A Modern Course in Statistical Physics

2nd Edition

L. E. REICHL

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This book is dedicated to
Ilya Prigogine
for his encouragement and support
and because
he has changed our view of the world.

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PREFACE

In 1992 after finishing my book, "The Transition of Chaos," I realized that I needed to write a new edition of "A Modern Course in Statistical Physics". I wanted to adjust the material to better prepare students for what I believe are the current directions of statistical physics. I wanted to place more emphasis on nonequilibrium processes and on the thermodynamics underlying biological processes. I also wanted to be more complete in the presentation of material. It turned out to be a greater task than I had anticipated, and now five years later I am finally finishing the second edition. One reason it has taken so long is that I have created a detailed solution manual for the second edition and I have added many worked out exercises to the text. In this way I hope I have made the second edition much more student and instructor friendly than the first edition was.

There are two individuals who have had a particularly large influence on this book and whom I want to thank, even though they took no part in writing the book. (Any negative features of this book are totally my responsibility.) The biggest influence has been Ilya Prigogine, and for that reason I have dedicated this book to him. When I first came to the University of Texas to join the Physics faculty, I became a member of what was then the Center for Thermodynamics and Statistical Mechanics (now known as the Prigogine Center for Statistical Mechanics and Complex Systems). My training was in equilibrium statistical mechanics. But that changed when I learned that the focus of this unique research Center, deep in the heart of Texas, was on nonequilibrium nonlinear phenomena, most of it far from equilibrium. I began to work on nonequilibrium and nonlinear phenomena, but followed my own path. The opportunity to teach and work in this marvelous research center and to listen to the inspiring lectures of Ilya Prigogine and lectures of the many visitors to the Center has opened new worlds to me, some of which I have tried to bring to students through this book.

The other individual who has had a large influence on this book is Nico van Kampen, a sometimes visitor to the University of Texas. His beautiful lectures on stochastic processes were an inspiration and spurred my interest in the subject.

I want to thank the many students in my statistical mechanics classes who helped me shape the material for this book and who also helped me correct the manuscript.

This book covers a huge range of material. I could not reference all the work by the individuals who have contributed in all these areas. I have referenced work which most influenced my view of the subject and which could lead students to other related work. I apologize to those whose work I have not been able to include in this book.

L. E. Reichl

Austin, Texas
September 1997

1

INTRODUCTION

1.A. OVERVIEW

The field of statistical physics has expanded dramatically in recent years. New results in ergodic theory, nonlinear chemical physics, stochastic theory, quantum fluids, critical phenomena, hydrodynamics, transport theory, and biophysics have revolutionized the subject, and yet these results are rarely presented in a form that students who have little background in statistical physics can appreciate or understand. This book has been written in an effort to incorporate these subjects into a basic course on statistical physics. It includes in a unified and integrated manner the foundations of statistical physics and develops from them most of the tools needed to understand the concepts underlying modern research in all of the above fields.

In the field of ergodic theory, for example, chaos theory has deepened our understanding of the structure and dynamical behavior of a variety of nonlinear systems and has made ergodic theory a modern field of research. Indeed, one of the frontiers of science today is the study of the spectral properties of decay processes in nature, based on the chaotic nature of the underlying dynamics of those systems. Advances in this field have been aided by the development of ever more powerful computers. In an effort to introduce this field to students, a careful discussion is given of the behavior of probability flows in phase space, including specific examples of ergodic and mixing flows.

Nonlinear chemical physics is still in its infancy, but it has already given a conceptual framework within which we can understand the thermodynamic origin of life processes. The discovery of *dissipative structures* (nonlinear spatial and temporal structures) in nonlinear nonequilibrium chemical systems has opened a new field in chemistry and biophysics. In this book, material has been included on chemical thermodynamics, chemical hydrodynamics, and nonequilibrium phase transitions in chemical and hydrodynamic systems.

The use of stochastic theory to study fluctuation phenomena in chemical and hydrodynamic systems, along with its growing use in population dynamics and complex systems theory, has brought new life to this field. The discovery of scaling behavior at all levels of the physical world, along with the appearance of Levy flights which often accompanies scaling behavior, has forced us to think

beyond the limits of the Central Limit Theorem. In order to give students some familiarity with modern concepts from the field of stochastic theory, we have placed probability theory in a more general framework and discuss, within that framework, classical random walks, Levy flights, and Brownian motion.

The theory of superfluids rarely appears in general textbooks on statistical physics, but the theory of such systems is incorporated at appropriate places throughout this book. We discuss the thermodynamic properties of superfluid and superconducting systems, the Ginzburg–Landau theory of superconductors, the BCS theory of superconductors, and superfluid hydrodynamics. Also included in the book is an extensive discussion of properties of classical fluids and their thermodynamic and hydrodynamic properties.

The theory of phase transitions has undergone a revolution in recent years. In this book we define critical exponents and use renormalization theory to compute them. We also derive an exact expression for the specific heat of the two-dimensional Ising system, one of the simplest exactly solvable systems which can exhibit a phase transition. At the end of the book we include an introduction to the theory of nonequilibrium phase transitions.

Hydrodynamics is a very powerful tool for understanding long-wavelength phenomena in classical fluids, solids, liquid crystals, superfluids, and biological systems. This book contains a thorough grounding in hydrodynamics based on the underlying symmetries and stability properties of matter. We discuss properties of correlation functions, causality, the fluctuation–dissipation theorem, the theory of light scattering, and the origin of hydrodynamics in terms of conserved quantities and broken symmetries. We also include a variety of applications of the hydrodynamics of mixtures, a subject essential for biophysics.

Transport theory is discussed from many points of view. We derive Onsager's relations for transport coefficients. We derive expressions for transport coefficients based on simple "back of the envelope" mean free path arguments. The Boltzmann and Lorentz–Boltzmann equations are derived and microscopic expressions for transport coefficients are obtained, starting from spectral properties of the Boltzmann and Lorentz–Boltzmann collision operators. The difficulties in developing a convergent transport theory for dense gases are also reviewed.

Concepts developed in statistical physics underlie all of physics. Once the forces between microscopic particles are determined, statistical physics gives us a picture of how microscopic particles act in the aggregate to form the macroscopic world. As we see in this book, what happens on the macroscopic scale is sometimes surprising.

1.B. PLAN OF BOOK

Thermodynamics is a consequence and a reflection of the symmetries of nature. It is what remains after collisions between the many degrees of freedom of

macroscopic systems randomize and destroy most of the coherent behavior. The quantities which cannot be destroyed, due to underlying symmetries of nature and their resulting conservation laws, give rise to the *state variables* upon which the theory of thermodynamics is built. Thermodynamics is therefore a solid and sure foundation upon which we can construct theories of matter out of equilibrium. That is why we place heavy emphasis on it in this book.

The book is divided into four parts. Chapters 2 and 3 present the foundations of thermodynamics and the thermodynamics of phase transitions. Chapters 4 through 6 present probability theory, stochastic theory, and the foundations of statistical mechanics. Chapters 7 through 9 present equilibrium statistical mechanics, with emphasis on phase transitions and the equilibrium theory of classical fluids. Chapters 10 through 12 deal with nonequilibrium processes, both on the microscopic and macroscopic scales, both near and far from equilibrium. The first two parts of the book essentially lay the foundations for the last two parts.

There seems to be a tendency in many books to focus on equilibrium statistical mechanics and derive thermodynamics as a consequence. As a result, students do not get the experience of traversing the vast world of thermodynamics and do not understand how to apply it to systems which are too complicated for statistical mechanics. For this reason, we begin the book with a thorough grounding in thermodynamics. In Chapter 2 we review the foundations of thermodynamics and thermodynamic stability theory and devote a large part of the chapter to a variety of applications which do not involve phase transitions, such as the cooling of gases, mixing, osmosis, and chemical thermodynamics. Chapter 3 is devoted to the thermodynamics of phase transitions and the use of thermodynamic stability theory in analyzing these phase transitions. We discuss first-order phase transitions in liquid–vapor–solid transitions, with particular emphasis on the liquid–vapor transition and its critical point and critical exponents. We also introduce the Ginzburg–Landau theory of continuous phase transitions and discuss a variety of transitions which involve broken symmetries.

Having developed some intuition concerning the macroscopic behavior of complex equilibrium systems, we then turn to microscopic foundations. Chapters 4 through 6 are devoted to probability theory and the foundations of statistical mechanics. Chapter 4 contains a review of basic concepts from probability theory and then uses these concepts to describe classical random walks and Levy flights. The Central Limit Theorem and the breakdown of the Central Limit Theorem for scaling processes is described. In Chapter 5 we study the dynamics of discrete stochastic variables based on the master equation. We also introduce the theory of Brownian motion and the idea of separation of time scales, which has proven so important in describing nonequilibrium phase transitions. The theory developed in Chapter 5 has many applications in chemical physics, laser physics, population dynamics, and biophysics, and it prepares the way for more complicated topics in statistical mechanics.

Chapter 6 lays the probabilistic foundations of statistical mechanics, starting from ergodic theory. In recent years, there has been a tendency to sidestep this aspect of statistical physics completely and to introduce statistical mechanics using information theory. The student then misses one of the current frontiers of modern physics, the study of the spectral behavior of decay processes in nature, based on the chaotic nature of the underlying dynamics of those systems. While we cannot go very far into this subject in this book, we at least discuss the issues. We begin by deriving the Liouville equation, which is the equation of motion for probability densities, both in classical mechanics and in quantum mechanics. We look at the types of flow that can occur in mechanical systems and introduce the concepts of ergodic and mixing flows, which appear to be minimum requirements if a system is to decay to thermodynamic equilibrium.

Chapters 7–9 are devoted entirely to equilibrium statistical mechanics. In Chapter 7 we derive the probability densities (the microcanonical, canonical, and grand canonical ensembles) for both closed and opened systems and relate them to thermodynamic quantities and the theory of fluctuations. We then use them to derive the thermodynamic properties of a variety of model systems, including harmonic lattices, spin systems, ideal quantum gases, and superconductors.

In Chapter 8 we introduce the equilibrium fluctuation theory of spin systems and show qualitatively how the spatial extent of correlations between fluctuations diverges as we approach the critical point. We also introduce the idea of scaling and use renormalization theory to obtain microscopic expressions for the critical exponents of spin lattices. Finally we conclude Chapter 8 by obtaining an exact expression for the heat capacity of the two-dimensional Ising lattice, and we compare our exact expressions to those of mean field theory.

Chapter 9 is devoted to the equilibrium theory of classical fluids. In this chapter we relate the thermodynamic properties of classical fluids to the underlying radial distribution function, and we use the Ursell–Mayer cluster expansion to obtain a virial expansion of the the equation of state of a classical fluid. We also discuss how to include quantum corrections for nondegenerate gases.

The last part of the book, Chapters 10–12, deals with nonequilibrium processes. Chapter 10 is devoted to hydrodynamic processes for systems near equilibrium. We begin by deriving the Navier–Stokes equations from the symmetry properties of a fluid of point particles, and we use the derived expression for entropy production to obtain the transport coefficients for the system. We use the solutions of the linearized Navier–Stokes equations to predict the outcome of light-scattering experiments. We go on to derive Onsager's relations between transport coefficients, and we use causality to derive the fluctuation–dissipation theorem. We also derive a general expression for the entropy production in systems with mixtures of particles which can undergo chemical reactions. We then use this theory to describe thermal and chemical transport processes in mixtures, across membranes, and in electrical circuits. The hydrodynamic equations describe the behavior of just a few slowly

varying degrees of freedom in fluid systems. If we assume that the remainder of the fluid can be treated as a background noise, we can use the fluctuation–dissipation theorem to derive the correlation functions for this background noise. In Chapter 10 we also consider hydrodynamic modes which result from broken symmetries, and we derive hydrodynamic equations for superfluids and consider the types of sound that can exist in such fluids.

In Chapter 11 we derive microscopic expressions for the coefficients of diffusion, shear viscosity, and thermal conductivity, starting both from mean free path arguments and from the Boltzmann and Lorentz–Boltzmann equations. In deriving microscopic expressions for the transport coefficients from the Boltzmann and Lorentz–Boltzmann equations, we use a very elegant method which relies on use of the eigenvalues and eigenfunctions of the collision operators associated with those equations. We obtain explicit microscopic expressions for the transport coefficients of a hard sphere gas.

Finally, in Chapter 12 we conclude with the fascinating subject of nonequilibrium phase transitions. We discuss thermodynamic stability theory for systems far from equilibrium. We also show how nonlinearities in the rate equations for chemical reaction–diffusion systems lead to nonequilibrium phase transitions which give rise to chemical clocks, nonlinear chemical waves, and spatially periodic chemical structures, while nonlinearities in the Rayleigh–Benard hydrodynamic system lead to spatially periodic convection cells. We shall also examine the nature of fluctuations in the neighborhood of the critical point for these transitions and show that they are characterized by a critical slowing down of certain unstable modes.

1.C. USE AS A TEXTBOOK

Even though this book contains a huge amount of material, it has been designed to be used as a textbook. In each chapter the material has been divided into *core topics* and *special topics*. The core topics provide key basic material in each chapter, while special topics illustrate these core ideas with a variety of applications. The instructor can select topics from the special topics sections, according to the emphasis he/she wishes to give the course.

In many sections, we have included nontrivial demonstration exercises to help the students understand the material and to help in solving homework problems. Each chapter has a variety of problems at the end of the chapter that can be used to help the students test their understanding.

Even if one covers only the core topics of each chapter, there may be too much material to cover in a one-semester course. However, the book is designed so that some chapters may be omitted completely. The choice of which chapters to use depends on the interests of the instructor. Our suggestion for a basic well-rounded one-semester course in statistical physics is to cover the core topics in Chapters 2, 3, 4, 7, 10, and 11 (only Section 11.B if time is running short).

The book is intended to introduce the students to a variety of subjects and resource materials which they can then pursue in greater depth if they wish. We have tried to use standardized notation as much as possible. In writing a book which surveys the entire field of statistical physics, it is impossible to include or even to reference everyone's work. We have included references which were especially pertinent to the points of view we take in this book and which will lead students easily to other work in the same field.

PART ONE

THERMODYNAMICS

2

INTRODUCTION TO THERMODYNAMICS

2.A. INTRODUCTORY REMARKS

The science of thermodynamics began with the observation that matter in the aggregate can exist in macroscopic states which are stable and do not change in time. These stable "equilibrium" states are characterized by definite mechanical properties, such as color, size, and texture, which change as the substance becomes hotter or colder (changes its temperature). However, any given equilibrium state can always be reproduced by bringing the substance back to the same state. Once a system reaches its equilibrium state, all changes cease and the system will remain forever in that state unless some external influence acts to change it. This inherent stability and reproducibility of the equilibrium states can be seen everywhere in the world around us.

Thermodynamics has been able to describe, with remarkable accuracy, the macroscopic behavior of a huge variety of systems over the entire range of experimentally accessible temperatures (10^{-4} K to 10^{6} K). It provides a truly universal theory of matter in the aggregate. And yet, the entire subject is based on only four laws, which may be stated rather simply as follows: Zeroth Law—it is possible to build a thermometer; First Law—energy is conserved; Second Law—not all heat energy can be converted into work; and Third Law—we can never reach the coldest temperature using a finite set of reversible steps. However, even though these laws sound rather simple, their implications are vast and give us important tools for studying the behavior and stability of systems in equilibrium and, in some cases, of systems far from equilibrium.

The *core topics* in this chapter focus on a review of various aspects of thermodynamics that will be used throughout the remainder of the book. The *special topics* at the end of this chapter give a more detailed discussion of some applications of thermodynamics which do not involve phase transitions. Phase transitions will be studied in Chapter 3.

We shall begin this chapter by introducing the variables which are used in thermodynamics and the mathematics needed to calculate changes in the thermodynamic state of a system. As we shall see, many different sets of

mechanical variables can be used to describe thermodynamic systems. In order to become familiar with some of these mechanical variables, we shall write the experimentally observed equations of state for a variety of thermodynamic systems.

As we have mentioned above, thermodynamics is based on four laws. We shall discuss the content of these laws in some detail, with particular emphasis on the second law. The second law is extremely important both in equilibrium and out of equilibrium because it gives us a criterion for testing the stability of equilibrium systems and, in some cases, nonequilibrium systems.

There are a number of different thermodynamic potentials that can be used to describe the behavior and stability of thermodynamic systems, depending on the type of constraints imposed on the system. For a system which is isolated from the world, the internal energy will be a minimum for the equilibrium state. However, if we couple the system thermally, mechanically, or chemically to the outside world, other thermodynamic potentials will be minimized. We will introduce the five most commonly used thermodynamic potentials (internal energy, enthalpy, Helmholtz free energy, Gibbs free energy, and the grand potential), and we will discuss the conditions under which each one is minimized at equilibrium and why they are called potentials.

When experiments are performed on thermodynamic systems, the quantities which are easiest to measure are the response functions. Generally, we change one parameter in the system and see how another parameter responds to that change, under highly controlled conditions. The quantity that measures the way in which the system responds is called a *response function.* In this chapter we shall introduce a variety of thermal and mechanical response functions and give relations between them.

Isolated equilibrium systems are systems in a state of maximum entropy. Any fluctuations which occur in such systems must cause a decrease in entropy if the equilibrium state is to be stable. We can use this fact to find relations between the intensive state variables for different parts of a system if those parts are to be in mechanical, thermal, and chemical equilibrium. In addition, we can find restrictions on the sign of the response functions which must be satisfied for stable equilibrium. We shall find these conditions and discuss the restrictions they place on the Helmholtz and Gibbs free energy.

Thermodynamics becomes most interesting when it is applied to real systems. In order to demonstrate its versatility, in the section on special topics, we shall apply it to a number of systems which have been selected for their practical importance or conceptual importance.

We begin with a subject of great practical and historic importance, namely, the cooling of gases. it is often necessary to cool substances below the temperature of their surroundings. The refrigerator most commonly used for this purpose is based on the Joule–Kelvin effect. There are two important ways to cool gases. We can let them do work against their own intermolecular forces by letting them expand freely (Joule effect); or we can force them through a small constriction, thus causing cooling at low temperatures or heating at high

temperatures (Joule-Kelvin effect). The Joule-Kelvin effect is by far the more effective of the two methods. We shall discuss both methods in this chapter and use the van der Waals equation of state to obtain estimates of the coolling effects for some real gases.

For reversible processes, changes in entropy content can be completely accounted for in terms of changes in heat content. For irreversible processes, this is no longer true. We can have entropy increase in an isolated system, even though no heat has been added. Therefore, it is often useful to think of an increase in entropy as being related to an increase in disorder in a system. One of the most convincing illustrations of this is the entropy change which occurs when two substances, which have the same temperature and pressure but different identities, are mixed. Thermodynamics predicts that the entropy will increase solely due to mixing of the substances.

When the entropy of a system changes due to mixing, so will other thermodynamic quantities. One of the most interesting examples of this is osmosis. We can fill a container with water and separate it into two parts by a membrane permeable to water but not salt, for example. If we put a small amount of salt into one side, the pressure of the resulting salt solution will increase markedly because of mixing.

Chemical reactions can be characterized in a rather simple way in terms of a thermodynamic quantity called the *affinity*. The affinity gives a measure of the distance of a chemical reaction from thermodynamic equilibrium and will be useful in later chapters when we discuss chemical systems out of equilibrium. We can obtain an expression for the affinity by using the conditions for thermodynamic equilibrium and stability introduced in Chapter 2, and at the same time we can learn a number of interesting facts about the thermodynamic behavior of chemical reactions. A special example of a type of reaction important to biological systems is found in electrolytes, which consist of salts which can dissociate but maintain an electrically neutral solution.

2.B. STATE VARIABLES AND EXACT DIFFERENTIALS

Thermodynamics describes the behavior of systems with many degrees of freedom after they have reached a state of thermal equilibrium—a state in which all past history is forgotten and all macroscopic quantities cease to change in time. The amazing feature of such systems is that, even though they contain many degrees of freedom ($\sim 10^{23}$) in chaotic motion, their thermodynamic state can be specified completely in terms of a few parameters—called *state variables*. In general, there are many state variables which can be used to specify the thermodynamic state of a system, but only a few (usually two or three) are independent. In practice, one chooses state variables which are accessible to experiment and obtains relations between them. Then, the "machinery" of thermodynamics enables one to obtain the values of any other state variables of interest.

State variables may be either *extensive* or *intensive*. Extensive variables always change in value when the size (spatial extent and number of degrees of freedom) of the system is changed, and intensive variables need not. Certain pairs of intensive and extensive state variables often occur together because they correspond to generalized forces and displacements which appear in expressions for thermodynamic work. Some examples of such extensive and intensive pairs are, respectively, volume, V, and pressure, P; magnetization, $\mathbf{M}$, and magnetic field strength, $\mathbf{H}$; length, L, and tension, J; area, A, and surface tension, σ; electric polarization, $\mathbf{P}$, and electric field, $\mathbf{E}$. The pair of state variables related to heat content of thermodynamic system are the temperature, T, which is intensive, and the entropy, S, which is extensive. There is also a pair of state variables associated with "chemical" properties of a system. They are the number of particles, N, which is extensive, and the chemical potential per particle, μ', which is intensive. In this book we shall sometimes use the number of moles, n, and the chemical potential per mole, μ (molar chemical potential); or the mass of a substance, M, and the chemical potential per unit mass, $\tilde{\mu}$, (specific chemical potential), as the chemical state variables. If there is more than one type of particle in the system, then there will be a·mole number and chemical potential associated with each type of particle.

Other state variables used to describe the thermodynamic behavior of a system are the various response functions, such as heat capacity, C; compressibility, κ; magnetic susceptibility, χ; and various thermodynamic potentials, such as the internal energy, U; enthalpy, H; Helmholtz free energy, A; Gibbs free energy, G; and the grand potential, Ω. We shall become thoroughly acquainted with these state variables in subsequent sections.

If we change the thermodynamic state of our system, the amount by which the state variables change must be independent of the path taken. If this were not so, the state variables would contain information about the history of the system. It is precisely this property of state variables which makes them so useful in studying changes in the equilibrium state of various systems. Mathematically changes in state variables correspond to exact differentials [1]; therefore, before we begin our discussion of thermodynamics, it is useful to review the theory of exact differentials. This will be the subject of the remainder of this section.

Given a function $F = F(x_1, x_2)$ depending on two independent variables x_1 and x_2, the differential of F is defined as follows:

$$dF = \left(\frac{\partial F}{\partial x_1}\right)_{x_2} dx_1 + \left(\frac{\partial F}{\partial x_2}\right)_{x_1} dx_2, \tag{2.1}$$

where $(\partial F/\partial x_1)_{x_2}$ is the derivative of F with respect to x_1 holding x_2 fixed. If F and its derivatives are continuous and

$$\left[\frac{\partial}{\partial x_1}\left(\frac{\partial F}{\partial x_2}\right)_{x_1}\right]_{x_2} = \left[\frac{\partial}{\partial x_2}\left(\frac{\partial F}{\partial x_1}\right)_{x_2}\right]_{x_1}, \tag{2.2}$$

then dF is an exact differential. If we denote

$$c_1(x_1,x_2) \equiv \left(\frac{\partial F}{\partial x_1}\right)_{x_2} \quad \text{and} \quad c_2(x_1,x_2) \equiv \left(\frac{\partial F}{\partial x_2}\right)_{x_1},$$

then the variables c_1 and x_1 and variables c_2 and x_2 are called "conjugate" variables with respect to the function F.

The fact that dF is exact has the following consequences:

(a) The value of the integral

$$F(B) - F(A) = \int_A^B dF = \int_A^B (c_1 dx_1 + c_2\, dx_2)$$

is independent of the path taken between A and B and depends only on the end points A and B.

(b) The integral of dF around a closed path is zero:

$$\oint_{\text{closed}} dF = \oint_{\text{closed}} (c_1 dx_1 + c_2 dx_2) \equiv 0.$$

(c) If one knows only the differential dF, then the function F can be found to within an additive constant.

If F depends on more than two variables, then the statements given above generalize in a simple way: Let $F = F(x_1, x_2, \ldots, x_n)$, then the differential, dF, may be written

$$dF = \sum_{i=1}^{n} \left(\frac{\partial F}{\partial x_i}\right)_{\{x_{j\neq i}\}} dx_i. \tag{2.3}$$

The notation $(\partial F/\partial x_i)_{\{x_{j\neq i}\}}$ means that the derivative of F is taken with respect to x_i holding *all* variables *but* x_i constant. For any pair of variables, the following relation holds:

$$\left[\frac{\partial}{\partial x_l}\left(\frac{\partial F}{\partial x_k}\right)_{\{x_{j\neq k}\}}\right]_{\{x_{j\neq l}\}} = \left[\frac{\partial}{\partial x_k}\left(\frac{\partial F}{\partial x_l}\right)_{\{x_{j\neq l}\}}\right]_{\{x_{j\neq k}\}}. \tag{2.4}$$

An example for the case of three independent variables is

$$dF = c_1 dx_1 + c_2 dx_2 + c_3 dx_3.$$

The Eq. (2.4) leads to the result

$$\left(\frac{\partial c_1}{\partial x_2}\right)_{x_1,x_3} = \left(\frac{\partial c_2}{\partial x_1}\right)_{x_2,x_3}, \left(\frac{\partial c_1}{\partial x_3}\right)_{x_1,x_2} = \left(\frac{\partial c_3}{\partial x_1}\right)_{x_3,x_2},$$

$$\left(\frac{\partial c_2}{\partial x_3}\right)_{x_2,x_1} = \left(\frac{\partial c_3}{\partial x_2}\right)_{x_3,x_1}.$$

Differentials of all state variables are exact and have the above properties. Given four state variables, x, y, z, and w, where w is a function of any two of the variables x, y, or z, one can obtain the following useful relations along paths for which $F(x, y, z) = 0$:

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}. \tag{2.5}$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1. \tag{2.6}$$

$$\left(\frac{\partial x}{\partial w}\right)_z = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial w}\right)_z. \tag{2.7}$$

$$\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial x}{\partial y}\right)_w + \left(\frac{\partial x}{\partial w}\right)_y \left(\frac{\partial w}{\partial y}\right)_z. \tag{2.8}$$

It is a simple matter to derive Eqs. (2.5)–(2.8). We will first consider Eqs. (2.5) and (2.6). Let us choose variables y and z to be independent, $x = x(y, z)$, and then choose x and z to be independent, $y = y(x, z)$, and write the following differentials; $dx = (\partial x/\partial y)_z dy + (\partial x/\partial z)_y dz$ and $dy = (\partial y/\partial x)_z dx + (\partial y/\partial z)_x dz$.

If we eliminate dy between these equations, we obtain

$$\left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z - 1\right] dx + \left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y\right] dz = 0.$$

Because dx and dz may be varied independently, their coefficients may be set equal to zero separately. The result is Eqs. (2.5) and (2.6).

To derive Eq. (2.7) we let y and z be independent so that $x = x(y, z)$ and write the differential for dx. If we then divide by dw, we obtain

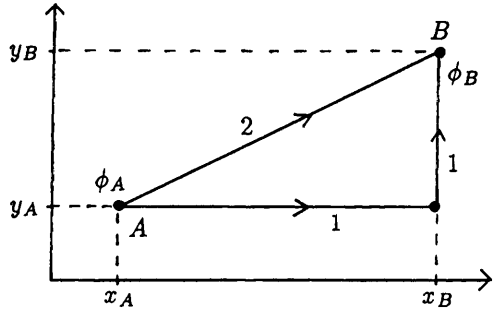
$$\frac{dx}{dw} = \left(\frac{\partial x}{\partial y}\right)_z \frac{dy}{dw} + \left(\frac{\partial x}{\partial z}\right)_y \frac{dz}{dw}.$$

For constant $z, dz = 0$ and we find Eq. (2.7)

Finally, to derive Eq. (2.8) we let x be a function of y and w, $x = x(y, w)$. If we write the differential of x, divide it by dy, and restrict the entire equation to constant z, we obtain Eq. (2.8).

When integrating exact differentials, one must be careful not to lose terms. In Exercise 2.1, we illustrate two different methods for integrating exact differentials.

■ **EXERCISE 2.1.** Consider the differential $d\phi = (x^2 + y)dx + xdy$. (a) Show that it is an exact differential. (b) Integrate $d\phi$ between the points A and B in the figure below, along the two different paths, 1 and 2. (c) Integrate $d\phi$ between points A and B using indefinite integrals.



Answer:

(a) From the expression $d\phi = (x^2 + y)dx + xdy$, we can write $(\partial\phi/\partial x)_y = x^2 + y$ and $(\partial\phi/\partial y)_x = x$. Since $[(\partial/\partial y)(\partial\phi/\partial x)_y]_x = [(\partial/\partial x)(\partial\phi/\partial y)_x]_y = 1$, the differential, $d\phi$, is exact.

(b) Let us first *integrate the differential, $d\phi$, along path 1:*

$$\begin{aligned}\phi_B - \phi_A &= \int_{x_A}^{x_B} (x^2 + y_A)\,dx + \int_{y_A}^{y_B} x_B\,dy \\ &= \tfrac{1}{3}x_B^3 + x_B y_B - \tfrac{1}{3}x_A^3 - x_A y_A.\end{aligned} \tag{1}$$

Let us next *integrate the differential, $d\phi$, along path* 2. Note that along *path* 2, $y = y_A + (\Delta y/\Delta x)(x - x_A)$, where $\Delta y = y_B - y_A$ and $\Delta x = x_B - x_A$. If we substitute this into the expression for $d\phi$, we find $d\phi = (x^2 + y)dx + xdy = [x^2 + y_A + (\Delta y/\Delta x)(2x - x_A)]dx$. Therefore

$$\begin{aligned}\phi_B - \phi_A &= \int_{x_A}^{x_B} dx\left[x^2 + y_A + \frac{\Delta y}{\Delta x}(2x - x_A)\right] \\ &= \tfrac{1}{3}x_B^3 + x_B y_B - \tfrac{1}{3}x_A^3 - x_A y_A.\end{aligned} \tag{2}$$

Note that the change in ϕ in going from point A to point B is independent of the path taken. This is a property of exact differentials.

(c) We now integrate the differential, $d\phi$, in a different way. Let us first do the indefinite integrals

$$\int \left(\frac{\partial \phi}{\partial x}\right)_y dx = \int (x^2 + y) dx = \tfrac{1}{3}x^3 + xy + K_1(y), \tag{3}$$

where $K_1(y)$ is an unknown function of y. Next do the integral

$$\int \left(\frac{\partial \phi}{\partial y}\right)_x dy = \int x dy = xy + K_2(x), \tag{4}$$

where $K_2(x)$ is an unknown function of x. In order for Eqs. (3) and (4) to be consistent, we must choose $K_2(x) = \frac{1}{3}x^3 + K_3$ and $K_1(y) = K_3$, where K_3 is a constant. Therefore, $\phi = \frac{1}{3}x^3 + xy + K_3$ and again, $\phi_B - \phi_A = \frac{1}{3}x_B^3 + x_B y_B - \frac{1}{3}x_A^3 - x_A y_A$.

2.C. SOME MECHANICAL EQUATIONS OF STATE

An equation of state is a functional relation between the state variables for a system in equilibrium which reduces the number of independent degrees of freedom needed to describe the state of the system. It is an equation which relates the thermal state variables, T or S, to the mechanical and chemical state variables for that system and contains a great deal of information about the thermodynamic behavior of the system. It is useful to give some examples of empirically obtained equations of state.

2.C.1. Ideal Gas Law

The best-known equation of state is the ideal gas law

$$PV = nRT, \tag{2.9}$$

where n is the number of moles, T is temperature in degrees Kelvin, P is the pressure in Pascals, V is the volume in cubic meters, and $R = 8.314$ J/mol· K is the universal gas constant. The ideal gas law gives a good description of a gas which is so dilute that the effect of interaction between particles can be neglected.

If there are m different types of particles in the gas, then the ideal gas law takes the form

$$PV = \sum_{i=1}^{m} n_i RT, \tag{2.10}$$

where n_i is the number of moles of the ith constituent.

2.C.2. Virial Expansion [2]

The virial expansion,

$$P = \left(\frac{nRT}{V}\right)\left[1 + \frac{n}{V}B_2(T) + \left(\frac{n}{V}\right)^2 B_3(T) + \cdots\right], \tag{2.11}$$

expresses the equation of state of a gas as a density expansion. The quantities $B_2(T)$ and $B_3(T)$ are called the second and third virial coefficients and are functions of temperature only. As we shall see in Chapter 9, the virial coefficients may be computed in terms of the interparticle potential. Comparison between experimental and theoretical values for the virial coefficients is an important method for obtaining the force constants for various interparticle potentials. In Fig. 2.1 we have plotted the second virial coefficient for helium and argon. The curves are typical of most gases. At low temperatures, B_2(T) is negative because the kinetic energy is small and the attractive forces between particles reduce the pressure. At high temperatures the attractive forces have little effect and corrections to the pressure become positive. At high temperature the second virial coefficient has a maximum.

For an ideal classical gas all virial coefficients, $B_i (i \geq 2)$, are zero, but for an ideal quantum gas (Bose–Einstein or Fermi–Dirac) the virial coefficients are

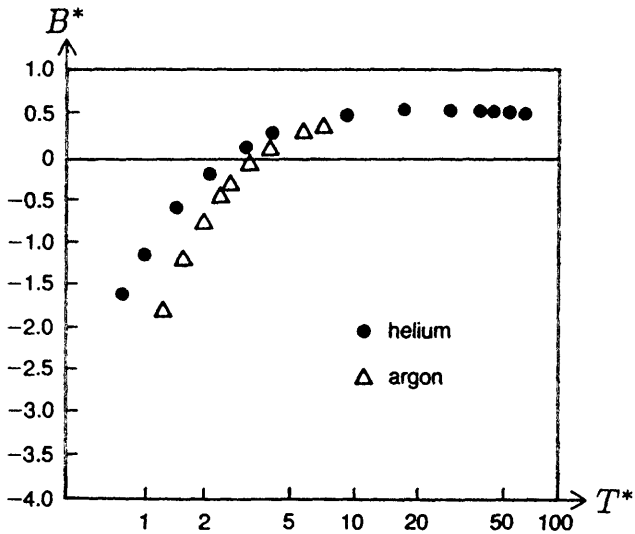


Fig. 2.1. A plot of the second virial coefficients for helium and argon in terms of the dimensionless quantities, $B^* = B_2/b_0$ and $T^* = k_B T/\varepsilon$, where b_0 and ε are constants, k_B is Boltzmann's constant, and T is the temperature. For helium, $b_0 = 21.07 \times 10^{-6}\text{m}^3/\text{mol}$ and $\varepsilon/k_B = 10.22$ K. For argon, $b_0 = 49.8 \times 10^{-6}\text{m}^3/\text{mol}$ and $\varepsilon/k_B = 119.8$ K. (Based on Ref. 2.)

nonzero. The "statistics" of quantum particles give rise to corrections to the classical ideal gas equation of state.

2.C.3. Van der Waals Equation of State [3]

The van der Waals equation of state is of immense importance historically because it was the first equation of state which applies to both the gas and liquid phases and exhibits a phase transition. It contains most of the important qualitative features of the gas and liquid phases although it becomes less accurate as density increases. The van der Waals equation contains corrections to the ideal gas equation of state, which take into account the form of the interaction between real particles. The interaction potential between molecules in a gas contains a strong repulsive core and a weaker attractive region surrounding the repulsive core. For an ideal gas, as the pressure is increased, the volume of the system can decrease without limit. For a real gas this cannot happen because the repulsive core limits the close-packed density to some finite value. Therefore, as pressure is increased, the volume tends to some minimum value, $V = V_{min} = nb$, where b is an experimental constant. The ideal gas equation of state must be corrected to take account of the existence of the repulsive core and assumes the form

$$P = \frac{nRT}{V - nb}.$$

The attracive region of the potential causes the pressure to be decreased slightly relative to that of a noninteracting gas because it introduces a "cohesion" between molecules. The decrease in pressure will be proportional to the probability that two molecules interact; this, in turn, is proportional to the square of the density of particles $(N/V)^2$. We therefore correct the pressure by a factor proportional to the square of the density, which we write $a(n^2/V^2)$. The constant a is an experimental constant which depends on the type of molecule being considered. The equation of state can now be written

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT. \tag{2.12}$$

In Table 2.1 we have given values of a and b for simple gases.

The second virial coefficient for a van der Waals gas is easily found to be

$$B_2^{(VW)}(T) = \left(b - \frac{a}{RT}\right). \tag{2.13}$$

We see that $B_2^{(VW)}(T)$ will be negative at low temperatures and will become positive at high temperatures but does not exhibit the maximum observed in real gases. Thus, the van der Waals equation does not predict all the observed

Table 2.1. Van der Waals Constants for Some Simple Gases [4]

	$a(\text{Pa} \cdot \text{m}^6/\text{mol}^2)$	$b(\text{m}^3/\text{mol})$
H_2	0.02476	0.02661
He	0.003456	0.02370
CO_2	0.3639	0.04267
H_2O	0.5535	0.03049
O_2	0.1378	0.03183
N_2	0.1408	0.03913

features of real gases. However, it describes enough of them to make it a worthwhile equation to study. In subsequent chapters, we will repeatedly use the van der Waals equation to study the thermodynamic properties of interacting fluids.

2.C.4. Solids

Solids have the property that their coefficient of thermal expansion, $\alpha_P = (1/v)(\partial v/\partial T)_P$, and their isothermal compressibility, $\kappa_T = -(1/v)(\partial v/\partial P)_T$, where $v = V/n$ is the molar volume, are very small. Therefore, for solids at fairly low temperature we can expand the molar volume of a solid in a Taylor series about zero temperature and zero pressure value, v_0, and obtain the following equation of state:

$$v = v_0(1 + \alpha_P T - \kappa_T P), \tag{2.14}$$

where T is measured in Kelvins. Typical values [5] of κ_T are of the order of 10^{-10}/Pa or 10^{-5}/atm. For example, for solid Ag (silver) at room temperature, $\kappa_T = 1.3 \times 10^{-10}$/Pa (for $P = 0$ Pa), and for diamond at room temperature, $\kappa_T = 1.6 \times 10^{-10}$/Pa (for $P = 4.0 \times 10^8$ Pa $- 10^{10}$ Pa). Typical values of α_P are of the order 10^{-4}/K. For example, for solid Na (sodium) at room temperature we have $\alpha_P = 2 \times 10^{-4}$/K, and for solid K (potassium) we have $\alpha_P = 2 \times 10^{-4}$/K.

2.C.5. Elastic Wire or Rod

For a stretched wire or rod in the elastic limit, Hook's law applies and we can write

$$J = A(T)(L - L_0), \tag{2.15}$$

where J is the tension measured in Newtons per meter, $A(T)$ is temperature dependent coefficient, L is the length of the stretched wire or rod, and L_0 is the

length of the wire when $J = 0$. The coefficient, $A(T)$, may be written $A(T) = A_0 + A_1 T$, where A_0 and A_1 are constants. The constant, A_1, is negative for most substances but may be positive for some substances (including rubber).

2.C.6. Surface Tension [6]

Pure liquids in equilibrium with their vapor phase have a well-defined surface layer at the interface between the liquid and vapor phases. The mechanical properties of the surface layer can be described by thermodynamic state variables. The origin of the surface layer is the unequal distribution of intermolecular forces acting on the molecules at the surface. Molecules in the interior of the liquid are surrounded by, and interact with, molecules on all sides. Molecules at the surface interact primarily with molecules in the liquid, since the vapor phase (away from the critical point) is far less dense than the liquid. As a result, there is a strong tendency for the molecules at the surface to be pulled back into the liquid and for the surface of the liquid to contract. The molecular forces involved are huge. Because of this tendency for the surface to contract, work must be done to increase the free surface of the liquid. When the surface area is increased, molecules from the interior must be brought to the surface and therefore work must be done against interior molecular forces. The *work per unit area* needed to extend the surface area is called the *surface tension of* the liquid. For most pure liquids, the surface tension does not depend on the area and the equation of state has the form

$$\sigma = \sigma_0 \left(1 - \frac{t}{t'}\right)^n, \tag{2.16}$$

where t is the temperature in degrees Celius, σ_0 is the surface tension at $t = 0°\text{C}$, t' is experimentally determined temperature within a few degrees of the critical temperature, and n is an experimental constant which has a value between one and two.

2.C.7. Electric Polarization [6–8]

When an electric field $\mathbf{E}$ is applied to a dielectric material, the particles composing the dielectric will be distorted and an electric polarization field, $\mathbf{P}$ ($\mathbf{P}$ is the induced electric dipole moment per unit volume), will be set up by the material. The polarization is related to the electric field, $\mathbf{E}$, and the electric displacement, $\mathbf{D}$, by the equation

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} \tag{2.17}$$

where ε_0 is the permittivity constant, $\varepsilon_0 = 8.854 \times 10^{-12} \text{C}^2/\text{N} \cdot \text{m}^2$. The electric field, $\mathbf{E}$, has units of Newtons per coulomb (N/C), and the electric displacement and electric polarization have units of coulomb per square meter

(C/m^2). **E** results from both external and surface charges. The magnitude of the polarization field, **P**, will depend on the temperature. A typical equation of state for a homogeneous dielectric is

$$\mathbf{P} = \left(a + \frac{b}{T}\right)\mathbf{E} \tag{2.18}$$

for temperatures not too low. Here a and b are experimental constants and T is temperature in degrees Kelvin.

2.C.8. Curie's Law [6–8]

If we consider a paramagnetic solid at constant pressure, the volume changes very little as a function of temperature. We can then specify the state in terms of applied magnetic field and induced magnetization. When the external field is applied, the spins line up to produce a magnetization **M** (magnetic moment per unit volume). The magnetic induction field, **B** (measured in units of teslas, 1 T=1 weber/m^2), the magnetic field strength, **H** (measured in units of amphere/meter), and the magnetization are related through the equation

$$\mathbf{B} = \mu_0\mathbf{H} + \mu_0\mathbf{M}, \tag{2.19}$$

where μ_0 is the permeability constant ($\mu_0 = 4\pi \times 10^{-7}$ T · m/A). The equation of state for such a system at room temperature is well approximated by Curie's law:

$$M = \frac{nD}{T}\mathbf{H}, \tag{2.20}$$

where n is the number of moles, D is an experimental constant dependent on the type of material used, and the temperature, T, is measured in Kelvins.

2.D. THE LAWS OF THERMODYNAMICS [6]

Thermodynamics is based upon four laws. Before we can discuss these laws in a meaningful way, it is helpful to introduce some basic concepts.

A system is in *thermodynamic equilibrium* if the mechanical variables do not change in time and if there are no macroscopic flow processes present. Two systems are separated by a fixed *insulating wall* (a wall that prevents transfer of matter heat and mechanical work between the systems) if the thermodynamic state variables of one can be changed arbitrarily without causing changes in the thermodynamic state variables of the other. Two systems are separated by a *conducting wall* if arbitrary changes in the state variables of one cause changes in the state variables of the other. A conducting wall allows transfer of heat. An insulating wall prevents transfer of heat.

It is useful to distinguish among three types of thermodynamic systems. An *isolated system* is one which is surrounded by an insulating wall, so that no heat or matter can be exchanged with the surrounding medium. A *closed system* is one which is surrounded by a conducting wall so that heat can be exchanged but matter cannot. An *open system* is one which allows both heat and matter exchange with the surrounding medium.

It is possible to change from one equilibrium state to another. Such changes can occur reversibly or irreversibly. A reversible change is one for which the system remains infinitesimally close to the thermodynamic equilibrium—that is, is performed quasi-statically. Such changes can always be reversed and the system brought back to its original thermodynamic state without causing any changes in the thermodynamic state of the universe. For each step of a reversible process, the state variables have a well-defined meaning.

An irreversible or spontaneous change from one equilibrium state to another is one in which the system does not stay infinitesimally close to equilibrium during each step. Such changes often occur rapidly and give rise to flows and "friction" effects. After an irreversible change the system cannot be brought back to its original thermodynamic state without causing a change in the thermodynamic state of the universe. With these ideas in mind, we an now discuss the four laws of thermodynamics.

2.D.1. Zeroth Law: Two Bodies, Each in Thermodynamic Equilibrium with a Third System, are in Thermodynamic Equilibrium with Each Other

The zeroth law is of fundamental importance to experimental thermodynamics because it enables us to introduce the concept of a thermometer and to measure temperatures of various systems in a reproducible manner. If we place a thermometer in contact with a given reference system, such as water at the triple point (where ice, water, and vapor coexist), then the mechanical variables describing the thermodynamic state of the thermometer (e.g., the height of a mercury column, the resistance of a resistor, or the pressure of a fixed volume container of gas) always take on the same values. If we then place the thermometer in contact with a third system and the mechanical variables do not change, then we say that the third system, the thermometer, and water at the triple point all have the same "temperature." Changes in the mechanical variables of the thermometer as it is cooled or heated are used as a measure of temperature change.

2.D.2. First Law: Energy Is Conserved

The first law tells us that there is a store of energy in the system, called the internal energy, U, which can be changed by causing the system to do work, $đW$, or by adding heat, $đQ$, to the system. We use the notation, $đW$, to indicate that the differential is not exact.) The change in the internal energy which

results from these two processes is given by

$$dU = đQ - đW. \tag{2.21}$$

The work, $đW$, may be due to changes in any relevant extensive "mechanical" or chemical variable. In general it can be written

$$đW = PdV - JdL - \sigma dA - \mathbf{E} \cdot d\mathbf{P} - \mathbf{H} \cdot d\mathbf{M} - \phi de - \sum_j \mu_j' dN_j, \tag{2.22}$$

where $dU, dV, dL, dA, d\mathbf{P}, d\mathbf{M}, de$, and dN_j are exact differentials, but $đQ$ and $đW$ are not because they depend on the path taken (on the way in which heat is added or work is done). The meaning of the first five terms in Eq. (2.22) was discussed in Section (2.C). The term, $-\phi de$, is the work the system needs to do it is has an electric potential, ϕ, and increases its charge by an amount, de. The last term, $-\mu_j' dN_j$, is the chemical work required for the system to add dN_j neutral particles if it has chemical potential, μ_j'. We may think of $-P, J, \sigma, \mathbf{E}, \mathbf{H}, \phi$, and μ_j' as generalized forces, and we may think of $dV, dL, dA, d\mathbf{P}, \mathrm{d}\mathbf{M}, de$ and dN_j as generalized displacements.

It is useful to introduce a generalized mechanical force, Y, which denotes quantities such as, $-P, J, \sigma, \mathbf{E}, \mathbf{H}$, and ϕ , and a generalized displacement, X, which denotes the corresponding displacements, $V, L, A, \mathbf{P}, \mathbf{M}$, and e, respectively. Then the first law can be written in the form

$$dU = đQ + YdX + \sum_j \mu_j' dN_j. \tag{2.23}$$

Note that μ_j' is a chemical force and dN_j is a chemical displacement. Note also that the pressure, P, has a different sign from the other generalized forces. If we increase the pressure, the volume increases, whereas if we increase the force, Y, for all other cases, the extensive variable, X, decreases.

2.D.3. Second Law: Heat Flows Spontaneously from High Temperatures to Low Temperatures

There are a number of ways to state the second law, with the one given above being the simplest. Three alternative versions are [6]:

(a) *The spontaneous tendency of a system to go toward thermodynamic equilibrium cannot be reversed without at the same time changing some organized energy, work, into disorganized energy, heat.*

(b) *In a cyclic process, it is not possible to convert heat from a hot reservoir into work without at the same time transferring some heat to a colder reservoir.*

(c) *The entropy change of any system and its surroundings, considered together, is positive and approaches zero for any process which approaches reversibility.*

The second law is of immense importance from many points of view. From it we can compute the maximum possible efficiency of an engine which transforms heat into work. It also enables us to introduce a new state variable, the entropy, S, which is conjugate to the temperature. The entropy gives us a measure of the degree of disorder in a sysem and also gives us a means for determining the stability of equilibrium states, and, in general, it forms an important link between reversible and irreversible processes.

The second law is most easily discussed in terms of an ideal heat engine first introduced by Carnot. The construction of all heat engines is based on the observation that if heat is allowed to flow from a high temperature to a lower temperature, part of the heat can be turned into work. Carnot observed that temperature differences can disappear spontaneously without producing work. Therefore, he proposed a very simple heat engine consisting only of reversible steps, thereby eliminating wasteful heat flows. The Carnot engine consists of the four steps shown in Fig. 2.2. These include:

(a) Isothermal (constant temperature) absorption of heat ΔQ_{12} from a reservoir at a high temperature τ_h (we use Δ to indicate a finite rather than an infinitesimal amount of heat) (the process $1 \rightarrow 2$).

(b) Adiabatic (constant heat content) change in temperature from τ_h to the lower value τ_c (the process $2 \rightarrow 3$).

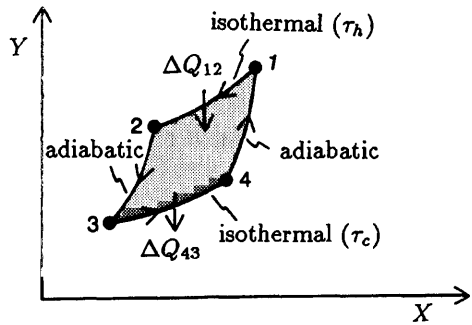


Fig. 2.2. A Carnot engine which runs on a substance with state variables, X and Y. The processes $1 \rightarrow 2$ and $3 \rightarrow 4$ occur isothermally at temperatures τ_h and τ_c, respectively. The processes $2 \rightarrow 3$ and $4 \rightarrow 1$ occur adiabatically. The heat absorbed is ΔQ_{12} and the heat ejected is ΔQ_{43}. The shaded area is equal to the work done during the cycle. The whole process takes place reversibly.

(**c**) Isothermal expulsion of heat ΔQ_{43} into a reservoir at temperature τ_c (the process $3 \rightarrow 4$).

(**d**) Adiabatic return to the initial state at temperature τ_h (the process $4 \rightarrow 1$).

The work done by the engine during one complete cycle can be found by integrating the differential element of work $Y\,dX$ about the entire cycle. We see that the total work ΔW_{tot} done by the engine is given by the shaded area in Fig. 2.2.

The total efficiency η of the heat engine is given by the ratio of the work done to heat absorbed:

$$\eta = \frac{\Delta W_{\text{tot}}}{\Delta Q_{12}} \tag{2.24}$$

Since the internal energy U is state variable and independent of path, the total change ΔU_{tot} for one complete cycle must be zero. The first law then enables us to write

$$\Delta U_{\text{tot}} = \Delta Q_{\text{tot}} - \Delta W_{\text{tot}} = 0 \tag{2.25}$$

and thus

$$\Delta W_{\text{tot}} = \Delta Q_{\text{tot}} = \Delta Q_{12} + \Delta Q_{34} = \Delta Q_{12} - \Delta Q_{43}. \tag{2.26}$$

If we combine Eqs. (2.24) and (2.26), we can write the efficiency in the form

$$\eta = 1 - \frac{\Delta Q_{43}}{\Delta Q_{12}} \tag{2.27}$$

A 100% efficient engine is one which converts all the heat it absorbs into work. However, as we shall see, no such engine can exist in nature.

The great beauty and utility of the Carnot engine lies in the fact that it is the most efficient of all heat engines operating between two heat reservoirs, each at a (different) fixed temperature. This is a consequence of the second law. To prove this let us consider two heat engines, A and B (cf. Fig. 2.3), which run between the same two reservoirs τ_h and τ_c. Let us assume that engine A is a heat engine with irreversible elements and B is a reversible Carnot engine. We will adjust the mechanical variables X and Y so that during one cycle both engines perform the same amount of work (note that X_{A} and Y_{A} need not be the same mechanical variables as X_{B} and Y_{B}):

$$\Delta W_{\text{tot}}^{\text{A}} = \Delta W_{\text{tot}}^{\text{B}} \equiv \Delta W. \tag{2.28}$$

Let us now assume that engine A is more efficient than engine B:

$$\eta_{\text{A}} > \eta_{\text{B}} \tag{2.29}$$

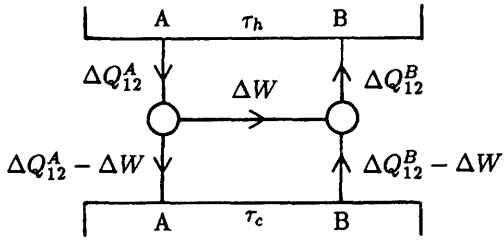


Fig. 2.3. Two heat engines, *A* and *B*, work together. Engine *B* acts as a heat pump while engine *A* acts as a heat engine with irreversible elements. Engine *A* cannot have a greater efficiency than engine *B* without violating the second law.

and thus

$$\frac{\Delta W}{\Delta Q_{12}^{\mathrm{A}}} > \frac{\Delta W}{\Delta Q_{12}^{\mathrm{B}}} \tag{2.30}$$

or

$$\Delta Q_{12}^{\mathrm{B}} > \Delta Q_{12}^{\mathrm{A}}. \tag{2.31}$$

We can use the work produced by engine A to drive the Carnot engine as a refrigerator. Since the Carnot engine is reversible, it will have the same efficiency whether it runs as a heat engine or as a heat pump. The work, ΔW, produced by A will be used to enable the Carnot engine B to pump heat from the low-temperature reservoir to the high-temperature reservoir. The net heat extracted from reservoir τ_c and delivered to reservoir τ_h is

$$\Delta Q_{12}^{\mathrm{B}} - \Delta W - (\Delta Q_{12}^{\mathrm{A}} - \Delta W) = \Delta Q_{12}^{\mathrm{B}} - \Delta Q_{12}^{\mathrm{A}}. \tag{2.32}$$

If engine A is more efficient than engine B, then the combined system has caused heat to flow from low temperature to high temperature without any work being expended by an outside source. This violates the second law and therefore engine A cannot be more efficient than the Carnot engine. If we now assume that both engines are Carnot engines, we can show, by similar arguments, that they both must have the same efficiency. Thus, we reach the following conclusion: *No engine can be more efficient than a Carnot engine, and all Carnot engines have the same efficiency.*

From the above discussion, we see that the efficiency of a Carnot engine is completely independent of the choice of mechanical variables X and Y and therefore can only depend on the temperatures τ_h and τ_c of the two reservoirs. This enables us to define an absolute temperature scale. From Eq. (2.27) we see that

$$\frac{\Delta Q_{43}}{\Delta Q_{12}} = f(\tau_h, \tau_c), \tag{2.33}$$

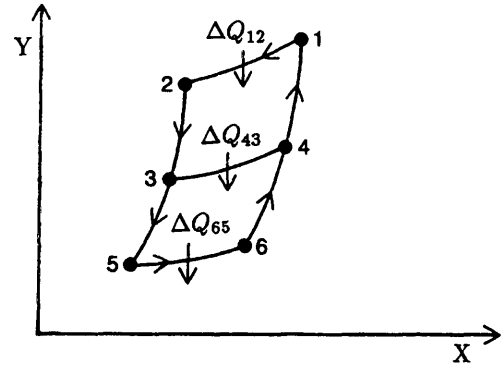


Fig. 2.4. Two Carnot engines running between three reservoirs with temperatures $\tau_h > \tau > \tau_c$ have the same overall efficiency as one Carnot engine running between reservoirs with temperatures $\tau_h > \tau c$.

where $f(\tau_h, \tau_c)$ is some function of temperatures τ_h and τ_c. The function $f(\tau_h, \tau_c)$ has a very special form. Let us consider two heat engines running between three reservoirs $\tau_h > \tau' > \tau_c$ (cf. Fig. 2.4). We can write

$$\frac{\Delta Q_{43}}{\Delta Q_{12}} = f(\tau_h, \tau'), \tag{2.34}$$

$$\frac{\Delta Q_{65}}{\Delta Q_{43}} = f(\tau', \tau_c), \tag{2.35}$$

and

$$\frac{\Delta Q_{65}}{\Delta Q_{12}} = f(\tau_h, \tau_c), \tag{2.36}$$

so that

$$f(\tau_h, \tau_c) = f(\tau_h, \tau')f(\tau', \tau_c). \tag{2.37}$$

Thus, $f(\tau_h, \tau_c) = g(\tau_h)g^{-1}(\tau_c)$ where $g(\tau)$ is some function of temperature.

One of the first temperature scales proposed but not widely used is due to W. Thomson (Lord Kelvin) and is called the *Thomson scale* [9]. It has the form

$$\frac{\Delta Q_{43}}{\Delta Q_{12}} = \frac{e^{\tau_c^\circ}}{e^{\tau_h^\circ}} \tag{2.38}$$

The Thomson scale is defined so that a given unit of heat ΔQ_{12} flowing between temperatures $\tau^\circ \to (\tau^\circ - 1)$ always produces the same amount of work, regardless of the value of τ°.

A more practical scale, the Kelvin scale, was also introduced by Thomson. It is defined as

$$\frac{\Delta Q_{43}}{\Delta Q_{12}} = \frac{\tau_c}{\tau_h}. \tag{2.39}$$

As we will see below, the Kelvin scale is identical to the temperature used in the ideal gas equation of state and is the temperature measured by a gas thermometer. For this reason, the Kelvin scale is the internationally accepted temperature scale at the present time.

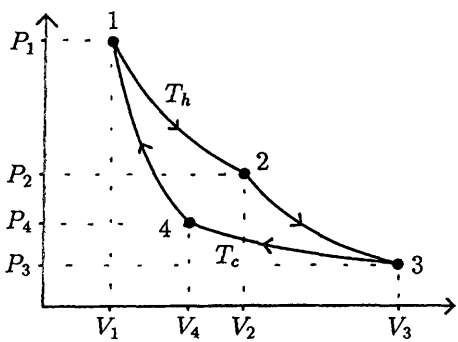
The units of degrees Kelvin are the same as degrees Celsius. The ice point of water at atmospheric pressure is defined as 0 °C, and the boiling point is defined as 100 °C. The triple point of water is 0.01 °C. To obtain a relation between degrees Kelvin and degrees Celsius, we can measure pressure of a real *dilute* gas as a function of temperature at fixed volume. It is found experimentally that the pressure varies linearly with temperature and goes to zero at $t_c = -273.15\,^{\circ}\mathrm{C}$. Thus, from the ideal gas law, we see that degrees Kelvin, T, are related to degrees Celsius, t_c, by the equation

$$T = (t_c + 273.15). \tag{2.40}$$

The triple point of water is fixed at $T = 273.16$ K.

In Exercise 2.2, we compute the efficiency of a Carnot engine which uses an ideal gas as an operating substance. However, Carnot engines can be constructed using any of a variety of substances (some examples are left as problems). Regardless of the operating substance, all Carnot engines have the same efficiency.

■ **Exercise 2.2.** Compute the efficiency of a Carnot cycle (shown in the figure below) which uses a monatomic ideal gas as an operating substance.



Answer: The equation of state of an ideal gas is $PV = nRT$, where $P = -Y$ is the pressure and $V = X$ is the volume, T is the temperature in Kelvins, and n is the number of moles. The internal energy is $U = (3/2)nRT$. The Carnot

cycle for an ideal gas is shown in the figure below. The part $1 \rightarrow 2$ is an isothermal expansion of the system, and the path $3 \rightarrow 4$ is an isothermal contraction. It is clear from the equation of state that the temperature, T_h, of path $1 \rightarrow 2$ is higher than the temperature, T_c, of path $3 \rightarrow 4$. The path $2 \rightarrow 3$ is an adiabatic expansion of the system, and the path $4 \rightarrow 1$ is an adiabatic contraction. We shall assume that n is constant during each cycle.

Let us first consider the isothermal paths. Since the temperature is constant along these paths, $dU = \frac{3}{2}nRdT = 0$. Thus, along the path $1 \rightarrow 2, \not{d}Q = \not{d}W = nRT_h(dV/V)$. The heat absorbed along the path $1 \rightarrow 2$ is

$$\Delta Q_{12} = nRT_h \int_{V_1}^{V_2} \frac{dV}{V} = nRT_h \ln\left(\frac{V_2}{V_1}\right). \tag{1}$$

The heat absorbed along the path $3 \rightarrow 4$ is

$$\Delta Q_{34} = nRT_c \ln\left(\frac{V_4}{V_3}\right). \tag{2}$$

Since $V_2 > V_1, \Delta Q_{12} > 0$ and heat is absorbed along the path $1 \rightarrow 2$. Since $V_3 > V_4$, $\Delta Q_{34} < 0$ and heat is ejected along the path $3 \rightarrow 4$.

Let us next consider the adiabatic paths. Along the adiabatic path, $\not{d}Q = 0 = dU + PdV = (3/2)nRdT + PdV$. If we make use of the equation of state, we find $(3/2)(dT/T) = -(dV/V)$. We now integrate to find $T^{3/2}V =$ constant for an adiabatic process. Thus, along the paths $2 \rightarrow 3$ and $4 \rightarrow 1$, respectively, we have

$$T_c V_3^{2/3} = T_h V_2^{2/3} \quad \text{and} \quad T_c V_4^{2/3} = T_h V_1^{2/3}. \tag{3}$$

For the entire cycle, we can write $\Delta U_{\text{tot}} = \Delta Q_{\text{tot}} - \Delta W_{\text{tot}} = 0$. Thus $\Delta W_{\text{tot}} = \Delta Q_{\text{tot}} = \Delta Q_{12} + \Delta Q_{34}$. The efficiency of the Carnot cycle is

$$\eta = \frac{\Delta W_{\text{tot}}}{\Delta Q_{12}} = 1 + \frac{\Delta Q_{34}}{\Delta Q_{12}} = 1 - \frac{T_c}{T_h}\frac{\ln(V_3/V_4)}{\ln(V_2/V_1)} = 1 - \frac{T_c}{T_h}, \tag{4}$$

since from Eq. (3) we have

$$\frac{V_3}{V_4} = \frac{V_2}{V_1}.$$

We can use the Carnot engine to define a new state variable called the *entropy*. All Carnot engines have an efficiency

$$\eta = 1 - \frac{\Delta Q_{43}}{\Delta Q_{12}} = 1 - \frac{T_c}{T_h}. \tag{2.41}$$

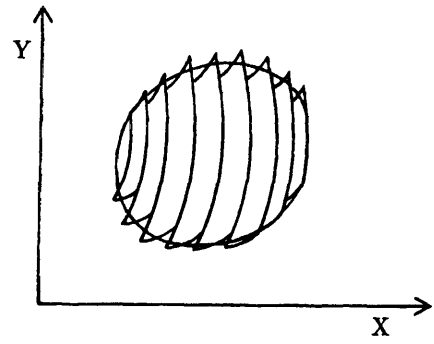


Fig. 2.5. An arbitrary reversible heat engine is composed of many infinitesimal Carnot engines. The area enclosed by the curve is equal to the work done by the heat engine.

(cf. Exercise 2.2) regardless of operating substance. Using Eq. (2.41), we can write the following relation for a Carnot cycle:

$$\frac{\Delta Q_{12}}{T_h} + \frac{\Delta Q_{34}}{T_c} = 0. \tag{2.42}$$

(note the change in indices in ΔQ_{34}). Equation (2.42) can be generalized to the case of an arbitrary *reversible* heat engine because we can consider such an engine as being composed of a sum of many infinitesimal Carnot cycles (cf. Fig. 2.5). Thus, for an arbitrary reversible heat engine we have

$$\oint \frac{đQ}{T} = 0. \tag{2.43}$$

The quantity

$$dS \equiv \frac{đQ}{T} \tag{2.44}$$

is an exact differential and the quantity S, called the *entropy*, may be considered a new state variable since the integral of dS about a closed path gives zero.

No heat engine can be more efficient than a Carnot engine. Thus, an engine which runs between the same two reservoirs but contains spontaneous or irreversible processes in some part of the cycle will have a lower efficiency, and we can write

$$\frac{\Delta Q_{43}}{\Delta Q_{12}} > \frac{T_c}{T_h} \tag{2.45}$$

and

$$\frac{\Delta Q_{12}}{T_h} - \frac{\Delta Q_{43}}{T_c} < 0. \tag{2.46}$$

For an arbitrary heat engine which contains an irreversible part, Eq. (2.46) gives

the very important relation

$$\oint \frac{đQ}{T} < 0. \tag{2.47}$$

For an irreversible process, $đQ/T$ can no longer be considered an exact differential.

A system may evolve between two thermodynamic states either by a reversible path or by a spontaneous, irreversible path. For any process, reversible or irreversible, the entropy change depends only on the initial and final thermodynamic states of the system, since the entropy is a state variable. If the system evolves between the initial and final states via a reversible path, then we can compute the entropy change along that path. However, if the system evolves between the initial and final states via an irreversible path, then we must construct a hypothetical reversible path between the initial and final states in order to use the equations of thermodynamics to compute the entropy change during the spontaneous process. For the irreversible path, the heat absorbed by the system will be less than that along the reversible path [cf. Eqs. (2.45)–(2.47)]. Therefore, $\int_{\text{irrev}} đQ/T < \int_{\text{rev}} đQ/T$. This means that *for an irreversible process, $\int_{\text{irrev}} đQ/T$ does not contain all contributions to the entropy change.* Some of it comes from the disorder created by spontaneity. This result is usually written in the form

$$dS = \frac{đQ}{T} + d_iS, \tag{2.48}$$

where d_iS denotes the *entropy production* due to spontaneous processes. For a reversible process, $d_iS = 0$ and $dS = (1/T)đQ$ so the entropy change is entirely due to a flow of heat into or out of the system. For a spontaneous (irreversible)) process, $d_iS > 0$.

For an isolated system we have $đQ = 0$, and we obtain the important relation

$$dS = d_iS \geq 0, \tag{2.49}$$

where the equality holds for a reversible process and the inequality holds for a spontaneous or irreversible process. Since the equilibrium state is, by definition, a state which is stable against spontaneous changes, Eq. (2.49) tells us that the equilibrium state is a state of maximum entropy. As we shall see, this fact gives an important criterion for determining the stability of the equilibrium state for an isolated system.

2.D.4. Third Law: The Difference in Entropy Between States Connected by a Reversible Process Goes to Zero in the Limit $T \to 0$ K [9–11]

The third law was first proposed by Nernst in 1906 on the basis of experimental observations and is a consequence of quantum mechanics. Roughly speaking, a

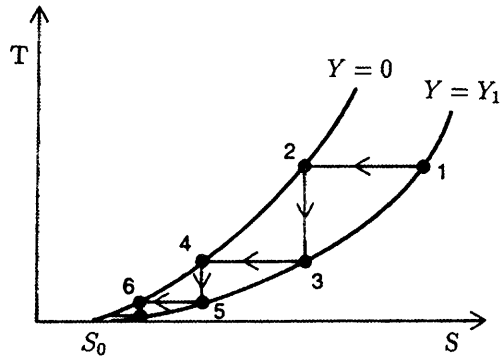


Fig. 2.6. The fact that curves $Y = 0$ and $Y = Y_1$ must approach the same point (the third law) makes it impossible to reach absolute zero by a finite number of reversible steps.

system at zero temperature drops into its lowest quantum state and in this sense becomes completely ordered. If entropy can be thought of as a measure of disorder, then at $T = 0$ K it must take its lowest value.

An alternative statement of the third law, and a direct consequence of the above statement, is, *It is impossible to reach absolute zero in a finite number of steps if a reversible process is used.* This alternative statement is easily demonstrated by means of a plot in the S–T plane. In Fig. 2.6 we have plotted the curves as a function of S and T for two states $Y = 0$ and $Y = Y_1$ for an arbitrary system. (A specific example might be a paramagnetic salt with $Y = H$.) We can cool the system by alternating between the two states, adiabatically and isothermally. From Eqs. (2.5) and (2.6), we write

$$\left(\frac{\partial T}{\partial Y}\right)_{S,N} = -\left(\frac{\partial T}{\partial S}\right)_{Y,N} \cdot \left(\frac{\partial S}{\partial Y}\right)_{T,N}. \tag{2.50}$$

As we shall show in Section 2.H, thermal stability requires that $(\partial S/\partial T)_Y \geq 0$. Equation (2.50) tells us that if T decreases as Y increases isentropically, then S must decrease as Y decreases isothermally, as shown in Fig. 2.6. For the process $1 \rightarrow 2$ we change from state $Y = Y_1$ to state $Y = 0$ isothermally, thus squeezing out heat, and the entropy decreases. For process $2 \rightarrow 3$, we increase Y adiabatically from $Y = 0$ to $Y = Y_1$ and thus decrease the temperature. We can repeat these processes as many times as we wish. However, as we approach $T = 0$ K, we know by the third law that the two curves must approach the same point and must therefore begin to approach each other, thus making it impossible to reach $T = 0$ K in a finite number of steps.

Another consequence of the third law is that certain derivatives of the entropy must approach zero as $T \rightarrow 0$ K. Let us consider a process at $T = 0$ K such that $Y \rightarrow Y + dY$ and $X \rightarrow X + dX$. Then the change in entropy if Y, T, and

N are chosen as independent variables is (assume $dN = 0$)

$$dS = \left(\frac{\partial S}{\partial Y}\right)_{N,T=0} dY, \tag{2.51}$$

or if X, T, and N are chosen as independent we obtain

$$dS = \left(\frac{\partial S}{\partial X}\right)_{N,T=0} dX. \tag{2.52}$$

Thus, if the states $(Y, T = 0\,\mathrm{K})$ and $(Y + dY, T = 0\,\mathrm{K})$ or the states $(X, T = 0\,\mathrm{K})$ and $(X + dX, T = 0\,\mathrm{K})$ are connected by a reversible process, we must have $dS = 0$ (third law) and therefore

$$\left(\frac{\partial S}{\partial Y}\right)_{N,T=0} = 0 \tag{2.53}$$

and

$$\left(\frac{\partial S}{\partial X}\right)_{N,T=0} = 0 \tag{2.54}$$

Equations (2.53) and (2.54) appear to be satisfied by real substances.

2.E. FUNDAMENTAL EQUATION OF THERMODYNAMICS [10]

The entropy plays a central role in both equilibrium and nonequilibrium thermodynamics. It can be thought of as a measure of the disorder in a system. As we shall see in Chapter 7, entropy is obtained microscopically by state counting. The entropy of an isolated system is proportional to the logarithm of the number of states available to the system. Thus, for example, a quantum system in a definite quantum state (pure state) has zero entropy. However, if the same system has finite probability of being in any of a number of quantum states, its entropy will be nonzero and may be quite large.

The entropy is an extensive, additive quantity. If a system is composed of a number of independent subsystems, then the entropy of the whole system will be the sum of the entropies of the subsystems. This additive property of the entropy is expressed mathematically by the relation

$$S(\lambda U, \lambda X, \{\lambda N_i\}) = \lambda S(U, X, \{N_i\}). \tag{2.55}$$

That is, the entropy is a first-order homogeneous function of the extensive state variables of the system. If we increase *all* the extensive state variables by a factor λ, then the entropy must also increase by a factor λ.

Differential changes in the entropy are related to differential changes in the extensive state variables through the combined first and second laws of thermodynamics:

$$TdS \geq \not{d}Q = dU - YdX - \sum_j \mu_j' dN_j. \tag{2.56}$$

The equality holds if changes in the thermodynamic state are reversible. The inequality holds if they are spontaneous or irreversible. Equations (2.55) and (2.56) now enable us to define the Fundamental Equation of thermodynamics. Let us take the derivative of λS with respect to λ:

$$\begin{aligned}\frac{d}{d\lambda}(\lambda S) = &\left(\frac{\partial S}{\partial \lambda U}\right)_{X,\{N_j\}} \frac{d}{d\lambda}(\lambda U) + \left(\frac{\partial S}{\partial \lambda X}\right)_{U,\{N_j\}} \frac{d}{d\lambda}(\lambda X) \\ &+ \sum_j \left(\frac{\partial S}{\partial \lambda N_j}\right)_{U,X,\{N_{i\neq j}\}} \frac{d(\lambda N_j)}{d\lambda}.\end{aligned} \tag{2.57}$$

However, from Eq. (2.56) we see that

$$\left(\frac{\partial S}{\partial U}\right)_{X,\{N_j\}} = \frac{1}{T}, \tag{2.58}$$

$$\left(\frac{\partial S}{\partial X}\right)_{U,\{N_j\}} = -\frac{Y}{T}, \tag{2.59}$$

and

$$\left(\frac{\partial S}{\partial N_j}\right)_{U,X,\{N_{i\neq j}\}} = -\frac{\mu_j'}{T}. \tag{2.60}$$

Equations (2.58)–(2.60) are called the thermal, mechanical, and chemical *equations of state*, respectively. The mechanical equation of state, Eq. (2.59), is the one most commonly seen and is the one which is described in Section 2.C. If we now combine Eqs (2.57)–(2.60), we obtain

$$TS = U - XY - \sum_j \mu_j' N_j. \tag{2.61}$$

Equation (2.61) is called the *Fundamental Equation of thermodynamics* (it is also known as *Euler's equation*) because it contains all possible thermodynamic information about the thermodynamic system. If we take the differential of Eq. (2.61) and subtract Eq. (2.56) (we will take the reversible case), we obtain

another important equation,

$$SdT + XdY + \sum_j N_j d\mu'_j = 0, \tag{2.62}$$

which is called the *Gibbs–Duhem* equation. The Gibbs–Duhem equation relates differentials of intensive state variables.

For a monatomic system, the above equations simplify somewhat if we work with densities. As a change of pace, let us work with molar densities. For single component system the Fundamental Equation can be written $TS = U - YX - \mu n$ and the combined first and second laws (for reversible processes) can be written $TdS = dU - YdX - \mu dn$. Let us now introduce the molar entropy, $s = S/n$, the molar density, $x = X/n$, and the molar internal energy, $u = U/n$. Then the Fundamental Equation becomes

$$Ts = u - Yx - \mu, \tag{2.63}$$

and the combined first and second laws become (for reversible processes)

$$Tds = du - Ydx. \tag{2.64}$$

Therefore, $(\partial s/\partial u)_x = 1/T$ and $(\partial s/\partial x)_u = -Y/T$. The Gibbs–Duhem equation is simply

$$d\mu = -sdT - xdY, \tag{2.65}$$

and therefore the chemical potential has the form, $\mu = \mu(T, Y)$, and is a function only of the intensive variables, T and Y. Note also that $s = -(\partial\mu/\partial T)_Y$ and $x = -(\partial\mu/\partial Y)_T$. In Exercise 2.3, we use these equations to write the Fundamental Equation for an ideal monatomic gas.

■ **EXERCISE 2.3.** The entropy of n moles of a monatomic ideal gas is $S = (5/2)nR + nR\ln[(V/V_0)(n_0/n)(T/T_0)^{3/2}]$, where V_0, n_0, and T_0 are constants (this is called the *Sackur–Tetrode equation*). The mechanical equation of state is $PV = nRT$. (a) Compute the internal energy. (b) Compute the chemical potential. (c) Write the Fundamental Equation for an ideal monatomic ideal gas and show that it is a first-order homogeneous function of the extensive state variables.

Answer: It is easiest to work in terms of densities. The molar entropy can be written $s = (5/2)R + R\ln[(v/v_0)(T/T_0)^{3/2}]$ ($v = V/n$ is the molar volume), and the mechanical equation of state is $Pv = RT$.

(a) The combined first and second law gives $du = Tds - Pdv$. If we further note that $ds = (\partial s/\partial T)_v dT + (\partial s/\partial v)_T dv$, then

$$du = T\left(\frac{\partial s}{\partial T}\right)_v dT + \left[T\left(\frac{\partial s}{\partial v}\right)_T - P\right]dv = \frac{3}{2}RdT, \tag{1}$$

since $(\partial s/\partial T)_v = (3R/2T)$ and $(\partial s/\partial v)_T = R/v$. Therefore, the molar internal energy is $u = \frac{3}{2}RT + u_0$ where u_0 is a constant, and the total internal energy is $U = nu = \frac{3}{2}nRT + U_0$, where $U_0 = nu_0$.

(b) Let us rewrite the molar entropy in terms of pressure instead of molar volume. From the mechanical equation of state, $v = (RT/P)$ and $v_0 = (RT_0/P_0)$. Therefore, $s = \frac{5}{2}R + R\ln[(P_0/P)(T/T_0)^{5/2}]$. From the Gibbs–Duhem equation, $(\partial\mu/\partial T)_P = -s = -(\frac{5}{2}R + R\ln[(P_0/P)(T/T_0)^{5/2}])$ and $(\partial\mu/\partial P)_T = v = RT/P$. If we integrate these we obtain the following expression for the molar chemical potential:

$$\mu = -RT\ln\left[\frac{P_0}{P}\left(\frac{T}{T_0}\right)^{5/2}\right]. \tag{2}$$

(c) Let us rewrite the entropy in terms of the internal energy, volume, and number of moles. We obtain

$$S = \frac{5}{2}nR + nR\ln\left[\frac{V}{V_0}\left(\frac{n_0}{n}\right)^{5/2}\left(\frac{U}{U_0}\right)^{3/2}\right]. \tag{3}$$

Equation (3) is the Fundamental Equation for an ideal monatomic gas. It clearly is a first-order homogeneous function of the extensive variables.

It is interesting to note that this classical ideal gas does not obey the third law of thermodynamics and cannot be used to describe systems at very low temperatures. At very low temperatures we must include quantum corrections to the ideal gas equation of state.

2.F. THERMODYNAMIC POTENTIALS [11]

In conservative mechanical systems, such as a spring or a mass raised in a gravitational field, work can be stored in the form of potential energy and subsequently retrieved. *Under certain circumstances* the same is true for thermodynamic systems. We can store energy in a thermodynamic system by doing work on it through a reversible process, and we can eventually retrieve that energy in the form of work. The energy which is stored and retrievable in the form of work is called the *free energy*. There are as many different forms of free energy in a thermodynamic system as there are combinations of

constraints. In this section, we shall discuss the five most common ones: internal energy, U; the enthalpy, H; the Helmholtz free energy, A; the Gibbs free energy, G; and the grand potential, Ω. These quantities play a role analogous to that of the potential energy in a spring, and for that reason they are also called the *thermodynamic potentials*.

2.F.1. Internal Energy

From Eq. (2.61) the fundamental equation for the internal energy can be written

$$U = ST + YX + \sum_j \mu_j' N_j, \tag{2.66}$$

where T, Y, and μ_j' are considered to be functions of S, X, and $\{N_j\}$ [cf. Eqs. (2.58)–(2.60)]. From Eq. (2.56), the total differential of the internal energy can be written

$$dU \leq TdS + YdX + \sum_j \mu_j' dN_j. \tag{2.67}$$

The equality holds for reversible changes, and the inequality holds for changes which are spontaneous. From Eq. (2.67) we see that

$$T = \left(\frac{\partial U}{\partial S}\right)_{X,\{N_j\}}, \tag{2.68}$$

$$Y = \left(\frac{\partial U}{\partial X}\right)_{S,\{N_j\}}, \tag{2.69}$$

and

$$\mu_j' = \left(\frac{\partial U}{\partial N_j}\right)_{S,X,\{N_{l\neq j}\}}. \tag{2.70}$$

We can use the fact that dU is an exact differential to find relations between derivatives of the intensive variables, T, Y, and μ_j'. From Eq. (2.4) we know, for example, that

$$\left[\frac{\partial}{\partial X}\left(\frac{\partial U}{\partial S}\right)_{X,\{N_j\}}\right]_{S,\{N_j\}} = \left[\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial X}\right)_{S,\{N_j\}}\right]_{X,\{N_j\}}. \tag{2.71}$$

From Eqs. (2.68), (2.69), and (2.71), we obtain

$$\left(\frac{\partial T}{\partial X}\right)_{S,\{N_j\}} = \left(\frac{\partial Y}{\partial S}\right)_{X,\{N_j\}}. \tag{2.72}$$

$(i+1)$ additional relations like Eq. (2.72) exist and lead to the identities

$$\left(\frac{\partial T}{\partial N_j}\right)_{S,X,\{N_{l\neq j}\}} = \left(\frac{\partial \mu_j'}{\partial S}\right)_{X,\{N_j\}}, \tag{2.73}$$

$$\left(\frac{\partial Y}{\partial N_j}\right)_{S,X,\{N_{l\neq j}\}} = \left(\frac{\partial \mu_j'}{\partial X}\right)_{S,\{N_j\}}, \tag{2.74}$$

and

$$\left(\frac{\partial \mu_j'}{\partial N_i}\right)_{S,X,\{N_{l\neq i}\}} = \left(\frac{\partial \mu_i'}{\partial N_j}\right)_{S,X,\{N_{l\neq j}\}}. \tag{2.75}$$

Equations (2.72)–(2.75) are extremely important both theoretically and experimentally because they provide a relation between rates of change of seemingly diverse quantities. They are called *Maxwell relations.*

For a substance with a single type of particle, the above equations simplify if we work with densities. Let $u = U/n$ denote the molar internal energy. Then the Fundamental Equation can be written $u = Ts + Yx + \mu$, where s is the molar entropy and x is a molar density. The combined first and second laws (for reversible processes) are $du = Tds + Ydx$. Therefore we obtain the identities $(\partial u/\partial s)_x = T$ and $(\partial u/\partial x)_s = Y$. Maxwell relations reduce to $(\partial T/\partial x)_s = (\partial Y/\partial s)_x$.

The internal energy is a thermodynamic potential or free energy because for processes carried out reversibly in an isolated, closed system at fixed X and $\{N_j\}$, the change in internal energy is equal to the maximum amount of work that can be done on or by the system. As a specific example, let us consider a *PVT* system (cf. Fig. 2.7). We shall enclose a gas in an insulated box with fixed total volume and divide it into two parts by a movable conducting wall. We can do work on the gas or have the gas do work by attaching a mass in a gravitational field to the partition via a pulley and insulated string. To do work reversibly, we assume that the mass is composed of infinitesimal pieces which can be added or removed one by one. If $P_1A + mg > P_2A$, then work is done on the gas by the mass, and if $P_1A + mg < P_2A$, the gas does work on the mass. The first law can be written

$$\Delta U = \Delta Q - \Delta W, \tag{2.76}$$

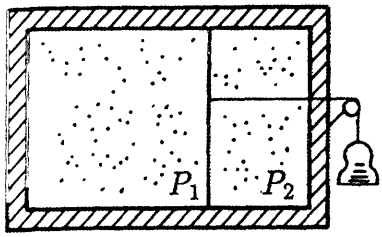


Fig. 2.7. For a reversible process in a closed, insulated box of fixed size ($\Delta S = 0$, $\Delta V = 0$, $\Delta N_j = 0$), the work done in lifting the weight will be equal to the change in the internal energy, $(\Delta U)_{S,V,N} = -\Delta W_{\text{free}}$.

where ΔU is the change in total internal energy of the gas, ΔQ is the heat flow through the walls, and ΔW can be divided into work done due to change in size of the box, $\int P dV$, and work done by the gas in raising the weight, ΔW_{free}:

$$\Delta W = \int P dV + \Delta W_{\text{free}}. \tag{2.77}$$

For a reversible process, $\Delta Q = \int T dS$. For the reversible process pictured in Fig. 2.7, $\Delta Q = 0, \Delta V = 0$, and $\Delta N_j = 0$ (if no chemical reactions take place). Therefore,

$$(\Delta U)_{S,V,\{N_j\}} = -\Delta W_{\text{free}}. \tag{2.78}$$

Thus, *for a reversible process at constant S, V,* and N_j, *work can be stored in the form of internal energy and can be recovered completely.* Under these conditions, internal energy behaves like a potential energy.

For a spontaneous process, work can only be done at constant S, V, and $\{N_i\}$ if we allow heat to leak through the walls. The first and second laws for a spontaneous process take the form

$$\int dU = \Delta U < \int T\, dS - \int P\, dV - \Delta W_{\text{free}} + \sum_j \int \mu_j' dN_j, \tag{2.79}$$

where the integrals are taken over a reversible path between initial and final states and not the actual spontaneous path. We can do work on the gas spontaneously by allowing the mass to drop very fast. Then part of the work goes into stirring up the gas. In order for the process to occur at constant entropy, some heat must leak out since $\Delta Q < \int T\, dS = 0$. Thus, for a spontaneous process

$$(\Delta U)_{S,V,\{N_j\}} < -\Delta W_{\text{free}}. \tag{2.80}$$

Not all work is changed to internal energy and is retrievable. Some is wasted in stirring the gas. (Note that for this process the entropy of the universe has increased since heat has been added to the surrounding medium.)

For processes involving mechanical variables Y and X we can write Eqs. (2.78) and (2.80) in the form

$$(\Delta U)_{S,X,\{N_j\}} \leq (-\Delta W_{\text{free}}), \tag{2.81}$$

where ΔW_{free} is any work done by the system other than that required to change X. *For a reversible process at constant S, X, and $\{N_j\}$, work can be stored as internal energy and can be recovered completely.*

If a process takes place in which no work is done on or by the system, then Eq. (2.81) becomes

$$(\Delta U)_{S,X,\{N_j\}} \leq 0 \tag{2.82}$$

and the internal energy either does not change (reversible process) or decreases (spontaneous process). Since a system in equilibrium cannot change its state spontaneously, we see that *an equilibrium state at fixed S, X,* and $\{N_j\}$ *is a state of minimum internal energy.*

2.F.2. Enthalpy

The internal energy is the convenient potential to use for processes carried out at constant X, S, and $\{N_j\}$. However, it often happens that we wish to study the thermodynamics of processes which occur at constant S, Y, and $\{N_j\}$. Then it is more convenient to use the enthalpy.

The enthalpy, H, is useful for systems which are thermally isolated and closed but mechanically coupled to the outside world. It is obtained by adding to the internal energy an additional energy due to the mechanical coupling:

$$H \equiv U - XY = ST + \sum_j \mu_j' N_j. \tag{2.83}$$

The addition of the term $-XY$ has the effect of changing the independent variables from (S, X, N_j) to (S, Y, N_j) and is called a *Legendre transformation.* If we take the differential of Eq. (2.83) and combine it with Eq. (2.67), we obtain

$$dH \leq T\,dS - X\,dY + \sum_j \mu_j' dN_j \tag{2.84}$$

and, therefore,

$$T = \left(\frac{\partial H}{\partial S}\right)_{Y,\{N_j\}}, \tag{2.85}$$

$$X = -\left(\frac{\partial H}{\partial Y}\right)_{S,\{N_j\}}, \tag{2.86}$$

and

$$\mu_j' = \left(\frac{\partial H}{\partial N_j}\right)_{S,Y,\{N_{l\neq j}\}}. \tag{2.87}$$

Since dH is an exact differential, we can use Eq. (2.4) to obtain a new set of Maxwell relations:

$$\left(\frac{\partial T}{\partial Y}\right)_{S,\{N_j\}} = -\left(\frac{\partial X}{\partial S}\right)_{Y,\{N_j\}}, \tag{2.88}$$

$$\left(\frac{\partial T}{\partial N_j}\right)_{S,Y,\{N_{l\neq j}\}} = \left(\frac{\partial \mu_j'}{\partial S}\right)_{Y,\{N_j\}}, \tag{2.89}$$

$$\left(\frac{\partial X}{\partial N_j}\right)_{S,Y,\{N_{l\neq j}\}} = -\left(\frac{\partial \mu_j'}{\partial Y}\right)_{S,\{N_j\}}, \tag{2.90}$$

and

$$\left(\frac{\partial \mu_j'}{\partial N_i}\right)_{S,Y,\{N_{l\neq i}\}} = \left(\frac{\partial \mu_i'}{\partial N_j}\right)_{S,Y,\{N_{l\neq j}\}}, \tag{2.91}$$

which relate seemingly diverse partial derivatives.

For a substance with a single type of molecule, Eqs. (2.84)–(2.91) become particularly simple if we work with densities. Let $h = H/n$ denote the molar enthalpy. Then the fundamental equation for the molar enthalpy can be written $h = u - xY = sT + \mu$. The exact differential of the molar enthalpy is $dh = Tds - xdY$ (for reversible processes), which yields the identities $(\partial h/\partial s)_Y = T$ and $(\partial h/\partial Y)_s = x$. Maxwell's relations reduce to $(\partial T/\partial Y)_s = -(\partial x/\partial s)_Y$. In Exercise 2.4, we compute the enthalpy for a monatomic ideal gas in terms of its natural variables.

■ **EXERCISE 2.4.** Compute the enthalpy for n moles of a monatomic ideal gas and express it in terms of its natural variables. The mechanical equation of state is $PV = nRT$ and the entropy is $S = \frac{5}{2}nR + nR\ln[(V/V_0)(n_0/n)(T/T_0)^{3/2}]$.

Answer: Let us write the molar entropy in terms of temperature and pressure. It is $s = \frac{5}{2}R + R\ln[(P_0/P)(T/T_0)^{5/2}]$. Also note that when $P = P_0$ and $T = T_0$, $s = s_0 = \frac{5}{2}R$. Now since $dh = Tds + vdP$ we have

$$\left(\frac{\partial h}{\partial s}\right)_P = T = T_0\left(\frac{P}{P_0}\right)^{2/5} e^{(s-s_0)/s_0} \tag{1}$$

and

$$\left(\frac{\partial h}{\partial P}\right)_s = +\frac{RT}{P}. \tag{2}$$

If we integrate, we find $h = \frac{5}{2}RT_0(P/P_0)^{2/5}e^{(s-s_0)/s_0} = \frac{5}{2}RT$. In terms of temperature, the enthalpy is $h = \frac{5}{2}RT$. There is an easier way to obtain these results. From Exercise 2.3, the molar internal energy is $u = \frac{3}{2}RT$. The fundamental equation for the molar enthalpy is $h = u + vP$, where $v = V/n$ is the molar volume. Since $v = RT/P$, we obtain $h = \frac{5}{2}RT$ and $H = \frac{5}{2}nRT$.

For a *YXT* system, the enthalpy is a thermodynamic potential for reversible processes carried out at constant Y. The discussion for the enthalpy is completely analogous to that for the internal energy except that now we allow the extensive variable X to change and maintain the system at constant Y. We then find

$$\Delta H \leq \int T\,dS - \int X\,dY - \Delta W_{\text{free}} + \sum_j \int \mu_j' dN_j, \tag{2.92}$$

where the equality holds for a reversible process and the inequality holds for a spontaneous process (ΔW_{free} is defined in Section 2.F.1). Therefore,

$$(\Delta H)_{S,Y,\{N_j\}} \leq (-\Delta W_{\text{free}}) \tag{2.93}$$

and we conclude that, *for a reversible process at constant S, Y, and $\{N_j\}$, work can be stored as enthalpy and can be recovered completely.*

If a process takes place at constant S, Y, and $\{N_j\}$ in which no work is done on or by the system, then

$$(\Delta H)_{S,Y,\{N_j\}} \leq 0. \tag{2.94}$$

Since the equilibrium state cannot change spontaneously, we find that *the equilibrium state at fixed S, Y, and $\{N_j\}$ is a state of minimum enthalpy.*

2.F.3. Helmholtz Free Energy

For processes carried out at constant T, X, and $\{N_j\}$, the Helmholtz free energy corresponds to a thermodynamic potential. The Helmholtz free energy, A, is useful for systems which are closed and thermally coupled to the outside world but are mechanically isolated (held at constant X). We obtain the Helmholtz free energy from the internal energy by adding a term due to the thermal coupling:

$$A = U - ST = YX + \sum_j \mu_j' N_j. \tag{2.95}$$

The addition of $-ST$ is a Legendre transformation which changes the independent variables from $(S, X, \{N_j\})$ to $(T, X, \{N_j\})$. If we take the differential of Eq. (2.95) and use Eq. (2.67), we find

$$dA \leq -S\,dT + Y\,dX + \sum_j \mu_j' dN_j. \tag{2.96}$$

Therefore,

$$S = -\left(\frac{\partial A}{\partial T}\right)_{X,\{N_j\}}, \tag{2.97}$$

$$Y = \left(\frac{\partial A}{\partial X}\right)_{T,\{N_j\}}, \tag{2.98}$$

and

$$\mu_j' = \left(\frac{\partial A}{\partial N_j}\right)_{T,X,\{N_{l\neq j}\}}. \tag{2.99}$$

Again, from Eq. (2.4), we obtain Maxwell relations

$$\left(\frac{\partial S}{\partial X}\right)_{T,\{N_j\}} = -\left(\frac{\partial Y}{\partial T}\right)_{X,\{N_j\}}, \tag{2.100}$$

$$\left(\frac{\partial S}{\partial N_j}\right)_{T,X,\{N_{l\neq j}\}} = -\left(\frac{\partial \mu_j'}{\partial T}\right)_{X,\{N_j\}}, \tag{2.101}$$

$$\left(\frac{\partial Y}{\partial N_j}\right)_{T,X,\{N_{l\neq j}\}} = \left(\frac{\partial \mu_j'}{\partial X}\right)_{T,\{N_j\}}, \tag{2.102}$$

and

$$\left(\frac{\partial \mu_j'}{\partial N_i}\right)_{T,X,\{N_{l\neq i}\}} = \left(\frac{\partial \mu_i'}{\partial N_j}\right)_{T,X,\{N_{l\neq j}\}} \tag{2.103}$$

for the system.

We can write the corresponding equations in terms of densities. Let us consider a monatomic substance and let $a = A/n$ denote the molar Helmholtz free energy. Then the fundamental equations for the molar Helmholtz free energy is $a = u - sT = xY + \mu$. The combined first and second laws (for reversible processes) can be written $da = -s\,dT + Y\,dx$ so that $(\partial a/\partial T)_x = -s$

and $(\partial a/\partial x)_T = Y$. Maxwells relations reduce to $(\partial s/\partial x)_T = -(\partial Y/\partial T)_x$. In Exercise 2.5, we compute that Helmholtz free energy for a monatomic ideal gas in terms of its natural variables.

■ **EXERCISE 2.5.** Compute the Helmholtz free energy for n moles of a monatomic ideal gas and express it in terms of its natural variables. The mechanical equation of state is $PV = nRT$ and the entropy is $S = \frac{5}{2}nR + nR\ln[(V/V_0)(n_0/n)(T/T_0)^{3/2}]$.

Answer: Since $da = -sdT - Pdv$ we have

$$\left(\frac{\partial a}{\partial T}\right)_v = -s = -\frac{5}{2}R - R\ln\left[\frac{v}{v_0}\left(\frac{T}{T_0}\right)^{3/2}\right] \tag{1}$$

and

$$\left(\frac{\partial a}{\partial v}\right)_T = -P = -\frac{RT}{v}. \tag{2}$$

If we integrate, we find $a = -RT - RT\ln[(v/v_0)(T/T_0)^{3/2}]$ and $A = -nRT - nRT\ln[(V/V_0)(n_0/n)(T/T_0)^{3/2}]$.

For a *YXT* system, the Helmholtz free energy is a thermodynamic potential for reversible processes carried out at constant T, X, and $\{N_j\}$. For a change in the thermodynamic state of the system, the change in the Helmholtz free energy can be written

$$\Delta A \leq -\int S\,dT + \int Y\,dX - \Delta W_{\text{free}} + \sum_j \int \mu_j' dN_j, \tag{2.104}$$

where the inequality holds for spontaneous processes and the equality holds for reversible processes (ΔW_{free} is defined in Section 2.66). For a process carried out at fixed T, X, and $\{N_j\}$, we find

$$(\Delta A)_{T,X\{N_j\}} \leq (-\Delta W_{\text{free}}), \tag{2.105}$$

and we conclude that *for a reversible process at constant T, X, and $\{N_j\}$, work can be stored as Helmholtz free energy and can be recovered completely.*

If no work is done for a process occurring at fixed T, X, and $\{N_j\}$, Eq. (2.105) becomes

$$(\Delta A)_{T,X,\{N_j\}} \leq 0. \tag{2.106}$$

Thus, *an equilibrium state at fixed T, X, and $\{N_j\}$ is a state of minimum Helmholtz free energy.*

2.F.4. Gibbs Free Energy

For processes carried out at constant Y, T, and $\{N_j\}$, the Gibbs free energy corresponds to the thermodynamic potential. Such a process is coupled both thermally and mechanically to the outside world. We obtain the Gibbs free energy, G, from the internal energy by adding terms due to the thermal and mechanical coupling,

$$G = U - TS - XY = \sum_j \mu_j' N_j. \tag{2.107}$$

In this way we change from independent variables $(S, X, \{N_i\})$ to variables $(T, Y, \{N_i\})$. If we use the differential of Eq. (2.106) in Eq. (2.67), we obtain

$$dG \leq -S\,dT - X\,dY + \sum_j \mu_j' dN_j, \tag{2.108}$$

so that

$$S = -\left(\frac{\partial G}{\partial T}\right)_{Y,\{N_j\}}, \tag{2.109}$$

$$X = -\left(\frac{\partial G}{\partial Y}\right)_{T,\{N_j\}}, \tag{2.110}$$

and

$$\mu_j' = \left(\frac{\partial G}{\partial N_j}\right)_{T,Y,\{N_{l\neq j}\}}. \tag{2.111}$$

The Maxwell relations obtained from the Gibbs free energy are

$$\left(\frac{\partial S}{\partial Y}\right)_{T,\{N_j\}} = \left(\frac{\partial X}{\partial T}\right)_{Y,\{N_j\}}, \tag{2.112}$$

$$\left(\frac{\partial S}{\partial N_j}\right)_{T,Y,\{N_{l\neq j}\}} = -\left(\frac{\partial \mu_j'}{\partial T}\right)_{Y,\{N_j\}}, \tag{2.113}$$

$$\left(\frac{\partial X}{\partial N_j}\right)_{T,Y,\{N_{l\neq j}\}} = -\left(\frac{\partial \mu_j'}{\partial Y}\right)_{T,\{N_j\}}, \tag{2.114}$$

and

$$\left(\frac{\partial \mu_j'}{\partial N_i}\right)_{T,Y,\{N_{l\neq i}\}} = \left(\frac{\partial \mu_i'}{\partial N_j}\right)_{T,Y,\{N_{l\neq j}\}} \tag{2.115}$$

and again relate seemingly diverse partial derivatives.

As we found in earlier sections, we can write the corresponding equations in terms of densities. We will consider a monomolecular substance and let $g = G/n$ denote the molar Gibbs free energy. Then the fundamental equation for the molar Gibbs free energy is $g = u - sT - xY = \mu$ and the molar Gibbs free energy is equal to the chemical potential (for a monomolelcular substance). The combined first and second laws (for reversible processes) can be written $dg = -sdT - xdY$ so that $(\partial g/\partial T)_Y = -s$ and $(\partial g/\partial Y)_T = -x$. Maxwells relations reduce to $(\partial s/\partial Y)_T = +(\partial x/\partial T)_Y$. For a monatomic substance, the molar Gibbs free energy is equal to the chemical potential.

For a *YXT* system, the Gibbs free energy is a thermodynamic potential for reversible processes carried out at constant T, Y, and $\{N_j\}$. For a change in the thermodynamic state of the system, the change in Gibbs free energy can be written

$$\Delta G \leq -\int S\,dT - \int X\,dY - \Delta W_{\text{free}} + \sum_j \int \mu_j'\,dN_j, \tag{2.116}$$

where the equality holds for reversible processes and the inequality holds for spontaneous processes (ΔW_{free} is defined in Section 2.F.1). For processes at fixed T, Y, and $\{N_j\}$, we obtain

$$(\Delta G)_{T,Y,\{N_j\}} \leq (-\Delta W_{\text{free}}). \tag{2.117}$$

Thus, *for a reversible process at constant T, Y, and $\{N_j\}$, work can be stored as Gibbs free energy and can be recovered completely.*

For a process at fixed T, Y, and $\{N_j\}$ for which no work is done, we obtain

$$(\Delta G)_{T,Y,\{N_j\}} \leq 0, \tag{2.118}$$

and we conclude that *an equilibrium state at fixed T, Y, and $\{N_j\}$ is a state of minimum Gibbs free energy.*

■ **EXERCISE 2.6.** Consider a system which has the capacity to do work, $đW = -Y\,dX + đW'$. Assume that processes take place spontaneously so that $dS = (1/T)đQ + d_iS$, where d_iS is a differential element of entropy due to the spontaneity of the process. Given the fundamental equation for the Gibbs free energy, $G = U - XY - TS$, show that $-(dG)_{Y,T} = đW' + Td_iS$. Therefore, at fixed Y and T, all the Gibbs free energy is available to do work for reversible processes. However, for spontaneous processes, the amount of work that can be done is diminished because part of the Gibbs free energy is used to produce entropy. This result is the starting point of nonequilibrium thermodynamics.

Answer: From the fundamental equation for the Gibbs free energy, we know that $dG = dU - X\,dY - Y\,dX - T\,dS - S\,dT$. Also we know that $dU = đQ + Y\,dX - đW'$, so we can write $dG = đQ - đW' - X\,dY - T\,dS - S\,dT$. For fixed Y and T we have $(dG)_{Y,T} = đQ - đW' - T\,dS$. Now remember that $dS = (1/T)đQ + d_iS$. Then we find $(dG)_{Y,T} = -đW' - Td_iS$. Note that the fundamental equation, $G = U - XY - TS$ contains the starting point of nonequilibrium thermodynamics.

For mixtures held at constant temperature, T, and pressure, P, the Gibbs free energy is a first-order homogeneous function of the particle numbers or particle mole numbers and this allows us to introduce a "partial" free energy, a "partial" volume, a "partial" enthalpy, and a "partial" entropy for each type of particle. For example, the chemical potential of a particle of type i, when written as $\mu_i = (\partial G/\partial n_i)_{T,P,\{n_{j\neq i}\}}$, is a partial molar Gibbs free energy. The total Gibbs free energy can be written

$$G = \sum_{i=1}^{N} n_i\mu_i = \sum_{i=1}^{n} n_i\left(\frac{\partial G}{\partial n_i}\right)_{T,P,\{n_{j\neq i}\}}. \tag{2.119}$$

The partial molar volume for a particle of type i is $v_i = (\partial V/\partial n_i)_{T,P,\{n_{j\neq i}\}}$, and the total volume can be written

$$V = \sum_{i=1}^{N} n_iv_i = \sum_{i=1}^{N} n_i\left(\frac{\partial V}{\partial n_i}\right)_{T,P,\{n_{j\neq i}\}}. \tag{2.120}$$

The partial molar entropy for particle of type i is $s_i = (\partial S/\partial n_i)_{T,P,\{n_{j\neq i}\}}$, and the total entropy can be written

$$S = \sum_{i=1}^{N} n_is_i = \sum_{i=1}^{N} n_i\left(\frac{\partial S}{\partial n_i}\right)_{T,P,\{n_{j\neq i}\}}. \tag{2.121}$$

Because the enthalpy is defined, $H = G + TS$, we can also define a partial molar enthalpy, $h_i = (\partial H/\partial n_i)_{T,P,\{n_{j\neq i}\}} = \mu_i + Ts_i$. Then the total enthalpy can be written $H = \sum_{i=1}^{N} n_ih_i$. These quantities are very useful when we describe the properties of mixtures in later chapters.

■ **EXERCISE 2.7.** Consider a fluid with electric potential, ϕ, containing ν different kinds of particles. Changes in the internal energy can be written, $dU = đQ - P\,dV + \phi de + \sum_j^{\nu} \mu_j dn_j$. Find the amount of Gibbs free energy needed to bring dn_i moles of charged particles of type i into the system at fixed temperature, pressure, and particle number, $n_j (j \neq i)$, in a reversible

manner. Assume that particles of type i have a valence, z_i. Note that the amount of charge in one mole of protons is called a *Faraday, F.*

Answer: The fundamental equation for the Gibbs free energy, $G = U + PV - TS$, yields $dG = dU + P\,dV + V\,dP - T\,dS - S\,dT$. Therefore, $dG = \not{d}Q + \phi de + \sum_j^\nu \mu_j dn_j + V\,dP - TdS - S\,dT$. For a reversible process, $dS = (1/T)\not{d}Q$, and $dG = \phi de + \sum_j^\nu \mu_j dn_j + V\,dP - S\,dT$. Now note that the charge carried by dn_i moles of particles of type, i, is $de = z_i F dn_i$. Thus, the change in the Gibbs free energy can be written

$$\begin{aligned} dG &= \phi de + VdP - SdT + \sum_j^\nu \mu_j dn_j \\ &= +V\,dP - S\,dT + (z_i F\phi + \mu_i)dn_i + \sum_{j\neq i}^\nu \mu_j dn_j. \end{aligned} \tag{1}$$

For fixed P, T, and $n_j (j \neq i)$, the change in the Gibbs free energy is

$$(dG)_{P,T,n_{j\neq i}} = (z_i F\phi + \mu_i)dn_i. \tag{2}$$

From Exercise 2.6, we see that this is just the work needed to add dn_i moles of charged particles of type, i, keeping all other quantities fixed. The quantity

$$\tilde{\mu}_i \equiv z_i F\phi + \mu_i, \tag{3}$$

is called the *electrochemical potential.*

2.F.5. Grand Potential

A thermodynamic potential which is extremely useful for the study of quantum systems is the grand potential. It is a thermodynamic potential energy for processes carried out in open systems where particle number can vary but T, X, and $\{\mu_j'\}$ are kept fixed.

The grand potential, Ω, can be obtained from the internal energy by adding terms due to thermal and chemical coupling of the system to the outside world:

$$\Omega = U - TS - \sum_j \mu_j' N_j = XY. \tag{2.122}$$

The Legendre transformation in Eq. (2.122) changes the independent variables from $(S, X, \{N_i\})$ to $(T, X, \{\mu_j'\})$. If we add the differential of Eq. (2.122) to Eq. (2.67), we obtain

$$d\Omega \leq -S\,dT + Y\,dX - \sum_j N_j d\mu_j', \tag{2.123}$$

and thus

$$S = -\left(\frac{\partial \Omega}{\partial T}\right)_{X,\{\mu_j'\}}, \tag{2.124}$$

$$Y = \left(\frac{\partial \Omega}{\partial X}\right)_{T,\{\mu_j'\}}, \tag{2.125}$$

and

$$N_j = -\left(\frac{\partial \Omega}{\partial \mu_j'}\right)_{T,X,\{\mu_{l\neq j}'\}}. \tag{2.126}$$

The Maxwell relations obtained from the grand potential are

$$\left(\frac{\partial S}{\partial X}\right)_{T,\{\mu_j'\}} = -\left(\frac{\partial Y}{\partial T}\right)_{X,\{\mu_j'\}}, \tag{2.127}$$

$$\left(\frac{\partial S}{\partial \mu_j'}\right)_{T,X,\{\mu_{l\neq j}'\}} = \left(\frac{\partial N_j}{\partial T}\right)_{X,\{\mu_i'\}}, \tag{2.128}$$

$$\left(\frac{\partial Y}{\partial \mu_j'}\right)_{T,X,\{\mu_{l\neq j}'\}} = -\left(\frac{\partial N_j}{\partial X}\right)_{T,\{\mu_i'\}}, \tag{2.129}$$

and

$$\left(\frac{\partial N_i}{\partial \mu_j'}\right)_{T,V,\{\mu_{l\neq j}'\}} = \left(\frac{\partial N_j}{\partial \mu_i'}\right)_{T,V,\{\mu_{l\neq i}'\}} \tag{2.130}$$

and are very useful in treating open systems. The grand potential is a thermodynamic potential energy for a reversible process carried out at constant T, X, and $\{\mu_j'\}$. For a change in the thermodynamic state of the system, the change in the grand potential can be written

$$\Delta\Omega \leq -\int S\,dT + \int Y\,dX - \Delta W_{\text{free}} - \sum_j \int N_j\,d\mu_j', \tag{2.131}$$

where the equality holds for reversible changes and the inequality holds for spontaneous changes (ΔW_{free} is defined in Section 2.F.1). For a process at fixed

T, X, and $\{\mu_j'\}$, we obtain

$$(\Delta\Omega)_{T,X,\{\mu_j'\}} \leq (-\Delta W_{\text{free}}). \tag{2.132}$$

Thus, *for a reversible process at constant T, X, and $\{\mu_j'\}$, work can be stored as grand potential and can be recovered completely.*

For a process at fixed T, X, and $\{\mu_j'\}$ for which no work is done, we obtain

$$(\Delta\Omega)_{T,X,\{\mu_j'\}} \leq 0, \tag{2.133}$$

and we find that *an equilibrium state at fixed T, X, and $\{\mu_j'\}$ is a state of minimum grand potential.*

2.G. RESPONSE FUNCTIONS

The response functions are the thermodynamic quantities most accessible to experiment. They give us information about how a specific state variable changes as other independent state variables are changed under controlled conditions. As we shall see in later chapters, they also provide a measure of the size of fluctuations in a thermodynamic system. The response functions can be divided into (a) thermal response functions, such as heat capacities, (b) mechanical response functions, such as compressibility and susceptibility, and (c) chemical response functions. We shall introduce some thermal and mechanical response functions in this section.

2.G.1. Thermal Response Functions (Heat Capacity)

The heat capacity, C, is a measure of the amount of heat needed to raise the temperature of a system by a given amount. In general, it is defined as the derivative, $C = (đQ/dT)$. When we measure the heat capacity, we try to fix all independent variables except the temperature. Thus, there are as many different heat capacities as there are combinations of independent variables, and they each contain different information about the system. We shall derive the heat capacity at constant X and $\{N_j\}$, $C_{X,\{N_j\}}$, and we shall derive the heat capacity at constant Y and $\{N_j\}$, $C_{Y,\{N_j\}}$. We will derive these heat capacities in two different ways, first from the first law and then from the definition of the entropy.

To obtain an expression of $C_{X,\{N_j\}}$, we shall assume that X, T, and $\{N_j\}$ are independent variables. Then the first law can be written

$$đQ = dU - Y\,dX - \sum_j \mu_j' dN_j = \left(\frac{\partial U}{\partial T}\right)_{X,\{N_j\}} dT + \left[\left(\frac{\partial U}{\partial X}\right)_{T,\{N_j\}} - Y\right] dX$$
$$+ \sum_j \left[\left(\frac{\partial U}{\partial N_j}\right)_{T,X,\{N_{i\neq j}\}} - \mu_j'\right] dN_j. \tag{2.134}$$

For constant X and $\{N_j\}$, we have $[đQ]_{X,\{N_j\}} = C_{X,\{N_j\}}dT$ and we find

$$C_{X,\{N_j\}} = \left(\frac{\partial U}{\partial T}\right)_{X,\{N_j\}} \tag{2.135}$$

for the heat capacity at constant X and $\{N_j\}$.

To obtain an expression for $C_{Y,\{N_j\}}$, we shall assume that Y, T, and $\{N_j\}$ are independent variables. Then we can write

$$dX = \left(\frac{\partial X}{\partial T}\right)_{Y,\{N_j\}} dT + \left(\frac{\partial X}{\partial Y}\right)_{T,\{N_j\}} dY + \sum_j \left(\frac{\partial X}{\partial N_j}\right)_{T,Y,\{N_{i\neq j}\}} dN_j. \tag{2.136}$$

If we substitute the expression for dX into Eq. (2.134), we obtain

$$\begin{aligned} đQ = &\left\{ C_{X,\{N_j\}} + \left[\left(\frac{\partial U}{\partial X}\right)_{T,\{N_j\}} - Y\right]\left(\frac{\partial X}{\partial T}\right)_{Y,\{N_j\}} \right\} dT \\ &+ \left[\left(\frac{\partial U}{\partial X}\right)_{T,\{N_j\}} - Y\right]\left(\frac{\partial X}{\partial Y}\right)_{T,\{N_j\}} dY \\ &+ \sum_j \left\{ \left[\left(\frac{\partial U}{\partial X}\right)_{T,\{N_j\}} - Y\right]\left(\frac{\partial X}{\partial N_j}\right)_{T,Y,\{N_{i\neq j}\}} + \left(\frac{\partial U}{\partial N_j}\right)_{T,X,\{N_{i\neq j}\}} - \mu_j' \right\} dN_j. \end{aligned} \tag{2.137}$$

For constant Y and $\{N_j\}$ we have $[đQ]_{Y,\{N_j\}} = C_{Y,\{N_j\}}dT$ and we find

$$C_{Y,\{N_j\}} = C_{X,\{N_j\}} + \left[\left(\frac{\partial U}{\partial X}\right)_{T,\{N_j\}} - Y\right]\left(\frac{\partial X}{\partial T}\right)_{Y,\{N_j\}} \tag{2.138}$$

for the heat capacity at constant Y and $\{N_j\}$.

For n moles of a monatomic substance, these equations simplify. Let us write them in terms of molar quantities. We can write the heat capacity in the form $C_{X,n} = (\partial U/\partial T)_{X,n} = n(\partial u/\partial T)_x$, where $u = U/n$ is the molar internal energy and $x = X/n$ is a molar density of the mechanical extensive variable. The molar heat capacity is then $c_x = (\partial u/\partial T)_x$ so that $C_{X,n} = nc_x$. Similarly, let us note that $(\partial X/\partial T)_{Y,n} = n(\partial x/\partial T)_Y$ and $(\partial U/\partial X)_{T,n} = (\partial u/\partial x)_T$. Therefore, the molar heat capacity at constant Y is $c_Y = c_x + [(\partial u/\partial x)_T - Y]\ (\partial x/\partial T)_Y$.

It is useful to rederive expressions for $C_{X,\{N_j\}}$ and $C_{Y,\{N_j\}}$ from the entropy. Let us first assume that T, X, and $\{N_j\}$ are independent. Then for a reversible process, we obtain

$$đQ = T\,dS = T\left(\frac{\partial S}{\partial T}\right)_{X,\{N_j\}} dT + T\left(\frac{\partial S}{\partial X}\right)_{T,\{N_j\}} dX + \sum_j T\left(\frac{\partial S}{\partial N_j}\right)_{T,X,\{N_{i\neq j}\}} dN_j. \tag{2.139}$$

For a processes which occurs at constant X and $\{N_j\}$, Eq. (2.139) becomes

$$[đQ]_{X,\{N_j\}} = T\left(\frac{\partial S}{\partial T}\right)_{X,\{N_j\}} dT, \tag{2.140}$$

and therefore

$$C_{X,\{N_j\}} = T\left(\frac{\partial S}{\partial T}\right)_{X,\{N_j\}} = -T\left(\frac{\partial^2 A}{\partial T^2}\right)_{X,\{N_j\}}. \tag{2.141}$$

The second term comes from Eq. (2.97).

Let us now assume that T, Y and $\{N_j\}$ are independent. For a reversible process, we obtain

$$đQ = T\,dS = T\left(\frac{\partial S}{\partial T}\right)_{Y,\{N_j\}} dT + T\left(\frac{\partial S}{\partial Y}\right)_{T,\{N_j\}} dY + \sum_j T\left(\frac{\partial S}{\partial N_j}\right)_{T,Y,\{N_{i\neq j}\}} dN_j. \tag{2.142}$$

If we combine Eqs. (2.136) and (2.139), we can also write

$$\begin{aligned} đQ = T\,dS = T&\left[\left(\frac{\partial S}{\partial T}\right)_{X,\{N_j\}} + \left(\frac{\partial S}{\partial X}\right)_{T,\{N_j\}}\left(\frac{\partial X}{\partial T}\right)_{Y,\{N_j\}}\right] dT \\ &+ T\left(\frac{\partial S}{\partial X}\right)_{T,\{N_j\}}\left(\frac{\partial X}{\partial Y}\right)_{T,\{N_j\}} dY \\ &+ T\sum_j\left[\left(\frac{\partial S}{\partial X}\right)_{T,\{N_j\}}\left(\frac{\partial X}{\partial N_j}\right)_{T,Y,\{N_{i\neq j}\}} + \left(\frac{\partial S}{\partial N_j}\right)_{T,X,\{N_{i\neq j}\}}\right] dN_j. \end{aligned} \tag{2.143}$$

If we now compare Eqs. (2.142) and (2.143), we find

$$\begin{aligned} C_{Y,\{N_j\}} &= T\left(\frac{\partial S}{\partial T}\right)_{Y,\{N_j\}} = C_{X,\{N_j\}} + T\left(\frac{\partial S}{\partial X}\right)_{T,\{N_j\}}\left(\frac{\partial X}{\partial T}\right)_{Y,\{N_j\}} \\ &= -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{Y,\{N_j\}}. \end{aligned} \tag{2.144}$$

The last term in Eq. (2.144) comes from Eq. (2.109).

We can obtain some additional useful identities from the above equations. If we compare Eqs. (2.100), (2.138), and (2.144), we obtain the identity

$$\left(\frac{\partial S}{\partial X}\right)_{T,\{N_j\}} = \frac{1}{T}\left[\left(\frac{\partial U}{\partial X}\right)_{T,\{N_j\}} - Y\right] = -\left(\frac{\partial Y}{\partial T}\right)_{X,\{N_j\}}. \tag{2.145}$$

Therefore,

$$\left(\frac{\partial^2 Y}{\partial T^2}\right)_{X,\{N_j\}} = -\frac{1}{T}\left(\frac{\partial C_{X,\{N_j\}}}{\partial X}\right)_{T,\{N_j\}}, \tag{2.146}$$

where we have used Eqs. (2.4) and (2.145).

For a monatomic substance, it is fairly easy to show that the molar heat capacity at constant mechanical molar density, x, is $c_x = T(\partial s/\partial T)_x = -T(\partial^2 a/\partial T^2)_x$, and the molar heat capacity at constant Y is $c_Y = T(\partial s/\partial T)_Y = -T(\partial^2 a/\partial T^2)_Y$. We also obtain the useful identities $(\partial s/\partial x)_T = (1/T)[(\partial u/\partial x)_T - Y] = -(\partial Y/\partial T)_x$ and $(\partial^2 Y/\partial T^{2])}_x = -(1/T)(\partial c_x/\partial x)_T$.

2.G.2. Mechanical Response Functions

There are three mechanical response functions which are commonly used. They are the *isothermal susceptibility*,

$$\chi_{T,\{N_j\}} = \left(\frac{\partial X}{\partial Y}\right)_{T,\{N_j\}} = -\left(\frac{\partial^2 G}{\partial Y^2}\right)_{T,\{N_j\}}, \tag{2.147}$$

the *adiabatic susceptibility*,

$$\chi_{S,\{N_j\}} = \left(\frac{\partial X}{\partial Y}\right)_{S,\{N_j\}} = -\left(\frac{\partial^2 H}{\partial Y^2}\right)_{S,\{N_j\}}, \tag{2.148}$$

and the *thermal expansivity*,

$$\alpha_{Y,\{N_j\}} = \left(\frac{\partial X}{\partial T}\right)_{Y,\{N_j\}}. \tag{2.149}$$

Using the identities in Section 2.B, the thermal and mechanical response functions can be shown to satisfy the identities

$$\chi_{T,\{N_j\}}(C_{Y,\{N_j\}} - C_{X,\{N_j\}}) = T(\alpha_{Y,\{N_j\}})^2, \tag{2.150}$$

$$C_{Y,\{N_j\}}(\chi_{T,\{N_j\}} - \chi_{S,\{N_j\}}) = T(\alpha_{Y,\{N_j\}})^2, \tag{2.151}$$

and

$$\frac{C_{Y,\{N_j\}}}{C_{X,\{N_j\}}} = \frac{\chi_{T,\{N_j\}}}{\chi_{S,\{N_j\}}}. \tag{2.152}$$

The derivation of these identities is left as a homework problem.

For *PVT* systems, the mechanical response functions have special names. Quantities closely related to the isothermal and adiabatic susceptibilities are the *isothermal compressibility,*

$$\kappa_{T,\{N_j\}} = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,\{N_j\}} = -\frac{1}{V}\left(\frac{\partial^2 G}{\partial P^2}\right)_{T,\{N_j\}}, \tag{2.153}$$

and *adiabatic compressibility,*

$$\kappa_{S,\{N_j\}} = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{S,\{N_j\}} = -\frac{1}{V}\left(\frac{\partial^2 H}{\partial P^2}\right)_{S,\{N_j\}}, \tag{2.154}$$

respectively. The *thermal expansivity* for a *PVT* is defined slightly differently from above. It is

$$\alpha_{P,\{N_j\}} = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,\{N_j\}}. \tag{2.155}$$

For a monatomic *PVT* system the mechanical response functions become even simpler if written in terms of densities. The isothermal and adiabatic compressibilities are $\kappa_T = -(1/v)(\partial v/\partial P)_T$ and $\kappa_s = -(1/v)(\partial v/\partial P)_s$, respectively, where $u = V/n$ is the molar volume. The thermal expansivity is $\alpha_P = (1/v)(\partial v/\partial T)_P$.

■ **EXERCISE 2.8.** Compute the molar heat capacities, c_v and c_P, the compressibilities, κ_T and κ_s, and the thermal expansivity, α_P, for a monatomic ideal gas. Start from the fact that the molar entropy of the gas is $s = \frac{5}{2}R + R\ln[(v/v_0)(T/T_0)^{3/2}]$ ($v = V/N$ is the molar volume), and the mechanical equation of state is $Pv = RT$.

Answer:

(a) *The molar heat capacity,* c_v: The molar entropy is $s = \frac{5}{2}R + R\ln[(v/v_0)(T/T_0)^{3/2}]$. Therefore $(\partial s/\partial T)_v = (3R/2T)$ and $c_v = T(\partial s/\partial T)_v = 3R/2$.

(b) *The molar heat capacity,* c_P: The molar entropy can be written $s = \frac{5}{2}R + R\ln[(P_0/P)(T/T_0)^{5/2}]$. Then $(\partial s/\partial T)_P = 5R/2T$ and $c_P = T(\partial s/\partial T)_P = 5R/2$.

(c) *The isothermal compressibility,* κ_T: From the mechanical equation of state, we have $v = (RT/P)$. Therefore, $(\partial v/\partial P)_T = -(v/P)$ and $\kappa_T = -(1/v)(\partial v/\partial P)_T = (1/P)$.

(**d**) *The adiabatic compressibility*, κ_s: We must first write the molar volume as a function of s and P. From the expressions for the molar entropy and mechanical equation of state given above we find $v = v_0(P_0/P)^{3/5} \exp[(2s/5R) - 1]$. Then $(\partial v/\partial P)_s = -(3v/5P)$ and $\kappa_s = -(1/v)(\partial v/\partial P)_s = (3/5P)$.

(**e**) *Thermal Expansivity*, α_P: Using the mechanical equation of state, we find $\alpha_P = (1/v)(\partial v/\partial T)_P = (1/T)$.

2.H. STABILITY OF THE EQUILIBRIUM STATE

The entropy of an isolated equilibrium system (cf. Section 2.D.3) must be a maximum. However, for a system with a finite number of particles in thermodynamic equilibrium, the thermodynamic quantities describe the average behaviour of the system. If there are a finite number of particles, then there can be spontaneous fluctuations away from this average behaviour. However, fluctuations must cause the entropy to decrease. If this were not so, the system could spontaneously move to new equilibrium state with a higher entropy because of spontaneous fluctuations. For a system in a stable equilibrium state, this, by definition, cannot happen.

We can use the fact that the entropy must be maximum to obtain conditions for local equilibrium and for local stability of equilibrium systems. We will restrict ourselves to PVT systems. However, our arguments also apply to general YXT systems.

2.H.1. Conditions for Local Equilibrium in a PVT System

Let us consider a mixture of l types of particles in an isolated box of volume, V_T, divided into two parts, A and B, by a conducting porous wall which is free to move and through which particles can pass (cf. Fig. 2.8). With this type of dividing wall there is a free exchange of heat, mechanical energy, and particles between A and B. One can think of A and B as two different parts of a fluid (gas or liquid), or perhaps as a solid (part A) in contact with its vapor (part B). We shall assume that no chemical reactions occur. Since the box is closed and isolated, the total internal energy, U_T, is

$$U_T = \sum_{\alpha=A,B} U_\alpha, \tag{2.156}$$

where U_α is the internal energy of compartment α. The total volume, V_T, is

$$V_T = \sum_{\alpha=A,B} V_\alpha, \tag{2.157}$$

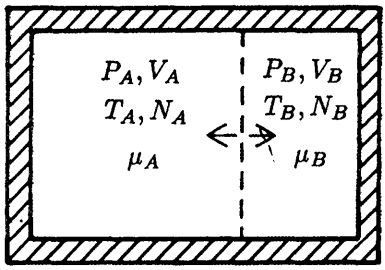


Fig. 2.8. An isolated, closed box containing fluid separated into two parts by a movable porous membrane.

where V_α is the volume of compartment α. The total number of particles, $N_{j,T}$, of type j is

$$N_{j,T} = \sum_{\alpha=A,B} N_{j,\alpha}, \tag{2.158}$$

where $N_{j,\alpha}$ is the total number of particles of type j in compartment α. The total entropy, S_T, is

$$S_T = \sum_{\alpha=A,B} S_\alpha, \tag{2.159}$$

where S_α is the total entropy of compartment α.

Let us now assume that spontaneous fluctuations can occur in the energy, volume, and particle number of each cell subject to the constraints

$$\Delta U_T = \Delta V_T = \Delta N_{j,T} = 0 \tag{2.160}$$

(assume that no chemical reactions occur) so that $\Delta U_A = -\Delta U_B$, $\Delta V_A = -\Delta V_B$, and $\Delta N_{j,A} = -\Delta N_{j,B}$. The entropy change due to these spontaneous fluctuations can be written

$$\Delta S_T = \sum_{\alpha=A,B} \left[\left(\frac{\partial S_\alpha}{\partial U_\alpha} \right)_{V_\alpha,\{N_{j,\alpha}\}} \Delta U_\alpha + \left(\frac{\partial S_\alpha}{\partial V_\alpha} \right)_{U_\alpha,\{N_{j,\alpha}\}} \Delta V_\alpha + \sum_{j=1}^{l} \left(\frac{\partial S_\alpha}{\partial N_{j,\alpha}} \right)_{U_\alpha,V_\alpha,\{N_{k\neq j,\alpha}\}} \Delta N_{j,\alpha} \right] + \cdots \tag{2.161}$$

From Eqs. (2.58)–(2.60) and (2.160), we can write Eq. (2.161) in the form

$$\Delta S_T = \left(\frac{1}{T_A} - \frac{1}{T_B} \right) \Delta U_A + \left(\frac{P_A}{T_A} - \frac{P_B}{T_B} \right) \Delta V_A - \sum_{j=1}^{l} \left(\frac{\mu'_{j,A}}{T_A} - \frac{\mu'_{j,B}}{T_B} \right) \Delta N_{j,A} + \cdots, \tag{2.162}$$

where T_α and P_α are the temperature and pressure, respectively, of the material in compartment α, and $\mu'_{j,\alpha}$ is the chemical potential of particles of type j in compartment α.

For a system in equilibrium, the entropy is a maximum. Therefore, any spontaneous changes must cause the entropy to decrease. However, $\Delta U_A, \Delta V_A$, and $\Delta N_{j,A}$ can be positive or negative. Thus, in order to ensure that $\Delta S_T \leq 0$, we must have

$$T_A = T_B, \tag{2.163}$$

$$P_A = P_B, \tag{2.164}$$

and

$$\mu'_{j,A} = \mu'_{j,B}, \qquad j = 1, \ldots, l. \tag{2.165}$$

Equations (2.163)–(2.165) give the conditions for local equilibrium in a system in which no chemical reactions occur. Thus, if the interface between A and B can transmit heat, mechanical energy, and particles of all types, then the two systems must have the same temperature, pressure, and chemical potential for each type of particle in order to be in equilibrium. It is important to note that if the partition cannot pass particles of type, i, then $\Delta N_{i,A} = \Delta N_{i,B} = 0$ and we can have $\mu'_{i,A} \neq \mu'_{i,B}$. If the partition is nonporous and fixed in position so no particles can pass and no mechanical work can be transmitted, then we can have $P_A \neq P_B$ and $\mu'_{j,A} \neq \mu'_{j,B}$ $(j = 1, \ldots, l)$ and still have equilibrium.

2.H.2. Conditions for Local Stability in a PVT System [12, 13]

Stability of the equilibrium state places certain conditions on the sign of the response functions. To see this, let us consider a closed isolated box with volume V_T, total entropy S_T, total internal energy U_T, and a total number of particles $N_{j,T}$ of type j, where $j = 1, \ldots, l$. We shall assume that the box is divided into M cells which can exchange thermal energy, mechanical energy, and particles. We shall denote the equilibrium volume, entropy, internal energy, and number of particles of type j for the αth cell by V^0_α, S^0_α, U^0_α, and $N^0_{j,\alpha}$, respectively. The equilibrium pressure, temperature, and chemical potentials of the various cells are P^0, T^0, and μ'^0_j, respectively (they must be the same for all the cells).

Because there are a finite number of particles in the box, there will be spontaneous fluctuations of the thermodynamic variables of each cell about their respective equilibrium values. These spontaneous fluctuations must be such that V_T, and U_T, and $N_{j,T}$ remain fixed. However, since the equilibrium state is stable, fluctuations must cause S_T to decrease. If it did not decrease, the equilibrium state would be unstable and spontaneous fluctuations would cause the system to move to a more stable equilibrium state of higher entropy.

We shall assume that fluctuations about the equilibrium state are small and expand the entropy of the αth cell in a Taylor expansion about its equilibrium value

$$
\begin{aligned}
&S_\alpha(U_\alpha, V_\alpha, \{N_{j,\alpha}\}) \\
&\quad = S_\alpha^0(U_\alpha^0, V_\alpha^0, \{N_{j,\alpha}^0\}) + \left(\frac{\partial S}{\partial U}\right)^0_{V,\{N_j\}} \Delta U_\alpha + \left(\frac{\partial S}{\partial V}\right)^0_{U,\{N_j\}} \Delta V_\alpha \\
&\qquad + \sum_{j=1}^{l} \left(\frac{\partial S}{\partial N_j}\right)^0_{U,V,\{N_{k\neq j}\}} \Delta N_{j,\alpha} + \frac{1}{2}\left\{ \Delta\left(\frac{\partial S_\alpha}{\partial U_\alpha}\right)_{V_\alpha,\{N_{j,\alpha}\}} \Delta U_\alpha \right. \\
&\qquad \left. + \Delta\left(\frac{\partial S_\alpha}{\partial V_\alpha}\right)_{U_\alpha,\{N_{j,\alpha}\}} \Delta V_\alpha + \sum_{j=1}^{l} \Delta\left(\frac{\partial S_\alpha}{\partial N_{j,\alpha}}\right)_{U_\alpha,V_\alpha,\{N_{k\neq j,\alpha}\}} \Delta N_{j,\alpha} \right\} + \cdots .
\end{aligned}
\tag{2.166}
$$

In Eq. (2.166), we define

$$
\begin{aligned}
\Delta\left(\frac{\partial S_\alpha}{\partial U_\alpha}\right)_{V_\alpha,\{N_{j,\alpha}\}} \equiv &\left(\frac{\partial^2 S}{\partial U^2}\right)^0_{V,\{N_j\}} \Delta U_\alpha + \left(\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial U}\right)_{V,\{N_j\}}\right)^0_{U,\{N_j\}} \Delta V_\alpha \\
&+ \sum_{j=1}^{l} \left(\frac{\partial}{\partial N_j}\left(\frac{\partial S}{\partial U}\right)_{V,\{N_j\}}\right)^0_{U,V,\{N_{k\neq j}\}} \Delta N_{j,\alpha}.
\end{aligned}
\tag{2.167}
$$

A similar expression holds for $\Delta(\partial S_\alpha/\partial V_\alpha)_{U_\alpha,\{N_{j,\alpha}\}}$. For $\Delta(\partial S_\alpha/\partial N_{j,\alpha})_{U_\alpha,V_\alpha,\{N_{k\neq j,\alpha}\}}$, we have

$$
\begin{aligned}
\Delta\left(\frac{\partial S_\alpha}{\partial N_{j,\alpha}}\right)_{U_\alpha,V_\alpha,\{N_{k\neq j,\alpha}\}} \equiv &\left(\frac{\partial}{\partial U}\left(\frac{\partial S}{\partial N_j}\right)_{U,V,\{N_{k\neq j}\}}\right)^0_{V,\{N_j\}} \Delta U_\alpha \\
&+ \left(\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial N_j}\right)_{U,V,\{N_{k\neq j}\}}\right)^0_{U,\{N_j\}} \Delta V_\alpha \\
&+ \sum_{i=1}^{l} \left(\frac{\partial}{\partial N_i}\left(\frac{\partial S}{\partial N_j}\right)_{U,V,\{N_{k\neq j}\}}\right)^0_{U,V,\{N_{k\neq i}\}} \Delta N_{i,\alpha}.
\end{aligned}
\tag{2.168}
$$

In Eqs. (2.166)–(2.168), the superscripts 0 on partial derivatives indicate that they are evaluated at equilibrium. The fluctuations $\Delta U_\alpha, \Delta V_\alpha$, and $\Delta N_{j,\alpha}$ are defined as $\Delta U_\alpha = U_\alpha - U_\alpha^0, \Delta V_\alpha = V_\alpha - V_\alpha^0$, and $\Delta N_{j,\alpha} = N_{j,\alpha} - N_{j,\alpha}^0$ and denote the deviation of the quantities U_α, V_α, and $N_{j,\alpha}$ from their absolute equilibrium values.

We can obtain the total entropy by adding the contributions to the entropy from each of the M cells. Because the entropy can only decrease due to fluctuations, the terms which are first order in the fluctuations, ΔU_α, ΔV_α, and $\Delta N_{j,\alpha}$ must add to zero (this is just the condition for local equilibrium obtained in Section 2.H.1). Therefore, the change in the entropy due to fluctuations must have the form

$$\Delta S_T = \frac{1}{2}\sum_{\alpha=1}^{M}\left\{\Delta\left(\frac{\partial S_\alpha}{\partial U_\alpha}\right)_{V_\alpha,\{N_{j,\alpha}\}}\Delta U_\alpha + \Delta\left(\frac{\partial S_\alpha}{\partial V_\alpha}\right)_{U_\alpha,\{N_{j,\alpha}\}}\Delta V_\alpha + \sum_{j=1}^{l}\Delta\left(\frac{\partial S_\alpha}{\partial N_{j,\alpha}}\right)_{U_\alpha,V_\alpha,\{N_{k\neq j,\alpha}\}}\Delta N_{j,\alpha}\right\} + \cdots. \tag{2.169}$$

Equation (2.169) can be written in simpler form if we make use of Eqs. (2.58)–(2.60). We than find

$$\Delta S_T = \frac{1}{2}\sum_{\alpha=1}^{M}\left[\Delta\left(\frac{1}{T}\right)_\alpha \Delta U_\alpha + \Delta\left(\frac{P}{T}\right)_\alpha \Delta V_\alpha - \sum_{j=1}^{l}\Delta\left(\frac{\mu_j'}{T}\right)_\alpha \Delta N_{j,\alpha}\right] + \cdots \tag{2.170}$$

or

$$\Delta S_T = -\frac{1}{2T}\sum_{\alpha=1}^{M}\left[\Delta T_\alpha \Delta S_\alpha - \Delta P_\alpha \Delta V_\alpha + \sum_{j=1}^{l}\Delta\mu_{j,\alpha}'\Delta N_{j,\alpha}\right] + \cdots. \tag{2.171}$$

In Eq. (2.171), we have used the relation $T\Delta S = \Delta U + P\Delta V - \sum_{j=1}^{l}\mu_j'\Delta N_j$. Equation (2.171) gives the entropy change, due to spontaneous fluctuations, in a completely general form. We can now expand ΔS_T in terms of any set of independent variables we choose.

Let us choose T, P, and N_j as the independent variables. Then we can write

$$\Delta S_\alpha = \left(\frac{\partial S}{\partial T}\right)^0_{P,\{N_j\}}\Delta T_\alpha + \left(\frac{\partial S}{\partial P}\right)^0_{T,\{N_j\}}\Delta P_\alpha + \sum_{j=1}^{l}\left(\frac{\partial S}{\partial N_j}\right)^0_{T,P,\{N_{k\neq j}\}}\Delta N_{j,\alpha}, \tag{2.172}$$

$$\Delta V_\alpha = \left(\frac{\partial V}{\partial T}\right)^0_{P,\{N_j\}}\Delta T_\alpha + \left(\frac{\partial V}{\partial P}\right)^0_{T,\{N_j\}}\Delta P_\alpha + \sum_{j=1}^{l}\left(\frac{\partial V}{\partial N_j}\right)^0_{T,P,\{N_{k\neq j}\}}\Delta N_{j,\alpha}, \tag{2.173}$$

and

$$\Delta\mu'_{j,\alpha} = \left(\frac{\partial\mu'_j}{\partial T}\right)^0_{P,\{N_j\}} \Delta T_\alpha + \left(\frac{\partial\mu'_j}{\partial P}\right)^0_{T,\{N_j\}} \Delta P_\alpha + \sum_{i=1}^{l} \left(\frac{\partial\mu'_j}{\partial N_i}\right)^0_{T,P,\{N_{k\neq i}\}} \Delta N_{i,\alpha}. \tag{2.174}$$

If we now substitute Eqs. (2.172)–(2.174) into Eq. (2.171) and use the Maxwell relations (2.112)–(2.115), the entropy change becomes

$$\Delta S_T = -\frac{1}{2T}\sum_{\alpha=1}^{M}\left[\left(\frac{\partial S}{\partial T}\right)^0_{P,\{N_j\}} (\Delta T_\alpha)^2 - 2\left(\frac{\partial V}{\partial T}\right)^0_{P,\{N_j\}} \Delta T_\alpha \Delta P_\alpha - \left(\frac{\partial V}{\partial P}\right)^0_{T,\{N_j\}} (\Delta P_\alpha)^2 + \sum_{i=1}^{l}\sum_{j=1}^{l}\left(\frac{\partial\mu'_j}{\partial N_i}\right)^0_{T,P,\{N_{k\neq i}\}} \Delta N_{i,\alpha}\Delta N_{j,\alpha}\right] + \cdots. \tag{2.175}$$

If we make use of Eqs. (2.6), (2.8) and (2.100), we can write

$$\left(\frac{\partial S}{\partial T}\right)_{P,\{N_j\}} = \left(\frac{\partial S}{\partial T}\right)_{V,\{N_j\}} - \left(\frac{\partial P}{\partial V}\right)_{T,\{N_j\}} \left(\frac{\partial V}{\partial T}\right)^2_{P,\{N_j\}}. \tag{2.176}$$

If we plug this into Eq. (2.175), we obtain

$$\Delta S_T = -\frac{1}{2T}\sum_{\alpha=1}^{M}\left[\left(\frac{\partial S}{\partial T}\right)^0_{V,\{N_j\}} (\Delta T_\alpha)^2 - \left(\frac{\partial P}{\partial V}\right)^0_{T,\{N_j\}} [\Delta V_\alpha]^2_{\{N_j\}} + \sum_{i=1}^{l}\sum_{j=1}^{l}\left(\frac{\partial\mu'_j}{\partial N_i}\right)^0_{T,P,\{N_{k\neq i}\}} \Delta N_{i,\alpha}\Delta N_{j,\alpha}\right] + \cdots, \tag{2.177}$$

where

$$[\Delta V_\alpha]_{\{N_j\}} \equiv \left(\frac{\partial V}{\partial T}\right)^0_{P,\{N_j\}} \Delta T_\alpha + \left(\frac{\partial V}{\partial P}\right)^0_{T,\{N_j\}} \Delta P_\alpha. \tag{2.178}$$

Because the fluctuations ΔT_α, ΔP_α, and $\Delta N_{j,\alpha}$ are independent, the requirement that $\Delta S_T \leq 0$ for a stable equilibrium state leads to the requirement that

$$C_{V,\{N_j\}} = T\left(\frac{\partial S}{\partial T}\right)_{V,\{N_j\}} \geq 0, \qquad \kappa_{T,\{N_j\}} = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,\{N_j\}} \geq 0,$$

$$\text{and} \qquad \sum_{i=1}^{l}\sum_{j=1}^{l}\left(\frac{\partial\mu'_j}{\partial N_i}\right)_{T,P,\{N_{k\neq i}\}} \Delta N_i \Delta N_j \geq 0. \tag{2.179}$$

Conditions (2.179) are a realization of Le Châteliers's famous principle: *If a system is in stable equilibrium, then any spontaneous change in its parameters must bring about processes which tend to restore the system to equilibrium.*

The first condition in Eq. (2.179), $C_{V,\{N_j\}} \geq 0$, is a condition for *thermal stability.* If a small excess of heat is added to a volume element of fluid, then the temperature of the volume element must increase relative to its surroundings so that some of the heat will flow out again. This requires that the heat capacity be positive. If the heat capacity were negative, the temperature would decrease and even more heat would flow in, thus leading to an instability. From Eqs. (2.150) and (2.179) we can also show that

$$C_{P,\{N_j\}} > C_{V,\{N_j\}} \geq 0. \tag{2.180}$$

The second condition in Eq. (2.179), $\kappa_{T,\{N_j\}} \geq 0$, is a condition for *mechanical stability.* If a small volume element of fluid spontaneously increases, the pressure of the fluid inside the fluid element must decrease relative to its surroundings so that the larger pressure of the surroundings will stop the growth of the volume element. This requires that the compressibility be positive. If the compressibility were negative, the pressure would increase and the volume element would continue to grow, thus leading to an instability. From Eqs. (2.151) and (2.179) we can show that

$$\kappa_{T,\{N_j\}} > \kappa_{S,\{N_j\}} \geq 0. \tag{2.181}$$

The third condition, $\sum_{i=1}^{l}\sum_{j=1}^{l}(\partial\mu'_j/\partial N_i)_{T,P,\{N_{k\neq i}\}}\,\Delta N_i \Delta N_j \geq 0$, where ΔN_i and ΔN_j are arbitrary variations, is the condition for *chemical stability.* We can write the condition for chemical stability in matrix form:

$$(\Delta N_1, \Delta N_2, \ldots, \Delta N_l)\begin{pmatrix} \mu'_{1,1} & \mu'_{1,2} & \cdots & \mu'_{1,l} \\ \mu'_{2,1} & \mu'_{2,2} & \cdots & \mu'_{2,l} \\ \vdots & \vdots & \ddots & \vdots \\ \mu'_{l,1} & \mu'_{l,2} & \cdots & \mu'_{l,l} \end{pmatrix}\begin{pmatrix} \Delta N_1 \\ \Delta N_2 \\ \vdots \\ \Delta N_l \end{pmatrix} \geq 0, \tag{2.182}$$

where $\mu'_{j,i} \equiv (\partial\mu'_j/\partial N_i)_{T,P,\{N_{k\neq i}\}}$. Because of the Maxwell relation $\mu'_{j,i} = \mu'_{i,j}$ [cf. Eq. (2.115)], the matrix

$$\bar{\mu}' \equiv \begin{pmatrix} \mu'_{1,1} & \mu'_{1,2} & \cdots & \mu'_{1,l} \\ \mu'_{2,1} & \mu'_{2,2} & \cdots & \mu'_{2,l} \\ \vdots & \vdots & \ddots & \vdots \\ \mu'_{l,1} & \mu'_{l,2} & \cdots & \mu'_{l,l} \end{pmatrix} \tag{2.183}$$

is symmetric. In addition, in order to satisfy the condition for chemical stability, the matrix $\bar{\mu}'$ must be a positive definite matrix. A symmetric matrix is

positive definite if $\mu_{ii} > 0$ $(i = 1, \ldots, l)$ and if every principal minor is positive or zero.

■ **EXERCISE 2.9.** A mixture of particles, A and B, has a Gibbs free energy of the form

$$G = n_A\mu_A^0(P,T) + n_B\mu_B^0(P,T) + RTn_A\ln(x_A) + RTn_B\ln(x_B) + \lambda\frac{n_An_B}{n},$$

where $n = n_A + n_B, x_A = n_A/n$, and $x_B = n_B/n$ (n indicates mole number), μ_A^0 and μ_B^0 are functions only of P and T. Plot the region of thermodynamic instability in the $x_A - T$ plane.

Answer: For chemical stability, the matrix

$$\begin{pmatrix} \mu_{A,A} & \mu_{A,B} \\ \mu_{B,A} & \mu_{B,B} \end{pmatrix}$$

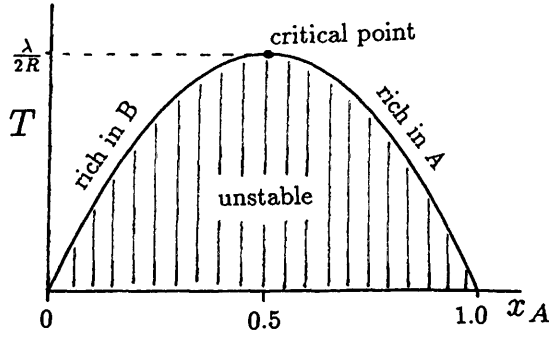
must be symmetric positive definite. This requires that $(\partial\mu_A/\partial n_A)_{P,T,n_B} > 0$, $(\partial\mu_B/\partial n_B)_{P,T,n_A} > 0$, and $(\partial\mu_A/\partial n_B)_{P,T,n_A} = (\partial\mu_B/\partial n_A)_{P,T,n_B} < 0$. The chemical potential of the A-type particle is

$$\mu_A = \left(\frac{\partial G}{\partial n_A}\right)_{P,T,n_B} = \mu_A^0(P,T) + RT\ln(x_A) + \lambda\frac{n_B}{n} - \lambda\frac{n_An_B}{n^2}. \qquad (2)$$

A condition for thermodynamic stability is

$$\left(\frac{\partial\mu_A}{\partial n_A}\right)_{P,T,n_B} = \frac{RT}{x_A}\frac{n_B}{n^2} - 2\frac{\lambda n_B}{n^2} + 2\frac{\lambda n_An_B}{n^3} > 0, \qquad (3)$$

or $x_A^2 - x_A + RT/2\lambda > 0$. For $T > \lambda/2R$, this is always satisfied. A plot of $T = (2\lambda/R)(x_A - x_A^2)$ is given below.



The shaded region corresponds to $x_A^2 - x_A + RT/2\lambda < 0$ and is thermodynamically unstable. The unshaded region is thermodynamically stable. For $T < \lambda/2R$, two values of x_A satisfy the condition $x_A^2 - x_A + RT/2\lambda > 0$ for

each value of T. These two values of x_A lie outside and on either side of the shaded region and are the mole fractions of two coexisting phases of the binary mixture, one rich in A and the other rich in B. For $T > \lambda/2R$, only one value of x_A satisfies the condition $x_A^2 - x_A + RT/2\lambda > 0$, so only one phase of the substance exists. (As we shall see in Chapter 3, a thermodynamically stable state may not be a state of thermodynamic equilibrium. For thermodynamic equilibrium we have the additional condition that the free energy be minimum or the entropy be maximum. A thermodynamically stable state which is not an equilibrium state is sometimes called a *metastable* state. It can exist in nature but eventually will decay to an absolute equilibrium state.)

2.H.3. Implications of the Stability Requirements for the Free Energies

The stability conditions place restrictions on the derivatives of the thermodynamic potentials. Before we show this, it is useful to introduce the concept of concave and convex functions [14]:

(**a**) A function $f(x)$ is a *convex* function if $d^2f(x)/dx^2 \geq 0$ for all x (cf. Fig. 2.9). For any x_1 and x_2 the chord joining the points $f(x_1)$ and $f(x_2)$ lies above or on the curve $f(x)$ for all x in the interval $x_1 < x < x_2$. If $df(x)/dx$ exists at a given point, the tangent at that point always lies below the function except at the point of tangency.

(**b**) A function $f(x)$ is a *concave* function of x if the function $-f(x)$ is convex.

We can now consider the effect of the stability requirements on the Helmholtz and Gibbs free energies.

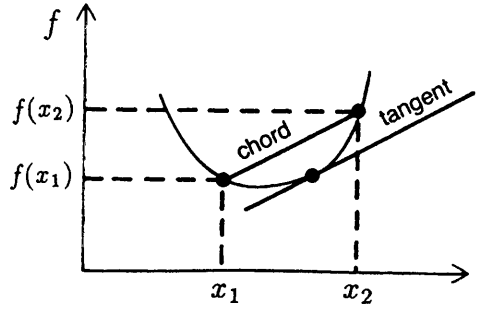


Fig. 2.9. The function $f(x)$ is a convex function of x.

From Eq. (2.97) and the stability condition, Eq. (2.180), we can write

$$\left(\frac{\partial^2 A}{\partial T^2}\right)_{V,\{N_j\}} = -\left(\frac{\partial S}{\partial T}\right)_{V,\{N_j\}} = -\frac{C_{V,\{N_j\}}}{T} < 0, \tag{2.184}$$

and from Eq. (2.98) and the stability condition, Eq. (2.181), we can write

$$\left(\frac{\partial^2 A}{\partial V^2}\right)_{T,\{N_j\}} = -\left(\frac{\partial P}{\partial V}\right)_{T,\{N_j\}} = \frac{1}{V\kappa_{T,\{N_j\}}} > 0 \tag{2.185}$$

The Helmholtz free energy is a concave function of temperature and a convex function of volume.

From Eq. (2.109) and the stability condition, Eq. (2.180), we can write

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,\{N_j\}} = -\left(\frac{\partial S}{\partial T}\right)_{P,\{N_j\}} = -\frac{C_{P,\{N_j\}}}{T} < 0, \tag{2.186}$$

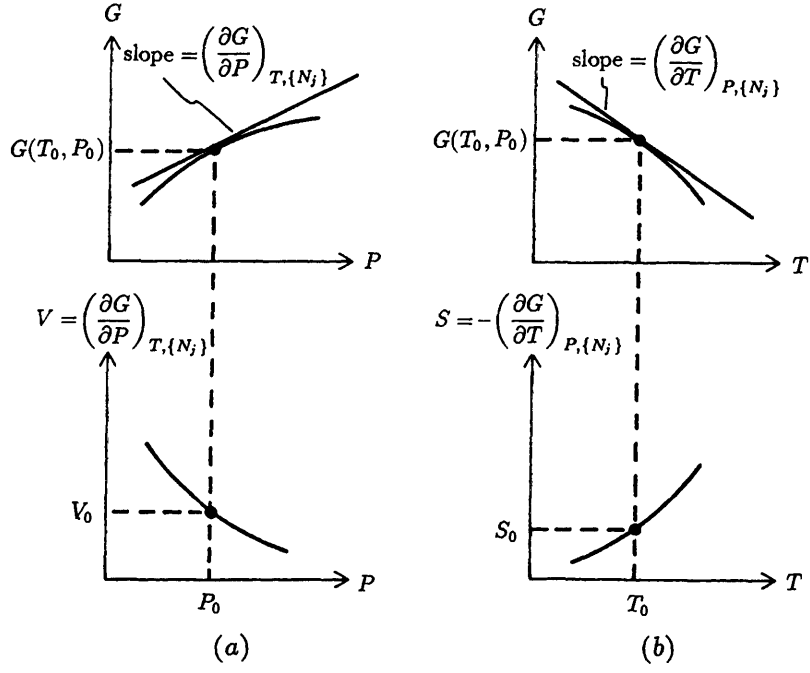


Fig. 2.10. (a) A plot of the Gibbs free energy and its slope as a function of pressure. (b) A plot of the Gibbs free energy and its slope as a function of temperature. Both plots are done in a region which does not include a phase transition.

and from Eq. (2.110) and the stability condition, Eq. (2.181), we can write

$$\left(\frac{\partial^2 G}{\partial P^2}\right)_{T,\{N_j\}} = \left(\frac{\partial V}{\partial P}\right)_{T,\{N_j\}} = -V\kappa_{T,\{N_j\}} < 0, \tag{2.187}$$

Thus, *the Gibbs free energy is a concave function of temperature and a concave function of pressure.*

It is interesting to sketch the free energy and its slope as function of pressure and temperature. A sketch of the Gibbs free energy, for a range of pressure and temperature for which no phase transition occurs, is given in Fig. 2.10. The case of phase transitions is given in Chapter 3.

The form of the Gibbs and Helmholtz free energies for a magnetic system is not so easy to obtain. However, Griffiths [15] has shown that for system of uncharged particles with spin, $G(T,H)$ is a concave function of T and H and $A(T,M)$ is a concave function of T and convex function of M. In Fig. 2.11, we sketch the Gibbs free energy and its slope as a function of T and H for a paramagnetic system.

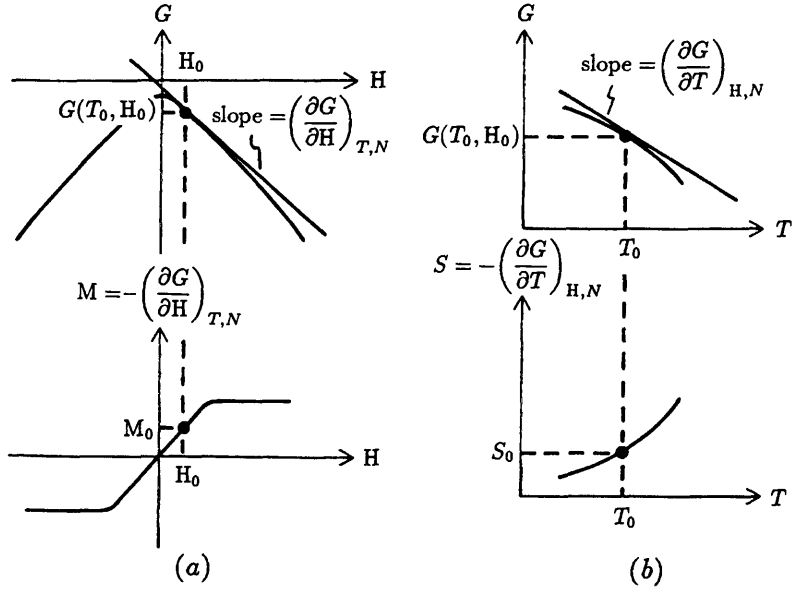


Fig. 2.11. (a) A plot of the Gibbs free energy and its slope as a function of applied field. (b) A plot of the Gibbs free energy and its slope as a function of temperature. Both plots are done in a region which does not include a phase transition.

▶ SPECIAL TOPICS

▶ S2.A. Cooling and Liquefaction of Gases [6]

All neutral gases (if we exclude gravitational effects) interact via a potential which has a hard core and outside the core a short-ranged attractive region. If such a gas is allowed to expand, it must do work against the attractive forces and its temperature will decrease. This effect can be used to cool a gas, although the amount of cooling that occurs via this mechanism alone is very small. We shall study two different methods for cooling: one based solely on free expansion and one which involves throttling of the gas through a porous plug or constriction. The second method is the basis for gas liquefiers commonly used in the laboratory.

▶ S2.A.1. The Joule Effect: Free Expansion

Experiments which attempted to measure cooling due to free expansion were first performed by Gay-Lussac in 1807 and were improved upon by Joule in 1843. The free expansion process is shown schematically in Fig. 2.12. The gas is initially confined to an insulated chamber with volume V_i at pressure P_i and temperature T_i. It is then allowed to expand suddenly into an insulated evacuated chamber with volume V_f. Since the gas expands freely, no work will be done and $\Delta W = 0$. Furthermore, since both chambers are insulated, no heat will be added and $\Delta Q = 0$. Thus, from the first law the internal energy must remain constant, $\Delta U = 0$, during the process. The only effect of free expansion is a transfer of energy between the potential energy and kinetic energy of the particles.

Because free expansion takes place spontaneously, the entropy of the gas will increase even though no heat is added. During the expansion we cannot use thermodynamics to describe the state of the system because it will not be in equilibrium, even locally. However, after the system has settled down and

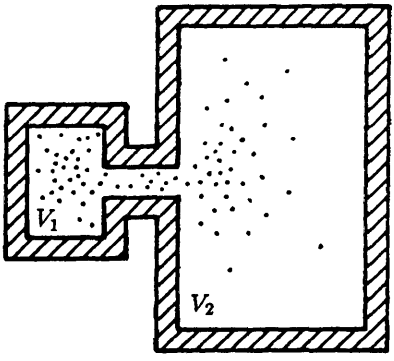


Fig. 2.12. The Joule effect. Free expansion of a gas from an insulated chamber of volume, V_1, into an insulated evacuated chamber of volume, V_2, causes cooling.

reached a final equilibrium state, we can use the thermodynamics to relate the initial and final states by finding an imaginary reversible path between them.

During the expansion the internal energy does not change and the particle number does not change. Thus, the internal energies and particle numbers of the initial and final states must be the same, and for our imaginary reversible path we can write

$$[dU]_n = 0 = \left(\frac{\partial U}{\partial T}\right)_{V,n} dT + \left(\frac{\partial U}{\partial V}\right)_{T,n} dV, \tag{2.188}$$

where n is the number of moles of gas. From Eq. (2.188), we can write

$$dT = -\frac{\left(\frac{\partial U}{\partial V}\right)_{T,n}}{\left(\frac{\partial U}{\partial T}\right)_{V,n}} dV = \left(\frac{\partial T}{\partial V}\right)_{U,n} dV, \tag{2.189}$$

where we have made use of the chain rule, Eq. (2.6). The quantity $(\partial T/\partial V)_{U,n}$ is called the *Joule coefficient.*

Let us compute the Joule coefficient for various gases. From Eq. (2.145), we know that

$$\left(\frac{\partial U}{\partial V}\right)_{T,n} = T\left(\frac{\partial P}{\partial T}\right)_{V,n} - P. \tag{2.190}$$

For an ideal gas we have the equation of state, $PV = nRT$, and we find that $(\partial U/\partial V)_{T,n} = 0$. Therefore, for an ideal gas the Joule coefficient, $(\partial T/\partial V)_{U,n} = 0$, and the temperature of an ideal gas cannot change during free expansion.

For a van der Waals gas [cf. Eq. (2.12)], we have

$$\left(\frac{\partial U}{\partial V}\right)_{T,n} = \frac{an^2}{V^2}. \tag{2.191}$$

For this case, there will be a change in internal energy due to interactions as volume changes if temperature is held fixed. To obtain the Joule coefficient, we must also find the heat capacity of the van der Waals gas. From Eq. (2.146), we obtain

$$\left(\frac{\partial C_{V,n}}{\partial V}\right)_{T,n} = T\left(\frac{\partial^2 P}{\partial T^2}\right)_{V,n} = 0. \tag{2.192}$$

Therefore, for a van der Waals gas the heat capacity, $C_{V,n}$, is independent of volume and can depend only on mole number and temperature:

$$C_{V,n} = C_{V,n}(T, n). \tag{2.193}$$

Since the heat capacity, $C_{V,n}$, contains no volume corrections due to interactions, it is thermodynamically consistent to choose its value to be equal to that of an ideal gas (at least in the regime where the van der Waals equation describes a gas). If we neglect internal degrees of freedom, we can write $C_{V,n} = \frac{3}{2}nR$. The Joule coefficient for a van der Waals gas then becomes

$$\left(\frac{\partial T}{\partial V}\right)_{U,n} = -\frac{2}{3}\frac{an}{RV^2}. \tag{2.194}$$

Using Eq. (2.194), we can integrate Eq. (2.189) between initial and final states. We find

$$T_f = \frac{2an}{3R}\left(\frac{1}{V_f} - \frac{1}{V_i}\right) + T_i. \tag{2.195}$$

The fractional change in temperature is therefore

$$\bar{\Delta}T = \left(\frac{T_f - T_i}{T_i}\right) = \frac{2an}{3RT_i}\left(\frac{1}{V_f} - \frac{1}{V_i}\right). \tag{2.196}$$

If $V_f > V_i$, the temperature will always decrease. We can use values of the van der Waals constant, a, given in Table 2.1 to estimate the change in temperature for some simple cases. Let us assume that $V_i = 10^{-3}\,\mathrm{m}^3$, $T_i = 300\,\mathrm{K}$, $n = 1$ mol, and $V_f = \infty$ (this will give maximum cooling). For oxygen we have $\bar{\Delta}T \approx -0.037$, and for carbon dioxide we obtain, $\bar{\Delta}T \approx -0.097$. We must conclude that free expansion alone is not a very effective way to cool a gas.

▶ S2.A.2. The Joule–Kelvin Effect: Throttling

Throttling of a gas through a porous plug or a small constriction provides a much more efficient means of cooling than free expansion and is the basis of most liquification machines. The throttling process in its simplest form is depicted in Fig. 2.13. A gas initially at a pressure, P_i, temperature, T_i, and volume, V_i, is forced through a porous plug into another chamber, maintained at pressure, $P_f < P_i$. All chambers and the plug are insulated so $\Delta Q = 0$ for the process. The gas inside the plug is forced through narrow twisting chambers irreversibly. Work must be done to force the gas through the plug. Even though the entire process is irreversible, we can use thermodynamics to relate the initial and final states.

The net work done by the gas is

$$\Delta W = \int_0^{V_f} P_f dV + \int_{V_i}^{0} P_i dV = P_f V_f - P_i V_i. \tag{2.197}$$

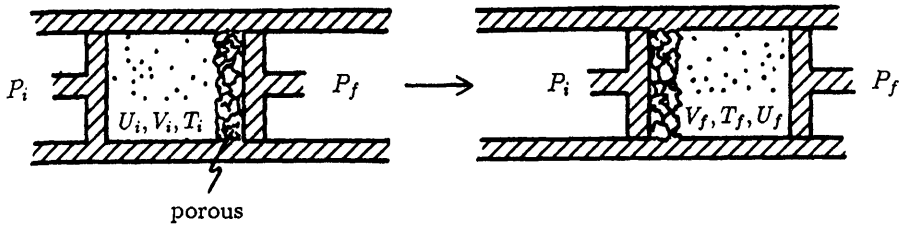


Fig. 2.13. The Joule–Kelvin effect. Throttling of a gas through a porous plug can cause cooling or heating.

From the first law, $\Delta U = -\Delta W$ since $\Delta Q \equiv 0$. Thus,

$$U_f + P_f V_f = U_i + P_i V_i \tag{2.198}$$

or, in terms of enthalpy,

$$H_f = H_i. \tag{2.199}$$

Thus, the throttling process is one which takes place at constant enthalpy.

Let us now construct a hypothetical reversible path to describe the constant enthalpy process. For each differential change along the reversible path, we have (assuming the total particle number remains constant)

$$[dH]_n = 0 = T\,dS + V\,dP. \tag{2.200}$$

We see that the increase in entropy due to the throttling process is accompanied by a decrease in pressure. It is convenient to use temperature and pressure as independent variables rather than entropy and pressure. We therefore expand the entropy

$$[dS]_n = \left(\frac{\partial S}{\partial T}\right)_{P,n} dT + \left(\frac{\partial S}{\partial P}\right)_{T,n} dP \tag{2.201}$$

and obtain

$$[dH]_n = 0 = C_{P,n} dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_{P,n}\right] dP. \tag{2.202}$$

In Eq. (2.202) we have used Eqs. (2.144) and (2.112). Equation (2.202) can be rewritten in the form

$$dT = \left(\frac{\partial T}{\partial P}\right)_{H,n} dP, \tag{2.203}$$

where $(\partial T/\partial P)_{H,n}$ is the *Joule–Kelvin coefficient* and is defined

$$\mu_{JK} = \left(\frac{\partial T}{\partial P}\right)_{H,n} = -\frac{\left(\frac{\partial H}{\partial P}\right)_{T,n}}{\left(\frac{\partial H}{\partial T}\right)_{P,n}} = \frac{1}{C_{P,n}}\left[T\left(\frac{\partial V}{\partial T}\right)_{P,n} - V\right]. \tag{2.204}$$

Let us now compute the Joule–Kelvin coefficient for various gases. For an ideal gas, $(\partial V/\partial T)_{P,n} = (V/T)$ and therefore the Joule–Kelvin coefficient, $(\partial T/\partial P)_{H,n}$, equals 0. There will be no temperature change during the throttling process for an ideal gas. Furthermore, since $T_i = T_f$ for ideal gases, $P_f V_f = P_i V_i$ and no net work will be done ($\Delta W = 0$). If work had been done on or by the gas, we would expect a temperature change since the process is adiabatic.

For a van der Waals gas, assuming that $C_{V,n} = \frac{3}{2}nR$, we find

$$\left(\frac{\partial T}{\partial P}\right)_{H,n} = \frac{1}{R}\left[\frac{2a}{RT}\left(\frac{v-b}{v}\right)^2 - b\right] \Bigg/ \left[\frac{5}{2} - \frac{3a}{RTv}\left(\frac{v-b}{v}\right)^2\right], \tag{2.205}$$

where $v = V/n$ is the molar volume. Equation (2.205) is straightforward to obtain from the righthand term in Eg. (2.204) and from Egs. (2.12), (2.144), and (2.100). For an interacting gas, such as the van der Waals gas, the Joule–Kelvin coefficient can change sign. This is easiest to see if we consider low densities so that $RTv \gg a$ and $v \gg b$. Then

$$\left(\frac{\partial T}{\partial P}\right)_{H,n} \approx \frac{2}{5R}\left[\frac{2a}{RT} - b\right]. \tag{2.206}$$

For low temperatures $(\partial T/\partial P)_{H,n} > 0$, and gases cool in the throttling process, but at high temperatures, we have $(\partial T/\partial P)_{H,n} < 0$, and they heat up. Two effect determine the behaviour of the Joule–Kelvin coefficient. On the one hand, the gas expand, which gives rise to cooling. On the other hand, work can be done on or by the gas. If $P_i V_i > P_f V_f$, then net work is done on the gas, which causes heating. If $P_i V_i < P_f V_f$, then net work is done by the gas, which causes cooling.

The inversion temperature (the temperature at which the sign of μ_{JK} changes) for the Joule–Kelvin coefficient will be a function of pressure. Since $C_{P,n} > 0$, the condition for inversion [from Eq. (2.204)] is

$$\left(\frac{\partial V}{\partial T}\right)_{P,n} = \frac{V}{T} \tag{2.207}$$

or, for a van der Waals gas [cf. Eq. (2.205)],

$$\frac{2a}{RT}\left(\frac{v-b}{v}\right)^2 = b. \tag{2.208}$$

We can use the van der Waals equation, (2.12), to write Eq. (2.208) in terms of pressure and temperature. First solve Eq. (2.208) for v as a function R, T, a, and b, and substitute into the van der Waals equation. This gives

$$P = \frac{2}{b}\sqrt{\frac{2aRT}{b} - \frac{3RT}{2b} - \frac{a}{b^2}}. \tag{2.209}$$

The inversion curve predicted by the van der Waals equation has the shape of a parabola with a maximum at $T_{\max}^{VW} = 8a/9bR$. For CO_2, $T_{\max}^{VW} = 911\,\mathrm{K}$ while the experimental value [15] is $T_{\max}^{VW} = 1500\,\mathrm{K}$. For H_2, $T_{\max}^{VW} = 99\,\mathrm{K}$ while the experimental value [15] is $T_{\max}^{VW} = 202\,\mathrm{K}$. In Fig. 2.14, we plot the van der Waals and the experimental inversion curves for N_2. The van der Waals equation predicts an inversion curve which lies below the experimental curve but qualitatively has the correct shape. For nitrogen at $P = 10^5\,\mathrm{Pa}$, $\mu_{JK} = 1.37 \times 10^{-7}\,\mathrm{K/Pa}$ at $T = 573\,\mathrm{K}$, $\mu_{JK} = 1.27 \times 10^{-6}\,\mathrm{K/Pa}$ at $T = 373\,\mathrm{K}$, $\mu_{JK} = 6.40 \times 10^{-6}\,\mathrm{K/Pa}$ at $T = 173\,\mathrm{K}$, and $\mu_{JK} = 2.36 \times 10^{-5}\,\mathrm{K/Pa}$ at $T = 93\,\mathrm{K}$. (For experimental value of μ_{JK} for other substances, see the International Critical Tables [5].) We see that the cooling effect can be quite large for throttling.

A schematic drawing of a liquefaction machine which utilizes the Joule–Kelvin effect is shown in Fig. 2.15. Gas is precooled in a vessel, A, below its inversion temperature and expanded through a small orifice into vessel, B, thus causing it to cool due to the Joule–Kelvin effect. The cooled gas is allowed to circulate about the tube in B so that the gas in the tube becomes progressively

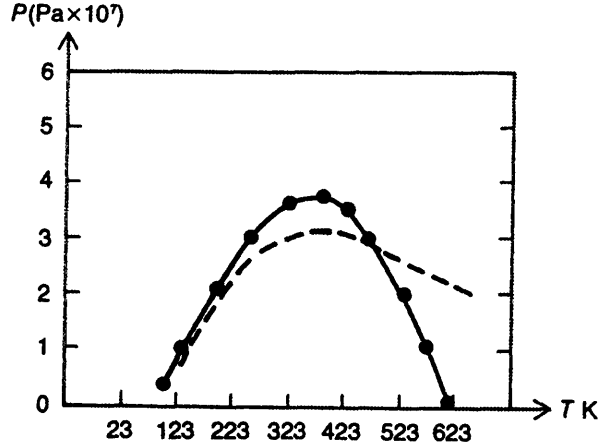


Fig. 2.14. A plot of the inversion temperature versus pressure for the Joule–Kelvin coefficient of N_2. The solid line is the experimental curve [6]. The dashed line is the curve predicted by the van der Waals equation for $a = 0.1408$ Pa. $\mathrm{M}^6/\mathrm{mol}^2$ and $b = 0.03913\mathrm{m}^3/\mathrm{mol}$.

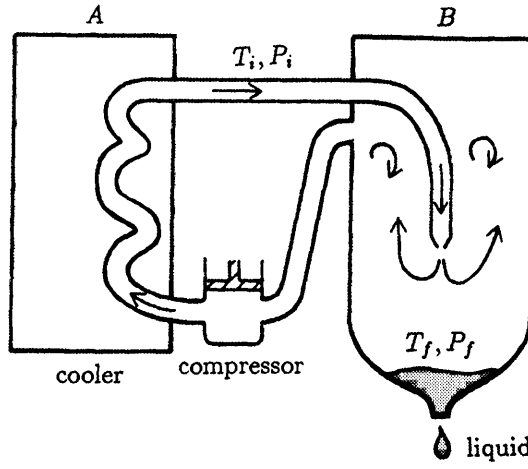


Fig. 2.15. Schematic drawing of a gas liquefier using the Joule–Kelvin effect.

cooler before expanding through the orifice. The process is run continuously and eventually the gas liquefies and collects below.

At times the Joule–Kelvin effect can lead to serious difficulties. For example, highly compressed H_2, which has a low inversion temperature, can ignite spontaneously when leaking from a damaged container, because of Joule–Kelvin heating.

▶ S2.B. Entropy of Mixing and the Gibbs Paradox [6]

If entropy is a measure of disorder in a system, then we expect that an entropy increase will be associated with the mixing of distinguishable substances, since this causes an increase in disorder. As we shall now show, this does indeed occur even for ideal gases.

Let us consider an ideal gas containing n_1 moles of atoms of type A_1, n_2 moles of atoms of type $A_2, \ldots$, and n_m moles of atoms of type A_m in a box of volume V and held at temperature T. The equation of state for the ideal gas mixture can be written

$$P = \sum_{j=1}^{m} P_j, \tag{2.210}$$

where P_j is the pressure of the j th component (partial pressure) and is defined as follows:

$$P_j = \frac{n_j RT}{V}. \tag{2.211}$$

The mole fraction of atoms of type A_j is defined as follows:

$$x_j = \frac{n_j}{\sum_{i=1}^{m} n_i} = \frac{P_j}{P}. \tag{2.212}$$

The change in the Gibbs free energy for an arbitrary change in the variables, $P, T, n_1, \ldots, n_m$, is

$$dG = -S\,dT + V\,dP + \sum_{j=1}^{m} \mu_j dn_j, \tag{2.213}$$

where μ_j is the chemical potential and S, V, and μ_j are given by Eqs. (2.109)–(2.111), but with mole number replacing particle number.

Let us now find the entropy of mixing for a mixture of distinguishable monatomic ideal gases. The Gibbs free energy of n moles of a monatomic ideal gas is

$$G(T, P, n) = -nRT \ln\left[\frac{T^{5/2}}{P}\right] + G^{(0)}, \tag{2.214}$$

where $G^{(0)}$ is a constant [cf. Eq. (2.107) and Exercise 2.3]. We will first consider a box held at temperature T and pressure P partitioned into m compartments, and let us assume the following: compartment 1 contains n_1 moles of atoms of type A_1 at pressure P and temperature T; compartment 2 contains n_2 moles of atoms of type A_2 at pressure P and temperature T; and so on. The compartments are separated by walls that can transmit heat and mechanical energy, so the pressure and temperature is uniform throughout the system. The Gibbs free energy of the system is the sum of the free energies of each compartment and can be written

$$G_I(P, T, n_1, \ldots, n_m) = -\sum_{j=1}^{m} n_j RT \ln\left[\frac{T^{5/2}}{P}\right] + G_I^{(0)}, \tag{2.215}$$

where $G_I^{(0)}$ is a constant. If we now remove the partitions and let the gases mix so that the final temperature and pressure are T and P, the Gibbs free energy of the mixture will be

$$\begin{aligned} G_F(P, T, n_1, \ldots, n_m) &= -\sum_{j=1}^{m} n_j RT \ln\left[\frac{T^{5/2}}{P_j}\right] + G_F^{(0)} \\ &= G_I(P, T, n_1, \ldots, n_m) + \sum_{j=1}^{m} n_j RT \ln(x_j) + G_F^{(0)} - G_I^{(0)}, \end{aligned} \tag{2.216}$$

where $G_F^{(0)}$ is a constant and we have used the relation $P_j = Px_j$. The change in the Gibbs free energy during the mixing process is therefore

$$\Delta G = G_F - G_I = \sum_{j=1}^{m} n_j RT \ln(x_j) + G_F^{(0)} - G_I^{(0)}. \tag{2.217}$$

From Eqs. (2.109) and (2.217), the increase in entropy due to mixing is

$$\Delta S_{\text{mix}} = -\sum_{j=1}^{m} n_j R \ln(x_j). \tag{2.218}$$

If $x_j = 1$ (one compartment and one substance), then $\Delta S_{\text{mix}} \equiv 0$, as it should be. If there are two compartments, each containing one mole, then $x_1 = (1/2)$ and $x_2 = (1/2)$ and $\Delta S_{\text{mix}} = 2R\ln(2)$ and the entropy increases during mixing.

It is important to note that Eq. (2.218) contains no explicit reference to the type of particles in the various compartments. As long as they are different, mixing increases the entropy. However, if they are identical, Eq. (2.218) tells us that there will still be an increase in entropy when the partitions are removed, even though the concept of mixing loses its meaning. Clearly, Eq. (2.218) does not work for identical particles. This was first noticed by Gibbs and is called the *Gibbs paradox*. The resolution of the Gibbs paradox lies in quantum mechanics, as we shall see when we come to statistical mechanics, (cf. Chapter 7). Identical particles must be counted in a different way from distinguishable particles (they have different "statistics"). This difference between identical and distinguishable particles persists even in the classical limit and leads to a resolution of the Gibbs paradox.

▶ S2.C. Osmotic Pressure in Dilute Solutions

Each spring, when the weather begins to warm up, sap rises in the trees, and the yearly cycle of life starts again. The rising of sap is one of many examples in biological systems of the phenomenon called *osmosis*. We can easily demonstrate the effect in the laboratory. Let us take a beaker of water and immerse a long tube (open at both ends) in it. The water levels of the tube and of the beaker will be the same. Next, close off the bottom end of the tube with a membrane which is permeable to water but not sugar. The water levels will still be the same in the tube and the beaker. Now add a bit of sugar to the water in the tube. Water will begin to enter the tube through the membrane, and the level of the sugar solution will rise a distance h above the level of the water in the beaker (cf. Fig. 2.16). The excess pressure created in the tube, $\pi = \rho_s hg$, is called the *osmotic pressure* (ρ_s is the density of the sugar solution and g is the acceleration of gravity). After equilibrium is reached, the pressure on the side of the membrane with sugar solution will be greater than that on the water side, by a factor π. The membrane must sustain the unbalanced force.

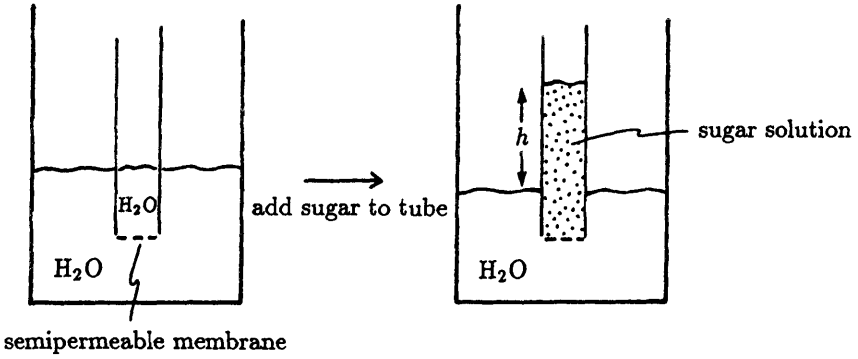


Fig. 2.16. The osmotic pressure of the sugar solution is $\pi = \rho_s hg$, where ρ_s is the density of the sugar solution and g is the acceleration of gravity.

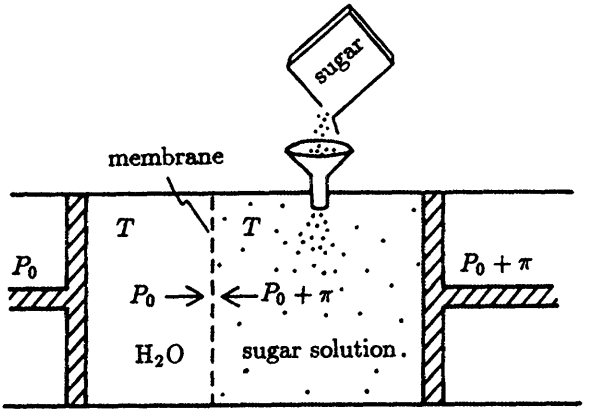


Fig. 2.17. A schematic representation of osmosis.

It is instructive to show the same phenomenon in another way (cf. Fig. 2.17). We will consider a system consisting of pure water, separated by a permeable (to water) membrane from a solution of sugar and water. The entire system is kept at a fixed temperature T, and the membrane is rigid. At equilibrium, there will be an imbalance in the pressures of the two sides. If P_0 is the pressure of the pure water, than the sugar solution will have a pressure $P = P_0 + \pi$, where π is the *osmotic pressure*. This imbalance of pressures is possible because the membrane is rigid and cannot transmit mechanical energy. Since the water is free to move through the membrane, the chemical potential of the pure water must be equal to the chemical potential of the water in the sugar solution.

Let us first write the thermodynamic relations for this system. First consider the sugar solution. A differential change in the Gibbs free energy, $G =$

$G(P, T, n_w, n_s)$, of the sugar solution (with n_w moles of water and n_s moles of sugar solution) can be written

$$dG = -S\,dT + V\,dP + \mu_w dn_w + \mu_s dn_s, \tag{2.219}$$

where $S = -(\partial G/\partial T)_{P,n_w,n_s}$ is the entropy of the solution, $V = (\partial G/\partial P)_{T,n_w,n_s}$ is the volume of the solution, and $\mu_w = (\partial G/\partial n_w)_{P,T,n_s}$ and $\mu_s = (\partial G/\partial n_s)_{P,T,n_w}$ are the chemical potentials of the water and sugar, respectively, in the solution. The chemical potentials are intensive and depend only on ratios n_s/n_w. It is convenient to introduce mole fractions

$$x_w = \frac{n_w}{n_w + n_s} = \frac{1}{1 + n_s/n_w} \quad \text{and} \quad x_s = \frac{n_s}{n_w + n_s} = \frac{n_s/n_w}{1 + n_s/n_w}. \tag{2.220}$$

Since $x_w + x_s = 1$, the chemical potentials can be written as a function of mole fraction, x_s. Thus, $\mu_w = \mu_w(P, T, x_s)$ and $\mu_s = \mu_s(P, T, x_s)$.

At equilibrium the chemical potentials of the pure water and the water in the sugar solution will be equal. If we let $\mu_w^{(0)}(P_0, T)$ denote the chemical potential of the pure water, we can write

$$\mu_w^{(0)}(P_0, T) = \mu_w(P, T, x_s) \tag{2.221}$$

as the condition for thermodynamic equilibrium.

We want to obtain an expression for the osmotic pressure in terms of measurable quantities. We will simplify properties of the solution as much as possible. We will assume that the solution is dilute so that $n_s/n_w \ll 1$ and $x_s \approx n_s/n_w \ll 1$. We can construct a fairly simple model to describe the solution. We write the Gibbs free energy of the solution in the form

$$\begin{aligned} G(P, T, n_s, n_w) = {} & n_w \mu_w^{(0)}(P, T) + n_s \mu_s^{(0)}(P, T) - \lambda \frac{n_s n_w}{n} \\ & + n_w RT \ln(x_w) + n_s RT \ln(x_s). \end{aligned} \tag{2.222}$$

The chemical potential $\mu_w^{(0)}(\mu_s^{(0)})$ contains contributions to the Gibbs free energy due to the presence of water (sugar) molecules and due to self-interactions. The term $-\lambda(n_s n_w/n)$ gives the contribution to the free energy due to interactions between sugar and water molecules. The last two terms on the right give contributions to the free energy due to mixing [cf. Eq. 3.57]. The chemical potential of the water in the solution can now be written

$$\mu_w(P, T, x_s) = \left(\frac{\partial G}{\partial n_w}\right)_{P,T,n_s} = \mu_w^{(0)}(P, T) - \lambda x_s^2 + RT \ln(1 - x_s), \tag{2.223}$$

where $\mu_w^{(0)}(P, T)$ is the chemical potential of pure water at pressure P and temperature T. For a dilute solution, $x_s = n_s/n \ll 1$ and $\ln(1 - x_s) =$

$-x_s - (1/2)x_s^2 - \cdots$. Thus, to lowest order in $x_s = n_s/n$, we find

$$\mu_w(P, T, x_s) \approx \mu_w^{(0)}(P, T) - x_s RT \tag{2.224}$$

for the chemical potential of water in a dilute sugar solution.

We now can find an expression for the osmotic pressure, $\pi = P - P_0$. Let us note that water, as well as most liquids, is very incompressible. The compressibility, κ_T, of water at 0 °C is $\kappa_T = 4.58 \times 10^{-11}$ cm^2/dyne. Therefore the quantity $(\partial\mu_w^0/\partial P)_{T,n_w} = (\partial V^0/\partial n_w)_{T,P} \equiv v_w^0$ (v_w^0 is the partial molar volume of water in the absence of solute and V^0 is the volume of water in the absence of solute) remains approximately constant for small changes in pressure. With this observation we can integrate $(\partial\mu_w^0/\partial P)_{T,n_w}$ to find

$$\mu_w^0(P, T) - \mu_w^0(P_0, T) \approx v_w^0(P - P_0) = v_w^0\pi. \tag{2.225}$$

Let us now assume that the change in the volume of water as we increase the number of moles is proportional to the number of moles so that $V^0 = n_w v_w^0$. Also, for very small concentrations of solute, we can assume that the change in the volume of water due to the presence of the solute is negligible so that $V^0 \approx V$, where V is the volume of the mixture. Then we can combine Eqs. (2.221), (2.224), and (2.225) to obtain

$$\pi \approx \frac{n_s RT}{V}. \tag{2.226}$$

Equation (2.226) is called *van't Hoff's law* and, surprisingly, looks very much like the ideal gas law, although we are by no means dealing with a mixture of ideal gases. Equation (2.226) is well verified for all dilute neutral solvent–solute systems.

■ **EXERCISE 2.10.** An experiment is performed in which the osmotic pressure of a solution, containing n_{suc} moles of sucrose ($C_{12}H_{22}O_{11}$) and 1 kg of water (H_2O), is found to have the following values [2]: (a) for $n_{suc} = 0.1, \pi = 2.53 \times 10^5$ Pa, (b) for $n_{suc} = 0.2, \pi = 5.17 \times 10^5$ Pa, and (c) for $n_{suc} = 0.3, \pi = 7.81 \times 10^5$ Pa. Compute the osmotic pressure of this system using van't Hoff's law. How do the computed values compare with the measured values?

Answer: The molecular weight of water (H_2O) is $M_{H_2O} = 18$ gr/mol. Therefore, 1 kg of water contains 55.56 mol of water. The molar volume of water is $v_{H_2O} = 18 \times 10^{-6}$ m^3/mol. The osmotic pressure of the solution, according to van't Hoff's law, is

$$\pi = \frac{n_{suc}}{55.56} \frac{(8.317\,\text{J/K})(303\,\text{K})}{18 \times 10^{-6}\,\text{m}^3/\text{mol}}.$$

The computed values are as follows: (a) For $n_{suc} = 0.1$, $\pi = 2.52 \times 10^5$ Pa, (b) for $n_{suc} = 0.2, \pi = 5.04 \times 10^5$ Pa, and (c) for $n_{suc} = 0.3, \pi = 7.56 \times 10^5$ Pa. The predictions of van't Hoff's law are good for a dilute solution of sucrose in water, but begin to deviate as the mole fraction of sucrose increases.

▶ S2.D. The Thermodynamics of Chemical Reactions [16–18]

Chemical reactions occur in systems containing several species of molecules (which we will call A, B, C, and D), which can transform into one another through inelastic collisions. A typical case might be one in which molecules A and B can collide inelastically to form molecules C and D. Conversely, molecules C and D can collide inelastically to form molecules A and B. The collisions occur at random and can be either elastic or inelastic. To be inelastic and result in a reaction, the two molecules must have sufficient energy to overcome any potential barriers to the reaction which might exist. Chemical equilibrium is a dynamical state of the system. It occurs when the rate of production of each chemical species is equal to its rate of depletion through chemical reactions. The chemical reactions themselves never stop, even at equilibrium.

In the early part of this century a Belgium scientist, de Donder, found that it was possible to characterize each chemical reaction by a single variable ξ, called the *degree of reaction*. In terms of ξ, it is then possible to determine when the Gibbs free energy has reached its minimum value (chemical reactions usually take place in systems with fixed temperature and pressure) and therefore when the chemical system reaches chemical equilibrium. It is important to notice that the concept of degree of reaction assumes that we can generalize the concept of Gibbs free energy to systems out of equilibrium.

▶ S2.D.1. The Affinity

Let us consider a chemical reaction of the form

$$-\nu_A A - \nu_B B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \nu_C C + \nu_D D. \tag{2.227}$$

The quantities ν_A, ν_B, ν_C, and ν_D are called *stoichiometric coefficients*; ν_j is the number of molecules of type j needed for the reaction to take place. By convention, ν_A and ν_B are negative. The constant k_1 is the rate constant for the forward reaction, and k_2 is the rate constant for the backward reaction. The rate constants give the probability per unit time that a chemical reaction takes place. If the rate constants are known, then one can find the rate of change in the

number of each type of molecule involved in the chemical reaction. For example, the rate of change in the number, N_A, of molecules of type A is given by

$$\frac{dN_A}{dt} = -k_1 N_A^{|\nu_A|} N_B^{|\nu_B|} + k_2 N_C^{|\nu_C|} N_D^{|\nu_D|}, \tag{2.228}$$

where $|\nu_A|$ denotes the absolute value of ν_A. Equation (2.228) reflects the fact that $|\nu_A|$ molecules of A and $|\nu_B|$ molecules of B must collide to destroy A molecules while $|\nu_C|$ molecules of C and $|\nu_D|$ molecules of D must collide to create A molecules.

Let us now assume that initially there are $n_A = -\nu_A n_0$ moles of A, $n_B = -\nu_B n_0 + N_B$ moles of B, $n_C = \nu_C n_0'$ moles of C, and $n_D = \nu_D n_0' + N_D$ moles of D. The reaction to the right will be complete when

$$n_A = 0, \qquad n_B = N_B, \qquad n_C = \nu_C(n_0 + n_0'), \qquad n_D = \nu_D(n_0 + n_0') + N_D.$$

We next define the *degree of reaction* by the equation

$$\xi = (n_0 + n_0') + \frac{n_A}{\nu_A}. \tag{2.229}$$

As we have defined it, ξ has the units of moles. In terms of ξ, the number of moles of each substance can be written

$$n_A = -\nu_A(n_0 + n_0') + \nu_A \xi, \tag{2.230}$$

$$n_B = -\nu_B(n_0 + n_0') + N_B + \nu_B \xi, \tag{2.231}$$

$$n_C = \nu_C \xi, \tag{2.232}$$

and

$$n_D = \nu_D \xi + N_D. \tag{2.233}$$

Any changes in the concentrations due to the reaction can therefore be written

$$dn_A = \nu_A d\xi, \quad dn_B = \nu_B d\xi, \quad dn_C = \nu_C d\xi, \quad dn_D = \nu_D d\xi \tag{2.234}$$

or

$$\frac{dn_A}{\nu_A} = \frac{dn_B}{\nu_B} = \frac{dn_C}{\nu_C} = \frac{dn_D}{\nu_D} = d\xi. \tag{2.235}$$

Equations (2.234) and (2.235) are very important because they tell us that any

changes in the thermodynamic properties of a system due to a given reaction can be characterized by a single variable.

From Eq. (2.108), differential changes in the Gibbs free energy may be written

$$dG = -S\,dT + V\,dP + \sum_{j=1}^{m} \mu_j dn_j = -S\,dT + V\,dP + \sum_{j=1}^{m} \mu_j \nu_j d\xi, \qquad (2.236)$$

where the sum is over the species which participate in the reaction. Therefore

$$\left(\frac{\partial G}{\partial \xi}\right)_{P,T} = \sum_{j=1}^{m} \mu_j \nu_j, \qquad (2.237)$$

and the quantity

$$A \equiv \sum_{j=1}^{m} \mu_j \nu_j \qquad (2.238)$$

is called the *affinity* (in some books the affinity is defined with an opposite sign). At chemical equilibrium, the Gibbs free energy must be a minimum,

$$\left(\frac{\partial G}{\partial \xi}\right)_{P,T}^{0} = A^0 = 0 \qquad (2.239)$$

(the superscript 0 denotes equilibrium) and, therefore, at chemical equilibrium the affinity must be zero.

We can easily find the sign of the affinity as the system moves toward chemical equilibrium from the left or right. At constant P and T, the Gibbs free energy, G, must always decrease as the system moves toward chemical equilibrium (at equilibrium G is a minimum). Therefore,

$$[dG]_{P,T} = \left(\frac{\partial G}{\partial \xi}\right)_{P,T} d\xi < 0. \qquad (2.240)$$

If the reaction goes to the right, then $d\xi > 0$ and $A < 0$. If the reaction goes to the left, then $d\xi < 0$ and $A > 0$. This decrease in the Gibbs free energy is due to spontaneous entropy production resulting from the chemical reactions (see Exercise 2.6).

If there are r chemical reactions in the system involving species, j, then there will be r parameters, ξ_k, needed to describe the rate of change of the number of moles, n_j:

$$dn_j = \sum_{k=1}^{r} \nu_{jk} d\xi_k. \qquad (2.241)$$

Table 2.2. Values of the Chemical Potential, μ^0, for Some Molecules in the Gas Phase at Pressure $P_0 = 1$ atm and Temperature $T_0 = 298$ K

Molecule	μ^0 (kcal/mol)
H_2	0.00
HI	0.31
I_2	4.63
N_2	0.00
NO_2	12.39
NH_3	−3.98
N_2O_4	23.49

The sum over k is over all chemical reactions in which molecules of type j participate.

Using ideal gas laws, some useful relations can be obtained for reactions in the gas phase. Consider a gas composed of four different kinds of molecules (A, B, C, and D) which undergo the reaction in Eq. (2.227). If the partial pressure of the ith constituent is P_i, the chemical potential of the ith constituent can be written

$$\mu_i(P_i, T) = \mu_i^0(P_0, T_0) - RT \ln\left[\left(\frac{T}{T_0}\right)^{5/2}\left(\frac{P_0}{P_i}\right)\right], \tag{2.242}$$

where $\mu_i^0(P_0, T_0)$ is the chemical potential of the ith constituent at pressure P_0 and temperature T_0. Values of μ_i^0, with $P_0 = 1$ atm and $T_0 = 298$ K, have been tabulated for many kinds of molecules [20]. A selection is given in Table 2.2. If we use Eq. (2.242), the Gibbs free energy can be written

$$\begin{aligned} G(T, P, \xi) &= \sum_i n_i \mu_i = \sum_i n_i \mu_i^0(P_0, T_0) - \sum_i n_i RT \ln\left[\left(\frac{T}{T_0}\right)^{5/2}\left(\frac{P_0}{P_i}\right)\right] \\ &= \sum_i n_i \mu_i^0(P_0, T_0) - \sum_i n_i RT \ln\left[\left(\frac{T}{T_0}\right)^{5/2}\left(\frac{P_0}{P}\right)\right] \\ &\quad + RT \ln[x_A^{n_A} x_B^{n_B} x_C^{n_C} x_D^{n_D}], \end{aligned} \tag{2.243}$$

and the affinity can be written

$$\begin{aligned} A(T,P,\xi) &= \sum_i \nu_i \mu_i^0(P_0,T_0) - \sum_i \nu_i RT \ln\left[\left(\frac{T}{T_0}\right)^{5/2}\left(\frac{P_0}{P_i}\right)\right] \\ &= \sum_i \nu_i \mu_i^0(P_0,T_0) - \sum_i \nu_i RT \ln\left[\left(\frac{T}{T_0}\right)^{5/2}\left(\frac{P_0}{P}\right)\right] \\ &\quad + RT \ln\left[\frac{x_C^{\nu_C} x_D^{\nu_D}}{x_A^{|\nu_A|} x_B^{|\nu_B|}}\right], \end{aligned} \tag{2.244}$$

where $P = \sum_i P_i$ is the pressure and T is the temperature at which the reaction occurs.

For "ideal gas reactions" the equilibrium concentrations of the reactants can be deduced from the condition that at equilibrium the affinity is zero, $A^0 = 0$. From Eq. (2.243) this gives the equilibrium condition

$$\ln\left[\frac{x_C^{\nu_C} x_D^{\nu_D}}{x_A^{|\nu_A|} x_B^{|\nu_B|}}\right] = \sum_i \nu_i \ln\left[\left(\frac{T}{T_0}\right)^{5/2}\left(\frac{P_0}{P}\right)\right] - \frac{1}{RT}\sum_i \nu_i \mu_i^0(P_0,T_0), \tag{2.245}$$

where $P_0 = 1$ atm and $T_0 = 298$ K. Equation (2.245) is called the *law of mass action*. As we shall show in Exercise 2.11, we can use it to compute the value of the degree of reaction, and therefore the mole fractions, at which chemical equilibrium occurs as a function of pressure and temperature.

▶ S2.D.2. Stability

Given the fact that the Gibbs free energy for fixed P and T is minimum at equilibrium, we can deduce a number of interesting general properties of chemical reactions. First, let us note that at equilibrium we have

$$\left(\frac{\partial G}{\partial \xi}\right)_{P,T}^0 = A^0 = 0 \tag{2.246}$$

and

$$\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{P,T}^0 = \left(\frac{\partial A}{\partial \xi}\right)_{P,T}^0 > 0. \tag{2.247}$$

Equations (2.246) and (2.247) are statements of the fact that the Gibbs free energy, considered as a function of P, T, and ξ, is minimum at equilibrium for fixed T and P.

From the fundamental equation, $H = G + TS$, we obtain several important relations. First, let us note that at equilibrium

$$\left(\frac{\partial H}{\partial \xi}\right)_{P,T}^{0} = T\left(\frac{\partial S}{\partial \xi}\right)_{P,T}^{0} \tag{2.248}$$

[we have used Eq. (2.246)]. Thus, changes in enthalpy are proportional to the changes in entropy. The left-hand side of Eq. (2.248) is called the *heat of reaction*. It is the heat absorbed per unit reaction in the neighborhood of equilibrium. For an exothermic reaction, $(\partial H/\partial \xi)_{P,T}^{0}$ is negative. For an endothermic reaction, $(\partial H/\partial \xi)_{P,T}^{0}$ is positive. From Eq. (2.109), Eq. (2.248) can be written

$$\left(\frac{\partial H}{\partial \xi}\right)_{P,T}^{0} = -T\left[\frac{\partial}{\partial \xi}\left(\frac{\partial G}{\partial T}\right)_{P,\xi}\right]_{P,T} = -T\left[\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial \xi}\right)_{P,T}\right]_{P,\xi} = -T\left(\frac{\partial A}{\partial T}\right)_{P,\xi}^{0}. \tag{2.249}$$

For an "ideal gas reaction," we can use Eqs. (2.244) and (2.249) to obtain an explicit expression for the heat of reaction. We find

$$\left(\frac{\partial H}{\partial \xi}\right)_{P,T}^{0} = \frac{5}{2}\sum_i \nu_i RT + \sum_i \nu_i RT \ln\left[\left(\frac{T}{T_0}\right)^{5/2}\left(\frac{P_0}{P}\right)\right] - RT \ln\left[\frac{x_C^{\nu_C} x_D^{\nu_D}}{x_A^{|\nu_A|} x_B^{|\nu_B|}}\right]. \tag{2.250}$$

If the total number of particles changes during the reaction ($\sum_i \nu_i \neq 0$), there will be contributions to the heat of reaction from two sources: (1) There will be a change in the heat capacity of the gas due to the change in particle number, and (2) there will be a change in the entropy due to the change in the mixture of the particles. If the total number of particles remains unchanged ($\sum_i \nu_i = 0$), the only contribution to the heat of reaction will come from the change in the mixture of particles (assuming we neglect changes to the heat capacity due to changes in the internal structure of the molecules).

Let us now obtain some other general properties of chemical reactions. From the chain rule [Eq. (2.6)] we can write

$$\left(\frac{\partial \xi}{\partial T}\right)_{P,A} = -\frac{\left(\frac{\partial A}{\partial T}\right)_{P,\xi}}{\left(\frac{\partial A}{\partial \xi}\right)_{P,T}} = \frac{1}{T}\frac{\left(\frac{\partial H}{\partial \xi}\right)_{P,T}}{\left(\frac{\partial A}{\partial \xi}\right)_{P,T}}. \tag{2.251}$$

The denominator in Eq. (2.251) is always positive. Thus, at equilibrium any small increase in temperature causes the reaction to shift in a direction in which heat is absorbed.

Let us next note the Maxwell relation

$$\left(\frac{\partial A}{\partial P}\right)_{T,\xi} = \left(\frac{\partial V}{\partial \xi}\right)_{P,T} \tag{2.252}$$

[cf. Eqs. (2.236) and (2.238)]. It enables us to write

$$\left(\frac{\partial \xi}{\partial P}\right)_{T,A} = -\frac{\left(\frac{\partial A}{\partial P}\right)_{T,\xi}}{\left(\frac{\partial A}{\partial \xi}\right)_{P,T}} = -\frac{\left(\frac{\partial V}{\partial \xi}\right)_{P,T}}{\left(\frac{\partial A}{\partial \xi}\right)_{P,T}}. \tag{2.253}$$

At equilibrium an increase in pressure at fixed temperature will cause the reaction to shift in a direction which decreases the total volume.

■ **EXERCISE 2.11.** Consider the reaction

$$N_2O_4 \rightleftharpoons 2NO_2,$$

which occurs in the gas phase. Start initially with 1 mol of N_2O_4 and no NO_2. Assume that the reaction occurs at temperature T and pressure P. Use ideal gas equations for the chemical potential. (a) Compute and plot the Gibbs free energy $G(T, P, \xi)$, as a function of the degree of reaction, ξ, for (i) $P = 1$ atm and $T = 298$ K and (ii) $P = 1$ atm and $T = 596$K. (b) Compute and plot the affinity, $A(T, P, \xi)$, as a function of the degree of reaction, ξ, for (i) $P = 1$ atm and $T = 298$ K and (ii) $P = 1$ and $T = 596$ K. (c) What is the degree of reaction, ξ, at chemical equilibrium for $P = 1$ atm and temperature $T = 298$ K? How many moles of N_2O_4 and NO_2 are present at equilibrium? (d) If initially the volume is V_0, what is the volume at equilibrium for $P = 1$ atm and $T = 298$ K? (e) What is the heat of reaction for $P = 1$ atm and $T = 298$ K?

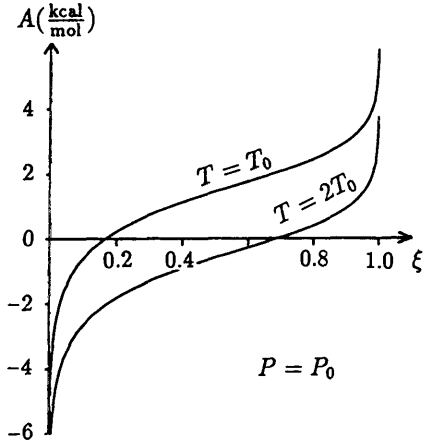
Answer: The number of moles can be written $n_{N_2O_4} = 1 - \xi$ and $n_{NO_2} = 2\xi$. The mole fractions are

$$x_{N_2O_4} = \frac{1-\xi}{1+\xi}, \qquad x_{NO_2} = \frac{2\xi}{1+\xi}. \tag{1}$$

(a) The Gibbs free energy is

$$G(T,P) = \sum_i n_i \mu_i^0(P_0, T_0) - \sum_i n_i RT \ln\left[\left(\frac{T}{T_0}\right)^{5/12}\left(\frac{P_0}{P}\right)\right] + RT \ln\left[\frac{(1-\xi)^{(1-\xi)}(2\xi)^{(2\xi)}}{(1+\xi)^{(1+\xi)}}\right], \tag{2}$$

where $i = (N_2O_4,\ NO_2)$. From Table 2.2, for $P_0 = 1$ atm and $T_0 = 298\,\text{K}$, $\mu^0_{N_2O_4} = 23.49\,\text{kcal/mol}$ and $\mu^0_{NO_2} = 12.39\,\text{kcal/mol}$. Plots of $G(T,P)$ are given below. Chemical equilibrium occurs for the value of ξ at the minimum of the curve.



(b) The affinity is

$$A(T,P) = \sum_i \nu_i \mu_i^0(P_0,T_0) - \sum_i \nu_i RT \ln\left[\left(\frac{T}{T_0}\right)^{5/2}\left(\frac{P_0}{P}\right)\right] + RT\ln\left[\frac{(2\xi)^2}{(1-\xi)(1+\xi)}\right]. \tag{3}$$

Plots of $A(T,P)$ are given in the figures.

(c) Chemical equilibrium occurs for the value of ξ at which $A = 0$. From the plot of the affinity, the equilibrium value of the degree of reaction is $\xi_{eq} \approx 0.166$. Thus, at equilibrium $n_{N_2O_4} = 0.834$ and $n_{NO_2} = 0.332$. At equilibrium the mole fractions are $x_{N_2O_4} = (0.834/1.166) = 0.715$ and $x_{NO_2} = (0.332/1.166) = 0.285$.

(d) Initially there are $n_{N_2O_4} = 1$ mol of N_2O_4 and $x_{NO_2} = 0$ mol of NO_2 and a total of 1 mol of gas present. At chemical equilibrium, there are $n_{N_2O_4} = 0.834$ mol of N_2O_4 and $n_{NO_2} = 0.332$ mol of NO_2 and a total of 1.166 mol of gas present. The reaction occurs at temperature T_0 and pressure P_0. Therefore, the initial volume is $V_0 = ((1)RT_0/P_0)$ and the final volume is $V = ((1.166)RT_0/P_0) = 1.166V_0$.

(e) The heat of reaction for the reaction occurring at temperature T_0 and pressure P_0 is

$$\left(\frac{\partial H}{\partial \xi}\right)^0_{P,T} = \frac{5}{2}RT_0 - RT_0 \ln\left[\frac{x^2_{NO_2}}{x_{N_2O_4}}\right] = \frac{5}{2}RT_0 - RT_0 \ln\left[\frac{(0.285)^2}{0.715}\right] = 4.68\,RT_0. \tag{4}$$

▶ S2.E. The Thermodynamics of Electrolytes [19–21]

A very important phenomenon in biological systems is the flow of charged ions in electrically neutral solutions. Of particular interest is the behaviour of dilute solutions of salt (the solutes), such as NaCl, KCl, or $CaCl_2$, in water (the solvent). If we denote the negative ion (the anion) as A^- and the positive ion (the cation) as C^+, the dissociation of the salt into charged ions can be denoted

$$A^-_{\nu_a} C^+_{\nu_c} \rightleftharpoons \nu_a A^- + \nu_c C^+ \tag{2.254}$$

(e.g., $CaCl_2 \rightleftharpoons 2Cl^- + Ca^+$), where ν_a and ν_c are the stoichiometric coefficients for the dissociation. The condition for equilibrium is

$$\mu_{ac} = \nu_a \mu_a^e + \nu_c \mu_c^e, \tag{2.255}$$

where $\mu_a^e(\mu_c^e)$ is the electrochemical of ion, A^- (C^+) and μ_{ac} is the chemical potential of the undissociated salt. Electrical neutrality of the fluid requires that

$$\nu_a z_a + \nu_c z_c = 0, \tag{2.256}$$

where $z_a e(z_c e)$ is the charge of the ion, A^- (C^+), and e is the charge of an electron. It is important to note that the mixture of a salt, such as NaCl, and water must be dealt with as a two-component system consisting of NaCl molecules and H_2O molecules. The salt can dissociate, but the numbers of anions and cations are not independent of one another. However, a thermodynamic framework can be set up to deal with the ions as separate entities, and that is what we will describe below.

The chemical potential of the salt in aqueous solution is extremely complicated, but experiments show that it can be written in the form

$$\mu_{ac}(P, T, x_{ac}) = \mu_{ac}^0(P, T) + RT \ln(\alpha_{ac}), \tag{2.257}$$

where α_{ac} is called the *activity* and will be defined below, and $\mu_{ac}^0(P, T)$ is the chemical potential of the salt in aqueous solution at temperature T and pressure P in the limit of infinite dilution. $\mu_{ac}^0(P, T)$ is *proportional* to the energy needed to add one salt molecule to pure water. We now define a reference value for the Gibbs free energy to be

$$G^0(P, T, n_{ac}, n_w) = n_{ac}\mu_{ac}^0(P, T) + n_w \mu_w^0(P, T), \tag{2.258}$$

where $n_{ac}(n_w)$ is the number of moles of salt (water) molecules in the system of interest and $\mu_w^0(P, T)$ is the chemical potential of pure water. In principle, we can obtain a numerical value for G^0. The difference between this reference

Gibbs free energy and the actual Gibbs free energy can be written

$$G - G^0 = n_{ac}(\mu_{ac} - \mu_{ac}^0) + n_w(\mu_w - \mu_w^0) = n_{ac}RT\ln(\alpha_{ac}) + n_w(\mu_w - \mu_w^0). \tag{2.259}$$

We can now relate the activity, α_{ac}, for the salt molecule to activities for the ions. We define

$$\alpha_{ac} = \alpha_a^{\nu_a}\alpha_c^{\nu_c}. \tag{2.260}$$

Then

$$\ln(\alpha_{ac}) = \nu_a \ln(\alpha_a) + \nu_c \ln(\alpha_c). \tag{2.261}$$

The condition for equilibrium, Eq. (2.255), is satisfied if we define the electrochemical potentials of the ions to be

$$\mu_a^e = \mu_a^0(P,T)) + RT\ln(\alpha_a) + z_a\mathrm{F}\phi \tag{2.262}$$

and

$$\mu_c^e = \mu_c^0(P,T) + RT\ln(\alpha_c) + z_c\mathrm{F}\phi, \tag{2.263}$$

where $\mu_{ac}^0 = \mu_a^0 + \mu_c^0$, and we use the condition for charge neutrality. Here ϕ is the electric potential, F is a Faraday, and z_i is the charge of the ith ion $(i = a, b)$.

The quantities α_a and α_c are defined to be the activities of the anion and cation, respectively. It is found experimentally that in the limit of infinite dilution, $\alpha_a = f_a c_a$ and $\alpha_c = f_c c_c$, where c_a and c_c are the concentrations (moles/volume) of the anions and cations, respectively. The quantities f_c and f_c are called *activity coefficients*. In the limit $c_i \to 0, f_i \to 1$ $(i = a, c)$. Solutions for which $f_c = 1$ and $f_a = 1$ are said to be *ideal*. For *ideal* solutions the electrochemical potentials of the ions can be written

$$\mu_a^e = \mu_a^0(P,T) + RT\ln(c_a) + z_a\mathrm{F}\phi \tag{2.264}$$

and

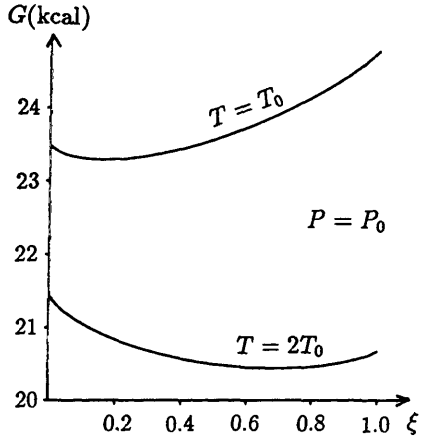
$$\mu_c^e = \mu_c^0(P,T) + RT\ln(c_c) + z_c\mathrm{F}\phi. \tag{2.265}$$

Because of these relationships, we can write changes in the Gibbs free energy as

$$\begin{aligned} dG &= -S\,dT + V\,dP + \mu_{ab}dn_{ab} + \mu_w dn_w \\ &= -S\,dT + V\,dP + \mu_a^e dn_a + \mu_c^e dn_c + \mu_w dn_w, \end{aligned} \tag{2.266}$$

where $dn_a = \nu_a dn_{ac}$ and $dn_c = \nu_c dn_{ac}$. Therefore, changes in the Gibbs free energy can be expressed either in terms of the salt or in terms of the ions. In Exercise 2.12, we give some examples of how these quantities can be used.

■ **EXERCISE 2.12.** Consider a vessel held at constant temperature T and pressure P, separated into two disjoint compartments, I and II, by a membrane. In each compartment there is a well-stirred, dilute solution of a solute and a solvent. Assume that the membrane is permeable to the solute, but not permeable to the solvent. Compute the ratios of the concentrations of solute in the two compartments for the following two cases. (a) The solute is uncharged, but the solvents in the two compartments are different. (b) The solute is charged and the fluids in the two compartments are maintained at different electric potentials, but the solvents are the same.



Answer:

(a) Denote the chemical potential of the solute in compartment I (II) as $(\mu_s)_I((\mu_s)_{II})$. Since the solute is uncharged, the chemical potential can be written $\mu_s = \mu_s^0 + RT \ln(c_s)$, where μ_s^0 is the chemical potential of the solute in the solvent in the limit of infinite dilution, and c_s is the concentration of the solute. The condition for equilibrium of the solute in the two compartments is

$$(\mu_s^0)_I + RT \ln(c_s^I) = (\mu_s^0)_{II} + RT \ln(c_s^{II}). \tag{1}$$

Thus, at equilibrium the ratio of the concentrations of solute in the two compartments is

$$\frac{c_s^I}{c_s^{II}} = \exp\left(\frac{(\mu_s^0)_{II} - (\mu_s^0)_I}{RT}\right). \tag{2}$$

The ratio $\beta_s \equiv c_s^I/c_s^{II}$ is called the *partition coefficient.* It is a measure of the different solubility of solute in the two solvents.

(b) Since the solute is charged, the chemical potential can be written $\mu_s = \mu_s^0 + RT \ln (c_s) + z_s F\phi$, where ϕ is the electric potential and z_s is the charge of the solute particles. Since the solvents are the same, the condition for equilibrium of the solute in the two compartment is

$$RT \ln (c_s^I) + z_s F\phi_I = RT \ln (c_s^{II}) + z_s F\phi_{II}. \tag{3}$$

Thus, at equilibrium the ratio of the concentrations of solute in the two compartments is

$$\frac{c_s^I}{c_s^{II}} = \exp\left(\frac{z_s F \Delta\phi}{RT}\right), \tag{3}$$

where $\Delta\phi = \phi_{II} - \phi_I$. Conversely, the potential difference for a given ratio of concentrations is

$$\Delta\phi = \phi_{II} - \phi_I = \frac{RT}{z_s F} \ln\left(\frac{c_s^I}{c_s^{II}}\right). \tag{4}$$

The potential difference, $\Delta\phi$, needed to maintain the concentration difference is called the *Nernst potential.*

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PROBLEMS

Problem 2.1. Test the following differentials for exactness. For those cases in which the differential is exact, find the function $u(x, y)$.

(**a**) $du_a = \frac{-y\,dx}{x^2+y^2} + \frac{x\,dy}{x^2+y^2}$.

(**b**) $du_b = (y - x^2)dx + (x + y^2)dy$.

(**c**) $du_c = (2y^2 - 3x)dx - 4xy\,dy$.

Problem 2.2. Consider the two differentials (1) $du_1 = (2xy + x^2)dx + x^2dy$ and (2) $du_2 = y(x - 2y)dx - x^2dy$. For both differentials, find the change in $u(x, y)$ between two points, (a, b) and (x, y). Compute the change in two different ways: (a) Integrate along the path $(a, b) \to (x, b) \to (x, y)$, and (b) integrate along the path $(a, b) \to (a, y) \to (x, y)$. Discuss the meaning of your results.

Problem 2.3. Electromagnetic radiation in an evacuated vessel of volume V at equilibrium with the walls at temperature T (black body radiation) behaves like a gas of photons having internal energy $U = aVT^4$ and pressure $P = (1/3)aT^4$, where a is Stefan's constant. (a) Plot the closed curve in the P–V plane for a Carnot cycle using blackbody radiation. (b) Derive *explicitly* the efficiency of a Carnot engine which uses blackbody radiation as its working substance.

Problem 2.4. A Carnot engine uses a paramagnetic substance as its working substance. The equation of state is $M = (nDH/T)$, where M is the magnetization, H is the magnetic field, n is the number of moles, D is a constant determined by the type of substance, and T is the temperature. (a) Show that the internal energy U, and therefore the heat capacity C_M, can only depend on the temperature and not the magnetization. Let us assume that $C_M = C =$ constant. (b) Sketch a typical Carnot cycle in the M–H plane. (c) Compute the total heat absorbed and the total work done by the Carnot engine. (d) Compute the efficiency of the Carnot engine.

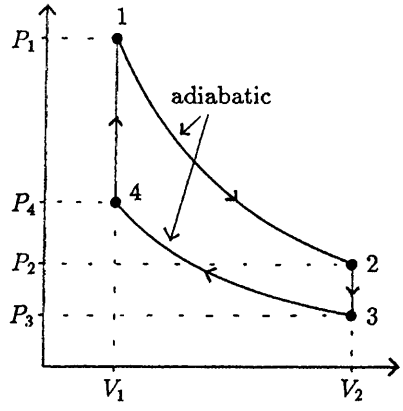


Fig. 2.18.

Problem 2.5. Find the efficiency of the engine shown in Fig. 2.18. Assume that the operating substance is an ideal monatomic gas. Express your answer in terms of V_1 and V_2. (The processes $1 \rightarrow 2$ and $3 \rightarrow 4$ are adiabatic. The processes $4 \rightarrow 1$ and $2 \rightarrow 3$ occur at constant volume.)

Problem 2.6. One kilogram of water is compressed isothermally at 20 °C from 1 atm to 20 atm. (a) How much work is required? (b) How much heat is ejected? Assume that the average isothermal compressibility of water during this process is $\kappa_T = 0.5 \times 10^{-4}$/atm and the average thermal expansivity of water during this process is $\alpha_P = 2 \times 10^{-4}/°\text{C}$.

Problem 2.7. Compute the efficiency of the heat engine shown in Fig. 2.19. The engine uses a rubber band whose equation of state is $J = \alpha LT$, where α is a constant, J is the tension, L is the length per unit mass, and T is the temperature in Kelvins. The specific heat (heat capacity per unit mass) is a constant, $c_L = c$.

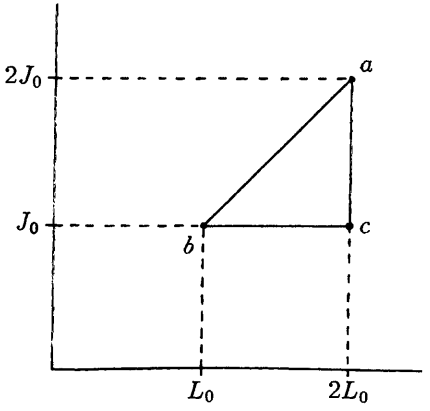


Fig. 2.19.

Problem 2.8. Experimentally one finds that for a rubber band

$$\left(\frac{\partial J}{\partial L}\right)_T = \frac{aT}{L_0}\left(1+2\left(\frac{L_0}{L}\right)^3\right) \quad \text{and} \quad \left(\frac{\partial J}{\partial T}\right)_L = \frac{aL}{L_0}\left(1-\left(\frac{L_0}{L}\right)^3\right),$$

where J is the tension, $a = 1.0 \times 10^3$ dyne/K, and $L_0 = 0.5$ m is the length of the band when no tension is applied. The mass of the rubber band is held fixed. (a) Compute $(\partial L/\partial T)_J$ and discuss its physical meaning. (b) Find the equation of state and show that dJ is an exact differential. (c) Assume that the heat capacity at constant length is $C_L = 1.0$J/K. Find the work necessary to stretch the band reversibly and adiabatically to a length of 1 m. Assume that when no tension is applied, the temperature of the band is $T = 290$ K. What is the change in temperature?

Problem 2.9. Blackbody radiation in a box of volume V and at temperature T has internal energy $U = aVT^4$ and pressure $P = (1/3)aT^4$, where a is the Stefan–Boltzmann constant. (a) What is the fundamental equation for blackbody radiation (the entropy)? (b) Compute the chemical potential.

Problem 2.10. Two vessels, insulated from the outside world, one of volume V_1 and the other of volume V_2, contain equal numbers N of the same ideal gas. The gas in each vessel is orginally at temperature T_i. The vessels are then connected and allowed to reach equilibrium in such a way that the combined vessel is also insulated from the outside world. The final volume is $V = V_1 + V_2$. What is the maximum work, ΔW_{free}, that can be obtained by connecting these insulated vessels? Express your answer in terms of T_i, V_1, V_2, and N.

Problem 2.11. For a low-density gas the virial expansion can be terminated at first order in the density and the equation of state is

$$P = \frac{Nk_BT}{V}\left[1+\frac{N}{V}B_2(T)\right],$$

where $B_2(T)$ is the second virial coefficient. The heat capacity will have corrections to its ideal gas value. We can write it in the form

$$C_{V,N} = \frac{3}{2}N\,k_B - \frac{N^2k_B}{V}F(T).$$

(a) Find the form that $F(T)$ must have in order for the two equations to be thermodynamically consistent. (b) Find $C_{P,N}$. (c) Find the entropy and internal energy.

Problem 2.12. Prove that

$$C_{Y,N} = \left(\frac{\partial H}{\partial T}\right)_{Y,N} \quad \text{and} \quad \left(\frac{\partial H}{\partial Y}\right)_{T,N} = T\left(\frac{\partial X}{\partial T}\right)_{Y,N} - X.$$

Problem 2.13. Compute the entropy, enthalpy, Helmholtz free energy, and Gibbs free energy of a paramagnetic substance and write them explicitly in terms of their natural variables when possible. Assume that the mechanical equation of state is $m = (DH/T)$ and that the molar heat capacity at constant magnetization is $c_m = c$, where m is the molar magnetization, H is the magnetic field, D is a constant, c is a constant, and T is the temperature.

Problem 2.14. Compute the Helmholtz free energy for a van der Waals gas. The equation of state is $(P + (\alpha n^2/V^2))(V - nb) = nRT$, where a and b are constants which depend on the type of gas and n is the number of moles. Assume that the heat capacity is $C_{V,n} = (3/2)nR$. Is this a reasonable choice for the heat capacity? Should it depend on volume?

Problem 2.15. Prove that (a) $\kappa_T(C_P - C_V) = TV\alpha_P^2$ and (b) $(C_P/C_V) = (\kappa_T/\kappa_S)$.

Problem 2.16. Show that $Tds = c_x(\partial T/\partial Y)_x dY + c_Y(\partial T/\partial x)_Y dx$, where $x = X/n$ is the amount of extensive variable, X, per mole, c_x is the heat capacity per mole at constant x, and c_Y is the heat capacity per mole at constant Y.

Problem 2.17. Compute the molar heat capacity c_P, the compressibilities κ_T and κ_s, and the thermal expansivity α_P for a monatomic van der Waals gas. Start from the fact that the mechanical equation of state is $P = (RT/(v - b)) - (\alpha/v^2)$ and the molar heat capacity is $c_v = 3R/2$, where $v = V/n$ is the molar volume.

Problem 2.18. Compute the heat capacity at constant magnetic field $C_{H,n}$, the susceptibilities $\chi_{T,n}$ and $\chi_{S,n}$, and the thermal expansivity $\alpha_{H,n}$ for a magnetic system, given that the mechanical equation of state is $M = nDH/T$ and the heat capacity is $C_{M,n} = nc$, where M is the magnetization, H is the magnetic field, n is the number of moles, D is a constant, c is the molar heat capacity, and T is the temperature.

Problem 2.19. A material is found to have a thermal expansivity $\alpha_P = (R/Pv) + (a/RT^2v)$ and an isothermal compressibility $\kappa_T = (1/v)(Tf(P) + (b/P))$, where $v = (V/n)$ is the molar volume. (a) Find $f(P)$. (b) Find the equation of state. (c) Under what conditions is this material stable?

Problem 2.20. Compute the efficiency of the reversible two heat engines in Fig. 2.20. Which engine is the most efficient? (Note that these are not Carnot cycles. The efficiency of a heat engine is $\eta = \Delta W_{total}/\Delta Q_{absorbed}$.)

Problem 2.21. It is found for a gas that $\kappa_T = Tvf(P)$ and $\alpha_P = (Rv/P) + (Av/T^2)$, where T is the temperature, v is the molar volume, P is the pressure, A is a constant, and $f(P)$ is an unknown function of P. (a) What is $f(P)$? (b) Find $v = v(P, T)$.

Problem 2.22. A monomolecular liquid at volume V_L and pressure P_L is separated from a gas of the same substance by a rigid wall which is permeable to the molecules, but does not allow liquid to pass. The volume of the gas is held fixed at V_G, but the volume

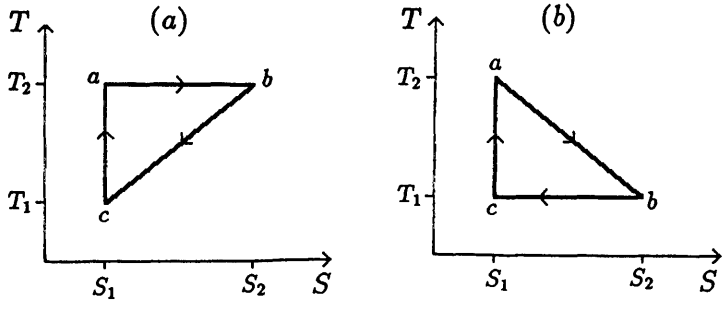


Fig. 2.20.

of the liquid can be varied by moving a piston. If the pressure of the liquid is increased by pushing in on the piston, by how much does the pressure of the gas change? [Assume the liquid is incompressible (its *molar volume* is independent of pressure) and describe the gas by the ideal gas equation of state. The entire process occurs at fixed temperature T.]

Problem S2.1. Consider a gas obeying the Dieterici equation of state,

$$P = \frac{nRT}{(V - nb)} \exp\left(-\frac{na}{VRT}\right),$$

where a and b are constants. (a) Compute the Joule coefficient. (b) Compute the Joule–Kelvin coefficient. (c) For the throttling process, find an equation for the inversion curve and sketch it. What is the maximum inversion temperature?

Problem S2.2. An insulated box is partitioned into two compartments, each containing an ideal gas of different molecular species. Assume that each compartment has the same temperature but different number of moles, different pressure, and different volume [the thermodynamic variables of the ith box are (P_i, T, n_i, V_i)]. The partition is *suddenly* removed and the system is allowed to reach equilibrium. (a) What are the final temperature and pressure? (b) What is the change in the entropy?

Problem S2.3. Two containers, each of volume V, contain ideal gas held at temperature T and pressure P. The gas in chamber 1 consists of $N_{1,a}$ molecules of type a and $N_{1,b}$ molecules of type b. The gas in chamber 2 consists of $N_{2,a}$ molelcules of type a and $N_{2,b}$ molecules of type b. Assume that $N_{1,a} + N_{1,b} = N_{2,a} + N_{2,b}$. The gases are allowed to mix so the final temperature is T and the final pressure is P (cf. Fig. 2.21). (a) Compute the entropy of mixing. (b) What is the entropy of mixing if $N_{1,a} = N_{2,a}$ and $N_{1,b} = N_{2,b}$. (c) What is the entropy of mixing if $N_{1,a} = N_{2,b}$ and $N_{1,b} = N_{2,a} = 0$. Discuss your results for (b) and (c).

Problem S2.4. An insulated box with fixed total volume V is partitioned into m insulated compartments, each containing an ideal gas of a different molecular species. Assume that each compartment has the same pressure but a different number of moles, a different temperature, and a different volume. (The thermodynamic variables for the ith compartment are (P, n_i, T_i, V_i).) If all partitions are suddenly removed and the system is allowed to reach equilibrium: (a) Find the final temperature and pressure, and the entropy of mixing. (Assume that the particles are monatomic.) (b) For the special case of $m = 2$ and parameters $n_1 = 1$ mol, $T_1 = 300$ K, $V_1 = 1$ liter, $n_2 = 3$ mol, and $V_2 = 2$ liters, obtain numerical values for all parameters in part (a).

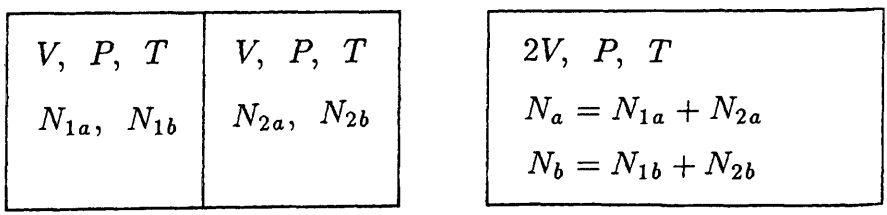


Fig. 2.21.

Problem S2.5. A tiny sack made of membrane permeable to water but not NaCl (sodium chloride) is filled with a 1% solution (by weight) of NaCl and water and is immersed in an open beaker of pure water at 38 °C at a depth of 1 ft. (a) What osmotic pressure is experienced by the sack? (b) What is the total pressure of the solution in the sack (neglect surface tension)? Assume that the sack is small enough that the pressure of the surrounding water can be assumed constant. (An example of such a sack is a human blood cell.)

Problem S2.6. A solution of particles A and B has a Gibbs free energy

$$G(P,T,n_A,n_B) = n_A g_A(P,T) + n_B g_B(P,T) + \frac{1}{2}\lambda_{AA}\frac{n_A^2}{n} + \frac{1}{2}\lambda_{BB}\frac{n_B^2}{n} + \lambda_{AB}\frac{n_A n_B}{n} + n_A RT\ln(x_A) + n_B RT\ln(x_B).$$

Initially, the solution has n_A moles of A and n_B moles of B. (a) If an amount, Δn_B, of B is added keeping the pressure and temperature fixed, what is the change in the chemical potential of A? (b) For the case $\lambda_{AA} = \lambda_{BB} = \lambda_{AB}$, does the chemical potential of A increase or decrease?

Problem S2.7. Consider the reaction

$$2\mathrm{HI} \rightleftharpoons 2\mathrm{H_2} + \mathrm{I_2},$$

which occurs in the gas phase. Start initially with 2 mol of HI and 0 mol each of H_2 and I_2. Assume that the reaction occurs at temperature T and pressure P. Use ideal gas equations for the chemical potential. (a) Compute and plot the Gibbs free energy, $G(T,P,\xi)$, as a function of the degree of reaction, ξ, for (i) $P = 1$ atm and $T = 298$ K and (ii) $P = 1$ atm and $T = 596$ K. (b) Compute and plot the affinity, $A(T,P,\xi)$, as a function of the degree of reaction, ξ, for (i) $P = 1$ atm and $T = 298$ K and (ii) $P = 1$ atm and $T = 596$ K. (c) What is the degree of reaction, ξ, at chemical equilibrium for $P = 1$ atm and temperature $T = 298$ K? How many moles of HI, H_2, and I_2 are present at equilibrium? (d) If initially the volume is V_0, what is the volume at equilibrium for $P = 1$ atm and $T = 298$ K? (e) What is the heat of reaction for $P = 1$ atm and $T = 298$ K?

Problem S2.8. Consider the reaction

$$2\mathrm{NH_3} \rightleftharpoons \mathrm{N_2} + 3\mathrm{H_2},$$

which occurs in the gas phase. Start initially with 2 mol of NH_3 and 0 mol each of H_2 and N_2. Assume that the reaction occurs at temperature T and pressure P. Use ideal gas equations for the chemical potential. (a) Compute and plot the Gibbs free energy, $G(T,P,\xi)$, as a function of the degree of reaction, ξ, for (i) $P = 1$ atm and $T = 298$ K and (ii) $P = 1$ atm and $T = 894$ K. (b) Compute and plot the affinity, $A(T,P,\xi)$, as a function of the degree of reaction, ξ, for (i) $P = 1$ atm and $T = 298$ K and (ii) $P = 1$ atm and $T = 894$ K. (c) What is the degree of reaction, ξ, at chemical equilibrium for $P = 1$ atm and temperature $T = 894$ K? How many moles of HI, H_2, and I_2 are present at equilibrium? (d) If initially the volume is V_0, what is the volume at equilibrium for $P = 1$ atm and $T = 894$ K? (e) What is the heat of reaction for $P = 1$ atm and $T = 894$ K?

3

THE THERMODYNAMICS OF PHASE TRANSITIONS

3.A. INTRODUCTORY REMARKS

A thermodynamic system can exist in a number of different phases whose macroscopic behavior can differ dramatically. Generally, systems become more ordered as temperature is lowered because forces of cohesion begin to overcome thermal motion and atoms can rearrange themselves into more ordered states. Phases changes occur abruptly at some critical temperature, although evidence that one will occur can be found on a macroscopic scale as the critical temperature is approached. In this chapter we will be concerned with the thermodynamics of phase transitions—that is, the description of phase transitions in terms of macroscopic variables. In later chapters we shall study them from a microscopic point of view.

The first step in trying to understand the phase changes that can occur in a system is to map out the phase diagram for the system. At a transition point, two (or more) phases can coexist in equilibrium with each other. The condition for equilibrium between phases is obtained from the equilibrium conditions derived in Chapter 2. Since phases can exchange matter and energy, equilibrium occurs when the chemical potentials of the phases become equal for given values of Y and T. From the equilibrium condition, we can determine the maximum number of phases that can coexist and, in principle, find equations for the regions of coexistence (the Clausius–Clapeyron equation).

At a phase transition the chemical potentials of the phases, and therefore the Gibbs free energy, must change continuously. However, phase transitions can be divided into two classes according the behavior of derivatives of the Gibbs free energy. Phase transitions which are accompanied by a discontinuous change of state (discontinuous first derivatives of the Gibbs free energy with respect to temperature and displacement) are called *first-order phase transitions*. Phase transitions which are accompanied by a continuous change of state (but discontinuous higher-order derivatives) are called *continuous phase transitions*. We give examples of both in this chapter.

Classical fluids provide some of the most familiar examples of first-order phase transitions. The vapor–liquid, vapor–solid, and liquid–solid transitions

are all first order. We shall discuss the phase transitions in classical fluids in some detail. For the vapor–solid and vapor–liquid transitions, we can use the Clausius–Clapeyron equation to find explicit approximate equations for the coexistence curves. Since the vapor–liquid transition terminates in a critical point, we will focus on it and compare the observed behavior of the vapor–liquid coexistence region to that predicted by the van der Waals equation.

Superconductors and superfluids are especially interesting from the standpoint of thermodynamics because they exhibit both first-order and continuous phase transitions and they provide a test for the third law of thermodynamics. In the absence of a magnetic field, the transition from a normal to a superconducting state in a metal is a continuous phase transition. It is a phase transition which is purely quantum mechanical in nature and results from a macroscopic condensation of pairs of electrons into a single quantum state. The superfluid transitions in liquid He^3 and liquid He^4 are of similar quantum origin. The superfluid transitions in liquid He^3 involve pairs of "dressed" He^3 atoms which condense, on a macroscopic scale, into a single quantum state. In liquid He^4 a macroscopic number of "dressed" He^4 atoms condense into the ground state. When liquid He^3 and liquid He^4 are mixed together, they form a binary mixture which can undergo both a continuous superfluid phase transition and a first-order binary phase transition.

Most phase transitions have associated with them a critical point (the liquid–solid transition does not). There is a well-defined temperature above which one phase exists and, as the temperature is lowered, a new phase appears. When the new phase appears, it often has different symmetry properties and a new thermodynamic variable, *the order parameter*, appears which characterizes the new phase. For first-order phase transitions there need not be a connection between the symmetries of the high-temperature phase and those of the low-temperature phase. For continuous phase transitions, there is always a well-defined connection between the symmetry properties of the two phases. Ginzburg and Landau developed a completely general theory of continuous symmetry-breaking phase transitions which involves an analytic expansion of the free energy in terms of the order parameter. We shall discuss the Ginzburg–Landau theory in this chapter and show how it can be applied to magnetic systems at the Curie point and to superfluid systems.

The critical point plays a unique role in the theory of phase transitions. As a system approaches its critical point from the high temperature side, it begins to adjust itself on a microscopic level. Large fluctuations occur which signal the emergence of a new order parameter which finally does appear at the critical point itself. At the critical point, some thermodynamic variables can become infinite. Critical points occur in a huge variety of systems, but regardless of the particular substance or mechanical variable involved, there appears to be a great similarity in the behaviour of all systems as they approach their critical points. One of the best ways to characterize the behavior of systems as they approach the critical point is by means of critical exponents. We shall define critical exponents in this chapter and give explicit examples of some of them for the

liquid-vapor transition in simple fluids. At the end of the chapter in the *special topics* section we define critical exponents for the Curie point.

The section on *special topics* contains further applications of thermodynamics at phase transitions and at the interface of different phases. In Chapter 2 we derived conditions for mechanical thermodynamic equilibrium between two parts of a system in equilibrium. If the system consists of two phases, such as a liquid and a gas phase, then the interface between the two phases may be under tension due to an imbalance of molecular forces at the interface. If the interface is under tension, the condition for mechanical equilibrium must be modified to include mechanical effects due to the surface tension.

A rather spectacular phenomenon which occurs in superfluid systems is the thermomechanical, or fountain, effect. As we shall see, it is possible to use a heat source to drive a superfluid fountain. Even though superfluids are highly degenerate quantum systems, the fountain effect surprisingly can be described in terms of classical thermodynamics. All we need is a system composed of two interpenetrating fluids, one of which carries no entropy. Then simple arguments give us the fountain effect.

A binary mixture of molecules in the fluid state provides a different example of a first-order phase transition. For that system, below a certain critical temperature we can have a physical separation of the mixture into two fluids, each of which is rich in one of the types of molecules.

Finally we conclude the special topics section with the application of Ginzburg–Landau theory to superconductors in the presence of a magnetic field.

3.B. COEXISTENCE OF PHASES: GIBBS PHASE RULE

Most systems can exist in a number of different phases, each of which can exhibit quite different macroscopic behavior. The particular phase that is realized in nature for a given set of independent variables is the one with the lowest free energy. For certain values of the independent variables, two or more phases of a system can coexist. There is a simple rule, called the *Gibbs phase rule*, which tells us the number of phases that can coexist. Generally, coexisting phases are in thermal and mechanical equilibrium and can exchange matter. Under these conditions, the temperature and chemical potentials of the phases must be equal (cf. Section 2.H) and there will be another condition between mechanical variables expressing mechanical equilibrium. For example, for a simple *PVT* system, the pressures of the two phases may be equal (if surface tension can be neglected).

For simplicity, let us first consider a *YXT* system which is pure (composed of one kind of particle). For a pure system, two phases, *I* and *II*, can coexist at a fixed value of Y and T if their respective chemical potentials are equal:

$$\mu^I(Y,T) = \mu^{II}(Y,T). \tag{3.1}$$

(The chemical potentials are functions only of intensive variables.) Equation (3.1) gives a relation between the values of Y and T for which the phases can coexist,

$$Y = Y(T), \tag{3.2}$$

and in the Y–T plane it defines a coexistence curve for the two phases. If the pure system has three phases, *I*, *II*, and *III*, they can only coexist at a single point in the Y–T plane (the triple point). Three coexisting phases must satisfy the equations

$$\mu^I(Y,T) = \mu^{II}(Y,T) = \mu^{III}(Y,T). \tag{3.3}$$

Since we have two equations and two unknowns, the triple point is uniquely determined. For a pure system, four phases cannot coexist, because we would then have three equations and two unknowns and there would be no solution.

As an example of the Gibbs phase rule for pure substances, we show the coexistence curves for various solid phases of water (cf. Fig. 3.1). We see that although water can exist in many different solid phases, no more than three phases can coexist at a given temperature and pressure.

For a mixture of l different types of particles, at most $l+2$ phases can coexist. To show this, we note that if there are l types of particles in each phase, then there will be $l+1$ independent variables for each phase, namely, $(Y, T, x_1, \ldots, x_{l-1})$, where x_i is the mole fraction of particles of type i. If we have several phases coexisting, the chemical potential for a given type of

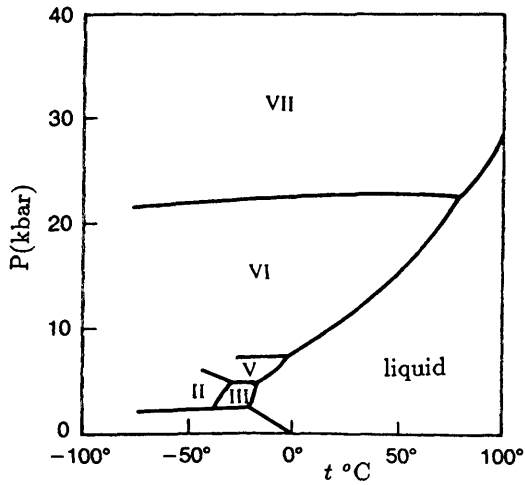


Fig. 3.1. Coexistence curves for the solid and liquid phases of water. In accordance with the Gibbs phase rule, no more than three phases can coexist [1]. (Based on Ref. 2.)

particle must have the same value in each of the various phases. Thus, if there are r coexisting phases at a given value of Y and T, the condition for equilibrium is

$$\begin{aligned}\mu_1^I(Y,T,x_1^I,x_2^I,\ldots,x_{l-1}^I) &= \mu_1^{II}(Y,T,x_1^{II},x_2^{II},\ldots,x_{l-1}^{II}) = \cdots \\ &= \mu_1^r(Y,T,x_1^r,\ldots,x_{l-1}^r). \end{aligned} \tag{3.4}$$

$$\begin{aligned}\mu_2^I(Y,T,x_1^I,\ldots,x_{l-1}^I) &= \mu_2^{II}(Y,T,x_1^{II},\ldots,x_{l-1}^{II}) = \cdots \\ &= \mu_2^r(Y,T,x_1^r,\ldots,x_{l-1}^r). \end{aligned} \tag{3.5}$$

$$\vdots \qquad\qquad \vdots$$

$$\begin{aligned}\mu_l^I(Y,T,x_1^I,\ldots,x_{l-1}^I) &= \mu_l^{II}(Y,T,x_1^{II},\ldots,x_{l-1}^{II}) = \cdots \\ &= \mu_l^r(Y,T,x_1^r,\ldots,x_{l-1}^r). \end{aligned} \tag{3.6}$$

Equations (3.4)–(3.6) give $l(r-1)$ equations to determine $2+r(l-1)$ unknowns. For a solution, the number of equations cannot be greater than the number of unknowns. Thus, we must have $l(r-1) \leqslant 2+r(l-1)$ or $r \leqslant l+2$. The number of coexisting phases must be less than or equal to $l+2$, where l is the number of different types of particle. For a pure state, $l=1$ and $r \leqslant 3$ as we found before. For a binary mixture, $l=2$ and $r \leqslant 4$, and, at most, four different phases can coexist.

3.C. CLASSIFICATION OF PHASE TRANSITIONS

As we change the independent intensive variables $(Y,T,x_1,\ldots,x_l)$ of a system, we reach values of the variables for which a phase change can occur. At such points the chemical potentials (which are functions only of intensive variables) of the phases must be equal and the phases can coexist.

The fundamental equation for the Gibbs free energy, in a system with l different kinds of molecules, is

$$G = \sum_{j=1}^{l} n_j \mu_j, \tag{3.7}$$

where n_j is the number of moles of the jth constituent, and μ_j is its chemical potential (cf. Section 2.F.4). For processes which occur at constant Y and T, changes in the Gibbs free energy can be written

$$[dG]_{Y,T} = \sum_{j=1}^{l} \mu_j dn_j. \tag{3.8}$$

Thus, at a phase transition, the derivatives $\mu_j = (\partial G/\partial n_j)_{Y,T,\{n_{i\neq j}\}}$ must be equal

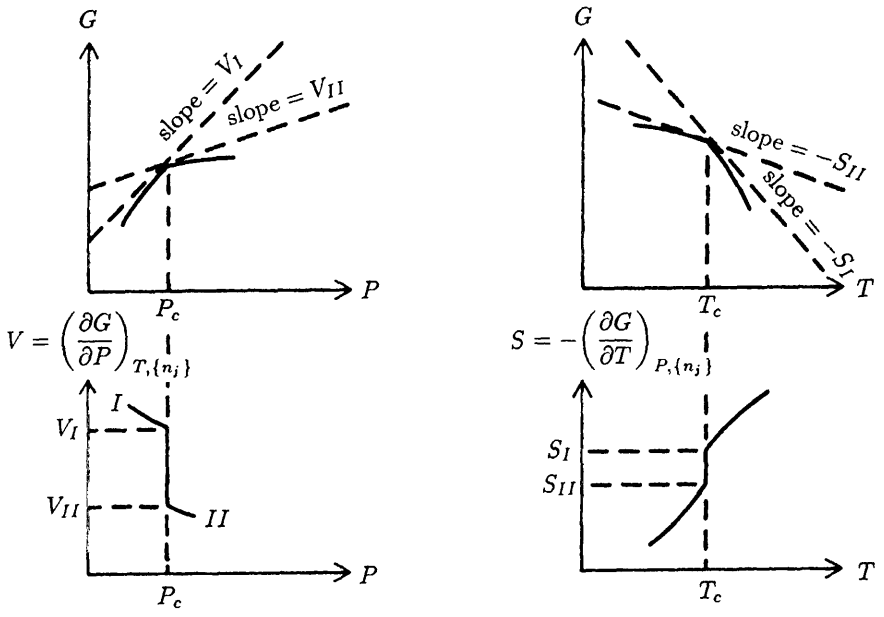


Fig. 3.2. Typical behavior for the Gibbs free energy at a first-order phase transition.

and the Gibbs free energy of each phase has the same value. However, no restriction is placed on the derivatives $X = -(\partial G/\partial Y)_{T,\{n_j\}}$ and $S = -(\partial G/\partial T)_{Y,\{n_j\}}$. The behavior of these derivatives is used to classify phase transitions. If the derivatives $(\partial G/\partial Y)_{T,\{n_j\}}$ and $(\partial G/\partial T)_{Y,\{n_j\}}$ are discontinuous at the transition point (that is, if the extensive variable X and the entropy S have different values in the two phases), the transition is called "first-order." If the derivatives $(\partial G/\partial T)_{Y,\{n_j\}}$ and $(\partial G/\partial Y)_{T,\{n_j\}}$ are continuous at the transition but higher-order derivatives are discontinuous, then the phase transition is continuous. (The terminology "nth-order phase transition" was introduced by Ehrenfest to indicate a phase transition for which the nth derivative of G was the first discontinuous derivative. However, for some systems, higher-order derivatives are infinite, and the theory proposed by Ehrenfest breaks down for those cases.)

Let us now plot the Gibbs free energy for first-order and continuous transitions in a PVT system. For such a system the Gibbs free energy must be a concave function of P and T (cf. Section 2.H.3). The Gibbs free energy and its first derivatives are plotted in Fig. 3.2 for a first-order phase transition. A discontinuity in $(\partial G/\partial P)_{T,\{n_j\}}$ means that there is the discontinuity in the volume of the two phases,

$$\Delta V = V^I - V^{II} = \left(\frac{\partial G}{\partial P}\right)^I_{T,\{n_j\}} - \left(\frac{\partial G}{\partial P}\right)^{II}_{T,\{n_j\}}, \tag{3.9}$$

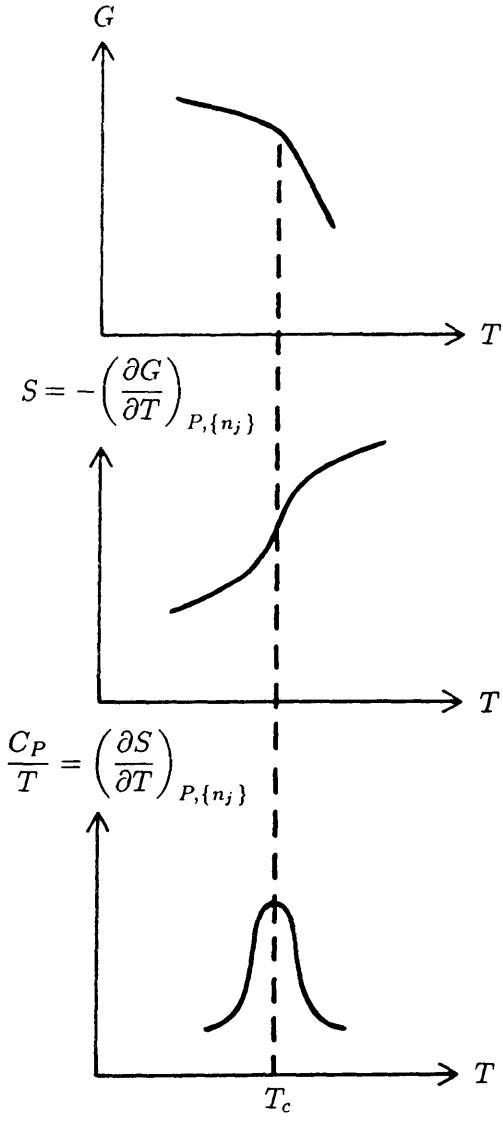


Fig. 3.3. Typical behavior for the Gibbs free energy at a continuous phase transition. The heat capacity can exhibit a peak at the transition.

and a discontinuity in $(\partial G/\partial T)_{P,\{n_j\}}$ means there is a discontinuity in the entropy of the two phases,

$$\Delta S = S^I - S^{II} = \left(\frac{\partial G}{\partial T}\right)^{II}_{P,\{n_j\}} - \left(\frac{\partial G}{\partial T}\right)^{I}_{P,\{n_j\}}. \tag{3.10}$$

Since the Gibbs free energy is the same for both phases at the transition, the fundamental equation $H = G + TS$ shows that the enthalpy of the two phases is different,

$$\Delta H = H^I - H^{II} = T\Delta S, \tag{3.11}$$

for a first-order phase transition. The enthalpy difference, ΔH, is also called the *latent heat.*

For a continuous phase transition, the Gibbs free energy is continuous but its slope changes rapidly. This in turn leads to a peaking in the heat capacity at the transition point. An example is given in Fig. 3.3. For a continuous transition, there is no abrupt change in the entropy or the extensive variable (as a function of Y and T) at the transition.

In the subsequent sections we shall give examples of first-order and continuous phase transitions.

3.D. PURE *PVT* SYSTEMS [3–5]

A pure *PVT* system is a system composed of only one type of molecule. The molecules generally have a repulsive core and a short-range attractive region outside the core. Such systems have a number of phases: a gas phase, a liquid phase, and various solid phases. A familiar example of a pure *PVT* system is water. Below we shall examine the properties of phase transitions in such systems. Since we deal with pure substances in this section, it is convenient to describe their phase transitions in terms of molar densities.

3.D.1. Phase Diagrams

A typical set of coexistence curves for pure substances is given in Fig. 3.4 (Note that Fig. 3.4 does not describe the isotopes of helium, He^3 or He^4, which have superfluid phases, but it is typical of most other pure substances.) Point A on the diagram is the *triple point*, the point at which the gas, liquid, and solid phases can coexist. Point C is the *critical point*, the point at which the vaporization curve terminates. The fact that the vaporization curve has a critical point means that we can go continuously from a gas to a liquid without ever going through a phase transition, if we choose the right path. The fusion curve does not have a critical point (none has ever been found). We must go through a phase transition in going from the liquid to the solid state. This difference between the gas–liquid and liquid–solid transitions indicates that there is a much greater fundamental difference between liquids and solids than between liquids and gases, as one would expect. The major difference lies in their symmetry properties. Solids exhibit spatial ordering, while liquids and gases do not. (We will use "vapor" and "gas" interchangeably.)

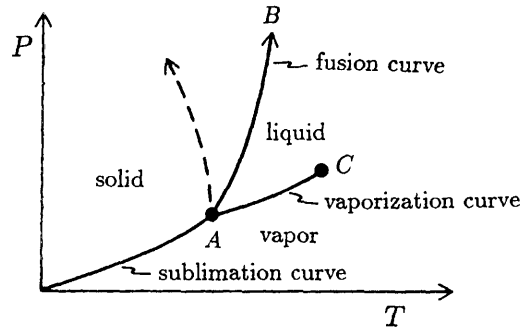


Fig. 3.4. Coexistence curves for a typical pure *PVT* system. Point *A* is the triple point and point *C* is the critical point. The dashed line is an example of a fusion curve with negative slope.

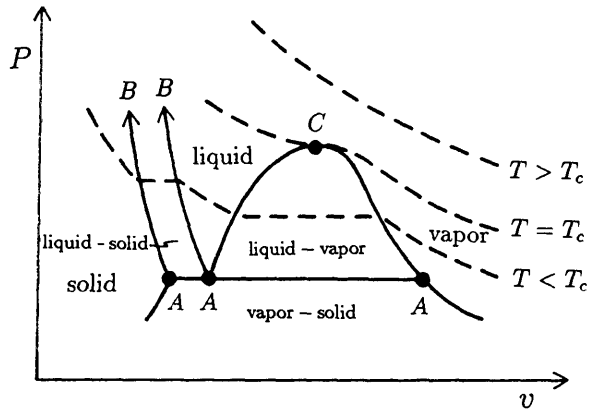


Fig. 3.5. A plot of the coexistence regions for a typical *PVT* system. All the phase transitions here are first order. The dashed lines represent isotherms.

The transitions from gas to liquid phase, from liquid to solid phase, and from gas to solid phase are all first-order transitions and are accompanied by a latent heat and a change in volume. In Fig. 3.5, we have drawn the phase diagram in the P–v plane. The dashed lines are lines of constant temperature. We notice that the slope of the dashed lines is negative, $(\partial P/\partial v)_T < 0$. This is a statement of the stability condition, $\kappa_T > 0$ (cf. Section 2.H.2). In the region of coexistence of phases, the isotherms (dashed lines) are always flat, indicating that in these regions the change in volume occurs for constant P and T.

It is interesting to plot the pressure as a function of molar volume and temperature in a three-dimensional figure. As we can see in Fig. 3.6, the result is similar to that of a mountain with ski slopes. The height of the mountain at any given value of v and T is the pressure. Fig. 3.6 actually corresponds to a plot of the equation of state for the pure system. The shaded region is the region of

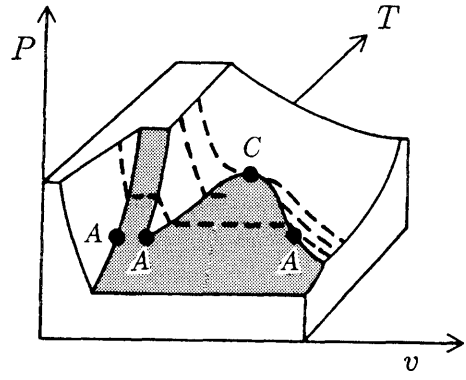


Fig. 3.6. Three-dimensional sketch of the equation for the typical pure PVT system.

coexistence of more than one phase. Figure 3.4 is a projection of Fig. 3.6 on the *P–T* plane and Fig. 3.5 is a projection of Fig. 3.6 on the *P–v* plane.

3.D.2. Coexistence Curves: Clausius–Clapyron Equation

The molar Gibbs free energies (the chemical potentials), $g = G/n$, of two coexisting phases (which we call *I* and *II*) of a pure *PVT* system must be equal. If we change the pressure and temperature at which the two phases coexist (that is, if we move to a new point on the coexistence curve), the molar Gibbs free energy of the two phases must change by equal amounts. Thus, $dg^I = dg^{II}$ along the coexistence curve. We can use this fact to find an equation for the coexistence curve. We use Eq. (2.108) to write

$$v^I dP - s^I dT = v^{II} dP - s^{II} dT \tag{3.12}$$

along the coexistence curve, where v is the molar volume and s is the molar entropy. Thus,

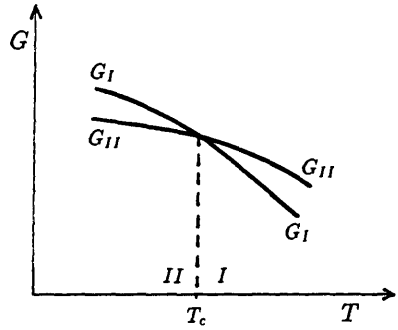
$$\left(\frac{dP}{dT}\right)_{coex} = \frac{s^I - s^{II}}{v^I - v^{II}} = \frac{\Delta s}{\Delta v} \tag{3.13}$$

along the coexistence curve, where $\Delta s = s^I - s^{II}$ is the difference in the molar entropy of the two phases and $\Delta v = v^I - v^{II}$ is the difference in the molar volume of the two phases. Equation (3.13) can also be written in terms of the latent heat, $\Delta h = T\,\Delta s$ [cf. Eq. (3.11)] so that

$$\left(\frac{dP}{dT}\right)_{coex} = \frac{\Delta h}{T\,\Delta v}. \tag{3.14}$$

Equation (3.14) is called the *Clausius–Clapeyron equation*. The latent heat, Δh, is the heat absorbed per mole in the transition from phase *II* to phase *I*. It is of interest to discuss the Clausius–Clapeyron equation for the three coexistence curves in Fig. 3.4.

■ **Exercise 3.1.** Prove that the latent heat must always be positive (heat is absorbed) when making a transition from a low-temperature phase to a high-temperature phase.



Answer: Let us assume that phase *I* is the high-temperature phase and phase *II* is the low-temperature phase. Since for fixed pressure and temperature the equilibrium state is a state of minimum Gibbs free energy, we must have $G_I < G_{II}$ above the transition temperature and $G_I > G_{II}$ below the transition temperature. As the drawing indicates, this implies that $(\partial G_I/\partial T)_{P,\{n_j\}} < (\partial G_{II}/\partial T)_{P,\{n_j\}}$ both above and below the transition temperature. Therefore $S_I = -(\partial G_I/\partial T)_{P,\{n_j\}} > S_{II} = -(\partial G_{II}/\partial T)_{P,\{n_j\}}$ and $\Delta S = T\Delta H$ is always positive in going from the low-temperature phase to the high-temperature phase.

3.D.2.a. Vaporization Curve

If we evacuate a chamber and partially fill it with a pure substance, then for the temperatures and pressures along the coexistence curve (the *vaporization curve*) from the triple point to the critical point (point *A* to point *C* in Fig. 3.4) the vapor and liquid phases will coexist in the chamber. For a given temperature *T*, the pressure of the vapor and liquid is completely determined and is called the *saturated vapor pressure*. As we change the temperature of the system the vapor pressure will also change. The Clausius–Clapeyron equation tells us how the vapor pressure changes as a function of temperature along the coexistence curve.

We can obtain a rather simple equation for the vaporization curve if we make some approximations. Let us assume that changes in the molar volume of the liquid may be neglected relative to changes in the molar volume of the vapor (gas) as we move along the coexistence curve, and let us assume the vapor

obeys the ideal gas law. Then $\Delta v \approx RT/P$, and the Clausius–Clapeyron equation for the vapor pressure curve takes the form

$$\left(\frac{dP}{dT}\right)_{coex} = \frac{P\Delta h_{lg}}{RT^2}, \tag{3.15}$$

where Δh_{lg} is the *latent heat of vaporization.* If we assume that the latent heat of vaporization is roughly constant over the range of temperatures considered, we can integrate Eq. (3.15) to obtain

$$P = P_0 e^{-\Delta h_{lg}/RT}. \tag{3.16}$$

Thus, as the temperature is increased, the vapor pressure increases exponentially along the vaporization curve. Conversely, if we increase the pressure, the temperature of coexistence (boiling point) increases.

■ **Exercise 3.2.** Compute the molar heat capacity of a vapor along the vaporization curve.

Answer: Along the vaporization curve there is only one independent variable, which we choose to be the temperature. In general, the entropy of the vapor is a function of both the pressure and temperature, but along the vaporization curve the pressure is related to the temperature by the Clausius–Clapeyron equation. The molar heat capacity along the vaporization curve can be written

$$\begin{aligned} c_{coex} &= T\left(\frac{\partial s}{\partial T}\right)_{coex} = T\left(\frac{\partial s}{\partial T}\right)_P + T\left(\frac{\partial s}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_{coex} \\ &= c_P - T\left(\frac{\partial v}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_{coex}, \end{aligned} \tag{1}$$

where we have used Eqs. (2.8) and (2.112). The molar heat capacity, c_P, is the heat capacity of the vapor held at constant pressure as we approach the coexistence curve. If we use the ideal gas equation of state to describe the properties of the vapor phase and if we use the Clausius–Clapeyron equation, we obtain the following expression for the molar heat capacity along the coexistence curve,

$$c_{coex} = c_P - \frac{\Delta h_{lg}}{T}. \tag{2}$$

At low enough temperatures, it is possible for the heat capacity, c_{coex}, to be negative. This would mean that if the temperature of the vapor is raised and it is maintained in equilibrium with liquid phase, the vapor would give off heat.

3.D.2.b. Fusion Curve

The fusion curve does not terminate at a critical point but can have either positive or negative slope. In Fig. 3.4 we used a solid line for the fusion curve with a positive slope and a dashed line for the case of negative slope. The Clausius–Clapeyron equation for the liquid–solid transition is

$$\left(\frac{dP}{dT}\right)_{coex} = \frac{\Delta h_{sl}}{T\,\Delta v_{sl}}, \tag{3.17}$$

where Δv_{sl} is the change in molar volume in going from the solid to the liquid phase and Δh_{sl} is the *latent heat of fusion.* If the volume of the solid is greater than that of the liquid, then Δv_{sl} will be negative and the slope, $(dP/dT)_{coex}$, will be negative. For the case of a fusion curve with positive slope, if we increase the pressure at a fixed temperature, we simply drive the system deeper into the solid phase. However, if the fusion curve has a negative slope, then increasing the pressure at fixed temperature can drive the system into the liquid phase. Water is an example of a system whose fusion curve has negative slope. The negative slope of the fusion curve for water makes ice skating possible. As the skate blades exert pressure on the ice, it turns to water and the skater floats along on a narrow puddle.

3.D.2.c. Sublimation Curve [3]

If a solid is placed in an evacuated chamber and maintained at some pressure and temperature along the sublimation curve, a vapor will coexist in equilibrium with the solid phase. The Clausius–Clapeyron equation for the sublimation curve is

$$\left(\frac{dP}{dT}\right)_{coex} = \frac{\Delta h_{sg}}{T\,\Delta v_{sg}}, \tag{3.18}$$

where Δv_{sg} is the change in molar volume in going from the solid to the gas phase and Δh_{sg} is the *latent heat of sublimation.* If we again assume that the gas phases obeys the ideal gas equation of state, the Clausius–Clapeyron equation takes the form

$$\left(\frac{dP}{dT}\right)_{coex} = \frac{P\Delta h_{sg}}{RT^2}. \tag{3.19}$$

If the vapor pressure is known over a small temperature interval, then the latent heat of sublimation can be obtained from Eq. (3.19). We can rewrite Eq. (3.19) in the form

$$\Delta h_{sg} = -R\frac{d\,\ln(P)}{d(1/T)}. \tag{3.20}$$

Then Δh_{sg} is proportional to the slope of the curve, $\ln(P)$ versus $1/T$.

■ **EXERCISE 3.3.** In the neighborhood of the triple point of ammonia (NH_3), the equation for the sublimation curve is $\ln(P) = 27.79 - 3726/T$ and the equation for the vaporization curve is $\ln(P) = 24.10 - 3005/T$, where P is measured in pascals and T is measured in kelvins. (a) Compute the temperature and pressure of the triple point. (b) What is the latent heat of sublimation? What is the latent heat of vaporization?.

Answer:

(**a**) At the triple point, the pressure and temperature of the vapor, liquid, and solid are the same. Therefore, the equation for the triple point temperature, T_t, is $27.79 - 3726/T_t = 24.10 - 3005/T_t$ or $T_t = 195.4\,\text{K}$. The triple point pressure, P_t, is $P_t = 6.13\,\text{kPa}$.

(**b**) The slope of the sublimation curve is

$$\left(\frac{\partial P}{\partial T}\right)_{coex} = \frac{3726\,P}{T^2} \approx \frac{P\,\Delta h_{sg}}{RT^2}. \tag{1}$$

Therefore, $\Delta h_{sg} \approx 31\,\text{kJ/mol}$. The slope of the vaporization curve is

$$\left(\frac{\partial P}{\partial T}\right)_{coex} = \frac{3005\,P}{T^2} \approx \frac{P\,\Delta h_{lg}}{RT^2}. \tag{2}$$

Therefore, $\Delta h_{lg} \approx 25\,\text{kJ/mol}$.

At moderately low temperatures (but not low enough for quantum effects to cause significant deviations from the classical gas equation of state), the vapor pressure along the sublimation curve is very low. We can use this fact to obtain a fairly simple equation for the sublimation curve which includes temperature variations in the latent heat and heat capacity of the vapor and solid. Let us first note that infinitesimal changes in the molar enthalpy of the solid can be written

$$dh = T\,ds + v dP = c_P dT + v(1 - T\alpha_P)dP, \tag{3.21}$$

where α_P is the thermal expansivity (cf. Eqs. (2.155), (2.112), (2.144)). We can use Eq. (3.21) to find an approximate expression for the difference between the enthalpy of the solid at two different points along the sublimation curve. We restrict ourselves to regions where the vapor pressure along the sublimation curve is small and we neglect pressure variations in Eq. (3.21). Note that $dh_g - dh_s = (c_P^s - c_P^g)dT$ along the coexistence curve. We then can integrate Eq. (3.21) and write

$$\Delta h_{sg} = \Delta h_{sg}^0 + \int_{T_0}^{T} (c_P^g - c_P^s)dT, \tag{3.22}$$

where $\Delta h_{sg} = h_g - h_s$ is the latent heat of sublimation at temperature T, $\Delta h^0_{sg} = h^0_g - h^0_s$ is the latent heat of sublimation at temperature T_0, h_s and h_g (h^0_s and h^0_g) are the enthalpies of the solid and gas phases, respectively, at temperature T (T_0) and very low pressure, and c^g_P and c^s_P are the moler heat capacities of the gas and solid, respectively. If we now integrate the Clausius–Clapeyron equation, (3.21), using Eq. (3.22) for Δh_{sg}, we obtain the following equation for the sublimation curve:

$$\ln\left(\frac{P}{P_0}\right) = \frac{\Delta h^0_{sg}}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right) + \int_{T_0}^{T} \frac{dT''}{RT''^2} \int_{T_0}^{T''} dT'(c^g_P - c^s_P). \tag{3.23}$$

Equation (3.23) can be useful for extending the results of experimental measurements [3].

3.D.3. Liquid–Vapor Coexistence Region [4, 5]

The liquid–vapor coexistence region culminates in a critical point and will be of special interest later. Therefore, it is useful at this point to examine the coexistence region under the critical point more closely. Let us redraw the coexistence curve (vaporization curve) for the liquid–vapor transition in the P–v plane (cf. Fig. 3.7). The isotherms for stable thermodynamic states are indicated by the solid lines. As we decrease the molar volume of the gas with temperature fixed at $T_0 < T_c$, the pressure increases until we reach the coexistence curve (point A). At point A, the vapor starts to condense and the pressure remains fixed until all vapor has changed to liquid (point B). Then the pressure begins to rise again.

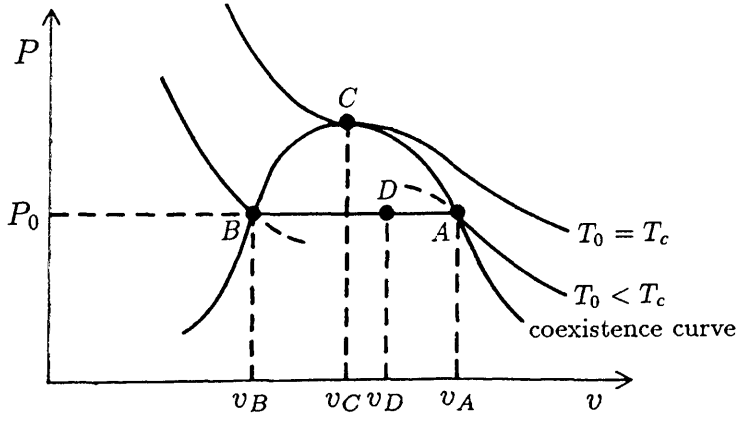


Fig. 3.7. The coexistence curve for the vapro–liquid coexistence region for a pure PVT system.

The amounts of liquid and vapor which coexist are given by the lever rule. Let us consider a system with temperature $T_0 < T_c$, pressure P_0, and total molar volume v_D. The system is then in a state in which the liquid and vapor phases coexist. The total molar volume, v_D, is given in terms of the molar volume of the liquid at point B, v_l, and the molar volume of vapor at point A, v_g, by

$$v_D = x_l v_l + x_g v_g, \tag{3.24}$$

where x_l is the mole fraction of liquid at point D and x_g is the mole fraction of gas at point D. If we multiply Eq. (3.24) by $x_l + x_g \equiv 1$, we find

$$\frac{x_l}{x_g} = \frac{(v_g - v_D)}{(v_D - v_l)}. \tag{3.25}$$

Equation (3.25) is called *the lever rule*. It tells us that the ratio of the mole fractions of liquid to gas at point D is equal to the inverse ratio of the distance between point D and points A and B.

As long as $(\partial v/\partial P)_T < 0$, the system is mechanically stable (cf. Eq. (2.179)). If we continue the isotherm, T_0, past the points A and B (the dashed line), we obtain curves which are mechanically stable but no longer correspond to a minimum of free energy. States along the dashed line at point A correspond to supercooled vapor states, while those along the dashed line at point B correspond to superheated liquid states. Such states are metastable and can be produced in the laboratory for very pure samples. It is possible that the superheated liquid curve can extend into the region of negative pressure. Such states can also be realized in the laboratory but require walls to maintain them. Systems with negative pressure are under tension and pull in on walls rather than push out against them. As we approach the critical temperature, the region of metastable states becomes smaller, and at the critical temperature it disappears. Thus, no metastable states can exist at the critical temperature. Also, as we approach the critical temperature the molar volumes of the liquid and vapor phases approach one another, and at the critical temperature they become equal.

The actual shape of the coexistence curve in the T–ρ plane (ρ is the mass density) has been given by Guggenheim [6] for a variety of pure substances and is reproduced in Fig. 3.8. Guggenheim plots the coexistence curve in terms of the reduced quantitites T/T_c and ρ/ρ_c, where T_c and ρ_c are the critical temperature and density, respectively, of a given substance. The reduced quantities T/T_c and ρ/ρ_c give a measure the distance of the particular substance from its critical point (T_c and ρ_c are different for each substance). Most substances, when plotted in terms of reduced temperature and density, lie in approximately the same curve. This is an example of the so-called *law of corresponding states*, which says that all pure classical fluids, when described in terms of reduced quantities, obey the same equation of state [7]. We shall see this again when we return to the van der Waals equation. The reduced densities

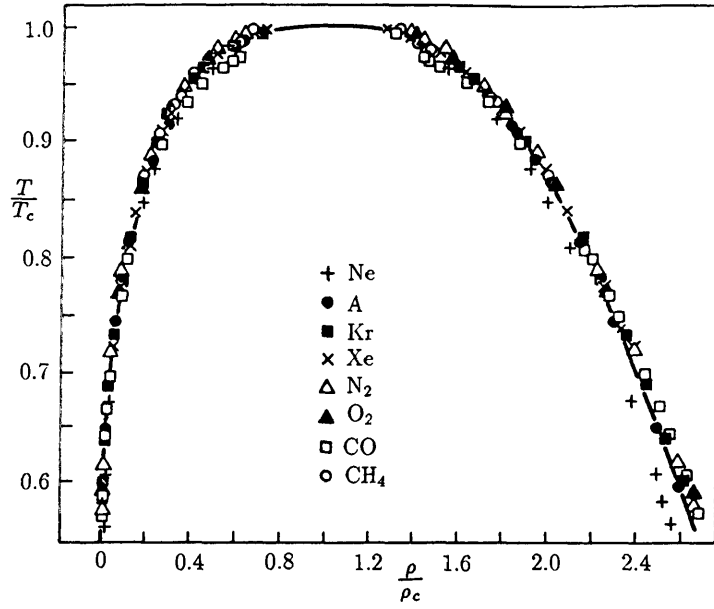


Fig. 3.8. Experimental vapor–liquid coexistence curve for a variety of substances. The plot is of the reduced temperature versus reduced density. (Based on Ref. 6.)

of the liquid and gas phases along the coexistence curves obey the following equations [6]:

$$\frac{\rho_l + \rho_g}{2\rho_c} = 1 + \frac{3}{4}\left(1 - \frac{T}{T_c}\right) \tag{3.26}$$

and

$$\frac{\rho_l - \rho_g}{\rho_c} = \frac{7}{2}\left(1 - \frac{T}{T_c}\right)^{1/3}. \tag{3.27}$$

These equations will be useful later.

It is possible to obtain expressions for response functions in the coexistence region. As an example, we will consider the molar heat capacity, c_v, for a liquid and vapor coexisting at a fixed molar volume, v_D (cf. Fig. 3.7). If we neglect any effects of gravity, then the system will consist of droplets of liquid in equilibrium with and floating in vapor. The internal energy per mole of the liquid at point D is $u_l(v_B, T_0)$ and that of the vapor at point D is $u_g(v_A, T_0)$ (the thermodynamic properties of the liquid and the vapor at point D are the same as on their respective sides of the coexistence curve). The total internal energy at point D is

$$U_{\text{tot}} = n_g u(v_g, T_0) + n_l u(v_l, T_0), \tag{3.28}$$

where $v_g = v_A$, $v_l = v_B$, and n_g and n_l are the number of moles of gas and liquid, respectively, at point D. The total internal energy per mole at point D is

$$u_{\text{tot}} = x_g u(v_g, T_0) + x_l u(v_l, T_0). \tag{3.29}$$

Let us now look at the variation of the internal energy with temperature along a line of fixed molar volume at point D (the molar heat capacity at point D),

$$c_v = \left(\frac{\partial u_{\text{tot}}}{\partial T}\right)_{v_D} = x_g \left(\frac{\partial u_g}{\partial T}\right)_{coex} + x_l \left(\frac{\partial u_l}{\partial T}\right)_{coex} + (u_l - u_g)\left(\frac{\partial x_l}{\partial T}\right)_{coex}, \tag{3.30}$$

where we have used the fact that $dx_l = -dx_g$. Equation (3.30) can be expressed in terms of directly measurable quantities. There are several steps involved which we itemize below.

(i) First consider the quantity $(\partial u_l/\partial T)_{coex}$. From Eq. (2.8), we can write

$$\left(\frac{\partial u_l}{\partial T}\right)_{coex} = \left(\frac{\partial u_l}{\partial T}\right)_{v_l} + \left(\frac{\partial u_l}{\partial v_l}\right)_T \left(\frac{\partial v_l}{\partial T}\right)_{coex} = c_{v_l} + \left(\frac{\partial u_l}{\partial v_l}\right)_T \left(\frac{\partial v_l}{\partial T}\right)_{coex}, \tag{3.31}$$

where c_{v_l} is the molar heat capacity of the liquid at point B. Similarly,

$$\left(\frac{\partial u_g}{\partial T}\right)_{coex} = c_{v_g} + \left(\frac{\partial u_g}{\partial v_g}\right)_T \left(\frac{\partial v_g}{\partial T}\right)_{coex}, \tag{3.32}$$

where c_{v_g} is the molar heat capacity of the vapor at point A.

(ii) Next consider the difference $\Delta u = u_g - u_l$ between the molar internal energies of the gas and liquid. From the Clausius–Clapeyron equation (3.14) and the fundamental equation for the enthalpy, Eq. (2.83), we can write

$$\left(\frac{dP}{dT}\right)_{coex} = \frac{\Delta h}{T\,\Delta v} = \frac{\Delta u}{T\,\Delta v} + \frac{\Delta(Pv)}{T\,\Delta v} = \frac{\Delta u}{T\,\Delta v} + \frac{P}{T}, \tag{3.33}$$

where $\Delta h = h_g - h_l$ and $\Delta v = v_g - v_l$ ($\Delta P = 0$ because the pressure of the two coexisting phases are the same). Therefore,

$$\Delta u = u_g - u_l = \left[\left(T\left(\frac{dP}{dT}\right)_{coex} - P\right)(v_g - v_l)\right]_{coex}. \tag{3.34}$$

(iii) Finally, let us consider the quantity $(\partial x_l/\partial T)_{coex}$. Since the total molar volume at point D can be written $v_D = x_g v_g + x_l v_l$, we can write

$$\left(\frac{\partial v_D}{\partial v_g}\right)_{v_D} = 0 = (v_l - v_g)\left(\frac{\partial x_l}{\partial T}\right)_{coex} + x_g \left(\frac{\partial v_g}{\partial T}\right)_{coex} + x_l \left(\frac{\partial v_l}{\partial T}\right)_{coex}. \tag{3.35}$$

Here we have used the fact that as we vary the temperature along the line v_D =constant, the liquid and vapor vary along their respective sides of the coexistence curve. We can rewrite Eq. (3.35) in the form

$$\left(\frac{\partial x_l}{\partial T}\right)_{coex} = \frac{1}{(v_g - v_l)}\left[x_g\left(\frac{\partial v_g}{\partial T}\right)_{coex} + x_l\left(\frac{\partial v_l}{\partial T}\right)_{coex}\right]. \tag{3.36}$$

We can now combine Eqs. (3.30), (3.32), (3.34), and (3.36) to obtain the following expression for the heat capacity along the line v_D =constant;

$$\begin{aligned} c_v = {} & x_g c_{v_g} + x_l c_{v_l} + x_g\left(\frac{\partial u_g}{\partial v_g}\right)_T\left(\frac{\partial v_g}{\partial T}\right)_{coex} + x_l\left(\frac{\partial u_l}{\partial v_l}\right)_T\left(\frac{\partial v_l}{\partial T}\right)_{coex} \\ & - \left[T\left(\frac{dP}{dT}\right)_{coex} - P\right]\left[x_g\left(\frac{\partial v_g}{\partial T}\right)_{coex} + x_l\left(\frac{\partial v_l}{\partial T}\right)_{coex}\right]. \end{aligned} \tag{3.37}$$

We now can make two final changes to Eq. (3.37). We can use the identity

$$\left(\frac{\partial u_g}{\partial v_g}\right)_T = T\left(\frac{\partial P_g}{\partial T}\right)_{v_g} - P \tag{3.38}$$

and an analogous one for $(\partial u_l/\partial v_l)_T$ [cf. Eq. (2.145)]. Also, we can use the identity (2.8) to write

$$\left(\frac{\partial P}{\partial T}\right)_{v_g} = \left(\frac{\partial P}{\partial T}\right)_{coex} - \left(\frac{\partial P}{\partial v_g}\right)_T\left(\frac{\partial v_g}{\partial T}\right)_{coex} \tag{3.39}$$

and an analogous expression for $(\partial P/\partial T)_{v_l}$. If Eqs. (3.38) and (3.39) and the analogous expressions for the liquid are substituted into Eq. (3.37), we find

$$c_v = x_g\left[c_{v_g} - T\left(\frac{\partial P}{\partial v_g}\right)_T\left(\frac{\partial v_g}{\partial T}\right)^2_{coex}\right] + x_l\left[c_{v_l} - T\left(\frac{\partial P}{\partial v_l}\right)_T\left(\frac{\partial v_l}{\partial T}\right)^2_{coex}\right]. \tag{3.40}$$

All quantities in Eq. (3.40) are measurable, and therefore a numerical value for the heat capacity can be obtained without much difficulty. Equation (3.40) will be useful later when we consider critical exponents.

The heat capacity at constant volume is finite in the coexistence region. However, the heat capacity at constant pressure is infinite in the coexistence region. If we add heat to a system with coexisting liquid and vapor phases and keep the pressure fixed, liquid will turn to vapor but the temperature will not change. Thus, $c_P = \infty$ in the coexistence region, while c_v can remain finite.

3.D.4. The van der Waals Equation

The van der Waals equation was first derived by van der Waals in his doctoral dissertation in 1873. It was the first, and to this day is the simplest, equation of state which exhibits many of the essential features of the liquid–vapor phase transition. The van der Waals equation is cubic in the molar volume and can be written in the form

$$v^3 - \left(b + \frac{RT}{P}\right)v^2 + \frac{a}{P}v - \frac{ab}{P} = 0. \tag{3.41}$$

An isotherm of the van der Waals equation is plotted in Fig. 3.9. For small values of T and P, the cubic equation has three distinct real roots (three values of v) for each value of P and T (this case is shown in Fig. 3.9). As T increases, the roots coalesce at a critical temperature, T_c, and above T_c two of the roots become imaginary and therefore unphysical. As $T \to \infty$, Eq. (3.41) reduces to the ideal gas equation of state, $v = RT/P$. The critical point is the point at which the roots of Eq. (3.41) coalesce. It is also the point at which the critical isotherm ($T = T_c$) has a vanishing slope $(\partial P/\partial v)_{T=T_c} = 0$ and an inflection point $(\partial^2 P/\partial v^2)_{T=T_c} = 0$. [An inflection point is a point where the curve changes from convex to concave and $(\partial^2 P/\partial v^2)_T$ changes sign.] If one uses the fact that

$$\left(\frac{\partial P}{\partial v}\right)_{T=T_c} = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial v^2}\right)_{T=T_c} = 0 \tag{3.42}$$

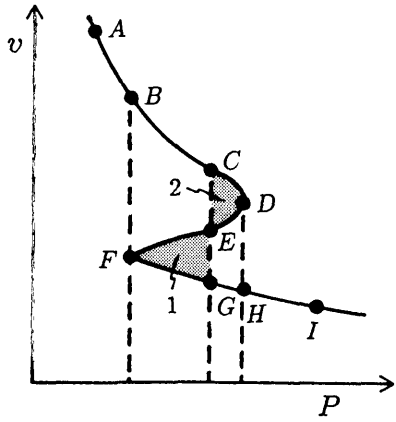


Fig. 3.9. A sketch of a typical van der Waals isotherm. The line from D to F corresponds to mechanical unstable states. The area, CDE, is labeled 2, and the area EFG is labeled 1. The area under the curve, $v = v(P)$, between any two points, is equal to the difference in molar Gibbs free energy between the points.

at the critical point, then we obtain the following values for the temperature T_c, pressure P_c, and molar volume v_c, at the critical point:

$$P_c = \frac{a}{27b^2}, \qquad v_c = 3b, \qquad T_c = \frac{8a}{27bR}. \tag{3.43}$$

If we introduce reduced variables $\bar{P} = P/P_c, \bar{T} = T/T_c$, and $\bar{v} = v/v_c$, then we may write the van der Waals equation in the form

$$\left(\bar{P} + \frac{3}{\bar{v}^2}\right)(3\bar{v} - 1) = 8\bar{T}. \tag{3.44}$$

It is important to note that Eq. (3.44) is independent of a and b. We are now measuring pressure, volume, and temperature in terms of their distance from the critical point. The values of v_c, T_c, and P_c will differ for different gases, but *all gases obey the same equation if they are the same distance from their respective critical points*—that is, if they have the same values of $\bar{P} = P/P_c$, $\bar{T} = T/T_c$, and $\bar{v} = v/v_c$. Thus, we see again the *law of corresponding states.*

An unphysical aspect of the van der Waals equation is its prediction of positive slope, $(\partial P/\partial v)_T$, for certain segments of the isotherms below T_c (the segment between D and F in Fig. (3.9). This region corresponds to mechanically unstable thermodynamic states. However, the unphysical parts of the P–V curve can be removed by use of the so-called Maxwell construction, which we will now describe.

From Eq. (2.108), we can write the equation for infinitesimal changes in the molar Gibbs free energy in the form

$$dg = -s\,dT + v\,dP. \tag{3.45}$$

If we now restrict ourselves to one of the van der Waals isotherms so $dT = 0$, we can determine how g varies with pressure along that isotherm. In Fig. 3.9 we plot the molar volume as a function of pressure along a typical van der Waals isotherm, and in Fig. 3.10 we plot the molar Gibbs free energy as a function of pressure for the isotherm in Fig. 3.9. Along the isotherm the difference in molar Gibbs free energy between any two points is equal to the area under the curve, $v = v(P)$, between those two points:

$$g_2 - g_1 = \int_{P_1}^{P_2} v(P)\,dP. \tag{3.46}$$

The Gibbs free energy increases and is concave between A and D. Between D and F it decreases and is convex. Then between F and I it becomes concave again and increases. We see that between D and F the states are mechanically unstable since mechanical stability requires that g be concave (cf. Section 2.H.3). The regions from A to D and from F to I are both mechanically stable

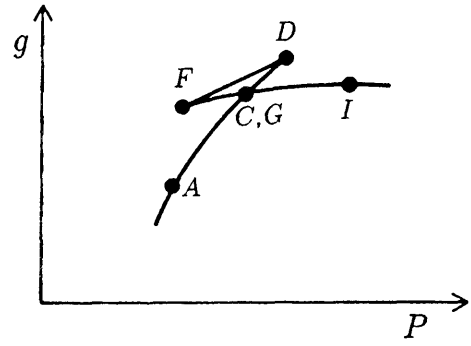


Fig. 3.10. A plot of the molar Gibbs free energy as a function of pressure for the isotherm in Fig. 3.9.

since g is concave. However, only the curve ACI in Fig. 3.10 corresponds to states in thermodynamic equilibrium because for these states the Gibbs free energy is a minimum. The states FCD are metastable. The equilibrium states thus correspond to those states whose Gibbs free enegy has values lying along the curve ACI. To obtain the equilibrium states on the isotherm between C and G we must draw a straight line (line of constant pressure) between them, since this is the only way the Gibbs free energy will remain constant in going from C to G. The physical isotherm (isotherm containing equilibrium states) is the line $ABCEGHI$ in Fig. (3.9).

Before we can complete our construction of isotherms, we must decide where C and G lie. For the points C and G, the molar Gibbs free energies are equal. Thus

$$0 = \int_{P_C}^{P_G} v(P)\,dP = \int_{P_C}^{P_D} v(P)\,dP + \int_{P_D}^{P_E} v(P)dP + \int_{P_E}^{P_F} v(P)\,dP + \int_{P_F}^{P_G} v(P)\,dP \tag{3.47}$$

or, after rearranging,

$$\int_{P_C}^{P_D} v(P)dP - \int_{P_E}^{P_D} v(P)\,dP = \int_{P_F}^{P_E} v(P)\,dP - \int_{P_F}^{P_G} v(P)\,dP. \tag{3.48}$$

The left-hand side is equal to area 2 in Fig. 3.9 and the right-hand side is equal to area 1. Thus, the line from C to G must be drawn so that the areas 1 and 2 are equal:

$$\text{Area 1} = \text{Area 2}. \tag{3.49}$$

If this is done, the curve *ACEGI* then gives the equilibrium states of the system. The condition given in Eq. (3.49) is called the *Maxwell construction.* Thus, with the Maxwell construction, we obtain the equilibrium isotherms from the van der Waals equation and the curves for metastable states.

3.E. SUPERCONDUCTORS [8–10]

Superconductivity was first observed in 1911 by Kamerlingh Onnes. He found that the resistance to current flow in mercury drops to zero at about 4.2 K (cf. Fig. 3.11). At first this was interpreted as a transition to a state with infinite conductivity. However, infinite conductivity imposes certain conditions on the magnetic field which were not subsequently observed. The relation between the electric current, **J**, and the applied electric field, **E**, in a metal is given by Ohm's law,

$$\mathbf{J} = \sigma \mathbf{E}, \tag{3.50}$$

where σ is the conductivity. The electric field **E** is related to the magnetic field **B** by Faraday's law,

$$\nabla_{\mathrm{r}} \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}. \tag{3.51}$$

If we substitute Eq. (3.50) into Eq. (3.51), we see that for infinite conductivity $\sigma \to \infty$ and $\partial \mathbf{B}/\partial t = 0$. This in turn implies that the state of the system depends on its history. If we first cool the sample below the transition temperature and then apply an external magnetic field, **H**, surface currents must be created in the sample to keep any field from entering the sample, since **B** must remain zero inside (cf. Fig. 3.12). However, if we place the sample in the **H**-field before cooling, a **B**-field is created inside. Then, if we cool the sample, the **B**-field must stay inside. Thus, the final states depend on how we prepare the sample. With the hypothesis of infinite conductivity, the state below the

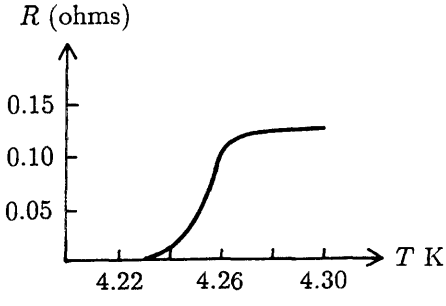


Fig. 3.11. The resistance of mercury drops to zero at about 4.2 K. (Based on Ref. 10.)

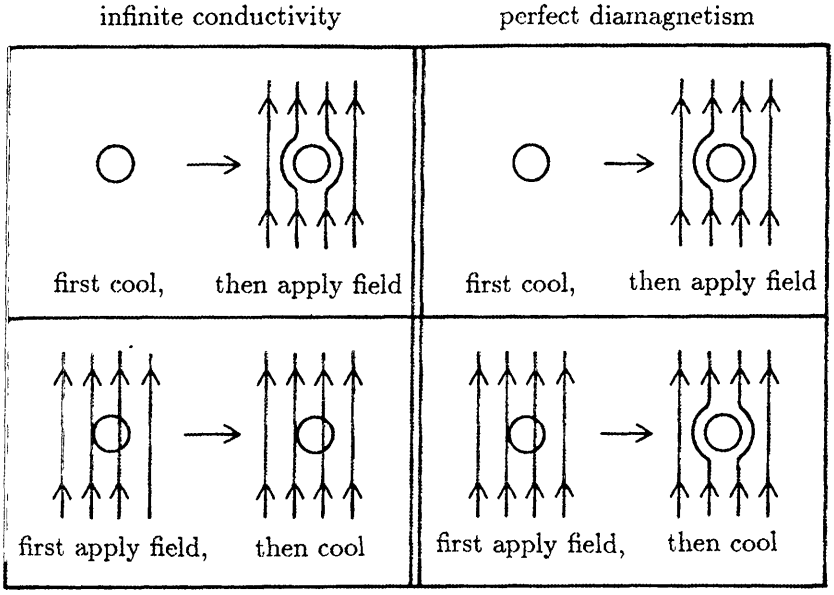


Fig. 3.12. A superconducting sample has different behavior if it is a perfect conductor or perfect diamagnet (the circle is the sample).

transition temperature cannot be a thermodynamic state since it depends on history.

In 1933, Meissner and Ochsenfeld [11] cooled a monocrystal of tin in a magnetic field and found that the field inside the sample was expelled below the transition point for tin. This is contrary to what is expected if the transition is to a state with infinite conductivity; it instead implies a transition to a state of perfect diamagnetism, $\mathbf{B} = 0$. It is now known that superconductors are perfect diamagnets. When superconducting metals are cooled below their transition point in the presence of a magnetic field, currents are set up on the surface of the sample in such a way that the magnetic fields created by the currents cancel any magnetic fields initially inside the medium. Thus $\mathbf{B} = 0$ inside a superconducting sample regardless of the history of its preparation.

No electric field is necessary to cause a current to flow in a superconductor. A magnetic field is sufficient. In a normal conductor, an electric field causes electrons to move at a constant average velocity because interaction with lattice impurities acts as a friction which removes energy from the electron current. In a superconductor, an electric field accelerates part of the electrons in the metal. No significant frictional effects act to slow them down. This behavior is reminiscent of the frictionless superflow observed in liquid He^4 below 2.19 K (cf. Section S3.B). Indeed, the superfluid flow in He^4 and the supercurrents in superconductors are related phenomena. The origin of the apparently frictionless flow in both cases lies in quantum mechanics. It is now known

that electrons in a superconducting metal can experience an effective attractive interaction due to interaction with lattice phonons. Because of this attraction, a fraction of the electrons (we never know which ones) can form "bound pairs." The state of minimum free energy is the one in which the bound pairs all have ths same quantum numbers. Thus, the bound pairs form a single macroscopically occupied quantum state which acts coherently and forms the condensed phase. As we shall see, the order parameter of the condensed phase behaves like an effective wave function of the pairs. Because the pairs in the condensed phase act coherently (as one state), any friction effects due to lattice impurities must act on the entire phase (which will contain many pairs and have a large mass) and not on a single pair. Thus, when an electric field is applied, the condensed phase moves as a whole and is not slowed significantly by frictional effects.

The condensed phase flows at a steady rate when a magnetic field is present, and it is accelerated when an electric field is applied. Just below the transition temperature, only a small fraction of electrons in the metal are condensed and participate in superflow. As temperature is lowered, thermal effects which tend to destroy the condensed phase become less important and a larger fraction of the electrons condense.

If a superconductor is placed in a large enough external magnetic field, the superconducting state can be destroyed. A plot of magnetic induction, B, versus applied field, H, appears as in Fig. 3.13. For applied field, H, with a value less than some temperature-dependent critical value, $H_{coex}(T)$, the system is a perfect diamagnet. That is, the permeability $\mu = 0$ and therefore $B = 0$. However, for $H > H_{coex}(T)$ the system becomes normal and $B = \mu H$. (For normal metals $\mu \approx \mu_0$, where μ_0 is the permeability of the vacuum.) Thus,

$$B = \begin{cases} 0 & \text{if } H < H_{coex}(T) \\ \mu_0 H & \text{if } H > H_{coex}(T) \end{cases} \tag{3.52}$$

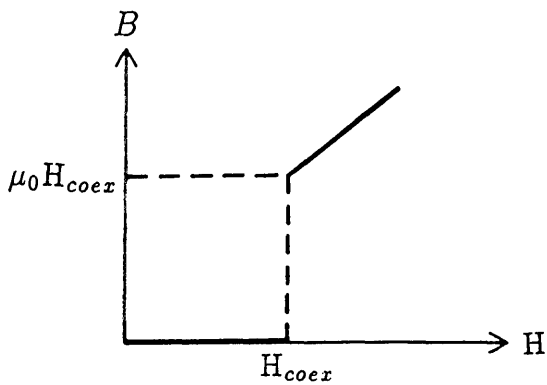


Fig. 3.13. A plot of the magnetic induction, **B**, versus the applied magnetic field, H, in a superconductor.

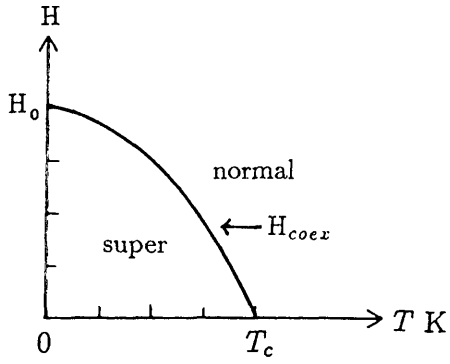


Fig. 3.14. The coexistence curve for normal and superconducting states.

The field, $H_{coex}(T)$ lies on the coexistence curve for the two phases. It has been measured as a function of the temperature and has roughly the same behaviour for most metals (cf. Fig. 3.14). The coexistence curve for the normal and superconducting phases is well approximated by the equation

$$H_{coex}(T) = H_0\left(1 - \frac{T^2}{T_c^2}\right), \tag{3.53}$$

where T_c is the critical temperature when no external fields are present. The slope $(dH/dT)_{coex} = 0$ at $T = 0\,\mathrm{K}$ and is negative at $T = T_c$. The phase diagram for a superconducting metal has analogies to the vapor–liquid transition in a *PVT* system, if we let H_{coex} replace the specific volume. Inside the coexistence curve, condensate begins to appear.

Along the coexistence curve, the chemical potentials of the superconducting and normal phases must be equal and, therefore, any changes in the chemical potentials must be equal. Thus, along the coexistence curve

$$-s_n dT - B_n dH = -s_s dT - B_s dH \tag{3.54}$$

or

$$s_n - s_s = -\mu_0 H_{coex}(T)\left(\frac{dH}{dT}\right)_{coex} \tag{3.55}$$

Equation (3.55) is the Clausius–Clapeyron equation for superconductors. We have used the fact that $B_s = 0$ and $B_n = \mu_0 H_{coex}(T)$ on the coexistence curve. Here $s_{n(s)}$ is the entropy per unit volume of the normal (superconducting) phase. We see that the transition has a latent heat (is first order) for all temperatures except $T = T_c$ where $H_{coex} = 0$. When no external magnetic fields are present, the transition is continuous.

The change in the heat capacity per unit volume at the transition is

$$(c_n - c_s)_{coex} = \left[T\frac{\partial(s_n - s_s)}{\partial T}\right]_{coex} = 2\mu_0 \frac{H_0^2}{T_c}\left(\frac{T}{T_c} - \frac{3T^3}{T_c^3}\right). \tag{3.56}$$

We have used Eq. (3.53) to evaluate the derivatives $(dH/dT)_{coex}$. At low temperatures the heat capacity of the normal phase is higher than that of the superconducting phase. At $T = T_c$ (the critical point) the heat capacity is higher in the superconductor and has a finite jump, $(c_s - c_n)_{T=T_c} = (4\mu_0/T_c)H_0^2$. It is worthwhile noting that as $T \to 0, (s_s - s_n) \to 0$ since $(dH/dT)_{coex} \to 0$ as $T \to 0$. This is in agreement with the third law of thermodynamics.

It is useful to obtain the difference between the Gibbs free energies of the normal and superconducting phases for $H = 0$. The differential of the Gibbs free energy per unit volume, g, is

$$dg = -s\,dT - B\,dH. \tag{3.57}$$

If we integrate Eq. (3.57) at a fixed temperature, we can write

$$g(T,H) - g(T,0) = -\int_0^H B\,dH. \tag{3.58}$$

For the normal phase we have

$$g_n(T,H) - g_n(T,0) = -\frac{\mu_0}{2}H^2. \tag{3.59}$$

For the superconducting phase ($H < H_{coex}$), we have

$$g_s(T,H) - g_s(T,0) = 0 \tag{3.60}$$

since $B = 0$ inside the superconductor. If we next use the fact that

$$g_n(T,H_{coex}) = g_s(T,H_{coex}), \tag{3.61}$$

we obtain the desired result

$$g_s(T,0) = g_n(T,0) - \frac{\mu_0}{2}H_{coex}^2(T). \tag{3.62}$$

Thus, the Gibbs free energy per unit volume of the superconductor in the absence of a magnetic field is lower than that of the normal phase by a factor $\mu_0/2H_{coex}^2(T)$ (the so-called condensation energy) at a temperature T. Since the Gibbs free energy must be a minimum for fixed H and T, the condensed phase is a physically realized state. Note that $g_s(T_c,0) = g_n(T_c,0)$ as it should.

3.F. THE HELIUM LIQUIDS

From the standpoint of statistical physics, helium has proven to be one of the most unique and interesting elements in nature. Because of its small atomic mass and weak attractive interaction, helium remains in the liquid state for a wide range of pressures and for temperatures down to the lowest measured values.

The helium atom occurs in nature in two stable isotopic forms, He^3 and He^4. He^3, with nuclear spin (1/2), obeys Fermi–Dirac statistics; while He^4, with nuclear spin 0, obeys Bose–Einstein statistics. At very low temperatures, where quantum effects become important, He^3 and He^4 provide two of the few examples in nature of quantum liquids.

Chemically, He^3 and He^4 are virtually identical. The only difference between them is a difference in mass. However, at low temperatures the two systems exhibit very different behavior due to the difference in their statistics. Liquid He^4, which is a boson liquid, exhibits a rather straightforward transition to a superfluid state at 2.19 K. This can be understood as a condensation of particles into a single quantum state. Liquid He^3 also undergoes a transition to a superfluid state, but at a much lower temperature (2.7×10^{-3} K). The mechanism for the superfluid transition in liquid He^3 is quite different from that of liquid He^4. In liquid He^3, particles (more accurately, quasiparticles) form bound pairs with a spin $s = 1$ and relative angular momentum, $l = 1$. The mechanism is similar to the formation of bound pairs in a superconductor except that the pairs in a superconductor are formed with spin $s = 0$ and angular momentum $l = 0$. Thus, the bound pairs in a superconductor are spherical with no magnetic moment, while those in liquid He^3 are flatter along one axis, carry angular momentum, and have a net magnetic moment. The fact that the bound pairs in liquid He^3 have structure leads to many fascinating effects never before observed in any other physical system.

When He^3 and He^4 are combined to form a binary mixture, a new type of phase point occurs (called a *tricritical point*) in which a λ-line connects to the critical point of a binary phase transition.

While we cannot discuss the theory of these systems at this point, it is worthwhile to look at their phase diagrams since they present such a contrast to those of classical fluids and they tend to confirm the third law.

3.F.1. Liquid He^4 [12–14]

He^4 was first liquefied in 1908 by Kamerlingh Onnes at a temperature of 4.215 K at a pressure of 1 atm. Unlike the classical liquids we described in Section 3.D, it has two triple points. The coexistence curves for liquid He^4 are shown in Fig. 3.15 (compare them with the coexistence curve for a classical liquid in Fig. 3.4). He^4 at low temperature has four phases. The solid phase only appears for pressures above 25 atm, and the transition between the liquid and

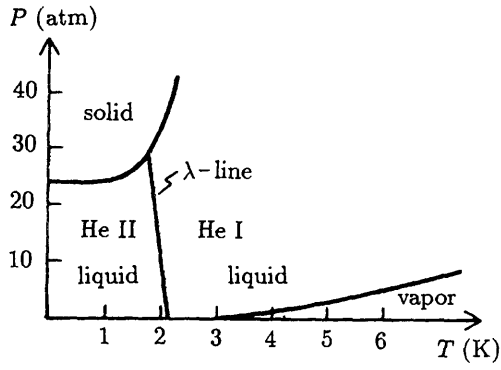


Fig. 3.15. The coexistence curves for He^4.

solid phases is first order. The liquid phase continues down to temperatures approaching $T = 0\,K$. However, there are in fact two liquid phases. As the normal liquid [liquid He(I)] is cooled, a line of λ-points occurs at about $T = 2\,K$ (the exact temperature depends on the pressure), indicating that a continuous symmetry-breaking phase transition occurs at this line. There is a triple point at each end of the — line. The symmetry that is broken is gauge symmetry. Below the λ-line, the liquid phase (which was called liquid He(II) by Keesom and Wolfke [15]) begins to exhibit very strange properties. The first experimenters who worked with liquid He^4 found that it was able to leak out of their containers through cracks so tiny that even He^4 gas could not leak through. This apparently frictionless flow is a consequence of the fact that the condensed phase is a highly coherent macroscopic quantum state. It is analogous to the apparent frictionless flow of the condensed phase in superconductors. The order parameter for the condensed phase in liquid He^4 is a macroscopic "wave function," and the Ginzburg–Landau theory for the condensed phase of He^4 is very similar to that of the condensed phase in superconductors, except that in liquid He^4 the particles are not charged. The specific heat of liquid He^4 along the λ-line is shown in Fig. 3.16. We can see that it has the lambda shape characteristic of a continuous phase transition.

The phase diagram of He^4 provides a good example of the third law. The vapor–liquid and solid–liquid coexistence curves approach the P-axis with zero slope. From Eqs. (2.54) and (2.100), we see that this is a consequence of the third law.

3.F.2. Liquid He^3 [16–18]

The He^3 atom is the rarer of the two helium isotopes. Its relative abundance in natural helium gas is one part in a million. Therefore, in order to obtain it in large quantities, it must be "grown" artificially from tritium solutions through

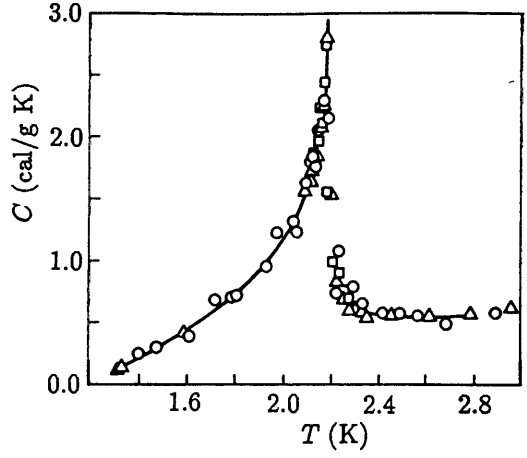


Fig. 3.16. The specific heat of He^4 at vapor pressure at the λ-point [12].

β-decay of the tritium atom. Thus, He^3 was not obtainable in large enough quantities to study until the late 1940s and it was first liquefied in 1948 by Sydoriack, Grilly, and Hammel [19]. Since the He^3 atom has only (3/4) the mass of a He^4 atom, it has a larger zero point energy than the He^4 atom. As a result, He^3 boils at temperature about 25% lower than He^4, and it requires a pressure about 25% greater than that of He^4 to solidify.

The phase diagram for He^3 (on the same scale as that for He^4) is given in Fig. 3.17. On this scale there appears to be no transition to a superfluid state. There is, however, a minimum in the liquid–solid coexistence curve. This is attributed to the spin of the He^3 atom. At low temperature the spin lattice of the He^3 solid has a higher entropy than the liquid. The entropy difference,

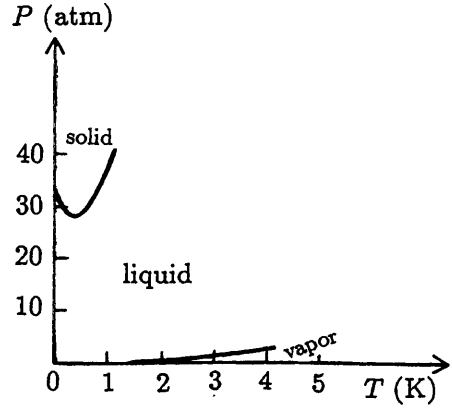


Fig. 3.17. Coexistence curves for He^3 [16].

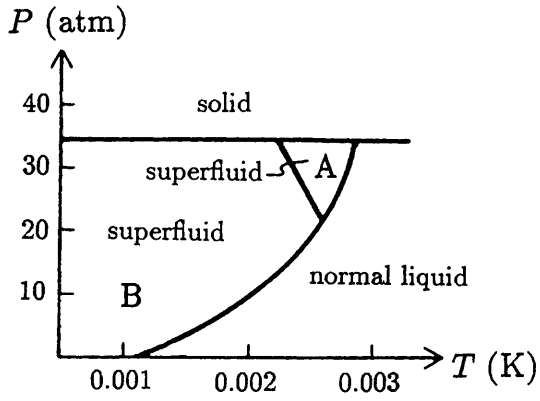


Fig. 3.18. Coexistence curves for superfluid phases of He^3 when no magnetic field is applied [16].

$\Delta S = S_{\text{liquid}} - S_{\text{solid}}$, is positive at high temperature, vanishes at about $T = 0.3\,\text{K}$ and becomes negative below 0.3 K. Since volume differences remain virtually unchanged, the Clausius–Clapeyron equation $dP/dT = \Delta S/\Delta V$ leads to a positive slope at high temperature and a negative slope at low temperature. At low temperature, if the third law is to be satisfied, the slope of the liquid–solid coexistence curve must become flat as $T \to 0\,\text{K}$.

Superfluidity was first observed in liquid He^3 in 1971 by Osheroff, Richardson, and Lee [20]. In 1997, they received the Nobel prize for this work. The transition occurs at 2.7×10^{-3} K at a pressure of about 34 atm. The phase diagram for a small temperature interval is shown in Fig. 3.18. There are, in fact, several superfluid phases in liquid He^3, depending on how the bound pairs orient themselves. The so-called A-phase is an anisotropic phase. The bound pairs (which have shape) all orient on the average in the same direction. This defines a unique axis in the fluid and all macroscopic properties depend on their orientation with respect to that axis. The B-phase is a more isotropic phase and has many features in common with the superfluid phase of a superconductor. If we apply a magnetic field to liquid He^3, a third superfluid phase appears. The transition between the normal and superfluid phases appears to be continuous, while that between the A and B superfluid phases appears to be first order.

3.F.3. Liquid He^3–He^4 Mixtures

When He^3 and He^4 are mixed together and condensed to the liquid state, some interesting phenomena occur. We will let x_3 denote the mole fraction of He^3. In 1949, Abraham, Weinstock, and Osborne [21] showed that He^3–He^4 mixtures can undergo a transition to a superfluid state. In this early experiment, they

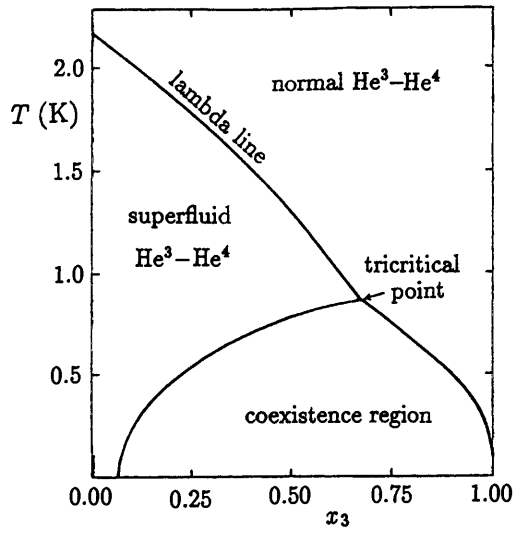


Fig. 3.19. The phase diagram for a liquid He^3–He^4 mixture plotted as a function of temperature T and mole fraction x_3 of He^3.

found that the λ-line extended from $T = 2.19\,\mathrm{K}$ for $x_3 = 0$ to about $T = 1.56\,\mathrm{K}$ for $x_3 = 0.282$. Later experiments extended the λ-line down to $T = 0.87\,\mathrm{K}$ for $x_3 = 0.67$ (cf. Fig. 3.19).

In 1954, Prigogine, Bingen, and Bellemans [22] predicted the existence of a phase separation of liquid He^3–He^4 mixtures into an He^3-rich phase and an He^4-rich phase. (The theory of binary phase separation in classical mixtures is discussed in Sect. (S3.E).) This phase separation was found in 1956 by Walters and Fairbank [23] using nuclear magnetic resonance techniques. They were able to measure the magnetic susceptibility of the liquid in different vertical layers of the mixture. In the coexistence region the magnetic susceptibility, which is a measure of the concentration of He^3 atoms varies with height. The critical point for this binary phase transition lies at the end of the λ-line at $T = 0.87\,\mathrm{K}$ and $x_3 = 0.67$. The phase transition along the λ-line is second order. The binary phase separation is a first-order phase transition. In 1982, the region of metastable states for this first-order phase transition was measured by Alpern, Benda, and Leiderer [24].

The end point of the λ-line is the critical point of the first-order binary phase transition. It was first called a *tricritical point* by Griffiths [25]. He pointed out that *in a suitable space* it is meeting point of three lines of second-order phase transitions. One line is the λ-line. The other two are lines of critical points associated with the first-order phase transition. Thus, the tricritical point is different from the triple points we have seen in classical fluids.

3.G. GINZBURG–LANDAU THEORY [26]

In the late 1930s, Ginzburg and Landau proposed a mean field theory of continuous phase transitions which relates the order parameter to the underlying symmetries of the system. One of the features which distinguishes first-order and continuous phase transitions is the behavior of the order parameter at the transition point. In a first-order phase transition, the order parameter changes discontinuously as one crosses the coexistence curve (except at the critical point). Also, first-order phase transitions may or may not involve the breaking of a symmetry of the system. For example, in the liquid–solid and vapor–solid transitions, the translational symmetry of the high-temperature phase (liquid or vapor) is broken, but for the vapor–liquid transition no symmetry of the system is broken. In the liquid and gas phases, the average particle density is independent of position and therefore is invariant under all elements of the translation group. The solid phase, however, has a periodic average density and is translationally invariant only with respect to a subgroup of the translation group. Solids may also exhibit first-order phase transitions in which the lattice structure undergoes a sudden rearrangement from one symmetry to another and the state of the solid changes discontinuously.

At a first-order phase transition, the slope of the free energy curve changes discontinuously as a function of Y and T at the transition point and a symmetry may or may not be broken. At a continuous phase transition, the slope of the free energy curve changes continuously and a symmetry is always broken. In such transitions, a new macroscopic parameter (the order parameter) appears in the less symmetric phase. The order parameter may be a scalar, a vector, a tensor, a complex number or some other quantity. The form of the order parameter is determined by the type of symmetry that is broken (an extensive discussion of this point may be found in Ref. 26). For example, in the transition from a paramagnetic to a ferromagnetic system, rotational symmetry is broken because a spontaneous magnetization occurs which defines a unique direction in space. The order parameter is a vector. In the transition from normal liquid He^4 to superfluid liquid He^4, gauge symmetry is broken. The order parameter is a complex scalar. In a solid, the lattice might begin to undergo a gradual reorientation as the temperature is lowered. The order parameter is the change in the spatially varying number density. In continuous transitions, one phase will always have a lower symmetry than the other. Usually the lower temperature phase is less symmetric, but this need not always be the case.

All transitions which involve a broken symmetry and a continuous change in the slope of the free energy curve can be described within the framework of a mean field theory due to Ginzburg and Landau [26]. Ginzburg–Landau theory does not describe all features of continuous phase transitions correctly, but it does give us a good starting point for understanding such transitions. Near a continuous phase transition the free energy is an analytic function of the order parameter associated with the less symmetric phase. In real systems, the free energy is not an analytic function of the order parameter near the critical

point. Nevertheless, Ginzburg–Landau theory still describes enough qualitative features of continuous phase transitions that it is well worth studying.

We will let η denote the order parameter and let ϕ denote the free energy and write

$$\phi(T, Y, f) = \phi_0(T, Y) + \alpha_2(T, Y)\eta^2 + \alpha_3(T, Y)\eta^3 + \alpha_4(T, Y)\eta^4 + \cdots - f\eta, \tag{3.63}$$

where Y is a generalized thermodynamic force and f is the force conjugate to the order parameter (one can usually be found, even though it may only be a mathematical construct and not realizable in the laboratory). There is no term in Eq. (3.63) which is first order in η because that would ensure a nonzero value for the order parameter above the transition point. The molar free energy, $\phi_0(T, Y)$, describes the thermodynamic quantities not directly involved in the transition and generally will depend on other state variables. For example, if we are studying the transition from the paramagnetic to the ferromagnetic state of a magnetic crystal, free energy $\phi_0(T, Y)$ would contain all the nonmagnetic contributions to the thermodynamic state of the crystal.

The actual value of the order parameter, η, which is realized in nature is the one that gives a minimum of the free energy. By plotting the free energy as a function of η for various choices of the coefficients $\alpha_2, \alpha_3, \alpha_4$, and f, it is easy to see under what conditions various types of phase transition can occur. The types of terms which are present in the free energy are determined by the symmetry properties of a system and the fact that the free energy is a scalar quantity. If the order parameter is a vector or tensor, then only invariant combinations can appear in the free energy. For example, the order parameter for a magnetic crystal is the magnetization. The magnetization, which is a vector, changes sign under time reversal. However, the free energy must be invariant under time reversal, and therefore a cubic term in the magnetization is ruled out. There are a number of different types of phase transition which can be described by the free energy in Eq. (3.63). We shall now consider several of these.

3.G.1. Continuous Phase Transitions

A continuous phase transition can occur if the cubic term in Eq. (3.63) cannot appear and if no external field is present. The free energy then takes the form

$$\phi(T, Y, \eta) = \phi_0(T, Y) + \alpha_2(T, Y)\eta^2 + \alpha_4(T, Y)\eta^4 + \cdots \tag{3.64}$$

The dependence of $\alpha_2(T, Y)$ on temperature is chosen so that for temperatures above and at the critical temperature the free energy will only be minimized for $\eta = 0$, while below the critical temperature it will be minimized for $|\eta| > 0$.

In general, the free energy will be minimum if

$$\left(\frac{\partial \phi}{\partial \eta}\right)_{T,Y} = 0 \quad \text{and} \quad \left(\frac{\partial^2 \phi}{\partial \eta^2}\right)_{T,Y} \geqslant 0. \tag{3.65}$$

Equations (3.65) give us conditions that must be satisfied for equilibrium states. The right-hand equation in (3.65) is the condition for stability (not all stable states are equilibrium states). In order to have global stability, we must have

$$\alpha_4(T, Y) > 0. \tag{3.66}$$

This will ensure that as we increase η to very large values, the free energy will continue to increase. The critical point occurs when $\alpha_2(T, Y) = 0$. This happens at a temperature $T = T_c(Y)$. If the critical temperature is a function of another variable, Y, then there will be a line of critical points in the (T, Y) plane. If we choose $\alpha_2(T, Y) > 0$ for $T > T_c(Y)$ and $\alpha_2(T, Y) < 0$ for $T < T_c(Y)$, then the free energy, Φ, will have its minimum value at $\eta = 0$ when $T > T_c(Y)$ and will have its minimum value for $\eta \neq 0$ when $T < T_c(Y)$. Since the free energy must vary continuously through the transition point, at $T = T_c(Y)$ we must have $\alpha_2(T_c, Y) = 0$. We can combine all this information if we write $\alpha_2(T, Y)$, in the neighborhood of the transition point, in the form

$$\alpha_2(T, Y) = \alpha_0(T, Y)(T - T_c(Y)), \tag{3.67}$$

where α_0 is a slowly varying function of T and Y.

In Fig. 3.20, we sketch the free energy for three values of α_2. In curve (A), the free energy has a minimum for $\eta = 0$. Curve (B) shows the critical point. The free energy becomes flattened in the neighborhood of $\eta = 0$. In curve (C), the free energy has minima at $\eta = \pm\eta_0 \neq 0$. The system will randomly select one of these two nonzero values of the order parameter, η, below the critical point. The region on curve (C) for which $(\partial^2\phi/\partial\eta^2)_{T,Y} < 0$ corresponds to a region of unstable states. The free energy has *extrema* when

$$\left(\frac{\partial\phi}{\partial\eta}\right)_{T,Y} = 2\alpha_2\eta + 4\alpha_4\eta^3 = 0 \tag{3.68}$$

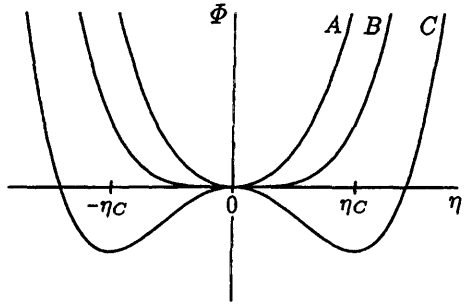


Fig. 3.20. The behavior of the free energy, $\Phi = \alpha_2\eta^2 + \alpha_4\eta^4$, for a continuous phase transition for $\alpha_4 = 4.0$ and (A) $\alpha_2 = 0.6$, (B) $\alpha_2 = 0.0$, and (C) $\alpha_2 = -0.6$. In the figure, $\eta_C = 2.7386$.

and therefore when

$$\eta = 0 \quad \text{or} \quad \eta = \pm\sqrt{\frac{-\alpha_2}{2\alpha_4}} = \pm\sqrt{\frac{\alpha_0}{2\alpha_4}(T_c - T)}. \tag{3.69}$$

When $T > T_c$, the *minimum* occurs for $\eta = 0$. When $T < T_c$, the *minimum* occurs for $\eta = \pm\sqrt{(\alpha_0/2\alpha_4)(T_c - T)}$. Thus, below the critical temperature, the order parameter is nonzero and increases as $\sqrt{T_c - T}$. From the above discussion, the free energy takes the following form:

$$\begin{aligned} \phi(T, Y, \eta) &= \phi_0(T, Y) \qquad \text{for} \quad T > T_c, \\ \phi(T, Y, \eta) &= \phi_0(T, Y) - \frac{\alpha_0^2 (T_c - T)^2}{4\alpha_4} \qquad \text{for} \quad T < T_c, \end{aligned} \tag{3.70}$$

where we have suppressed the dependence of T_c on Y and the dependence of α_0 and α_4 on T and Y.

The molar heat capacity is

$$c_Y = -T\left(\frac{\partial^2 \phi}{\partial T^2}\right)_Y. \tag{3.71}$$

If we neglect derivatives of α_0 and α_4 (we assume that they vary slowly with temperature), we find that the molar heat capacity has a finite jump at the critical point:

$$c_Y(T_c^-) - c_Y(T_c^+) = \frac{T_c \alpha_0^2}{2\alpha_4}. \tag{3.72}$$

The jump in the heat capacity has the shape of a λ, as shown in Fig. 3.21, and therefore the critical point for a continuous phase transition is sometimes called a λ-point.

The transition from normal to superfluid in liquid He^4 is an example of a continuous phase transition. The order parameter, η, is the macroscopic wave function, Ψ, for the condensed phase and the generalized force, Y, is just the pressure, P (the force P is not conjugate to Ψ). The free energy can be written

$$\phi(T, P, \Psi) = \phi_0(T, P) + \alpha_2 |\Psi|^2 + \alpha_4 |\Psi|^4 + \cdots, \tag{3.73}$$

where $\alpha_2(T, P) = \alpha_0(T, P)(T - T_c)$ and $\alpha_0(T, P)$ and $\alpha_4(T, P)$ are slowly varying functions of T and P. The order parameter, $\Psi = 0$, above the critical temperature, and $\Psi = e^{i\theta}\sqrt{(\alpha_0/2\alpha_4)(T_c - T)}$ below the critical temperature. The phase factor, θ, can be choosen to be zero as long as no currents flow in the system. As we see in Fig. 3.15 there is in fact a line of continuous transition points in the (P, T) plane. In Fig. 3.16 we showed the behavior of the heat

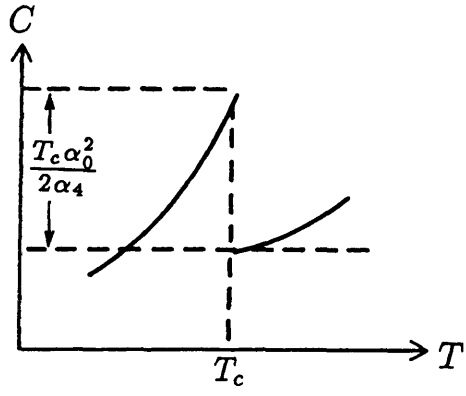


Fig. 3.21. The jump in the heat capacity at the critical point (lambda point) as predicted by Landau theory.

capacity as we passed through the line of critical points. As we see from the figure, there is a finite lambda-shaped jump in the heat capacity of the liquid.

If we turn on an external force, f, which couples to the order parameter, then the continuous phase transtion is destroyed. In the presence of an external force, the free energy has the form

$$\phi'(T, Y, f) = \phi(T, Y, \eta) - f\eta = \phi_0(T, Y) + \alpha_2\eta^2 + \alpha_4\eta^4 + \cdots - f\eta, \quad (3.74)$$

where $\alpha_2 = \alpha_2(T, Y)$ and $\alpha_4 = \alpha_4(T, Y)$. The order parameter is nonzero for all temperatures. A plot of the free energy in the presence of a force is shown in Fig. 3.22 for the same parameters as Fig. 3.20.

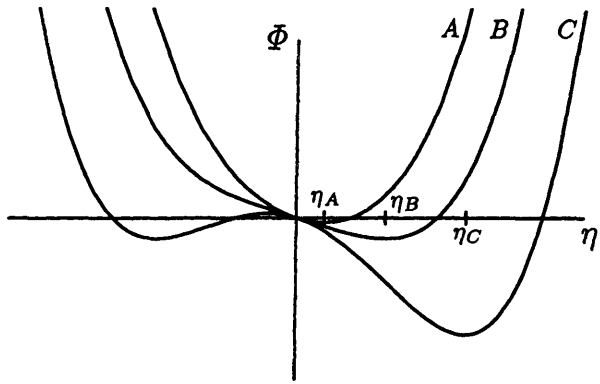


Fig. 3.22. The behavior of the free energy, $\phi = \alpha_2\eta^2 + \alpha_4\eta^4 - f\eta$, for a continuous phase transition for $\alpha_4 = 4.0$, $f = 0.06$, and (A) $\alpha_2 = 0.6$, (B) $\alpha_2 = 0.0$, and (C) $\alpha_2 = -0.6$. η_A, η_B, and η_C locate the minima of the curves. In the figure $\eta_A = 0.0485, \eta_B = 0.1554$, and $\eta_C = 0.2961$.

From Eq. (3.74), we can obtain the susceptibility, $\chi = (\partial\eta/\partial f)_{T,Y} = -(\partial^2\phi'/\partial f^2)_{T,Y}$. The equilibrium state is a solution of the equation

$$\left(\frac{\partial\phi'}{\partial\eta}\right)_{T,Y} = 2\alpha_2\eta + 4\alpha_4\eta^3 - f = 0. \tag{3.75}$$

If we take the derivative of Eq. (3.75) with respect to f and solve for $(\partial\eta/\partial f)_{T,Y}$, we obtain

$$\chi(f) = \left(\frac{\partial\eta}{\partial f}\right)_{T,Y} = \frac{1}{2\alpha_2 + 12\alpha_4\eta^2}. \tag{3.76}$$

In the limit, $f \to 0, \eta = 0$ for $T > T_c$ and $\eta = \sqrt{-\alpha_2/2\alpha_4}$ for $T < T_c$. Therefore, in the limit $f \to 0$ the susceptibility will be different above and below the critical point. We find

$$\begin{aligned} \chi &= \lim_{f\to 0}\left(\frac{\partial\eta}{\partial f}\right)_{T,Y} = \frac{1}{2\alpha_2} = \frac{1}{2\alpha_0(T - T_c)} \quad \text{for } T > T_c, \\ \chi &= \lim_{f\to 0}\left(\frac{\partial\eta}{\partial f}\right)_{T,Y} = -\frac{1}{4\alpha_2} = \frac{1}{4\alpha_0(T_c - T)} \quad \text{for } T < T_c. \end{aligned} \tag{3.77}$$

Note that the susceptibility diverges at the critical point.

The transition from a paramagnetic to ferromagnetic system is one of the simplest examples of a continuous phase transition. A system which exhibits this behaviour is a magnetic solid, such as nickel, whose lattice sites contain atoms with a magnetic moment. The critical temperature is called the Curie temperature. Above the Curie temperature, the magnetic moments are oriented at random and there is no net magnetization. However, as the temperature is lowered, magnetic interaction energy between lattice sites becomes more important than randomizing thermal energy. Below the Curie temperature, the magnetic moments became ordered on the average and a spontaneous magnetization appears. The symmetry that is broken at the Curie point is rotation symmetry. Above the Curie point, the paramagnetic system is rotationally invariant, while below it the spontaneous magnetization selects a preferred direction in space. The order parameter for this continuous phase transition is the magnetization, **M**. The magnetization is a vector and changes sign under time reversal. The free energy is a scalar and does not change sign under time reversal. If a magnetic field, **H**, is applied to the system, the Ginzburg–Landau free energy can be written in the form

$$\phi(T, \mathbf{H}) = \phi_0(T) - \mathbf{M}\cdot\mathbf{H} + \alpha_2\mathbf{M}\cdot\mathbf{M} + \alpha_4(\mathbf{M}\cdot\mathbf{M})^2 + \cdots, \tag{3.78}$$

where the coefficients α_2 and α_4 have the same properties as described above. For the case when the applied field **H** equals 0, the magnetization **M** equals 0

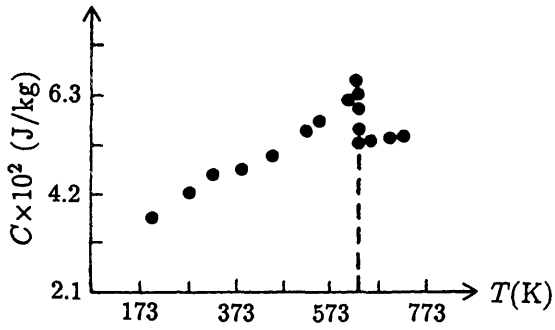


Fig. 3.23. The specific heat of nickel in the neighborhood of the Curie point. The dashed line gives the Curie point [34]. (Based on Ref. 34.)

above the Curie temperature and $\mathbf{M} = \pm\sqrt{(\alpha_0/2\alpha_4)(T_c - T)}\hat{\mathbf{M}}$ below the Curie temperature. $\hat{\mathbf{M}}$ is a unit vector which gives the direction of the magnetization vector. The actual direction of the magnetization vector, if $\mathbf{H} = 0$, will be determined by random fluctuations or outside influences. The heat capacity at the Curie point exhibits the characteristic λ-shaped peak. As an example, the λ-point in nickel is shown in Fig. 3.23.

3.G.2. First-Order Transitions

If the order parameter is a scalar, then there is no reason to exclude a third-order term in the molar free energy, ϕ. Also, if the order parameter is a second-order tensor, there are ways to contract a product of three such tensors to yield a scalar and again the free energy can have a third-order term. Such systems cannot exhibit a continuous transition. To see why, let us write the free energy in the form

$$\phi(T, Y, \eta) = \phi_0(T, Y) + \alpha_2\eta^2 + \alpha_3\eta^3 + \alpha_4\eta^4 + \cdots, \tag{3.79}$$

where $\alpha_2 = \alpha_2(T, Y), \alpha_3 = \alpha_3(T, Y)$, and $\alpha_4 = \alpha_4(T, Y)$.

The extrema of the free energy are given by the equation $(\partial\phi/\partial\eta)_{T,Y} = 0$, which has solutions $\eta = 0$ and $\eta = ((-3\alpha_3 \pm \sqrt{9\alpha_3^2 - 32\alpha_2\alpha_4})/8\alpha_4)$. As long as $9\alpha_3^2 - 32\alpha_2\alpha_4 < 0$, the only minimum of the free energy occurs at $\eta = 0$ because other values of η will be complex and therefore unphysical. When $9\alpha_3^2 - 32\alpha_2\alpha_4 > 0$, two minima and one maximum can exist. A plot of the free energy for $\alpha_2 > 0, \alpha_4 > 0$, and a range of values of α_3 is given in Fig. 3.24. For curves A, B, and C the state of minimum free energy (the equilibrium state) occurs for $\eta = 0$. Curve D shows the behavior of the free energy at the critical temperature for this system. At this point the equilibrium state shifts from one with order parameter $\eta = 0$ to one with order parameter $\eta = \eta_D$. Therefore, this is a discontinuous transition and is of the type one expects for a first-order transition. The transition point for the first-order transition (curve D in Fig.

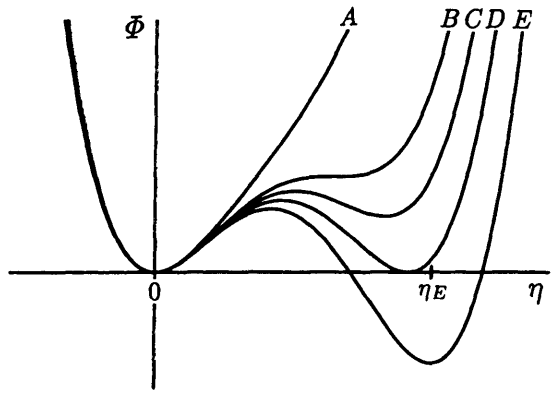


Fig. 3.24. The behavior of the free energy, $\phi = \alpha_2\eta^2 + \alpha_3\eta^3 + \alpha_4\eta^4$, for $\alpha_2 = 2.0$, $\alpha_4 = 4.0$, and (A) $\alpha_3 = -4.5$, (B) $\alpha_3 = -5.333$, (C) $\alpha_3 = -5.5$, (D) $\alpha_3 = -5.6568$, and (E) $\alpha_3 = -5.85$. In the figure, $\eta_E = 0.7738$.

3.24) is easily found. It must satisfy the conditions $\phi - \phi_0 = 0$ and $(\partial\phi/\partial\eta)_{T,Y} = 0$. These two conditions give $\eta = -\alpha_3/2\alpha_4$ and $\alpha_2 = \alpha_3^2/4\alpha_4$. Therefore, the first-order transition occurs when $\alpha_2 > 0$, and therefore it occurs before any continuous transition as the temperature is lowered. If $\alpha_3 < 0$, then it occurs for a positive value of the order parameter. If $\alpha_3 > 0$, then it occurs for a negative value of the order parameter.

3.H. CRITICAL EXPONENTS [27–29]

The critical point is the point at which the order parameter of a new phase begins to grow continuously from zero. We have seen many examples of critical points. In the liquid–vapor transition, a critical point terminated the liquid–vapor coexistence curve and was the one point for which the free energy slope changed continuously. For the binary mixture, the critical point marked the temperature at which phase separation could first take place as we lowered the temperature. In the spin system the critical point for transition from a paramagnetic state to ferromagnetic state was the Curie point. In the superconductor, the critical point was the point at which the condensate first appeared as we lowered the temperature in the absence of an external field. In liquid He^4, the condensed and normal phases were separated by a line of critical points in the (P, T) plane.

Systems exhibit dramatically new behavior below the critical point. As we approach the critical point from above (higher temperature), the system anticipates its new behavior by making "adjustments" on a microscopic scale. These "adjustments" appear in the form of fluctuations in density, magnetization, and so on, which become very large as the critical point is approached. Just

below the critical point, the order parameter of the new phase first becomes nonzero.

3.H.1. Definition of Critical Exponents

A subject of great interest is the way in which various systems approach the critical point. For this purpose it is useful to introduce the idea of critical exponents. As one approaches the critical point, various thermodynamic functions may diverge or go to zero or even remain finite. It is therefore convenient to introduce an expansion parameter

$$\varepsilon = \frac{T - T_c}{T_c}, \tag{3.80}$$

where T_c is the critical temperature, which is a measure of the distance from the critical point in terms of reduced variables.

Near the critical point all thermodynamic functions can be written in the form

$$f(\varepsilon) = A\varepsilon^{\lambda}(1 + B\varepsilon^{y} + \cdots) \tag{3.81}$$

where $y > 0$. The critical exponent for the function $f(\varepsilon)$ is defined

$$\lambda = \lim_{\varepsilon \to 0} \frac{\ln f(\varepsilon)}{\ln \varepsilon}. \tag{3.82}$$

If λ is negative, $f(\varepsilon)$ diverges at the critical point. If λ is positive, $f(\varepsilon)$ goes to zero at the critical point. In Fig. 3.25 we have plotted $f(\varepsilon) = \varepsilon^{\lambda}$ for $\lambda = -1, -3/2, 1/2$, and $1/4$. The case where $\lambda = 0$ may correspond to several different possibilities; for example, it may correspond to a logarithmic divergence $f(\varepsilon) = A|\ln \varepsilon| + B$ or to a dependence on ε of the form $f(\varepsilon) = A + B\varepsilon^{1/2}$. For such cases a modified exponent is introduced. If j is the smallest integer, such that $d^j f(\varepsilon)/d\varepsilon^j = f^{(j)}(\varepsilon)$ diverges, then

$$\lambda' = j + \lim_{\varepsilon \to 0} \frac{\ln |f^{(j)}(\varepsilon)|}{\ln \varepsilon}. \tag{3.83}$$

In Fig. 3.26 we have plotted $f(\varepsilon)$ as a function of ε for some cases when $\lambda = 0$. Although we have chosen to write ε in terms of temperature, it is also of interest to introduce exponents for the approach to the critical point involving quantities other than temperature, such as pressure, density, magnetic field, and so on. Thus, there are a number of different critical exponents that can be defined for a system depending on how the critical point is approached. We shall give some examples in the next section.

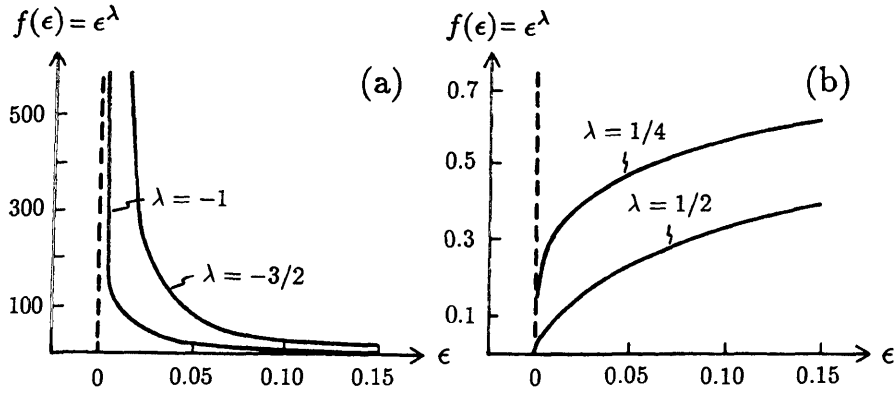


Fig. 3.25. Plots of $f(\varepsilon) = \varepsilon^{\lambda}$ for cases when $\lambda \neq 0$ (a) Plots for $\lambda = -1$ and $\lambda = -\frac{3}{2}$. (b) Plots for $\lambda = \frac{1}{4}$ and $\lambda = \frac{1}{2}$.

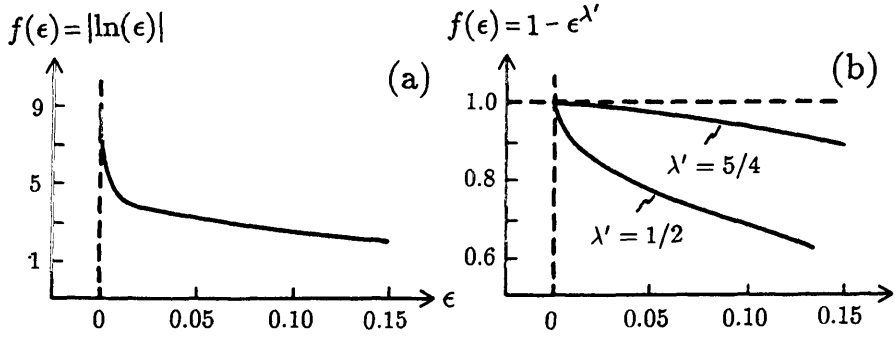


Fig. 3.26. Plots of $f(\varepsilon) = \varepsilon^{\lambda}$ for cases when $\lambda = 0$, (a) Plot of $f(\varepsilon) = |\ln(\varepsilon)|$. (b) Plot of $f(\varepsilon) = 1 - e^{\lambda'}$.

3.H.2. The Critical Exponents for Pure *PVT* Systems

There are four critical exponents which are commonly used to describe the bulk thermodynamic properties of *PVT* systems. We define them and give their experimental values below.

(a) Degree of the Critical Isotherm. The deviation of the pressure $(P - P_c)$ from its critical value varies *at least* as the fourth power of $(V - V_c)$ as the critical point is approached along the critical isotherm. It is convenient to express this fact by introducing a critical exponent, δ, such that

$$\frac{P - P_c}{P_c^0} \equiv A_\delta \left| \frac{\rho - \rho_c}{\rho_c} \right|^{\delta} \operatorname{sign}(\rho - \rho_c), \qquad T = T_c, \tag{3.84}$$

where P_c is the critical pressure, ρ_c is the critical density, A_δ is a constant, and P_c^0 is the pressure of an ideal gas at the critical density and temperature. Experimentally it is found that $6 > \delta \gtrsim 4$. The exponent δ is called the *degree of the critical isotherm.*

(b) Degree of the Coexistence Curve. Guggenheim [6] has shown that the deviation $(T - T_c)$ varies approximately as the third power of $(V - V_c)$ as the critical point is approached along the coexistence curve from either direction. One expresses this fact by introducing a critical exponent β, such that

$$\frac{\rho_l - \rho_g}{\rho_c} = A_\beta(-\varepsilon)^\beta, \tag{3.85}$$

where ρ_l is the density of liquid at temperature $T < T_c$, ρ_g is the density of gas at temperature $T < T_c$, each evaluated on the coexistence curve, and A_β is a constant. The quantity $\rho_l - \rho_g$ is the order parameter of system. It is zero above the critical point and nonzero below it. The exponent β is called the *degree of the coexistence curve* and is found from experiment to have values $\beta \approx 0.34$.

(c) Heat Capacity. The heat capacity at constant volume appears to have a logarithmic divergence for $T \to T_c$ along the critical isochore $(V = V_c)$. The critical exponent for heat capacity is denoted α and is defined as follows:

$$C_V = \begin{cases} A'_\alpha(-\varepsilon)^{-\alpha'}, & T < T_c, \quad \rho = \rho_c, \\ A_\alpha(+\varepsilon)^{-\alpha}, & T > T_c, \quad \rho = \rho_c, \end{cases} \tag{3.86}$$

where A'_α and A_α are constants. The exponents α and α' are found experimentally to have values $\alpha \sim 0.1$ and $\alpha' \sim 0.1$.

(d) Isothermal Compressibility. The isothermal compressibility diverges approximately as a simple pole:

$$\frac{\kappa_T}{\kappa_T^0} = \begin{cases} A'_\gamma(-\varepsilon)^{-\gamma'}, & T < T_c, \quad \rho = \rho_l(T) \text{ or } \rho_g(T) \\ A_\gamma(\varepsilon)^{-\gamma}, & T > T_c, \quad \rho = \rho_c, \end{cases} \tag{3.87}$$

where A'_γ and A_γ are constants. For $T < T_c$ one approaches the critical point along the coexistence curve; for $T > T_c$ one approaches it along the critical isochore. Typical experimental values of γ' and γ are $\gamma' \sim 1.2$ and $\gamma \sim 1.3$.

(e) Exponent Inequalities. It is possible to obtain inequalities between the critical exponents using thermodynamic arguments. We shall give an example here. Equation (3.40) can be rewritten in terms of the mass density as

$$c_v = x_g c_{v_g} + x_l c_{v_l} + \frac{x_g T}{\rho_g^3 \kappa_T^g}\left(\frac{\partial \rho_g}{\partial T}\right)^2_{coex} + \frac{x_l T}{\rho_l^3 \kappa_T^l}\left(\frac{\partial \rho_l}{\partial T}\right)^2_{coex}, \tag{3.88}$$

where c_v, c_{v_g} and c_{v_l} are now specific heats (heat capacity per kilogram), and κ_T is the isothermal compressibility. All terms on the right-hand side of Eq. (3.88) are positive. Thus, we can write

$$c_v \geqslant \frac{x_g T}{\rho_g^3 \kappa_T^g} \left(\frac{\partial \rho_g}{\partial T}\right)^2_{coex}. \tag{3.89}$$

As the critical point is approached for fixed volume, $x_g \to (1/2), \rho_g \to \rho_c$ (ρ_c is the critical density), κ_T diverges as $(T_c - T)^{-\gamma'}$ [cf. Eq. (3.87)], and $(\partial \rho_g / \partial T)_{coex}$ diverges as $(T_c - T)^{\beta - 1}$ if we assume that $[(1/2)(\rho_l + \rho_g) - \rho_c]$ goes to zero more slowly than $(\rho_l - \rho_g)$ [cf. Eqs. (3.26) and (3.27)]. Thus,

$$c_v \geqslant \frac{1}{2} \frac{T_c B (T_c - T)^{\gamma' + 2\beta - 2}}{\rho_c^3} \tag{3.90}$$

where B is a constant, and

$$\ln c_v \geqslant (2 - \gamma' - 2\beta) |\ln(-\varepsilon)|. \tag{3.91}$$

If we next divide by $|\ln(-\varepsilon)|$ and take the limit $T \to T_c^-$, we find

$$\alpha' + 2\beta + \gamma' \geqslant 2. \tag{3.92}$$

The inequality in Eq. (3.92) is roughly satisfied by real fluids. If we choose $\alpha' = 0.1, \beta = (1/3)$, and $\gamma' = 1.3$, then $\alpha' + 2\beta + \gamma' \approx 2$. Equation (3.92) is called the *Rushbrook inequality.*

The critical exponents can be computed fairly easily starting from mean field theories such as the van der Waals equation (cf. Exercise (3.4)) or Ginzburg–Landau theory. All mean field theories give similar results. The common feature of these theories is that they can be derived assuming that the particles move in a mean field due to all other particles. The mean field theories do not properly take into account the effects of short-ranged correlations at the critical point and do not give the correct results for the critical exponents. We shall return to this point when we discuss Wilson renormalization theory of critical points. In Section S3.C, we define the critical exponents for the Curie point in a magnetic system.

■ **EXERCISE 3.4.** Compute the critical exponents, α, β, δ, and γ for a gas whose equation of state is given by the van der Waals equation.

Answer: The van der Waals equation in terms of reduced variables is $(\overline{P} + (3/\overline{v}^2))(3\overline{v} - 1) = 8\overline{T}$. In order to examine the neighborhood of the critical point, we introduce expansion parameters $\varepsilon = (T/T_c) - 1$, $\omega = (v/v_c) - 1$, and $\pi = (P/P_c) - 1$. In terms of these parameters, the

van der Waals equation can be written

$$\left[(1+\pi)+\frac{3}{(1+\omega)^2}\right][3(\omega+1)-1]=8(1+\varepsilon). \tag{1}$$

If we solve for π, we find

$$\pi=\frac{8\varepsilon+16\varepsilon\omega+8\varepsilon\omega^2-3\omega^3}{2+7\omega+8\omega^2+3\omega^3}. \tag{2}$$

(**a**) *The degree of the critical isotherm*, δ. Let $\varepsilon=0$ in Eq. (2) and expand π in powers of ω. This gives

$$\pi=-\frac{3}{2}\omega^3+\cdots. \tag{3}$$

Thus, the degree of the critical isotherm is $\delta=3$.

(**b**) *The isothermal compressibility exponent*, γ. Let us compute $(\partial\pi/\partial\omega)_\varepsilon$ and then set $\omega=0$. We obtain

$$\left(\frac{\partial\pi}{\partial\omega}\right)_\varepsilon=-6\varepsilon \tag{4}$$

for $\omega=0$. Thus, the critical exponent, γ, is $\gamma=1$.

(**c**) *The degree of the coexistence curve*, β. In the neighborhood of the critical point, the van der Waals equation can be written

$$\pi=4\varepsilon-6\varepsilon\omega+9\varepsilon\omega^2-\frac{3}{2}\omega^3+\cdots. \tag{5}$$

The values of ω on either side of the coexistence curve can be found from the conditions that along the isotherm,

$$\int_{\bar{v}_g}^{\bar{v}_l}\bar{v}d\bar{P}=0 \quad \text{and} \quad \bar{P}(\bar{v}_g)=\bar{P}(\bar{v}_l), \tag{6}$$

where $\bar{P}=P/P_c$ is the reduced pressure and $\bar{v}_g=v_g/v_c$ and $\bar{v}_l=v_l/v_c$ are the reduced molar volumes of the gas and liquid, respectively, on the coexistence curve. The condition that the pressure and temperature of the liquid and gas in the coexistence region be equal yields

$$-\tfrac{3}{2}\omega_l^3-6\varepsilon\omega_l+9\varepsilon\omega_l^2=-\tfrac{3}{2}\omega_g^3-6\,\varepsilon\omega_g+9\varepsilon\omega_g^2. \tag{7}$$

If we note that ω_l is negative and write $\omega_l=-\tilde{\omega}_l$ and $\omega_g=+\tilde{\omega}_g$, then Eq. (7) gives

$$4\varepsilon(\tilde{\omega}_l+\tilde{\omega}_g)+6\varepsilon(\tilde{\omega}_l^2-\tilde{\omega}_g^2)+\tilde{\omega}_l^3+\tilde{\omega}_g^3=0. \tag{8}$$

The fact that the molar Gibbs free energy of the liquid and gas phases are equal means that $\int_{v_g}^{v_l} v dP = 0$ or that

$$\int_{\omega_g}^{\omega_l} d\omega(1+\omega)\left(-6\varepsilon + 18\omega\varepsilon - \frac{9}{2}\omega^2 + \cdots\right) \approx -6\varepsilon(\omega_l - \omega_g) + 6\varepsilon(\omega_l^2 - \omega_g^2) - \frac{3}{2}(\omega_l^3 - \omega_g^3) + \cdots = 0. \tag{9}$$

or

$$4\varepsilon(\tilde{\omega}_l + \tilde{\omega}_g) + 4\varepsilon(\tilde{\omega}_l^2 - \tilde{\omega}_g^2) + \tilde{\omega}_l^3 + \tilde{\omega}_g^3 = 0. \tag{10}$$

In order for Eqs. (8) and (10) to be consistent, we must have $\tilde{\omega}_g = \tilde{\omega}_l$. If we plug this into Eq. (8) or (10), we get $\tilde{\omega}_l = \tilde{\omega}_g = \tilde{\omega}$. This gives $\tilde{\omega}^2 \approx -4\varepsilon$. Note that ε is negative.

Thus,

$$\tilde{\omega}_g \approx \tilde{\omega}_l = 2|\varepsilon|^{1/2} \tag{11}$$

and the degree of the coexistence curve is $\beta = 1/2$.

(d) *The heat capacity exponent,* α. The jump in the heat capacity can be obtained from Eq. (3.40). Let us approach the critical point along the critical isochore, $v = v_c$. Then as $T \to T_c, x_l \approx x_g \to 1/2$ and $c_{v_g} \to c_{v_l}$. Thus, the jump in the heat capacity is given by

$$c_{v_c}(T_c^-) - c_{v_c}(T_c^+) = \lim_{T \to T_c} \left\{ -\frac{T}{2}\left[\left(\frac{\partial P_g}{\partial v_g}\right)_T \left(\frac{\partial v_g}{\partial T}\right)^2_{coex} + \left(\frac{\partial P_l}{\partial v_l}\right)_T \left(\frac{\partial v_l}{\partial T}\right)^2_{coex}\right]\right\}. \tag{12}$$

Along the coexistence curve $(\partial \bar{v}/\partial \bar{T})_{coex} = \pm|\varepsilon|^{-1/2}$, where the minus sign applies to the liquid and the plus sign applies to the gas. From Eqs. (5) and (11) we find

$$\left(\frac{\partial \bar{P}_l}{\partial \bar{v}_l}\right)_T \equiv \left(\frac{\partial \bar{P}_g}{\partial \bar{v}_g}\right)_T = 6|\varepsilon| - \frac{9}{2}\omega^2 - 18\omega|\varepsilon| + \cdots = -12|\varepsilon| \pm O(|\varepsilon|^{3/2}). \tag{13}$$

If we note that $(P_c v_c/RT_c) = (3/8)$, we find

$$c_{v_c}(T_c^-) - c_{v_c}(T_c^+) = \frac{9}{2}R + O(\varepsilon). \tag{14}$$

Thus, the van der Waals equation predicts a finite jump in the heat capacity at the critical point and therefore it predicts $\alpha' = \alpha = 0$.

▶ SPECIAL TOPICS

▶ S3.A. Surface Tension

In Section 2.H.1, we showed that two parts of a thermodynamic system, at equilibrium, must have the same pressure if the interface between them is free to move and transmit mechanical energy. In deriving the condition for mechanical equilibrium however, we neglected any contributions due to surface tension. In this section we shall show that, if the surface moves in such a way that its area changes, surface tension can affect the mechanical equilibrium condition.

For simplicity, let us consider a monomolecular thermodynamic system consisting of two phases, gas (vapor) and liquid in contact and in thermodynamic equilibrium. A typical example would be water droplets in contact with water vapor. As we discussed in Section 2.C.6, very strong unbalanced molecular forces at the liquid surface act to contract the surface. If the liquid droplet grows and the surface area increases, then work must be done against these surface forces. This provides an additional contribution to the mechanical energy of the system.

In order to obtain corrections to the condition for mechanical equilibrium due to surface effects, let us consider a single liquid droplet of radius, R, floating in gas (we neglect gravity). We assume that the entire system is held at temperature T and is contained in a fixed total volume, $V_{\text{tot}} = V_g + V_l$, where $V_l = (4/3)\pi R^3$ is the volume of the liquid droplet and $V_g = V_{\text{tot}} - V_l$ is the volume of the gas phase (cf. Fig. 3.27). The surface area of the droplet is $A = 4\pi R^2$ and its surface tension is σ. The number of molecules in the gas phase is N_g and in the liquid phase is N_l. The number of molecules comprising the surface, N_s, generally will be very small compared to those in the liquid or

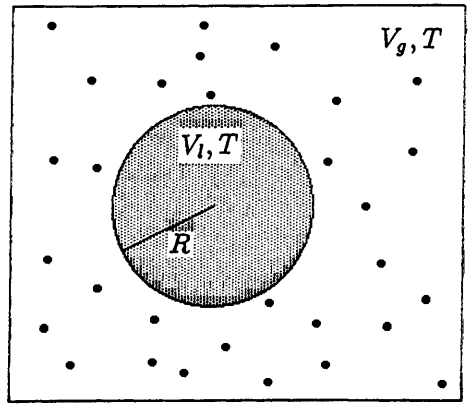


Fig. 3.27. A single liquid droplet in equilibrium with its vapor.

gas phases, so we take $N_s \approx 0$. Since the gas and liquid phases are free to exchange particles and heat, at equilibrium the chemical potentials $\tilde{\mu}_g$ and $\tilde{\mu}_l$, of the gas and liquid phases respectively, will be equal and the temperature will be uniform throughout. However, the pressures of the gas and liquid phases need not be equal if surface effects are included. Since we are dealing with a monomolecular substances, the chemical potential will be a function only of pressure and temperature. Therefore, at thermodynamic equilibrium we have

$$\mu_l(P_l, T) = \mu_g(P_g, T). \tag{3.93}$$

Because we are dealing with a system at fixed temperature, total volume, and chemical potential, it is convenient to work with the grand potential (cf. Section 2.F.5). The grand potential for the entire system can be written

$$\Omega = -P_g V_g - P_l V_l + \sigma A = -(V_{\text{tot}} - \tfrac{4}{3}\pi R^3)P_g - \tfrac{4}{3}\pi R^3 P_l + \sigma 4\pi R^2. \tag{3.94}$$

For a system at equilibrium with fixed temperature, total volume, and chemical potential, the grand potential must be a minimum. Therefore, we obtain the condition for thermodynamic equilibrium:

$$\left(\frac{d\Omega}{dR}\right)_{T,V_{\text{tot}},\mu} = 4\pi R^2(P_g - P_l) + 8\pi R\sigma = 0 \tag{3.95}$$

or

$$P_l - P_g = \frac{2\sigma}{R}. \tag{3.96}$$

If the interface between the two parts of a thermodynamic system has a surface tension and if the surface has curvature, then the condition for mechanical equilibrium must be corrected to include the effects of surface tension. The pressures in the two parts of the system need no longer be equal. The surface

Table 3.1. The Surface Tension for Various Liquids in Contact with Air

Substance	σ (dynes/cm)	T(°C)
Water	72.0	25
Water	67.9	50
Alcohol	21.8	25
Alcohol	19.8	50
Soap solution	25.0	25
Mercury	487	15

tension varies with temperature and generally decreases as the temperature is raised. The addition of impurities to the liquid will reduce the surface tension because it disrupts the tight network of "unbalanced" intermolecular forces at the interface. Some values of the surface tension of several substances are given in Table 3.1. Equation (3.96) was obtained by thermodynamic arguments. In Exercise 3.5, we show that it can also be obtained by purely mechanical arguments.

■ **EXERCISE 3.5.** Use purely mechanical arguments to derive Eq. (3.96) for a spherical liquid droplet, with radius R, floating in a gas. Assume that the liquid has pressure P_l, the gas has pressure P_g, and interface has surface tension σ.

Answer: Consider the forces acting on an area element, $d\mathbf{A} = \hat{\mathbf{r}}R^2 \sin(\theta)d\theta d\phi$, located in the interval $\theta \to \theta + d\theta$ and $\phi \to \phi + d\phi$ on the surface of the droplet. There will be a force outward (inward) along the direction, $\hat{\mathbf{r}}$, due to the pressure of the liquid (gas). The net force on the area element due to the pressure difference is

$$d\mathbf{F}_P = (P_l - P_g)\hat{\mathbf{r}}R^2 \sin\theta d\theta d\phi, \tag{1}$$

where $\hat{\mathbf{r}} = \sin(\theta)\cos(\phi)\hat{\mathbf{x}} + \sin(\theta)\sin(\phi)\hat{\mathbf{y}} + \cos(\theta)\hat{\mathbf{z}}$. The surface tension exerts force on the edges of the area element which are tangent to the surface and perpendicular outward at each edge, and it tends to stretch the area element in all four directions (note that the units of surface tension are (work/area)=(force/length)). The side, $(\theta \to \theta + d\theta, \phi)$, of the area element, $d\mathbf{A}$, experiences a force

$$d\mathbf{f}_1 = -\hat{\boldsymbol{\varphi}}\sigma R\, d\theta, \tag{2}$$

where $R\,d\theta$ is the length of the side and the unit vector, $\hat{\boldsymbol{\varphi}}$, can be written $\hat{\boldsymbol{\varphi}} = -\sin(\phi)\hat{\mathbf{x}} + \cos(\phi)\hat{\mathbf{y}}$. The side, $(\theta \to \theta + d\theta, \phi + d\phi)$, of the area element, $d\mathbf{A}$, experiences a force

$$d\mathbf{f}_2 = (\hat{\phi} + d\hat{\phi})\sigma R\, d\theta, \tag{3}$$

where $R\,d\theta$ is the length of the side and the unit vector, $\hat{\phi} + d\hat{\phi}$, can be written $\hat{\boldsymbol{\varphi}} + d\hat{\boldsymbol{\varphi}} \equiv -\sin(\phi + d\phi)\hat{\mathbf{x}} + \cos(\phi + d\phi)\hat{\mathbf{y}}$. The side, $(\theta, \phi \to \phi + d\phi)$, of the area element, $d\mathbf{A}$, experiences a force

$$d\mathbf{f}_3 = -\hat{\boldsymbol{\theta}}\sigma R \sin(\theta)d\phi, \tag{4}$$

where $R\sin(\theta)d\phi$ is the length of the side and the unit vector, $\hat{\boldsymbol{\theta}}$, can be written $\hat{\boldsymbol{\theta}} = \cos(\theta)\cos(\phi)\hat{\mathbf{x}} + \cos(\theta)\sin(\phi)\hat{\mathbf{y}} + \sin(\theta)\hat{\mathbf{z}}$. The side, $(\theta + d\theta, \phi \to \phi + d\phi)$, of the area element, $d\mathbf{A}$, experiences a force

$$d\mathbf{f}_4 = (\hat{\boldsymbol{\theta}} + d\hat{\boldsymbol{\theta}})\sigma R \sin(\theta + d\theta)d\phi, \tag{5}$$

where $R\sin(\theta + d\theta)d\phi$ is the length of the side and the unit vector, $\hat{\boldsymbol{\theta}} + d\hat{\boldsymbol{\theta}}$, can be written $\hat{\boldsymbol{\theta}} + d\hat{\boldsymbol{\theta}} \equiv \cos(\theta + d\theta)\cos(\phi)\hat{\mathbf{x}} + \cos(\theta + d\theta)\sin(\phi)\hat{\mathbf{y}} + \sin(\theta + d\theta)\hat{\mathbf{z}}$. If the droplet is to be in equilibrium, these forces must add to zero.

The condition for mechanical equilibrium takes its simplest form if we integrate these forces over the top hemisphere of the droplet—that is, if we integrate the forces over the interval $0 \geqslant \theta \geqslant \pi/2$ and $0 \geqslant \phi \geqslant 2\pi$. [Before we integrate, we must expand Eqs. (3) and (5) and only keep terms of order $d\theta\, d\phi$]. The integration over ϕ causes all contributions in the $\hat{\mathbf{x}}$ and $\hat{\mathbf{y}}$ directions to drop out and we get

$$\int_{hemisphere} [d\mathbf{F}_P + d\mathbf{f}_1 + d\mathbf{f}_2 + d\mathbf{f}_3 + d\mathbf{f}_4] = [(P_l - P_g)\pi R^2 - 2\pi\sigma R]\hat{\mathbf{z}}. \quad (6)$$

If the droplet is to be in equilibrium, these forces must add to zero. Therefore,

$$(P_l - P_g)R - 2\sigma = 0, \quad (7)$$

and we obtain the same condition for mechanical equilibrium as was obtained from thermodynamic arguments.

It is interesting to obtain the equilibrium vapor pressure of the gas as a function of the radius of the droplet. Let us assume that a reversible change in the pressure of the liquid and gas occurs in such a way as to keep the system in equilibrium and keep the temperature fixed. Since we are dealing with a monomolecular substance, we know that reversible changes in the chemical potential of the liquid and vapor can be written $d\mu' = vdP - sdT$, where $v = V/N$ is the volume per particle and $s = S/N$ is the entropy per particle. If the radius of the droplet changes, keeping the droplet in equilibrium with the vapor and keeping the temperature fixed ($dT = 0$), then $d\mu'_l = d\mu'_g$ and

$$v_l dP_l = v_g dP_g, \quad (3.97)$$

where $v_l = V_l/N_l$ and $v_g = V_g/N_g$. However, from Eqs. (3.96) and (3.97), we can write $dP_l - dP_g = d(2\sigma/R)$ and

$$\left(\frac{v_g - v_l}{v_l}\right) dP_g = d\left(\frac{2\sigma}{R}\right). \quad (3.98)$$

Let us now restrict ourselves to the case when the volume per particle of the liquid is much smaller than that of the gas (far from the critical point) so that $v_l \ll v_g$. Then we can approximate the volume per particle of the gas by the ideal gas value, $v_g = (k_B T/P_g)$, and Eq. (3.98) takes the form

$$\frac{k_B T}{v_l}\frac{dP_g}{P_g} = d\left(\frac{2\sigma}{R}\right). \quad (3.99)$$

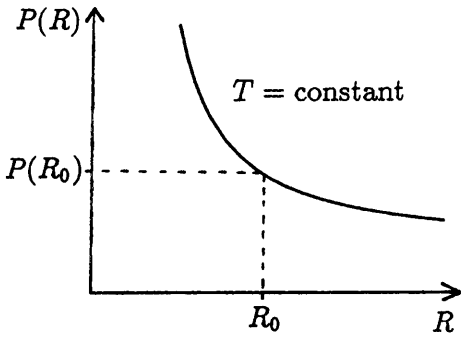


Fig. 3.28. A plot of the equilibrium vapor pressure of the droplet as a function of the radius of the droplet.

From Eq. (3.99), we can now find how the equilibrium vapor pressure of the gas varies as a function of the radius of the droplet. We will neglect changes in v_l as the pressure changes because liquids are very incompressible. Let us integrate the right-hand side of Eq. (3.99) from $R = \infty$ to R and the left-hand side from $P_g(\infty)$ to $P_g(R)$. Then we find

$$P_g(R) \approx P_g(\infty) \exp\left(\frac{2\sigma v_l}{k_B T R}\right). \tag{3.100}$$

The quantity $P_g(\infty)$ is the vapor pressure when the interface has no curvature (i.e., is flat). For a curved interface, the vapor pressure must be greater to maintain the droplet in equilibrium with the vapor then. Equation (3.100) tells us that only droplets of a given size can exist in equilibrium with a vapor at fixed P and T. Drops of different size will be unstable.

A plot of the equilibrium vapor pressure as a function of the radius of the droplet is given in Fig. 3.28. For a given radius, $R = R_0$, the equilibrium vapor pressure is $P_g(R_0)$. If there happens to be a droplet with radius, $R > R_0$, then the pressure, $P_g(R_0)$, is too high and the droplet will absorb fluid in an effort to reduce the pressure of the gas and eventually will condense out. If $R < R_0$, the pressure of the gas is too low and the droplet will give up fluid in an effort to increase the pressure and will disappear. As a result, the droplets tend to be a uniform size.

▶ S3.B. Thermomechanical Effect [30]

The behavior of liquid He^4 below 2.19 K can be described in terms of a model which assumes that liquid He^4 is composed of two interpenetrating fluids. One fluid (superfluid) can flow through cracks too small for He^4 gas to leak through, and it appears to carry no entropy. The other fluid (normal fluid) behaves normally. The fact that the superfluid carries no entropy leads to some very

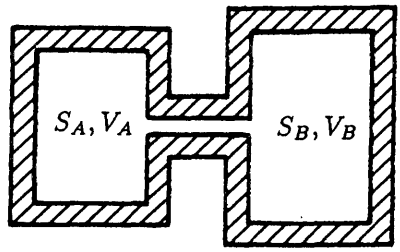


Fig. 3.29. Two vessels containing liquid He^4 below 2.19 K and connected by a very fine capillary. Only superfluid can pass between the two vessels.

interesting behavior, some of which can be described with classical thermodynamics. Let us consider two vessels, A and B, filled with liquid He^4 at a temperature below 2.19 K, and let us assume that they are connected by a capillary so thin that only the superfluid can flow through it (cf. Fig. 3.29). Let us further assume that the vessels are insulated from the outside world. This means that the total entropy must remain constant if no irreversible processes take place. Let us also assume that the total mass and total volume of the system remain constant. Under these conditions, the equilibrium state is a state of minimum internal energy.

We can obtain the condition for equilibrium between the vessels if we assume that matter can flow between them but entropy cannot. The total internal energy will be denoted U_T, and u_l will denote internal energy per kilogram (specific internal energy) in vessel l. The total internal energy is then given by

$$U_T = \sum_{l=A,B} M_l u_l, \tag{3.101}$$

where M_l is the total mass of liquid He^4 in vessel l. At equilibrium, the total internal energy must be a minimum. Thus,

$$\delta U_T = 0 = \sum_{l=A,B} (u_l \delta M_l + M_l \delta u_l). \tag{3.102}$$

Let us now assume that the total volume, V_l, and the total entropy, S_l, of liquid He^4 in vessel l (for $l = A, B$) are constant (this is possible because only superfluid can flow between the vessels and superfluid carries no entropy). The entropy of liquid He^4 in vessel l can be written $S_l = M_l s_l$, where M_l and s_l are the total mass and specific entropy of liquid He^4 in vessel l. Similarly, $V_l = M_l v_l$, where v_l is the specific volume of liquid He^4 in vessel l. Since S_l and V_l are constants, we can write $\delta S_l = M_l \delta s_l + s_l \delta M_l = 0$ and $\delta V_l = M_l \delta v_l + v_l \delta M_l = 0$. Therefore,

$$\delta s_l = -s_l \frac{\delta M_l}{M_l} \tag{3.103}$$

and

$$\delta v_l = -v_l \frac{\delta M_l}{M_l}. \tag{3.104}$$

Let us now expand the differential, δu_l, in Eq. (3.102) in terms of specific entropy and specific volume. Equation (3.102) then takes the form

$$\sum_{l=A,B} \left(u_l \delta M_l + M_l \left[\left(\frac{\partial u_l}{\partial s_l} \right)_{v_l} \delta s_l + \left(\frac{\partial u_l}{\partial v_l} \right)_{s_l} \delta v_l \right] \right) = 0. \tag{3.105}$$

If we note that $(\partial u/\partial s)_v = T$ and $(\partial u/\partial v)_s = -P$ [cf. Eqs. (2.68) and (2.69)] and make use of Eqs. (3.103) and (3.104), we obtain

$$\sum_{l=A,B} (u_l - s_l T_l + v_l P_l) \delta M_l = \sum_{l=A,B} \tilde{\mu}_l \delta M_l = 0, \tag{3.106}$$

where $\tilde{\mu}_l$ is the specific chemical potential of liquid He^4 in vessel l. Since the total mass is conserved, we can write $\delta M_A = -\delta M_B$ and we obtain the equilibrium condition

$$\tilde{\mu}_A(T_A, P_A) = \tilde{\mu}_B(T_B, P_B). \tag{3.107}$$

Since atoms can be exchanged, the chemical potentials of liquid He^4 in the two vessels must be equal. However, since heat cannot be exchanged and volume cannot change (no mechanical energy transfer), the pressure and temperature of the two vessels need not be the same.

We can now vary the temperature and pressure in one of the vessels (vessel A, for example) in such a way that the two vessels remain in equilibrium. The change in chemical potential in vessel A is

$$\Delta \tilde{\mu}_A = -s \Delta T_A + v \Delta P_A, \tag{3.108}$$

where $s = -(\partial \tilde{\mu}/\partial T)_P$ and $v = (\partial \tilde{\mu}/\partial P)_T$. But to maintain equilibrium, we must have $\Delta \tilde{\mu}_A = 0$ so the chemical potentials of the two vessels remain equal. Therefore,

$$\Delta P_A = \frac{s}{v} \Delta T_A. \tag{3.109}$$

Thus, a change in temperature of vessel A must be accompanied by a change in pressure of vessel A. If the temperature increases, the pressure will increase. This is called the *thermomechanical effect.*

The thermomechanical effect is most dramatically demonstrated in terms of the so-called fountain effect. Imagine a small elbow tube filled with very fine

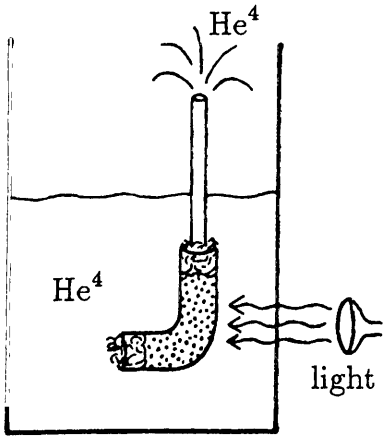


Fig. 3.30. The fountain effect.

powder, with cotton stuffed in each end. Assume that a long, thin capillary tube is put in one end and the elbow tube is immersed in liquid He^4 at a temperature below 2.19 K. If we now irradiate the elbow tube with a burst of light, the pressure of helium in the elbow tube will increase and helium will spurt out of the capillary tube (cf. Fig. 3.30). This is called the *fountain effect* and is a consequence of Eq. (3.109). When helium in the elbow tube is heated by radiation, superfluid will flow into the elbow tube to equalize the chemical potentials and increase the pressure in the elbow tube. It is interesting that in the fountain effect there is a spontaneous flow of matter from a cooler to hotter vessel. However, since the superfluid does not carry entropy, this does not violate the second law.

▶ S3.C. The Critical Exponents for the Curie Point

For magnetic systems, exponents α, β, γ, and δ can be defined in analogy with pure fluids. The phase diagrams for simple magnetic systems are given in Figs. 3.31–3.33. In Fig. 3.31, we sketch the coexistence curve for a ferromagnetic system. Below some critical temperature the spins begin to order spontaneously. The coexistence curve separates the two directions of magnetization. In Fig. 3.32 we plot some isotherms of the magnetic system, and in Fig. 3.33 we plot the magnetization as a function of temperature. It is helpful to refer to these curves when defining the various exponents.

(a) Degree of the Critical Isotherm. The exponent δ describes the variation of magnetization with magnetic field along the critical isotherm

$$\frac{H}{H_c^0} = B_\delta \left| \frac{M_H(T_c)}{M_0(0)} \right|^\delta, \tag{3.110}$$

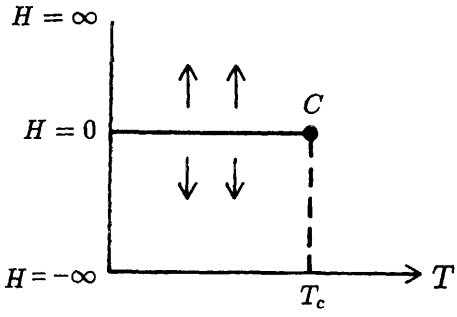


Fig. 3.31. Coexistence curve for a typical magnetic system. Below the Curie point the magnetization occurs spontaneously. The curve $H = 0$ separates the two possible orientations of the magnetization.

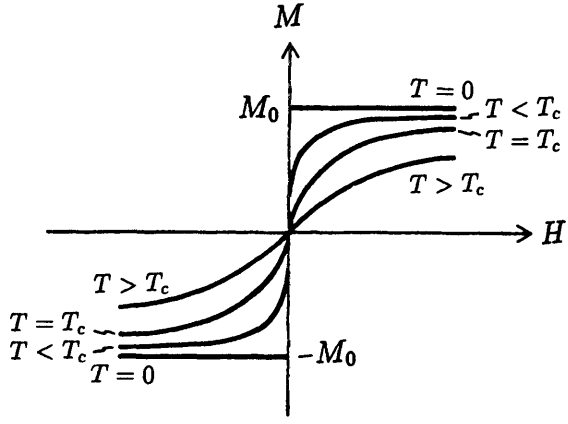


Fig. 3.32. A sketch of the isotherms for a ferromagnetic system.

where $H_c^0 = k_B T/m_0$, $M_0(0)$ is the magnetization in zero field at zero temperature, m_0 is the magnetic moment per spin, and B_δ is a proportionality constant. Experimentally, δ has values $4 \leqslant \delta \leqslant 6$ in agreement with the values of δ for pure fluids.

(b) Magnetization Exponent. In a magnetic system, the exponent β describes how the magnetization approaches its value at the critical point when no external field is present. It is defined as follows:

$$\frac{M_0(T)}{M_0(0)} = B_\beta(-\epsilon)^\beta, \tag{3.111}$$

where B_β is a constant. For magnetic systems, $\beta \approx \frac{1}{3}$ as it is for fluids.

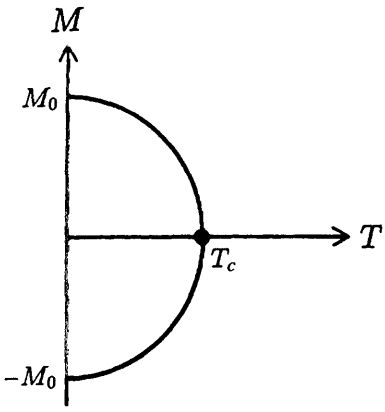


Fig. 3.33. A sketch of the magnetization for a simple ferromagnetic system.

(c) The Heat Capacity. For magnetic systems, the coefficients α and α' are defined as follows:

$$C_H(H=0) = \begin{cases} B'_\alpha(-\epsilon)^{-\alpha'}, & T < T_c, \\ B_\alpha \epsilon^{-\alpha}, & T > T_c, \end{cases} \tag{3.112}$$

where B_α and B'_α are constants. Experimentally, one finds $\alpha \sim \alpha' \sim 0$.

(d) The Magnetic Susceptibility. The magnetic susceptibility in the vicinity of the critical point can be written

$$\frac{\chi_T}{\chi_T^0} = \begin{cases} B'_\gamma(-\epsilon)^{-\gamma'}, & T < T_c, \quad H = 0, \\ B_\gamma \epsilon^{-\gamma}, & T > T_c, \quad H = 0, \end{cases} \tag{3.113}$$

where B'_γ and B_γ are constants and χ_T^0 is the susceptibility of a noninteracting system at the critical temperature. For real systems, γ has been found to be $\gamma \sim 1.3$.

The striking feature about the critical exponents for fluids and for magnetic systems is that the values are roughly the same. Indeed, there appears to be a great similarity in the way in which many systems approach their critical points.

▶ S3.D. Tricritical Points

Ginzberg–Landau theory allows us to describe a tricritical point (a point where a line of λ points meets the critical point for a line of discontinuous transitions). Let us consider a free energy of the form

$$\phi(T, Y, \eta) = \phi_0(T, Y) + \alpha_2 \eta^2(T, Y) + \alpha_4 \eta^4(T, Y) + \alpha_6 \eta^6(T, Y) + \cdots, \tag{3.114}$$

where $\alpha_2 = \alpha_2(T, Y), \alpha_4 = \alpha_4(T, Y)$, and $\alpha_6 = \alpha_6(T, Y)$.The extrema of the free energy are given by

$$\left(\frac{\partial \phi}{\partial \eta}\right)_{T,Y} = 2\alpha_2\eta + 4\alpha_4\eta^3 + 6\alpha_6\eta^5 = 0. \tag{3.115}$$

This has solutions

$$\eta = 0 \quad \text{and} \quad \eta^2 = \frac{-\alpha_4 \pm \sqrt{\alpha_4^2 - 3\alpha_2\alpha_6}}{3\alpha_6}. \tag{3.116}$$

Because there is no cubic or fifth-order term in the free energy, we can have a regime in which there is a line discontinuous transitions and a regime in which there is a line of continuous phase transitions. The conditions that must be satisfied for a discontinuous transition to occur are $\phi - \phi_0 = 0$ and $(\partial\phi/\partial\eta)_{T,Y} = 0$. These two conditions give $\eta^2 = -\alpha_4/2\alpha_6$ (the discontinuous transition can only occur for $\alpha_4 < 0$ so η^2 is non-negative) and

$$\alpha_2(T, Y) = \frac{\alpha_4^2(T, Y)}{4\alpha_6(T, Y)}. \tag{3.117}$$

The line of discontinuous transitions is given by the values of T and Y which satisfy Eq. (3.117). The line of continuous phase transition is given by the condition

$$\alpha_2(T, Y) = 0. \tag{3.118}$$

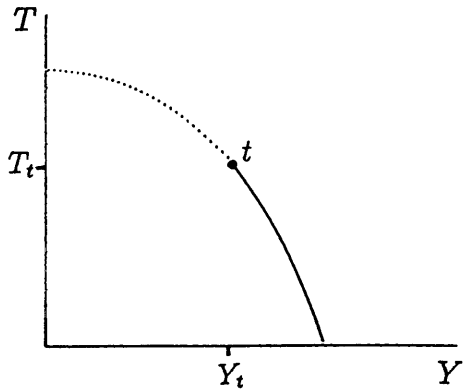


Fig. 3.34. A plot of the neighborhood of the tricritical point in the (T, Y) plane. The point t connecting the line of continuous phase transitions (dotted line) and the line of first-order phase transitions (solid line) is a tricritical point. It is the meeting point of three phases.

The lines of discontinuous and continuous phase transitions meet at a point, (T_t, Y_t), determined by the conditions $\alpha_2(T_t, Y_t) = 0$ and $\alpha_4(T_t, Y_t) = 0$. A schematic picture is given in Fig. 3.34. The point, t, was called a *tricritical point* by Griffiths [25]. He showed that in a suitable space it is the meeting point of three lines of critical points (two of them associated with the discontinuous transition).

A tricritical point occurs in He^3–He^4 mixtures (cf. Fig. 3.19). It is simultaneously the critical point for the binary phase transition and the end point of a line of λ points associated with superfluid phase transition.

▶ S3.E. Binary Mixtures [2, 31–33]

If we consider a fluid which is a mixture of several different types of interacting particles, a phase transition can occur in which there is a physical separation of the fluid into regions containing different concentrations of the various types of particles. The simplest example of this type of phase transition occurs for binary mixtures.

It is useful first to obtain a number of thermodynamic relations applicable to all binary mixtures. The Gibbs free energy for a binary mixture composed of n_1 moles of type 1 particles and n_2 moles of type 2 particles is

$$G = G(T, P, n_1, n_2) = n_1\mu_1 + n_2\mu_2, \tag{3.119}$$

and differential changes in the Gibbs free energy can be written

$$dG = -SdT + VdP + \mu_1 dn_1 + \mu_2 dn_2. \tag{3.120}$$

The molar Gibbs free energy, $g = G/n (n = n_1 + n_2)$, is

$$g = x_1\mu_1 + x_2\mu_2, \tag{3.121}$$

where x_1 and x_2 are the mole fractions of particles of type 1 and 2, respectively. From Eqs. (3.120) and (3.121), it is easy to show that

$$dg = -sdT + vdP + (\mu_1 - \mu_2)dx_1, \tag{3.122}$$

so that $g = g(T, P, x_1)$.

The chemical potential of type 1 particles is

$$\mu_1 = \left(\frac{\partial G}{\partial n_1}\right)_{P,T,n_2} = g + (1 - x_1)\left(\frac{\partial g}{\partial x_1}\right)_{P,T} \tag{3.123}$$

and the chemical potential of type 2 particles is

$$\mu_2 = \left(\frac{\partial G}{\partial n_2}\right)_{P,T,n_1} = g - x_1\left(\frac{\partial g}{\partial x_1}\right)_{P,T}, \tag{3.124}$$

where we have used the fact that

$$\left(\frac{\partial x_1}{\partial n_1}\right)_{n_2} = \frac{x_2}{n} \quad \text{and} \quad \left(\frac{\partial x_1}{\partial n_2}\right)_{n_1} = -\frac{x_1}{n}. \tag{3.125}$$

From Eqs. (3.122)–(3.124), we see that the chemical potential depends on the mole numbers n_1 and n_2, only through its dependence on the mole fraction, x_1. We can also show that

$$\left(\frac{\partial \mu_1}{\partial x_1}\right)_{P,T} = (1 - x_1)\left(\frac{\partial^2 g}{\partial x_1^2}\right)_{P,T} \tag{3.126}$$

and

$$\left(\frac{\partial \mu_2}{\partial x_1}\right)_{P,T} = -x_1\left(\frac{\partial^2 g}{\partial x_1^2}\right)_{P,T} \tag{3.127}$$

▶ S3.E.1. Stability Conditions

In Section 2.H.2, we found that chemical stability and Maxwell's relations require that the matrix

$$\begin{pmatrix} \mu_{1,1} & \mu_{1,2} \\ \mu_{2,1} & \mu_{2,2} \end{pmatrix}$$

must be symmetric positive definite, where $\mu_{i,j} = (\partial \mu_i / \partial n_j)_{P,T,\{n_k \neq n_j\}}$. This requires that $\mu_{i,i} > 0$ $(i = 1, 2)$ and that every principal minor be positive or zero. Thus, for a binary mixture we must have

$$\mu_{1,1} > 0, \qquad \mu_{2,2} > 0, \qquad \det\begin{pmatrix} \mu_{1,1} & \mu_{1,2} \\ \mu_{2,1} & \mu_{2,2} \end{pmatrix} \geq 0, \quad \text{and} \quad \mu_{1,2} = \mu_{2,1}. \tag{3.128}$$

For processes that occur at constant T and P, we have some additional conditions. From the Gibbs–Duhem equation (2.62), for processes in which $dT = 0$ and $dP = 0$ we have

$$n_1[d\mu_1]_{P,T} + n_2[d\mu_2]_{P,T} = 0. \tag{3.129}$$

Furthermore, we can write

$$[d\mu_1]_{P,T} = \left(\frac{\partial \mu_1}{\partial n_1}\right)_{P,T,n_2} dn_1 + \left(\frac{\partial \mu_1}{\partial n_2}\right)_{P,T,n_1} dn_2 \tag{3.130}$$

and

$$[d\mu_2]_{P,T} = \left(\frac{\partial \mu_2}{\partial n_1}\right)_{P,T,n_2} dn_1 + \left(\frac{\partial \mu_2}{\partial n_2}\right)_{P,T,n_1} dn_2. \tag{3.131}$$

If we combine Eqs. (3.129)–(3.131) and use the fact that the differentials dn_1 and dn_2 are independent, we find that

$$n_2\left(\frac{\partial \mu_2}{\partial n_2}\right)_{P,T,n_1} + n_1\left(\frac{\partial \mu_1}{\partial n_2}\right)_{P,T,n_1} = 0 \tag{3.132}$$

and

$$n_1\left(\frac{\partial \mu_1}{\partial n_1}\right)_{P,T,n_2} + n_2\left(\frac{\partial \mu_2}{\partial n_1}\right)_{P,T,n_2} = 0. \tag{3.133}$$

Thus, if $\mu_{1,1} > 0$, then $\mu_{2,1} < 0$, then for binary systems the conditions for chemical stability for a process at constant T and P reduce to

$$\left(\frac{\partial \mu_1}{\partial n_1}\right)_{P,T,n_2} > 0, \qquad \left(\frac{\partial \mu_2}{\partial n_2}\right)_{P,T,n_1} > 0, \qquad \left(\frac{\partial \mu_2}{\partial n_1}\right)_{P,T,n_2} = \left(\frac{\partial \mu_1}{\partial n_2}\right)_{P,T,n_1} < 0. \tag{3.134}$$

From Eq. (3.127), the molar Gibbs free energy must satisfy the condition

$$\left(\frac{\partial^2 g}{\partial x_1^2}\right)_{P,T} > 0. \tag{3.135}$$

Thus, *for chemical stability, the molar Gibbs free energy must be a convex function of the mole fraction.*

▶ S3.E.2. Equilibrium Conditions

In Section 2.H.2, we found that for a binary mixture to be in equilibrium the pressure P, the temperature T, and the chemical potential of each type of particle must be equal (uniform) throughout the system. The chemical potentials of different types of particles need not be equal.

If a phase separation occurs in a binary mixture, the chemical potential of type 1 particles must be equal in the two phases and similarily for the chemical potential of type 2 particles. This equality of chemical potentials between the two phases gives us a condition for locating the coexistence curve. For type 1

particles we have $\mu_1^I = \mu_1^{II}$ or

$$g^I + (1 - x_1^I)\left(\frac{\partial g}{\partial x_1}\right)^I_{P,T} = g^{II} + (1 - x_1^{II})\left(\frac{\partial g}{\partial x_1}\right)^{II}_{P,T}, \tag{3.136}$$

and for type 2 particles we have $\mu_2^I = \mu_2^{II}$ or

$$g^I - x_1^I\left(\frac{\partial g}{\partial x_1}\right)^I_{P,T} = g^{II} - x_1^{II}\left(\frac{\partial g}{\partial x_1}\right)^{II}_{P,T}, \tag{3.137}$$

where I and II denote the two phases. If we combine Eqs. (3.136) and (3.137), we can write the conditions for equilibrium in the form

$$\left(\frac{\partial g}{\partial x_1}\right)^I_{P,T} = \left(\frac{\partial g}{\partial x_1}\right)^{II}_{P,T} \tag{3.138}$$

and

$$(x_1^I - x_1^{II})\left(\frac{\partial g}{\partial x_1}\right)^I_{P,T} = g^I - g^{II}. \tag{3.139}$$

Equations (3.138) and (3.139) tell us that the equilibrium points in the (g, x_1) plane have equal slopes, and they have a common tangent. Equations (3.138) and (3.139) locate the coexistence curve.

In Fig. 3.35 we show a sketch of the molar Gibbs free energy which illustrates these various properties. It shows a region where two phases can

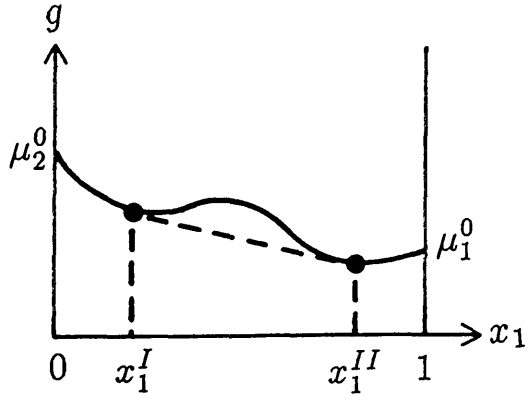


Fig. 3.35. A sketch of the molar Gibbs free energy of a phase separated binary mixture. The two points with common tangent are equilibrium states.

coexist. The points that have a common tangent are the equilibrium points. The concave region in the middle is unstable. In this region the two phases, one rich type 1 particles and the other rich in type 2 particles, can coexist. In a test tube, the heavier phase will sink to the bottom and the lighter one will float to the top.

As long as $(\partial\mu_2/\partial x_1)_{P,T} < 0$, the binary mixture will be stable and exist in one phase. However, if $(\partial\mu_2/\partial x_1)_{P,T} > 0$ the system has an unstable region and phase separation occurs. The critical point for this phase separation is given by $(\partial\mu_2/\partial x_1)^c_{P,T} = 0$. The critical point is the point where the x_1 first becomes a double-valued function of μ_1 or μ_2 as the temperature is changed. That is, two different values of x_1 give the same value of the chemical potential. Thus, in analogy to the liquid–vapor critical point (with $P \to \mu_2$ and $v \to x_1$), the critical point is a point of inflection of the curve $\mu_2 = \mu_2(T, P, x_1)$ for T and P constant. Therefore, we have the additional condition that $(\partial^2\mu_2/\partial x_1^2)^c_{P,T} = 0$ at the critical point.

A sketch of the coexistence curve, and the curve separating stable from unstable states is given in Fig. 3.36. The region outside and above the coexistence curve corresponds to allowed single-phase equilibrium states. Below the coexistence curve is a coexistence region in which two equilibrium states with different concentrations of type 1 particles can coexist at the same temperature. The shaded region corresponds to metastable states. These are single-phase states which are not in thermodynamic equilibrium but are chemically stable. All single-phase states below the dashed line are unstable and cannot be realized in nature. Let us follow the horizontal line at temperature, $T' < T_c$, in Fig. 3.36. At $x_1 = 0$, we have a system consisting only of type 2 particles. As we start adding type 1 particles, the concentration of type 1 particles increases until we reach the coexistence curve at point I. At this point, the system separates into two phases, one in which type 1 particles have concentration x_1^I and another in which type 1 particles have concentration x_1^{II}. As we increase the number of type 1 particles relative to type 2 particles, the

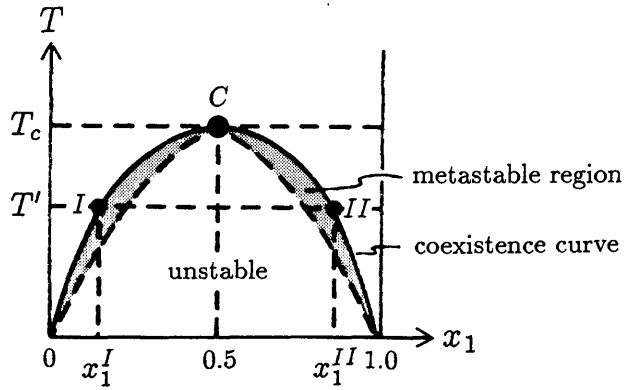


Fig. 3.36. The phase diagram for a binary mixture. The point C is the critical point.

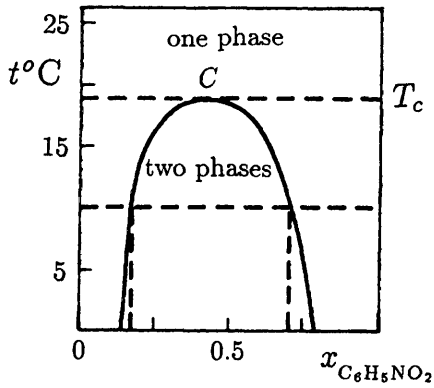


Fig. 3.37. The phase diagram for a mixture of *n*-hexane and nitrobenzene ($C_6\,H_5\,NO_2$) at atmospheric pressure. The solid line is the coexistence curve. (Based on Ref. 2.)

amount of phase II increases and the amount of phase I decreases until we reach the coexistence curve at point II. At point II, phase I has disappeared and we again have a single-phase equilibrium state of concentration, x_1^{II}.

We see that there many analogies between the liquid–gas transition and the separation of a binary mixture into two phases. An example of a system exhibiting this type of behavior is a mixture of *n*-hexane and nitrobenzene at atmospheric pressure. The phase diagram for this system is given in Fig. 3.37.

■ **EXERCISE 3.6.** Consider a binary mixture of particles of types 1 and 2, whose Gibbs free energy is given by

$$G = n_1\mu_1^0(P,T) + n_2\mu_2^0(P,T) + RTn_1\ln(x_1) + RTn_2\ln(x_2) + \lambda n x_1 x_2,$$

where $n = n_1 + n_2, n_1$ and n_2 are the mole numbers, and x_1 and x_2 are the mole fractions of particles of types 1 and 2, respectively. (a) Plot the molar Gibbs free energy $g(P,T,x_1)$ versus x_1 for fixed P and T (for definiteness assume that $\mu_1^0 = 1.0, \mu_2^0 = 1.05, RT = 0.8$, and $\lambda = 1$). What are x_1^I and x_1^{II}? (*b*) Use conditions $(\partial\mu_1/\partial x_1)^c_{P,T} = (\partial^2\mu_1/\partial x_1^2)^c_{P,T} = 0$ to locate the critical point. (c) Find the condition for equilibrium between the two phases. Show that the conditions $\mu_1^I = \mu_1^{II}$ and $\mu_2^I = \mu_2^{II}$ and the condition $(\partial g/\partial x_1)^I_{P,T} = (\partial g/\partial x_1)^{II}_{P,T}$ are equivalent.

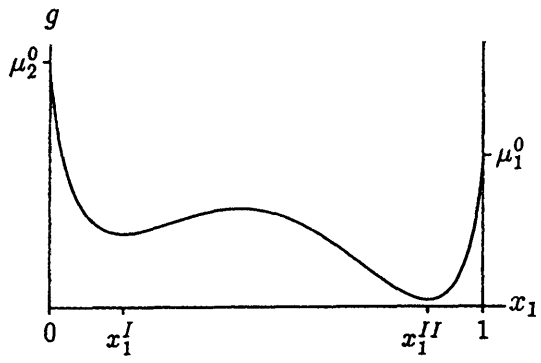
Answer:

(**a**) The molar Gibbs free energy is

$$g = \frac{G}{n} = x_1\mu_1^0 + x_2\mu_2^0 + RTx_1\ln(x_1) + RTx_2\ln(x_2) + \lambda x_1 x_2, \quad (1)$$

A plot of g versus x_1 is given below for $\mu_1^0 = 1.0$, $\mu_2^0 = 1.05$, $RT = 0.8$, and $\lambda = 1$.

The equilibrium concentrations are $x_1^I = 0.169$ and $x_1^{II} = 0.873$.



(b) The chemical potential, μ_2, is

$$\mu_2 = \left(\frac{\partial G}{\partial n_2}\right)_{P,T,n_1} = \mu_2^0(P,T) + RT\ln(1-x_1) + \lambda x_1^2. \qquad (2)$$

Therefore, at the critical point we have $(\partial\mu_2/\partial x_1)^c_{P,T} = -RT/(1-x_1) + 2\lambda x_1 = 0$ and $(\partial^2\mu_2/\partial x_1^2)^c_{P,T} = -RT/(1-x_1)^2 + 2\lambda = 0$. If we solve these two equations for T and x_1, we find that the critical point is located at $x_1 = 1/2$ and $T = \lambda/2R$.

(c) There are two ways to obtain the condition for equilibrium between the two phases. (i) The condition $(\partial g/\partial x_1)^I_{P,T} = (\partial g/\partial x_1)^{II}_{P,T}$, together with Eq. (1), yields the equilibrium condition

$$\lambda(1-2x_1^I) + RT\ln\left(\frac{x_1^I}{1-x_1^I}\right) = \lambda(1-2x_1^{II}) + RT\ln\left(\frac{x_1^{II}}{1-x_1^{II}}\right). \qquad (3)$$

(ii) The conditions $\mu_1^I = \mu_1^{II}$ and $\mu_2^I = \mu_2^{II}$ yield the equilibrium conditions

$$RT\ln(x_1^I) + \lambda(1-x_1^I)^2 = RT\ln(x_1^{II}) + \lambda(1-x_1^{II})^2 \qquad (4)$$

and

$$RT\ln(1-x_1^I) + \lambda(x_1^I)^2 = RT\ln(1-x_1^{II}) + \lambda(x_1^{II})^2. \qquad (5)$$

If we subtract Eq. (5) from Eq. (4), we recover Eq. (3). Thus, the two equilibrium conditions are equivalent.

▶ S3.E.3. Coexistence Curve

Before we write an equation for the coexistence curve, it is necessary to introduce a new expression for the chemical potential. Let us first remember that the Gibbs free energy can be written $G = U - ST + PV = n_1\mu_1 + n_2\mu_2$. Therefore, the chemical potential for type 1 particles can be written

$$\mu_1 = \left(\frac{\partial G}{\partial n_1}\right)_{P,T,n_2} = \left(\frac{\partial U}{\partial n_1}\right)_{P,T,n_2} - T\left(\frac{\partial S}{\partial n_1}\right)_{P,T,n_2} + P\left(\frac{\partial V}{\partial n_1}\right)_{P,T,n_2}. \quad (3.140)$$

The quantity $u_1 \equiv (\partial U/\partial n_1)_{P,T,n_2}$ is a partial molar internal energy, $s_1 \equiv (\partial S/\partial n_1)_{P,T,n_2}$ is a partial molar entropy, and $v_1 \equiv (\partial V/\partial n_1)_{P,T,n_2}$ is a partial molar volume. Note that the chemical potential is a partial molar Gibbs free energy. Similar quantities exist for type 2 particles. In terms of these "partial" quantities, the chemical potentials can be written

$$\mu_1 = u_1 - s_1T + v_1P \quad \text{and} \quad \mu_2 = u_2 - s_2T + v_2P. \quad (3.141)$$

It is useful to note the relation between the molar volume, $v = V/n$ and the partial molar volume, $v_1 = (\partial V/\partial n_1)_{P,T,n_2}$. It is easy to show that

$$v_1 = \left(\frac{\partial V}{\partial n_1}\right)_{P,T,n_2} = v + (1 - x_1)\left(\frac{\partial v}{\partial x_1}\right)_{P,T}. \quad (3.142)$$

The partial molar enthalpies of the type 1 and type 2 particles are

$$h_1 \equiv \left(\frac{\partial H}{\partial n_1}\right)_{P,T,n_2} = u_1 + v_1P \quad \text{and} \quad h_2 \equiv \left(\frac{\partial H}{\partial n_2}\right)_{P,T,n_1} = u_2 + v_2P, \quad (3.143)$$

respectively.

If we are in a region of coexistence of the two different phases, then the temperature, pressure, and chemical potentials of each type of particle must be equal. As we move along the coexistence curve, changes in the chemical potentials, temperature, and pressure of the two phases must be equal. Let us now consider the differential of the quantity, μ_1/T. It is

$$\begin{aligned} d\left(\frac{\mu_1}{T}\right) = &\left[\frac{\partial}{\partial T}\left(\frac{\mu_1}{T}\right)\right]_{P,n_1,n_2} dT + \left[\frac{\partial}{\partial P}\left(\frac{\mu_1}{T}\right)\right]_{T,n_1,n_2} dP \\ &+ \left[\frac{\partial}{\partial n_1}\left(\frac{\mu_1}{T}\right)\right]_{P,T,n_2} dn_1 + \left[\frac{\partial}{\partial n_2}\left(\frac{\mu_1}{T}\right)\right]_{P,T,n_1} dn_2. \end{aligned} \quad (3.144)$$

However,

$$\left[\frac{\partial}{\partial T}\left(\frac{\mu_1}{T}\right)\right]_{P,n_1,n_2} = -\frac{h_1}{T^2}, \tag{3.145}$$

where we have used the fact that $(\partial\mu_1/\partial T)_{P,n_1,n_2} = -(\partial S/\partial n_1)_{P,T,n_2}$ and $\mu_1 = h_1 - s_1 T$. If we make use of the fact that $(\partial\mu_1/\partial P)_{T,n_1,n_2} = (\partial V/\partial n_1)_{P,T,n_2} = v_1$ and (3.145), we can write Eq. (3.144) in the form

$$d\left(\frac{\mu_1}{T}\right) = -\frac{h_1}{T^2}dT + \frac{v_1}{T}dP + \frac{1}{T}\left(\frac{\partial\mu_1}{\partial x_1}\right)_{P,T} dx_1, \tag{3.146}$$

and we can write

$$d\left(\frac{\mu_2}{T}\right) = -\frac{h_2}{T^2}dT + \frac{v_2}{T}dP + \frac{1}{T}\left(\frac{\partial\mu_2}{\partial x_1}\right)_{P,T} dx_1, \tag{3.147}$$

where v_1 and v_2 are partial molar volumes. However, along the coexistence curve, $d(\mu_1/T)^I = d(\mu_1/T)^{II} \equiv d(\mu_1/T)$, $dT^I = dT^{II} \equiv dT$, and $dP^I = dP^{II} \equiv dP$, but $dx_1^I \neq dx_1^{II}$. Therefore, we can write the following equations for the coexistence curves:

$$-\frac{\Delta h_1}{T}dT + \Delta v_1 dP + \left(\frac{\partial\mu_1}{\partial x_1}\right)^I_{P,T} dx_1^I - \left(\frac{\partial\mu_1}{\partial x_1}\right)^{II}_{P,T} dx_1^{II} = 0 \tag{3.148}$$

and

$$-\frac{\Delta h_2}{T}dT + \Delta v_2 dP + \left(\frac{\partial\mu_2}{\partial x_1}\right)^I_{P,T} dx_1^I - \left(\frac{\partial\mu_2}{\partial x_1}\right)^{II}_{P,T} dx_1^{II} = 0 \tag{3.149}$$

where $\Delta h_i = h_i^I - h_i^{II}$ and $\Delta v_i = v_i^I - v_i^{II}$ for $(i = 1, 2)$.

Let us now obtain an equation for the coexistence curve in the (T, x_1) plane for constant pressure processes, $dP = 0$. The equations for the coexistence curve reduce to

$$-\frac{\Delta h_1}{T} + \left(\frac{\partial\mu_1}{\partial x_1}\right)^I_{P,T}\left(\frac{dx_1^I}{dT}\right)_P - \left(\frac{\partial\mu_1}{\partial x_1}\right)^{II}_{P,T}\left(\frac{dx_1^{II}}{dT}\right)_P = 0 \tag{3.150}$$

and

$$-\frac{\Delta h_2}{T} + \left(\frac{\partial\mu_2}{\partial x_1}\right)^I_{P,T}\left(\frac{dx_1^I}{dT}\right)_P - \left(\frac{\partial\mu_2}{\partial x_1}\right)^{II}_{P,T}\left(\frac{dx_1^{II}}{dT}\right)_P = 0. \tag{3.151}$$

We can solve Eqs. (3.150) and (3.151) for $(dx_1^I/dT)_P$ and $(dx_1^{II}/dT)_P$. If we use Eqs. (3.126) and (3.127), we obtain

$$\left(\frac{dx_1^I}{dT}\right)_P = \frac{x_1^{II}\Delta h_1 + (1 - x_1^{II})\Delta h_2}{T(x_1^{II} - x_1^I)(\partial^2 g/\partial x_1^2)_{P,T}^I} \tag{3.152}$$

and

$$\left(\frac{dx_1^{II}}{dT}\right)_P = \frac{x_1^I \Delta h_1 + (1 - x_1^I)\Delta h_2}{T(x_1^{II} - x_1^I)(\partial^2 g/\partial x_1^2)_{P,T}^{II}}. \tag{3.153}$$

Thus, in general there is a latent heat associated with this phase transition and it is a first-order transition.

▶ S3.F. The Ginzburg–Landau Theory of Superconductors [9, 26, 35]

One of the most interesting applications of the Ginzburg–Landau theory involves a sample of superconducting material which may contain both normal and condensed regions or is of finite size. For such systems we must allow the order parameter to vary in position. Assume that a constant external magnetic field, $\mathbf{H}$, is applied to the sample, but allow for the possibility of a spatially varying order parameter, $\Psi(\mathbf{r})$. If the sample contains both normal and condensed regions, then there will also be a local spatially varying induction field, $\mathbf{B}(\mathbf{r})$. The order parameter is treated in a manner similar to the wave function of a quantum particle. Gradients in the order parameter (spatial variations) will give contributions to the free energy of a form similar to the kinetic energy of a quantum particle. Furthermore, if a local induction field $\mathbf{B}(\mathbf{r})$ is present, the canonical momentum of the condensed phase will have a contribution from the vector potential $\mathbf{A}(\mathbf{r})$ associated with $\mathbf{B}(\mathbf{r})$. The local vector potential $\mathbf{A}(\mathbf{r})$ is related to the local induction field, $\mathbf{B}(\mathbf{r})$, through the relation

$$\mathbf{B}(\mathbf{r}) = \nabla_{\mathbf{r}} \times \mathbf{A}(\mathbf{r}). \tag{3.154}$$

The Helmholtz free energy $a_s(\mathbf{r}, \mathbf{B}, T)$ per unit volume is given by

$$\begin{aligned} a_s(\mathbf{r}, \mathbf{B}, T) =& a_n(T) + \alpha_2(T)|\Psi(\mathbf{r})|^2 + \alpha_4(T)|\Psi(r)|^4 \\ &+ \frac{1}{2m}|-i\hbar\nabla_{\mathbf{r}}\Psi - e\mathbf{A}\Psi|^2 + \frac{B^2}{2\mu_0}, \end{aligned} \tag{3.155}$$

where e and m are the charge and mass, respectively, of the electron pairs, and $\hbar$ is Planck's constant. The quantity, $(-i\hbar\nabla_{\mathbf{r}} - e\mathbf{A})$, is the canonical

momentum operator associated with the condensate. It has exactly the same form as the canonical momentum of a charged quantum particle in a magnetic field. The Gibbs free energy per unit volume is given by a Legendre transformation,

$$g(\mathbf{r}, \mathbf{H}, T) = a(\mathbf{r}, \mathbf{B}, T) - \mathbf{B} \cdot \mathbf{H}. \tag{3.156}$$

The total Gibbs free energy is found by integrating $g(\mathbf{r}, \mathbf{H}, T)$ over the entire volume. Thus,

$$G_s(\mathbf{H}, T) = \int d\mathbf{r} \Big[a_n(T) + \alpha_2(T)|\Psi(\mathbf{r})|^2 + \alpha_4(T)|\Psi(\mathbf{r})|^4 + \frac{1}{2m}|-i\hbar\nabla_{\mathbf{r}}\Psi - e\mathbf{A}\Psi|^2 + \frac{B^2}{2\mu_0} - \mathbf{B}\cdot\mathbf{H} \Big]. \tag{3.157}$$

If we now extremize $G_s(\mathbf{H}, T)$ with respect to variations in $\Psi^*(\mathbf{r})$ and assume that on the boundary of the sample the normal component of the canonical momentum, $(i\hbar\nabla_{\mathbf{r}}\Psi - e\mathbf{A}\Psi)$, is zero, we find

$$\alpha_2\Psi + 2\alpha_4\Psi|\Psi|^2 + \frac{1}{2m}(-i\hbar\nabla_{\mathbf{r}} - e\mathbf{A}(\mathbf{r}))^2\Psi = 0. \tag{3.158}$$

To obtain Eq. (3.158) we have had to integrate by parts. If we next extremize $G_s(\mathbf{H}, T)$ with respect to variations in $\mathbf{A}(\mathbf{r})$, we obtain

$$\frac{1}{\mu_0}\nabla_{\mathbf{r}} \times \mathbf{B} = +\frac{e\hbar}{2mi}(\Psi^*\nabla_{\mathbf{r}}\Psi - \Psi\nabla_{\mathbf{r}}\Psi^*) - \frac{e^2}{m}\mathbf{A}|\Psi|^2. \tag{3.159}$$

To obtain Eq. (3.159), we have used the vector identities

$$\int dV\mathbf{C}\cdot(\nabla_{\mathbf{r}} \times \mathbf{A}) = \oint d\mathbf{S}\cdot(\mathbf{A}\times\mathbf{C}) + \int dV\mathbf{A}\cdot\nabla_{\mathbf{r}}\times\mathbf{C} \tag{3.160}$$

and

$$\oint d\mathbf{S}\cdot(\mathbf{E}\times\mathbf{F}) = \oint \mathbf{E}\cdot(\mathbf{F}\times d\mathbf{S}), \tag{3.161}$$

where $\int dV$ is an integral over the total volume V of the sample and $\oint d\mathbf{S}$ is an integral over the surface enclosing the volume V. We have assumed that $(\mathbf{B} - \mu_0\mathbf{H}) \times \hat{\mathbf{n}} = 0$, where $\hat{\mathbf{n}}$ is the unit vector normal to the surface of the sample. Thus, right on the surface the tangent component of the induction field is the same as that of a normal metal. However, it will go to zero in the sample.

The local supercurrent in a superconductor is driven by the local magnetic induction field and is defined as

$$\mathbf{J}_s(\mathbf{r}) = \frac{1}{\mu_0}\nabla_r \times \mathbf{B}(\mathbf{r}) = \frac{e\hbar}{2mi}(\Psi^*\nabla_r\Psi - \Psi\nabla_r\Psi^*) - \frac{e^2}{m}\mathbf{A}|\Psi|^2 \qquad (3.162)$$

as we would expect. It is a combination of the current induced by $\mathbf{H}$ and the magnetization current. If we compare Eqs. (3.159) and (3.162) we see that the supercurrent $\mathbf{J}_s(\mathbf{r})$ has the same functional form as the probability current of a free particle. Inside a sample, where $\mathbf{B}(\mathbf{r}) = 0$, there is no supercurrent. The supercurrent is confined to the surface of the sample.

We can use Eqs. (3.158) and (3.159) to determine how the order parameter, $\Psi(\mathbf{r})$, varies in space at the edge of the sample. Let us assume that $\mathbf{A}(\mathbf{r}) \equiv 0$, but that Ψ can vary in space in the z direction $\Psi = \Psi(z)$. Under these conditions, we can assume that $\Psi(z)$ is a real function, and therefore there is no supercurrent, $\mathbf{J}_s = 0$. Let us next introduce a dimensionless function,

$$f(z) = \Psi(z)\sqrt{\frac{\alpha_4}{2|\alpha_2|}}. \qquad (3.163)$$

Then Eq. (3.158) takes the form

$$-\xi^2(T)\frac{d^2f}{dz^2} - f + f^3 = 0, \qquad (3.164)$$

where $\xi(T)$ is called the Ginzburg–Landau coherence length and is defined as

$$\xi(T) = \sqrt{\frac{\hbar^2}{2m|\alpha_2|}}. \qquad (3.165)$$

Equation (3.164) can be used to find how the order parameter varies in space on the boundary of a superconducting sample.

Let us consider a sample that is infinitely large in the x and y directions but extends only from $z = 0$ to $z = \infty$ in the z direction. The region from $z = -\infty$ to $z = 0$ is empty. We will assume that at $z = 0$ there is no condensate, $f(z = 0) = 0$; but deep in the interior of the sample it takes its maximum value $f(z = \infty) = 1$ [that is, $\Psi(z) = (|\alpha_2|/2\alpha_4)^{1/2}$ deep in the interior of the sample]. Equation 3.164 is a nonlinear equation for f, but it can be solved. To solve it we must find its first integral. Let us multiply Eq. (3.164) by df/dz and rearrange and integrate terms. We then find

$$-\xi^2\left(\frac{df}{dz}\right)^2 = f^2 - \frac{1}{2}f^4 + C, \qquad (3.166)$$

where C is an integration constant. We will choose C so that the boundary conditions

$$\frac{df}{dz} \underset{z\to\infty}{\longrightarrow} 0 \quad \text{and} \quad f \underset{z\to\infty}{\longrightarrow} 1$$

are satisfied. This gives $C = -(1/2)$ and Eq. (3.166) takes the form

$$\xi^2 \left(\frac{df}{dz}\right)^2 = \frac{1}{2}(1 - f^2)^2. \tag{3.167}$$

We can now solve Eq. (3.167) and find

$$f(z) = \tanh \frac{z}{\sqrt{2}\xi} \tag{3.168}$$

[$f(z)$ is plotted in Fig. 3.38]. Most of the variation of the order parameter occurs within a distance $z = 2\xi(T)$ from the boundary. Thus, the order parameter is zero on the surface but increases to its maximum size within a distance $2\xi(T)$ of the surface. Near a critical point, $\xi(T)$ will become very large.

It is also useful to introduce the penetration depth for the magnetic field and determine the manner in which the induction field $\mathbf{B}(\mathbf{r})$ dies away at the surface of the sample. Let us assume that the order parameter is constant throughout the superconductor (we neglect variations at the surface, although this is often a bad assumption). Let us also assume that the vector potential is pointed in the y direction and can vary in the z direction $A = A_y(z)\hat{\mathbf{y}}$. Then Eq. (3.162) reduces to

$$A_y(z) = \lambda^2 \frac{d^2 A_y}{dz^2}, \tag{3.169}$$

where

$$\lambda = \sqrt{\frac{2m\alpha_4}{|\alpha_2| e^2 \mu_0}} \tag{3.170}$$

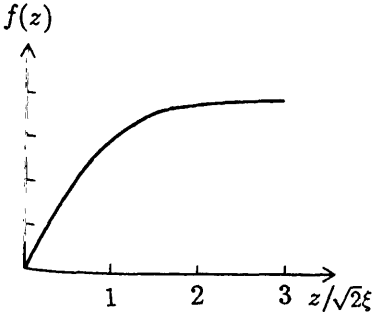


Fig. 3.38. A plot of $f(z) = \tanh(z/(\sqrt{2}\xi))$ versus $z/(\sqrt{2}\xi)$.

is the penetration depth. Thus the vector potential drops off exponentially inside the superconductor,

$$A_y = A_0 e^{-z/\lambda}, \tag{3.171}$$

and we obtain the result that all supercurrents are confined to within a distance λ of the surface. Note that the penetration depth also becomes very large near the critical point.

There are many more applications of the Ginzburg–Landau theory of superconductors than can be presented here. The interested reader should see Ref. 9.

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PROBLEMS

Problem 3.1. A condensible vapor has a molar entropy $s = s_0 + R \ln[C(v-b)(u+(a/v))^{5/2}]$, where C and s_0 are constants. (a) Compute the equation of state. (b) Compute the molar heat capacities, c_v and c_P. (c) Compute the latent heat between liquid and vapor phases at temperature T in terms of the temperature T, the gas constant R, and the liquid and gas molar volumes v_l and v_g. How can you find explicit values of v_l and v_g if you need to?

Problem 3.2. Find the coefficient of thermal expansion, $\alpha_{coex} = (1/v)(\partial v/\partial T)_{coex}$, for a gas maintained in equilibrium with its liquid phase. Find an approximate explicit expression for α_{coex}, using the ideal gas equation of state. Discuss its behavior.

Problem 3.3. Prove that the slope of the sublimation curve of a pure substance at the triple point must be greater than that of the vaporization curve at the triple point.

Problem 3.4. Consider a monatomic fluid along its liquid–gas coexistence curve. Compute the rate of change of chemical potential along the coexistence curve, $(d\mu/dT)_{coex}$, where μ is the chemical potential and T is the temperature. Express your answer in terms of s_l, v_l and s_g, v_g, which are the molar entropy and molar volume of the liquid and gas, respectively.

Problem 3.5. A system in its solid phase has a Helmholtz free energy per mole, $a_s = B/Tv^3$, and in its liquid phase it has a Helmholtz free energy per mole, $a_l = A/Tv^2$, where A and B are constants, v is the volume per mole, and T is the temperature. (a) Compute the molar Gibbs free energy density of the liquid and solid phases. (b) How are the molar volumes, v, of the liquid and solid related at the liquid–solid phase transition? (c) What is the slope of the coexistence curve in the P–T plane?

Problem 3.6. Deduce the Maxwell construction using stability properties of the Helmholtz free energy rather than the Gibbs free energy.

Problem 3.7. For a van der Waals gas, plot the isotherms in the $\overline{P}$–$\overline{V}$ plane ($\overline{P}$ and $\overline{V}$ are

the reduced pressure and volume) for reduced temperatures $\overline{T} = 0.5$, $\overline{T} = 1.0$, and $\overline{T} = 1.5$. For $\overline{T} = 0.5$, is $\overline{P} = 0.1$ the equilibrium pressure of the liquid–gas coexistence region?

Problem 3.8. Consider a binary mixture composed of two types of particles, A and B. For this system the fundamental equation for the Gibbs free energy is $G = n_A\mu_A + n_B\mu_B$, the combined first and second laws are $dG = -S\,dT + V\,dP + \mu_A dn_A + \mu_B dn_B$ (S is the total entropy and V is the total volume of the system), and the chemical potentials μ_A and μ_B are intensive so that $\mu_A = \mu_A(P, T, x_A)$ and $\mu_B = \mu_B(P, T, x_A)$, where x_A is the mole fraction of A. Use these facts to derive the relations

$$s\,dT - v\,dP + \sum_{\alpha=A,B} x_\alpha d\mu_\alpha = 0 \tag{a}$$

and

$$\sum_{\alpha=A,B} x_\alpha(d\mu_\alpha + s_\alpha dT - v_\alpha dP) = 0, \tag{b}$$

where $s = S/n, v = V/n, n = n_A + n_B, s_\alpha = (\partial S/\partial n_\alpha)_{P,T,n_{\beta\neq\alpha}}$, and $v_\alpha = (\partial V/\partial n_\alpha)_{P,T,n_{\beta/\alpha}}$ with $\alpha = A, B$ and $\beta = A, B$.

Problem 3.9. Consider liquid mixture (l) of particles A and B coexisting in equilibrium with vapor mixture (g) of particles A and B. Show that the generalization of the Clausius–Clapeyron equation for the coexistence curve between the liquid and vapor phases when the mole fraction of A in the liquid phase is held fixed is given by

$$\left(\frac{dP}{dT}\right)_{x_A^l} = \frac{x_A^g(s_A^g - s_A^l) + x_B^g(s_B^g - s_B^l)}{x_A^g(v_A^g - v_A^l) + x_B^g(v_B^g - v_B^l)},$$

where $s_\alpha = (\partial S/\partial n_\alpha)_{P,T,n_{\beta\neq\alpha}}$ and $v_\alpha = (\partial V/\partial n_\alpha)_{P,T,n_{\beta\neq\alpha}}$ with $\alpha = A, B$ and $\beta = A, B$. [*Hint*: Equation (b) of Problem (3.8) is useful.]

Problem 3.10. A PVT system has a line of continuous phase transitions (a lambda line) separating two phases, I and II, of the system. The molar heat capacity c_P and the thermal expansivity α_P are different in the two phases. Compute the slope $(dP/dT)_{\text{coex}}$ of the λ line in terms of the temperature T, the molar volume v, $\Delta c_P = c_P^I - c_P^{II}$, and $\Delta\alpha_P = \alpha_P^I - \alpha_P^{II}$.

Problem 3.11. Water has a latent heat of vaporization, $\Delta h = 540\,\text{cal/gr}$. One mole of steam is kept at its condensation point under pressure at $T = 373\,\text{K}$. The temperature is then lowered to $T = 336\,\text{K}$, keeping the volume fixed. What fraction of the steam condenses into water? (Treat the steam as an ideal gas and neglect the volume of the water.)

Problem 3.12. A liquid crystal is composed of molecules which are elongated (and often have flat segments). It behaves like a liquid because the locations of the center of mass of the molecules have no long-range order. It behaves like a crystal because the orientation of the molecules does have long range order. The order parameter for a liquid crystal is given by the dyatic $\mathbf{S} = \eta(\mathbf{nn} - (1/3)\mathbf{I})$, where $\mathbf{n}$ is a unit vector (called the director) which gives the average direction of alignment of the molecules. The free energy of the liquid crystal can be written

$$\phi = \phi_0 + \tfrac{1}{2}AS_{ij}S_{ij} - \tfrac{1}{3}BS_{ij}S_{jk}S_{ki} + \tfrac{1}{4}C\,S_{ij}S_{ij}S_{kl}S_{kl}$$

where $A = A_0(T - T^*), A_0, B$ and C are constants, $\mathbf{I}$ is the unit tensor so $\hat{\mathbf{x}}_\mathbf{i} \cdot \mathbf{I} \cdot \hat{\mathbf{x}}_\mathbf{j} = \delta_{ij}, S_{ij} = \hat{\mathbf{x}}_\mathbf{i} \cdot \mathbf{S} \cdot \hat{\mathbf{x}}_\mathbf{j}$, and the summation is over repeated indices. The quantities $\hat{\mathbf{x}}_\mathbf{i}$ are the unit vectors $\hat{\mathbf{x}}_\mathbf{1} = \hat{\mathbf{x}}, \hat{\mathbf{x}}_\mathbf{2} = \hat{\mathbf{y}}$, and $\hat{\mathbf{x}}_\mathbf{3} = \hat{\mathbf{z}}$. (a) Perform the summations in the expression for Φ and write Φ in terms of η, A, B, C. (b) Compute the critical temperature T_c at which the transition from isotropic liquid to liquid crystal takes place, and compute the magnitude of the order parameter η at the critical temperature. (c) Compute the difference in entropy between the isotropic liquid ($\eta = 0$) and the liquid crystal at the critical temperature.

Problem 3.13. The equation of state of a gas is given by the Berthelot equation $(P + a/Tv^2)(v - b) = RT$. (a) Find values of the critical temperature T_c, the critical molar volume v_c, and the critical pressure P_c, in terms of a, b, and R. (b) Does the Berthelot equation satisfy the law of corresponding states? (c) Find the critical exponents β, δ, and γ from the Berthelot equation.

Problem S3.1. A boy blows a soap bubble of radius R which floats in the air a few moments before breaking. What is the difference in pressure between the air inside the bubble and the air outside the bubble when (a) $R = 1$ cm and (b) $R = 1$ mm? The surface tension of the soap solution is $\sigma = 25$ dynes/cm. (Note that soap bubbles have two surfaces.

Problem S3.2. Imagine a droplet of water, in equilibrium with its vapor, placed on a wire frame that can stretch the surface area of the droplet, keeping the temperature fixed. Assume that the whole system, droplet, frame, and vapor is contained in a fixed total volume V and kept at temperature T. The grand potential of the system can be written $\Omega = \Omega_0 + \Omega_s$, where $\Omega_s = \sigma A$ is the surface grand potential, σ is the surface tension, A is the surface area of the liquid, and Ω_0 is the grand potential of the remainder of the system. Neglect contributions from the frame and changes in the volume of the water droplet as it is stretched. The surface tension of water can be written

$$\sigma = \sigma_0 \left(1 - \frac{t}{t'}\right)^n,$$

where $\sigma_0 = 75.5$ dynes/cm is the surface tension at temperature, $t = 0\,^\circ$C, $n = 1.2$, and $t' = 368\,^\circ$C. (a) Compute the internal energy per unit area of the surface assuming that the number of surface atoms, $N_s = 0$. (b) Plot the surface area and the surface internal energy per unit area for the temperature interval $t = 0\,^\circ$C to $t = t'$.

Problem S3.3. Assume that two vessels of liquid He^4, connected by a *very* narrow capillary, are maintained at constant temperature; that is, vessel A is held at temperature T_A, and vessel B is held at temperature T_B. If an amount of mass, ΔM, is transferred reversibly from vessel A to vessel B, how much heat must flow out of (into) each vessel? Assume that $T_A > T_B$.

Problem S3.4. Prove that at the tricritical point, the slope of the line of first-order phase transitions is equal to that of the line of continuous phase transitions.

Problem S3.5. For a binary mixture of particles of type 1 and 2, the Gibbs free energy is $G = n_1\mu_1 + n_2\mu_2$ and differential changes in the Gibbs free energy are $dG = -S\,dT + V\,dP + \mu_1 dn_1 + \mu_2 dn_2$. The Gibbs free energy of the mixture is assumed to be

$$G = n_1\mu_1^0(P, T) + n_2\mu_2^0(P, T) + RTn_1 \ln(x_1) + RTn_2 \ln(x_2) + \lambda n x_1 x_2,$$

where $\mu_1^0 = \mu_2^0$ are the chemical potentials of the pure substances. In the region in which the binary mixture separates into two phases, *I* and *II* with concentrations x_1^I and x_1^{II}, find the equation, $(\partial x_1^I/\partial T)_P$ for the coexistence curve. Write your answer in terms of x_1^I and $\tau = T/T_c$ where $T_c = \lambda/2R$.

Problem S3.6. Consider a mixture of molecules of type A and B to which a *small* amount of type C molecules is added. Assume that the Gibbs free energy of the resulting tertiary system is given by

$$G(P,T,n_A,n_B,n_C) = n_A\mu_A^0 + n_B\mu_B^0 + n_C\mu_C^0 + RTn_A \ln(x_A) + RTn_B \ln(x_B) + RTn_C \ln(x_C) + \lambda n_A n_B/n + \lambda_1 n_A n_C/n + \lambda_1 n_B n_C/n,$$

where $n = n_A + n_B + n_C, n_C \ll n_A$, and $n_C \ll n_B$. The quantities $\mu_A^0 = \mu_A^0(P,T)$, $\mu_B^0 = \mu_B^0(P,T)$, and $\mu_c^0 = \mu_C^0(P,T)$ are the chemical potentials of pure A, B, and C, respectively, at pressure P and temperature T. For simplicity, assume that $\mu_A^0 = \mu_B^0 = \mu_C^0$. To lowest order in the mole fraction x_C, compute the shift in the critical temperature and critical mole fraction of A due to the presence of C.

PART TWO

CONCEPTS FROM PROBABILITY THEORY

4

ELEMENTARY PROBABILITY THEORY AND LIMIT THEOREMS

4.A. INTRODUCTION

Thermodynamics is a theory which relates the average values of physical quantities, such as energy, magnetization, particle number, and so on, to one another. However, it tells us nothing about processes occurring at the microscopic level or how details of microscopic behavior affect thermodynamic behavior. The microscopic theory of systems with a large number of degrees of freedom is based on probabilistic concepts. In this chapter we will review some of the elementary concepts from probability theory that will occur again and again throughout the remainder of the book.

We will begin in a rather simple way by introducing ways of counting and classifying large numbers of objects, and we will give an intuitive definition of probability which will later be justified by the law of large numbers.

Stochastic variables are, by definition, variables whose values are determined by the outcome of experiments. The most we can know about a stochastic variable is the probability that a particular value of it will be realized in an experiment. We shall introduce the concept of probability distributions for both discrete and continuous stochastic variables and show how to obtain the moments of a stochastic variable by using characteristic functions. As examples we shall discuss in some detail the binomial distribution and its two limiting cases, the Gaussian and Poisson distributions.

The simple concepts of this chapter can be carried a long way. In the section on *special topics* we will use them to study random walks on simple lattices in one, two, and three spatial dimensions. With these simple examples we can explore the effects of spatial dimension on a stochastic process.

We have seen in Chapter 3 that there is a high degree of universality in the thermodynamic behaviour of systems with many degrees of freedom. In particular, we found that many systems have the same critical exponents, regardless of the microscopic structure of the system. This is an example of a *Limit Theorem* [1] involving highly correlated stochastic quantities. In this

chapter we will introduce Limit Theorems for uncorrelated stochastic quantities. We first introduce the concept of an infinitely divisible stochastic variable and then derive the *Central Limit Theorem*, which describes the limiting behavior of independent stochastic variables with finite variance. Finally, we study the limiting behavior of independent stochastic variables with infinite variance which are governed by Levy distributions. We use the Weierstrass random walk to show that such systems can develop fractal-like clustering in space.

4.B. PERMUTATIONS AND COMBINATIONS [2, 3]

When applying probability theory to real situations, we are often faced with counting problems which are complex. On such occasions it is useful to keep in mind two very important principles:

(a) *Addition principle*: If two operations are mutually exclusive and the first can be done in m ways while the second can be done in n ways, then one or the other can be done in $m + n$ ways.

(b) *Multiplication principle*: If an operation can be performed in n ways, and after it is performed in any one of these ways a second operation is performed which can be performed in any one of m ways, then the two operations can be performed in $n \times m$ ways.

These two principles will underlie much of our discussion in the remainder of this chapter.

When dealing with large numbers of objects it is often necessary to find the number of permutations and/or combinations of the objects. A *permutation* is any arrangement of a set of N distinct objects in a definite order. The number of different permutations of N distinct objects is $N!$ The number of different permutations of N objects taken R at a time is $(N!/(N-R)!)$.

Proof: Let us assume that we have N ordered spaces and N distinct objects with which to fill them. Then the first space can be filled N ways, and after it is filled, the second can be filled in $(N-1)$ ways, etc. Thus the N spaces can be filled in

$$N(N-1)(N-2) \times \cdots \times 1 = N!$$

ways. To find the number of permutations, P_R^N, of N distinct objects taken R at a time, let us assume we have R ordered spaces to fill. Then the first can be filled in N ways, the second in $(N-1)$ ways,..., and the Rth in $(N-R+1)$ ways. The total number of ways that R ordered spaces can be filled using N distinct objects is

$$P_R^N = N(N-1) \times \cdots \times (N-R+1) = \frac{N!}{(N-R)!}.$$

A *combination* is a selection of N distinct objects without regard to order. The number of different combinations of N objects taken R at a time is $(N!/(N-R)!R!)$.

Proof: R distinct objects have $R!$ permutations. If we let C_R^N denote the number of combinations of N distinct objects taken R at a time, then $R!C_R^N = P_R^N$ and $C_R^N = N!/(N-R)!R!$

The number of permutations of a set of N objects which contains n_1 identical elements of one kind, n_2 identical elements of another kind,..., and n_k identical elements of a kth kind is $N!/n_1!n_2!\cdots n_k!$, where $n_1 + n_2 + \cdots + n_k = N$.

■ **EXERCISE 4.1.** Find the number of permutations of the letters in the word, ENGINEERING. In how many ways are three E's together? In how many ways are (only) two E's together.

Answer: The number of permutations is $(11!/3!3!2!2!) = 277,200$, since there are 11 letters but two identical pairs (I and G) and two identical triplets (E and N). The number of permutations with three E's together = the number of permutations of ENGINRING $= (9!/3!2!2!) = 15,120$. The number of ways that only two E's are together $= 8 \times (15,120) = 120,960$, since there are eight ways to insert EE into ENGINRING and its permutations.

4.C. DEFINITION OF PROBABILITY [2–4]

Probability is a quantization of our *expectation* of the outcome of an event or experiment. Suppose that one possible outcome of an experiment is A. Then, the probability of A occurring is $P(A)$ if, out of N identical experiments, we *expect* that $NP(A)$ will result in the outcome A. As N becomes very large $(N \to \infty)$ we *expect* that the fraction of experiments which result in A will approach $P(A)$. An important special case is one in which an experiment can result in any of n different equally likely outcomes. If exactly m of these outcomes corresponds to event A, then $P(A) = m/n$.

The concept of a sample space is often useful for obtaining relations between probabilities and for analyzing experiments. A *sample space* of an experiment is a set, S, of elements such that any outcome of the experiment corresponds to one or more elements of the set. An *event* is a subset of a sample space S of an experiment. The probability of an event A can be found by using the following procedure:

(a) Set up a sample space S of all possible outcomes.

(b) Assign probabilities to the elements of the sample space (the sample points). For the special case of a sample space of N equally likely outcomes, assign a probability $1/N$ to each point.

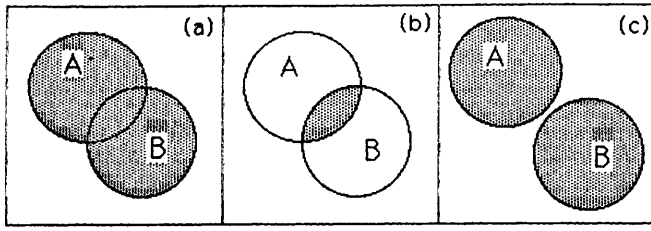


Fig. 4.1. (a) The shaded area is the union of A and B, $A \cup B$; (b) the shaded area is the intersection of A and B, $A \cap B$; (c) when A and B are mutually exclusive there is no overlap.

(c) To obtain the probability of an event A, add the probabilities assigned to elements of the subset of S that corresponds to A.

In working with probabilities, some ideas from set theory are useful. The *union* of two events A and B is denoted $A \cup B$. $A \cup B$ is the set of all points belonging to A or B or both (cf. Fig. 4.1a). The *intersection* of two events is denoted $A \cap B$. $A \cap B$ is the set of all points belonging to both A and B (cf. Fig. 4.1b). If the events A and B are *mutually exclusive*, then $A \cap B = \emptyset$ where $\emptyset$ is the empty set ($A \cap B =$ contains no points) (cf. Fig. 4.1c).

We can obtain some useful relations between the probabilities of different events. We shall let $P(A)$ denote the probability that event A is the outcome of an experiment ($P(\emptyset) = 0, P(S) = 1$); we shall let $P(A \cap B)$ denote the probability that *both* events A and B occur as the result of an experiment; and finally we shall let $P(A \cup B)$ denote the probability that event A or event B or both occur as the outcome of an experiment. Then the probability $P(A \cup B)$ may be written

$$P(A \cup B) = P(A) + P(B) - P(A \cap B). \tag{4.1}$$

In writing $P(A) + P(B)$, we take the region $A \cap B$ into account twice. Therefore, we have to subtract a factor $P(A \cap B)$.

If the two events A and B are mutually exclusive, then they have no points in common and

$$P(A \cup B) = P(A) + P(B). \tag{4.2}$$

If events $A_1, A_2, \ldots, A_m$ are *mutually exclusive* and *exhaustive*, then $A_1 \cup A_2 \cup \cdots \cup A_m = S$ and the m events form a *partition* of the sample space S into m subsets. If $A_1, A_2, \ldots, A_m$ form a partition, then

$$P(A_1) + P(A_2) + \cdots + P(A_m) = 1. \tag{4.3}$$

We shall see Eq. (4.3) often in this book.

The events A and B are *independent if and only if*

$$P(A \cap B) = P(A)P(B). \tag{4.4}$$

Note that since $P(A \cap B) \neq 0$, A and B have some points in common. Therefore, independent events are not mutually exclusive events. They are completely different concepts. For mutually exclusive events, $P(A \cap B) = 0$.

The *conditional probability* $P(B|A)$ gives us the probability that event A occurs as the result of an experiment *if* B also occurs. $P(B|A)$ is defined by the equation

$$P(B|A) = \frac{P(A \cap B)}{P(B)}. \tag{4.5}$$

Since $P(A \cap B) = P(B \cap A)$, we find also that

$$P(A)P(A|B) = P(B)P(B|A). \tag{4.6}$$

From Eq. (4.4) we see that if A and B are independent, then

$$P(B|A) = P(A). \tag{4.7}$$

The conditional probability $P(B|A)$ is essentially the probability of event A if we use the set B as the sample space rather than S.

■ **EXERCISE 4.2.** Consider a sample space consisting of events A and B such that $P(A) = \frac{3}{5}, P(B) = \frac{2}{3}$, and $P(A \cup B) = 1$. Compute $P(A \cap B), P(B|A)$, and $P(A|B)$. Are A and B independent?

Answer: From Eq. (4.1), $P(A \cap B) = P(A) + P(B) - P(A \cup B) = \frac{4}{15}$. But $P(A \cap B) \neq P(A)P(B)$ so A and B are not independent. The conditional probabilities are $P(A|B) = P(A \cap B)/P(A) = \frac{4}{9}$ and $P(B|A) = P(A \cap B)/P(B) = \frac{2}{5}$. Thus, $\frac{4}{9}$ of the points in A also belong to B and $\frac{2}{5}$ of the points in B also belong to A.

4.D. STOCHASTIC VARIABLES AND PROBABILITY

In order to apply probability theory to the real world, we must introduce the concept of a stochastic, or random, variable (the two words are interchangeable, but we shall refer to them as stochastic variables). A quantity whose value is a number determined by the outcome of an experiment is called a *stochastic variable*. A stochastic variable, X, on a sample space, S, is a function which maps elements of S into the set of real numbers, $\{R\}$, in such a way that the

inverse mapping of every interval in $\{R\}$ corresponds to an event in S (in other words, a stochastic variable is a function which assigns a real number to each sample point). It is useful to note that the statement *select at random* means that all selections are equally probable.

In a given experiment, a stochastic variable may have any one of a number of values. Therefore, one must be careful to distinguish a stochastic variable (usually denoted by a capital letter X) from its possible realizations, $\{x_i\}$. Some examples of stochastic variables are (i) the number of heads which appear each time three coins are tossed; (ii) the velocity of each molecule leaving a furnace.

In this section we introduce the concept of a *probability distribution function*, a *probability density function*, and a *characteristic function* which can be associated with a stochastic variable and which contain all possible information about the stochastic variable. We also generalize these quantities to the case when several stochastic variables are necessary to fully describe a system.

4.D.1. Distribution Functions

4.D.1.1a. Discrete Stochastic Variables

Let X be a stochastic variable on the sample space, S, and assume that X has a countable set of realizations, x_i, where $i = 1, 2, \ldots, n$ (n is either a finite integer or $n = \infty$). One can make S a probability space by assigning a probability, p_i, to each realization, x_i. The set of values, $\{p_i\}$, is the probability distribution on S and must satisfy the conditions $p_i \geqslant 0$ and $\sum_{i=1}^{\infty} p_i = 1$.

We can introduce a probability density function, $P_X(x)$, defined as

$$P_X(x) = \sum_{i=1}^{n} p_i \delta(x - x_i), \tag{4.8}$$

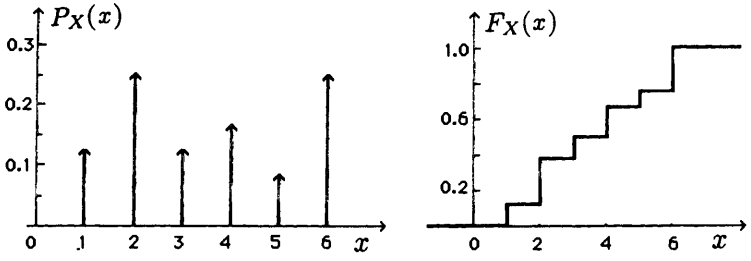
and a distribution function, $F_X(x)$, defined as

$$F_X(x) = \int_{-\infty}^{x} dy\, P_X(y) = \sum_{i=1}^{n} p_i \Theta(x - x_i). \tag{4.9}$$

where $\Theta(x - x_i)$ is a Heaviside function and has values $\Theta(x) = 0$ for $x < 0$ and $\Theta(x) = 1$ for $x > 0$. Note that the probability density function is just the derivative of the distribution function, $P_X(x) = dF_X(x)/dx$. The distribution function, $F_X(x)$, is the probability that the stochastic variable, X, has a realization in the interval $(-\infty, x)$. In order that the probability density, $P_X(x)$, always be positive, the distribution function, $F_X(x)$, must be monotonically increasing function of x. It has limiting values $F_X(-\infty) = 0$ and $F_X(+\infty) = 1$.

■ **EXERCISE 4.3.** Consider a weighted six-sided die. Let $x_i = i$ $(i = 1, 2, \ldots, 6)$ denote the realization that the i^{th} side faces up when the die is thrown. Assume that $p_i = \frac{1}{8}, p_2 = \frac{1}{4}, p_3 = \frac{1}{8}, p_4 = \frac{1}{6}, p_5 = \frac{1}{12}, p_6 = \frac{3}{12}$, in Eqs. (4.8) and (4.9). Plot $P_X(x)$ and $F_X(x)$ for this system.

Answer:



Note: we have represented the delta function, $\delta(x - x_i)$, as an arrow with height equal to p_i.

4.D.1.1b. Continuous Stochastic Variables

Let X be a stochastic variable which can take on a continuous set of values, such as an interval on the real axis. From the definition of a stochastic variable, we know that an interval $\{a \leqslant x \leqslant b\}$, corresponds to an event. Let us assume that there exists a piecewise continuous function, $P_X(x)$, such that the probability that X has a value in the interval $\{a \leqslant x \leqslant b\}$ is given by the area under the curve, $P_X(x)$ versus x, between $x = a$ and $x = b$,

$$\text{Prob}\,(a \leqslant x \leqslant b) = \int_a^b dx\, P_X(x). \tag{4.10}$$

Then X is a continuous stochastic variable, $P_X(x)$ is the probability density for the stochastic variable, X, and $P_X(x)dx$ is the probability to find the stochastic variable, X, in the interval $x \to x + dx$. The probability density must satisfy the conditions $P_X(x) \geqslant 0$ and $\int_{-\infty}^{\infty} dx\, P_X(x) = 1$ (we have assumed that the range of X is $-\infty \leqslant x \leqslant \infty$).

We can also define the distribution function, $F_X(x)$, for the continuous stochastic variable, X. As before, it is given by

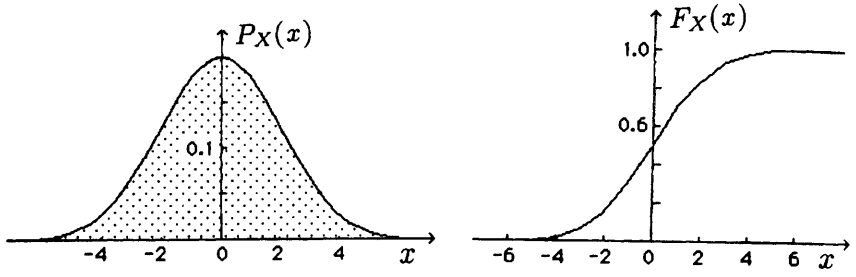
$$F_X(x) = \int_{-\infty}^{x} dy\, P_X(y), \tag{4.11}$$

and it is the probability to find the stochastic variable, X, in the interval $\{-\infty \leqslant x\}$. The distribution function, $F_N(x)$, must be a monotonically

increasing function of x, and it has limiting values $F_X(-\infty) = 0$ and $F_X(+\infty) = 1$.

■ **EXERCISE 4.4.** Plot the probability density, $P_X(x)$, and the distribution function, $F_X(x)$, for the Gaussian probability density, $P_X(x) = (1/2\sqrt{2\pi})e^{-x^2/8}$.

Answer:



Often we wish to find the probability density, not for the stochastic variable, X, but for some new stochastic variable, $Y = H(X)$, where $H(X)$ is a known function of X. The probability density, $P_Y(y)$, for the stochastic variable, Y, is defined as

$$P_Y(y) = \int_{-\infty}^{\infty} dx\, \delta(y - H(x))\, P_X(x), \tag{4.12}$$

where $\delta(y - H(x))$ is the Dirac delta function.

4.D.2. Moments

If we can determine the probability density, $P_X(x)$, for the stochastic variable, X, then we have obtained all possible information about it. In practice, this usually is difficult. However, if we cannot determine $P_X(x)$, we can often obtain information about the moments of X. The nth moment of X is defined

$$\langle x^n \rangle = \int_{-\infty}^{\infty} dx\, x^n P_X(x). \tag{4.13}$$

Some of the moments have special names. The moment, $\langle x \rangle$, is called the mean value of X. The combination, $\langle x^2 \rangle - \langle x \rangle^2$, is called the variance of X, and the standard derivation of X, σ_X, is defined as

$$\sigma_X \equiv \sqrt{\langle x^2 \rangle - \langle x \rangle^2}. \tag{4.14}$$

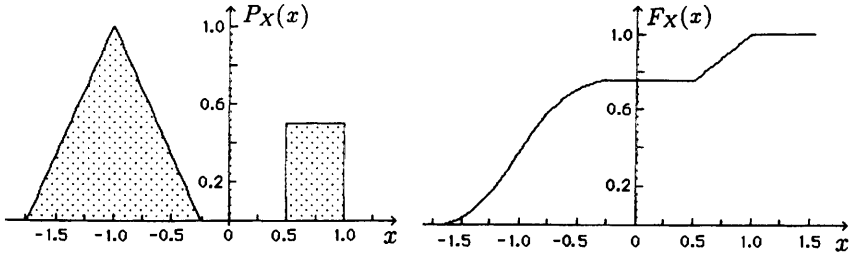
The moments give us information about the spread and shape of the probability density, $P_X(x)$. The most important moments are the lower-order ones since they contain information about the overall behavior of the probability density. We give some examples below.

4.D.2.1a. The First Moment

The first moment, $\langle x \rangle$, gives the position of the "center of mass" of the probability density, $P_X(x)$. It is sometimes confused with two other quantities, the most probable value, x_p, and the median, x_m. The most probable value, x_p, locates the point of largest probability in $P_X(x)$. The median, x_m, is the value of x which divides the area under the curve, $P_X(x)$ versus x, into equal parts. In other words, $F_X(x_m) = \frac{1}{2}$.

In Exercise (4.4), because of the symmetric shape of the Gaussian distributions shown there, the mean, $\langle x \rangle$, the most probable value, x_p, and the median, x_m, all occur at the same point, $x = 0$. In Exercise 4.5, we give an example in which they all occur at different points.

■ **EXERCISE 4.5.** Locate $\langle x \rangle$, x_p, and x_m for the probability density, $P_X(x)$, and the probability distribution, $F_X(x)$, shown below.



Answer: The mean is $\langle x \rangle = -0.5625$. The most probable value is $x_p = -1.0$. The median is $x_m = -0.862$.

4.D.2.1b. The Second Moment

The second moment, $\langle x^2 \rangle$, gives the "moment of inertia" of the probability about the origin. The standard deviation, σ_X [cf. Eq. 4.14] gives a measure of how far the probability spreads away from the mean, $\langle x \rangle$. It is interesting to consider some examples. In Exercise (4.4), $\langle x^2 \rangle = 4$, $\langle x \rangle = 0$, and $\sigma_X = 2$. In Exercise 4.5, $\langle x^2 \rangle = 0.966$, $\langle x \rangle = -0.5625$, and $\sigma_X = 0.806$.

4.D.2.1c. The Third Moment

The third moment, $\langle x^3 \rangle$, picks up any skewness in the distribution of probability about $x = 0$. This can be seen in Exercise 4.4 and 4.5. For Exercise (4.4), $\langle x^3 \rangle = 0$ because the probability is symmetrically distributed about $x = 0$. However, for the probability distribution in Exercise 4.5, $\langle x^3 \rangle = -0.844$, indicating that most of the probability lies to the left of $x = 0$.

4.D.3. Characteristic Functions

The characteristic function, $f_X(k)$, corresponding to the stochastic variable, X, is defined as

$$f_X(k) = \langle e^{ikx} \rangle = \int_{-\infty}^{\infty} dx\, e^{ikx} P_X(x) = \sum_{n=0}^{\infty} \frac{(ik)^n \langle x^n \rangle}{n!}. \tag{4.15}$$

The series expansion in Eq. (4.15) is meaningful only if the higher moments, $\langle x^n \rangle$, are small so that the series converges. From the series expansion in Eq. (4.15) we see that it requires all the moments to completely determine the probability density, $P_X(x)$. Characteristic functions are continuous functions of k and have the property that $f_X(0) = 1, |f_X(k)| \leqslant 1$, and $f_X(-k) = f_X^*(k)$ ($*$ denotes complex conjugation). The product of two characteristic functions is always a characteristic function.

If the characteristic function is known, then the probability density, $P_X(x)$, is given by the inverse transform

$$P_X(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk\, e^{-ikx} f_X(k). \tag{4.16}$$

Furthermore, if we know the characteristic function we can obtain moments by differentiating:

$$\langle x^n \rangle = \lim_{k \to 0} (-i)^n \frac{d^n f_X(x)}{dk^n}. \tag{4.17}$$

Equation (4.17) provides a simple way to obtain moments if we know $f_X(k)$.

It is often useful to write the characteristic function, $f_X(k)$, in terms of cumulants, $C_n(X)$, rather than expand it directly in terms of moments. The cumulant expansion is defined

$$f_X(k) = \exp\left(\sum_{n=1}^{\infty} \frac{(ik)^n}{n!} C_n(X) \right), \tag{4.18}$$

where $C_n(X)$ is the n^{th}-order cumulant. If we expand Eqs. (4.15) and (4.18) in powers of k and equate terms of the same order in k, we find the following expressions for the first four cumulants:

$$C_1(X) = \langle x \rangle, \tag{4.19}$$

$$C_2(X) = \langle x^2 \rangle - \langle x \rangle^2, \tag{4.20}$$

$$C_3(X) = \langle x^3 \rangle - 3\langle x \rangle \langle x^2 \rangle + 2\langle x \rangle^3, \tag{4.21}$$

and

$$C_4(X) = \langle x^4 \rangle - 3\langle x^2 \rangle^2 - 4\langle x \rangle \langle x^3 \rangle + 12\langle x \rangle^2 \langle x^2 \rangle - 6\langle x \rangle^4, \tag{4.22}$$

If higher-order cumulants rapidly go to zero, we can often obtain a good approximation to $f_X(k)$ by retaining only the first few cumulants in Eq. (4.18). We see that $C_1(X)$ is just the mean value of X and $C_2(X)$ is the variance.

■ **EXERCISE 4.6.** Consider a system with stochastic variable, X, which has probability density, $P_X(x)$, given by the circular distribution; $P_X(x) = \frac{2}{\pi}\sqrt{1-x^2}$ for $|x| \leqslant 1$, and $P_X(x) = 0$ for $|x| > 1$. Find the characteristic function and use it to find the first four moments and the first four cumulants.

Answer: The characteristic function is

$$f_X(k) = \frac{2}{\pi}\int_{-1}^{1} dx e^{ikx}\sqrt{1-x^2} = \frac{2}{k}J_1(k),$$

(cf. Gradshteyn and Ryzhik [8]) where $J_1(k)$ is a Bessel function. Now expand $f_X(k)$ in powers of k

$$f_X(k) = \frac{2}{k}\left[\frac{k}{2} - \frac{k^3}{16} + \frac{k^5}{384} + \cdots\right] = 1 - \frac{1}{4}\frac{k^2}{2!} + \frac{1}{8}\frac{k^4}{4!} - \cdots.$$

From Eq. (4.17), the moments are $\langle x\rangle = \langle x^3\rangle = 0$, $\langle x^2\rangle = \frac{1}{4}$, and $\langle x^4\rangle = \frac{1}{8}$. The cumulents are $C_1 = C_3 = 0$, $C_2 = \frac{1}{4}$, and $C_4 = -\frac{1}{16}$.

4.D.4. Jointly Distributed Stochastic Variables

The stochastic variables, $X_1, X_2, \ldots, X_n$, are jointly distributed if they are defined on the same sample space, S. The joint distribution function for the stochastic variables, $X_1, X_2, \ldots, X_n$, can be written

$$F_{X_1,\ldots,X_n}(x_1,\ldots,x_n) \equiv \text{Prob}\{X_1 < x_1, \ldots, X_n < x_n\}, \tag{4.23}$$

where $\{X_1 < x_1, \ldots, X_n < x_n\} = \{X_1 < x_1\} \cap \cdots \cap \{X_n < x_n\}$. In other words, $F_{X_1,\ldots,X_n}(x_1,\ldots,x_n)$ is the probability that simultaneously the stochastic variables, X_i, have values in the intervals $\{-\infty < X_i < x_i\}$ for $i = 1, \ldots, n$. The joint probability density, $P_{X_1,\ldots,X_n}(x_1,\ldots,x_n)$ is defined as

$$P_{X_1,\ldots,X_n}(x_1,\ldots,x_n) = \frac{\partial^n F_{X_1,\ldots,X_n}(x_1,\ldots,x_n)}{\partial x_1 \cdots \partial x_n}, \tag{4.24}$$

so that

$$F_{X_1,\ldots,X_n}(x_1,\ldots,x_n) = \int_{-\infty}^{x_1}\cdots\int_{-\infty}^{x_n} dx_1 \cdots dx_n P_{X_1,\ldots,X_n}(x_1,\ldots,x_n). \tag{4.25}$$

For simplicity, let us now consider the joint distribution function, $F_{X,Y}(x,y)$, and joint probability density, $P_{X,Y}(x,y)$, for two stochastic variables, X and Y.

The distribution function satisfies the conditions $F_{X,Y}(-\infty, y) = F_{X,Y}(x, -\infty) = F_{X,Y}(-\infty, -\infty) = 0$ and $F_{X,Y}(\infty, \infty) = 1$. Furthermore,

$$F_{X,Y}(x_2, y) - F_{X,Y}(x_1, y) = \text{Prob}\{x_1 < X \leqslant x_2; Y \leqslant y\} \geqslant 0 \qquad \text{for} \quad x_2 > x_1. \tag{4.26}$$

The probability density, $P_{X,Y}(x, y)$, satisfies the condition $0 \leqslant P_{XY}(x, y) \leqslant 1$, and is normalized to one:

$$\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy\, P_{X,Y}(x, y) = 1. \tag{4.27}$$

If we want the reduced distribution function, $F_X(x)$, for the stochastic variable, X, it is defined as

$$F_X(x) = F_{X,Y}(x, \infty) = \int_{-\infty}^{x} dx' \int_{-\infty}^{\infty} dy\, P_{X,Y}(x', y). \tag{4.28}$$

Similarly, the reduced probability density, $P_X(x)$, for the stochastic variable, X, is defined as

$$P_X(x) = \int_{-\infty}^{\infty} dy\, P_{X,Y}(x, y). \tag{4.29}$$

We can obtain the reduced distribution function, $F_Y(y)$, and the reduced probability density, $P_Y(y)$, in a similar manner.

The nth moment of the stochastic variable, X, is defined as

$$\langle x^n \rangle = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy\, x^n P_{X,Y}(x, y). \tag{4.30}$$

Joint moments of the stochastic variables, X and Y, are defined as

$$\langle x^m y^n \rangle = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy\, x^m y^n P_{X,Y}(x, y). \tag{4.31}$$

There are two related joint moments that are commonly used in the physics literature. They are the covariance,

$$\text{Cov}(X, Y) = \langle (x - \langle x \rangle)(y - \langle y \rangle) \rangle = \langle xy \rangle - \langle x \rangle \langle y \rangle, \tag{4.32}$$

and even more commonly the *correlation function*

$$\text{Cor}(X, Y) = \frac{\langle (x - \langle x \rangle)(y - \langle y \rangle) \rangle}{\sigma_X \sigma_Y}, \tag{4.33}$$

where σ_X and σ_Y are the standard deviations of the stochastic variables X and Y, respectively. The correlation function, $\mathrm{Cor}(X,Y)$, is dimensionless and is a measure of the degree of dependence of the stochastic variables X and Y on one another (cf. Exercise 4.7). The correlation function has the following properties:

(i) $\mathrm{Cor}(X,Y) = \mathrm{Cor}(Y,X)$.
(ii) $-1 \leqslant \mathrm{Cor}(X,Y) \leqslant 1$.
(iii) $\mathrm{Cor}(X,X) = 1, \mathrm{Cor}(X,-X) = -1$.
(iv) $\mathrm{Cor}(aX+b, cY+d) = \mathrm{Cor}(X,Y)$ if $a,c \neq 0$.

The notion of joint correlation function can be extended to any number of stochastic variables.

For two stochastic variables, X and Y, which are *independent*, the following properties hold:

(i′) $P_{X,Y}(x,y) = P_X(x)P_Y(y)$.
(ii′) $\langle XY\rangle = \langle X\rangle\langle Y\rangle$.
(iii′) $\langle (X+Y)^2\rangle - \langle (X+Y)\rangle^2 = \langle X^2\rangle - \langle X\rangle^2 + \langle Y^2\rangle - \langle Y\rangle^2$.
(iv′) $\mathrm{Cor}(X,Y) = 0$.

Note that the converse of (iv′) does not necessarily hold. If $\mathrm{Cor}(X,Y) = 0$, it does not always means that X and Y are independent.

■ **EXERCISE 4.7.** Show that the correlation function, $\mathrm{Cor}(X,Y)$, is a measure of the degree to which X depends on Y.

Answer: Let $X = aY + b$ and choose a and b to minimize the mean square error, $e = \langle (x - ay - b)^2\rangle$. Set $\delta e = (\partial e/\partial a)\delta a + (\delta e/\delta b)\delta b = 0$, and set the coefficients of δa and δb separately to zero. This gives two equations, $-2\langle xy\rangle + 2a\langle y^2\rangle + 2b\langle y\rangle = 0$ and $-2\langle x\rangle + 2a\langle y\rangle + 2b = 0$. Eliminate b and solve for a to find $a = -\mathrm{Cor}(X,Y)\sigma_X/\sigma_Y$. Thus when $\mathrm{Cor}(X,Y) = 0, a = 0$ and the random variables, X and Y, appear to be independent, at least when viewed by this statistical measure.

When we deal with several stochastic variables, we often wish to find the probability density for a new stochastic variable which is a function of the old stochastic variables. For example, if we know the joint probability density, $P_{X,Y}(x,y)$, we may wish to find the probability density for a variable $Z = G(X,Y)$, where $G(X,Y)$ is a known function of X and Y. The probability density, $P_Z(z)$, for the stochastic variable, Z, is defined as

$$P_Z(z) = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy\, \delta(z - G(x,y)) P_{X,Y}(x,y). \tag{4.34}$$

From Eq. (4.34), the characteristic function for the stochastic variable, Z, is easily found to be

$$f_Z(k) = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy\, e^{ikG(x,y)} P_{X,Y}(x,y). \tag{4.35}$$

■ **EXERCISE 4.8.** The stochastic variables, X and Y, are independent and are Gaussian distributed with first moments, $\langle x\rangle = \langle y\rangle = 0$, and standard deviations, $\sigma_X = \sigma_Y = 1$. Find the joint distribution function for the stochastic variables, $V = X + Y$ and $W = X - Y$. Are V and W independent?

Answer: The probability densities for X and Y are $P_X(x) = (1/\sqrt{2\pi})e^{-(1/2)x^2}$ and $P_Y(y) = (1/\sqrt{2\pi})e^{-(1/2)y^2}$. Since X and Y are independent, Eq. (4.34) gives

$$P_{V,W}(v,w) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy\, \delta(v - v'(x,y))\delta(w - w'(x,y))e^{-(1/2)(x^2+y^2)}, \tag{1}$$

where $v'(x,y) = x + y$ and $w'(x,y) = x - y$. Now note that

$$\delta(v - v'(x,y))\delta(w - w'(x,y)) = J\begin{pmatrix} x & y \\ w & v \end{pmatrix}\delta(x - x'(v,w))\delta(y - y'(v,w)), \tag{2}$$

where $x'(v,w) = \frac{1}{2}(v + w)$, $y'(v,w) = \frac{1}{2}(v - w)$, and $J\begin{pmatrix} x & y \\ w & v \end{pmatrix} = \frac{1}{2}$ is the Jacobian of the coordinate transformation. Thus,

$$P_{V,W}(v,w) = \frac{1}{4\pi}e^{-(1/4)(v^2+w^2)}. \tag{3}$$

V and W are independent since $P_{V,W}(v,w)$ is factorizable.

We can also introduce characteristic functions for jointly distributed stochastic variables. They are often useful for obtaining moments. We define

$$f_{X_1,\ldots,X_N}(k_1,\ldots,k_N) = \int_{-\infty}^{\infty} dx_1 \cdots \int_{-\infty}^{\infty} dx_N e^{i(k_1x_1+\cdots+k_Nx_N)} \times P_{X_1,\ldots,X_N}(x_1,\ldots,x_N). \tag{4.36}$$

The joint moment, $\langle x_i \cdots x_n\rangle$ $(n \leqslant N)$, is then given by

$$\langle x_i \cdots x_n\rangle = \lim_{k_1\to 0} \cdots \lim_{k_N\to 0} (-i)^n \frac{\partial}{\partial k_1} \times \cdots \times \frac{\partial}{\partial k_n} f_{X_1,\ldots,X_N}(k_1,\ldots,k_N). \tag{4.37}$$

One of the most important multivariant distributions, and one which we will use repeatedly in this book, is the multivariant Gaussian distribution with zero mean. Some of its properties are discussed in Exercise (4.9).

■ **EXERCISE 4.9.** The multivariant Gaussian distribution with zero mean can be written

$$P_{X_1,\ldots,X_N}(x_1,\ldots,x_N) = \sqrt{\frac{\det(\bar{\mathbf{g}})}{(2\pi)^N}} e^{-(1/2)\mathbf{x}^T\cdot\bar{\mathbf{g}}\cdot\mathbf{x}},$$

where $\bar{\mathbf{g}}$ is a symmetric $N \times N$ positive definite matrix, $\mathbf{x}$ is a column vector, and the transpose of $\mathbf{x}$, $\mathbf{x}^T = (x_1,\ldots,x_N)$, is a row vector. Thus, $\mathbf{x}^T\cdot\bar{\mathbf{g}}\cdot\mathbf{x} = \sum_{i=1}^N \sum_{j=1}^N g_{ij}x_ix_j$. (a) Show that $P_{X_1,\ldots,X_N}(x_1,\ldots,x_N)$ is normalized to one. (b) Compute the characteristic function, $f_{X_1,\ldots,X_N}(k_1,\ldots,k_N)$. (c) Show that the moments, $\langle x_i\rangle = 0$ and that all higher moments can be expressed in terms of products of the moments, $\langle x_i^2\rangle$ and $\langle x_ix_j\rangle$. This is the simplest form of Wick's theorem used in field theory.

Answer:

(**a**) Since $\bar{\mathbf{g}}$ is a symmetric matrix, it can be diagonalized using an orthogonal matrix, $\bar{\mathbf{O}}$, where $\bar{\mathbf{O}}^{-1} = \bar{\mathbf{O}}^T$ and $\bar{\mathbf{O}}^{-1}\cdot\bar{\mathbf{O}} = \bar{\mathbf{I}}$ ($\bar{\mathbf{I}}$ is the unit matrix). Note that the determinant of $\bar{\mathbf{O}}$ is one, $\det(\bar{\mathbf{O}}) = 1$. We can write $\bar{\mathbf{O}}\cdot\bar{\mathbf{g}}\cdot\bar{\mathbf{O}}^T = \bar{\Gamma}$, where $\bar{\Gamma}$ is diagonal ($\Gamma_{ii} = \gamma_i$ and $\Gamma_{ij} = 0$ for $i \neq j$). The orthogonal matrix, $\bar{\mathbf{O}}$, transforms the stochastic variables. We will let $\boldsymbol{\alpha} = \bar{\mathbf{O}}\cdot\mathbf{x} = (\alpha_1,\ldots,\alpha_N)$. Since $\det(\bar{\mathbf{O}}) = 1$, the Jacobian of the transformation is one. Thus, $dx_1\cdots dx_n = d\alpha_1\cdots d\alpha_N$. Furthermore, $\mathbf{x}^T\cdot\bar{\mathbf{g}}\cdot\mathbf{x} = \boldsymbol{\alpha}^T\cdot\bar{\Gamma}\cdots\boldsymbol{\alpha}$. Thus,

$$\int\cdots\int dx_1\cdots dx_N e^{-(1/2)\mathbf{x}^T\cdot\bar{\mathbf{g}}\cdot\mathbf{x}} = \int\cdots\int d\alpha_1\cdots d\alpha_N e^{-(1/2)\sum_i^N \gamma_i\alpha_i^2}$$
$$= \sqrt{\frac{(2\pi)^N}{\gamma_1\cdots\gamma_N}} = \sqrt{\frac{(2\pi)^N}{\det(\bar{\mathbf{g}})}},$$

since $\det(\bar{\mathbf{g}}) = \det(\bar{\Gamma}) = \gamma_1\cdots\gamma_n$.

(**b**) The characteristic function is

$$f_{X_1,\ldots,X_N}(k_1,\ldots,k_N) = \sqrt{\frac{\det(\bar{\mathbf{g}})}{(2\pi)^N}} \int_{-\infty}^{\infty}\cdots$$
$$\int_{-\infty}^{\infty} dx_1\cdots dx_N e^{i\mathbf{k}^T\cdot\mathbf{x}} e^{-(1/2)\mathbf{x}^T\cdot\bar{\mathbf{g}}\cdot\mathbf{x}},$$

where $\mathbf{k}^T = (k_1,\ldots,k_N)$. If we transform the integral into diagonal

form, as we did in part (a), it is straightforward to show that

$$f_{X_1,\ldots,X_N}(k_1,\ldots,k_N) = e^{-(1/2)\mathbf{k}^T\cdot\bar{\mathbf{g}}^{-1}\cdot\mathbf{k}}.$$

(c) The first moment is $\langle x_i\rangle = \lim_{k_i\to 0}(-i)(\partial/\partial k_i)f_{X_1,\ldots,X_N}(k_1,\ldots,k_N) = 0$, since the derivative brings down a factor of k_j. In fact, all odd moments will be zero for the same reason. The second moment is easily seen to be $\langle x_i x_j\rangle = (\bar{\mathbf{g}}^{-1})_{ij}$. Inspection shows that all higher moments depend only on sums of products of factors of the form $(\bar{\mathbf{g}}^{-1})_{ij}$, and therefore only on sums of products of second moments. More generally, *the average of a product of 2n stochastic variables is equal to the sum of all possible combinations of different pairwise averages of the stochastic variables.* For example,

$$\langle x_1x_2x_3x_4\rangle = \langle x_1x_2\rangle\langle x_3x_4\rangle + \langle x_1x_3\rangle\langle x_2x_4\rangle + \langle x_1x_4\rangle\langle x_2x_3\rangle.$$

(Note that $\langle x_ix_j\rangle = \langle x_jx_i\rangle$.) More generally, if we have $2n$ stochastic variables, the number of terms in the expression for the $2n$th moment,

$$\langle x_1x_2\cdots x_{2n}\rangle = \langle x_1x_2\rangle\langle x_3x_4\rangle\times\cdots\times\langle x_{2n-1}x_{2n}\rangle + \cdots,$$

is $(2n)!/n!2^n$. We determine this as follows. There are $((2n)(2n-1)/2)$ ways to form the first pair. After that there are $((2n-2)(2n-3)/2)$ ways to form the second pair, and so on. After all the pairs are formed in this way, by the multiplication rule, there will be $\prod_{i=0}^{n-1}((2n-2i)(2n-(2i+1)))/2) = ((2n)!/2^n)$ different combinations of pairs. Of these, $n!$ will be identical because they are different permutations of the same pairs. Thus, the total number of different terms in the expression for $\langle x_1x_2\cdots x_{2n}\rangle$ is $(2n)!/n!2^n$.

4.E. BINOMIAL DISTRIBUTIONS

A commonly found application of probability theory is for the case of a large number, N, of independent experiments, each having two possible outcomes. The probability distribution for one of the outcomes is called the *binomial distribution.* In the limit of large N, the binomial distribution can be approximated by either the Gaussian or the Poisson distribution, depending on the size of the probability of a given outcome during a single experiment. We shall consider all three distributions in this section. We shall also use the binomial distribution to find the probability density for a random walk in one dimension.

4.E.1. The Binomial Distribution [2–5]

Let us carry out a sequence of N statistically independent trials and assume that each trial can have only one of two outcomes, 0 or +1. Let us denote the

probability of outcome, 0, by q and the probability of outcome, $+1$, by p so that $p+q=1$. In a given sequence of N trials, the outcome, 0, can occur n_0 times and the outcome, $+1$ times, where $N=n_0+n_1$. The probability for a given *permutation* of n_0 outcomes, 0, and n_1 outcomes, $+1$, is $q^{n_0}p^{n_1}$ since the N trials are statistically independent. The probability for any *combination* of n_0 outcomes, 0, and n_1 outcomes, $+1$, is

$$P_N(n_1)=\frac{N!}{n_0!n_1!}q^{n_0}p^{n_1} \tag{4.38}$$

since a *combination* of n_2 outcomes, 0, and n_1 outcomes, $+1$, contains $(N!/n_0!n_1!)$ permutations. Equation (4.38) is often called the *binomial distribution* even though it is not a distribution function in the sence of Section 4.D. From the binomial theorem, we have the normalization condition

$$\sum_{n_1=0}^{N}P_N(n_1)=\sum_{n_1=0}^{N}\frac{N!}{n_1!(N-n_1)!}p^{n_1}q^{N-n_1}=(p+q)^N=1. \tag{4.39}$$

We can view the sequence of trials in another way. Let X_i be the stochastic variable describing the outcome of the ith trial and let X_i have two realizations: $x=0$ with probability q and $x=+1$ with probability p. The probability density for the ith trial is $P_{X_i}(x)=q\delta(x)+p\delta(x-1)$, and the characteristic function for the ith trial is $f_{X_i}(k)=q+pe^{ik}$.

■ **EXERCISE 4.10.** The probability of an archer hitting his target is $\frac{1}{3}$. If he shoots five times, what is the probability of hitting the target at least three times?

Answer: Let n_1 be the number of hits. Then $N=n_0+n_1=5, p=\frac{1}{3}$, and $q=\frac{2}{3}$. The probability of having n_1 hits in $N=5$ trials is $P_5(n_1)=(5!/n_1!(5-n_1)!)\left(\frac{1}{3}\right)^{n_1}\left(\frac{2}{3}\right)^{5-n_1}$. The probability of at least three hits $=P_5(3)+P_5(4)+P_5(5)=\frac{51}{243}\approx 0.21$.

We will now let $Y_N=X_1+X_2+\cdots+X_N$ be the stochastic variable which describes the additive outcome of N trials. Since the trials are independent, the probability density for the stochastic variable, Y_N, is just

$$P_{Y_N}(y)=\int\cdots\int dx_1\cdots dx_N\delta(y-x_1-\cdots-x_N)P_{X_1}(x_1)\times\cdots\times P_{X_N}(x_N). \tag{4.40}$$

From Eq. (4.35), the characteristic function for the random variable, Y_N, is

$$\begin{aligned} f_{Y_N}(k) &= \int dx_1 \cdots \int dx_N e^{ik(x_1+x_2+\cdots+x_N)} P_{X_1}(x_1) \times \cdots \times P_{X_N}(x_N) \\ &= f_{X_1}(k) \times \cdots \times f_{X_N}(k) = (q + pe^{ik})^N. \end{aligned} \tag{4.41}$$

We can expand the characteristic function using the binomial theorem. We obtain

$$f_{Y_N}(k) = \sum_{n_1=0}^{N} \frac{N!}{n_1!(N-n_1)!} p^{n_1} q^{N-n_1} e^{in_1 k}. \tag{4.42}$$

The probability density, $P_{Y_N}(x)$, for the stochastic variable, Y_N, is

$$\begin{aligned} P_{Y_N}(y) &= \frac{1}{2\pi} \int dk e^{-iky} f_{Y_N}(k) = \sum_{n_1=0}^{N} \frac{N!}{n_1!(N-n_1)!} p^{n_1} q^{N-n_1} \delta(y - n_1) \\ &= \sum_{n_1=0}^{N} P_N(n_1) \delta(y - n_1), \end{aligned} \tag{4.43}$$

where $P_N(n_1)$ is the probability that the outcome, $+1$, will occur n_1 times in N trials.

The moments, $\langle y \rangle = \langle n_1 \rangle$, are easily found by direct summation or by differentiating the characteristic function. For example,

$$\langle n_1 \rangle = \sum_{n_1=0}^{N} n_1 P_N(n_1) = \sum_{n_1=0}^{N} \frac{n_1 N!}{n_1!(N-n_1)!} p^{n_1} q^{N-n_1} = p \frac{\partial}{\partial p} (p+q)^N = pN. \tag{4.44}$$

Also, it is easy to see that

$$\langle y \rangle = \lim_{k \to 0} (-i) \frac{\partial}{\partial k} f_{Y_N}(k) = pN = \langle n_1 \rangle. \tag{4.45}$$

In a similar manner, we obtain for the second moment

$$\langle y^2 \rangle = \langle n_1^2 \rangle = \sum_{n_1=0}^{N} n_1^2 P_N(n_1) = (Np)^2 + Npq. \tag{4.46}$$

The variance is given by $\langle n_1^2 \rangle - \langle n_1 \rangle^2 = Npq$, and the standard deviation is

$$\sigma_N = \sqrt{Npq}. \tag{4.47}$$

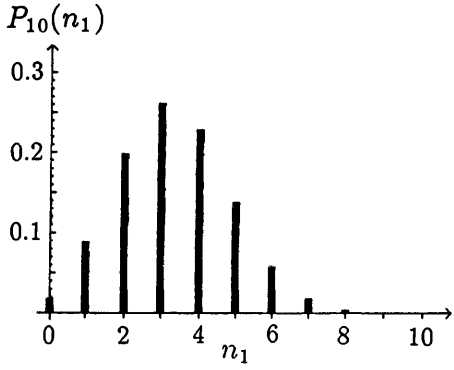


Fig. 4.2. The binomial distribution for $p = \frac{1}{3}$ and $N = 10$; for this case, $\langle n_1 \rangle = \frac{10}{3}$.

The fractional deviation is

$$\frac{\sigma_N}{\langle n_1 \rangle} = \sqrt{\frac{q}{p}} \frac{1}{\sqrt{N}}. \tag{4.48}$$

The fractional deviation is a measure of the deviation of the fraction, n_1/N, of trials with outcome, $+1$, from its expected value, p, in any single sequence of N trials. A small value of $\sigma_N/\langle n_1 \rangle$ means that n_1/N will likely be close to p. For $N \to \infty$, $\sigma_N/\langle n_1 \rangle \to 0$ so that $n_1/N \to p$. The binomial distribution, for the case $N = 10$ and $p = \frac{1}{3}$ is plotted in Fig. 4.2.

4.E.2. The Gaussian (or Normal) Distribution

Let us make a change of stochastic variables, $Z_N = (y_N - \langle y \rangle)/\sigma_Y = ((Y_N - p_N)/\sqrt{pqN})$. Z_N is a stochastic variable whose average value, $\langle z \rangle$, equals 0 when $\langle y \rangle = pN$. The probability density for the stochastic variable, Z_N, is

$$P_{Z_N}(z) = \int_{-\infty}^{\infty} dy \delta\left(z - \frac{(y - pN)}{\sqrt{pqN}}\right) P_{Y_N}(y). \tag{4.49}$$

The characteristic function is

$$\begin{aligned} f_{Z_N}(k) &= \int_{-\infty}^{\infty} dz e^{ikz} P_{Z_N}(z) = e^{-ik\sqrt{pN/q}} f_{Y_N}\left(\frac{k}{\sqrt{pqN}}\right) \\ &= (q\, e^{-ik\sqrt{p/qN}} + p\, e^{-ik\sqrt{q/pN}})^N, \end{aligned} \tag{4.50}$$

where $f_{Y_N}(k)$ is defined in Eq. (4.41) and we make use of the fact that $q = 1 - p$. We now will take the limit $N \to \infty$. We first expand the quantity in

brackets in powers of k and obtain

$$f_{Z_N}(k) = \left(1 - \frac{k^2}{2N}(1 + R_N)\right)^N, \tag{4.51}$$

where

$$R_N = 2\sum_{m=3}^{\infty} \frac{1}{m!}\left(\frac{ik}{\sqrt{N}}\right)^{m-2} \frac{pq^m + q(-p)^m}{\sqrt{(pq)^m}}. \tag{4.52}$$

As $N \to \infty$, we have $R_N \to 0$ and

$$f_Z(k) \equiv \lim_{N\to\infty} f_{Z_N}(k) = \lim_{N\to\infty}\left(1 - \frac{k^2}{2N}(1 + R_N)\right)^N = e^{-(k^2)/2}, \tag{4.53}$$

where we have used the definition

$$\lim_{N\to\infty}\left(1 + \frac{z}{N}\right)^N = e^z. \tag{4.54}$$

Thus, in the limit $N \to \infty$, we obtain

$$P_Z(z) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dk e^{-ikz} e^{-k^2/2} = \frac{1}{\sqrt{2\pi}} e^{-z^2/2}. \tag{4.55}$$

It is easy to show that the first moment, $\langle z\rangle$, equals 0 and that the standard deviation, σ_Z, equals 1.

For the case $N \gg 1$ but N finite, we still have $P_{Z_N}(z) \approx (1/\sqrt{2\pi})e^{-z^2/2}$. Transform back to the stochastic variables, $y = \sigma_Y z + \langle y\rangle$. Then

$$P_{Y_N}(y) \approx \int_{-\infty}^{\infty} dz \delta(y - \sigma_Y z - \langle y\rangle) P_Z(z) = \frac{1}{\sigma_Y\sqrt{2\pi}} \exp\left(-\frac{(y - \langle y\rangle)^2}{2\sigma_Y^2}\right). \tag{4.56}$$

Equation (4.56) is the Gaussian probability density for the number of outcomes, $+1$, after many trials. It is also the most general form of a Gaussian probability density. It is important to note that the Gaussian probability density is entirely determined in terms of the first and second moments, $\langle y\rangle$ and $\langle y^2\rangle$ (since $\sigma_Y = \sqrt{\langle y^2\rangle - \langle y\rangle^2}$). In Exercise 4.4, we have plotted a Gaussian probability density for $\langle y\rangle = 0$ and $\sigma_Y = 2$.

4.E.3. The Poisson Distribution

The Poisson distribution can be obtained from the binomial distribution in the limit $N \to \infty$ and $p \to 0$, such that $Np = a \ll N$ (a is a finite constant). Let us

return to Eq. (4.41) and let $p = (a/N)$. Then

$$f_{Y_N}(k) = \left(1 - \frac{a}{N} + \frac{a}{N}e^{ik}\right)^N. \tag{4.57}$$

If we now take the limit, $N \to \infty$, we obtain

$$\begin{aligned} f_Y(k) &\equiv \lim_{N\to\infty} f_{Y_N}(k) = \lim_{N\to\infty}\left(1 + \frac{a}{N}(e^{ik} - 1)\right)^N = \exp(a(e^{ik} - 1)) \\ &= e^{-a}\sum_{m=0}^{\infty}\frac{a^m}{m!}e^{imk}. \end{aligned} \tag{4.58}$$

Thus the probability density is

$$P_Y(y) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dk e^{-iky} f_Y(k) = \sum_{n_1=0}^{\infty}\frac{a^{n_1}}{n_1!}e^{-a}\delta(y - n_1). \tag{4.59}$$

The coefficient

$$P(n_1) = \frac{a^{n_1}}{n_1!}e^{-a}, \tag{4.60}$$

is commonly called the *Poisson distribution.* It is the probability for finding n_1 outcomes, $+1$, after many trials, when the probability, p (for an outcome, $+1$, in a single trial), is very small ($p \ll 1$). The first moment, $\langle n_1 \rangle$, equals a. The Poisson distribution depends only on the first moment, and therefore it is sufficient to know only the first moment in order to find the probability density for a Poisson process. In Fig. 4.3, we plot the Poisson distribution for $a = 2$.

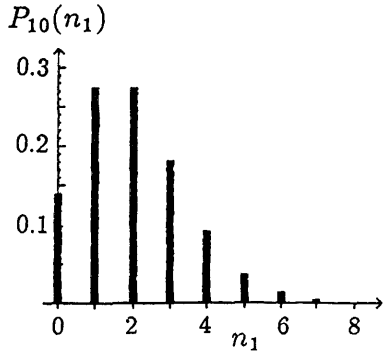


Fig. 4.3. The Poisson distribution for $\langle n \rangle = a = 2$.

■ **EXERCISE 4.11.** A thin sheet of gold foil (one atom thick) is fired upon by a beam of neutrons. The neutrons are assumed equally likely to hit any part of the foil but only "see" the gold nuclei. Assume that for a beam containing many neutrons, the average number of hits is two. (a) What is the probability that no hits occur? (b) What is the probability that two hits occur?

Answer: Since the ratio (area nucleus/area atoms) $\approx 10^{-12}$, the probability of a hit is small. Since the number of trials is large, we can use the Poisson distribution. Let n_1 denote the number hits. Then $\langle n_1 \rangle = 2$ and the Poisson distribution can be written $P(n_1) = e^{-2}2^{n_1}/n_1!$.

(**a**) The probability that no hits occur is $P(0) = e^{-2}2^0/0! = 0.135$.
(**b**) The probability that two hits occur is $P(2) = e^{-2}2^2/2! = 0.27$.

4.E.4. Binomial Random Walk

The problem of random walk is an example of an application of the binomial distribution to a problem in physics. Consider a particle which is constrained to move along the x axis. It has probability, $p = \frac{1}{2}$, of taking a step of length, Δ, to the right and a probability, $q = \frac{1}{2}$, of taking a step of length, Δ, to the left. Let us assume that the particle takes N steps and that the outcome of each step is independent of previous steps (the steps are statistically independent). For the ith step, let the stochastic variable, X_i, have realization, $x = +\Delta$, for a step to the right and $x = -\Delta$ for a step the left. The probability density for the ith step is $P_{X_i}(x) = \frac{1}{2}(\delta(x + \Delta) + \delta(x - \Delta))$. The characteristic function for the ith step is $f_{X_i}(k) = \cos(k\Delta)$.

The net displacement, Y_N (along the x axis), of the particle after N steps is given by $Y_N = X_1 + \cdots + X_N$. The characteristic function for the stochastic variable, Y_N, is

$$f_{Y_N}(k) = (\cos(k\Delta))^N = \left(1 - \frac{k^2\Delta^2}{2!} + \cdots\right)^N \approx 1 - \frac{Nk^2\Delta^2}{2!} + \cdots \qquad (4.61)$$

[cf. Eqs. (4.40) and (4.41)]. The first and second moments are $\langle y \rangle = 0$ and $\langle y^2 \rangle = N\Delta^2$, respectively, and the standard deviation is $\sigma_{Y_N} = \Delta\sqrt{N}$. In Fig. 4.4 we show three realizations of this random walk for $N = 2000$ steps and $\Delta = 1$. There are 2^N possible realizations for a given value of N.

We can find a differential equation for the characteristic function in the limit when the step size, Δ, and the time between steps, τ, become infinitesimally small. Let us write the characteristic function, $f_{Y_N}(k) \equiv f_Y(k, N\tau)$, where $t = N\tau$ is the time at which the Nth step occurs. Also note that initially ($N = 0$) the walker is at $y = 0$. Thus, $P_{Y_0}(y) = \delta(y)$ and $f_Y(k, 0) = 1$. From Eq. (4.61), we

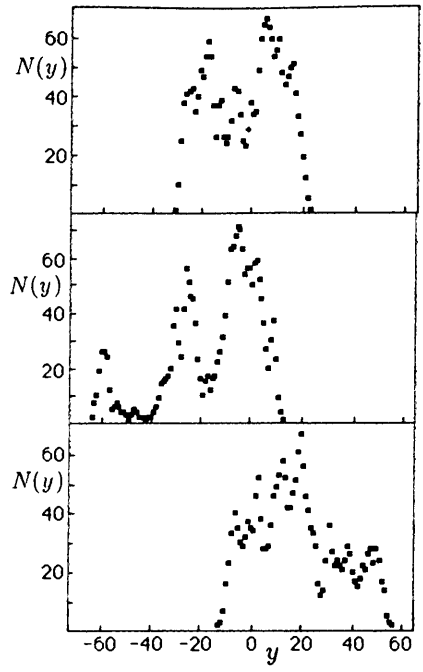


Fig. 4.4. Three of the 2^N possible realizations of the binomial random walk for $p = q = \frac{1}{2}$, step size, $\Delta = 1$, and number of steps, $N = 2000$. $N(y)$ is the number of times the walker reaches point y. For this case $\langle y \rangle = 0$ and $\sigma_Y \approx 44.7$. In each case the walker starts at $y = 0$.

can write

$$f_Y(k,(N+1)\tau) - f_Y(k,N\tau) = (\cos(k\Delta) - 1) f_Y(k,N\tau)$$
$$= \left(-\frac{k^2\Delta^2}{2} + \cdots\right) f_Y(k,N\tau), \tag{4.62}$$

where we have expanded $\cos(k\Delta)$ in powers of $k\Delta$. Now take the limits $N \to \infty$, $\tau \to 0$, and $\Delta \to 0$ so that $D = (\Delta^2/2\tau)$ is finite and $N\tau = t$. If we note that

$$\lim_{N\to\infty} \lim_{\tau\to 0} \frac{f_Y(k,(N+1)\tau) - f_Y(k,N\tau)}{\tau} = \frac{\partial f_Y(k,t)}{\partial t} \tag{4.63}$$

and

$$\lim_{N\to\infty} \lim_{\tau\to 0} \lim_{\Delta\to 0} \left(-\frac{k^2\Delta^2}{2\tau} + \cdots\right) f_Y(k,N\tau) = -Dk^2 f_Y(k,t), \tag{4.64}$$

then combining these equations we obtain

$$\frac{\partial f_Y(k,t)}{\partial t} = -Dk^2 f_Y(k,t). \tag{4.65}$$

For the case $f_Y(k,0) = 1$, Eq. (4.65) has the solution

$$f_Y(k,t) = e^{-Dk^2 t}. \tag{4.66}$$

The probability distribution is

$$P(y,t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dk e^{-iky} e^{-Dk^2 t} = \sqrt{\frac{1}{4\pi Dt}}\exp\left(-\frac{y^2}{4Dt}\right). \tag{4.67}$$

The probability density for the random walker is a Gaussian whose standard deviation is $\sigma = \sqrt{2Dt}$. The probability density spreads with time.

We can derive Eq. (4.67) in a completely different way. If we make the change of stochastic variables, $Z_N = (Y_N/\Delta\sqrt{N})$, then the characteristic function, $f_{Z_N}(k)$, associated with the stochastic variable, Z_N, is

$$f_{Z_N}(k) = (\cos(k/\sqrt{N}))^N \tag{4.68}$$

[cf. Eq. (4.50)]. Following Section 4.E.2, we can take the limit $N \to \infty$ and find

$$f_Z(k) \equiv \lim_{N\to\infty} f_{Z_N}(k) = \exp\left(-\frac{k^2}{2}\right), \tag{4.69}$$

and therefore $P_Z(z) = (1/\sqrt{2\pi})\exp(-z^2/2)$. For very large N, we can write $P_{Z_N}(z) \approx P_Z(z)$. The probability density for the net displacement, Y_N, then becomes

$$P_{Y_N}(y) \approx \int_{-\infty}^{\infty} dz\delta(y - \Delta\sqrt{N}z)P_Z(z) = \frac{1}{\sqrt{2\pi\Delta^2 N}}\exp\left(-\frac{y^2}{2\Delta^2 N}\right). \tag{4.70}$$

If the particle takes n steps per unit time, then $N = nt$ and the probability density that the particle lies in the interval, $y \to y + dy$, along the x axis, at time t is

$$P(y,t) \approx \int_{-\infty}^{\infty} dz\delta(y - \Delta\sqrt{N}z)P_Z(z) = \frac{1}{\sqrt{4\pi Dt}}\exp\left(-\frac{y^2}{4Dt}\right), \tag{4.71}$$

where $D = \frac{1}{2}n\Delta^2$ is the diffusion coefficient for the random walk. The probability density as a function of time is plotted in Fig. 4.5. Initially, $P(y,t)$ has the form of a delta function, $\delta(y)$. As time passes, it spreads in such a way

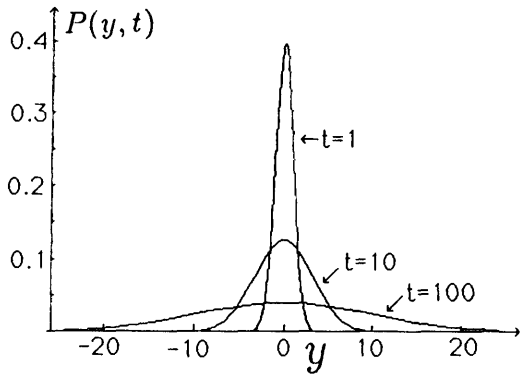


Fig. 4.5. A plot of the probability density, P (y, t) [cf. Eq. (4.71)], for $D = \frac{1}{2}$, $t = 1, 10, 100$.

that the total area underneath the curve is equal to one, but the probability of finding the particles at some distance along the x axis grows with time since the standard deviation, $\sigma = \sqrt{\Delta^2 N} = \sqrt{2Dt}$, grows as the square-root of the time.

4.F. A Central Limit Theorem [6] and Law of Large Numbers

It can be shown that the probability density describing the distribution of outcomes of a large number of events universally approaches a Gaussian form (provided the moments of the distribution for the individual events are finite). This is called the *Central Limit Theorem.* The central limit theorem has been proved in complete generality in Section S4.C. Below we give a slightly weaker version, directly applicable to measurements. This result shows why Gaussian distributions are so widely seen in nature. Another result of considerable importance is the *law of large numbers.* The law of large numbers gives quantitative justification to the use of probabilities.

4.F.1. A Central Limit Theorem

The Central Limit Theorem (cf. Section S4.C) can be stated in a simplified form which has direct relevance to the statistics of measurements. Let us consider a stochastic variable, Y_N, which is the deviation from the average of N statistically independent measurements of a stochastic variable, X. We write Y_N as

$$Y_N = \frac{1}{N}(X_1 + \cdots + X_N) - \langle x \rangle = Z_1 + \cdots + Z_N, \tag{4.72}$$

where

$$Z_i = \frac{1}{N}(X_i - \langle x \rangle)$$

The characteristic function, $f_Z(k;N)$, for the stochastic variable, $Z_i = (1/N)(X_i - \langle x \rangle)$, can be written

$$f_Z(k;N) = \int_{-\infty}^{\infty} dx e^{i(k/N)(x-\langle x \rangle)} P_X(x) = 1 - \frac{1}{2}\frac{k^2}{N^2}\sigma_X^2 + \cdots, \tag{4.73}$$

where $\sigma_X^2 = \langle x^2 \rangle - \langle x \rangle^2$. For large N and finite variance, higher-order terms in the expansion of the right-hand side can be neglected. (Note that the oscillatory character of the integrand ensures that the integral goes to zero for large k.) The characteristic function for Y_N is then

$$f_{Y_N}(k) = \left(1 - \frac{1}{2}\frac{k^2}{N^2}\sigma_X^2 + \cdots\right)^N \to \exp\left(-\frac{k^2\sigma_X^2}{2N}\right) \quad \text{as} \quad N \to \infty. \tag{4.74}$$

In Eq. (4.74), we have used the identity $\lim_{N\to\infty}(1 + x/N)^N = e^x$. Thus

$$P_{Y_N}(y) \to \frac{1}{2\pi}\int_{-\infty}^{\infty} dk e^{iky} \exp\left(-\frac{k^2\sigma_X^2}{2N}\right) = \sqrt{\frac{N}{2\pi\sigma_X^2}} \exp\left(-\frac{Ny^2}{2\sigma_X^2}\right) \tag{4.75}$$

as $N \to \infty$. Regardless of the form of $P_X(x)$, if it has finite moments, the average of a large number of statistically independent measurements of X will be a Gaussian centered at $\langle x \rangle$, with a standard deviation which is $1/\sqrt{N}$ times the standard deviation of the probability density of X.

4.F.2. The Law of Large Numbers [3, 4]

The law of large numbers underlies the intuitive concept of probability that we introduced in Section 4.C. Much of the content of the law of large numbers is contained in the Central Limit Theorem as applied to measurements. We will give a simple version of it here.

The law of large numbers applies to N independent experiments and may be stated as follows: *If an event, A, has a probability, p, of occurring, then the fraction of outcomes, A, approaches p in the limit* $N \to \infty$. The proof has two steps. The first step involves the derivation of the Tchebycheff inequality. The second step uses this inequality do derive the law of large numbers.

The Tchebycheff inequality establishes a relation between the variance and the probability that a stochastic variable can deviate by an arbitrary amount, ε (ε is positive), from its average value. The variance, σ_Z, of a stochastic variable, Z, is written

$$\sigma_Z^2 = \int_{-\infty}^{\infty} dz(z - \langle z \rangle)^2 P_Z(z). \tag{4.76}$$

If we now delete that range of the variable, z, for which $|z - \langle z \rangle| \leqslant \varepsilon$, we can

write

$$\sigma_Z^2 \geqslant \int_{-\infty}^{\langle z\rangle-\varepsilon} dz(z-\langle z\rangle)^2 P_Z(z) + \int_{\langle z\rangle+\varepsilon}^{\infty} dz(z-\langle z\rangle)^2 P_Z(z). \tag{4.77}$$

Since under the integral $|z-\langle z\rangle| \geqslant \varepsilon^2$, we can replace $(z-\langle z\rangle)^2$ by ε^2 in Eq. (4.77) and write

$$\sigma_Z^2 \geqslant \varepsilon^2 \left(\int_{-\infty}^{\langle z\rangle-\varepsilon} dz P_Z(z) + \int_{\langle z\rangle+\varepsilon}^{\infty} dz P_Z(z) \right) = \varepsilon^2 P(|z-\langle z\rangle| \geqslant \varepsilon), \tag{4.78}$$

where $P(|z-\langle z\rangle| \geqslant \varepsilon)$ is the probability that the stochastic variable, Z, deviates from $\langle z\rangle$ by more than $\pm\varepsilon$. From Eq. (4.78), we obtain the Tchebycheff inequality

$$P(|z-\langle z\rangle| \geqslant \varepsilon) \leqslant \frac{\sigma_Z^2}{\varepsilon^2}. \tag{4.79}$$

Thus, for fixed variance, σ_Z^2, the probability that Z can differ from its average value by more than $\pm\varepsilon$ decreases as ε^{-2} for increasing ε.

We now come to the law of large numbers. Let us consider N independent measurements of the stochastic variable, Z. Let Y_N be the mean value of the outcomes, $Y_N = (1/N)(Z_1 + \cdots + Z_N)$, where Z_i is the outcome of the ith measurement. The law of large numbers states that the probability that Y_N deviates from $\langle z\rangle$ goes to zero as $N \to \infty$. Thus, the $\lim_{N\to\infty} P(|y_N - \langle z\rangle| \geqslant \varepsilon) = 0$. To prove this, let us first note that $\langle y_N\rangle = \langle z\rangle$. Since we have independent events, the variance, σ_{Y_N}, behaves as $\sigma_{Y_N}^2 = \sigma_Z^2/N$. We now use the Tchebycheff inequality to write

$$P(|y_N - \langle z\rangle| \geqslant \varepsilon) \leqslant \frac{\sigma_{Y_N}^2}{\varepsilon^2} = \frac{\sigma_Z^2}{N\varepsilon^2}. \tag{4.80}$$

Thus, we find

$$\lim_{N\to\infty} P(|y_N - \langle z\rangle| \geqslant \varepsilon) = 0, \tag{4.81}$$

provided that σ_Z is finite.

▶ SPECIAL TOPICS

▶ S4.A. Lattice Random Walk [7]

Random walks on lattices provide some of the simplest examples of the effect of spatial dimension on physical processes. This type of random walk is so

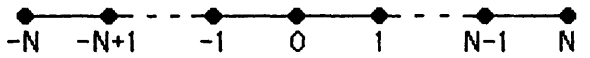


Fig. 4.6. A one-dimensional lattice with period $2N + 1$. If the walker steps right at site $l = N$, it enters from the left at site $l = -N$.

simple that we can use the concepts of the previous sections to compute the probability that the walker will reach any other part of the lattice. This section is based on a discussion of lattice random walks by E. Montroll [7]. We will find that random walks can have quite different properties in three dimensions than in one or two dimensions.

▶ S4.A.1. One-Dimensional Lattice

Let us consider a random walker on a periodic one-dimensional lattice with $2N + 1$ lattice sites (cf. Fig. 4.6). Let $P_s(l)$ be the probability to find the walker at site, l, at discrete time, s. Since the lattice is periodic, $P_s(l) = P_s(l \pm [2N + 1])$. If the walker steps from site N to the right, he enters again from the left at site $-N$. We will assume that at each step the walker steps one step to the right with probability $p = \frac{1}{2}$, or he steps to the left with probability $q = \frac{1}{2}$. The probability density for the ith step is

$$p(l_i) = \tfrac{1}{2}(\delta_{l_i,+1} + \delta_{l_i,-1}). \tag{4.82}$$

We will assume that each step is independent of previous steps and that the walker starts at site $l = 0$ at time $s = 0$. Then the position of the walker at time s (after s steps) is $l = l_1 + l_2 + \cdots + l_s$. From Eq. (4.40), the probability, $P_s(l)$, is given by

$$P_s(l) = \sum_{l_1=-N}^{N} \cdots \sum_{l_s=-N}^{N} \delta_{l,l_1+l_2+\cdots+l_s} p(l_1)p(l_2) \times \cdots \times p(l_s). \tag{4.83}$$

Since $P_s(l)$ is a periodic function of l, we can expand it in a Fourier series

$$P_s(l) = \frac{1}{2N+1} \sum_{n=-N}^{N} f_s(n) \exp\left(-\frac{2\pi i n l}{2N+1}\right), \tag{4.84}$$

where $f_s(n)$ is the Fourier amplitude and is also the characteristic function for this stochastic process. We can revert this equation and write the Fourier amplitude in terms of $P_s(l)$,

$$f_s(n) = \sum_{l=-N}^{N} P_s(l) \exp\left(+\frac{2\pi i n l}{2N+1}\right). \tag{4.85}$$

We have used the identity

$$\sum_{l=-N}^{N} \exp\left(\pm\frac{2\pi inl}{2N+1}\right) = (2N+1)\delta_{n,0}.$$

We can also Fourier transform the transition probability, $p(l)$ (cf. Eq. (4.82)), to obtain

$$\lambda(n) \equiv \sum_{l=-N}^{N} p(l) \exp\left(+\frac{2\pi inl}{2N+1}\right) = \cos\left(\frac{2\pi n}{2N+1}\right), \tag{4.86}$$

where $\lambda(n)$ is the Fourier amplitude. From Eqs. (4.83) and (4.85), we can write

$$f_s(n) = (\lambda(n))^s \tag{4.87}$$

for the characteristic function of the stochastic process.

Let us now take the limit $N \to \infty$. First we introduce the variable $\phi = (2\pi n/(2N+1))$. Then for large N,

$$\frac{1}{(2N+1)}\sum_{n=-N}^{N} = \frac{1}{(2N+1)}\int_{-N}^{N} dn \approx \frac{1}{2\pi}\int_{-\pi}^{\pi} d\phi,$$

and the probability, $P_s(l)$, in the limit $N \to \infty$, becomes

$$P_s(l) = \frac{1}{2\pi}\int_{-\pi}^{\pi} d\phi f_s(\phi) e^{-il\phi} \tag{4.88}$$

and

$$f_s(\phi) = \sum_{l=-\infty}^{\infty} P_s(l) e^{il\phi}. \tag{4.89}$$

The single-step probability becomes

$$p(l_i) = \frac{1}{2\pi}\int_{-\pi}^{\pi} d\phi \lambda_s(\phi) e^{-il_i\phi}. \tag{4.90}$$

From Eq. (4.87) we obtain

$$f_s(\phi) = (\lambda(\phi))^s. \tag{4.91}$$

(Note that if the walker starts at $l = 0$ at time $s = 0$, then $f_0(\phi) = 1$.)

It is now easy to compute $P_s(l)$ for a random walk on a one-dimensional lattice. If the walker starts from site, $l = 0$, we obtain

$$P_s(l) = \frac{1}{2\pi}\int_{-\pi}^{\pi} d\phi(\cos(\phi))^s e^{-il\phi}$$
$$= \begin{cases} \left(\frac{1}{2}\right)^s \dfrac{s!}{\left(\frac{s-l}{2}\right)!\left(\frac{s+l}{2}\right)!} & \text{for } s-l \text{ even and } s \geqslant l, \\ 0 & \text{otherwise.} \end{cases} \tag{4.92}$$

It is useful to ask another question about the walker. What is the probability that the walker will *escape* from the origin? To formulate this in a simple way, we first introduce a generating function, $U(z, l)$, for $P_s(l)$:

$$U(z,l) = \sum_{s=0}^{\infty} z^s P_s(l) = \frac{1}{2\pi}\int_{-\pi}^{\pi} d\phi f_0(\phi)\frac{e^{-il\phi}}{1 - z\lambda(\phi)}. \tag{4.93}$$

To obtain the term on the right, we have used Eqs. (4.88) and (4.91) and we have summed over s. The probability, $P_s(l)$, is then obtained from $U(z, l)$ by the equation

$$P_s(l) = \lim_{z\to 0}\frac{1}{s!}\frac{\partial^s}{\partial z^s}U(z,l). \tag{4.94}$$

■ **EXERCISE 4.12.** Compute the generating function, $U(z, 0)$, for the probability to be at site $l = 0$, at time s, given that the walker was at site $l = 0$ at time $s = 0$.

Answer: Since $f_0(\phi) = 1, U(z,0)$ is given by $U(z,0) = (1/2\pi)\int_{-\pi}^{\pi} d\phi(1/[1 - z\cos(\phi)])$. We can make the change of variables, $x = \tan(\phi/2)$. Then $\cos(\phi) = ((1-x^2)/(1+x^2))$ and $d\phi = 2dx/(1+x^2)$ and $U(z,0) = (2/\pi)\int_0^{\infty}(dx/[(1-z)+x^2(1+z)]) = (1-z^2)^{-1/2}$.

We will now let $Q_s(l)$ denote the probability that the walker arrives at site l for the *first* time after s steps. We can introduce a generating function $V(z, l)$ for $Q_s(l)$:

$$V(z,l) = \sum_{s=1}^{\infty} z^s Q_s(l). \tag{4.95}$$

Thus, $V(1, l)$ is the total probability that the walker reaches site l during the random walk.

We can now relate the generating functions $V(z,l)$ and $U(z,l)$. The walker can arrive at a lattice site l for the first time after s steps or for the first time after one step and then again after $s-1$ steps in any manner, and so on. Thus, if the walker starts at $l=0$,

$$P_0(l) = \delta_{l,0}, \tag{4.96}$$

and we can write

$$P_s(l) = \sum_{j=1}^{s} Q_j(l) P_{s-j}(0) \qquad \text{for} \quad s > 0. \tag{4.97}$$

If we combine Eqs. (4.93), (4.96), and (4.97), we obtain

$$U(z,l) = \delta_{l,0} + \sum_{s=1}^{\infty} z^s P_s(l) = \delta_{l,0} + \sum_{s=1}^{\infty} \sum_{j=1}^{s} Q_j(l) P_{s-j}(0) z^s. \tag{4.98}$$

We can change the order of the summation in Eq. (4.98) ($\sum_{s=1}^{\infty}\sum_{j=1}^{s} = \sum_{j=1}^{\infty}\sum_{s=j}^{\infty}$) and perform the summation. Then we find that $U(z,l) = \delta_{l,0} + V(z,l)U(z,0)$ and

$$V(z,l) = \frac{U(z,l) - \delta_{l,0}}{U(z,0)}. \tag{4.99}$$

The total probability to return to the origin is given by

$$V(1,0) = 1 - \frac{1}{U(1,0)}, \tag{4.100}$$

and the total probability that the walker *escapes* from the origin is

$$P_{escape} = \frac{1}{U(1,0)}. \tag{4.101}$$

For the one-dimensional walker, $U(1,0) = \infty$ and $P_{escape} = 0$ (cf. Exercise 4.12). Thus, for random walk on a one-dimensional lattice, the walker will return to the origin with probability equal to one if it starts at the origin. The walker cannot escape.

It is very interesting to generalize the above discussion to random walks in two or more dimensions, as we shall see below.

▶ S4.A.2. Random Walk in Higher Dimension

To generalize the above results to d-dimensional lattices, we introduce unit vectors, $\hat{\mathbf{x}}_i$ $(i = 1, 2, \ldots, d)$ for the various orthogonal directions in space. If the

lattice sites are a unit distance apart, we can denote their position by the vector, $\mathbf{l} = l_1\hat{\mathbf{x}}_i + \cdots + l_d\hat{\mathbf{x}}_d$, where l_i are integers. The probability to find the walker at site, $\mathbf{l}$ at time s is $P_s(\mathbf{l}) = P_s(l_1, \ldots, l_d)$. We will let the lattice have $2N + 1$ sites in each spatial direction so that $-N \leqslant l_i \leqslant N$ $(i = 1, \ldots, d)$. We will assume that the lattice is periodic in each direction. That is,

$$\begin{aligned} P_s(l_1, l_2, \ldots, l_d) &= P_s(l_1 \pm [2N+1], l_2, \ldots, l_d) \\ &= P_s(l_1, l_2 \pm [2N+1], \ldots, l_d) = \cdots \\ &= P_s(l_1, l_2, \ldots, l_d \pm [2N+1]). \end{aligned} \tag{4.102}$$

The probability, $P_s(\mathbf{l})$, can be expanded in the Fourier series:

$$P_s(\mathbf{l}) = \left(\frac{1}{2N+1}\right)^d \sum_{n_1=-N}^{N} \cdots \sum_{n_d=-N}^{N} f_s(\mathbf{n}) \exp\left(-\frac{2\pi\mathbf{n}\cdot\mathbf{l}}{2N+1}\right), \tag{4.103}$$

where $\mathbf{n} = n_1\hat{\mathbf{x}}_1 + \cdots + n_d\hat{\mathbf{x}}_d$, and the Fourier amplitude, $f_s(\mathbf{n}) = f_s(n_1, \ldots, n_d)$, is given by

$$f_s(\mathbf{n}) = \sum_{l_1=-N}^{N} \cdots \sum_{l_d=-N}^{N} P_s(\mathbf{l}) \exp\left(\frac{2\pi\mathbf{n}\cdot\mathbf{l}}{2N+1}\right). \tag{4.104}$$

Let us now take the limit $N \to \infty$. We introduce the variable, $\phi_i = 2\pi n_i/(2N+1)$ $(i = 1, \ldots, d)$, and $\boldsymbol{\varphi} = \phi_1\hat{\mathbf{x}}_i + \cdots + \phi_d\hat{\mathbf{x}}_d$. Then we find

$$P_s(\mathbf{l}) = \left(\frac{1}{2\pi}\right)^d \int_{-\pi}^{\pi} d\phi_1 \cdots \int_{-\pi}^{\pi} d\phi_d f_s(\phi) e^{-i\mathbf{l}\cdot\boldsymbol{\varphi}}, \tag{4.105}$$

and

$$f_s(\boldsymbol{\varphi}) = \sum_{l_1=-\infty}^{\infty} \cdots \sum_{l_d=-\infty}^{\infty} P_s(\mathbf{l}) e^{+i\mathbf{l}\cdot\boldsymbol{\varphi}}. \tag{4.106}$$

It is of interest to consider a random walk on two- and three-dimensional simple square lattices, where the walker steps to one of its nearest neighbors at each step. Let us first consider the case, $d = 2$. Such a lattice is shown in Fig. 4.7. If the lattice spacing is $a = 1$ and the walker is equally likely to step in any direction, the single step probability can be written

$$p(\mathbf{l}) = \frac{1}{4} \sum_{\varepsilon=\pm 1} (\delta_{l_1,\varepsilon}\delta_{l_2,0} + \delta_{l_1,0}\delta_{l_2,\varepsilon}), \tag{4.107}$$

where $\mathbf{l} = l_1\hat{\mathbf{x}}_1 + l_2\hat{\mathbf{x}}_2$. The characteristic function for the single-step

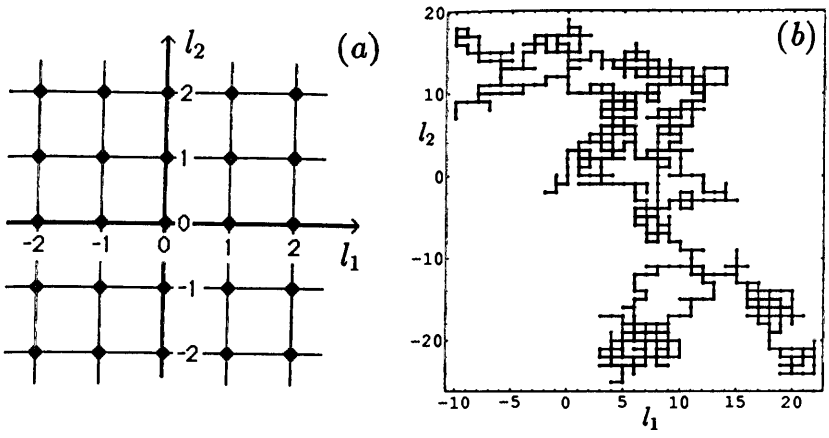


Fig. 4.7. (a) A simple square two-dimensional lattice. (b) Random walk for 1000 steps on a square two-dimensional lattice. The walker starts at $\mathbf{l} = \mathbf{0}$.

probability is

$$\lambda(\boldsymbol{\varphi}) = \sum_{l_1=-\infty}^{\infty} \sum_{l_2=-\infty}^{\infty} p(\mathbf{l}) e^{+i\mathbf{l}\cdot\boldsymbol{\varphi}} = \frac{1}{2}(\cos(\phi_1) + \cos(\phi_2)), \tag{4.108}$$

where

$$\boldsymbol{\varphi} = \phi_1 \hat{\mathbf{x}}_1 + \phi_2 \hat{\mathbf{x}}_2.$$

If the walker starts at $\mathbf{l} = \mathbf{0}$, then $f_0(\boldsymbol{\varphi}) = 1$ and the generating function, $U(z, \mathbf{l})$, is given by [cf. Eq. (4.93)]

$$U(z, \mathbf{l}) = \left(\frac{1}{2\pi}\right)^2 \int_{-\pi}^{\pi} d\phi_1 \int_{-\pi}^{\pi} d\phi_2 \frac{e^{-i\mathbf{l}\cdot\boldsymbol{\varphi}}}{1 - \frac{z}{2}(\cos(\phi_1) + \cos(\phi_2))}. \tag{4.109}$$

Let us compute $U(z, \mathbf{0})$. We make the change of variables, $x_i = \cos(\phi_i)$. Then

$$U(1, \mathbf{0}) = \left(\frac{1}{\pi}\right)^2 \int_{-1}^{1} \int_{-1}^{1} \frac{dx_1 dx_2}{\sqrt{1 - x_1^2}\sqrt{1 - x_2^2}\left(1 - \frac{z}{2}(x_1 + x_2)\right)}. \tag{4.110}$$

We first integrate over x_2 and obtain

$$U(1, \mathbf{0}) = \frac{1}{\pi} \int_{-1}^{1} \frac{dx_1}{\sqrt{1 - x_1^2}\sqrt{\left(1 - \frac{z}{2}x_1\right)^2 - \left(\frac{z}{2}\right)^2}} \tag{4.111}$$

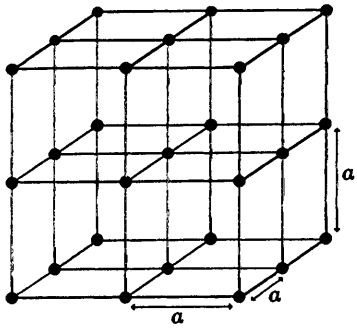


Fig. 4.8. A simple cubic lattice with lattice spacing, a.

(cf. Ref. 8). We next integrate over x_1 and find

$$U(1,\mathbf{0}) = \frac{2}{\pi}K(z), \tag{4.112}$$

where $K(k)$ is the complete elliptic integral of the first kind (k is the modulus). When $k \to 1, K(k) \to \infty$, and when $z \to 1, U(1,\mathbf{0}) \to \infty$. Thus, the escape probability for a random walker on this two-dimensional square lattice is zero, $P_{escape} = 0$ [cf. Eqs. (4.100) and (4.101)]. In Fig. 4.7, we show one realization of a random walk on the $d = 2$ square lattice. The walker starts from $\mathbf{l} = \mathbf{0}$ and 1000 steps are shown.

Let us now consider a random walk on a simple cubic lattice with lattice spacing, $a = 1$ (cf. Fig. 4.8). In this case, the single-step probability is

$$p(\mathbf{l}) = \frac{1}{6}\sum_{\varepsilon=\pm 1}(\delta_{l_1,\varepsilon}\delta_{l_2,0}\delta_{l_3,0} + \delta_{l_1,0}\delta_{l_2,\varepsilon}\delta_{l_3,0}) + \delta_{l_1,0}\delta_{l_2,0}\delta_{l_3,\varepsilon}) \tag{4.113}$$

and the characteristic function is

$$\lambda(\boldsymbol{\varphi}) = \tfrac{1}{3}(\cos(\phi_1) + \cos(\phi_2) + \cos(\phi_3)). \tag{4.114}$$

If the walker starts at $\mathbf{l} = \mathbf{0}$, the generating function, $U(z,\mathbf{0})$, is

$$U(z,\mathbf{0}) = \left(\frac{1}{2\pi}\right)^3 \int_{-\pi}^{\pi} d\phi_1 \int_{-\pi}^{\pi} d\phi_2 \int_{-\pi}^{\pi} d\phi_3 \frac{1}{1 - \frac{z}{3}(\cos(\phi_1) + \cos(\phi_2) + \cos(\phi_3))}. \tag{4.115}$$

Let us now compute the escape probability, $P_{escape} = 1/U(1,\mathbf{0})$. We may write

$$U(1,\mathbf{0}) = \left(\frac{1}{\pi}\right)^3 \int_0^{\pi}\int_0^{\pi}\int_0^{\pi} \frac{d\phi_1 d\phi_2 d\phi_3}{1 - \frac{1}{3}(\cos(\phi_1) + \cos(\phi_2) + \cos(\phi_3))}. \tag{4.116}$$

With a change of variables, $x_i = \cos(\phi_i)$, $U(1,\mathbf{0})$ takes the form

$$U(1,\mathbf{0}) = \left(\frac{1}{\pi}\right)^3 \int_{-1}^{1}\int_{-1}^{1}\int_{-1}^{1} \frac{dx_1 dx_2 dx_3}{\sqrt{1-x_1^2}\sqrt{1-x_2^2}\sqrt{1-x_3^2}(1-\frac{1}{3}(x_1+x_2+x_3))}. \tag{4.117}$$

We first integrate over x_3 and obtain

$$U(1,\mathbf{0}) = \left(\frac{1}{\pi}\right)^2 \int_{-1}^{1}\int_{-1}^{1} \frac{dx_1 dx_2}{\sqrt{1-x_1^2}\sqrt{1-x_2^2}\sqrt{(1-\frac{1}{3}(x_1+x_2))^2-\frac{1}{9}}}. \tag{4.118}$$

(cf. Ref. 8). We next integrate over x_2 and find

$$U(1,\mathbf{0}) = \frac{6}{\pi^2}\int_{-1}^{1} \frac{dx_1}{(3-x_1)\sqrt{1-x_1^2}} K\left(\frac{2}{3-x_1}\right) \approx 1.516 \tag{4.119}$$

(cf. Ref. 7), where $K(k)$ is the complete elliptic integral of the first kind (k is the modulus). From Eq. (4.119) we have computed $U(1,\mathbf{0})$ numerically. An analytic expression is obtained in Ref. 9. The escape probability for a random walker on a simple cubic lattice is $P_{escape} = 1/U(1,\mathbf{0}) \approx 0.66$. Thus, for this three dimensional simple cubic lattice there is a large probability that a random walker, who starts at the origin, will never return to the origin. The walker can escape.

The results of this section are special cases of a more general result due to Polya [10] where he shows that random walkers (whose step size distribution has finite variance) on one- and two-dimensional lattices can never escape their origin. They eventually will return to their starting point. But in three dimensions, there is a finite probability that a walker can escape forever from its starting point. Random walks for which the escape probability is zero are said to *persistent*. Random walks with finite escape probability are said to be *transient*.

▶ S4.B. Infinitely Divisible Distributions [6, 11]

The concept of an infinitely divisible distribution function is important to all limit theorems in statistical physics. The limiting distribution can only belong to this class of distributions. A stochastic variable, Y, is infinitely divisible if *for any integer N*, it can be represented by a sum

$$Y = X_1 + X_2 + \cdots + X_N \tag{4.120}$$

of identically distributed stochastic variables, $X_i (i = 1, \ldots, N)$. The distribution

functions, $F_Y(y)$, for infinitely divisible stochastic variables, Y, are called *infinitely divisible distribution functions*. The distribution function, $F_Y(y)$, is infinitely divisible if and only if, for any N, its characteristic function $f_Y(k)$ is the Nth power of some characteristic function, $f_X(k, 1/N)$. Thus, $f_Y(k) = (f_X(k, 1/N))^N$ or

$$f_X(k, 1/N) = (f_Y(k))^{1/N} \tag{4.121}$$

(we take the principal branch of the Nth root). Infinitely divisible distributions may have either finite or infinite variance. We give some examples of infinitely divisible distributions below.

■ **EXERCISE 4.13.** Show that the characteristic function for an infinitely divisible distribution has no real zeros.

Answer: Let $g(k) = \lim_{N\to\infty}(f(k))^{1/N}$. Then either $g(k) = 0$ or $g(k) = 1$ since $g(k) = 0$ when $f(k) = 0$ and $g(k) = 1$ when $f(k) \neq 0$. Since $f(0) = 1$ and $f(k)$ is continuous, $f(k) \neq 0$ in a neighborhood of the origin and $g(k) = 1$ in a neighborhood of the origin. But since $g(k)$ is also a characteristic function, it is continuous and cannot jump from value $g(k) = 1$ to $g(k) = 0$ at some value of k. Therefore, $g(k) = 1$ for all k and $f(k) \neq 0$ for all k. The converse, however, need not be true. If a characteristic function has no real zeros, it still might not be infinitely divisible.

▶ S4.B.1. Gaussian Distribution

The Gaussian distribution is infinitely divisible. To see this, let us consider the most general form of the Gaussian probability density for the stochastic variable, Y. The probability density is

$$P_Y(y) = \sqrt{\frac{1}{2\pi\sigma_Y^2}}\exp\left(-\frac{(y-a)^2}{2\sigma_Y^2}\right), \tag{4.122}$$

with average $\langle y\rangle = a$ and standard deviation σ_Y. The characteristic function is

$$f_Y(k) = \exp\left(iak - \frac{\sigma_Y^2}{2}k^2\right). \tag{4.123}$$

The Nth root is $f_X(k; 1/N) = (f_Y(k))^{1/N} = \exp\left(i(a/N)/k - (\sigma_Y^2/2N)k^2\right)$. Thus, the probability density for each of the identically distributed stochastic variables, X_i is

$$P_X(x; 1/N) = \sqrt{\frac{1}{2\pi(\sigma_Y^2/N)}}\exp\left(-\frac{(x-a/N)^2}{2(\sigma_Y^2/N)}\right), \tag{4.124}$$

and the average value and standard deviation of the stochastic variable X_i are $\langle x \rangle = (a/N)$ and $\sigma_X = (\sigma_Y/\sqrt{N})$, respectively.

▶ S4.B.2. Poisson Distribution

The Poisson distribution is infinitely divisible. The Poisson probability density for a stochastic variable, Y, is given by

$$P_Y(y) = \sum_{m=0}^{\infty} \frac{\lambda^m e^{-\lambda}}{m!} \delta(y - a - mh) \tag{4.125}$$

where $\langle y \rangle = a + \lambda h$ is the average value of Y and $\sigma_Y = h\sqrt{\lambda}$ is its standard deviation. The characteristic function for stochastic variable Y is

$$f_Y(k) = \exp(iak + \lambda(e^{ikh} - 1)). \tag{4.126}$$

The Nth root is $f_X(k; 1/N) = (f_Y(k))^{1/N} = \exp(i(a/N)k + \lambda/N(e^{ikh} - 1))$. Thus, the probability density for each of the N identically distributed stochastic variables X_i is

$$P_X(x; 1/N) = \sum_{m=0}^{\infty} \frac{1}{m!} \left(\frac{\lambda}{N}\right)^m e^{-\lambda/N} \delta\left(x - \frac{a}{N} - mh\right) \tag{4.127}$$

and the Poisson distribution is infinitely divisible. The average of X and its standard deviation are given by $\langle x \rangle = (a + \lambda h)/N$ and $\sigma_X = (\sigma_Y/\sqrt{N})$, respectively.

▶ S4.B.3. Cauchy Distribution

The Cauchy distribution function,

$$F_Y(y) = \frac{1}{\pi}\left(\frac{\pi}{2} + \tan^{-1}\left(\frac{y - b}{a}\right)\right) \tag{4.128}$$

($a > 0$ and b are finite constants) for stochastic variable Y, is an example of an infinitely divisible distribution which has an infinite variance. The probability density for a stochastic variable, Y, is

$$P_Y(y) = \frac{dF_Y}{dy} = \frac{1}{\pi} \frac{a}{a^2 + (y - b)^2}. \tag{4.129}$$

The first moment is $\langle y \rangle = b$, but the variance and the standard deviation are infinite. The characteristic function for stochastic variable Y is

$$f_Y(k) = \exp(ikb - |k|a). \tag{4.130}$$

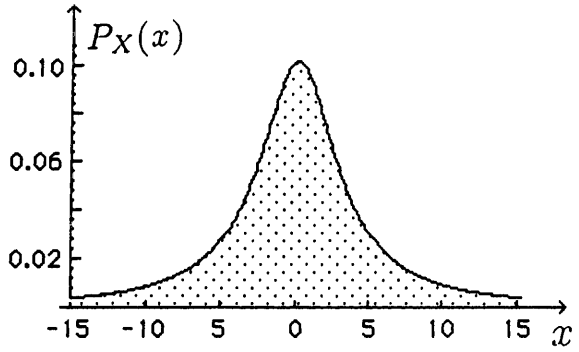


Fig. 4.9. A plot of the Cauchy probability density for $b = 0$ and $a = \pi$.

The Nth root is $f_X(k, 1/N) = (f_Y(k))^{1/N} = \exp(ik(b/N) - |k|(a/N))$. Thus, the Cauchy distributions is infinitely divisible. The probability density for each of the N identically distributed stochastic variables X_i is

$$P_X(x; 1/N) = \frac{1}{\pi} \frac{a/N}{(a/N)^2 + (x - b/N)^2}. \tag{4.131}$$

From Eq. (4.131) we find $\langle x \rangle = b/N$. The Cauchy distribution is plotted in Fig. 4.9.

▶ S4.B.4. Levy Distribution

The Cauchy distribution is a special case of a more general distribution, called the Levy distribution. The Levy distribution has infinite variance and has a characteristic function of the form

$$f_Y(k) = \exp(-c|k|^\alpha), \tag{4.132}$$

where $0 < \alpha < 2$. We can only obtain an analytic expression for $P_Y(y)$, for a few special cases. We shall discuss the properties of these distributions in more detail in Section (S4.D).

■ **EXERCISE 4.14.** Consider the characteristic function $f(k) = (1 - b)/(1 - be^{ik})(0 < b < 1)$. Show that it is infinitely divisible.

Answer: First note that

$$\ln f(k) = \ln(1 - b) - \ln(1 - be^{ik}) = \sum_{m=1}^{\infty} \frac{b^m}{m}(e^{ikm} - 1).$$

Thus

$$f(k) = \prod_{m=1}^{\infty} e^{(b^m/m)(e^{ikm}-1)}.$$

Since $f(k)$ is a product of Poisson characteristic functions, it is infinitely divisible.

▶ S4.C. The Central Limit Theorem

We wish to consider the sum, Y_N, of N independent identically distributed stochastic variables X_i such that

$$Y_N = X_1 + \cdots + X_N. \tag{4.133}$$

We will let $F_{Y_N}(y)$ denote the distribution function, and $f_{Y_N}(k)$ the characteristic function, of stochastic variable Y_N. We will let $F_X(x; 1/N)$ denote the distribution function, and $f_X(k; 1/N)$ the characteristic function, of stochastic variables $X_i^{(N)}$. The characteristic function for the stochastic variable Y_N can be written

$$\begin{aligned} f_{Y_N}(k) &= \int_{-\infty}^{\infty} dx_1 \cdots \int_{-\infty}^{\infty} dx_N e^{ik(x_1+\cdots+x_N)} P_X(x_1; 1/N) \times \cdots \times P_X(x_N; 1/N) \\ &= (f_X(k; 1/N))^N \end{aligned} \tag{4.134}$$

[cf. Eq. (4.35)], where $P_X(x; 1/N) = dF_X(x; 1/N)/dx$ is the probability density of X_i.

The Central Limit Theorem describes the limiting behavior ($N \to \infty$) of the stochastic variable Y_N for the case where the stochastic variables X_i have finite variance. We will also assume that X_i has zero mean, $\langle x \rangle = 0$, since this causes no loss of generality. More specifically, we consider system for which

$$\lim_{N\to\infty} f_X(k; 1/N) = 1 \tag{4.135}$$

and

$$\lim_{N\to\infty} N\langle x^2 \rangle = C, \tag{4.136}$$

where C is a finite constant. For such systems, the limiting distribution function, $F_Y(y) = \lim_{N\to\infty} F_{Y_N}(y)$ is infinitely divisible even though Y_N and X_i might not infinitely divisible. Furthermore, *the limiting distribution is a Gaussian.* This is the content of the *Central Limit Theorem.*

Before we take the limit, $N \to \infty$, and prove the Central Limit Theorem, it useful in the next section to obtain some inequalities.

▶ S4.C.1. Useful Inequalities

Let us first define

$$\begin{aligned}\Delta f_{X,N} &= f_X(k; 1/N) - 1 = \int (e^{ikx} - 1) dF_X(x; 1/N) \\ &= \int (e^{ikx} - 1 - ikx) dF_X(x, 1/N).\end{aligned} \tag{4.137}$$

where we have used the fact that $\langle x \rangle = 0$ in the last inequality. Next note that

$$|e^{ikx} - 1 - ikx| \leqslant \tfrac{1}{2} kx^2 \tag{4.138}$$

(we have plotted the left- and right-hand sides of Eq. (4.138) in Fig. 4.10. If we combine Eqs. (4.137) and (4.138), we obtain

$$|\Delta f_{X,N}| = |f_X(k; 1/N) - 1| \leqslant \tfrac{1}{2} k \langle x^2 \rangle. \tag{4.139}$$

This is our first inequality.

Let us now obtain a second inequality. *For sufficiently large N*, we can assume that $\Delta f_{X,N} < \frac{1}{2}$ [cf. Eq. (4.135)]. Then

$$\begin{aligned}&|\ln[f_X(k; 1/N)] - \Delta f_{X,N}| = |\ln[1 + \Delta f_{X,N}] - \Delta f_{X,N}| \\ &= \left| \sum_{m=2}^{\infty} \frac{1}{m} (\Delta f_{X,N})^m \right| \leqslant \sum_{m=2}^{\infty} \frac{1}{m} |\Delta f_{X,N}|^m \leqslant \frac{1}{2} \sum_{m=2}^{\infty} |\Delta f_{X,N}|^m \\ &= \frac{1}{2} \frac{|\Delta f_{X,N}|^2}{1 - |\Delta f_{X,N}|} \leqslant |\Delta f_{X,N}|^2.\end{aligned} \tag{4.140}$$

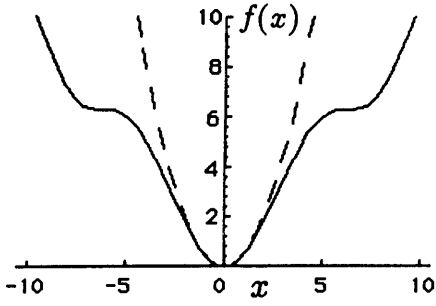


Fig. 4.10. Plot of $f(x) \equiv |e^{ikx} - 1 - ikx|$ (solid line) and of $f(x) \equiv \frac{1}{2} x^2$ (dashed line) for $k = 1$.

We can now combine the above inequalities to obtain

$$|\ln(f_{Y_N}) - N\Delta f_{X,N}| = N|\ln(f_X) - \Delta f_{X,N}| \leqslant N|\Delta f_{X,N}|^2 \quad \leqslant \tfrac{1}{2}Nk\langle x^2\rangle|\Delta f_{X,N}|, \tag{4.141}$$

where $\Delta f_{X,N}$ is defined in Eq. (4.137). We will use these inequalities below.

▶ S4.C.2. Convergence to a Gaussian

If we combine Eqs. (4.136) and (4.141), we find

$$\lim_{N\to\infty} |\ln f_{Y_N}(k) - N\int(e^{ikx} - 1 - ikx)dF_X(x; 1/N)| = 0, \tag{4.142}$$

since $\lim_{N\to\infty} f_X(k, 1/N) \to 1$. Therefore,

$$f_Y(k) = \lim_{N\to\infty} f_{Y_N}(k) = \lim_{N\to\infty} \exp\left(N\int(e^{ikx} - 1 - ikx)dF_X\right), \tag{4.143}$$

where $f_Y(k)$ is the limiting characteristic function.

It is useful to introduce a function

$$K_N(u) = N\int_{-\infty}^{u} x^2 dF_X(k; 1/N), \tag{4.144}$$

Then $K_N(-\infty) = 0$ and $K_N(+\infty) = N\langle x^2\rangle$. Furthermore, $K_N(u)$ is a non-decreassing bounded function. Using Eq. (4.144), we can write

$$N\int(e^{ikx} - 1 - ikx)dF_X(x; 1/N) = \int(e^{ikx} - 1 - ikx)\frac{1}{x^2}dK_N(x). \tag{4.145}$$

Thus, the limiting characteristic function, $f_Y(k)$, takes the form

$$f_Y(k) = \lim_{N\to\infty} \exp\left[\int(e^{ikx} - 1 - ikx)\frac{1}{x^2}dK_N(x)\right]. \tag{4.146}$$

Equation (4.146) is the *Kolmogorov formula* (cf. Section S4.E). In Section S4.E we give a general proof that since $K(u)$ is a bounded monotonically increasing function, $f_Y(k)$ is infinitely divisible. Below we show this for the special case of variables, X_i, with finite variance.

Let us introduce a new stochastic variable, Z_i, which is independent of N, such that

$$X_i = \frac{Z_i - \langle z\rangle}{\sqrt{N}\sigma_Z}. \tag{4.147}$$

Here σ_Z is the standard deviation of Z_i and is finite. We assume that the stochastic variables Z_i are identically distributed. We see that $\langle x \rangle = 0$ and $\langle x^2 \rangle = (\langle z^2 \rangle - \langle z \rangle^2)/N\sigma_Z^2$. Thus,

$$N\langle x^2 \rangle = \frac{\langle z^2 \rangle - \langle z \rangle^2}{\sigma_Z^2} = 1 \tag{4.148}$$

and Eq. (4.136) is satisfied. Furthermore, we have

$$\lim_{N\to\infty} f_X(k; 1/N) = \lim_{N\to\infty} e^{-ik\langle z \rangle/\sqrt{N}\sigma_Z} f_Z\left(\frac{k}{\sqrt{N}\sigma_Z}\right) = 1 \tag{4.149}$$

(see Eq. 4.50) and Eq. (4.135) is satisfied.

Let us look at the limiting behavior of $K_N(u)$ in Eq. (4.144). First note that

$$\begin{aligned} K_N(u) &= N \int_{-\infty}^{u} dx\, x^2 P_X(x; 1/N) \\ &= \int_{-\infty}^{\sqrt{N}\sigma_Z u} dz \frac{(z - \langle z \rangle)^2}{\sigma_Z^2} P_Z(z) \end{aligned} \tag{4.150}$$

so that

$$\lim_{N\to\infty} K_N(u) = \begin{cases} 1 & \text{for } u > 0 \\ 0 & \text{for } u < 0 \end{cases} \tag{4.151}$$

It is easy to show that this is just the condition that the limiting distribution be a Gaussian. We can write Eq. (4.151) in the form $\lim_{N\to\infty} K_N(u) = \Theta(u)$, where $\Theta(u)$ is the Heaviside function. Therefore, $\lim_{N\to\infty} dK_N(u) = \delta(u)\, du$. If we substitute this into Eq. (4.146), we obtain

$$f_Y(k) = e^{-k^2/2}. \tag{4.152}$$

From Eq. (4.55), this corresponds to a Gaussian probability density, $P_Y(y) = e^{y^2/2}$, centered at $\langle y \rangle = 0$ with standard deviation equal to one. This result is the *Central Limit Theorem.*

▶ S4.D. Weierstrass Random Walk [12, 13]

One of the simplest random walks which does not satisfy the conditions of the Central Limit Theorem is the Weierstrass random walk. In the continuum limit, the Weierstrass random walk is governed by a Levy distribution and not a Gaussian. We will first consider the discrete case and then the continuum limit.

▶ S4.D.1. Discrete One-Dimensional Random Walk

Let us consider a walker constrained to move along the x axis. At discrete time intervals, τ, the walker takes a step of length $b^n\Delta$ to the left or to the right with probability $(a-1)/2a^{n+1}$ (n can be any integer, $n = 0, 1, \ldots$). We assume that each step is independent of all the others. The displacement of the walker after N steps is $Y_N = X_1 + \cdots + X_N$, where X_i is the displacement at the ith step. The probability density for the displacement X_i is

$$P_{X_i}(x) = \frac{a-1}{2a}\sum_{n=0}^{\infty}\frac{1}{a^n}[\delta(x-b^n\Delta)+\delta(x+b^n\Delta)], \tag{4.153}$$

where $a \geqslant 1$ and $b \geqslant 1$. It is easy to show that $\langle x\rangle = 0$ and $\langle x^2\rangle = (a-1)\Delta^2/(a-b^2)$. Thus for $b^2 < a$ we have $\langle x^2\rangle < \infty$, and we expect the limiting distribution to be a Gaussian. For $b^2 = a$ we have $\langle x^2\rangle = \infty$, and for $b^2 > a$, $\langle x^2\rangle$ is undefined. Therefore, for $b^2 \geqslant a$ the conditions of the Central Limit Theorem are not satisfied, and as $N \to \infty$ the probability density for Y_N need not approach a Gaussian.

The characteristic function for the ith step is

$$f(k) \equiv f_{X_i}(k) = \int_{-\infty}^{\infty} dx e^{ikx} P_{X_i}(x) = \left(\frac{a-1}{a}\right)\sum_{n=0}^{\infty}\frac{1}{a^n}\cos(kb^n\Delta). \tag{4.154}$$

which is known as the *Weierstrass function*. We will consider $f(k)$ for the case $a = 4$ and various values of b. For $a = 4$ and $b = 1$, $\langle x\rangle = \Delta^2$ and $f(k) = \cos(k\Delta)$. Thus, for this case the random walk reduces to a binomial random walk. In Fig. 4.11, we plot $f(k)$ for the cases $(a = 4, b = 3)$ and $(a = 4, b = 5)$. The characteristic function, $f(k)$, has the very interesting property that for $b > a$ it has finite derivatives at *no* value of k [14]. In fact, except for special cases, the characteristic function has structure to as small a scale as we wish to look.

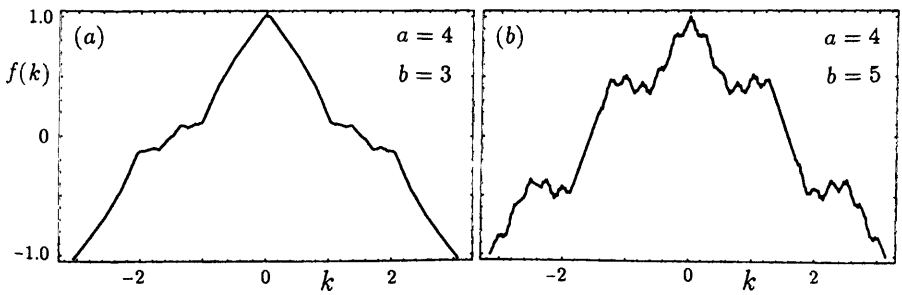


Fig. 4.11. The Weierstrass characteristic function, $f(k)$, for (a) $a = 4$, $b = 3$ ($\mu = \ln(a)/\ln(b) = 1.26$) (b) $a = 4$, $b = 5$ ($\mu = \ln(a)/\ln(b) = 0.86$).

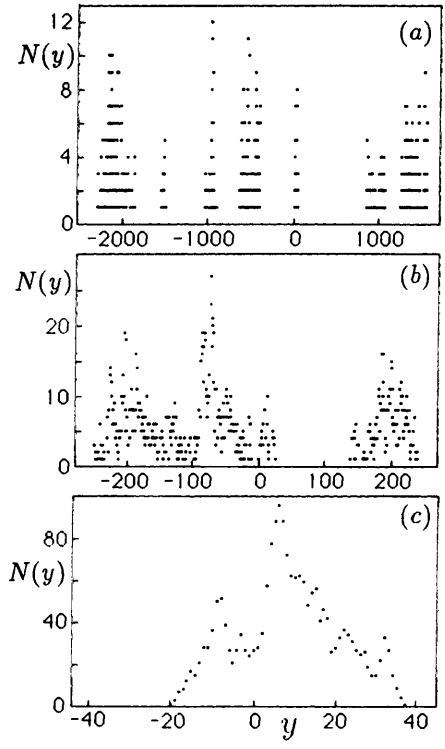


Fig. 4.12. One realization of the Weierstrass random walk for $N = 2000$, $\Delta = 1$, $a = 4$, and (a) $b = 5$, (b) $b = 3$, and (c) $b = 1$.

The characteristic function for the displacement $Y_N = X_1 + \cdots + X_N$ is

$$f_{Y_N}(k) = (f(k))^N, \tag{4.155}$$

where $f(k)$ is defined in Eq. (4.154). In Fig. 4.12 we show one realization of the Weierstrass random walk for $N = 2000$ and for cases $(a = 4, b = 1)$, $(a = 4, b = 3)$, and $(a = 4, b = 5)$. For the case $(a = 4, b = 5)$, the random walk shows clustering with a spread that is growing dramatically with N. For the case $(a = 4, b = 3)$ the random walk no longer clusters but still is spreading rapidly with N. For the case $(a = 4, b = 1)$ the random walk reduces to a binomial random walk which spreads as $\sqrt{N}$.

It has been shown in Ref. 15 that this phenomenon of clustering persists as $N \to \infty$ for the parameter range $0 < \mu = \ln(a)/\ln(b) < 1$. In the limit $N \to \infty$, there will be clusters on all scales down to size Δ and the probability will have a fractal-like structure in space. In the parameter range $0 < \mu < 1$, it has been shown that the walker has a finite probability of escaping the origin. The random walk is *transient*. Therefore the walker does not return to smooth out the clusters. For $1 < \mu < 2$, the random walk is *persistent* and the clusters get smoothed out.

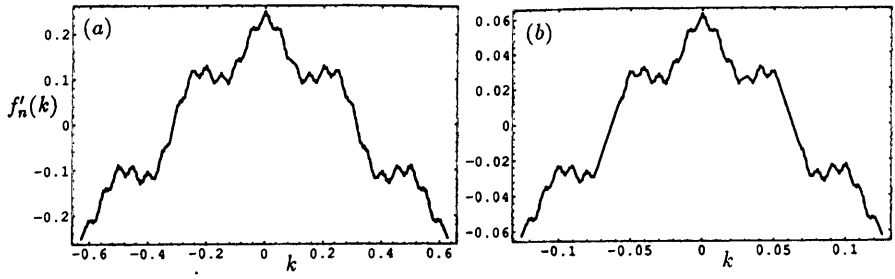


Fig. 4.13. Self-similarity embedded in the Weierstrass function. We plot $f'_n(k) \equiv (1/a_{m+1}) f(b^{n+1}k)$ for $a = 4$, $b = 5$, and (a) $n = 0$ and (b) $n = 1$. In going from (a) to (b) we are enlarging the central peak.

The characteristic function, $f(k)$, has embedded in it a self-similar structure. To see this let us rewrite $f(k)$ in the form

$$f(k) = \frac{1}{a} f(bk) + \frac{a-1}{a} \cos(\Delta k) \tag{4.156}$$

or, more generally,

$$\frac{1}{a^n} f(b^n k) = \frac{1}{a^{n+1}} f(b^{n+1}k) + \frac{a-1}{a} \frac{1}{a^n} \cos(\Delta b^n k). \tag{4.157}$$

We show this behavior in Fig. 4.13 where we plot $(1/a)f(bk)$ and $(1/a^2)f(b^2k)$ for $(a = 4, b = 5)$. As we move to a smaller scale (increasing n) we focus on the central peak of the previous scale. The figure is self-similar to as small a scale (in k) as we wish to examine.

It is important to note that $f(k)$ is not infinitely divisible because $f(k)$ can go to zero for some values of k (cf Exercise 4.13 and Fig. 4.11).

▶ S4.D.2. Continuum Limit of One-Dimensional Discrete Random Walk

Let us now take the continuum limit of the Weierstrass random walk. We proceed as in Section 4.E.4. Let us assume that the time between steps is τ, and rewrite the characteristic function, $f_{Y_N}(k) \equiv f_Y(k, N\tau)$. We assume that initially the walker is at $y = 0$ so that $P_{Y_0}(y) = \delta(y)$ and the characteristic function, $f_Y(k, 0)$, equals 1. We can write

$$f_Y(k, (N+1)\tau) - f_Y(k, N\tau) = (f(k) - 1) f_Y(k, N\tau), \tag{4.158}$$

where $f(k)$ is defined in Eqs. (4.154). We will now let $a = 1 + \alpha\Delta$ and $b = 1 + \beta\Delta$ and take the limits $N \to \infty, \Delta \to 0$, and $\tau \to 0$ so that

$\mu = \ln(a)/\ln(b) \to \alpha/\beta, N\tau \to t$, and $\Delta^\mu/\tau \to \delta$. It can be shown that [13]

$$\lim_{\tau\to 0}\lim_{\Delta\to 0}\frac{1}{\tau}(f(k)-1) = \mu\delta|k|^\mu\cos\left(\frac{\pi\mu}{2}\right)\Gamma(-\mu), \tag{4.159}$$

where $\Gamma(-\mu)$ is the Gamma function.

For $0 < \mu < 1, \Gamma(-\mu)$ is negative and $\cos(\mu\pi/2)$ is positive. For $1 < \mu < 2, \Gamma(-\mu)$ is positive and $\cos(\mu\pi/2)$ is negative. From Eq. (4.159), we can write

$$\frac{\partial f(k,t)}{\partial t} = -D_L|k|^\mu f(k,t), \tag{4.160}$$

where

$$D_L = \mu\delta\cos\left(\frac{\pi\mu}{2}\right)\Gamma(-\mu). \tag{4.161}$$

The solution to Eq. (4.160), for the case when $f(k,0) = 1$, is

$$f(k,t) = \exp(-D_L|k|^\mu t). \tag{4.162}$$

This is the Levy distribution. The probability density, $P(y,t)$, for the displacement of the random walker in the continuum limit is given by

$$P(y,t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dk e^{-iky}e^{-D_L|k|^\mu t}. \tag{4.163}$$

Bochner [16] has shown that $P(y,t)$ is only a nonnegative function for $0 < \mu \leqslant 2$ and therefore can only be interpreted as a probability for this range of μ. It is easy to check that $P(y,t)$ is normalized to one.

There are only a few values of μ for which Eq. (4.163) can be integrated and obtained in closed form. The case $\mu = 1$ gives the Cauchy distribution [cf. Eq. (4.163)], while the case $\mu = 2$ gives the Gaussian distribution. In Fig. 4.14 we show plots of $P(y,t)$ for $t = 1/D_L$ and for $\mu = 0.86$ and $\mu = 1.26$, the cases considered in Fig. 4.11. $P(y,t)$ has a very long tail indicating that there is no cutoff in the structure for small k (long wavelength).

▶ S4.D.3. Two-Dimensional Discrete Random Walk (Levy Flight)

The Levy flight is a special case of the more general Rayleigh–Pearson random walk [17, 18] in two and three dimensions. We will first set up the Rayleigh–Pearson random walk and then consider the case of a discrete Levy flight.

Let us consider a random walk in the (x,y) plane such that at the ith step the particle takes a step of length a_i along a path that makes an angle θ_i with respect

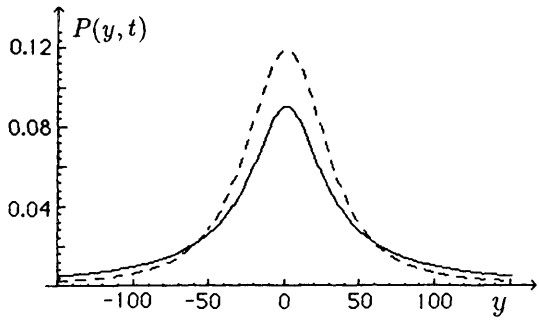


Fig. 4.14. Plots of $P(y,t)$ for $\mu = 0.86$ (solid line) and $\mu = 1.26$ (dashed line) for time $t = 1/D_L$.

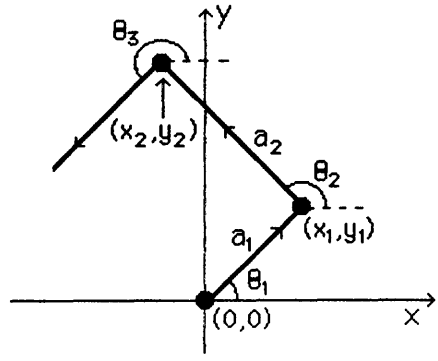


Fig. 4.15. The coordinates for a two-dimensional random walk.

to the x-axis (cf. Fig. 4.15). We will assume that r_i and θ_i are independent stochastic variables, that a_i has a probability density $P(r_i)$, and that θ_i is uniformly distributed over the interval $0 \rightarrow 2\pi$ so that the probability density $P(\theta_i) = (1/2\pi)$. If the walker is at $(x = 0, y = 0)$ at the initial time, then after N steps it will be at $(x = x_N, y = y_N)$, where $x_N = r_1\cos(\theta_1) + r_2\cos(\theta_2) + \cdots + r_N\cos(\theta_N)$ and $y_N = r_1\sin(\theta_1) + r_2\sin(\theta_2) + \cdots + r_N\sin(\theta_N)$.

If we assume that the ith step is independent of the $(i+1)$th step for all i, then the probability density to find the particle at $x \rightarrow x + dx$ and $y \rightarrow y + dy$ after N steps is

$$P_N(x,y) = \left(\frac{1}{2\pi}\right)^N \int_0^{2\pi} d\theta_1 \cdots \int_0^{2\pi} d\theta_N \int_0^{\infty} dr_1 \cdots \int_0^{\infty} dr_N P(r_1) \times \cdots \times P(r_N)$$
$$\times \delta(x - r_1\cos(\theta_1) - r_2\cos(\theta_2) - \cdots - r_N\cos(\theta_N))$$
$$\times \delta(y - r_1\sin(\theta_1) - r_2\sin(\theta_2) - \cdots - r_N\sin(\theta_N)). \qquad (4.164)$$

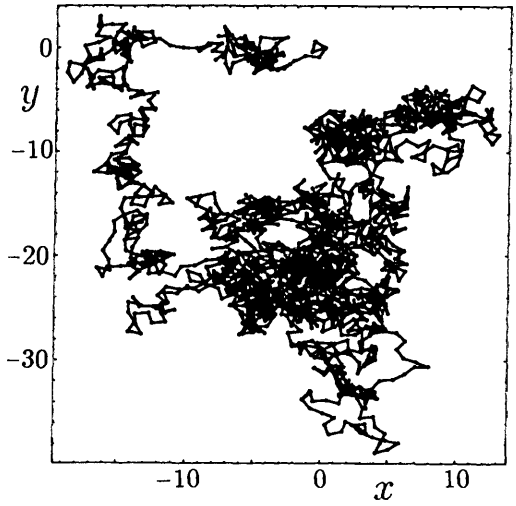


Fig. 4.16. One realization of a Rayleigh–Pearson random walk for the case when all steps are of unit length ($a = 1$). The total number of steps is $N = 2000$. The walker starts at $(x = 0, y = 0)$.

In Fig. 4.16 we show a two-dimensional Rayleigh–Pearson random walk for the case when the step lengths $r_i (i = 1, \ldots, N)$ are identically distributed with probability density $P(r_i) = P(r) = \delta(r - 1)$. For this case, the walker always takes steps of unit length, although the direction of the steps is completely random.

In Fig. 4.17 we show a Rayleigh–Pearson random walk for the case when the step lengths r are variable and probability density $P(r)$ is given by a Weierstrass probability density:

$$P(r) = \frac{a-1}{a} \sum_{n=0}^{\infty} \frac{1}{a^n} [\delta(r - b^n \Delta))]. \tag{4.165}$$

Note that the step lengths are all positive. With this distribution of step lengths, there is a small chance that at a given step the walker will take a very long step. Therefore the behavior of this random walk is completely different from that of a binomial random or simple lattice random walk. Figure 4.17 is an example of a discrete Levy flight. For $0 < \mu < 2$ and in both two and three spatial dimensions the random walk is transient [15]. Therefore, as $N \to \infty$ the random walk will form fractal-like clusters on all scales down to scale size Δ. In the continuum limit, it will form clusters on all scales.

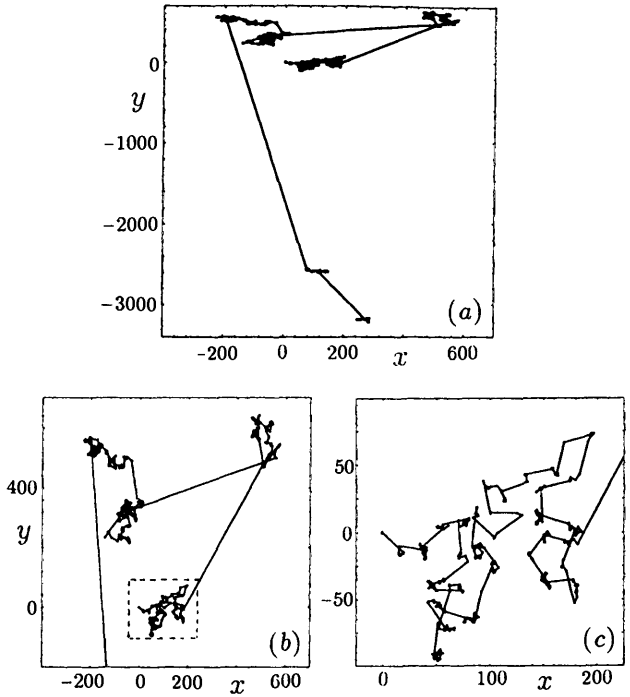


Fig. 4.17. One realization of a Rayleigh–Pearson random walk for the case when the distribution of step lengths is given by the Weierstrass probability density. The total number of steps is $N = 2000$. The walker starts at $(x = 0, y = 0)$. The sequence of angles is the same as in Fig. 4.16 (a) The complete walk. (b) Magnification of the upper section of (a). (c) Magnification of hatched box in (b).

It is also possible to obtain a Levy-type random walk by haviing the walker move on a lattice which has self-similar structure. Such types of random walks are discussed in Ref. [19].

▶ S4.E. General Form of Infinitely Divisible Distributions

The definition of an infinitely divisible distribution function is given in Section S4.B. For the case of infinitely divisible distributions with finite variance, A. N. Kolmogorov [6, 20] has given a general form of the characteristic function, called *Kolmogorov's formula*, which is also unique. P. Levy [21, 22] and A. Khintchine [23] have generalized Kolmogorov's result to the case of infinitely divisible distributions with infinite variance. Their formula is called the *Levy–Khintchine formula*. In Sections S4.E.1–S4.E.2 below, we describe these two formulas.

▶ S4.E.1. Levy–Khintchine Formula [22, 23]

The most general form of an infinitely divisible characteristic function has the form

$$f(k) = \exp\left[ik\alpha + \int_{-\infty}^{\infty}\left(e^{ikx} - 1 - \frac{ikx}{1+x^2}\right)\frac{1+x^2}{x^2}dG(x)\right], \tag{4.166}$$

where α is a constant and $G(x)$ is a real, bounded, nondecreasing function of x such that $G(-\infty) = 0$. The integrand at $x = 0$ is

$$\left\{\left(e^{ikx} - 1 - \frac{ikx}{1+x^2}\right)\frac{1+x^2}{x^2}\right\}_{x=0} = -\frac{k^2}{2}. \tag{4.167}$$

Both α and $G(x)$ are uniquely determined by $f(k)$. Equation (4.166) is called the *Levy–Khintchine formula.*

It is fairly easy to see that the Levy–Khintchine formula is infinitely divisible. We can write Eq. (4.166) in the form

$$f(k) = e^{ik\alpha - k^2\sigma^2/2}e^{I(k)}, \tag{4.168}$$

where $\sigma^2 = G(0^+) - G(0^-)$ and

$$\begin{aligned} I(k) &= \lim_{\varepsilon\to 0}\int_{|x|>\varepsilon}\left(e^{ikx} - 1 - \frac{ikx}{1+x^2}\right)\frac{1+x^2}{x^2}dG(x) \\ &= \lim_{\varepsilon\to 0}\lim_{m\to\infty}\sum_{l=1}^{m}\left(e^{ikx_l} - 1 - \frac{ikx_l}{1+x_l^2}\right)\frac{1+x_l^2}{x_l^2}(G(x_l) - G(x_{l-1})). \end{aligned} \tag{4.169}$$

Thus $f(k)$ is the product of a Gaussian characteristic function and the limit of a product of Poisson characteristic functions, all of which are infinitely divisible. Therefore, $f(k)$ is infinitely divisible.

The quantities α and $G(x)$ can be obtained if we know $F_N(x)$, the distribution function associated with $(f(k))^{1/N}$. Let us write

$$\begin{aligned} \ln f(k) &= \lim_{N\to\infty} N(f_N(k) - 1) \\ &= \lim_{N\to\infty}(ik\alpha_N + \int\left(e^{ikx} - 1 - \frac{ikx}{1+x^2}\right)\frac{1+x^2}{x^2}dG_N(x). \end{aligned} \tag{4.170}$$

But $N(f_N(k) - 1) = N\int_{-\infty}^{\infty}(e^{ikx} - 1)dF_N(x)$, so that

$$\alpha_N = N\int_{-\infty}^{\infty}\frac{x}{1+x^2}dF_N(x) \quad \text{and} \quad dG_N(x) = \frac{Nx^2}{1+x^2}dF_N(x). \tag{4.171}$$

■ **EXERCISE 4.15.** Show that the characteristic function, $f(k) = [(1-b)/(1+a)][(1+ae^{ik})/(1-be^{-ik})](0 < a \leqslant b < 1)$ is *not* infinitely divisible.

Answer: Note that

$$\begin{aligned}\ln(f(k)) &= \ln(1-b) + \ln(1+ae^{ik}) - \ln(1+a) - \ln(1-be^{-ik}) \\ &= \sum_{n=1}^{\infty}\left[\frac{b^n}{n}(e^{-ink}-1) + (-1)^{n+1}\frac{a^n}{n}(e^{ink}-1)\right] \\ &\equiv i\alpha k + \int_{-\infty}^{\infty}(e^{-iku}-1)\frac{1+u^2}{u^2}dG(u) - ik\int_{-\infty}^{\infty}\frac{1}{u}dG(u).\end{aligned}$$

We can satisfy the above equation if we let

$$G(u) = \sum_{n=1}^{\infty}\left[\frac{nb^n}{1+n^2}\Theta(u+n) - (-1)^n\frac{na^n}{1+n^2}\Theta(u-n)\right]$$

and

$$\alpha = -\sum_{n=1}^{\infty}\left(\frac{b^n + (-1)^n a^n}{1+n^2}\right).$$

But $G(u)$ is not a monotonically increasing function of u. Therefore, $f(k)$ is not infinitely divisible.

It is easy to see that for the Gaussian characteristic function, Eq. (4.123), $\alpha = a$ and $G(x) = \sigma_Y^2\Theta(x)$. For the Poisson characteristic function, Eq. (4.126), $\alpha = a + \lambda h/(1+h^2)$ and $G(x) = \lambda h^2/(1+h^2)\Theta(x-h)$. For the Cauchy characteristic function, Eq. (4.130), $\alpha = b$ and $G(x) = (a/\pi)\tan^{-1}(x) + (a/2)$.

▶ S4.E.2. Kolmogorov Formula [6, 20]

Kolmogorov was the first to find a general formula for infinitely divisible distributions, although his formula only applies to distributions *with finite variance*. He obtained

$$f_Y(k) = \exp\left[i\gamma k + \int_{-\infty}^{\infty}\{e^{iku} - 1 - iku\}\frac{1}{u^2}dK(u)\right], \tag{4.172}$$

where γ is a constant and the function $K(u)$ [whose differential, $dK(u)$, appears in Eq. (4.172)] is a nondecreasing function with bounded variation. Note that $\lim_{k\to 0}(df/dk) = i\gamma$ and $\lim_{k\to 0}(d^2f/dk^2) = -\gamma^2 - K(\infty)$. Thus the first moment is $\langle y\rangle = \gamma$ and the standard deviation $\sigma = \sqrt{K(\infty)}$. Equation (4.172) is called *Kolmogorov's formula* and it is unique.

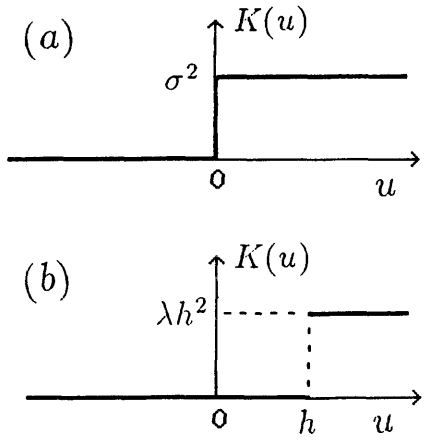


Fig. 4.18. Plots of $K(u)$ for (a) the Gaussian distribution and (b) the Poisson distribution.

The Kolmogorov formula can be obtained from the Levy–Khintchine formula if we let $K(x) = \int_{-\infty}^{x}(1+y^2)dG(y)$ and $\gamma = \alpha + \int_{-\infty}^{\infty} ydG(y)$. If we compare Eq. (4.172) to the characteristic function for a Poisson distribution [cf. Eq. (4.126)], the function $K(u)$ is proportional to the distribution function of spacings between realizations of the stochastic variable, Y (spacings between discrete jumps in $F_Y(x)$). For example, for the Poisson distribution, $K(u) = \lambda h^2 \Theta(u-h)$ and $dK(u) = \lambda h^2 \delta(u-h)$. For the Gaussian distribution, Eq. (4.123), the realizations of Y form a continuum (zero spacing between realizations) and $K(u) = \sigma_Y^2 \Theta(u)$ (we plot $K(u)$ for the Gaussian and Poisson distributions in Fig. 4.18). The Kolmogorov formula does not apply to the Cauchy distribution, since the Cauchy distribution has infinite variance.

■ **EXERCISE 4.16.** Consider the characteristic function, $f(k) = (1-b)/(1-b^{ik})(0<b<1)$ (cf. Exercise 4.15). Find the Kolmogorov function, $K(u)$.

Answer: First note that

$$\ln f(k) = \sum_{m=1}^{\infty} \frac{b^m}{m}(e^{ikm}-1) = ik\sum_{m=1}^{\infty} b^m + \sum_{m=1}^{\infty}\frac{b^m}{m} + \sum_{m=1}^{\infty}\frac{b^m}{m}(e^{ikm}-1-ikm)$$

$$= ik\frac{b}{(1-b)} + \sum_{m=1}^{\infty}\frac{b^m}{m}(e^{ikm}-1-ikm).$$

By comparison with Eq. (4.172), we find $dK(u) = \sum_{m=1}^{\infty} mb^m \delta(u-m)$ and $K(u) = \sum_{m=1}^{\infty} mb^m \Theta(u-m)$. Thus, $\gamma = b/(1-b)$ and $\sigma^2 = \sum_{m=1}^{\infty} mb^m = b/(1-b)^2$. Furthermore, $K(u)$ is a nondecreasing function of u and has bounded variation. Thus, conditions of Kolmogorov's formula are satisfied and $f(k)$ is an infinitely divisible characteristic function.

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PROBLEMS

Problem 4.1. A bus has nine seats facing forward and eight seats facing backward. In how many ways can seven passengers be seated if two refuse to ride facing forward and three refuse to ride facing backward?

Problem 4.2. Find the number of ways in which eight persons can be assigned to two rooms (A and B) if each room must have at least three persons in it.

Problem 4.3. Find the number of permutations of the letters in the word MONOTONOUS. In how many ways are four O's together? In how many ways are (only) 3 O's together?

Problem 4.4. In how many ways can five red balls, four blue balls, and four white balls be placed in a row so that the balls at the ends of the row are the same color?

Problem 4.5. Three coins are tossed. (a) Find the probability of getting *no* heads. (b) Find the probability of getting *at least one head.* (c) Show that the event "heads on the first coin" and the event "tails on the last two coins" are independent. (d) Show that the event "only two coins heads" and the event "three coins heads" are dependent and mutually exclusive.

Problem 4.6. Various six digit numbers can be formed by permuting the digits 666655. All arrangements are equally likely. Given that a number is even, what is the probability that two fives are together? (*Hint*: You must find a conditional probability.)

Problem 4.7. Fifteen boys go hiking. Five get lost, eight get sunburned, and six return home without problems. (a) What is the probability that a sunburned boy got lost? (b) What is the probability that a lost boy got sunburned?

Problem 4.8. A stochastic variable X can have values $x = 1$ and $x = 3$. A stochastic variable Y can have values $y = 2$ and $y = 4$. Denote the joint probability density $P_{X,Y}(x, y) = \sum_{i=1,3} \sum_{j=2,4} p_{ij} \delta(x - i)\delta(y - j)$. Compute the covariance of X and Y for the following two cases: (a) $p_{1,2} = p_{1,4} = p_{3,2} = p_{3,4} = \frac{1}{4}$ and (b) $p_{1,2} = p_{3,4} = 0$ and $p_{1,4} = p_{3,2} = \frac{1}{2}$. For each case, decide if X and Y are independent.

Problem 4.9. The stochastic variables X and Y are independent and Gaussian distributed with first moment $\langle x \rangle = \langle y \rangle = 0$ and standard deviations $\sigma_X = \sigma_Y = 1$. Find the characteristic function for the random variable $Z = X^2 + Y^2$, and compute the moments $\langle z \rangle, \langle z^2 \rangle$, and $\langle z^3 \rangle$. Find the first three cumulants.

Problem 4.10. A die is loaded so that even numbers occur three times as often as odd numbers. (a) If the die is thrown $N = 12$ times, what is the probability that odd numbers occur three times? If it is thrown $N = 120$ times, what is the probability that odd numbers occur thirty times? Use the binomial distribution. (b) Compute the same quantities as in part (a) but use the Gaussian distribution. [Note: For parts (a) and (b) compute your answers to four places.] (c) Compare answers for (a) and (b). Plot the binomial and Gaussian distributions for the case $N = 12$.

Problem 4.11. A book with 700 misprints contains 1400 pages. (a) What is the probability that one page contains 0 misprints? (b) What is the probability that one page contains 2 misprints?

Problem 4.12. Three old batteries and a resistor, R, are used to construct a circuit. Each battery has a probability p to generate voltage $V = v_0$ and has a probability $1 - p$ to generate voltage $V = 0$. Neglect any internal resistance in the batteries. Find the average power, $\langle V^2 \rangle / R$, dissipated in the resistor if (a) the batteries are connected in series and (b) the batteries are connected in parallel. In cases (a) and (b), what would be the average power dissipated if all batteries were certain to generate voltage $V = v_0$? (c) How would you realize the conditions and results of this problem in a laboratory?

Problem 4.13. Consider a random walk in one dimension. In a single step the probability of a displacement between x and $x + dx$ is given by

$$P(x)dx = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{(x-a)^2}{2\sigma^2}\right).$$

After N steps the displacement of the walker is $S = X_1 + \cdots + X_N$, where X_i is the displacement during the ith step. Assume the steps are independent of one another. After N steps, (a) what is the probability density for the displacement, S, of the walker and (b) what are the average displacement, $\langle S \rangle$, and the standard deviation of the walker?

Problem 4.14. Consider a random walk in one dimension for which the walker at each step is equally likely to take a step with displacement anywhere in the interval $d - a \leqslant x \leqslant d + a$, where $a < d$. Each step is independent of the others. After N steps the walker's displacement is $S = X_1 + \cdots + X_N$, where X_i is the displacement during the ith step. After N steps, (a) what is the average displacement, $\langle S \rangle$, and (b) what is his standard deviation?

Problem 4.15. Consider a random walk for which the probability of taking of step of length, $x \to x + dx$, is given by $P(x)dx = \frac{1}{\pi}(a/(x^2 + a^2))dx$. Find the probability density for the displacement of the walker after N steps. Does it satisfy the Central Limit Theorem? Should it?

Problem S4.1. Consider a random walk on an infinite one dimensional ($d = 1$) lattice where the walker starts at site $l = 0$. (a) Compute the generating functions $U(z, l)$ and $V(z, l)$. (b) Compute the probability to reach site, l, during the random walk. (c) Compute the probability that the walker reaches site $l = 0$ and site $l = 1$ after $s = 3$ and after $s = 4$ steps. Compute the probability that the walker reaches sites $l = 0$ and site $l = 1$ *for the first time* after $s = 3$ and after $s = 4$ steps. (d) Compute the average number of steps needed to reach site, $l = 1$, during the random walk. Explain your result.

Problem S4.2. Consider a random walk along *nearest neighbors* on an infinite, periodic face centered two-dimensional ($d = 2$) square lattice. A unit cell is shown in Fig. 4.19. Assume that the lattice spacing is $a = 2$ and that the walker starts at site $l_1 = 0, l_2 = 0$. (a) By counting paths (draw them), find the probability, $P_4(\mathbf{0})$, that the walker returns to the origin after four steps. Find the probability, $Q_4(\mathbf{0})$, that the walker returns to the origin *for the first time* after four steps. (b) Compute the generating function, $U(z, 0)$. Use this result to compute $P_4(\mathbf{0})$ and $Q_4(\mathbf{0})$. (c) Compute the escape probability.

Problem S4.3. Consider a random walk along *nearest neighbors* on an infinite, periodic body-centered three-dimensional ($d = 3$) cubic lattice. A unit cell is shown in Fig. 4.20. Assume that the lattice spacing is $a = 2$ and that the walker starts at site,

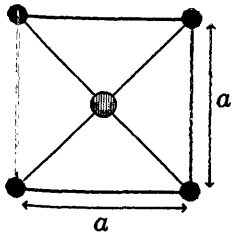


Fig. 4.19. Unit cell for a face-centered square lattice.

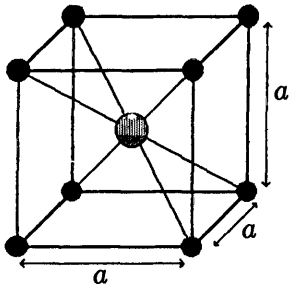


Fig. 4.20. Unit cell for a body-centered cubic lattice.

$(l_1 = 0, l_2 = 0, l_3 = 0)$. Compute the generating function. $U(1,0)$, and the escape probability. [*Hint*: Make a change of variables, $x_i = \tan(\phi_i/2)$. Then change to spherical coordinates, $x_1 = r\sin(\theta)\cos(\phi), x_2 = r\sin(\theta)\sin(\phi)$, and $x_1 = r\cos(\theta)$. Replace the integration over r by an integration over t, where $t = r\sin(\theta)\sqrt{\frac{1}{2}\cos(\theta)\sin(\frac{\phi}{2})}$. The three integrations over t, θ, and ϕ then separate.]

Problem S4.4. Consider a Rayleigh–Pearson random walk in which the walker has a probability $P(r)dr = rdr/(1+r^2)^{3/2}$ to take a step of length $r \to r + dr$. If the walker starts at the origin, compute the probability $P_N(R)$ to find the walker within a circle of radius R after N steps.

Problem S4.5. A stochastic variable X has characteristic function $f_X(k) = 1/(1+k^2)$. (a) Compute the probability density, $P_X(x)$, the average, $\langle x \rangle$, and variance. (b) Write Kolmogorov's formula for this characteristic function. What is $K(u)$? Is the stochastic variable X infinitely divisible?

Problem S4.6. Consider the gamma distribution function for stochastic variable X:

$$F(x) = \left(\frac{1}{2}\right)^{n/2} \frac{1}{\Gamma(n/2)} \int_0^x dy y^{(n/2)-1} e^{-y/2} \qquad \text{for} \quad x > 0$$

and $F(x) = 0$ for $x < 0$ (n is an integer). (a) Find the characteristic function for this distribution. (b) Write the Levy–Khintchine formula for the characteristic function. That is, find α and $G(x)$. Is X infinitely divisible? [*Hint*: First find $F_N(x)$ and use it to find $G_N(x)$ and take the limit.]

5

STOCHASTIC DYNAMICS AND BROWNIAN MOTION

5.A. INTRODUCTION

Now that we have reviewed some of the basic ideas of probability theory (cf. Chapter 4), we will begin to study more complicated situations in which probability can evolve in time. In Chapter 4 we already considered some simple random walks which are elementary stochastic processes that can be built from repeated application of the same transition process at discrete time intervals. In this chapter we will derive differential equations of motion for the evolution of probability distributions and densities in time. The level at which we discuss this time evolution is phenomenological because we will not concern ourselves with the relation of these equations to Newtonian mechanics. That will be the subject of Chapter 6. Also, in this chapter we will limit ourselves to Markov processes, which are stochastic processes with a very limited memory of previous events.

The equation which governs the stochastic dynamics of Markov processes is the *master equation.* It is one of the most important equations in statistical physics because of its almost universal applicability. It has been applied to problems in chemistry, biology, population dynamics, laser physics, Brownian motion, fluids, and semiconductors, to name a few cases. As a system of stochastic variables evolves in time, transitions occur between various realizations of the stochastic variables. Because of these transitions, the probability of finding the system in a given state changes until the system reaches a final steady state in which transitions cannot cause further changes in the probability distribution (it can happen that the system never reaches a steady state, but we will be most concerned with cases for which it can). To derive the master equation, we must assume that the probability of each transition depends only on the preceding step and not on any previous history. This assumption applies to many different types of physical system found in nature.

One of the simplest types of Markov processes that we will consider is the Markov chain. Markov chains are processes in which transitions occur between realizations of discrete stochastic variables at discrete times, as in the case for

the random walks we treated in Chapter 4 using simple probability theory. In this chapter we will formulate such problems in a more elegant manner. We will get a very good picture of how stochastic systems can decay to a unique steady state for the case in which the transition matrix is "regular" and we can introduce the concept of *ergodicity*, which we shall come back to in Chapter 6. The dynamics of Markov chains is totally governed by a "transition matrix" which is real and generally is nonsymmetric. We shall show how the stochastic dynamics can be expressed in terms of a spectral decomposition of the probability in terms of the left and right eigenvectors of the transition matrix.

If the time interval between events can vary in a continuous manner, then we must introduce the *master equation* which is a differential difference equation governing the time evolution of the probability. For the very special case when the transition rate between realizations exhibits *detailed balance*, solutions of the master equation can also be expressed in terms of a spectral decomposition. Detailed balance holds for many types of systems which are near thermal equilibrium or do not have internal probability currents as they reach the long time state. Some examples for which detailed balance holds can include chemical reactions near equilibrium, electronic transitions, and some random walks. The master equation for birth–death processes, which include chemical reactions and population dynamics, is derived in the section on *special topics*.

One often encounters systems with many degrees of freedom but for which a few of the degrees of freedom evolve on a much slower time scale than the others. An example of this is Brownian motion, in which a relatively massive particle, such as a grain of pollen, is immersed in a fluid, such as water. The grain of pollen is observed to undergo rapid, apparently random, agitated motion. Brownian motion, which was first made popular by the work of biologist Robert Brown, was used by Einstein as evidence of the atomic nature of matter. Indeed, it only occurs because of the discrete particulate nature of matter. A phenomenological theory of this motion can be obtained by writing Newton's equation of motion for the massive particle and including in it a systematic friction force and a random force to mimic the effects of the many degrees of freedom of the fluid in which the massive particle is immersed. This gives rise to the Langevin equation of motion for the massive particle.

Given a Langevin equation for a Brownian motion process, we can obtain an equation for time evolution of the probability distribution in phase space of the Brownian particle, called the Fokker–Planck equation. In the sections devoted to *special topics* we will derive the Fokker–Planck equation and we will solve it for Brownian motion with one spatial degree of freedom in the presence of strong friction. We shall also mention the interesting connection of Fokker–Planck dynamics to chaos theory when one considers more than one spatial degree of freedom. For cases in which the master equation cannot be solved exactly, it can sometimes be approximated by a Fokker–Planck equation. We will discuss some of those cases in this chapter. In later chapters we will use the concepts developed here to describe other types of Brownian motion in many body systems.

5.B. GENERAL THEORY [1–4]

Let us consider a system whose properties can be described in terms of a single stochastic variable Y. Y could denote the velocity of a Brownian particle, the number of particles in a box, or the number of people in a queue, to name a few of many possibilities.

We will use the following notation for the probability density for the stochastic variable Y:

$$P_1(y_1, t_1) \equiv \text{(the probability density that the stochastic variable } Y \text{ has value } y_1 \text{ at time } t_1); \tag{5.1}$$

$$P_2(y_1, t_1; y_2, t_2) \equiv \text{(the joint probability density that the stochastic variable } Y \text{ has value } y_1 \text{ at time } t_1 \text{ and } y_2 \text{ at time } t_2); \tag{5.2}$$

$$P_n(y_1, t_1; y_2, t_2; \ldots; y_n, t_n) \equiv \text{(the joint probability density that the stochastic variable } Y \text{ has value } y_1 \text{ at time } t_1, y_2 \text{ at time } t_2, \ldots, y_n \text{ at time } t_n. \tag{5.3}$$

The joint probability densities are positive:

$$P_n \geqslant 0; \tag{5.4}$$

they can be reduced:

$$\int P_n(y_1, t_1; y_2, t_2, ; \ldots; y_n, t_n) dy_n = P_{n-1}(y_1, t_1; y_2, t_2; \ldots; y_{n-1}, t_{n-1}); \tag{5.5}$$

and they are normalized:

$$\int P_1(y_1, t_1) dy_1 = 1. \tag{5.6}$$

In Eqs. (5.5) and (5.6) we have assumed that Y is a continuous stochastic variable. However, if Y is discrete we simply replace the integrations by summations. We can introduce time-dependent moments of the stochastic variables, $\langle y_1(t_1) y_2(t_2) \times \cdots \times y_n(t_n) \rangle$. They are defined as

$$\langle y_1(t_1) y_2(t_2) \cdots y_n(t_n) \rangle = \int\int y_1 y_2 \cdots y_n P_n(y_1, t_1; \ldots; y_n, t_n) dy_1 \cdots y_n \tag{5.7}$$

and give the correlation between values of the stochastic variable at different

times. A process is called *stationary* if

$$P_n(y_1, t_1; y_2, t_2; \ldots; y_n, t_n) = P_n(y_1, t_1 + \tau; y_2, t_2 + \tau; \ldots; y_n, t_n + \tau) \quad (5.8)$$

for all n and τ. Thus, for a stationary process

$$P_1(y_1, t_1) = P_1(y_1), \quad (5.9)$$

and $\langle y_1(t_1) y_2(t_2) \rangle$ depends only on $|t_1 - t_2|$—the absolute value of the difference in times. All physical processes in equilibrium are stationary.

We shall also introduce a conditional probability:

$$P_{1|1}(y_1, t_1 \,|\, y_2, t_2) = \text{(the conditional probability density for the stochastic variable } Y \text{ to have value } y_2 \text{ at time } t_2 \text{ given that it had value } y_1 \text{ at time } t_1) \quad (5.10)$$

It is defined by the identity

$$P_1(y_1, t_1) P_{1|1}(y_1, t_1 \,|\, y_2, t_2) = P_2(y_1, t_1; y_2, t_2). \quad (5.11)$$

Combining Eqs. (5.5) and (5.11) we obtain the following relation between the probability densities at different times:

$$P_1(y_2, t_2) = \int P_1(y_1, t_1) P_{1|1}(y_1, t_1 \,|\, y_2, t_2) dy_1 \quad (5.12)$$

where the conditional probability $P_{1|1}(y_1, t_1 \,|\, y_2, t_2)$ has the property

$$\int P_{1|1}(y_1, t_1 \,|\, y_2, t_2) dy_2 = 1, \quad (5.13)$$

as can be demonstrated easily.

We can also introduce a joint conditional probability density as follows:

$$P_{k|l}(y_1, t_1; \ldots; y_k, t_k \,|\, y_{k+1}, t_{k+1}, ; \ldots; y_{k+l}, t_{k+l}) = \text{(the joint conditional probability density that the stochastic variable } Y \text{ has values } (y_{k+1}, t_{k+1}; \ldots; y_{k+l}, t_{k+l}) \text{ given that } (y_1, t_1; \ldots; y_k, t_k) \text{ are fixed).} \quad (5.14)$$

The joint conditional probability density is defined as

$$P_{k|l}(y_1, t_1; \ldots; y_k, t_k \,|\, y_{k+1}, t_{k+1}; \ldots; y_{k+l}, t_{k+l}) = \frac{P_{k+1}(y_1, t_1; \ldots; y_k, t_k; y_{k+1}, t_{k+1}; \ldots; y_{k+l}, t_{k+l})}{P_k(y_1, t_1; \ldots; y_k, t_k)}. \quad (5.15)$$

The joint probability densities are important when there are correlations between values of the stochastic variable at different times—that is, if the stochastic variable has some memory of its past. However, if the stochastic variable has memory only of its immediate past, then the expressions for the joint probability densities and the joint probability densities simplify considerably.

If the stochastic variable has memory only of its immediate past, the joint conditional probability density $P_{n-1|1}(y_1, t_1; \ldots; y_{n-1}, t_{n-1}|y_n, t_n)$, where $t_1 < t_2 < \cdots < t_n$, must have the form

$$P_{n-1|1}(y_1, t_1; \ldots; y_{n-1}, t_{n-1}|y_n, t_n) = P_{1|1}(y_{n-1}, t_{n-1}|y_n, t_n). \tag{5.16}$$

That is, the conditional probability density for y_n at t_n is fully determined by the value of y_{n-1} at t_{n-1} and is not affected by any knowledge of the stochastic variable Y at earlier times. The conditional probability density $P_{1|1}(y_1, t_1|y_2, t_2)$ is called the *transition probability.* A process for which Eq (5.16) is satisfied is called a *Markov process.* A Markov process is fully determined by the two functions $P_1(y,t)$ and $P_{1|1}(y_1, t_1|y_2, t_2)$. The whole hierarchy of probability densities can be constructed from them. For example,

$$\begin{aligned} P_3(y_1, t_1; y_2, t_2; y_3, t_3) &= P_2(y_1, t_1; y_2, t_2)P_{2|1}(y_1, t_1; y_2, t_2|y_3, t_3) \\ &= P_1(y_1, t_1)P_{1|1}(y_1, t_1|y_2, t_2)P_{1|1}(y_2, t_2|y_3, t_3). \end{aligned} \tag{5.17}$$

If we integrate Eq. (5.17) over y_2 assuming $t_1 < t_2 < t_3$, we obtain

$$P_2(y_1, t_1; y_3, t_3) = P_1(y_1, t_1) \int P_{1|1}(y_1, t_1|y_2, t_2)P_{1|1}(y_2, t_2|y_3, t_3)dy_2. \tag{5.18}$$

If we now divide Eq. (5.18) by $P_1(y_1, t_1)$, we obtain

$$P_{1|1}(y_1, t_1|y_3, t_3) = \int P_{1|1}(y_1, t_1|y_2, t_2)P_{1|1}(y_2, t_2|y_3, t_3)dy_2. \tag{5.19}$$

Equation (5.19) is called the *Chapman–Kolmogorov equation.* Notice that we have broken the probability of transition from y_1, t_1 to y_3, t_3 into a process involving two successive steps, first from y_1, t_1, to y_2, t_2 and then from y_2, t_2 to y_3, t_3. The Markov character is exhibited by the fact that the probability of the two successive steps is the product of the probability of the individual steps. The successive steps are statistically *independent.* The probability of the transition $y_2, t_2 \to y_3, t_3$ is not affected by the fact that it was preceded by a transition $y_1, t_1 \to y_2, t_2$.

In the next section we will use these equations to study some of the simplest Markov processes, namely those of Markov chains.

5.C. MARKOV CHAINS [2–6]

One of the simplest examples of a Markov process is that of a Markov chain. This involves transitions, at discrete times, between values of a discrete stochastic variable, Y. Let us assume that Y has realizations $\{y(n)\}$, where $n = 1, 2, \ldots, M$, and that transitions occur at times $t = s\tau$, where $s = 0, 1, \ldots, \infty$. We let $P(n, s)$ denote the probability that Y has realization, $y(n)$, at "time" $t = s$. We let $P_{1|1}(n_1, s_1 | n_2, s_2)$ denote the conditional probability that Y has realization $y(n_2)$ at time s_2, given that it had realization $y(n_1)$ at time s_1. The two quantities $P(n, s)$ and $P_{1|1}(n_1, s_1 | n_2, s_2)$ completely determine the evolution of a Markov chain.

We can write Eq. (5.12) for the probability $P(n, s)$ in the form

$$P(n, s+1) = \sum_{m=1}^{M} P(m, s) P_{1|1}(m, s | n, s+1) \tag{5.20}$$

and from the Chapman–Kolmogorov equation, (5.19), we can write the conditional probability in the form

$$P_{1|1}(n_0, s_0 | n, s+1) = \sum_{m=1}^{M} P_{1|1}(n_0, s_0 | m, s) P_{1|1}(m, s | n, s+1). \tag{5.21}$$

The quantity $P_{1|1}(m, s | n, s+1)$ is called the *transition probability.* It is the conditional probability that if the system is in state m at time s, it will jump to state n in the next step. It therefore contains all necessary information about the basic transition mechanism in the system.

Let us now introduce the transition matrix $\mathbf{Q}(s)$, whose (m, n)th element is the transition probability

$$Q_{m,n}(s) \equiv P_{1|1}(m, s | n, s+1). \tag{5.22}$$

In this section we will consider Markov chains for which the transition matrix is independent of time, $\mathbf{Q}(s) = \mathbf{Q}$. In Section S5.A, we consider the case when the transition matrix depends periodically on time $\mathbf{Q}(s) = \mathbf{Q}(s+N)$.

5.C.1. Spectral Properties

For the case of a time-independent transition matrix, we have

$$\mathbf{Q}_{m,n} = P_{1|1}(m, 0 | n, 1) = P_{1|1}(m, s | n, s+1). \tag{5.23}$$

The formal solution of Eq. (5.21) for the conditional probability can be obtained by iteration and is given by

$$P_{1|1}(m, s_0 | n, s) = (\mathbf{Q}^{s-s_0})_{m,n}, \tag{5.24}$$

where the right-hand side denotes the (m, n)th element of the matrix $\mathbf{Q}$ raised to the $s - s_0$ power. The probability $P(n, s)$ is given by

$$P(n, s) = \sum_{m=1}^{M} P(m, 0)(\mathbf{Q}^s)_{m,n}. \tag{5.25}$$

It is useful at this point to introduce Dirac vector notation. We will let $P(n, s) \equiv \langle \mathbf{p}(s) | n \rangle$, and $P_{1|1}(m, s_0 | n, s) \equiv \langle m | \mathbf{P}(s_0 | s) | n \rangle$. Here $\langle \mathbf{p}(s) |$ is the probability vector and $\mathbf{P}(s_0 | s)$ is the conditional probability matrix. The left and right states, $\langle n |$ and $| n \rangle$ respectively, denote the possible realizations of the stochastic variable Y and are assumed to be complete, $\sum_{n=1}^{M} | n \rangle \langle n | = 1$, and orthonormal, $\langle m | n \rangle = \delta_{m,n}$. The probability $P(n, s) \equiv \langle \mathbf{p}(s) | n \rangle$ can be thought of as the nth component of a row vector. We shall now express $\mathbf{P}(s_0 | s)$ and $\langle \mathbf{p}(s) |$ in terms of eigenstates of the transition matrix, $\mathbf{Q}$.

The transition matrix, $\mathbf{Q}$, in general is not a symmetric matrix. Therefore, the right and left eigenvectors of $\mathbf{Q}$ will be different. The eigenvalues, λ_i $(i = 1, \ldots, M)$, of $\mathbf{Q}$ are given by values of λ which satisfy the condition that the determinant of the matrix, $\mathbf{Q} - \lambda \mathbf{I}$, be zero. That is,

$$\det | \mathbf{Q} - \lambda \mathbf{I} | = 0 \tag{5.26}$$

($\mathbf{I}$ is the unit matrix). If $\mathbf{Q}$ is an $M \times M$ matrix, it will have M eigenvalues, which may or may not all be real. Corresponding to the ith eigenvalue, there will be a left eigenstate, $\langle \chi_i |$, and a right eigenstate, $| \psi_i \rangle$. The left eigenstate satisfies the eigenvalue equation, $\langle \chi_i | \lambda_i = \langle \chi_i | \mathbf{Q}$, or

$$\chi_i(n) \lambda_i = \sum_{m=1}^{M} \chi_i(m) Q_{m,n}, \tag{5.27}$$

where $\chi_i(n) \equiv \langle \chi_i | n \rangle$ and $Q_{m,n} \equiv \langle m | \mathbf{Q} | n \rangle$. The right eigenstate satisfies the eigenvalue equation, $\lambda_i | \psi_i \rangle = \mathbf{Q} | \psi_i \rangle$, or

$$\lambda_i \psi_i(n) = \sum_{m=1}^{M} Q_{n,m} \psi_i(m), \tag{5.28}$$

where $\psi_i(n) \equiv \langle n | \psi_i \rangle$.

We can prove that the left and right eigenvectors of $\mathbf{Q}$ are complete and orthogonal. Let us first prove *orthogonality*. Consider the eigenvalue equations $\lambda_j | \psi_j \rangle = \mathbf{Q} | \psi_j \rangle$ and $\langle \chi_i | \lambda_i = \langle \chi_i | \mathbf{Q}$. Multiply the first equation by $\langle \chi_i |$ and the second equation by $| \psi_j \rangle$, and subtract the first equation from the second. We get

$$(\lambda_i - \lambda_j) \langle \chi_i | \psi_j \rangle = \langle \chi_i | \mathbf{Q} | \psi_j \rangle - \langle \chi_i | \mathbf{Q} | \psi_j \rangle = 0. \tag{5.29}$$

Thus, if $\lambda_i \neq \lambda_j$, then $\langle \chi_i | \psi_j \rangle = 0$. If $\lambda_i = \lambda_j$, then $\langle \chi_i | \psi_i \rangle$ can be nonzero. We shall always normalize the left and right eigenvectors so that

$$\langle \chi_i | \psi_j \rangle = \delta_{i,j}. \tag{5.30}$$

Let us next consider *completeness*. Let us expand a probability vector $\langle \mathbf{p}|$, in terms of left eigenvectors so that $\langle \mathbf{p}| = \sum_{i=1}^{M} \alpha_i \langle \chi_i|$. We then multiply on the right by $|\psi_j\rangle$ and use the orthonormality condition, Eq. (5.30). We find $\alpha_j = \langle \mathbf{p}|\psi_j\rangle$ so that

$$\langle \mathbf{p}| = \sum_{i=1}^{M} \langle \mathbf{p}|\psi_i\rangle\langle \chi_i|$$

This expresses the completeness condition

$$\sum_{i=1}^{M} |\psi_i\rangle\langle \chi_i| = \mathbf{I} \tag{5.31}$$

for the left and right eigenstates.

We next obtain some general properties of the eigenvalues, λ_i. First, we will prove that $|\lambda_i| \leqslant 1$ for all i. To do this, first take the absolute value of Eq. (5.28), $|\lambda_i \psi_i(n)| = |\sum_{m=1}^{M} Q_{n,m}\psi_i(m)|$. Both λ_i and $\psi_i(n)$ are complex (or real) numbers while $Q_{m,n}$ is a real number. It is easy to show that $|\lambda_i\psi_i(n)| = |\lambda_i||\psi_i(n)|$. We next use the triangle inequality, $|\sum_{i=1}^{M} x_i| \leqslant \sum_{i=1}^{M} |x_i|$, where x_i is a complex number. Thus, we find

$$|\lambda_i||\psi_i(n)| \leqslant \sum_{m=1}^{M} Q_{n,m}|\psi_i(m)|. \tag{5.32}$$

Let us assume that $|\psi_i(n)| \leqslant C$ for all n, where C is a positive constant. Then

$$\sum_{m=1}^{M} Q_{n,m}|\psi_i(m)| \leqslant C\sum_{m=1}^{M} Q_{n,m} = C. \tag{5.33}$$

Assume that for $n = n_0$, $|\psi_i(n_0)| = C$. Then Eqs. (5.32) and (5.33) give $|\lambda_i|C \leqslant C$ and

$$|\lambda_i| \leqslant 1. \tag{5.34}$$

Thus, all eigenvalues of the transition matrix have a magnitude less than or equal to one.

Now that we have established that $|\lambda_i| \leqslant 1$, we can also prove that $\lambda_i = 1$ is always an eigenvalue. Let us first note that the particular choice, $\psi_i(n) = 1$ for

all n, is a right eigenvector with eigenvalue, $\lambda_i = 1$ [cf. Eq. (5.28) and note that $\sum_{m=1}^{M} Q_{nm} = 1$]. The corresponding left eigenvector, $\langle \chi_i |$, with eigenvalue, $\lambda_i = 1$, must satisfy the eigenvalue equation

$$\chi_i(n) = \sum_{m=1}^{M} \chi_i(m) Q_{m,n}. \tag{5.35}$$

Equation (5.35) is the equation for a stationary probability vector, $\chi_i(n) \equiv P_{ST}(n)$—that is, one that does not change with time.

We can expand the transition matrix, $\mathbf{Q}$, in terms of its left and right eigenvectors. Consider the left eigenvalue equation, $\langle \chi_i | \lambda_i = \langle \chi_i | \mathbf{Q}$. Multiply from the left by the right eigenstate, $|\psi_i\rangle$, and sum over i. If we use the completeness relation, Eq. (5.31), we obtain $\mathbf{Q} = \sum_{i=1}^{M} \lambda_i |\psi_i\rangle\langle\chi_i|$ or

$$Q_{m,n} = \sum_{i=1}^{M} \lambda_i \psi_i(m) \chi_i(n). \tag{5.36}$$

If we now combine Eqs. (5.24) and (5.36) and use the orthonormality of the left and right eigenvectors, we obtain

$$P_{1|1}(m, s_0 | n, s) = \sum_{i=1}^{M} \lambda_i^{s-s_0} \psi_i(m) \chi_i(n). \tag{5.37}$$

Thus, we have obtained the general solution for the discrete Markov process in terms of the eigenvalues and left and right eigenvectors of the transition matrix $\mathbf{Q}$.

The detailed behavior of the conditional probability depends on the structure of the transition matrix. There is one case that we are particularly interested in, and that is the case when the transition matrix is regular. The transition matrix $\mathbf{Q}$ is called *regular* if all elements of some power $\mathbf{Q}^N$ (N an integer) are nonzero. If $\mathbf{Q}$ is regular, the probability $P(n, s)$ tends to a unique stationary state $P_{ST}(n)$ after a long time. This means that there will be only one eigenvalue of $\mathbf{Q}$ with eigenvalue $\lambda = 1$. Let us denote it $\lambda_1 = 1$. Then Eq. (5.37) can be written

$$P_{1|1}(m, s_0 | n, s) = \psi_1(m) P_{ST}(n) + \sum_{i=2}^{M} \lambda_i^{s-s_0} \psi_i(m) \chi_i(n), \tag{5.38}$$

where $\psi_1(m) = 1$ for all m. Since $\lambda_i < 1$ for $i \neq 1$, we can take the limit $s \to \infty$ and obtain

$$\lim_{s\to\infty} P_{1|1}(m, s_0 | n, s) = \psi_1(m) P_{ST}(n) \qquad \text{with } \psi_1(m) = 1 \text{ for all } m. \tag{5.39}$$

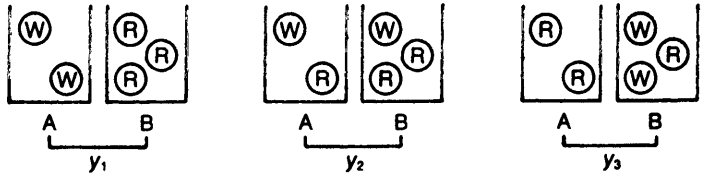
Thus, for regular transition matrices, the conditional probability tends to a unique value for long times. Similarly,

$$\lim_{s\to\infty} P(n, s) = P_{ST}(n). \tag{5.40}$$

In Exercise 5.1, we shall illustrate these ideas with an example.

Markov chains which are governed by regular transition matrices are *ergodic*. That is, it is possible, starting from any one realization of the stochastic variable, to reach every other realization through transitions during the evolution of the system. This is no longer true if, for example, the transition matrix is block-diagonal. Then some realizations will be decoupled from others. When the transition matrix is block-diagonal, the system can have multiple long-time states.

■ **EXERCISE 5.1.** Consider two pots, A and B, with three red balls and two white balls distributed between them so that A always has two balls and B always has three balls. There are three different configurations for the pots, as shown in the figure below. We obtain transitions between these three configurations by picking a ball out of A at random and one out of B at random and interchanging them. (a) Compute the transition matrix **Q** and the conditional probability $P_{1|1}(m, s_0|n, s)$. (b) If initially $P_i(1, 0) = 1$, $P_1(2, 0) = 0$, and $P_1(3, 0) = 0$, compute the probability $P_1(n, s)$ ($n = 1, 2,$ and 3) at time s. (c) Assume that the realization, $y(n) = n$. Compute the first moment, $\langle y(s)\rangle$, and the autocorrelation function, $\langle y(0)y(s)\rangle$, for the same initial conditions as in part (b).



Answer:

(**a**) Inspection shows that we can make the following transitions from y_i to y_j with transition probability, Q_{ij}, such that $Q_{11} = 0$, $Q_{12} = 1$, $Q_{13} = 0$, $Q_{21} = \frac{1}{6}$, $Q_{22} = \frac{1}{2}$, $Q_{23} = \frac{1}{3}$, $Q_{31} = 0$, $Q_{32} = \frac{2}{3}$, and $Q_{33} = \frac{1}{3}$. The transition matrix and its square are given by

$$\mathbf{Q} = \begin{pmatrix} 0 & 1 & 0 \\ \frac{1}{6} & \frac{1}{2} & \frac{1}{3} \\ 0 & \frac{2}{3} & \frac{1}{3} \end{pmatrix} \quad \text{and} \quad \mathbf{Q}^2 = \begin{pmatrix} \frac{1}{6} & \frac{1}{2} & \frac{1}{3} \\ \frac{1}{12} & \frac{23}{36} & \frac{10}{36} \\ \frac{1}{9} & \frac{20}{36} & \frac{1}{3} \end{pmatrix},$$

respectively. The transition matrix is regular so this system has a

unique long-time stationary state. The eigenvalues of $\mathbf{Q}$ are $\lambda_1 = 1$, $\lambda_2 = \frac{1}{6}$, and $\lambda_3 = -\frac{1}{3}$. The right eigenstates can be written

$$|\psi_1\rangle = \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}, \qquad |\psi_2\rangle = \begin{pmatrix} -\frac{3}{2} \\ -\frac{1}{4} \\ 1 \end{pmatrix}, \qquad |\psi_3\rangle = \begin{pmatrix} 3 \\ -1 \\ 1 \end{pmatrix}.$$

The left eigenstates can be written

$$\langle\chi_1| = \left(\tfrac{1}{10} \quad \tfrac{6}{10} \quad \tfrac{3}{10}\right), \qquad \langle\chi_2| = \left(-\tfrac{4}{15} \quad -\tfrac{4}{15} \quad \tfrac{8}{15}\right),$$
$$\langle\chi_3| = \left(\tfrac{1}{6} \quad -\tfrac{1}{3} \quad \tfrac{1}{6}\right).$$

We can now construct the conditional probability matrix

$$\mathbf{P}(s_0|s) = \sum_{i=1}^{3} \lambda_i^{s-s_0} |\psi_i\rangle\langle\chi_i| = \begin{pmatrix} \frac{1}{10} & \frac{6}{10} & \frac{3}{10} \\ \frac{1}{10} & \frac{6}{10} & \frac{3}{10} \\ \frac{1}{10} & \frac{6}{10} & \frac{3}{10} \end{pmatrix}$$
$$+ \left(\tfrac{1}{6}\right)^{s-s_0} \begin{pmatrix} \frac{2}{5} & \frac{2}{5} & -\frac{4}{5} \\ \frac{1}{15} & \frac{1}{15} & -\frac{2}{15} \\ -\frac{4}{15} & -\frac{4}{15} & \frac{8}{15} \end{pmatrix}$$
$$+ \left(-\tfrac{1}{3}\right)^{s-s_0} \begin{pmatrix} \frac{1}{2} & -1 & \frac{1}{2} \\ -\frac{1}{6} & \frac{1}{3} & -\frac{1}{6} \\ \frac{1}{6} & -\frac{1}{3} & \frac{1}{6} \end{pmatrix}.$$

Note that all the probabiliy is carried by the long-time state.

(b) Denote the probability vector as $\langle \mathbf{p}(s)| = (P(1, s), P(2, s), P(3, s))$. Then $\langle \mathbf{p}(s)| = \langle \mathbf{p}(0)|\mathbf{P}(0|s)$. If we assume an initial condition $\langle \mathbf{p}(0)| = (1, 0, 0)$, then the probability vector at time s is

$$\langle \mathbf{p}(s)| = \left\{ \left[\frac{1}{10} + \frac{2}{5}\left(\frac{1}{6}\right)^s + \frac{1}{2}\left(-\frac{1}{3}\right)^s\right], \left[\frac{3}{5} + \frac{2}{5}\left(\frac{1}{6}\right)^s - \left(-\frac{1}{3}\right)^s\right], \right.$$
$$\left. \left[\frac{3}{10} - \frac{4}{5}\left(\frac{1}{6}\right)^s + \frac{1}{2}\left(-\frac{1}{3}\right)^s\right] \right\}.$$

(c) The first moment is given by $\langle y(s)\rangle = \sum_{n=1}^{3} nP_1(n, s)$. From the expression for $\langle \mathbf{p}(s)|$ we obtain

$$\langle y(s)\rangle = \frac{11}{5} - \frac{6}{5}\left(\frac{1}{6}\right)^s.$$

Finally, we compute the autocorrelation function,

$$\langle y(0)y(s)\rangle = \sum_{m=1}^{3}\sum_{n=1}^{3} mnP_1(m, 0)P_{1|1}(m, 0|n, s).$$

We obtain

$$\langle y(0)y(s)\rangle = \frac{66}{5} + \frac{4}{5}\left(\frac{1}{6}\right)^s.$$

Note that the eigenvalue $\lambda_3 = -\frac{1}{3}$ does not contribute to $\langle y(s)\rangle$ and $\langle y(0)y(s)\rangle$. However, if we choose the dependence of $y(n)$ on n differently, it will, in general, contribute to these.

5.C.2. Random Walk

The problem of random walk on a lattice which was considered in Sections 4.E and 4.F can be formulated as a Markov chain of transition probabilities. For simplicity, let us consider random walk on an infinite one dimensional lattice with lattice spacing, Δ, along the x axis, and let us assume that the time between steps is τ. Let $P_1(n\Delta, s\tau)$ be the probability to find the particle at point $x = n\Delta$ after s steps. Then

$$P_1(n\Delta, (s+1)\tau) = \sum_{m=-\infty}^{\infty} P_1(m\Delta, s\tau) P_{1|1}(m\Delta, s\tau \,|\, n\Delta, (s+1)\tau), \quad (5.41)$$

where $P_{1|1}(m\Delta, s\tau|n\Delta, (s+1)\tau)$ is the transition probability to go from site $x = m\Delta$ to site $x = n\Delta$ in one step.

As a specific example, let us consider the case in which the random walker has an equal probability to go one lattice site to the left or right during each step. Then the transition probability is

$$P_{1|1}(m\Delta, s\tau \,|\, n\Delta, (s+1)\tau) = \tfrac{1}{2}\delta_{n,m+1} + \tfrac{1}{2}\delta_{n,m-1} \quad (5.42)$$

and Eq. (5.41) takes the form

$$P_1(n\Delta, (s+1)\tau) = \tfrac{1}{2}P_1((n+1)\Delta, s\tau) + \tfrac{1}{2}P_1((n-1)\Delta, s\tau). \quad (5.43)$$

We can obtain a differential equation for the probability $P_1(n\Delta, s\tau)$ in the continuum limit. Let us subtract $P_1(n\Delta, s\tau)$ from both sides of Eq. (5.43) and divide by τ. We then can write

$$\frac{P_1(n\Delta, s\tau + \tau) - P_1(n\Delta, s\tau)}{\tau} = \frac{\Delta^2}{2\tau}\left[\frac{P_1(n\Delta + \Delta, s\tau) + P_1(n\Delta - \Delta, s\tau) - 2P_1(n\Delta, s\tau)}{\Delta^2}\right]. \quad (5.44)$$

If we now let $x = n\Delta$, $t = s\tau$, and take the limit $\Delta \to 0$ and $\tau \to 0$ so that $D \equiv \Delta^2/2\tau$ is finite and x and t are finite, we obtain the following differential equation for $P(x,t)$:

$$\frac{\partial P_1(x,t)}{\partial t} = D\frac{\partial^2 P_1(x,t)}{\partial x^2.} \tag{5.45}$$

(cf. Egs. (4.62)–(4.64)). Equation (5.45) is a *diffusion equation* for the probability density $P_1(x,t)$.

Let us solve Eq. (5.45) for the case $P_1(x,0) = \delta(x)$. We first introduce the Fourier transform of $P_1(x, t)$:

$$\tilde{P}_1(k, t) = \int_{-\infty}^{\infty} dx\, P_1(x, t)e^{ikx}.$$

Then Eq. (5.45) takes the form

$$\frac{\partial \tilde{P}(k, t)}{\partial t} = -Dk^2\tilde{P}_1(k,t). \tag{5.47}$$

We can solve Eq. (5.47) to obtain

$$\tilde{P}(k, t) = e^{-Dk^2t}, \tag{5.48}$$

where we have used the fact that $\tilde{P}(k, 0) = 1$ since $P_1(x, 0) = \delta(x)$. We can now take the inverse transform to obtain

$$P_1(x, t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dk\, e^{-ikx}e^{-Dk^2t} = \frac{1}{\sqrt{4\pi Dt}}e^{-x^2/4Dt}. \tag{5.49}$$

It is easy to show that $\langle x(t)\rangle = 0$ and $\langle x^2(t)\rangle = 2Dt$.

5.D. THE MASTER EQUATION [3, 4]

We often need to consider processes for which the time interval between events can vary in a continuous and random manner, but as in Section 6.C the realizations of the stochastic variable Y are discrete. For such processes, we need to obtain a differential equation for the time dependence of the probability $P_1(n, t)$. In this section we consider processes for which the elementary events or transitions occur over a very short time interval compared to the time during which the stochastic process evolves. The time evolution of such processes is governed by the *master equation.*

5.D.1. Derivation of the Master Equation

To begin, let us rewrite Eq. (5.12) in the form

$$P_1(n, t+\Delta t) = \sum_{m=1}^{M} P_1(m, t) P_{1|1}(m, t \mid n, t+\Delta t). \tag{5.50}$$

The differential equation for $P_1(n, t)$ can be constructed from Eq. (5.50) if we note that

$$\begin{aligned} \frac{\partial P_1(n, t)}{\partial t} &\equiv \lim_{\Delta t \to 0} \left(\frac{P_1(n, t+\Delta t) - P_1(n, t)}{\Delta t} \right) \\ &= \lim_{\Delta t \to 0} \frac{1}{\Delta t} \sum_{m=1}^{M} P_1(m, t)(P_{1|1}(m, t \mid n, t+\Delta t) - \delta_{m,n}). \end{aligned} \tag{5.51}$$

Since we will take the limit $\Delta t \to 0$, we can expand the transition probability $P_{1|1}(m, t \mid n, t+\Delta t)$ in a power series in Δt and keep only the lowest-order term. In order to conserve probability at all times, its most general form is

$$P_{1|1}(m, t \mid n, t+\Delta t) = \delta_{m,n} \left[1 - \Delta t \sum_{l=1}^{M} w_{m,l}(t) \right] + w_{m,n}(t) \Delta t + \ldots, \tag{5.52}$$

where $w_{m,n}(t)$ is the *transition probability rate*. In Eq. (5.52), $w_{m,n}(t)\Delta t$ is the probability of a transition from state m to state n during the time interval $t \to t + \Delta t$. Similarly, $[1 - \sum_{l=1}^{M} w_{m,l}(t)\Delta t]$ is the probability that *no* transition occurs during the time interval $t \to t + \Delta t$. If we now substitute Eq. (5.52) into Eq. (5.51), we obtain

$$\frac{\partial P_1(n, t)}{\partial t} = \sum_{m=1}^{M} [P_1(m, t) w_{m,n}(t) - P_1(n, t) w_{n,m}(t))]. \tag{5.53}$$

Equation (5.53) is called the *master equation*. The master equation gives the rate of change of the probability $P_1(n, t)$ due to transitions into the state n from all others states (first term on the right) and due to transitions out of state n into all others states (second term on the right).

The conditional probability $P_{1|1}(n_0, 0 \mid n, t)$ also satisfies a master equation

$$\frac{\partial P_{1|1}(n_0, 0 \mid n, t)}{\partial t} = \sum_{m=1}^{M} [P_{1|1}(n_0, 0 \mid m, t) w_{m,n}(t) - P_{1|1}(n_0, 0 \mid n, t) w_{n,m}(t))], \tag{5.54}$$

where $P_{1|1}(n_0, 0|n, t)$ is the probability to find the system in the state n at time t, given that it was in the state n_0 at time $t = 0$. The conditional probability satisfies an initial condition $P_{1|1}(n_0, 0|n, 0) = \delta_{n,n_0}$.

The master equation can be written in a more concise form if we introduce the transition matrix

$$W_{m,n}(t) = w_{m,n}(t) - \delta_{m,n} \sum_{n'=1}^{M} w_{n,n'}(t). \tag{5.55}$$

The master equation then takes the form

$$\frac{\partial P_1(n, t)}{\partial t} = \sum_{m=1}^{M} P_1(m, t) W_{m,n}(t). \tag{5.56}$$

From Eq. (5.55), we see that the transition matrix must satisfy the conditions

$$W_{m,n} \geqslant 0 \text{ for } n \neq m \quad \text{and} \quad \sum_{n} W_{m,n} = 0 \qquad \text{for each } m. \tag{5.57}$$

Thus, the entries in the rows of $W_{m,n}$ must add to zero.

We can write Eq. (5.56) in still more concise form if we introduce Dirac notation. We let $P_1(n, t) = \langle \mathbf{p}(t) | n \rangle$, where $\langle \mathbf{p}(t) |$ is the probability vector, and $P_{1|1}(n_0, t_0|n, t) = \langle n_0 | \mathbf{P}(t_0|t) | n \rangle$, where $\mathbf{P}(t_0|t)$ is the conditional probability operator. Similarly we let $W_{m,n}(t) = \langle m | \mathbf{W}(t) | n \rangle$. The master equation for the probability vector becomes

$$\frac{\partial \langle \mathbf{p}(t) |}{\partial t} = \langle \mathbf{p}(t) | \mathbf{W}(t), \tag{5.58}$$

and the master equation for the conditional probability operator becomes

$$\frac{\partial \mathbf{P}(0|t)}{\partial t} = \mathbf{P}(0|t)\mathbf{W}(t), \tag{5.59}$$

The transition matrix, $W_{m,n}(t)$, in general is not symmetric so its left and right eigenvectors will be different. However, one can often use the method of Section 5.C.1 to obtain a spectral decomposition of $\mathbf{W}(t)$ and therefore of $\langle \mathbf{p}(t) |$ and $\mathbf{P}(0|t)$. However, care must be used. There may be cases where the eigenvectors of $\mathbf{W}(t)$ do not span the solution space [7]. Then the spectral decomposition cannot be used. There is one type of system for which a spectral decomposition can always be done, and that is the case for which the transition rates $w_{m,n}(t)$ satisfy detailed balance.

5.D.2. Detailed Balance [3, 4, 8]

The transition rates satisfy *detailed balance* if

$$P^s(n)w_{n,m} = P^s(m)w_{m,n}, \tag{5.60}$$

where $P^s(n) \equiv \lim_{t\to\infty} P_1(n, t)$ is the long-time stationary probability of the system (we assume the transition rates, $w_{m,n}$, are independent of time) and is independent of time. $P^{s](n)}$ is the left eigenvector of the transition matrix, $\mathbf{W}$, so that $\langle \mathbf{p}^s | \mathbf{W} = 0$ where $P^s(n) = \langle \mathbf{p}^s | n \rangle$. Equation (5.60) tells us that at equilibrium, the flow of probability into level n from level m is equal to the flow of probability from level m to level n. It is useful to note that the state, $P^s(n)$, can be obtained from Eq. (5.60) by iterating. For example, $P^s(2) = P^s(1)(w_{1,2}/w_{2,1})$, $P^s(3) = P^s(2)(w_{2,3}/w_{3,2}) = P^s(1)(w_{1,2}/w_{2,1})(w_{2,3}/w_{3,2})$ and so on. $P^s(1)$ can then be found by requiring that the probability be normalized to one, $\sum_{n=1}^{M} P^{s](n)=1}$.

Given Eq. (5.60), we can show that the dynamical evolution of the master equation is governed by a symmetric matrix. Let us define

$$\begin{aligned} V_{n,m} &= \sqrt{\frac{P^s(n)}{P^s(m)}} W_{n,m} = \sqrt{\frac{P^s(n)}{P^s(m)}} w_{n,m} - \delta_{n,m} \sum_{n'} w_{n,n'} \\ &= \sqrt{\frac{P^s(m)}{P^s(n)}} w_{m,n} - \delta_{n,m} \sum_{n'} w_{m,n'} = V_{m,n}, \end{aligned} \tag{5.61}$$

where we have used Eq. (5.60). If we now introduce a new function, $\tilde{P}(n, t) = P_1(n, t)/\sqrt{P^s(n)}$, the master equation takes the form

$$\frac{\partial \tilde{P}(n, t)}{\partial t} = \sum_{m=1}^{M} \tilde{P}(m, t) V_{m,n}. \tag{5.62}$$

Let us again use Dirac notation to write $\langle \tilde{\mathbf{p}}(t) | n \rangle = \tilde{P}(n, t)$ and $V_{n,m} = \langle n | \mathbf{V} | m \rangle$. Then the solution of the master equation becomes

$$\langle \tilde{\mathbf{p}}(t) | = \langle \tilde{\mathbf{p}}(0) | e^{\mathbf{V}t}. \tag{5.63}$$

Since $V_{n,m}$ is a symmetric matrix, it has a complete orthonormal set of eigenvectors. We shall denote the eigenvalues of $\mathbf{V}$ by λ_i and left and right eigenvectors by $\langle \psi_i |$ and $| \psi_i \rangle$, respectively, where $i = 0, \ldots, M-1$. The left and right eigenvectors are the same. Thus, $\langle \psi_i | \mathbf{V} = \langle \psi_i | \lambda_i$ and $\mathbf{V} | \psi_i \rangle = \lambda_i | \psi_i \rangle$. Since the eigenvectors form a complete orthonormal set, we can write orthonormality condition as $\langle \psi_i | \psi_j \rangle = \delta_{i,j}$ and the completeness condition as $\sum_{i=0}^{M-1} | \psi_i \rangle \langle \psi_i | = \mathbf{1}$.

The solution to the master equation can now be written in terms of a spectral decomposition

$$\langle \tilde{\mathbf{p}}(t)| = \sum_{i=0}^{M-1} \langle \tilde{\mathbf{p}}(0)|\psi_i\rangle e^{\lambda_i t}\langle \psi_i|. \tag{5.64}$$

In terms of the probability $P_1(n, t)$, it takes the form

$$P_1(n, t) = \sum_{i=0}^{M-1}\sum_{m=1}^{M} \sqrt{\frac{P^s(n)}{P^s(m)}}\, P_1(m, 0)\langle m|\psi_i\rangle e^{\lambda_i t}\langle \psi_i|n\rangle. \tag{5.65}$$

The eigenvalues λ_i must be negative or zero. Let $i = 0$ denote the zero eigenvalue, $\lambda_0 = 0$. Then

$$P^s(n) = \lim_{t\to\infty} P_1(n, t) = \sum_{m=1}^{M} \sqrt{\frac{P^s(n)}{P^s(m)}}\, P_1(m, 0)\langle m|\psi_0\rangle\langle \psi_0|n\rangle. \tag{5.66}$$

In order to be consistent we must have $\langle m|\psi_0\rangle = \langle \psi_0|m\rangle = \sqrt{P^s(m)}$, for all m, since $\sum_m P_1(m, 0) = 1$. Thus,

$$P_1(n, t) = P^s(n) + \sum_{i=1}^{M-1}\sum_{m=1}^{M} \sqrt{\frac{P^s(n)}{P^s(m)}}\, P_1(m, 0)\langle m|\psi_i\rangle e^{\lambda_i t}\langle \psi_i|n\rangle. \tag{5.67}$$

In Exercise 5.2 we give an example of a random walk which obeys detailed balance and in Exercise 5.3 we give an example of one that does not obey detailed balance.

■ **EXERCISE 5.2** Consider an asymmetric random walk on an open-ended lattice with four lattice sites. The transition rates are $w_{1,2} = w_{4,3} = 1, w_{2,3} = w_{3,4} = \frac{3}{4}, w_{2,1} = w_{3,2} = \frac{1}{4}$, and $w_{i,j} = 0$ for all other transitions. (a) Write the transition matrix, **W**, and show that this system obeys detailed balance. (b) Compute **V** and find its eigenvalues and eigenvectors. (c) Write $P_1(n, t)$ for the case $P_1(n, 0) = \delta_{n,1}$. What is $P_1(2, t)$?

Answer:

(a) The transition matrix, **W**, is given by

$$\mathbf{W} = \begin{pmatrix} -1 & 1 & 0 & 0 \\ \frac{1}{4} & -1 & \frac{3}{4} & 0 \\ 0 & \frac{1}{4} & -1 & \frac{3}{4} \\ 0 & 0 & 1 & -1 \end{pmatrix}.$$

It has eigenvalues $\lambda_0 = 0$, $\lambda_1 = -1 + \frac{\sqrt{3}}{4}$, $\lambda_2 = -2$, and $\lambda_3 = -1 - \frac{\sqrt{3}}{4}$. The left eigenvector of $\mathbf{W}$ with eigenvalue, $\lambda_0 = 0$, is the stationary probability distribution, $\langle \mathbf{p}^s | = (\frac{1}{26}, \frac{2}{13}, \frac{6}{13}, \frac{9}{26})$. This system satisfies detailed balance because $P^s(n)w_{n,n+1} = P^s(n+1)w_{n+1,n}$. For example, $P^s(1)w_{1,2} = (\frac{1}{26})(1) = \frac{1}{26}$ and $P^s(2)w_{2,1} = (\frac{2}{13})(\frac{1}{4}) = \frac{1}{26}$.

(b) The matrix $\mathbf{V}$ is given by

$$\mathbf{V} = \begin{pmatrix} -1 & \frac{1}{2} & 0 & 0 \\ \frac{1}{2} & -1 & \frac{\sqrt{3}}{4} & 0 \\ 0 & \frac{\sqrt{3}}{4} & -1 & \frac{\sqrt{3}}{2} \\ 0 & 0 & \frac{\sqrt{3}}{2} & -1 \end{pmatrix}.$$

It also has eigenvalues $\lambda_0 = 0$, $\lambda_1 = -1 + \frac{\sqrt{3}}{4}$, $y_2 = -2$, and $\lambda_3 = -1 - \frac{\sqrt{3}}{4}$. The orthonormalized eigenstates are

$$\langle \psi_0 | = \left(\sqrt{\frac{1}{26}}, \sqrt{\frac{2}{13}}, \sqrt{\frac{6}{13}}, \sqrt{\frac{9}{26}} \right) \approx (0.196, 0.392, 0.679, 0.588),$$

$$\langle \psi_1 | \approx (0.679, 0.588, -0.196, -0.392),$$

$$\langle \psi_2 | \approx (-0.196, 0.392, -0.679, 0.588),$$

and $\langle \psi_3 | \approx (-0.679, 0.588, 0.196, -0.392)$.

(c) For the initial condition, $P_1(n, 0) = \delta_{n,1}, P_1(n, t)$ can be written

$$P_1(n, t) = P(n)^s + \sum_{i=1}^{3} \sqrt{\frac{P^s(n)}{P^s(1)}} \langle 1 | \psi_i \rangle e^{\lambda_i t} \langle \psi_i | n \rangle.$$

Using the numbers from (b) we find

$$P_1(2, t) \approx 0.154 + (0.799)e^{-0.567t} - (0.154)e^{-2t} - (0.799)e^{-1.433t}.$$

Note that $P_1(2, 0) = 0$ as it should.

■ **EXERCISE 5.3** Consider an asymmetric random walk on a periodic lattice with four lattice sites. The transition rates are $w_{1,2} = w_{2,3} = w_{3,4} = w_{4,1} = \frac{3}{4}$, $w_{2,1} = w_{3,2} = w_{4,3} = w_{1,4} = \frac{1}{4}$, and $w_{i,j} = 0$ for all other transitions. Write the transition matrix, $\mathbf{W}$, and show that this system does not obey detailed balance.

Answer:

The transition matrix, $\mathbf{W}$, is given by

$$\mathbf{W} = \begin{pmatrix} -1 & \frac{3}{4} & 0 & \frac{1}{4} \\ \frac{1}{4} & -1 & \frac{3}{4} & 0 \\ 0 & \frac{1}{4} & -1 & \frac{3}{4} \\ \frac{3}{4} & 0 & \frac{1}{4} & -1 \end{pmatrix}.$$

The left eigenvector of $\mathbf{W}$ with eigenvalue, $\lambda_0 = 0$, is the stationary probability distribution, $\langle \mathbf{p}^s | = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. Therefore, detailed balance cannot be satisfied and we cannot find a symmetric matrix which governs the dynamics of this system. It is interesting that the long-time state is one for which it is equally likely to find the random walker at any lattice site. Yet because detailed balance is not satisfied, there is also a probability current around the lattice.

5.D.3. Mean First Passage Time [9]

One of the useful quantities we can compute is a *mean first passage time*. If we consider the random walk problem, the mean first passage time is the average time for the walker to reach some site, n_p, *for the first time* assuming that the walker started at site n_0 at time $t = 0$. Computing this quantity involves a trick. We will assume that $P_1(n_p, t) \equiv 0$ for all time. This way, if the walker steps on site n_p, it can never return to the random walk. This is called an *absorbing boundary condition* at site n_p.

To be clear about what we are doing, we will let $Q_n(t)$ denote the conditional probability to find the walker at site n, assuming that it starts at site n_0 at time $t = 0$ (we suppress its dependence on n_0 for simplicity). Then $Q_n(0) = \delta_{n,n_0}$ and $Q_{n_p}(t) = 0$ (the absorbing boundary condition). The equations of motion for $Q_n(t)$ are the same as for $P_1(n, t)$ [cf. Eqs. (5.55) and (5.56)], except that we set $Q_{n_p}(t) = 0$. Thus,

$$\frac{\partial Q_n(t)}{\partial t} = \sum_{m(\neq n_p)=1}^{M} Q_m(t) w_{m,n}(t) - Q_n(t) \sum_{m=1}^{M} w_{m,n}(t)) \qquad \text{for } n \neq n_p. \tag{5.68}$$

Note that we set $Q_{n_P}(t) = 0$ but $w_{n_P,n} \neq 0$ in Eq. (5.68). In Dirac notation we write Eq. (5.68) as

$$\frac{\partial \mathbf{Q}(t)}{\partial t} = \mathbf{QM}, \tag{5.69}$$

where $Q_n(t) \equiv \langle n_0 | \mathbf{Q}(t) | n \rangle$ and $\langle m | \mathbf{M} | n \rangle = w_{m,n} - \delta_{m,n} \sum_{n'=1}^{M} w_{n,n'}$ with $m \neq n_p$. The matrix $\mathbf{M}$ is not symmetric in general, and therefore its left and right eigenvectors will not be the same. We can use the methods of Section 5.C to expand the solution of Eq. (5.69) in terms of left and right eigenvectors of $\mathbf{M}$ and its eigenvalues (see Exericse 5.4). However, when using this approach one must check that the eigenvectors are complete. Since $Q_n(t)$ must decay, at least for a finite lattice (the walker eventually steps on site, n_p), all the eigenvalues of $\mathbf{M}$ must be negative.

The probability that the walker is still "alive" (i.e., has not stepped on the site, $n = n_p$) at time t is

$$P_{n_0}(t) \equiv \sum_{n(\neq n_p)=1}^{M} Q_n(t). \tag{5.70}$$

We now define

$$f_{n_0,n_P}(t) \equiv \{\text{the probability to reach the site, } n_P, \text{ during the time interval } t \to t + dt\} \tag{5.71}$$

We then note that to be "alive" at time t, the probability must equal the sum of the probabilities to either have "died" during the time $t \to t + dt$ or still be alive at time $t + dt$. Thus, we can write

$$P_{n_0}(t) = f_{n_0,n_P}(t)dt + P_{n_0}(t + dt). \tag{5.72}$$

If we now note that $P_{n_0}(t + dt) = P_{n_0}(t) + (dP_{n_0}(t)/dt)dt + \cdots$, then we can write

$$f_{n_0,n_P}(t) = -\frac{dP_{n_0}(t)}{dt}. \tag{5.73}$$

From Eqs. (5.68) and (5.70), the probability density, $f_{n_0,n_P}(t)$, can also be written

$$\begin{aligned} f_{n_0,n_P}(t) &= -\sum_{n(\neq n_P)=1}^{M} \frac{dQ_n(t)}{dt} \\ &= \sum_{n'(\neq n_P)=1}^{M} \sum_{m(\neq n_P)=1}^{M} Q_m(t)w_{m,n'}(t) - \sum_{n'(\neq n_P)=1}^{M} Q_{n'}(t) \sum_{m=1}^{M} w_{m,n'}(t) \\ &= -\sum_{n'(\neq n_P)=1}^{M} Q_{n'}(t)w_{n_P,n'}(t)). \end{aligned} \tag{5.74}$$

Thus $f_{n_0,n_P}(t)$ can be expressed in terms of the probability to find the walker on neighbors of the site n_P and the transition rate between n_P and its neighbors.

The average time it takes the walker to reach the site n_p, given that it starts at site n_0 at time $t = 0$, is

$$\langle t \rangle = \int_0^\infty dt\, t f_{n_0,n_P}(t) = \int_0^\infty dt P_{n_0}(t), \tag{5.75}$$

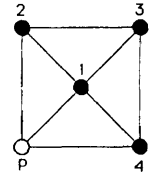
where we have used Eq. (5.72) and have integrated by parts. $\langle t \rangle$ is the *mean first passage time*.

■ **EXERCISE 5.4** Consider an asymmetric random walk on a lattice with five lattice sites. Assume that the fifth site, P, absorbs the walker. The transition rates $w_{1,2} = w_{1,3} = w_{1,4} = w_{1,P} = \frac{1}{4}$, $w_{2,1} = w_{2,3} = w_{2,P} = \frac{1}{3}$, $w_{3,1} = w_{3,2} = w_{3,4} = \frac{1}{3}$, $w_{4,1} = w_{4,3} = w_{4,P} = \frac{1}{3}$, $w_{P,1} = w_{P,2} = w_{P,4} = \frac{1}{3}$, and $w_{i,j} = 0$ for all other transitions. (a) Write the transition matrix, **M**, and compute its eigenvalues and left and right eigenvectors. (b) If the walker starts at site $n = 3$ at time $t = 0$, compute the mean first passage time.

Answer:

(**a**) The transition matrix, **M**, is given by

$$\mathbf{W} = \begin{pmatrix} -1 & \frac{1}{4} & \frac{1}{4} & \frac{1}{4} \\ \frac{1}{3} & -1 & \frac{1}{3} & 0 \\ \frac{1}{3} & \frac{1}{3} & -1 & \frac{1}{3} \\ \frac{1}{3} & 0 & \frac{1}{3} & -1 \end{pmatrix}.$$



It has eigenvalues $\lambda_1 \approx -0.216$, $\lambda_2 = -1.0$, $\lambda_3 \approx -1.284$, and $\lambda_4 = -1.5$. The left eigenvectors are

$$\langle \chi_1^L | \approx (0.286, 0.204, 0.265, 0.204),$$
$$\langle \chi_2^L | = (0, -0.5, 0, 0.5),$$
$$\langle \chi_3^L | \approx (0.614, -0.054, -0.415, -0.054),$$
$$\langle \chi_4^L | = (-0.2, 0.3, -0.3, 0.3).$$

The right eigenvectors are

$$|\chi_1^R\rangle \approx \begin{pmatrix} 1.0 \\ 0.950 \\ 1.234 \\ 0.950 \end{pmatrix}, \qquad |\chi_2^R\rangle = \begin{pmatrix} 0 \\ -1.0 \\ 0 \\ 1.0 \end{pmatrix},$$

$$|\chi_3^R\rangle \approx \begin{pmatrix} 1.0 \\ -0.117 \\ -0.901 \\ -0.117 \end{pmatrix}, \qquad |\chi_4^R\rangle = \begin{pmatrix} -0.5 \\ 1.0 \\ -1.0 \\ 1.0 \end{pmatrix}.$$

(b) The spectral decomposition of the matrix $\mathbf{Q}(t)$ can be written

$$\mathbf{Q}(t) = \mathbf{Q}(0) \sum_{i=1}^{4} e^{\lambda_i t} |\chi_i^R\rangle\langle\chi_i^L|. \tag{1}$$

If we take matrix elements and note that $\langle n_0 | \mathbf{Q}(0) | n\rangle = \delta_{n,n_0}$, we find

$$\langle n_0 | \mathbf{Q}(t) | n\rangle = \sum_{i=1}^{4} e^{\lambda_i t} \langle n_0 | \chi_i^R\rangle\langle\chi_i^L | n\rangle. \tag{2}$$

The mean first passage time is

$$\begin{aligned} \langle t\rangle &= \int_0^\infty dt P_{n_0}(t) = \sum_{n=1}^{4} \int_0^\infty dt \langle n_0 | \mathbf{Q}(t) | n\rangle \\ &= \sum_{n=1}^{4}\sum_{i=1}^{4} \langle n_0 | \chi_i^R\rangle \left(\frac{-1}{\lambda_i}\right) \langle\chi_i^L | n\rangle. \end{aligned} \tag{3}$$

If we now let $n_0 = 3$ and use the numbers from part (a), we find $\langle t\rangle \approx 5.33$.

5.E. BROWNIAN MOTION

Brownian motion provides some of the most spectacular evidence, on the "macroscopic" scale, for the discrete or atomic nature of matter on the "microscopic" scale. The discreteness of matter causes fluctuations in the density of matter, which, in turn, causes observable effects on the motion of the Brownian particle. This can be seen if one immerses a large particle (usually about one micron in diameter) in a fluid with the same density as the particle. When viewed under a microscope, the large particle (the Brownian particle) appears to be in a state of agitation, undergoing rapid and random movements. Early in the nineteenth century, the biologist Robert Brown wrote a paper on this phenomenon [10] which received wide attention, and as a result it has been named for him.

The modern era in the theory of Brownian motion began with Albert Einstein, who, initially unaware of the widely observed phenomenon of Brownian motion, was looking for a way to confirm the atomic nature of matter. Einstein obtained a relation between the macroscopic diffusion coefficient, D, and the atomic properties of matter. This relation is $D = RT/N_A 6\pi\eta a$, where R is the gas constant, $N_A = 6.02 \times 10^{23}\,\text{mol}^{-1}$ is Avogadro's number, T is the temperature in kelvins, η is the viscosity, and a is the radius of the Brownian particle [11, 12]. It has since been confirmed by many experiments on Brownian motion [13].

In this section we derive the theory of Brownian motion starting from the Langevin equations for a Brownian particle. That is, we focus on a large particle (the Brownian particle) immersed in a fluid of much smaller atoms. The agitated motion of the large particle is much slower than that of the atoms and is the result of random and rapid kicks due to density fluctuations in the fluid. Since the time scales of the Brownian motion and the atomic motions are vastly different, we can separate them and focus on the behavior of the Brownian particle. The effect of the fluid on the Brownian particle can be reduced to that of a random force and a systematic friction acting on the Brownian particle.

The Langevin theory of Brownian motion provides a paradigm theory for treating many-body systems in which a separation of time scales can be identified between some of the degrees of freedom. For this reason we consider it in some detail here.

5.E.1. Langevin Equation [3, 4]

Consider a particle in a fluid undergoing Brownian motion. For simplicity we will consider motion in one dimension. The results can easily be generalized to three dimensions. We assume that the particle is free to move in the fluid but that the effect of the fluid is included by adding a friction, which is proportional to the velocity, and a random force, $\xi(t)$, due to random density fluctuations in the fluid. The equations of motion of the Brownian particle are

$$\frac{dv(t)}{dt} = -\frac{\gamma}{m}v(t) + \frac{1}{m}\xi(t), \tag{5.76}$$

$$\frac{dx(t)}{dt} = v(t), \tag{5.77}$$

where $v(t)$ and $x(t)$ are the velocity and position, respectively, of the particle at time t, m is the mass of the particle, and γ is the friction coefficient. Equations (5.76) and (5.77) are the *Langevin equations* of motion for the Brownian particle.

The random force, $\xi(t)$, is a stochastic variable giving the effect of background noise, due to the fluid, on the Brownian particle. We will assume that $\xi(t)$ is a Gaussian white noise process with zero mean so that $\langle \xi(t) \rangle_\xi = 0$. The noise is Markovian and stationary and the average, $\langle \ \rangle_\xi$, is an average with respect to the probability distribution of realizations of the stochastic variable $\xi(t)$. We will not write the probability distribution explicitly. The assumption that the noise is *white* means that the noise is delta-correlated,

$$\langle \xi(t_1)\xi(t_2) \rangle_\xi = g\delta(t_2 - t_1), \tag{5.78}$$

and therefore (as we shall show in Section 5.E.2 its power spectrum contains all frequency components. The weighting factor, g, is a measure of the strength of the noise. Such a correlation function indicates that the noise is not correlated

from one instant to the next, and therefore it is impossible to represent a single realization of $\xi(t)$ in terms of a continuously drawn line. The fact that the noise is *Gaussian* with zero mean (cf. Exercise 4.9 means that correlation functions containing an odd number of terms, $\xi(t)$, are zero and that correlation functions containing an even number of terms, $\xi(t)$, can be expressed in terms of sums of products of the pairwise correlation function, $\langle \xi(t_1)\xi(t_2)\rangle_\xi$. For example,

$$\langle \xi(t_1)\xi(t_2)\xi(t_3)\xi(t_4)\rangle_\xi = \langle \xi(t_1)\xi(t_2)\rangle_\xi \langle \xi(t_3)\xi(t_4)\rangle_\xi + \langle \xi(t_1)\xi(t_3)\rangle_\xi \langle \xi(t_2)\xi(t_4)\rangle_\xi + \langle \xi(t_1)\xi(t_4)\rangle_\xi \langle \xi(t_2)\xi(t_3)\rangle_\xi.$$

Equations (5.76) and (5.77) can be solved fairly easily. Let us assume that at time $t = 0$, the velocity and position of the Brownian particle are $v(0) = v_0$ and $x(0) = x_0$, respectively. Then the solution the Eqs (5.76) and (5.77) is

$$v(t) = v_0 e^{-(\gamma/m)t} + \frac{1}{m}\int_0^t ds e^{-(\gamma/m)(t-s)}\xi(s) \tag{5.79}$$

and

$$x(t) = x_0 + \frac{m}{\gamma}(1 - e^{-(\gamma/m)t})v_0 + \frac{1}{\gamma}\int_0^t ds(1 - e^{-(\gamma/m)(t-s)})\xi(s). \tag{5.80}$$

Equations (5.79) and (5.80) give $v(t)$ and $x(t)$ for a single realization of $\xi(t)$. Since $\xi(t)$ is a stochastic variable, $v(t)$ and $x(t)$ are also stochastic variables whose properties are determined by $\xi(t)$. The average velocity (subject to the condition that $v(0) = v_0$) is $\langle v(t)\rangle_\xi = v_0 e^{-(\gamma/m)t}$ and the average displacement is $\langle (x(t) - x_0)\rangle_\xi = \frac{m}{\gamma}(1 - e^{-(\gamma/m)t})v_0$.

We can also obtain correlation functions from Eqs. (5.78), (5.79), and (5.80). If we make use of the fact that $\langle v_0\xi(t)\rangle_\xi = 0$, then we can write

$$\langle v(t_2)v(t_1)\rangle_\xi = v_0^2 e^{-(\gamma/m)(t_2+t_1)} + \frac{g}{m^2}\int_0^{t_2} ds_2 \int_0^{t_1} ds_1 \delta(s_2 - s_1) e^{(\gamma/m)(s_1-t_1)} e^{(\gamma/m)(s_2-t_2)}. \tag{5.81}$$

The integral is easily done to yield

$$\langle v(t_2)v(t_1)\rangle_\xi = \left(v_0^2 - \frac{g}{2m\gamma}\right) e^{-(\gamma/m)(t_2+t_1)} + \frac{g}{2m\gamma} e^{-(\gamma/m)(t_2-t_1)}. \tag{5.82}$$

We can also obtain the variance in the displacement. If we use Eqs. (5.78) and (5.80) and the fact that $\langle x_0\xi(t)\rangle_\xi = 0$, we can write

$$\langle (x(t) - x_0)^2\rangle_\xi = \frac{m^2}{\gamma^2}\left(v_0^2 - \frac{g}{2m\gamma}\right)(1 - e^{-(\gamma/m)t})^2 + \frac{g}{\gamma^2}\left[t - \frac{m}{\gamma}(1 - e^{-(\gamma/m)t})\right]. \tag{5.83}$$

Thus, after a long time the variance goes as $\langle (x(t_2) - x_0)^2 \rangle_\xi = (g/\gamma^2)t$ (neglecting some constant terms). This is the same behavior that we saw for random walks in Chapter 4, if we choose a *diffusion coefficient*, $D = g/2\gamma^2$.

We can use a simple trick to determine the value of g for a Brownian particle in equilibrium with a fluid. Let us assume that the Brownian particle is in equilibrium with the fluid and average over all possible initial velocities, v_0. We denote this "thermal" average by $\langle \rangle_T$. By the equipartition theorem, for a particle in equilibrium the average kinetic energy is $\frac{1}{2}k_BT$ for each degree of freedom, $\frac{1}{2}m\langle v_0^2 \rangle_T = \frac{1}{2}k_BT$, where k_B is Boltzmann's constant and T is the temperature in kelvins. If the Brownian particle is in equilbrium, its velocity correlation function must be stationary. Therefore, we must have $v_0^2 = g/2m\gamma$ so the first term on the right in Eq. (5.82) is removed. If we now take the thermal average of Eq. (5.82), we see that we must have $g = 2\gamma k_BT$. The correlation function can be written

$$\langle \langle v(t_2)v(t_1) \rangle_\xi \rangle_T = \frac{k_BT}{m} e^{-(\gamma/m)|t_2 - t_1|}. \tag{5.84}$$

The absolute value on the time difference ensures that correlations always decay as the time difference increases. Information about the initial velocity of the Brownian particle decays exponentially.

For the case when the Brownian particle is in equilibrium with the fluid, the variance of the displacement becomes

$$\langle \langle (x(t) - x_0)^2 \rangle_\xi \rangle_T = \frac{2k_BT}{\gamma} \left[t - \frac{m}{\gamma}(1 - e^{-(\gamma/m)t}) \right]. \tag{5.85}$$

where we have assumed that $\langle x_0 \rangle_T = \langle v_0 \rangle_T = 0$ and that x_0 and v_0 are statistically independent so that $\langle x_0 v_0 \rangle = 0$. Thus, after a long time, $\langle \langle (x(t) - x_0)^2 \rangle_\xi \rangle_T = (2k_BT/\gamma)t$ and the *diffusion coefficient* becomes $D = k_BT/\gamma$. The friction coefficient, γ, can also be determined from properties of the fluid and and hydrodynamics. For large spherical Brownian particles, we can assume that the fluid sticks to the surface. The friction coefficient is then the Stokes friction, $\gamma = 6\pi\eta R$, where η is the shear viscosity of the fluid and R is the radius of the Brownian particle (see Sect. (S10.G)). For very small Brownian particles, stick boundary conditions might not apply and the friction coefficient, γ, might be different.

■ **EXERCISE 5.5.** Consider a Brownian particle of mass m which is attached to a harmonic spring with force constant k and is constrained to move in one dimension. The Langevin equations are

$$\frac{dv}{dt} = -\frac{\gamma}{m}v - \omega_0^2 x + \frac{1}{m}\xi(t) \quad \text{and} \quad \frac{dx}{dt} = v,$$

where $\omega_0 = \sqrt{k/m}$. Let x_0 and v_0 be the initial position and velocity, respectively, of the Brownian particle and assume that it is initially in equilibrium with the fluid. Then by the equipartition theorem, the average kinetic energy is $\frac{1}{2}m\langle v_0^2\rangle_T = \frac{1}{2}k_BT$ and average vibrational potential energy is $\frac{1}{2}\omega_0^2\langle x_0^2\rangle_T = \frac{1}{2}k_BT$. We also assume that x_0 and v_0 are statistically independent so $\langle x_0 v_0\rangle_T = 0$. (a) Show that a condition for the process to be stationary is that the noise strength is $g = 4\gamma k_BT$. (b) Compute the velocity correlation function, $\langle\langle v(t_2)v(t_1)\rangle_\xi\rangle_T$.

Answer: The Langevin equations can be solved and give the following expression for the velocity at time t:

$$v(t) = v_0 e^{-\Gamma t}C(t) - \frac{\omega_0^2}{\Delta}x_0 e^{-\Gamma t}\sinh(\Delta t) + \frac{1}{m}\int_0^t dt'\xi(t')e^{-\Gamma(t-t')}C(t-t'),$$

where $C(t) = \cosh(\Delta t) - (\Gamma/\Delta)\sinh(\Delta t)$, $\Gamma = \gamma/m$, and $\Delta = \sqrt{\Gamma^2 - \omega_0^2}$. If we use the fact that $\langle x_0 v_0\rangle_T = 0$ and assume that $t_2 > t_1$, the velocity correlation function can be written

$$\begin{aligned}\langle\langle v(t_2)v(t_1)\rangle_\xi\rangle_T =& e^{-\Gamma(t_2+t_1)}C(t_2)C(t_1)\langle v_0^2\rangle_T \\ &+ \frac{\omega_0^4}{\Delta^2}\langle x_0^2\rangle_T e^{-\Gamma(t_2+t_1)}\sinh(\Delta t_2)\sinh(\Delta t_1) \\ &+ \frac{g}{m^2}\int_0^{t_1} dt e^{-\Gamma(t_2+t_1-2t)}C(t_2-t)C(t_1-t).\end{aligned}$$

If we choose $g = 4\gamma k_BT$ to ensure stationarity then after some algebra we obtain

$$\langle\langle v(t_2)v(t_1)\rangle_\xi\rangle_T = \frac{k_BT}{m}e^{-\Gamma(t_2-t_1)}\left[\cosh(\Delta(t_2-t_1)) - \frac{\Gamma}{\Delta}\sinh(\Delta(t_2-t_1))\right].$$

A similar calculation for $t_1 > t_2$ yields the same answer but with $t_1 \leftrightarrow t_2$. Thus,

$$\langle\langle v(t_1+\tau)v(t_1)\rangle_\xi\rangle_T = \frac{k_BT}{m}e^{-\Gamma|\tau|}\left[\cosh(\Delta\tau) - \frac{\Gamma}{\Delta}\sinh(\Delta|\tau|)\right].$$

5.E.2. The Spectral Density (Power Spectrum)

A quantity of great interest in studying *stationary* stochastic processes is the spectral density (or power spectrum). If one has experimental data on a stochastic variable $\psi(t)$—that is, if one has a time series for $\psi(t)$—then it is useful to compute the power spectrum because this contains a great deal of information about the stochastic process, as we shall see below.

In practice, in dealing with data from experiments, one has a finite length of time series to work with. Let us assume that we have a time series of length T. We denote it $\psi(t;T)$, where $\psi(t;T) = \psi(t)$ for $-T/2 \leqslant t \leqslant T/2$ and $\psi(t;T) = 0$ otherwise. The $\lim_{T\to\infty}\psi(t;T) = \psi(t)$. The Fourier transform of $\psi(t;T)$ is

$$\tilde{\psi}(\omega;T) = \int_{-\infty}^{\infty} dt\psi(t;T)e^{i\omega t}. \tag{5.86}$$

Because $\psi(t;T)$ is real, we have $\tilde{\psi}(\omega;T) = \tilde{\psi}^*(-\omega;T)$, where $*$ denotes complex conjugation.

The spectral density is defined as

$$S_{\psi,\psi}(\omega) \equiv \lim_{T\to\infty}\frac{1}{T}\tilde{\psi}^*(\omega;T)\tilde{\psi}(\omega;T). \tag{5.87}$$

If we substitute Eq. (5.86) into (5.87), we find

$$\begin{aligned} S_{\psi,\psi}(\omega) &= \lim_{T\to\infty}\frac{1}{T}\int_{-\infty}^{\infty} dt_2 \int_{-\infty}^{\infty} dt_1\psi(t_2;T)\psi(t_1;T)e^{-i\omega(t_2-t_1)} \\ &= \int_{-\infty}^{\infty} d\tau\, e^{-i\omega(\tau)} \lim_{T\to\infty}\frac{1}{T}\int_{-\infty}^{\infty} dt_1\psi(t_1+\tau;T)\psi(t_1;T) \\ &= \int_{-\infty}^{\infty} d\tau\, e^{-i\omega(\tau)}\langle\psi(t_1+\tau)\psi(t_1)\rangle_{\bar{t}}, \end{aligned} \tag{5.88}$$

where $\langle\psi(t_1+\tau)\psi(t_1)\rangle_{\bar{t}}$ denotes the time average:

$$\langle\psi(t_1+\tau)\psi(t_1)\rangle_{\bar{t}} \equiv \lim_{T\to\infty}\frac{1}{T}\int_{-\infty}^{\infty} dt_1\psi(t_1+\tau;T)\psi(t_1;T). \tag{5.89}$$

Equation (5.89) denotes the average of the product of numbers, $\psi(t_1;T)\psi(t_1+\tau;T)$, over each point of the time series, $\psi(t)$. Since we assume that the stochastic process is stationary, the stochastic properties of the time series don't change as we shift along the time series. Therefore we expect that the time average, $\langle\psi(t_1+\tau)\psi(t_1)\rangle_{\bar{t}}$, should be equal to the statistical average, $\langle\psi(t_1+\tau)\psi(t_1)\rangle_{\psi}$, in which we average the product, $\psi(t_1+\tau)\psi(t_1)$, at a given point, $t = t_1$, but over an infinite number of realizations of the time series, $\psi(t)$, at time t. Therefore, for a stationary process, we expect that

$$C_{\psi,\psi}(\tau) \equiv \langle\psi(t_1+\tau)\psi(t_1)\rangle_{\psi} = \langle\psi(t_1+\tau)\psi(t_1)\rangle_{\bar{t}} \tag{5.90}$$

If we now combine Eqs. (5.89) and (5.90), we obtain the following expression for the spectral density:

$$S_{\psi,\psi}(\omega) = \int_{-\infty}^{\infty} d\tau e^{-i\omega\tau}\langle\psi(t_1+\tau)\psi(t_1)\rangle_{\psi} = \int_{-\infty}^{\infty} d\tau e^{-i\omega\tau}C_{\psi,\psi}(\tau), \tag{5.91}$$

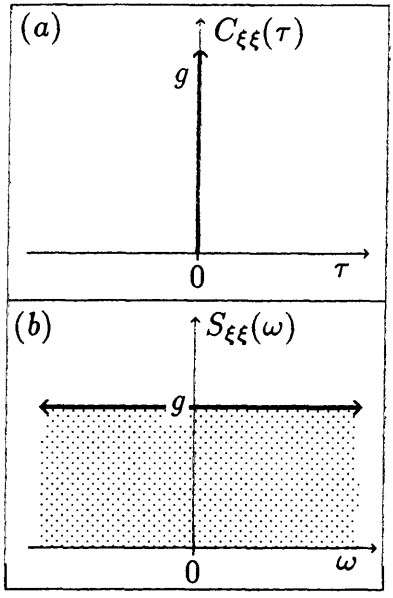


Fig. 5.1. (a) The correlation function, $C_{\xi\xi}(t)$. (b) The spectral density, $S_{\xi\xi}(\omega)$.

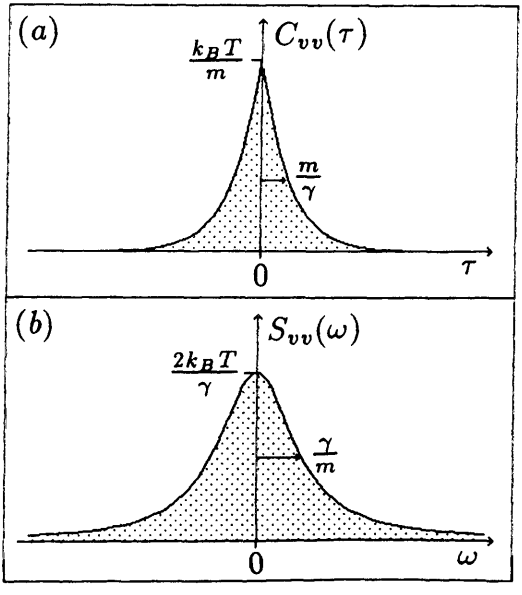


Fig. 5.2. (a) The correlation function, $C_{vv}(t)$. (b) The spectral density, $S_{vv}(\omega)$.

It is interesting to compute the spectral densities for the Brownian motion described in Section 5.E.1. Let us consider the case when the Brownian particle is in thermal equilibrium with the fluid and the process is stationary. From Eq. (5.78), the spectral density for the white noise is

$$S_{\xi,\xi}(\omega) = \int_{-\infty}^{\infty} d\tau e^{-i\omega\tau} \langle \xi(t_1 + \tau)\xi(t_1) \rangle_\xi = g = 2\gamma k_B T. \tag{5.92}$$

Thus, a white noise process contains all frequencies with equal weight. The correlation function, $C_{\xi\xi}(t)$, and spectral density, $S_{\xi\xi}(\omega)$, are shown in Fig. 5.1.

The spectral density for the velocity time series is

$$S_{v,v}(\omega) = \int_{-\infty}^{\infty} d\tau e^{-i\omega\tau} \langle v(t_1 + \tau)v(t_1) \rangle_\xi = \frac{2k_B T\gamma}{m^2\omega^2 + \gamma^2}. \tag{5.93}$$

Plots of the velocity correlation function and spectral density for the Brownian particle are given in Fig. 5.2.

■ **EXERCISE 5.6.** Compute the spectral density, $S_{v,v}(\omega)$, for the harmonically bound Brownian particle considered in Exercise 5.5. Plot the velocity correlation function, $C_{v,v}(\tau)$, and spectral density $S_{v,v}(\omega)$ for the case $\omega_0 > \Gamma$ (this corresponds to an *underdamped* Brownian particle).

Answer: The velocity correlation function can be written

$$C_{v,v}(\tau) = \langle \langle v(t_1 + \tau)v(t_1) \rangle_\xi \rangle_T = \frac{\Gamma k_B T}{m} e^{-\Gamma|\tau|} \left[\frac{1}{\Gamma} \cos(\delta|\tau|) - \frac{1}{\delta} \sin(\delta|\tau|) \right],$$

where $\Gamma = \frac{\gamma}{m}$ and $\delta = \sqrt{\omega_0^2 - \Gamma^2} = -i\Delta$. The spectral density can be written

$$\begin{aligned} S_{v,v}(\omega) &= \int_0^{\infty} d\tau \cos(\omega\tau) e^{-\Gamma|\tau|} \left[\frac{1}{\Gamma} \cos(\delta|\tau|) - \frac{1}{\delta} \sin \delta|\tau| \right] \\ &= \frac{4\gamma k_B T\omega^2}{m(\omega_0^2 - 2\delta\omega + \omega^2)(\omega_0^2 + 2\delta\omega + \omega^2)} \end{aligned}.$$

Both $C_{v,v}(\tau)$ and $S_{v,v}(\omega)$ are plotted in the accompanying graphs.

Because the Brownian particle is underdamped, the velocity correlation function, $C_{v,v}(\tau)$, oscillates as it is damped out exponentially. The spectral density, $S_{v,v}(\omega)$, has peaks near $\omega = \pm\omega_0$ and the peaks have an approximate width, $\frac{2\gamma}{m}$.

When the noise is not "white", the spectral density still affords a means of making contact with experiment [14].

▶ SPECIAL TOPICS

▶ S5.A. Time Periodic Markov Chain

Let us now consider the case in which the transition probability is time-dependent but periodic in time with period N. That is, $Q_{n,m}(s) \equiv P_{1|1}(n, s|m, s+1) = P_{1|1}(n, s+N|m, s+N+1)$. The probability vector after one period of the transition probability can be written

$$\langle \mathbf{P}(N)| = \langle \mathbf{P}(0)|\mathbf{Q}(0)\mathbf{Q}(1) \times \cdots \times \mathbf{Q}(N-1) \equiv \langle \mathbf{P}(0)|\mathbf{U}, \tag{5.94}$$

where $\mathbf{U} = \mathbf{Q}(0)\mathbf{Q}(1) \times \cdots \times \mathbf{Q}(N-1)$ is the transition probability that takes the system from the initial state, $\langle \mathbf{P}(0)|$, to the state after one period, $\langle \mathbf{P}(N)|$. More generally, the probability vector after l periods of the transition matrix is

$$\langle \mathbf{P}(lN)| = \langle \mathbf{P}(0)|\mathbf{U}^l. \tag{5.95}$$

We can expand the probability vector, $\langle \mathbf{P}(lN)|$, in terms of left and right eigenvectors of the transition matrix, $\mathbf{U}$. Let Λ_α be the αth eigenvalue of $\mathbf{U}$, and let $\langle \chi_\alpha|$ and $|\psi_\alpha\rangle$ denote the left and right normalized eigenvectors of $\mathbf{U}$, respectively, where $\alpha = 1, \ldots, M$. Thus, $\mathbf{U}|\psi_\alpha\rangle = \Lambda_\alpha|\psi_\alpha\rangle$ and $\langle \chi_\alpha|\mathbf{U} = \langle \chi_\alpha|\Lambda_\alpha$. We then proceed as we did in Section 5.C.1. If $\mathbf{U}$ is an $M \times M$ matrix, then its spectral decomposition is given by

$$\mathbf{U} = \sum_{\alpha=1}^{M} \Lambda_\alpha |\psi_\alpha\rangle\langle \chi_\alpha|. \tag{5.96}$$

The probability vector after l periods of the transition matrix is given by

$$\langle \mathbf{P}(lN)| = \sum_{\alpha=1}^{M} \Lambda_\alpha^l \langle \mathbf{P}(0)|\psi_\alpha\rangle\langle \chi_\alpha|. \tag{5.97}$$

The probability for the nth realization of the stochastic variable Y at time $s = lN$ is given by

$$P(n, lN) = \sum_{m=1}^{M}\sum_{\alpha=1}^{M} \Lambda_\alpha^l P(m, 0)\psi_\alpha(m)\chi_\alpha(n). \tag{5.98}$$

We will demonstrate the use of these equations in Exercise 5.7.

■ **EXERCISE 5.7.** Let us consider a stochastic variable Y with three realizations, $y(1)$, $y(2)$, and $y(3)$. Let us assume that the transition

probabilities between these states are $Q_{1,1}(s) = Q_{2,2}(s) = Q_{3,3}(s) = 0$, $Q_{1,2}(s) = Q_{2,3}(s) = Q_{3,1}(s) = \cos^2(2\pi s/3)$, and $Q_{1,3}(s) = Q_{2,1}(s) = Q_{3,2}(s) = \sin^2(2\pi s/3)$. If initially the system is in the state $y(1)$, what is the probability to find it in the state $y(2)$ after l periods of the transition matrix?

Answer: The transition matrix has a period $N = 3$. In general it is given by

$$\mathbf{Q}(s) = \begin{pmatrix} 0 & \cos^2(\frac{2\pi s}{3}) & \sin^2(\frac{2\pi s}{3}) \\ \sin^2(\frac{2\pi s}{3}) & 0 & \cos^2(\frac{2\pi s}{3}) \\ \cos^2(\frac{2\pi s}{3}) & \sin^2(\frac{2\pi s}{3}) & 0 \end{pmatrix}.$$

Therefore,

$$\mathbf{Q}(0) = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} \quad \text{and} \quad \mathbf{Q}(1) = \mathbf{Q}(2) = \begin{pmatrix} 0 & \frac{1}{4} & \frac{3}{4} \\ \frac{3}{4} & 0 & \frac{1}{4} \\ \frac{1}{4} & \frac{3}{4} & 0 \end{pmatrix},$$

and the transition matrix $\mathbf{U}$ becomes

$$\mathbf{U} = \mathbf{Q}(0)\mathbf{Q}(1)\mathbf{Q}(2) = \begin{pmatrix} \frac{1}{16} & \frac{3}{8} & \frac{9}{16} \\ \frac{9}{16} & \frac{1}{16} & \frac{3}{8} \\ \frac{3}{8} & \frac{9}{16} & \frac{1}{16} \end{pmatrix}.$$

The eigenvalues of $\mathbf{U}$ are $\Lambda_1 = 1$, $\Lambda_2 = -\frac{7}{16}e^{-i\theta}$, and $\Lambda_3 = -\frac{7}{16}e^{+i\theta}$, where $\theta = \tan^{-1}(3\sqrt{3}/13)$.

The right eigenstates can be written

$$|\psi_1\rangle = \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}, \qquad |\psi_2\rangle = \begin{pmatrix} -e^{+i\pi/3} \\ -e^{-i\pi/3} \\ 1 \end{pmatrix}, \qquad |\psi_3\rangle = \begin{pmatrix} -e^{-i\pi/3} \\ -e^{+i\pi/3} \\ 1 \end{pmatrix}.$$

The left eigenstates can be written

$$\langle\chi_1| = (\tfrac{1}{3}, \tfrac{1}{3}, \tfrac{1}{3}), \qquad \langle\chi_2| = (-\tfrac{1}{3}e^{-i\pi/3}, -\tfrac{1}{3}e^{+i\pi/3}, \tfrac{1}{3})$$

and

$$\langle\chi_3| = (-\tfrac{1}{3}e^{+i\pi/3}, -\tfrac{1}{3}e^{-i\pi/3}, \tfrac{1}{3}).$$

We can now compute the probability $P(2, 3l)$. The initial probability density is $P(n, 0) = \delta_{n,1}$. From Eq. (5.98), the probability $P(2, 3l)$ is

$$\begin{aligned} P(2, 3l) &= \Lambda_1^l \psi_1(1)\chi_1(2) + \Lambda_2^l \psi_2(1)\chi_2(2) + \Lambda_3^l \psi_3(1)\chi_3(2) \\ &= \frac{1}{3} + (-1)^l \frac{2}{3}\left(\frac{7}{16}\right)^l \cos\left(l\theta - \frac{2\pi}{3}\right). \end{aligned}$$

▶ S5.B. Master Equation for Birth–Death Processes [3, 4]

One of the most common applications of the master equation is the description of *birth–death processes* such as one finds in chemistry and population dynamics. Birth–death processes are processes in which transitions can only take place between nearest-neighbor states. For example, if one considers a population in which only one individual is produced at each birth and one individual dies at each death, then we have a typical birth–death process.

▶ S5.B.1. The Master Equation

For concreteness let us consider a population of bacteria. We assume that at time t, there are n bacteria and we make the following assumptions:

(1) The probability of a bacterium dying during the time $t \to t + \Delta t$ is given by $w_{n,n-1}(t)\Delta t = d_n(t)\Delta t$.
(2) The probability of a bacterium being created in time $t \to t + \Delta t$ is given by $w_{n,n+1}(t)\Delta t = b_n(t)\Delta t$.
(3) The probability that no change occurs in the bacteria population in time $t \to t + \Delta t$ is given by $[1 - \sum_{l=1}^{M} w_{m,l}(t)\Delta t] = [1 - (b_m(t) + d_m(t))\Delta t]$.
(4) The probability of more than one birth or death in time $t \to t + \Delta t$ is zero.

The transition probability can be written

$$P_{1|1}(m, t|n, t + \Delta t) = [1 - (b_m(t) + d_m(t))\Delta t]\delta_{m,n} + (b_m(t)\delta_{n,m+1} + d_m(t)\delta_{n,m-1}\Delta t + \cdots \tag{5.99}$$

and the master equation takes the form

$$\frac{\partial P_1(n, t)}{\partial t} = b_{n-1}(t)P_1(n-1, t) + d_{n+1}(t)P_1(n+1, t) - (b_n(t) + d_n(t))P(n, t). \tag{5.100}$$

Note that we have allowed the birth and death rates, $b_n(t)$ and $d_n(t)$ respectively, to depend on time. In most applications of Eq. (5.100) that we will consider here, they will be independent of time.

Let us consider the case in which b_n and d_n are independent of time. Then the master equation will have at least one stationary state, $P_n^s \equiv P(n, \infty)$, which is independent of time and satisfies the condition $\partial P_n^s/\partial t = 0$. (If the transition matrix, **W**, is made up of uncoupled blocks, then there may be more than one stationary state.) The master equation for the stationary state can be written in

the form

$$0 = d_{n+1}P^s_{n+1} - b_nP^s_n - (d_nP^s_n - b_{n-1}P^s_{n-1}). \tag{5.101}$$

Note that since $d_{n+1}P^s_{n+1} - b_nP^s_n = d_nP^s_n - b_{n-1}P^s_{n-1}$, the quantity $J \equiv b_{n-1}P^s_{n-1} - d_nP^s_n$ must be independent of n. The quantity J is just the net probability current between pairs of sites.

The case where no probability flows, $J = 0$, is equivalent to detailed balance since

$$b_{n-1}P^s_{n-1} = d_nP^s_n. \tag{5.102}$$

Systems obeying detailed balance are very similar to systems in thermodynamic equilibrium, since no net probability current flows between microscopic states of those systems. For systems obeying detailed balance, we can iterate Eq. (5.102) to obtain an expression for P^s_n in terms of P^s_0:

$$P^s_n = \frac{b_{n-1}b_{n-2}\ldots b_0}{d_nd_{n-1}\ldots d_1}P^s_0. \tag{5.103}$$

The value of P^s_0 is obtained by the condition that the total probability be normalized to one, $\sum_{n=0}^{M} P^s_n = 1$.

The full master equation can only be solved exactly for some special cases. In the following two sections, we give some techniques for solving it exactly for some of the few cases where that is possible. In Section S5.B.2 we consider the case when the birth and death rates depend linearly on the population number. In Section S5.B.3 we consider the case when the birth and death rates depend nonlinearly on the population number. We will discuss some approximation schemes for solving the master equation in Section S5.D.

▶ S5.B.2. Linear Birth–Death Processes

Let us assume that the probability of a birth or death is proportional to the number of bacteria present and is independent of time. Then $b_n = \beta n$ and $d_n = \gamma n$, where β and γ are constants, and the master equation takes the form

$$\frac{\partial P_1(n, t)}{\partial t} = \beta(n-1)P_1(n-1, t) + \gamma(n+1)P_1(n+1, t) - (\beta n + \gamma n)P(n, t). \tag{5.104}$$

Equation (5.104) describes a linear birth-death process because the coefficients of P_1 on the right-hand side of the equation depend linearly on n. Note that n is the number of bacteria and therefore $n \geqslant 0$. Thus, Eq. (5.104) must never allow probability to flow into regions where $n < 0$. We see that

Eq. (5.104) satisfies that condition. If $n = -1$, the coefficient of $P_1(n+1, t)$ is zero so flow can never occur from positive to negative values of n. Equation (5.104) is said to have a *natural boundary* at $n = 0$. This may not always be the case and one must be careful when using such master equations.

Linear master equations depending on discrete stochastic variables are often most easily solved by means of a generating function, $F(z, t)$. We will use this method to solve Eq. (5.104). The generating function is defined as

$$F(z, t) = \sum_{n=-\infty}^{\infty} z^n P_1(n, t). \tag{5.105}$$

Since we have a natural boundary at $n = 0$, it does not matter that the summation in Eq. (5.105) extends to $n = -\infty$. Various moments of the population number, n, are obtained by taking derivatives of $F(z, t)$ with respect of z and then allowing $z \to 1$. For example,

$$\langle n(t) \rangle = \lim_{z \to 1} \frac{\partial F(z, t)}{\partial z} = \sum_{n=-\infty}^{\infty} n P_1(n, t) \tag{5.106}$$

and

$$\langle n^2(t) \rangle - \langle n(t) \rangle = \lim_{z \to 1} \frac{\partial^2 F(z, t)}{\partial z^2} = \sum_{n=-\infty}^{\infty} (n^2 - n) P_1(n, t). \tag{5.107}$$

Higher moments may be obtained in an analogous manner.

We can now obtain a differential equation for the generating function, $F(z, t)$. Let us multiply Eq. (5.104) by z^n and sum over n. Note, for example, that

$$\sum_{n=-\infty}^{\infty} z^n (n-1) P_1(n-1, t) = z^2 \frac{d}{dz} \sum_{n=-\infty}^{\infty} z^{n-1} P_1(n-1, t) = z^2 \frac{dF(z, t)}{dz}$$

and

$$\sum_{n=-\infty}^{\infty} z^n (n+1) P_1(n+1, t) = \frac{d}{dz} \sum_{n=-\infty}^{\infty} z^{n+1} P_1(n+1, t) = \frac{dF(z, t)}{dz}.$$

We obtain the following differential equation for $F(z, t)$:

$$\frac{\partial F}{\partial t} = (z - t)(\beta z - \gamma) \frac{\partial F}{\partial z}. \tag{5.108}$$

If we substitute Eq. (5.105) into Eq. (5.108) and equate like powers of z, we

retrieve Eq. (5.104). Equation (5.108) is a first-order linear partial differential equation and may be solved using the method of characteristics.

■ **Method of Characteristics [15].** Let us consider a first order linear differential equation of the form

$$\frac{\partial F(z,t)}{\partial t} + g(z)\frac{\partial F(z,t)}{\partial z} + h(z)F(z,t) = 0, \tag{1}$$

where $g(z)$ and $h(z)$ are arbitrary functions of z. Write $F(z,t)$ in the form

$$F(z,t) = \left[e^{-\int^z \frac{h(x)}{g(z)}}\right]\Phi(z,t), \tag{2}$$

where $\Phi(z,t)$ is an unknown function of z and t. If we substitute Eq. (2) into Eq. (1), we find a partial differential equation for $\Phi(z,t)$:

$$\frac{\partial \Phi(z,t)}{\partial t} + g(z)\frac{\partial \Phi(z,t)}{\partial z} = 0. \tag{3}$$

We now find the characteristics for Eq. (3). These are lines in the z–t plane along which $\Phi(z,t)$ is constant. These lines satisfy the equation $dt = dz/g(z)$ or $\int^z dz/g(z) - t = C_1$, where C_1 is a constant. It is easy to show that any function of $\int^z dz/g(z) - t$ is a solution of Eq. (3). Generally we write the solution as $\Phi(z,t) = \Phi(e^{\int^z dz/g(z) - t})$, and the solution to Eq. (1) takes the form

$$F(z,t) = e^{\int^z [h(z)/g(z)]dz}\Phi(e^{\int^z dz/g(z) - t}). \tag{4}$$

If we use the method of characteristics to solve Eq. (5.108), we find

$$F(z,t) = F\left(\left(\frac{\beta(z-1)}{\beta z - \gamma}\right)e^{(\beta-\gamma)t}\right) \tag{5.109}$$

Although we know that $F(z,t)$ is a rather complicated function of β, γ, and t, we still do not know the exact form of $F(z,t)$. This we obtain from the initial conditions. Let us assume that at time $t = 0$ there are exactly m bacteria in the population. Thus, $P(n,0) = \delta_{n,m}$ and $F(z,0) = z^m$. From Eq. (5.109) we find

$$F\left(\frac{\beta(z-1)}{\beta z - \gamma}\right) = z^m. \tag{5.110}$$

If we now let $u = \beta(z-1)/(\beta z - \gamma)$, then we can write $z = (\gamma u - \beta)/\beta(u-1)$, so

$$F(u) = \left(\frac{\gamma u - \beta}{\beta(u-1)}\right)^m \tag{5.111}$$

and

$$F(z, t) = \left(\frac{\gamma(z-1)e^{(\beta-\gamma)t} - \beta z + \gamma}{\beta(z-1)e^{(\beta-\gamma)t} - \beta z + \gamma}\right)^m. \tag{5.112}$$

Equation (5.112) is exact and contains all possible information about the linear birth–death process. We can now obtain $P_1(n, t)$ and all the moments of n from Eq. (5.112). In order to obtain $P_1(n, t)$ we must expand Eq. (5.112) in a Taylor series in z. $P_1(n, t)$ is the coefficient of z^n. The first moment is

$$\langle n(t)\rangle = \left(\frac{\partial F}{\partial z}\right)_{z=1} = me^{(\beta-\gamma)t}. \tag{5.113}$$

The variance is

$$\langle n^2(t)\rangle - \langle n(t)\rangle^2 = m\left(\frac{\beta+\gamma}{\gamma-\beta}\right)e^{(\beta-\gamma)t}(1 - e^{(\beta-\gamma)t}) \tag{5.114}$$

If the birth rate is greater than the death rate, the population will grow exponentially with time. If the death rate is greater than the birth rate, the population will die out. Of course, Eq. (5.104) gives a vastly oversimplified description of the dynamics of a bacteria population. We have left out factors involving food supply, temperature, and so on, but it does give a good starting point. For an excellent discussion of the application of master equations to population dynamics, see Ref. 16.

Birth–death equations can also be applied to chemical reaction kinetics. For example, in Problem S5.2 we consider the reaction

$$\mathrm{A} + \mathrm{X} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{A} + \mathrm{Y},$$

where the number of A molecules is kept constant but the number of X molecules and Y molecules can vary. $k_1(k_2)$ is the probability per unit time that a reaction takes place if an X molecule (Y molecule) collides with an A molecule. The reaction in the forward direction requires n_A A molecules, $n_X + 1$ X molecules, and $n_y - 1$ Y molecules to produce a system containing n_A A molecules, n_X X molecules, and n_Y Y molecules. Similarly, the backward reaction requires n_A A molecules, $n_X - 1$ X molecules, and $n_Y + 1$ Y molecules to produce a system containing n_A A molecules, n_X X molecules, and n_Y Y molecules. The transition rate for the forward reaction depends on the number of binary collisions, $n_A(n_X + 1)$, between A molecules and X molecules. Similarly, the transition rate for the backward reaction depends on the product, $n_A(n_Y + 1)$. Thus, the transition rate for the forward reaction is $w_1 = k_1 n_A(n_X + 1)$, and for the backward reaction it is $w_2 = k_2 n_A(n_Y + 1)$.

If we assume that the total number of X molecules and Y molecules is constant and equal to N, then the master equation can be written

$$\frac{\partial P_1(n,t)}{\partial t} = k_2(N-n+1)P_1(n-1,t) + k_1(n+1)P_1(n+1,t) - (k_1 n + k_2(N-n))P(n,t). \tag{5.115}$$

where n is the number of X molecules and $N-n$ is the number of Y molecules. For simplicity we have absorbed n_A into k_1 and k_2. We leave it as a homework problem to solve this master equation.

▶ S5.B.3. Nonlinear Birth–Death Processes [3, 4, 17]

Some of the simplest examples of nonlinear birth-death processes come from population dynamics and chemical reaction kinetics. A nonlinear birth–death process is one for which one or both of the transition rates, $b_n(t)$ and $d_n(t)$, depend nonlinearly on n. The master equation for nonlinear birth–death processes usually cannot be solved exactly, except for the long-time state. However, for binary nonlinear processes they sometimes can be solved exactly because the partial differential equation for the generating function might be solvable in terms of orthogonal polynomials.

An example of an exactly soluble nonlinear system is the binary chemical reaction [18]

$$2\mathrm{X} \xrightarrow{k} \mathrm{B}.$$

The transition rate for this reaction is proportional both to the reaction rate, k, and to the number of different ways, $\frac{1}{2}n_X(n_X-1)$, to form pairs of X molecules if there are n_X X molecules in the system. If the system has n_X+2 X molecules and n_B-1 B molecules before the reaction, then it will have n_X X molecules and n_B B molecules after the reaction. The transition rate is $w = \frac{k}{2}(n_X+2)(n_X+1)$. The master equation can be written

$$\frac{\partial P(n,t)}{\partial t} = \frac{k}{2}(n+2)(n+1)P(n+2,t) - \frac{k}{2}n(n-1)P(n,t). \tag{5.116}$$

This equation has a natural boundary at $n=0$ since probability cannot flow into $P(-1,t)$ from above. The equation for the generating function takes the form

$$\frac{\partial F}{\partial t} = \frac{k}{2}(1-z^2)\frac{\partial^2 F}{\partial z^2}. \tag{5.117}$$

The generating function, $F(z, t)$, in terms of Gegenbauer polynomials can be written

$$F(z, t) = \sum_{n=0}^{\infty} A_n e^{-(k/2)n(n-1)t} C_n^{-1/2}(z). \tag{5.118}$$

The coefficient A_n depends on initial conditions. The first few Gegenbauer polynomials are $C_0^{-1/2}(z) = 1$, $C_1^{-1/2}(z) = -z$, $C_2^{-1/2}(z) = \frac{1}{2}(1 - z^2)$, and $C_3^{-1/2}(z) = \frac{1}{2}z(1 - z^2)$. We shall not attempt to compute A_n here. Solutions can be found in Ref. 17.

It is important to note that most nonlinear master equations cannot be solved exactly. It is then often necessary to resort to approximation schemes or numerical methods for solutions.

▶ S5.C. The Fokker–Planck Equation [3, 4, 19]

The Fokker–Planck equation is the equation governing the time evolution of the probability density for the Brownian particle. It is a second-order differential equation and is exact for the case when the noise acting on the Brownian particle is Gaussian white noise. The derivation of the Fokker–Planck equation is a two-step process. We first derive the equation of motion for the probability density $\rho(x, v, t)$ to find the Brownian particle in the interval $x \to x + dx$ and $v \to v + dv$ at time t for one realization of the random force $\xi(t)$. We then obtain an equation for $P(x, v, t) = \langle \rho(x, v, t) \rangle_\xi$, the average of $\rho(x, v, t)$ over many realizations of the random force $\xi(t)$. The probability density $P(x, v, t)$ is the macroscopically observed probability density for the Brownian particle. Its dynamical evolution is governed by the Fokker–Planck equation.

▶ S5.C.1. Probability Flow in Phase Space

Let us obtain the probability to find the Brownian particle in the interval $x \to x + dx$ and $v \to v + dv$ at time t. We will consider the space of coordinates, $\mathbf{X} = (x, v)$ (x and v the displacement and velocity, respectively, of the Brownian particle), where $-\infty < x < \infty$ and $-\infty < v < \infty$. The Brownian particle is located in the infinitesimal area, $dxdv$, with probability $\rho(x, v, t)dxdv$. We may view the probability as a fluid whose density at point (x, v) is given by $\rho(x, v, t)$. The speed of the fluid at point (x, v) is given by $\dot{\mathbf{X}} = (\dot{x}, \dot{v})$. Since the Brownian particle must lie somewhere in this space, we have the condition

$$\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dv \rho(x, v, t) = 1. \tag{5.119}$$

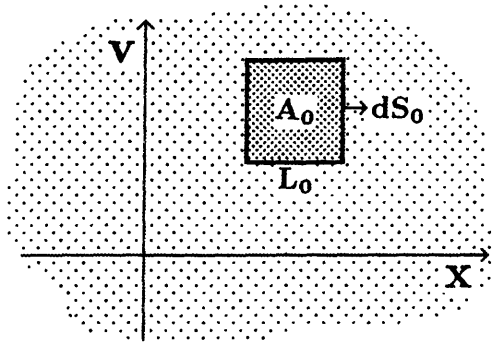


Fig. 5.3. A finite area in Brownian particle phase space.

Let us now consider a fixed finite area, A_0, in this space (cf. Fig. 5.3). The probability to find the Brownian particle in this area at time t is $P(A_0) = \int_{A_0} dxdv\rho(x,v,t)$. Since the Brownian particle cannot be destroyed, and change in the probability contained in A_0 must be due to a flow of probability through the sides of A_0. Thus

$$\frac{\partial}{\partial t}P(A_0) = \frac{\partial}{\partial t}\int\int_{A_0} dxdv\rho(x,v,t) = -\oint_{L_0} \rho(x,v,t)\dot{\mathbf{X}}\cdot d\mathbf{S_0}, \tag{5.120}$$

where $d\mathbf{S_0}$ denotes a differential surface element along the edge of area A_0, $\rho\dot{\mathbf{X}}$ is the probability current through the edge, and L_0 is the line around the edge of area element A_0. We can now use Gauss's theorem to change the surface integral into an area integral, $\oint_{L_0} \rho(x,v,t)\dot{\mathbf{X}}\cdot d\mathbf{S_0} = \int_{A_0} dxdv\nabla_{\mathbf{X}}\cdot(\dot{\mathbf{X}}\rho(x,v,t))$, where $\nabla_{\mathbf{X}}$ denotes the gradient, $\nabla_{\mathbf{X}} = (\partial/\partial x, \partial/\partial v)$. We find

$$\frac{\partial}{\partial t}\int\int_{A_0} dxdv\rho(x,v,t) = -\int_{A_0} dxdv\nabla_{\mathbf{X}}\cdot(\dot{\mathbf{X}}\rho(x,v,t)). \tag{5.121}$$

Since the area A_0, is fixed, we can take the time derivative inside the integral. Since the area A_0, is arbitrary, we can equate integrands of the two integrals in Eq. (5.121). Then we find that $(\partial\rho(t)/\partial t) = -\nabla_{\mathbf{X}}\cdot(\dot{\mathbf{X}}\rho(t))$, or

$$\frac{\partial\rho(t)}{\partial t} = -\nabla_{\mathbf{X}}\cdot(\dot{\mathbf{X}}\rho(t)) = -\frac{\partial(\dot{x}\rho(t))}{\partial x} - \frac{\partial(\dot{v}\rho(t))}{\partial v} \tag{5.122}$$

where we have let $\rho(t) = \rho(x,v,t)$.

▶ S5.C.2. Probability Flow for Brownian Particle

In order to write Eq. (5.122) explicitly for a Brownian particle, we first must know the Langevin equation governing the evolution of the Brownian particle.

Let us assume that Brownian particle moves in the presence of a potential, $V(x)$. The Langevin equations are then

$$\frac{dv(t)}{dt} = -\frac{\gamma}{m}v(t) + \frac{1}{m}F(x) + \frac{1}{m}\xi(t) \quad \text{and} \quad \frac{dx(t)}{dt} = v(t), \tag{5.123}$$

where the force, $F(x)$ equals $-(dV(x)/dx)$. If we substitute these equations into Eq. (5.122), we find

$$\begin{aligned}\frac{\partial\rho(t)}{\partial t} &= -\frac{\partial(v\rho(t))}{\partial x} + \frac{\gamma}{m}\frac{\partial(v\rho(t))}{\partial v} - \frac{1}{m}F(x)\frac{\partial\rho(t)}{\partial v} - \frac{1}{m}\xi(t)\frac{\partial\rho(t)}{\partial v} \\ &= -\hat{L}_0\rho(t) - \hat{L}_1(t)\rho(t),\end{aligned} \tag{5.124}$$

where the differential operators $\hat{L}_0$ and $\hat{L}_1$ are defined as

$$\hat{L}_0 = v\frac{\partial}{\partial x} - \frac{\gamma}{m} - \frac{\gamma}{m}v\frac{\partial}{\partial v} + \frac{1}{m}F(x)\frac{\partial}{\partial v} \quad \text{and} \quad \hat{L}_1 = \frac{1}{m}\xi(t)\frac{\partial}{\partial v}. \tag{5.125}$$

Since $\xi(t)$ is a stochastic variable, the time evolution of $\rho(x, v, t)$ will be different for each realization of $\xi(t)$. However, when we observe an actual Brownian particle we are observing the average effect of the random force on it. Therefore, we introduce an *observable* probability, $P(x, v, t)dxdv$, to find the Brownian particle in the interval $x \to x + dx$ and $v \to v + dv$. We define this observable probability to be

$$P(x, v, t) = \langle\rho(x, v, t)\rangle_\xi. \tag{5.126}$$

We now must find the equation of motion of $P(x, v, t)$.

Since the random force, $\xi(t)$, has zero mean and is a Gaussian white noise, the derivation of $P(x, v, t)$ is straightforward and very instructive. It only takes a bit of algebra. We first introduce a new probability density, $\sigma(t)$, such that

$$\rho(t) = e^{-\hat{L}_0 t}\sigma(t). \tag{5.127}$$

Using Eqs. (5.124), (5.126), and (5.127), it is easy to show that $\sigma(t)$ obeys the equation of motion:

$$\frac{\partial\sigma(t)}{\partial t} = -\hat{V}(t)\sigma(t), \tag{5.128}$$

where $\hat{V}(t) = e^{+\hat{L}_0 t}\hat{L}_1(t)e^{-\hat{L}_0 t}$. Equation (5.128) has the formal solution

$$\sigma(t) = \exp\left[-\int_0^t dt'\hat{V}(t')\right]\sigma(0). \tag{5.129}$$

Let us now expand the exponential in Eq. (5.129) in a power series. Using the identity $e^x = \sum_{n=0}^{\infty}(x^n/n!)$, we obtain

$$\sigma(t) = \left[\sum_{n=0}^{\infty} \frac{(-1)^n}{n!}\left(\int_0^t dt' \hat{V}(t')\right)^n\right]\sigma(0). \tag{5.130}$$

We now can take the average, $\langle\rangle_\xi$, of Eq. (5.130). Because the noise, $\xi(t)$, has zero mean and is Gaussian, only even values of n will remain (cf. Exercise 4.9). Thus, we find

$$\langle\sigma(t)\rangle_\xi = \left[\sum_{n=0}^{\infty} \frac{1}{(2n)!}\left\langle\left(\int_0^t dt' \hat{V}(t')\right)^{2n}\right\rangle_\xi\right]\sigma(0). \tag{5.131}$$

We can use some results from Exercise 4.9 to simplify Eq. (5.131). The average, $\langle(\int_0^t dt' \hat{V}(t'))^{2n}\rangle_\xi$, will decompose into $(2n!/n!2^n)$ identical terms, each containing a product of n pairwise averages, $\langle\int_0^t dt_i \hat{V}(t_i)\int_0^t dt_j \hat{V}(t_j)\rangle_\xi$. Thus, Eq. (5.131) takes the form

$$\langle\sigma(t)\rangle_\xi = \left[\sum_{n=0}^{\infty} \frac{1}{n!}\left(\frac{1}{2}\int_0^t dt_2 \int_0^t dt_1 \langle\hat{V}(t_2)\hat{V}(t_1)\rangle_\xi\right)^n\right]\sigma(0). \tag{5.132}$$

We can now sum this series to obtain

$$\langle\sigma(t)\rangle_\xi = \exp\left[\frac{1}{2}\int_0^t dt_2 \int_0^t dt_1 \langle\hat{V}(t_2)\hat{V}(t_1)\rangle_\xi\right]\sigma(0). \tag{5.133}$$

Let us compute the integral in Eq. (5.133),

$$\begin{aligned}
&\frac{1}{2}\int_0^t dt_2 \int_0^t dt_1 \langle\hat{V}(t_2)\hat{V}(t_1)\rangle_\xi \\
&= \frac{g}{2m^2}\int_0^t dt_2 \int_0^t dt_1 \delta(t_2 - t_1) e^{+\hat{L}_0 t_2}\frac{\partial}{\partial v} e^{-\hat{L}_0(t_2 - t_1)}\frac{\partial}{\partial v} e^{-\hat{L}_0 t_1} \\
&= \frac{g}{2m^2}\int_0^t dt_1 e^{+\hat{L}_0 t_1}\frac{\partial^2}{\partial v^2} e^{-\hat{L}_0 t_1}.
\end{aligned} \tag{5.134}$$

If we substitute Eq. (5.134) into Eq. (5.133) and take the derivative of Eq. (5.133) with respect to time t, we find the following equation of motion for $\langle\sigma(t)\rangle_\xi$,

$$\frac{\partial\langle\sigma(t)\rangle_\xi}{\partial t} = \frac{g}{2m^2} e^{+\hat{L}_0 t}\frac{\partial^2}{\partial v^2} e^{-\hat{L}_0 t}\langle\sigma(t)\rangle_\xi. \tag{5.135}$$

With this result, we can obtain the equation of motion of $P(x, v, t) = \langle\rho(x, v, t)\rangle_\xi$.

Let us note that $\langle \rho(t) \rangle_\xi = \hat{U}(t) \langle \sigma(t) \rangle_\xi$, where $\hat{U}(t) = e^{-\hat{L}_0 t}$, and take the derivative of $\langle \rho(t) \rangle_\xi$ with respect to time t. We then obtain

$$\frac{\partial \langle \rho(t) \rangle_\xi}{\partial t} = -\hat{L}_0 \langle \rho(t) \rangle_\xi + \hat{U}(t) \frac{\partial \langle \sigma(t) \rangle_\xi}{\partial t} = -\hat{L}_0 \langle \rho(t) \rangle_\xi + \frac{g}{2m^2} \frac{\partial \langle \rho(t) \rangle_\xi}{\partial v^2}. \tag{5.136}$$

If we combine Eqs. (5.125), (5.126), and (5.136), the equation for the observable probability density, $P(x, v, t)$, becomes

$$\frac{\partial P}{\partial t} = -v \frac{\partial P}{\partial x} + \frac{\partial}{\partial v} \left[\left(\frac{\gamma}{m} v - \frac{1}{m} F(x) \right) P \right] + \frac{g}{2m^2} \frac{\partial^2 P}{\partial v^2}, \tag{5.137}$$

where $P = P(x, v, t)$. Equation (5.134) is the *Fokker–Planck equation* for the probability $P(x, v, t)dxdv$ to find the Brownian particle in the interval $x \to x + dx$ and $v \to v + dv$ at time t.

It is important to note that the Fokker–Planck equation conserves probability. We can write it in the form of a *continuity equation*

$$\frac{\partial P}{\partial t} = -\nabla \cdot \mathbf{J}, \tag{5.138}$$

where $\nabla = \hat{\mathbf{x}}(\partial/\partial x) + \hat{\mathbf{v}}(\partial/\partial v)$ is a gradient operator in the (x, v) phase space and $\mathbf{J}$ is the probability current or flux,

$$\mathbf{J} = \hat{\mathbf{x}} v P - \hat{\mathbf{v}} \left(\frac{\gamma}{m} v P - \frac{1}{m} F(x) P + \frac{g}{2m^2} \frac{\partial P}{\partial v} \right), \tag{5.139}$$

in the (x, v) phase space. By the same arguments used in Eqs. (5.120) and (5.121), we see that any change in the probability contained in a given area of the (x, v) phase space must be due to flow of probability through the sides of the area, and therefore the probability is a conserved quantity. It cannot be created or destroyed locally.

In this section we have derived the Fokker–Planck equation for a Brownian particle which is free to move in one spatial dimension. The Fokker–Planck can be generalized easily to three spatial dimensions. However, when the force $\mathbf{F}(\mathbf{x})$ couples the degrees of freedom, little is known about the details of its dynamical evolution. Below we consider Brownian motion in the limit of very large friction. For this case, detailed balance holds, the force can be expressed in terms of a potential, and we can begin to understand some of the complex phenomena governing the dynamics of the Fokker–Planck equation.

▶ S5.C.3. The Strong Friction Limit

Let us now consider a Brownian particle moving in one dimension in a potential well, $V(x)$, and assume that the friction coefficient, γ, is very large so that the

velocity of the Brownian particle relaxes to its stationary state very rapidly. Then we can neglect time variations in the velocity and in the Langevin equations [Eq. (5.123)], we assume that $(dv/dt) \approx 0$. The Langevin equations then reduce to

$$\frac{dx(t)}{dt} = \frac{1}{\gamma}F(x) + \frac{1}{\gamma}\xi(t), \tag{5.140}$$

where $F(x) = -(dV(x)/dx)$. We now can use the method of Section S5.C.2 to find the probability $P(x,t)dx$ to find the Brownian particle in the interval $x \to x + dx$ at time t. The probability density, $P(x,t)$, is defined as the average, $P(x,t) = \langle \rho(x,t) \rangle_\xi$, where the equation of motion for the density, $\rho(x,t)$, is given by

$$\begin{aligned} \frac{\partial \rho(t)}{\partial t} &= -\frac{\partial(\dot{x}\rho)}{\partial x} = -\frac{1}{\gamma}\frac{\partial(F(x)\rho)}{\partial x} - \frac{1}{\gamma}\xi(t)\frac{\partial \rho}{\partial x} \\ &= -L_0\rho(t) - L_1(t)\rho(t). \end{aligned} \tag{5.141}$$

The differential operators L_0 and L_1 are defined as

$$L_0 = \frac{1}{\gamma}\frac{\partial F(x)}{\partial x} + \frac{1}{\gamma}F(x)\frac{\partial}{\partial x} \quad \text{and} \quad L_1 = \frac{1}{\gamma}\xi(t)\frac{\partial}{\partial x}. \tag{5.142}$$

If we now substitute into Eqs. (5.136) and (5.137), we obtain

$$\frac{\partial P(x,t)}{\partial t} = \frac{1}{\gamma}\frac{\partial}{\partial x}\left(\frac{dV}{dx}P(x,t) + \frac{g}{2\gamma}\frac{\partial P(x,t)}{\partial x}\right) = -\frac{\partial J}{\partial x}, \tag{5.143}$$

where $J = -(1/\gamma)(dV/dx)P + (g/2\gamma^2)(dP/dx)$ is the probability current. Equation (5.143) is now a Fokker–Planck equation for the probability density $P(x,t)$ to find the Brownian particle in the interval $x \to x + dx$ at time t. Because Eq. (5.143) has the form of a continuity equation, the probability is conserved.

▶ S5.C.4. Solution of Fokker–Planck Equations with One Variable

For the case of a "free" Brownian particle, one for which $V(x) = 0$, the Fokker–Planck equation (5.143) reduces to the *diffusion equation*

$$\frac{\partial P(x,t)}{\partial t} = \frac{g}{2\gamma^2}\frac{\partial^2 P(x,t)}{\partial x^2} = D\frac{\partial^2 P(x,t)}{\partial x^2}. \tag{5.144}$$

As we showed in Section 4.E, this has a solution

$$P(x,t) = \sqrt{\frac{1}{4\pi Dt}}\exp\left(\frac{-x^2}{4Dt}\right). \tag{5.145}$$

Note that $(1/D) = (2\gamma^2/g) = (\gamma/k_BT)$. Thus for large friction coefficient, γ, the spatial relaxation is very slow.

For the case when $V(x) \neq 0$, we can obtain a spectral decomposition of the probability density $P(x,t)$. Let us first introduce a rescaled time $\tau = t/\gamma$ and write the Fokker-Planck equation (5.143) as

$$\frac{\partial P(x,\tau)}{\partial \tau} = \frac{d^2V}{dx^2}P + \frac{dV}{dx}\frac{\partial P}{\partial x} + \frac{g}{2\gamma}\frac{\partial^2 P}{\partial x^2} = -\hat{L}_{FP}P(x,\tau). \tag{5.146}$$

The operator, $\hat{L}_{LP} = (d^2V/dx^2) + (dV/dx)(\partial/\partial x) + (g/2\gamma)(\partial^2/\partial x^2)$, is a non-self-adjoint operator because of its dependence on the first-order partial derivative. However, it is possible to rewrite the Fokker–Planck equation in terms of a self-adjoint operator via a simple transformation. Then the solutions become more intuitive.

Let us write the probability in the form

$$P(x,\tau) = e^{-\gamma V(x)/g}\Psi(x,\tau), \tag{5.147}$$

where $\Psi(x,\tau)$ is a function to be determined. If we now substitute into Eq. (5.146) we obtain the following equation for $\Psi(x,\tau)$:

$$\frac{\partial \Psi(x,\tau)}{\partial \tau} = \left(\frac{1}{2}\frac{d^2V}{dx^2} - \frac{\gamma}{2g}\left(\frac{dV}{dx}\right)^2\right)\Psi(x,\tau) + \frac{g}{2\gamma}\frac{\partial^2\Psi}{\partial x^2} = -\hat{H}_{FP}\Psi(x,\tau). \tag{5.148}$$

The operator, $\hat{H}_{FP} = -(\frac{1}{2}(d^2V/dx^2) - (\gamma/2g)(dV/dx)^2) - (g/2\gamma)(\partial^2/\partial x^2)$, is a self-adjoint operator and we can use the many well established techniques for dealing with such operators. We will let $\phi_n(x)$ and λ_n denote the nth eigenvector and eigenvalue, respectively, of H_{FP} so that $H_{FP}\phi_n(x) = \lambda_n\phi_n(x)$. The eigenvectors are complete and can be made orthonormal so that

$$\int_{-\infty}^{\infty} dx\phi_{n'}(x)\phi_n(x) = \delta_{n',n}. \tag{5.149}$$

Furthermore, the eigenvalues are real and must have zero or positive values in order that the probability remains finite. We can expand $\Psi(x,t)$ in terms of the eigenvectors and eigenvalues of $\hat{H}_{FP}$:

$$\Psi(x,\tau) = \sum_{n=0}^{\infty} a_n e^{-\lambda_n\tau}\phi_n(x). \tag{5.150}$$

It is interesting to note that $\hat{H}_{FP}$ has at least one zero eigenvalue, which we denote $\lambda_0 = 0$, and a corresponding eigenvector, $\phi_0(x)$, which satisfies the equation

$$\left(\frac{1}{2}\frac{d^2V}{dx^2} - \frac{\gamma}{2g}\left(\frac{dV}{dx}\right)^2\right)\phi_0(x) + \frac{g}{2\gamma}\frac{\partial^2\phi_0(x)}{\partial x^2} = 0. \tag{5.151}$$

Equation (5.150) has the solution

$$\phi_0(x) = Ce^{-\gamma V(x)/g}, \tag{5.152}$$

where C is a normalization constant. This is just the transformation used in Eq. (5.146). Therefore we can now combine Eqs. (5.147), (5.150), and (5.152) and write the probability as

$$P(x,\tau) = \phi_0^2(x) + \sum_{n=1}^{\infty} a_n e^{-\lambda_n \tau}\phi_0(x)\phi_n(x). \tag{5.153}$$

In this form, it is clear that the probability is conserved due to the orthonormality of the eigenstates. If we integrate over Eq. (5.153), we obtain

$$\int_{-\infty}^{\infty} dx P(x,\tau) = \int_{-\infty}^{\infty} dx \phi_0(x)^2 = 1. \tag{5.154}$$

The coefficients, a_n, can be determined from the initial conditions. Let us assume that we are given $P(x,0)$. Then we write

$$P(x,0) = \phi_0^2(x) + \sum_{n=1}^{\infty} a_n \phi_0(x)\phi_n(x). \tag{5.155}$$

If we now divide through by $\phi_0(x)$, multiply by $\phi_{n_0}(x)$, and integrate over x, we obtain

$$a_{n_0} = \int_{-\infty}^{\infty} dx \frac{\phi_{n_0}(x)}{\phi_0(x)} P(x,0). \tag{5.156}$$

After a long time, the probability approaches the stationary state:

$$P(x,\infty) = \phi_0^2(x). \tag{5.157}$$

There are several examples of Fokker–Planck equations with one variable which can be solved analytically. We will consider one of them in Exercise (5.8) and leave the others as homework problems.

This method can also be extended to Fokker–Planck equations with two or more spatial degrees of freedom when a transformation analogous to Eq. (5.146) can be found which allows us to write the Fokker–Planck equation in terms of a self-adjoint operator. For such cases, it is possible that the dynamics governed by the self-adjoint operator can undergo a transition to chaos. Examples of such cases have been studied in Refs. 22–24.

■ **EXERCISE 5.8.** Consider the "short-time" relaxation of a free Brownian particle. The Langevin equation for the velocity is $m(dv/dt) = -\gamma v + \xi(t)$. (a) Find the Fokker–Planck equation for the probability $P(v,t)dv$ to find the Brownian particle with velocity $v \to v + dv$ at time t. (b) Solve the Fokker–Planck equation, assuming that at time $t = 0$ the velocity is $v = v_0$.

Answer:

(**a**) To obtain the Fokker–Planck equation, we will follow the method of Section S5.C. The equation for the probability $\rho(v,t)$ for a specific realization of the random force $\xi(t)$ is

$$\frac{\partial \rho}{\partial t} = -\frac{\partial \dot{v}\rho}{\partial v} = \frac{\gamma}{m}\frac{\partial v\rho}{\partial v} - \frac{1}{m}\xi(t)\frac{\partial \rho}{\partial v}. \tag{1}$$

From Eq. (1) we see that $\hat{L}_0 = -(\gamma/m)(1 + v(\partial/\partial v))$. We can now plug into Eq. (5.136) to obtain a Fokker–Planck equation for the probability density $P(v,t)$. We find

$$\frac{\partial P}{\partial t} = \frac{\gamma}{m}\frac{\partial (vP)}{\partial v} + \frac{g}{2m^2}\frac{\partial^2 P}{\partial v^2}. \tag{2}$$

(**b**) To solve the Fokker–Planck equation, we follow the method of Section S5.C.3. Make a transformation, $P(v,t) = e^{-m\gamma v^2/2g}\Psi(v,t)$. If we plug this into Eq. (2), we obtain the following equation for $\Psi(v,t)$,

$$\frac{m}{\gamma}\frac{\partial \Psi}{\partial t} = \left(\frac{1}{2} - \frac{1}{4A}v^2 + A\frac{\partial^2}{\partial v^2}\right)\Psi \equiv \hat{H}\Psi. \tag{3}$$

where $A = (g/2m\gamma)$. The operator $\hat{H} = \frac{1}{2} - (1/4A)v^2 + A(\partial^2/\partial v^2)$ is self-adjoint and has eigenfunctions $\phi_n(v)$ $(n = 0, 1, 2, \ldots, \infty)$ which can be expressed in terms of Hermite polynomials [20]. The nth normalized eigenfunction of $\hat{H}$ is

$$\phi_n(v) = \frac{1}{\sqrt{2^n n!}\sqrt{2\pi A}} H_n\left(\frac{v}{\sqrt{2A}}\right) e^{-v^2/4A}, \tag{4}$$

where $H_n(y)$ is the nth-order Hermite polynomial and can be written $H_n(y) = (-1)^n e^{y^2}(d^n/dy^n)e^{-y^2}$. The operator $\hat{H}$ satisfies the eigen-

value equation $\hat{H}\phi_n(v) = -n\phi_n(v)$, so the nth eigenvalue is $\lambda_n = -n$. The eigenfunctions satisfy the orthonormality condition

$$\int_{-\infty}^{\infty} dv \phi_{n'}(v)\phi_n(v) = \delta_{n',n}. \tag{5}$$

If we redefine the time to be $\tau = (\gamma/m)t$, then we obtain the following spectral decomposition of $\Psi(v,t)$,

$$\Psi(v,t) = \sum_{n=0}^{\infty} a_n e^{-n\tau}\phi_n(v). \tag{6}$$

The probability $P(v,\tau)$ is

$$P(v,\tau) = \sum_{n=0}^{\infty} a_n e^{-n\tau}\phi_0(v)\phi_n(v). \tag{7}$$

The initial probability distribution is $P(v,0) = \delta(v - v_0)$. This gives $a_n = \phi_n(v_0)/\phi_0(v_0)$ and we obtain

$$\begin{aligned} P(v,\tau) &= \sum_{n=0}^{\infty} e^{-n\tau}\phi_n(v_0)\phi_n(v)\phi_0(v)/\phi_0(v_0) \\ &= \frac{1}{\sqrt{2\pi A}} e^{-v^2/2A} \sum_{n=0}^{\infty} \frac{1}{2^n n!} e^{-n\tau} H_n\left(\frac{v_0}{\sqrt{2A}}\right) H_n\left(\frac{v}{\sqrt{2A}}\right). \end{aligned} \tag{9}$$

We now can make use of an identity

$$\frac{1}{\sqrt{1-z^2}} \exp\left(\frac{-(x^2+y^2-2xyz)}{1-z^2}\right) = e^{-x^2-y^2} \sum_{n=0}^{\infty} \left(\frac{z^n}{2^n n!}\right) H_n(x) H_n(y) \tag{10}$$

(see Ref. 21, page 786). Using this identity, the probability can be written

$$P(v,\tau) = \frac{1}{\sqrt{2\pi A(1-e^{-2\tau})}} \exp\left(\frac{-(v - v_0 e^{-\tau})^2}{2A(1-e^{-2\tau})}\right). \tag{11}$$

Thus, the probability density has the form of a Gaussian. The average velocity decays as $\langle v(t)\rangle = v_0 e^{-\tau}$, and the velocity distribution has a standard deviation, $\sigma_v = \sqrt{A(1-e^{-2\tau})}$. In the limit of "long time" the probability density takes the form

$$P(v,t) \approx \frac{1}{\sqrt{2\pi\gamma k_B T/m^2}} \exp\left(\frac{-m^2 v^2}{2\gamma k_B T}\right). \tag{12}$$

Thus, for large friction coefficient, γ, the relaxation time for the

velocity distribution goes as γ^{-1} while the relaxation time for the spatial distribution goes as γ.

▶ S5.D. Approximations to the Master Equation [3, 4]

The master equation, under some conditions, may be reduced to a Fokker–Planck equation. For example, if the step size shrinks and the transition rate grows as a small parameter decreases to zero, then we can use the Kramers–Moyal expansion to obtain a Fokker–Planck equation from the master equation. We have already used this fact in Chapter 4 when we obtained the continuum limit for discrete random walks.

Let us consider a random walk in which the step size is given by Δ. The master equation can be written

$$\frac{\partial P_1(n\Delta,t)}{\partial t} = \sum_{m=-\infty}^{\infty} [P_1(m\Delta,t)w_{m,n}(\Delta) - P_1(n\Delta,t)w_{n,m}(\Delta)], \tag{5.158}$$

where $P_1(n\Delta,t)$ is the probability to find the walker at point $x = n\Delta$ at time t. Let us choose the transition rate to be

$$w_{n',n}(\Delta) = \frac{1}{\Delta^2}(\delta_{n',n+1} + \delta_{n',n-1}). \tag{5.159}$$

Then the master equation becomes

$$\frac{\partial P_1(n\Delta,t)}{\partial t} = \frac{1}{\Delta^2}[P_1((n+1)\Delta,t) + P_1((n-1)\Delta,t) - 2P_1(n\Delta,t)]. \tag{5.160}$$

We now let $x = n\Delta$ in Eq. (5.159) and let $\Delta \to 0$. To determine what becomes of the left-hand side in this limit, we expand it in a Taylor series in the small parameter, Δ keeping $x = n\Delta$. Then

$$\begin{aligned}\frac{\partial P_1(x,t)}{\partial t} &= \lim_{\Delta\to 0}\frac{1}{\Delta^2}[P_1(x+\Delta,t) + P_1(x-\Delta,t) - 2P_1(x,t)] \\ &= \lim_{\Delta\to 0}\frac{1}{\Delta^2}\left[P_1(x,t) + \left(\frac{\partial P_1}{\partial x}\right)_{\Delta=0}\Delta + \frac{1}{2}\left(\frac{\partial^2 P_1}{\partial x^2}\right)_{\Delta=0}\Delta^2 + \cdots\right. \\ &\quad \left. + P_1(x,t) - \left(\frac{\partial P_1}{\partial x}\right)_{\Delta=0}\Delta + \frac{1}{2}\left(\frac{\partial^2 P_1}{\partial x^2}\right)_{\Delta=0}\Delta^2 + \cdots - 2P_1(x,t)\right] \\ &= \frac{\partial^2 P_1}{\partial x^2}. \end{aligned} \tag{5.161}$$

Thus, in the limit $\Delta \to 0$ the random walk is described by a simple Fokker–

Planck equation. Higher-order derivatives in the Taylor series do not contribute because their coefficients go to zero. Lower-order terms in the Taylor series cancel. We see that the condition to obtain a Fokker–Planck equation is that the step size, Δ, decreases and the transition rate, $w_{m,n}(\Delta)$, increases as $1/\Delta^2$. This is a simple example of a Kramers–Moyal-type expansion [25, 26].

It is useful to consider a more general example. Let us write the master equation for the continuous stochastic variable x:

$$\frac{\partial P_1(x,t)}{\partial t} = \int_{-\infty}^{\infty} dx' [P_1(x',t)w(x'|x) - P_1(x,t)w(x|x')], \tag{5.162}$$

where $w(x'|x)$ is the transition rate. Let $y = x' - x$ denote the change in stochastic variable x at a transition, and introduce the notation $\tau(x,y) = w(x|x+y)$ so that $\tau(x-y,y) = w(x-y|y)$. In Eq. (5.162), make the change of variables $x' = x + y$, and in the first term under the integral let $y \to -y$. Then the master equation can be rewritten

$$\frac{\partial P_1(x,t)}{\partial t} = \int_{-\infty}^{\infty} dy [P_1(x-y,t)\tau(x-y,y) - P_1(x)\tau(x,y)]. \tag{5.163}$$

We can now expand $P_1(x-y,t)\tau(x-y,y)$ in a Taylor series in y. This, of course, only makes sense if the function $\tau(x,y)$ is sharply peaked about $y = 0$. Equation (5.163) takes the form

$$\begin{aligned}\frac{\partial P_1(x,t)}{\partial t} &= \int_{-\infty}^{\infty} dy \left[\left(\sum_{n=0}^{\infty} \frac{(-y)^n}{n!} \frac{\partial^n}{\partial x^n} (P_1(x,t)\tau(x,y)) \right) - P_1(x,t)\tau(x,y) \right] \\ &= \int_{-\infty}^{\infty} dy \sum_{n=1}^{\infty} \frac{(-y)^n}{n!} \frac{\partial^n}{\partial x^n} (P_1(x,t)\tau(x,y)).\end{aligned} \tag{5.164}$$

Thus,

$$\frac{\partial P_1(x,t)}{\partial t} = \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \frac{\partial^n}{\partial x^n} (\alpha_n(x) P_1(x,t)), \tag{5.165}$$

where $\alpha_n(x)$ is the nth moment,

$$\alpha_n(x) = \int_{-\infty}^{\infty} dy\, y^n \tau(x,y) = \int_{-\infty}^{\infty} dy\, y^n\, w(x|x+y). \tag{5.166}$$

Equation (5.165) is the *Kramers–Moyal* expansion of the master equation. It only has meaning for those special forms of $w(x|x+y) = \tau(x,y)$ for which the infinite series of higher-order derivatives truncates. We shall now give an example of such a case.

Let us choose $w(x|x+y) = \tau(x,y)$ to be of the form

$$w(x|x+y) = \tau(x,y) = \frac{1}{\sqrt{\pi}\Delta^3}\exp\left(-\frac{(y-A(x)\Delta^2)^2}{\Delta^2}\right). \tag{5.167}$$

Then

$$\alpha_1 = \int_{-\infty}^{\infty} dy\, y\, w(x|x+y) = A(x), \tag{5.168}$$

and

$$\alpha_2 = \int_{-\infty}^{\infty} dy\, y^2\, w(x|x+y) = \tfrac{1}{2} + \Delta^2 A^2(x). \tag{5.169}$$

Higher-order odd moments are identically zero, and higher-order even moments are proportional to powers of Δ. Thus, for the choice of $w(x|x+y)$ given in Eq. (5.167), as $\Delta \to 0$, the master equation reduces to

$$\frac{\partial P_1(x,t)}{\partial t} = -A(x)\frac{\partial P_1(x,t)}{\partial x} + \frac{1}{4}\frac{\partial^2 P_1(x,t)}{\partial x^2}. \tag{5.170}$$

For this process the step size decreases because the width of the Gaussian shrinks, and the transition rate increases as $\Delta \to 0$. If this occurs in the particular manner shown in Eq. (5.167), then the Kramers–Moyal expansion has meaning.

For the case when the step size in a master equation cannot be made arbitrarily small, as is the case for chemical reactions or population dynamics, the Kramers–Moyal expansion of the master equation may not give a good approximation. Then one must use some other approximation scheme or solve the equation numerically. An alternative approximation scheme has been introduced by van Kampen. He has shown that it is still possible to approximate the master equation by a Fokker–Planck equation if the system has a large parameter, such as a volume or total particle number, and if the transition rates depend on that large parameter in a certain way. A full discussion of this method may be found in van Kampen's book [3].

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PROBLEMS

Problem 5.1. Urn A initially has one white and one red marble, and urn B initially has one white and three red marbles. The marbles are repeatedly interchanged. In each step of the process one marble is selected from each urn at random and the two marbles selected are interchanged. Let the stochastic variable Y denote "configuration of the urns." Three configurations are possible: (1) Urn A—2 white balls, Urn B—4 red balls;

(2) Urn A—one white and one red ball, Urn B—one white and three red balls; (3) Urn A—two red balls, Urn B—two white and two red balls. We shall denote these three realizations as y(1), y(2), and y(3), respectively. (a) Compute the transition matrix, $\mathbf{Q}$, and the conditional probability matrix, $\mathbf{P}(s_0|s)$. (b) Compute the probability vector, $\langle \mathbf{P}(s)|$, at time s, given the initial condition stated above. What is the probability that there are 2 red marbles in urn A after 2 steps? After many steps? (c) Assume that the realization, $y(n)$, equals n^2. Compute the first moment, $\langle y(s)\rangle$, and the autocorrelation function, $\langle y(0)y(s)\rangle$, for the same initial conditions as in part (b).

Problem 5.2. Three boys, A, B, and C, stand in a circle and play catch (B stands to the right of A). Before throwing the ball, each boy flips a coin to decide whether to throw to the boy on his right or left. If "heads" comes up, the boy throws to his right. If "trials" comes up, he throws to his left. The coin of boy A is "fair" (50% heads and 50% tails), the coin of boy B has heads on both side, and the coin of boy C is weighted (75% heads and 25% tails). (a) Compute the transition matrix, its eigenvalues, and its left and right eigenvectors. (b) If the ball is thrown at regular intervals, approximately what fraction of time does each boy have the ball (assuming they throw the ball many times)? (c) If boy A has the ball to begin with, what is the chance he will have it after two throws? What is the chance he will have it after s throws?

Problem 5.3. A trained mouse lives in the house shown in the Fig. 5.4. A bell rings at regular intervals (short compared to the mouses lifetime). Each time it rings, the mouse changes rooms. When he changes rooms, he is equally likely to pass through any of the doors of the room he is in. Let the stochastic variable Y denote "mouse in a particular room." There are three realizations of Y: "mouse in room A," "mouse in room B," and "mouse in room C," which we denote as y(1), y(2), and y(3), respectively. (a) Compute the transition matrix, $\mathbf{Q}$, and the conditional probability matrix, $\mathbf{P}(s_0|s)$. (b) Compute the probability vector, $\langle \mathbf{P}(s)|$, at time s, given that the mouse starts in room C. Approximately what fraction of his life does he spend in each room? (c) Assume that the realization, $y(n)$, equals n. Compute the first moment, $\langle y(s)\rangle$, and the autocorrelation function, $\langle y(0)y(s)\rangle$, for the same initial conditions as in part (b).

Problem 5.4. The doors of the mouse's house in Fig. 5.4 are fixed so that they periodically get larger and smaller. This causes the mouse's transition probability between rooms to become time periodic. Let the stochastic variable Y have the same meaning as in Problem 5.3. The transition matrix is now given by $Q_{1,1}(s) = Q_{2,2}(s) = Q_{3,3}(s) = 0$, $Q_{1,2}(s) = \cos^2(\pi s/2), Q_{1,3}(s) = \sin^2(\pi s/2)$, $Q_{2,1}(s) = \frac{1}{4} + \frac{1}{2}\sin^2(\pi s/2), Q_{2,3}(s) = \frac{1}{4} + \frac{1}{2}\cos^2(\pi s/2), Q_{3,1}(s) = \frac{1}{2}\cos^2(\pi s/2)$, and $Q_{3,2}(s) = \frac{1}{2} + \frac{1}{2}\sin^2(\pi s/2)$. (a) If initially the mouse is in room A, what is the

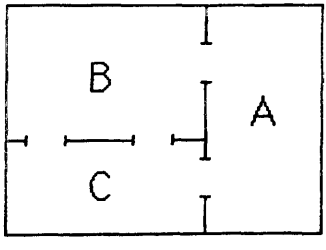


Fig. 5.4. Mouse's house.

probability to find it in room A after $2s$ room changes? In room B? (b) If initially the mouse is in room B, what is the probability to find it in room A after $2s$ room changes? In room B?

Problem 5.5. Consider a discrete random walk on a one-dimensional periodic lattice with $2N+1$ lattice sites (label the sites from $-N$ to N). Assume that the walker is equally likely to move one lattice site to the left or right at each step. Treat this problem as a Markov chain. (a) Compute the transition matrix, $\mathbf{Q}$, and the conditional probability matrix, $\mathbf{P}\ (s_0|s)$. (b) Compute the probability $P_1(n,s)$ at time s, given the walker starts at site $n=0$. (c) If the lattice has five lattice sites ($N=2$), compute the probability to find the walker on each site after $s=2$ steps and after $s=\infty$ steps. Assume that the walker starts at site $n=0$.

Problem 5.6. At time t, a radioactive sample contains n identical undecayed nuclei, each with a probability per unit time, λ, of decaying. The probability of a decay during the time $t \to t+\Delta t$ is $\lambda n \Delta t$. Assume that at time $t=0$ there are n_0 undecayed nuclei present. (a) Write down and solve the master equation for this process [find $P_1(n,t)$]. (b) Compute the mean number of undecayed nuclei and the variance as a function of time. (c) What is the half-life of this decay process?

Problem 5.7. Consider a random walk on the lattice shown in Fig. 5.5. The transition rates are $w_{1,2}=w_{1,3}=\frac{1}{2}$, $w_{2,1}=w_{2,3}=w_{2,4}=\frac{1}{3}$, $w_{3,1}=w_{3,2}=w_{3,4}=\frac{1}{3}$, $w_{4,2}=w_{4,3}=\frac{1}{2}$, and $w_{1,4}=w_{4,1}=0$. (a) Write the transition matrix, $\mathbf{W}$, and show that this system obeys detailed balance. (b) Compute the symmetric matrix, $\mathbf{V}$, and find its eigenvalues and eigenvectors. (c) Write $P_1(n,t)$ for the case $P_1(n,0)=\delta_{n,1}$. What is $P_1(4,t)$?

Problem 5.8. Consider a random walk on the lattice shown in Fig. 5.6. The site, P, absorbs the walker. The transition rates are $w_{1,2}=w_{1,3}=\frac{1}{2}$, $w_{2,1}=w_{2,3}=w_{2,P}=\frac{1}{3}$, $w_{3,1}=w_{3,2}=w_{3,P}=\frac{1}{3}$, and $w_{P,1}=w_{P,2}=\frac{1}{2}$. (a) Write the transition matrix, $\mathbf{M}$, and compute its eigenvalues and and left and right eigenvectors. (b) If the walker starts at site $n=1$ at time $t=0$, compute the mean first passage time.

Problem 5.9. Let us consider on RL electric circuit with resistance, R, and inductance, L, connected in series. Even though no average electromotive force (EMF) exists across the resistor, because of the discrete character of the electrons in the circuit and their random motion, a fluctuating EMF, $\xi(t)$, exists whose strength is determined by the temperature, T. This, in turn, induces a fluctuating current, $I(t)$, in the circuit. The Langevin equation of motion for the current is

$$L\frac{dI(t)}{dt}+RI(t)=\xi(t),$$

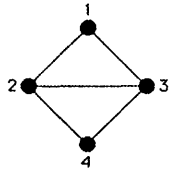


Fig. 5.5.

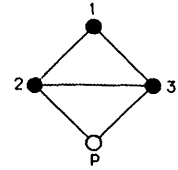


Fig. 5.6.

If the EMF is delta-correlated, $\langle \xi(t_2)\xi(t_1)\rangle_\xi = g\delta(t_2 - t_1)$ and $\langle \xi(t)\rangle_\xi = 0$, compute, g, and the current correlation function, $\langle\langle I(t_2)I(t_1)\rangle_\xi\rangle_T$. Assume that the average magnetic energy in the inductor is $\frac{1}{2}L\langle I_0^2\rangle_T = \frac{1}{2}k_BT$ and $\langle I_0\rangle_T = 0$, where $I(0) = I_0$.

Problem 5.10. Due to the random motion and discrete nature of electrons, and LRC series circuit experiences a random electromotive from (EMF), $\xi(t)$. This, in turn, induces a random varying charge, $Q(t)$, on the capacitor plates and a random current, $I(t) = (dQ(t)/dt)$, through the resistor and inductor. The random charge, $Q(t)$, satisfies the Langevin equation

$$L\frac{d^2Q(t)}{dt^2} + R\frac{dQ(t)}{dt} + \frac{Q(t)}{C} = \xi(t).$$

Assume that the EMF is delta-correlated, $\langle \xi(t_2)\xi(t_1)\rangle_\xi = g\delta(t_2 - t_1)$, and $\langle \xi(t)\rangle_\xi = 0$. Assume that the circuit is at temperature T and that the average magnetic energy in the inductor and average electric energy in the capacitor satisfy the equipartition theorem, $\frac{1}{2}L\langle I_0^2\rangle_T = \frac{1}{2}k_BT$ and $\frac{1}{2C}\langle Q_0^2\rangle_t = \frac{1}{2}k_BT$, where $Q(0) = Q_0$ and $I(0) = I_0$. Assume that $\langle Q_0\rangle_T = \langle I_0\rangle_T = \langle Q_0I_0\rangle_T = 0$. (a) Compute the current correlation function, $\langle\langle I(t_2)I(t_1)\rangle_\xi\rangle_T$. (b) Compute the variance of the charge distribution, $\langle\langle (Q(t) - Q_0)^2\rangle_\xi\rangle_T$.

Problem 5.11. Consider a Brownian particle of mass m moving in one dimension in the presence of a constant force f_0 (such as a gravitational or electric field) in a fluid with force constant γ and in the presence of a delta-correlated random force $\xi(t)$ such that $\langle \xi(t_2)\xi(t_1)\rangle_\xi = g\delta(t_2 - t_1)$ and $\langle \xi(t)\rangle_\xi = 0$. Assume that the velocity and displacement of the Brownian particle at time $t = 0$ are v_0 and x_0, respectively. (a) Compute the velocity correlation function $\langle v(t_2)v(t_1)\rangle_\xi$. (b) Compute the variance $\langle (x(t) - x_0)^2\rangle_\xi$.

Problem S5.1. Consider a linear birth–death process which includes the possibility of a change in population due to immigration in addition to the change that occurs due to the birth and death of individuals in the population. Assume that at time t the population has n members. Let $\alpha\Delta t$ be the probability that one individual enters the society due to immigration in time $t \to t + \Delta t$. Let $\beta n\Delta t(\gamma n\Delta t)$ be the probability of a birth (death) in time $t \to t + \Delta t$. Assume that at time $t = 0$ the population has $n = m$ members. (a) Write the master equation and compute the generating function, $F(z,t) = \sum_{n=-\infty}^{\infty} z^n P_1(n,t)$, for this process. (b) Compute the first moment $\langle n(t)\rangle$, and the variance, $\langle n^2(t)\rangle - \langle n(t)\rangle^2$, for this process.

Problem S5.2. Consider the chemical reaction

$$A + X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A + Y,$$

where molecule A is a catalyst whose concentration is maintained constant. Assume that the total number of molecules X and Y is constant and equal to N. $k_1(k_2)$ is the probability per unit time that molecule X (Y) interacts with a molecule A to produce a molecule Y (X). (a) Find the equation of motion for the probability $P_1(n,t)$ to find n X molecules in the system at time t, and find the generating function, $F(z,t) = \sum_{n=-\infty}^{\infty} z^n P_1(n,t)$. (b) Find the average number of X molecules in the system at time t, and find the variance in the distribution of X molecules. In the limit, $N \to \infty$, how does the variance for the particle distribution compare with that of a Gaussian distribution?

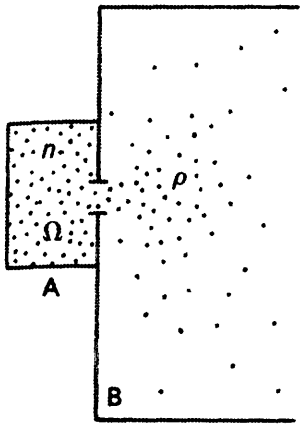


Fig. 5.7. Diffusion through a small hole.

Problem S5.3. Consider a box (A) of volume Ω, connected to another box (B) of infinite volume via a small hole (cf. Fig. 5.7). Assume that the probability that a particle moves from box A to box B in time Δt is $(n/\Omega)\Delta t$ and that the probability that a particle moves from box B to box A in time Δt is $\rho \Delta t$, where ρ is the density (assumed constant) of particles in box B. (a) Write down the master equation for the probability $P_1(n,t)$ to find n particles in box A at time t, and compute the generating function, $F(z,t) = \sum_{n=-\infty}^{\infty} z^n P_1(n,t)$. Assume that there are m particles in box A at time $t = 0$. (b) Compute $P_1(n,t)$ for the same initial conditions as part (a). (c) Find the average number of particles in box A and find the variance in particle number as a function of time.

Problem S5.4. Consider the chemical reaction in Problem S5.2 and let $N = 3, k_1 = 2$, and $k_2 = 1$. (a) Write the transition matrix, **W** and compute its eigenvalues and left and right eigenvectors. (b) If initially there are zero X-molecules in the system, what is the probability of finding three X-molecules at time t. What is the probability of finding three X-molecules at time $t = \infty$?

Problem S5.5. Consider the following chemical reaction,

$$\mathrm{A} + \mathrm{M} \xrightarrow{k_1} \mathrm{X} + \mathrm{M} \quad \text{and} \quad 2\mathrm{X} \xrightarrow{k_2} \mathrm{E} + \mathrm{D},$$

where molecules A, M, E, and D are obtained from large reservoirs and can be assumed constant. (a) Find the probability to have n X molecules in the system after a very long time, $t \to \infty$. (b) Find the average number of X molecules after a very long time. [*Some hints*: Use the boundary conditions $F(1) = 1$ and $F(-1) = 0$ for the generating function, $F(z)$. The generating function can be found in terms of modified Bessel functions. The transformation $F(z) = \sqrt{s}G(s)$, where $s = (1+z)/2$, might be helpful.]

Problem S5.6. The motion of an harmonically bound Brownian particle moving in one dimension is governed by the Langevin equations,

$$m\frac{dv(t)}{dt} = -\gamma v(t) - m\omega_0^2 x(t) + \xi(t) \quad \text{and} \quad \frac{dx(t)}{dt} = v(t),$$

where $v(t)$ and $x(t)$ are the velocity and displacement of the particle at time t, m is the

mass, γ is the friction coefficient, ω_0 is the natural frequency of the harmonic oscillator, and $\xi(t)$ is a delta-correlated random force. If the particle at time $t = 0$ is in equilibrium with the fluid, compute the variance, $\langle\langle(x(t) - x_0)^2\rangle_\xi\rangle_T$. [Note that for this case, $\langle\xi(t_2)\xi(t_1)\rangle_\xi = 4\gamma k_B T\delta(t_2 - t_1)$, and by the equipartition theorem, $\langle x_0^2\rangle_T = k_B T/m\omega_0^2$ and $\langle v_0^2\rangle_T = k_B T/m$. Also assume $\langle v_0\rangle_T = \langle x_0\rangle_T = \langle x_0 v_0\rangle_T = 0$.]

Problem S5.7. Consider a Brownian rotor with moment of inertia, I, constrained to rotate through angle, θ, about the z axis. The Langevin equations of motion for the rotor are $I(d\omega/dt) = -\Gamma\omega + \xi(t)$ and $(d\theta/dt) = \omega$, where ω is the angular velocity of the rotor, Γ is the friction coefficient, and $\xi(t)$ is a Gaussian white noise torque. The torque is delta-correlated, $\langle\xi(t')\xi(t)\rangle_\xi = G\delta(t' - t)$, where G is the noise strength. (a) For the case of large friction coefficient, Γ, write the Fokker–Planck equation for the probability density, $P(\theta, t)$, to find the Brownian rotor in the interval $\theta \to \theta + d\theta$ at time, t. (b) Solve the Fokker–Planck equation assuming that at time $t = 0$ the rotor is at $\theta = \theta_0$. (c) Compute the probability current at time t.

Problem S5.8. A Brownian particle of mass m moves in one dimension in the presence of a harmonic potential $V(x) = \frac{1}{2}kx^2$, where k is the force constant. The Langevin equations are given by $m[dv(t)/dt] = -\gamma v(t) - dV(x)/dx + \xi(t)$ and $dx(t)/dt = v(t)$, where γ is the friction coefficient and $\xi(t)$ is a Gaussian white noise force. The noise is delta-correlated, $\langle\xi(t')\xi(t)\rangle_\xi = g\delta(t' - t)$, where g is the noise strength. (a) Write the Fokker–Planck equation for the probability density, $P(x, t)$, in the limit of large friction coefficient. (b) Solve the Fokker–Planck equation and write the solution, $P(x, t)$, for arbitrary times. Assume that at time $t = 0$, the Brownian particle is at $x = x_0$. (c) Write an approximate expression for $P(x, t)$ for very long times.

Problem S5.9. Consider a biased random walk along the x axis with step size Δ and transition rate

$$w(n\Delta|n'\Delta) = \left(\frac{\alpha(n\Delta)}{\Delta} + \frac{\beta(n\Delta)}{\Delta^2}\right)\delta_{n',n+1} + \left(-\frac{\alpha(n\Delta)}{\Delta} + \frac{\beta(n\Delta)}{\Delta^2}\right)\delta_{n',n-1},$$

where $-\infty \leqslant n \leqslant \infty$ and $-\infty \leqslant n' \leqslant \infty$. Use the Kramers–Moyal expansion to obtain a Fokker–Planck equation for this random walk in the limit $\Delta \to 0$ with $n\Delta = x$.

6

THE FOUNDATIONS OF STATISTICAL MECHANICS

6.A. INTRODUCTION

In Chapter 5 we studied the time evolution of probability distributions in the Markov approximation, where the dynamics of the process was determined in terms of a single transition probability. The transition probability itself is usually determined phenomenologically; and thus the equations we derived, the master equation and the Fokker–Planck equation, may be considered as phenomenological equations. However, they exhibit exactly the type of behavior we need to describe the observed irreversible decay of systems to a unique equilibrium state. In this chapter we will set up the machinery for a microscopic probabilistic description of matter for both classical and quantum mechanical systems. That is, we shall lay the foundations for statistical mechanics and we will learn how thermodynamics and irreversible processes are thought to arise from the reversible laws of dynamics.

We want to describe the behavior of systems with a large number of degrees of freedom, such as N interacting particles in a box or N interacting objects on a lattice. The motion of such objects is governed by Newton's laws or, equivalently, by Hamiltonian dynamics. In three dimensions, such a system has $3N$ degrees of freedom (if we neglect internal degrees of freedom) and classically is specified by $6N$ independent position and momentum coordinates whose motion is uniquely determined from Hamiltonian dynamics. If we set up a $6N$-dimensional phase space, whose $6N$ coordinates consist of the $3N$ momentum and $3N$-position variables of the particles, then the state of the system is given by a single point in the phase space, which moves according to Hamiltonian dynamics as the state of the system changes. If we are given a real N-particle system, we never know exactly what its state is. We only know with a certain probability that it is one of the points in the phase space. Thus, the state point can be regarded as a stochastic variable and we can assign a probability distribution to the points in phase space in accordance with our knowledge of the state of the system. We then can view the phase space as a probability fluid which flows according to Hamiltonian dynamics. In this way, we obtain a connection between the mechanical description and a probabilistic description

of the system. The problem of finding an equation of motion for the probability density reduces to a problem in fluid dynamics. In this chapter, we shall also lay the foundations for equilibrium statistical mechanics. For classical dynamical systems which are *ergodic*, an equilibrium probability distribution can be constructed which gives excellent agreement with experiment.

When we deal with quantum systems the phase space variables no longer commute and it is often useful to use representations other than the coordinate representation to describe the state of the system. Thus, we introduce the idea of a probability density operator (a positive definite Hermitian operator), which can be used to find the probability distribution in any desired representation. We then can use the Schrödinger equation to find the equation of motion for the probability density operator.

The N-body probability density for a classical system contains more information about the system than we need. In practice, the main use of the probability density is to find expectation values or correlation functions for various observables, since those are what we measure experimentally and what we deal with in thermodynamics. The observables we deal with in physics are generally one- or two-body operators, and to find their expectation values we only need reduced one- or two-body probability densities and not the full N-body probability density. In the *special topics* section we shall find that the equations of motion for the reduced probability densities form a hierarchy of equations called the BBGKY hierarchy (after Born, Bogoliubov, Green, Kirkwood, and Yvon, who discovered it), which makes them impossible to solve without some approximation which terminates the hierarchy. This, in fact, is a general feature of all reduced descriptions.

In quantum systems, we cannot introduce probability densities which specify both the position and momentum of the particle, because these quantities do not commute. However, we can introduce quantities which are formally analogous, namely, the Wigner functions. The Wigner functions are not probability densities, because they can become negative. However, they can be used to obtain expectation values in a manner formally analogous to that of classical systems, and the reduced Wigner functions form a hierarchy which in the classical limit reduces to the classical BBGKY hierarchy.

Finally, in the last sections of the *special topics* section, we shall describe conditions under which systems which are governed by the reversible laws of Newtonian dynamics display irreversible behavior.

6.B. THE CLASSICAL PROBABILITY DENSITY [1–3]

If we view the flow of points in the phase space of a classical N-body Hamiltonian system as a fluid whose dynamics is governed by Hamilton's equations, then we can derive the equation of motion for the probability density of the classical system in phase space. This equation of motion is called the *Liouville equation*. Because Hamilton's equations preserve volume in phase

space, the probability fluid flow is incompressible. It is also nondissipative, unlike the probability flow governed by the Fokker-Planck equation.

Let us consider a closed classical system with $3N$ degrees of freedom (for example, N particles in a three-dimensional box). The state of such a system is completely specified in terms of a set of $6N$ independent real variables $(\mathbf{p}^N, \mathbf{q}^N)$ ($\mathbf{p}^N$ and $\mathbf{q}^N$ denote the set of vectors $\mathbf{p}^N = (\mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N)$ and $\mathbf{q}^N = (\mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_N)$, respectively; $\mathbf{p}_l$ and $\mathbf{q}_l$ are the momentum and position of the lth particle. If the state vector $\mathbf{X}^N = \mathbf{X}^N(\mathbf{p}^N, \mathbf{q}^N)$ is known at one time, then it is completely determined for any other time from Newton's laws.

If we know the Hamiltonian, $H(\mathbf{X}^N, t)$, for the system, then the time evolution of the quantities $\mathbf{p}_l$ and $\mathbf{q}_l$ $(l = 1, \ldots, N)$ is given by Hamilton's equations,

$$\dot{\mathbf{p}}_l \equiv \frac{d\mathbf{p}_l}{dt} = -\frac{\partial H^N}{\partial \mathbf{q}_l} \tag{6.1}$$

and

$$\dot{\mathbf{q}}_l \equiv \frac{d\mathbf{q}_l}{dt} = \frac{\partial H^N}{\partial \mathbf{p}_l}. \tag{6.2}$$

If the Hamiltonian does not depend explicitly on the time, then it is a global constant of the motion and we can write

$$H^N(\mathbf{X}^N) = E, \tag{6.3}$$

where the constant, E, is the total energy of the system. In this case the system is called *conservative*.

Let us now associate to the system a $6N$-dimensional phase space, Γ. The state vector $\mathbf{X}^N(\mathbf{p}^N, \mathbf{q}^N)$ then specifies a point in the phase space. As the system evolves in time and its state changes, the system point $\mathbf{X}^N$ traces out a trajectory in Γ-space (cf. Fig. 6.1). Since the subsequent motion of a classical system is uniquely determined from the initial conditions, it follows that no two trajectories in phase space can cross. If they could, one could not uniquely determine the subsequent motion of the trajectory.

When we deal with real physical systems, we can never specify exactly the state of the system. There will always be some uncertainty in the initial conditions. Therefore, it is useful to consider $\mathbf{X}^N$ as a stochastic variable and to introduce a probability density $\rho(\mathbf{X}^N, t)$ on the phase space, where $\rho(\mathbf{X}^N, t)d\mathbf{X}^N$ is the probability that the state point, $\mathbf{X}^N$, lies in the volume element $\mathbf{X}^n \to \mathbf{X}^n + d\mathbf{X}^N$ at time t. (Here $d\mathbf{X}^N = d\mathbf{q}_1 \times \cdots \times d\mathbf{q}_N d\mathbf{p}_1 \times \cdots \times d\mathbf{p}_N$.) In so doing we introduce a picture of phase space filled with a continuum (or fluid) of state points. If the fluid were composed of discrete points, then each point would be assigned a probability in accordance with our initial knowledge of the system and would carry this probability for all time (probability is conserved).

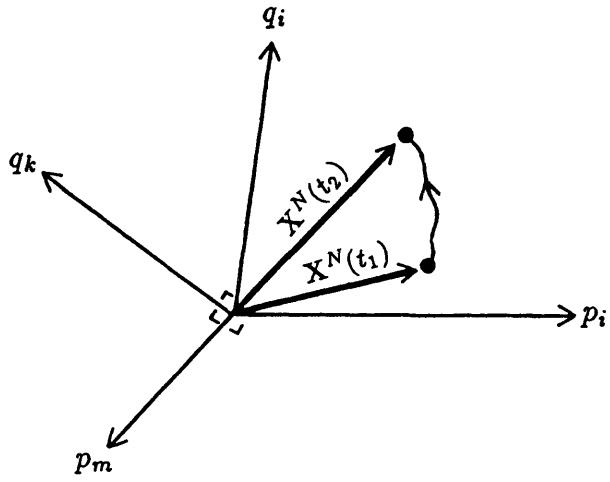


Fig. 6.1. Movement of a system point, $\mathbf{X}^N(t)$, in a $6N$-dimensional phase space ($t_2 > t_1$). We show only four of the $6N$ coodinate directions.

The change in our knowledge of the state of the system with time is determined by the way in which the fluid flows. Since for real systems the state points form a continuum, we must introduce a probability density, $\rho(\mathbf{X}^N, t)$, on the phase space.

Because state points must always lie somewhere in the phase space, we have the normalization condition

$$\int_\Gamma \rho(\mathbf{X}^N, t) d\mathbf{X}^N = 1 \tag{6.4}$$

where the integration is taken over the entire phase space. If we want the probability of finding the state point in a small finite region R of Γ space at time t, then we simply integrate the probability density over that region. If we let $P(R)$ denote the probability of finding the system in region R, then

$$P(R) = \int_R \rho(\mathbf{X}^N, t) d\mathbf{X}^N. \tag{6.5}$$

If at some time there is only a small uncertainty in the state of the system, the probability density will be sharply peaked in the region where the state is known to be located, and zero elsewhere. As time passes, the probability density may remain sharply peaked (although the peaked region can move through phase space) and we do not lose any knowledge about the state of the system. On the other hand, it might spread and become rather uniformly distributed, in which case all knowledge of the state of the system becomes lost.

Probability behaves like a fluid in phase space. We can therefore use arguments from fluid mechanics to obtain the equation of motion for the probability density (cf. Section S10.A). We will let $\dot{\mathbf{X}}^N = (\dot{\mathbf{q}}^N, \dot{\mathbf{p}}^N)$ denote the velocity of a state point, and we will consider a small volume element, V_0, at a fixed point in phase space. Since probability is conserved, the total decrease in the amount of probability in V_0 per unit time is entirely due to the flow of probability through the surface of V_0. Thus,

$$\frac{d}{dt}P(V_0) = \frac{\partial}{\partial t}\int_{V_0} \rho(\mathbf{X}^N, t)d\mathbf{X}^N = -\oint_{S_0} \rho(\mathbf{X}^N, t)\dot{\mathbf{X}}^N \cdot d\mathbf{S}^N, \tag{6.6}$$

where S_0 denotes the surface of volume element V_0, and $d\mathbf{S}^N$ is a differential area element normal to S_0. If we use Gauss's theorem and change the surface integral to a volume integral, we find

$$\frac{\partial}{\partial t}\int_{V_0} \rho(\mathbf{X}^N, t)d\mathbf{X}^N = -\int_{V_0} \nabla_{\mathbf{X}^N} \cdot (\rho(\mathbf{X}^N, t)\dot{\mathbf{X}}^N)d\mathbf{X}^N, \tag{6.7}$$

where $\nabla_{\mathbf{X}^N}$ denotes the gradient with respect to phase space variables $\nabla_{\mathbf{X}^N} = ((\partial/\partial\mathbf{q}_1), (\partial/\partial\mathbf{q}_2), \ldots, (\partial/\partial\mathbf{q}_N); (\partial/\partial\mathbf{p}_1), \ldots, (\partial/\partial\mathbf{p}_N))$. We can take the derivative inside the integral because V_0 is fixed in space. If we equate arguments of the two integrals in Eq. (6.7), we obtain

$$\frac{\partial}{\partial t}\rho(\mathbf{X}^N, t) + \nabla_{\mathbf{X}^N} \cdot (\rho(\mathbf{X}^N, t)\dot{\mathbf{X}}^N) = 0. \tag{6.8}$$

Equation (6.8) is the balance equation for the probability density in the $6N$-dimensional phase space.

We can use Hamilton's equations to show that the probability behaves like an incompressible fluid. A volume element in phase space changes in time according to the equation

$$d\mathbf{X}_t^N = \mathscr{J}^N(t, t_0)d\mathbf{X}_{t_0}^N, \tag{6.9}$$

where $\mathscr{J}^N(t, t_0)$, the Jacobian of the transformation, is the determinant of a $6N \times 6N$-dimensional matrix which we write symbolically as

$$\mathscr{J}^N(t, t_0) = \det \begin{vmatrix} \frac{\partial \mathbf{p}_t^N}{\partial \mathbf{p}_{t_0}^N} & \frac{\partial \mathbf{p}_t^N}{\partial \mathbf{q}_{t_0}^N} \\ \frac{\partial \mathbf{q}_t^N}{\partial \mathbf{p}_{t_0}^N} & \frac{\partial \mathbf{q}_t^N}{\partial \mathbf{q}_{t_0}^N} \end{vmatrix}. \tag{6.10}$$

The Jacobian $\mathscr{J}^N(t, t_0)$ can be shown to satisfy the relation

$$\mathscr{J}^N(t, t_0) = \mathscr{J}^N(t, t_1)\mathscr{J}^N(t_1, t_0) \tag{6.11}$$

if we remember that the product of the determinant of two matrices is equal to the determinant of the products.

Let us now assume that the system evolves for a short time interval $\Delta t = t - t_0$. Then the coordinates of a state point can be written

$$\mathbf{p}_t^N = \mathbf{p}_{t_0}^N + \dot{\mathbf{p}}_{t_0}^N \Delta t + 0(\Delta t)^2 \tag{6.12}$$

and

$$\mathbf{q}_t^N = \mathbf{q}_{t_0}^N + \dot{\mathbf{q}}_{t_0}^N \Delta t + 0(\Delta t)^2. \tag{6.13}$$

[Again Eqs. (6.12) and (6.13) have been written symbolically to denote the set of $6N$ equations for the components of $\mathbf{X}^N$.] If we combine Eqs. (6.10), (6.12), and (6.13), we find

$$\mathscr{J}^N(t, t_0) = \det \begin{vmatrix} 1 + \frac{\partial \dot{\mathbf{p}}_{t_0}^N}{\partial \mathbf{p}_{t_0}^N} \Delta t & \frac{\partial \dot{\mathbf{p}}_{t_0}^N}{\partial \mathbf{q}_{t_0}^N} \Delta t \\ \frac{\partial \dot{\mathbf{q}}_{t_0}^N}{\partial \mathbf{p}_{t_0}^N} \Delta t & 1 + \frac{\partial \dot{\mathbf{q}}_{t_0}^N}{\partial \mathbf{q}_{t_0}^N} \Delta t \end{vmatrix} = 1 + \left(\frac{\partial \dot{\mathbf{q}}_{t_0}^N}{\partial \mathbf{q}_{t_0}^N} + \frac{\partial \dot{\mathbf{p}}_{t_0}^N}{\partial \mathbf{p}_{t_0}^N} \right) \Delta t + 0(\Delta t)^2 \tag{6.14}$$

(cf. Appendix A). However, from Hamilton's equations [cf. Eqs. (6.1) and (6.2)] we obtain

$$\left(\frac{\partial \dot{\mathbf{q}}_{t_0}^N}{\partial \mathbf{q}_{t_0}^N} + \frac{\partial \dot{\mathbf{p}}_{t_0}^N}{\partial \mathbf{p}_{t_0}^N} \right) \equiv 0 \tag{6.15}$$

and, therefore,

$$\mathscr{J}^N(t, t_0) = 1 + 0(\Delta t)^2. \tag{6.16}$$

From Eq. (6.11) we can write

$$\mathscr{J}^N(t, 0) = \mathscr{J}^N(t, t_0)\mathscr{J}^N(t_0, 0) = \mathscr{J}^N(t_0, 0)(1 + 0(\Delta t)^2), \tag{6.17}$$

and the time derivative of the Jacobian becomes

$$\frac{d\mathscr{J}^N}{dt} = \lim_{\Delta t \to 0} \frac{\mathscr{J}^N(t_0 + \Delta t, 0) - \mathscr{J}^N(t_0, 0)}{\Delta t} = 0. \tag{6.18}$$

Thus, for a system whose dynamics is determined by Hamilton's equations, the Jacobian does not change in time and

$$\mathscr{J}^N(t, 0) = \mathscr{J}^N(0, 0) = 1. \tag{6.19}$$

Equation (6.19) is extremely important for several reasons. First, it tells us that volume elements in phase space do not change in size during the flow (although they can change in shape):

$$d\mathbf{X}_t^N = d\mathbf{X}_{t_0}^N. \tag{6.20}$$

Second, it tells us that the probability behaves like an incompressible fluid since

$$\nabla_{\mathbf{X}^N} \cdot \dot{\mathbf{X}}^N \equiv 0 \tag{6.21}$$

[cf. Eq. (6.15)]. If we combine Eqs. (6.8) and (6.21) the equation of motion for the probability density takes the form

$$\frac{\partial \rho(\mathbf{X}^N, t)}{\partial t} = -\dot{\mathbf{X}}^N \cdot \nabla_{\mathbf{X}^N} \rho(\mathbf{X}^N, t). \tag{6.22}$$

Note that Eq. (6.22) gives the time rate of change of $\rho(\mathbf{X}^N, t)$ at a *fixed point* in phase space. If we want the time rate of change as seen by an observer moving with the probability fluid, then we must find the equation for the total time derivative of $\rho(\mathbf{X}^N, t)$. The total or convective time derivative is defined as

$$\frac{d}{dt} = \left(\frac{\partial}{\partial t} + \dot{\mathbf{X}}^N \cdot \nabla_{\mathbf{X}^N} \right) \tag{6.23}$$

[cf. Appendix A, Eq. (A.5)] and, therefore, from Eq. (6.22) we obtain

$$\frac{d\rho(\mathbf{X}^N, t)}{dt} = 0. \tag{6.24}$$

Thus, the probability density remains constant in the neighborhood of a point moving with the probability fluid.

If we use Hamilton's equations, we can write Eq. (6.22) in the form

$$\frac{\partial \rho(\mathbf{X}^N, t)}{\partial t} = -\hat{\mathscr{H}}^N \rho(\mathbf{X}^N, t), \tag{6.25}$$

where the differential operator, $\hat{H}^N$, is just the Poisson bracket

$$\hat{\mathscr{H}}^N = \sum_{j=1}^{N} \left(\frac{\partial H^N}{\partial \mathbf{p}_j} \cdot \frac{\partial}{\partial \mathbf{q}_j} - \frac{\partial H^N}{\partial \mathbf{q}_j} \cdot \frac{\partial}{\partial \mathbf{p}_j} \right) \tag{6.26}$$

(we put a hat on $\hat{\mathscr{H}}^N$ to indicate that it is differential operator). Equation (6.25) is often written in the form

$$i\frac{\partial \rho(\mathbf{X}^N, t)}{\partial t} = \hat{L}^N \rho(\mathbf{X}^N, t), \tag{6.27}$$

where $\hat{L}^N = -i\hat{\mathscr{H}}^N$. Equation (6.27) is called the *Liouville equation* and the differential operator, $\hat{L}^N$, is called the *Liouville operator.* The Liouville operator is a Hermitian differential operator.

If we know the probability density, $\rho(\mathbf{X}^N, 0)$, at time, $t = 0$, then we may solve Eq. (6.27) to find the probability density, $\rho(\mathbf{X}^N, t)$, at time t. The formal solution is

$$\rho(\mathbf{X}^N, t) = e^{-i\hat{L}^N t}\rho(\mathbf{X}^N, 0). \tag{6.28}$$

A probability density, $\rho_s(\mathbf{X}^N)$, which remains constant in time must satisfy the condition

$$\hat{L}^N \rho_s(\mathbf{X}^N) = 0 \tag{6.29}$$

and is called a stationary solution of the Liouville equation. The Liouville equation is particularly simple to solve explicitly if the mechanical system is integrable and one can make a canonical transformation from phase variables, $(\mathbf{p}_1, \ldots, \mathbf{p}_N, \mathbf{q}_1, \ldots, \mathbf{q}_N)$, to action-angle variables $(\mathbf{J}_1, \ldots, \mathbf{J}_N, \theta_1, \ldots, \theta_N)$ [4, 5]. We show how this is done in Exercise 6.1.

The Liouville equation, (6.27), is the equation of motion for the probability density of a classical dynamical system. Its properties differ in an important respect from the properties of the Fokker–Planck equation in Chapter 5. The Liouville operator is Hermitian, whereas the Fokker–Planck operator is not. Thus, the solution of the Liouville equation will oscillate and not decay to a unique equilibrium state. Furthermore, if we reverse the time in Eq. (6.28), we do not change the equation of motion for the probability density since the Liouville operator changes sign under time reversal. This is different from the Fokker–Planck equation, which changes into a different equation under time reversal. Thus, Eq. (6.27) does not admit an irreversible decay of the system to a unique equilibrium state and thus cannot describe the decay to equilibrium that we observe so commonly in nature. And yet, if we believe that the dynamics of systems is governed by Newton's laws, it is all we have. The problem of obtaining irreversible decay from the Liouville equation is one of the central problems of statistical physics and is one that we shall say more about in subsequent sections.

■ **EXERCISE 6.1.** Consider a particle which bounces elastically and vertically off the floor under the influence of gravity (assume no friction acts). At time $t = 0$, the particle is located at $z = 0$ and has upward momentum, $p = p_0$. It rises to a maximum height, $z = h$. Solve the Liouville equation to find the probability density, $\rho(p, z, t)$, at time t.

Answer: The Hamiltonian for the particle can be written $H = (p^2/2m) + V(z) = E$, where $V(z) = mgz$ for $z \geq 0$ and $V(z) = \infty$ for

$z < 0$. The turning point (the point where the momentum goes to zero) of the orbit is at $z = h$, the energy is $E = mgh$, and the initial momentum is $p_0 = m\sqrt{2gh}$. Hamilton's equations are $\dot{p} = -(\partial H/\partial z) = -mg$ and $\dot{z} = (p/m)$. Hamiltonian's equations may be solved to give

$$z(t) = \sqrt{2gh}t - \frac{g}{2}t^2 \quad \text{and} \quad p(t) = m\sqrt{2gh} - mgt \qquad \text{for} \quad 0 \le t \le T, \tag{1}$$

where $T = 2\sqrt{(2h/g)}$ is the period of the motion. Both $z(t)$ and $p(t)$ are periodic functions of time with period T.

We can also describe this system in terms of action-angle variables. The action is

$$J = \frac{1}{2\pi}\oint p dz = \frac{\sqrt{2m}}{\pi}\int_0^h dz\sqrt{E - mgz} = \frac{2}{3\pi g}\sqrt{\frac{2}{m}}E^{3/2} \tag{2}$$

so the energy, as a function of action, is

$$H = \left(\frac{9\pi^2 g^2 m}{8}\right)^{1/3} J^{2/3} = E. \tag{3}$$

From Hamilton's equations we have $\dot{J} = (\partial H/\partial\theta) = 0$, so the action is a constant of the motion, and the angle evolves according to the equation

$$\dot{\theta} = \frac{\partial H}{\partial J} \equiv \omega(J) = g\pi\left(\frac{m}{2E}\right)^{1/2} = \left(\frac{\pi^2 g^2 m}{3J}\right)^{1/3} = \pi\sqrt{\frac{g}{2h}}. \tag{4}$$

We see again that the period of the motion is $T = (2\pi/\omega) = 2\sqrt{(2h/g)}$. If the angle variable at time $t = 0$ is $\theta = 0$, then at time t it is $\theta = \omega t$. We can now use Eqs. (1), (3), and (4) and the fact that $t = \theta/\omega$ to write the canonical transformation from phase space variables (p, z) to phase space variables (J, θ). We find

$$\begin{aligned} z(J,\theta) &= \frac{1}{g\pi^2}\left(\frac{3\pi g J}{m}\right)^{2/3}\left(\pi\theta - \frac{1}{2}\theta^2\right) \\ \text{and} \quad p(J,\theta) &= \frac{m}{\pi}\left(\frac{3g\pi J}{m}\right)^{1/3}(\pi - \theta) \qquad \text{for} \quad 0 \le \theta \le 2\pi. \end{aligned} \tag{5}$$

Because the transformation (5) is canonical, the Jacobian of the transformation

$$J = \det\begin{pmatrix} \frac{\partial p}{\partial J} & \frac{\partial p}{\partial \theta} \\ \frac{\partial z}{\partial J} & \frac{\partial z}{\partial \theta} \end{pmatrix}, \tag{6}$$

is equal to one as can be easily shown. Thus, $dpdz = dJd\theta$ and

$\delta(p-p_0)\delta(z-z_0)=\delta(J-J_0)\delta(\theta-\theta_0)$, where $p_0=p(J_0,\theta_0)$ and $z_0=z(J_0,\theta_0)$. We can write the Liouville equation in terms of the canonical variables (p,z),

$$\frac{\partial\rho}{\partial t}+\dot{p}\frac{\partial\rho}{\partial p}+\dot{z}\frac{\partial\rho}{\partial z}=0, \tag{7}$$

or in terms of canonical variables (J,θ),

$$\frac{\partial\rho'}{\partial t}+\dot{\theta}\frac{\partial\rho'}{\partial\theta}=0, \tag{8}$$

where $\rho(p,z,t)=\rho'(J,\theta,t)$ are the probability densities. The initial conditions are given by $\rho(p,z,0)=\delta(p-p_0)\delta(z)$ and $\rho'(J,\theta,0)=\delta(J-J_0)\delta(\theta)$, where $J_0=(2m/3\pi)\sqrt{2gh^3}$. Because the probability density, $\rho'(J,\theta,t)$, is a periodic function of θ, we can expand it in a Fourier series

$$\rho'(J,\theta,t)=\frac{1}{2\pi}\sum_{n=-\infty}^{\infty}\tilde{\rho}_n(J,t)e^{in\theta}. \tag{9}$$

If we plug Eq. (9) into the Liouville equation, (8), and use the fact that $\sum_{n=-\infty}^{\infty}e^{in\theta}=2\pi\delta(\theta)$ and $(1/2\pi)\int_0^{2\pi}d\theta e^{in\theta}=\delta_{n,0}$, then we find that the Fourier coefficient evolves in time as

$$\tilde{\rho}_n(J,t)=\tilde{\rho}_n(J,0)e^{-in\omega(J)t}, \tag{10}$$

where $\dot{\theta}=\omega(J)$. Therefore

$$\rho'(J,\theta,t)=\frac{1}{2\pi}\sum_{n=-\infty}^{\infty}\tilde{\rho}_n(J,0)e^{in(\theta-\omega(J)t)}. \tag{11}$$

If we now make use of the initial conditions, we obtain

$$\rho'(J,\theta,t)=\delta(J-J_0)\delta(\theta-\omega(J)t) \tag{12}$$

and

$$\rho(p,z,t)=\delta(p-p(J_0,\omega t))\delta(z-z(J_0,\omega t)), \tag{13}$$

where $p(J_0,\omega t)$ and $z(J_0,\omega t)$ are given by Eq. (5).

We shall often be interested in obtaining the expectation value of phase functions, $O^N(\mathbf{X}^N)$. The expectation value of $O^N(\mathbf{X}^N)$ at time t is given by

$$\begin{aligned}\langle O(t)\rangle&=\int d\mathbf{X}_1\cdots\int d\mathbf{X}_N O^N(\mathbf{X}^N)\rho(\mathbf{X}^N,t)\\&=\int d\mathbf{X}_1\cdots\int d\mathbf{X}_N O^N(\mathbf{X}^N)e^{-i\hat{L}^N t}\rho(\mathbf{X}^N,0).\end{aligned} \tag{6.30}$$

We have written the expectation value in the "Schrödinger" picture. That is, we have allowed the state function, $\rho(\mathbf{X}^N, t)$, to evolve in time and we have kept the phase function, $O^N(\mathbf{X}^N)$, fixed in time. We could equally well allow the phase function to vary in time and keep the state function fixed. We note that the Liouville operator, $\hat{L}^N$, contains derivatives with respect to $\mathbf{p}^N$ and $\mathbf{q}^N$. If we expand the exponential in a power series and integrate by parts, there will be a change of sign for each partial derivative and we find

$$\begin{aligned}\langle O(t)\rangle &= \int d\mathbf{X}_1 \cdots \int d\mathbf{X}_N O^N(\mathbf{X}^N, t)\rho(\mathbf{X}^N, 0) \\ &= \int d\mathbf{X}_1 \cdots \int d\mathbf{X}_N \rho(\mathbf{X}^N, 0) e^{+\hat{L}^N t} O^N(\mathbf{X}^N, 0).\end{aligned} \tag{6.31}$$

(we assumed that $\rho(\mathbf{X}^N, 0) \to 0$ for large $\mathbf{X}^N$). Thus, we obtain the classical version of the "Heisenberg" picture. We see that phase functions and state functions evolve according to different laws. The equation of motion of a phase function is given by

$$i\frac{\partial O^N(\mathbf{X}^N, t)}{\partial t} = -\hat{L}^N O^N(\mathbf{X}^N, t), \tag{6.32}$$

where Eq. (6.32) gives the evolution of $O^N(\mathbf{X}^N, t)$ at a fixed point in phase space.

■ **EXERCISE 6.2.** A system of N particles has a Hamiltonian $H = \sum_{i=1}^{N} p_i^2/2m + \sum_{i<j}^{N(N-1)/2} V(|\mathbf{q}_i - \mathbf{q}_j|)$. The phase function which gives the particle density at position $\mathbf{R}$ in configuration space is $n(\mathbf{q}^N, \mathbf{R}) = \sum_{i=1}^{N} \delta(\mathbf{q}_i - \mathbf{R})$. Write the equation of motion of $n(\mathbf{q}^N, \mathbf{R})$.

Answer: The equation of motion of $n(\mathbf{q}^N, \mathbf{R})$ is given by Eq. (6.32). Since $n(\mathbf{q}^N, \mathbf{R})$ does not depend on momentum, Eq. (6.32) reduces to

$$\frac{\partial n}{\partial t} = \sum_{i=1}^{N} \dot{\mathbf{q}}_i \cdot \frac{\partial}{\partial \mathbf{q}_i} \delta(\mathbf{q}_i - \mathbf{R}). \tag{1}$$

If we now replace the differentiation with respect to $\mathbf{q}_i$ by a differentiation with respect to $\mathbf{R}$, we obtain

$$\frac{\partial n}{\partial t} = -\nabla_{\mathbf{R}} \cdot \sum_{i=1}^{N} \frac{\mathbf{p}_i}{m} \delta(\mathbf{q}_i - \mathbf{R}). \tag{2}$$

(since $\dot{\mathbf{q}}_i = (\mathbf{p}_i/m)$) or

$$\frac{\partial n}{\partial t} = -\nabla_{\mathbf{R}} \cdot \mathbf{J}(\mathbf{p}^N, \mathbf{q}^N; \mathbf{R}), \tag{3}$$

where $\mathbf{J}(\mathbf{p}^N, \mathbf{q}^N; \mathbf{R}) = \sum_{i=1}^{N} (\mathbf{p}_i/m)\delta(\mathbf{q}_i - \mathbf{R})$ is the particle current phase function. Equation (3) is a balance equation which reflects the conservation of particle number on the microscopic level.

It is interesting to note that the probability density, $\rho(\mathbf{X}^N, t)$, is often interpreted in terms of an "ensemble" of systems. This was the view originally taken by W. Gibbs. Let us consider an ensemble of η identical systems (η very large). If we look at each system at a given time, it will be represented by a point in the $6N$-dimensional phase space. The distribution of points representing our ensemble of systems will be proportional to $\rho(\mathbf{X}^N, t)$. That is, the density of system points in phase space will be given by $\eta\rho(\mathbf{X}^N, t)$.

6.C. ERGODIC THEORY AND THE FOUNDATIONS OF STATISTICAL MECHANICS [6–13]

The subject of ergodic theory was primarily the domain of mathematicians until the advent of modern computers. However, in recent years it has become an even more important subject of research because of its importance in such diverse fields as celestial mechanics (stability of the solar system) and chemistry (stability of isolated excited molecules) and because it asks questions which lie at the very foundations of statistical mechanics.

As we shall see, the flow of probability in phase space is of a very special type. There are absolutely no diffusion processes present. Historically, two types of probability flow have been important in understanding the behaviour of phase space, namely, ergodic flow and mixing flow. For systems with ergodic flow, we obtain a unique stationary probability density (a constant on the energy surface) which characterizes systems with a fixed energy at equilibrium. However, a system with ergodic flow cannot necessarily reach this equilibrium state if it does not start out there. For decay to equilibrium, we must have at least the additional property of mixing. Mixing systems are ergodic (the converse is not always true, however) and can exhibit random behavior. In addition, reduced distribution functions can be defined which decay to an equilibrium state. We give examples of mixing flow in the special topics Section (S6.D).

Ergodic and mixing behavior for real systems is difficult to establish in general. It has been done only for a few model systems. However, there is a large class of conservative systems, the anharmonic oscillators, which are of great importance in mechanics, chemistry, and the theory of solids. These systems are neither ergodic nor mixing but exhibit behavior reminiscent of both in local regions of their phase space. They have been studied extensively with computers in recent years and give great insight into the behavior of flows in phase space and the possible mechanism behind the irreversibility we observe in nature. We briefly discuss such systems in the special topics in Section (S6.E).

Let us now define ergodic flow. Consider a Hamiltonian system with $3N$ degrees of freedom with Hamiltonian $H(\mathbf{p}^N, \mathbf{q}^N) = E$. If we relabel the momentum coordinates so $p_1 = p_{x,1}$, $p_2 = p_{y,1}$, $p_3 = p_{z,1}$, $p_4 = p_{x,2}, \ldots$, $p_{3N} = p_{z,N}$ (with similar relabeling for the position coordinates), then Hamilton's equations can be written

$$\frac{dq_1}{(\partial H/\partial p_1)} = \cdots = \frac{dq_{3N}}{(\partial H/\partial p_{3N})} = \cdots = -\frac{dp_1}{(\partial H/\partial q_1)} = \cdots = -\frac{dq_{3N}}{(\partial H/\partial q_{3N})} = dt. \tag{6.33}$$

Equation (6.33) provides us with $6N - 1$ equations between phase space coordinates which, when solved, give us $6N - 1$ constants, or integrals, of the motion,

$$f_i(p_1, \ldots, p_{3N}, q_1, \ldots, q_{3N}) = C_i, \tag{6.34}$$

where $i = 1, 2, \ldots, 6N - 1$ and C_i is a constant. However, these integrals of the motion can be divided into two kinds: isolating and nonisolating. Isolating integrals define a whole surface in the phase space and are important in ergodic theory, while nonisolating integrals do not define a surface and are unimportant [6, 14]. One of the main problems of ergodic theory is to determine how many isolating integrals a given system has. An example of an isolating integral is the total energy, $H(\mathbf{p}^N, \mathbf{q}^N) = E$. For N particles in a box, it is the only isolating integral (at least for hard spheres).

Let us consider a system for which the only isolating integral of the motion is the total energy and assume that the system has total energy, E. Then trajectories in Γ space (the $6N$-dimensional phase space) which have energy, E, will be restricted to the energy surface, S_E. The energy surface, S_E, is a $(6N - 1)$-dimensional "surface" in phase space which exists because of the global integral of the motion, $H(p_1, \ldots, p_{3N}, q_1, \ldots, q_{3N}) = E$. The flow of state points on the energy surface is defined to be *ergodic* if almost all points, $\mathbf{X}(p_1, \ldots, p_{3N}, q_1, \ldots, q_{3N})$, on the surface move in such a way that they pass through every small finite neighborhood, R_E, on the energy surface. Or, in other words, each point samples small neighborhoods over the entire surface during the course of its motion (a given point, $\mathbf{X}(p_1, \ldots, p_{3N}, q_1, \ldots, q_{3N})$ cannot pass through every point on the surface, because a line which cannot intersect itself cannot fill a surface of two or more dimensions). Note that not all points need sample the surface, only "almost all." We can exclude a set of measure zero from this requirement.

A criterion for determining if a system is ergodic was established by Birkhoff [15] and is called the *ergodic theorem*. Let us consider an integrable phase function $f(\mathbf{X}^N)$ of the state point $\mathbf{X}^N$. We may define a phase average of

the function $f(\mathbf{X}^N)$ on the energy surface by the equation

$$\langle f\rangle_S = \frac{1}{\sum(E)}\int_{S_E} f(\mathbf{X}^N)dS_E = \frac{1}{\sum(E)}\int_\Gamma \delta(H^N(\mathbf{X}^N) - E)f(\mathbf{X}^N)d\mathbf{X}^N, \quad (6.35)$$

where dS_E is an area element of the energy surface which is invariant (does not change size) during the evolution of the system and $\sum(E)$ is the area of the energy surface and is defined as

$$\sum(E) = \int_{S_E} dS_E = \int_\Gamma \delta(H^N(\mathbf{X}^N) - E)d\mathbf{X}^N \quad (6.36)$$

(we are using the notation of Section 6.B). We may define a time average of the function $f(\mathbf{X}^N)$ by the equation

$$\langle f\rangle_T = \lim_{T\to\infty}\frac{1}{T}\int_{t_0}^{t_0+T} f(\mathbf{X}^N(t))dt \quad (6.37)$$

for all trajectories for which the time average exists. Birkhoff showed that the time average in Eq. (6.37) exists for all integrable phase functions of physical interest (that is, for smooth functions).

It terms of averages, the *ergodic theorem* may be stated as follows: *A system is ergodic if for all phase functions,* $f(\mathbf{X}^N)$: *(i) the time average,* $\langle f\rangle_T$, *exists for almost all* $\mathbf{X}^N$ *(all but a set of measure zero), and (ii) when it exists it is equal to the phase average,* $\langle f\rangle_T = \langle f\rangle_S$.

To find the form of the invariant area element, dS_E, let us first write an expression for the volume of phase space, $\Omega(E)$, with energy less than E—that is, the region of phase space for which $0 < H^N(X^N) < E$. We shall assume that the phase space can be divided into layers, each with different energy, and that the layers can be arranged in the order of increasing energy. (This is possible for all systems that we will consider.) The volume, $\Omega(E)$, can then be written

$$\Omega(E) = \int_{0<H^N(\mathbf{X}^N)<E} d\mathbf{X}^N = \int_{0<H^N(\mathbf{X}^N)<E} dA_H dn_H, \quad (6.38)$$

where dA_H is an area element on a surface of constant energy and dn_H is normal to that surface. Since $\nabla_{\mathbf{X}}H^N$ is a vector perpendicular to the surface $H^N(\mathbf{X}^N)$ =constant, we can write $dH^N = |\nabla_{\mathbf{X}}H^N|dn_H$ and the volume becomes

$$\Omega(E) = \int_0^E dH^N \sum(H^N), \quad (6.39)$$

where

$$\sum(H^N) = \int_{S_H}\frac{dA_H}{|\nabla_{\mathbf{X}}H^N|} \quad (6.40)$$

is a function of H^N and is an invariant measure of the surface area for a given value of H^N. If we take the derivative of $\Omega(E)$, we find

$$\frac{d\Omega(E)}{dE} = \sum(E) = \int_{S_E} \frac{dA_E}{|\nabla_{\mathbf{X}} H^N|_{H=E}}. \tag{6.41}$$

The area, $\sum(E)$, is called the *structure function*. By the same argument, if we wish to take the average value of a function $f(\mathbf{X}^N)$ over the surface, we can write

$$\langle f \rangle_S = \frac{1}{\sum(E)} \int_{S_E} f(\mathbf{X}^N) \frac{dA_E}{|\nabla_{\mathbf{X}} H^N|_{H^N=E}} = \frac{1}{\sum(E)} \frac{d}{dE} \int_{0<H^N(\mathbf{X}^N)<E} f(\mathbf{X}^N) d\mathbf{X}^N. \tag{6.42}$$

Thus, the differential

$$dS_E = \frac{dA_E}{|\nabla_{\mathbf{X}} H^N|_{H^N=E}} \tag{6.43}$$

is the invariant surface area element.

■ **EXERCISE 6.3.** Compute the structure function for a gas of N noninteracting particles in a box of volume V. Assume that the system has a total energy E.

Answer: The Hamiltonian for the gas is

$$H^N = \sum_{i=1}^{3N} \frac{p_i^2}{2m} = E. \tag{1}$$

The volume of phase space with energy less than E is

$$\Omega(E) = \int_V d\mathbf{q}_1 \cdots \int_V d\mathbf{q}_N \int d\mathbf{p}_1 \cdots \int d\mathbf{p}_N \qquad \text{for} \quad \mathbf{p}_1^2 + \cdots + \mathbf{p}_N^2 \leq 2mE. \tag{2}$$

This can be written $\Omega(E) = V^N \Omega_p$, where

$$\Omega_p = \int d\mathbf{p}_1 \cdots \int d\mathbf{p}_N \Theta(R^2 - \mathbf{p}_1^2 - \cdots - \mathbf{p}_N^2). \tag{3}$$

is the volume enclosed in momentum space and $R^2 = 2mE$. The volume in momentum space, Ω_p, has the form $\Omega_p = A_{3N} R^{3N}$. Let us find A_{3N}. This can be done by a trick. First do the integral

$$\int_{-\infty}^{\infty} dp_{1,x} \cdots \int_{-\infty}^{\infty} dp_{3N,z} \exp[-(p_{1,x}^2 + \cdots + p_{3N,z}^2)] = \left(\int_{-\infty}^{\infty} dp e^{-p^2} \right)^{3N} = \pi^{3N/2}. \tag{4}$$

Next note that $(d\Omega_p/dE) = \int d\mathbf{p}_1 \cdots \int d\mathbf{p}_N \delta(R^2 - \mathbf{p}_1^2 - \cdots - \mathbf{p}_N^2)$ so that

$$\begin{aligned}\int_0^\infty dR \frac{d\Omega_p}{dR} e^{-R^2} &= \int_{-\infty}^{\infty} dp_{1,x} \cdots \int_{-\infty}^{\infty} dp_{3N,z} \exp[-(p_{1,x}^2 + \cdots + p_{3N,z}^2)] \\ &= 3NA_{3N} \int_0^\infty dR R^{3N-1} e^{-R^2} = \frac{3}{2} NA_{3N} \Gamma\left(\frac{3}{2}N\right),\end{aligned} \tag{5}$$

where $\Gamma(x)$ is the gamma function. If we equate Eq. (4) to Eq. (5), we find

$$A_{3N} = \frac{2\pi^{3N/2}}{3N\Gamma(3N/2)}. \tag{6}$$

Thus, the volume of the region of phase space with energy less than E is

$$\Omega(E) = \frac{2V^N \pi^{3N/2} R^{3N}}{3N\Gamma(3N/2)} = \frac{V^N (2\pi mE)^{3N/2}}{\Gamma(3N/2+1)}, \tag{7}$$

The structure function, $\sum(E)$, equals $(d\Omega(E)/dE)$.

If a system is ergodic, the fraction of time that its state, $X^N(\mathbf{p}^N, \mathbf{q}^N)$, spends in a given region R_E of the energy surface will be equal to the fraction of the surface S_E occupied by R_E. Let us consider a function $\phi(R_E)$ such that $\phi(R_E) = 1$ when X^N is in R_E and $\phi(R_E) = 0$ otherwise. Then it is easy to see that, for an ergodic system,

$$\lim_{T\to\infty} \frac{\tau_{R_E}}{T} = \frac{\sum(R_E)}{\sum(E)}, \tag{6.44}$$

where τ_{R_E} is the time the trajectory spends in R_E and $\sum(R_E)$ is the area occupied by R_E.

A system can exhibit ergodic flow on the energy surface only if there are no other isolating integrals of the motion which prevent trajectories from moving freely on the energy surface. If no other isolating integrals exist, the system is said to be metrically transitive (trajectories move freely on the energy surface). If a system is ergodic, it will spend equal times in equal areas of the energy surface. If we perform measurements to decide where on the surface the system point is, we should find that result. We can also ask for the probability of finding the system in a given region R_E of the energy surface. Since we have nothing to distinguish one region from another, the best choice we can make is to assume that the probability $P(R_E)$ of finding the system in R_E is equal to the fraction of the energy surface occupied by

R_E. Thus,

$$P(R_E) = \frac{1}{\sum(E)} \int_{R_E} dS_E = \frac{\sum(R_E)}{\sum(E)}. \tag{6.45}$$

From Eq. (6.45) it is a simple matter to write down a normalized probability density for the energy surface, namely,

$$\rho(\mathbf{X}^N, S_E) = \frac{1}{\sum(E)}. \tag{6.46}$$

Equation (6.46) is called the *fundamental distribution law* by Khintchine and called the *microcanonical ensemble* by Gibbs. Since it is a function only of the energy, it is a stationary state of the Liouville equation (6.27). It says that all states on the energy surface are equally probable. Equation (6.46) forms the foundation upon which all of equilibrium and most of nonequilibrium statistical mechanics are built. Its importance cannot be overemphasized. In Exercise 6.2, we give a simple example of ergodic flow.

In this section, we have discussed ergodic theory for classical systems. However, it is also possible to formulate analogous definitions for quantum systems. In fact, the criterion is rather sample. A quantum system is ergodic if and only if the system has a nondegenerate energy spectrum [16]. This means, of course, that there are no other observables which commute with the Hamiltonian.

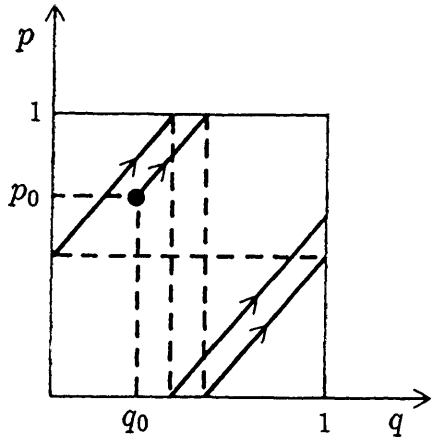
■ **EXERCISE 6.4.** Consider a dynamical flow on the two-dimensional unit square, $0 \leq p \leq 1$ and $0 \leq q \leq 1$, given by the equations of motion, $(dp/dt) = \alpha$ and $(dq/dt) = 1$. Assume that the system has periodic boundary conditions. (a) Show that this flow is ergodic. (b) If the initial probability density at time, $t = 0$, is $\rho(p, q, 0)$, compute the probability density at time, t.

Answer:

(a) The equations of motion are easily solved to give

$$p(t) = p_0 + \alpha t \quad \text{and} \quad q(t) = q_0 + t, \tag{1}$$

where p_0 and q_0 are the initial momentum and position, respectively. If we eliminate the time t, we obtain the phase space trajectory, $p = p_0 + \alpha(q - q_0)$, on the square surface. If α is a rational number, $\alpha = (m/n)$ (m and n integers), then the trajectory will be periodic and repeat itself after a period, n. If α is irrational, the trajectory will be dense on the unit square (but will not fill it)). A trajectory is shown in the accompanying figure.



When α is irrational, the system is ergodic. Let us show this explicitly. Since the phase space is periodic, any integrable function, $f(p,q)$, can be expanded in a Fourier series,

$$f(p,q) = \sum_{m=-\infty}^{\infty} \sum_{n=-\infty}^{\infty} A_{m,n} e^{2\pi i(mq+np)}. \tag{2}$$

We wish to show that the time average and the phase average of the function, $f(p,q)$, are equal for α irrational. The time average is given by

$$\begin{aligned}\langle f \rangle &= \lim_{T\to\infty} \frac{1}{T} \int_{t_0}^{t_0+T} dt \sum_{m=-\infty}^{\infty} \sum_{n=-\infty}^{\infty} A_{m,n} e^{2\pi i[m(q_0+t)+n(p_0+\alpha t)]} \\ &= A_{0,0} + \lim_{T\to\infty} \frac{1}{T} \sum_{m=-\infty}^{\infty}{}' \sum_{n=-\infty}^{\infty}{}' A_{m,n} e^{2\pi i[m(q_0+t_0)+n(p_0+\alpha t_0)]} \\ &\quad \times \left(\frac{e^{2\pi i(m+n)T} - 1}{2\pi i(m+\alpha n)} \right). \end{aligned} \tag{3}$$

The primes on the summations indicate that the values $m = 0$ and $n = 0$ are excluded from the summation. For irrational values of α, the denominator can never equal zero. Therefore

$$\langle f \rangle_T = A_{0,0}. \tag{4}$$

Similarly, we can show that

$$\langle f \rangle_s = \int_0^1 \int_0^1 dpdq\, f(p,q) = A_{0,0}. \tag{5}$$

Hence, the system is ergodic (note that $dpdq = dp_0 dq_0$, so area is preserved).

(b) The probability density satisfies periodic boundary conditions, so we can write

$$\rho(p,q,t) = \sum_{m=-\infty}^{\infty} \sum_{n=-\infty}^{\infty} \rho_{m,n}(t) e^{2\pi i m q} e^{2\pi i n p}. \tag{6}$$

It is easy to show that $\rho_{m,n}(t) = \rho_{m,n}(0) e^{2\pi i (m+\alpha n)t}$. Next note that $\int_0^1 dq e^{2\pi i m q} = \delta_{m,0}$ and $\sum_{m=-\infty}^{\infty} e^{2\pi i m q} = \delta(q)$. Using these relations, we find

$$\rho(p,q,t) = \rho(p + \alpha t, q + t, 0). \tag{7}$$

From Eq. (7) we see that ergodicity is not sufficient to cause a system which initially has a nonstationary distribution (localized on the energy surface) to approach a stationary state (spread throughout the energy surface). The probability density in Eq. (7) does not change shape with time, but simply wanders intact through the phase space. In order to approach a stationary state the system must be 'mixing'. Conditions for mixing flow are discussed in special topics Section S6.D.

6.D. THE QUANTUM PROBABILITY DENSITY OPERATOR

For quantum systems, the phase space coordinates do not commute so we cannot introduce a probability density function directly on the phase space. Because of the noncommutivity of phase space coordinates, we cannot simultaneously know the values of all the phase space coordinates. Instead we will introduce a *probability density operator* or *density operator* as it is commonly called. The density operator contains all possible information about the state of the quantum system. If we wish we can use it to construct the Wigner distribution, which is a function that reduces to the classical probability density in the limit where Planck's constant goes to zero.

The probability density operator $\hat{\rho}(t)$ (we shall call it the density operator), contains all possible information about the state of the quantum system. It is a positive definite Hermitian operator. Given that we know the density operator, $\hat{\rho}(t)$, for a system, we can use it to obtain the expectation value of any observable $\hat{O}$ at time t. The expectation value is defined as

$$\langle O(t) \rangle = \mathrm{Tr}\, \hat{O}\hat{\rho}(t), \tag{6.47}$$

where Tr denotes the trace. The density operator is normalized so that

$$\mathrm{Tr}\, \hat{\rho}(t) = 1. \tag{6.48}$$

In Eqs. (6.47) and (6.48), the trace can be evaluated using any convenient complete set of states. For example, we could use the eigenstates of the operator, $\hat{O}$, or any other Hermitian operator, $\hat{A}$, which may or may not commute with $\hat{O}$. We will let $\{|o_i\rangle\}$ and $\{|a_i\rangle\}$ denote the complete orthonormal sets of eigenstates of the operators, $\hat{O}$ and $\hat{A}$, respectively, and let $\{o_i\}$ and $\{a_i\}$ be the corresponding sets of eigenvalues ($\hat{O}|o_i\rangle = o_i|o_i\rangle$ and ($\hat{A}|a_i\rangle = a_i|a_i\rangle$). For simplicity we use Dirac notation (cf. Appendix B). The trace can be evaluated in either of these basis. Thus, we can write

$$\langle O(t)\rangle = \sum_i o_i \langle o_i|\hat{\rho}(t)|o_i\rangle = \sum_i \sum_j \langle a_i|\hat{O}|a_j\rangle\langle a_j|\hat{\rho}(t)|a_i\rangle, \tag{6.49}$$

where $o_i = \langle o_i|\hat{O}|o_i\rangle$ and we have used the completeness relation, $\sum_i |a_i\rangle\langle a_i| = \hat{1}$, where $\hat{1}$ is the unit operator. The diagonal matrix element, $\langle o_i|\hat{\rho}(t)|o_i\rangle$ ($\langle a_i|\hat{\rho}(t)|a_i\rangle$), gives the probability to find the system in the state $|o_i\rangle$ ($|a_i\rangle$), at time t. The set of numbers, $\langle a_j|\hat{\rho}(t)|a_i\rangle$, forms a matrix representation of the density operator (called the *density matrix*) with respect to the basis states, $\{|a_i\rangle\}$. The density matrix is a positive definite Hermitian matrix. The off-diagonal matrix element, $\langle a_j|\hat{\rho}(t)|a_i\rangle$ for $i \neq j$, cannot be interpreted as a probability.

The introduction of a density operator allows a more general description of a quantum system than does the Schrödinger equation. As we shall see, it can also be used to describe the equilibrium and near equilibrium states of a many-body system. To see this it is useful to distinguish between "pure states" and "mixed states." Consider a quantum system in the state $|\psi(t)\rangle$ which evolves according to the Schrödinger equation,

$$i\hbar \frac{\partial|\psi(t)\rangle}{\partial t} = \hat{H}|\psi(t)\rangle, \tag{6.50}$$

where $\hat{H}$ is the Hamiltonian operator, and $\hbar$ is Planck's constant. The density operator which describes this "pure state" is simply

$$\hat{\rho}(t) = |\psi(t)\rangle\langle\psi(t)|. \tag{6.51}$$

A "mixed state" is an incoherent mixture of states $|\psi_i(t)\rangle$:

$$\hat{\rho}(t) = \sum_i p_i |\psi_i(t)\rangle\langle\psi_i(t)|, \tag{6.52}$$

where p_i is the probability to be in the state $|\psi_i(t)\rangle$, and the states $|\psi_i(t)\rangle$ each satisfy the Schrödinger equation. Equilibrium and near-equilibrium states of many-body systems are of this type.

Using the Schrödinger equation, the equation of motion of the density operator is easily found to be

$$i\frac{\partial\hat{\rho}(t)}{\partial t} = \frac{1}{\hbar}[\hat{H}, \hat{\rho}(t)] = \hat{L}\hat{\rho}(t), \tag{6.53}$$

where $[\hat{H}, \hat{\rho}(t)]$ is the commutator of the Hamiltonian, $\hat{H}$, with $\hat{\rho}(t)$, and the operator $\hat{L} \equiv \frac{1}{\hbar}[\hat{H}]$, is proportional to the commutator of $\hat{H}$ with everything on its right. The operator $\hat{L}$ is the quantum version of the *Liouville operator* and is a Hermitian operator. Equation (6.53) is called the *Liouville equation* and gives the evolution of the *state* of the system (in the Schrödinger picture). If the density operator is known at time $t = 0$, then its value at time t is given by

$$\hat{\rho}(t) = e^{-i\hat{L}t}\hat{\rho}(0) = e^{-(i/\hbar)\hat{H}t}\hat{\rho}(0)e^{+(i/\hbar)\hat{H}t} \tag{6.54}$$

If we substitute Eq. (6.54) into Eq. (6.47) and use the invariance of the trace under cyclic rotation of operators, then Eq. (6.47) takes the form

$$\langle O(t)\rangle = \mathrm{Tr}\,\hat{O}(t)\hat{\rho}(0), \tag{6.55}$$

where

$$\hat{O}(t) = e^{+(i/\hbar)\hat{H}t}\hat{O}(0)e^{-(i/\hbar)\hat{H}t}. \tag{6.56}$$

Thus the operator, $\hat{O}$, obeys a different equation of motion,

$$-i\frac{\partial\hat{O}(t)}{\partial t} = \frac{1}{\hbar}[\hat{H}, \hat{O}(t)] = \hat{L}\hat{O}(t), \tag{6.57}$$

which is different from that of the density matrix. Equation (6.57) gives the evolution of the system in the "Heisenberg" picture.

It is often convenient to expand the density operator in terms of a complete orthonormal set of eigenstates $\{|E_i\rangle\}$ of the Hamiltonian, $\hat{H}$, where E_i is the eigenvalue corresponding to eigenstate $|E_i\rangle$. If we note the completeness relation $\sum_i |E_i\rangle\langle E_i| = \hat{1}$, then Eq. (6.54) takes the form

$$\hat{\rho}(t) = \sum_i \sum_j \langle E_i|\hat{\rho}(0)|E_j\rangle e^{-(i/\hbar)(E_i - E_j)t}|E_i\rangle\langle E_j|. \tag{6.58}$$

From Eq. (6.58), we see that a stationary state, $\hat{\rho}_s$, occurs when all off-diagonal matrix elements $\langle E_i|\hat{\rho}(0)|E_j\rangle$ with $i \neq j$, of $\hat{\rho}(0)$ vanish of $E_i \neq E_j$. Thus, for a state with no degenerate energy levels, the stationary state, $\hat{\rho}_s$, must be diagonal in the energy basis. This can only happen if $\hat{\rho}_s$ is a function of the

Hamiltonian,

$$\hat{\rho}_s = f(\hat{H}). \tag{6.59}$$

For a system with degenerate energy levels, one may still diagonalize both $\hat{\rho}$ and $\hat{H}$ simultaniously by introducing additional invariants of the motion, $\hat{I}$ which commute with each other and with $\hat{H}$. Thus, in general, a stationary state will be a function of all mutually commuting operators, $\hat{H}, \hat{I}_1, \ldots, \hat{I}_n$,

$$\hat{\rho}_s = f(\hat{H}, \hat{I}_1, \ldots, \hat{I}_n). \tag{6.60}$$

For systems which approach thermodynamic equilibrium, the stationary state may be an equilibrium state.

■ **EXERCISE 6.5.** Consider a harmonic oscillator with Hamiltonian, $\hat{H} = (1/2m)(\hat{p}^2 + \frac{1}{2}m\omega^2\hat{x}^2)$. Assume that at time $t = 0$ the oscillator is a state described by the density operator, $\hat{\rho}(0) = \hbar\sqrt{ab}(e^{-a\hat{x}^2}e^{-b\hat{p}^2} + e^{-b\hat{p}^2}e^{-a\hat{x}^2})$, where a and b are constants with the dimensions of inverse length squared and inverse momentum squared, respectively. (a) Compute the probability to find the particle in the interval $x \to x + dx$ at time $t = 0$. (b) Write the Liouville equation in the position basis. (c) Compute the probability to find the particle in the interval $x \to x + dx$ at time t.

Answer:

(a) The probability to find the particle in the interval $x \to x + dx$ at time $t = 0$ is $\langle x|\hat{\rho}(0)|x\rangle dx$, where $|x\rangle$ is an eigenstate of the position operator $\hat{x}$. We will use the notation $\rho_{x',x}(0) \equiv \langle x'|\hat{\rho}(0)|x\rangle$. Then

$$\begin{aligned}\rho_{x',x}(0) &= \hbar\sqrt{ab}(e^{-ax'^2} + e^{-ax^2})\langle x'|e^{-b\hat{p}^2}|x\rangle \\ &= \frac{\sqrt{ab}}{2\pi}(e^{ax'^2} + e^{-ax^2})\int_{-\infty}^{\infty} dp e^{-bp^2}e^{i(p/\hbar)(x'-x)} \\ &= \frac{1}{2}\sqrt{\frac{a}{\pi}}(e^{-ax'^2} + e^{-ax^2})\exp\left(-\frac{(x'-x)^2}{4b\hbar^2}\right),\end{aligned} \tag{1}$$

where we have used the completeness relation, $\int_{-\infty}^{\infty} dp|p\rangle\langle p| = \hat{1}$, for momentum eigenstates and the conventions of Appendix B. The probability to find the particle in the interval $x \to x + dx$ is $\rho_{x,x}(0)dx$, where

$$\rho_{x,x}(0) = \sqrt{\frac{a}{\pi}}\, e^{-ax^2}. \tag{2}$$

(b) The Liouville equation in the position basis is

$$
\begin{aligned}
i\hbar\frac{\partial\rho_{x',x}(t)}{\partial t} &= \frac{1}{2m}\int_{-\infty}^{\infty} dx''(\langle x'|\hat{p}^2|x''\rangle\rho_{x'',x}(t) - \rho_{x',x''}(t)\langle x''|\hat{p}^2|x\rangle) \\
&\quad + \frac{1}{2}m\omega^2(x'^2 - x^2)\rho_{x',x}(t) \\
&= \frac{1}{4m\pi\hbar}\int_{-\infty}^{\infty} dp\int_{-\infty}^{\infty} dx'' p^2(e^{i(p/\hbar)(x'-x'')}\rho_{x'',x}(t) \\
&\quad - \rho_{x',x''}(t)e^{i(p/\hbar)(x''-x)}) + \frac{1}{2}m\omega^2(x'^2 - x^2)\rho_{x',x}(t) \\
&= \frac{-\hbar}{4m\pi}\int_{-\infty}^{\infty} dp\int_{-\infty}^{\infty} dx''\left(\left(\frac{\partial^2}{\partial x''^2}e^{i(p/\hbar)(x'-x'')}\right)\rho_{x'',x}(t)\right. \\
&\quad \left. - \rho_{x',x''}(t)\left(\frac{\partial^2}{\partial x''^2}e^{i(p/\hbar)(x''-x)}\right)\right) \\
&\quad + \frac{1}{2}m\omega^2(x'^2 - x^2)\rho_{x',x}(t). \qquad (3)
\end{aligned}
$$

If we now assume that $\rho_{x',x}(t) \to 0$ as $x' \to \infty$ or $x \to \infty$, then we can integrate by parts in Eq. (3) and obtain

$$
i\hbar\frac{\partial\rho_{x',x}(t)}{\partial t} = \frac{\hbar^2}{2m}\left(\frac{\partial^2\rho_{x',x}(t)}{\partial x'^2} - \frac{\partial^2\rho_{x',x}(t)}{\partial x^2}\right) + \frac{1}{2}m\omega^2(x'^2 - x^2)\rho_{x',x}(t). \qquad (4)
$$

(c) To find $\rho_{x,x}(t)$, let us first solve the Liouville equation in the basis of eigenstates of the Hamiltonian, $\hat{H} = (1/2m)\hat{p}^2 + \frac{1}{2}m\omega^2\hat{x}^2$. From Exercise 5.8, we see that the Hamiltonian has eigenvalues $E_n = \hbar\omega(n + \frac{1}{2})$ and eigenstates $|n\rangle$, $(\hat{H}|n\rangle = E_n|n\rangle)$, which in the position basis are

$$
\langle x|n\rangle = \sqrt{\frac{1}{2^n n!}}\left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\mathrm{H}_n\left(\sqrt{\frac{m\omega}{\hbar}}\,x\right)e^{m\omega x^2/2\hbar}, \qquad (5)
$$

where $\mathrm{H}_n(\sqrt{(m\omega/\hbar)}x)$ is a Hermite polynomial. The Liouville equation in the basis of eigenstates $|n\rangle$ is

$$
i\hbar\frac{\partial\rho_{n',n}(t)}{\partial t} = \hbar\omega(n' - n)\rho_{n',n}(t), \qquad (6)
$$

where $\rho_{n',n}(t) = \langle n'|\hat{\rho}(t)|n\rangle$. The solution to Eq. (6) is

$$
\rho_{n',n}(t) = e^{-i\omega(n'-n)t}\rho_{n',n}(0). \qquad (7)
$$

Let us now note that $\rho_{n',n}(0) = \int_{-\infty}^{\infty} dx'_0 \int_{-\infty}^{\infty} dx_0 \langle n'|x'_0\rangle \rho_{x'_0,x_0}(0)\langle x_0|n\rangle$. Then the density matrix, $\rho_{x',x}(t)$, can be written

$$\rho_{x',x}(t) = \sum_{n'=0}^{\infty}\sum_{n=0}^{\infty}\int_{-\infty}^{\infty} dx'_0 \times \int_{-\infty}^{\infty} dx_0 \langle x'|n'\rangle\langle n|x\rangle\langle x_0|n\rangle\langle n'|x'_0\rangle e^{-i\omega(n'-n)t}\rho_{x'_0,x_0}(0). \tag{8}$$

If we use the initial condition in part (a), the probability density, $\rho_{x,x}(t)$, can be written

$$\rho_{x,x}(t) = \frac{1}{2}\sqrt{\frac{a}{\pi}}\sum_{n'=0}^{\infty}\sum_{n=0}^{\infty}\int_{-\infty}^{\infty} dx'_0 \times \int_{-\infty}^{\infty} dx_0 \langle x|n'\rangle\langle n|x\rangle\langle x_0|n\rangle\langle n'|x'_0\rangle e^{-i\omega(n'-n)t} \times (e^{-ax_0'^2} + e^{-ax_0^2})\exp\left(-\frac{(x'_0 - x_0)^2}{4b\hbar^2}\right). \tag{9}$$

Let us now use Eq. (5) and note the identity in Eq. (10) of Exercise 5.8. With this we can write

$$\sum_{n=0}^{\infty}\langle x_0|n\rangle\langle n|x\rangle e^{+in\omega t} = \left(\frac{m\omega}{\pi\hbar}\right)^{1/2}\sqrt{f(t)}e^{m\omega(x^2+x_0^2)/2\hbar} \times \exp\left(-\frac{m\omega}{\hbar}f(t)(x^2 + x_0^2 - 2x_0xe^{i\omega t})\right), \tag{10}$$

where $f(t) = ie^{-i\omega t}/2\sin(\omega t)$. If we use Eq. (10) to perform the summations in Eq. (9), then we are left integrals over x'_0 and x_0 which can be performed explicitly. After considerable algebra, we find

$$\rho_{x,x}(t) = \sqrt{\frac{a}{\pi}}\,\mathrm{Re}\left[\frac{1}{\sqrt{B(t)}}e^{-ax^2/B(t)}\right], \tag{11}$$

where Re denotes the real part and

$$B(t) = \cos^2(\omega t) + \frac{a}{bm^2\omega^2}\sin^2(\omega t) + i\frac{2a\hbar}{m\omega}\cos(\omega t)\sin(\omega t). \tag{12}$$

■ **EXERCISE 6.6.** An ensemble of silver atoms (each with spin $\frac{1}{2}$) is prepared so that 60% of the atoms are in the $S_z = +\frac{\hbar}{2}$ eigenstate of $\hat{S}_z$ and 40% of the atoms are in the $S_x = -\frac{\hbar}{2}$ eigenstate of $\hat{S}_x$ ($\hat{S}_x$ and $\hat{S}_z$ are the x and z components of the spin angular momentum operator). (a) Compute the density matrix at time $t = 0$ in the basis of eigenstates of $\hat{S}_z$. (b) Assume that

the silver atoms sit in a magnetic field, $\mathbf{B} = B_0\hat{\mathbf{y}}$, and have a magnetic Hamiltonian, $\hat{H} = \mu\mathbf{S}\cdot\mathbf{B}$, where μ is the magnetic moment of a silver atom. Compute the density matrix at time t (in the basis of eigenstates of $\hat{S}_z$). (c) Compute $\langle S_z(t)\rangle$ at time $t = 0$ and at time t.

Answer:

(**a**) Let $|i_\pm\rangle$ denote the eigenstates of $\hat{S}_k (k = x, y, z)$ with eigenvalues $\pm(\hbar/2)$ so $(\hat{S}_k|k_\pm\rangle = \pm(\hbar/2)|k_\pm\rangle)$. The density operator at time $t = 0$ is the mixed state

$$\hat{\rho}(0) = \frac{6}{10}|z_+\rangle\langle z_+| + \frac{4}{10}|x_-\rangle\langle x_-|. \tag{1}$$

Now note that the matrix representation of the components $\hat{S}_x, \hat{S}_y$, and $\hat{S}_z$ in the basis of eigenstates of $\hat{S}_z$ are

$$S_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad S_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \text{and} \quad S_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{2}$$

The eigenstates of $\hat{S}_x$ and $\hat{S}_y$, in the basis of eigenstates of $\hat{S}_z$ are

$$\begin{pmatrix} \langle z_+|x_\pm\rangle \\ \langle z_-|x_\pm\rangle \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ \pm 1 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} \langle z_+|y_\pm\rangle \\ \langle z_-|y_\pm\rangle \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ \pm i \end{pmatrix}, \tag{3}$$

respectively. The eigenstates of $\hat{S}_z$ in the basis of eigenstates of $\hat{S}_z$ are

$$\begin{pmatrix} \langle z_+|z_+\rangle \\ \langle z_-|z_+\rangle \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} \langle z_+|z_-\rangle \\ \langle z_-|z_-\rangle \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{4}$$

Using these results we find the initial density matrix in the $|z_\pm\rangle$ basis,

$$\rho(0) = \begin{pmatrix} \frac{4}{5} & -\frac{1}{5} \\ -\frac{1}{5} & \frac{1}{5} \end{pmatrix}. \tag{5}$$

(**b**) The Hamiltonian is $\hat{H} = \frac{1}{2}\mu\hbar B_0(|y_+\rangle\langle y_+| - |y_-\rangle\langle y_-|)$ (this is its spectral decomposition). If we let $\rho_{y++} \equiv \langle y_+|\hat{\rho}|y_+\rangle$, then the Liouville equation for various matrix elements of the density matrix in basis $|y_\pm\rangle$ is given by

$$\begin{aligned} i\frac{\partial\rho_{y++}(t)}{\partial t} = 0, \quad i\frac{\partial\rho_{y+-}(t)}{\partial t} &= \mu B_0\rho_{y+-}(t), \quad i\frac{\partial\rho_{y-+}(t)}{\partial t} \\ &= -\mu B_0\rho_{y-+}(t) \quad \text{and} \quad i\frac{\partial\rho_{y--}(t)}{\partial t} = 0, \end{aligned} \tag{6}$$

Now note that the initial density matrix in the basis $|y_\pm\rangle$ is given by

$$\rho(0) = \begin{pmatrix} \frac{1}{2} & \frac{3+2i}{10} \\ \frac{3-2i}{10} & \frac{1}{2} \end{pmatrix}. \tag{7}$$

Using Eq. (7), we can solve Eqs. (6) and write the density matrix at time t in the basis $|y_\pm\rangle$. We find

$$\rho(t) = \begin{pmatrix} \frac{1}{2} & \frac{3+2i}{10} e^{-i\mu B_0 t} \\ \frac{3-2i}{10} e^{+i\mu B_0 t} & \frac{1}{2} \end{pmatrix}. \tag{8}$$

We now can transform Eq. (8) to the basis $|z_\pm\rangle$ to obtain

$$\rho(t) = \begin{pmatrix} \frac{1}{2}+\frac{3}{10}\cos(\mu B_0 t)+\frac{1}{5}\sin(\mu B_0 t) & \frac{3}{10}\sin(\mu B_0 t)-\frac{1}{5}\cos(\mu B_0 t) \\ \frac{3}{10}\sin(\mu B_0 t)-\frac{1}{5}\cos(\mu B_0 t) & \frac{1}{2}-\frac{3}{10}\cos(\mu B_0 t)-\frac{1}{5}\sin(\mu B_0 t) \end{pmatrix}. \tag{9}$$

(c) The average z-component of spin angular momentum at time, $t = 0$ is

$$\langle S_z(0)\rangle = \mathrm{Tr}\,\hat{S}_z\hat{\rho}(0) = \frac{\hbar}{2}\mathrm{Tr}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} \frac{4}{5} & -\frac{1}{5} \\ -\frac{1}{5} & \frac{1}{5} \end{pmatrix} = \frac{3}{10}\hbar. \tag{10}$$

The average z component of spin angular momentum at time t is

$$\langle S_z(t)\rangle = \frac{3}{10}\hbar\cos(\mu B_0 t) + \frac{1}{5}\hbar\sin(\mu B_0 t). \tag{11}$$

▶ SPECIAL TOPICS

▶ S6.A. Reduced Probability Densities and the BBGKY Hierarchy [2, 5, 17]

The N-particle probability density, $\rho(\mathbf{X}^N, t)$, contains much more information than we would ever need or want. Most quantities we measure experimentally can be expressed in terms of one-body or two-body phase functions. One-body phase functions are usually written in the form

$$O^N_{(1)}(\mathbf{X}^N) = \sum_{i=1}^{N} O(\mathbf{X}_i), \tag{6.61}$$

and two-body phase functions are written in the form

$$O_{(2)}^{N}(\mathbf{X}^N) = \sum_{i<j}^{N(N-1)/2} O(\mathbf{X}_i, \mathbf{X}_j), \tag{6.62}$$

An example of a one-body phase function is the kinetic energy, $\sum_{i=1}^{N} p_i^2/2m$, of an N-particle system. An example of a two-body phase function is the potential energy, $\sum_{i<j}^{N(N-1)/2} V(|\mathbf{q}_i - \mathbf{q}_j|)$, of an N-particle system. To find the expectation value of a one-body phase function, we only need to know the one-body reduced probability density. Similarly, to find the expectation value of a two-body phase function, we only need to know the two-body reduced probability density.

The one-body reduced probability density is given by

$$\rho_1(\mathbf{X}_1, t) = \int \cdots \int d\mathbf{X}_2 \cdots d\mathbf{X}_N \, \rho(\mathbf{X}_1, \ldots, \mathbf{X}_N, t), \tag{6.63}$$

where $\rho(\mathbf{X}_1, \ldots, \mathbf{X}_N, t) \equiv \rho(\mathbf{X}^N, t)$. The s-body reduced probability density is given by

$$\rho_s(\mathbf{X}_1, \ldots, \mathbf{X}_s, t) = \int \cdots \int d\mathbf{X}_{s+1} \ldots d\mathbf{X}_N \, \rho(\mathbf{X}_1, \ldots, \mathbf{X}_N, t). \tag{6.64}$$

If the probability density, $\rho(\mathbf{X}_1, \ldots, \mathbf{X}_N, t)$, is known at time t, then the expectation value of the one-body phase function at time t is given by

$$\langle O_{(1)}(t) \rangle = \sum_{i=1}^{N} \int \cdots \int d\mathbf{X}_1 \ldots d\mathbf{X}_N \, O(\mathbf{X}_i) \rho(\mathbf{X}^N, t) = N \int d\mathbf{X}_1 O(\mathbf{X}_1, t) \rho_1(\mathbf{X}_1, t). \tag{6.65}$$

Similarly, the expectation value of the two-body phase function at time t is

$$\begin{aligned} \langle O_{(2)}(t) \rangle &= \sum_{i<j}^{N(N-1)/2} \int \cdots \int d\mathbf{X}_1 \ldots d\mathbf{X}_N \, O(\mathbf{X}_i, \mathbf{X}_j) \rho(\mathbf{X}^N, t) \\ &= \frac{N(N-1)}{2} \int \int d\mathbf{X}_1 d\mathbf{X}_2 O(\mathbf{X}_1, \mathbf{X}_2, t) \rho_2(\mathbf{X}_1, \mathbf{X}_2, t). \end{aligned} \tag{6.66}$$

In Eqs. (6.65) and (6.66), we have assumed that the probability density is symmetric under interchange of particle labels if the Hamiltonian is symmetric.

The equation of motion of $\rho_s(\mathbf{X}_1, \ldots, \mathbf{X}_s, t)$ can be obtained from the Liouville equation. It is convenient to first introduce another quantity,

$F_s(\mathbf{X}_1, \ldots, \mathbf{X}_s, t)$, defined as

$$F_s(\mathbf{X}_1, \ldots, \mathbf{X}_s, t) \equiv V^s \int \cdots \int d\mathbf{X}_{s+1} \ldots d\mathbf{X}_N \rho(X_1, \ldots, \mathbf{X}_N, t), \tag{6.67}$$

and

$$F_N(\mathbf{X}_1, \ldots, \mathbf{X}_N, t) \equiv V^N \rho(\mathbf{X}_1, \ldots, \mathbf{X}_N, t). \tag{6.68}$$

Let us assume that the evolution of the system is governed by a Hamiltonian of the form

$$H^N(\mathbf{X}^N) = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i<j}^{N(N-1)/2} \phi(|\mathbf{q}_i - \mathbf{q}_j|), \tag{6.69}$$

where $\phi(|\mathbf{q}_i - \mathbf{q}_j|)$ is a two-body spherically symmetric interaction potential between particles i and j. The Liouville operator is

$$\hat{L}^N = -i \sum_{i=1}^{N} \frac{\mathbf{p}_i}{m} \cdot \frac{\partial}{\partial \mathbf{q}_i} + i \sum_{i<j}^{N(N-1)/2} \hat{\Theta}_{ij}, \tag{6.70}$$

where

$$\hat{\Theta}_{ij} = \frac{\partial \phi_{ij}}{\partial \mathbf{q}_i} \cdot \frac{\partial}{\partial \mathbf{p}_i} + \frac{\partial \phi_{ij}}{\partial \mathbf{q}_j} \cdot \frac{\partial}{\partial \mathbf{p}_j} \tag{6.71}$$

and $\phi_{ij} = \phi(|\mathbf{q}_i - \mathbf{q}_j|)$. If we integrate the Liouville equation, (6.27), over $\mathbf{X}_{s+1}, \ldots, \mathbf{X}_N$ and multiply by V^s, we obtain

$$\begin{aligned} \frac{\partial F_s}{\partial t} + i\hat{L}^s F_s = & V^s \int \cdots \int d\mathbf{X}_{s+1} \cdots d\mathbf{X}_N \\ & \times \left\{ -\sum_{i=s+1}^{N} \frac{\mathbf{p}_i}{m} \cdot \frac{\partial}{\partial \mathbf{q}_i} + \sum_{i \le s; s+1 \le j \le N} \hat{\Theta}_{ij} + \sum_{s+1 \le k < l} \hat{\Theta}_{kl} \right\} \\ & \times \rho^N(\mathbf{X}_1, \ldots, \mathbf{X}_N, t). \end{aligned} \tag{6.72}$$

If we assume that $\rho(\mathbf{X}_1, \ldots, \mathbf{X}_N, t) \to 0$ for large values of $\mathbf{X}_i$, then the first and third terms on the right-hand side of Eqs. (6.72) go to zero. One can see this by using Gauss's theorem and changing the volume integration to surface integration. For a large system the contribution from $\rho(\mathbf{X}_1, \ldots, \mathbf{X}_N, t)$ on the surface goes to zero. The second term on the right-hand side can be written in

the form

$$V^s \int \cdots \int d\mathbf{X}_{s+1} \cdots d\mathbf{X}_N \sum_{i \le s; s+i \le j \le N} \hat{\Theta}_{ij} \rho^N(\mathbf{X}_1, \ldots, \mathbf{X}_N, t)$$

$$= V^s (N-s) \sum_{i=1}^{s} \int d\mathbf{X}_{s+1} \hat{\Theta}_{i,s+1} \int \cdots \int d\mathbf{X}_{s+2} \cdots d\mathbf{X}_N \rho^N(\mathbf{X}_1, \ldots, \mathbf{X}_N, t)$$

$$= \frac{(N-s)}{V} \sum_{i=1}^{s} \int d\mathbf{X}_{s+1} \hat{\Theta}_{i,s+1} F_{s+1}(\mathbf{X}_1, \ldots, \mathbf{X}_{s+1}, t).$$

Equation (6.72) then becomes

$$\frac{\partial F_s}{\partial t} + i\hat{L}^s F_s = \frac{(N-s)}{V} \sum_{i=1}^{s} \int d\mathbf{X}_{s+1} \hat{\Theta}_{i,s+1} F_{s+1}(\mathbf{X}_1, \ldots, \mathbf{X}_{s+1}, t). \tag{6.73}$$

For a fixed values of s we may take the limit $N \to \infty, V \to \infty$, such that $v \equiv V/N$ remains constant (this is called the thermodynamic limit) and Eq. (6.73) becomes

$$\frac{\partial F_s}{\partial t} + i\hat{L}^s F_s = \frac{1}{v} \sum_{i=1}^{s} \int d\mathbf{X}_{s+1} \hat{\Theta}_{i,s+1} F_{s+1}(\mathbf{X}_1, \ldots, \mathbf{X}_{s+1}, t). \tag{6.74}$$

Equation (6.74) gives a hierarchy of equations of motion for the reduced probability densities $F_s(\mathbf{X}_1, \ldots, \mathbf{X}_N, t)$. It is called the BBGKY hierarchy after authors Bogoliubov [17], Born and Green [18], Kirkwood [19], and Yvon [20]. The most useful equations in the hierarchy are those for $F_1(\mathbf{X}_1, t)$ and $F_2(\mathbf{X}_1, \mathbf{X}_2, t)$:

$$\frac{\partial F_1}{\partial t} + \frac{\mathbf{p}_1}{m} \cdot \frac{\partial F_1}{\partial \mathbf{q}_1} = \frac{1}{v} \int d\mathbf{X}_2 \hat{\Theta}_{12} F_2(\mathbf{X}_1, \mathbf{X}_2, t) \tag{6.75}$$

and

$$\frac{\partial F_2}{\partial t} + \left(\frac{\mathbf{p}_1}{m} \cdot \frac{\partial}{\partial \mathbf{q}_1} + \frac{\mathbf{p}_2}{m} \cdot \frac{\partial}{\partial \mathbf{q}_2} - \hat{\Theta}_{12} \right) F_2 = \frac{1}{v} \int d\mathbf{X}_3 (\hat{\Theta}_{13} + \hat{\Theta}_{23}) F_3(\mathbf{X}_1, \mathbf{X}_2, \mathbf{X}_3, t). \tag{6.76}$$

Notice that the equation of motion of F_1 depends on F_2, the equation of motion for F_2 depends on F_3, and so on. This makes the equations of the hierarchy impossible to solve unless some way can be found to truncate it. For example, if we could find some way to write $F_2(\mathbf{X}_1, \mathbf{X}_2, t)$ in terms of $F_1(\mathbf{X}_1, t)$ and $F_1(\mathbf{X}_2, t)$, then we could in principle solve Eq. (6.75) for the reduced probability density $F_1(\mathbf{X}_1, t)$. Equation (6.75) is called the *kinetic equation.*

▶ S6.B. Reduced Density Matrices and the Wigner Distribution [16, 21–25]

For quantum mechanical system, the phase space coordinates of particles do not commute, and therefore it is impossible to specify simultaneously the position and momentum of the particles. As a result, it is also not possible to define a distribution function on the phase space which can be interpreted as a probability density. However, Wigner [16] was first to show that it is possible to introduce a function which formally analogous to the classical probability density and which reduces to it in the classical limit.

Before we introduce the Wigner function, it is useful to introduce the idea of one- and two-body reduced density matrices. In quantum mechanics, as in classical mechanics, we generally deal with one-body operators,

$$\hat{O}_{(1)}^{N} = \sum_{i=1}^{N} \hat{O}(\hat{\mathbf{p}}_i, \hat{\mathbf{q}}_i), \tag{6.77}$$

such as the N-body kinetic energy operator, and we also deal with two-body operators,

$$\hat{O}_{(2)}^{N} = \sum_{i<j}^{N(N-1)/2} \hat{O}(\hat{\mathbf{p}}_i, \hat{\mathbf{p}}_j, \hat{\mathbf{q}}_i, \hat{\mathbf{q}}_j), \tag{6.78}$$

such as the interaction potential. The trace of a one-body operator, in the position basis, can be written

$$\begin{aligned}
\langle O_{(1)}(t)\rangle &= \mathrm{Tr}\, \hat{O}_{(1)}^{N} \hat{\rho}(t) \\
&= \sum_{i=1}^{N} \int dx_1 \cdots \int dx_N \int dx_1' \cdots \int dx_N' \langle x_1, \ldots, x_N | \hat{O}_i | x_1', \ldots, x_N' \rangle \\
&\quad \times \langle x_1', \ldots, x_N' | \hat{\rho}(t) | x_1, \ldots, x_N \rangle \\
&= N \int dx_1 \cdots \int dx_N \int dx_1' \langle x_1 | \hat{O}_1 | x_1' \rangle \langle x_1', x_2, \ldots, x_N | \hat{\rho}(t) | x_1, \ldots, x_N \rangle \\
&\equiv \int dx_1 \int dx_1' \langle x_1 | \hat{O}_1 | x_1' \rangle \langle x_1' | \hat{\rho}_{(1)}(t) | x_1 \rangle,
\end{aligned} \tag{6.79}$$

where $\hat{O}_i = \hat{O}(\hat{\mathbf{p}}_i, \hat{\mathbf{q}}_i)$ and

$$\langle x_1' | \hat{\rho}_{(1)}(t) | x_1 \rangle = N \int dx_2 \cdots \int dx_N \langle x_1', x_2, \ldots, x_N | \hat{\rho}(t) | x_1, \ldots, x_N \rangle \tag{6.80}$$

is the one-body reduced density matrix. (We use the notation of Appendix B.)

The two-body reduced density matrix is defined in an analogous manner. The trace of a two-body operator in the position basis can be written

$$\begin{aligned}\langle O_{(2)}(t)\rangle &= \mathrm{Tr}\,\hat{O}^N_{(2)}\hat{\rho}(t)\\ &= \sum_{i<j}^{N(N-1)/2}\int dx_1\cdots\int dx_N\int dx'_1\cdots\int dx'_N\langle x_1,\ldots,x_N|\hat{O}_{i,j}|x'_1,\ldots,x'_N\rangle\\ &\quad\times\langle x'_1,\ldots,x'_N|\hat{\rho}(t)|x_1,\ldots,x_N\rangle\\ &= \frac{N(N-1)}{2}\int dx_1\cdots\int dx_N\int dx'_1\int dx'_2\langle x_1,x_2|\hat{O}_{1,2}|x'_1,x'_2\rangle\\ &\quad\times\langle x'_1,x'_2,x_3,\ldots,x_N|\hat{\rho}(t)|x_1,\ldots,x_N\rangle\\ &\equiv \frac{1}{2}\int dx_1\int dx_2\int dx'_1\int dx'_2\langle x_1,x_2|\hat{O}_{1,2}|x'_1,x'_2\rangle\langle x'_1,x'_2|\hat{\rho}_{(2)}(t)|x_1,x_2\rangle,\end{aligned} \tag{6.81}$$

where $\hat{O}_{i,j}=\hat{O}(\hat{\mathbf{p}}_i,\hat{\mathbf{p}}_j,\hat{\mathbf{q}}_i,\hat{\mathbf{q}}_j)$ and

$$\begin{aligned}\langle x'_1,x'_2|\hat{\rho}_{(2)}(t)|x_1,x_2\rangle &= N(N-1)\int dx_3\cdots\int dx_N\\ &\quad\times\langle x'_1,x'_2,x_3,\ldots,x_N|\hat{\rho}(t)|x_1,\ldots,x_N\rangle\end{aligned} \tag{6.82}$$

is the two-body reduced density matrix.

We can now introduce the one- and two-particle reduced Wigner functions. The one-particle reduced Wigner function is defined as

$$f_1(\mathbf{k},\mathbf{R},t)\equiv\int d\,\mathbf{r}e^{i\mathbf{k}\cdot\mathbf{r}}\left\langle\mathbf{R}+\frac{\mathbf{r}}{2}|\hat{\rho}_{(1)}(t)|\mathbf{R}-\frac{\mathbf{r}}{2}\right\rangle, \tag{6.83}$$

and the two-particle reduced Wigner function is defined as

$$\begin{aligned}f_2(\mathbf{k}_1,\mathbf{k}_2,\mathbf{R}_1,\mathbf{R}_2;t) &= \int\int d\,\mathbf{r}_1 d\,\mathbf{r}_2 e^{i\mathbf{k}_1\cdot\mathbf{r}_1}e^{i\cdot\mathbf{k}_2\mathbf{r}_2}\\ &\quad\times\left\langle\mathbf{R}_1+\frac{\mathbf{r}_1}{2};\mathbf{R}_2+\frac{\mathbf{r}_2}{2}|\rho_{(2)}(t)|\mathbf{R}_1-\frac{\mathbf{r}_1}{2},\mathbf{R}_2-\frac{\mathbf{r}_2}{2}\right\rangle.\end{aligned} \tag{6.84}$$

Higher-order Wigner functions can be defined in a similar manner.

In analogy to the classical distribution function, the one-particle Wigner function obeys the relations

$$\int\frac{d\,\mathbf{k}}{(2\pi)^3}f_1(\mathbf{k},\mathbf{R},t)=\langle\mathbf{R}|\hat{\rho}_{(1)}(t)|\mathbf{R}\rangle=n(\mathbf{R},t), \tag{6.85}$$

where $n(\mathbf{R}, t)$ is the average number of particles at point $\mathbf{R}$ and time, t, and

$$\int d\mathbf{R} f_1(\mathbf{k}, \mathbf{R}, t) = \langle \mathbf{k} | \hat{\rho}_{(1)}(t) | \mathbf{k} \rangle = n(\mathbf{k}, t), \tag{6.86}$$

and $n(\mathbf{k}, t)$ is the average number of particles with wavevector, $\mathbf{k}$, at time t. The Wigner function can be used to take phase space averages in the same way as the classical distribution functions. For example, the average current is defined as

$$\langle \mathbf{j}(\mathbf{R}, t) \rangle = \int \frac{d\mathbf{k}}{(2\pi)^3} \hbar \mathbf{k} f_1(\mathbf{k}, \mathbf{R}, t), \tag{6.87}$$

where $\hbar$ is Planck's constant. However, the Wigner function can become negative and therefore cannot always be interpreted as a probability density.

We can derive the equation of motion for $f_1(\mathbf{k}, \mathbf{R}, t)$ in the following way. For a system with a Hamiltonian

$$\hat{H} = \sum_{i=1}^{N} \frac{\hbar^2 k_i^2}{2m} + \sum_{i<j}^{N(N-1)/2} V(\hat{\mathbf{q}}_i - \hat{\mathbf{q}}_j), \tag{6.88}$$

the equation of motion for the one-particle reduced density matrix is

$$\begin{aligned} \frac{\partial}{\partial t} \langle \mathbf{r}_1 | \hat{\rho}_{(1)}(t) | \mathbf{r}_2 \rangle = & -\frac{i\hbar}{2m} (\nabla_{\mathbf{r}_1} + \nabla_{\mathbf{r}_2}) \cdot (\nabla_{\mathbf{r}_1} - \nabla_{\mathbf{r}_2}) \langle \mathbf{r}_1 | \hat{\rho}_{(1)}(t) | \mathbf{r}_2 \rangle \\ & - \frac{i}{\hbar} \int d\mathbf{r}' [V(\mathbf{r}_2 - \mathbf{r}') - V(\mathbf{r}_1 - \mathbf{r}')] \langle \mathbf{r}_1, \mathbf{r}' | \hat{\rho}_{(2)}(t) | \mathbf{r}_2, \mathbf{r}' \rangle, \end{aligned} \tag{6.89}$$

where $V(\mathbf{r}_1 - \mathbf{r}_2) = \langle \mathbf{r}_1, \mathbf{r}_2 | V(\hat{\mathbf{q}}_i - \hat{\mathbf{q}}_j) | \mathbf{r}_1, \mathbf{r}_2 \rangle$.

Let us now change to relative and center-of-mass coordinates, $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ and $\mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)$, respectively. We then multiply by $e^{i\mathbf{k}\cdot\mathbf{r}}$ and integrate over $d\mathbf{r}$ and find

$$\begin{aligned} & \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \frac{\partial}{\partial t} \left\langle \mathbf{R} + \frac{\mathbf{r}}{2} | \hat{\rho}_{(1))}(t) | \mathbf{R} - \frac{\mathbf{r}}{2} \right\rangle \\ & = -\frac{i\hbar}{m} \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \nabla_{\mathbf{R}} \cdot \nabla_{\mathbf{r}} \left\langle \mathbf{R} + \frac{\mathbf{r}}{2} | \hat{\rho}_{(1)}(t) | \mathbf{R} - \frac{\mathbf{r}}{2} \right\rangle \\ & \quad - \frac{i}{\hbar} \int d\mathbf{r}' \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \left[V\left(\mathbf{R} - \frac{\mathbf{r}}{2} - \mathbf{r}'\right) - V\left(\mathbf{R} + \frac{\mathbf{r}}{2} - \mathbf{r}'\right) \right] \\ & \quad \times \left\langle \mathbf{R} + \frac{\mathbf{r}}{2}, \mathbf{r}' | \hat{\rho}_{(2)}(t) | \mathbf{R} - \frac{\mathbf{r}}{2}, \mathbf{r}' \right\rangle. \end{aligned} \tag{6.90}$$

In Eq. (6.90) we can integrate the first term on the right by parts to remove the derivative with respect to $\mathbf{r}$. We can also introduce dummy variables into the second term on the right and make use of definitions in Eqs. (6.83) and (6.84) to obtain

$$\frac{\partial}{\partial t} f_1(\mathbf{k}, \mathbf{R}, t) = -\frac{\hbar}{m}\mathbf{k} \cdot \nabla_{\mathbf{R}} f_1(\mathbf{k}, \mathbf{R}, t) - \frac{i}{\hbar}\int \frac{d\mathbf{k}'}{(2\pi)^3}\int d\mathbf{r}'\left[V\left(\mathbf{R} - \mathbf{r}' - \frac{1}{2i}\frac{\partial}{\partial \mathbf{k}}\right) - V\left(\mathbf{R} - \mathbf{r}' + \frac{1}{2i}\frac{\partial}{\partial \mathbf{k}}\right)\right] \times f_2(\mathbf{k}, \mathbf{R}; \mathbf{k}', \mathbf{r}'; t). \tag{6.91}$$

Equation (6.91) is the quantum kinetic equation for the one-particle reduced Wigner function. If we rewrite it in terms of momenta $\mathbf{p} = \hbar\mathbf{k}$ and $\mathbf{p}' = \hbar\mathbf{k}'$, it takes the form

$$\frac{\partial}{\partial t} f_1'(\mathbf{p}, \mathbf{R}, t) + \frac{\mathbf{p}}{m} \cdot \nabla_{\mathbf{R}} f_1'(\mathbf{p}, \mathbf{R}, t) = -\frac{i}{\hbar}\int \frac{d\mathbf{p}}{(2\pi)^3}\int d\mathbf{r}'\left[V\left(\mathbf{R} - \mathbf{r}' - \frac{\hbar}{2i}\frac{\partial}{\partial \mathbf{p}}\right) - V\left(\mathbf{R} - \mathbf{r}' + \frac{\hbar}{2i}\frac{\partial}{\partial \mathbf{p}}\right)\right] \times f_2'(\mathbf{p}, \mathbf{R}; \mathbf{p}', \mathbf{r}'; t), \tag{6.92}$$

where

$$f_n'(\mathbf{p}_1, \mathbf{r}_1; \ldots; \mathbf{p}_n, \mathbf{r}_n) = \frac{1}{\hbar^{3n}} f_n\left(\frac{1}{\hbar}\mathbf{p}_1, \mathbf{r}_1; \ldots; \frac{1}{\hbar}\mathbf{p}_n, \mathbf{r}_n\right). \tag{6.93}$$

We can now expand the potential on the right-hand side in powers of $\hbar$ and take the limit $\hbar \to 0$. We then retrieve the classical kinetic equation.

The Wigner function can be used to take the average value of a large class of ordinary functions of momentum and position but in some cases it will give the wrong answer. The average value of any quantity which is only a function of position or only a function of momentum can always be taken (this is easily seen from Eqs. (6.85) and (6.86)). However, only those functions which involve both position and momentum can be used for which the Weyl correspondence between the quantum and classical version of the operators holds. To see this, let us consider the classical function $O(\mathbf{p}, \mathbf{q})$ of phase space variables $\mathbf{p}$ and $\mathbf{q}$. We can find the quantum version of this function as follows. We first introduce its Fourier transform, $\tilde{O}(\boldsymbol{\sigma}, \boldsymbol{\eta})$, with the equation

$$O(\mathbf{p}, \mathbf{q}) = \int\int d\boldsymbol{\sigma} d\boldsymbol{\eta}\, \tilde{O}(\boldsymbol{\sigma}, \boldsymbol{\eta}) e^{i(\boldsymbol{\sigma}\cdot\mathbf{p} + \boldsymbol{\eta}\cdot\mathbf{q})}. \tag{6.94}$$

Matrix elements of the quantum operator corresponding to $O(\mathbf{p}, \mathbf{q})$ can be obtained from the Fourier transform, $\tilde{O}(\boldsymbol{\sigma}, \boldsymbol{\eta})$, via the equation

$$\langle \mathbf{r}' | \hat{O} | \mathbf{r}'' \rangle = \int\int d\boldsymbol{\sigma} d\boldsymbol{\eta}\, \tilde{O}(\boldsymbol{\sigma}, \boldsymbol{\eta}) \langle \mathbf{r}' | e^{i(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}} - \boldsymbol{\eta}\cdot\hat{\mathbf{q}})} | \mathbf{r}'' \rangle, \tag{6.95}$$

where $\hat{\mathbf{p}}$ and $\hat{\mathbf{q}}$ are momentum and position operators. If the classical function $O(\mathbf{p}, \mathbf{q})$ and matrix elements of the corresponding operator $\hat{O}$ are related by the above procedure, then the expectation value of $\hat{O}$ is given by

$$\langle O(t) \rangle = \int\int d\mathbf{p} d\mathbf{r} O(\mathbf{p}, \mathbf{r}) f_1'(\mathbf{p}, \mathbf{r}, t). \tag{6.96}$$

There are some cases for which the Weyl procedure does not give the correct correspondence between classical and quantum operators (such as the commutator $[\hat{\mathbf{p}}, \hat{\mathbf{r}}]_-$, the square of the Hamiltonian $\hat{H}^2$, the square of the angular momentum $\mathbf{L}^2$, etc.) and the Wigner function gives the wrong result. Then it is necessary to introduce more general quantum phase space distributions which may in general be complex functions [25].

■ **EXERCISE 6.7.** Compute the Wigner function for a system with a density operator, $\hat{\rho} = \hbar\sqrt{ab}(e^{-a\hat{x}^2} e^{-b\hat{p}^2} + e^{-b\hat{p}^2} e^{-a\hat{x}^2})$.

Answer: First compute the matrix element of the density operator in the position basis,

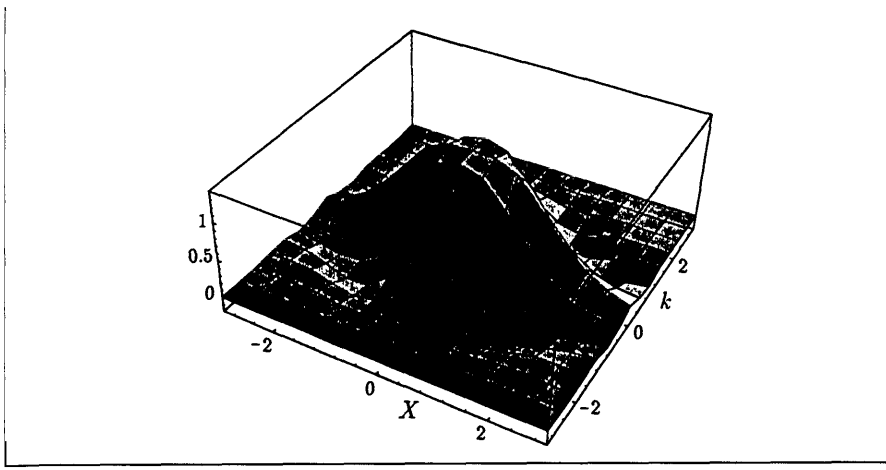
$$\langle x_1 | \hat{\rho} | x_2 \rangle = \frac{1}{2}\sqrt{\frac{a}{\pi}}(e^{-ax_1^2} + e^{-ax_2^2}) \exp\left(-\frac{(x_1 - x_2)^2}{4b\hbar^2}\right). \tag{1}$$

Now let $x_1 = X + (x/2)$ and $x_1 - (x/2)$. The Wigner function is then given by (after some algebra)

$$f(k, X) = \int_{-\infty}^{\infty} dx e^{ikx} \left\langle X + \frac{x}{2} | \hat{\rho} | X - \frac{x}{2} \right\rangle$$

$$= \sqrt{\frac{4ab\hbar^2}{1 + ab\hbar^2}} \exp\left(\frac{-aX^2}{1 + ab\hbar^2}\right) \exp\left(\frac{-bk^2\hbar^2}{1 + ab\hbar^2}\right) \cos\left(\frac{2ab\hbar^2 kX}{1 + ab\hbar^2}\right). \tag{2}$$

A plot of the Wigner function is shown here for $a = 1$ and $b\hbar^2 = 2$. Note that there are some regions where it becomes negative, indicating that it is not a probability density.



▶ S6.C. Microscopic Balance Equations [26]

For quantum systems with short-ranged interactions and long-wavelength inhomogeneities, we can derive microscopic balance equations for the particle density, momentum density, and energy density in a manner analogous to the derivation for classical systems. We first note, however, that the position and momentum operators satisfy the commutation relations,

$$[\hat{\mathbf{p}}_i, \hat{\mathbf{p}}_j]_- = 0, \qquad [\hat{\mathbf{q}}_i, \hat{\mathbf{q}}_j]_- = 0, \quad \text{and} \quad [\hat{\mathbf{q}}_i, \hat{\mathbf{p}}_j]_- = i\hbar\delta_{ij}. \tag{6.97}$$

The commutator of the momentum operator $\hat{\mathbf{p}}_i$ with an arbitrary function of coordinate operators is

$$[\hat{\mathbf{p}}_i, F(\hat{\mathbf{q}}_1, \ldots, \hat{\mathbf{q}}_N)]_- = -i\hbar \frac{\partial F}{\partial \hat{\mathbf{q}}_i}, \tag{6.98}$$

while the commutator of $\hat{\mathbf{q}}_i$ with an arbitrary function of momenta $G(\hat{\mathbf{p}}_1, \ldots, \hat{\mathbf{p}}_N)$ is

$$[\hat{\mathbf{q}}_i, G(\hat{\mathbf{p}}_1, \ldots, \hat{\mathbf{p}}_N)]_- = i\hbar \frac{\partial G}{\partial \hat{\mathbf{p}}_i}. \tag{6.99}$$

Let us assume that the dynamics of the system is governed by a Hamiltonian of the form

$$\hat{H}^N = \sum_{i=1}^{N} \frac{|\hat{\mathbf{p}}_i|^2}{2m} + \sum_{i<j}^{(1/2)N(N-1)} V(|\hat{\mathbf{q}}_i - \hat{\mathbf{q}}_j|). \tag{6.100}$$

Then from Eq. (6.57) the equation of motion for the operator $\hat{\mathbf{q}}_i$ is

$$\frac{\partial \hat{\mathbf{q}}_i}{\partial t} = \frac{i}{\hbar}[\hat{H}, \hat{\mathbf{q}}_i]_- = \frac{\hat{\mathbf{p}}_i}{m}. \tag{6.101}$$

The equation of motion of $\hat{\mathbf{p}}_i$ is given by

$$\frac{\partial \hat{\mathbf{p}}_i}{\partial t} = -\sum_{l \neq i}\left[\frac{\partial V(|\hat{\mathbf{q}}_i - \hat{\mathbf{q}}_l|)}{\partial \hat{\mathbf{q}}_i}\right] = \sum_{l \neq i} \hat{\mathbf{F}}_{il}. \tag{6.102}$$

These equations have the same form as the classical equations.

For quantum systems, the microscopic expressions for the densities must be Hermitian in order to be observable. Thus, we must have symmetrized expressions for operators which involve both momentum and position. Using Eq. (6.57) and the above equations, we can show that the balance equation for the particle number density is given by

$$\frac{\partial}{\partial t}\hat{n}(\hat{\mathbf{q}}^N; \mathbf{R}) = -\nabla_{\mathbf{R}} \cdot \hat{\mathbf{J}}^n(\hat{\mathbf{p}}^N, \hat{\mathbf{q}}^N; \mathbf{R}), \tag{6.103}$$

where the particle density is defined as

$$\hat{n}(\hat{\mathbf{q}}^N; \mathbf{R}) = \sum_{i=1}^{N} \delta(\hat{\mathbf{q}}_i - \mathbf{R}) \tag{6.104}$$

and the particle current density is defined as

$$\hat{\mathbf{J}}^n(\hat{\mathbf{p}}^N, \hat{\mathbf{q}}^N; \mathbf{R}) = \frac{1}{2}\sum_{i=1}^{N}\left[\frac{\hat{\mathbf{p}}_i}{m}\delta(\hat{\mathbf{q}}_i - \mathbf{R}) + \delta(\hat{\mathbf{q}}_i - \mathbf{R})\frac{\hat{\mathbf{p}}_i}{m}\right]. \tag{6.105}$$

As usual, we let $\hat{\mathbf{p}}^N$ denote the set of momenta $\hat{\mathbf{p}}^N = (\hat{\mathbf{p}}_1, \ldots, \hat{\mathbf{p}}_N)$ and we let $\hat{\mathbf{q}}^N$ denote the set of positions $\hat{\mathbf{q}}^N = (\hat{\mathbf{q}}_1, \ldots, \hat{\mathbf{q}}_N)$.

The balance equation for the momentum density takes the form

$$m\frac{\partial}{\partial t}\hat{\mathbf{J}}^n(\hat{\mathbf{p}}^N, \hat{\mathbf{q}}^N; \mathbf{R}) = -\nabla_{\mathbf{R}} \cdot \hat{\mathbf{J}}^p(\hat{\mathbf{p}}^N, \hat{\mathbf{q}}^N; \mathbf{R}), \tag{6.106}$$

where the momentum current tensor, $\hat{\mathbf{J}}^p(\hat{\mathbf{p}}^N, \hat{\mathbf{q}}^N; \mathbf{R})$, is defined as

$$\begin{aligned}\hat{\mathbf{J}}^p(\hat{\mathbf{p}}^N, \hat{\mathbf{q}}^N; \mathbf{R}) = &\frac{1}{4m}\sum_{i=1}^{N}[\hat{\mathbf{p}}_i\hat{\mathbf{p}}_i\delta(\hat{\mathbf{q}}_i - \mathbf{R}) + (\hat{\mathbf{p}}_i\delta(\hat{\mathbf{q}}_i - \mathbf{R})\hat{\mathbf{p}}_i)^T \\ &+ \hat{\mathbf{p}}_i\delta(\hat{\mathbf{q}}_i - \mathbf{R})\hat{\mathbf{p}}_i + \delta(\hat{\mathbf{q}}_i - \mathbf{R})\hat{\mathbf{p}}_i\hat{\mathbf{p}}_i] \\ &+ \frac{1}{2}\sum_{i \neq l}^{N}\sum^{N}(\hat{\mathbf{q}}_i - \hat{\mathbf{q}}_l) \cdot \mathbf{F}_{il}\delta(\mathbf{q}_i - \mathbf{R}).\end{aligned} \tag{6.107}$$

In Eqs. (6.106) and (6.107) the notation

$$\nabla_{\mathbf{R}} \cdot (\hat{\mathbf{p}}_i \delta(\hat{\mathbf{q}}_i - \mathbf{R})\hat{\mathbf{p}}_i)^T \equiv \hat{\mathbf{p}}_i \nabla_{\mathbf{R}} \cdot \delta(\hat{\mathbf{q}}_i - \mathbf{R})\hat{\mathbf{p}}_i \tag{6.108}$$

has been used.

Finally, the balance equation for the energy density can be written

$$\frac{\partial}{\partial t}\hat{h}(\hat{\mathbf{p}}^N, \hat{\mathbf{q}}^N; \mathbf{R}) = -\nabla_{\mathbf{R}} \cdot \hat{\mathbf{J}}^h(\hat{\mathbf{p}}^N, \hat{\mathbf{q}}^N; \mathbf{R}), \tag{6.109}$$

where the energy density is defined as

$$\hat{h}(\hat{\mathbf{p}}^N, \hat{\mathbf{q}}^N; \mathbf{R}) \equiv \frac{1}{2}\sum_{i=1}^{N} [\hat{h}_i \delta(\hat{\mathbf{q}}_i - \mathbf{R}) + \delta(\hat{\mathbf{q}}_i - \mathbf{R})\hat{h}_i] \tag{6.110}$$

with

$$\hat{h}_i = \frac{|\hat{\mathbf{p}}_i|^2}{2m} + \frac{1}{2}\sum_{j \neq i} V(|\hat{\mathbf{q}}_i - \hat{\mathbf{q}}_j|) \tag{6.111}$$

and the energy current density is defined as

$$\begin{aligned}\hat{\mathbf{J}}^h(\hat{\mathbf{p}}^N, \hat{\mathbf{q}}^N; \mathbf{R}) \equiv & \frac{1}{4}\sum_{i=1}^{N}\left[\hat{h}_i \frac{\hat{\mathbf{p}}_i}{m}\delta(\hat{\mathbf{q}}_i - \mathbf{R}) + \hat{h}_i \delta(\hat{\mathbf{q}}_i - \mathbf{R})\frac{\hat{\mathbf{p}}_i}{m}\right. \\ & \left. + \frac{\hat{\mathbf{p}}_i}{m}\delta(\hat{\mathbf{q}}_i - \mathbf{R})\hat{h}_i + \delta(\hat{\mathbf{q}}_i - \mathbf{R})\frac{\hat{\mathbf{p}}_i}{m}\hat{h}_i\right] \\ & + \frac{1}{4}\sum_{i \neq j}^{N}\sum^{N}\left[\frac{(\hat{\mathbf{p}}_i + \hat{\mathbf{p}}_j)}{m} \cdot \hat{\mathbf{F}}_{ij}(\hat{\mathbf{q}}_i - \hat{\mathbf{q}}_j)\delta(\hat{\mathbf{q}}_i - \mathbf{R})\right. \\ & \left. + \delta(\hat{\mathbf{q}}_i - \mathbf{R})(\hat{\mathbf{q}}_i - \hat{\mathbf{q}}_j)\hat{\mathbf{F}}_{ij} \cdot \frac{(\hat{\mathbf{p}}_i + \hat{\mathbf{p}}_j)}{m}\right].\end{aligned} \tag{6.112}$$

To obtain Eq. (6.112), one must use the fact that the center-of-mass coordinates commute with the relative coordinates.

▶ S6.D. Mixing Flow [7–9]

Ergodicity is not a sufficient condition on a dynamical flow to ensure that a probability distribution that initially is localized on an energy surface will spread, in a course grained manner, throughout the energy surface. Spreading throughout the energy surface is the type of behavior that we need for a

Newtonian system to approach a state that might be used as an equilibrium state. A type of flow that does have this feature, and therefore might exhibit irreversibility in a course-grained sense (because of the unstable nature of its dynamics!) is *mixing flow.* Mixing flow is chaotic and causes any initial probability distribution to spread throughout the energy surface. *Mixing flow is ergodic, but ergodic flows are not always mixing* (the exceptions, however, are rare).

A system is mixing if, for all square integrable functions, $f(\mathbf{X}^N)$ and $g(\mathbf{X}^N)$, on the energy surface, S_E, we obtain

$$\lim_{t\to\pm\infty} \frac{1}{\sum(E)} \int_{S_E} f(\mathbf{X}^N) g(\mathbf{X}^N(t)) dS_E = \frac{\int_{S_E} f(\mathbf{X}^N) dS_E \int_{S_E} g(\mathbf{X}^N) dS_E}{(\sum(E))^2}, \quad (6.113)$$

where $\sum(E)$ is the structure function defined in Section 6.C.

Equation (6.113) ensures that the average value of a dynamical function $f(\mathbf{X}^N)$ will approach a stationary value in the limit $t \to \pm\infty$. Let $g(\mathbf{X}^N) = \rho(\mathbf{X}^N)$, where $\rho(\mathbf{X}^N)$ is a nonstationary probability density. Then

$$\langle f(t) \rangle = \int_{S_E} f(\mathbf{X}^N) \rho(\mathbf{X}^N(t)) dS_E \underset{t\to\pm\infty}{\longrightarrow} \frac{1}{\sum(E)} \int_{S_E} f(\mathbf{X}^N) dS_E. \quad (6.114)$$

Thus, $f(t)$ approaches an average with respect to the stationary state $\rho_s = [\sum(E)]^{-1}$.

It is important to emphasize that mixing gives a coarse-grained and not a fine-grained approach to a stationary state. The average of the probability density becomes uniform, but the probability density itself cannot because of Eq. (6.24). The probability density does not change in a neighborhood of a moving phase point, but it can change at a given point in space. We can visualize this if we consider a beaker containing oil and water. We add the oil and water carefully so that they are initially separated, and we assume that they cannot diffuse into one another. We then stir them together (Fig. 6.2). The local density and the total volume of the oil remain constant, but the oil will get stretched into filaments throughout the water. Therefore, on the average, the density of the oil will become uniform throughout the beaker. If we are careful enough, we can also stir the oil back into its original shape. Therefore, while we get an approach to uniformity, the whole process can be reversed. However, as we shall see, mixing does lead to the appearance of random behavior in deterministic systems and coarse-grained irreversibility.

The meaning of Eq. (6.113) may therefore be summarized as follows. Let A and B be two finite arbitrary regions on the surface S_E. Let us assume that all phase points initially lie in A. If the system is mixing, and we let it evolve in time, the fraction of points which lie in A or B in the limit $t \to \pm\infty$ will equal the fraction of area S_E occupied by A or B, respectively.

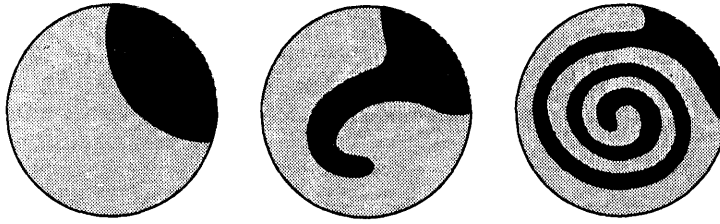


Fig. 6.2. Stirring oil and water together leads to uniformity, *on the average*.

An example of a discrete dynamical system which is mixing is the Baker's map. The dynamics evolves on a unit square, $0 \le p \le 1$ and $0 \le q \le 1$. The state points evolve in discrete time steps and change value in a discontinuous manner. The dynamical evolution is governed by an "alphabet" with two letters, 0 and 1, and the set, $\{S\}$, of all possible infinite sequences of letters. Each infinite sequence has the form $S = (\ldots, S_{-2}, S_{-1}, S_0, S_1, S_2 \ldots)$, where S_k =(0 or 1) and $k = (0, \pm 1, \pm 2, \ldots)$, and corresponds to a state point in the two-dimensional phase space. Each sequence maps onto the unit square according to the rules,

$$p = \sum_{k=0}^{-\infty} S_k 2^{k-1} = \frac{S_0}{2} + \frac{S_{-1}}{4} + \frac{S_{-2}}{8} + \cdots \quad \text{and}$$
$$q = \sum_{k=1}^{\infty} S_k 2^{-k} = \frac{S_1}{2} + \frac{S_2}{4} + \frac{S_3}{8} + \cdots . \tag{6.115}$$

Thus, if all $S_k = 0$, then $p = q = 0$, and if all $S_k = 1$, then $p = q = 1$ since $\sum_{k=1}^{\infty} (\frac{1}{2})^k = 1$. All other cases also lie on the unit square, $0 \le p \le 1$ and $0 \le q \le 1$.

The dynamics is introduced into the phase space by means of the Bernoulli shift, U, which is defined so that $US_k = S_{k+1}$. That is, the operator, U, acting on a sequence, S, shifts each element to the right one place. The shift acting on the sequence, S, is equivalent to the following transformation (the Baker's transformation) on the unit square:

$$U(p,q) = \begin{cases} (2p, \frac{1}{2}q), & 0 \le p \le \frac{1}{2} \\ (2p-1, \frac{1}{2}q + \frac{1}{2}), & \frac{1}{2} \le p \le 1. \end{cases} \tag{6.116}$$

The inverse transformations is

$$U^{-1}(p,q) = \begin{cases} (\frac{1}{2}p, 2q), & 0 \le q \le \frac{1}{2} \\ (\frac{1}{2}p + \frac{1}{2}, 2q-1), & \frac{1}{2} \le q \le 1. \end{cases} \tag{6.117}$$

The Jacobian of the transformation is equal to one. Therefore, the mapping, U, is area-preserving. Let us now look at how the probability density evolves under the action of the shift, U. Let $\rho_0(p,q)$ be the initial probability density and let us assume that it is continuous and smooth. After we allow U to act n times, we obtain

$$\rho_n(p,q) = U^n\rho_0(p,q) = \rho_0(U^{-n}p, U^{-n}q). \tag{6.118}$$

More explicitly,

$$\rho_{n+1}(p,q) = \begin{cases} \rho_n(\frac{1}{2}p, 2q), & 0 \le q \le \frac{1}{2} \\ \rho_n(\frac{1}{2}p + \frac{1}{2}, 2q - 1), & \frac{1}{2} \le q \le 1 \end{cases} \tag{6.119}$$

The time evolution operator, U, is an example of a Frobenius–Perron operator [27] and [28].

The effect of the Baker's transformation is to stretch an initial area element into filaments throughout the unit square, much as a baker does in kneading dough. Note that whenever $S_0 = 0$ the point corresponding to the sequence, S, will lie to the left of $p = \frac{1}{2}$ and when $S_0 = 1$ it will lie to the right of $p = \frac{1}{2}$. Therefore, points corresponding to sequences with 0 and 1 distributed at random in the positions, S_k, will be shifted to the right or left of $p = \frac{1}{2}$ by U at random. If initially the probability density is $\rho_0(p,q) = 0$ for $0 \le p \le \frac{1}{2}$ and $0 \le q \le 1$ and $\rho(p,q) = 2$ for $\frac{1}{2} \le p \le 1$ and $0 \le q \le 1$, then the probability density at times $n = 1, 2, 3$, are shown in Fig. 6.3.

As we have seen above, there is an element of randomness in the position of a point in the p direction. Let us look at the reduced probability density, $\phi(p)$, in the p direction. The quantity $\phi_n(p)dp$ is the probability of finding a point in the interval $p \to dp$ at 'time' n. It is defined as $\phi_n \equiv \int_0^1 dq\rho_n(p,q)$. Using Eq. (6.119), $\phi_{n+1}(p)$ becomes

$$\phi_{n+1}(p) = \frac{1}{2}\phi_n\left(\frac{p}{2}\right) + \frac{1}{2}\phi_n\left(\frac{p}{2} + \frac{1}{2}\right). \tag{6.120}$$

The reduced probability evolves in a Markovian manner. We can show that $\lim_{n\to\infty}\phi_n(p) = 1$ and, therefore, that the reduced or coarse-grained probability

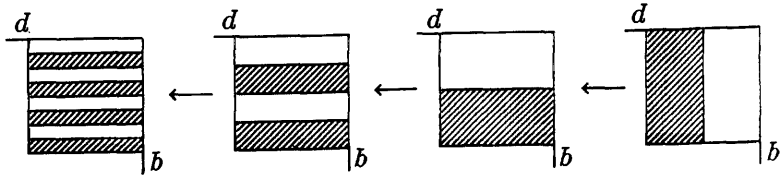


Fig. 6.3. Evolution of an initial probability under the action of the Baker's map.

density approaches a constant. If we iterate Eq. (6.120), we obtain

$$\phi_n(p) = \frac{1}{2^n}\sum_{k=0}^{2^n-1}\phi_0\left(\frac{p}{2^n}+\frac{k}{2^n}\right). \tag{6.121}$$

For a continuous and smooth function, $\phi_0(p)$, we obtain

$$\lim_{n\to\infty}\phi_n(p) = \lim_{n\to\infty}\int_0^{1-1/2^n} dy\,\phi_0\left(\frac{p}{2^n}+y\right) = \int_0^1 dy\phi_0(y) = 1, \tag{6.122}$$

where we have let $y = k2^{-n}$. Notice that for $n \to -\infty$, $\phi_n(p)$ will *not* approach a constant. However, a reduced probability density, defined in terms of the variable q, does. Therefore, the Baker's transformation exhibits irreversibility in a course-grained sense.

■ **EXERCISE 6.8.** Compute the trace of the Baker map, $\hat{U}^n$.

Answer: Let us denote $\hat{U}^n(p,q) = (p^n(p,q), q^n(p,q))$, where $p^n(p,q)$ and $q^n(p,q)$ are functions of p and q. The trace of U^n can be written

$$\mathrm{Tr}\,\hat{U}^n = \int_0^1 dp\int_0^1 dp\delta(p-p^n(p,q))\delta(q-q^n(p,q)). \tag{1}$$

Before we evaluate Eq. (1), let us note the following property of the Dirac delta function. Let us consider a function, $f(x)$, which has zeros at points $x_{0,k}$ (where $k = 1,2,\ldots,M$), so that $f(x_{0,k}) = 0$. Then

$$\delta(f(x)) \equiv \sum_{k=1}^{M}\frac{\delta(x-x_{0,k})}{|f'(x_{0,k})|}, \tag{2}$$

where $f'(x) = (df/dx)$.

We now can evaluate the trace of $\hat{U}^n$. Notice that the delta functions will give contributions when $p^n = p$ and $q^n = q$. That is, for all 2^n nth-order periodic *points* of the map, $\hat{U}^n$. First note that $(dp_n/dp_0) = 2^n$ and $(dq_n/dq_0) = (1/2^n)$. Thus,

$$\mathrm{Tr}\,\hat{U}^n = \sum_{\text{Period } n \text{ points}}\left|\frac{dp_n}{dp_0}-1\right|^{-1}\left|\frac{dq_n}{dq_0}-1\right|^{-1} = 2^n(2^n-1)^{-1}\left(1-\frac{1}{2^n}\right)^{-1}$$

$$= \left(1-\frac{1}{2^n}\right)^{-2} = \sum_{m=0}^{\infty}(m+1)\left(\frac{1}{2^m}\right)^n \tag{3}$$

(cf. Ref. 28). The trace of U^n is equal to the sum of the eigenvalues of U^n.

▶ S6.E. Anharmonic Oscillator Systems [4]

The study of anharmonic oscillator systems has long been important in statistical mechanics in connection with the theory of heat transport in solids [29]. One would like to know the mechanism of heat conduction. If heat is added to a harmonic lattice and divided unequally between the normal modes, there is no way for the system to reach equilibrium because the normal modes do not interact. However, if slight anharmonicities exist in the lattice, it was expected that equipartition of energy would occur and that the system would thus reach equilibrium.

In 1955, Fermi, Pasta, and Ulam [30] conducted a computer experiment intending to show this. They studied a system of 64 oscillators with cubic and broken linear coupling. They found that when energy was added to a few of the lower modes there was no tendency for the energy to spread to the other modes. This behavior is quite different from what one would expect if the anharmonic oscillator system were an ergodic system. Then one expects the system to reach a stationary state in which all states with the same energy would be equally probable, and one expects to see energy sharing among the modes.

The type of behavior that Fermi, Pasta, and Ulam observed is now fairly well understood in terms of a theorem due to Kolmogorov [31], Arnold [32], and Moser [33] (commonly called the KAM theorem). The theorem states that for a system with weak anharmonic coupling (which satisfies the conditions of the KAM theorem), most of the energy surface will be composed of invariant tori and the system will exhibit behavior in many respects similar to that of an unperturbed harmonic oscillator system. The energy surface will not be metrically transitive. As the coupling is increased, however, the invariant regions of phase space break down and at some point one expects to see a sharp transition to chaotic behavior and something similar to equipartition of energy between the modes. (True equipartition requires ergodicity, and it is not clear that anharmonic oscillator systems are ergodic above the transition energy.)

There is now a variety of nonlinear oscillator systems which have been studied and which exhibit a transition from stable to chaotic behavior as certain parameters are changed [4]. Henon and Heiles [34] studied the bounded motion of orbits for a system with two degrees of freedom governed by the Hamiltonian

$$H = \tfrac{1}{2}(p_1^2 + p_2^2 + q_1^2 + q_2^2) + q_1 q_2^2 - \tfrac{1}{3} q_1^3. \tag{6.123}$$

The trajectories move in a four-dimensional phase space but are restricted to a three-dimensional surface because the total energy is a constant of the motion. It is possible to study a two-dimensional cross section of the three-dimensional energy surface. For example, we can consider the surface $q_2 = 0$ and look at a trajectory each time it passes through the surface with positive velocity $p_2 > 0$. It is then possible to plot successive points of the trajectory ($q_2 = 0, p_2 > 0$) in the p_1, q_1 plane. If the only constant of motion is the total energy, E, then the points should be free to wander through the region of the p_1, q_1 plane

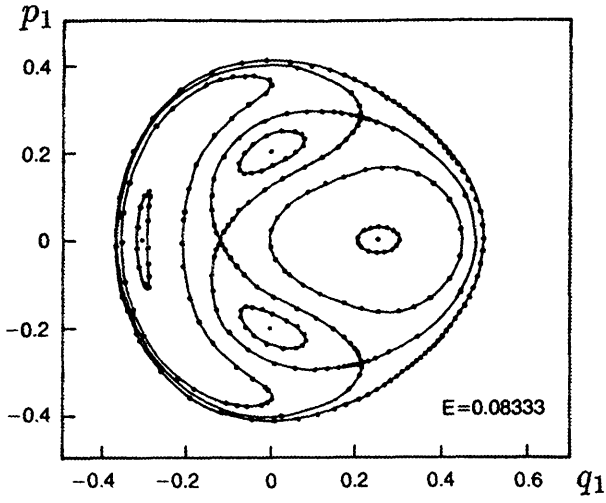


Fig. 6.4. Henon–Heiles result for $E = 0.08333$. (Based on Ref 34.)

corresponding to the energy surface. The motion we see will appear to be quite similar to ergodic motion. If there is an additional constant of the motion, the points will lie on a smooth curve in the p_1, q_1 plane.

Henon and Heiles studied trajectories whose motion was governed by Eq. (6.123) for a variety of energies. The results are sketched in Fig. 6.4. For an energy, $E = 0.08333$, they found only smooth curves, indicating that to computer accuracy there was an additional constant of the motion. Each closed curve in Fig. 6.4 corresponds to one trajectory. The three points of intersection of lines are hyperbolic fixed points, and the four points surrounded by curves are elliptic fixed points [4]. However, at an energy $E = 0.12500$, the picture begins to break down (cf. Fig. 6.5). Each closed curve in Fig. 6.5 corresponds to one trajectory. The five islands correspond to one trajectory, and the random dots outside the closed curve correspond to one trajectory. At an energy of $E = 0.16667$, almost no stable motion remains (cf. Fig. 6.6). A single trajectory is free to wander over almost the entire energy surface. In a very small energy range the system has undergone a transition from stable to chaotic behavior. Additional studies of the Henon–Helies system [35, 36] have shown that trajectory points move apart linearly in the stable regions, whereas they move apart exponentially in the chaotic regions.

The change from stable to chaotic behavior sets in rather abruptly. This has been understood in terms of an overlapping of resonances in the system. The Hamiltonian for a general anharmonic system with two degrees of freedom can be written in terms of action angle variables in the form

$$H = H_0(J_1, J_2) + \lambda V(J_1, J_2, \phi_1, \phi_2) \tag{6.124}$$

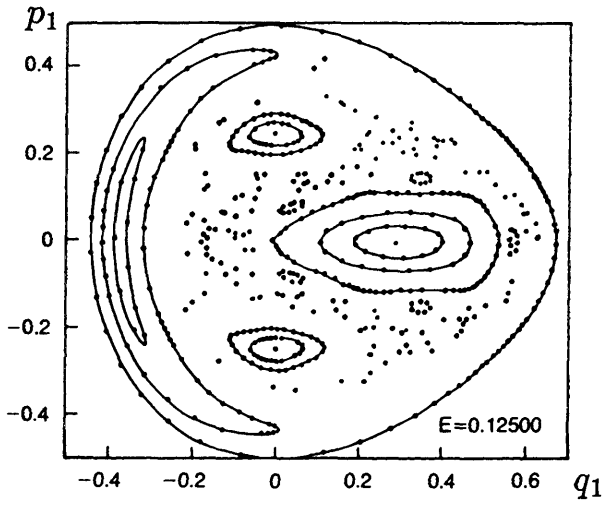


Fig. 6.5. Henon–Heiles result for $E = 0.12500$. (Based on Ref 34.)

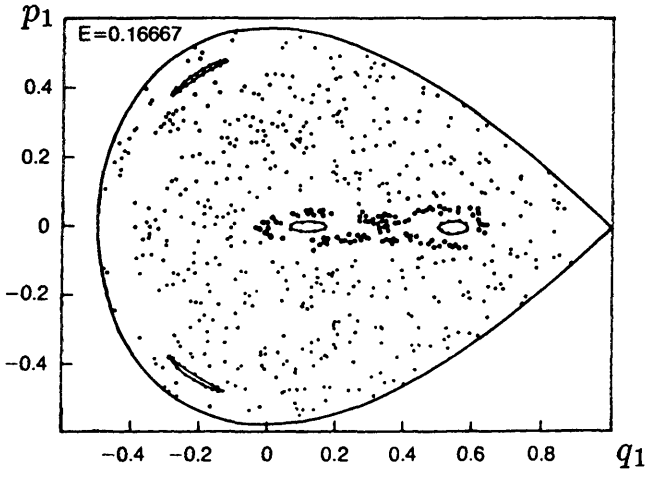


Fig. 6.6. Henon–Heiles result for $E = 0.16667$. (Based on Ref 34.)

by means of the transformation

$$p_i = -(2m\omega J_i)^{1/2}\sin\phi_i \quad \text{and} \quad q_i = \left(\frac{2J_i}{m\omega}\right)^{1/2}\cos\phi_i.$$

The function $H_0(J_1, J_2)$ has a polynomial dependence on the action variables J_1 and J_2 (not merely a linear dependence as would be the case for a harmonic system) and no angle dependence, while $V(J_1, J_2, \phi_1, \phi_2)$ depends on both

action and angle variables and is a periodic function of the angles. When $\lambda = 0$ the action variables will be constants of the motion, and the angles ϕ_1 and ϕ_2 will change in time according to the equations

$$\phi_i = \omega_i(J_1, J_2)t + \phi_{i,0} \tag{6.125}$$

for $(i = 1, 2)$ where

$$\omega_i(J_1, J_2) = \frac{\partial H_0}{\partial J_i}. \tag{6.126}$$

For the anharmonic case, the frequencies $\omega_i(J_1, J_2)$ will be continuous because they depend on the action variables, even for two degrees of freedom. This continuous dependence on the action variables is quite different from a harmonic oscillator system where the frequencies, ω_i, are constant.

For systems which satisfy the conditions of the KAM theorem (namely, small λ and nonzero Hessian, $\det|\partial^2 H_0/\partial_{J_i}\partial_{J_j}| \neq 0$ for $(i,j) = 1$ and 2), only a very small region of phase space, the resonance regions, will exhibit chaotic behavior. The rest of the phase space will correspond to stable motion. If one tries to construct new action variables $\mathscr{J}_i$ which are constants of the motion when $\lambda \neq 0$ but small, one finds that this can be done for most of the phase space, except for the resonance zones. In the resonance zones, perturbation expansions for $\mathscr{J}_i$ diverge. Let us construct a perturbation expansion [37] for the action variables $\mathscr{J}_i$ to lowest order in λ. Let us consider a Hamiltonian of the form

$$H = H_0(J_1, J_2) + \lambda \sum_{n_1, n_2} V_{n_1, n_2}(J_1, J_2)\cos(n_1\phi_1 + n_2\phi_2) \tag{6.127}$$

and let us introduce the generator

$$F(\mathscr{J}_1, \mathscr{J}_2, \phi_1, \phi_2) = \mathscr{J}_1\phi_1 + \mathscr{J}_2\phi_2 + \sum_{n_1, n_2} B_{n_1, n_2}\sin(n_1\phi_1 + n_2\phi_2) \tag{6.128}$$

of a canonical transformation from variables J_i, ϕ_i to variables $\mathscr{J}_i, \Phi_i$, such that the variables $\mathscr{J}_i$ are constants of the motion. Then

$$J_i = \frac{\partial F}{\partial \phi_i} = \mathscr{J}_i + \sum_{n_1, n_2} n_i B_{n_1, n_2}\cos(n_1\phi_1 + n_2\phi_2) \tag{6.129}$$

for $i = 1, 2$ and

$$\Phi_i = \frac{\partial F}{\partial \mathscr{J}_i} \tag{6.130}$$

for $i = 1, 2$. If we substitute Eq. (6.129) into Eq. (6.127) and keep terms to lowest order in λ (this requires a Taylor series expansion of H_0), we obtain

$$H = H_0(\mathscr{J}_1, \mathscr{J}_2) + \sum_{n_1,n_2} \{(n_1\omega_1 + n_2\omega_2)B_{n_1,n_2} + \lambda V_{n_1,n_2}\}\cos(n_1\phi_1 + n_2\phi_2). \tag{6.131}$$

To lowest order in λ, $\mathscr{J}_1$ and $\mathscr{J}_2$ will be constants of motion if we choose

$$B_{n_1,n_2} = \frac{-\lambda V_{n_1,n_2}}{(n_1\omega_1 + n_2\omega_2)}. \tag{6.132}$$

Then

$$H = H_0(\mathscr{J}_1 \mathscr{J}_2) + O(\lambda^2) \tag{6.133}$$

and

$$\mathscr{J}_1 = J_1 + \sum_{n_1,n_2} \frac{\lambda V_{n_1,n_2}}{(n_1\omega_1 + n_2\omega_2)} \cos(n_1\phi_1 + n_2\phi_2) + O(\lambda^2) \tag{6.134}$$

Note, however, that since ω_1 and ω_2 are functions of J_1 and J_2, there are values of J_1 and J_2 for which the denominator $(n_1\omega_1 + n_2\omega_2)$ can be zero, and the perturbation expansion becomes meaningless. Indeed, as long as

$$|n_1\omega_1 + n_2\omega_2| \leq \lambda V_{n_1,n_2}, \tag{6.135}$$

the perturbation expansion will diverge and $\mathscr{J}_i$ is not a well-behaved invariant. This region of phase space is called the resonance zone and $(n_1\omega_1 + n_2\omega_2) = 0$ is the resonance condition. It is in the resonance zones that one observes chaotic behavior.

If the regions of phase space which contain resonances, and a small region around each resonance, are excluded from the expansion for $\mathscr{J}_1$, then one can have a well-behaved expression for $\mathscr{J}_1$. Thus, one can exclude regions which satisfy the condition

$$[n_1\omega_1(J_1, J_2) + n_2\omega_2(J_1, J_2)] \ll \lambda V_{n_1,n_2}.$$

For smooth potentials, V_{n_1,n_2} decreases rapidly for increasing n_1 and n_2. Thus for increasing n_1 and n_2, ever smaller regions of the phase space are excluded.

Kolmogorov, Arnold, and Moser proved that as $\lambda \to 0$ the amount of excluded phase space approaches zero. The idea behind their proof is easily seen in terms of a simple example [38]. Consider the unit line (a line of length one). It contains an infinite number of rational fractions, but they form a set of

measure zero on the line. If we exclude a region

$$\left(\frac{m}{n}-\frac{\varepsilon}{n^3}\right)\leq\frac{m}{n}\leq\left(\frac{m}{n}-\frac{\varepsilon}{n^3}\right)$$

around each rational fraction, the total length of the unit line that is excluded is

$$\sum_{n=1}^{\infty}\sum_{m=1}^{n}\left(\frac{2\varepsilon}{n^3}\right)=2\varepsilon\sum_{n=1}^{\infty}\frac{1}{n^2}=\frac{\varepsilon\pi^2}{3}\underset{\varepsilon\to 0}{\longrightarrow}0.$$

Thus, for small λ, we can exclude the resonance regions in the expansion of $\mathscr{J}_1$ and still have a large part of the phase space in which $\mathscr{J}_1$ is well-defined and invariant tori can exist.

Walker and Ford [37] give a simple exactly soluble example of the type of distortion that a periodic potential can create in phase space. It is worth repeating here. They consider a Hamiltonian of the type

$$H=H_0(J_1,J_2)+\lambda J_1J_2\cos(2\phi_1-2\phi_2)=E, \tag{6.136}$$

where

$$H_0(J_1,J_2)=J_1+J_2-J_1^2-3J_1J_2+J_2^2. \tag{6.137}$$

For this model, there are two constants of the motion, namely, the total energy $H=E$ and

$$I=J_1+J_2. \tag{6.138}$$

Therefore, we do not expect to see any chaotic behavior for this system. However, the unperturbed phase space will still be distorted when $\lambda\neq 0$. The frequencies ω_i for this model are given by

$$\omega_1=\frac{\partial H_0}{\partial J_1}=1-2J_1-3J_2 \tag{6.139}$$

and

$$\omega_2=\frac{\partial H_0}{\partial J_2}=1-3J_1+2J_2. \tag{6.140}$$

If we want the frequencies to remain positive, we must choose $0\leq J_1\leq\frac{5}{13}$ and $0\leq J_2\leq\frac{1}{13}$ and, therefore, $E\leq\frac{3}{13}$.

Let us plot trajectories for the Walker–Ford case ($q_2=0, p_2>0$) (note that $q_i=(2J_i)^{1/2}\cos\phi_i$ and $p_i=-(2J_i)^{1/2}\sin\phi_i$). We find that for $\lambda=0$ the trajectories trace out concentric circles in the p_1,q_1 plane. When the

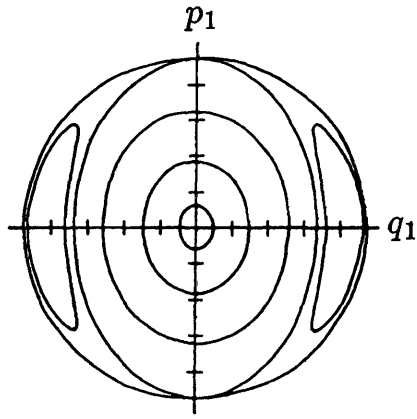


Fig. 6.7. Cross–section of the energy surface for the Hamiltonian, $H = J_1 + J_2 - J_1^2 - 3J_1J_2 + J_2^2 + \lambda J_1 J_2 \cos(2\phi_1 - 2\phi_2) = E$. There is no chaotic behavior. (Based on Ref. 37.)

perturbation is turned on ($\lambda \neq 0$), the phase space becomes highly distorted. If we set $\phi_2 = \frac{3}{2}\pi$ (this means $q_2 = 0, p_2 > 0$) and substitute Eq. (6.138) into Eq. (6.136), we obtain the following equation for the perturbed level curves:

$$(3 + \lambda \cos 2\phi_1)J_1^2 - (5I + \lambda I \cos 2\phi_1)J_1 + I + I^2 - E = 0. \tag{6.141}$$

They are sketched in Fig. 6.7. Most of the phase space is only slightly distorted from the unperturbed case. However, there is a region which is highly distorted and in which two elliptic fixed points (surrounded by orbits) and two hyperbolic fixed points appear [4]. The fixed points occur for values of J_i and ϕ_i such that $\dot{J}_1 + \dot{J}_2 = (\dot{\phi}_1 - \dot{\phi}_2) = 0$. If we use the fact that $\dot{J}_i = -\partial H/\partial \phi_i$ and $\dot{\phi}_i = \partial H/\partial J_i$ and condition $\phi_2 = 3\pi/2$, we find that the hyperbolic orbits occur when

$$J_1 = \frac{(5-\lambda)}{(1-\lambda)} J_2 \quad \text{and} \quad (\phi_1 - \phi_2) = 0 \quad \text{and} \quad \pi, \tag{6.142}$$

while the elliptic orbits occur for

$$J_1 = \frac{(5+\lambda)}{(1+\lambda)} J_2, \qquad (\phi_1 - \phi_2) = \frac{\pi}{2} \quad \text{and} \quad \frac{3\pi}{2}. \tag{6.143}$$

The first-order resonance condition for this model [cf. Eq. (6.135)] is $2\omega_1 - 2\omega_2 = 0$ or, from Eqs. (6.139) and (6.140), $J_1 = 5J_2$. Therefore, from Eqs. (6.142) and (6.143) we see that the distorted region of phase space lies in the resonance zone.

In general, for a Hamiltonian of the form

$$H = H_0(J_1, J_2) + \lambda V(J_1, J_2)\cos(n_1\phi_1 + n_2\phi_2) \tag{6.144}$$

there will be no chaotic behavior because there is always an extra constant of motion,

$$I = n_2 J_1 - n_1 J_2. \tag{6.145}$$

However, when the Hamiltonian is of the more general form given in Eq. (6.127), the extra constant of motion is destroyed and the resonance zones become more complicated and begin to overlap. When this occurs one begins to see chaotic behavior.

Walker and Ford study the example

$$H = H_0(J_1, J_2) + \lambda_1 J_1 J_2 \cos(2\phi_1 - 2\phi_2) + \lambda_2 J_1 J_2^{3/2}\cos(2\phi_1 - 3\phi_2), \tag{6.146}$$

where an extra cosine term has been added to Eq. (6.136). For this model there is no longer an extra constant of motion. There are two primary resonances which grow as λ_1 and λ_2 are increased. In Fig. 6.8, we sketch their results. For low energies there is no chaotic behavior (to computer accuracy). However, as the resonance zones grow and begin to overlap, the trajectories in the regions of overlap become unstable and begin to exhibit chaotic behavior. In Fig. 6.8 the dots correspond to a single trajectory.

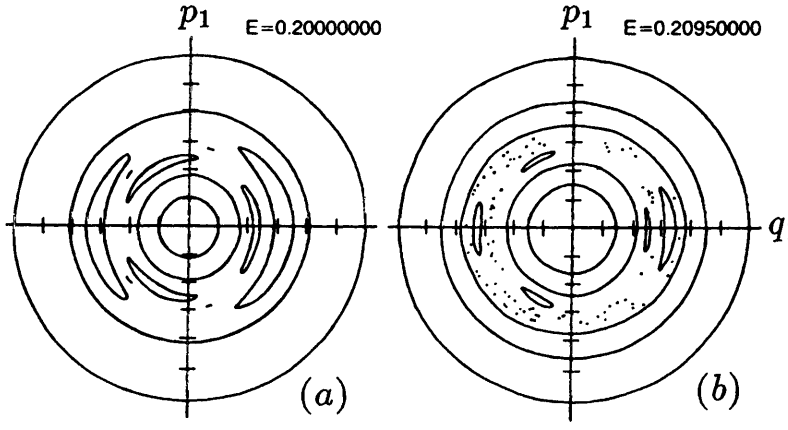


Fig. 6.8. Cross section of the energy surface for the Hamiltonian, $H = J_1 + J_2 - J_1^2 - 3J_1J_2 + J_2^2 + \lambda_1 J_1 J_2 \cos(2\phi_1 - 2\phi_2) + \lambda_2 J_1 J_2 \cos(2\phi_1 - 3\phi_2) = E$. (a) Phase space trajectories below the energy of primary resonance overlap. (b) Phase space trajectories above the energy of primary resonance overlap. When primary resonances overlap, large-scale chaos occurs in their neighborhood. (Based on Ref. 37.)

Thus, from these simple examples we see that the chaotic, or ergodiclike, behavior of phase space for the anharmonic oscillator system appears to be caused by the overlapping of resonances. If the energy surface is filled with resonance zones, as is often the case, then we expect chaotic behavior to set in at very low energy.

Anharmonic oscillator systems are a rather special type of system and their ergodicity has never been established, for obvious reasons. A completely different type of system is a system of hard spheres. For systems of hard spheres, ergodicity and mixing behavior have been established [39]. A proof that systems with Lennard-Jones types of potential are ergodic has never been given. However, when the number of degrees of freedom becomes large, the "regular" regions of the phase space appear to become relatively less important than the chaotic regions and statistical mechanics, which is built on the assumption that ergodicity appears to work perfectly for those systems.

The chaotic behavior illustrated in this section is indicative of unstable flow in phase space. Orbits in the chaotic region which initially neighbor one another move apart exponentially and may move to completely different parts of the energy surface. If we start with an ensemble of orbits in some region of phase space and assign a probability distribution to them, the probability distribution will spread on the energy surface, and we will become less certain about the actual state of the system. Systems with unstable flow have the potential of exhibiting decay to thermodynamic equilibrium: An initially localized probability distribution can spread and, in a coarse-grained sense, can fill the energy surface.

▶ S6.F. Newtonian Dynamics and Irreversibility [40, 41]

The instability and chaos that we have described in the baker map, Eq. (6.116), and that we have illustrated in the Henon–Heiles system appears to be a source of the irreversibility seen in nature. One of the great paradoxes of physics is the fact that Newton's equations are reversible, but much of nature evolves in an irreversible manner: Nature appears to have an "arrow of time." There is a new field of statistical physics which finally is resolving this paradox [40–44]. The resolution of the paradox is most easily seen in the spectral properties of chaotic maps such as the baker map. Individual trajectories in chaotic systems move apart exponentially and become impossible to compute even after a fairly short time. However, in such systems, smooth initial probability distributions generally relax to a smooth final distribution after some time. There are now several "reversible" chaotic maps for which a spectral decomposition can be obtained in terms of the decay rates and their associated eigenstates [28, 42, 43]. The decay rates are related to the Lyopounov exponents for the underlying chaos, and determine the physically observable decay properties of such

systems. The spectral theory of these systems can be formulated outside of Hilbert space.

Considerable progress has also been made in understanding the emergence of irreversible behavior in unstable Hamiltonian systems, at least for the case when the dynamical phase space contains dense sets of resonances. For such systems a spectral theory can also be formulated outside the Hilbert space [45–46]. We don't have space to say more about this beautiful new area of statistical physics, but the cited references should give interested readers a fairly readable entrance to the field. Ref. 41 gives a historial overview.

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PROBLEMS

Problem 6.1. Consider a system of N uncoupled harmonic oscillators with Hamiltonian, $H = \sum_{i=1}^{N}(p_i^2/2m_i + k_i q_i^2/2)$. Assume that the system initially has a probability density $\rho(\mathbf{p}^N, \mathbf{q}^N, 0) = \prod_{i=1}^{N} \delta(p_i - p_{i0})\delta(q_i - q_{i0})$. Compute the probability density $\rho(\mathbf{p}^N, \mathbf{q}^N, t)$ at time t, where $\mathbf{p}^N = (p_1, \ldots, p_N)$ and $\mathbf{q}^N = (q_1, \ldots, q_N)$.

Problem 6.2. Consider a particle which bounces vertically in a gravitational field, as discussed in Exercise 6.1. Assume an initial probability distribution, $\rho(p,z,0) = \frac{10}{9}\delta(z)\Theta(1.0-p)\Theta(p-0.1)$($\Theta(x)$ is the Heaviside function; $\Theta(x)=1$ for $x>0$ and $\Theta(x)=0$ for $x<0$). What is $\rho'(J,\theta,0)$? Sketch $\rho(p,z,t)$ and $\rho'(J,\theta,t)$ for $t=0.4$, mass $m=1$, and gravitational acceleration $g=1$.

Problem 6.3. Consider a particle with mass $m=1$ moving in an infinite square well potential, $V(x)=0$ for $-1<x<1$ and $V(x)=\infty$ otherwise. Assume that initially the particle lies at $x=-1$ with momentum, $p=p_0$ for $0.1\le p_0\le 1.0$ in the positive x direction. (a) Find the solution of the Liouville equation in action-angle space at time t. (b) At what time does the initial distribution of points begin to break apart in (p,x) space?

Problem 6.4. For a noninteracting gas of N particles in a cubic box of volume $V=L^3$, where L is the length of the side of box, find the solution, $\rho(\mathbf{p}^{3N},\mathbf{q}^{3N},t)$, of the Liouville equation at time t, where $\mathbf{p}^{3N}=(\mathbf{p}_1,\ldots,\mathbf{p}_N)$ and $\mathbf{q}^{3N}=(\mathbf{q}_1,\ldots,\mathbf{q}_N)$ with $\mathbf{p}_i=(p_{ix},p_{iy},p_{iz})$ and $\mathbf{q}_i=(q_{ix},q_{iy},q_{iz})$. Assume periodic boundary conditions, and assume that the probability density at time $t=0$ is given by

$$\rho(\mathbf{p}^{3N}\cdot\mathbf{q}^{3N},0)=\left(\frac{\sqrt{\pi}}{2L}\right)^{3N}\prod_{i=1}^{N}\prod_{\alpha=x,y,z}e^{-p_{i\alpha}^2}\sin\left(\frac{\pi q_{i\alpha}}{L}\right)\quad\text{for}\quad 0\le q_{i\alpha}\le L.$$

Problem 6.5. Consider a system with one degree of freedom whose dynamics is governed by a Hamiltonian of the form $H(p,q)=\frac{1}{2}p^2+\frac{1}{4}q^4=E$, where E is the total energy. Assume that initially $\rho(p,q,0)=(1/\sqrt{\pi})\delta(p)e^{-q^4}$. Solve the Liouville equation for $\rho(p,q,t)$. (*Hint*: It is useful to first transform to action-angle variables. The solution involves elliptic functions.)

Problem 6.6. A two-level system has a Hamiltonian matrix

$$\begin{pmatrix}H_{1,1}&H_{1,2}\\H_{2,1}&H_{2,2}\end{pmatrix}=\begin{pmatrix}3&4i\\-4i&-3\end{pmatrix},$$

where, for example, $H_{1,2}\equiv\langle 1|\hat{H}|2\rangle$. The density matrix at time $t=0$ is

$$\begin{pmatrix}\rho_{1,1}(0)&\rho_{1,2}(0)\\\rho_{2,1}(0)&\rho_{2,2}(0)\end{pmatrix}=\begin{pmatrix}1&0\\0&0\end{pmatrix}.$$

(a) Find the density matrix

$$\begin{pmatrix}\rho_{1,1}(t)&\rho_{1,2}(t)\\\rho_{2,1}(t)&\rho_{2,2}(t)\end{pmatrix}$$

at time t. (b) What is the probability to be in the state $|1\rangle$ at time $t=0$? At time t? For simplicity, assume that $\hbar=1$.

Problem 6.7. An atom with spin 1 has a Hamiltonian $\hat{H}=AS_z^2+B(\hat{S}_x^2-\hat{S}_y^2)$, where $\hat{S}_x$, $\hat{S}_y$, and $\hat{S}_z$ are the x, y, and z components of the spin angular momentum operator. In the basis of eigenstates of the operator, $\hat{S}_z$, these three operators have the matrix representations

$$\hat{S}_z=\hbar\begin{pmatrix}1&0&0\\0&0&0\\0&0&-1\end{pmatrix},\quad \hat{S}_x=\frac{\hbar}{\sqrt{2}}\begin{pmatrix}0&1&0\\1&0&1\\0&1&0\end{pmatrix},\quad\text{and}\quad \hat{S}_y=\frac{\hbar}{i\sqrt{2}}\begin{pmatrix}0&1&0\\-1&0&1\\0&-1&0\end{pmatrix}.$$

(a) Write the density matrix (in the basis of eigenstates of $\hat{S}_z$) at time $t = 0$ for two different cases: (i) The atom is initially in an eigenstate of $\hat{S}_z$ with eigenvalue $+\hbar$; (ii) the atom is initially in an eigenstate of $\hat{S}_x$ with eigenvalue $+\hbar$. (b) Compute the density matrix (in the basis of eigenstates of $\hat{S}_z$) at time t for each of the two cases in (a). (c) Compute the average z component of spin at time t for the two cases in (a).

Problem 6.8. Consider a harmonic oscillator with Hamiltonian $\hat{H} = (1/2m)\hat{p}^2 + \frac{1}{2}m\omega^2\hat{x}^2$. Assume that at time $t = 0$ the oscillator is in an eigenstate of the momentum operator, $\hat{\rho}(0) = |p_0\rangle\langle p_0|$. (a) Write the Liouville equation in the momentum basis. (b) Compute the density matrix $\langle p'|\hat{\rho}(t))|p\rangle$, at time t.

Problem S6.1. Locate all period-3 points of the Baker map in the (p, q) plane.

PART THREE

EQUILIBRIUM STATISTICAL MECHANICS

7

EQUILIBRIUM STATISTICAL MECHANICS

7.A. INTRODUCTION

Most systems in nature, if they are isolated (i.e., do not exchange energy or matter with the outside world), will tend to a time-independent state (thermodynamic equilibrium) whose macroscopic properties may be described in terms of only a few state variables. For such stationary states the entropy is a maximum and the energy is fixed. However, even though the energy is fixed, the system could exist in any one of a number of different microscopic states consistent with that energy. If we only know the total energy, we have no way of distinguishing one microscopic state from another, nor do we have a way of assigning probability to those various microstates. As we have seen in Chapter 6, for the special case of ergodic systems, we can assign a probability to various microscopic states based on the mechanical properties of the system. If a system is ergodic, it is equally probable to find the state of the system in different regions of the energy surface if those regions are equal in size. This leads naturally to the following probability distribution on the energy surface:

$$\rho(\mathbf{X}^N, E) = \begin{cases} \dfrac{1}{\Sigma(E)} & \text{for } H(\mathbf{X}^n) = E, \\ 0 & \text{otherwise,} \end{cases} \tag{7.1}$$

where $\sum(E)$ is the area of the energy surface (the structure function). This choice of probability density for an isolated system forms the foundation upon which statistical mechanics is built.

Once the distribution function is given, it is a straightforward matter to compute the expectation values of various quantities, such as energy, magnetization, and so on. However, there is one quantity which still eludes us, and that is the entropy. We know that the entropy must be additive and positive and must have a maximum value at equilibrium. An entropy of the form $S = \int d\mathbf{X}^N [\rho(\mathbf{X}^N)]^{2n} C_N$, where n is some positive integer and C_N is a constant, is one type that could be used. However, the form that we shall use in

this book is the *Gibbs entropy*

$$S = -k_B \int d\mathbf{X}^N \rho(\mathbf{X}^N) \ln[C_N \rho(\mathbf{X}^N)], \tag{7.2}$$

where $k_B = 1.38 \times 10^{-23}$ J/K is the Boltzmann constant. The constant, C_N, is inserted to give the correct units, but also has important physical meaning. It is determined from quantum mechanics. The form of entropy in Eq. (7.2) was chosen by Gibbs [1] because it gives the correct expression for the temperature of systems which are closed but not isolated. For quantum systems, the Gibbs entropy can be written

$$S = -k_B Tr[\hat{\rho} \ln(\hat{\rho})], \tag{7.3}$$

where $\hat{\rho}$ is the density operator and the trace is taken over any complete orthonormal set of basis states.

As we have seen in Chapter 2, we must have the ability to describe the behavior of systems under a variety of external constraints. *Closed isolated systems* have fixed total energy and fixed particle number. *Closed systems* have fixed particle number but varying energy so that only the average energy is specified. *Open systems* can have varying particle number and energy. A closed isolated system has an equilibrium probability density (the microcanonical ensemble) of the form given in Eq. (7.1). However, the probability densities for closed and open systems (the canonical and grand canonical ensembles, respectively) will be determined below. Once the equilibrium probability density for a system is known, the problem of computing thermodynamic quantities is straightforward.

In this chapter we have selected a variety of fairly simple examples to illustrate how the equilibrium probability densities can be applied to real systems. We have selected the examples for their historical and practical importance or because they illustrate important concepts that we shall need later. The models and systems we will study in this chapter are all exactly soluble. In subsequent chapters, we will introduce a variety of approximation schemes for systems which cannot be solved exactly.

This chapter is divided more or less into three sections. We begin by deriving the thermodynamic properties of two closed isolated systems (fixed energy and particle number), namely, an ideal gas and an Einstein solid using the microcanonical ensemble. Following a method due to Einstein, we can also use the microcanonical ensemble to derive a probability distribution for fluctuations of thermodynamic quantities about the equilibrium state. The Einstein method is based on a Taylor series expansion of the entropy about absolute equilibrium, and therefore it breaks down near the critical point where fluctuations can become very large. However, it still gives us valuable insight concerning the behavior of fluctuations near a critical point. In this chapter we will apply Einstein fluctuation theory to fluid systems.

We next consider closed systems in which the temperature and particle

number is fixed but the energy can fluctuate. Such systems are described by the canonical ensemble. As examples of closed systems, we consider in some detail the effect of lattice vibrations on the thermodynamic properties of solids. We also compute the thermodynamic properties of an Ising spin lattice. We can obtain exact expressions for the thermodynamic properties of one-dimensional spin lattices, and we use a mean field model to obtain approximate expressions for the thermodynamic properties of higher-dimensional spin lattices. Mean field theory predicts that a phase transition from a disordered state to an ordered state occurs on the spin lattice.

Finally we consider open systems in which both the energy and particle number can fluctuate but the temperature and chemical potential are fixed. Such systems are described by the grand canonical ensemble. The grand canonical ensemble is especially suitable for describing systems in which phase transitions occur which break gauge symmetry because particle number need not be conserved. We will use the grand canonical ensemble to compute the thermodynamic properties of ideal quantum gases, both Bose–Einstein and Fermi–Dirac.

An ideal Bose–Einstein gas is composed of identical bosons and at very low temperatures can exhibit a phase transition (even though the particles do not interact) in which a macroscopic number of particles condense into a single momentum state merely because of Bose–Einstein statistics. An ideal Fermi–Dirac gas on the other hand does not exhibit a phase transition but, because of the Pauli exclusion principle, has interesting behavior of its own. No two fermions can have the same set of quantum numbers. Therefore, at low temperature the fermions begin to fill all the low energy momentum states and even at $T = 0$ K some particles can have a very large momentum. Thus a Fermi gas, even at $T = 0$ K, will have a large pressure.

For an ideal Fermi gas, there is no condensation into a single momentum state. However, if we allow an attraction between fermions, then they can form bound pairs which can condense in momentum space. This is what happens to electrons in a superconductor. In a superconducting solid, electrons interact with lattice phonons and with one another through a phonon-mediated interaction which is attractive in the neighborhood of the Fermi surface. The fermion pairs condense in momentum space and act coherently, thus giving rise to the unusual superconducting properties observed in such systems.

7.B. THE MICROCANONICAL ENSEMBLE [1–3]

For an ergodic mechanical system with fixed particle number (closed) and fixed energy (isolated), all states on the energy surface are equally probable. This fact forms the basis upon which equilibrium statistical mechanics is built and is the origin of the microcanonical ensemble. As we shall now show, this distribution extremizes the Gibbs entropy and therefore allows us to make contact with thermodynamics. Let us first consider a quantum system. As we saw in Chapter 6, the equilibrium probability density, in order to be a stationary state, must be a

function of the Hamiltonian, $\hat{\rho} = \hat{\rho}(\hat{H})$. Let $|E, n\rangle$ denote a set of states of energy E with respect to which the density operator is diagonal. The integer, n, takes values $n = 1, \ldots, N(E)$, where $N(E)$is the total number of states with energy E. The probability to find the system in state $|E, n\rangle$ is $P_n = \langle E, n|\hat{\rho}|E, n\rangle$, and the entropy can be written

$$S = -k_B \operatorname{Tr}[\hat{\rho} \ln(\hat{\rho})] = -k_B \sum_{n=1}^{N(E)} P_n \ln(P_n). \tag{7.4}$$

We must determine the set of probabilities, $\{P_n\}$, which extremize the entropy subject to the constraint, $\operatorname{Tr}(\hat{\rho}) = \sum_{n=1}^{N(E)} P_n = 1$. The simplest way to do this is to use Lagrange multipliers. Since we have one constraint, we need one Lagrange multiplier, which we call α_0. We then require the following variation to be zero:

$$\delta\left[\sum_{n=1}^{N(E)} (\alpha_0 P_n - k_B P_n \ln(P_n))\right] = \sum_{n=1}^{N(E)} (\alpha_0 - k_B - k_B \ln(P_n))\delta P_n = 0. \tag{7.5}$$

Since the variation, δP_n, is arbitrary we must have $\alpha_0 - k_B - k_B \ln(P_n) = 0$ or

$$P_n = e^{1-\alpha_0/k_B} = \text{constant}. \tag{7.6}$$

The Lagrange multiplier, α_0, is determined by the normalization condition, $\operatorname{Tr}(\hat{\rho}) = \sum_{n=1}^{N(E)} P_n = 1$. We find that the probability, P_n, is given by

$$P_n = \frac{1}{N(E)}. \tag{7.7}$$

Thus, the probability distribution which extremizes the Gibbs entropy is the one for which all states of the same energy are equally probable. This is called the *microcanonical ensemble*. If we substitute Eq. (7.7) into (7.4), we find that the entropy is given by

$$S = k_B \ln(N(E)). \tag{7.8}$$

The entropy is proportional to the logarithm of the number of states with energy E.

If we are given a thermodynamic system with a fixed mechanical energy E and if we know the number of microscopic states with energy E, then we can use Eq. (7.8) to compute the thermodynamic properties of the system. The internal energy of the system is just U=E. Therefore, the temperature can be found from the thermodynamic relation $(\partial S/\partial E)_{N,X} = 1/T$. The generalized force is $Y = (\partial E/\partial X)_{N,S}$. The chemical potential is $\mu' = (\partial E/\partial N)_{S,X}$. As an illustration, in Exercise 7.1, we compute the thermodynamic properties of an Einstein solid.

■ **EXERCISE 7.1.** An Einstein solid consists of a lattice in three-dimensional space with N lattice sites. Each lattice site contains three harmonic oscillators (one for each direction in space), each of which has frequency ω. Neither the lattice sites nor the harmonic oscillators are coupled to one another. The total energy of the lattice is $H = \hbar\omega \sum_{i=1}^{3N} n_i + \frac{3}{2}N\hbar\omega = E$, where n_i is the number of quanta of energy on the ith harmonic oscillator. The total number of quanta on the lattice is fixed at $M = \sum_{i=1}^{3N} n_i$. Assume that M and N are very large. (a) What is the total number of microscopic states with energy E? (b) Compute the entropy as a function of temperature, T, and number of lattice sites, N. (c) Compute the heat capacity of this solid.

Answer: Because the harmonic oscillators are spatially separated on different lattice sites and at a given lattice site are associated with different spatial directions, they are distinguishable. The quanta are indistinguishable.

(**a**) The number of ways to assign M identical quanta to $3N$ distinguishable oscillators is

$$\text{Number of states with energy } E = \frac{(3N + M - 1)!}{M!(3N - 1)!}. \tag{1}$$

An easy way to see this is to imagine M white dots and $3N - 1$ black dots mixed together on a line. The M white dots represent quanta. The $3N - 1$ black dots represent the boundaries between $3N$ "pots" (harmonic oscillators) which hold the quanta. The total number of different states is simply the number of different permutations of the black and white dots.

(**b**) The entropy is

$$S = k_B \ln\left(\frac{(3N + M - 1)!}{M!(3N - 1)!}\right). \tag{2}$$

For M and N large we can simplify this since by *Stirlings formula*, $\ln(N!) \approx N \ln(N) - N$. Using this formula we find

$$S = k_B \ln\left(\frac{\left(1 + \dfrac{M}{3N}\right)^{M+3N}}{(M/3N)^M}\right). \tag{3}$$

Now note that $1/T = (\partial S/\partial E)_N = (1/\hbar\omega)(\partial S/\partial M)_N$ and

$$\left(\frac{\partial S}{\partial M}\right)_N = \frac{\hbar\omega}{T} = k_B \ln\left(\frac{3N}{M} + 1\right). \tag{4}$$

Solving for M, we find

$$M = \frac{3N}{e^{\beta\hbar\omega} - 1}, \tag{5}$$

where $\beta = 1/k_B T$. The entropy is

$$S = 3Nk_B \ln(1 - e^{-\beta\hbar\omega}) + \frac{3Nk_B \beta\hbar\omega e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}. \tag{6}$$

The internal energy is

$$U = E = \frac{3N\hbar\omega e^{-\beta\hbar\omega}}{(1 - e^{\beta\hbar\omega})} + \frac{3}{2} N\hbar\omega. \tag{7}$$

The heat capacity is

$$C_N = \frac{3N\hbar^2\omega^2}{k_B T^2} \frac{e^{-\beta\hbar\omega}}{(1 - e^{-\beta\hbar\omega})^2}. \tag{8}$$

It is useful to perform a similar calculation for a classical system. Let us consider a closed isolated system with a configuration space volume, V, and a fixed number of particles, N, which is constrained to the energy shell, $E \to E + \Delta E$. We now consider an energy shell rather than just the energy surface because it simplifies calculations without changing the physics. We can make ΔE as small as we like. The volume of the energy shell is $\Omega_{\Delta E}(E, V, N) = \sum(E, V, N)\Delta E$,where $\sum(E, V, N)$ is the structure function, Eq. (6.41) (the area of the energy surface). To obtain the equilibrium probability density we must find an extremum of the Gibbs entropy subject to the normalization condition

$$\int_{E<H(\mathbf{E})<E+\Delta E} d\mathbf{X}^N \rho(\mathbf{X}^N) = 1, \tag{7.9}$$

where the integration is restricted to the energy shell. We again use the method of Lagrange multipliers and write

$$\begin{aligned} &\delta\left[\int_{E<H(\mathbf{E})<E+\Delta E} d\mathbf{X}^N(\alpha_0\rho(\mathbf{X}^N) - k_B\rho(\mathbf{X}^N) \ln[C_N\rho(\mathbf{X}^N)])\right] \\ &\quad = \int_{E<H(\mathbf{E})<E+\Delta E} d\mathbf{X}^N(\alpha_0 - k_B - k_B \ln[C_N\rho(\mathbf{X}^N)])\delta\rho(\mathbf{X}^N) = 0. \end{aligned} \tag{7.10}$$

Since $\delta\rho(\mathbf{X}^N)$ is arbitrary, we must have $\rho(\mathbf{X}^N) = C_N^{-1} e^{\alpha_0/k_B - 1} = \text{constant}$. The Lagrange multiplier, α_0, is determined from the normalization condition,

Eq. (7.9). We find

$$\rho(\mathbf{X}^N) = \begin{cases} \dfrac{1}{\Omega_{\Delta E}(E,V,N)} & \text{for } E < H(\mathbf{E}) < E + \Delta E, \\ 0 & \text{otherwise.} \end{cases} \tag{7.11}$$

If we substitute Eq. (7.11) into Eq. (7.2) for the entropy, we find

$$S = k_B \ln\left(\frac{\Omega_{\Delta E}(E,V,N)}{C_N}\right). \tag{7.12}$$

Comparison with Eq. (7.8) shows that $\Omega_{\Delta E}(E,V,N)/C_N$ is just the number of states in the energy shell, $E \to E + \Delta E$. The constant, C_N, can be determined from quantum mechanics. The volume of a single quantum state in a $6N$-dimensional phase space is h^{3N}, where h 6.63×10^{-34} J·S is Planck's constant. Therefore, the constant, C_N, is chosen as follows. For distinguishable particles, $C_N = h^{3N}$ so $\Omega_{\Delta E}/C_N$ is just the number of quantum states confined to the energy surface. For indistinguishable particles, $C_N = N!h^{3N}$. The factor of $N!$ is included to avoid overcounting of states when the particles are indistinguishable. It is purely quantum mechanical in origin and cannot be justified classically except that it solves Gibb's paradox. In Section 7.D, we shall show exactly where it comes from.

In practice, when computing the thermodynamic properties of a system of energy E, it is easiest to work with the total volume of phase space, $\Omega(E,V,N)$, enclosed by the energy surface, rather than the volume of the energy shell. In the *thermodynamic limit* (the limit $N \to \infty$ and $V \to \infty$ such that $N/V =$ constant), both quantities give the same entropy. To see this, let us divide the volume enclosed by the surface of energy E into $E/\Delta E$ shells each of width ΔE. These shells will range in energy from 0 to E. Shells with low energy will have a smaller volume than shells with higher energy. The total volume can be written as a sum of the volumes of all the shells.

$$\Omega(E,V,N) = \sum_{i=1}^{E/\Delta E} \Omega_{\Delta E}(E_i,V,N). \tag{7.13}$$

The shell with the largest volume will be that with energy $E \to E + \Delta E$. Thus, we can write

$$\Omega_{\Delta E}(E,V,N) \leqslant \Omega(E,V,N) \leqslant \frac{E}{\Delta E}\Omega_{\Delta E}(E,V,N). \tag{7.14}$$

If we take the logarithm of each term in Eq. (7.14), we find

$$\ln(\Omega_{\Delta E}) \leqslant \ln(\Omega) \leqslant \ln(\Omega_{\Delta E}) - \ln\left(\frac{\Delta E}{E}\right). \tag{7.15}$$

But $\ln(\Omega) \sim N$ and $\ln(E/\Delta E) \sim \ln(N)$. Therefore, in the limit $N \to \infty$, $\ln(\Omega) = \ln(\Omega_{\Delta E})$, because we can neglect terms of order $\ln(N)$ relative to terms of order N. Thus, in the thermodynamic limit the entropy can be written

$$S = k_B \ln\left(\frac{\Omega(E,V,N)}{C_N}\right), \tag{7.16}$$

where $C_N = h^{3N}$ for distinguishable particles and $C_N = N!h^{3N}$ for indistinguishable particles. In Exercise 7.2, we compute the thermodynamic properties of an ideal classical gas using Eq. (7.16) and the phase space volume, $\Omega(E,V,N)$, computed in Exercise 6.2.

■ **EXERCISE 7.2.** Use the microcanonical ensemble to find the entropy and equation of state of an ideal gas of N identical particles of mass m confined to a box of volume V. Assume that N and V are very large.

Answer: From Exercise 6.2, the volume of phase space with energy less than E is

$$\Omega(E) = \frac{V^N(2\pi mE)^{3N/2}}{\Gamma(3N/2+1)}. \tag{1}$$

For very large N and V, the entropy is given by

$$S = k_B \ln\left(\frac{\Omega(E)}{N!h^{3N}}\right) = k_B \ln\left(\frac{V^N(2\pi mE)^{3N/2}}{N!h^{3N}\Gamma(3N/2+1)}\right). \tag{2}$$

Let us note that for large N, we have $\ln(N!) \approx N\ln(N) - N$ and $\Gamma(3N/2+1) = (3N/2)! \approx (3N/2e)^{3N/2}$. We can rewrite the entropy in the form

$$\begin{aligned} S &= \frac{3Nk_B}{2} + Nk_B \ln\left[V\left(\frac{4\pi mE}{3h^2N}\right)^{3/2}\right] + Nk_B - Nk_B \ln(N) \\ &= \frac{5Nk_B}{2} + Nk_B \ln\left[\frac{V}{N}\left(\frac{4\pi mE}{3h^2N}\right)^{3/2}\right]. \end{aligned} \tag{3}$$

In the middle term we have explicitly separated off the contribution $(+Nk_B - Nk_B\ln(N))$ coming from the Gibbs counting factor. We see that without it, the entropy is not a homogeneous function. In the last term, the Gibbs counting factor is combined into the rest of the terms, and we see that the entropy is just the expected Sackur–Tetrode entropy and is a homogeneous function of the extensive variables.

If we remember that the internal energy, U, equals E, then Eq. (3) is the fundamental equation for the entropy. The pressure is given by

$P = -(\partial U/\partial V)_{S,N}$. If we take the derivative of Eq. (3) with respect to V holding S and N fixed, we obtain an equation for $P = -(\partial U/\partial V)_{S,N}$ which we can solve to give $P = 2U/3V$. Next note that $T = (\partial U/\partial S)_{V,N}$. If we take the derivative of U with respect to S holding V and N fixed, we obtain an equation for $(\partial U/\partial S)_{V,N}$ which we can solve to yield $U = \frac{3}{2}Nk_BT$. If we combine these two results, we obtain the ideal gas equation of state $PV = Nk_BT$.

7.C. EINSTEIN FLUCTUATION THEORY [4, 5]

There is a very simple method due to Einstein [5] for obtaining the probability distribution for fluctuations about the equilibrium state. This theory uses the microcanonical ensemble. We first derive the general formalism and then apply it to thermodynamic systems

7.C.1. General Discussion

Let us consider a closed adiabatically isolated system with energy in the range $E \rightarrow E + \Delta E$. We shall assume that the system is ergodic so that all possible microscopic states of the system are equally probable. Let $\Gamma(E)$ denote the number of microscopic states with energy $E \rightarrow E + \Delta E$. Then the entropy of the system is given by

$$S = k_B \ln[\Gamma(E)]. \tag{7.17}$$

Often it is useful to have a more detailed microscopic description of the system than that given by Eq. (7.17). For example, we might want to subdivide a system into cells and to specify its state according the thermodynamic behavior of each cell (each cell would be an open system). We can do this if we assume that, in addition to the energy, the macroscopic state of the system is describable in terms of n independent macroscopically measurable parameters (state variables) $A_i (i = 1, 2, \ldots, n)$, where A_i could denote quantities such as energy, pressure, temperature, and so on of the ith cell.

Let $\Gamma(E, A_1, \ldots, A_n)$ denote the number of microstates with energy E and parameters $A_1, \ldots, A_n$. Then the probability that the system is in a macroscopic state described by parameters $E, A_1, \ldots, A_n$, is given by

$$P(E, A_1, \ldots, A_n) = \frac{\Gamma(E, A_1 \ldots, A_n)}{\Gamma(E)}. \tag{7.18}$$

The entropy of the system in a state with parameters $(E, A_1, \ldots, A_n)$ is given by

$$S(E, A_1, \ldots, A_n) = k_B \ln[\Gamma(E, A_1, \ldots, A_n)]. \tag{7.19}$$

Hence

$$P(E, A_1, \ldots, A_n) = \frac{1}{\Gamma(E)} \exp\left[\frac{1}{k_B} S(E, A_1, \ldots, A_n)\right]. \tag{7.20}$$

The entropy will be a maximum when the system is in an equilibrium sate, $A_1^0, \ldots, A_n^0$. Any fluctuation about the equilibrium state must cause the entropy to decrease. If we let α_i denote the fluctuations

$$\alpha_i = A_i - A_i^0, \tag{7.21}$$

then we can expand the entropy about its equilibrium value to obtain

$$S(E, A_1, \ldots, A_n) = S(E, A_1^0, \ldots, A_n^0) - \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n} g_{ij}\,\alpha_i\,\alpha_j + \cdots, \tag{7.22}$$

where

$$g_{ij} \equiv -\left(\frac{\partial^2 S}{\partial A_i \partial A_j}\right)_{A_i = A_i^0;\, A_j = A_j^0} \tag{7.23}$$

Einstein fluctuation theory is based on the assumption that fluctuations about the equilibrium state are small. Therefore, we can terminate the expansion of the entropy at second order. This approximation is not good near a phase transition where fluctuations can become very large. The matrix g_{ij} is positive definite since the entropy must decrease and is symmetric since the quantities, A_i, are state variables. (A matrix is positive definite if every principal minor is positive.) Equation (7.22) contains no terms which are first order in A_i to ensure that spontaneous fluctuations about the equilibrium do not cause a decrease in the entropy. Equilibrium is a state of maximum entropy.

We can now substitute Eq. (7.22) into Eq. (7.20) and obtain the following expression for the probability distribution of fluctuations about the equilibrium state (cf. Exercise 4.9):

$$\begin{aligned} P(\boldsymbol{\alpha}) &= \sqrt{\frac{\det|\bar{\mathbf{g}}|}{(2\pi k_B)^n}} \exp\left[-\frac{1}{2k_B}\boldsymbol{\alpha}^T \cdot \bar{\mathbf{g}} \cdot \boldsymbol{\alpha}\right] \\ &= \sqrt{\frac{\det|\bar{\mathbf{g}}|}{(2\pi k_B)^n}} \exp\left[-\frac{1}{2k_B}\sum_{i=1}^{n}\sum_{j=1}^{n} g_{ij}\alpha_i\alpha_j\right]. \end{aligned} \tag{7.24}$$

The vector $\boldsymbol{\alpha}^T$ is the row vector $\boldsymbol{\alpha}^T = (\alpha_1, \ldots, \alpha_n)$ and is the transpose of the column vector $\boldsymbol{\alpha}$. The quantity g_{ij} is the ijth element of the $n \times n$ matrix, $\bar{\mathbf{g}}$. The quantity $\det|\bar{\mathbf{g}}|$ is the determinant of the matrix $\bar{\mathbf{g}}$. The probability $P(\boldsymbol{\alpha})$ is

normalized to one:

$$\int_{-\infty}^{\infty} D\boldsymbol{\alpha} P(\boldsymbol{\alpha}) \equiv \int_{-\infty}^{\infty} d\alpha_1 \times \cdots \times \int_{-\infty}^{\infty} d\alpha_n P(\boldsymbol{\alpha}) = 1 \tag{7.25}$$

Since only small fluctuations are assumed to be probable, there is no difficulty in extending the limits of integration in Eq. (7.25) from $-\infty$ to $+\infty$.

We often want to find expectation values of various moments of the fluctuations. To do this, it is convenient to introduce a more general integral,

$$I(\mathbf{h}) \equiv \sqrt{\frac{\det|\bar{\mathbf{g}}|}{(2\pi k_B)^n}} \int_{-\infty}^{\infty} D\overline{\alpha} \exp\left[-\frac{1}{2k_B}\boldsymbol{\alpha}^T \cdot \bar{\mathbf{g}} \cdot \boldsymbol{\alpha} + \mathbf{h}^T \cdot \boldsymbol{\alpha}\right] = e^{\frac{1}{2}k_B \mathbf{h}^T \cdot \bar{\mathbf{g}}^{-1} \cdot \mathbf{h}}, \tag{7.26}$$

where $I(\mathbf{h})$ is a characteristic function (cf. Exercise 4.9). The moment, $\langle \alpha_i \alpha_j \rangle$, is defined as

$$\langle \alpha_i \alpha_j \rangle = \lim_{\mathbf{h}\to 0} \left(\frac{\partial^2}{\partial h_i \partial h_j} I(\mathbf{h}) \right) = k_B (\bar{\mathbf{g}}^{-1})_{ij}. \tag{7.27}$$

Since the probability density, $P(\boldsymbol{\alpha})$, is a multivariant Gaussian with zero mean, the first moment, $\langle \alpha_i \rangle = 0$, and all higher moments can be expressed in terms of the moments $\langle \alpha_i^2 \rangle$ and $\langle \alpha_i \alpha_j \rangle$ (cf. Exercise 4.9).

7.C.2. Fluid Systems

Let us consider a closed isolated box with volume, V_T, which contains a fluid with total entropy, S_T, total energy, E_T, and total number of particles, N_T, and total mass, M_T. We shall assume that the box is divided into ν cells of equal size and that at equilibrium the volume, entropy, internal energy, and mass of particles in the ith cell are $V_i = V_0, S_i, U_i$, and M_i, respectively (cf. Fig. 7.1). The total volume of the box is then $V_T = \nu V_0$. The equilibrium pressure, temperature, and chemical potential of the whole system are denoted P_0, T_0, and $\tilde{\mu}_0$, respectively.

From Eq. (2.171), the entropy change due to deviations in various thermodynamic quantities from their equilibrium state will be given by

$$\Delta S_T = \frac{1}{2T_0} \sum_{i=1}^{\nu} [-\Delta T_i \Delta S_i + \Delta P_i \Delta V_i - \Delta \tilde{\mu}_i \Delta M_i]. \tag{7.28}$$

If we now use the expressions obtained in Section 7.C.1, we can write an expression for the probability of a given set of fluctuations. To obtain an explicit expression, we must choose a particular set of independent variables.

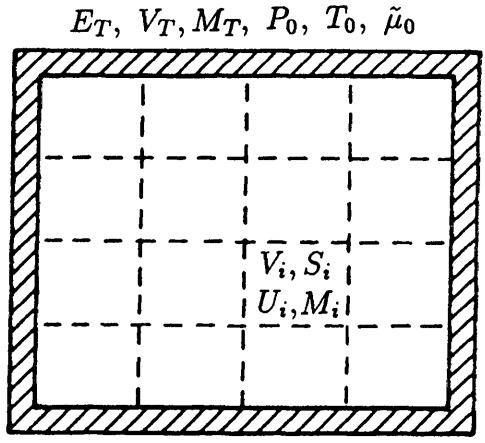


Fig. 7.1. A system with fixed total energy, E_T, total volume, V_T, total mass, M_T, equilibrium pressure, P_0, equilibrium temperature, T_0, and equilibrium chemical potential, $\tilde{\mu}_0$. To describe local fluctuations about absolute equilibrium, we divide the system into cells. Cell i has volume, entropy, internal energy, and mass given by $V_i = V_0, S_i, U_i$, and M_i, respectively.

Schematically, we can write the probability as

$$P(\Delta S_T) = \sqrt{\frac{\det|\mathbf{g}|}{(2\pi k_B)^{3\nu}}} \exp\left[-\frac{1}{2k_B T_0}\sum_{i=1}^{\nu}\left[\Delta T_i \Delta S_i - \Delta P_i \Delta V_i + \Delta\tilde{\mu}_i \Delta M_i\right]\right]. \tag{7.29}$$

where the matrix $\mathbf{g}$ is determined once the independent variables are decided upon.

Let us first pull the volume dependence out of Eq. (7.28). We will write $S = Vs$ and $M = V\rho$, where s is entropy/volume and ρ is mass/volume. Let us next note that the Gibbs–Duhem equation, when written in terms of mass density, ρ, takes the form $\rho d\tilde{\mu} = -sdT + dP$. Therefore, $\Delta T\Delta S - \Delta P\Delta V + \Delta\tilde{\mu}\Delta M = V(\Delta T\Delta s + \Delta\tilde{\mu}\Delta\rho)$. The differential of the Helmholtz free energy/volume, a, satisfies the equation $da = -sdT + \tilde{\mu}d\rho$, so $(\partial\tilde{\mu}/\partial T)_\rho = -(\partial s/\partial\rho)_T$. If we now choose temperature, T, and mass density, ρ, as independent variables, we find

$$\Delta T\Delta S - \Delta P\Delta V + \Delta\tilde{\mu}\Delta M = V\left[\frac{c_\rho}{T}(\Delta T)^2 + \left(\frac{\partial\tilde{\mu}}{\partial\rho}\right)_T(\Delta\rho)^2\right], \tag{7.30}$$

where c_ρ is the equilibrium specific heat. The row vector, $\boldsymbol{\alpha}^T$, can be written

$\boldsymbol{\alpha} = (Y_\varsigma, \ldots, Y_\nu, \rho_\varsigma, \ldots, \rho_\nu)$ and the matrix, $\mathbf{g}$, has matrix elements

$$g_{ij} = \begin{cases} \dfrac{Vc_\rho}{T^2} & \text{if } i = j \text{ and } 1 \leqslant i \leqslant \nu; \\ \dfrac{V}{T}\left(\dfrac{\partial \tilde{\mu}}{\partial \rho}\right)_T & \text{if } i = j \text{ and } \nu + 1 \leqslant i \leqslant 2\nu; \\ 0 & \text{otherwise.} \end{cases} \tag{7.31}$$

The probability of a fluctuation, $\boldsymbol{\alpha}^T = (\Delta T_1, \ldots, \Delta T_\nu, \Delta\rho_1, \ldots, \Delta\rho_\nu)$, is therefore

$$P(\{\Delta T_i, \Delta\rho_i\}) = \sqrt{\frac{\left(\frac{Vc_\rho}{T^2}\right)^\nu \left(\frac{V}{T}\left(\frac{\partial\tilde{\mu}}{\partial\rho}\right)_T\right)^\nu}{(2\pi k_B)^{2\nu}}} \times \exp\left[-\frac{1}{2k_B}\sum_{i=1}^{\nu}\left[\frac{Vc_\rho}{T^2}(\Delta T_i)^2 + \frac{V}{T}\left(\frac{\partial\tilde{\mu}}{\partial\rho}\right)_T(\Delta\rho_i)^2\right]\right]. \tag{7.32}$$

We can now obtain expressions for variances and for correlations between fluctuations in various cells. It is easy to see that

$$\langle \Delta\rho_j \Delta T_k \rangle = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} d(\Delta\rho_1) \ldots d(\Delta\rho_\nu) d(\Delta T_1) \ldots d(\Delta T_\nu) \times P(\{\Delta T_i, \Delta\rho_i\})\, \Delta\rho_j\, \Delta T_k = 0, \tag{7.33}$$

$$\langle (\Delta\rho_j)^2 \rangle = \frac{T}{V}\left(\frac{\partial\tilde{\mu}}{\partial\rho}\right)_T^{-1}, \tag{7.34}$$

$$\langle (\Delta T_j)^2 \rangle = \frac{T^2 k_B}{Vc_\rho}, \tag{7.35}$$

and

$$\langle \Delta\rho_j \rangle = \langle \Delta T_j \rangle = 0. \tag{7.36}$$

Thus, we have found that fluctuations in temperature and density are statistically independent. One can also show that pressure and entropy fluctuations are statistically independent. However, fluctuations in most other pairs of thermodynamic variables are not independent.

It is important to note that in Eq. (7.33) we found no correlation between various cells. This result was built into the theory because Eq. (7.33) contains no information about coupling between cells. In real systems, there is coupling between cells. This can be included in the theory by expressing ΔS_i and ΔP_i in

terms of temperature and volume variations in other cells and not just those of cell i. The more general expression will then contain coupling constants which reflect the strength of the coupling between the cells.

In this section, we have analyzed fluid systems by dividing them into discrete cells. This, of course, is a rather artificial way to proceed, but it is conceptually very simple and gives us good intuition about what thermodynamic quantities govern the behavior of fluctuations about the equilibrium state. It is a simple matter to change the summations over discrete cells to integrations over continuously varying densities, provided that the spatial variations have sufficiently long wavelengths (vary slow enough). We shall look at the spatial dependence of fluctuations in later chapters.

7.D. THE CANONICAL ENSEMBLE

A closed system can exchange heat with its surroundings and as a consequence will have a fluctuating total energy. We therefore need to find a probability density which corresponds to an extremum of the entropy closed systems. This probability distribution is the basis of the canonical ensemble. In Section 7.D.1 we derive the probability density operator for a closed equilibrium system, and in Sections 7.D.2 and 7.D.3 we show how to compute thermodynamic properties for systems of indistinguishable particles and for systems of distinguishable particles, respectively.

7.D.1. Probability Density Operator

In order to obtain the probability density operator for a closed system we must extremize the Gibbs entropy subject to two constraints. We require that the probability density operator, $\hat{\rho}$, be normalized.

$$\mathrm{Tr}_N(\hat{\rho}) = 1, \tag{7.37}$$

and we require that the average energy be fixed to some value $\langle E \rangle$,

$$\mathrm{Tr}_N(\hat{H}_N\hat{\rho}) = \langle E \rangle. \tag{7.38}$$

If we introduce the Lagrange multipliers, α_0 and α_E, we can find the probability density operator, $\hat{\rho}$, which extremizes the entropy subject to the constraints, Eqs. (7.37) and (7.38). The extremization condition is

$$\begin{aligned} &\delta\{\mathrm{Tr}_N[\alpha_0\hat{\rho} + \alpha_E\hat{H}_N\hat{\rho} - k_B\hat{\rho}\,\ln(\hat{\rho})]\} \\ &\quad = \mathrm{Tr}_N[\{(\alpha_0 - k_B)\hat{I} + \alpha_E\hat{H}_N - k_B\ln(\hat{\rho})\}\delta\hat{\rho}] = 0, \end{aligned} \tag{7.39}$$

where $\hat{I}$ is the unit operator. Since $\delta\hat{\rho}$ is arbitrary, we must have

$$(\alpha_0 - k_B)\hat{I} + \alpha_E\hat{H}_N - k_B\ln(\hat{\rho}) = 0, \tag{7.40}$$

and therefore

$$\hat{\rho} = \exp\left[\left(\frac{\alpha_0}{k_B} - 1\right)\hat{I} + \frac{\alpha_E}{k_B}\hat{H}_N\right]. \tag{7.41}$$

The two Lagrange multipliers, α_0 and α_E, can be determined from the constraints Eqs. (7.37) and (7.38). From Eqs. (7.37) and (7.41) we find

$$Z_N(\alpha_E) \equiv \exp\left(1 - \frac{\alpha_0}{k_B}\right) = \mathrm{Tr}\left(e^{\alpha_E \hat{H}_N/k_B}\right). \tag{7.42}$$

The quantity $Z_N(T)$ is called the *partition function*. We next determine the Lagrange multiplier, α_E. Let us multiply Eq. (7.40) by $\hat{\rho}$ and take the trace. We obtain

$$\mathrm{Tr}_N[(\alpha_0 - k_B)\hat{\rho} + \alpha_E \hat{H}_N \hat{\rho} - k_B \hat{\rho} \ln(\hat{\rho})] = -k_B \ln[Z_N(\alpha_E)] + \alpha_E \langle E \rangle + S = 0, \tag{7.43}$$

where we have made use of the constraints, Eqs. (7.37) and (7.38), and the definitions of the partition function Eq. (7.42) and the Gibbs entropy Eq. (7.3). From Section 2.F.3 the fundamental equation for the Helmholtz free energy can be written $A - U + ST = 0$. If we note that the internal energy is $U = \langle E \rangle$, then we can make the identification $\alpha_E = -1/T$ and we find that the Helmholtz free energy is

$$A = -k_B T \ln[Z_N(T)]. \tag{7.44}$$

The *partition function*, $Z_N(T)$, takes the form

$$Z_N(T) = e^{-\beta A} = \mathrm{Tr}_N\left(e^{-\beta \hat{H}_N}\right), \tag{7.45}$$

where $\beta = 1/k_B T$. The probability density operator can be written

$$\hat{\rho} = e^{-\beta(\hat{H}_N - A)} = \frac{e^{-\beta \hat{H}_N}}{\mathrm{Tr}_N\left(e^{-\beta \hat{H}_N}\right)}. \tag{7.46}$$

Equation (7.46) is the probability density for the *canonical ensemble*. The trace is evaluated using any convenient complete orthonormal set of N-particle basis states. However, as we shall show below, we must make a distinction between systems of N distinguishable particles and systems of N indistinguishable particles.

It is important to note that Eq. (7.46) was obtained by extremizing the Gibbs entropy. Historically, the Gibbs entropy was chosen because it gave this result [1, 2] for the probability density of a system at temperature T. At high

temperature, where equipartition of energy occurs, Eq. (7.46) gives the correct relation between the temperature and the average energy.

Equation (7.44) is the Fundamental Equation for a closed system. From it we can obtain all thermodynamic quantities. For example, the entropy is given by $S = -(\partial A/\partial T)_{X,N}$. The generalized force is given by $Y = (\partial A/\partial X)_{T,N}$. The chemical potential is given by $\mu' = (\partial A/\partial N)_{T,X}$. Another useful relation for the internal energy is $U = (\partial \beta A/\partial \beta)_{X,N}$.

In the canonical ensemble the temperature, T, is fixed and the *average energy*, $U = \langle E \rangle$, is fixed. However, because there can be a flow of energy in and out of this system, it is important to know how large the fluctuations in the energy about the average, $\langle E \rangle$, will be. Let us therefore compute the variance of the energy fluctuations. We first write the normalization condition

$$\mathrm{Tr}_N(e^{\beta[A(T,X,N)-\hat{H}_N]}) = 1, \tag{7.47}$$

If we differentiate Eq. (7.47) twice with respect to β, we find

$$0 = \mathrm{Tr}_N\left(\left[\left(\frac{\partial^2 \beta A}{\partial \beta^2}\right)_{X,N} + \left(-\hat{H}_N + \left(\frac{\partial \beta A}{\partial \beta}\right)_{X,N}\right)^2\right] e^{\beta[A(T,X,N)-\hat{H}_N]}\right), \tag{7.48}$$

This gives

$$\langle E^2 \rangle - \langle E \rangle^2 = -\left(\frac{\partial^2 \beta A}{\partial \beta^2}\right)_{X,N} = k_B T^2 C_{X,N}, \tag{7.49}$$

where $C_{X,N}$ is the heat capacity at constant X and N. The heat capacity, $C_{X,N}$, and average energy, $\langle E \rangle$, are each proportional to N. Therefore, the fractional deviation behaves as

$$\frac{\sqrt{\langle E^2 \rangle - \langle E \rangle^2}}{\langle E \rangle} \sim N^{-1/2} \tag{7.50}$$

and goes to zero as the number of degrees of freedom becomes infinite. This means that the fluctuations in energy become very small relative to the magnitude of the energy itself. In the thermodynamic limit, most microstates will have an energy approximately equal to the average energy, $U = \langle E \rangle$, and the canonical ensemble becomes equivalent to the microcanonical ensemble.

In evaluating the trace in Eq. (7.45) we must distinguish between systems of indistinguishable particles and systems of distinguishable particles. A system of N indistinguishable particles, by definition, has the property that the Hamiltonian and all other physical observable remain invariant under permutation of the particles. We will consider both cases below.

7.D.2. Systems of Indistinguishable Particles

As we show in Appendix B, for systems of identical particles we can evaluate the trace either in terms of complete sets of symmetrized or antisymmetrized N-body position or momentum eigenstates, or in terms of the "number" representation. However, the fact that in the canonical ensemble the number of particles is restricted to N makes the particle number representation unwieldy when using the canonical ensemble. As we have shown in Appendix B [Eqs. (B.30) and (B.32)], the trace of the probability density for a set of N identical particles may be written

$$\mathrm{Tr}_N(\hat{\rho}) = \frac{1}{N!} \sum_{k_1,\ldots,k_N} \langle k_1 \ldots, k_N | \hat{\rho} | k_1, \ldots, k_N \rangle^{(\pm)} = 1, \tag{7.51}$$

where the states $|k_1, \ldots, k_N\rangle$ denote "momentum" eigenstates for the N-body system. The symmetrized state $|k_1, \ldots, k_N\rangle^{(+)}$ must be used for bosons. The antisymmetrized state $|k_1, \ldots, k_N\rangle^{(-)}$ must be used for fermions. The "momentum" eigenstates may be written as the direct product of the "momentum" eigenstates of the constituent particles,

$$|k_a, k_b, \ldots, k_l\rangle \equiv |k_a\rangle_1 |k_b\rangle_2 \times \cdots \times |k_l\rangle_N. \tag{7.52}$$

On the left-hand side of Eq. (7.52), we use the convention that the "momenta" of the particles labelled from 1 to N are ordered from left to right from 1 to N. Thus, particle 1 has "momentum" k_a, particle 2 has "momentum" $k_b, \ldots$, particle N has "momentum" k_l. (When we say "momentum" we include spin and any other internal degrees of freedom of a particle that might affect the thermodynamic properties of the system.) The state $|k_a\rangle_1$ is the "momentum" eigenstate for particle 1. The state $|k_1, \ldots, k_N\rangle^{(\pm)}$ is defined as

$$|k_1, \ldots, k_N\rangle^{(\pm)} = \sum_P (\pm 1)^P P |k_1, \ldots, k_N\rangle, \tag{7.53}$$

where $\sum_P P$ denotes the sum over all permutations of the momentum in the state $|k_1, \ldots, k_N\rangle$ (cf. Appendix B). In Exercise 7.3 we evaluate the partition function for the (unrealistic) case of a three-body system of identical particles.

■ **EXERCISE 7.3.** Compute the partition function, $Z_3(T)$, for an ideal gas of three identical particles (bosons or fermions) in a cubic box of volume $V = L^3$. Assume the walls of the box are infinitely hard. For symplicity, neglect any spin or other internal degrees of freedom. What approximations can be made for a high-temperature and low-density gas?

Answer: The Hamiltonian for this three-body ideal gas is $\hat{H}_3 = \hat{p}_1^2/2m + \hat{p}_2^2/2m + \hat{p}_3^2/2m$, where $\hat{\mathbf{p}}_i = \hbar\hat{\mathbf{k}}_i$ is the momentum operator for the ith particle and $\hat{\mathbf{k}}_i$ is the wave vector of the ith particle.

It is instructive first to work out the partition function for a single particle, $Z_1(T) = \mathrm{Tr}_1[\exp(-\beta\hat{p}^2/2m)] = \sum_{\mathbf{k}}\langle\mathbf{k}|exp(-\beta\hbar^2\hat{k}^2/2m)|\mathbf{k}\rangle$, where $|\mathbf{k}\rangle$ is orthonormal eigenstate of the wavevector operator, $\hat{\mathbf{k}} = \hat{\mathbf{p}}/\hbar$ and $\langle\mathbf{k}\,|\,\mathbf{k}'\rangle = \delta_{\mathbf{k},\mathbf{k}'}$. Since the particle is confined to a cubic box of volume $V = L^3$ and the walls of the box are infinitely hard, the kinetic energy eigenstates can be written

$$\psi_{n_x,n_y,n_z}(x, y, z) = A\,\sin\left(\frac{n_x\pi x}{L}\right)\sin\left(\frac{n_y\pi y}{L}\right)\sin\left(\frac{n_z\pi z}{L}\right), \tag{1}$$

where n_x, n_y, and n_z are integers $1, 2, \ldots, \infty$, and A is a normalization constant. The allowed wavevectors are

$$\mathbf{k} = \frac{n_x\pi}{L}\mathbf{i} + \frac{n_y\pi}{L}\mathbf{j} + \frac{n_z\pi}{L}\mathbf{k}, \tag{2}$$

where $\mathbf{i}$, $\mathbf{j}$, and $\mathbf{k}$ are unit vectors in the x, y, and z directions, respectively. The single particle partition function can be written

$$Z_1(T) = \sum_{n_x=1}^{\infty}\sum_{n_y=1}^{\infty}\sum_{n_z=1}^{\infty}\exp\left[-\frac{\beta\pi^2\hbar^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2)\right]. \tag{3}$$

If the volume, V, is very large on microscopic scales, we can change the summation to an integration in Eq. (3). Let us note that $\sum_{n_x=1}^{\infty} = \int_1^{\infty} dn_x$, and make a change of variables, $p_x = n_x\pi\hbar/L$. For very large L, $\hbar\pi/L \approx 0$ and we find

$$\begin{aligned} Z_1(T) &= \left(\frac{L^3}{\pi^3\hbar^3}\right)\int_0^{\infty} dp_x\int_0^{\infty} dp_y\int_0^{\infty} dp_z\exp\left[-\frac{\beta}{2m}(p_x^2 + p_y^2 + p_z^2)\right] \\ &= \left(\frac{V}{h^3}\right)\int_{-\infty}^{\infty} dp_x\int_{-\infty}^{\infty} dp_y\int_{-\infty}^{\infty} dp_z\exp\left[-\frac{\beta}{2m}(p_x^2 + p_y^2 + p_z^2)\right] = \frac{V}{\lambda_T^3}, \end{aligned} \tag{4}$$

where

$$\lambda_T = \frac{h}{\sqrt{2\pi mk_BT}} \tag{5}$$

is the *thermal wavelength* and has units of length. As we shall show below, the thermal wavelength is a measure of the distance over which the particles maintain phase coherence in the gas.

The three-body partition function can be written

$$Z_3(T) = \mathrm{Tr}_3(e^{-\beta\hat{H}}) = \frac{1}{3!}\sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3} \langle \mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, |\hat{\rho}|\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3\rangle^{(\pm)}, \tag{6}$$

where

$$\begin{aligned}|\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3\rangle^{(\pm)} = |\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3\rangle \pm |\mathbf{k}_1, \mathbf{k}_3, \mathbf{k}_2\rangle \pm |\mathbf{k}_2, \mathbf{k}_1, \mathbf{k}_3\rangle \\ \pm |\mathbf{k}_3, \mathbf{k}_2, \mathbf{k}_1\rangle + |\mathbf{k}_3, \mathbf{k}_1, \mathbf{k}_2\rangle + |\mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_1\rangle.\end{aligned} \tag{7}$$

If we note the orthonormality condition, $\langle \mathbf{k}_a, \mathbf{k}_b, \mathbf{k}_c \,|\, \mathbf{k}_d, \mathbf{k}_e, \mathbf{k}_f\rangle = \delta_{\mathbf{k}_a,\mathbf{k}_d}\delta_{\mathbf{k}_b,\mathbf{k}_e}\delta_{\mathbf{k}_c,\mathbf{k}_f}$ then Eq. (6) becomes

$$\begin{aligned}Z_3(T) &= \frac{1}{3!}\left[(Z_1(T))^3 \pm 3Z_1(T)Z_1\left(\frac{T}{2}\right) + 2Z_1\left(\frac{T}{3}\right)\right] \\ &= \frac{1}{3!}\left[\left(\frac{V}{\lambda_T^3}\right)^3 \pm \frac{3}{(2)^{3/2}}\left(\frac{V}{\lambda_T^3}\right)^2 + \frac{2}{(3)^{3/2}}\left(\frac{V}{\lambda_T^3}\right)\right] \\ &= \frac{1}{3!}\left(\frac{V}{\lambda_T^3}\right)^3\left[1 \pm \frac{3}{(2)^{3/2}}\left(\frac{\lambda_T^3}{V}\right) + \frac{2}{(3)^{3/2}}\left(\frac{\lambda_T^3}{V}\right)^2\right].\end{aligned} \tag{8}$$

The semiclassical limit corresponds to high temperatures and/or low densities (large V). In that case, we see from Eq. (8) that we can neglect terms proportional to λ_T^3/V and we obtain the semiclassical partition function for a gas of three identical particles:

$$Z_3(T) \approx \frac{1}{3!}\left(\frac{V}{\lambda_T^3}\right)^3. \tag{9}$$

For a gas of N identical particles, the semiclassical limit gives an approximate partition function:

$$Z_N(T) \approx \frac{1}{N!}\left(\frac{V}{\lambda_T^3}\right)^N. \tag{10}$$

The factor $N!$ in Eq. (10) is exactly the counting factor used in the microcanonical ensemble for indistinguishable particles. It resolves the Gibbs paradox.

As we have shown in Exercise 7.3, symmetrized and antisymmetrized states must be used when computing the partition function for systems of identical particles at low temperatures and/or high densities where quantum effects

strongly influence the translational degrees of freedom. However, for moderately high temperatures and/or moderate densities the partition function takes the approximate form

$$Z_N(T) = \mathrm{Tr}_N\left(e^{-\beta\hat{H}}\right) \approx \frac{1}{N!}\sum_{k_1,\ldots,k_N} \langle k_1,\ldots,k_N|e^{-\beta\hat{H}}|k_1,\ldots,k_N\rangle, \qquad (7.54)$$

where we now neglect the contributions from permuted states. In doing so, we are neglecting terms of order, $(N/V)\lambda_T^3$, where $\lambda_T = h/\sqrt{2\pi m k_B T}$ is the thermal wavelength. Equation (7.54) gives a good description of a semiclassical gas of N identical particles. Quantum effects still must be taken into account in computing any contributions to the partition function due to internal degrees of freedom. To see this, let us consider a gas of noninteracting molecules which have internal degrees of freedom which can absorb energy. Such internal degrees of freedom might include the rotational and vibrational motions of the molecule and electronic or nuclear excitations. For such a system, the Hamiltonian of the ith molecule can be written $\hat{H}_i = \hat{p}_i^2/2m + \hat{H}_{i(rot)} + \hat{H}_{i(vib)} + \hat{H}_{i(elec)} + \hat{H}_{i(nuc)} + \cdots$, where $\hat{H}_{i(rot)}, \hat{H}_{i(vib)}, \hat{H}_{i(elec)}$, and $\hat{H}_{i(nuc)}$ denote the rotational, vibrational, electronic, and nuclear internal degrees of freedom, respectively. In writing this Hamiltonian as we have, we have assumed that these various internal degrees of freedom are uncoupled from one another. For a gas of N uncoupled particles in a box of volume V, the partition function can be written

$$Z_N(V,T) = \frac{1}{N!}\mathrm{Tr}_N\left(\exp\left[-\beta\sum_{i=1}^{N}\left(\frac{\hat{p}_i^2}{2m} + \hat{H}_{i(rot)} + \hat{H}_{i(vib)} + \hat{H}_{i(el)} + \hat{H}_{i(nuc)} + \cdots\right)\right]\right). \qquad (7.55)$$

The partition function takes a particularly simple form for this system *if the Hamiltonians in Eq. (7.55) commute with one another.* Then we find

$$Z_N(T,V) = \frac{1}{N!}\left(Z_{1(tr)}\, Z_{1(rot)}\, Z_{1vib}\, Z_{1(elec)}\, Z_{1(nuc)} \times \cdots\right)^N \qquad (7.56)$$

where $Z_{1(tr)} = \mathrm{Tr}_1(e^{-\beta\hat{p}^2/2m}), Z_{1(rot)} = \mathrm{Tr}_1(e^{-\beta\hat{H}_1(rot)})$, and so on. The trace, Tr_1 is taken over a complete set of single particle states appropriate for the Hamiltonian appearing under it.

For a semiclassical ideal gas with no internal degrees of freedom, the partition function is (cf. Exercise 7.3)

$$Z_N(T,V) = \frac{1}{N!}\left(\frac{V}{\lambda_T^3}\right)^N \approx \left(\frac{eV}{N\lambda_T^3}\right)^N, \qquad (7.57)$$

where we have made use of *Stirling's approximation*, $N! \approx (N/e)^N$. The Helmholtz

free energy is

$$A = -k_B T \ln(Z_N) = -N k_B T - N k_B T \ln\left[\frac{V}{N}\left(\frac{h^2}{2\pi m k_B T}\right)^{-3/2}\right]. \tag{7.58}$$

The entropy is

$$S = -\left(\frac{\partial A}{\partial T}\right)_{V,N} = \frac{5}{2} N k_B + N k_B \ln\left[\frac{V}{N}\left(\frac{h^2}{2\pi m k_B T}\right)^{-3/2}\right], \tag{7.59}$$

which is just the Sackur–Tetrode equation. In Exercise 7.4 we compute the thermodynamic properties for a semiclassical gas of N identical spin-$\frac{1}{2}$ particles in a magnetic field.

■ **EXERCISE 7.4.** A cubic box (with infinitely hard walls) of volume, $V = L^3$, contains an ideal gas of N identical atoms, each of which has spin, $s = \frac{1}{2}$, and magnetic moment, μ. A magnetic field, **B**, is applied to the system. (a) Compute the partition function for this system. (b) Compute the internal energy and the heat capacity. (c) What is the magnetiziation?

Answer:

(a) The partition function takes the form

$$Z_N = \frac{1}{N!}(Z_{1(tr)})^N (Z_{1(mag)})^N, \tag{1}$$

where $Z_{1(tr)}$ is the translational contribution for a single molecule and $Z_{1(mag)}$ is the magnetic contribution for a single molecule. The single particle translational partition function can be written $Z_{1(tr)} = V/\lambda_T^3$, where $\lambda_T = h/\sqrt{2\pi m k_B T}$ is the thermal wavelength.

Let us now compute the partition function due to the magnetic degrees of freedom. Each atom will have magnetic energy $E(s) = -\frac{1}{2} s\mu B$, where $s = \pm 1$. The magnetic partition function for a single atom is

$$Z_{1(mag)} = \sum_{s=\pm 1} e^{-s\beta\mu B/2} = 2\cosh\left(\frac{\beta\mu B}{2}\right). \tag{2}$$

The partition function for the gas is

$$Z_N = \frac{1}{N!}\left(\frac{2V}{\lambda_T^3}\right)^N \cosh^N\left(\frac{\beta\mu B}{2}\right). \tag{3}$$

(**b**) The internal energy is given by

$$U = -\left(\frac{\partial \ln Z_N}{\partial \beta}\right) = \frac{3}{2}Nk_BT - \frac{1}{2}N\mu B \tanh\left(\frac{\beta\mu B}{2}\right). \tag{4}$$

The heat capacity is

$$C_{V,N} = \left(\frac{\partial U}{\partial T}\right)_{V,N,B} = \frac{3}{2}Nk_B + Nk_B\left(\frac{\beta\mu B}{2}\right)^2 \operatorname{sech}^2\left(\frac{\beta\mu B}{2}\right). \tag{5}$$

(**c**) The magnetization is given by $M = -(\partial\Phi/\partial B)_{T,N}$, where Φ is the free energy for this problem (the translational part is like a Helmholtz free energy, a function of T, V, and N, and the magnetic part is like a Gibbs free energy, a function of T, B, and N). The free energy of the combined system doesn't have a name so we call it Φ. Then $\Phi = -K_BT \ln(Z_N)$ and

$$M = -\left(\frac{\partial \Phi}{\partial B}\right)_{T,N} = \frac{1}{2}N\mu \tanh\left(\frac{\beta\mu B}{2}\right). \tag{6}$$

7.D.3. Systems of Distinguishable Particles

For systems of distinguishable particles, the trace in Eq. (7.45) can be evaluated using a complete set of unsymmetrized N-body states. For example, if we use "momentum" eigenstates to evaluate the trace, we have

$$\mathrm{Tr}_N(\hat{\rho}) = \sum_{k_1,\ldots,k_N} \langle k_1, \ldots, k_N | \hat{\rho} | k_1, \ldots, k_N \rangle. \tag{7.60}$$

One of the best examples of such a system is a semiclassical solid composed of N lattice sites. Even if the atoms at each lattice site are identical they do not have translational kinetic energy. They are located at different points in space and they can be distinguished by their position in space. An Einstein solid is an example of a semiclassical solid in which the atoms can be considered to be distinguishable because they remain at well-defined lattice sites. In Exercise 7.5 we compute the thermodynamic properties of an Einstein solid using the canonical ensemble.

■ **EXERCISE 7.5** Use the canonical ensemble to compute the entropy, internal energy, and heat capacity of the Einstein solid described in Exercise 7.1.

Answer: The Hamiltonian for an Einstein solid with N lattice sites and $3N$ harmonic oscillators with frequency ω is

$$\hat{H} = \hbar\omega \sum_{i=1}^{3N} \left(\hat{n}_i + \frac{1}{2} \right), \tag{1}$$

where $\hat{n}_i$ is the number operator for energy quanta in the ith harmonic oscillator. The number operators have eigenvalues which are integers, $n_i = 0, 1, 2, \ldots, \infty$, and eigenvectors $|n_i\rangle$, so that $\hat{n}_i|n_i\rangle = n_i|n_i\rangle$. The partition function is given by

$$Z_N(T) = \mathrm{Tr}_N \left[\exp\left(-\beta\hbar\omega \sum_{i=1}^{3N} (\hat{n}_i + \tfrac{1}{2}) \right) \right]. \tag{2}$$

We can evaluate the trace in Eq. (2) using the basis states $|n_1, n_2, \ldots, n_{3N}\rangle = |n_1\rangle \times \cdots \times |n_{3N}\rangle$. Then

$$\begin{aligned} Z_N(T) &= \sum_{n_1=0}^{\infty} \cdots \sum_{n_{3N}=0}^{\infty} \langle n_1, \ldots, n_{3N} | \exp\left(-\beta\hbar\omega \sum_{i=1}^{3N} (\hat{n}_i + \tfrac{1}{2}) \right) | n_1, \ldots, n_{3N} \rangle \\ &= \sum_{n_1=0}^{\infty} \cdots \sum_{n_{3N}=0}^{\infty} \exp\left(-\beta\hbar\omega \sum_{i=1}^{3N} (n_i + \tfrac{1}{2}) \right) \\ &= \left(\sum_{n_1=0}^{\infty} e^{-\beta\hbar\omega(n_i + \frac{1}{2})} \right) \times \cdots \times \left(\sum_{n_{3N}=0}^{\infty} e^{-\beta\hbar\omega(n_{3N} + \frac{1}{2})} \right) = \left(\frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} \right)^{3N}. \end{aligned} \tag{3}$$

(Note that the number of particles is fixed at N. The number operator, $\hat{n}_i$ counts the number of vibrational quanta in the ith harmonic oscillator. Even though the number of particles is fixed at N, the number of vibrational quanta has no restriction.)

The Helmholtz free energy is

$$A(T, N) = -k_B T \ln(Z_N(T)) = \tfrac{3}{2} N\hbar\omega + 3Nk_B T \ln(1 - e^{-\beta\hbar\omega}). \tag{4}$$

The entropy is

$$S = -\left(\frac{\partial A}{\partial T} \right)_N = 3Nk_B \ln(1 - e^{-\beta\hbar\omega}) + \frac{3N\hbar\omega}{T} \frac{e^{-\beta\hbar\omega}}{(1 - e^{-\beta\hbar\omega})}. \tag{5}$$

The internal energy is

$$U = \left(\frac{\partial \beta A}{\partial \beta} \right)_N = \frac{3}{2} N\hbar\omega + 3N\hbar\omega \frac{e^{-\beta\hbar\omega}}{(1 - e^{-\beta\hbar\omega})}. \tag{6}$$

The heat capacity is

$$C_N = \left(\frac{\partial U}{\partial T}\right)_N = \frac{3N\hbar^2\omega^2}{k_B T^2} \frac{e^{-\beta\hbar\omega}}{(1-e^{-\beta\hbar\omega})^2}. \tag{7}$$

7.E. HEAT CAPACITY OF A DEBYE SOLID [6, 7]

The intermolecular cohesive forces which bind the simplest molecular crystals are the same as the forces which give the correction terms in the van der Waals equation of state (Section 2.C.3). The short-range repulsive forces between atoms make crystals virtually incompressible. The longer-range attractive force holds the atoms of the crystal in place at some fixed lattice spacing, although the atoms can undergo oscillations about their lattice positions. To first approximation, a crystal may be viewed as an ordered array of atoms, each one fixed to a lattice site and free to oscillate about the lattice site. While the potential which governs the oscillations is anharmonic, to lowest approximation, in deriving the heat capacity, we can treat it as harmonic. In this section we shall compute the heat capacity for a three-dimensional harmonically coupled lattice using a continuum approximation of the type first proposed by Debye and we will compare it to experiment. (In Section S7.A we obtain an exact expression for the heat capacity of lattice vibrations for a one-dimensional lattice and compare Debye theory to the exact result for that case.)

Let us consider the contribution to the heat capacity of the sound modes in a simple three-dimensional harmonic lattice. Consider a rectangular lattice with sides of lengths L_x, L_y, and L_z. We will assume that all sides are pinned so that the sound waves form standing waves with wavelengths $2L_x/l_x, 2L_y/l_y$, and $2L_z/l_z$ in the x, y, and z directions, respectively, where l_x, l_y, and l_z are integers. The α^{th} sound mode will have a dispersion relation of the form

$$\omega_\alpha^2 = c^2\left[\left(\frac{\pi l_{x\alpha}}{L_x}\right)^2 + \left(\frac{\pi l_y \alpha}{L_y}\right)^2 + \left(\frac{\pi l_{z\alpha}}{L_z}\right)^2\right]. \tag{7.61}$$

The Hamiltonian operator takes the form

$$\hat{H} = \sum_{\alpha=1}^{N} \hbar\omega_\alpha(\hat{a}_\alpha^\dagger \hat{a}_\alpha + \tfrac{1}{2}\hat{1}) = \sum_{\alpha=1}^{N} \hbar\omega_\alpha(\hat{n}_\alpha + \tfrac{1}{2}\hat{1}), \tag{7.62}$$

where $\hat{n}_\alpha = \hat{a}_\alpha^\dagger \hat{a}_\alpha$ is the number operator for energy quanta (phonons) in the α^{th} normal mode. Let $|n_\alpha\rangle$ be the eigenvector of the number operator, $\hat{n}_\alpha$. Then

$\hat{n}_\alpha|n_\alpha\rangle = n_\alpha|n_\alpha\rangle$. The partition function can be written

$$Z_N(T) = \mathrm{Tr}_N\left[\exp\left(-\beta\sum_{\alpha=1}^{N}\hbar\omega_\alpha\left(\hat{n}_\alpha+\tfrac{1}{2}\right)\right)\right] = \prod_{\alpha=1}^{N}\frac{e^{-\beta\hbar\omega_\alpha/2}}{1-e^{-\beta\hbar\omega_\alpha}} = \prod_{\alpha=1}^{N}\left(2\sinh\left(\frac{\beta\hbar\omega_\alpha}{2}\right)\right)^{-1}. \tag{7.63}$$

The average energy is

$$\langle E\rangle = -\frac{\partial\ln(Z_N)}{\partial\beta} = \sum_{\alpha=1}^{N}\frac{\hbar\omega_\alpha/2}{\tanh\left(\frac{\beta\hbar\omega_\alpha}{2}\right)} = \sum_{\alpha=1}^{N}\frac{\hbar\omega_\alpha}{2}+\sum_{\alpha=1}^{N}\frac{\hbar\omega_\alpha}{e^{\beta\hbar\omega_\alpha}-1}. \tag{7.64}$$

Since the average can also be written $\langle E\rangle = \langle\sum_{\alpha=1}^{N}\hbar\omega_\alpha(\hat{n}_\alpha+\frac{1}{2})\rangle$, comparison with Eq. (7.64) shows that the average number of quanta in the α^{th} phonon mode is

$$\langle\hat{n}_\alpha\rangle = \frac{1}{e^{\beta\hbar\omega_\alpha}-1}, \tag{7.65}$$

which is Planck's formula.

The allowed values of ω_α in Eq. (7.61) consist of discrete points in a three-dimensional frequency space. The distance between points in the x direction is $\pi c/L_x$, in the y direction it is $\pi c/L_y$, and in the z direction it is $\pi c/L_z$. The volume per point in frequency space is therefore $(\pi c)^3/V$, where $V = L_xL_yL_z$ is the volume of the crystal. The number points per unit volume in frequency space is $V/(\pi c)^3$. The total number of allowed values of ω_α less than some value ω is given by $\frac{1}{8}(4\pi\omega^3/3)(V/(\pi c)^3)$, where $\frac{1}{8}(4\pi\omega^3/3)$ is the volume of $\frac{1}{8}$ of a sphere of radius ω (the phonon frequency is positive). Thus, the number of allowed frequencies in the range $\omega \to \omega + d\omega$ is given by

$$dl = \frac{V}{2\pi^2c^3}\omega^2 d\omega. \tag{7.66}$$

In general, there will be two transverse sound modes and one longitudinal sound mode since crystals can sustain both longitudinal and transverse sound modes (a fluid can only sustain longitudinal sound modes). The transverse and longitudinal sound modes in a crystal propagate at different velocities which we shall denote as c_t and c_l, respectively. If the three different sound modes are taken into account the number of allowed frequencies, dn, in the interval, $\omega \to \omega + d\omega$, is

$$dn = \frac{V}{2\pi^2}\left(\frac{2}{c_t^3}+\frac{1}{c_l^3}\right)\omega^2 d\omega. \tag{7.67}$$

Since there is a minimum wavelength allowed on the lattice due to the finite spacing of the atoms, there will be a cutoff frequency, ω_D (the Debye frequency). If there are N atoms on the three-dimensional crystal, there will be $3N$ sound modes. We can then determine the Debye frequency by relating it to the total number of modes,

$$3N = \int_1^{3N} dn = \frac{V}{2\pi^2}\left(\frac{2}{c_t^3}+\frac{1}{c_l^3}\right)\int_0^{\omega_D}\omega^2 d\omega = \frac{V}{2\pi^2}\left(\frac{2}{c_t^3}+\frac{1}{c_l^3}\right)\frac{\omega_D^3}{3}. \tag{7.68}$$

If we solve for ω_D^3, we find that the Debye frequency is given by

$$\omega_D^3 = \frac{18N\pi^2}{V}\left(\frac{2}{c_t^3}+\frac{1}{c_l^3}\right)^{-1}. \tag{7.69}$$

The density of states can be written

$$g(\omega) = \frac{dn}{d\omega} = \frac{V\omega^2}{2\pi^2}\left(\frac{2}{c_t^3}+\frac{1}{c_l^3}\right) = \frac{9N\omega^2}{\omega_D^3}. \tag{7.70}$$

Once we are given the density of states, $g(\omega)$, the average energy is given by

$$\langle E\rangle = \frac{1}{2}\int_0^{\omega_D}\hbar\omega g(\omega)\,d\omega + \int_0^{\omega_L}\hbar\omega n(\omega)g(\omega)d\omega. \tag{7.71}$$

We then find

$$\langle E\rangle = \frac{9N\hbar\omega_D}{8} + \frac{9N}{\omega_D^3}\int_0^{\omega_D}\frac{\hbar\omega^3 d\omega}{e^{\beta\hbar\omega}-1}. \tag{7.72}$$

The heat capacity is

$$C_N = \frac{9Nk_B}{\hbar^2\beta^2\omega_D^3}\int_0^{\omega_D} d\omega\frac{(\beta\hbar\omega)^4 e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2} = \frac{9Nk_B}{(\hbar\beta\omega_D)^3}\int_0^{T_D/T} dx\frac{x^4e^x}{(e^x-1)^2}, \tag{7.73}$$

where the Debye temperature, T_D, is defined $T_D = \hbar\omega_D/k_B$.In the limit $T \to 0$, the heat capacity becomes approximately

$$C_N \approx \frac{9Nk_B}{(\hbar\beta\omega_D)^3}\int_0^{\infty} dx\frac{x^4e^x}{(e^x-1)^2} = \frac{12Nk_B\pi^4T^3}{5T_D^3}, \tag{7.74}$$

These results are in good qualitative agreement with the experimentally observed heat capacity of many solids. We give two examples in Fig. 7.2 where we have plotted the prediction of Debye theory and have compared

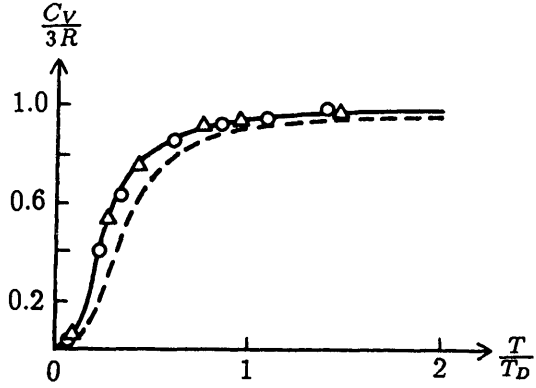


Fig. 7.2. The solid line is the heat capacity curve predicted by Debye theory. The dashed line is that predicted for Einstein solid. The circles and triangles are experimental values for the heat capacity of Al ($T_D = 390$ K) and Cu ($T_D = 315$ K), respectively. (Based on Ref. 8.)

it to experimental results for aluminium and copper (using the appropriate Debye temperatures for those substances). Experimentally, one finds that at high temperatures the heat capacity, C_N, is roughly constant with $C_N \approx 3Nk_B = 3nR$, where n is the number of moles and R is the gas constant. However, as the temperature approaches $T = 0$ K, the heat capacity goes to zero as T^3.

It is interesting that classical physics cannot give the correct behavior for the heat capacity of solids at low temperature. A classical harmonically coupled lattice with N atoms has a heat capacity, $C_N = 3Nk_B$, which is independent of temperature. The first theory to give the correct qualitative behavior of solids at all but very low temperatures was due to Einstein. He assumed that the solid was composed of N *uncoupled* harmonic oscillators. The thermodynamic properties of the Einstein solid have been computed in Exercises 7.1 and 7.5. The heat capacity of an Einstein solid goes to zero as $T \to 0\,K$ and therefore gives a vast improvement over classical theory. It accounts for the fact that only the longest-wavelength phonons can be excited at very low temperature, whereas classical theory allows them all to be excited. However, Einstein theory gives a vastly oversimplified density of states. It assumes that all phonon modes have a single frequency and therefore that the density of states is $g(\omega) = 3N\delta(\omega - \omega_0)$, where ω_0 is the frequency of all the phonon modes. In real solids, the phonon modes have a distribution of frequencies, and this is more accurately taken into account by the Debye (continuum) theory. The heat capacity for the Einstein solid goes to zero exponentially with temperature and therefore does not give the correct low-temperature behavior for a solid. In Fig. 7.3 we compare the density of states for the Einstein solid and the Debye solid.

The actual density of states for some solids has been measured using neutron scattering techniques. Neutrons interact with the nuclei of atoms in the solid

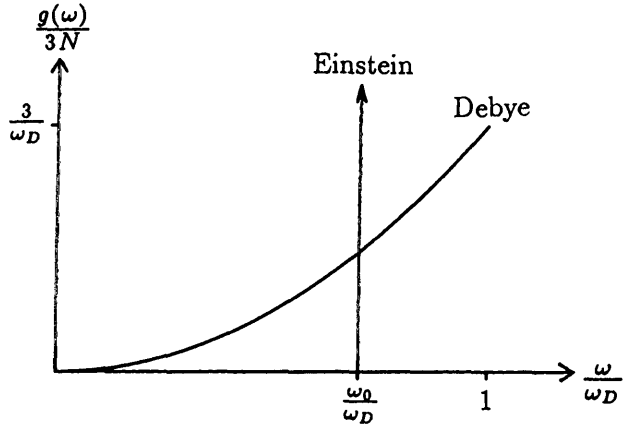


Fig. 7.3. Plots of the density of states of Einstein and Debye solids.

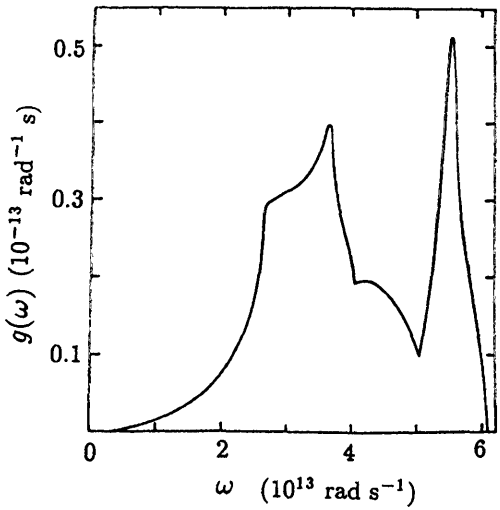


Fig. 7.4. The density of states for aluminum, obtained from neutron scattering experiments. Reprinted, by permission, from R. Stedman, et al., *Phys. Rev.* **162**, 549 (1967).

and are scattered by phonons, which are simply the normal modes of the atomic oscillations. In Fig. 7.4 we show the density of states for aluminum. The low-frequency contribution looks somewhat like the Debye result, but at high frequencies the Debye density of states is completely inadequate. It is interesting to note in Fig. 7.2 that the heat capacity of aluminum at high temperatures is not sensitive to the density of states. This is a result of the equipartition principle. At high temperatures the average energy of an oscillator is $k_B T$ and is independent of frequency of the oscillator.

7.F. ORDER–DISORDER TRANSITIONS

An important class of systems that can be studied using methods of equilibrium statistical mechanics are those which exhibit a transition from a disordered to an ordered state. One of the simplest examples of such a system consists of a lattice of N spin-$\frac{1}{2}$ objects with magnetic moment μ. Each lattice site can interact with the magnetic fields of their nearest neighbors and with any external applied magnetic fields that might be present. The Hamiltonian for such a system can be written

$$H = \sum_{\{ij\}} \epsilon_{ij} s_i s_j - \mu B \sum_{i=1}^{N} s_i, \tag{7.75}$$

where $\sum_{ij}$ denotes the sum over nearest-neighbor pairs ij (one must be careful to count each pair only once), ϵ_{ij} is the magnetic interaction energy between nearest neighbors i and j, s_i is the z component of spin at the ith lattice site, and B is the external magnetic field. For spin-$\frac{1}{2}$ objects, $s_i = +1(-1)$ if the spin of site i is oriented in the positive (negative) z direction. There is no kinetic energy in Eq. (7.75). *The Hamiltonian only contains information about spin orientation and the spatial distribution of lattice sites.* If $\epsilon_{ij} < 0$, then for $B = 0$ the lattice will have its lowest energy when all the lattice sites have spin up or all the lattice sites have spin down, both cases being equally probable. If $B \neq 0$, then the configuration in which all lattice sites are oriented with spin up will be energetically favored. Similarly, if $\epsilon_{ij} > 0$, then for $B = 0$ the configuration in which neighboring spins are oriented opposite to one another will be favored.

The partition function for this spin lattice can be written

$$Z_N(T) = \sum_{\text{all config.}} \exp\left[-\beta \sum_{\{ij\}} \epsilon_{ij} s_i s_j + \beta \mu B \sum_{i=1}^{N} s_i\right], \tag{7.76}$$

where $\sum_{\text{allconfig.}}$ denotes the sum over all 2^N possible different configurations of spin on the lattice. The partition function introduces an additional influence, that of thermal energy, $k_B T$. While the magnetic interaction energy, H, will cause the spins on the lattice to become ordered, the thermal energy, $k_B T$, will tend to randomize the spins on the lattice. It is these two competing influences which lead to an *order–disorder phase transition* on the spin lattice. At low temperature, the lattice will be ordered. As we raise the temperature, at some point the order dissappears and the spins become randomly oriented. The system, described by the partition function, Eq. (7.76), is called the *Ising model* and was originally used by Ising [10] as a model for ferromagnetism. However, the model also has been used to describe the behavior of lattice gases, binary alloys "melting" of DNA, and so on.

The Ising model can be solved exactly, and analytic expressions for its thermodynamic properties can be found in one and two dimensions, but no one has ever succeeded in solving it analytically in three dimensions. In one dimension it does not exhibit a phase transition at finite temperature, but in two dimensions it does. In one dimension the lattice does not have enough nearest neighbors for the ordering effects of the interaction energy to compete effectively with the disordering thermal energy. However, for two or more spatial dimensions it does. The Ising model was first solved in two dimensions by Onsager [11–13]. It is one of the few exactly soluble models which exhibit a phase transition.

In this section we shall consider two simple versions of the Ising model. We will first obtain exact expressions for the thermodynamic properties of a one-dimensional Ising lattice. The one-dimensional lattice does not exhibit a phase transition at finite temperature. However, the method of solution contains some ideas which are used to solve the much more difficult case of a two-dimensional lattice. We will solve the two-dimensional case in Chapter 8. In this section we will also compute the thermodynamic properties of an Ising lattice with d dimensions in the mean field approximation. The mean field approximation of the d-dimensional lattice does have a phase transition at finite temperature.

7.F.1. Exact Solution for a One-Dimensional Lattice

Let us consider a one-dimensional periodic lattice that consists of N lattice sites evenly spaced, as shown in Fig. 7.5. We will assume that all nearest neighbors have the same interaction energy, $\epsilon_{ij} = -\epsilon$, so that the configuration with lowest energy is one in which the spins are totally aligned. The periodicity of the lattice is imposed by assuming that $s_{i+N} = s_i$. The total energy for a given configuration, $\{s_i\}$, is

$$E\{s_i\} = -\epsilon \sum_{i=1}^{N} s_i s_{i+1} - \mu B \sum_{i=1}^{N} s_i. \tag{7.77}$$

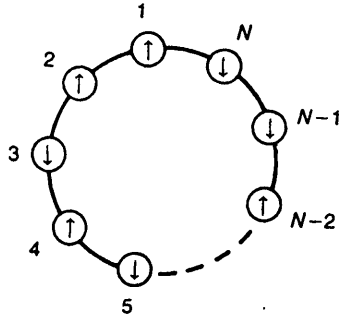


Fig. 7.5. A one-dimensional periodic lattice with N lattice sites.

The partition function can be written

$$Z_N(T,B) = \sum_{s_1=\pm 1} \cdots \sum_{s_N=\pm 1} \exp\left[\beta \sum_{i=1}^{N} \left(\epsilon s_i s_{i+1} + \frac{1}{2}\mu B(s_i + s_{i+1})\right)\right], \tag{7.78}$$

where we have used the fact that $\sum_{i=1}^{N} s_i = \frac{1}{2}\sum_{i=1}^{N}(s_i + s_{i+1})$ for a periodic lattice. It is now convenient to introduce a 2×2 matrix,

$$\bar{\mathbf{P}} = \begin{pmatrix} e^{\beta(\epsilon+\mu B)} & e^{-\beta\epsilon} \\ e^{-\beta\epsilon} & e^{\beta(\epsilon-\mu B)} \end{pmatrix}, \tag{7.79}$$

whose matrix elements are defined as

$$\langle s_i|\bar{\mathbf{P}}|s_{i+1}\rangle = e^{\beta(\epsilon s_i s_{i+1} + \frac{1}{2}\mu B(s_i + s_{i+1}))}. \tag{7.80}$$

The partition function may then be written

$$\begin{aligned} Z_N(T,B) &= \sum_{s_1=\pm 1} \cdots \sum_{s_N=\pm 1} \langle s_1|\bar{\mathbf{P}}|s_2\rangle\langle s_2|\bar{\mathbf{P}}|s_3\rangle \cdots \langle s_N|\bar{\mathbf{P}}|s_1\rangle \\ &= \sum_{s_1=\pm 1} \langle s_1|\bar{\mathbf{P}}^N|s_1\rangle = \mathrm{Tr}[\bar{\mathbf{P}}^N] = \lambda_+^N + \lambda_-^N = \lambda_+^N\left[1 + \left(\frac{\lambda_-}{\lambda_+}\right)^N\right], \end{aligned} \tag{7.81}$$

where $\lambda_\pm$ are the eigenvalues of the matrix $\bar{\mathbf{P}}$. We shall use the convention $\lambda_+ > \lambda_-$. The eigenvalues of $\bar{\mathbf{P}}$ are easily found to be

$$\lambda_\pm = e^{\beta\epsilon}\left[\cosh(\beta\mu B) \pm \sqrt{\cosh^2(\beta\mu B) - 2e^{-2\beta\epsilon}\sinh(2\beta\epsilon)}\right]. \tag{7.82}$$

In the limit $N \to \infty$, only the largest eigenvalue, λ_+, contributes to the thermodynamic quantities. This is easily seen if we note that the Gibbs free energy per site is

$$\begin{aligned} g(T,B) &= \lim_{N\to\infty} \frac{1}{N} G_N(T,B) = -k_B T \lim_{N\to\infty} \frac{1}{N} \ln[Z_N(T,B)] \\ &= -k_B T \ln[\lambda_+]. \end{aligned} \tag{7.83}$$

In Eq. (7.83), we have used the fact that $\lim_{N\to\infty}(\lambda_-/\lambda_+)^N = 0$. Thus the Gibbs free energy per site is

$$g(T,B) = -\epsilon - k_B \ln\left[\cosh(\beta\mu B) + \sqrt{\cosh^2(\beta\mu B) - 2e^{-2\beta\epsilon}\sinh(2\beta\epsilon)}\right]. \tag{7.84}$$

The order parameter is given by

$$\langle s\rangle = -\left(\frac{\partial g}{\partial \mu B}\right)_T = \frac{\sinh(\beta\mu B)}{\sqrt{\cosh^2(\beta\mu B) - 2e^{-2\beta\epsilon}\sinh(2\beta\epsilon)}}. \tag{7.85}$$

From Eq. (7.85) we see that the one-dimensional Ising model cannot exhibit a phase transition because when $B \to 0$ the order parameter also goes to zero. Hence, no spontaneous nonzero value of the order parameter is possible. The exact solution to the two-dimensional Ising model is givin in Chapter 8, and it does allow a phase transition.

7.F.2. Mean Field Theory for a *d*-Dimensional Lattice

We can obtain approximate analytic expressions for the thermodynamic properties of a d-dimensional Ising lattice using the mean field approximation first introduced by Weiss [14]. In the mean field approximation, the Hamiltonian of a d-dimensional spin lattice with N lattice sites can be written

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N} \nu\epsilon\langle s\rangle s_i - \mu B\sum_{i=1}^{N} s_i = -\sum_{i=1}^{N} E(\epsilon, B)s_i, \tag{7.86}$$

where ϵ is the coupling constant, ν is the number of nearest-neighbor spins, and $E(\epsilon, B) = \frac{1}{2}\nu\epsilon\langle s\rangle + \mu B$. The factor of $\frac{1}{2}$ ensures that we don't count the same pair of spins twice. The quantity $\langle s\rangle \equiv \langle s_i\rangle$ is the average spin per site. The quantity $\nu\epsilon\langle s\rangle s_i$ is an average magnetic interaction energy between site i and its nearest neighbours, assuming that the neigbors all have spin $\langle s\rangle$. As we shall show below, the average spin per site, $\langle s\rangle$, must be determined in a self-consistent manner.

The partition function can be written

$$Z_N = \left(\sum_{s_i=\pm 1} e^{\beta E s_i}\right)^N = (2\cosh(\beta E))^N. \tag{7.87}$$

The Gibbs free energy per site is

$$g(\epsilon, B) = -k_B T \lim_{N\to\infty}\left(\frac{1}{N}\ln(Z_N)\right) = -k_B T \ln[2\cosh(\beta E)]. \tag{7.88}$$

The probability $P(s_i)$ that site i has spin s_i is

$$P(s_i) = \frac{e^{\beta E s_i}}{\sum_{s_i=\pm 1} e^{\beta E s_i}} = \frac{e^{\beta E s_i}}{2\cosh(\beta E)}. \tag{7.89}$$

Note that the probability $P(s_i)$has an especially simple form in the mean field approximation because coupling to nearest neighbours is taken into account in such a simple manner.

The average magnetization of the lattice is given by

$$\langle M \rangle = N\mu\langle s \rangle, \tag{7.90}$$

where

$$\langle s \rangle = \frac{\sum_{s_i=\pm 1} s_i e^{\beta E s_i}}{\sum_{s_j=\pm 1} e^{\beta E s_j}} = \tanh[\beta E] = \tanh\left[\beta\left(\frac{1}{2}\nu\epsilon\langle s \rangle + \mu B\right)\right]. \tag{7.91}$$

The magnetization is the order parameter for the spin lattice. If $B = 0$, the magnetization will be zero for the high-temperature paramagnetic phase of the lattice (randomly ordered spins) and it will be nonzero at lower temperatures where the spins have spontaneously aligned.

We can determine the critical temperature, T_c, at which the lattice starts to become ordered as temperature is lowered (the Curie point) from the expression for the average spin per site, $\langle s \rangle$. Let us write $\langle s \rangle$ for the case $B = 0$;

$$\langle s \rangle = \tanh\left[\frac{1}{2}\beta\nu\epsilon\langle s \rangle\right] = \tanh\left[\frac{\nu\epsilon\langle s \rangle}{2k_B T}\right]. \tag{7.92}$$

We must solve Eq. (7.92) for $\langle s \rangle$. This can be done graphically by plotting $f_1 \equiv \langle s \rangle$ versus $\langle s \rangle$ and $f_2 \equiv \tanh(\alpha\langle s \rangle)$ versus $\langle s \rangle$ on the same graph. The solution to Eq. (7.92) is given by those points where the two curves cross—that is, where $f_1 = f_2$. In Figs. 7.6a and 7.6b, we plot f_1 and f_2 versus $\langle s \rangle$ for $\alpha < 1$ and $\alpha > 1$, respectively. For the case $\alpha < 1$, there is only one crossing point and it is at $\langle s \rangle = 0$. For $\alpha > 1$, there are three crossing points, at $\langle s \rangle = 0$ and at $\langle s \rangle = \pm s_0$. The free energy per site for these various cases is

$$g(\epsilon, 0) = \begin{cases} -k_B T \ln(2) & \text{if } \langle s \rangle = 0, \\ -k_B T \ln[2\cosh(\frac{1}{2}\beta\nu\epsilon s_0)] & \text{if } \langle s \rangle = \pm s_0. \end{cases} \tag{7.93}$$

Thus, the values, $\langle s \rangle = \pm s_0$ [when they are solutions to Eq. (7.92)] describe possible states of thermodynamic equilibrium since they minimize the free energy. The transition point (critical point) occurs at $\alpha = 1$ in Fig. 7.6 and therefore when $\nu\epsilon/2k_B T = 1$. Thus the critical temperature in the mean field approximation is $T = T_c = \nu\epsilon/2k_B$. In Fig. 7.7, we plot the order parameter $\langle s \rangle$, versus T/T_c.

We see that mean field theory predicts a phase transition at a finite temperature for a d-dimensional lattice. This does not agree with our exact

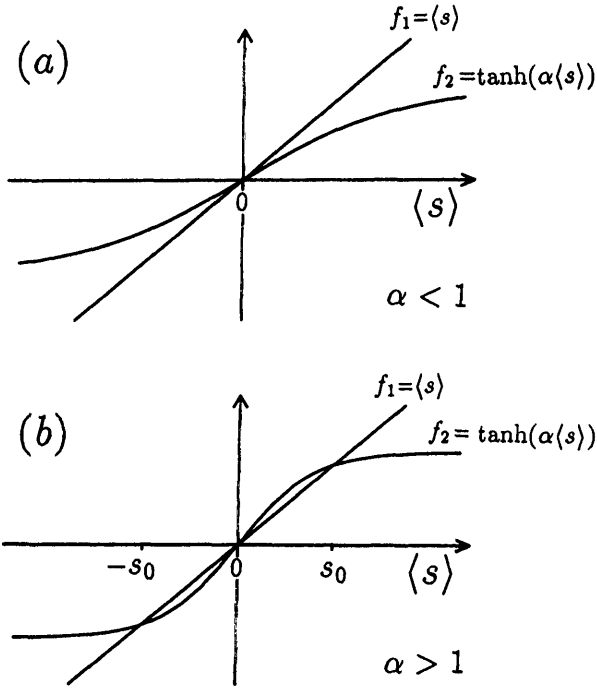


Fig. 7.6. Plots of $f_1 \equiv \langle s\rangle$ versus $\langle s\rangle$ and $f_2 \equiv \tanh(\alpha\langle s\rangle)$ versus $\langle s\rangle$. (a) $\alpha < 1$. (b) $\alpha > 1$.

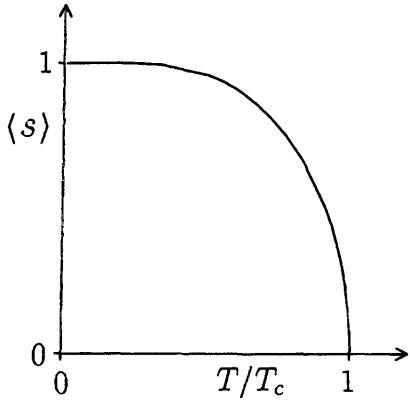


Fig. 7.7. A plot of the order parameter, $\langle s\rangle$, versus the reduced temperature, T/T_c.

result for the case $d = 1$ (cf. Section 7.F.1) where we found no phase transition at finite temperature. As we shall see in Chapter 8, mean field theory gives too high an estimate of the critical temperature for spatial dimensions, $d \leq 3$. It gives good estimates for $d \geq 4$ which is not of physical interest but is of mathematical interest.

Let us next examine the behavior of the heat capacity in the neighborhood of the critical temperature. The internal energy for $B = 0$ is

$$U = -\frac{1}{Z_N}\frac{\partial Z_N}{\partial \beta} = -\frac{1}{2}N\nu\epsilon\langle s\rangle^2. \tag{7.94}$$

The heat capacity is

$$C_N = \left(\frac{\partial U}{\partial T}\right)_N = -k_B\beta^2\left(\frac{\partial U}{\partial \beta}\right)_N = Nk_B\nu\epsilon\beta^2\langle s\rangle\left(\frac{\partial\langle s\rangle}{\partial\beta}\right)_N. \tag{7.95}$$

But

$$\left(\frac{\partial\langle s\rangle}{\partial\beta}\right)_N = \operatorname{sech}^2\left(\beta\frac{\nu\epsilon}{2}\langle s\rangle\right)\left[\frac{\nu\epsilon}{2}\langle s\rangle + \beta\frac{\nu\epsilon}{2}\left(\frac{\partial\langle s\rangle}{\partial\beta}\right)_N\right] \tag{7.96}$$

so

$$\left(\frac{\partial\langle s\rangle}{\partial\beta}\right)_N = \frac{\nu\epsilon\langle s\rangle}{3\cosh^2\left(\beta\frac{\nu\epsilon}{2}\langle s\rangle\right) - \beta\nu\epsilon}. \tag{7.97}$$

The heat capacity finally becomes

$$C_N = \frac{Nk_B\beta^2\nu^2\epsilon^2\langle s\rangle^2}{2\cosh^2\left(\beta\frac{\nu\epsilon}{2}\langle s\rangle\right) - \beta\nu\epsilon} = \frac{2Nk_B\langle s\rangle^2(T_c/T)^2}{[\cosh^2(\langle s\rangle T_c/T) - T_c/T]}. \tag{7.98}$$

In Fig. 7.8 we plot the heat capacity as a function of temperature. We see that the heat capacity has a finite jump at the critical temperature. It reaches a maximum value of $3Nk_B$ at $T = T_c$.

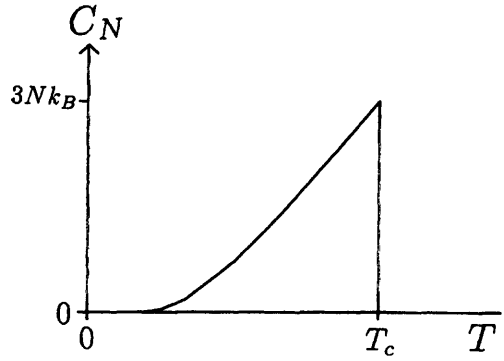


Fig. 7.8. A plot of the heat capacity, C_N, as a function of temperature in the neighborhood of the critical point.

The final quantity we wish to compute is the magnetic susceptibility, $\chi_{T,N}(B)$. The magnetic susceptibility is defined as

$$\chi_{T,N}(B) = \left(\frac{\partial\langle M\rangle}{\partial B}\right)_{T,N} = N\mu\left(\frac{\partial\langle s\rangle}{\partial B}\right)_{T,N}. \tag{7.99}$$

From Eq. (7.91) we can write

$$\left(\frac{\partial\langle s\rangle}{\partial B}\right)_{T,N} = \operatorname{sech}^2\left[\beta\frac{\nu\epsilon}{2}\langle s\rangle + \beta\mu B\right]\left[\beta\frac{\nu\epsilon}{2}\left(\frac{\partial\langle s\rangle}{\partial B}\right)_{T,N} + \beta\mu\right], \tag{7.100}$$

or

$$\left(\frac{\partial\langle s\rangle}{\partial B}\right)_{T,N} = \frac{2\beta\mu}{2\cosh^2\left[\beta\frac{\nu\epsilon}{2}\langle s\rangle + \beta\mu B\right] - \beta\nu\epsilon}. \tag{7.101}$$

The magnetic susceptibility, $\chi_{T,N}(B)$, is then given by

$$\chi_{T,N}(B) = \frac{2\beta N\mu^2}{2\cosh^2\left[\beta\frac{\nu\epsilon}{2}\langle s\rangle + \beta\mu B\right] - \beta\nu\epsilon}. \tag{7.102}$$

The magnetic susceptibility in the limit $B = 0$ is

$$\chi_{T,N}(0) = \frac{2\beta N\mu^2}{2\cosh^2\left[\beta\frac{\nu\epsilon}{2}\langle s\rangle\right] - \beta\nu\epsilon} = \frac{2N\mu^2}{\nu\epsilon}\frac{(T_c/T)}{\cosh^2(\langle s\rangle T_c/T) - T_c/T}, \tag{7.103}$$

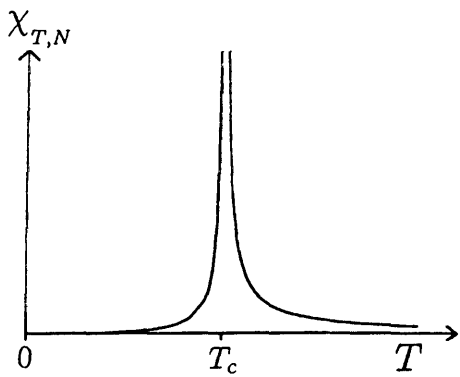


Fig. 7.9. A plot of the magnetic susceptibility, $\chi(0)_{T,N}$, as a function of temperature in the neighborhood of the critical point.

with $\langle s \rangle$ given by Eq. (7.92). Examination of Eq. (7.103) shows that the magnetic susceptibility has an infinite jump at the critical point. In Fig. 7.9, we plot $\chi_{T,N}(0)$ as a function of temperature.

The results we have obtained in this section for the thermodynamic properties of a spin lattice in the neighborhood of the phase transition are qualitatively similar to the results we obtained in Chapter 3 using mean field theories. Using statistical mechanics to obtain these results allows us to compute various constants that appear in the thermodynamic expressions in terms of microscopic interaction energies and magnetic moments. A generalization of mean field methods has been used by Suzuki to study critical phenomena [15]. As we shall see in Chapter 8, where we give some exact results for the two-dimensional spin lattice and use renormalization theory, mean field theory gives a rough qualitative picture of the phase transition, but it is not quantitatively correct.

7.G. THE GRAND CANONICAL ENSEMBLE

An open system can exchange both heat and matter with its surroundings and, therefore, both energy and particle number will fluctuate. For an open system in equilibrium, we fix both the average energy, $\langle E \rangle$, and the average particle number, $\langle N \rangle$. To obtain the equilibrium probability density in such a fluctuating environment, we use the method of Lagrange multipliers to extremize the Gibbs entropy subject to the following three constraints. We require that the normalization take the form

$$\mathrm{Tr}(\hat{\rho}) = 1. \tag{7.104}$$

We require that the average energy have a fixed value, $\langle E \rangle$, so that

$$\mathrm{Tr}(\hat{H}\hat{\rho}) = \langle E \rangle. \tag{7.105}$$

And finally, we require that the average particle number have a fixed value, $\langle N \rangle$, so that

$$\mathrm{Tr}(\hat{N}\hat{\rho}) = \langle N \rangle, \tag{7.106}$$

where $\hat{N}$ is the total particle number operator.

We can now find the probability density operator, $\hat{\rho}$, which extremizes the Gibbs entropy subject to the constraints, Eqs. (7.104)–(7.106). The extremization condition is

$$\begin{aligned} &\delta\{\mathrm{Tr}[\alpha_0\hat{\rho} + \alpha_E\hat{H}\hat{\rho} + \alpha_N\hat{N}\hat{\rho} - k_B\hat{\rho}\ln(\hat{\rho})]\} \\ &= \mathrm{Tr}[\{(\alpha_0 - k_B)\hat{I} + \alpha_E\hat{H} + \alpha_N\hat{N} - k_B\ln(\hat{\rho})\}\delta\hat{\rho}] = 0, \end{aligned} \tag{7.107}$$

where α_0, α_E, and α_N are Lagrange multipliers. Since $\delta\hat{\rho}$ is arbitrary, we have

$$(\alpha_0 - k_B)\hat{I} + \alpha_E\hat{H} + \alpha_N\hat{N} - k_B\ln(\hat{\rho}) = 0. \tag{7.108}$$

We can now use Eq. (7.108) and the three constraints, Eqs. (7.104)–(7.106) to determine the Lagrange multipliers. The normalization condition, Eq. (7.104), allows us to introduce the grand partition function,

$$Z(\alpha_E, \alpha_N) \equiv \exp\left(1 - \frac{\alpha_0}{k_B}\right) = \mathrm{Tr}\left[\exp\left(\frac{\alpha_E}{k_B}\hat{H} + \frac{\alpha_N}{k_B}\hat{N}\right)\right], \tag{7.109}$$

and relates α_0 to α_E and α_N. To determine α_E and α_N, let us multiply Eq. (7.108) by $\hat{\rho}$ and take the trace. We find

$$-k_B\ln[Z(\alpha_E, \alpha_N)] + \alpha_E\langle E\rangle + \alpha_N\langle N\rangle + S = 0. \tag{7.110}$$

If we compare Eq. (7.110) to the fundamental equation for the grand potential, $\Omega = U - TS - \mu' N$ (cf. Section 2.F.5), we can make the identifications, $\alpha_E = -1/T$ and $\alpha_N = \mu'/T$, and

$$\Omega(T, \mu') = -k_B T\ln[Z_\mu(T)]. \tag{7.111}$$

Equation (7.111) is the Fundamental Equation for the grand potential. It is written in terms of the *grand partition function*, which is defined as

$$Z_\mu(T) = e^{-\beta\Omega(T,\mu')} = \mathrm{Tr}(e^{-\beta(\hat{H}-\mu'\hat{N})}), \tag{7.112}$$

with $\beta = 1/k_B T$. The probability density operator can be written

$$\hat{\rho} = e^{-\beta(\hat{H}-\mu'\hat{N}-\Omega)} = \frac{e^{-\beta(\hat{H}-\mu'\hat{N})}}{\mathrm{Tr}(e^{-\beta(\hat{H}-\mu'\hat{N})})}. \tag{7.113}$$

Equation (7.113) is the probability density operator for the *grand canonical ensemble.* Equation (7.112) is the Fundamental Equation for an open system. While we have not written it explicitly, the grand potential will generally depend on a generalized displacement, X, whose form depends on the mechanical properties of the system being considered. For example, for a gas, X=V is the volume and for a magnetic system, $X = M$ is the magnetization. Once we know the grand partition function, we can compute the grand potential, and from it we can obtain all thermodynamic quantities. The entropy is given by $S = -(\partial\Omega/\partial T)_{X,\mu'}$.The generalized force is given by $Y = (\partial\Omega/\partial X)_{T,\mu'}$. The average particle number is given by $\langle N\rangle = -(\partial\Omega/\partial\mu')_{T,X}$. In exercise 7.6 we use the grand canonical ensemble to compute the thermodynamic properties of a gas of photons.

■ **EXERCISE 7.6** A cubic box of volume $V = L^3$ contains electromagnetic energy (photons) in equilibrium with the walls at temperature T (black-body variation). The allowed photon energies are determined by the standing waves formed by the electromagnetic field in the box. The photon energies are $\hbar\omega_i = \hbar c k_i$, where k_i is the wavevector of the ith standing wave. Compute the pressure of this photon gas. (Note that since photons have no mass, the gas has chemical potential, $\mu' = 0$.)

Answer: Since there are in infinite number of standing waves allowed, the grand partition function is

$$Z_\mu(T) = \sum_{n_1=0}^{\infty} \cdots \sum_{n_\infty=0}^{\infty} \exp\left(-\beta \sum_{i=1}^{\infty} n_i \hbar\omega_i\right) = \prod_{i=1}^{\infty} \left(\frac{1}{1 - e^{-\beta\hbar\omega_i}}\right). \quad (1)$$

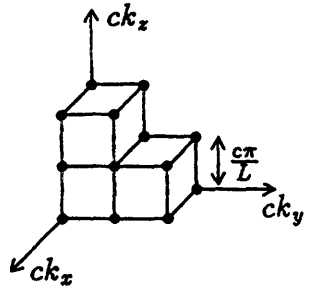
The grand potential is

$$\Omega = -PV = k_B T \sum_{i=1}^{\infty} \ln(1 - e^{-\beta\hbar\omega_i}). \quad (2)$$

We can change the summation to an integration in the following way. The standing waves have wavevectors, $\mathbf{k} = (n_x\pi/L)\mathbf{i} + (n_y\pi/L)\mathbf{j} + (n_z\pi/L)\mathbf{k}$. These correspond to allowed frequencies, ω, such that

$$\omega^2 = c^2\left[\left(\frac{n_x\pi}{L}\right)^2 + \left(\frac{n_y\pi}{L}\right)^2 + \left(\frac{n_z\pi}{L}\right)^2\right]. \quad (3)$$

If we imagine a lattice of allowed frequencies, $\omega = ck$, the spacing per point in ω space is $c\pi/L$ (see the figure below). The volume per point is $(c\pi/L)^3$. The number of points per unit volume is $(L/c\pi)^3$.



The number, ν of allowed frequencies less than some value ω is therefore

$$\nu = \frac{1}{8}\left(\frac{4}{3}\pi\omega^3\right)\left(\frac{L}{c\pi}\right)^3 = \frac{L^3\omega^3}{6c^3\pi^2}. \quad (4)$$

For each allowed frequency of the electromagnetic field, there are two

transverse modes. Thus, $\sum_{i=1}^{\infty} = 2\int d\nu = (L^3/\pi^2 c^3)\int_0^\infty \omega^2 d\omega$. The pressure therefore becomes

$$P = -\frac{k_B T}{\pi^2 c^3}\int_0^\infty \omega^2 d\omega \ln\left(1 - e^{-\beta\hbar\omega}\right). \tag{5}$$

If we integrate by parts, we find

$$P = \frac{\hbar}{3c^3\pi^2}\int_0^\infty \omega^3 d\omega \frac{1}{e^{-\beta\hbar\omega} - 1} = \frac{\pi^2 k_B^4 T^4}{45c^3\hbar^3} = \frac{1}{3}\sigma T^4, \tag{6}$$

where $\sigma = \pi^2 k_B^4/15c^3\hbar^3$ is the Stefan-Boltzmann constant.

In the grand canonical ensemble, the temperature, T, and chemical potential, μ', are fixed and the average energy, $U = \langle E\rangle$, and average particle number, $\langle N\rangle$, are fixed. However, because there can be a flow of energy and particles in and out of this system, it is important to know how large the fluctuations are. The derivation of the variance in energy fluctuations is similar to the derivation given in Section 7.D.1. Let us derive the variance in particle number fluctuations. We first write the normalization condition in the form

$$\mathrm{Tr}\left(e^{\beta[\Omega(T,\mu) - \hat{H} + \mu'\hat{N}]}\right) = 1. \tag{7.114}$$

If we differentiate Eq. (7.114) twice with respect to μ', we can obtain

$$\langle N^2\rangle - \langle N\rangle^2 = -k_B T\left(\frac{\partial^2\Omega}{\partial\mu'^2}\right)_{T,X} = k_B T\left(\frac{\partial\langle N\rangle}{\partial\mu'}\right)_{T,X}. \tag{7.115}$$

Thus, the fractional deviation behaves as

$$\frac{\sqrt{\langle N^2\rangle - \langle N\rangle^2}}{\langle N\rangle} \sim N^{-1/2}. \tag{7.116}$$

As the average number of particles increases, the size of the fluctuations in particle number comes small compared to the size of the average particle number. Most microstates will have a particle number approximately equal to the average number and we retrieve the canonical ensemble.

It is useful to write Eq. (7.115) in terms of the isothermal compressibility. From Eq. (2.6), $(\partial N/\partial\mu')_{T,V} = -(\partial N/\partial V)_{T,\mu'}(\partial V/\partial\mu')_{T,N}$. From Eq. (2.102), $(\partial\mu'/\partial V)_{T,N} = -(\partial P/\partial N)_{T,V}$. From Eq. (2.6), $(\partial P/\partial N)_{T,V} = -(\partial P/\partial V)_{T,N}(\partial V/\partial N)_{T,P}$. If we now combine these equations and note that $(\partial N/\partial V)_{T,\mu'} = (\partial N/\partial V)_{T,P} = \langle N\rangle/V$ since $\mu' = \mu'(T,P)$, we find

$$\langle N^2\rangle - \langle N\rangle^2 = k_B T\left(\frac{\partial\langle N\rangle}{\partial\mu'}\right)_{T,X} = -k_B T\frac{\langle N\rangle^2}{V^2}\left(\frac{\partial\langle V\rangle}{\partial P}\right)_{T,N} = \frac{k_B T\langle N\rangle^2}{V}\kappa_T. \tag{7.117}$$

Thus, the variance in particle number fluctuations is proportional to the isothermal compressibility. Near a critical point, the compressibility can become infinite and, therefore, fluctuations in the particle number (or density) become very large.

7.H. IDEAL QUANTUM GASES

When a collection of identical particles forms a gas, the particles must be regarded as indistinguishable. Therefore, at low temperatures, where the thermal wavelength of particles becomes large and overlapping of wave functions occurs, the statistics of the particles plays a crucial role in determining the thermodynamic behavior of the gas. All particles which are known today obey either Bose–Einstein or Fermi–Dirac statistics. At very low temperatures, Bose–Einstein and Fermi-Dirac gases behave in completely different ways because their different statistics introduce different kinds of correlations between particles even though they do not interact via Newtonian forces. At high temperatures, the statistics play no role and all ideal gases, regardless of statistics, behave in the same way.

When working with systems of identical particles, it is often easiest to use the grand cononical ensemble because then it is not necessary to conserve particle number. The grand canonical ensemble allows the number of particles in the system to fluctuate, but keeps the chemical potential fixed. This becomes especially useful when dealing with systems which can undergo a phase transition to a superfluid or superconducting state. For an ideal gas of identical particles each of mass m, the grand partition function can be written

$$Z_\mu(T, V) = \mathrm{Tr}[e^{-\beta(\hat{H}_0 - \mu'\hat{N})}], \tag{7.118}$$

where $\hat{H}_0$ is the kinetic energy operator and total particle number operator $\hat{N}$ is the number operator.

For an ideal gas, it is most convenient to evaluate the trace in the number representation since both the energy operator and the number operator are diagonal in that representation (cf. Appendix B). We shall assume that our gas is contained in a "box" with periodic boundary conditions. We will let the volume of the "box" be $V = L_x L_y L_z$, where L_x, L_y, and L_z are the lengths of the sides of the box in the x, y, and z directions, respectively. The momentum operator for a single particle can be written $\hat{\mathbf{p}} = \hbar\hat{\mathbf{k}}$, where $\hat{\mathbf{k}}$ is the wave-vector of the particle. For a "box" with periodic boundary conditions, the momentum operator has eigenvalues

$$\mathbf{p}_l = \hbar\left(\frac{2\pi l_x}{L_x}\mathbf{i} + \frac{2\pi l_y}{L_y}\mathbf{j} + \frac{2\pi l_z}{L_z}\mathbf{k}\right), \tag{7.119}$$

where l_x, l_y, and l_z are integers each ranging from $-\infty$ to ∞. Let us denote the

set of integers, $\boldsymbol{l} = (l_x, l_y, l_z)$. Each different choice of integers l_x, l_y, l_z corresponds to a possible state of the system. The kinetic energy operator for a single particle is $\hat{p}^2/2m$ and has eigenvalues

$$\frac{p_1^2}{2m} = \varepsilon \equiv \varepsilon_{l_x,l_y,l_z} = \frac{\hbar^2}{2m}\left(\frac{4\pi^2 l_x^2}{L_x^2} + \frac{4\pi^2 l_y^2}{L_y^2} + \frac{4\pi^2 l_z^2}{L_z^2}\right). \tag{7.120}$$

Let $n_l \equiv n_{l_x,l_y,l_z}$ denote the number of particles with momentum $\mathbf{p}_\mathbf{l}$. Then the kinetic energy operator can be written $\hat{H}_0 = \sum_l \hat{n}_l \varepsilon_l$, and the number operator can be written $\hat{N}_0 = \sum_l \hat{n}_l$. The summation, $\sum_l$, ranges over all possible values of the integers l_x, l_y, and l_z.

The difference between Bose–Einstein and Fermi–Dirac particles lies in the numbers of particles that can occupy a given momentum (and therefore kinetic energy) eigenstate. For a gas of identical Bose–Einstein particles there is no restriction on the number of particles that can have a given set of quantum numbers, l_x, l_y, and l_z. Therefore, the trace in Eq. (7.118) must include the possibility that any numbr of particles, $n_\mathbf{l}$, ranging from 0 to ∞, can occupy the momentum state, $\mathbf{p}_\mathbf{l}$. This will be true for each possible momentum state. Thus, for a Bose–Einstein gas the grand partition function is

$$Z_{BE}(T, V, \mu') = \prod_l \left[\sum_{n_l=0}^{\infty} \exp(-\beta n_l(\varepsilon_l - \mu'))\right]. \tag{7.121}$$

In Eq. (7.121), the product $\prod_\mathbf{l}(\Sigma_{n_\mathbf{l}=0}^{\infty})$ can be written more explicitly as

$$\prod_l \left(\sum_{n_l=0}^{\infty}\right) = \sum_{n_{-\infty,-\infty,-\infty}=0}^{\infty} \times \cdots \times \sum_{n_{-1,0,0}=0}^{\infty} \times \sum_{n_{0,0,0}=0}^{\infty} \times \sum_{n_{1,0,0}=0}^{\infty} \times \cdots \times \sum_{n_{\infty,\infty,\infty}=0}^{\infty} \tag{7.122}$$

In Eq. (7.121) we have not explicitly included the possibility that the particles have (integer) spin or other internal degrees of freedom. However, it is straightforward to include them.

For a gas of identical Fermi–Dirac particles, again, each different set of quantum numbers, l_x, l_y, and l_z, corresponds to a state of the system. However, for Fermi–Dirac particles the Pauli exclusion principle restricts the number of particles, $n_\mathbf{l}$, which can occupy a given state, $\mathbf{l}$, to $n_\mathbf{l} = 0$ or $n_\mathbf{l} = 1$. Thus, for a Fermi–Dirac gas the grand partition function becomes

$$Z_{FD}(T, V, \mu') = \prod_l \left[\sum_{n_l=0}^{1} \exp(-\beta n_l(\varepsilon_l - \mu'))\right]. \tag{7.123}$$

In writing the partition function for the Fermi–Dirac gas, we have not explicitly

included the (half-integer) spin or other internal degrees of the freedom of the particles. We will do this below in Section 7.H.2, where we describe the behavior of Fermi–Dirac gases in more detail.

7.H.1. Bose–Einstein Gases

The grand partition function for a Bose–Einstein ideal gas is given by Eq. (7.121). It implicitly assumes that the bosons have spin $s = 0$, so spin degrees of freedom do not have to be taken into account. If we expand the exponential into a product of exponentials, each depending on a different value of $\boldsymbol{l}$, then we can rearrange terms in Eq. (7.121) and write the grand partition function in the form

$$Z_{BE}(T, V, \mu') = \prod_{\boldsymbol{l}} \left(\sum_{n_{\boldsymbol{l}}=0}^{\infty} e^{-\beta n_{\boldsymbol{l}}(\varepsilon_{\boldsymbol{l}} - \mu')} \right) = \prod_{\boldsymbol{l}} \left(\frac{1}{1 - e^{-\beta(\varepsilon_{\boldsymbol{l}} - \mu')}} \right). \tag{7.124}$$

From Eq. (8.B.52), the grand potential can be written

$$\Omega_{BE}(T, V, \mu') = -k_B T \ln[Z_{BE}(T, V, \mu')] = k_B T \sum_{\boldsymbol{l}} \ln(1 - e^{-\beta(\varepsilon_{\boldsymbol{l}} - \mu')}). \tag{7.125}$$

The average number of particles in the gas is

$$\langle N \rangle = -\left(\frac{\partial \Omega_{BE}}{\partial \mu'} \right)_{T,V} = \sum_{\boldsymbol{l}} \left(\frac{1}{e^{\beta(\varepsilon_{\boldsymbol{l}} - \mu')^{-1}}} \right) = \sum_{\boldsymbol{l}} \langle n_{\boldsymbol{l}} \rangle. \tag{7.126}$$

where $\langle n_{\boldsymbol{l}} \rangle$ is the average number of particles in the state $\boldsymbol{l}$ and is defined

$$\langle n_{\boldsymbol{l}} \rangle = \left(\frac{1}{e^{\beta(\varepsilon_{\boldsymbol{l}} - \mu')} - 1} \right) = \left(\frac{z}{e^{\beta \varepsilon_{\boldsymbol{l}}} - z} \right). \tag{7.127}$$

The quantity $z = e^{\beta \mu'}$ is called the *fugacity*.

The ideal Bose–Einstein gas is particularly interesting because it can undergo a phase transition. We get our first indication of this by looking at the way particles are distributed among the allowed states. Let us first note that since the exponential $e^{\beta \varepsilon_{\boldsymbol{l}}}$ can only have a range of values $1 \leq e^{\beta \varepsilon_{\boldsymbol{l}}} \leq \infty$, the fugacity must have values $0 \leq z \leq 1$. Otherwise, $\langle n_{\boldsymbol{l}} \rangle$ could become negative, and that would be unphysical since $\langle n_{\boldsymbol{l}} \rangle$ is an average particle number. Thus, for a Bose–Einstein gas the chemical potential, $\mu' = k_B T \ln(z)$, must be negative or zero. This means that it is "easy" to add additional particles to the gas. Let us notice something else about the average particle number, $\langle n_{\boldsymbol{l}} \rangle$. For the state with quantum numbers $\boldsymbol{l} = \boldsymbol{0} \equiv (l_x = 0, l_y = 0, l_z = 0)$, the energy, $\varepsilon_{\boldsymbol{0}} = 0$, and the

average particle number, $\langle n_0 \rangle$, can become very large as $z \to 1$, since

$$\langle n_0 \rangle = \left(\frac{z}{1-z} \right). \tag{7.128}$$

The fact that $\lim_{z \to 1} \langle n_0 \rangle = \infty$ means that the state with zero energy can become macroscopically occupied as $z \to 1$. This is precisely what happens at the phase transition.

Let us now compute some thermodynamic quantities for the Bose–Einstein gas. The summations in Eqs. (7.125) and (7.126) cannot be done explicitly, but for large enough volume, V, we can change the summation, $\sum_l$, to an integration. For simplicity, let us assume the gas is in a cubic box so that $L_x = L_y = L_z = L$ and $V = L_3$. We first compute the average particle number, $\langle N \rangle$, which from Eqs. (7.120) and (7.126) takes the form

$$\langle N \rangle = \sum_{l_x=-\infty}^{\infty} \sum_{l_y=-\infty}^{\infty} \sum_{l_z=-\infty}^{\infty} \left(\frac{z}{\exp[\frac{\beta}{2m}(p_x^2 + p_y^2 + p_z^2)] - z} \right), \tag{7.129}$$

where $p_x = 2\pi\hbar l_x/L$, $p_y = 2\pi\hbar l_y/L$, and $p_z = 2\pi\hbar l_z/L$. It is useful to change the summations in Eq. (7.129) to integrations. However, the term in the sum with $l_x = 0, l_y = 0$, and $l_z = 0$ can become infinite as $z \to 1$. Therefore it must be removed from the sum before we change the sum to an integration. The allowed values of the momentum, $\mathbf{p}$, form a grid of points located at $p_x = 2\pi\hbar l_x/L$, $p_y = 2\pi\hbar l_y/L$, and $p_z = 2\pi\hbar l_z/L$ in $\mathbf{p}$ space. If we explicitly remove the point at $p_x = 0, p_y = 0$, and $p_z = 0$, and change from Cartesian to spherical coordinates, we obtain

$$\sum_l{}' \approx \int' dl = \frac{V}{(2\pi\hbar)^3} \int' d\mathbf{p} = \frac{4\pi V}{(2\pi\hbar)^3} \int_{2\pi\hbar/L}^{\infty} p^2 dp. \tag{7.130}$$

The summation, $\sum_l{}'$, and integration, $\int' dl$, exclude the point at $l_x = 0$, $l_y = 0$, and $l_z = 0$. The integration, $\int' d\mathbf{p}$, excludes a sphere of radius $p < 2\pi\hbar/L$ about the origin. We can now rewrite the average particle number as

$$\langle N \rangle = \frac{z}{1-z} + \frac{4\pi V}{(2\pi\hbar)^3} \int_{2\pi\hbar/L}^{\infty} p^2 dp \left(\frac{z}{\exp(\beta p^2/2m) - z} \right). \tag{7.131}$$

Similarly, we can write the grand potential in the form

$$\Omega_{BE}(T, V, \mu) = k_B T \ln(1-z) + \frac{4\pi V k_B T}{(2\pi\hbar)^3} \int_{2\pi\hbar/L}^{\infty} p^2 dp \ln[1 - z\exp(-\beta p^2/2m)], \tag{7.132}$$

where we again have separated out the point at the origin.

It is useful to introduce dimensionless variables. If we let $x^2 = \beta p^2/2m$, the grand potential becomes

$$\Omega_{BE}(T, V, \mu) = k_B T \ln(1 - z) + \frac{4k_B TV}{\lambda_T^3 \sqrt{\pi}} \int_{\lambda_T \sqrt{\pi}/L}^{\infty} x^2 dx \ln[1 - ze^{-x^2}] \quad (7.133)$$

and the average particle number becomes

$$\langle N \rangle = \frac{z}{1 - z} + \frac{4V}{\lambda_T^3 \sqrt{\pi}} \int_{\lambda_T \sqrt{\pi}/L}^{\infty} x^2 dx \left(\frac{z}{e^{x^2} - z} \right), \quad (7.134)$$

where

$$\lambda_T = \left(\frac{2\pi\hbar^2}{mk_B T} \right)^{1/2} \quad (7.135)$$

is the *thermal wavelength.* The thermal wavelength is the deBroglie wavelength of a quantum particle with kinetic energy $k_B T$, and it is a measure of the spread of a wavefunction of the particles. As long as λ_T is much less than the average interparticle spacing, the quantum statistics of the particles will not have a significant influence on the thermodynamic properties of the gas. However, when λ_T becomes of the same order as the average interparticle spacing, the thermodynamic properties of the gas will begin to depend strongly on whether the particles are bosons or fermions.

Let us now write Eqs. (7.133) and (7.134) in terms of intensive variables and examine the volume dependence of various terms. From Eq. (2.122), the pressure can be written

$$P = -\frac{\Omega_{BE}}{V} = -\frac{k_B T}{V} \ln(1 - z) + \frac{k_B T}{\lambda_T^3} g_{5/2}(z) - I_P \left(z, \frac{\lambda_T \sqrt{\pi}}{L} \right), \quad (7.136)$$

where

$$g_{5/2}(z) = -\frac{4}{\sqrt{\pi}} \int_0^{\infty} x^2 dx \ln[1 - ze^{-x^2}] = \sum_{\alpha=1}^{\infty} \frac{z^\alpha}{\alpha^{5/2}} \quad (7.137)$$

and

$$I_P(z, a) = -\frac{4k_B T}{\lambda_T^3 \sqrt{\pi}} \int_0^a x^2 dx \ln[1 - ze^{-x^2}]. \quad (7.138)$$

In Eq. (7.137), the summation is obtained by expanding the integrand in powers of z and integrating each term.

We can also rearrange Eq. (7.134) to obtain an equation for the average particle density,

$$\langle n\rangle = \frac{\langle N\rangle}{V} = \frac{1}{V}\frac{z}{1-z} + \frac{1}{\lambda_T^3} g_{3/2}(z) - I_n\left(z, \frac{\lambda_T\sqrt{\pi}}{L}\right), \tag{7.139}$$

where

$$g_{3/2}(z) = z\frac{d}{dz} g_{5/2}(z) = \frac{4}{\sqrt{\pi}}\int_0^\infty x^2 dx \left(\frac{z}{e^{x^2} - z}\right) = \sum_{\alpha=1}^{\infty} \frac{z^\alpha}{\alpha^{3/2}} \tag{7.140}$$

and

$$I_n(z, a) = \frac{4}{\sqrt{\pi}\lambda_T^3}\int_0^a x^2 dx \left(\frac{z}{e^{x^2} - z}\right). \tag{7.141}$$

It is straightforward to show $\lim_{a\to 0} I_P(1, a) = 0.$ and $\lim_{a\to 0} I_n(1, a) = 0.$ Therefore, in changing from the summation to the integration, if the singular term $\boldsymbol{l} = \mathbf{0}$ had not been explicitly removed, its effect would have been lost.

The quantities $g_{5/2}(z)$ and $g_{3/2}(z)$, which appear in Eqs. (7.136) and (7.139), are well-behaved functions of z. We plot them in Fig. 7.10. Both $g_{5/2}(z)$ and $g_{3/2}(z)$ remain bounded and approach finite values,

$$g_{5/2}(1) - \zeta\left(\frac{5}{2}\right) \approx 1.342\cdots \quad \text{and} \quad g_{3/2}(1) = \zeta\left(\frac{3}{2}\right) \approx 2.612\cdots, \tag{7.142}$$

as $z \to 1$, where $\zeta(\frac{5}{2})$ and $\zeta(\frac{3}{2})$ are Riemann zeta functions.

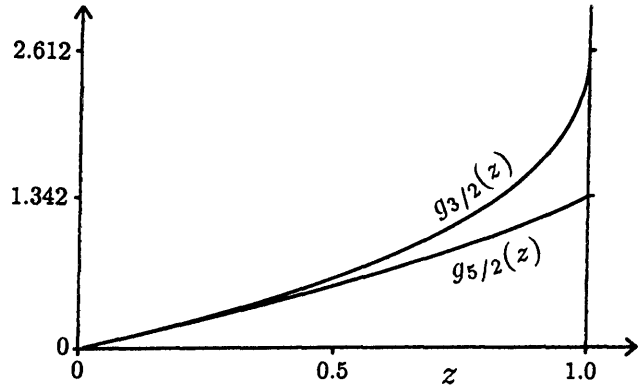


Fig. 7.10. Plots of $g_{5/2}(z)$ and $g_{3/2}(z)$ versus z.

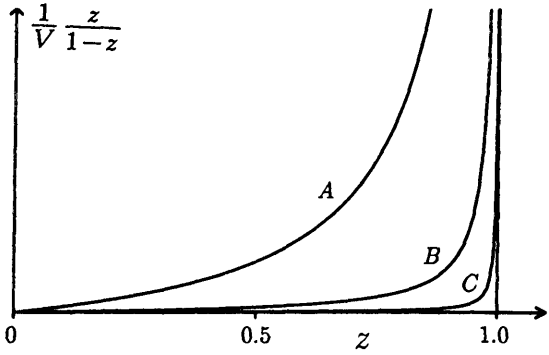


Fig. 7.11. Plots of $(1/V)[z/(1-z)]$ versus z for (A) $V = 10$, (B) $V = 100$, (C) $V = 1000$.

Finally, let us examine the functions $-(1/V)\ln(1-z)$ and $(1/V)[z/(1-z)]$ which appear in Eqs. (7.136) and (7.139). In Eq. (7.139), the intensive variables $\langle n \rangle$ and T appear explicitly. Let us fix $\langle n \rangle$ and T and let $V \to \infty$ and $z \to 1$. In the neighborhood of $z = 1$, we will write $z = 1 - 1/(n_0 V)$, where n_0 is a constant, so $z \to 1$ in a systematic manner as $V \to \infty$. Then it is easy to see that

$$\lim_{V\to\infty}\left(-\frac{1}{V}\ln(1-z(V))\right) = 0 \quad \text{and} \quad \lim_{V\to\infty}\left(\frac{1}{V}\frac{z(V)}{1-z(V)}\right) = n_0. \tag{7.143}$$

Thus, in the limit $V \to \infty$, we can neglect the contribution to pressure due to the term $-(1/V)\ln(1-z)$, but we must retain the contribution to the average particle density due to the term $(1/V)[z/(1-z)]$. Let us now examine the behavior of the function $(1/V)[z/(1-z)]$. In Fig. 7.11 we plot $(1/V)[z/(1-z)]$, as a function of z for increasing values of the volume, V. Note that for any given value V, it always becomes infinite as $z \to 1$. The larger the volume, the closer z must be to $z = 1$ before the term $(1/V)[z/(1-z)]$ becomes significant.

Let us now take the thermodynamic limit in Eqs. (7.136) and (7.139). We let $V \to \infty$ and $\langle N \rangle \to \infty$ so that $\langle n \rangle = \langle N \rangle / V$ remains finite. The pressure then takes the form

$$P = \begin{cases} \dfrac{k_B T}{\lambda_T^3} g_{5/2}(z) & \text{if } z < 1, \\ \dfrac{k_B T}{\lambda_T^3} g_{5/2}(1) & \text{if } z = 1. \end{cases} \tag{7.144}$$

The average particle density takes the form

$$\langle n \rangle = \frac{\langle N \rangle}{V} = \begin{cases} \dfrac{1}{\lambda_T^3} g_{3/2}(z) & \text{if } z < 1, \\ n_0 + \dfrac{1}{\lambda_T^3} g_{3/2}(1) & \text{if } z = 1. \end{cases} \tag{7.145}$$

A somewhat exaggerated plot of $\langle n \rangle \lambda_T^3, n_0 \lambda_T^3$, and $g_{3/2}(z)$ as a function of z is shown in Fig. 7.12. The plot is actually done at large but finite volume, so the growth of $n_0 \lambda_T^3$ can be seen more clearly. The main contribution to the growth of the quantity $\langle n \rangle \lambda_T^3$ comes from $g_{3/2}(z)$ until z approaches $z = 1$. Then as $z \to 1, g_{3/2}(z)$ approaches a constant and $n_0 \lambda_T^3$ determines the further growth of $\langle n \rangle \lambda_T^3$. This is called *Bose–Einstein condensation*. What we are seeing as $z \to 1$ is the macroscopic condensation of particles into lowest energy state of the gas. The number density, n_0, of particles in the zero energy state, ε_0, becomes macroscopic in size.

In the thermodynamic limit, Bose–Einstein condensation begins to occur when the fugacity, z, equals 1 (or when the chemical potential $\mu'(T, \langle n \rangle) = k_B T \ln(z) = 0$). Therefore, Bose–Einstein condensation begins to occur when the temperature and average particle number satisfy the condition

$$\langle n \rangle \lambda_T^3 = g_{3/2}(1) \approx 2.612 \tag{7.146}$$

[cf. Eq. (7.145)]. Equation (7.146) enables us to write the critical particle density, $\langle n \rangle_c$ (the particle density at which condensation occurs), as a function

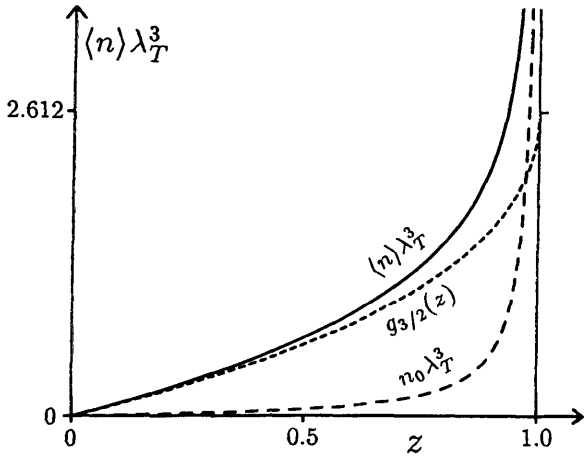


Fig. 7.12. Plots of $\langle n \rangle \lambda_T^3$, $g_{3/2}(z)$, and $n_0 \lambda_T^3$ versus z. (The contribution of $n_0 \lambda_T^3$ for $z < 1$ has been exaggerated by taking $V = 100$ rather than $V = \infty$.)

of temperature:

$$\langle n\rangle_c = \frac{1}{\langle v\rangle_c} = \frac{g_{3/2}(1)}{\lambda_T^3} \approx 2.612\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2}, \tag{7.147}$$

where $\langle v\rangle_c$ is the critical volume per particle. The critical temperature, T_c (the temperature at which condensation occurs), as a function of particle density is given by

$$\lambda_{T_c}^3 = \frac{g_{3/2}(1)}{\langle n\rangle} \quad \text{or} \quad T_c = \left(\frac{2\pi\hbar^2}{mk_B}\right)\left(\frac{\langle n\rangle}{g_{3/2}(1)}\right)^{2/3} \approx \left(\frac{2\pi\hbar^2}{mk_B}\right)\left(\frac{\langle n\rangle}{2.612}\right)^{2/3}. \tag{7.148}$$

The order parameter, η, for Bose–Einstein condensation is the fraction of particles in the condensed phase, $\eta = n_0/\langle n\rangle$. From Eqs. (7.145) and (7.148), we can write

$$\eta = \frac{n_0}{\langle n\rangle} = 1 - \frac{g_{3/2}(1)}{\langle n\rangle\lambda_T^3} = 1 - \frac{\lambda_{T_c}^3}{\lambda_T^3} = 1 - \left(\frac{T}{T_c}\right)^{3/2}. \tag{7.149}$$

A plot of the order parameter as a function of temperature is given in Fig. 7.13.

Equation (7.146) also determines the shape of the coexistence curve between the "normal" phase and the "condensed" phase of the gas. From Equation (7.144), we see that for particle densities, $\langle n\rangle > \langle n\rangle_c (\langle v\rangle < \langle v\rangle_c)$, the pressure

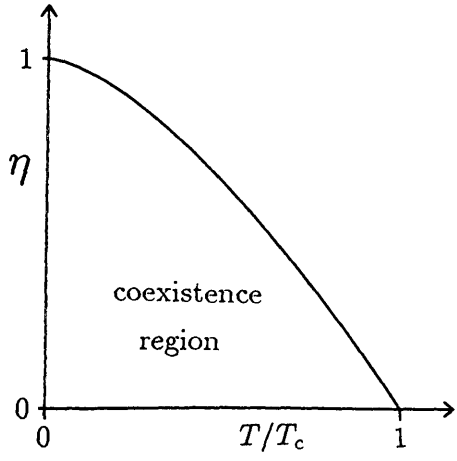


Fig. 7.13. A plot of the order parameter, $\eta = n_0/\langle n\rangle$, versus temperature, T, for Bose–Einstein condensation.

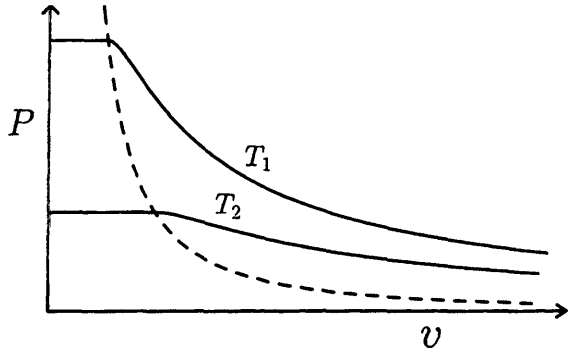


Fig. 7.14. A plot of the coexistence curve (dashed line) and some isotherms in the $P - v$ plane for the phase transition in a Bose–Einstein gas.

becomes independent of particle density. If we now use Eq. (7.147), we can write the critical pressure, P_c, as a function of the critical volume per particle, $\langle v \rangle_c$:

$$P_c = \frac{2\pi\hbar^2 g_{5/2}(1)}{m(g_{3/2}(1))^{5/3}} \frac{1}{\langle v \rangle_c^{5/3}}. \tag{7.150}$$

A plot of the coexistence curve, Eq. (7.150), together with some isotherms in the P–v plane, is given in Fig. 7.14. The region under the dashed curve is the coexistence region, the region where both condensed particles and non-condensed particles can coexist.

Another quantity of great interest in the neighborhood of a phase transition is the heat capacity. From Eq. (2.127), the entropy per unit volume is $s = (\partial S/\partial V)_{T,\mu'} = (\partial P/\partial T)_{V,\mu'}$ ($s = (\partial S/\partial V)_{T,\mu'}$ only if the gas is composed of single type of particle). Therefore, from Eq. (7.144) we can compute the entropy and we obtain

$$s = \left(\frac{\partial P}{\partial T}\right)_{V,\mu'} = \begin{cases} k_B \frac{5}{2} \frac{1}{\lambda_T^3} g_{5/2}(z) - k_B \langle n \rangle \ln(z) & \text{if } z < 1, \\ k_B \frac{5}{2} \frac{1}{\lambda_T^3} g_{5/2}(1) & \text{if } z = 1, \end{cases} \tag{7.151}$$

where we have made use of Eq. (7.145). Given Eq. (7.151) for the entropy density, we can now compute the heat capacity/volume at constant density, $c_n = T(\partial s/\partial T)_n$. It is important to note that in order to compute c_n, we hold n fixed and not μ'. The computation of c_n requires the following quantity,

$$\left(\frac{\partial \beta\mu'}{\partial T}\right)_n = -\frac{3}{2T} \frac{g_{3/2}(z)}{g_{1/2}(z)}. \tag{7.152}$$

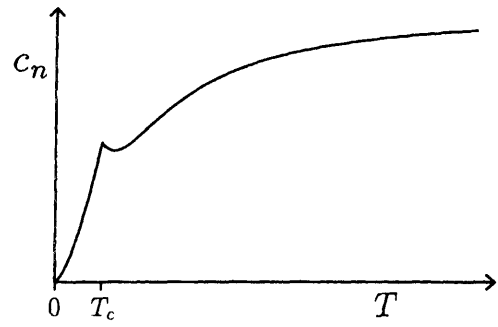


Fig. 7.15. A plot of the heat capacity per unit volume for a Bose–Einstein ideal gas as a function of the temperature. The temperature, T_c, is the critical temperature for the onset of Bose–Einstein condensation.

Equation (7.152) is obtained by differentiating Eq. (7.145) with respect to T holding $\langle n \rangle$ fixed. The computation of c_n is then straightforward. We find

$$c_n = T\left(\frac{\partial s}{\partial T}\right)_n = \begin{cases} k_B \frac{15}{4} \frac{1}{\lambda_T^3} g_{5/2}(z) - \langle n \rangle k_B \frac{9}{4} \frac{g_{3/2}(z)}{g_{1/2}(z)} & \text{if } z < 1, \\ k_B \frac{15}{4} \frac{1}{\lambda_T^3} g_{5/2}(1), & \text{if } z = 1. \end{cases} \tag{7.153}$$

In Fig. 7.15 we plot the heat capacity per unit volume for the Bose–Einstein gas. The location of the critical point is clear in the plot. Also, the Bose–Einstein gas clearly obeys the third law of thermodynamics. In the limit $T \to 0\,K$, the entropy approaches zero with temperature dependence, $T^{3/2}$. In the high-temperature limit, the heat capacity approaches a constant value as we would expect for a classical ideal gas. In the high-temperature limit the effect of statistics becomes negligible. The phase transition in an ideal Bose–Einstein gas in entirely the result of statistics. As we shall see, the Fermi–Dirac gas exhibits no such transition.

The high-temperature behavior of the Bose–Einstein gas is readily obtained. At high temperature, $z \to 0$ and $g_{5/2}(z) \approx g_{3/2}(z) \approx g_{1/2}(z) = z$. From Eq. (7.145) we obtain

$$\langle n \rangle = \frac{\langle N \rangle}{V} = \frac{z}{\lambda_T^3} = \left(\frac{m k_B T}{2\pi\hbar^2}\right)^{3/2} e^{\beta\mu}, \tag{7.154}$$

for the particle density, and from Eq. (7.144) we obtain

$$P = \frac{k_B T z}{\lambda_T^3} = \frac{\langle N \rangle k_B T}{V}. \tag{7.155}$$

for the pressure. From Eq. (7.153) we obtain

$$c_n = \frac{15k_B z}{4\lambda_T^3} - \frac{9k_B\langle N\rangle}{4V} = \frac{3}{2}\frac{\langle N\rangle k_B}{V} \tag{7.156}$$

for the heat capacity per unit volume. Thus, at high temperature the Bose–Einstein gas behaves like an ideal classical gas.

■ **EXERCISE 7.7.** Compute the variance, $\langle (N - \langle N\rangle)^2\rangle$, in the number of particles for an ideal boson gas (below the critical temperature) in the neighborhood of $T = 0K$.

Answer: The variance in the particle number is given by

$$\langle (N - \langle N\rangle)^2\rangle = \frac{1}{\beta}\left(\frac{\partial\langle N\rangle}{\partial\mu'}\right)_{T,V}. \tag{1}$$

The average number of particles in a boson gas below the critical temperature is

$$\langle N\rangle = \frac{z}{1-z} + \frac{V}{\lambda_T^3} g_{3/2}(z), \tag{2}$$

where $g_{3/2}(z) = \Sigma_{\alpha=1}^{\infty} \frac{z^\alpha}{\alpha^{3/2}}$. The variance is then

$$\langle (N - \langle N\rangle)^2\rangle = \frac{z}{1-z} + \left(\frac{z}{1-z}\right)^2 + \frac{V}{\lambda_T^3} g_{1/2}(z) \geq \langle N\rangle + \langle N\rangle^2, \tag{3}$$

For an ideal boson gas at low temperature, the particle number distribution has a huge variance so it is not possible to give good predictions about how many particles are in the system at any given instant.

7.H.2. Fermi–Dirac Ideal Gases

We shall now examine the thermodynamic behavior of a gas of identical, non-interacting spin $s = \frac{1}{2}$ particles of mass m. For simplicity, we shall assume the gas is in a cubic box so $L_x = L_y = L_z = L$ and we shall assume periodic boundary conditions. When we include the effects of spin we must generalize the expression for the grand partition function given in Eq. (7.123). Spin $\frac{1}{2}$ particles can exist in two spin states, $s_z = \pm\frac{1}{2}\hbar$. Therefore, each momentum state can have two particles, one particle for each of the two spin states, and still not violate the Pauli exclusion principle. We will let $n_{l,\sigma}$ denote the number of particles with quantum numbers $\boldsymbol{l} = (l_x, l_y, l_z)$ and spin σ, where $\sigma = \uparrow (\downarrow)$ for

$s_z = +\frac{1}{2}\hbar(-\frac{1}{2}\hbar)$. The grand partition function takes the form

$$Z_{FD}(T,V,\mu') = \prod_{l=0}^{\infty}\left(\sum_{n_{l\uparrow}=0}^{1} e^{-\beta n_{l,\uparrow}(\varepsilon_l-\mu')} \sum_{n_{l,\downarrow}=0}^{1} e^{-\beta n_{l,\downarrow}(\varepsilon_l-\mu')}\right)$$
$$= \prod_{l}(1+e^{-\beta(\varepsilon_l-\mu')})^2. \tag{7.157}$$

The power of 2 is due to the fact that there are two possible spin states for each set of quantum numbers, l. If we are dealing with a gas of spin-s fermions, then there will be $g = 2s + 1$ spin states for each value of l and the partition function is given by

$$Z_{FD}(T,V,\mu) = \prod_{l}(1+e^{-\beta(\varepsilon_l-\mu')})^g. \tag{7.158}$$

The grand potential is given y [cf. Eq. (8.B.52)]

$$\Omega_{FD}(T,V,\mu') = -k_BT\ln[Z_{FD}(T,V,\mu')] = -k_BTg\sum_{l}\ln(1+e^{-\beta(\varepsilon_l-\mu')}), \tag{7.159}$$

where $g = 2$ for spin-$\frac{1}{2}$ particles. The average number of particles in the gas is

$$\langle N\rangle = -\left(\frac{\partial\Omega_{FD}}{\partial\mu'}\right)_{T,V} = \sum_{l}\left(\frac{g}{e^{\beta(\varepsilon_l-\mu')}+1}\right) = \sum_{l}\langle n_l\rangle, \tag{7.160}$$

where $\langle n_l\rangle$, the average number of particles with quantum numbers l, is defined as

$$\langle n_l\rangle = \left(\frac{g}{e^{\beta(\varepsilon_l-\mu')}+1}\right) = \left(\frac{g_z}{e^{\beta\varepsilon_l}+z}\right). \tag{7.161}$$

In Eq. (7.161) the quantity $z = e^{\beta\mu'}$ is the fugacity. For Fermi–Dirac particles, the average particle number has no possibility of diverging. The fugacity can take on the entire range of values $0 \le z \le \infty$, and the average particle number can take on a range of value $0 \le \langle n_l\rangle \le g$. In Fig. 7.16 we plot $\langle n_l\rangle$ as a function of ε_l at low temperature (solid line) and at $T = 0$K (dashed line). We see that at low temperature the particles completely fill all the states with lowest energy. Only those states at higher energy are partly occupied. At zero temperature, all states below a cutoff energy, $\varepsilon_l = \varepsilon_f = \mu_0$, is called the *Fermi energy*. The momentum, $p_f = \sqrt{2m\varepsilon_f}$, is called the *Fermi momentum*. The distribution of particles in momentum space at low temperature is like a "sea" with all the lower states filled with particles. Only particles in states near the "top" of the

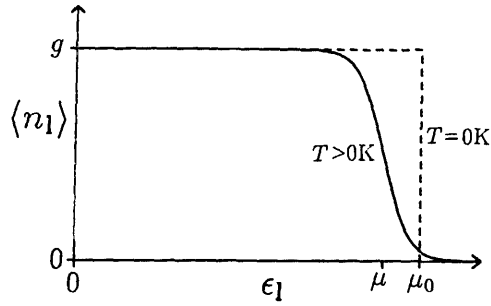


Fig. 7.16. Plots of the average occupation number, $\langle n_l \rangle$, as a function of energy, ε_l, at very low temperature. The solid line is a plot for $T > 0$ K, and the dashed line is a plot for $T = 0$ K. μ is the chemical potential.

"sea" can change their state. For this reason this distribution of particles is called the *Fermi sea.*

Let us now compute the thermodynamic properties of the Fermi–Dirac gas. For large enough volume, V, we can again change the summation, Σ_l, to an integration,

$$\sum_l \approx \frac{4\pi V}{(2\pi\hbar)^3} \int_0^\infty p^2 dp \tag{7.162}$$

[cf. Eq. (7.130)]. For the Fermi–Dirac gas there are no singular terms to remove from the summation before we approximate the sum, Σ_l, by an integral. Therefore, the magnitude of the momentum, p, in Eq. (7.162) ranges from 0 to ∞. The grand potential takes the form

$$\Omega_{FD}(T, V, \mu) = -PV = -\frac{4\pi k_B T V}{(2\pi\hbar)^3} \int_0^\infty p^2 dp \ln[1 + ze^{\beta p^2/2m}]. \tag{7.163}$$

Similarly, the average particle number takes the form

$$\langle N \rangle = \frac{4\pi g V}{(2\pi\hbar)^3} \int_0^\infty p^2 dp \left(\frac{z}{e^{\beta p^2/2m} + z} \right). \tag{7.164}$$

Let us now make the change of variables, $x^2 = \beta p^2/2m$, in Eqs. (7.163) and (7.164). Then the pressure of the Fermi–Dirac gas can be written

$$P = -\frac{\Omega_{FD}}{V} = \frac{g k_B T}{\lambda_T^3} f_{5/2}(z), \tag{7.165}$$

where λ_T is the thermal wavelength [cf. Eq. (7.135)] and the function $f_{5/2}(z)$ is

defined as

$$f_{5/2}(z) = \frac{4}{\sqrt{\pi}} \int_0^\infty x^2 dx \ln[1 + ze^{-x^2}] = \sum_{\alpha=1}^{\infty} (-1)^{\alpha+1} \frac{z^\alpha}{\alpha^{5/2}}. \tag{7.166}$$

The average particle density can be written

$$\langle n \rangle = \frac{\langle N \rangle}{V} = \frac{g}{\lambda_T^3} f_{3/2}(z), \tag{7.167}$$

where

$$f_{3/2}(z) = z \frac{d}{dz} f_{5/2}(z) = \frac{4}{\sqrt{\pi}} \int_0^\infty x^2 dx \left(\frac{z}{e^{x^2} + z} \right) = \sum_{\alpha=1}^{\infty} (-1)^{\alpha+1} \frac{z^\alpha}{\alpha^{3/2}}. \tag{7.168}$$

In Fig. 7.17 we plot $f_{5/2}(z)$ and $f_{3/2}(z)$ as a function of z.

It is interesting to compare the pressure of an ideal Fermi gas with that of an ideal classical gas and an ideal Bose–Einstein gas. In Fig. 7.18 we plot P versus the average volume per particle, $v = \langle n \rangle^{-1}$ and show one isotherm of the same temperature for each gas. For the Fermi–Dirac gas we set $g = 1$ so we are comparing only the effect of statistics. The pressure of the Bose–Einstein gas is dramatically lower than the classical or Fermi–Dirac gas for small v. This happens because in a Bose–Einstein gas at low v (below the critical volume per particle) a macroscopic number of particles condense into the zero momentum state and can no longer contribute to the pressure. The pressure of the Fermi–Dirac gas, on the other hand, always lies a little above that of the classical gas. This happens because for a Fermi–Dirac gas only one or zero particles can occupy a given momentum state, whereas in a classical gas any number can occupy a given momentum state. As a result, when comparing a Fermi–Dirac ideal gas to a classical ideal gas with the same particle density, $\langle n \rangle = v^{-1}$, the

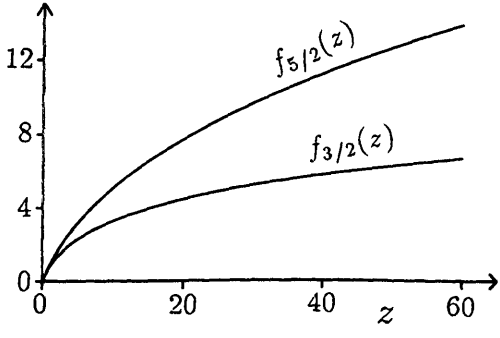


Fig. 7.17. Plots of $f_{5/2}(z)$ and $f_{3/2}(z)$ versus z.

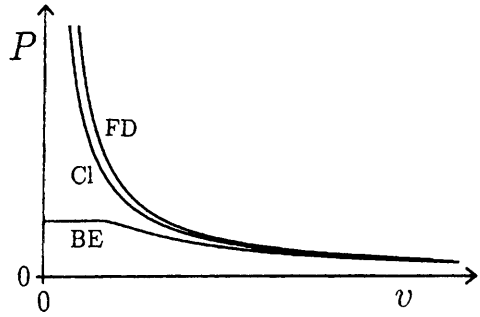


Fig. 7.18. Plots of the pressure of a Fermi–Dirac (FD), a Bose–Einstein (BE), and a classical (Cl) ideal gas as a function of volume per particle assuming the particles have the same mass and neglecting spin. One isotherm for each gas is shown. The temperatures of the three isotherms are the same.

Fermi–Dirac gas will contain more particles at higher momentum. The Fermi–Dirac gas will therefore tend to have a higher pressure than the classical gas.

It is interesting also to examine the behavior of the quantity, $\langle n \rangle \lambda_T^3$, as a function of the chemical potential, μ'. In Fig. 7.19 we plot $\langle n \rangle \lambda_T^3$ versus the product, $\beta\mu'$, for both a Fermi–Dirac and Bose–Einstein ideal gas. We see that the chemical potential of the Bose–Einstein gas remains negative and that the dominant growth in $\langle n \rangle \lambda_T^3$ occurs as $\mu' \to 0$. For the Fermi–Dirac gas the product, $\beta\mu'$, can be positive or negative and the dominant growth in $\langle n \rangle \lambda_T^3$ occurs when $\beta\mu'$ is positive and growing in value. As we shall see below when we focus on behavior of the Fermi–Dirac gas in the neighorhood of $T = 0K$, the chemical potential for a Fermi-Dirac gas approaches a positive finite constant as $T \to 0$ K. This is not evident in Fig. 7.19. We can revert the series expansion of $\langle n \rangle \lambda_T^3 / g$ [cf. Eqs. (7.167) and (7.168)] and obtain a series expansion for the fugacity, $z = e^{\beta\mu'}$, which is convergent for sufficiently low density and high

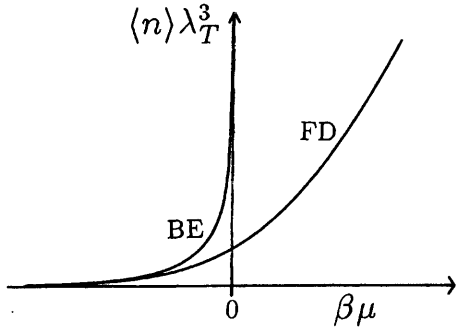


Fig. 7.19. Plots of $\langle n \rangle \lambda_T^3$ versus $\beta\mu$ for a Bose–Einstein (BE) and Fermi–Dirac (FD) gas.

temperature. We obtain

$$z = e^{\beta\mu'} = \frac{\langle n\rangle\lambda_T^3}{g} + \frac{1}{2^{3/2}}\left(\frac{\langle n\rangle\lambda_T^3}{g}\right)^2 + \left(\frac{1}{2^2} - \frac{1}{3^{3/2}}\right)\left(\frac{\langle n\rangle\lambda_T^3}{g}\right)^3 + \cdots \quad (7.169)$$

The coefficients of various powers of the quantity, $\langle n\rangle\lambda_T^3/g$, will always be positive. Thus, as $T \to \infty$, $z \to 0$ and the product, $\beta\mu'$, must be large and negative. Since $\beta \to 0$ the chemical potential $\mu \to -\infty$ at high temperature. For low temperatures, $z \to \infty$ and $\beta\mu' \to \infty$. Since $\beta \to \infty$, in the limit $T \to 0$ the chemical potential can remain finite and indeed it does.

Let us now compute the thermodynamic properties of the ideal Fermi–Dirac gas at low temperatures. Let us first examine the behavior of $f_{3/2}(z)$ at low temperatures. We may write it in the form

$$\begin{aligned} f_{3/2}(z) &= \frac{4}{\sqrt{\pi}}\int_0^\infty dx \frac{x^2}{[e^{x^2-\nu}+1]} = \frac{2}{\sqrt{\pi}}\int_0^\infty dy \frac{\sqrt{y}}{[e^{y-\nu}+1]} \\ &= \frac{4}{3\sqrt{\pi}}\int_0^\infty dy y^{3/2}\frac{e^{y-\nu}}{[1+e^{y-\nu}]^2}, \end{aligned} \quad (7.170)$$

where we have let $y = x^2$ in the second integral and $\nu = \beta\mu'$. To obtain the last integral we have integrated by parts. The function $\Delta(y,\nu) \equiv e^{y-\nu}/[1+e^{y-\nu}]^2$, which appears in the last integral, is essentially the derivative of the occupation number $\langle n_l\rangle$, and at low temperature is sharply peaked about $y = \nu = \beta\mu'$ where the strongest variation in $\langle n_l\rangle$ occurs (cf. Fig. 7.20). Thus, to perform the integration in Eq. (7.170), we may expand $y^{3/2}$ in a Taylor series about $y = \nu$. If we then let $t = (y - \nu)$, we can write $f_{3/2}(z)$ as

$$f_{3/2}(z) = \frac{4}{3\sqrt{\pi}}\int_{-\nu}^\infty dt \frac{e^t}{(1+e^t)^2}\left(\nu^{3/2} + \frac{3}{2}\nu^{1/2}t + \frac{3}{8}\nu^{-1/2}t^2 + \cdots\right). \quad (7.171)$$

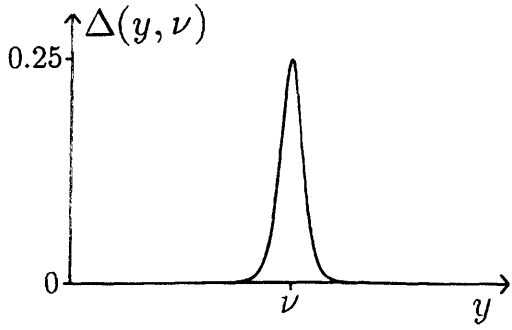


Fig. 7.20. A plot of $\Delta(y,\nu) \equiv e^{y-\nu}/[1+e^{y-\nu}]^2$ versus y.

The contribution from the lower limit in the integral will be of order $e^{-\beta\mu}$. At low temperatures we can neglect it and extend the lower limit to $-\infty$ so that

$$f_{3/2}(z) = \frac{4}{3\sqrt{\pi}} \int_{-\infty}^{\infty} dt \frac{e^t}{(1+e^t)^2} \left(\nu^{3/2} + \frac{3}{2}\nu^{1/2}t + \frac{3}{8}\nu^{-1/2}t^2 + \cdots \right). \quad (7.172)$$

To evaluate Eq. (7.172), we must evaluate integrals of the form

$$I_n = \int_{-\infty}^{\infty} dt \frac{t^n e^t}{(1+e^t)^2}. \quad (7.173)$$

The result is $I_n = 0$ for n odd, $I_0 = 1$, and $I_n = (n-1)!(2n)(1-2^{1-n})\zeta(n)$ for n even, where $\zeta(n)$ is a Riemann zeta function [$\zeta(2) = \frac{\pi^2}{6}$, $\zeta(4) = \frac{\pi^4}{90}$, $\zeta(6) = \frac{\pi^6}{945}$], etc.

We can use the above results to obtain an expansion for the quantity $\langle n \rangle \lambda_T^3/g$ which is valid at low temperature. From Eqs. (7.167), (7.172) and (7.173), we find

$$\langle n \rangle \frac{\lambda_T^3}{g} = \frac{4}{3\sqrt{\pi}} \left[(\beta\mu')^{3/2} + \frac{\pi^2}{8}(\beta\mu')^{-1/2} + \cdots \right]. \quad (7.174)$$

If we take the limit $T \to 0$ K in Eq. (7.174), we find the following density-dependent expression for the chemical potential

$$\mu'(T=0) = \mu_0 \equiv \varepsilon_F = \frac{\hbar^2}{2m} \left(\frac{6\pi^2 \langle n \rangle}{g} \right)^{2/3}. \quad (7.175)$$

The chemical potential, $\mu_0 \equiv \varepsilon_F$, at $T = 0$ K is also called the *Fermi energy*, because at $T = 0$ K it is the maximum energy that a particle in the gas can have (cf. Fig. 7.16). At very low temperatures, only particles within a distance, $k_B T$, of the Fermi surface can participate in physical processes in the gas, because they can change their momentum state. Particles lower down in the Fermi sea have no empty momentum states available for them to jump to and do not contribute to changes in the thermodynamic properties. Equation (7.174) may be reverted to find the chemical potential a a function of temperature and density. The result is

$$\mu' = \varepsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\varepsilon_F} \right)^2 + \cdots \right]. \quad (7.176)$$

Thus, the chemical potential approaches a finite constant as $T \to 0$ K. In Fig. 7.21 we plot the chemical potential of an ideal Fermi–Dirac gas a function of temperature for fixed particle density.

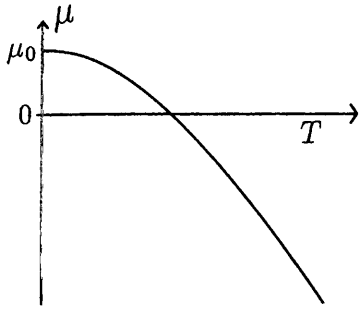


Fig. 7.21. A plot of the chemical potential of a Fermi–Dirac gas as a function of temperature for fixed particle density.

The internal energy, $U = \langle \hat{H} \rangle = \sum_l \varepsilon_l n_l$, can be computed in a similar manner. At low temperature, it is given by

$$U = \frac{3}{5}\langle N \rangle \varepsilon_F \left[1 + \frac{5}{12}\left(\frac{k_B T}{\varepsilon_F} \right)^2 + \cdots \right]. \tag{7.177}$$

From Eq. (7.177) we obtain the heat capacity of the Fermi–Dirac gas in the limit $T \to 0$ K. We find

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{V,\langle N \rangle} = \frac{\langle N \rangle \pi^2}{2} \frac{k_B^2 T}{\varepsilon_F} + \cdots. \tag{7.178}$$

Thus, the heat capacity of an ideal Fermi–Dirac gas depends linearly on the temperature at very low temperatures and goes to zero at $T = 0$ K in accordance with the third law. It is important to note, however, that particles in an ideal Fermi–Dirac gas can have a large zero-point momentum and, therefore, a large pressure and energy even at $T = 0$ K. This is a result of the Pauli exchange principle.

It is a simple matter to show that at high temperatures, all quantities approach values expected for an ideal classical gas.

■ **EXERCISE 7.8.** Compute the variance in particle number, $\langle (N - \langle N \rangle)^2 \rangle$, for a Fermi–Dirac gas for temperatures near $T = 0$ K.

Answer: First note the thermodynamic identity,

$$\langle (N - \langle N \rangle)^2 \rangle = k_B T \left(\frac{\partial \langle N \rangle}{\partial \mu'} \right)_{T,V}. \tag{1}$$

Near $T = 0$ K, we can write

$$\frac{\langle N \rangle}{V} \frac{\lambda_T^3}{g} \approx \frac{4}{3\sqrt{\pi}} (\beta \mu')^{3/2}. \tag{2}$$

where g is a multiplicity factor due to the degeneracy of spin states, and $\lambda_T = \sqrt{2\pi\hbar^2/mk_BT}$ is the thermal wavelength. From Eq. (2), we find

$$\langle N\rangle = \frac{4gV}{3\sqrt{\pi}}\left(\frac{m\mu'}{2\pi\hbar^2}\right)^{3/2}. \tag{3}$$

If we now take the derivative of Eq. (3), we obtain

$$\left(\frac{\partial\langle N\rangle}{\partial\mu'}\right)_{T,V} = \frac{2gV\mu'^{1/2}m^{3/2}}{\sqrt{\pi}(2\pi\hbar^2)^{3/2}}. \tag{4}$$

Let us now solve Eq. (3) for μ' as a function of $\langle N\rangle$ and substitute into Eq. (4). We find

$$\left(\frac{\partial\langle N\rangle}{\partial\mu'}\right)_{T,V} = V\frac{m}{\hbar^2}\left(\frac{3g^2\langle N\rangle}{4\pi^4V}\right)^{1/3}. \tag{5}$$

The variance then becomes

$$\langle(N-\langle N\rangle)^2\rangle = k_BTV\frac{m}{\hbar^2}\left(\frac{3g^2\langle N\rangle}{4\pi^4V}\right)^{1/3}. \tag{6}$$

The variance in particle number for a Fermi-Dirac gas at low temperature is much smaller than that of a Bose-Einstein gas.

■ **EXERCISE 7.9.** Compute the density of states at the Fermi surface for an ideal Fermi–Dirac gas confined to a box of volume V.

Answer: For simplicity we assume the box is cubic with volume $V = L^3$. The momentum is

$$\mathbf{p}_\mathbf{l} = \hbar\left(\frac{2\pi l_x}{L}\mathbf{i} + \frac{2\pi l_y}{L}\mathbf{j} + \frac{2\pi l_z}{L}\mathbf{k}\right), \tag{1}$$

where l_x, l_y, and l_z are integers each ranging from $-\infty$ to ∞. Let us denote the set of integers $\boldsymbol{l} = l_x, l_y l_z$. Each different choice of integers l_x, l_y, and l_z corresponds to a possible state of the system. The allowed values of the momentum, $\mathbf{p}$, form a grid of points located at $p_x = 2\pi\hbar l_x/L$, $p_y = 2\pi\hbar l_y/L$, and $p_z = 2\pi\hbar l_z/L$ in $\mathbf{p}$ space. The volume per point in $\mathbf{p}$ space is $(2\pi\hbar/L)^3$. The number of points per unit volume is $(L/2\pi\hbar)^3$. The number of points (states), ν, inside a spherical volume of $\mathbf{p}$ space with radius less than p is

$$\nu = \frac{4}{3}\pi p^3\left(\frac{L}{2\pi\hbar}\right)^3. \tag{2}$$

The energy of a particle with momentum $\mathbf{p} = \hbar\mathbf{k}$ is $\varepsilon_{\mathbf{k}} = \hbar^2 k^2/2m$. The number of states in the interval $\nu \to \nu + d\nu$ is

$$d\nu = \frac{d\nu}{d\varepsilon_{\mathbf{k}}} d\varepsilon_{\mathbf{k}} = \frac{m^{3/2} V \sqrt{\varepsilon_{\mathbf{k}}}}{\sqrt{2}\pi^2 \hbar^3} d\varepsilon_{\mathbf{k}}. \tag{3}$$

The density of states at the Fermi surface is

$$N(0) = \left(\frac{d\nu}{d\varepsilon_{\mathbf{k}}}\right)_{k=k_f} = \frac{m^{3/2} V \sqrt{\varepsilon_f}}{\sqrt{2}\pi^2 \hbar^3}, \tag{4}$$

where ε_f is the Fermi energy. It should be noted that Eq. (4) is the density of state for a single spin component.

▶ SPECIAL TOPICS

▶ S7.A. Heat Capacity of Lattice Vibrations on a One-Dimensional Lattice—Exact Solution

We can find an exact expression for the heat capacity of a one-dimensional lattice of harmonically coupled atoms. Let us consider a lattice of N atoms of mass m coupled to one another with harmonic springs, all of which have force constant, κ. For simplicity, we will assume that the end masses are coupled to rigid infinitely massive walls by the same harmonic springs (cf. Fig. 7.22). The momentum and displacement operators for the jth atom are $\hat{p}_j$ and $\hat{q}_j$, respectively (the displacement, q_j, is measured relative to the left wall). When the lattice is completely at rest, the springs have length a. The distance between the walls is $L = (N+1)a$. The Hamiltonian operator is

$$\hat{H} = \sum_{j=1}^{N} \frac{\hat{p}_j^2}{2m} + \frac{\kappa}{2} \sum_{j=1}^{N-1} (\hat{q}_{j+1} - \hat{q}_j - a\hat{1})^2 + \frac{\kappa}{2}(\hat{q}_1 - a\hat{1})^2 + \frac{\kappa}{2}(\hat{q}_N - Na\hat{1})^2, \tag{7.179}$$

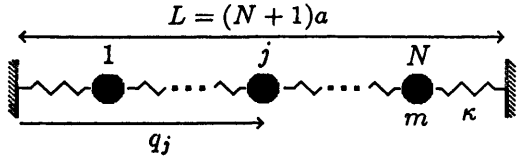


Fig. 7.22. A one-dimensional lattice of N masses, m, coupled by harmonic forces with force constant κ. The lattice is attached to rigid, infinitely massive walls at each end. q_j measures the displacement of the jth mass from the left wall. The distance between walls is $L = (N+1)a$, where a is the spacing between masses when the lattice is at "rest" (for a quantum lattice, there will always be zero point motion).

where $\hat{1}$ is the unit operator. The position and momentum operators obey the commutation relations $[\hat{q}_j, \hat{p}_{j'}] = i\hbar\delta_{jj'}$, $[\hat{p}_j, \hat{p}_{j'}] = 0$, and $[\hat{q}_j, \hat{q}_{j'}] = 0$.

We can also measure the displacement, $\hat{u}_j$, of the jth atom relative to its equilibrium position. If we let $\hat{q}_j = ja\hat{1} + \hat{u}_j$, the Hamiltonian operator takes the simpler form

$$\hat{H} = \sum_{j=1}^{N} \frac{\hat{p}_j^2}{2m} + \frac{\kappa}{2}\sum_{j=1}^{N-1}(\hat{u}_{j+1} - \hat{u}_j)^2 + \frac{\kappa}{2}\hat{u}_1^2 + \frac{\kappa}{2}\hat{u}_N^2. \tag{7.180}$$

Let us now introduce the interaction matrix,

$$\bar{V} = \frac{\kappa}{m}\begin{pmatrix} 2 & -1 & 0 & \cdots & 0 & 0 \\ -1 & 2 & -1 & \cdots & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & 2 & -1 \\ 0 & 0 & 0 & \cdots & -1 & 2 \end{pmatrix}. \tag{7.181}$$

Then the Hamiltonian operator takes the form

$$\hat{H} = \frac{1}{2m}\bar{p}^T \cdot \bar{1} \cdot \bar{p} + \frac{m}{2}\bar{u}^T \cdot \bar{V} \cdot \bar{u}, \tag{7.182}$$

where $\bar{p} = (\hat{p}_1, \hat{p}_2, \ldots, \hat{p}_N)$ and $\bar{u} = (\hat{u}_1, \hat{u}_2, \ldots, \hat{u}_N)$ are row matrices containing the momentum and position operators, respectively, of the N atoms. The quantities $\bar{p}^T$ and $\bar{u}^T$ denote the transpose of column matrices and $\bar{1}$ is the unit matrix.

The interaction matrix, $\bar{V}$, is symmetric and therefore can be diagonalized by an orthogonal matrix, $\bar{X}$. Since $\bar{X}$ is orthogonal it satisfies the conditions, $\bar{X}^T \cdot \bar{X} = \bar{X} \cdot \bar{X}^T = \bar{1}$. Because $\bar{V}$ is an $N \times N$ matrix it has N eigenvalues which we denote by ω_α^2, where $\alpha = 1, 2, \ldots N$. Then

$$\bar{X}^T \cdot \bar{V} \cdot \bar{X} = \bar{\Lambda}, \tag{7.183}$$

where $\bar{\Lambda}$ is the diagonal matrix

$$\bar{\Lambda} = \begin{pmatrix} \omega_1^2 & 0 & \cdots & 0 \\ 0 & \omega_2^2 & \cdots & 0 \\ & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \omega_N^2 \end{pmatrix}. \tag{7.184}$$

One can easily check that the eigenvalues are

$$\omega_\alpha^2 = 4\omega_0^2 \sin^2\left(\frac{\pi\alpha}{2(N+1)}\right), \tag{7.185}$$

where $\omega_0 = \sqrt{\kappa/m}$ is the natural frequency of a harmonic oscillator with force constant κ and mass m. Matrix elements of the orthogonal matrix are

$$X_{j,\alpha} = \sqrt{\frac{2}{N+1}} \sin\left(\frac{\pi j \alpha}{N+1}\right). \tag{7.186}$$

We can now use the orthogonal matrix to transform to normal mode coordinates, (P_α, Q_α). Let $\hat{u}_j = \sum_{\alpha=1}^{N} X_{j,\alpha}\hat{Q}_\alpha$ and $\hat{p}_j = \sum_{\alpha=1}^{N} X_{j,\alpha}\hat{P}_\alpha$. Then the Hamiltonian operator becomes

$$\hat{H} = \frac{1}{2m}\sum_{\alpha=1}^{N} \hat{P}_\alpha^2 + \frac{m}{2}\sum_{\alpha=1}^{N} \omega_\alpha^2 \hat{Q}_\alpha^2. \tag{7.187}$$

Thus, the normal modes consist of a collection of uncoupled harmonic oscillators, each with different frequency, ω_α. They correspond to standing sound waves on the lattice. Since the orthogonal transformation is also canonical, the commutation relations are preserved so that $[\hat{Q}_\alpha, \hat{P}_{\alpha'}] = i\hbar\delta_{\alpha,\alpha'}$, $[\hat{P}_\alpha, \hat{P}_{\alpha'}] = 0$ and $[\hat{Q}_\alpha, \hat{Q}_{\alpha'}] = 0$.

We now have one last step in order to put the Hamiltonian operator in particularly simple form. Let us introduce the creation operator $\hat{a}_\alpha^\dagger$, and annihilation operator, $\hat{a}_\alpha$, for quanta in the αth normal mode (sound mode),

$$\hat{a}_\alpha = \sqrt{\frac{m\omega_\alpha}{2\hbar}}\left(\hat{Q}_\alpha + \frac{i\hat{P}_\alpha}{m\omega_\alpha}\right) \quad \text{and} \quad \hat{a}_\alpha^\dagger = \sqrt{\frac{m\omega_\alpha}{2\hbar}}\left(\hat{Q}_\alpha - \frac{i\hat{P}_\alpha}{m\omega_\alpha}\right). \tag{7.188}$$

Note that $\hat{Q}_\alpha$ and $\hat{P}_\alpha$ are Hermition operators.

Using the commutation relations for the normal mode coordinates, we can show that the creation and annihilation operators satisfy the commutation relations, $[\hat{a}_\alpha, \hat{a}_{\alpha'}^\dagger] = \hat{1}\delta_{\alpha,\alpha'}$. The Hamiltonian operator then takes the form

$$\hat{H} = \sum_{\alpha=1}^{N} \hbar\omega_\alpha(\hat{a}_\alpha^\dagger\hat{a}_\alpha + \tfrac{1}{2}\hat{1}) = \sum_{\alpha=1}^{N} \hbar\omega_\alpha(\hat{n}_\alpha + \tfrac{1}{2}\hat{1}), \tag{7.189}$$

where $\hat{n}_\alpha = \hat{a}_\alpha^\dagger\hat{a}_\alpha$ is the number operator for energy quanta (phonons) in the αth normal mode, $|n_\alpha\rangle$ is its eigenstate and $\hat{n}_\alpha|n_\alpha\rangle = n_\alpha|n_\alpha\rangle$.

The partition function can be written in terms of the Hamiltonian, Eq. (7.180) or (7.189), since inside the trace we can use the orthogonal matrix to transform between them. We simply insert the identity, $\bar{X}\cdot\bar{X}^T = \bar{1}$, into the trace and obtain

$$\mathrm{Tr}_N\,(e^{-\beta\hat{H}}) = \mathrm{Tr}_N\,(\bar{X}\cdot\bar{X}^T\cdot e^{-\beta\hat{H}}) = \mathrm{Tr}_N\,(\bar{X}^T\cdot e^{-\beta\hat{H}}\cdot\bar{X}) = \mathrm{Tr}_N\,(e^{-\beta\bar{X}^T\cdot\hat{H}\cdot\bar{X}}). \tag{7.190}$$

Therefore, the partition function can be written

$$Z_N(T) = \mathrm{Tr}_N\left[\exp\left(-\beta\sum_{\alpha=1}^{N}\hbar\omega_\alpha(\hat{n}_\alpha+\tfrac{1}{2})\right)\right] = \prod_{\alpha=1}^{N}\frac{e^{-\beta\hbar\omega_\alpha/2}}{1-e^{-\beta\hbar\omega_\alpha}}. \tag{7.191}$$

The average energy is

$$\langle E\rangle = -\frac{\partial\ln(Z_N)}{\partial\beta} = \sum_{\alpha=1}^{N}\frac{\hbar\omega_\alpha}{2}+\sum_{\alpha=1}^{N}\frac{\hbar\omega_\alpha}{e^{\beta\hbar\omega_\alpha}-1}. \tag{7.192}$$

The average number of quanta in the αth phonon mode is

$$\langle\hat{n}_\alpha\rangle = \frac{1}{e^{\beta\hbar\omega_\alpha}-1}, \tag{7.193}$$

which is Planck's formula. The heat capacity is

$$C_N = \frac{\partial\langle E\rangle}{\partial T} = k_B\sum_{\alpha=1}^{N}\frac{(\beta\hbar\omega_\alpha)^2e^{\beta\hbar\omega_\alpha}}{(e^{\beta\hbar\omega_\alpha}-1)^2}. \tag{7.194}$$

The summation cannot be done explicitly, but for large N we can change the summation to an integration to obtain a manageable form for the heat capacity as we shall show below.

It is easy to see that at high temperature, Eq. (7.194) gives the correct classical expression for the heat capacity. First note that as $T\to\infty$, $\beta\hbar\omega_\alpha \ll 1$ and $e^{\beta\hbar\omega_\alpha}\approx 1+\beta\hbar\omega_\alpha+$. Then the lowest order term in an expansion in powers of $\beta\hbar\omega_\alpha$ is $C_N = Nk_B$, which is the correct expression for the heat capacity of N classical harmonic oscillators on a one-dimensional lattice.

▶ S7.A.1. Exact Expression—Large N

If the number of atoms in the chain is very large, then in Eqs. (7.192) and (7.194) we can change the summation into an integration. The normal mode frequency, ω, as a function of mode number, α, is

$$\omega = 2\omega_0\sin\left(\frac{\pi\alpha}{2(N+1)}\right). \tag{7.195}.$$

where $2\omega_0$ is the maximum allowed phonon (sound) frequency. Let us denote this "cutoff" frequency by $\omega_L = 2\omega_0$. For $N\gg 1$ we can write

$$\sum_{\alpha=1}^{N}\approx\int_1^N d\alpha\approx\int_0^{\omega_L}g(\omega)d\omega\approx\frac{2N}{\pi}\int_0^{\omega_L}\frac{d\omega}{\sqrt{\omega_L^2-\omega^2}} = N, \tag{7.196}$$

where

$$g(\omega) \equiv \frac{d\alpha}{d\omega} = \frac{2N}{\pi\sqrt{\omega_L^2 - \omega^2}} \tag{7.197}$$

is the density of states (obtained by differentiating Eq. (7.195) with respect to ω) and $g(\omega)d\omega$ is the number of phonon modes (not quanta) in the frequency interval $\omega \to \omega + d\omega$. The average energy can be written

$$\langle E\rangle = \frac{1}{2}\int_0^{\omega_L} \hbar\omega g(\omega)d\omega + \int_0^{\omega_L} \hbar\omega n(\omega)g(\omega)d\omega = \frac{N\hbar\omega_L}{\pi} + \int_0^{\omega_L} \hbar\omega n(\omega)g(\omega)d\omega, \tag{7.198}$$

where $n(\omega) = (e^{\beta\hbar\omega} - 1)^{-1}$ is the average number of quanta in the phonon mode with frequency ω. The quantity $N\hbar\omega_L/\pi$ is the zero point energy of the lattice. In the limit $T \to 0$, $n(\omega) \to 0$ and $\langle E\rangle \to N\hbar\omega_L/\pi$. Thus, the quantum lattice always has some motion even at absolute zero kelvin. This is a consequence of the Heisenberg uncertainty relation, which does not allow the momentum of the masses to be zero if the masses are constrained to remain in the neighborhood of their lattice sites.

From Eqs. (7.194) and (7.196), the heat capacity can be written

$$C_N = k_B\int_0^{\omega_L} g(\omega)d\omega\frac{(\beta\hbar\omega)^2 e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2} = \frac{2Nk_B}{\pi}\int_0^{\omega_L} d\omega\frac{(\beta\hbar\omega)^2 e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2\sqrt{\omega_L^2 - \omega^2}}. \tag{7.199}$$

It is useful, however, to make one last change of variables. Let $x = \beta\hbar\omega$ and define a lattice temperature, $T_L = \hbar\omega_L/k_B$. This is the temperature the lattice must have so the thermal energy, k_BT, is equal to the largest allowed quantum of energy, $\hbar\omega_L$. The heat capacity then takes the form

$$C_N = \frac{2Nk_B}{\pi}\int_0^{T_L/T} \frac{dxx^2e^x}{(e^x - 1)^2\sqrt{(T_L/T)^2 - x^2}}. \tag{7.200}$$

In the limit $T \to 0$, the heat capacity becomes approximately

$$C_N = \frac{2Nk_BT}{\pi T_L}\int_0^{\infty} \frac{dxx^2e^x}{(e^x - 1)^2} + O(T^3) = \frac{2Nk_BT\pi}{3T_L} + O(T^3), \tag{7.201}$$

where we have used the fact that

$$I_n \equiv \int_0^{\infty} \frac{dxx^ne^x}{(e^x - 1)^2} = \sum_{\alpha=0}^{\infty} \frac{n!}{(\alpha + 1)^n} \tag{7.202}$$

(expand the integrand in powers of e^{-x} and integrate). For special values of n the sum can be performed. For example, $I_2 = \pi/3$ and $I_4 = 4\pi^4/15$. Thus, at very low temperatures the heat capacity of this one-dimensional lattice goes to zero linearly with the temperature. Notice also that at very low temperatures the high-frequency (short-wavelength) phonon modes give almost no contribution to the heat capacity of the lattice because there is not enough thermal energy to excite them.

▶ S7.A.2. Continuum Approximation—Large N

We will assume that we do not know the exact dispersion relation [Eq. (7.185)] for the phonon modes, and we will use the information we do have. We know that there are N atoms on the lattice, that it has length L, and that it is pinned on the ends. The allowed wavelengths for phonons on an elastic lattice of length L which is pinned at its ends are given by $\lambda_\alpha = 2L/\alpha$, where $\alpha = 1, 2, \ldots, N$. The allowed phonon wavevectors are $k_\alpha = 2\pi/\lambda_\alpha = \pi\alpha/L$. The minimum allowed wavelengths are of the order of the lattice spacing, and therefore there is a cutoff frequency which we shall call the Debye frequency, ω_D. The dispersion relation for the phonons is $\omega_\alpha = ck_\alpha = c(\pi\alpha/L)$, where c is the speed of sound. The Debye frequency can be found as follows. The number of phonon modes is equal to the number of atoms, so

$$N = \sum_{\alpha=1}^{N} 1 \approx \int_{\alpha=1}^{N} d\alpha \approx \int_0^{\omega_D} g_D(\omega)d\omega = \frac{L}{c\pi}\int_0^{w_D} d\omega = \frac{L\omega_D}{c\pi}. \tag{7.203}$$

Therefore, the Debye frequency is $\omega_D = Nc\pi/L$ and the density of states is

$$g_D(\omega) \equiv \frac{d\alpha}{d\omega} = \frac{L}{c\pi} = \frac{N}{\omega_D}. \tag{7.204}$$

The density of states in the continuum approximation is a constant, whereas the exact solution gives a frequency-dependent density of states. In Fig. 7.23 we plot the exact density of states and the density of states obtained using the continuum approximation. The continuum approximation dramatically underestimates the density of states near the cutoff frequency.

The average energy is given by Eq. (7.198) if we simply replace the lattice density of states, $g(\omega)$, by the continuum density of states, $g_D(\omega)$. We then find

$$\langle E\rangle = \frac{N\hbar\omega_D}{4} + \frac{N}{\omega_D}\int_0^{\omega_D} \hbar\omega n(\omega)d\omega. \tag{7.205}$$

The heat capacity is

$$C_N = \frac{Nk_B}{\omega_D}\int_0^{\omega_D} \frac{(\beta\hbar\omega)^2 e^{\beta\hbar\omega}d\omega}{(e^{\beta\hbar\omega}-1)^2} = \frac{Nk_BT}{T_D}\int_0^{T_D/T} \frac{dx\,x^2e^x}{(e^x-1)^2}, \tag{7.206}$$

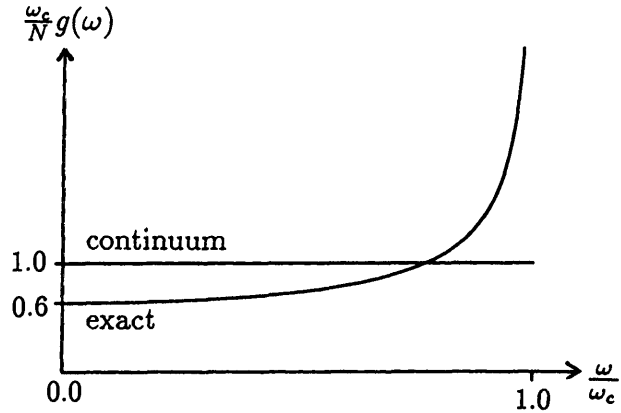


Fig. 7.23. Plots of the exact density of states and the density of states obtained using the continuum approximation, both for the one-dimensional lattice. Here we take $\omega_c = \omega_L = \omega_D$.

where in the second term we have again made the change of variables, $x = \beta\hbar\omega$, and have defined the Debye temperature, $T_D = \hbar\omega_D/k_B$.

In the limit $T \to 0$, the heat capacity in the continuum approximation becomes

$$C_N = \frac{Nk_BT}{T_D}\int_0^\infty \frac{dx\, x^2 e^x}{(e^x-1)^2} + O(T^3) = \frac{Nk_BT\pi^2}{3T_D} + O(T^3). \tag{7.207}$$

At very low temperatures the continuum approximation also gives a heat capacity for the one-dimensional lattice which goes to zero linearly with the temperature. The coefficient differs slightly from the exact result in Eq. (7.201).

▶ S7.B. Momentum Condensation in an Interacting Fermi Fluid [15–17]

An ideal Bose–Einstein gas can condense in momentum space and thereby undergo a phase transition, but an ideal Fermi–Dirac gas is prevented from doing so because the Pauli exclusion principle does not allow more than one fermion to occupy a given quantum state. Electrons in a conducting solid are free to wander through the lattice and form a Fermi fluid. At low temperatures the electrons form a Fermi sea and only those near the Fermi surface affect the thermodynamic properties of the electron fluid (cf. Section 7.H). The electrons experience a mutual Coulomb repulsion which is screened by lattice ions. However, as first noted by Frohlich [18], those electrons in the neighborhood of the Fermi surface also experience a lattice-phonon-mediated effective attraction

(two electrons may in effect be attracted to one another because they are both attracted to the same lattice ion). Cooper [15] showed that this effective attraction at the Fermi surface could cause bound pairs of electrons to form, and these pairs could then condense in momentum space, giving rise to a phase transition in the interacting Fermi fluid. Bardeen, Schrieffer and Cooper, [16] showed that this momentum space condensation of *Cooper pairs* is the origin of superconductivity in materials. In 1972, they received the Nobel Prize for this work.

We shall now derive the thermodynamic properties of a Fermi fluid which can form Cooper pairs. It is found experimentally that Cooper pairs have zero total angular momentum and zero total spin. If the pairs are not undergoing a net translation through the fluid (no supercurrent), then we can assume that only those electrons at the Fermi surface with equal and opposite momentum and opposite spin components are attracted to one another. We shall assume that all other electrons behave like an ideal gas. With these assumptions, we can write the Hamiltonian of the electron fluid in the form

$$\hat{H} = \sum_{\mathbf{k},\lambda} \varepsilon_{\mathbf{k}} \hat{a}^{\dagger}_{\mathbf{k},\lambda} \hat{a}_{-\mathbf{k},\lambda} + \sum_{\mathbf{k}} \sum_{\mathbf{l}} V_{\mathbf{k},\mathbf{l}} \hat{a}^{\dagger}_{\mathbf{k},\uparrow} \hat{a}^{\dagger}_{-\mathbf{k},\downarrow} \hat{a}_{-\mathbf{l},\downarrow} \hat{a}_{\mathbf{l},\uparrow}, \tag{7.208}$$

where $\varepsilon_{\mathbf{k}} = \hbar^2 k^2 / 2m$, and λ denotes the z component of spin of a given electron and takes values $\lambda = \uparrow$ or $\lambda = \downarrow$ (spin component $+\frac{1}{2}\hbar$ or $-\frac{1}{2}\hbar$, respectively). The operators, $\hat{a}^{\dagger}_{\mathbf{k},\lambda}$ and $\hat{a}_{\mathbf{k},\lambda}$, respectively create and annihilate an electron with momentum $\hbar\mathbf{k}$ and spin component λ (cf. Appendix B). They satisfy fermion anticommutation relations. The interaction term in Eq. (7.208) destroys a pair of electrons with momenta $\hbar\mathbf{l}$ and $-\hbar\mathbf{l}$ and opposite spin components, and it creates a pair of electrons with momenta $\hbar\mathbf{k}$ and $-\hbar\mathbf{k}$ and opposite spin components. Since the electrons only experience an attraction at the Fermi surface, the interaction energy, $V_{\mathbf{k},\mathbf{l}}$, can be written

$$V_{\mathbf{k},\mathbf{l}} = \begin{cases} -V_0 & \text{if } |\mu' - \varepsilon_{\mathbf{k}}| \leqslant \Delta\varepsilon \text{ and } |\mu' - \varepsilon_{\mathbf{l}}| \leqslant \Delta\varepsilon, \\ 0 & \text{otherwise,} \end{cases} \tag{7.209}$$

where V_0 is a positive constant, μ' is the chemical potential of the fermi fluid, and $\Delta\varepsilon$ is a small energy of order $k_B T$.

In order to simplify our calculations, we shall compute the thermodynamic properties of this interacting Fermi fluid in the mean field approximation. We write the Hamiltonian in the form

$$\hat{H}_{mf} = \sum_{\mathbf{k},\lambda} \varepsilon_{\mathbf{k}} \hat{a}^{\dagger}_{\mathbf{k},\lambda} \hat{a}_{\mathbf{k},\lambda} + \sum_{\mathbf{k}} \Delta^{*}_{\mathbf{k}} \hat{a}_{-\mathbf{k},\downarrow} \hat{a}_{\mathbf{k},\uparrow} + \sum_{\mathbf{k}} \Delta_{\mathbf{k}} \hat{a}^{\dagger}_{\mathbf{k},\uparrow} \hat{a}^{\dagger}_{-\mathbf{k},\downarrow}, \tag{7.210}$$

where

$$\Delta_{\mathbf{k}} = \begin{cases} \Delta & \text{if } |\mu - \varepsilon_{\mathbf{k}}| \leqslant \Delta\varepsilon, \\ 0 & \text{otherwise} \end{cases} \tag{7.211}$$

and

$$\Delta \equiv -V_0 \sum_{\mathbf{k}}{}' \langle \hat{a}_{-\mathbf{k},\downarrow} \hat{a}_{\mathbf{k},\uparrow} \rangle \text{ and } \quad \Delta^* \equiv -V_0 \sum_{\mathbf{k}}{}' \langle \hat{a}^\dagger_{\mathbf{k},\uparrow} \hat{a}^\dagger_{-\mathbf{k},\downarrow} \rangle. \tag{7.212}$$

The prime on the summation, $\sum'_{\mathbf{k}}$, means that the summation is restricted to a distance, $\Delta\varepsilon$, on either side of the Fermi surface. The average, $\langle \hat{a}_{-\mathbf{k},\downarrow} \hat{a}_{\mathbf{k},\uparrow} \rangle$, is defined as

$$\langle \hat{a}_{-\mathbf{k},\downarrow} \hat{a}_{\mathbf{k},\uparrow} \rangle = \mathrm{Tr}[\hat{\rho} \hat{a}_{-\mathbf{k},\downarrow} \hat{a}_{\mathbf{k},\uparrow}], \tag{7.213}$$

where the density operator, $\hat{\rho}$, is defined as

$$\hat{\rho} = \frac{e^{-\beta(\hat{H}_{mf} - \mu\hat{N})}}{\mathrm{Tr}[e^{-\beta(\hat{H}_{mf} - \mu\hat{N})}]}. \tag{7.214}$$

The average, $\langle \hat{a}^\dagger_{\mathbf{k},\uparrow} \hat{a}^\dagger_{-\mathbf{k},\downarrow} \rangle$, is similarly defined. The number operator, $\hat{N}$, is defined as

$$\hat{N} = \sum_{\mathbf{k},\lambda} \hat{a}^\dagger_{\mathbf{k},\lambda} \hat{a}_{\mathbf{k},\lambda}. \tag{7.215}$$

The quantity Δ is called the *gap function* and may be real or complex. It is a thermodynamic quantity and is a measure of the average binding energy of all the Cooper pairs. If a macroscopic number of Cooper pairs form, then $\langle \hat{a}^\dagger_{\mathbf{k},\uparrow} \hat{a}^\dagger_{-\mathbf{k},\downarrow} \rangle \approx \sqrt{n_c}$ and $\langle \hat{a}^\dagger_{\mathbf{k},\uparrow} \hat{a}^\dagger_{-\mathbf{k},\downarrow} \rangle \approx \sqrt{n_c}$ where n_c is the average number of Cooper pairs in the fluid. Δ is the order parameter for this transition.

It is important to notice that the Hamiltonian, $\hat{H}_{mf}$, does not commute with the number operator, $\hat{N}$, if $\Delta \neq 0$. This means that if a macroscopic number of Cooper pairs form, the system does not conserve the particle (electron) number and the gauge symmetry is broken. The formation of a macroscopic number of Cooper pairs is a phase transition somewhat analogous to Bose–Einstein condensation (cf. Section 7.H). In both cases, gauge symmetry is broken. Since we are working in the grand canonical ensemble and only specify the average particle number, the fact that gauge symmetry is broken is not a problem. If a macroscopic number of Cooper pairs form, the total energy of the system is lowered. The transition to the condensed phase occurs when the thermal energy, $k_B T$, which tends to break Cooper pairs apart, becomes less important than the phonon-mediated attraction between electrons.

It is useful now to introduce an effective Hamiltonian

$$\hat{K} = \sum_{\mathbf{k}} \xi_{\mathbf{k}} (\hat{a}^\dagger_{\mathbf{k},\uparrow} \hat{a}_{\mathbf{k},\uparrow} - \hat{a}_{-\mathbf{k},\downarrow} \hat{a}^\dagger_{-\mathbf{k},\downarrow}) + \sum_{\mathbf{k}} \Delta^*_{\mathbf{k}} \hat{a}_{-\mathbf{k},\downarrow} \hat{a}_{\mathbf{k},\uparrow} + \sum_{\mathbf{k}} \Delta_{\mathbf{k}} \hat{a}^\dagger_{\mathbf{k},\uparrow} \hat{a}^\dagger_{-\mathbf{k},\downarrow}, \tag{7.216}$$

where

$$\xi_{\mathbf{k}} = \varepsilon_{\mathbf{k}} - \mu' = \frac{\hbar^2 k^2}{2m} - \mu', \tag{7.217}$$

and we have made use of the fermion anticommutation relations. The effective Hamiltonian, $\hat{K}$, differs from $\hat{H}_{mf} - \mu\hat{N}$ only by a constant term. Therefore the density operator can also be written

$$\hat{\rho} = \frac{e^{-\beta(\hat{H}_{mf}-\mu\hat{N})}}{\mathrm{Tr}\left[e^{-\beta(\hat{H}_{mf}-\mu\hat{N})}\right]} = \frac{e^{\beta\hat{K}}}{\mathrm{Tr}\left[e^{-\beta\hat{K}}\right]}. \tag{7.218}$$

The effective Hamiltonian, $\hat{K}$, can be written in matrix form:

$$\hat{K} = \sum_{\mathbf{k}} \bar{\alpha}_{\mathbf{k}}^{\dagger} \bar{K}_{\mathbf{k}} \bar{\alpha}_{\mathbf{k}}, \tag{7.219}$$

where

$$\bar{K}_{\mathbf{k}} \equiv \begin{pmatrix} \xi_{\mathbf{k}} & \Delta_{\mathbf{k}} \\ \Delta_{\mathbf{k}}^* & -\xi_{\mathbf{k}} \end{pmatrix}, \qquad \bar{\alpha}_{\mathbf{k}} = \begin{pmatrix} \hat{a}_{\mathbf{k},\uparrow} \\ \hat{a}_{-\mathbf{k},\downarrow}^{\dagger} \end{pmatrix}, \qquad \bar{\alpha}_{\mathbf{k}}^{\dagger} = (\hat{a}_{\mathbf{k},\uparrow}^{\dagger} \quad \hat{a}_{-\mathbf{k},\downarrow}). \tag{7.220}$$

As was first shown by Bogoliubov [19], the effective Hamiltonian, $\hat{K}$, can be diagonalized by means of a unitary transformation which preserves the fermion anticommutation relations. In so doing, we obtain the Hamiltonian for effective excitations (called bogolons) of the system. To diagonalize the effective Hamiltonian, we introduce a 2×2 unitary matrix,

$$\bar{U}_{\mathbf{k}} \equiv \begin{pmatrix} u_{\mathbf{k}}^* & v_{\mathbf{k}} \\ -v_{\mathbf{k}}^* & u_{\mathbf{k}} \end{pmatrix}, \tag{7.221}$$

Since $\bar{U}_{\mathbf{k}}^{\dagger}\bar{U}_{\mathbf{k}} = \bar{U}_{\mathbf{k}}\bar{U}_{\mathbf{k}}^{\dagger} = \bar{1}$ (unitarity), we must have $|u_{\mathbf{k}}|^2 + |v_{\mathbf{k}}|^2 = 1$. We also introduce the vectors

$$\bar{\Gamma}_{\mathbf{k}} = \begin{pmatrix} \hat{\gamma}_{\mathbf{k},0} \\ \hat{\gamma}_{\mathbf{k},1}^{\dagger} \end{pmatrix}, \qquad \bar{\Gamma}_{\mathbf{k}}^{\dagger} = (\hat{\gamma}_{\mathbf{k},0}^{\dagger} \ \hat{\gamma}_{\mathbf{k},1}), \tag{7.222}$$

which are related to the vectors, $\bar{\alpha}_{\mathbf{k}}$, via the unitary transformation

$$\bar{\alpha}_{\mathbf{k}} = \bar{U}_{\mathbf{k}}\bar{\Gamma}_{\mathbf{k}}. \tag{7.223}$$

The physical significance of the vectors, $\bar{\Gamma}_{\mathbf{k}}$, will become clear below. It is easy to show that since $\hat{a}_{\mathbf{k},\lambda}^{\dagger}$ and $\hat{a}_{\mathbf{k},\lambda}$ obey fermion anticommutation relations, the

operators, $\hat{\gamma}^{\dagger}_{\mathbf{k},\mathbf{i}}$ and $\hat{\gamma}_{\mathbf{k},\mathbf{i}}$ $(i = 0, 1)$, must also obey fermion anticommutation relations

$$[\hat{\gamma}_{\mathbf{k},\mathbf{i}}, \hat{\gamma}^{\dagger}_{\mathbf{k}',\mathbf{i}'}]_+ = \delta_{\mathbf{k},\mathbf{k}'}\delta_{\mathbf{i},\mathbf{i}'}, \qquad [\hat{\gamma}_{\mathbf{k},\mathbf{i}}, \hat{\gamma}_{\mathbf{k}',\mathbf{i}'}]_+ = [\hat{\gamma}^{\dagger}_{\mathbf{k},\mathbf{i}}, \hat{\gamma}^{\dagger}_{\mathbf{k}',\mathbf{i}'}]_+ = 0. \tag{7.224}$$

If we revert Eq. (7.223), we see that $\hat{\gamma}_{\mathbf{k},0}$ decreases the momentum of the system by $\hbar\mathbf{k}$ and lowers the spin by $\hbar$ (it destroys a particle with quantum numbers, $(\mathbf{k}, \uparrow)$, and creates one with quantum numbers, $(-\mathbf{k}, \downarrow)$, whereas $\hat{\gamma}_{\mathbf{k},1}$ increases the momentum of the system by $\hbar\mathbf{k}$ and raises the spin by $\hbar$.

We now require that the unitary matrix, $\bar{U}_{\mathbf{k}}$, diagonalize the effective Hamiltonian, $\bar{K}_K$. That is,

$$\bar{U}^{\dagger}_{\mathbf{k}}\bar{K}_{\mathbf{k}}\bar{U}_{\mathbf{k}} = \bar{E}_{\mathbf{k}} \qquad \text{with } \bar{E}_{\mathbf{k}} = \begin{pmatrix} E_{\mathbf{k},0} & 0 \\ 0 & E_{\mathbf{k},1} \end{pmatrix}. \tag{7.225}$$

We find that $E_{\mathbf{k},0} = E_{\mathbf{k}}$ and $E_{\mathbf{k},1} = -E_{\mathbf{k}}$ with

$$E_{\mathbf{k}} = \sqrt{\xi^2_{\mathbf{k}} + |\Delta_{\mathbf{k}}|^2}. \tag{7.226}$$

With this transformation, we have succeeded in reducing the interacting Fermi gas of electrons to an ideal Fermi gas of bogolons. In terms of bogolon operators, the effective Hamiltonian becomes

$$\begin{aligned} \hat{K} &= \sum_{\mathbf{k}} \bar{\alpha}^{\dagger}_{\mathbf{k}} \bar{U}_{\mathbf{k}} \bar{U}^{\dagger}_{\mathbf{k}} \bar{K}_{\mathbf{k}} \bar{U}_{\mathbf{k}} \bar{U}^{\dagger}_{\mathbf{k}} \bar{\alpha}_{\mathbf{k}} = \sum_{\mathbf{k}} \bar{\gamma}^{\dagger}_{\mathbf{k}} \bar{E}_{\mathbf{k}} \bar{\gamma}_{\mathbf{k}} \\ &= \sum_{\mathbf{k}} (E_{\mathbf{k},0}\, \hat{\gamma}^{\dagger}_{\mathbf{k},0}\, \hat{\gamma}_{\mathbf{k},0} - E_{\mathbf{k},1}\, \hat{\gamma}^{\dagger}_{\mathbf{k},1}\, \hat{\gamma}_{\mathbf{k},1} + E_{\mathbf{k},1}). \end{aligned} \tag{7.227}$$

The effective Hamiltonian, when written in terms of bogolon operators, looks like that of an ideal Fermi gas. The bogolons are collective modes of the system and play a role analogous to that of phonons in a Debye solid, although their dispersion relation is quite different.

We can now obtain a self-consistent equation for the gap function, Δ. First note that

$$\langle \hat{\gamma}^{\dagger}_{\mathbf{k},0} \hat{\gamma}_{\mathbf{k},0} \rangle = \frac{1}{(1 + e^{\beta E_{\mathbf{k},0}})} = \frac{1}{2}\left[1 - \tanh\left(\frac{\beta E_{\mathbf{k},0}}{2}\right)\right] \tag{7.228}$$

and

$$\langle \hat{\gamma}^{\dagger}_{\mathbf{k},1} \hat{\gamma}_{\mathbf{k},1} \rangle = \frac{1}{(1 + e^{-\beta E_{\mathbf{k},1}})} = \frac{1}{2}\left[1 + \tanh\left(\frac{\beta E_{\mathbf{k},1}}{2}\right)\right] \tag{7.229}$$

Then

$$\langle \bar{\alpha}_{\mathbf{k}} \bar{\alpha}_{\mathbf{k}}^{\dagger} \rangle = \begin{pmatrix} 1 - \langle \hat{a}_{\mathbf{k},\uparrow}^{\dagger} \hat{a}_{\mathbf{k},\uparrow} \rangle & -\langle \hat{a}_{-\mathbf{k},\downarrow} \hat{a}_{\mathbf{k},\uparrow} \rangle \\ -\langle \hat{a}_{\mathbf{k},\uparrow}^{\dagger} \hat{a}_{-\mathbf{k},\downarrow}^{\dagger} \rangle & \langle \hat{a}_{-\mathbf{k},\downarrow}^{\dagger} \hat{a}_{-\mathbf{k},\downarrow} \rangle \end{pmatrix}$$

$$= \bar{U}_{\mathbf{k}} \begin{pmatrix} 1 - \langle \hat{\gamma}_{\mathbf{k},0}^{\dagger} \hat{\gamma}_{\mathbf{k},0} \rangle & 0 \\ 0 & \langle \hat{\gamma}_{\mathbf{k},1}^{\dagger} \hat{\gamma}_{\mathbf{k},1} \rangle \end{pmatrix} \bar{U}_{\mathbf{k}}^{\dagger}$$

$$= \frac{1}{2} \hat{1} + \frac{1}{2} \bar{U}_{\mathbf{k}} \begin{pmatrix} \tanh\,(\beta E_{\mathbf{k}}/2) & 0 \\ 0 & -\tanh\,(\beta E_{\mathbf{k}}/2) \end{pmatrix} \bar{U}_{\mathbf{k}}^{\dagger}$$

$$= \frac{1}{2} \hat{1} + \frac{1}{2E_{\mathbf{k}}} \bar{U}_{\mathbf{k}} \begin{pmatrix} E_{\mathbf{k}} & 0 \\ 0 & -E_{\mathbf{k}} \end{pmatrix} \bar{U}_{\mathbf{k}}^{\dagger} \tanh\,(\beta E_{\mathbf{k}}/2)$$

$$= \frac{1}{2} \hat{1} + \frac{1}{2E_{\mathbf{k}}} \bar{K}_{\mathbf{k}} \tanh\,(\beta E_{\mathbf{k}}/2). \tag{7.230}$$

Let us now equate off-diagonal matrix elements. We write

$$-\langle \hat{a}_{-\mathbf{k},\downarrow} \hat{a}_{\mathbf{k},\uparrow} \rangle = \frac{\Delta_{\mathbf{k}}}{2E_{\mathbf{k}}} \tanh\,(\beta E_{\mathbf{k}}/2) \tag{7.231}$$

If we multiply Eq. (7.231) by $V_{\mathbf{k},\mathbf{l}}$, integrate over $\mathbf{k}$, and use Eqs. (7.211) and (7.212), we obtain

$$1 = V_0 \sum_{\mathbf{k}}{}' \frac{1}{2E_{\mathbf{k}}} \tanh\,(\beta E_{\mathbf{k}}/2). \tag{7.232}$$

It is useful to note that under the primed summation the bogolon energy can be written $E_{\mathbf{k}} = \sqrt{\xi_{\mathbf{k}}^2 + |\Delta|^2}$. Equation (7.232) is the equation for the gap function. It has been obtained from the grand canonical ensemble. Therefore, the solutions of the gap equation correspond to extrema of the free energy. The solution at a given temperature which corresponds to the stable thermodynamic state is the one which minimizes the free energy. Since the energy, $E_{\mathbf{k}}$, depends on the gap, Eq. (7.232) is rather complicated.

Let us now determine some properties of the gap function from Eq. (7.232). If we assume that the system is contained in a large volume, V, we can change the summation to an integration [cf. Eq. (7.162)]. Note that

$$\sum_{\mathbf{k}} \approx \frac{V}{2\pi^2} \int_0^{\infty} dk\, k^2 = \frac{m^{3/2} V}{\sqrt{2}\pi^2 \hbar^3} \int_{-\mu'}^{\infty} d\xi_{\mathbf{k}} \sqrt{\xi_{\mathbf{k}} + \mu'}, \tag{7.233}$$

where we have Eg. (7.217). The summation, $\sum_{\mathbf{k}}'$, which is restricted to the

neighborhood of the Fermi surface, can be written

$$\sum_{\mathbf{k}}{}' \approx \frac{m^{3/2}V}{\sqrt{2}\pi^2\hbar^3}\int_{-\Delta\varepsilon}^{\Delta\varepsilon}\sqrt{\varepsilon_f}\,d\xi_{\mathbf{k}} \approx N(0)\int_{-\Delta\varepsilon}^{\Delta\varepsilon} d\xi_{\mathbf{k}}, \tag{7.234}$$

where we have set $\mu \approx \varepsilon_f$ (ε_f is the Fermi energy) and $N(0) = mVk_f/2\pi^2\hbar^2$ is the density of states at the Fermi surface for a single spin state (cf. Exercise 7.9). We can now write Eq. (7.232) as

$$1 = V_0N(0)\int_0^{\Delta\varepsilon} d\xi_{\mathbf{k}}\frac{\tanh\left[\frac{\beta}{2}\sqrt{\xi_{\mathbf{k}}^2 + |\Delta(T)|^2}\right]}{\sqrt{\xi_{\mathbf{k}}^2 + |\Delta(T)|^2}}. \tag{7.235}$$

Equation (7.235) determines the temperature dependence of the gap, $\Delta(T)$, and can be used to find the transition temperature.

The energy of bogolons (measured from the Fermi surface) with momentum $\hbar\mathbf{k}$ is $E_{\mathbf{k}} = \sqrt{\xi_{\mathbf{k}}^2 + |\Delta(T)|^2}$. It takes a finite energy to excite them, regardless of their momentum, because there is a gap in the energy spectrum. At the critical temperature, T_c, the gap goes to zero and the excitation spectrum reduces to that of an ideal Fermi gas. The critical temperature can be obtained from Eq. (7.235). It is the temperature at which the gap becomes zero. Thus, at the critical temperature we have

$$\begin{aligned} 1 &= V_0N(0)\int_0^{\Delta\varepsilon} d\xi_{\mathbf{k}}\frac{\tanh\left[\frac{\beta\xi_{\mathbf{k}}}{2}\right]}{\xi_{\mathbf{k}}} = N(0)V_0\int_0^{\beta_c\Delta\varepsilon/2} dx\frac{\tanh(x)}{x} \\ &= N(0)V_0\ln\left[\frac{\alpha}{2}\beta_c\Delta\varepsilon\right], \end{aligned} \tag{7.236}$$

where $\beta_c = (k_BT_c)^{-1}$, $\alpha = 2.26773$, and we have used the fact that

$$\int_0^b \frac{\tanh(x)}{x}dx = \ln(\alpha b), \tag{7.237}$$

for $b > 100$. Thus, Eq. (7.236) holds when $\beta_c\Delta\varepsilon/2 > 100$. This means that $N(0)V_0 < 0.184$ and therefore use of Eq. (7.236) restricts us to fairly weakly coupled systems. From Eqs. (7.236) and (7.237) we obtain

$$k_BT_c = \frac{\alpha}{2}\Delta\varepsilon e^{-1/N(0)V_0}, \tag{7.238}$$

for $\beta_c\Delta\varepsilon/2 > 100$. Thus, the critical temperature, T_c, varies exponentially with the strength of the attractive interaction.

We can also use Eq. (7.235) to find the gap, $\Delta(0) \equiv \Delta_0$, at $T = 0$ K. Since $\tanh(\infty) = 1$, we can write

$$1 = V_0 N(0) \int_0^{\Delta\varepsilon} d\xi_{\mathbf{k}} \frac{1}{\sqrt{\xi_{\mathbf{k}}^2 + \Delta_0^2}} = V_0 N(0) \sinh^{-1}\left(\frac{\Delta\varepsilon}{\Delta_0}\right), \tag{7.239}$$

or

$$\Delta_0 = \frac{\Delta\varepsilon}{\sinh\,(1/V_0 N(0))} \approx 2\Delta\varepsilon e^{-1/N(0)V_0}. \tag{7.240}$$

The rightmost expression for Δ_0 applies for weakly coupled systems when $N(0)V_0 < 0.184$. Comparing Eqs. (7.238) and (7.240), we obtain the following relation between the critical temperature and the zero temperature gap *for weakly coupled systems*:

$$\frac{\Delta_0}{k_B T_c} = \frac{4}{\alpha} = 1.764. \tag{7.241}$$

Equation (7.241) is in good agreement with experimental values of this ratio for superconductors. Equation (7.235) may be solved numerically to obtain a plot of the gap as a function of temperature. The gap function is a real function for the case (such as we are considering here) when no supercurrent is present. We show the behavior of $\Delta(T)$ in Fig. 7.24 for weakly coupled systems.

Since bogolons form an ideal gas, the entropy can be written in the form

$$S = -2k_B \sum_{\mathbf{k}} [n_{\mathbf{k}} \ln(n_{\mathbf{k}}) + (1 - n_{\mathbf{k}}) \ln(1 - n_{\mathbf{k}})], \tag{7.242}$$

where $n_{\mathbf{k}} = (1 + e^{\beta E_{\mathbf{k}}})^{-1}$ (cf. Problem 7.23). The heat capacity, $C_{V,N}$, is easy to

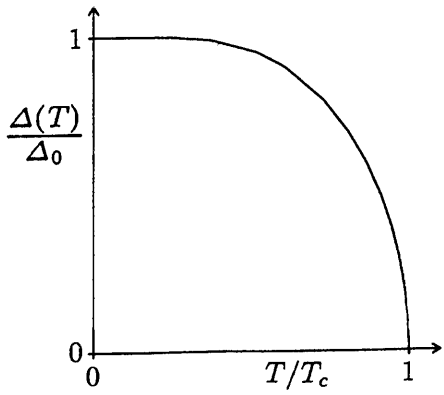


Fig. 7.24. A plot of the ratio $\Delta(T)/\Delta_0$ versus the reduced temperature, T/T_c, for a weakly coupled system.

find from Eq. (7.242). let us first note that for a Fermi gas at very low temperature we have $\mu \approx \varepsilon_f$, where ε_f is the Fermi energy, and $(\partial\mu/\partial T)_{V,\langle N\rangle} \approx 0$. Thus,

$$\begin{aligned} C_{V,N} = T\left(\frac{\partial S}{\partial T}\right)_{V,\langle N\rangle} &\approx 2\beta k_B \sum_{\mathbf{k}} \frac{\partial n_{\mathbf{k}}}{\partial \beta} \ln\left(\frac{n_{\mathbf{k}}}{1-n_{\mathbf{k}}}\right) \\ &= -2\beta k_B \sum_{\mathbf{k}} \frac{\partial n_{\mathbf{k}}}{\partial E_{\mathbf{k}}}\left(E_{\mathbf{k}}^2 + \frac{1}{2}\beta \frac{\partial |\Delta_{\mathbf{k}}|^2}{\partial \beta}\right). \end{aligned} \tag{7.243}$$

We can now examine the heat capacity, both at the critical temperature and in the limit $T \to 0$ K.

Let us first look at the neighborhood of the critical point. The first term in Eq. (7.243) is continuous at $T = T_c$, but the second term is not since $\partial|\Delta_{\mathbf{k}}|^2/\partial\beta$ has a finite value for $T < T_c$ but is zero for $T > T_c$. Near $T = T_c$, we may let $E_{\mathbf{k}} \to |\xi_{\mathbf{k}}|$. Then the heat capacity just below the critical temperature is

$$C_{V,N}^{<} \approx -2\beta_c k_B \sum_{\mathbf{k}} \frac{\partial n_{\mathbf{k}}}{\partial |\xi_{\mathbf{k}}|}\left(\xi_{\mathbf{k}}^2 + \frac{1}{2}\beta_c \left(\frac{\partial |\Delta_{\mathbf{k}}|^2}{\partial \beta}\right)_{T=T_c}\right), \tag{7.244}$$

and just above the critical temperature it is

$$C_{V,N}^{>} \approx -2\beta_c k_B \sum_{\mathbf{k}} \frac{\partial n_{\mathbf{k}}}{\partial |\xi_{\mathbf{k}}|} \xi_{\mathbf{k}}^2. \tag{7.245}$$

The discontinuity in the heat capacity at the critical temperature is

$$\begin{aligned} \Delta C_{V,N} = C_{V,\langle N\rangle}^{<} - C_{V,\langle N\rangle}^{>} &= -\beta_c^2 k_B {\sum_{\mathbf{k}}}' \left(\frac{\partial |\Delta|^2}{\partial \beta}\right)_{T=T_c} \frac{\partial n_{\mathbf{k}}(|\xi_{\mathbf{k}}|)}{\partial |\xi_{\mathbf{k}}|} \\ &= -k_B \beta_c^2 N(0)\left(\frac{\partial |\Delta|^2}{\partial \beta}\right)_{T=T_c} = N(0)\left(\frac{\partial |\Delta|^2}{\partial T}\right)_{T=T_c} \end{aligned} \tag{7.246}$$

Thus, the heat capacity has a finite discontinuity at the critical temperature, as we would expect for a mean field theory.

Let us now compute the heat capacity in the limit $T \to 0$. As we can see from Fig. 7.24, the gap function, Δ, approaches a finite value, Δ_0, as $T \to 0$ and $\partial\Delta/\partial T \to 0$ as $T \to 0$. As a result the heat capacity takes a fairly simple form in the limit $T \to 0$. If we assume that $\mu' \approx \varepsilon_f$ and $\Delta \approx \Delta_0$ in Eq. (7.243), then the heat capacity takes the form

$$C_{V,N} \approx -2\beta k_B \sum_{\mathbf{k}} E_{\mathbf{k}}^2 \frac{\partial n_{\mathbf{k}}}{\partial E_{\mathbf{k}}} = 2\beta^2 k_B \sum_{\mathbf{k}} E_{\mathbf{k}}^2 \frac{e^{\beta E_{\mathbf{k}}}}{(1+e^{\beta E_{\mathbf{k}}})^2}, \tag{7.247}$$

where $E_{\mathbf{k}} = \sqrt{\xi_{\mathbf{k}}^2 + \Delta_0^2}$. In order to change Eq. (7.247) it is useful to introduce the bogolon density of states. We can write

$$\sum_{\mathbf{k}} = \frac{m^{3/2}V}{\sqrt{2}\pi^2\hbar^3}\int_0^\infty \sqrt{\varepsilon_{\mathbf{k}}}d\varepsilon_{\mathbf{k}} = \frac{m^{3/2}V}{\sqrt{2}\pi^2\hbar^3}\int_{\Delta_0}^\infty \left[\sqrt{E_{\mathbf{k}}^2 - \Delta_0^2} + \varepsilon_f\right]^{1/2} \frac{E_{\mathbf{k}}dE_{\mathbf{k}}}{\sqrt{E_{\mathbf{k}}^2 - \Delta_0^2}}. \tag{7.248}$$

For momenta, $k \approx k_f$, the density of states is singular. Therefore, the dominant contribution to the integral comes from the neighborhood of the Fermi surface and we can write

$$\sum_{\mathbf{k}} \approx N(0)\int_{\Delta_0}^\infty \frac{E_{\mathbf{k}}dE_{\mathbf{k}}}{\sqrt{E_{\mathbf{k}}^2 - \Delta_0^2}}. \tag{7.249}$$

Let us next note that in the limit $T \to 0$ we can write $e^{\beta E_{\mathbf{k}}}/(1 + e^{\beta E_{\mathbf{k}}})^2 \approx e^{-\beta E_{\mathbf{k}}}$. Thus, the heat capacity takes the form

$$C_{V,N} \approx 2\beta^2 k_B N(0)\int_{\Delta_0}^\infty \frac{E_{\mathbf{k}}^3 dE_{\mathbf{k}}}{\sqrt{E_{\mathbf{k}}^2 - \Delta_0^2}} e^{-\beta E_{\mathbf{k}}}. \tag{7.250}$$

The integral in Eq. (7.250) is easy to do if we use a trick. Note that

$$I \equiv \int_{\Delta_0}^\infty \frac{E_{\mathbf{k}}dE_{\mathbf{k}}}{\sqrt{E_{\mathbf{k}}^2 - \Delta_0^2}} e^{-\beta E_{\mathbf{k}}} = \Delta_0 K_1(\beta\Delta_0), \tag{7.251}$$

where K_1 is a modified Bessel function [19]. But

$$\int_{\Delta_0}^\infty \frac{E_{\mathbf{k}}^3 dE_{\mathbf{k}}}{\sqrt{E_{\mathbf{k}}^2 - \Delta_0^2}} e^{-\beta E_{\mathbf{k}}} = \frac{\partial^2 I}{\partial\beta^2} = \frac{1}{4}\Delta_0^3[3K_1(\beta\Delta_0) + K_3(\beta\Delta_0)]. \tag{7.252}$$

Thus, the heat capacity takes the form

$$C_{V,N} = \frac{1}{2}\beta^2 k_B N(0)\Delta_0^3[3K_1(\beta\Delta_0) + K_3(\beta\Delta_0)]. \tag{7.253}$$

If we now make use of the asymptotic form of the modified Bessel functions, $K_n(\beta\Delta_0) \approx \sqrt{\pi/2\beta\Delta_0}\, e^{-\beta\Delta_0}$, the heat capacity takes the form

$$C_{V,N} \approx \sqrt{2\pi}\beta^{3/2} k_B N(0)\Delta_0^{5/2} e^{-\beta\Delta_0} \tag{7.254}$$

in the limit $T \to 0$. Thus, the heat capacity of the condensed Fermi fluid goes to zero exponentially with temperature rather than linearly as in the case for an ideal Fermi gas. In Fig. 7.25 we show a sketch of the heat capacity of the interacting Fermi fluid (superconductor). The solid line is the Fermi fluid, and the dashed line is an ideal Fermi gas.

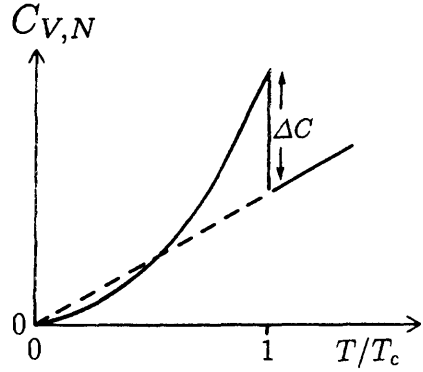


Fig. 7.25. A sketch of the heat capacity for a superconductor. The straight dashed line gives the heat capacity in the absence of interaction (ideal Fermi gas). The solid line shows the jump in the heat capacity at the critical point and the exponential decay for temperatures below the critical point.

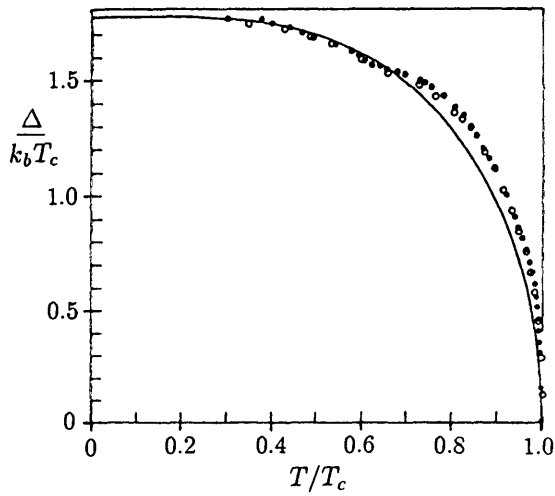


Fig. 7.26. Variation of $\Delta/k_B T_c$ with reduced temperature, T/T_c, for tin. The data points are obtained from ultrasonic acoustic attenuation measurements [20] for two different frequencies. The solid line is BCS theory. Reprinted, by permission, from R. W. Morse and H. V. Bohm, *Phys. Rev.* **108**, 1094 (1954).

The mean field theory gives a surprisingly good description of the behavior of real superconductors. In Fig. 7.26 we show experimental measurements of the gap function, Δ, as a function of temperature for tin. The solid line is the mean field theory of Bardeen, Cooper, and Schrieffer. The experimental points, which are obtained from ultrasonic accoustic attenuation measurements [21], fit it very well.

▶ S7.C. The Yang–Lee Theory of Phase Transitions [22, 23]

Yang and Lee have used very simple arguments involving the grand canonical ensemble to arrive at a mechanism by which a phase transition can take place in a classical fluid. We present it here because it gives valuable insight into the structure of the grand partition function.

Let us consider a classical system of particles interacting via a potential,

$$V(|\mathbf{q}_{ij}|) = \begin{cases} \infty & \text{if } |\mathbf{q}_{ij}| < a \\ -\varepsilon_{ij}, & \text{if } a \leqslant |\mathbf{q}_{ij}| \leqslant b, \\ 0 & \text{if } b < |\mathbf{q}_{ij}|, \end{cases} \tag{7.255}$$

where $\mathbf{q}_{ij} - \mathbf{q}_i - \mathbf{q}_j$ Because the particles have an infinite hard core, there is a maximum number of particles, M, which can be fitted into a box of volume V. Therefore, the grand partition function must have the form

$$\begin{aligned} Z_\mu(T,V) &= \sum_{N=0}^{M} \frac{e^{\beta\mu N}}{N!h^{3N}} \int \cdots \int d\mathbf{p}^N d\mathbf{q}^N \exp\left\{ -\beta \left(\sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i<j=1}^{N(N-1)/2} V(|\mathbf{q}_{ij}|) \right) \right\} \\ &= \sum_{N=0}^{M} \frac{e^{\beta\mu N}}{N!\lambda_T^{3N}} Q_N(V,T), \end{aligned} \tag{7.256}$$

where λ_T is the thermal wavelength and $Q_N(T,V)$ is called the *configuration integral* and is defined as

$$Q_N(T,V) = \int d\mathbf{q}^N \exp\left\{ -\beta \sum_{i<j=1}^{N(N-1)/2} V(|\mathbf{q}_{ij}|) \right\} \tag{7.257}$$

In the last term in Eq. (7.256), we have performed the momentum integrations. Since we are now dealing with classical particles, the phase space coordinates commute and the momentum integrations are trivial. Information about deviations from ideal gas behavior is contained in the configuration integral. For $N > M, Q_N(T,V) = 0$ because the hard core in the potential prevents more than M particles from occupying a box of volume V.

Let us now introduce a new variable, $y \equiv e^{\beta\mu}/\lambda_T^3$. Then, Eq. (7.256) can be written in the form

$$Z_\mu(T,V) = \sum_{N=0}^{M} \frac{y^N}{N!} Q_N(T,V). \tag{7.258}$$

We see that for finite volume, V, the grand partition function, $Z_\mu(T,V)$, is a polynomial of order M in the parameter y. The coefficients of y^N are positive

and real for all N. Since $Z_\mu(T, V)$ is a polynomial of order M, we can rewrite it in the form

$$Z_\mu(T, V) = \prod_{i=1}^{M} \left(1 - \frac{y}{y_i}\right). \tag{7.259}$$

where the quantities y_i, are the M roots of the equation $Z_\mu(T, V) = 0$. Because the coefficients $Q_N/N!$ are all real and positive, none of the roots y_i can be real and positive for finite M if we wish to satisfy the equation $Z_\mu(T, V) = 0$. Therefore, for finite M all roots of y must be either real and negative or complex. If they are complex, then they must occur in complex conjugate pairs since $Z_\mu(T, V)$ is real. As the volume is increased, the number of roots, M, will increase and move around in the complex plane. In the limit $V \to \infty$, it can happen that some of the roots will touch the positive real axis (cf. Fig. 7.27). When this happens, a phase transition occurs because the system can have different behavior for $y < y_0$ and $y > y_0$, where y_0 is the value of the root on the real axis. In general, the pressure, P, will be continuous across the point y_0, but the density and/or higher derivatives of P will be discontinuous (we give an example later).

The pressure and density, in the limit of infinite volume, are given by

$$\frac{P}{k_B T} = \lim_{V \to \infty} \left(\frac{1}{V} \ln[Z_\mu(T, V)]\right) \tag{7.260}$$

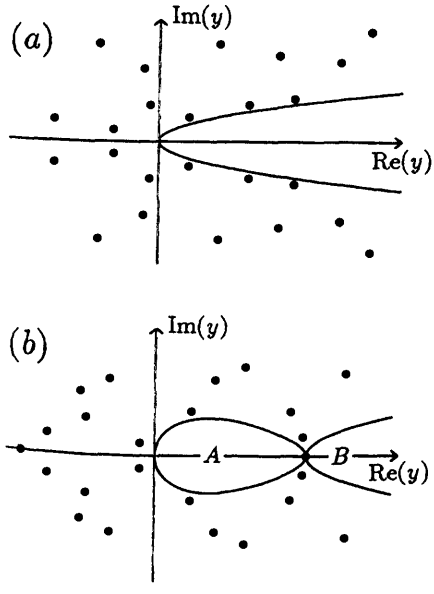


Fig. 7.27. A schematic plot of the roots of $Z_\mu(T, V) = 0$ in the complex y plane. (a) For finite V, no roots lie on the positive real axis. (b) For $V = \infty$, roots can touch the positive real axis and separate regions, A and B, with different phase.

and

$$\frac{1}{\nu} = \lim_{V\to\infty} \frac{\langle N\rangle}{V} = \lim_{V\to\infty} \left(y\frac{\partial}{\partial y}\frac{1}{V}\ln[Z_\mu(T,V)] \right). \tag{7.261}$$

In general, the two operations $\lim_{V\to\infty}$ and $y(\partial/\partial y)$ cannot be interchanged freely. However, Yang and Lee proved that for the type of interaction considered in Eq. (7.255), the limit in Eq. (7.261) exist and the operations $\lim_{V\to\infty}$ and $y(\partial/\partial_y)$ can be interchanged. The results of Yang and Lee are contained in the following theorems (proofs can be found in Ref. 22).

Theorem I. For all positive real values of y, $(1/V)\ln[Z_\mu(T,V)]$ approaches, as $V\to\infty$, a limit which is independent of the shape of the volume V. Furthermore, the limit is a continuous monotonically increasing function of y.

Theorem II. If in the complex y plane a region R containing a segment of the positive real axis is always free of roots, then in this region as $V\to\infty$ the quantities

$$\frac{1}{V}\ln[Z_\mu(T,V)] \quad \text{and} \quad \left(y\frac{\partial}{\partial y}\right)^n \frac{1}{V}\ln[Z_\mu(T,V)] \qquad \text{for } n = 1,2,\ldots,\infty,$$

approach limits which are analytic with respect to y. Furthermore, the operations $y(\partial/\partial y)$ and $\lim_{V\to\infty}$ commute in R so that

$$\lim_{V\to\infty}\left(y\frac{\partial}{\partial y}\frac{1}{V}\ln[Z_\mu(T,V)] \right) = y\frac{\partial}{\partial y}\lim_{V-\infty}\left(\frac{1}{V}\ln[Z_\mu(T,V)] \right).$$

Theorems I and II, together with Eqs. (7.260) and (7.261), enable us to obtain the following relation between ν and P:

$$\frac{1}{\nu} = y\frac{\partial}{\partial y}\left(\frac{P}{k_BT}\right). \tag{7.262}$$

They tell us that the pressure must be continuous for all y but that the derivatives of the pressure need only be continuous in regions of the positive real y axis where roots of $Z_\mu(T,V) = 0$ do not touch the real axis. At points where roots touch, the derivatives of the pressure can be discontinuous. In general, if $\partial P/\partial y$ is discontinuous, then the system undergoes a first-order phase transition. If a higher-order derivative is the first to be discontinuous, then the phase transition is continuous.

If ν is discontinuous at a point y_0 (where y_0 is a root of $Z_\mu(T,V) = 0$), then it will decrease with y in the direction of increasing y. This can be proved as follows. Note that

$$y\frac{\partial}{\partial y}\left(\frac{1}{\nu}\right) = \left(y\frac{\partial}{\partial y}\right)^2\left[\frac{1}{V}\ln[Z_\mu]\right] = \frac{1}{V}\langle(N-\langle N\rangle)^2\rangle.$$

The quantity, $\langle (N - \langle N \rangle)^2 \rangle$, is always greater than zero. Therefore, $1/\nu$ always increases and ν always decreases with increasing y.

Yang and Lee applied this theory of phase transitions to the two-dimensional Ising model [21, 23]. They found that for the Ising model the roots of $Z_\mu(T, V) = 0$ all lie on the unit circle and close onto the positive real y axis in the limit of an infinite system. The point at which the roots touch the real axis gives the value of y for which the system undergoes a phase transition.

It is of interest to consider an explicit example [24]. We will consider a system with the following grand partition function:

$$Z_\mu = \frac{(1+y)^V(1-y^V)}{(1-y)}, \tag{7.263}$$

where V is an integer. Z_μ has V real roots at $y = -1$ and it has complex roots of the form $y = e^{2\pi ik/V}$, where $k = 1, 2, \ldots, V-1$. As the value of V increases, the density of roots on the unit circle increases and the roots get closer to the point $y = 1$ (cf. Fig. 7.28).

The function $P/k_BT = \lim_{V\to\infty}(1/V)\ln[Z_\mu]$ has different limiting values for $y < 1$ and $y > 1$ as $V \to \infty$. We find

$$\frac{P}{k_BT} = \lim_{V\to\infty}\frac{1}{V}\ln\left[\frac{(1+y)^V(1-y^V)}{(1-y)}\right] = \begin{cases} \ln(1+y) & \text{if } y < 1 \\ \ln(1+y) + \ln(y) & \text{if } y > 1. \end{cases} \tag{7.264}$$

Note that the pressure is continuous at $y = 1$. The volume per particle, v, is easily found from Eqs. (7.262) and (7.264):

$$\frac{1}{v} = y\frac{\partial}{\partial y}\left(\frac{P}{k_BT}\right) = \begin{cases} \dfrac{y}{(1+y)} & \text{if } y < 1, \\ \dfrac{2y+1}{(1+y)}, & \text{if } y > 1. \end{cases} \tag{7.265}$$

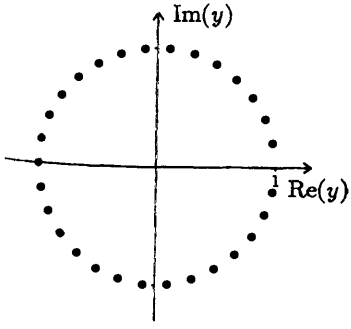


Fig. 7.28. An example where the roots of the grand partition function lie on the unit circle in the complex y plane.

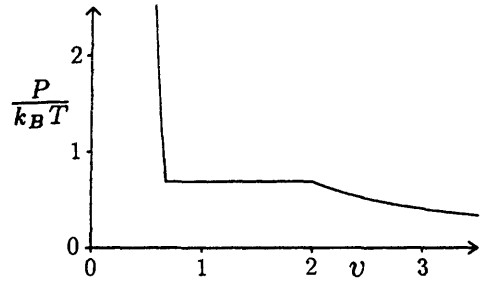


Fig. 7.29. A plot of P/k_BT versus v for a system with grand partition function, $Z_\mu = (1+y)^V(1-y)^V/(1-y)$.

Thus the volume per particle is discontinuous at $y = 1$ and we have a first-order phase transition. If we combine Eqs. (7.264) and (7.265), it is straightforward to show that the system has the following equation of state.

$$\frac{P}{k_BT} = \begin{cases} \ln\left[\dfrac{v}{v-1}\right] & \text{if } v > 2, \\ \ln[2] & \text{if } 2 > v > \frac{2}{3}, \\ \ln\left[\dfrac{v(1-v)}{(2v-1)^2}\right] & \text{if } \frac{2}{3} > v > \frac{1}{2}. \end{cases} \tag{7.266}$$

In Fig. 7.29 we plot P/k_BT as a function of volume per particle, v. We see that it has the behavior expected for a first-order phase transition.

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PROBLEMS

Problem 7.1. Compute the structure function for N noninteracting harmonic oscillators, each with frequency ω and mass m. Assume the system has total energy E. Using this structure function and the microcanonical ensemble, compute the entropy and the heat capacity of the system.

Problem 7.2. A system consists of N noninteracting, distinguishable two-level atoms. Each atom can exist in one of two energy states, $E_0 = 0$ or $E_1 = \varepsilon$. The number of atoms in energy level, E_0, is n_0 and the number of atoms in energy level, E_1, is n_1. The internal energy of this system is $U = n_0E_0 + n_1E_1$. (a) Compute the entropy of this system as a function of internal energy. (b) Compute the temperature of this system. Under what conditions can it be negative? (c) Compute the heat capacity for a fixed number of atoms, N.

Problem 7.3. A lattice contains N normal lattice sites and N interstitial lattice sites. The lattice sites are all distinguishable. N identical atoms sit on the lattice, M on the interstitial sites, and $N - M$ on the normal sites ($N \gg M \gg 1$). If an atom occupies a normal site, it has energy $E = 0$. If an atom occupies an interstitial site, it has energy $E = \varepsilon$. Compute the internal energy and heat capacity as a function of temperature for this lattice.

Problem 7.4. Consider a lattice with N spin-1 atoms with magnetic moment μ. Each atom can be in one of three spin states, $S_z = -1, 0, +1$. Let n_{-1}, n_0, and n_1 denote the respective number of atoms in each of those spin states. Find the total entropy and the configuration which maximizes the total entropy. What is the maximum entropy? (Assume that no magnetic field is present, so all atoms have the same energy. Also assume that atoms on different lattice sites cannot be exchanged, so they are distinguishable).

Problem 7.5. A system has three distinguishable molecules at rest, each with a quantized magnetic moment which can have z components $+\frac{1}{2}\mu$ or $-\frac{1}{2}\mu$. Find an expression for the distribution function, f_i (i denotes the ith configuration), which maximizes entropy subject to the conditions $\sum_i f_i = 1$ and $\sum_i M_{i,z} f_i = \gamma\mu$, where $M_{i,z}$ is the magnetic moment of the system in the ith configuration. For the case $\gamma = \frac{1}{2}$, compute the entropy and compute f_i.

Problem 7.6. A fluid in equilibrium is contained in an insulated box of volume V. The fluid is divided (conceptually) into m cells. Compute the variance of enthalpy fluctuations, $\langle(\Delta H_i)^2\rangle$, in the ith cell (For simplicity assume the fluctuations occur at fixed particle number, N_i). (*Hint*: Use P and S as independent variables.)

Problem 7.7. A fluid in equilibrium is contained in an insulated box of volume V. The fluid is divided (conceptually) into m cells. Compute the variance of internal energy fluctuations, $\langle(\Delta U_i)^2\rangle$, in the ith cell (For simplicity assume the fluctuations occur at fixed particle number, N_i). What happens to the internal energy fluctuations near a critical point?

Problem 7.8. What is the partition function for a van der Waals gas with N particles? Note that the result is phenomenological and might involve some guessing. It is useful to compare it to the partition function for an ideal gas. Remember that the particles are indistinquishable, so when using the partition function one must insert a counting factor. Use this partition function to compute the internal energy, $U(N, T, V)$, the pressure, $P(N, T, V)$, and the entropy, $S(U, V, N)$.

Problem 7.9. Consider a solid surface to be a two-dimensional lattice with N_s sites. Assume that N_a atoms ($N_a \ll N_s$) are adsorbed on the surface, so that each lattice site has either zero or one adsorbed atom. An adsorbed atom has energy $E = -\varepsilon$, where $\varepsilon > 0$. Assume the atoms on the surface do not interact with one another.

(a) If the surface is at temperature T, compute the chemical potential of the adsorbed atoms as a function of T, ε, and N_a/N_s (use the canonical ensemble).

(b) If the surface is in equilibrium with an ideal gas of similar atoms at temperature T, compute the ratio N_a/N_s as a function of pressure, P, of the gas. Assume the gas has number density n. (*Hint*: Equate the chemical potentials of the adsorbed surface atoms and the gas.)

Problem 7.10. Consider a two-dimensional lattice in the x–y plane with sides of length L_x and L_y which contains N atoms (N very large) coupled by nearest-neighbor harmonic forces. (a) Compute the Debye frequency for this lattice. (b) In the limit $T \to 0$, what is the heat capacity?

Problem 7.11. A cubic box (with infinitely hard walls) of volume $V = L^3$ contains an ideal gas of N rigid HCl molecules (assume that the effective distance between the H atom and the Cl atom is $d = 1.3$Å. (a) If $L = 1.0$ cm, what is the spacing between translational energy levels? (b) Write the partition function for this system (include both translation and rotational contributions). At what temperature do rotational degrees of freedom become important? (c) Write expressions for the Helmholtz free energy, the entropy, and the heat capacity of this system for temperatures where the rotational degrees of freedom make a significant contribution.

Problem 7.12. An ideal gas is composed of N "red" atoms of mass m, N "blue" atoms of mass m, and N "green" atoms of mass m. Atoms of the same color are

indistinguishable. Atoms of different color are distinguishable. (a) Use the canonical ensemble to compute the entropy of this gas. (b) Compute the entropy of an ideal gas of $3N$ "red" atoms of mass m. Does it differ from that of the mixture? If so, by how much?

Problem 7.13. An ideal gas consists of a mixture of "green" and "red" spin-$\frac{1}{2}$ particles. All particles have mass m. A magnetic field, B, is applied to the system. The "green" particles have magnetic moment γ_G, and the "red" particles have magnetic moment γ_R, where $\gamma_R < \gamma_G$. Assume the temperature is high enough that Fermi statistics can be neglected. The system will be in equilibrium if the chemical potentials of the "red" and "green" gases are equal. Compute the ratio N_R/N_G, where N_R is the number of "red" particles and N_G is the number of "green" particles. Use the canonical ensemble (no other ensemble will be accepted).

Problem 7.14. Consider a one-dimensional lattice with N lattice sites and assume that the ith lattice site has spin $s_i = \pm 1$. the Hamiltonian describing this lattice is $H = -\varepsilon \sum_{i=1}^{N} s_i s_{i+1}$. Assume periodic boundary conditions, so $s_{N+1} \equiv s_1$. Compute the correlation function, $\langle s_1 s_2 \rangle$. How does it behave at very high temperature and at very low temperature?

Problem 7.15. In the mean field approximation to the Ising lattice, the order parameter, $\langle s \rangle$, satisfies the equation $\langle s \rangle = \tanh(\langle s \rangle \frac{T_c}{T})$, where $T_c = \nu\varepsilon/2k_B$ with ε the strength of the coupling between lattice sites and ν the number of nearest neighbors. (a) Show that $\langle s \rangle$ has the following temperature dependence: (i) $\langle s \rangle \approx 1 - 2e^{-2T_c/T}$ if $T \sim 0$ K, and (ii) $\langle s \rangle \approx \sqrt{3(1 - T/T_c)}$ if $T \sim T_c$. (b) Compute the jump in the heat capacity at $T = T_c$. (c) Compute the magnetic susceptibility, $\chi_{T,N}(B = 0)$, in the neighborhood of $T = T_c$ for both $T > T_c$ and $T < T_c$. What is the critical exponent for both cases?

Problem 7.16. The density of states of an ideal Bose–Einstein gas is

$$g(E) = \begin{cases} \alpha E^2 & \text{if } E > 0, \\ 0 & \text{if } E < 0, \end{cases}$$

where α is a constant. Compute the critical temperature for Bose–Einstein condensation.

Problem 7.17. An ideal Bose–Einstein gas consists of noninteracting bosons of mass m which have an internal degree of freedom which can be described by assuming, that the bosons are two-level atoms. Bosons in the ground state have energy $E_0 = p^2/2m$, while bosons in the excited state have energy $E_1 = p^2/2m + \Delta$, where p is the momentum and Δ is the excitation energy. Assume that $\Delta \gg k_B T$. Compute the Bose–Einstein condensation temperature, T_c, for this gas of two-level bosons. Does the existence of the internal degree of freedom raise or lower the condensation temperature?

Problem 7.18. Compute the Clausius–Clapyron equation for an ideal Bose–Einstein gas and sketch the coexistence curve. Show that the line of transition points in the P–v plane obeys the equation

$$Pv^{5/3} = \frac{2\pi\hbar^2}{m} \frac{g_{5/2}(1)}{(g_{3/2}(1))^{5/3}}.$$

Problem 7.19. Show that the pressure, P, of an ideal Bose–Einstein gas can be written in the form $P = \alpha u$, where u is the internal energy per unit volume and α is a constant. (a) What is u? (b) What is α?

Problem 7.20. Electrons in a piece of copper metal can be assumed to behave like an ideal Fermi gas. Copper metal in the solid state has a mass density of 9gr/cm^3. Assume that each copper atom donates one electron to the Fermi gas. Assume the system is at $T = 0$ K. (a) Compute the Fermi energy, ε_F, of the electron gas. (b) Compute the Fermi "temperature," $T_F = \varepsilon_F/k_B$.

Problem 7.21. The density of states of an ideal Fermi–Dirac gas is

$$g(E) = \begin{cases} D & \text{if } E > 0, \\ 0 & \text{if } E < 0, \end{cases}$$

where D is a constant. (a) Compute the Fermi energy. (b) Compute the heat capacity at very low temperature.

Problem 7.22. Compute the magnetization of an ideal gas of spin-$\frac{1}{2}$ fermions in the presence of a magnetic field. Assume that the fermions each have magnetic moment μ_e. Find an expression for the magnetization in the limit of weak magnetic field and $T \to 0$ K.

Problem 7.23. Show that the entropy for an ideal Fermi–Dirac ideal gas (neglecting spin) can be written in the form

$$S = -k_B \sum_{\mathbf{l}} \{\langle n_{\mathbf{l}} \rangle \ln[\langle n_{\mathbf{l}} \rangle] + (1 - \langle n_{\mathbf{l}} \rangle) \ln[1 - \langle n_{\mathbf{l}} \rangle]\},$$

where $\langle n_{\mathbf{l}} \rangle = (e^{\beta(\varepsilon_{\mathbf{l}} - \mu)} + 1)^{-1}$.

Problem 7.24. To lowest order in the density, find the difference in the pressure and isothermal compressibility between an ideal boson and an ideal fermion gas. Assume that the fermions and bosons have the same mass and both are spinless. (*Note*: You are now considering fairly high temperature.)

Problem S7.1. Show that near the critical temperature the gap function, $\Delta(T)$, in a weakly coupled, condensed Fermi fluid (superconductor) in the mean field approximation has temperature dependence

$$\frac{\Delta(T)}{\Delta(0)} = 1.74\left(1 - \frac{T}{T_c}\right)^{1/2},$$

where T_c is the critical temperature and $\Delta(0)$ is the gap function at $T = 0$ K.

Problem S7.2. The unitary matrix, $\bar{U}_{\mathbf{k}} \equiv \begin{pmatrix} u_{\mathbf{k}}^* & v_{\mathbf{k}} \\ -v_{\mathbf{k}}^* & u_{\mathbf{k}} \end{pmatrix}$, diagonalizes the effective Hamiltonian $\bar{K}_{\mathbf{k}} \equiv \begin{pmatrix} \varepsilon_{\mathbf{k}} & \Delta_{\mathbf{k}} \\ \Delta_{\mathbf{k}}^* & -\varepsilon_{\mathbf{k}} \end{pmatrix}$. Compute $v_{\mathbf{k}}$ and $u_{\mathbf{k}}$.

8

ORDER–DISORDER TRANSITIONS AND RENORMALIZATION THEORY

8.A. INTRODUCTION

In previous chapters we have used mean field theory to construct a variety of models of equilibrium systems which undergo second-order phase transitions. In this chapter we will show how the idea of *scaling* leads to a universal theory of critical phenomena, and we will derive some exact results for order–disorder transitions.

A useful way to obtain information about fluctuations in an equilibrium system is linear response theory. Experimentally, we can probe equilibrium systems with a weak external field which couples to the thermodynamic quantities of interest. For example, a magnetic field couples to the magnetization and allows us to probe magnetization fluctuations in a system. The way in which a system responds to an external field is determined by the type of fluctuations which occur in it. Indeed, as we shall see, the response function can be expressed directly in terms of the correlation functions for equilibrium fluctuations. In this chapter we shall use time-independent linear response theory to obtain a relation between the long-wavelength part of the equilibrium correlation functions and the static response functions. We will then use mean field theory to show that near critical points, fluctuations become correlated over a wide region of space, indicating that long-range order has set in.

If we are to describe the thermodynamic behavior of systems as they approach a critical point, we must have a systematic way of treating thermodynamic functions in the neighborhood of the critical point. Such a method exists and is called *scaling*. We can write the singular part (the part affected by the phase transition) of thermodynamic functions near a critical point in terms of distance from the critical point. Widom was first to point out that as the distance from the critical point is varied, thermodynamic functions change their scale but not their functional form. The idea of scaling can be expressed mathematically by saying that the thermodynamic functions are *homogeneous functions* of their distance from the critical point. As we shall see, the idea of scaling underlies all theories of critical phenomena and enables us to obtain new equalities between various critical exponents. The scaling behavior

of thermodynamic functions near a critical point has been verified experimentally.

Kadanoff was able to apply the idea of scaling in a very clever way to the Ising model and in so doing opened the way for the modern theory of critical phenomena introduced by Wilson. The idea behind Kadanoff scaling is the following. As the correlation length increases, we can rescale (increase) the size of the interacting units on the lattice. That is, instead of describing the lattice in terms of interacting spins, we describe it in terms of interacting *blocks* of spin. We take the average spin of each block and consider it as the basic unit. As the system approaches the critical point, the correlation length gets larger and the block size gets larger in such a way that the thermodynamic functions do not change their form, but they do rescale. With this picture, Kadanoff was able to find a relation between the critical exponents associated to the correlation length of fluctuations and the critical exponents which were introduced in Section 3.H.

Wilson carried Kadanoff's idea a step farther and introduced a means of computing critical exponents microscopically. Wilson's approach is based on a systematic rescaling of the effective Hamiltonian which describes a system near the critical point. As the correlation length increases near a critical point, one repeatedly integrates out the effect of shorter-ranged correlations and requires that the Hamiltonian retain the same functional form. This leads to nonlinear recursion relations between the effective coupling constants on different length scales. The critical point corresponds to a fixed point of these recursion relations. The eigenvalues of the transformation matrix (linearized about the fixed points) which yields the recursion relations can be expressed in terms of the critical exponents. Therefore, if we can find the eigenvalues, the problem is solved. In this chapter we will show how Wilson's theory can be applied to some simple models, such as the triangular planar spin lattice, and in the *special topics* section section we will apply it to the S^4 model. We will leave some examples for homework problems.

Finally, as a *special topic*, we shall derive Onsager's exact expression for the heat capacity of a two-dimensional square planar Ising spin lattice, and we shall show that this system does indeed have a critical point. The method we use to derive Onsager's original result is not the same as that used by Onsager. Instead we follow a procedure developed by Kasteleyn and by Fisher using dimer graphs. The derivation of the Onsager result is then fairly straightforward.

8.B. STATIC CORRELATION FUNCTIONS AND RESPONSE FUNCTIONS [1, 2]

In this section we will investigate some general properties of static correlation functions and response functions in an equilibrium system. These will prove useful when we discuss scaling properties of equilibrium systems in subsequent

sections. We will first give some general relations and then use mean field theory to help build intuition about their qualitative behavior.

8.B.1. General Relations

Let us consider a system of N particles in a container of volume V at a fixed temperature T. We will assume that the ith particle has spin $\hat{s}_i$, magnetic moment μ, momentum operator $\hat{\mathbf{p}}_i$, and position operator $\hat{\mathbf{q}}_i$. The magnetization density operator is defined as

$$\hat{\mathbf{m}}(\mathbf{r}) = \mu \sum_{i=1}^{N} \hat{s}_i \, \delta(\hat{\mathbf{q}}_i - \mathbf{r}). \tag{8.1}$$

The total magnetization operator is

$$\hat{\mathbf{M}} = \int_V d\mathbf{r}\, \hat{\mathbf{m}}(\mathbf{r}) = \mu \sum_{i=1}^{N} \hat{s}_i. \tag{8.2}$$

If a magnetic induction field, $\mathbf{B}(\mathbf{r})$, is present, the total Hamiltonian may be written

$$\hat{H} = \hat{H}_0 - \int_V d\mathbf{r}\, \hat{\mathbf{m}}(\mathbf{r}) \cdot \mathbf{B}(\mathbf{r}), \tag{8.3}$$

where $\hat{H}_0$ is the unperturbed Hamiltonian:

$$\hat{H}_0 = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{(ij)} V(\hat{\mathbf{q}}_i, \hat{\mathbf{q}}_j, s_i, s_j). \tag{8.4}$$

In Eq. (8.4), the first term on the right is the kinetic energy. The second term on the right is the interaction energy between particles, and the summation is over all pairs of particles.

Let us now assume that the applied magnetic field, $\mathbf{B}$, is constant throughout the volume, V. The average magnetization in the presence of this field is

$$\langle \mathbf{M} \rangle_{\mathbf{B}} = \frac{\mathrm{Tr}\,[e^{-\beta \hat{H}} \hat{\mathbf{M}}]}{\mathrm{Tr}\,[e^{-\beta \hat{H}}]}. \tag{8.5}$$

If we let $\hat{M}_\alpha$ denote the α^{th} component of the magnetization operator, $\hat{\mathbf{M}}$, where $\alpha = x, y, z$, then we can write for the static magnetic susceptibility

$$\begin{aligned} \chi_{\alpha,\alpha'} &= \left(\frac{\partial \langle M_\alpha \rangle_{\mathbf{B}}}{\partial B_{\alpha'}} \right)_{T,N,B=0} = \beta(\langle \hat{M}_\alpha \hat{M}_{\alpha'} \rangle - \langle M_\alpha \rangle \langle M_{\alpha'} \rangle) \\ &= \beta \langle (\hat{M}_\alpha - \langle \hat{M}_\alpha \rangle)(\hat{M}_{\alpha'} - \langle M_{\alpha'} \rangle) \rangle. \end{aligned} \tag{8.6}$$

Note that the susceptibility as we have defined it is independent of the applied magnetic field. It contains information about the thermodynamic properties of the unperturbed system.

Let us now introduce the magnetization density fluctuation, $\delta\hat{m}_\alpha(\mathbf{r}) = m_\alpha(\mathbf{r}) - \langle m_\alpha(\mathbf{r})\rangle$. Then the static susceptibility can be written

$$\chi_{\alpha,\alpha'} = \beta \int_V d\mathbf{r}_1 \int_V d\mathbf{r}_2 \langle \delta\hat{m}_\alpha(\mathbf{r}_1)\delta\hat{m}_{\alpha'}(\mathbf{r}_2)\rangle \equiv \beta \int_V d\mathbf{r}_1 \int_V d\mathbf{r}_2 C_{\alpha,\alpha'}(\mathbf{r}_1, \mathbf{r}_2), \tag{8.7}$$

where

$$C_{\alpha,\alpha'}(\mathbf{r}_1, \mathbf{r}_2) = \langle \delta\hat{m}_\alpha(\mathbf{r}_1)\delta\hat{m}_{\alpha'}(\mathbf{r}_2)\rangle \tag{8.8}$$

is the static spatial correlation function between magnetization density fluctuations at points $\mathbf{r}_1$ and $\mathbf{r}_2$ in the system.

For systems with very large volume, V, we can neglect boundary effects if there are no spatially varying external forces present, and the static spatial correlation function will depend only on the relative displacement, $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$, of the two points in the system. Then we can write

$$C_{\alpha,\alpha'}(\mathbf{r}) = \langle \delta\hat{m}_\alpha(\mathbf{r})\delta\hat{m}_{\alpha'}(\mathbf{0})\rangle. \tag{8.9}$$

The static susceptibility becomes

$$\chi_{\alpha,\alpha'} = \beta V \int_V d\mathbf{r}\, C_{\alpha,\alpha'}(\mathbf{r}). \tag{8.10}$$

It is useful to introduce yet another quantity, the static structure factor,

$$G_{\alpha,\alpha'}(\mathbf{k}) \equiv \int_V d\mathbf{r}\, e^{i\mathbf{k}\cdot\mathbf{r}} C_{\alpha,\alpha'}(\mathbf{r}). \tag{8.11}$$

This can also be written

$$\begin{aligned} G_{\alpha,\alpha'}(\mathbf{k}) &= \frac{1}{V}\int_V d\mathbf{r}_1 \int_V d\mathbf{r}_2 e^{i\mathbf{k}\cdot(\mathbf{r}_1-\mathbf{r}_2)} \langle \delta\hat{m}_\alpha(\mathbf{r}_1)\delta\hat{m}_{\alpha'}(\mathbf{r}_2)\rangle \\ &= \frac{1}{V}\langle \delta\hat{m}_\alpha(\mathbf{k})\delta\hat{m}_{\alpha'}(-\mathbf{k})\rangle. \end{aligned} \tag{8.12}$$

In Eq. (8.12) we have made use of the Fourier decomposition of the spatially varying fluctuations

$$\delta\hat{m}_\alpha(\mathbf{r}) = \frac{1}{V}\sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{r}} \delta\hat{m}_\alpha(\mathbf{k}). \tag{8.13}$$

If we now compare Eqs. (8.7) and (8.12), we see that the static susceptibility can be written in terms of the infinite wavelength component of the static structure factor

$$\chi_{\alpha,\alpha'} = \beta V G_{\alpha,\alpha'}(\mathbf{k} = \mathbf{0}). \tag{8.14}$$

Thus, we see that the way in which a system responds to a constant external field is completely determined by the long-wavelength equilibrium fluctuations. In Chapter 3 we found that the static susceptibility becomes infinite as we approach the critical point. Thus, Eq. (8.14) tells us that near the critical point the correlation function will have a large long-wavelength component, indicating that long-range order has begun to occur.

8.B.2. Application to the Ising Lattice

Consider now a three-dimensional Ising lattice with volume V. Assume that the lattice has N lattice sites. Let us break the lattice into blocks of volume Δ, so each block has $n = (\Delta/V)N$ spins. Let us assume the lattice has a temperature, T, which is above the critical point so the total magnetization is zero, $\langle \mathbf{M} \rangle = 0$. Let us assume that the z component of magnetization of the l^{th} block is m_l (m_l can be positive or negative and can have values ranging from $m_l = -n\mu$ to $m_l = +n\mu$). Since the total magnetization is zero, we must have $\sum_l \langle m_l \rangle = 0$. If the block sizes are large enough so that n is large and each block achieves equilibrium locally, then we can also assume that $\langle m_l \rangle = 0$.

Let us now analyze the system using Ginzburg-Landau mean field theory (cf. Section 3.G). We can write a phenomenological expression for the partition function

$$Z_N(T) = \sum_{\{m_l\}} e^{-V\phi\{m_l\}}, \tag{8.15}$$

where $\phi\{m_l\}$ is the free energy density of the system, $e^{-V\phi\{m_l\}}$ is the probability of finding the lattice in a configuration $\{m_l\}$, and the summation is over all possible configurations of the lattice. Since we require that $\langle m_l \rangle = 0$, $\phi\{m_l\}$ must be an even function of m_l.

If we assume that the lattice is very large, then we can let the discrete spatial variation of the local magnetization density become continuous, $m_\alpha \to \delta m(\mathbf{r})$. For small fluctuations away from equilibrium we can write

$$\begin{aligned} \phi\{\delta m(\mathbf{r})\} = \beta a(T) &+ \frac{1}{2} C_1(T) \int_V d\mathbf{r} (\delta m(\mathbf{r}))^2 \\ &+ \frac{1}{2} C_2(T) \int_V d\mathbf{r} (\nabla \delta m(\mathbf{r})) \cdot (\nabla \delta m(\mathbf{r})) + \cdots, \end{aligned} \tag{8.16}$$

where $a(T)$ is the nonmagnetic free energy density. Let us next note that

$$\int_V d\mathbf{r}(\delta m(\mathbf{r}))^2 = \frac{1}{V}\sum_{\mathbf{k}} \delta m(\mathbf{k})\delta m(-\mathbf{k}), \tag{8.17}$$

where $\delta m(-\mathbf{k}) = \delta m^*(\mathbf{k})$ and

$$\int_V d\mathbf{r}(\nabla\delta m(\mathbf{r}))\cdot(\nabla\delta m(\mathbf{r})) = \frac{1}{V}\sum_{\mathbf{k}} k^2\delta m(\mathbf{k})\delta m(-\mathbf{k}). \tag{8.18}$$

The free energy can then be written

$$\phi\{\delta m(\mathbf{k}\} = \beta a(T) + \frac{1}{2V}\sum_{\mathbf{k}}(C_1(T) + k^2C_2(T))\delta m(\mathbf{k})\delta m(-\mathbf{k}) + \cdots. \tag{8.19}$$

We can use this free energy to obtain the probability for a fluctuation, $\delta m(\mathbf{k})$, to occur. It is

$$P(\delta m(\mathbf{k})) = C\exp\left(-\frac{1}{2}(C_1 + k^2C_2)|\delta m(\mathbf{k})|^2\right), \tag{8.20}$$

where C is a normalization constant. With the probability density in Eq. (8.20), we can compute the static structure factor. We find

$$\begin{aligned} G(\mathbf{k}) &= \int_{-\infty}^{\infty} d[\delta m(\mathbf{k})]P(\delta m(\mathbf{k}))|\delta m(\mathbf{k})|^2 \\ &= \langle|\delta m(\mathbf{k})|^2\rangle = \frac{1}{C_1 + k^2C_2}. \end{aligned} \tag{8.21}$$

The static susceptibility is given by

$$\chi = \beta VG(\mathbf{k} = 0) = \frac{\beta V}{C_1}. \tag{8.22}$$

Near a phase transition, the susceptibility behaves as $\chi \approx (T - T_c)^{-1}$ (cf. Section S3.C). Therefore, $C_1 \approx (T - T_c)$.

The static correlation function is given by

$$C(\mathbf{r}) = \frac{1}{V}\sum_{\mathbf{k}} G(\mathbf{k})e^{-i\mathbf{k}\cdot\mathbf{r}} = \int \frac{d\,\mathbf{k}}{(2\pi)^3}\frac{e^{-i\mathbf{k}\cdot\mathbf{r}}}{(C_1 + k^2C_2)} = \frac{1}{4\pi C_2 r}e^{-r\sqrt{C_1/C_2}}. \tag{8.23}$$

The correlation function has a length $\xi \approx \sqrt{C_2/C_1}$. Since $C_1 \approx (T - T_c)$ near a critical point, the range $\xi \approx \sqrt{C_2/(T - T_c)}$ goes to infinity as $(T - T_c)^{-1/2}$ as

we approach a critical point. Therefore, at the critical point the spatial correlations between fluctuations extend across the entire system.

8.C. SCALING [1, 3]

As we approach the critical point, the distance over which fluctuations are correlated approaches infinity and all effects of the finite lattice spacing are wiped out. There are no natural length scales left. Thus we might expect that in the neighborhood of the critical point, as we change the distance from the critical point (for example, by changing the temperature), we do not change the form of the free energy but only *its scale*.

The idea of scaling underlies all critical exponent calculations. To understand scaling, we must first introduce the concept of a homogeneous function.

8.C.1. Homogeneous Functions

A function $F(\lambda x)$ is homogeneous if for all values of λ, we obtain

$$F(\lambda x) = g(\lambda)F(x). \tag{8.24}$$

The general form of the function $g(\lambda)$ can be found easily. We first note that

$$F(\lambda\mu x) = g(\lambda\mu)F(x) = g(\lambda)g(\mu)F(x) \tag{8.25}$$

so that

$$g(\lambda\mu) = g(\lambda)g(\mu). \tag{8.26}$$

If we take the derivative with respect to μ, we find

$$\frac{\partial}{\partial\mu}g(\lambda\mu) = \lambda g'(\lambda\mu) = g(\lambda)g'(\mu), \tag{8.27}$$

where $g'(\mu) = dg(\mu)/d\mu$. We next set $\mu = 1$ and $g'(1) = p$. Then

$$\lambda g'(\lambda) = pg(\lambda). \tag{8.28}$$

If we integrate from 1 to λ and note that $g(1) = 1$, we find

$$g(\lambda) = \lambda^p. \tag{8.29}$$

Thus,

$$F(\lambda x) = \lambda^p F(x) \tag{8.30}$$

and $F(x)$ is said to be a homogeneous function of degree p. A homogeneous function has a very special form. In Eq. (8. 30), if we let $\lambda = x^{-1}$, we obtain

$$F(x) = F(1)x^p. \tag{8.31}$$

Thus, the homogeneous function $F(x)$ has power-law dependence on its arguments.

Let us now consider a homogeneous function of two variables $f(x, y)$. Such a function can be written in the form

$$f(\lambda^p x, \lambda^q y) = \lambda f(x, y) \tag{8.32}$$

and is characterized by two parameters, p and q. It is convenient to write $f(x, y)$ in another form. We will let $\lambda = y^{-1/q}$. Then

$$f(x, y) = y^{1/q} f\left(\frac{x}{y^{p/q}}, 1\right), \tag{8.33}$$

and we see that the homogeneous function, $f(x, y)$, depends on x and y only through the ratio $x/y^{p/q}$ aside from a multiplicative factor. We can now apply these ideas to thermodynamic quantities near the critical point.

8.C.2. Widom Scaling [4]

As we have seen in numerous examples, when a phase transition occurs in a system, part of the free energy begins to behave in a manner which leads to singular behavior in some of the thermodynamic response functions. If we assume that the "singular" part of the free energy scales, then we can find a relation between various critical exponents which agrees with experiment. We will consider magnetic systems since they give a simple picture, and we shall assume that a magnetic induction field, $\mathbf{B}$, is present. Let us write the free energy per lattice site in terms of a regular part, $g_r(T, \mathbf{B})$, which does not change in any significant way as we approach the critical point, and a singular part, $g_s(\varepsilon, \mathbf{B})$, which contains the important singular behavior of the system in the neighborhood of the critical point. Then

$$g(T, \mathbf{B}) = g_r(T, \mathbf{B}) + g_s(\varepsilon, \mathbf{B}), \tag{8.34}$$

where $\varepsilon = (T - T_c)/T_c$ and T_c is the critical temperature.

We shall assume that the singular part of the free energy is generalized homogeneous function of its parameters,

$$g_s(\lambda^p \varepsilon, \lambda^q B) = \lambda g_s(\varepsilon, B). \tag{8.35}$$

We now write the free energy as a function of the magnitude of $\mathbf{B}$. For

the systems we consider here, its direction does not play an important role. The critical exponents in Section 3H can all be determined in terms of p and q. Let us first find an expression for β, which is defined [cf. Eq. (3.85)] as

$$M(\varepsilon, B = 0) \sim (-\varepsilon)^{\beta}. \tag{8.36}$$

If we differentiate Eq. (8.35) with respect to B, we obtain

$$\lambda^q M(\lambda^p \varepsilon, \lambda^q B) = \lambda M(\varepsilon, B). \tag{8.37}$$

If we next let $\lambda = (-\varepsilon)^{-1/p}$ and set $B = 0$, we obtain

$$M(\varepsilon, 0) = (-\varepsilon)^{(1-q)/p} M(-1, 0). \tag{8.38}$$

Thus,

$$\beta = \frac{1-q}{p} \tag{8.39}$$

and we obtain our first relation.

Let us next determine the exponent δ (the degree of the critical isotherm), which is defined [cf. Eq. (3.84)] as

$$M(0, B) = |B|^{1/\delta} \operatorname{sign} B. \tag{8.40}$$

If we set $\varepsilon = 0$ and $\lambda = B^{-1/q}$ in Eq. (8.35), we can differentiate with respect to B and obtain

$$M(0, B) = B^{(1-q)/q} M(0, 1). \tag{8.41}$$

Thus,

$$\delta = \frac{q}{1-q} \tag{8.42}$$

and we obtain our second relation.

The magnetic susceptibility is obtained from the thermodynamic relation

$$\chi = -\left(\frac{\partial^2 g}{\partial B^2}\right)_T \sim \begin{cases} (-\varepsilon)^{-\gamma'}, & T < T_c, \\ (\varepsilon)^{-\gamma}, & T > T_c. \end{cases} \tag{8.43}$$

By differentiating Eq. (8.37) with respect to B, we can write

$$\lambda^{2q} \chi(\lambda^p \varepsilon, \lambda^q B) = \lambda \chi(\varepsilon, B). \tag{8.44}$$

If we now set $B = 0$ and let $\lambda = (\varepsilon)^{-1/p}$, we find

$$\chi(\varepsilon, 0) = \varepsilon^{(1-2q)/p}\chi(1, 0). \tag{8.45}$$

Thus, the critical exponent for the susceptibility is

$$\gamma = \frac{2q - 1}{p}, \tag{8.46}$$

and we obtain our third relation between p and q and the critical exponents. By a similar calculation, we find that $\gamma = \gamma'$.

The heat capacity at constant B is given by

$$C_B = -T\left(\frac{\partial^2 g}{\partial T^2}\right)_B \sim (\varepsilon)^{-\alpha} \tag{8.47}$$

[cf. Eq. (3.86)]. From Eq. (8.35), we obtain

$$\lambda^{2p} C_B(\lambda^p \varepsilon, \lambda^q B) = \lambda C_B(\varepsilon, B). \tag{8.48}$$

If we set $B = 0$ and $\lambda = (\varepsilon)^{-1/p}$, we find

$$C_B(\varepsilon, 0) = \varepsilon^{(1-2p)/p} C_B(1, 0), \tag{8.49}$$

and therefore

$$\alpha = 2 - \frac{1}{p} \tag{8.50}$$

is our fourth relation. By a similar calculation we find $\alpha = \alpha'$.

In Eqs. (8.39), (8.42), (8.46), and (8.50), we have obtained the four critical exponents, α, β, γ, and δ, in terms of the two parameters p and q. If we combine Eqs. (8.39), (8.42), and (8.46), we find

$$\gamma' = \gamma = \beta(\delta - 1). \tag{8.51}$$

From Eqs. (8.39), (8.42), and (8.50) we find

$$\alpha + \beta(\delta + 1) = 2. \tag{8.52}$$

Thus, the Widom scaling assumption allows us to obtain *exact* relations between the critical exponents. These relations agree with mean field theory ($\alpha = 0$, $\beta = \frac{1}{2}$, $\delta = 3$, $\gamma = 1$) as one can easily check. They also agree with experimentally obtained values of the critical exponents which generally differ from mean field results (cf. Table 8.1).

For later reference, it is useful to express p and q in terms of the critical exponents. We find

$$p = \frac{1}{\beta}\frac{1}{(\delta+1)} \tag{8.53}$$

and

$$q = \delta\frac{1}{(\delta+1)}. \tag{8.54}$$

The scaling property for systems near the critical point has been verified experimentally for fluids [5] and magnetic systems [1].

8.C.3. Kadanoff Scaling [6]

Kadanoff has shown how to apply the idea of scaling to the Ising model. Let us consider a d-dimensional Ising system with nearest-neighbor coupling (Γ nearest neighbors). The Hamiltonian is

$$H\{S\} = -K\sum_{(ij)}^{\Gamma N/2} S_i S_j - B\sum_{i=1}^{N} S_i, \tag{8.55}$$

where N is the number of lattice sites. We will divide the lattice into blocks of length La, where a is the distance between sites (cf. Fig. 8.1). We choose L so that $La \ll \xi$ where ξ is the correlation length of spin fluctuations on the lattice [cf. Eq. (8.23)]. The total number of spins in each block is L^d. The total number of blocks is NL^{-d}. The total spin in block I is

$$S_I' = \sum_{i\varepsilon I} S_i. \tag{8.56}$$

Since L is chosen so that $La \ll \xi$, the spins in each block will be highly correlated and it is likely that they will be aligned to some extent. In view of this, it is useful to define a new spin variable, S_I, through the relation

$$S_I' = ZS_I, \tag{8.57}$$

where $S_I = \pm 1$ and $Z = L^y$.

Spins interact with nearest-neighbor spins, so blocks should also interact with nearest-neighbor blocks. Thus, the block Hamiltonian will be of the form

$$H\{S_L\} = -K_L\sum_{(IJ)}^{\Gamma NL^{-d}/2} S_I S_J - B_L\sum_{I=1}^{NL^{-d}} S_I \tag{8.58}$$

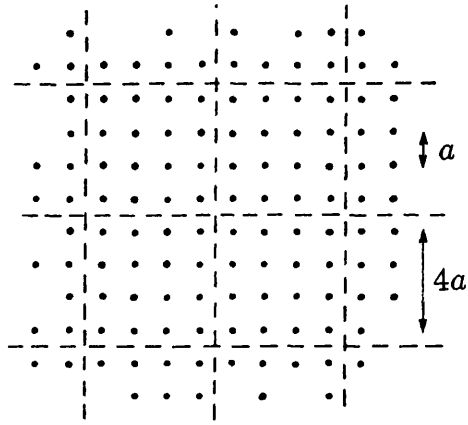


Fig. 8.1. Decomposition of a square lattice into square blocks whose sides have length $La = 4a$.

where K_L is the new effective interaction between nearest-neighbor blocks. The block Hamiltonian looks exactly like the site Hamiltonian except that all quantities are rescaled. Therefore, we expect the free energy per block, $g(\varepsilon_L, B_L)$, to have the same functional form as the free energy per site, $g(\varepsilon, B)$. Since there are L^d sites per block, we have

$$g(\varepsilon_L, B_L) = L^d g(\varepsilon, B). \tag{8.59}$$

If we rescale our system and describe it in terms of blocks rather than sites, we reduce the effective correlation length (measured in units of La) and therefore we move farther away from the critical point. Thus, the correlation length will behave as

$$\xi_L(\varepsilon_L, B_L) = L^{-1}\xi(\varepsilon, B). \tag{8.60}$$

Since rescaling moves us away from the critical point, the temperature ε and magnetic field B must also rescale. We assume that

$$\varepsilon_L = \varepsilon L^x, \tag{8.61}$$

where x is positive. Similarly,

$$B\sum_{i=1}^{N} S_i = B\sum_{I=1}^{NL^{-d}}\sum_{i\in I} S_i = B\sum_{I=1}^{NL^{-d}} S_I{}' = BZ\sum_{I=1}^{NL^{-d}} S_I, \tag{8.62}$$

so that

$$B_L = BZ = L^y B. \tag{8.63}$$

Equation (8.58) now becomes

$$g(L^x\varepsilon, L^y B) = L^d g(\varepsilon, B). \tag{8.64}$$

If we compare Eq. (8.64) with Eq. (8.35), we find $x = pd$ and $y = qd$. Thus,

$$q < 1 \tag{8.65}$$

in agreement with experiment

The Kadanoff view of scaling allows us to introduce two new critical exponents which are associated with the spatial correlations of spin fluctuations in the system. The block correlation function is defined

$$C(r_L, \varepsilon_L) = \langle S_I S_J \rangle - \langle S_I \rangle \langle S_J \rangle, \tag{8.66}$$

where r_L is the distance between blocks I and J in units of La. We can write Eq. (8.66) as

$$\begin{aligned} C(r_L, \varepsilon_L) &= Z^{-2}[\langle S'_I S'_J \rangle - \langle S'_I \rangle \langle S'_J \rangle] \\ &= Z^{-2} \sum_{i \in I} \sum_{j \in J} [\langle S_i S_j \rangle - \langle S_i \rangle \langle S_j \rangle] \\ &= Z^{-2}(L^d)^2 [\langle S_i S_j \rangle - \langle S_i \rangle \langle S_j \rangle] = Z^{-2}(L^d)^2 C(r, \varepsilon), \end{aligned} \tag{8.67}$$

where r is the distance between sites i and j on different blocks. The distances r_L and r are related by the expression

$$r_L = L^{-1} r, \tag{8.68}$$

and we write

$$C(L^{-1}r, \varepsilon L^x) = L^{2(d-y)} C(r, \varepsilon). \tag{8.69}$$

If we choose $L = r/a$, the correlation function takes the form

$$C(r, \varepsilon) = \left(\frac{r}{a}\right)^{2(y-d)} C\left(a, \varepsilon \left(\frac{r}{a}\right)^x\right). \tag{8.70}$$

We can now introduce two new exponents for the correlation function. We first define a critical exponent, ν, for the correlation length as

$$\xi \sim (T - T_c)^{-\nu}. \tag{8.71}$$

For mean field theories $\nu = \frac{1}{2}$. From Eq. (8.23) we see that the correlation function away from the critical point depends on r and ε in the combination $r/\xi = r\varepsilon^\nu$. In Eq. (8.70) the correlation function depends on r and ε in the

combination εr^x. Thus,

$$x = pd = \nu^{-1}. \tag{8.72}$$

At the critical point, $\varepsilon = 0$ and the correlation function varies as

$$C(r,0) \sim (r)^{2(y-d)}. \tag{8.73}$$

In three dimensions, we expect the correlation function at the critical point to behave as

$$C(r,0) \sim \left(\frac{1}{r}\right)^{1+\eta}, \tag{8.74}$$

where η is another new exponent. For mean field theories, $\eta = 0$. In d dimensions, $C(r,0)$ varies as

$$C(r,0) = \left(\frac{1}{r}\right)^{(d-2+\eta)} \tag{8.75}$$

and we can make the identification

$$(d-2+\eta) = 2(d-y) = 2d(1-q) \tag{8.76}$$

Thus, the exponents for the correlation function can be written in terms of the exponents for the thermodynamic quantities we have already considered. From Eqs. (8.50) and (8.72) we find

$$\nu = \frac{2-\alpha}{d} \tag{8.77}$$

and from Eqs. (8.54) and (8.76) we find,

$$\eta = 2 - d\left(\frac{\delta-1}{\delta+1}\right) = 2 - \frac{d\gamma}{2\beta+\gamma}. \tag{8.78}$$

Thus, Kadanoff scaling allows us to obtain two new critical exponents and new identities between all the exponents.

8.D. MICROSCOPIC CALCULATION OF CRITICAL EXPONENTS [3, 7–11]

The Kadanoff picture of scaling was given firm mathematical foundation by Wilson [12], who developed a technique for computing the critical exponents microscopically. We shall outline Wilson's procedure for the case of spin systems, and then in Exercise 8.1 we apply it to a triangular planar lattice.

Let us consider a system described by the partition function

$$Z(\mathbf{K},N)=\sum_{\{S_i\}}\exp[-\mathscr{H}(\mathbf{K},\{S_i\},N)]. \tag{8.79}$$

The effective Hamiltonian, $\mathscr{H}(\mathbf{K},\{S_i\},N)$ (which includes temperature), can be written in the form

$$\begin{aligned}\mathscr{H}(\mathbf{K},\{S_i\},N)=K_0+K_1\sum_i S_i+K_2\sum_{(i,j)}^{(1)}S_iS_j+K_3\sum_{(i,j)}^{(2)}S_iS_j\\ +K_4\sum_{(i,j,k)}^{(1)}S_iS_jS_k+\cdots,\end{aligned} \tag{8.80}$$

where $\mathbf{K}$ is an infinite-dimensional vector containing all coupling constants, and the summation $\sum^{(i)}$ means that only (ith) nearest neighbors are included. The coupling constants, K_i, contain the temperature. For the Ising model, $K_1=-\beta B$, $K_2=-\beta J$ where J is the strength of the coupling between spins, and $K_3=K_4=\cdots=0$.

We can introduce blocks and sum over spins, σ_I, interior to each block. Thus,

$$\begin{aligned}Z(\mathbf{K},N)&=\sum_{\{S_I.\sigma_I\}}\exp[-\mathscr{H}(\mathbf{K},\{S_I,\sigma_I\},N)]\\ &=\sum_{\{S_I\}}\exp[-\mathscr{H}(\mathbf{K}_L,\{S_I\},NL^{-d})]=Z(\mathbf{K}_L,NL^{-d}).\end{aligned} \tag{8.81}$$

Since the new partition function has the same functional form as the old one, we can write the following expression for the free energy density per site:

$$g(\mathbf{K})=\lim_{N\to\infty}\frac{1}{N}\ln Z(\mathbf{K},N)=\lim_{N\to\infty}\frac{1}{N}\ln Z(\mathbf{K}_L,NL^{-d})=L^{-d}g(\mathbf{K}_L). \tag{8.82}$$

The coupling constant vectors, $\mathbf{K}$ and $\mathbf{K}_L$, of the site spin and block spin systems, respectively, will be related by a transformation,

$$\mathbf{K}_L=\mathbf{T}(\mathbf{K}), \tag{8.83}$$

where $\mathbf{K}_L$ will be a vector whose elements are nonlinear functions of the components of $\mathbf{K}$. Since our new Hamiltonian is identical in form to the old one, we can repeat the process and transform to even larger blocks nL. After n transformations we find

$$\mathbf{K}_{nL}=\mathbf{T}(\mathbf{K}_{(n-1)L}). \tag{8.84}$$

If the system is not critical, there will be a finite correlation range. Thus, when we transform to larger blocks the effective correlation range appears to shrink and we move away from the critical point. However, when the system is critical, the correlation range is infinite and we reach a fixed point of the transformation. At the fixed point, the transformation $\mathbf{T}$ can no longer change the vector $\mathbf{K}$. Thus, the critical point occurs for values of the coupling constant vectors, $\mathbf{K}^*$, which satisfy the condition

$$\mathbf{K}^* = \mathbf{T}(\mathbf{K}^*). \tag{8.85}$$

The sequence of transformations $\mathbf{T}$ is called the renormalization group (although $\mathbf{T}$ only has properties of a semigroup). The motion of the vector $\mathbf{K}$ in coupling constant space is similar to the motion of the vector describing a state point in phase space, except that the motion of $\mathbf{K}$ occurs in discrete jumps rather than continuously.

It is useful to illustrate the possible motions of $\mathbf{K}$ for the case of a two-dimensional vector, $\mathbf{K} = (K_1, K_2)$. Equation (8.84) can be thought to describe the motion of $\mathbf{K}$ in $\mathbf{K}$ space (the space of components of $\mathbf{K}$) as we change block size. To locate a critical point in $\mathbf{K}$ space, we must locate the fixed points of Eq. (8.84). The procedure is identical to that used to find and classify the fixed points of classical dynamical equations. Let us assume that a fixed point of the transformation $\mathbf{K}_L = \mathbf{T}(\mathbf{K})$ occurs at $\mathbf{K}^* = (K_1^*, K_2^*)$. We will want to know how the vector $\mathbf{K}$ moves in the neighborhood of the point $\mathbf{K}^*$. We must linearize Eq. (8.84) about $\mathbf{K}^*$. We will let $\delta\mathbf{K}_L = (\mathbf{K}_L - \mathbf{K}^*)$ and $\delta\mathbf{K} = (\mathbf{K} - \mathbf{K}^*)$. Then for small $\delta\mathbf{K}_L$ and $\delta\mathbf{K}$ we get a linearized transformation

$$\delta\mathbf{K}_L = \mathbb{A} \cdot \delta\mathbf{K}, \tag{8.86}$$

where

$$\mathbb{A} = \begin{pmatrix} \dfrac{\partial K_{1L}}{\partial K_1} & \dfrac{\partial K_{1L}}{\partial K_2} \\ \dfrac{\partial K_{2L}}{\partial K_1} & \dfrac{\partial K_{2L}}{\partial K_2} \end{pmatrix}_{\substack{K_{1L}=K_1^* \\ K_{2L}=K_2^*}} \tag{8.87}$$

We next find the eigenvalues and eigenvectors of the matrix $\mathbb{A}$. Since $\mathbb{A}$, in general, will be nonsymmetric, we must use the method of Section 5.C. The eigenvectors can be written

$$\delta\mathbf{u}_L = \bar{\bar{\Lambda}}\,\delta\mathbf{u}, \tag{8.88}$$

where $\bar{\bar{\Lambda}}$ is the matrix of eigenvalues,

$$\bar{\bar{\Lambda}} = \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix}, \tag{8.89}$$

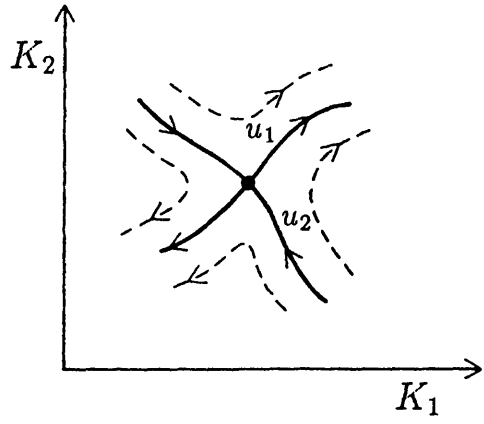


Fig. 8.2. A hyperbolic fixed point with its eigencurves and the flow of points in the neighborhood of the fixed point.

and $\delta\mathbf{u}$ is the right eigenvector,

$$\delta\mathbf{u} = \begin{pmatrix} \delta u_1 \\ \delta u_2 \end{pmatrix}. \tag{8.90}$$

The eigenvalues λ_1 and λ_2 of the matrix $\mathbb{A}$ determine the behavior of trajectories in the neighborhood of the fixed point. In Fig 8.2 we have drawn the case of a hyperbolic fixed point and its eigencurves. Points along the eigencurves move as

$$\delta u_{nL,1} = (\lambda_1)^n \delta u_1, \tag{8.91}$$

$$\delta u_{nL,2} = (\lambda_2)^n \delta u_2. \tag{8.92}$$

Thus, for $\lambda > 1$ the point moves away from the fixed point under the transformation, and for $\lambda < 1$ it moves toward the fixed point. The dashed lines represent the trajectories of points which do not lie on the eigencurves. For a hyperbolic fixed point, they will always move away from the fixed point after many transformations. All systems with vectors $\mathbf{K}$ lying on an eigencurve with eigenvalue $\lambda < 1$ are critical, since with enough transformations they will come arbitrarily close to the fixed point. Such systems are said to exhibit "universality." The behavior of a point along an eigencurve with $\lambda > 1$ is reminiscent of the actual behavior of noncritical systems. As we increase the block size, we move away from the critical point. Thus, an eigenvalue $\lambda > 1$ is called relevant and its eigenvector is identified as one of the physical quantities (ε or B, for example) which measure the distance of the system from the critical point.

In general we write the singular part of the free energy density in terms of the eigenvectors δu_i and eigenvalues λ_i as follows:

$$g_s(\delta u_1, \delta u_2, \delta u_3, \ldots) = L^{-d} g_s(\lambda_1 \delta u_1, \lambda_2 \delta u_2, \lambda_3 \delta u_3, \ldots) \tag{8.93}$$

[cf. Eq. (8.82)]. This looks very much like Widom scaling. Indeed, for the case of an Ising system for which there are two relevant physical parameters which measure the distance of the system from the critical point, we expect that two of the eigenvalues will be relevant, let us say $\lambda_1 > 1$ and $\lambda_2 > 1$. If we compare Eq. (8.93) with Widom scaling of the Ising model,

$$g(\varepsilon, B) = \frac{1}{\lambda} g(\lambda^p \varepsilon, \lambda^q B), \tag{8.94}$$

we can make the identification $\delta u_1 = \varepsilon$ and $\delta u_2 = B$. Thus,

$$\lambda = L^d, \tag{8.95}$$

$$\lambda_1 = (L^d)^p \Rightarrow p = \frac{\ln \lambda_1}{d \ln L}, \tag{8.96}$$

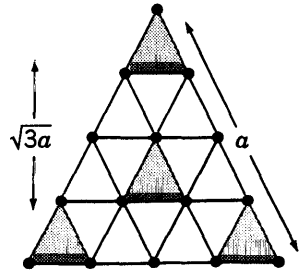
and

$$\lambda_2 = (L^d)^q \Rightarrow q = \frac{\ln \lambda_2}{d \ln L}. \tag{8.97}$$

If we now use Eqs. (8.53) and (8.54), we have expressed the critical exponents in terms of the relevant eigenvalues.

In Exercise 8.1 we use Wilson's theory to obtain approximate expressions for the critical exponents of a triangular planar lattice [13].

■ **EXERCISE 8.1.** Compute the critical exponents for 3-spin blocks on the triangular planar lattice for the two dimensional nearest-neighbor Ising model. Retain terms to lowest order in $\langle V \rangle$.



(a)

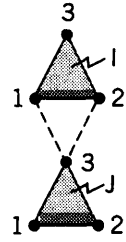
Answer: The Hamiltonian can be written

$$H = -K\sum_{ij} s_i s_j - B\sum_i s_i. \tag{1}$$

We assign to a single block (block I in the figure below) a spin given by $S_I = \text{sign}(s_1^I + s_2^I + s_3^I)$. Therefore, $S_I = +1$ for the following configurations:

$$(\alpha = 1; \downarrow\uparrow\uparrow)(\alpha = 2; \uparrow\downarrow\uparrow)(\alpha = 3; \uparrow\uparrow\downarrow)(\alpha = 4; \uparrow\uparrow\uparrow)$$

The internal spin degrees of freedom are defined, $\sigma_I^\alpha = |s_1^I + s_2^I + s_3^I|_\alpha$. For configurations defined above we have: $\sigma_I^1 = \sigma_I^2 = \sigma_I^3 = 1$, and $\sigma_I^4 = 3$.



(*b*)

The partition function can be written

$$Z(K_L, N) = \sum_{\{S_I\}} \exp[-H(\mathbf{K}_L, \{S_I\})] = \sum_{\{S_I\}}\sum_{\{\sigma_I\}} \exp[-H(\mathbf{K}, \{S_I, \sigma_I\})]. \tag{2}$$

Now define

$$H(\mathbf{K}, \{S_I, \sigma_I\}) = H_0(\mathbf{K}, \{S_I, \sigma_I\}) + V(\mathbf{K}, \{S_I, \sigma_I\}), \tag{3}$$

where

$$H_0(\mathbf{K}, \{S_I, \sigma_I\}) = -K\sum_I \sum_{i\in I}\sum_{j\in I} s_i s_j \tag{4}$$

and

$$V(K, \{S_I, \sigma_I\}) = -K\sum_{I\neq J}\sum_{i\in I}\sum_{j\in J} s_i s_j - B\sum_I\sum_{i\in I} s_i. \tag{5}$$

We next define the expectation value

$$\langle A(\{S_I\})\rangle = \frac{\sum_{\sigma_I} A(\{S_I,\sigma_I\})\exp[-H_0(\mathbf{K},\{S_I,\sigma_I\})]}{\sum_{\sigma_I}\exp[-H_0(\mathbf{K},\{S_I,\sigma_I\})]}. \tag{6}$$

Now note that

$$\begin{aligned}\exp[-H(\mathbf{K}_L,\{S_I\})] &= \left(\sum_{\sigma_I}\exp[-H_0(\mathbf{K},\{S_I,\sigma_I\})]\right)\langle e^{-V}\rangle \\ &\approx \left(\sum_{\sigma_I} e^{-H_0}\right)(e^{\langle V\rangle+\frac{1}{2}[\langle V^2\rangle-\langle V\rangle^2]}+\cdots).\end{aligned} \tag{7}$$

We can perform the summations in the unperturbed part to get

$$[Z_0(\mathbf{K})]^M = \sum_{\sigma_I}\exp[-H_0(\mathbf{K},\{S_I,\sigma_I\})], \tag{8}$$

where M is the number of blocks and $Z_0(\mathbf{K})$ is the partition function of a single block and is defined as

$$Z_0(\mathbf{K}) = \sum_{\sigma_I}\exp[K(s_1^I s_2^I + s_1^I s_3^I + s_2^I s_3^I)] = e^{3K} + 3e^{-K}. \tag{9}$$

The interaction is $V_{IJ} = -K(s_1^I s_3^J + s_2^I s_3^J)$. The average value of a single spin index is

$$\begin{aligned}\langle s_3^I\rangle &= Z_0(K)^{-1}\sum_{\sigma_I} s_3^I \exp[K(s_1^I s_2^I + s_2^I s_3^I + s_3^I s_1^I)] \\ &= Z_0(K)^{-1} S_I(e^{3K} + e^{-K}).\end{aligned} \tag{10}$$

If we take the logarithm of Eq. (7), we obtain

$$\begin{aligned}H(K_L,B_L,\{S_I\}) &= M\ln(Z_0(K)) + \langle V\rangle + \frac{1}{2}[\langle V^2\rangle - \langle V^2\rangle]\cdots \\ &= M\ln(Z_0(K)) - 2K\sum_{I\neq J}\left(\frac{e^{3K}+e^{-K}}{e^{3K}+3e^{-K}}\right)^2 S_I S_J \\ &\quad - 3\sum_I\left(\frac{e^{3K}+e^{-K}}{e^{3K}+3e^{-K}}\right)S_I B + \cdots,\end{aligned} \tag{11}$$

where we have retained terms up to $\langle V\rangle$. Thus the Hamiltonian for the blocks

has been written in the form

$$H(K_L, B_L, \{S_I\}) = -K_L \sum_{IJ} S_I S_J - B_L \sum_I S_I. \tag{12}$$

If we now compare Eqs. (1) and (12), we find

$$K_L = 2K\left(\frac{e^{3K} + e^{-K}}{e^{3K} + 3e^{-K}}\right)^2 \tag{13}$$

and

$$B_L = 3B\left(\frac{e^{3K} + e^{-K}}{e^{3K} + 3e^{-K}}\right). \tag{14}$$

Fixed points occur for $(K^* = 0, B^* = 0)$ and for $(K^* = K_f, B^* = 0)$ where K_f is the solution to the equation

$$\frac{1}{2} = \left(\frac{e^{3K_f} + e^{-K_f}}{e^{3K_f} + 3e^{-K_f}}\right)^2. \tag{15}$$

Equation (15) has eight solutions, only one of which is real and positive. This solution gives $K_f = \frac{1}{4}\ln(1 + 2\sqrt{2}) \approx 0.3356$. Thus the fixed points occur for $(K^* = 0, B^* = 0)$ and for $(K^* = 0.3356, B^* = 0)$.

Let us first consider the fixed point, $(K^* = 0, B^* = 0)$. If we let $K = \delta K$ and $B = \delta B$ and linearize Eqs. (13) and (14) in δK and δB, we obtain

$$\delta K_L = 0.5\delta K \quad \text{and} \quad \delta B_L = 1.5\delta B. \tag{16}$$

This fixed point corresponds to temperature, $T = \infty K$.

Let us next consider the fixed point, $(K^* = 0.3356, B^* = 0)$. If we let $K = 0.3356 + \delta K$ and $B = \delta B$ and linearize Eqs. (13) and (14) in δK and δB, we obtain

$$\delta K_L = 1.623\delta K \quad \text{and} \quad \delta B_L = 2.121\delta B, \tag{17}$$

so the eigenvalues are $\lambda_K = 1.623$ and $\lambda_B = 2.121$. The Widom scaling exponents become

$$p = \frac{\ln(\lambda_K)}{2\ln(\sqrt{3})} = 0.441 \quad \text{and} \quad q = \frac{\ln(\lambda_B)}{2\ln(\sqrt{3})} = 0.684. \tag{18}$$

The critical exponents are

$$\alpha = 2 - \frac{1}{p} = -0.27, \qquad \beta = \frac{1-q}{p} = 0.72,$$
$$\gamma = \frac{2q-1}{p} = 0.83, \quad \text{and} \quad \delta = \frac{q}{1-q} = 2.2 \tag{19}$$

The exact solution of this two-dimensional Ising model yields $(\lambda_K)_{\text{exact}} = 1.73$ and $(\lambda_B)_{exact} = 2.80$. Thus, we are close for λ_K but our calculation of λ_B is not very good. It is possible to carry the calculation to higher orders in $\langle V^n \rangle$. In so doing, more elements of the vector, **K**, are introduced and better agreement with the exact results is obtained.

▶ SPECIAL TOPICS

▶ S8.A. Critical Exponents for the S^4 Model [3, 7, 8]

Let us consider a d-dimensional cubic Ising lattice with N lattice sites. The partition function can be written in the form

$$Z(K) = \sum_{\{s_n\}} \exp\left(K \sum_{\mathbf{n}} \sum_{\mathbf{e}} S_{\mathbf{n}} S_{\mathbf{n}+\mathbf{e}} \right), \tag{8.98}$$

where $K = \beta J$ is the effective interaction and **e** is the vector indicating the positions of various nearest neighbors of the site, **n**. The summation is over all possible configurations of the lattice. We can change the summation to an integration if we introduce a weighting factor, $W(S_{\mathbf{n}}) = \delta(S_{\mathbf{n}}^2 - 1)$. Then Eq. (8.98) can be written

$$Z(K) = \left[\prod_{\mathbf{m}} \int_{-\infty}^{\infty} dS_{\mathbf{m}} W(S_{\mathbf{m}}) \right] \exp\left[K \sum_{\mathbf{n}} \sum_{\mathbf{e}} S_{\mathbf{n}} S_{\mathbf{n}+\mathbf{e}} \right]. \tag{8.99}$$

The partition function is now in a form which allows some generalization.

Let us choose the weighting function in a slightly different manner. We will let

$$W(S_{\mathbf{n}}) = e^{-(b/2)S_{\mathbf{n}}^2 - uS_{\mathbf{n}}^4}. \tag{8.100}$$

If we choose $b = -4u$, the $W(S_{\mathbf{n}})$ takes the simple form

$$W(S_{\mathbf{n}}) = e^{-u(S_{\mathbf{n}}^2 - 1)^2}, \tag{8.101}$$

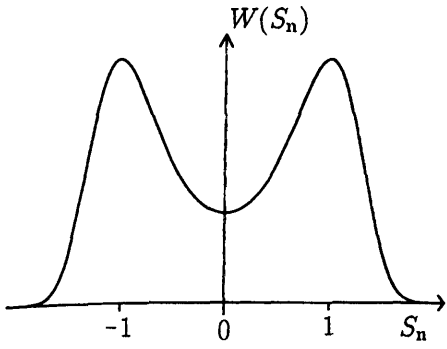


Fig. 8.3. The weighting function, $W(S_n) = e^{-u(S_n^2-1)^2}$, for $u = 1$.

and gives a fairly good approximation to the Ising partition function, Eq. (8.98) since it is peaked at $S_n = \pm 1$ (cf. Fig. 8.3). With this weighting factor, the partition function takes the form

$$Z(K,b,u) = \left[\prod_{\mathbf{m}} \int_{-\infty}^{\infty} dS_{\mathbf{m}}\right] \exp\left[K \sum_{\mathbf{n}} \sum_{\mathbf{e}} S_{\mathbf{n}} S_{\mathbf{n}+\mathbf{e}} - \sum_{\mathbf{n}} \left(\frac{b}{2} S_{\mathbf{n}}^2 + u S_{\mathbf{n}}^4\right)\right]. \tag{8.102}$$

The system now has an effective Hamiltonian

$$\begin{aligned} H &= K \sum_{\mathbf{n}} \sum_{\mathbf{e}} S_{\mathbf{n}} S_{\mathbf{n}+\mathbf{e}} + \sum_{\mathbf{n}} \left(\frac{b}{2} S_{\mathbf{n}}^2 + u S_{\mathbf{n}}^4\right) \\ &= \frac{1}{2} K \sum_{\mathbf{n}} \left[\sum_{\mathbf{e}}{}' (S_{\mathbf{n}+\mathbf{e}} - S_{\mathbf{n}})^2 + \left(\frac{b}{K} - 2d\right) S_{\mathbf{n}}^2\right] + u \sum_{\mathbf{n}} S_{\mathbf{n}}^4, \end{aligned} \tag{8.103}$$

where the sum $\sum_{\mathbf{e}}'$ is restricted to positive values of $\mathbf{e}$ and $\sum_{\mathbf{e}}' = d$ for a cubic lattice. The system described by Eq. (8.103) is called the S^4 model of the Ising system.

It is useful now to rewrite the Hamiltonian and partition function in terms of continuous variables. To do this we first introduce a spin field. Let $S_{\mathbf{n}}$ denote the spin at point $\mathbf{x} = \mathbf{n}a$ (we assume an infinitely large cubic lattice with spacing, a, between lattice sites). Then we introduce the Fourier amplitude, $S(\mathbf{k})$,

$$S(\mathbf{k}) = a^d \sum_{\mathbf{n}} S_{\mathbf{n}} e^{i\mathbf{k}\cdot\mathbf{n}a}. \tag{8.104}$$

The components, $k_i (i = 1, \ldots, d)$, of the wavevectors, $\mathbf{k}$, can only take on values in the range $-\frac{\pi}{2} < k_i < \frac{\pi}{a}$ since wavelengths smaller than the lattice

spacing are not allowed. It is also useful to note the identities

$$\left(\frac{a}{2\pi}\right)^d \int_{-\pi/a}^{\pi/a} dk_1 \cdots \int_{-\pi/a}^{\pi/a} dk_d e^{i\mathbf{k}\cdot\mathbf{n}a} = \delta_{\mathbf{n},0} \tag{8.105}$$

and

$$a^d \sum_{\mathbf{n}} e^{i\mathbf{k}\cdot\mathbf{n}a} = \delta(\mathbf{k}). \tag{8.106}$$

From Eq. (8.104), we can define a continuous spin field

$$S(\mathbf{x}) = \left(\frac{1}{2\pi}\right)^d \int_{-\pi/a}^{\pi/a} dk_1 \cdots \int_{-\pi/a}^{\pi/a} dk_d e^{i\mathbf{k}\cdot\mathbf{x}} S(\mathbf{k}). \tag{8.107}$$

The spin field, $S(\mathbf{x})$, is dimensionless. Note also that $S(\mathbf{x} = \mathbf{n}a) = S_{\mathbf{n}}$, but $S(\mathbf{x})$ need not be zero between lattice sites.

Let us now rewrite the Hamiltonian in terms of the spin field, $S(\mathbf{k})$. First note that

$$\sum_{\mathbf{n}} \sum_{\mathbf{e}}{}' (S_{\mathbf{n}+\mathbf{e}} - S_{\mathbf{n}})^2 = \left(\frac{1}{2\pi a}\right)^d \int d\mathbf{k} \sum_{\mathbf{e}}{}' S(\mathbf{k}) S(-\mathbf{k}) \left|e^{i\mathbf{k}\cdot\mathbf{e}a} - 1\right|^2. \tag{8.108}$$

and

$$\begin{aligned} \sum_{\mathbf{n}} S_{\mathbf{n}}^4 = \left(\frac{1}{2\pi}\right)^{4d} \frac{1}{a^d} \int d\mathbf{k}_1 \int d\mathbf{k}_2 \int d\mathbf{k}_3 \int d\mathbf{k}_4 \\ \times S(\mathbf{k}_1) S(\mathbf{k}_2) S(\mathbf{k}_3) S(\mathbf{k}_4) \delta(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 + \mathbf{k}_4). \end{aligned} \tag{8.109}$$

The Hamiltonion then takes the form

$$\begin{aligned} H = &\frac{K}{2} \left(\frac{1}{2\pi a}\right)^d \int d\mathbf{k} \sum_{\mathbf{e}}{}' |S(\mathbf{k})|^2 \left|e^{i\mathbf{k}\cdot\mathbf{e}a} - 1\right|^2 \\ &+ \frac{K}{2} \left(\frac{b}{K} - 2d\right) \left(\frac{1}{2\pi a}\right)^d \int d\mathbf{k} |S(\mathbf{k})|^2 \\ &+ \frac{u}{a^d} \left(\frac{1}{2\pi}\right)^{4d} \int d\mathbf{k}_1 \int d\mathbf{k}_2 \int d\mathbf{k}_3 \int d\mathbf{k}_4 \\ &\times S(\mathbf{k}_1) S(\mathbf{k}_2) S(\mathbf{k}_3) S(\mathbf{k}_4) \delta(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 + \mathbf{k}_4). \end{aligned} \tag{8.110}$$

Near the critical point, spin fluctuations begin to exhibit long-range order. Therefore we only need to be concerned with long-wavelength (small-

wavevector) phenomena. If we note that $|e^{i\mathbf{k}\cdot\mathbf{e}a} - 1|^2 \approx k^2a^2$ for small k (note that $\sum_{\mathbf{e}}' |\mathbf{k}\cdot\mathbf{e}|^2 = k^2$), then the Hamiltonian can be written

$$\begin{aligned} H = &\frac{1}{2}\left(\frac{1}{2\pi}\right)^d \int d\mathbf{k}(C_1 + C_2k^2)|S(\mathbf{k})|^2 \\ &+ \frac{u}{a^d}\left(\frac{1}{2\pi}\right)^{4d} \int d\mathbf{k}_1 \int d\mathbf{k}_2 \int d\mathbf{k}_3 \int d\mathbf{k}_4 \\ &\times S(\mathbf{k}_1)S(\mathbf{k}_2)S(\mathbf{k}_3)S(\mathbf{k}_4)\delta(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 + \mathbf{k}_4), \end{aligned} \tag{8.111}$$

where

$$C_2 = Ka^{-d+2} \quad \text{and} \quad C_1 = \left(\frac{b}{K} - 2d\right)Ka^{-d}. \tag{8.112}$$

It is useful to rescale the spin fields. We will let $S'(\mathbf{k}) = S(\mathbf{k})(Ka^{2-d})^{1/2}$, $r = (b/K - 2d)a^{-2}$, and $u' = u(Ka^{2-d})^{-2}$. The Hamiltonian then becomes

$$\begin{aligned} H(r, u', \{S'\}) = &\frac{1}{2}\left(\frac{1}{2\pi}\right)^d \int d\mathbf{k}(r + k^2)|S'(\mathbf{k})|^2 \\ &+ u'\left(\frac{1}{2\pi}\right)^{4d} \int d\mathbf{k}_1 \int d\mathbf{k}_2 \int d\mathbf{k}_3 \int d\mathbf{k}_4 \\ &\times S'(\mathbf{k}_1)S'(\mathbf{k}_2)S'(\mathbf{k}_3)S'(\mathbf{k}_4)\delta(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 + \mathbf{k}_4). \end{aligned} \tag{8.113}$$

The partition function is given by

$$Z(r, u', \{S'\}) = \int DS' e^{H(r,u',\{S'\})}, \tag{8.114}$$

where DS' now denotes a functional integral over values of the spin variables, $S'(\mathbf{k})$. Equation (8.113) is the starting point for the renormalization theory, for the S^4 model. When $u' = 0$, the model is called the "Gaussian model". In order to find a scaled Hamiltonian for the system, we follow a procedure similar to that for the triangular lattice in Exercise 8.1, but now we work in wavevector space and not real space.

Our first step is obtain a block Hamiltonian. In order to do this, we will introduce a scaling parameter. $L > 1$, and divide the momentum intervals $0 < k_i < \pi/a$ into short-wavelength intervals $\pi/La < k_i < \pi/a$ and long-wavelength intervals $0 < k_i < \pi/La$. We then separate the spin fields into their long-wavelength and short-wavelength parts:

$$S'(\mathbf{k}) = \mathscr{S}_L(\mathbf{k}) \qquad \text{for } 0 < k_i < \frac{\pi}{La}(i = 1, \ldots, d) \tag{8.115}$$

and

$$S'(\mathbf{k}) = \sigma_L(\mathbf{k}) \qquad \text{for } \frac{\pi}{La} < k_i < \frac{\pi}{a} (i = 1, \ldots, d). \tag{8.116}$$

From Eq. (8.107), we introduce the corresponding spin fields $\mathscr{S}_L(\mathbf{x})$ and $\sigma_L(\mathbf{x})$. The spin field $\mathscr{S}_L(\mathbf{x})$ is defined as

$$\mathscr{S}(\mathbf{x}) = \left(\frac{1}{2\pi}\right)^d \int \cdots \int_{-\pi/La}^{\pi/La} d\mathbf{k} \mathscr{S}_L(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{x}} \tag{8.117}$$

and is slowly varying over a region the size of the block, while the spin field $\sigma_L(\mathbf{x})$ is defined as

$$\sigma_L(\mathbf{x}) = \left(\frac{1}{2\pi}\right)^d \int \cdots \int_{-\pi/La}^{\pi/a} \tilde{d}\mathbf{k} \sigma_L(\mathbf{k}) e^{ik\cdot x}, \tag{8.118}$$

where $\int_a^b \tilde{d}\mathbf{k} \equiv \int_a^b d\mathbf{k} + \int_{-b}^{-a} d\mathbf{k}$ and $\sigma_L(\mathbf{x})$ is rapidly varying inside a block.

We now decompose the quadratic part of the effective Hamiltonian into its long-wavelength and short-wavelength parts and define the quantities

$$\mathscr{H}_0(\{\mathscr{S}_L\}, r) = \frac{1}{2}\left(\frac{1}{2\pi}\right)^d \int_{-\pi/La}^{\pi/La} d\mathbf{k}(k^2 + r)\mathscr{S}_L(\mathbf{k})\mathscr{S}_L(-\mathbf{k}), \tag{8.119}$$

$$\mathscr{H}_0(\{\sigma_L\}, r) = \frac{1}{2}\left(\frac{1}{2\pi}\right)^d \int_{\pi/La}^{\pi/a} \tilde{d}\mathbf{k}(k^2 + r)\sigma_L(\mathbf{k})\sigma_L(-\mathbf{k}), \tag{8.120}$$

and

$$V(\{\mathscr{S}_L, \sigma_L\}, u') = u'\left(\frac{1}{2\pi}\right)^{4d} \int \cdots \int_{-\pi/a}^{\pi/a} d\mathbf{k}_1 d\mathbf{k}_2 d\mathbf{k}_3 d\mathbf{k}_4 \times S'(\mathbf{k}_1)S'(\mathbf{k}_2)S'(\mathbf{k}_3)S'(\mathbf{k}_4)\delta(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 + \mathbf{k}_4), \tag{8.121}$$

where $\mathscr{S}_L(\mathbf{k})$ and $\sigma_L(\mathbf{k})$ are defined in Eqs. (8.115) and (8.116). We now can introduce an expectation value defined as

$$\langle A(\{\mathscr{S}_L\})\rangle = \frac{\int D\sigma_L e^{-\mathscr{H}_0(\{\sigma_L\})} A(\{\sigma_L, \mathscr{S}_L\})}{\int D\sigma_L e^{-\mathscr{H}_0(\{\sigma_L\})}} \tag{8.122}$$

and write the partition function in the form

$$\begin{aligned} Z(r, u') &= \left[\int D\sigma_L e^{-\mathscr{H}_0(\{\sigma_L\})}\right] \int D\mathscr{S}_L e^{-\mathscr{H}_0(\{\mathscr{S}_L\})} \langle e^{-V(\{\mathscr{S}_L, \sigma_L\})}\rangle \\ &= \left[\int D\sigma_L e^{-\mathscr{H}_0(\{\sigma_L\})}\right] \int D\mathscr{S}_L e^{-\mathscr{H}_0(\{\mathscr{S}_L\}) - \langle V\rangle + \frac{1}{2}[\langle V^2\rangle - \langle V\rangle^2]} + \cdots, \end{aligned} \tag{8.123}$$

where we have introduced a cumulant expansion are before. We are only concerned with those parts of the partition function which contribute to the singular part of the free energy. Thus, the term in brackets, which comes from short-wavelength variations, can be neglected and the effective Hamiltonian takes the form

$$\mathscr{H}(\{\mathscr{S}_L\}, r_L, u'_L) = \frac{1}{2}\left(\frac{1}{2\pi}\right)^d \int_{-\pi/La}^{\pi/La} d\mathbf{k}(k^2 + r)\mathscr{S}_L(\mathbf{k})\mathscr{S}_L(-\mathbf{k}) + \langle V\rangle - \frac{1}{2}[\langle V^2\rangle - \langle V\rangle^2] + \cdots \tag{8.124}$$

After a scale transformation, we seek a new Hamiltonian of the form

$$\begin{aligned}\mathscr{H}_L(\{\mathscr{S}_L\}, r_L, u_L) = {} & \frac{1}{2}\left(\frac{1}{2\pi}\right)^d \int_{-\pi/a}^{\pi/a} d\mathbf{k}_L(k_L^2 + r_L)\mathscr{S}_L(\mathbf{k}_L)\mathscr{S}_L(-\mathbf{k}_L) \\ & + u_L\left(\frac{1}{2\pi}\right)^{4d} \int\cdots\int_{-\pi/a}^{\pi/a} d\mathbf{k}_{1L}\, d\mathbf{k}_{2L}\, d\mathbf{k}_{3L}\, d\mathbf{k}_{4L} \\ & \times \mathscr{S}_L(\mathbf{k}_{1L})\mathscr{S}_L(\mathbf{k}_{2L})\mathscr{S}_L(\mathbf{k}_{3L})\mathscr{S}_L(\mathbf{k}_{4L}) \\ & \times \delta(\mathbf{k}_{1L} + \mathbf{k}_{2L} + \mathbf{k}_{3L} + \mathbf{k}_{4L}).\end{aligned} \tag{8.125}$$

If we can write Eq. (8.124) in the same form as Eq (8.125), then we can obtain the new coupling constant, u_L. We first compute the expectation value, $\langle V\rangle$, and obtain

$$\begin{aligned}\langle V\rangle = {} & \left[\int D\sigma_L e^{-\mathscr{H}_0(\{\sigma_L\})}\right]^{-1} \int D\sigma_L e^{-\mathscr{H}_0(\{\sigma_L\})} \left(\frac{1}{2\pi}\right)^{4d} \\ & \times \left\{u' \int\cdots\int_{-\pi/La}^{\pi/La} d\mathbf{k}_1\, d\mathbf{k}_2\, d\mathbf{k}_3\, d\mathbf{k}_4 \right. \\ & \times \mathscr{S}_L(\mathbf{k}_1)\mathscr{S}_L(\mathbf{k}_2)\mathscr{S}_L(\mathbf{k}_3)\mathscr{S}_L(\mathbf{k}_4)\delta(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 + \mathbf{k}_4) \\ & + 6u' \int_{-\pi/La}^{\pi/La} d\mathbf{k}_1 \int_{-\pi/La}^{\pi/La} d\mathbf{k}_2 \left[\int_{\pi/La}^{\pi/a} \tilde{d}\mathbf{k}_3 \int_{\pi/La}^{\pi/a} \tilde{d}\mathbf{k}_4 \mathscr{S}_L(\mathbf{k}_1)\mathscr{S}_L(\mathbf{k}_2)\right. \\ & \left. \times \sigma_L(\mathbf{k}_3)\sigma_L(\mathbf{k}_4)\delta(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 + \mathbf{k}_4)\right] \\ & + u' \int\cdots\int_{\pi/La}^{\pi/a} \tilde{d}\mathbf{k}_1 \tilde{d}\mathbf{k}_2 \tilde{d}\mathbf{k}_3 \tilde{d}\mathbf{k}_4 \sigma_L(\mathbf{k}_1)\sigma_L(\mathbf{k}_2)\sigma_L(\mathbf{k}_3)\sigma_L(\mathbf{k}_4) \\ & \left. \times \delta(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 + \mathbf{k}_4)\right\}.\end{aligned} \tag{8.126}$$

The factor 6 enters because there are six terms with two factors of $\mathscr{S}_L(\mathbf{k})$ and

two factors of $\sigma_L(\mathbf{k})$. They each give identical contributions. The last term can be neglected since it contains only short-wavelength contributions and contributes to the regular part of the free energy. To evaluate the second term, we use Eq. (7.27) to obtain

$$\langle \sigma_L(\mathbf{k}_3)\sigma_L(\mathbf{k}_4)\rangle = \frac{(2\pi)^d}{k_3^2 + r}\delta(\mathbf{k}_3 + \mathbf{k}_4). \tag{8.127}$$

Then the singular part of $\langle V\rangle$ takes the form

$$\begin{aligned}\langle V\rangle_s = {} & u'\left(\frac{1}{2\pi}\right)^{4d}\int\cdots\int_{-\pi/La}^{\pi/La} d\mathbf{k}_1\cdots d\mathbf{k}_4 \\ & \times \mathscr{S}_L(\mathbf{k}_1)\mathscr{S}_L(\mathbf{k}_2)\mathscr{S}_L(\mathbf{k}_3)\mathscr{S}_L(\mathbf{k}_4)\delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4) \\ & + 6u'\left(\frac{1}{2\pi}\right)^{3d}\int\cdots\int_{-\pi/La}^{\pi/La} d\mathbf{k}_1\, d\mathbf{k}_2 \mathscr{S}_L(\mathbf{k}_1)\mathscr{S}_L(\mathbf{k}_2) \\ & \times \delta(\mathbf{k}_1+\mathbf{k}_2)\int_{\pi/La}^{\pi/a} \tilde{d}\mathbf{k}\,\frac{1}{k^2+r}.\end{aligned} \tag{8.128}$$

We see that $\langle V\rangle$ has a structure similar to the original Hamiltonian, but it yields no correction to the quartic part. The correction to the quartic part can be obtained from the second-order terms in the cumulant expansion.

Many terms contribute to the second-order cumulant, $\frac{1}{2}[\langle V^2\rangle - \langle V\rangle^2]$. To obtain explicit expressions for them, we must use Wick's theorem (see Ex. 4.9). We will not attempt to work out all the details here but will summarize the results. As Wilson and Kogut [8] have shown, the only term of interest in $\frac{1}{2}[\langle V^2\rangle - \langle V\rangle^2]$ is the correction to the quartic term in the effective Hamiltonian. They have shown that corrections to the quadratic terms can be neglected. Furthermore, contributions to the second-order cumulant coming from pairwise averages of spins which are both located on the same potential, V, give no contribution since for those terms $\langle V^2\rangle = \langle V\rangle^2$ and they cancel out. Thus, we only retain terms which have at least one pairwise average between spins on different factors, V. The only term which involves four spins, $\mathscr{S}_L(\mathbf{k})$, and which contributes to the second-order cumulant is

$$\begin{aligned}\frac{1}{2}\langle V^2\rangle_{\text{quartic}} = {} & \frac{1}{2}\left[\int D\sigma_L e^{-\mathscr{H}_0(\{\sigma_L\})}\right]^{-1}\int D\sigma_L e^{-\mathscr{H}_0(\{\sigma_L\})}\left(\frac{1}{2\pi}\right)^{8d} \\ & \times\left\{36u'^2\int\cdots\int_{-\pi/La}^{\pi/La} d\mathbf{k}_1\, d\mathbf{k}_2\, d\mathbf{k}_7 d\mathbf{k}_8\int\cdots\int_{\pi/La}^{\pi/a}\tilde{d}\mathbf{k}_3\tilde{d}\mathbf{k}_4\tilde{d}\mathbf{k}_5\tilde{d}\mathbf{k}_6\right. \\ & \times \mathscr{S}_L(\mathbf{k}_1)\mathscr{S}_L(\mathbf{k}_2)\sigma_L(\mathbf{k}_3)\sigma_L(\mathbf{k}_4)\sigma_L(\mathbf{k}_5)\sigma_L(\mathbf{k}_6)\mathscr{S}_L(\mathbf{k}_7)\mathscr{S}_L(\mathbf{k}_8) \\ & \left.+\cdots\right\}.\end{aligned} \tag{8.129}$$

The origin of the numerical factor, 36, can be understood if we note that there is a factor, $\frac{1}{2}$, in front of $\langle V^2\rangle_{\text{quartic}}$, there are six terms in each factor V with two $\mathscr{S}_L$'s and two σ_L 's, and there are two different ways of taking pairwise averages for each term in $V^2(\frac{1}{2}\times 6\times 6\times 2 = 36)$.

From the results of Exercise 4.9 and Section 7.C.1, we obtain

$$\begin{aligned}\frac{1}{2}\langle V^2\rangle_{\text{quartic}} = \left(\frac{1}{2\pi}\right)^{5d} 36u'^2 \int\cdots\int_{-\pi/La}^{\pi/La} d\mathbf{k}_1\cdots d\mathbf{k}_4 \\ \times \mathscr{S}_L(\mathbf{k}_1)\mathscr{S}_L(\mathbf{k}_2)\mathscr{S}_L(\mathbf{k}_3)\mathscr{S}_L(\mathbf{k}_4)\,\delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4) \\ \times \int_{\pi/La}^{\pi/a} \tilde{d}\mathbf{k}\left(\frac{1}{k^2+r}\right)\left(\frac{1}{(\mathbf{k}_3+\mathbf{k}_4-\mathbf{k})^2+r}\right) + \text{other terms.}\end{aligned} \tag{8.130}$$

If we combine contributions from Eqs. (8.128) and (8.130), the Hamiltonian $\mathscr{H}(\{\mathscr{S}_L\}, r_L, u_L)$ in Eq. (8.124) takes the following form:

$$\begin{aligned}\mathscr{H}(\{\mathscr{S}_L\}, r_L, u_L) = \frac{1}{2}\left(\frac{1}{2\pi}\right)^{d}\int_{-\pi/La}^{\pi/La} d\mathbf{k}\,\mathscr{S}_L(\mathbf{k})\,\mathscr{S}_L(-\mathbf{k}) \\ \times\left[(k^2+r)+\frac{12u'}{(2\pi)^d}\int_{\pi/La}^{\pi/a}\tilde{d}\mathbf{k}\frac{1}{k^2+r}\right] \\ +\left(\frac{1}{2\pi}\right)^{4d}\int\cdots\int_{-\pi/La}^{\pi/La} d\mathbf{k}_1\cdots d\mathbf{k}_4 \\ \times \mathscr{S}_L(\mathbf{k}_1)\mathscr{S}_L(\mathbf{k}_2)\mathscr{S}_L(\mathbf{k}_3)\mathscr{S}_L(\mathbf{k}_4)\,\delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4) \\ \times\left[u'-\frac{36u'^2}{(2\pi)^d}\int_{\pi/La}^{\pi/a}\tilde{d}\mathbf{k}\left(\frac{1}{k^2+r}\right)\left(\frac{1}{(\mathbf{k}_3+\mathbf{k}_4-\mathbf{k})^2+r}\right)\right] \\ +\cdots\end{aligned} \tag{8.131}$$

where we have neglected some contributions (terms not containing block spins), some second-order quadratic terms, and terms containing six or eight block spins. Also, we neglected all contributions from higher-order cumulants.

To obtain Eq (8.131) in a form similar to the original effective Hamiltonian, we must make a change of scale. We let

$$\mathbf{k}_L = L\mathbf{k} \tag{8.132}$$

and

$$\mathscr{S}_L(\mathbf{k}_L) = Z^{-1}\mathscr{S}_L(\mathbf{k}). \tag{8.133}$$

Then we find

$$
\begin{aligned}
&\mathscr{H}_L(\{\mathscr{S}_L\}, r_L, u_L) \\
&\quad = \frac{1}{2}\frac{Z^2 L^{-d}}{(2\pi)^d}\int_{-\pi/a}^{\pi/a} d\mathbf{k}_L \mathscr{S}_L(\mathbf{k}_L)\mathscr{S}_L(-\mathbf{k}_L) \\
&\quad \times \left[\frac{k_L^2}{L^2} + r + \frac{12u'}{(2\pi)^d}\int_{\pi/La}^{\pi/a} \tilde{d}\mathbf{k}\frac{1}{k^2+r}\right] \\
&\quad + \left(\frac{1}{2\pi}\right)^{4d}\frac{Z^4}{(L^d)^3}\int\cdots\int_{\pi/a}^{\pi/a} d\mathbf{k}_{1L}\times\cdots\times d\mathbf{k}_{4L} \\
&\quad \times \mathscr{S}_L(\mathbf{k}_{1L})\mathscr{S}_L(\mathbf{k}_{2L})\mathscr{S}_L(\mathbf{k}_{3L})\mathscr{S}_L(\mathbf{k}_{4L})\,\delta(\mathbf{k}_{1L}+\mathbf{k}_{2L}+\mathbf{k}_{3L}+\mathbf{k}_{4L}) \\
&\quad \times \left[u' - \frac{36u'^2}{(2\pi)^d}\int_{\pi/La}^{\pi/a}\tilde{d}\mathbf{k}\left(\frac{1}{k^2+r}\right)\left(\frac{1}{(\mathbf{k}_3+\mathbf{k}_4-\mathbf{k})^2+r}\right)\right].
\end{aligned}
\tag{8.134}
$$

Equation (8.134) is the transformed Hamiltonian that we have been looking for. If we let $Z = L^{1+d/2}$, then we obtain the following expression for r_L:

$$
r_L = L^2\left[r + \frac{12u'}{(2\pi)^d}\int_{\pi/La}^{\pi/a}\tilde{d}\mathbf{k}\frac{1}{k^2+r}\right]. \tag{8.135}
$$

The expression for u_L requires more discussion. To obtain an expression for u_L which is independent of the $\mathbf{k}$ integrations in Eq. (8.134), we must make an approximation. If we let $\mathbf{k}_3 + \mathbf{k}_4 = 0$, we obtain

$$
u_L = L^{\mathscr{E}}\left[u' - \frac{36u'^2}{(2\pi)^d}\int_{\pi/La}^{\pi/a}\tilde{d}\mathbf{k}\left(\frac{1}{k^2+r}\right)^2\right], \tag{8.136}
$$

where $\mathscr{E} = 4 - d$. This approximation is made every time we change the scale of the Hamiltonian. Eqs. (8.135) and (8.136) are the recursion relations we have been looking for. They are correct as long as $|\mathscr{E}| \ll 1$ (this will become clearer below).

To find the fixed points of Eqs. (8.135) and (8.136), we will turn them into differential equations. We first write the recursion relation for a transformation from block L to block sL,

$$
r_{sL} = s^2\left[r_L + \frac{12u_L}{(2\pi)^d}\int\cdots\int_{\pi/sa}^{\pi/a}\tilde{d}\mathbf{k}\frac{1}{k^2+r_L}\right], \tag{8.137}
$$

and

$$
u_{sL} = s^{\mathscr{E}}\left[u_L - \frac{36u_L^2}{(2\pi)^d}\int\cdots\int_{\pi/sa}^{\pi/a}\tilde{d}\mathbf{k}\left(\frac{1}{k^2+r_L}\right)^2\right], \tag{8.138}
$$

where s is now considered to be a continuous parameter. Let $s = 1 + h$ for $h \ll 1$. Then, Eqs. (8.137) and (8.138) can be approximated by

$$r_{(1+h)L} = (1 + 2h)\left[r_L + \frac{12u_L}{(2\pi)^d}\int_{(\pi/a)(1-h)}^{\pi/a} \tilde{d}\mathbf{k}\left(\frac{1}{k^2 + r_L}\right)\right] \tag{8.139}$$

and

$$u_{(1+h)L} = (1 + \mathscr{E}h)\left[u_L - \frac{36u_L^2}{(2\pi)^d}\int_{(\pi/a)(1-h)}^{\pi/a} \tilde{d}\mathbf{k}\left(\frac{1}{k^2 + r_L}\right)^2\right]. \tag{8.140}$$

We next evaluate the integrals. We can write for small h

$$\frac{1}{(2\pi)^d}\int_{(\pi/a)(1-h)}^{\pi/a} \tilde{d}\mathbf{k}\left(\frac{1}{k^2 + r_L}\right)^n = \frac{2}{(2\pi)^d}\left(\frac{1}{\left(\frac{\pi}{a}\right)^2 + r_L}\right)^n \int_{(\pi/a)(1-h)}^{\pi/a} \tilde{d}\mathbf{k}$$
$$\equiv \left(\frac{1}{\left(\frac{\pi}{a}\right)^2 + r_L}\right)^n \frac{Ah}{12},$$

where A is a constant. Thus, Eqs. (8.139) and (8.140) become (to first order in h)

$$r_{(1+h)L} - r_L = 2hr_L + \frac{u_L Ah}{\left(\left(\frac{\pi}{a}\right)^2 + r_L\right)} \tag{8.141}$$

and

$$u_{(1+h)L} - u_L = \mathscr{E}hu_L - \frac{3u_L^2 Ah}{\left(\left(\frac{\pi}{a}\right)^2 + r_L\right)^2}. \tag{8.142}$$

If we next divide by hL and take the limit $h \to 0$, we find

$$L\frac{dr_L}{dL} = 2r_L + \frac{Au_L}{\left(\left(\frac{\pi}{a}\right)^2 + r_L\right)} \tag{8.143}$$

and

$$L\frac{du_L}{dL} = \mathscr{E}u_L - \frac{3Au_L^2}{\left(\left(\frac{\pi}{a}\right)^2 + r_L\right)^2}. \tag{8.144}$$

Now let $t \equiv \ln L$ and choose the units of a such that $\pi/a = 1$. Then

$$\frac{dr}{dt} = 2r + \frac{Au}{1+r} \tag{8.145}$$

and

$$\frac{du}{dt} = \mathscr{E}u - \frac{3Au^2}{(1+r)^2}. \tag{8.146}$$

Higher-order terms can be neglected as long as $|\mathscr{E}| \ll 1$. The fixed points of Eqs. (8.145) and (8.146) occur when

$$\frac{dr^*}{dt} = 2r^* + \frac{Au^*}{1+r^*} = 0 \tag{8.147}$$

and

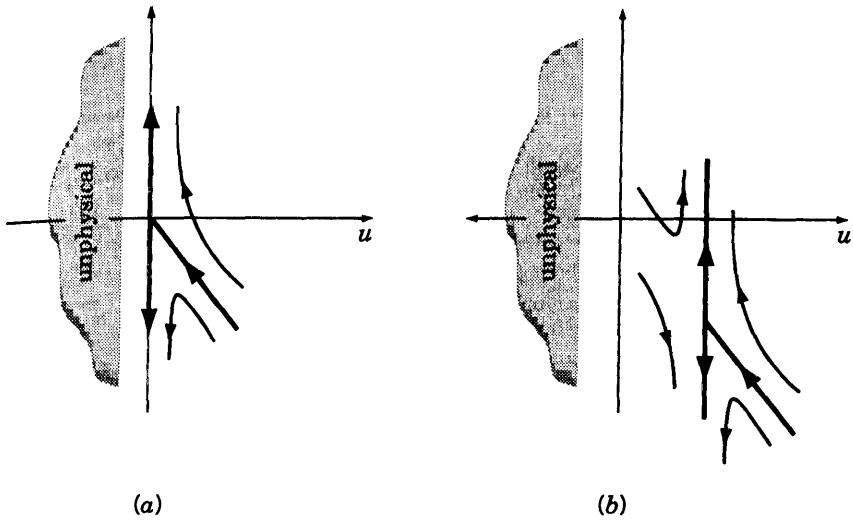
$$\frac{du^*}{dt} = \mathscr{E}u^* - \frac{3Au^{*2}}{(1+r^*)^2} = 0. \tag{8.148}$$

There are two sets of fixed points, $(u^* = 0, r^* = 0)$ and $(u^* = \mathscr{E}/3A$, $r^* = -\mathscr{E}/6)$. If we let $\delta u = u - u^*$ and $\delta r = r - r^*$, then the linearized transformation becomes (to first order in u^* and r^*)

$$\begin{pmatrix} \dfrac{d\delta r}{dt} \\ \dfrac{d\delta u}{dt} \end{pmatrix} = \begin{pmatrix} 2 - Au^* & A(1-r^*) \\ 0 & \mathscr{E} - 6Au^* \end{pmatrix} \begin{pmatrix} \delta r \\ \delta u \end{pmatrix} \tag{8.149}$$

and we obtain the eigenvalues $\lambda_r = 2 - Au^*$ and $\lambda_u = \mathscr{E} - 6Au^*$ for small u^* and r^*. Thus, λ_r is a relevant eigenvalue. For the fixed point ($u^* = 0$ and $r^* = 0$) the eigenvalues are $\lambda_r = 2$ and $\lambda_u = \mathscr{E}$ (this is just the Gaussian fixed point), and for the fixed point ($u^* = \mathscr{E}/3A$ and $r^* = -\mathscr{E}/6$) the eigenvalues are $\lambda_r = 2 - \mathscr{E}/3$ and $\lambda_u = -\mathscr{E}$. For $d > 4, \mathscr{E} < 0$ and the second fixed point is repulsive and therefore unphysical since both eigencurves are directed away from the fixed point and it can never be reached. Thus, for $d > 4$, the physics is governed by the Gaussian fixed point. For $d < 4$, the Gaussian fixed point is repulsive and for this case the fixed point $(u^* = \mathscr{E}/3A, r^* = -\mathscr{E}/6)$ is the physical one. For $d = 4$, the fixed points coalesce. In Fig. 8.4 we sketch the trajectories in the neighborhood of the two fixed points.

We can now obtain expressions for the critical exponents α and ν, but it requires a bit of algebra. To obtain the equations for the eigencurves of the S^4 model, we must rewrite the differential equations in Eq. (8.149) in terms of L.



(a) (b)

Fig. 8.4. A sketch of trajectories in the neighborhood of the physical fixed points for the S^4 model: (a) For $d > 4$ the Gaussian fixed point governs the physics; (b) for $d < 4$ the fixed point ($u^* = \varepsilon/3A$, $r^* = -\varepsilon/6$) governs the physics ($\varepsilon = 4 - d$).

We first write Eq. (8.149) in terms of its eigenvectors and eigenvalues. (Note that the left and right eigenvectors will be different since the matrix on the right-hand side is not symmetric (cf. Section 5.C). For our purposes, it is not necessary to find explicit expressions for the eigenvectors. If we let $\delta u_1(t)$ denote the relevant eigenvector, we can write

$$\frac{d\delta u_1(t)}{dt} = (2 - Au^*)\delta u_1(t). \tag{8.150}$$

The solution to Eq. (8.150) can be written

$$\delta u_1(t) = e^{(2-Au^*)t}\delta u_1(0). \tag{8.151}$$

If we now remember that $t = \ln L$, we find

$$\delta u_{1,L} = e^{(2-Au^*)\ln L}\delta u_1 \tag{8.152}$$

so that $\lambda_1 = \exp[(2 - Au^*) \ln L]$. We then make use of Eq. (9.E.18) to obtain

$$p = \left(\frac{2 - Au^*}{d}\right). \tag{8.153}$$

Using Eqs. (8.50) and (8.153) we obtain

$$\alpha = 2 - \frac{d}{2 - Au^*} \tag{8.154}$$

and using Eqs. (8.77) and (8.154) we obtain

$$\nu = \frac{1}{2 - Au^*}. \tag{8.155}$$

Since the fixed points which characterize the system are different for $d > 4$ and $d < 4$, the critical exponents will also differ for those two cases.

Let us first consider the case $d > 4$. Then $u^* = 0$ and we find

$$\alpha = 2 - \frac{d}{2} = \frac{\mathscr{E}}{2}, \tag{8.156}$$

where we have used the fact that $\mathscr{E} = 4 - d$. We also find

$$\nu = \frac{1}{2}. \tag{8.157}$$

When $d < 4$, $u^* = \mathscr{E}/3A$, and we find

$$\alpha = \frac{\mathscr{E}}{6 - \mathscr{E}} \approx \frac{\mathscr{E}}{6} \tag{8.158}$$

and

$$\nu \approx \frac{1}{2} + \frac{\mathscr{E}}{12}. \tag{8.159}$$

The magnetic critical exponent can also be computed and the result is

$$\delta \approx 3 + \mathscr{E} \tag{8.160}$$

as for the case $d > 4$. The other exponents can be obtained from the identities in Eqs. (8.51), (8.52), and (8.78). In Table 8.1 we compare the results of the S^4 model with the experimental results, with mean field results, and with the results due to exact calculations for the Ising model. The first thing to note is that, for $d = 4$, the mean field theories and the S^4 model give the same results. For $d = 3$, the S^4 model gives very good agreement with the experimental and Ising values of the exponents (the exact results for the three-dimensional Ising are obtained from a numerical calculation). However, there is really no reason why it should. We have retained only the lowest-order approximation for the exponents in the $\mathscr{E}$ expansion. If we take $\mathscr{E} = 1$ (as it is for $d = 3$), then the expansion need not converge. In fact, higher order terms in the series give large

Table 8.1 Values of the Critical Exponents from Experiment and from Various Theories

Critical Exponent	Experimental Value	Exact Ising $d = 2$	Exact Ising $d = 3$	Mean Field Theory	S^4 Model $d > 4$	S^4 Model $d = 4$	S^4 Model $d < 4$	S^4 Model $d = 3$
α	0–0.2	0	0.12	0	$\varepsilon/2$	0	$\varepsilon/6$	0.17
β	0.3–0.4	0.125	0.31	$\frac{1}{2}$	$1/2-\varepsilon/4$	$\frac{1}{2}$	$1/2-\varepsilon/6$	0.33
δ	4–5	15	5.2	3	$3+\varepsilon$	3	$3+\varepsilon$	4
γ	1.2–1.4	1.75	1.25	1	1	1	$1+\varepsilon/6$	1.17
ν	0.6–0.7	1.0	0.64	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$1/2+\varepsilon/12$	0.58
η	0.1	0.25	0.056	0	0	0	0	0

[a]Based on Refs. 3 and 8.

contributions and ruin the agreement. For this reason the $\mathscr{E}$ expansion is thought to be an asymptotic expansion—that is, one for which the first few terms give a result close to the result obtained by summing the entire series.

One may well ask the meaning of an expansion about $d = 4$ and in terms of noninteger d, when real physical systems correspond to $d = 1, 2$, or 3. However consideration of these "unphysical" values of d provides us with a theoretical tool for understanding the role of the dimension of space in physical phenomena, and it has led to a major advance in our understanding of critical phenomena.

▶ S8.B.EXACT SOLUTION OF THE TWO-DIMENSIONAL ISING MODEL [14, 15]

The two-dimensional Ising model is one of the simplest systems that exhibit a phase transition and one of the few that can be solved exactly. The phase transition in this system is an order–disorder transition. It has served as the paradigm system for describing order–disorder transitions in a variety of contexts. In physics it has been used to model the phase transition from the paramagnetic to the ferromagnetic state (the Curie point) in magnetic crystals. However, it has also had many applications outside of physics. It has been used to model learning [16] and information storage [17] in neural networks. In molecular biology, it as been used to model cooperative conformational changes due to ligand binding in macromolecules [18] and heat denaturation of DNA [19]. It has also been used in sociology to model cultural isolation [20]. In this section we shall use it in its physics context to model order–disorder in a spin system.

An analytic expression for the partition function of an Ising system can be obtained in one and two dimensions, but no one has succeeded in solving it analytically in three dimensions. In one dimension it does not have a phase transition. In two dimensions, it does have a phase transition. In Section 7.F we considered the one-dimensional Ising model and the mean field approximation to the Ising model. In this section we will consider the case of a planar Ising spin lattice and show how an analytic expression for the partition function may be obtained and how the phase transition appears [21].

▶ S8.B.1. Partition Function

Let us consider a planar lattice of N spin-$\frac{1}{2}$ objects with magnetic moment, μ. A planar lattice is one which can be laid out flat in a two-dimensional plane without any bonds intersecting. For example, a lattice with periodic boundary conditions is not planar. Each lattice site can interact with the magnetic fields of its nearest neighbors. Some examples of planar lattices are shown in Fig. 8.5.

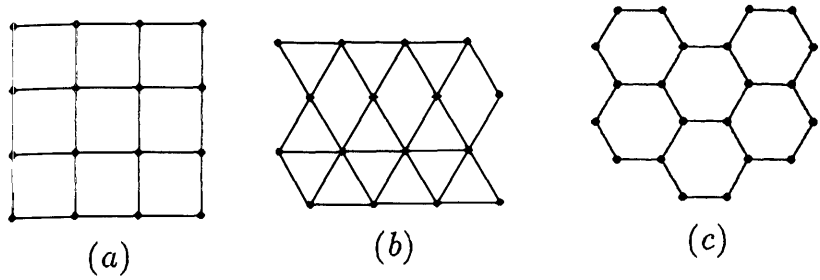


Fig. 8.5. Three types of planar lattice. (a) Square lattice. (b) Triangular lattice. (c) Hexagonal lattice.

The Hamiltonian for a two-dimensional planar lattice can be written

$$H = -\sum_{\{ij\}} J(s_i s_j - 1), \tag{8.161}$$

where $\Sigma_{\{ij\}}$ denotes the sum over nearest neighbors, i and j, J is the magnetic interaction energy between nearest-neighbor pairs, and s_i is the z component of spin at the ith lattice site. The factor, -1, in Eq. (8.161) merely shifts the zero point of energy and will prove useful in subsequent calculations. For spin-$\frac{1}{2}$ objects, $s_i = +1(-1)$ if the spin of site i is oriented in the positive (negative) z direction. If $J > 0$, the lattice will have its lowest energy when all the lattice sites have spin-oriented in like manner. If $J < 0$, the configuration in which neighboring spins are oriented opposite to one another will be favored.

The partition function for this planar lattice can be written

$$\begin{aligned} Z_N(T) &= \sum_{a.c.} \exp\left(\sum_{(ij)} K(s_i s_j - 1)\right) \\ &= e^{-N_{nn}K} \sum_{s_1=\pm 1} \cdots \sum_{s_N=\pm 1} \prod_{(ij)} e^{K s_i s_j}, \end{aligned} \tag{8.162}$$

where $K = \beta J$, $\Sigma_{a.c.}$ denotes the sum over all 2^N possible different configurations of spin on the lattice, and N_{nn} is the number of nearest neighbor pairs. The sum, $\Sigma_{(ij)}$ and the product, $\prod_{(ij)}$, are taken only over nearest-neighbor pairs. Let us now note that since $s_i = \pm 1$, we can write

$$e^{K s_i s_j} = \cosh(K) + s_i s_j \sinh(K) = \cosh(K)[1 + \tanh(K) s_i s_j]. \tag{8.163}$$

Therefore, the partition function can be written in the form

$$Z_N(T) = e^{-N_{nn}K}(\cosh(K))^{N_{nn}} \sum_{s_1=\pm 1} \cdots \sum_{s_N=\pm 1} \prod_{(ij)} [1 + \tanh(K) s_i s_j]. \tag{8.164}$$

To evaluate the partition function, we must expand the product and then sum over each spin variable, s_i. There are several properties of the spin that should be noticed and that simplify the expression for the partition function. First note that

$$\sum_{i=\pm 1} s_i^{2n} = 2 \quad \text{and} \quad \sum_{i=\pm 1} s_i^{2n+1} = 0, \tag{8.165}$$

where n is an integer (including zero). Thus, only even powers of the spin variable can appear in the partition function. Also, only nearest-neighbor pairs can appear and a given nearest-neighbor pair can appear only once. Each summation over a spin variable yields a factor of 2. Expansion of the product in Eq. (8.164) yields a sum of terms depending on varying powers of $\tanh(K)$. After summation over spins is performed, each term in the sum can be represented by a picture which we call a *closed graph.* We then can write the partition function in the form

$$Z_N(T) = 2^N e^{-N_{nn}K}(\cosh(K))^{N_{nn}} \sum(\text{all closed graphs}) \tag{8.166}$$

The closed graphs are obtained as follows:

(1) Lay out the grid of lattice sites as they appear on the original planer lattice (cf. Fig. 8.5) but do not yet draw connections between lattice sites.

(2) Find all different ways to draw nearest-neighbor bonds between lattice sites so they form closed loops (any number of closed loops including zero). We only require that no nearest-neighbor bond appears more than once. There may be more than one closed loop on a graph, and they may intersect, as long as they have *no bonds in common* (cf. Fig. 8.6) for an example of an allowed and forbidden graph).

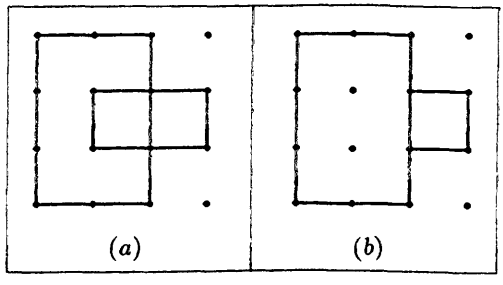


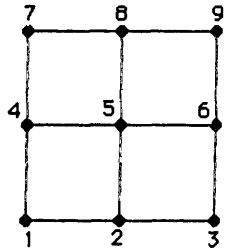
Fig. 8.6. Some closed graphs on a 3 × 3 square lattice. (a) An allowed graph. (b) A forbidden graph because two closed loops share a bond.

(3) A given graph contributes a factor, $\tanh^r(K)$, where r is the number of bonds in the graph.

An example of the use of these rules is given in Exercise 8.2

In writing Eq. (8.166), we have made progress toward obtaining an analytic expression for the partition function, but we still have a ways to go. In the next section, we will change the subject slightly and show how to represent an antisymmetric matrix in terms of a *directed graph.* We will also show how to represent the determinant of an antisymmetric matrix (actually its square root) in terms of *dimer graphs.* Then in Section S8.B.3 we will make a connection between the *closed graphs* described above and *dimer graphs.*

■ **EXERCISE 8.2** Consider the 3×3 spin lattice shown in the figure. Assign a coupling constant, $J_x(J_y)$ to horizontal (vertical) bonds. Obtain an analytic expression for the partition function.



Answer: First note that the lattice has $N = 9$ lattice sites and $N_{nn} = 12$ nearest-neighbor pairs. The partition function can be written

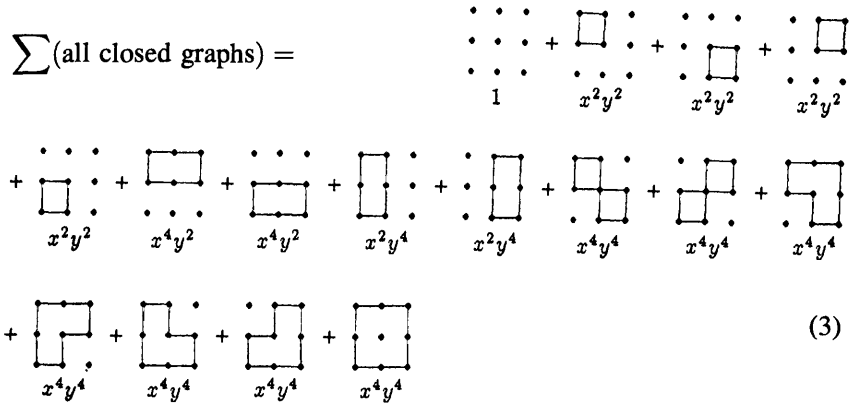
$$Z_9 = e^{-6K_x}e^{-6K_y}\sum_{s_1=\pm1}\cdots\sum_{s_9=\pm1} e^{K_x s_1 s_2}e^{K_y s_1 s_4}e^{K_x s_2 s_3}e^{K_y s_2 s_5}e^{K_y s_3 s_6} \times e^{K_y s_4 s_7}e^{K_x s_4 s_5}e^{K_x s_5 s_6}e^{K_y s_5 s_8}e^{K_y s_6 s_9}e^{K_x s_7 s_8}e^{K_x s_8 s_9}, \quad (1)$$

where $K_x = \beta J_x$ and $K_y = \beta J_y$. We may write this as

$$Z_9 = 2^9 e^{-6K_x}e^{-6K_y}\cosh^6(K_x)\cosh^6(K_y)\sum(\text{all closed graphs}). \quad (2)$$

Next we note that

$\sum$(all closed graphs) =



(3)

We therefore obtain the following analytic expression for Z_9:

$$Z_9 = 2^9 e^{-6K_x} e^{-6K_y} \cosh^6(K_x)\cosh^6(K_y) \times [1 + 4x^2y^2 + 2x^4y^2 + 2x^2y^4 + 7x^4y^4]$$

where $x \equiv \tanh(K_x)$ and $y \equiv \tanh(K_y)$.

▶ S8.B.2. Antisymmetric Matrices and Dimer Graphs [22]

Let us now return to the planar lattice whose partition function we wish to compute. We again draw a picture of the planar lattice, but now associate a direction to each bond. The resulting picture we call a *directed graph*. We can associate an antisymmetric matrix, A with a *directed graph* by assigning to the directed bond between lattice sites, i and j, a matrix element, a_{ij}. Only nearest-neighbor lattice sites give rise to nonzero matrix elements. We can associate the following matrix elements with the directed graph:

$$a_{ij} = \begin{cases} \alpha & \text{for bond directed } i \to j, \\ -\alpha & \text{for bond directed } i \leftarrow j, \\ = 0 & \text{if } i \text{ and } j \text{ have no bond} \end{cases} \quad (8.167)$$

Here $\alpha = \tanh(K)$. It is possible to generalize Eq. (8.167) and assign different weights, α, to different bonds. For the case of a square directed graph, for example, for the horizontal bonds we let $\alpha = x = \tanh(K_x)$ and for the vertical bonds we let $\alpha = y = \tanh(K_y)$ (such a case is considered in Exercise 8.3)

If we want all the terms in the determinant of the antisymmetric matrix, A, to be positive, then the choice of directions given the nearest-neighbor bonds must be carefully made. Kasteleyn [22] showed that *for graphs with an even number*

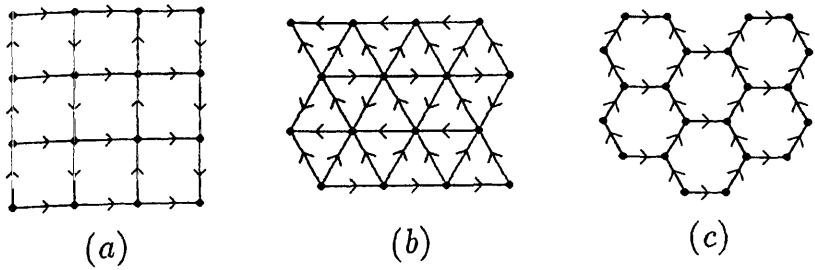
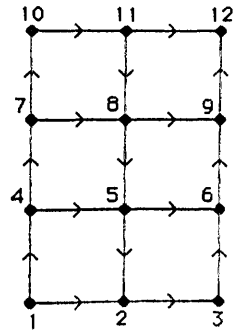


Fig. 8.7. Three types of directed planar lattice. (a) Directed square lattice. (b) Directed triangular lattice. (c) Directed hexagonal lattice

of lattice sites, directions can be chosen in such a way that all terms in the determinant of the antisymmetric matrix, A, are positive. This is important when we later connect the antisymmetric matrix generated by a directed graph to the partition function. The direction is chosen so that in going around any *even loop* on the directed graph in a clockwise manner, one encounters only an odd number of clockwise directed bonds. An *even loop* is a closed path containing an even number of lattice sites and enclosing an even number (including zero) of lattice sites. An even loop never passes through the same lattice site twice. Correct directions for some directed graphs are shown in Fig. 8.7. An example an antisymmetric graph obtained in this manner is given in Exercise 8.3.

■ **EXERCISE 8.3.** Consider the directed planar lattice shown in the accompanying figure. Write the 12 × 12 antisymmetric matrix, A, associated with this lattice, and compute the determinant of the matrix, A.



Answer: The antisymmetric matrix associated with the accompanying graph is

$$A = \begin{pmatrix}
0 & x & 0 & y & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
-x & 0 & x & 0 & -y & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & -x & 0 & 0 & 0 & y & 0 & 0 & 0 & 0 & 0 & 0 \\
-y & 0 & 0 & 0 & x & 0 & y & 0 & 0 & 0 & 0 & 0 \\
0 & y & 0 & -x & 0 & x & 0 & -y & 0 & 0 & 0 & 0 \\
0 & 0 & -y & 0 & -x & 0 & 0 & 0 & y & 0 & 0 & 0 \\
0 & 0 & 0 & -y & 0 & 0 & 0 & x & 0 & y & 0 & 0 \\
0 & 0 & 0 & 0 & y & 0 & -x & 0 & x & 0 & -y & 0 \\
0 & 0 & 0 & 0 & 0 & -y & 0 & -x & 0 & 0 & 0 & y \\
0 & 0 & 0 & 0 & 0 & 0 & -y & 0 & 0 & 0 & x & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & y & 0 & -x & 0 & x \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -y & 0 & -x & 0
\end{pmatrix}, \tag{1}$$

where $x = \tanh(K_x)$ and $y = \tanh(K_y)$. The determinant of this matrix is

$$\begin{aligned} \det(A) &= 16x^8y^4 + 48x^6y^6 + 44x^4y^8 + 12x^2y^{10} + y^{12} \\ &= (4x^4y^2 + 6x^2y^4 + y^6)^2. \end{aligned} \tag{2}$$

The determinant, det(**A**), of an antisymmetric matrix, **A**, can always be written as the square of a polynomial containing the weighting factors, α (or whatever weighting factors are assigned to the graph). Furthermore, it is possible to express $\sqrt{\det(\mathbf{A})}$ (**A** obtained from a directed graph) in terms of a sum of graphs which we shall call *dimer graphs*. A dimer graph is obtained in the following way:

(1) Lay out the grid of lattice sites (but do not yet draw bonds) as they appear in the original *directed graph*.

(2) Connect all pairs of lattice sites by bonds so that each lattice site is attached to only one bond and all lattice sites are members of a bond. The lattice consists of a set of unconnected bonds (we call them dimer bonds).

The quantity, $\sqrt{\det(\mathbf{A})}$, can be represented by the set of all different dimer graphs which may be obtained from the original planar lattice. Thus,

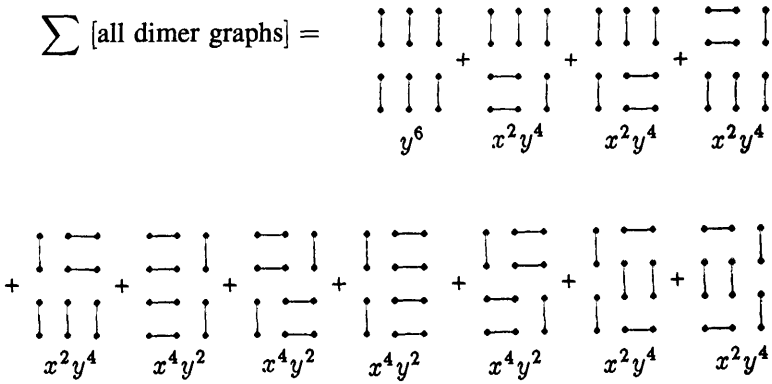
$$\sqrt{\det(A)} = \sum(\text{all different dimer graphs}). \tag{8.168}$$

Once a dimer graph is drawn, an analytic expression can be associated with it. If a graph has s dimer bonds, then we can assign a factor, $\tanh^s(K)$, to the graph. As we show in Exercise 8.4, we can also generalize this to give different weights to different bonds. For example, let us consider a square dimer graph with different bond strengths, K_x, for horizontal and, K_y, verticle bonds. If the graph has r horizontal dimer bonds and s verticle dimer bonds, we associate a factor, $\tanh^r(K_x)\tanh^s(K_y)$ with the graph. In Exercise 8.4, we construct the dimer graphs that represent $\sqrt{\det(\mathbf{A})}$ for the antisymmetric matrix, $\mathbf{A}$, obtained in Exercise 8.3.

■ **EXERCISE 8.4.** Consider the directed lattice shown in Exercise 8.3 and the antisymmetric matrix, $\mathbf{A}$, generated by that directed lattice. Draw all dimer graphs that represent $\sqrt{\det(\mathbf{A})}$ and show that they do indeed reproduce the analytic expression obtained in Exercise 8.3.

Answer: For the antisymmetric matrix, A, generated in Exercise 8.3, we want to show that $\sqrt{\det(\mathbf{A})} = \sum$ [all dimer graphs]. Note that

$\sum$ [all dimer graphs] =



(2)

Thus, if we add the contributions from the various graphs, we find

$$\sum[\text{all dimer graph}] = 4x^4y^2 + 6x^2y^4 + y^6,$$

in agreement with Exercise 8.3.

▶ S8.B.3. Closed Graphs and Mixed Dimer Graphs

Kasteleyn [22] and Fisher [23] have found a way to write the partition function in terms of dimer graphs and thereby have found a way to obtain an expression for the partition function in terms of the determinant of an antisymmetric

matrix. The method is based on the following observation. Consider a lattice with two different coupling constants, J and J^*, for example. A bond with coupling constant, J^*, will contribute factor, $2e^{-K^*}\cosh(K^*)$ and $\tanh(K^*)$, where $K^* = \beta J^*$, to the partition function. [Note that the factor -1 in Eq. (8.161)] gives rise to this property.] However, note that

$$\lim_{K^*\to\infty} 2e^{-K^*}\cosh(K^*) = 1 \quad \text{and} \quad \lim_{K^*\to\infty} \tanh(K^*) = 1. \tag{8.169}$$

The next thing to notice is that the partition function of a given planar lattice depends on a sum of terms depending on different powers of the weighting factor, $\tanh(K)$. However, the dimer graphs which are generated from a directed graph all depend on the same power of the weighting factor, $\tanh(K)$. Therefore we need to construct a directed graph which can generate dimer graphs depending on different powers of the weighting factors. The limiting behavior in Eq. (8.169) enables us to do this in a unique and unambiguous way for planar graphs.

The expansion of the partition function in terms of dimer graphs requires two important pieces of information. On the one hand, we use the theorem of Kasteleyn which says that it is possible to draw a directed graph which generates an antisymmetric matrix whose determinant has all positive terms. On the other hand, we use a method of expanding the vertices of a planar lattice so that a directed graph can be associated with it (we call it a *mixed directed graph*) which produces dimer graphs (we call them *mixed dimer graphs*) whose analytic expressions are in one-to-one correspondence with the closed graphs for that planar lattice. Kasteleyn [21] and Fisher [22] had different ways to accomplish this. In this section, we use Fisher's approach [23].

We can construct mixed directed graphs according to the following procedure.

(1) Draw the planar lattice of interest. (Figure 8.5 gives some examples of planar lattices.) The planar lattice will have N vertices and N_{nn} nearest-neighbor bonds. On the planar lattice we shall call the bonds *primary bonds*. Represent primary bonds by solid lines.

(2) Replace each vertex of degree $q (q \geq 4)$ by a cluster of $q-2$ vertices connected by $q-3$ *internal* bonds. (A vertex of degree, q, is one at which q bonds meet.) Represent internal bonds by dashed lines. (See Fig. 8.8 for an example of this replacement.) With this replacement, all vertices are now either of degree $q = 2$ or 3.

(3) Replace each vertex of degree, $q = 2$, by two vertices connected by one internal bond. Replace each vertex of degree, $q = 3$, by a cluster of three vertices connected by three internal bonds. (See Fig. 8.9 for examples.)

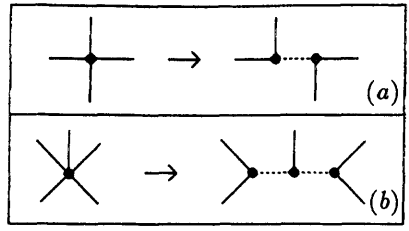


Fig. 8.8. Replace vertices of degree, $q(q \geqslant 4)$, by a cluster of $q-2$ vertices connected by $q-3$ internal bonds. (a) $q=4$. (b) $q=5$.

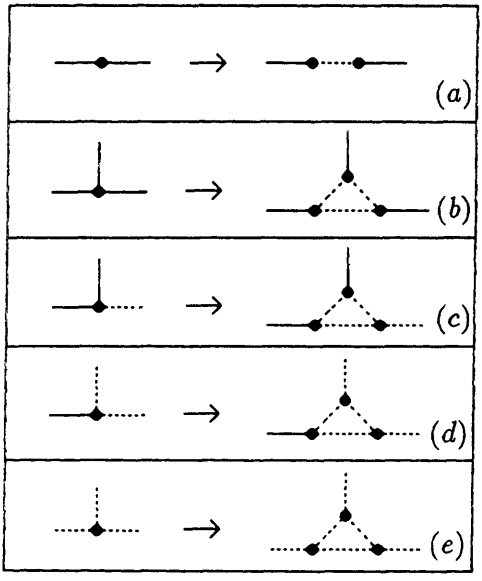


Fig. 8.9. (a) Replace vertex of degree 2 with two vertices and an internal bond. (b)–(e) Replace vertex of degree 3 with three vertices and three internal bonds.

(4) Assign directions to all the bonds (primary and internal) so that counterclockwise circulation around any *even loop* yields an odd number of clockwise directed bonds. (According to the theorem of Kasteleyn, this can always be done.)

The *mixed directed graph* which results from steps 1–4 is a collection of directed solid and dashed lines connecting vertices of degree 3 or smaller.

Once a *mixed directed graph* has been associated with a planar lattice, we can associate an *antisymmetric matrix*, A_m, with the directed mixed graph in the

following manner. The antisymmetric matrix, A_m, is constructed by assigning to matrix elements, a_{ij}, the following values:

$$a_{ij} = \begin{cases} 1/\alpha & \text{for a solid bond directed } i \rightarrow j, \\ -1/\alpha & \text{for a solid bond directed } i \leftarrow j, \\ 1 & \text{for dashed bond directed } i \rightarrow j, \\ -1 & \text{for a dashed bond directed } i \leftarrow j, \\ 0 & \text{if } i \text{ and } j \text{ have no bond.} \end{cases} \tag{8.170}$$

As we found in Section S8.B.2, we can associate a collection of dimer graphs (we shall call them *mixed dimer graphs*) with each directed mixed graph. Dimers can now be solid or dashed depending on whether they occur at the position of primary or internal bonds, respectively, on the mixed directed graph which generated them. No more than one dimer bond attaches to any given vertex. To each dimer bond we assign a factor $1/\alpha$, if the dimer bond is a solid line and assign a factor 1 if the dimer bond is a dashed line. A given dimer graph has a factor $(1/\alpha)^m(1)^n$ assocated with it if it has m primary (solid) dimer bonds and n internal (dashed) dimer bonds.

We can now relate $\sqrt{\det(\mathbf{A}_m)}$ to the sum over all mixed dimer graphs that can be derived from the mixed directed graph which generates the antisymmetric matrix, $\mathbf{A}_m$. We write

$$\sqrt{\det(\mathbf{A}_m)} = \sum(\text{all mixed dimer graphs}). \tag{8.171}$$

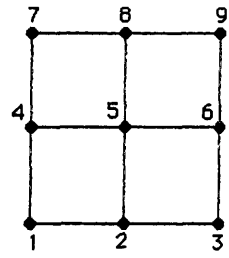
The mixed dimer graphs that result from a given planar lattice are in one-to-one correspondence with the closed graphs which are generated by that same planar lattice. The correspondence is "inverted," however. The primary (solid) dimer bonds on the mixed dimer graph correspond to the *lack* of bonds on the closed graph.

We can now relate $\sqrt{\det(\mathbf{A}_m)}$ to the partition function associated with the planar lattice. We can write

$$\begin{aligned} Z_N(T) &= 2^N e^{-N_{nn}K}(\cosh(K))^{N_{nn}}\alpha^s\sqrt{\det(\mathbf{A}_m)} \\ &= 2^N e^{-N_{nn}K}(\cosh(K))^{N_{nn}}\alpha^s\sum(\text{all mixed dimer graphs}), \end{aligned} \tag{8.172}$$

where s is the maximum number of primary (solid) dimer bonds that can appear on any of the mixed dimer graphs. With this definition, the dimer graph in which all dimers are primary (solid) bonds actually corresponds to the unit graph. In Exercise 8.5 we show these steps for the planar lattice considered in Exercise 8.2.

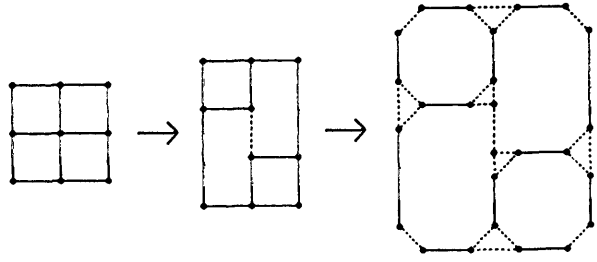
■ **EXERCISE 8.5.** Consider the planar lattice shown in the accompanying figure. (a) Construct a mixed directed graph for this lattice and construct the associated antisymmetric matrix, $\mathbf{A}_m$. (b) Compute the partition function from this antisymmetric matrix, $\mathbf{A}_m$. (c) Draw the mixed dimer graphs for this lattice and write an analytic expression for the partition function.



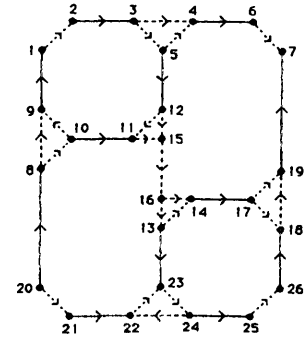
Answer:

(a) We first obtain the directed mixed lattice. We replace the vertex of degree 4 by two vertices of degree 3 and an internal line. We then replace each vertex of degree 2 by two vertices of degree 2 connected by an internal line. We replace each vertex of degree 3 by two vertices of degree 3 connected by three internal bonds. The results is a graph with 26 vertices.

This procedure is shown in the graphs below.



We next give directions to all the lines in the mixed graph so that for any *even loop*, clockwise circulation encounters an odd number of clockwise directed bonds. Such a choice is shown below. We have also numbered the vertices.



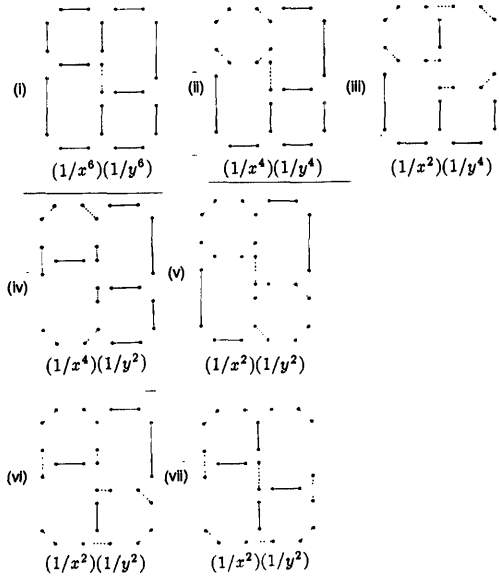
(**b**) Given the numbered mixed directed graph above, we can use it to construct an antisymmetric matrix, $\mathbf{A}_m$. Choose the matrix elements according to the directions of the bonds and their type. Assign a value, $\pm 1/x$, to horizontal bonds and assign a factor, $\pm\frac{1}{y}$ to vertical bonds. The nonzero matrix elements are $a_{1,2} = +1$, $a_{2,1} = -1$, $a_{2,3} = +1/x$, $a_{3,2} = -1/x$, $a_{3,5} = +1$, $a_{5,3} = -1$, $a_{5,12} = +1/y$, $a_{12,5} = -1/y$, $a_{1,3} = a_{3,1} = 0$, and so on. The matrix, A_L is too big to write here, but it is easy to construct given the directed graph above. Once it has been constructed we can find its determinant. It is

$$\det(A_L) = \frac{1}{x^{12}y^{12}}(1 + 4x^2y^2 + 2x^4y^2 + 2x^2y^4 + 7x^4y^4)^2. \qquad (1)$$

The partition function is

$$\begin{aligned} Z_N(T) &= 2^9 e^{-6K_x} e^{-6K_y} \cosh^6(K_x)\cosh^6(K_y) x^6 y^6 \\ &\quad \times \left[\frac{1}{x^6y^6}(1 + 4x^2y^2 + 2x^4y^2 + 2x^2y^4 + 7x^4y^4)\right] \\ &= 2^9 e^{-6K_x} e^{-6K_y} \cosh^6(K_x)\cosh^6(K_y) \\ &\quad \times (1 + 4x^2y^2 + 2x^4y^2 + 2x^2y^4 + 7x^4y^4). \end{aligned} \qquad (2)$$

Let us now draw the dimer graphs. There is one dimer graph for each closed graph in Eq. (3) of Exercise 8.2. We shall draw some of them here. We have



The analytic expression associated with each mixed dimer graph is shown below it. Graph (i) above corresponds to the first closed graph in Exercise 8.2, Eq. (3). Four mixed dimer graphs of the type (ii) above correspond to closed graphs, 2–5 in Exercise 8.2, Eq. (3). The two mixed dimer graphs of the type (iii) above correspond to closed graphs 6 and 7, and the two mixed dimer graphs of the type (iv) above correspond to closed graphs 8 and 9 in Exercise 8.2, Eq. (3). Two mixed dimer graphs of the type (v) above correspond to closed graphs 10 and 11 in Exercise 8.2, Eq. (3). Four mixed dimer graphs of the type (vi) above correspond to closed graphs 12–15 in Exercise 8.2, Eq. (3). And finally, graph (vii) corresponds to the last graph in Exercise 8.2, Eq. (3). Thus there are 16 possible mixed dimer graphs. They each consist of 26 vertices and a mixture of solid and dashed dimer bonds. The partition function is

$$Z_N(t) = 2^9 e^{-K_x} e^{-6K_y} \cosh^6(K_x)\cosh^6(K_y) \times x^6 y^6 \sum(\text{all mixed dimer graphs}). \quad (3)$$

▶ S8.B.4. Partition Function for the Infinite Planar Lattice

We now have enough information to obtain an analytic expression for the partition function of an infinite planar lattice. For simplicity we will consider a square planar lattice. The procedure is to extract an $n \times n$ segment from the infinite lattice, and then take the limit, $n \to \infty$. In order to demonstrate the procedure, we will first extract a 3×3 segment from the infinite planer lattice

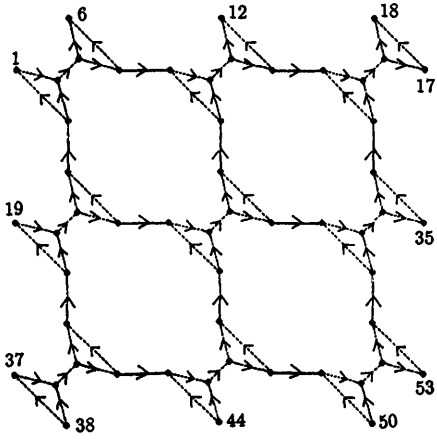


Fig. 8.10. A 3×3 segment of an infinite square directed graph corresponds to a 54×54 mixed directed graph.

and describe its properties in detail. Then we will go on to write partition function for an $n \times n$ segment and take the limit, $n \to \infty$.

▶ *S8.B.4.1. A 3 × 3 Segment of the Infinite Square Planar Lattice*

Let us consider a 3×3 segment of an infinite square planar lattice. We first construct a 54×54 mixed directed graph as shown in Fig 8.10 using the rules of Section S8.B.3. We can then assign an antisymmetric matrix, $\mathbf{A}_{54}$, to the directed mixed graph. We obtain

$$A_{54} = \begin{pmatrix} \Gamma & X & 0 & -Y^T & 0 & 0 & 0 & 0 & 0 \\ -X^T & \Gamma & X & 0 & -Y^T & 0 & 0 & 0 & 0 \\ 0 & -X^T & \Gamma & 0 & 0 & -Y^T & 0 & 0 & 0 \\ Y & 0 & 0 & \Gamma & X & 0 & -Y^T & 0 & 0 \\ 0 & Y & 0 & -X^T & \Gamma & X & 0 & -Y^T & 0 \\ 0 & 0 & Y & 0 & -X^T & \Gamma & 0 & 0 & -Y^T \\ 0 & 0 & 0 & Y & 0 & 0 & \Gamma & X & 0 \\ 0 & 0 & 0 & 0 & Y & 0 & -X^T & \Gamma & X \\ 0 & 0 & 0 & 0 & 0 & Y & 0 & -X^T & \Gamma \end{pmatrix}, \tag{8.173}$$

where "0" in the matrix (8.173) represents a 6×6 matrix with all elements zero:

$$\Gamma \equiv \Gamma_6 = \begin{pmatrix} 0 & 1 & 1 & 0 & 0 & 0 \\ -1 & 0 & 1 & 0 & 0 & 0 \\ -1 & -1 & 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 & 1 & 1 \\ 0 & 0 & 0 & -1 & 0 & 1 \\ 0 & 0 & 0 & -1 & -1 & 0 \end{pmatrix},$$

$$X \equiv X_6 = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 1/x & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}, \tag{8.174}$$

$$Y \equiv Y_6 = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1/y & 0 & 0 & 0 & 0 \end{pmatrix},$$

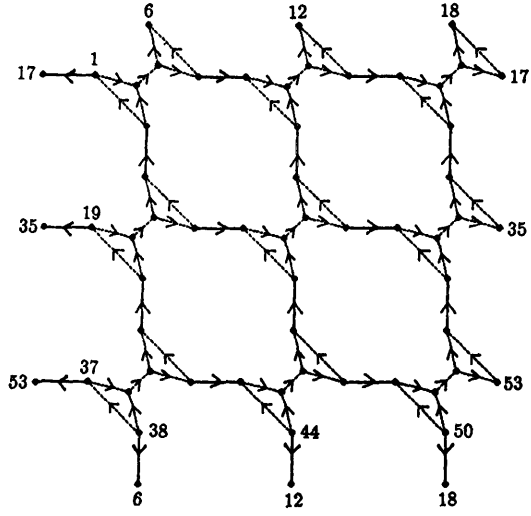


Fig. 8.11. The 54 × 54 directed lattice with bonds connecting opposite sides added.

The subscript 6 is added to show that Γ_6, X_6, and Y_6 are 6×6 matrices. This notation will be useful later. In constructing the mixed directed graph, Fig. 8.10, we have left out its connections to the rest of the infinite mixed directed graph, and the antisymmetric matrix, $\mathbf{A}_{54}$, does not include these bonds.

Let us now take our 54×54 directed lattice and change it by giving it periodic boundary conditions. We will connect opposite sides to one another by adding bonds and then add the contributions from these new bonds to the antisymmetric matrix. It turns out that as we consider larger and larger segments of the infinite planar lattice, these additional terms contribute less and less to the determinant of the antisymmetric matrix, and in the limit of an infinite lattice they do not affect the result. In Fig. 8.11 we redraw the 54×54 directed lattice so that bonds on opposite sides are connected. We then no longer have a planar lattice. Note the directions of these added bonds are opposite to normal connections to the infinite lattice. The antisymmetric matrix, $\tilde{A}_{54}$, that results from adding these new bonds to A_{54} is given by

$$A_{54} = \begin{pmatrix} \Gamma & X & X^T & -Y^T & 0 & 0 & -Y & 0 & 0 \\ -X^T & \Gamma & X & 0 & -Y^T & 0 & 0 & -Y & 0 \\ -X & -X^T & \Gamma & 0 & 0 & -Y^T & 0 & 0 & -Y \\ Y & 0 & 0 & \Gamma & X & X^T & -Y^T & 0 & 0 \\ 0 & Y & 0 & -X^T & \Gamma & X & 0 & -Y^T & 0 \\ 0 & 0 & Y & -X & -X^T & \Gamma & 0 & 0 & -Y^T \\ Y^T & 0 & 0 & Y & 0 & 0 & \Gamma & X & X^T \\ 0 & Y^T & 0 & 0 & Y & 0 & -X^T & \Gamma & X \\ 0 & 0 & Y^T & 0 & 0 & Y & -X & -X^T & \Gamma \end{pmatrix}, \tag{8.175}$$

The antisymmetric matrix, $\tilde{A}_{54}$, is now in a form that is easy to deal with. First note that we can write $\tilde{A}_{54}$ as the tensor product of smaller matrices (tensor products are defined in the subsection below). We can write

$$\begin{aligned}\tilde{A}_{54} &= \begin{pmatrix} D_{18} & -I_3 \otimes Y_6^T & -I_3 \otimes Y_6 \\ I_3 \otimes Y_6 & D_{18} & -I_3 \otimes Y_6^T \\ I_3 \otimes Y_6^T & I_3 \otimes Y_6 & D_{18} \end{pmatrix} \\ &= I_3 \otimes D_{18} + E_3 \otimes (I_3 \otimes Y_6^T) - E_3^{-1} \otimes (I_3 \otimes Y_6), \end{aligned} \tag{8.176}$$

where

$$D_{18} = \begin{pmatrix} \Gamma_6 & X_6 & X_6^T \\ -X_6^T & \Gamma_6 & X_6 \\ -X_6 & -X_6^T & \Gamma_6 \end{pmatrix}, \tag{8.177}$$

$$E_3 = \begin{pmatrix} 0 & -1 & 0 \\ 0 & 0 & -1 \\ 1 & 0 & 0 \end{pmatrix}, \quad \text{and} \quad I_3 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{8.178}$$

■ **Tensor Product of Matrices.** We introduce the tensor product of two matrices, $\bar{A}$ and $\bar{B}$, as follows. We write $\bar{\mathbb{C}} = \bar{A} \otimes \bar{B}$, where $\bar{\mathbb{C}}$ is a fourth-order tensor whose $(ijkl)$th element is given by

$$(\bar{\mathbb{C}})_{ijkl} = (\bar{A} \otimes \bar{B})_{ijkl} = A_{ij}B_{kl}. \tag{1}$$

where A_{ij} and B_{kl} are the (ij)th and (kl)th elements of matrices $\bar{A}$ and $\bar{B}$, respectively. The product of two fourth-order tensors, $\bar{\mathbb{Q}}$ and $\bar{\mathbb{R}}$, is given by

$$(\bar{\mathbb{Q}}\bar{\mathbb{R}})_{ijkl} = \sum_{m,n} \mathbb{Q}_{imkn}\mathbb{R}_{mjnl}, \tag{2}$$

where $\mathbb{Q}_{imkn}$ and $\mathbb{R}_{mjnl}$ are the $(imkn)$th and $(mjnl)$th elements of the tensors $\bar{\mathbb{Q}}$ and $\bar{\mathbb{R}}$, respectively. The tensor product of a matrix $\bar{A}$ with the unit matrix $\bar{I}$ is

$$(\bar{A} \otimes \bar{I})_{ijkl} = A_{ij}\delta_{k,l}, \tag{3}$$

where $\delta_{k,l}$ is the Kronecker delta function. *If $\bar{B}$ and $\bar{C}$ commute*, then we can write

$$(\bar{A} \otimes \bar{B})(\bar{C} \otimes \bar{D}) = (\bar{A}\bar{C}) \otimes (\bar{B}\bar{D}). \tag{4}$$

The matrix D_{18} can also be written as a tensor product:

$$D_{18} = I_3 \otimes \Gamma_6 - E_3 \otimes X_6 + E_3^{-1} \otimes X_6^T. \tag{8.179}$$

Therefore, the antisymmetric matrix $(\tilde{A})_{54}$ takes the form

$$\tilde{A}_{54} = I_3 \otimes (I_3 \otimes \Gamma_6) - I_3 \otimes (E_3 \otimes X_6) + I_3 \otimes (E_3^{-1} \otimes X_6^T) + E_3 \otimes (I_3 \otimes Y_6^T) - E_3^{-1} \otimes (I_3 \otimes Y_6), \tag{8.180}$$

where we have used the fact that $E_3^2 = E_3^{-1}$. Let us next introduce the matrix P_3, which diagonalizes E_3. That is,

$$P_3^{-1} E_3 P_3 = \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix}, \tag{8.181}$$

where λ_k is the kth eigenvalue ($k = 1, 2, 3$) of the matrix E_3 and is given by $\lambda_k = \exp(2\pi i k/3)$. Then we find that

$$\begin{aligned} \mathbf{A}'_{54} &\equiv (P_3^{-1} \otimes (P_3^{-1} \otimes I_6))\tilde{A}_{54}(P_3 \otimes (P_3 \otimes I_6)) \\ &= I_3 \otimes I_3 \otimes \Gamma_6 - I_3 \otimes (P_3^{-1} E_3 P_3) \otimes X_6 \\ &\quad + I_3 \otimes (P_3^{-1} E_3^{-1} P_3) \otimes X_6^T \\ &\quad + (P_3^{-1} E_3 P_3) \otimes I_3 \otimes Y_6^T - (P_3^{-1} E_3^{-1} P_3) \otimes I_3 \otimes Y_6. \end{aligned} \tag{8.182}$$

We next note, for example, that

$$I_3 \otimes \Gamma_6 = \begin{pmatrix} \Gamma_6 & 0 & 0 \\ 0 & \Gamma_6 & 0 \\ 0 & 0 & \Gamma_6 \end{pmatrix} \tag{8.183}$$

and

$$(P_3^{-1} E_3 P_3) \otimes X_6 = \begin{pmatrix} \lambda_1 X_6 & 0 & 0 \\ 0 & \lambda_2 X_6 & 0 \\ 0 & 0 & \lambda_3 X_6 \end{pmatrix}. \tag{8.184}$$

Then one can readily show we have obtained an expression for A'_{54} which is block diagonal. It can be written

$$\mathbf{A}'_{54} = \begin{pmatrix} D_{1,1}^{(3)} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & D_{1,2}^{(3)} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & D_{1,3}^{(3)} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & D_{2,1}^{(3)} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & D_{2,2}^{(3)} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & D_{2,3}^{(3)} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & D_{3,1}^{(3)} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & D_{3,2}^{(3)} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & D_{3,3}^{(3)} \end{pmatrix}, \tag{8.185}$$

where

$$D_{i,j}^{(3)} = \Gamma_6 - \lambda_i X_6 + \frac{1}{\lambda_i} X_6^T + \lambda_j Y_6^T - \frac{1}{\lambda_j} Y_6$$
$$= \begin{pmatrix} 0 & 1 & 1 & 0 & x/\lambda_i & 0 \\ -1 & 0 & 1 & 0 & 0 & y\lambda_j \\ -1 & -1 & 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 & 1 & 1 \\ -x\lambda_i & 0 & 0 & -1 & 0 & 1 \\ 0 & -y/\lambda_j & 0 & -1 & -1 & 0 \end{pmatrix}. \tag{8.186}$$

The determinant of $D_{i,j}^{(3)}$ is given by

$$\det[D_{i,j}^{(3)}] = 1 + \left(\frac{1}{x}\right)^2 + \left(\frac{1}{y}\right)^2 + \left(\frac{1}{x}\right)^2\left(\frac{1}{y}\right)^2 - 2\left(\frac{1}{x}\right)\cos\left(\frac{2\pi i}{3}\right) - 2\left(\frac{1}{y}\right)\cos\left(\frac{2\pi j}{3}\right) + 2\left(\frac{1}{x}\right)^2\left(\frac{1}{y}\right)\cos\left(\frac{2\pi j}{3}\right) + 2\left(\frac{1}{y}\right)^2\left(\frac{1}{x}\right)\cos\left(\frac{2\pi i}{3}\right). \tag{8.187}$$

Let us now note that due to the cyclic permeability of matrices under the determinant and the fact the determinant of a product of matrices is equal to the product of determinants of those matrices, we obtain

$$\det[\tilde{A}_{54}] = \det[A'_{54}] = \prod_{i=1}^{3}\prod_{j=1}^{3}\left[1 + \left(\frac{1}{x}\right)^2 + \left(\frac{1}{y}\right)^2 + \left(\frac{1}{x}\right)^2\left(\frac{1}{y}\right)^2 - 2\left(\frac{1}{x}\right)\cos\left(\frac{2\pi i}{3}\right) - 2\left(\frac{1}{y}\right)\cos\left(\frac{2\pi j}{3}\right) + 2\left(\frac{1}{x}\right)^2\left(\frac{1}{y}\right)\cos\left(\frac{2\pi j}{3}\right) + 2\left(\frac{1}{y}\right)^2\left(\frac{1}{x}\right)\cos\left(\frac{2\pi i}{3}\right)\right]. \tag{8.188}$$

These results are easily generalized to an $n \times n$ segment of the infinite planar lattice.

▶ *S8.B.4.2. An n × n Segment of an Infinite Square Planar Lattice*

Let us now consider an $n \times n$ segment of the infinite square spin lattice. The mixed directed lattice that we construct will have $6n^2$ lattice sites, and therefore the antisymmetric matrix that we associate with the directed lattice will be $6n^2 \times 6n^2$-dimensional. We proceed exactly as before. We introduce the $n \times n$-dimensional matrix, E_n, which consists of all zeros except for (i) matrix elements -1 along the nearest upper off-diagonal and (ii) the matrix element 1

in the bottom left corner. We shall restrict outselves of odd values of n. Then the eigenvalues of E_n are given by $\lambda_k = \exp(2\pi ik/n)$, where $k = 1, 2, \ldots, n$. The determinant of the antisymmetric matrix, $\tilde{A}_{6n^2}$, obtained by connecting opposite bonds of the $6n^2 \times 6n^2$-dimensional directed lattice will be given by

$$\det[\tilde{A}_{6n^2}] = \prod_{j=1}^{n}\prod_{k=1}^{n}\left[1 + \left(\frac{1}{x}\right)^2 + \left(\frac{1}{y}\right)^2 + \left(\frac{1}{x}\right)^2\left(\frac{1}{y}\right)^2 - 2\left(\frac{1}{x}\right)\cos\left(\frac{2\pi j}{n}\right)\right.$$
$$\left. - 2\left(\frac{1}{y}\right)\cos\left(\frac{2\pi k}{n}\right) + 2\left(\frac{1}{x}\right)^2\left(\frac{1}{y}\right)\cos\left(\frac{2\pi k}{n}\right) + 2\left(\frac{1}{y}\right)^2\left(\frac{1}{x}\right)\cos\left(\frac{2\pi j}{n}\right)\right]$$
$$= \prod_{j=1}^{n}\prod_{k=1}^{n} D_{jk}^{(n)}. \tag{8.189}$$

The partition function can be written

$$Z_n(T) = 2^{n^2} e^{-K_x n(n-1)} e^{-K_y n(n-1)} \cosh^{n(n-1)}(K_x) \cosh^{n(n-1)}(K_y)$$
$$\times x^{n(n-1)} y^{n(n-1)} \sqrt{\det[\tilde{\mathbf{A}}_{6n^2}]}. \tag{8.190}$$

If we remember that $x = \tanh(K_x)$ and $y = \tanh(K_y)$ and note that $e^{-K}\sinh(K) = \tanh(K)/[1 + \tanh(K)]$, then with the help of Eq. (8.189) we can write the partition function as

$$Z_n(T) = 2^{n^2}\left(\frac{x}{1+x}\right)^{n(n-1)}\left(\frac{y}{1+y}\right)^{n(n-1)}\sqrt{\prod_{j=1}^{n}\prod_{k=1}^{n} D_{jk}^{(n)}}. \tag{8.191}$$

The logarithm of the partition function becomes

$$\ln[Z_n(T)] = n^2\ln(2) + n(n-1)\ln\left(\frac{x}{1+x}\right) + n(n-1)\ln\left(\frac{y}{1+y}\right)$$
$$+ \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\ln(D_{ij}^{(n)}). \tag{8.192}$$

We now can take the thermodynamic limit. It is useful to note that $\lim_{n\to\infty}\sum_{i=1}^{n}(1/n)\cos(2\pi i/n) = (1/2\pi)\int_0^{2\pi} d\phi\cos(\phi)$. Then for the free energy density (free energy per lattice site), $a(T)$, we find

$$-\frac{a(T)}{k_B T} = \lim_{n\to\infty}\left[\frac{1}{n^2}\ln[Z_n(T)]\right] = \ln 2 + \ln\left(\frac{x}{1+x}\right) + \ln\left(\frac{y}{1+y}\right)$$
$$+ \frac{1}{2}\frac{1}{4\pi^2}\int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\phi_2 \ln\left[1 + \frac{1}{x^2} + \frac{1}{y^2} + \frac{1}{x^2y^2} - \frac{2}{x}\cos(\phi_1) - \frac{2}{y}\cos(\phi_2)\right.$$
$$\left. + \frac{2}{x^2y}\cos(\phi_2) + \frac{2}{xy^2}\cos(\phi_1)\right]. \tag{8.193}$$

We can simplify subsequent calculations if we let $J_x = J_y$. Then $x = y = \tanh(K)$ and the free energy density takes the form

$$\begin{aligned}-\frac{a(T)}{k_BT} &= \ln(2) + 2\ln\left(\frac{x}{1+x}\right) \\ &\quad + \frac{1}{2}\frac{1}{4\pi^2}\int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\phi_2 \ln\left[1 + \frac{2}{x^2} + \frac{1}{x^4}\right. \\ &\quad \left. - \left(\frac{2}{x} - \frac{2}{x^3}\right)(\cos(\phi_1) + \cos(\phi_2))\right] \\ &= \ln(2) - 2\ln(1+x) + \frac{1}{2}\frac{1}{4\pi^2}\int_0^{2\pi} d\phi_1 \\ &\quad \times \int_0^{2\pi} d\phi_2 \ln\left[1 + 2x^2 + x^4 + 2x(1-x^2)(\cos(\phi_1) + \cos(\phi_2))\right].\end{aligned} \tag{8.194}$$

We now can make use of the identities

$$2x(1-x^2) = \sinh(2K)/\cosh^4(K) \quad \text{and} \quad 1 + 2x^2 + x^4 = \cosh^2(2K)/\cosh^4(K). \tag{8.195}$$

Then the free energy density becomes

$$\begin{aligned}-\frac{a(T)}{k_BT} &= \ln(2) - 2K \\ &\quad + \frac{1}{2}\frac{1}{4\pi^2}\int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\phi_2 \ln[\cosh^2(2K) + \sinh(2K)(\cos(\phi_1) + \cos(\phi_2))].\end{aligned}$$

Equation (8.196) can be simplified still further. Note that $\cos(\phi_1) + \cos(\phi_2) = 2\cos[\frac{1}{2}(\phi_1 + \phi_2)]\cos[\frac{1}{2}(\phi_1 - \phi_2)]$. If we make the change of variables, $\theta_1 = \frac{1}{2}(\phi_1 - \phi_2)$ and $\theta_2 = \frac{1}{2}(\phi_1 + \phi_2)$, and let $\kappa = 2\sinh(2K)/\cosh^2(2K)$, then the free energy density becomes

$$\begin{aligned}-\frac{a(T)}{k_BT} &= \ln(2) - 2K + \ln[\cosh(2K)] \\ &\quad + \frac{1}{4\pi^2}\int_{-\pi}^{\pi} d\theta_1 \int_0^{2\pi} d\theta_2 \ln[1 + \kappa\cos(\theta_1)\cos(\theta_2)].\end{aligned} \tag{8.197}$$

We can integrate Eq. (8.197) if we note that [24]

$$\int_0^{2\pi} dx \ln(a + b\cos(x)) = 2\pi \ln[(a + \sqrt{a^2 - b^2})/2]. \tag{8.198}$$

Then we obtain

$$-\frac{a(T)}{k_BT} = \ln(2) - 2K + \ln[\cosh(2K)] + \frac{2}{\pi}\int_0^{\pi/2} d\theta \ln\left[\frac{1}{2}\left(1 + \sqrt{1-\kappa^2\sin^2(\theta)}\right)\right]. \tag{8.199}$$

The internal energy density is easily obtained from Eq. (8.199). We find

$$u(T) = J\frac{\partial}{\partial K}\left(\frac{a(T)}{k_BT}\right) = 2J - J\coth(2K)[1 + (2\tanh^2(2K) - 1)\frac{2}{\pi}\mathrm{K}(\kappa)], \tag{8.200}$$

where $\mathrm{K}(\kappa)$ is the complete elliptic integral of the first kind [25] and is defined as

$$\mathrm{K}(\kappa) = \int_0^{\pi/2} \frac{d\theta}{\sqrt{1-\kappa^2\sin^2(\theta)}}. \tag{8.201}$$

The specific heat is given by

$$c = \frac{\partial u}{\partial T} = -\frac{K}{T}\frac{\partial u}{\partial K} = \frac{2}{\pi}k_BK^2\coth^2(2K)\left\{2\mathrm{K}(\kappa) - 2\mathrm{E}(\kappa) - 2\,\mathrm{sech}^2(2K)\left[\frac{\pi}{2} + (2\tanh(2K) - 1)\mathrm{K}(\kappa)\right]\right\}. \tag{8.202}$$

The complete elliptic integral of the first kind, $\mathrm{K}(\kappa)$, has a singularity for $\kappa = 1$. The phase transition occurs at this point. The temperature at which the phase transition occurs is then given by the condition

$$\kappa_c = \frac{2\sinh(2K_c)}{\cosh^2(2K_c)} = 1. \tag{8.203}$$

This gives a critical temperature, $T_c = 2.269J/k_B$. In Fig 8.12 we plot the internal energy per site and the specific heat as a function of K, which is proportional to the inverse temperature.

Ising-like phase transitions have been measured in the two-dimensional Ising-like antiferromagnets, K_2CoF_4 and Rb_2CoF_4. These substances behave like two-dimensional spin systems because they consist of strongly coupled antiferromagnetic CoF_2 planes separated by weakly coupled planes containing the remaining molecules. In Fig 8.13 we show two measurements of the heat capacity of Rb_2CoF_4. We see the characteristic Ising-like singularity in the heat capacity.

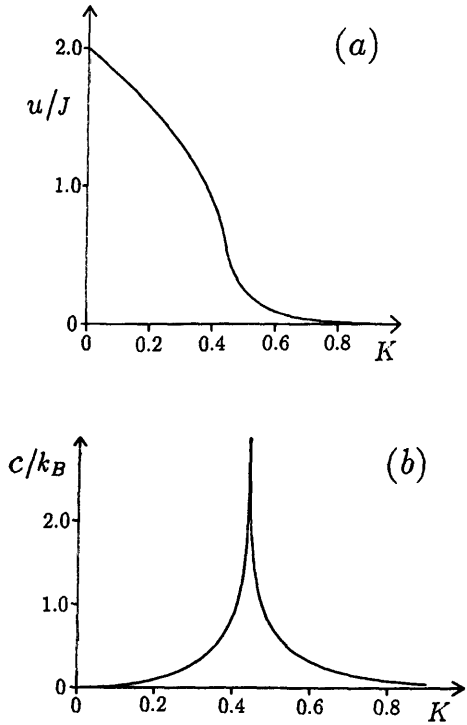


Fig. 8.12. (a) The internal energy per site as a function of K. (b) The specific heat as a function of K. The phase transition occurs at $K_c = 1/2.269 = 0.4407$.

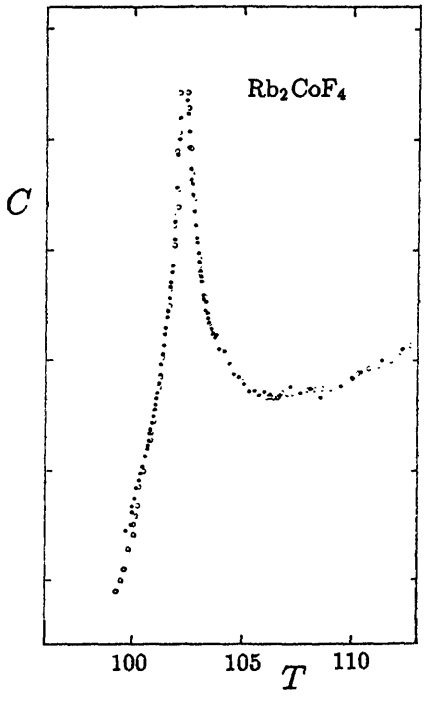


Fig. 8.13. The heat capacity of Rb_2CoF_4 (given in arbitrary units) as a function of temperature, T, measured in Kelvin. Two sets of experimental data are shown. Reprinted, by permission, from H. Ikeda, I. Hatta, and M. Tanaka, *J. Phys. Soc.* (Japan) **40**, 334 (1976).

In the section we have obtained analytic expressions for the free energy, the internal energy, and the heat capacity of a two-dimensional square planar Ising lattice. From Eq. (8.202) we can obtain the critical exponent, α. The type of singularity that occurs in the heat capacity is easy to find from properties of the complete elliptic integrals. Let us note that as $\kappa \to 1$, $E(\kappa) \to 1$ but $K(\kappa) \to \ln(4/\sqrt{1-\kappa^2})$. Thus, the singularity in the heat capacity is logarithmic and the critical exponent, α, for the two-dimensional Ising lattice is $\alpha = 0$.

It is interesting to compare Fig. 8.12, the exact heat capacity of the two-dimensional Ising lattice, to that of the mean field approximation given in Fig. 7.8. Mean field theory predicts a finite discontinuity, while the exact solution gives a logarithmic singularity. The two theories also give different critical temperatures.

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PROBLEMS

Problem 8.1. A one-dimensional lattice of spin-$\frac{1}{2}$ lattice sites can be decomposed into blocks of three spins each. Use renormalization theory to determine whether or not a phase transition can occur on this lattice. If a phase transition does occur, what are its critical exponents? Retain terms in the block Hamiltonian to order $\langle V \rangle$, where V is the coupling between blocks.

Problem 8.2. Find the critical exponents for five spin blocks on a square lattice for the two-dimensional nearest-neighbor Ising model. Retain terms to lowest order in $\langle V \rangle$, where V is the interaction energy between blocks (cf. Fig. 8.14).

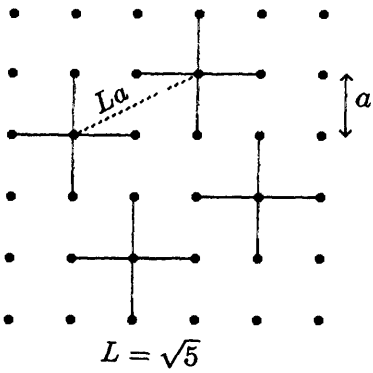
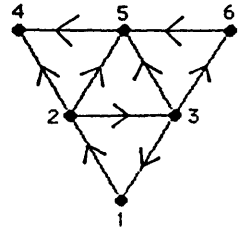
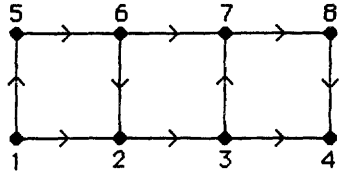


Fig. 8.14.

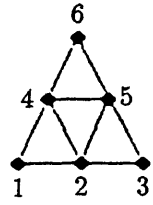
Problem S8.1. Consider the directed lattice shown in the figure. Assume that horizontal bonds have a coupling constant, J_x, and that tilted vertical bonds have coupling constant, J_y. (a) Find the antisymmetric matrix, A, associated with this lattice. Compute its determinant. (b) Draw all disconnected dimer graphs for this lattice. Show that they represent $\sqrt{A}$.



Problem S8.2. Consider the directed lattice shown in the Figure. Assume that horizontal bonds have coupling constant, J_x, and that vertical bonds have a coupling constant, J_y (a) Find the antisymmetric matrix, A, associated with this lattice. Compute its determinant. (b) Draw all disconnected dimer graphs for this lattice. Show that they represent $\sqrt{A}$.



Problem S8.3. Consider the planar triangular lattice shown in the figure. Assign a coupling constant, J, to each bond. (a) Compute the partition function and draw all closed graphs for this lattice. (b) Draw the directed mixed graph for this lattice and obtain the antisymmetric matrix it generates. Show that the determinant of the antisymmetric yields the correct expression for the partition function.



9

INTERACTING FLUIDS

9.A. INTRODUCTION

One of the great successes of equilibrium statistical mechanics has been the theory of interacting fluids. For real fluids, the interparticle potential has a hard core and a weak attractive region. Consequently, the usual perturbation theories do not work. For dilute or moderately dense fluids, the only small parameter is the density and therefore, various thermodynamic quantities can be formulated in terms of a density expansion.

In this chapter we shall restrict overselves primarily to neutral fluids with spherically symmetric potentials. The quantity of central importance in describing such systems is the radial distribution function, which is a measure of the probability of finding a particle at some distance, q, from any particle in the fluid. The radial distribution function can be measured directly by X-ray scattering experiments or it can be obtained from molecular dynamics experiments. We shall begin this chapter by deriving an expression for the internal energy in terms of the radial distribution function, and in the *special topics* section we will derive expressions for both the pressure and compressibility in terms of the radial distribution function, using both the canonical and grand canonical ensembles.

In the chapters on thermodynamics, we have already been introduced to the virial expansion of the equation of state. We shall now derive an expression for the virial coefficients using microscopic theory. The method involves writing the grand partition function in terms of a cumulant expansion and then expressing the grand potential and pressure in terms of the cumulants or cluster functions. The techniques for doing this were first developed by Ursell, whose work was later extended by Mayer. The analysis is greatly facilitated by the use of graph theory which enables one to give a simple physical interpretation to various terms in the virial expansion. The first few virial coefficients have been computed for a variety of interparticle potentials. We shall discuss the results for the hard-core potential, the square-well potential, and the Lennard-Jones 6–12 potential and compare them with experiment.

For very light molecules at low temperatures, quantum effects introduce significant deviation from classical behavior. In the *special topics* section we will construct the virial expansion for interacting degenerate quantum fluids.

9.B. THERMODYNAMICS AND THE RADIAL DISTRIBUTION FUNCTION [1–5]

In this chapter we will compute the equilibrium properties of a classical fluid consisting of N particles with mass m whose dynamics is determined by a Hamiltonian of the form

$$H^N(\mathbf{p}^N, \mathbf{q}^N) = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{(ij)=1}^{N(N-1)/2} \mathrm{V}(\mathbf{q}_{ij}), \tag{9.1}$$

where $\mathbf{q}_{ij} = \mathbf{q}_i - \mathbf{q}_j$ is the relative displacement of particles, i and j (we use the notation of Section 6.B). It is useful to introduce the one-body phase function, $O_1^N(\mathbf{q}^N) = \sum_{i=1}^{N} O_1(\mathbf{q}_i)$ (the kinetic energy is an example of a one-body phase function), and the two-body phase function, $O_2^N(\mathbf{q}^N) = \sum_{(ij)=1}^{N(N-1)/2} O_2(\mathbf{q}_i - \mathbf{q}_j)$ (the potential energy is an example of a two-body phase function). The average values of these phase functions can be written

$$\langle O_1^N \rangle = \frac{\int d\mathbf{p}^N d\mathbf{q}^N O_1^N(\mathbf{q}^N) e^{-\beta H^N}}{\int d\mathbf{p}^N d\mathbf{q}^N e^{-\beta H^N}} = \int d\mathbf{q}_1 O_1(\mathbf{q}_1) n_1^N(\mathbf{q}_1; V, T) \tag{9.2}$$

and

$$\langle O_2^N \rangle = \frac{1}{2} \int d\mathbf{q}_1 \int d\mathbf{q}_2 O_2(\mathbf{q}_1, \mathbf{q}_2) n_2^N(\mathbf{q}_1, \mathbf{q}_2; V, T), \tag{9.3}$$

where $n_1^N(\mathbf{q}_1; V, T)$ and $n_2^N(\mathbf{q}_1, \mathbf{q}_2; V, T)$ are the one-body and two-body reduced distribution functions, respectively, in the canonical ensemble. They are defined

$$n_l^N(\mathbf{q}_1, \ldots, \mathbf{q}_l; V, T) = \frac{1}{Q_N(V,T)} \frac{N!}{(N-l)!} \int d\mathbf{q}_{l+1} \cdots d\mathbf{q}_N \, e^{-\beta V^N}, \tag{9.4}$$

where $\mathrm{V}^N = \sum_{(ij)=1}^{N(N-1)/2} \mathrm{V}(\mathbf{q}_{ij})$ is the potential energy. In Eq. (9.4) the quantity $Q_N(V,T)$ is called the *configuration integral* and is defined as

$$Q_N(V,T) = \int d\mathbf{q}^N e^{-\beta \mathrm{V}^N}. \tag{9.5}$$

The reduced distribution functions have the property that

$$\int d\mathbf{q}_1 \cdots d\mathbf{q}_l n_l^N(\mathbf{q}_1, \ldots, \mathbf{q}_l; V, T) = \frac{N!}{(N-l)!}. \tag{9.6}$$

One of the simplest quantities to compute is the internal energy, $U(V,T,N)$. The internal energy is just the average value of the Hamiltonian and can be

written

$$U(V,T,N) = \langle H \rangle = \frac{3}{2}Nk_BT + \frac{\int d\mathbf{q}^N \mathrm{V}^N e^{-\beta V^N}}{\int d\mathbf{q}^N e^{-\beta V^N}} = \frac{3}{2}Nk_BT + \frac{1}{2}\int\int d\mathbf{q}_1 d\mathbf{q}_2 \mathrm{V}(\mathbf{q}_{12}) n_2^N(\mathbf{q}_1, \mathbf{q}_2; V, T). \tag{9.7}$$

The term $\frac{3}{2}Nk_BT$ is the kinetic contribution to the internal energy, and the remaining term is the contribution due to the interaction between the particles.

The expression for the internal energy simplifies considerably for systems whose particles interact via spherically symmetric potentials, $\mathrm{V}(\mathbf{q}_{ij}) = \mathrm{V}(q_{ij})$, where $q_{ij} = |\mathbf{q}_i - \mathbf{q}_j|$ is the magnitude of the relative displacement. Then the two-particle reduced probability density takes the form $n_2^N(\mathbf{q}_1, \mathbf{q}_2; V, T) = n_2^N(\mathbf{q}_{12}; V, T)$. Furthermore, it will depend only on the magnitude, q_{ij}, of the relative displacement. If we change the integration variables to relative, $\mathbf{q}_{ij}$, and center-of-mass, $\mathbf{Q}_{ij} = \frac{1}{2}(\mathbf{q}_i + \mathbf{q}_j)$, coordinates and let $n_2^N(\mathbf{q}_{12}; V, T) = (\frac{N}{V})^2 g_2^N(q_{ij}; V, T)$, then we can integrate over the center-of-mass coordinates and find

$$U(V,T,N) = \frac{3}{2}Nk_BT + \frac{1}{2}\frac{N^2}{V}\int 4\pi q^2 dq \mathrm{V}(q) g_2^N(q; V, T), \tag{9.8}$$

where $q = q_{12}$. The function $g_2^N(q; V, T)$ is called the *radial distribution function*. The radial distribution function is extremely important because it completely characterizes the behavior of a classical fluid of spherically symmetric particles. It also has a direct physical interpretation. The quantity $(N/V)g(q)4\pi q^2 dq$ is the average number of particles in a spherical shell of width $q \to q + dq$ at a distance q from any particle in the fluid.

The form of the radial distribution function can be determined from neutron scattering experiments in which slow neutrons scatter from atomic nuclei in a liquid. The angular dependence of the scattered neutrons is measured, and this information can be used to construct the static structure factor, $S_{nn}(k)$ (cf. Exercise 9.1), of the liquid. The structure function can be expressed in terms of the radial distribution function. In Fig. 9.1 we show the structure factor and the radial distribution function obtained from neutron scattering experiments on liquid ^{36}Ar at 85 K. The radial distribution function goes to zero at about the hard-core radius, indicating that no particles can penetrate the hard core. It has a maximum at about the distance of the minimum of the attractive potential between nearest-neighbor argon atoms in the liquid. The next peak is due to the high probability of finding next nearest neighbors at that position, and so on.

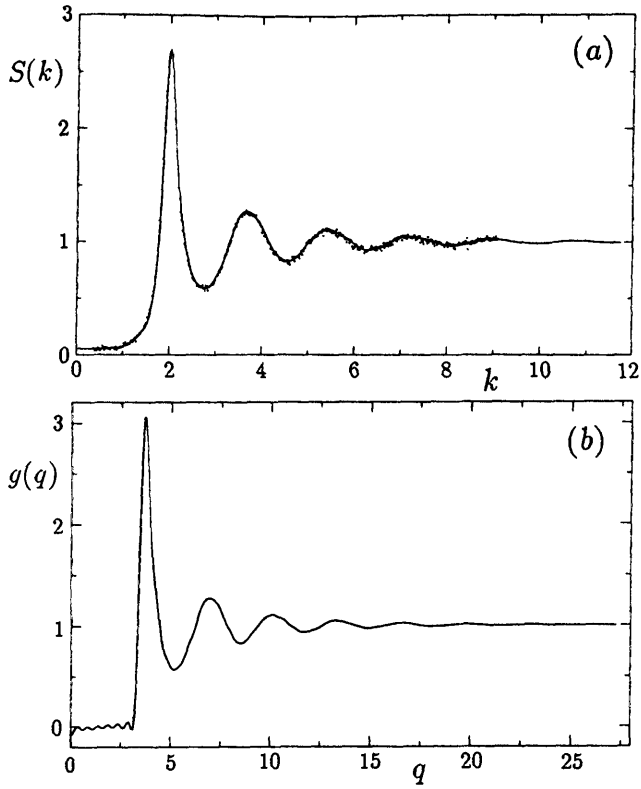


Fig. 9.1. (a) The structure factor, $S(k) = S_{nn}(k)$, versus k (in Å^{-1}) for liquid ^{36}Ar at 85 K obtained from neutron scattering experiments. The dots are data poins. The solid line is a best fit to the data. (b) The radial distribution function, $g(q)$, versus q (in Å) obtained from the data in (a). Reprinted, by permission, from J. L. Yarnell, et. al., *Phys. Rev.* **A7**, 2130 (1973).

■ **EXERCISE 9.1.** The static density correlation function, $C_{nn}(\mathbf{r})$, for an equilibrium fluid can be written $C_{nn}(\mathbf{r}) = (1/N)\int d\mathbf{r}'\langle n(\mathbf{r}'+\mathbf{r})n(\mathbf{r}')\rangle$, where the density phase function is defined $n(\mathbf{r},\mathbf{q}^N) = \sum_{i=1}^{N}\delta(\mathbf{q}_i - \mathbf{r})$. The static structure factor for the fluid is defined as $S_{nn}(\mathbf{k}) = \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} C_{nn}(\mathbf{r})$. Show that in the limit $N \to \infty$ and $V \to \infty$ with $n = N/V =$ constant, the static structure factor when written in terms of the pair correlation function has the form

$$S_{nn}(\mathbf{k}) = 1 + n\delta(\mathbf{k}) + \frac{4\pi}{k}\int_0^\infty qdq\sin(kq)(g_2(q) - 1).$$

Answer: The static structure factor may be written

$$S_{nn}(\mathbf{k}) = \frac{1}{N}\int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \int d\mathbf{r}' \langle n(\mathbf{r}'+\mathbf{r}) n(\mathbf{r}')\rangle$$
$$= \frac{1}{N}\int\int d\mathbf{r}' d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{i=1}^{N}\sum_{j=1}^{N} \langle \delta(\mathbf{q}_i - \mathbf{r}' - \mathbf{r})\delta(\mathbf{q}_j - \mathbf{r}')\rangle$$
$$= \frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{N} \langle e^{i\mathbf{k}\cdot(\mathbf{q}_i - \mathbf{q}_j)}\rangle. \tag{1}$$

If we evaluate the average value in the canonical ensemble, we find

$$S_{nn}(\mathbf{k}) = \frac{1}{N}\frac{1}{Q_N(V,T)}\sum_{i=1}^{N}\sum_{j=1}^{N}\int d\mathbf{q}_1 \cdots \int d\mathbf{q}_N e^{i\mathbf{k}\cdot(\mathbf{q}_i - \mathbf{q}_j)} e^{-\beta V(\mathbf{q}^N)}$$
$$= \frac{1}{N}\left[N + \frac{1}{Q_N(V,T)}\sum_{(i,j;i\neq j)}^{N(N-1)}\int d\mathbf{q}_1 \cdots \int d\mathbf{q}_N e^{i\mathbf{k}\cdot(\mathbf{q}_i - \mathbf{q}_j)} e^{-\beta V(\mathbf{q}^N)}\right]$$
$$= 1 + \frac{1}{N}\int d\mathbf{q}_1 \int d\mathbf{q}_2 e^{i\mathbf{k}\cdot\mathbf{q}_{ij}} n_2^N(\mathbf{q}_1, \mathbf{q}_2; V, T)$$
$$= 1 + \frac{N}{V}\int d\mathbf{q}_{12} e^{i\mathbf{k}\cdot\mathbf{q}_{12}} g_2^N(q_{12}; V, T). \tag{2}$$

The minimum value of the wavevector, $\mathbf{k}$, is determined by the size of the box. In the limit $N \to \infty$ and $V \to \infty$ with $n = N/V =$ constant, the length of the wavevector can be zero. We can separate this contribution from the remainder of the integral. We find

$$S_{nn}(\mathbf{k}) = 1 + n\delta(\mathbf{k}) + n\int d\mathbf{q}_{12} e^{i\mathbf{k}\cdot\mathbf{q}_{12}} (g_2^N(q_{12}; V, T) - 1). \tag{3}$$

The integration over angles in Eq. (3) can be performed to finally give

$$S_{nn}(\mathbf{k}) = 1 + n\delta(\mathbf{k}) + \frac{4\pi n}{k}\int q dq \sin(kq)(g_2^N(q; V, T) - 1). \tag{4}$$

The structure factor can be measured in neutron scattering experiments, and the term $n\delta(\mathbf{k})$ is the contribution due to coherent forward scattering.

9.C. VIRIAL EXPANSION OF THE EQUATION OF STATE [1–3, 7, 8]

The first step in obtaining tractable microscopic expressions for the thermodynamic properties of fluids is to find a small parameter that can be used as an

expansion parameter. For dilute or moderately dense gases, such a parameter is the density. In this section we shall first obtain a microscopic expression for the virial expansion of the equation of state (density expansion) for a classical fluid, and then we shall compare the predictions of the microscopic theory to experimental results.

9.C.1. Virial Expansion and Cluster Functions

Let us consider a classical gas of identical particles of mass m which interact via two-body short-ranged forces. We shall assume that the potential has a large repulsive core and short-ranged attraction (cf. Fig. 9.2). For such a system the grand partition function can be written in the form

$$Z_\mu(T,V) = \sum_{N=0}^{\infty} \frac{1}{N!} \frac{1}{\lambda_T^{3N}} e^{\beta N\mu'} Q_N(V,T), \tag{9.9}$$

where the momentum integrations have been performed and the configuration integral, $Q_N(V,T)$, is defined in Eq. (9.5).

If the interparticle potential, V_{ij}, is short-ranged, then for large values of separation between particles we obtain $\mathrm{V}_{ij} = 0$ and $\exp(-\beta \mathrm{V}_{ij}) = 1$. It is convenient to introduce a function, f_{ij}, such that

$$f_{ij} = e^{-\beta \mathrm{V}_{ij}} - 1. \tag{9.10}$$

The function f_{ij} becomes zero outside the range of the interaction. Furthermore, in the region of the hard core, where $\mathrm{V}_{ij} = \infty$, the function $f_{ij} = -1$. Thus f_{ij} is a much better expansion parameter than V_{ij} (cf. Fig. 9.2). In terms of the

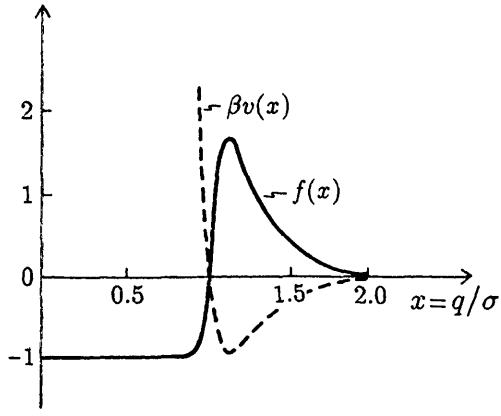


Fig. 9.2. The dashed line is a plot of a typical interparticle potential, $v(x)$ (Lennard-Jones 6–12), the solid line is a plot of $f(x) = e^{-\beta v(x)} - 1$, and σ is a measure of the hard-core radius ($v(1) = 0$). The plots are given for a fixed temperature.

function f_{ij}, the configuration integral can be written as

$$Q_N(V,T) = \int \cdots \int d\mathbf{q}_1 \cdots d\mathbf{q}_N \prod_{(ij)}^{N(N-1)/2} (1 + f_{ij}). \tag{9.11}$$

In Eq. (9.11) the product is taken over all pairs of particles (ij). There are $N(N-1)/2$ such pairs.

It was shown by Ursell [9] that the partition function can be written in terms of a cumulant expansion. We first write the configuration integral in the form

$$Q_N(V,T) = \int \cdots \int d\mathbf{q}_1 \cdots d\mathbf{q}_N W_N(\mathbf{q}_1, \ldots, \mathbf{q}_N), \tag{9.12}$$

so that

$$Z_\mu(T,V) = \sum_{N=0}^{\infty} \frac{1}{N!} \frac{1}{\lambda_T^{3N}} e^{\beta N \mu'} \int \cdots \int d\mathbf{q}_1 \cdots d\mathbf{q}_N W_N(\mathbf{q}_1, \ldots, \mathbf{q}_N). \tag{9.13}$$

We now define the following cumulant expansion for the grand partition function:

$$Z_\mu(T,V) = \exp\left[\sum_{l=1}^{\infty} \frac{1}{l!} \frac{1}{\lambda_T^{3l}} e^{\beta l \mu'} \int \cdots \int d\mathbf{q}_1 \cdots d\mathbf{q}_l U_l(\mathbf{q}_1, \ldots, \mathbf{q}_l)\right], \tag{9.14}$$

where $U_l(\mathbf{q}_1, \ldots, \mathbf{q}_l)$ is called a *cluster function* of *Ursell function*. In terms of the cluster functions, the grand potential takes a simple form:

$$\begin{aligned} \Omega(V,T,\mu) &= -k_B T \ln[Z_\mu(T,V)] \\ &= -k_B T \sum_{l=1}^{\infty} \frac{1}{l!} \frac{1}{\lambda_T^{3l}} e^{\beta l \mu'} \int \cdots \int d\mathbf{q}_1 \cdots d\mathbf{q}_l U_l(\mathbf{q}_1, \ldots, \mathbf{q}_l). \end{aligned} \tag{9.15}$$

If we know the function $W_N(\mathbf{q}, \ldots, \mathbf{q}_N)$, then we can easily find the cluster functions $U_N(\mathbf{q}_1, \ldots, \mathbf{q}_N)$. We simply expand Eqs. (9.13) and (9.14) in powers of $(\lambda_T^{-3}\exp(\beta\mu'))$ and equate coefficients. We then obtain the following hierarchy of equations:

$$U_1(\mathbf{q}_1) = W_1(\mathbf{q}_1), \tag{9.16}$$

$$U_2(\mathbf{q}_1, \mathbf{q}_2) = W_2(\mathbf{q}_1, \mathbf{q}_2) - W_1(\mathbf{q}_1) W_1(\mathbf{q}_2), \tag{9.17}$$

$$\begin{aligned} U_3(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3) = {} & W_3(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3) - W_1(\mathbf{q}_1) W_2(\mathbf{q}_2, \mathbf{q}_3) \\ & - W_1(\mathbf{q}_2) W_2(\mathbf{q}_1, \mathbf{q}_3) - W_1(\mathbf{q}_3) W_2(\mathbf{q}_1, \mathbf{q}_2) \\ & + 2 W_1(\mathbf{q}_1) W_1(\mathbf{q}_2) W_1(\mathbf{q}_3), \end{aligned} \tag{9.18}$$

and so on. We can revert Eqs. (9.16)–(9.18) and find

$$W_1(\mathbf{q}_1) = U_1(\mathbf{q}_1), \tag{9.19}$$

$$W_2(\mathbf{q}_1, \mathbf{q}_2) = U_2(\mathbf{q}_1, \mathbf{q}_2) + U_1(\mathbf{q}_1)U_1(\mathbf{q}_2), \tag{9.20}$$

$$\begin{aligned} W_3(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3) = {} & U_3(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3) + U_1(\mathbf{q}_1)U_2(\mathbf{q}_2, \mathbf{q}_3) + U_1(\mathbf{q}_2)U_2(\mathbf{q}_1, \mathbf{q}_3) \\ & + U_1(\mathbf{q}_3)U_2(\mathbf{q}_1, \mathbf{q}_2) + U_1(\mathbf{q}_1)U_1(\mathbf{q}_2)U_1(\mathbf{q}_3), \end{aligned} \tag{9.21}$$

and so on. The cumulant expansion we have just introduced is independent of the form of $W_N(\mathbf{q}_1, \ldots, \mathbf{q}_N)$.

For the systems we consider in this chapter, we can write

$$W_N(\mathbf{q}_1, \ldots, \mathbf{q}_N) = \prod_{(ij)}^{N(N-1)/2} (1 + f_{ij}). \tag{9.22}$$

Thus, the first few terms are

$$W_1(\mathbf{q}_1) = 1, \tag{9.23}$$

$$W_2(\mathbf{q}_1, \mathbf{q}_2) = (1 + f_{12}), \tag{9.24}$$

$$W_3(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3) = (1 + f_{12})(1 + f_{13})(1 + f_{23}), \tag{9.25}$$

$$W_4(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3, \mathbf{q}_4) = (1 + f_{12})(1 + f_{13})(1 + f_{14})(1 + f_{23})(1 + f_{24})(1 + f_{34}), \tag{9.26}$$

and so on. If we expand out the expressions for $W_N(\mathbf{q}_1, \ldots, \mathbf{q}_N)$, we see that the case $N = 1$ contains one term, the case $N = 2$ contains two terms, the case $N = 3$ contains eight terms, and the case $N = 4$ contains 64 terms. From Eqs. (9.16)–(9.18) we can find the first few cluster functions. They are

$$U_1(\mathbf{q}_1) = 1, \tag{9.27}$$

$$U_2(\mathbf{q}_1, \mathbf{q}_2) = f_{12}, \tag{9.28}$$

and

$$U_3(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3) = f_{12}f_{13} + f_{12}f_{23} + f_{13}f_{23} + f_{12}f_{13}f_{23}. \tag{9.29}$$

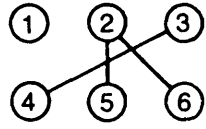
The expression for $U_4(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3, \mathbf{q}_4)$ is too long to write down here, so we will leave it as an exercise. It contains 38 terms. It is easy to see that the functions $W_N(\mathbf{q}_1, \ldots, \mathbf{q}_N)$ and $U_N(\mathbf{q}_1, \ldots, \mathbf{q}_N)$ rapidly become very complicated as N increases.

Since the grand partition function contains terms with arbitrarily large values of N, it is necessary to find a systematic procedure for categorizing and sorting various terms in the expressions for $W_N(\mathbf{q}_1, \ldots, \mathbf{q}_N)$ and $U_N(\mathbf{q}_1, \ldots, \mathbf{q}_N)$. Such

a procedure is called *graph theory*. We can represent $W_N(\mathbf{q}_1, \ldots, \mathbf{q}_N)$ in terms of graphs in the following way:

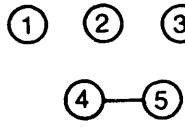
$$W_N(\mathbf{q}_1, \ldots, \mathbf{q}_N) = \sum (\text{all different } N\text{-particle graphs}). \tag{9.30}$$

An N-particle graph is obtained by drawing N-numbered circles and connecting them together with any number of lines (including zero) subject only to the condition that any two circles cannot be connected by more than one line. Two N-particle graphs are different if the numbered circles are connected differently. An algebraic expression can be associated with an N-particle graph by assigning a factor f_{ij} to each pair of numbered circles that are connected by a line. For example, the six-particle graph is expressed as



$$= f_{34} f_{25} f_{26}, \tag{9.31}$$

and the five-particle graph is expressed as



$$= f_{45}. \tag{9.32}$$

The graphical expression for $W_3(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3)$ can be written

$$W_3(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3) =$$ $$, \tag{9.33}$$

where we have grouped together all graphs with the same topological structure before labels are attached.

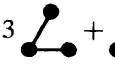
From Eqs. (9.16)–(9.18), it is not difficult to see that the cluster functions can also be represented by graphs, but of a special form. We find that

$$U_l(\mathbf{q}_1, \ldots, \mathbf{q}_l) = \sum (\text{all different } l\text{-clusters}). \tag{9.34}$$

An l-cluster is an l-particle graph in which all numbered circles are interconnected. Thus, in an l-cluster it must be possible to reach all numbered circles by continuously following the lines connecting the circles. Graphical expressions for the first few cluster functions are given by

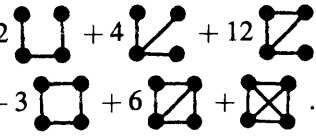
$$U_1(\mathbf{q}_1) =$$ $$, \tag{9.35}$$

$$U_2(\mathbf{q}_1, \mathbf{q}_2) =$$ $$ \tag{9.36}$$

$$U_3(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3) = 3$$  $$, \tag{9.37}$$

and

$$U_4(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3, \mathbf{q}_4) = 12 + 4 + 12 + 3 + 6 + . \tag{9.38}$$



Again, we have grouped together all graphs which have the same topological structure before lables are attached.

We see from graph theory that the cluster functions have a special meaning. An N-particle cluster function $U_N(\mathbf{q}_1, \ldots, \mathbf{q}_N)$ is nonzero only if all N-particles interact. Thus, they contain information about the way in which clusters occur among interacting particles in the gas. By writing the partition function in terms of a cumulant expansion, we have isolated the quantities which have physical content.

There is also another reason for writing $Z_\mu(T, V)$ as a cumulant expansion, which does not become apparent until we try to integrate over the functions $W_N(\mathbf{q}_1, \ldots, \mathbf{q}_N)$. Let us consider some examples and restrict ourselves to four-particle graphs.

(**a**) Each unconnected dot gives rise to a factor V. For example,

$$\int \cdots \int d\mathbf{q}_1 \cdots d\mathbf{q}_4 \left(\begin{array}{cc} \bullet & \bullet \\ \bullet & \bullet \end{array} \right) = \int \cdots \int d\mathbf{q}_1 \cdots d\mathbf{q}_4 1 = V^4$$

and

$$\int \cdots \int d\mathbf{q}_1 \cdots d\mathbf{q}_4 \left(\begin{array}{cc} \bullet & \bullet \\ \bullet - & \bullet \end{array} \right) = \int \cdots \int d\mathbf{q}_1 \cdots d\mathbf{q}_4 f_{24} f_{34}$$

$$= V \int\int\int d\mathbf{q}_2 \, d\mathbf{q}_3 \, d\mathbf{q}_4 \, f_{24} f_{34}.$$

(**b**) If two parts of a graph are not connected by a line, the corresponding algebraic expression factors into a product. For example,

$$\int \cdots \int d\mathbf{q}_1 \cdots d\mathbf{q}_4 \left(\begin{array}{cc} \bullet & \bullet \\ \bullet & \bullet \end{array} \right) = \int \cdots \int d\mathbf{q}_1 \cdots d\mathbf{q}_4 f_{12} f_{34}$$

$$= \left(\int\int d\mathbf{q}_1 d\mathbf{q}_2 f_{12} \right) \left(\int\int d\mathbf{q}_3 d\mathbf{q}_4 f_{34} \right).$$

(**c**) Each completely connected part of a graph (cluster) is proportional to the volume (this comes from integrating over the center of mass of a cluster).

For example,

$$\int \cdots \int d\mathbf{q}_1 \cdots d\mathbf{q}_4 \left(\begin{array}{cc} \bullet & \bullet \\ \bullet & \bullet \end{array} \right) = \left(V \int d\mathbf{q}_{12} f_{12} \right) \left(V \int d\mathbf{q}_{34} f_{34} \right)$$

and

$$\int\cdots\int d\mathbf{q}_1\cdots d\mathbf{q}_4\ \left(\right.\ \left.\right) = V\int\int\int d\mathbf{q}_1 d\mathbf{q}_2 d\mathbf{q}_3\, f_{12} f_{23} f_{13}$$

$$= V^2\int\int d\mathbf{q}_{31} d\mathbf{q}_{21}\, f(|\mathbf{q}_{31}|) f(|\mathbf{q}_{21}|) f(|\mathbf{q}_{31}-\mathbf{q}_{21}|),$$

where $\mathbf{q}_{31} = \mathbf{q}_3 - \mathbf{q}_1$ and $\mathbf{q}_{21} = \mathbf{q}_2 - \mathbf{q}_1$. In the second example, we have integrated over the position of particle 1 in the cluster. This gives a factor V since the cluster can be anywhere in the box. The positions of particles 2 and 3 are then specified relative to particle 1 (it is useful to draw a picture). Thus, the configuration integral $Q_N(V,T)$ contains terms which have volume dependence of the form V^α, where α can range anywhere from $\alpha = 1$ to $\alpha = N$. The integrals over cluster functions, however, are always proportional to the volume. We can write

$$b_l(V,T) = \frac{1}{Vl!}\int\cdots\int d\mathbf{q}_1\cdots d\mathbf{q}_l U_l(\mathbf{q}_1,\ldots,\mathbf{q}_l), \tag{9.39}$$

where $b_l(V,T)$ is called a cluster integral and, at most, depends on the density. Thus, the expression for the grand potential, $\Omega(V,T,\mu')$, in Eq. (9.15) is proportional to the volume.

We are now in a position to obtain the virial expansion of the equation of state. From Eqs. (9.15) and (9.39) we may write the grand potential as

$$\Omega(V,T,\mu') = -Vk_BT\sum_{l=1}^{\infty}\frac{b_l(T,V)e^{\beta l\mu'}}{\lambda_T^{3l}}. \tag{9.40}$$

The pressure then becomes

$$P = -\frac{\Omega(V,T,\mu')}{V} = k_BT\sum_{l=1}^{\infty}\frac{b_l(T,V)e^{\beta l\mu'}}{\lambda_T^{3l}}. \tag{9.41}$$

and the particle density is given by

$$\frac{\langle N\rangle}{V} = -\frac{1}{V}\left(\frac{\partial\Omega}{\partial\mu'}\right)_{V,T} = \sum_{l=1}^{\infty}\frac{lb_l(V,T)e^{\beta l\mu'}}{\lambda_T^{3l}}. \tag{9.42}$$

The virial expansion of the equation of state is an expansion in powers of the density,

$$\frac{PV}{\langle N\rangle k_BT} = \sum_{l=1}^{\infty}B_l(T)\left(\frac{\langle N\rangle}{V}\right)^{l-1}. \tag{9.43}$$

To determine the lth virial coefficient, B_l, let us for simplicity consider all equations in the thermodynamic limit ($V \to \infty, \langle N \rangle \to \infty$, such that $\langle N \rangle / V$ =constant). Then $b_l(T, V) \longrightarrow \lim its_{V\to\infty} \tilde{b}_l(T)$. If we combine Eqs. (9.41), (9.42), and (9.43), we obtain

$$\left(\sum_{l=1}^{\infty} \frac{\tilde{b}_l(T) e^{\beta l \mu'}}{\lambda_T^{3l}}\right)\left(\sum_{n=1}^{\infty} \frac{n\tilde{b}_n(T) e^{\beta n \mu'}}{\lambda_T^{3n}}\right)^{-1} = \sum_{l'=1}^{\infty} B_{l'}\left(\sum_{n'=1}^{\infty} \frac{n' \tilde{b}_{n'}(T) e^{\beta n' \mu'}}{\lambda_T^{3n'}}\right)^{l'-1}. \tag{9.44}$$

If we now expand both sides of Eq. (9.44) and equate coefficients of equal powers of $\lambda_T^{-3}\exp(\beta\mu')$, we obtain the following expressions for the first four virial coefficients:

$$B_1(T) = \tilde{b}_1(T) = 1, \tag{9.45}$$

$$B_2(T) = -\tilde{b}_2(T), \tag{9.46}$$

$$B_3(T) = 4\tilde{b}_2^2(T) - 2\tilde{b}_3(T), \tag{9.47}$$

$$B_4(T) = -20b_2^3(T) + 18\tilde{b}_2(T)\tilde{b}_3(T) - 3\tilde{b}_4(T), \tag{9.48}$$

and so on. The higher-order terms in the virial expansion are determined by larger and larger clusters of particles.

The functions f_{ij} depend only on relative coordinates. Consequently, we can show that

$$\frac{1}{V}\int\int\int d\mathbf{q}_1 d\mathbf{q}_2 d\mathbf{q}_3 \left(\begin{array}{c}\bullet\\ \bullet\quad\bullet\end{array}\right) = \left[\int d\mathbf{q}_1 \bullet\!\!-\!\!\bullet\right]^2.$$

Similarly,

$$\frac{1}{V}\int\cdots\int d\mathbf{q}_1\cdots d\mathbf{q}_4 \left(\begin{array}{cc}\bullet & \bullet\\ \bullet & \bullet\end{array}\right) = \frac{1}{V}\int\cdots\int d\mathbf{q}_1\cdots d\mathbf{q}_4 \left(\begin{array}{cc}\bullet & \\ \bullet & \bullet\\ & \bullet\end{array}\right) = \left[\int d\mathbf{q}_1 \left(\bullet\!\!-\!\!\bullet\right)\right]^3$$

and

$$\frac{1}{V}\int\cdots\int d\mathbf{q}_1\cdots d\mathbf{q}_4 \left(\begin{array}{cc}\bullet & \bullet\\ \bullet & \bullet\end{array}\right) = \left[\int d\mathbf{q}_1 \left(\bullet\!\!-\!\!\bullet\right)\right]\left[\int\cdots\int d\mathbf{q}_2 d\mathbf{q}_3 \left(\begin{array}{c}\bullet\\ \bullet\quad\bullet\end{array}\right)\right].$$

These identities enable us to simplify the expressions for the virial coefficients and write them as

$$B_n(V,T) = -\frac{1}{n}\frac{1}{(n-2)!}\int d\mathbf{q}_1\cdots d\mathbf{q}_n \tilde{V}_n(\mathbf{q}_1,\ldots,\mathbf{q}_n), \tag{9.49}$$

where $\tilde{V}_n(\mathbf{q}_1, \ldots, \mathbf{q}_n)$ is called a *star function* and

$$\tilde{V}_n(\mathbf{q}_1, \ldots, \mathbf{q}_n) = \sum (\text{all different } n\text{-particle star graphs}). \tag{9.50}$$

An n-particle star graph is a connected graph which is so tightly connected that if we remove any point and all lines that connect to it the remaining graph will still be connected.

In terms of graphs, the first few star functions are given by

$$\tilde{V}_2(\mathbf{q}_1, \mathbf{q}_2) =$$ (9.51)

$$\tilde{V}_3(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3) =$$ (9.52)

and

$$\tilde{V}_4(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3, \mathbf{q}_4) = 3$$ (9.53)

The numerical factors in front of each graph in Eq. (9.53) indicate that there are that many ways to assign the coordinates to the points and obtain topologically different graphs. Thus, there are that many different graphs. The nth-order virial coefficient is composed only of tightly bound connected n-particle graphs.

We are now in a position to compare the predictions of this theory to experimental observations.

9.C.2. The Second Virial Coefficient [1]

The second virial coefficient gives the correction to the ideal gas equation of state due to two-body clustering. For very dilute gases, two-body clusters give by far the dominant contribution from interactions in the fluid and it is sufficient to terminate the virial expansion at second order.

From Eqs. (9.10), (9.28), (9.39), and (9.46), the second virial coefficient can be written

$$B_2(T) = -\frac{1}{2V}\int\int d\mathbf{q}_1 d\mathbf{q}_2 f(\mathbf{q}_{12}) = -\frac{1}{2}\int d\mathbf{q}_{12}(e^{-\beta \mathbf{V}(\mathbf{q}_{12})} - 1), \tag{9.54}$$

where we have changed to center of mass and relative coordinates and have integrated over the center of mass. The behavior of the second virial coefficient has been studied for a variety of interparticle potentials. For very simple potentials it can be computed analytically, and for realistic potentials it must be computed numerically. We shall focus on two potentials which historically have been important in understanding the behavior of the virial coefficients. They are the square-well potential and the Lennard-Jones 6–12 potential (cf. Fig. 9.3).

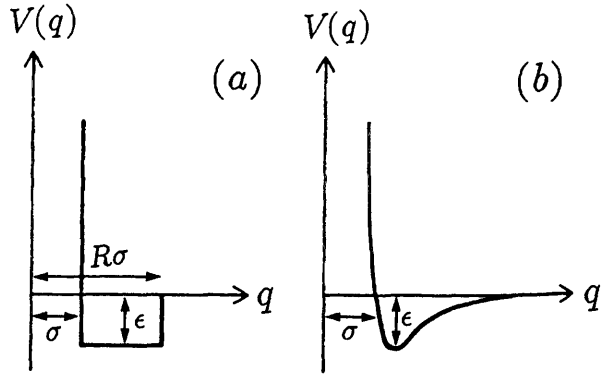


Fig. 9.3. Sketch of (a) the square-well potential and (b) the Lennard-Jones 6–12 potential.

9.C.2.1. Square-Well Potential.

The square-well potential is shown in Fig. (9.3.a) and has the form

$$V_{SW}(q) = \begin{cases} \infty & 0 < q < \sigma, \\ -\varepsilon & \sigma < q < R\sigma, \\ 0 & R\sigma < q. \end{cases} \tag{9.55}$$

The square-well potential has a hard core of radius, σ, and a square attractive region of depth ε and width $(R-1)\sigma$. The second virial coefficient can be computed analytically and has the form

$$B_2(T)_{SW} = \frac{2\pi\sigma^2}{3}[1 - (R^3 - 1)(e^{\beta\varepsilon} - 1)]. \tag{9.56}$$

Note that $B_2(T)_{SW}$ differs from $B_2(T)_{HC}$ by a temperature-dependent term (see Ex. 9.2). At low temperatures it is negative and at high temperatures it becomes positive. At low temperatures the attractive interaction energy due to the square well can compete with the thermal energy, k_BT, and causes a lowering of the pressure relative to the ideal gas value. At high temperature the hard core becomes dominant and the pressure increases relative to that of an ideal gas.

We can write $B_2(T)_{SW}$ in a reduced form if we let $B^*(T)_{SW} = B(T)_{SW}/b_0 (b_0 = 2\pi\sigma^3/3)$ and $T^* = k_BT/\varepsilon$. Then we find

$$B_2^*(T)_{SW} = [1 - (R^3 - 1)(e^{1/T^*} - 1)]. \tag{9.57}$$

Equation (9.57) will be useful when we compare the square-well results to experiment.

9.C.2.2. Lennard-Jones 6–12 Potential

A potential which gives a very good approximation to the interaction between atoms is the Lennard-Jones 6–12 potential,

$$V_{LJ}(q) = 4\varepsilon\left[\left(\frac{\sigma}{q}\right)^{12} - \left(\frac{\sigma}{q}\right)^{6}\right] \tag{9.58}$$

(cf. Fig. 9.3b). The Lennard-Jones potential has a gradually sloping hard core, which takes account of the fact that particles with high energy can, to some extent, penetrate the hard core. When $q = \sigma$ we obtain $V_{LJ}(\sigma) = 0$. Thus, $q = \sigma$ is the radius of the hard core when the potential changes from positive to negative. The minimum of the Lennard-Jones potential occurs when $q = (2)^{1/6}\sigma$ and the value of the potential at the minimum is $V_{LJ}((2)^{1/6}\sigma) = -\varepsilon$. Thus, ε is the depth of the Lennard-Jones potential.

The second virial coefficient for the Lennard-Jones potential can be found analytically in the form of a series expansion. If we integrate Eq. (9.54) by parts and introduce the notation $x = q/\sigma, T^* = k_B T/\varepsilon$, and $B_2^*(T)_{LJ} = B_2(T)_{LJ}/b_0$, we find

$$B_2^*(T)_{LJ} = \frac{4}{T^*}\int_0^\infty dx\, x^2\left[\frac{12}{x^{12}} - \frac{6}{x^6}\right]\exp\left\{-\frac{4}{T^*}\left[\left(\frac{1}{x}\right)^{12} - \left(\frac{1}{x}\right)^{6}\right]\right\}. \tag{9.59}$$

If we expand $\exp[(4/T^*)(1/x)^6]$ in an infinite series, each term of the series can be computed analytically and we obtain the following expansion for $B_2^*(T)_{LJ}$:

$$B_2^*(T)_{LJ} = \sum_{n=0}^{\infty} \alpha_n \left(\frac{1}{T^*}\right)^{((2n+1)/4)}, \tag{9.60}$$

where the coefficients α are defined in terms of gamma functions as

$$\alpha_n = -\frac{2}{4n!}\,\Gamma\left(\frac{2n-1}{4}\right). \tag{9.61}$$

Values of the coefficients α_n for $n = 0, \ldots, 40$ are given in Ref. 1, p. 1119. In Table 9.1 we give all values for $n = 0, \ldots, 12$. The expansion for $B_2^*(T)_{LJ}$ converges rapidly for $T^* > 4$, but more slowly for lower values of T^*. Values of $B_2^*(T)_{LJ}$ for T^* ranging from 0.3 to 400 are given in Table 9.2.

In Fig. 9.4 we plot $B_2^*(T)$ versus T^* for both the square-well potential and the Lennard-Jones potential. We also give experimental values of $B_2^*(T)$ for a variety of substances. The Lennard-Jones potential gives values of $B_2^*(T)$ in good agreement with experimental results. At high temperatures, $B_2^*(T)_{LJ}$ and the experimental points for He gas exhibit a maximum, while $B_2^*(T)_{SW}$ does not. The maximum occurs because at high temperatures, particles can penetrate

Table 9.1. Coefficients for the Expansion of the Second Virial Coefficient for Lennard-Jones 6–12 Potential[a]

n	α_n	n	α_n
0	+1.7330010	7	−0.0228901
1	−2.5636934	8	−0.0099286
2	−0.8665005	9	−0.0041329
3	−0.4272822	10	−0.0016547
4	−0.2166251	11	−0.0006387
5	−0.1068205	12	−0.0002381
6	−0.0505458		

[a]Based on Ref. 1.

Table 9.2 Values of the Reduced Second Virial Coefficient versus the Reduced Temperature for the Lennard-Jones Potential[a]

T^*	B_2^*	T^*	B_2^*
0.30	−27.8806	4.00	+0.1154
0.40	−13.7988	4.50	+0.1876
0.50	−8.7202	5.00	+0.2433
0.70	−4.7100	10.00	+0.4609
1.00	−2.5381	20.00	+0.5254
1.50	−1.2009	30.00	+0.5269
2.00	−0.6276	40.00	+0.5186
2.50	−0.3126	50.00	+0.5084
3.00	−0.1152	100.00	+0.4641
3.50	+0.0190	400.00	+0.3583

[a]Based on Ref. 1.

into the hard core and lower the amount of excluded volume. The square-well potential has a hard core with infinite slope and cannot account for this effect, while the Lennard-Jones potential, with a sloping hard core, can account for it. The data points for He deviate from the classical results at low temperature. These deviations are due to quantum effects and will be discussed in Sec. (S9.D). The second virial coefficients for all classical gases, when plotted in terms of reduced quantities, are identical. This is an example of the law of corresponding states.

In Table 9.3 we have given a list of values for the parameters ε/k_B and σ for various substances, assuming they interact via square-well or Lennard-Jones potentials. These parameters are obtained from experimental values for the

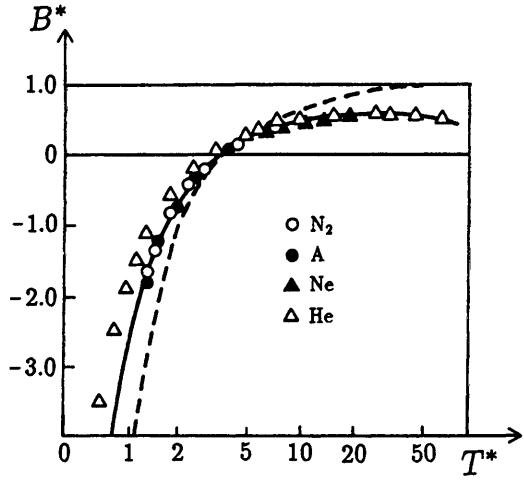


Fig. 9.4. The reduced second virial coefficient. The solid line is the calculated curve for the Lennard-Jones 6–12 potential. The dashed line is the calculated curve for the square-well potential (for $R = 1.6$). The points are experimental values for the gases listed. (Based on Ref. 1.)

second virial coefficient. Thus, measurements of the virial coefficients of real gases provide an extremely important way of determining the form of the effective interparticle potential for various molecules. The values of ε can be found if we take experimental values of $B_2(T)$ for two different temperatures,

Table 9.3 Values of the Parameters σ and ε for the Square-Well (S-W) and Lennard Jones (L-J) 6–12 Potentials Taken from Experimental Data on the Second Virial Coefficient[a]

	Potential	R	σ (Å)	ε/k_B (K)
Argon (A)	S-W	1.70	3.067	93.3
190 °C → 600 °C	L-J		3.504	117.7
Krypton (Kr)	S-W	1.68	3.278	136.5
160 °C → 600 °C	L-J		3.827	164.0
Nitrogen (N_2)	S-W	1.58	3.277	95.2
150 °C → 400 °C	L-J		3.745	95.2
Carbon dioxide (CO_2)	S-W	1.44	3.571	283.6
0 °C → 600 °C	L-J		4.328	198.2
Xenon (Xe)	S-W	1.64	3.593	198.5
0 °C → 700 °C	L-J		4.099	222.3
Methane (CH_4)	S-W	1.60	3.355	142.5
0 °C → 350 °C	L-J		3.783	148.9

[a]Based on Ref. 10.

say T_1 and T_2, equate the two ratios

$$\left(\frac{B_2(T_2)}{B_1(T_1)}\right)_{\text{exper}} = \left(\frac{B_2^*(\varepsilon, T_2)_{\text{theor}}}{B_2^*(\varepsilon, T_1)_{\text{theor}}}\right), \tag{9.62}$$

and solve for ε. In this ratio, all dependence on σ is eliminated. Once we find ε, we can find σ if we note that

$$B_2(T)_{\text{exper}} = \frac{2\pi\sigma^3}{3} B_2^*(\varepsilon, T)_{\text{theor}}. \tag{9.63}$$

The only unknown in Eq. (9.63) is σ.

The Lennard-Jones 6–12 potential is perhaps the most widely used interparticle potential, but there are many other forms of potential that may be used to compute the virial coefficients, and some of them give better agreement with experimental results over a wider range of temperature than does the Lennard-Jones potential.

Computation of the third virial coefficient is more challenging but still can be done for some simple potentials. However, new effects can enter, such as three body forces which are not included in the virial expansion given here. Some of these effects are described in Section S9.C. Also, in Section S9.C the third virial coefficients for hard spheres and for particles coupled by a square-well potential and by the Lennard-Jones potential are computed.

■ **EXERCISE 9.2.** Compute the second virial coefficient, $B_2(T)$, for a hard sphere gas of atoms of radius, R, confined to a box of volume, V. Write the equation of state for this gas as a virial expansion to first order in the density.

Answer: The second virial coefficient, $B_2(T)$, is defined as

$$B_2(T) = -\frac{1}{V}\frac{1}{2!}\int d\mathbf{q}_1 \int d\mathbf{q}_2 f(\mathbf{q}_{21}), \tag{1}$$

where $\mathbf{q}_{21} = \mathbf{q}_2 - \mathbf{q}_1$ and $f(\mathbf{q}_{21}) = (e^{-\beta \mathrm{V}(\mathbf{q}_{21})} - 1)$. The interaction potential, $\mathrm{V}(\mathbf{q}_{21})$, for hard spheres is given by $\mathrm{V}(\mathbf{q}_{21}) = \infty$ for $q_{21} < R$ and $\mathrm{V}(\mathbf{q}_{21}) = 0$ for $q_{21} > R$. We can make a change of variables and let $\mathbf{q} = \mathbf{q}_2 - \mathbf{q}_1$ and $\mathbf{Q} = \frac{1}{2}(\mathbf{q}_1 + \mathbf{q}_2)$. Then

$$\begin{aligned} B_2(T) &= -\frac{1}{V}\frac{1}{2}\int d\mathbf{Q} \int d\mathbf{q} f(\mathbf{q}) = -\frac{1}{2}\int d\mathbf{q}(e^{-\beta \mathrm{V}(\mathbf{q})} - 1) \\ &= +2\pi \int_0^R dq\, q^2 = \frac{2\pi R^3}{3} \equiv b_0. \end{aligned} \tag{2}$$

The equation of state, to first order in the density, is

$$\frac{PV}{Nk_BT} = 1 + b_0\frac{N}{V} + \cdots.$$

9.C.3. Higher-Order Viral Coefficients [2]

As we increase the density or decrease the temperature of a gas, at some point it will undergo a transition to a liquid or a solid phase. Past this point, and well before we reach it, the virial expansion ceases to give good agreement with the observed equation of state. It is possible to obtain some idea of the limits of the virial expansion for a hard-sphere gas. Although hard-sphere gases do not exist in nature, they can be constructed on a computer by means of molecular dynamics calculations. In these calculations, the motion of a finite number of particles is followed by solving the equations of motion of the system. The phase space coordinates of all the particles can be obtained at any given time, and the phase functions of interest can be computed. The thermodynamic properties are obtained by time averaging of the phase functions of interest.

The second through sixth virial coefficients for systems of hard spheres have been computed [11] and the results are $B_2(T) = b_0$, $B_3(T) = \frac{5}{8}b_0^2$, $B_4(T) = 0.29b_0^3$, $B_5(T) = 0.11b_0^4$, and $B_6(T) = 0.04b_0^5$, where $b_0 = 2\pi\sigma^3/3$ and σ is the hard-core radius. The virial expansion for the equation of state is plotted in Fig. 9.5 and compared to "experimental" results from molecular dynamics calculations. In the figure, a curve is given for the virial expansion up

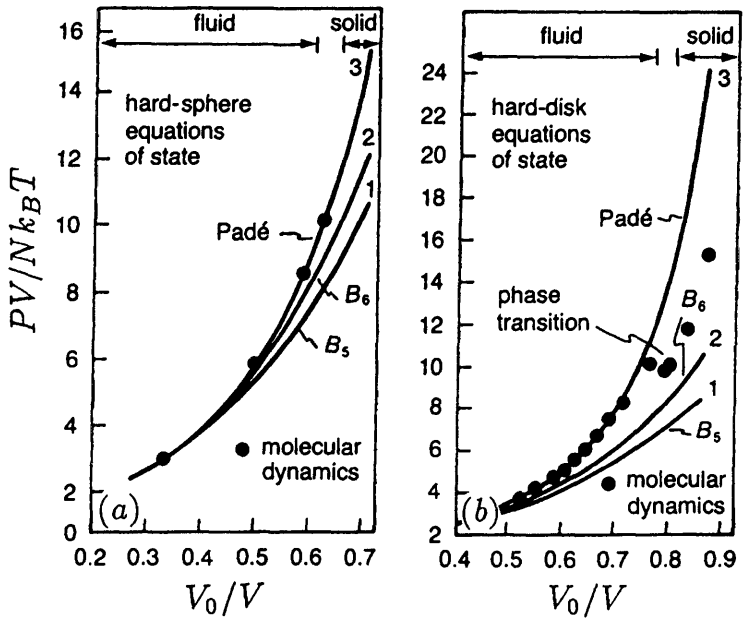


Fig. 9.5. Equation of state for hard-sphere and hard-disk fluids. (a) Hard-sphere fluid: Line 1 includes all virial coefficients up to B_5; line 3 gives the prediction of the Padé approximate; molecular dynamics results are indicated by the dots. (b) Hard-disk fluid: All quantities have meaning similar to part (a). (Based on Ref. 11.)

to and including $B_5(T)$ and the virial expansion up to and including $B_6(T)$. The agreement gets better as we add more terms, but it is not extremely good at higher densities. Better agreement occurs if we construct the so-called Padé approximate to the virial expansion. The Padé approximate is obtained as follows. If we are given a finite expansion for some function $F(x)$,

$$F(x) = a_0 + a_1 x + \cdots + a_n x^n, \tag{9.64}$$

we can construct the Padé approximate to $F(x)$ by writing it in the form

$$F(x) = \frac{b_0 + b_1 x + b_2 x^2 + \cdots + b_m x^m}{c_0 + c_1 x + \cdots + c_l x^l}. \tag{9.65}$$

If we expand Eq. (9.65) in a power series, we can find the coefficients b_i and c_j from the coefficients a_n. If we know a finite number of coefficients, a_n, then we can find a finite number of coefficients b_i and c_j. By doing this, we replace a finite series expansion by an infinite series expansion.

Ree and Hoover [11] have constructed the Padé approximate to the equation of state for a hard-sphere gas. They obtain

$$\frac{PV}{Nk_BT} = 1 + b_0 \frac{N}{V} \frac{\left(1 + 0.063507 b_0 \frac{N}{V} + 0.017329 b_0^2 \left(\frac{N}{V}\right)^2\right)}{\left(1 - 0.561493 b_0 \frac{N}{V} + 0.081313 b_0^2 \left(\frac{N}{V}\right)^2\right)}. \tag{9.66}$$

The Padé approximate to the equation of state is plotted in Fig. 9.5. It gives much better results than the simple virial expansion. It is worth noting that the hard-sphere gas exhibits a phase transition from a fluid state to a crystalline state as the density increases. While we will not give the details here, Fig. 9.5 shows the results of an analogous calculation for a system of hard disks. The drop in the pressure at about $V_0/V = 0.75$ indicates a transition to a crystalline state. The Padé approximate gives poor agreement for the crystal phase.

Expressions for higher virial coefficients for square-well potentials have been obtained, but, as we can see from the results for hard spheres, a simple virial expansion does not give very good agreement for dense systems.

▶ SPECIAL TOPICS

▶ S9.A. The Pressure and Compressibility Equations

It is possible to express other thermodynamic quantities in terms of the radial distribution function. Below we derive expressions for the pressure and the compressibility in terms of the radial distribution function.

▶ S9.A.1. The Pressure Equation

We can obtain an expression for the pressure by using a simple trick. Consider a box of volume $V = L^3$ (L is the length of a side) which contains N particles. We will assume the box is large enough that we can neglect the effects of the walls (in the thermodynamic limit this is rigorously true). From Eqs. (2.98) and (7.44), we can write

$$\begin{aligned} P &= k_B T\left(\frac{\partial}{\partial V}\ln[Z_N(V,T)]\right)_{T,N} = k_B T\left(\frac{\partial}{\partial V}\ln[Q_N(V,T)]\right)_{T,N} \\ &= \frac{k_B TL}{3V}\left(\frac{\partial}{\partial L}\ln[Q_N(V,T)]\right)_{T,N}. \end{aligned} \tag{9.67}$$

The configuration integral can be written

$$Q_N(V,T) = \int_0^L dq_1 \cdots \int_0^L dq_{3N} e^{-\beta \mathrm{V}(\mathbf{q}^N)} = V^N \int_0^1 \cdots \int_0^1 dx_1 \cdots dx_{3N} e^{-\beta \mathrm{V}(L\mathbf{x}^N)}, \tag{9.68}$$

where we have made the change of variables, $q_i = Lx_i$. The derivative of $Q_N(V,T)$ with respect to L gives

$$\begin{aligned} \left(\frac{\partial Q_N(V,T)}{\partial L}\right)_{T,N} &= \frac{3N}{L} Q_N(V,T) \\ &\quad - \beta V^N \int_0^1 \cdots \int_0^1 dx_1 \cdots dx_{3N} \left(\frac{\partial \mathrm{V}(L\mathbf{x}^N)}{\partial L}\right)_{T,N} e^{-\beta \mathrm{V}(L\mathbf{x}^N)}. \end{aligned} \tag{9.69}$$

If we now note

$$\frac{\partial \mathrm{V}(L\mathbf{x}^N)}{\partial L} = \frac{1}{2}\sum_{(ij)} \frac{\partial \mathbf{q}_{ij}}{\partial L} \cdot \frac{\partial \mathrm{V}(\mathbf{q}_{ij})}{\partial \mathbf{q}_{ij}} = \frac{1}{2L}\sum_{(ij)} \mathbf{q}_{ij} \cdot \frac{\partial \mathrm{V}(\mathbf{q}_{ij})}{\partial \mathbf{q}_{ij}}, \tag{9.70}$$

we can combine Eqs. (9.67), (9.69), and (9.70) to give

$$\frac{P}{k_B T} = \frac{N}{V} - \frac{\beta}{6V}\int d\mathbf{q}_1 \int d\mathbf{q}_2\, \mathbf{q}_{12} \cdot \frac{\partial \mathrm{V}(\mathbf{q}_{12})}{\partial \mathbf{q}_{12}} n_2^N(\mathbf{q}_1, \mathbf{q}_2; V, T). \tag{9.71}$$

For spherically symmetric potentials, Eq. (9.71) takes the form

$$\frac{P}{k_B T} = \frac{N}{V} - \frac{4\pi n^2 \beta}{6}\int_0^\infty q^3 dq \frac{\partial \mathrm{V}(q)}{\partial q} g_2^N(q; V, T). \tag{9.72}$$

Thus we find that the pressure depends only on the radial distribution function. Eq. (9.72) is called the *pressure equation.*

▶ S9.A.2. The Compressibility Equation

As a final example, let us obtain an expression for the isothermal compressibility, $\kappa_{T,N}$. For this, we need the variance of the particle number, as was shown in Eq. (7.117), and therefore we must now describe the system in the grand canonical ensemble. The average values of one- and two-body phase functions can be written

$$\langle O_1 \rangle = \int d\mathbf{q}_1 O_1(\mathbf{q}_1) n_1^{\mu}(\mathbf{q}_1; V, T) \tag{9.73}$$

and

$$\langle O_2 \rangle = \frac{1}{2} \int d\mathbf{q}_1 \int d\mathbf{q}_2 O_2(\mathbf{q}_1, \mathbf{q}_2) n_2^{\mu}(\mathbf{q}_1, \mathbf{q}_2; V, T) \tag{9.74}$$

where $n_1^{\mu}(\mathbf{q}_1; V, T)$ and $n_2^{\mu}(\mathbf{q}_1, \mathbf{q}_2; V, T)$ are the one-body and two-body reduced distribution functions, respectively, in the grand canonical ensemble. They are defined

$$n_l^{\mu}(\mathbf{q}_1, \ldots, \mathbf{q}_l; V, T) = \frac{1}{Z^{\mu}(V, T)} \sum_{N=l}^{\infty} \frac{1}{(N-l)!\, h^{3N}} \int d\mathbf{p}^N \int d\mathbf{q}_{l+1} \ldots d\mathbf{q}_N e^{-\beta(H^N - \mu' N)}. \tag{9.75}$$

The one-body and two-body reduced distribution functions, in the grand canonical ensemble, have the property that

$$\langle N \rangle = \int d\mathbf{q}_1 n_1^{\mu}(\mathbf{q}_1; V, T) \tag{9.76}$$

and

$$\langle N^2 \rangle - \langle N \rangle = \int d\mathbf{q}_1 \int d\mathbf{q}_2 n_2^{\mu}(\mathbf{q}_1, \mathbf{q}_2; V, T). \tag{9.77}$$

If we now combine Eqs. (7.117), (9.76), and (9.77), we can write

$$\frac{\langle N \rangle k_B T \kappa_T}{V} - 1 = \frac{1}{\langle N \rangle} \int d\mathbf{q}_1 \int d\mathbf{q}_2 [n_2^{\mu}(\mathbf{q}_1, \mathbf{q}_2; V, T) - n_1^{\mu}(\mathbf{q}_1; V, T) n_1^{\mu}(\mathbf{q}_2; V, T)]. \tag{9.78}$$

For a system whose particles interact via a spherically symmetric potential, it is useful again to let $n_2^{\mu}(\mathbf{q}_{12}; V, T) = (N/V)^2 g_2^{\mu}(q_{ij}; V, T)$. Then Eq. (9.78) takes the form

$$nk_BT\kappa_T = k_BT\left(\frac{\partial n}{\partial P}\right)_T = \left[1 + \langle n\rangle \int_0^{\infty} dq\, 4\pi q^2 [g_2^{\mu}(q; V, T) - 1]\right], \tag{9.79}$$

where $\langle n\rangle = \langle N\rangle/V$. Equation (9.79) is called the *compressibility equation.*

The compressibility equation can be written in terms of the *structure function,* $h(q) \equiv g_2^{\mu}(q) - 1$, and takes the form

$$k_BT\left(\frac{\partial n}{\partial P}\right)_T = 1 + \langle n\rangle \int h(q)d\mathbf{q}. \tag{9.80}$$

The structure function contains all possible information about correlations between particles a distance q apart. Near a phase transition, where $(\partial n/\partial P)_T \to \infty$, it must become very long-ranged so the integral will diverge.

▶ S9.B. Ornstein–Zernicke Equation

Ornstein and Zernicke [12] introduced the idea of decomposing the structure function into a short-ranged part, $C(q)$, and a long-ranged part. They wrote the structure function in the form

$$h(q_{12}) = C(q_{12}) + \langle n\rangle \int d\mathbf{q}_3\, C(q_{13})h(q_{32}). \tag{9.81}$$

Equation (9.81) is called the *Ornstein–Zernicke equation.* The first term, $C(q_{12})$ (called the *direct correlation function*), contains the effects of short-ranged correlations, and the second contains the effect of long-ranged correlations and allows for interactions between the particles 1 and 2 which first propagate through the medium. If we introduce the Fourier transform

$$\tilde{h}(\mathbf{k}) = \int d\mathbf{q}_{12} e^{i\mathbf{k}\cdot\mathbf{q}_{12}} h(q_{12}) \tag{9.82}$$

and a similar one for $c(q_{12})$, we can write Eq. (9.81) in the form

$$\tilde{h}(\mathbf{k}) = \tilde{C}(\mathbf{k}) + \langle n\rangle \tilde{C}(\mathbf{k})\tilde{h}(\mathbf{k}), \tag{9.83}$$

where $\tilde{C}(\mathbf{k})$ is the Fourier transform of the direct correlation function, $C(q_{12})$. In terms of the quantity $\tilde{h}(\mathbf{k})$, the compressibility equation takes the form

$$k_BT\left(\frac{\partial n}{\partial P}\right)_T = 1 + \langle n\rangle \tilde{h}(\mathbf{k} = 0). \tag{9.84}$$

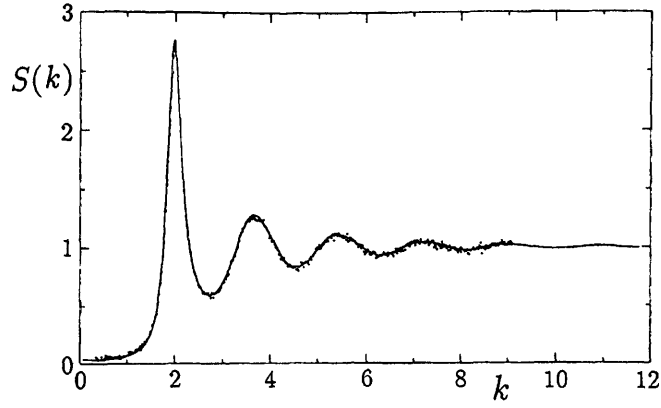


Fig. 9.6. The structure factor, $S(k) = S_{nn}(k)$, versus k (in Å^{-1}) for liquid ^{36}Ar obtained from neutron scattering experiments (dots), and from molecular dynamics (solid line) using the Lennard-Jones potential with parameters fitted to Argon. Reprinted, by permission, from J. L. Yarnell, et. al., *Phys. Rev.* **A7**, 2130 (1973).

If we take the reciprocal of Eq. (9.84), we find

$$\frac{1}{k_B T}\left(\frac{\partial P}{\partial n}\right)_T = \frac{1}{1 + \langle n\rangle \tilde{h}(\mathbf{k}=0)} = 1 - \langle n\, \tilde{C}(\mathbf{k}=0) = 1 - \langle n\rangle \int d\mathbf{q}\, C(q). \tag{9.85}$$

Since $(\partial P/\partial n)_T \to 0$ near the critical point, $C(q)$ must remain short-ranged.

The direct correlation function has been obtained from molecular dynamics simulation for a classical fluid of 864 atoms which interact via a Lennard-Jones potential, $V(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]$. In Fig. 9.6 we first make a comparison between the structure factor, $S_{nn}(k)$, obtained from neutron scattering experiments on argon and that obtained from molecular dynamics using the Lennard-Jones potential. The agreement is extremely good. The direct correlation function obtained from the molecular dynamics using the Lennard-Jones potential is shown in Fig. 9.7. The direct correlation function is negative in the region of the hard core and then rises sharply to a positive value outside the hard core.

The Ornstein–Zernicke equation, in general, must be solved numerically. However, Percus and Yevick [14] introduced an approximation which gives quite good agreement with the experimentally measured radial distribution function; and for the case of a hard sphere gas can be solved analytically. Percus and Yevick chose to write the direct correlation function in the form

$$C_{PY}(q) = g_{PY}(q)(1 - e^{\beta V(q)}). \tag{9.86}$$

When this is substituted into the Ornstein–Zernicke equation, one obtains the

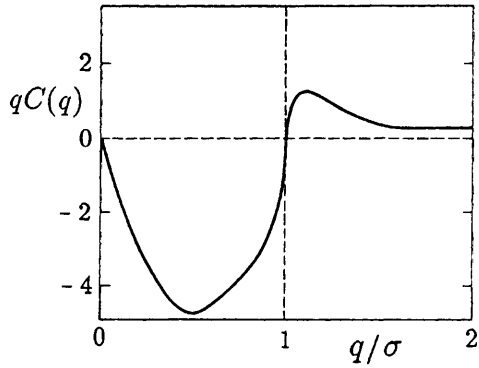


Fig. 9.7. The direct correlation function, $qC(q)$, versus q/σ (σ is the hard-core radius) for a Lennard-Jones fluid, obtained from a molecular dynamics simulation. Reprinted, by permission, from L. Verlet, *Phys. Rev.* **165**, 201 (1968)

Percus–Yevick equation

$$g_{PY}(q_{12}) = e^{\beta V(q_{12})} + ne^{\beta V(q_{12})} \int d\mathbf{q}_3 g_{PY}(q_{13})(1 - e^{\beta V(q_{13})})h_{PY}(q_{23}), \quad (9.87)$$

where $h_{PY}(q) = g_{PY}(q) - 1$.

Watts [15] has used the Percus–Yevick equation to compute the equation of state for a fluid whose particles interact via the Lennard-Jones potential. In Fig. 9.8 we show his results for a number of isotherms. The Percus–Yevick equation does predict the phase transition from the liquid to vapor phase. There is a large region where the Percus–Yevick equation has no solution. This region separates different branches of each isotherm of the equation of state and corresponds to the coexistence region.

Wertheim [16] and Thiele [17] independently showed that the Percus–Yevick equation for a hard-sphere fluid can be solved analytically. Since the radial distribution function obtained from the Percus–Yevick equation is approximate, we do not expect the pressure and compressibility equations to give the same results for the equation of state. Thiele obtained the following equation of state from the pressure equation:

$$P = \frac{N}{V} k_B T \frac{(1 + 2x + 3x^2)}{(1 - x)^2}, \quad (9.88)$$

where $x = \frac{1}{4}n$. From the compressibility equation, he obtained

$$P = \frac{\langle N \rangle}{V} k_B T \frac{(1 + x + x^2)}{(1 - x)^3}. \quad (9.89)$$

In both equations the pressure becomes infinite at $x = 1$, which is a density

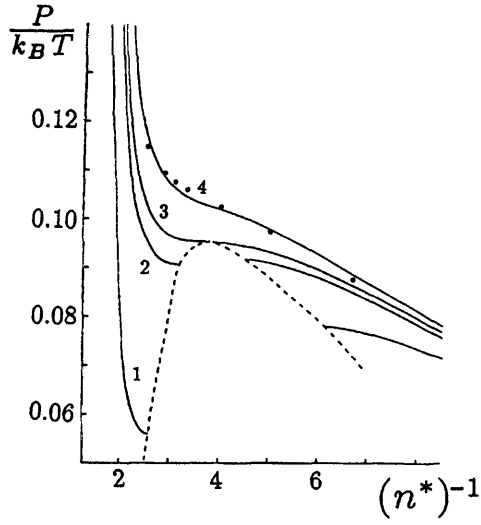


Fig. 9.8. Isotherms of the equation of state for a Lennard–Jones fluid obtained by solving the Percus–Yevick equation. Note that $n^* = n\sigma^3$ and $T^* = k_B T/\varepsilon$, where (1) $T^* = 1.2$, (2) $T^* = 1.263$, (3) $T^* = 1.275$, and (4) $T^* = 1.3$. The dots are experimental points for argon at $T^* = 1.3$. For the region enclosed by the dashed line, the Percus–Yevick equation has no solutions (based on Ref. [10]).

greater than the close-packed density, $x_{cp} = 2\pi\sqrt{2}/3$. Thus, the equations give unphysical results for very dense systems. However, at lower densities they give good agreement with the results of molecular dynamics experiments [18].

▶ S9.C. Third Virial Coefficient [1, 3]

The third virial coefficient contains the contribution from three-body clusters in the gas and may be written in the form

$$B_3(T) = -\frac{1}{3V}\int\int\int d\mathbf{q}_1\, d\mathbf{q}_2\, d\mathbf{q}_3\, U_3(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3) + \frac{1}{V^2}\left(\int\int d\mathbf{q}_1\, d\mathbf{q}_2\, U_2(\mathbf{q}_1, \mathbf{q}_2)\right)^2. \tag{9.90}$$

Equation (9.90) is completely general and does not depend on the form of the interparticle potential. In deriving microscopic expressions for the cluster functions, we have assumed that the N-particle potential was additive—that is, that it could be written as the sum of strictly two-body interactions:

$$\mathbf{V}^N(\mathbf{q}^N) = \sum_{(ij)}^{(1/2)N(N-1)} \mathbf{V}_{ij}(\mathbf{q}_{ij}). \tag{9.91}$$

In fact, in a real gas this is not sufficient. For example, if three bodies in a gas interact simultaneously, they become polarized and an additional three-body polarization interaction occurs. This polarization interaction has a significant effect on the third virial coefficient at low temperatures and must be included [19]. Let us write the total three-body interaction in the form

$$V^3(\mathbf{q}^3) = V(\mathbf{q}_{12}) + V(\mathbf{q}_{13}) + V(\mathbf{q}_{23}) + \Delta V_{123}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3), \tag{9.92}$$

where Δv_{123} is the three-body polarization interaction. The polarization interaction has been computed by several methods [20,21] and has the form

$$\Delta v_{123} = \frac{\alpha(1 + 3\cos(\gamma_1)\cos(\gamma_2)\cos(\gamma_3))}{q_{12}q_{13}q_{23}}, \tag{9.93}$$

where q_{ij} are the lengths of the sides of the atomic triangle, γ_i are the internal angles, and α is a parameter that depends on the polarizability and properties of the two-body interaction. Thus, the polarization interaction is repulsive.

If we include the correction due to polarization effects, we can write the third virial coefficient as

$$B_3(T) = B_3(T)^{\text{add}} + \Delta B_3(T), \tag{9.94}$$

where

$$B_3(T)^{\text{add}} = -\frac{1}{3V}\int\int\int d\mathbf{q}_1\, d\mathbf{q}_2\, d\mathbf{q}_3 f(\mathbf{q}_{12})f(\mathbf{q}_{13})f(\mathbf{q}_{23}) \tag{9.95}$$

and

$$\Delta B_3(T) = -\frac{1}{3V}\int\int\int d\mathbf{q}_1\, d\mathbf{q}_2\, d\mathbf{q}_3 (e^{-\beta\Delta V_{123}} - 1)e^{-\beta(V_{12}+V_{23}+V_{13})}. \tag{9.96}$$

The third virial coefficients for additive potentials and the corrections due to nonadditive polarization effects have been obtained for a number of potentials. We shall discuss some of these results below.

▶ S9.C.1. Square-Well Potential

An expression for the additive third virial coefficient for the square-well potential was first obtained analytically by Kihara [1, 21]. For $R \leqslant 2$, it has the form

$$\begin{aligned} B_3(T)^{\text{add}}_{SW} = \tfrac{1}{8}b_0^2[5 &- (R^6 - 18R^4 + 32R^3 - 15)x \\ &- (2R^6 - 36R^4 + 32R^3 + 18R^2 - 16)x^2 \\ &- (6R^6 - 18R^4 + 18R^2 - 6)x^3], \end{aligned} \tag{9.97}$$

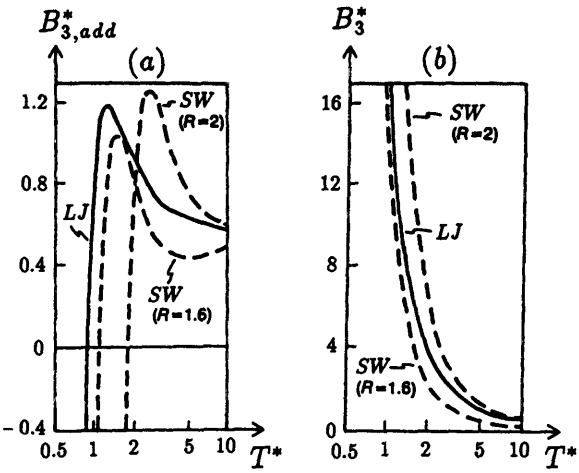


Fig. 9.9. The third virial coefficient. (a) The additive contribution as calculated for the Lennard-Jones 6–12 potential and the square-well potential for $R = 1.6$ and $R = 2$. (b) The polarization contribution for the potentials in (a). (Based on Ref. 10.)

while for $R \geqslant 2$, it has the form

$$B_3(T)^{\text{add}}_{SW} = \tfrac{1}{8}b_0^2[5 - 17x - (-32R^3 + 18R^2 + 48)x^2 - (5R^6 - 32R^3 + 18R^2 + 26)x^3] \tag{9.98}$$

where $x = [e^{\beta\varepsilon} - 1]$. In computing the third virial coefficient, the values of R, ε, and σ obtained from the second virial coefficient are generally used. Sherwood and Prausnitz have plotted values of $B_3(T)^{\text{add}}_{SW}$ and the correction $\Delta B_3(T)_{\text{SW}}$ for a variety of values of R. Their results are shown in Fig. 9.9. At low temperature, the contribution from polarization effects can have a large effect. The corrected values give better agreement with experimental results than does the additive part alone. In Fig. 9.10 we compare the additive and corrected results with experimental values of $B_3(T)$ for argon.

▶ S9.C.2. Lennard-Jones 6–12 Potential

The additive third virial coefficient for the Lennard-Jones potential can be obtained analytically in the form of a series expansion in a manner similar to that used for the second virial coefficient. However, it is much more complicated. The series expansion takes the form

$$B_3(T)_{\text{LJ}} = b_0^2 \sum_{n=0}^{\infty} \beta_n \left(\frac{1}{T^*}\right)^{-(n+1)/2} . \tag{9.99}$$

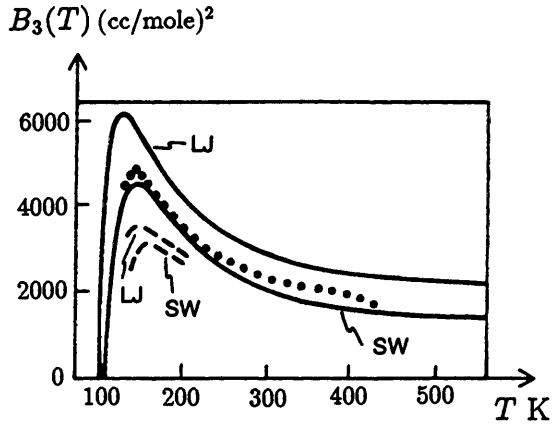


Fig. 9.10. Comparison of observed and calculated third virial coefficient for argon. The solid lines include the polarization effects. The dashed lines give only the additive contribution. (Based on Ref. 10.)

A table of values for the coefficients β_n may be found in Ref. 1; we will not give them here. Curves for $B_3(T)_{LJ}^{\text{add}}$ and $\Delta B_3(T)_{\text{LJ}}$ are shown in Fig. 9.9. They are very similar to the curves for the square-well potential. The Lennard-Jones curves for argon are compared with experimental results in Fig. 9.10. The Lennard-Jones potential does not give extremely good agreement with the experimental values for argon, probably because the potential well has insufficient curvature [10].

■ **EXERCISE 9.3.** Compute the third virial coefficient, $B_3(T)$, for a hard sphere gas of atoms of radius, R, confined to a box of volume, V. Use a geometrical method to find $B_3(T)$. Write the equation of state for this gas as a virial expansion to second order in the density.

Answer: The third virial coefficient is written

$$B_3(T) = -\frac{1}{3V}\int\int\int d\mathbf{q}_1\, d\mathbf{q}_2\, d\mathbf{q}_3 f(\mathbf{q}_{21}) f(\mathbf{q}_{31}) f(\mathbf{q}_{32}) \tag{1}$$

First we change from coordinates $(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3)$ to coordinates $(\mathbf{q}_1, \mathbf{q}_{21}, \mathbf{q}_{31})$, where $\mathbf{q}_{21} = \mathbf{q}_2 - \mathbf{q}_1$ and $\mathbf{q}_{31} = \mathbf{q}_3 - \mathbf{q}_1$. The Jacobian of this transformations is one. We can integrate over $\mathbf{q}_1$ to obtain

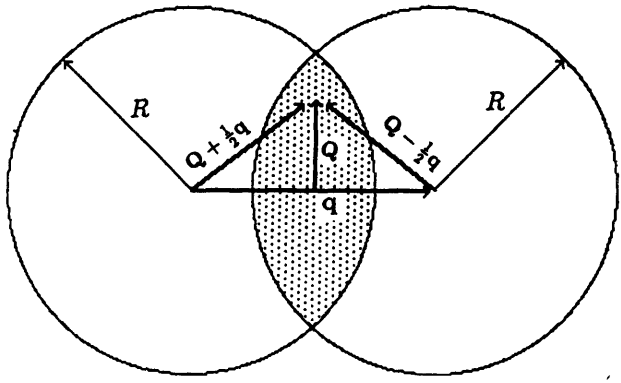
$$B_3(T) = -\frac{1}{3}\int\int d\mathbf{q}_{21} d\mathbf{q}_{31} f(\mathbf{q}_{21}) f(\mathbf{q}_{31}) f(\mathbf{q}_{31} - \mathbf{q}_{21}). \tag{2}$$

Next make the change of variables, $\mathbf{q} = \mathbf{q}_{31} - \mathbf{q}_{21}$ and $\mathbf{Q} = \frac{1}{2}(\mathbf{q}_{31} + \mathbf{q}_{21})$. The Jacobian of this transformation is one. The third virial coefficient then

takes the form

$$B_3(T) = -\frac{1}{3}\int\int d\mathbf{q}d\mathbf{Q} f\left(\mathbf{Q}-\frac{1}{2}\mathbf{q}\right) f\left(\mathbf{Q}+\frac{1}{2}\mathbf{q}\right) f(\mathbf{q}). \tag{3}$$

The integration over $\mathbf{Q}$ can be reduced to geometry. Consider the accompanying figure.



The circle on the left represents the sphere $Q \le R$ and $|\mathbf{q}+\frac{1}{2}\mathbf{Q}| \le R$. The sphere on the right represents the sphere $|\mathbf{q}-\frac{1}{2}\mathbf{Q}| \le R$. The integration over $\mathbf{Q}$ in Eq. (3) gives the volume of the shaded overlap region. This volume is twice the volume of a spherical cap (for sphere of radius R) of height $h = R - \frac{1}{2}q$. The volume of such a spherical cap is $\frac{1}{3}\pi h^2(3R-h)$. Thus, the integration over $\mathbf{Q}$ gives

$$B_3(T) = \frac{4\pi R^3}{9}\int d\mathbf{q}\left(1-\frac{3q}{4R}+\frac{q^3}{16R^3}\right), \tag{4}$$

(there are two spherical caps). Integration over $\mathbf{q}$ gives

$$B_3(T) = \frac{5\pi^2 R^6}{18} = \frac{5}{8}b_0^2. \tag{5}$$

The equation of state, to second order in the density, is

$$\frac{PV}{Nk_BT} = 1 + b_0\frac{N}{V} + \frac{5b_0^2}{8}\left(\frac{N}{V}\right)^2 + \cdots. \tag{6}$$

▶ S9.D. Virial Coefficients for Quantum Gases [1, 22]

For fluids composed of molecules of small mass, such as He, the classical expressions for the virial coefficients do not give very good results at lower temperatures (cf. Fig. 9.4). For such particles, the thermal wavelength

$\lambda_T = (2\pi\hbar^2/mk_BT)^{1/2}$ will be relatively large and quantum corrections must be taken into account. There are two kinds of quantum effects which must be considered: *diffraction effects*, which are important when the thermal wavelength is the size of the radius of the molecules, and the *effects of statistics*, which are important when the thermal wavelength is the size of the average distance between particles.

To find general expressions for the virial coefficients, we proceed along lines similar to those for a classical fluid except that, for the quantum case, momentum variables no longer commute with position variables and cannot be eliminated immediately. The grand partition function for a quantum system can be written in the form

$$Z_\mu(T,V) = \sum_{N=0}^{\infty} \frac{e^{\beta\mu' N}}{N!\lambda_T^{3N}} \mathrm{Tr}_N[\hat{W}_N(\beta)], \tag{9.100}$$

where λ_T is the thermal wavelength,

$$\hat{W}_N(\beta) = \lambda_T^{3N} N!\, e^{-\beta\hat{H}^N}, \tag{9.101}$$

and $\hat{H}^N$ is the N-body Hamiltonian; $\hat{W}_N(\beta)$ depends on the momentum and position operators for the N particles. As before, we can expand the grand partition function in a cumulant expansion,

$$Z_\mu(T,V) = \exp\left[\sum_{l=1}^{\infty} \frac{e^{\beta\mu' l}}{l!\lambda_T^{3l}} \mathrm{Tr}_l\, \hat{U}_l(\beta)\right], \tag{9.102}$$

where $\hat{U}_l(\beta)$ depends on the momentum and position operators for l particles. If we equate coefficients of equal powers of the parameter $e^{\beta\mu'}/\lambda_T^3$ in Eqs. (9.100) and (9.102), we obtain

$$\mathrm{Tr}_1[\hat{U}_1(\beta)] = \mathrm{Tr}_1[\hat{W}_1(\beta)], \tag{9.103}$$

$$\mathrm{Tr}_2[\hat{U}_2(\beta)] = \mathrm{Tr}_2[\hat{W}_2(\beta)] - (\mathrm{Tr}_1[\hat{W}_1(\beta)])^2, \tag{9.104}$$

$$\mathrm{Tr}_3[\hat{U}_3(\beta)] = \mathrm{Tr}_3[\hat{W}_3(\beta)] - 3(\mathrm{Tr}_1[\hat{W}_1(\beta)])(\mathrm{Tr}_2[\hat{W}_2(\beta)]) + 2(\mathrm{Tr}_1[\hat{W}_1(\beta)])^3, \tag{9.105}$$

and so on. From Eq. (9.102) we can write the grand potential in the form

$$\Omega(V,T,\mu) = -k_BT \sum_{l=1}^{\infty} \frac{e^{\beta\mu' l}}{l!\lambda_T^{3l}} \mathrm{Tr}_l\,[\hat{U}_l(\beta)], \tag{9.106}$$

and the average particle density takes the form

$$\langle n\rangle = -\frac{1}{V}\left(\frac{\partial\Omega}{\partial\mu'}\right)_{V,T} = \sum_{l=1}^{\infty} \frac{le^{\beta\mu' l}}{\lambda_T^{3l}} b_l(V,T), \tag{9.107}$$

where

$$b_l(V,T) \equiv \frac{1}{l!V}\,\mathrm{Tr}_l\,[\hat{U}_l(\beta)]. \tag{9.108}$$

The virial expansion for the equation of state may be written

$$\frac{P}{\langle n\rangle k_B T} = \sum_{l=1}^{\infty} \mathscr{B}_l(T)\langle n\rangle^{l-1}, \tag{9.109}$$

where the virial coefficients, $\mathscr{B}_l(T)$, are related to the quantities $b_l(V,T)$ through Eqs. (9.45)–(9.48). Thus, $\mathscr{B}_1 = b_1, \mathscr{B}_2 = -b_2, \mathscr{B}_3 = 4b_2^2 - 2b_3$, and so on. In Exercises 9.4 and 9.5 we give some examples of quantum corrections to the classical virial coefficients.

■ **EXERCISE 9.4.** Compute the second virial coefficient, $B_2^0(T)$, for an ideal Fermi–Dirac gas of spin, $S = \frac{1}{2}$, particles.

Answer: The second virial coefficient may be written

$$B_2^0(T) = -\frac{1}{2!V}\mathrm{Tr}_2[\hat{U}_2^0(\beta)] = -\frac{1}{2!V}\mathrm{Tr}_2[\hat{W}_2^0(\beta)] + \frac{1}{2!V}(\mathrm{Tr}_1[\hat{W}_1^0(\beta)])^2, \tag{1}$$

where $\hat{W}_2^0(\beta) = 2\lambda_T^6 e^{-\beta(\hat{T}_1+\hat{T}_2)}$ and $\hat{W}_1^0(\beta) = \lambda_T^3 e^{-\beta\hat{T}_1}, \hat{T}_i \equiv p_i^2/2m$ is the kinetic energy operator for the ith particle. From Appendix B, Eq. (B.30) we can write

$$\mathrm{Tr}_1[e^{-\beta\hat{T}_1}] = \sum_{k_1}\sum_{s_1=\pm1}\langle \mathbf{k}_1, s_1|e^{-\beta\hat{T}_1}|\mathbf{k}_1, s_1\rangle = 2\sum_{k_1}\exp\left(-\frac{\beta\hbar^2 k_1^2}{2m}\right) = 2\frac{V}{\lambda_T^3} \tag{2}$$

and

$$\begin{aligned}
\mathrm{Tr}_2[e^{-\beta(\hat{T}_1+\hat{T}_2)}] &= \frac{1}{2}\sum_{\mathbf{k}_1}\sum_{s_1=\pm1}\sum_{\mathbf{k}_2}\sum_{s_2=\pm1} \\
&\quad [\langle \mathbf{k}_1, s_1; \mathbf{k}_2, s_2|e^{-\beta(\hat{T}_1+\hat{T}_2)}|\mathbf{k}_1, s_1; \mathbf{k}_2, s_2\rangle \\
&\quad - \langle \mathbf{k}_1, s_1; \mathbf{k}_2, s_2|e^{-\beta(\hat{T}_1+\hat{T}_2)}|\mathbf{k}_2, s_2; \mathbf{k}_1, s_1\rangle], \\
&= \frac{1}{2}\left(\sum_{\mathbf{k}_1}\sum_{s_1=\pm1}\langle \mathbf{k}_1, s_1|e^{-\beta\hat{T}1}|\mathbf{k}_1, s_1\rangle\right)\left(\sum_{\mathbf{k}_2}\sum_{s_2=\pm1}\langle \mathbf{k}_2, s_2|e^{-\beta\hat{T}_2}|\mathbf{k}_2, s_2\rangle\right) \\
&\quad - \frac{1}{2}\sum_{\mathbf{k}_1}\sum_{s_1=\pm1}\sum_{\mathbf{k}_2}\sum_{s_2=\pm1}\langle \mathbf{k}_1, s_1|e^{-\beta\hat{T}_1}|\mathbf{k}_2, s_2\rangle\langle \mathbf{k}_2, s_2|e^{-\beta\hat{T}_2}|\mathbf{k}_1, s_1\rangle \\
&= \frac{1}{2}\frac{4V^2}{\lambda_T^6} - 2\frac{V}{2^{5/2}\lambda_T^3}.
\end{aligned} \tag{3}$$

If we combine the above equations, the second virial coefficient becomes

$$B_2^0 = \frac{\lambda_T^3}{2^{3/2}}. \tag{4}$$

Thus, Fermi–Dirac statistics causes an effective repulsion between particles in the gas.

The only case that we can hope to treat analytically for an interacting quantum system is the second virial coefficient; because the Schrödinger equation can sometimes be solved analytically for two-body interactions. Below we show how that may be done. The second virial coefficient may be written

$$B_2(T) = -\frac{1}{2!V}\mathrm{Tr}_2[\hat{W}_2(\beta)] + \frac{1}{2!V}(\mathrm{Tr}_1[\hat{W}_1(\beta)])^2, \tag{9.110}$$

where $\hat{W}_2(\beta) = 2!\,\lambda_T^6 e^{-\beta(\hat{T}_1+\hat{T}_2+\hat{\mathrm{V}}_{12})}$, $\hat{W}_1(\beta) = \lambda_T^3 e^{-\beta\hat{T}_1}$, $\hat{T}_i \equiv p_i^2/2m$ is the kinetic energy operator for the ith particle, and $\hat{\mathrm{V}}_{12}$ is the interaction potential between particles 1 and 2. We shall assume that the interaction potential depends on relative displacement, $\hat{\mathbf{q}} = \hat{\mathbf{q}}_1 - \hat{\mathbf{q}}_2$, of the two particles and it may or may not depend on the spin of the two particles, $\hat{\mathrm{V}}_{12} = \mathrm{V}(\hat{\mathbf{q}}, s_1, s_2)$. It is useful to separate the kinetic energy into a center of mass and a relative part. If we introduce the center-of-mass momentum, $\hat{\mathbf{P}} = \hat{\mathbf{p}}_1 + \hat{\mathbf{p}}_2$, and relative momentum, $\hat{\mathbf{p}} = \frac{1}{2}(\hat{\mathbf{p}}_2 - \hat{\mathbf{p}}_1)$, the total kinetic energy operator can be written $\hat{T}_1 + \hat{T}_2 = \hat{T}_{cm} + \hat{T}_{rel}$, where $\hat{T}_{cm} = (\hat{P}^2/4m)$ is the center-of-mass kinetic energy, and $\hat{T}_{rel} = (\hat{p}^2/m)$ is the kinetic energy associated with the relative motion of the two particles. Let us consider the difference between the second virial coefficient for the interacting and noninteracting gas. We can write

$$\Delta B_2 = B_2(T) - B_2^0(T) = -\frac{\lambda_T^6}{V}\mathrm{Tr}_2\left[e^{-\beta\hat{T}_{cm}}(e^{-\beta(\hat{T}_{rel}+V_{12})} - e^{-\beta\hat{T}_{rel}})\right]. \tag{9.111}$$

The trace must be taken using symmetrized states for a Bose–Einstein gas and antisymmetrized states for a Fermi–Dirac gas.

If we consider a spin zero boson gas, the symmetrized states are simply

$$|\mathbf{k}_1, \mathbf{k}_2\rangle^{(s)} = \frac{1}{\sqrt{2}}(|\mathbf{k}_1, \mathbf{k}_2\rangle + |\mathbf{k}_2, \mathbf{k}_1\rangle). \tag{9.112}$$

and we can write

$$\Delta B_{2,be} = -\frac{\lambda_T^6}{2V}\sum_{\mathbf{k}_1}\sum_{\mathbf{k}_2}{}^{(s)}\langle \mathbf{k}_1, \mathbf{k}_2|\left[e^{-\beta\hat{T}_{cm}}(e^{-\beta(\hat{T}_{rel}+V_{12})} - e^{-\beta\hat{T}_{rel}})\right]|\mathbf{k}_1, \mathbf{k}_2\rangle^{(s)}. \tag{9.113}$$

If the bosons have spin, then the states will also depend on spin and the expression for $\mathrm{Tr}_2\,[\hat{W}_2(\beta)]$ becomes more complicated.

Let us now consider a spin-$\frac{1}{2}$ fermion gas. We will let $\uparrow$ denote $s_z = +\frac{1}{2}$ and let $\downarrow$ denote $s_z = -\frac{1}{2}$. For each value of the momenta, $\mathbf{k}_1$ and $\mathbf{k}_2$, there are four spin states that must be considered. The total spin of the two particles can be $S = 0$ or $S = 1$. We let $|\mathbf{k}_1, \mathbf{k}_2; S, S_z\rangle^{(a)}$ denote an antisymmetric state with spin S and z component of spin S_z. Then the trace must be taken with respect to the states

$$\begin{aligned}
|\mathbf{k}_1, \mathbf{k}_2; 0, 0\rangle^{(a)} &= \tfrac{1}{2}(|\mathbf{k}_1, \mathbf{k}_2\rangle + |\mathbf{k}_2, \mathbf{k}_1\rangle)(|\uparrow,\downarrow\rangle - |\downarrow,\uparrow\rangle),\\
|\mathbf{k}_1, \mathbf{k}_2; 1, 1\rangle^{(a)} &= \tfrac{1}{\sqrt{2}}(|\mathbf{k}_1, \mathbf{k}_2\rangle - |\mathbf{k}_2, \mathbf{k}_1\rangle)|\uparrow,\uparrow\rangle,\\
|\mathbf{k}_1, \mathbf{k}_2; 1, 0\rangle^{(a)} &= \tfrac{1}{2}(|\mathbf{k}_1, \mathbf{k}_2\rangle - |\mathbf{k}_2, \mathbf{k}_1\rangle)(|\uparrow,\downarrow\rangle + |\downarrow,\uparrow\rangle),\\
|\mathbf{k}_1, \mathbf{k}_2; 1, -1\rangle^{(a)} &= \tfrac{1}{\sqrt{2}}(|\mathbf{k}_1, \mathbf{k}_2\rangle - |\mathbf{k}_2, \mathbf{k}_1\rangle)|\downarrow,\downarrow\rangle.
\end{aligned} \tag{9.114}$$

With these states, we can write

$$\begin{aligned}
\Delta B_{2,fd} = -\frac{\lambda_T^6}{2V}\sum_{\mathbf{k}_1}\sum_{\mathbf{k}_2}\sum_{(S,S_z)}\\
\times {}^{(a)}\langle \mathbf{k}_1, \mathbf{k}_2; S, S_z|[e^{-\beta\hat{T}_{cm}}(e^{-\beta(\hat{T}_{rel}+V_{12})} - e^{-\beta\hat{T}_{rel}})]|\mathbf{k}_1, \mathbf{k}_2; S, S_z\rangle^{(a)}.
\end{aligned} \tag{9.115}$$

If the interaction between particles does not depend explicitly on spin—that is, if $\hat{\mathrm{V}}_{12} = \mathrm{V}(\hat{\mathbf{q}})$—then the summation over spin can be performed easily and Eq. (9.115) reduces to

$$\begin{aligned}
\Delta B_{2,fd} = -\frac{\lambda_T^6}{2V}\sum_{\mathbf{k}_1}\sum_{\mathbf{k}_2}[{}^{(s)}\langle \mathbf{k}_1; \mathbf{k}_2|[e^{-\beta\hat{T}_{cm}}(e^{-\beta(\hat{T}_{rel}+V_{12})} - e^{-\beta\hat{T}_{rel}})]|\mathbf{k}_1, \mathbf{k}_2\rangle^{(s)}\\
+ 3\,{}^{(a)}\langle \mathbf{k}_1, \mathbf{k}_2|\left[e^{-\beta\hat{T}_{cm}}\,e^{-\beta(\hat{T}_{rel}+V_{12})} - e^{-\beta\hat{T}_{rel}}\right)]|\mathbf{k}_1, \mathbf{k}_2\rangle^{(a)}],
\end{aligned} \tag{9.116}$$

where

$$|\mathbf{k}_1; \mathbf{k}_2\rangle^{(a)} = \frac{1}{\sqrt{2}}(|\mathbf{k}_1, \mathbf{k}_2\rangle - |\mathbf{k}_2, \mathbf{k}_1\rangle). \tag{9.117}$$

The momentum eigenstates, $|\mathbf{k}_1, \mathbf{k}_2\rangle$, can be written in terms of center-of-mass momentum, $\hat{\mathbf{P}} = \hbar\hat{\mathbf{K}}$, and relative momentum, $\hat{\mathbf{p}} = \hbar\hat{\mathbf{k}}$. That is, $|\mathbf{k}_1, \mathbf{k}_2\rangle = |\mathbf{K}\rangle|\mathbf{k}\rangle$. The symmetrized and antisymmetrized states become

$$|\mathbf{k}_1, \mathbf{k}_2\rangle^{(s)} = \frac{1}{\sqrt{2}}|\mathbf{K}\rangle(|\mathbf{k}\rangle + |-\mathbf{k}\rangle) \quad \text{and} \quad |\mathbf{k}_1, \mathbf{k}_2\rangle^{(a)} = \frac{1}{\sqrt{2}}|\mathbf{K}\rangle(|\mathbf{k}\rangle - |-\mathbf{k}\rangle), \tag{9.118}$$

respectively. If we substitute Eqs. (9.118) into Eqs. (9.113) and (9.116) and perform the sum over the center-of-mass momentum (first change it to an integral), we find for the Bose–Einstein gas

$$\Delta B_{2,be} = \frac{-2^{3/2}\lambda_T^3}{2} \sum_{\mathbf{k}} {}^{(s)}\langle \mathbf{k} | (e^{-\beta(\hat{T}_{rel}+V_{12})} - e^{-\beta \hat{T}_{rel}})] | \mathbf{k} \rangle^{(s)} \tag{9.119}$$

and for the Fermi–Dirac gas

$$\begin{aligned} \Delta B_{2,fd} = \frac{-2^{3/2}\lambda_T^3}{2} \sum_{\mathbf{k}} [{}^{(s)}\langle \mathbf{k}| (e^{-\beta(\hat{T}_{rel}+V_{12})} - e^{-\beta \hat{T}_{rel}}) |\mathbf{k}\rangle^{(s)} \\ + 3\, {}^{(a)}\langle \mathbf{k}| (e^{-\beta(\hat{T}_{rel}+V_{12})} - e^{-\beta \hat{T}_{rel}}) |\mathbf{k}\rangle^{(a)}]. \end{aligned} \tag{9.120}$$

Before we can proceed further, we must compute the energy eigenstates, $|E_n\rangle$, of the relative Hamiltonian, $\hat{H}_{rel} = \hat{p}^2/m + \mathrm{V}(\hat{\mathbf{q}})$. Let us denote the position eigenstates by $|\mathbf{r}\rangle$ so that $\hat{\mathbf{q}}|\mathbf{r} = \mathbf{r}|\mathbf{r}\rangle$. Then the eigenvalue problem, $\hat{H}_{rel}|E_n\rangle = E_n|E_n\rangle$, in the position basis becomes

$$-\frac{\hbar^2}{m} \nabla_{\mathbf{r}}^2 \psi_n(\mathbf{r}) + \mathrm{V}(\mathbf{r})\psi_n(\mathbf{r}) = E_n \psi_n(\mathbf{r}), \tag{9.121}$$

where $\psi_n(\mathbf{r}) = \langle \mathbf{r}|E_n\rangle$. The energy eigenstates form a complete set which we can denote, $\sum_n |E_n\rangle\langle E_n| = 1$. Similarly, we will let $\sum_{n_o} |E_{n_o}\rangle\langle E_{n_o}| = 1$ denote the complete set of energy eigenstates of the relative kinetic energy operator, $\hat{T}_{rel}$. If the interaction potential is attractive, then the spectrum of $\hat{H}_{rel}$ may contain contributions from bound states, in addition to states which extend over the size of the container. In the limit of infinite volume, the spectrum may consist of bound states in addition to a continuum of states.

It is useful now to change to the position basis. If we also insert a complete set of energy eigenstates, we find

$$\Delta B_{2,be} = -2^{3/2}\lambda_T^3 \int d\mathbf{r} \left[\sum_n |\psi_n^{(s)}(\mathbf{r})|^2 e^{-\beta E_n} - \sum_{n_o} |\psi_{n_o}^{(s)}(\mathbf{r})|^2 e^{-\beta E_{n_o}} \right] \tag{9.122}$$

and for the Fermi–Dirac gas we have

$$\begin{aligned} \Delta B_{2,fd} = -2^{3/2}\lambda_T^3 \int d\mathbf{r} \left[\left(\sum_n |\psi_n^{(s)}(\mathbf{r})|^2 e^{-\beta E_n} - \sum_{n_o} |\psi_{n_o}^{(s)}(\mathbf{r})|^2 e^{-\beta E_{n_o}} \right) \right. \\ \left. + 3 \left(\sum_n |\psi_n^{(a)}(\mathbf{r})|^2 e^{-\beta E_n} - \sum_{n_o} |\psi_{n_o}^{(a)}(\mathbf{r})|^2 e^{-\beta E_{n_o}} \right) \right], \end{aligned} \tag{9.123}$$

where $\psi_n^{(s)}(\mathbf{r}) = {}^{(s)}\langle \mathbf{r}|E_n\rangle$ and $\psi_n^{(a)}(\mathbf{r}) = {}^{(a)}\langle \mathbf{r}|E_n\rangle$.

Let us now restrict ourselves to spherically symmetric potentials, $V(\mathbf{r}) = V(|\mathbf{r}|)$. The energy eigenstates may be written in the form

$$\psi_n(\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} R_{n,l}(r) Y_{l,m}(\theta, \phi), \tag{9.124}$$

where $\mathbf{r} = (r, \theta, \phi)$ denotes the relative displacement in spherical coordinates, and $Y_{l,m}(\theta, \phi)$ is a spherical harmonic. The coefficient, $R_{n,l}(r)$, satisfies the Schrödinger equation

$$-\frac{\hbar^2}{mr}\frac{d^2(rR_{n,l}(r))}{dr^2} + \frac{l(l+1)\hbar^2}{mr^2} R_{n,l}(r) + V(r)R_{n,l}(r) = E_{n,l}R_{n,l}(r). \tag{9.125}$$

If we note that

$$\psi_n(-\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} (-1)^l R_{n,l}(r) Y_{l,m}(\theta, \phi), \tag{9.126}$$

then

$$\psi_n^{(s)}(\mathbf{r}) = \frac{2}{\sqrt{2}} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} R_{n,2l}(r) Y_{2l,2m}(\theta, \phi) \tag{9.127}$$

and

$$\psi_n^{(a)}(-\mathbf{r}) = \frac{2}{\sqrt{2}} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} R_{n,2l+1}(r) Y_{2l+1,2m+1}(\theta, \phi). \tag{9.128}$$

We can now substitute Eqs. (9.127) and (9.128) into Eqs. (9.122) and (9.123). If we use the orthonormality of the spherical harmonics

$$\int_0^{2\pi} d\phi \int_{-1}^{1} d(\cos(\theta)) Y^*_{l',m'}(\theta, \phi) Y_{l,m}(\theta, \phi) = \delta_{l',l}\delta_{m',m}, \tag{9.129}$$

and use the fact that the energy eigenstates must be normalized to one so that $\int_0^\infty r^2 dr\, |R_{n,l}(r)|^2 = 1$, we then find for the spin-0 Bose–Einstein gas

$$\Delta B_{2,be} = -2^{3/2}\lambda_T^3 \sum_{l=0}^{\infty} (4l+1) \left[\sum_n e^{-\beta E_{n,2l}} - \sum_{n_o} e^{-\beta E_{n_0,2l}} \right] \tag{9.130}$$

and for the spin-$\frac{1}{2}$ Fermi-Dirac gas

$$\Delta B_{2,fd} = -2^{3/2}\lambda_T^3 \sum_{l=0}^{\infty} \left[(4l+1) \left(\sum_n e^{-\beta E_{n,2l}} - \sum_{n_0} e^{-\beta E_{n_0,2l}} \right) + 3(4l+3) \left(\sum_n e^{-\beta E_{n,2l+1}} - \sum_{n_0} e^{-\beta E_{n_0,2l+1}} \right) \right], \tag{9.131}$$

For the spin-0 Bose–Einstein gas, only even angular momentum states contribute to the second virial coefficient. For the spin-$\frac{1}{2}$ Fermi–Dirac gas, only even angular momentum states contribute for pairs of particles with total spin $S = 0$, and only odd angular momentum states contribute for pairs of particles with total spin $S = 1$.

We can simplify the calculation of the second virial coefficients still further with a simple trick. Let us assume that the system is contained in a large spherical box of radius R and that the surface of the sphere has infinitely hard walls. The most general form of solution of Eq. (9.125) can be written

$$R_{n,l}(r) = A_{n,l}[\cos(\delta_{n,l})j_l(k_{n,l}r) - \sin(\delta_{n,l})n_l(k_{n,l}r)], \tag{9.132}$$

where $k_{n,l} = \sqrt{mE_{nl}}/\hbar$ and $\delta_{n,l}$ is the phase shift of the wavefunction relative to its value for the noninteracting system. For the noninteracting system, $\delta_{n,l} = 0$. The Bessel functions have the property that for large argument, $\lim_{x\to\infty} j_l(x) \to (1/x)\sin[x - l\pi/2]$ and $\lim_{x\to\infty} n_l(x) \to -(1/x)\cos[x - l\pi/2]$. Thus, near the outer walls of the container we have

$$R_{n,l}(r) \approx \frac{A_{n,l}}{k_{n,l}r}\sin\left[k_{n,l}r - \frac{l\pi}{2} + \delta_{n,l}\right] \qquad \text{for} \quad r \approx R. \tag{9.133}$$

At the outer wall we must have $R_{n,l}(R) = 0$. Therefore, for the interacting gas we must have

$$k_{n,l}R - \tfrac{1}{2}l\pi + \delta_{n,l} = n_l\pi, \tag{9.134}$$

and for the noninteracting gas we must have

$$k_{n_o,l}R - \tfrac{1}{2}l\pi = n_{o,l}\pi, \tag{9.135}$$

where n_l and $n_{o,l}$ are integers which label the allowed energy levels in the spherical container. If we take the derivative of Eq. (9.133) [Eq. (9.134)] with respect to $k_{n,l}(k_{n_o,l})$ and then take the difference of the resulting equations, we find

$$\frac{1}{\pi}\frac{d\delta_{n,l}}{dk_{n,l}} = \frac{dn_l}{dk_{n,l}} - \frac{dn_{o,l}}{dk_{n_o,l}}. \tag{9.136}$$

This is useful if we note that in the limit as $R \to \infty$, the energy levels in the container form a continuum and we can write $\sum_n = \int dk(dn/dk)$, where dn/dk is the density of states.

Let us again consider the virial coefficient for the spin-0 Bose–Einstein gas [Eq. (9.130)]. If we explicitly separate out the bound state contributions (and

suppress their dependence on l), we can write

$$\Delta B_{2,be} = -2^{3/2}\lambda_T^3 \sum_{n,bd} e^{-\beta E_{n,bd}} - \frac{2^{3/2}\lambda_T^3}{\pi} \sum_{l=0}^{\infty} (4l+1) \int_0^\infty dk \frac{d\delta_{2l}(k)}{dk} e^{-\beta k^2/m}. \tag{9.137}$$

Similarly, we find for the spin-$\frac{1}{2}$ Fermi-Dirac gas

$$\Delta B_{2,fd} = -2^{3/2}\lambda_T^3 \sum_{n,bd} e^{-\beta E_{n,bd}} - \frac{2^{3/2}\lambda_T^3}{\pi} \sum_{l=0}^{\infty} (4l+1) \int_0^\infty dk \frac{d\delta_{2l}(k)}{dk} e^{-\beta k^2/m} + 3(4l+3) \int_0^\infty dk \frac{d\delta_{2l+1}(k)}{dk} e^{-\beta k^2/m}]. \tag{9.138}$$

We cannot say anything more about the second virial coefficient, unless we specify the shape of the spherically symmetric potential, $V(r)$. We leave this for an exercise.

■ **EXERCISE 9.5.** Compute the second virial coefficient for a dilute gas of hard sphere spin-0 bosons at fairly low temperature.

Answer: For hard spheres of radius $R = a$, in an infinitely large box, the scattering phase shift, $\delta_l(k)$, is given by

$$\tan(\delta_l(k)) = \frac{j_l(ka)}{n_l(ka)}. \tag{1}$$

For a dilute gas of bosons at fairly low temperature, the momenta, k, of the particles will be fairly low. Therefore, we can approximate the Bessel functions in Eq. (1) by their asymptotic limits for small argument, and we find

$$\tan(\delta_l(k)) \approx -\frac{(ka)^{2l+1}}{(2l+1)(1\cdot 3\cdots(2l-1))^2}. \tag{2}$$

Thus for small ka, the dominant term comes from the partial wave, $l = 0$, and $\delta_0(k) \approx -ka$. Hard spheres have no bound states. Therefore, the second virial coefficient can be written

$$B_2 = B_2^0 + \frac{2^{3/2}\lambda_T^3}{\pi} \int_0^\infty dk\, a e^{-\beta k^2/m} = B_2^0 + 2a\lambda_T^2. \tag{3}$$

The second virial coefficient for the noninteracting gas is $B_2^0 = -\lambda_T^3/2^{5/2}$. Thus, we find

$$B_2 = -\frac{\lambda_T^3}{2^{5/2}} + 2a\lambda_T^2 + \cdots. \tag{4}$$

While Bose–Einstein statistics tends to lower the pressure of the boson gas, the hard core tends to increase it.

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PROBLEMS

Problem 9.1. Compute the second virial coefficient for a gas which interacts via the potential

$$V(\mathbf{q}) = \begin{cases} \infty & \text{if } q < R, \\ \frac{\varepsilon}{R(\lambda-1)}(q - \lambda R) & \text{if } R \leqslant q \leqslant \lambda R, \\ 0 & \text{if } q > \lambda R. \end{cases}$$

Problem 9.2. Consider a classical gas in a box of volume V. Compute the second virial coefficient, B_2, for the Gaussian model, $f(q_{ij}) = e^{-aq_{ij}^2}$, where $a^{-1/2} \ll V^{1/3}$. Sketch the effective potential, $\beta V(q_{ij})$.

Problem 9.3. Compute the second coefficient for the weakly coupled particles with potential $V(\mathbf{q}) = V_0$ for $q \leq R$ and $V(\mathbf{q}) = 0$ for $q > R$.

Problem S9.1. Assume at low density the direct correlation function can be approximated by $C(\mathbf{q}) = (e^{-\beta V(\mathbf{q})} - 1)$. For a low-density hard-sphere gas (radius R), use the Ornstein–Zernicke equation to obtain the first-order correction (in density) to the ideal gas expression for the isothermal compressibility. Show that your result agrees with the result obtained when starting from the virial expansion, $P/nk_BT = 1 + nB_2$, where $n = N/V$ and B_2 is the second virial coefficient.

Problem S9.2. Consider a classical gas in a box of volume V. Compute the third virial coefficient, B_3, for the Gaussian model, $f(q_{ij}) = e^{-aq_{ij}^2}$, where $a^{-1/2} \ll V^{1/3}$.

Problem S9.3. The third virial coefficient can be written

$$B_3 = -\frac{1}{3}\int d\mathbf{q}_{12} \int d\mathbf{q}_{13} f(\mathbf{q}_{12}) f(\mathbf{q}_{13}) f(\mathbf{q}_{13} - \mathbf{q}_{12}).$$

where $f(\mathbf{q}) = (e^{-\beta V(\mathbf{q})} - 1)$ and $V(\mathbf{q})$ is the interaction potential between particles with relative position, $\mathbf{q}$. The Fourier transform of $f(\mathbf{q})$ is $\tilde{f}(\mathbf{k}) = \int e^{i\mathbf{k}\cdot\mathbf{q}} f(\mathbf{q})$. The inverse transform is $f(\mathbf{q}) = (1/2\pi)^3 \int e^{-i\mathbf{k}\cdot\mathbf{q}} \tilde{f}(\mathbf{k})$. (a) Show that the third virial coefficient can be written $B_3 = -\frac{1}{3}(1/2\pi)^3 \int d\mathbf{k} \tilde{f}(\mathbf{k}) \tilde{f}(-\mathbf{k}) \tilde{f}(-\mathbf{k})$. (b) Compute $\tilde{f}(\mathbf{k})$ for a gas of hard spheres with radius R. (c) Use part (b) to compute the third virial coefficient for a hard sphere gas.

Problem S9.4. Compute the third virial coefficient for weakly coupled particles with potential $V(\mathbf{q}) = V_0$ for $q \leq R$ and $V(\mathbf{q}) = 0$ for $q \geq R$.

Problem S9.5. Compute the third virial coefficient for an ideal Fermi–Dirac gas of spin, $s = \frac{1}{2}$, particles.

Problem S9.6. Compute the second virial coefficient for a dilute gas of soft-sphere spin-0 bosons at fairly low temperature. Assume that the spheres have radius $r = a$ and a potential $V(r) = +V_0$ for $r \leq a$ and $V(r) = 0$ for $r > a$. Assume also that $k^2 \ll mV_0/\hbar^2$.

PART FOUR

NONEQUILIBRIUM STATISTICAL MECHANICS

10

HYDRODYNAMIC PROCESSES NEAR EQUILIBRIUM

10.A. INTRODUCTION

When a system is disturbed from its equilibrium state, quantities which are not conserved during collisions, or which are not order parameters for an underlying broken symmetry, decay rapidly to their equilibrium values. After a few collision times, only quantities which are conserved during the collisions, or order parameters, remain out of equilibrium. The densities of conserved quantities and order parameters entirely characterize the nonequilibrium behavior of the fluid after long times. The equations of motion for the densities of the conserved quantities and for order parameters are called the *hydrodynamic equations.* Some examples of conserved quantities may include particle number, momentum, and energy. Examples of order parameters may include average magnetization, or a complex function characterizing a superfluid state. If there are inhomogeneities in the densities of conserved quantities, then particles, momentum, or kinetic energy must be transported from one part of the fluid to another to achieve equilibrium. Therefore, very-long-wavelength disturbances will take a long time relax, whereas short-wavelength disturbances relax more quickly. This dependence of relaxation time on wavelength is a feature that characterizes hydrodynamic processes.

Hydrodynamic equations describe the long-wavelength, low-frequency phenomena in a large variety of systems, including dilute gases, liquids, solids, liquid crystals, superfluids, and chemically reacting systems. For complicated systems, transport processes are often coupled. For example, in a multicomponent system, it is possible to have a temperature gradient drive a particle current and a concentration gradient drive a heat current. Some complicated systems can have as many as 10 or 20 (or more) transport coefficients to describe the decay to equilibrium from the hydrodynamic regime.

In 1932, Onsager showed that the reversibility of the dynamical laws on the microscopic level requires that certain relations exist between transport coefficients describing coupled transport processes. Onsager's relations are of

immense importance because they enable us to link seemingly independent transport processes and thereby reduce the number of experiments that must be performed in order to measure all the transport coefficients. In this chapter we will derive Onsager's relations and apply them to transport processes in reacting multicomponent systems and superfluid systems. At the same time we will show how the hydrodynamic equations for such complicated systems can be derived from a knowledge of the thermodynamics and symmetry properties of a system.

Fluctuations about the equilibrium state decay *on the average* according to the same linear macroscopic laws (hydrodynamic equations) which describe the decay of the system from a nonequilibrium state to the equilibrium state. If we can probe the equilibrium fluctuations, we have a means of probing the transport processes in the system. The *fluctuation–dissipation theorem* shows that it is possible to probe the equilibrium fluctuations by applying a weak external field which couples to particles in the medium but yet is too weak to affect the medium. The system will respond to the field and absorb energy from it in a manner which depends entirely on the spectrum of the equilibrium fluctuations. According to the fluctuation–dissipation theorem, the spectrum of equilibrium fluctuations and the rate of absorption of energy from the external field can be expressed in terms of a response matrix which is related to the correlation matrix for equilibrium fluctuations.

In this chapter we will derive the fluctuation–dissipation theorem and apply it to a variety of systems. The derivation requires several steps. We first introduce the *Wiener–Khinchine theorem*, which enables us to relate the spectral density matrix for fluctuations to the time-dependent correlation matrix for fluctuations in the system. We then introduce linear response theory and use the assumption of causality to obtain a relation between the real and imaginary parts of the response matrix.

One of the simplest applications of linear response theory involves a harmonically bound Brownian particle immersed in a medium. If the Brownian particle is pulled away from its equilibrium position, it will decay back to equilibrium and dissipate energy into the fluid. We will obtain an expression for the linear response function of the Brownian particle and in terms of it derive an expression for the correlation function for equilibrium fluctuations in the position for the oscillator.

In the *special topics* section we discuss important applications of the fluctuation–dissipation theory—for example, the scattering of light from a fluid. The electric field of the incident light wave polarizes the particles in the medium, thus allowing the light to couple to the medium. The light will be scattered by density fluctuations, and by measuring the spectrum of the scattered light we can measure the spectrum of the density fluctuations. We will find that the density fluctuations are of two types: thermal density fluctuations due to fluctuations in the local entropy and mechanical density fluctuations due to damped sound waves. For low-frequency and long-wavelength fluctuations, the spectrum of scattered light can be obtained from the linearized hydro-

dynamic equations, and, therefore, light scattering experiments give us a means of measuring transport coefficients in the fluid.

In the special topics section we shall apply hydrodynamic theory to transport processes in electric circuits composed of different metals coupled together and held at nonuniform temperature. We shall also discuss the transport of mixtures across membranes.

The hydrodynamic equations describe the long time behavior of a few hydrodynamic modes in a system with 10^{23} degrees of freedom. The non-hydrodynamic degrees of freedom decay on a much faster time scale than the hydrodynamic modes and provide background noise. We can use the fluctuation-dissipation theorem to find the correlation functions for this background noise as we will show in the special topics section.

It is also possible to derive correlation functions for microscopic Brownian particles using the hydrodynamic equations. The hydrodynamic flow of the medium around a Brownian particle creates memory effects which cause its velocity autocorrelation to decay with a slow long time tail.

The poles of the spectral density matrix give us information about the spectrum of fluctuations in an equilibrium system. The poles corresponding to very-low-frequency, long-wavelength processes are due to hydrodynamic modes in the system. By using projection operator techniques, it is possible to introduce projections onto the space of hydrodynamic modes and onto the space orthogonal to it. We can then write the spectral density matrix for hydrodynamic fluctuations in a very general form and show that hydrodynamic modes arise not only from conserved quantities but also from broken symmetries which occur at a continous phase transition.

10.B. NAVIER–STOKES HYDRODYNAMIC EQUATIONS [1–3]

The Navier–Stokes equations describe the macroscopic behavior of an isotropic fluid of point particles out of quilibrium. They are essentially the macroscopic "balance equations" (cf. Appendix A) for the quantities that are conserved during collision processes on the microscopic scale. The conserved quantities for an isotropic fluid of point particles include the particle number, the momentum, and the energy. The balance equations for the conserved quantities contain no source terms because the conserved quantities cannot be created or destroyed on the microscopic scale. In addition to the balance equations for conserved quantities, it is essential to write the balance equation for the entropy density of the fluid. Entropy is not a conserved quantity. For a fluid in which irreversible processes can occur, there will be an entropy source term. The entropy source term in a fluid is the hydrodynamic equivalent of the Joule heating which occurs in an electric circuit which has resistance. The entropy source term enables us to identify generalized forces and currents in the fluid.

The *conductance* in a fluid (the proportioality constant between force and resulting current) is called a *transport coefficient.* Once the transport coefficients for the fluid have been identified, we can write the Navier–Stokes equations.

10.B.1. Balance Equations

In this section we will derive the balance equations for the mass density, momentum density, energy density, and entropy density for an isotropic fluid of point particles. The balance equation for the mass density is especially simple since particles can't be created and there can be no dissipative particle currents. The balance equation for the momentum density is based on Newton's second law. Momentum can only be created in a fluid of external unbalanced forces act on the fluid, and therefore there can only be a momentum source term if external forces are present. The balance equations for the energy density and the entropy density can be written in a general form, and thermodynamic relations can be used to relate them.

10.B.1.1. Mass Balance Equation

In the absence of chemical reactions, the number of particles entering and leaving a collision in a fluid will be conserved. For nonrelativistic processes, the total mass of the particles involved in the collision process will also be conserved. As a result, if we consider a volume element of the fluid, $V(t)$ (with a given set of fluid particles), which moves with the fluid, the amount of mass inside this volume element must remain constant. Let $\rho = \rho(\mathbf{r}, t)$ denote the mass density (mass per unit volume) and let M denote the total mass in the volume, $V(t)$. Then

$$\frac{dM}{dt} = \frac{d}{dt}\int_{V(t)} \rho dV = \int_{V(t)} \left(\frac{d\rho}{dt} + \rho \nabla_r \cdot \mathbf{v}\right) dV = 0, \tag{10.1}$$

where $\mathbf{v} = \mathbf{v}(\mathbf{r}, \mathrm{t})$ is the average velocity of the fluid at point $\mathbf{r}$ and time t, and we have used Eq. (A.16) in Appendix A. Since the volume element, $V(t)$,is arbitrary, the integrand must be zero and we find

$$\frac{d\rho}{dt} + \rho \nabla_r \cdot \mathbf{v} = 0. \tag{10.2}$$

If we note that the convective derivative is given by $d/dt = \partial/\partial t + \mathbf{v} \cdot \nabla_{\mathrm{r}}$, then we can also write

$$\frac{\partial \rho}{\partial t} + \nabla_r \cdot (\rho \mathbf{v}) = 0, \tag{10.3}$$

The quantity, $\mathbf{J} \equiv \rho \mathbf{v}$ is the mass current or mass flux and has units mass/

area·time. It is also a momentum density. The derivative, $d\rho/dt$, gives the time rate of change of the mass density for an observer moving with the fluid. The derivative, $\partial\rho/\partial t$, gives the time rate of change of the mass density for an observer at a fixed point in the fluid (cf. Appendix A). Equation (10.3) is sometimes called the *continuity equation*. It is a direct consequence of the conservation of mass in the fluid.

10.B.1.2. Momentum Balance Equation

The total momentum, $\mathbf{P}(t) = \int_{V(t)} \rho \mathbf{v} dV$, of the volume element, $V(t)$, evolves acording to Newton's law. The time rate of change of the momentum, $\mathbf{P}(t)$, must be equal to the sum of the forces acting on the volume element, $V(t)$. Therefore we can write the equation of motion of the fluid element in the form

$$\frac{d\mathbf{P}(t)}{dt} = \frac{d}{dt}\int_{V(t)} \rho \mathbf{v} dV = \int_{V(t)} \rho \mathbf{F} dV + \int_{S(t)} \mathbf{f} dS, \tag{10.4}$$

where $\mathbf{F}$ is an external force per unit mass which couples to the particles inside the volume element (it could be an electric or magnetic field for example), $\mathbf{f}$ is a force per unit area acting on the walls of the volume element, and $S(t)$ denotes the surface of the volume element, $V(t)$. The surface force, $\mathbf{f}$, is due to the fluid surrounding the volume element. It will always have a component perpendicular to the surface of $V(t)$, and for a nonideal fluid (a fluid with dissipation) it will have a component tangent to the surface.

If we write a differential surface area element as a vector, $d\mathbf{S}$, directed outward perpendicular to the surface, then we can write $\mathbf{f}dS = d\mathbf{S} \cdot \bar{\mathbf{P}}$, where $\bar{\mathbf{P}}$ is the pressure tensor, $\mathbf{f} = \hat{\mathbf{n}} \cdot \bar{\mathbf{P}}$, and $\hat{\mathbf{n}}$ is a unit vector directed outward perpendicular to the surface. The pressure tensor has nine components. In Cartesian coordinates it can be written $\bar{\mathbf{P}} = P_{xx}\hat{\mathbf{x}}\hat{\mathbf{x}} + P_{xy}\hat{\mathbf{x}}\hat{\mathbf{y}} + \cdots + P_{zz}\hat{\mathbf{z}}\hat{\mathbf{z}}$, where $\hat{\mathbf{x}}, \hat{\mathbf{y}}$, and $\hat{\mathbf{z}}$ are unit vectors in the x, y, and z directions, respectively. The unit vector, $\hat{\mathbf{n}}$, can be written $\hat{\mathbf{n}} = n_x\hat{\mathbf{x}} + n_y\hat{\mathbf{y}} + n_z\hat{\mathbf{z}}$, where n_x, n_y, and n_z are components of $\hat{\mathbf{n}}$ in the x, y, and z directions, respectively. Note that the ith component of the vector, $\mathbf{f}$, can be written $f_i = \sum_j n_j P_{ji}$, where $i = x, y, z$ and $j = x, y, z$. If we use Gauss's theorem, we can write

$$\int_{S(t)} d\mathbf{S} \cdot \bar{\mathbf{P}} = \int_{V(t)} dV \nabla_r \cdot \bar{\mathbf{P}} \tag{10.5}$$

Here $\nabla_r \cdot \bar{\mathbf{P}}$ is a vector those ith component is $(\nabla_r \cdot \bar{\mathbf{P}})_i = \sum_j \partial_j P_{ji} = \partial P_{xi}/\partial x + \partial P_{yi}/\partial y + \partial P_{zi}/\partial z$ and $\partial_z = \partial/\partial x, \partial_y = \partial/\partial y$, and $\partial_z = \partial/\partial z$. Then the argument of Eq. (10.4) must satisfy the equation

$$\frac{d\rho\mathbf{v}}{dt} + \rho\mathbf{v}(\nabla_r \cdot \mathbf{v}) = \rho\mathbf{F} + \nabla_r \cdot \bar{\mathbf{P}} \tag{10.6}$$

[cf. Appendix A, Eq. (A.16)].

For an ideal fluid (no dissipation) the only force on the walls of $V(t)$ is due to the hydrostatic pressure, $P = P(\mathbf{r}, t)$, which is always perpendicular to the walls and pointed inward. Thus, for an ideal fluid we have $\mathbf{f} = -P\hat{\mathbf{n}}$ and $\bar{\mathbf{P}} = -P\bar{\mathbf{U}}$($\bar{\mathbf{U}}$ is the unit tensor, $\bar{\mathbf{U}} = \hat{\mathbf{x}}\hat{\mathbf{x}} + \hat{\mathbf{y}}\hat{\mathbf{y}} + \hat{\mathbf{z}}\hat{\mathbf{z}}$). For a nonideal fluid, there is also a dissipative contribution, $\bar{\mathbf{\Pi}}$, to the pressure tensor and Eq. (10.6) takes the form

$$\frac{d\rho\mathbf{v}}{dt} + \rho\mathbf{v}(\nabla_r \cdot \mathbf{v}) = \rho\mathbf{F} - \nabla_r P - \nabla_r \cdot \bar{\mathbf{\Pi}} \tag{10.7}$$

since $\nabla_r \cdot (P\bar{\mathbf{U}}) = \nabla_r P$. The tensor $\bar{\mathbf{\Pi}}$ is called the *stress tensor.* If we make use of the convective derivative, $d/dt = \partial/\partial t + \mathbf{v} \cdot \nabla$, we can also write Eq. (10.7) in the form

$$\frac{\partial\rho\mathbf{v}}{\partial t} + \nabla_r \cdot (P\bar{\mathbf{U}} + \rho\mathbf{v}\mathbf{v} + \bar{\mathbf{\Pi}}) = \rho\mathbf{F}. \tag{10.8}$$

The term $\rho\mathbf{v}\mathbf{v}$ is the momentum flux. It is a nine-component dyatic tensor, $\rho\mathbf{v}\mathbf{v} = \rho v_x v_x \hat{\mathbf{x}}\hat{\mathbf{x}} + \rho v_x v_y \hat{\mathbf{x}}\hat{\mathbf{y}} + \cdots + \rho v_z v_z \hat{\mathbf{z}}\hat{\mathbf{z}}$. Equations (10.7) and (10.8) are alternative versions of the *momentum balance equation* for an isotropic fluid of point particles. Equation (10.7) describes the time rate of change of momentum density as seen by an observer moving with the fluid, and Eq. (10.8) describes the time rate of change of momentum density a seen by an observer at a fixed point in space.

10.B.1.3. Energy and Entropy Balance Equations

The energy and entropy balance equations are easy to write down. We will let ϵ denote the energy per unit mass, and let ρe denote the energy per unit volume of the fluid. For the case when the external force has the form $\mathbf{F} = -\nabla_r \phi$($\phi$ is a potential energy per unit mass), the energy density can be written $\rho e = \rho u + \frac{1}{2}\rho v^2 + \rho\phi$, where u is the internal energy per unit mass. Thus the energy density has contributions from thermodynamic processes in the fluid, the kinetic energy of the fluid, and the external potential energy.

Since the energy inside the volume element cannot be created or destroyed by collisions, the only way the energy inside the volume element can change is by flow through the walls of $V(t)$. The balance equation for the total energy can be written

$$\frac{\partial\rho e}{\partial t} + \nabla_\mathbf{r} \cdot (\mathbf{J}_e^R + \mathbf{J}_e^D) = 0, \tag{10.9}$$

where $\mathbf{J}_e^R$ is the reactive (nondissipative) energy current and $\mathbf{J}_e^D$ is the dissipative energy current. Both $\mathbf{J}_e^R$ and $\mathbf{J}_e^D$ have yet to be determined.

The entropy balance equation can be written in an analogous fashion. However, now we must take account of the fact that entropy can be created inside the volume element due to spontaneous processes inside of $V(t)$. Let s denote the entropy per unit mass (the specific entropy) and ρs denote the

entropy per unit volume. The entropy balance equation then becomes

$$\frac{\partial \rho s}{\partial t} + \nabla_{\mathbf{r}} \cdot (\mathbf{J}_s^R + (\mathbf{J}_s^D) = \sigma_s, \tag{10.10}$$

where $\mathbf{J}_s^R$ is the reactive entropy current, $\mathbf{J}_s^D$ is the dissipative entropy current, and σ_s is an entropy source term due to disspative processes inside of $V(t)$. The explicit forms of $\mathbf{J}_s^R$, $\mathbf{J}_s^D$, and σ_s will be determined in the next section.

10.B.2. Entropy Source and Entropy Current

Let us now assume that spatial variations of deviations from thermodynamic equilibrium occur on very large length scales compared to microscopic distances. Then locally the system will be in equilibrium, but the actual values of thermodynamic quantities vary slowly in space and time. The fundamental equation for the internal energy is $\rho u = T\rho s - P + \rho\tilde{\mu}$, where $\tilde{\mu}$ is the chemical potential per unit mass [cf. Eq. (2.66)]. If we take the differential of this equation and use the Gibbs–Duhem equation, $\rho d\tilde{\mu} + \rho s dT - dP = 0$, we find $d(\rho u) = Td(\rho s) + \tilde{\mu} d\rho$. Therefore, we can write

$$\begin{aligned} &\frac{d\rho u}{dt} - T\frac{d\rho s}{dt} - \tilde{\mu}\frac{d\rho}{dt} = \frac{\partial \rho u}{\partial t} - T\frac{\partial \rho s}{\partial t} - \tilde{\mu}\frac{\partial \rho}{\partial t} \\ &\quad + \mathbf{v} \cdot \nabla_{\mathbf{r}}(\rho u) - T\mathbf{v} \cdot \nabla_{\mathbf{r}}(\rho s) - \tilde{\mu}\mathbf{v} \cdot \nabla_{\mathbf{r}}(\rho) = 0, \end{aligned} \tag{10.11}$$

where we have made use of the convective time derivative. Let us next note that

$$\begin{aligned} &\mathbf{v} \cdot \nabla_{\mathbf{r}}(\rho u) - T\mathbf{v} \cdot \nabla_{\mathbf{r}}(\rho s) - \tilde{\mu}\mathbf{v} \cdot \nabla_{\mathbf{r}}(\rho) \\ &\quad = \nabla_{\mathbf{r}} \cdot [(\rho u - T\rho s - \rho\tilde{\mu})\mathbf{v}] + \rho s\mathbf{v} \cdot \nabla_{\mathbf{r}} T + \rho\mathbf{v} \cdot \nabla_{\mathbf{r}}\tilde{\mu} + P\nabla_{\mathbf{r}} \cdot \mathbf{v} \\ &\quad = \mathbf{v} \cdot (\rho s\nabla_{\mathbf{r}} T + \rho\nabla_{\mathbf{r}}\tilde{\mu} - \nabla_{\mathbf{r}} P) = 0, \end{aligned} \tag{10.12}$$

where we have used the fundamental equation, $\rho u = T\rho s - P + \rho\tilde{\mu}$, and the last term is zero because of the Gibbs–Duhem equation, $\rho d\tilde{\mu} + \rho s dT - dP = 0$. Therefore

$$\frac{d\rho u}{dt} - T\frac{d\rho s}{dt} - \tilde{\mu}\frac{d\rho}{dt} = \frac{\partial \rho u}{\partial t} - T\frac{\partial \rho s}{\partial t} - \tilde{\mu}\frac{\partial \rho}{\partial t} = 0. \tag{10.13}$$

Let us now assume, for simplicity, that all external forces are zero so that $\mathbf{F} = 0$. Then the total energy per unit volume is $\rho e = \rho u + \frac{1}{2}\rho v^2$, and we can write

$$\frac{\partial \rho e}{\partial t} = \frac{\partial \rho u}{\partial t} + \mathbf{v} \cdot \frac{\partial \rho \mathbf{v}}{\partial t} - \frac{1}{2}v^2 \frac{\partial \rho}{\partial t}. \tag{10.14}$$

If we combine Eqs. (10.13) and (10.14), we find

$$T\frac{\partial \rho s}{\partial t} = \frac{\partial \rho e}{\partial t} - \mathbf{v}\cdot\frac{\partial \rho \mathbf{v}}{\partial t} + \left(\frac{1}{2}v^2 - \tilde{\mu}\right)\frac{\partial \rho}{\partial t}. \tag{10.15}$$

We can now use the balance equations to obtain an expression for the entropy current and source. If we combine Eqs. (10.3), (10.8), (10.9), and (10.15), we obtain

$$T\frac{\partial \rho s}{\partial t} = -\nabla_{\mathbf{r}}\cdot(\mathbf{J}_e^R + \mathbf{J}_e^D) + \mathbf{v}[\nabla_{\mathbf{r}}\cdot(P\bar{\mathbf{U}} + \rho\mathbf{v}\mathbf{v} + \bar{\mathbf{\Pi}})] - \left(\frac{1}{2}v^2 - \tilde{\mu}\right)\nabla_{\mathbf{r}}\cdot(\rho\mathbf{v}). \tag{10.16}$$

This equation can be simplified further. Note that

$$\mathbf{v}\cdot[\nabla_{\mathbf{r}}\cdot(\rho\mathbf{v}\mathbf{v})] = \sum_i\sum_j v_i\nabla_j(\rho v_j v_i) = \sum_i\sum_j[\rho v_i v_j(\nabla_j v_i) + v_i^2\nabla_j(\rho v_j)]. \tag{10.17}$$

Note also that

$$\nabla_j\left(\rho v_j\frac{1}{2}v_i^2\right) = \frac{1}{2}v_i^2\nabla_j(\rho v_j) + \rho v_j v_i\nabla_j v_i. \tag{10.18}$$

If we combine Eqs. (10.17) and (10.18), we find

$$\mathbf{v}\cdot[\nabla_{\mathbf{r}}\cdot(\rho\mathbf{v}\mathbf{v})] = \frac{1}{2}v^2\nabla_{\mathbf{r}}\cdot(\rho\mathbf{v}) + \frac{1}{2}\nabla_{\mathbf{r}}\cdot(\rho v^2\mathbf{v}). \tag{10.19}$$

Let us now substitute Eq. (10.19) into Eq. (10.16) and make use of the Gibbs–Duhem relation, $\rho s\nabla_{\mathbf{r}}T + \rho\nabla_{\mathbf{r}}\tilde{\mu} - \nabla_{\mathbf{r}}P = 0$. Then after some rearrangement we find

$$T\frac{\partial \rho s}{\partial t} = -\nabla_{\mathbf{r}}\cdot(\mathbf{J}_e^R + \mathbf{J}_e^D - \rho\mu''\mathbf{v} - \bar{\mathbf{\Pi}}\cdot\mathbf{v}) + \rho s\mathbf{v}\cdot\nabla_{\mathbf{r}}T - \bar{\mathbf{\Pi}} : \nabla_{\mathbf{r}}\mathbf{v}, \tag{10.20}$$

where $\bar{\mathbf{\Pi}} : \nabla_{\mathbf{r}}\mathbf{v} \equiv \sum_i\sum_j \Pi_{ij}\nabla_i v_j$ and $\mu'' = \tilde{\mu} + \frac{1}{2}v^2$. We can now write Eq. (10.20) in the form of a balance equation. If we divide through by the temperature, we can rearrange terms to obtain

$$\begin{aligned}\frac{\partial \rho s}{\partial t} = &-\nabla_{\mathbf{r}}\cdot\left(\frac{\mathbf{J}_e^R + \mathbf{J}_e^D - \rho\mu''\mathbf{v} - \bar{\mathbf{\Pi}}\cdot\mathbf{v}}{T}\right)\\ &+ (\mathbf{J}_e^R + \mathbf{J}_e^D - \rho\mu''\mathbf{v} - \rho sT\mathbf{v} - \bar{\mathbf{\Pi}}\cdot\mathbf{v})\cdot\nabla_{\mathbf{r}}\left(\frac{1}{T}\right) - \frac{1}{T}\bar{\mathbf{\Pi}} : \nabla_{\mathbf{r}}\mathbf{v}.\end{aligned} \tag{10.21}$$

We can simplify Eq. (10.21) still further if we first write its form for a nondissipative fluid.

Consider a fluid in which no dissipative processes occur. By definition, the stress tensor, $\bar{\Pi}$, equals 0 and the dissipative energy current, $\mathbf{J}_e^D$, equals 0 for such a fluid. Also there will be no entropy source term. Therefore, from Eq. (10.21) the reactive energy current must be given by

$$\mathbf{J}_e^R \equiv \rho\mu''\mathbf{v} + \rho sT\mathbf{v} = \rho(h + \tfrac{1}{2}v^2)\mathbf{v} = \rho(u + P + \tfrac{1}{2}v^2)\mathbf{v}, \tag{10.22}$$

where h is the enthalpy per unit mass. If we substitute Eq. (10.22) into Eq.(10.21) and set $\bar{\Pi} = 0$ and $\mathbf{J}_\epsilon^D = 0$, we obtain the entropy balance equation for a nondissipative fluid,

$$\frac{\partial \rho s}{\partial t} = -\nabla_{\mathbf{r}} \cdot (\rho s\mathbf{v}). \tag{10.23}$$

The entropy current in a nondissipative fluid is $\rho s\mathbf{v}$.

If we substitute the definition of the reactive energy current, $\mathbf{J}_e^R$, into Eq. (10.20), we obtain the final form of the entropy balance equation for a dissipative fluid:

$$\frac{\partial \rho s}{\partial t} = -\nabla_{\mathbf{r}} \cdot (\rho s\mathbf{v} + \mathbf{J}_s^D) - \frac{1}{T}\mathbf{J}_s^D \cdot \nabla_{\mathbf{r}} T - \frac{1}{T}\bar{\Pi} : \nabla_{\mathbf{r}}\mathbf{v}, \tag{10.24}$$

where the dissipative entropy current, $\mathbf{J}_s^D$, is

$$\mathbf{J}_s^D = \frac{1}{T}(\mathbf{J}_e^D - \bar{\Pi} \cdot \mathbf{v}). \tag{10.25}$$

The entropy source in a dissipative fluid is

$$\sigma_s = -\frac{1}{T}\mathbf{J}_s^D \cdot \nabla_{\mathbf{r}} T - \frac{1}{T}\bar{\Pi} : \nabla_{\mathbf{r}}\mathbf{v}. \tag{10.26}$$

One can easily check that the quantity $\mathbf{J}_s^D \cdot \nabla_{\mathbf{r}} T + \bar{\Pi} : \nabla_{\mathbf{r}}\mathbf{v}$ has units (energy/volume · time). It is the hydrodynamic version of Joule heating. In an electric circuit, Joule heating is given by $\mathbf{J} \cdot \mathbf{E}$, where $\mathbf{E}$ is the electric field and $\mathbf{J}$ is the electric current. This is the (energy/volume · time) dissipated in the electric circuit. We see that the hydrodynamic entropy production has the same form if we identify $\mathbf{J}_s^D$ and $\bar{\Pi}$ as the generalized currents and $\nabla_{\mathbf{r}} T$ and $\nabla_{\mathbf{r}}\mathbf{v}$ as the generalized forces driving those currents.

In an electric circuit the electric current and the electric field (driving force) are related by Ohm's law, $\mathbf{J} = \sigma\mathbf{E}$, where σ is the conductivity of the electric medium. Hydrodynamic media also have a version of Ohm's law in which the driving forces are linearly related to the currents. In hydrodynamic systems the

"conductivities" are called "transport coefficients." In the next section we will obtain the transport coefficients for an isotropic fluid of point particles, and in so doing we will be able to write the Navier–Stokes equations for the fluid.

■ **EXERCISE (10.1)** (a) Write the dyatic tensor $\nabla_{\mathbf{r}}\mathbf{v}$ in orthogonal curvilinear coordinates. Assume that the coordinates have unit vectors $\hat{\mathbf{e}}_1$, $\hat{\mathbf{e}}_2$, and $\hat{\mathbf{e}}_3$, coordinates u_1, u_2, and u_3, and scale factors h_1, h_2, and h_3. (b) Write the dyatic tensor $\nabla_{\mathbf{r}}\mathbf{v}$ for the special case of cylindrical coordinates $u_1 = r, u_2 = \phi$, and $u_3 = z$ with scale factors $h_1 = 1, h_2 = r$, and $h_3 = 1$ and unit vectors $\hat{\mathbf{e}}_1 = \hat{\mathbf{r}}, \hat{\mathbf{e}}_2 = \hat{\boldsymbol{\phi}}$, and $\hat{\mathbf{e}}_3 = \hat{\mathbf{z}}$.

Answer

(**a**) In orthogonal curvilinear cordinates the gradient is

$$\nabla = \frac{\hat{\mathbf{e}}_1}{h_1}\frac{\partial}{\partial u_1} + \frac{\hat{\mathbf{e}}_2}{h_2}\frac{\partial}{\partial u_2} + \frac{\hat{\mathbf{e}}_3}{h_3}\frac{\partial}{\partial u_3}, \tag{1}$$

and the velocity can be written $\mathbf{v} = v_1\hat{\mathbf{e}}_1 + v_2\hat{\mathbf{e}}_2 + v_3\hat{\mathbf{e}}_3$. Let x_i denote Cartesian coordinates, where $x_1 = x, x_2 = y$, and $x_3 = z$. Unit vectors in Cartesian coordinates will be denoted $\hat{\mathbf{x}}_\alpha$ with $\alpha = 1, 2, 3$. (Cartesian coordinates are orthogonal curvilinear coordinates with all scale factors equal to one.) In evaluating the dyatic, it is useful to note that derivatives of the Cartesian unit vectors $\hat{\mathbf{x}}_\alpha$ with respect to the generalized coordinates u_1, u_2, and u_3 are zero. That is, $\partial\hat{\mathbf{x}}_\alpha/\partial u_i = 0$. The unit vectors $\hat{\mathbf{e}}_i$ are related to the Cartesian unit vectors through a transformation

$$\hat{\mathbf{e}}_i = \sum_\alpha R_{i,\alpha}(u_1, u_2, u_3)\hat{\mathbf{x}}_\alpha \quad \text{and} \quad \hat{\mathbf{x}}_\alpha = \sum_i R^{-1}_{\alpha,i}(u_1, u_2, u_3)\hat{\mathbf{e}}_i. \tag{2}$$

We can now make use of the above relations to write the dyatic tensor, $\nabla_{\mathbf{r}}\mathbf{v}$ in the form

$$\nabla_{\mathbf{r}}\mathbf{v} = \sum_i\sum_j \frac{\hat{\mathbf{e}}_i\hat{\mathbf{e}}_j}{h_i}\frac{\partial v_j}{\partial u_i} + \sum_i\sum_j\sum_k\sum_\alpha \frac{\hat{\mathbf{e}}_i\hat{\mathbf{e}}_k}{h_i} v_j \frac{\partial R_{j,\alpha}}{\partial u_i} R^{-1}_{\alpha,k}. \tag{3}$$

(**b**) In cylindrical coordinates we have

$$\begin{pmatrix} \hat{\mathbf{r}} \\ \hat{\boldsymbol{\phi}} \\ \hat{\mathbf{z}} \end{pmatrix} = \begin{pmatrix} \cos(\phi) & \sin(\phi) & 0 \\ -\sin(\phi) & \cos(\phi) & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \hat{\mathbf{x}} \\ \hat{\mathbf{y}} \\ \hat{\mathbf{z}} \end{pmatrix}. \tag{4}$$

Therefore, we find

$$\nabla_{\mathbf{r}}\mathbf{v} = \hat{\mathbf{r}}\hat{\mathbf{r}}\frac{\partial v_r}{\partial r} + \hat{\mathbf{r}}\hat{\boldsymbol{\phi}}\frac{\partial v_\phi}{\partial r} + \hat{\mathbf{r}}\hat{\mathbf{z}}\frac{\partial v_z}{\partial r} + \hat{\boldsymbol{\phi}}\hat{\mathbf{r}}\left(\frac{1}{r}\frac{\partial v_r}{\partial \phi} - \frac{v_\phi}{r}\right) + \hat{\boldsymbol{\phi}}\hat{\boldsymbol{\phi}}\left(\frac{1}{r}\frac{\partial v_\phi}{\partial \phi} + \frac{v_r}{r}\right) + \hat{\boldsymbol{\phi}}\hat{\mathbf{z}}\frac{1}{r}\frac{\partial v_r}{\partial \phi} + \hat{\mathbf{z}}\hat{\mathbf{r}}\frac{\partial v_r}{\partial z} + \hat{\mathbf{z}}\hat{\boldsymbol{\phi}}\frac{\partial v_\phi}{\partial z} + \hat{\mathbf{z}}\hat{\mathbf{z}}\frac{\partial v_z}{\partial z}. \tag{5}$$

10.B.3. Transport Coefficients

Transport coefficients are the generalized conductivities of a hydrodynamic system. Before we can determine how many transport coefficients are needed for our isotropic fluid of point particles, we must determine how many independent driving forces and currents there are in the fluid. In the last section we found that the generalized driving forces are $\nabla_{\mathbf{r}}T$ and $\nabla_{\mathbf{r}}\mathbf{v}$ and the generalized currents are $\mathbf{J}_s^D$ and $\bar{\boldsymbol{\Pi}}$. Both $\nabla_{\mathbf{r}}\mathbf{v}$ and $\bar{\boldsymbol{\Pi}}$ are nine component tensors, and each can be decomposed into three orthogonal parts. For example, we can write the dyatic, $\nabla_{\mathbf{r}}\mathbf{v}$, in the form (see the insert "Useful Mathematics—Tensors", below)

$$\nabla_{\mathbf{r}}\mathbf{v} = \tfrac{1}{3}(\nabla_{\mathbf{r}}\cdot\mathbf{v})\bar{\mathbf{U}} + [\nabla_{\mathbf{r}}\mathbf{v}]^s + [\nabla_{\mathbf{r}}\mathbf{v}]^a. \tag{10.27}$$

In Cartesian coordinates, we have

$$[\nabla_{\mathbf{r}}\mathbf{v}]_{ij}^s = \tfrac{1}{2}(\partial_j v_i + \partial_i v_j) - \tfrac{1}{3}\delta_{ij}\nabla_{\mathbf{r}}\cdot\mathbf{v} \text{ and } [\nabla_{\mathbf{r}}\mathbf{v}]_{ij}^a = \tfrac{1}{2}(\partial_j v_i - \partial_i v_j). \tag{10.28}$$

Similarly, we can write the stress tensor as

$$\bar{\boldsymbol{\Pi}} = \tfrac{1}{3}[\mathrm{Tr}(\bar{\boldsymbol{\Pi}})]\bar{\mathbf{U}} + \bar{\boldsymbol{\Pi}}^s + \bar{\boldsymbol{\Pi}}^a. \tag{10.28}$$

For an isotropic fluid of point particles or particles which interact via a spherically symmetric potential, the antisymmetric part of the stress tensor is identically zero. The antisymmetric "force," $[\nabla_{\mathbf{r}}\mathbf{v}]^a = \nabla_{\mathbf{r}}\times\mathbf{v}$, is the curl of the velocity. It is the contribution from vortex motion in the fluid. For a fluid of particles which interact via spherically symmetric forces, there is no way to couple rotational motion of the particles to vortex motion of the fluid. Therefore, there is no way to dissipate energy from the fluid flow by transforming angular momentum of the fluid into angular momentum of the particles. Thus, for a fluid of point particles, $\bar{\boldsymbol{\Pi}}^a \equiv 0$. For a fluid of particles which interact via nonspherically symmetric forces, there will be coupling between angular momentum and translational flow [4].

■ **Useful Mathematics—Tensors**

An arbitrary tensor, $\bar{\mathbf{T}}$, can be decomposed into three orthogonal components. In cartesian coordinates we can write the nine component tensor in the form

$$\bar{\mathbf{T}} = T_{xx}\hat{\mathbf{x}}\hat{\mathbf{x}} + T_{xy}\hat{\mathbf{x}}\hat{\mathbf{y}} + \cdots + T_{zz}\hat{\mathbf{z}}\hat{\mathbf{z}}. \tag{1}$$

The nine terms in Eq. (1) can be regrouped into three orthogonal quantities. We may write $\bar{\mathbf{T}}$ as

$$\bar{\mathbf{T}} = \tfrac{1}{3}\mathrm{Tr}(\hat{\mathbf{T}})\bar{\mathbf{U}} + \bar{\mathbf{T}}^s + \bar{\mathbf{T}}^a, \tag{2}$$

where $\bar{\mathbf{U}} = \hat{\mathbf{x}}\hat{\mathbf{x}} + \hat{\mathbf{y}}\hat{\mathbf{y}} + \hat{\mathbf{z}}\hat{\mathbf{z}}$ is the unit tensor and $\mathrm{Tr}(\bar{\mathbf{T}}) = T_{xx} + T_{yy} + T_{zz}$. In Eq. (2), $\bar{\mathbf{T}}^s$ is a symmetric tensor with zero trace and is defined as

$$\bar{\mathbf{T}}^s = \tfrac{1}{2}(\bar{\mathbf{T}} + \bar{\mathbf{T}}^T) - \tfrac{1}{3}\mathrm{Tr}(\bar{\mathbf{T}})\bar{\mathbf{U}}, \tag{3}$$

where $\bar{\mathbf{T}}^T$ is the transpose of $\bar{\mathbf{T}}$. The symmetric tensor may also be written in the form

$$\bar{\mathbf{T}}^s = T^s_{xx}\hat{\mathbf{x}}\hat{\mathbf{x}} + T^s_{xy}\hat{\mathbf{x}}\hat{\mathbf{y}} + \cdots + T^s_{zz}\hat{\mathbf{z}}\hat{\mathbf{z}}, \tag{4}$$

where $T^s_{xx} = \frac{2}{3}T_{xx} - \frac{1}{3}T_{yy} - \frac{1}{3}T_{zz}, T^s_{xy} = \frac{1}{2}(T_{xy} + T_{yx})$, and so on. In Eq. (2), $\bar{\mathbf{T}}^a$ is an antisymmetric tensor with zero trace and is defined as

$$\bar{\mathbf{T}}^a = \tfrac{1}{2}(\bar{\mathbf{T}} - \bar{\mathbf{T}}^T). \tag{5}$$

The antisymmetric tensor may be written in the form

$$\bar{\mathbf{T}}^a = T^a_{xx}\hat{\mathbf{x}}\hat{\mathbf{x}} + T^a_{xy}\hat{\mathbf{x}}\hat{\mathbf{y}} + \cdots + T^a_{zz}\hat{\mathbf{z}}\hat{\mathbf{z}}, \tag{6}$$

where $T^a_{xx} = 0, T^a_{xy} = \frac{1}{2}(T_{xy} - T_{yx})$, and so on.

If we introduce a second tensor, $\bar{\mathbf{V}}$, then it also can be decomposed in the manner described above. The scalar product of the two tensors can be written

$$\bar{\mathbf{T}} : \bar{\mathbf{V}} = \tfrac{1}{3}[\mathrm{Tr}(\bar{\mathbf{T}})][\mathrm{Tr}(\bar{\mathbf{V}})] + \bar{\mathbf{T}}^s : \bar{\mathbf{V}}^s + \bar{\mathbf{T}}^a : \bar{\mathbf{V}}^a. \tag{7}$$

One can also show that

$$\bar{\mathbf{U}} : \bar{\mathbf{T}}^s = \bar{\mathbf{U}} : \bar{\mathbf{T}}^a = \bar{\mathbf{T}}^s : \bar{\mathbf{V}}^a = 0. \tag{8}$$

Thus, the tensor, $\bar{\mathbf{T}}$, can be decomposed into three independent orthogonal components.

In order to write "Ohm's law" for the fluid, we shall make use of Curie's principle, which states that *in an isotropic fluid, a given force cannot drive a current of a different tensor character.* Let us note that there are four forces in the fluid, each with a different tensor character. They are $\nabla_{\mathbf{r}}T$, a polar vector; $[\nabla_{\mathbf{r}}\mathbf{v}]^s$, a symmetric tensor; $\nabla_{\mathbf{r}}\cdot\mathbf{v}$, a scalar: and $[\nabla_{\mathbf{r}}\mathbf{v}]^a = \nabla_{\mathbf{r}}\times\mathbf{v}$, an axial vector. (Polar vectors and axial vectors behave differently under inversion through the origin of coordinates. Polar vectors change their sign. Axial vectors do not.) Since the antisymmetric part of the stress tensor is zero, the axial vector cannot drive a current. Thus, an isotropic fluid of point particles has three generalized forces. They are $\nabla_{\mathbf{r}}T, \nabla_{\mathbf{r}}\cdot\mathbf{v}$, and $[\nabla_{\mathbf{r}}\mathbf{v}]^s$. They drive the generalized currents, $\mathbf{J}_s^D, \Pi \equiv \frac{1}{3}\mathrm{Tr}(\bar{\boldsymbol{\Pi}})$, and $\bar{\boldsymbol{\Pi}}^s$. Since they are all of different tensor character, we find the following generalization of Ohm's law for the fluid:

$$\mathbf{J}_s^D = -\frac{K}{T}\nabla_{\mathbf{r}}T, \tag{10.29}$$

where K is the *coefficient of thermal conductivity,*

$$\bar{\boldsymbol{\Pi}}^s = -2\eta[\nabla_{\mathbf{r}}\mathbf{v}]^s, \tag{10.30}$$

where η is the *coefficient of shear viscosity,* and

$$\Pi = -\zeta\nabla_{\mathbf{r}}\cdot\mathbf{v}, \tag{10.31}$$

where ζ is the *coefficient of bulk viscosity.*

If we use Eqs. (10.29)–(10.31), the entropy production takes the form

$$\sigma_s = \frac{K}{T^2}|\nabla_{\mathbf{r}}T|^2 + 2\frac{\eta}{T}|[\nabla_{\mathbf{r}}\mathbf{v}]^s|^2 + \frac{\zeta}{T}|\nabla_{\mathbf{r}}\cdot\mathbf{v}|^2, \tag{10.32}$$

where $|\nabla_{\mathbf{r}}T|^2 = (\nabla_{\mathbf{r}}T)\cdot(\nabla_{\mathbf{r}}T)$ and $|[\nabla_{\mathbf{r}}\mathbf{v}]^s|^2 = [\nabla_{\mathbf{r}}\mathbf{v}]^s : [\nabla_{\mathbf{r}}\mathbf{v}]^s$. The mass balance, momentum balance, and entropy balance equations take the form

$$\frac{\partial\rho}{\partial t} + \nabla_{\mathbf{r}}\cdot(\rho\mathbf{v}) = 0, \tag{10.33}$$

$$\frac{\partial\rho\mathbf{v}}{\partial t} + \nabla_{\mathbf{r}}\cdot(\rho\mathbf{v}\mathbf{v}) = -\nabla_{\mathbf{r}}P + \eta\nabla_{\mathbf{r}}^2,\mathbf{v} + (\zeta + \tfrac{1}{3}\eta)\nabla_{\mathbf{r}}(\nabla_{\mathbf{r}}\cdot\mathbf{v}). \tag{10.34}$$

and

$$\frac{\partial\rho s}{\partial t} + \nabla_{\mathbf{r}}\cdot(\rho s\mathbf{v} + \mathbf{J}_s^D) = \frac{K}{T^2}|\nabla_{\mathbf{r}}T|^2 + 2\frac{\eta}{T}|[\nabla_{\mathbf{r}},\mathbf{v}]^s|^2 + \frac{\zeta}{T}(\nabla_{\mathbf{r}}\cdot\mathbf{v})^2. \tag{10.35}$$

respectively. The derivation of the specific form of Eq. (10.34) is given in Exercise (10.2). Equations (10.33)–(10.35) collectively are called the *Navier–*

Stokes equations or hydrodynamic equations. They describe the hydrodynamic behavior of an isotropic fluid of point particles. In the next section we describe how to solve the linearized version of these equations. The linearized hydrodynamic equations describe the behavior of the fluid if it is only slightly displaced from absolute equilibrium. They are also useful in describing the behavior of fluctuations for a fluid in equilibrium.

■ **EXERCISE 10.2.** Prove that

$$\nabla_{\mathbf{r}} \cdot \bar{\mathbf{\Pi}} = -\eta \nabla_{\mathbf{r}}^2 \mathbf{v} - (\zeta + \tfrac{1}{3}\eta) \nabla_{\mathbf{r}} (\nabla_{\mathbf{r}} \cdot \mathbf{v})$$

if $\bar{\mathbf{\Pi}}^s = -2\eta[\nabla_{\mathbf{r}}\mathbf{v}]^s$ and $\Pi = -\zeta(\nabla_{\mathbf{r}} \cdot \mathbf{v})$ with $\bar{\mathbf{\Pi}} = \Pi\bar{\mathbf{U}} + \bar{\mathbf{\Pi}}^s$. Note that $\bar{\mathbf{U}}$ is the unit tensor.

Answer: The stress tensor is $\bar{\mathbf{\Pi}} = -2\eta[\nabla_{\mathbf{r}}\mathbf{v}]^s - \zeta\bar{\mathbf{U}}(\nabla_{\mathbf{r}} \cdot \mathbf{v})$, where

$$[\nabla_{\mathbf{r}}\mathbf{v}]^s_{ij} = \tfrac{1}{2}(\partial_j v_i + \partial_i v_j) - \tfrac{1}{3}\delta_{ij} \nabla_{\mathbf{r}} \cdot \mathbf{v}. \tag{1}$$

The ijth component of the stress tensor is

$$\bar{\Pi}_{ij} = -\eta(\partial_j v_i + \partial_i v_j) + (\tfrac{2}{3}\eta - \zeta)\delta_{ij} \nabla_{\mathbf{r}} \cdot \mathbf{v}. \tag{2}$$

Then

$$\begin{aligned} (\nabla_{\mathbf{r}} \cdot \bar{\mathbf{\Pi}})_{ij} &= -\partial_i[\eta(\partial_j v_i + \partial_i v_j) - (\tfrac{2}{3}\eta - \zeta)\delta_{ij} \nabla_{\mathbf{r}} \cdot \mathbf{v}] \\ &= -[\eta\partial_j(\partial_i v_i) + \eta\partial_i^2 v_j - (\tfrac{2}{3}\eta - \zeta)\partial_j \nabla_{\mathbf{r}} \cdot \mathbf{v}] \\ &= -\eta\partial_i^2 v_j - (\tfrac{1}{3}\eta + \zeta)\partial_j \nabla_{\mathbf{r}} \cdot \mathbf{v}. \end{aligned} \tag{3}$$

Thus

$$\nabla_{\mathbf{r}} \cdot \bar{\mathbf{\Pi}} = -\eta \nabla_{\mathbf{r}}^2 \mathbf{v} - (\zeta + \tfrac{1}{3}\eta) \nabla_{\mathbf{r}} (\nabla_{\mathbf{r}} \cdot \mathbf{v}). \tag{4}$$

10.C. LINEARIZED HYDRODYNAMIC EQUATIONS [5]

The hydrodynamic equations, (10.33)–(10.35), depend nonlinearly on the thermodynamic variables and the average velocity. This makes them very difficult to solve and one generally must resort to numerical methods for solving them. However, if we restrict ourselves to the neighborhood of absolute equilibrium, then we can look at the behavior of small deviations from the equilibrium state, and it is possible to linearize the hydrodynamic equations.

10.C.1. Linearization of the Hydrodynamic Equations

Let ρ_0, T_0, s_0, and P_0, denote the equilibrium mass density, temperature, the specific entropy, and pressure, respectively. Then close to the equilibrium state, we can write $\rho(\mathbf{r},t) = \rho_0 + \Delta\rho(\mathbf{r},t), T = T_0 + \Delta T(\mathbf{r},t), s(\mathbf{r},t) = s_0 + \Delta s(\mathbf{r},t)$, and $P(\mathbf{r},t) = P_0 + \Delta P(\mathbf{r},t)$, respectively. The average velocity, $\mathbf{v}(\mathbf{r},t)$, is zero at equilibrium, so it is already first order in deviation from equilibrium. If we now substitute these expansions into the hydrodynamic equations (10.33)–(10.35), and only retain terms to first order in deviations from equilibrium, we find

$$\frac{\partial \Delta\rho}{\partial t} + \rho_0 \nabla_{\mathbf{r}} \cdot \mathbf{v} = 0, \tag{10.36}$$

$$\rho_0 \frac{\partial \mathbf{v}}{\partial t} = -\nabla_{\mathbf{r}} \Delta P + \eta \nabla_{\mathbf{r}}^2 \mathbf{v} + (\zeta + \tfrac{1}{3}\eta) \nabla_{\mathbf{r}} (\nabla_{\mathbf{r}} \cdot \mathbf{v}), \tag{10.37}$$

and

$$\rho_0 \frac{\partial \Delta s}{\partial t} = \frac{K}{T_0} \nabla_{\mathbf{r}}^2 \Delta T. \tag{10.38}$$

To obtain the final form of Eq. (10.38), we have used Eq. (10.36) to eliminate two terms and we have used Eq. (10.29).

The momentum balance equation, (10.37), is actually three equations since the velocity has three components. Thus, we have five equations but we have seven unknowns, $\Delta\rho, \Delta s, \Delta T, \Delta P, \mathbf{v}_x, \mathbf{v}_y$, and $\mathbf{v}_z$. In order to solve these equations, we can use thermodynamics to reduce the number of unknowns to five since the quantities $\Delta\rho, \Delta s, \Delta T$, and ΔP are related by thermodynamic equations. We can choose two of them to be independent and expand the other two in terms of them. The choice of the two independent variables depends on convenience for the problem of interest.

Let us choose $\Delta\rho$ and ΔT to be independent. Then we can write

$$\Delta s(\mathbf{r},t) = \left(\frac{\partial s}{\partial \rho}\right)_T^0 \Delta\rho(\mathbf{r},t) + \left(\frac{\partial s}{\partial T}\right)_\rho^0 \Delta T(\mathbf{r},t) \tag{10.39}$$

and

$$\Delta P(\mathbf{r},t) = \left(\frac{\partial P}{\partial \rho}\right)_T^0 \Delta\rho(\mathbf{r},t) + \left(\frac{\partial P}{\partial T}\right)_\rho^0 \Delta T(\mathbf{r},t). \tag{10.40}$$

The linearized hydrodynamic equations take the form

$$\frac{\partial \Delta\rho}{\partial t} + \rho_0 \nabla_{\mathbf{r}} \cdot \mathbf{v} = 0, \tag{10.41}$$

$$\rho_0 \frac{\partial \mathbf{v}}{\partial t} = -\left(\frac{\partial P}{\partial \rho}\right)_T^0 \nabla_{\mathbf{r}} \Delta\rho - \left(\frac{\partial P}{\partial T}\right)_\rho^0 \nabla_{\mathbf{r}} \Delta T + \eta \nabla_{\mathbf{r}}^2 \mathbf{v} + (\zeta + \tfrac{1}{3}\eta) \nabla_{\mathbf{r}} (\nabla_{\mathbf{r}} \cdot \mathbf{v}), \tag{10.42}$$

and

$$\rho_0 \left(\frac{\partial s}{\partial \rho}\right)_T^0 \frac{\partial \Delta\rho}{\partial t} + \rho_0 \left(\frac{\partial s}{\partial T}\right)_\rho^0 \frac{\partial \Delta T}{\partial t} = \frac{K}{T_0} \nabla_{\mathbf{r}}^2 \Delta T. \tag{10.43}$$

Equations (10.41)–(10.43) form a set of coupled equations which describe the behavior of small deviations from absolute equilibrium.

It is useful to consider the behavior of the linearized hydrodynamic equations for an ideal fluid in which the transport coefficients are $K = 0, \eta = 0$, and $\zeta = 0$. Then Eq. (10.43) gives

$$\frac{\partial \Delta T}{\partial t} = -\left(\frac{\partial T}{\partial s}\right)_\rho^0 \left(\frac{\partial s}{\partial \rho}\right)_T^0 \frac{\partial \Delta\rho}{\partial t} = \left(\frac{\partial T}{\partial \rho}\right)_s^0 \frac{\partial \Delta\rho}{\partial t}, \tag{10.44}$$

and Eq. (10.42) reduces to

$$\rho_0 \frac{\partial \mathbf{v}}{\partial t} = -\left(\frac{\partial P}{\partial \rho}\right)_T^0 \nabla_{\mathbf{r}} \Delta\rho - \left(\frac{\partial P}{\partial T}\right)_\rho^0 \nabla_{\mathbf{r}} \Delta T. \tag{10.45}$$

If we now take the time derivative of Eq. (10.45) and use Eqs. (10.41) and (10.44), we obtain

$$\frac{\partial^2 \mathbf{v}}{\partial t^2} - \left(\frac{\partial P}{\partial \rho}\right)_s^0 \nabla_{\mathbf{r}}^2 \mathbf{v} = 0, \tag{10.46}$$

where we have used the fact that $(\partial P/\partial \rho)_s^0 = (\partial P/\partial \rho)_T^0 + (\partial P/\partial T)_\rho^0 (\partial T/\partial \rho)_s^0$. Equation (10.46) is the wave equation for longitudinal velocity variations. It describes the behavior of sound waves with speed, $c = \sqrt{(\partial P/\partial \rho)_s^0}$, in the ideal fluid. Thus, an ideal fluid supports sound waves whose speed is determined by the adiabatic compressibility of the fluid.

In a dissipative fluid, sound modes can be damped. We will now determine the dispersion relations for normal modes of the dissipative fluid. As a first step, let us Fourier transform the space dependence of the linearized

hydrodynamic equaions. We let $\Delta\rho(\mathbf{r},t) = (1/2\pi)^3 \int d\mathbf{k}\rho_{\mathbf{k}}(t)e^{-i\mathbf{k}\cdot\mathbf{r}}$ so that $\rho_{\mathbf{k}}(t) = \int d\mathbf{r}\Delta\rho(\mathbf{r},t)e^{i\mathbf{k}\cdot\mathbf{r}}$. Similarly, $\mathbf{v}(\mathbf{r},t) = (1/2\pi)^3 \int d\mathbf{k}\mathbf{v}_{\mathbf{k}}(t)e^{-i\mathbf{k}\cdot\mathbf{r}}$ and $T(\mathbf{r},t) = (1/2\pi)^3 \int d\mathbf{k}T_{\mathbf{k}}(t)e^{-i\mathbf{k}\cdot\mathbf{r}}$. If we substitute these expressions into Eq. (10.41)–(10.43), we find

$$\frac{\partial\rho_{\mathbf{k}}}{\partial t} - i\rho_0\mathbf{k}\cdot\mathbf{v}_{\mathbf{k}} = 0, \tag{10.47}$$

$$\rho_0\frac{\partial\mathbf{v}_{\mathbf{k}}}{\partial t} = i\left(\frac{\partial P}{\partial\rho}\right)_T^0 \mathbf{k}\rho_{\mathbf{k}} + i\left(\frac{\partial P}{\partial T}\right)_\rho^0 \mathbf{k}T_{\mathbf{k}} - \eta k^2\mathbf{v}_{\mathbf{k}} - (\zeta + \tfrac{1}{3}\eta)\mathbf{k}(\mathbf{k}\cdot\mathbf{v}_{\mathbf{k}}), \tag{10.48}$$

and

$$\rho_0\left(\frac{\partial s}{\partial\rho}\right)_T^0 \frac{\partial\rho_{\mathbf{k}}}{\partial t} + \rho_0\left(\frac{\partial s}{\partial T}\right)_\rho^0 \frac{\partial T_{\mathbf{k}}}{\partial t} = -\frac{K}{T_0}k^2T_{\mathbf{k}}, \tag{10.49}$$

where $\rho_{\mathbf{k}} = \rho_{\mathbf{k}}(t), T_{\mathbf{k}} = T_{\mathbf{k}}(t)$, and $\mathbf{v}_{\mathbf{k}} = \mathbf{v}_{\mathbf{k}}(t)$.

We can simplify Eqs. (10.47)–(10.49) still further. Let us divide the velocity into longitudinal (parallel to $\mathbf{k}$) and transverse (perpendicular to $\mathbf{k}$) components:

$$\mathbf{v}_{\mathbf{k}}(t) = v_{\mathbf{k}}^{\parallel}(t)\hat{\mathbf{k}} + \mathbf{v}_{\mathbf{k}}^{\perp}(t), \tag{10.50}$$

where $\mathbf{k}\cdot\mathbf{v}_{\mathbf{k}}^{\perp}(t) \equiv 0$ and $\mathbf{k}\cdot\mathbf{v}_{\mathbf{k}}(t) \equiv \mathbf{k}v_{\mathbf{k}}^{\parallel}(t)$. The component $\mathbf{k}v_{\mathbf{k}}^{\parallel}(t)$ is the amplitude of a longitudinal velocity variation which has wavelength $\lambda = 2\pi/k$. These are velocity variations in the direction $\mathbf{k}$. The velocity vector, $\mathbf{v}_{\mathbf{k}}^{\perp}(t)$, is a two-component vector which describes velocity variations with wavelength $\lambda = 2\pi/k$, but transverse (perpendicular) to the direction of $\mathbf{k}$.

The transverse and longitudinal components of the average velocity decouple in the linearized hydrodynamic equations. They evolve according to different equations of motion. From Eqs. (10.47)–(10.49) and (10.50), we can write

$$\frac{\partial\rho_{\mathbf{k}}}{\partial t} - i\rho_0 k v_{\mathbf{k}}^{\parallel} = 0, \tag{10.51}$$

$$\rho_0\frac{\partial v_{\mathbf{k}}^{\parallel}}{\partial t} = ik\left(\frac{\partial P}{\partial\rho}\right)_T^0 \rho_{\mathbf{k}} + ik\left(\frac{\partial P}{\partial T}\right)_\rho^0 \mathrm{T}_{\mathbf{k}} - (\zeta + \tfrac{4}{3}\eta)\mathrm{k}^2\mathrm{v}_{\mathbf{k}}^{\parallel}, \tag{10.52}$$

$$\rho_0\left(\frac{\partial s}{\partial\rho}\right)_T^0 \frac{\partial\rho_{\mathbf{k}}}{\partial t} + \rho_0\left(\frac{\partial s}{\partial T}\right)_\rho^0 \frac{\partial T_{\mathbf{k}}}{\partial t} = -\frac{K}{T_0}k^2T_{\mathbf{k}}, \tag{10.53}$$

and

$$\rho_0\frac{\partial\mathbf{v}_{\mathbf{k}}^{\perp}}{\partial t} = -\eta k^2\mathbf{v}_{\mathbf{k}}^{\perp}. \tag{10.54}$$

Equations (10.51)–(10.53) govern the evolution of the coupled heat and sound modes (sound consists of longitudinal oscillations of the fluid). Equation (10.54) governs the evolution of shear modes (transverse velocity oscillations).

We want to solve the hydrodynamic equations, given some set of initial conditions $\rho_{\mathbf{k}}(0), T_{\mathbf{k}}(0)$, and $\mathbf{v}_{\mathbf{k}}(0)$. It is useful to introduce the Laplace transform

$$\tilde{\rho}_{\mathbf{k}}(z) = \int_0^\infty dt \rho_{\mathbf{k}}(t) e^{-zt} \quad \text{and} \quad \rho_{\mathbf{k}}(t) = \frac{1}{2\pi i} \int_{\delta - i\infty}^{\delta + i\infty} dz \tilde{\rho}_{\mathbf{k}}(z) e^{zt}, \tag{10.55}$$

where δ is a positive number. The Laplace transform of the time derivative is

$$\int_0^\infty dt \frac{\partial \rho_{\mathbf{k}}(t)}{\partial t} e^{-zt} = -\rho_{\mathbf{k}}(0) + z\tilde{\rho}_{\mathbf{k}}(z). \tag{10.56}$$

Similar Laplace transforms can be written for the other variables.

Let us now Laplace transform Eqs. (10.51)–(10.54). We find

$$z\tilde{\rho}_{\mathbf{k}}(z) - i\rho_0 k \tilde{v}_{\mathbf{k}}^{\parallel}(z) = \rho_{\mathbf{k}}(0), \tag{10.57}$$

$$\rho_0 z \tilde{v}_{\mathbf{k}}^{\parallel}(z) - ik \left(\frac{\partial P}{\partial \rho}\right)_T^0 \tilde{\rho}_{\mathbf{k}}(z) - ik \left(\frac{\partial P}{\partial T}\right)_\rho^0 \tilde{T}_{\mathbf{k}}(z) + (\zeta + \tfrac{4}{3}\eta) k^2 \tilde{v}_{\mathbf{k}}^{\parallel}(z) = \rho_0 v_{\mathbf{k}}^{\parallel}(0), \tag{10.58}$$

$$\rho_0 z \left(\frac{\partial s}{\partial \rho}\right)_T^0 \tilde{\rho}_{\mathbf{k}}(z) + \rho_0 z \left(\frac{\partial s}{\partial T}\right)_\rho^0 \tilde{T}_{\mathbf{k}}(z) + \frac{K}{T_0} k^2 \tilde{T}_{\mathbf{k}}(z) = \rho_0 \left(\frac{\partial s}{\partial \rho}\right)_T^0 \rho_{\mathbf{k}}(0) + \rho_0 \left(\frac{\partial s}{\partial T}\right)_\rho^0 T_{\mathbf{k}}(0), \tag{10.59}$$

and

$$\rho_0 z \tilde{\mathbf{v}}_{\mathbf{k}}^{\perp}(z) + \eta k^2 \tilde{\mathbf{v}}_{\mathbf{k}}^{\perp}(z) = \rho_0 \mathbf{v}_{\mathbf{k}}^{\perp}(0). \tag{10.60}$$

Let us now simplify these equations. First we note the following thermodynamic identities

$$\left(\frac{\partial P}{\partial \rho}\right)_T = \frac{c_0^2}{\gamma} \quad \text{and} \quad \left(\frac{\partial P}{\partial T}\right)_\rho = \frac{\rho_0 c_0^2 \alpha_P}{\gamma} = \frac{\rho_0}{T_0} \frac{c_P - c_\rho}{\alpha_P}, \tag{10.61}$$

where $\tilde{c}_\rho = T_0 (\partial s/\partial T)_\rho$ and $\tilde{c}_P = T_0 (\partial s/\partial T)_P$ are the specific heats at constant density and pressure, respectively, $c_0 = \sqrt{(\partial P/\partial \rho)_s}$ is the speed of sound, $\alpha_P = -(1/\rho_0)(\partial \rho/\partial T)_P$ is the thermal expansivity, and $\gamma = \tilde{c}_P/\tilde{c}_\rho$. Note the

Maxwell relation, $(\partial s/\partial \rho)_T = -(1/\rho_0^2)(\partial P/\partial T)_\rho$. Also, let us now introduce the *longitudinal kinetic viscosity*, ν_l, the *transverse kinetic viscosity*, ν_t, and the *thermal diffusivity*, χ, which are defined

$$\nu_l = \frac{1}{\rho_0}\left(\zeta + \frac{4}{3}\eta\right), \quad \nu_t = \frac{\eta}{\rho_0}, \quad \text{and} \quad \chi = \frac{K}{\rho_0 \tilde{c}_P}, \tag{10.62}$$

respectively, Then Eqs. (10.57)–(10.60) take the form

$$z\tilde{\rho}_k(z) - i\rho_0 k\tilde{v}_{\mathbf{k}}^{\parallel}(z) = \rho_{\mathbf{k}}(0), \tag{10.63}$$

$$(z + \nu_l k^2)\tilde{v}_{\mathbf{k}}^{\parallel}(z) - ik\frac{c_0^2}{\gamma\rho_0}\tilde{\rho}_{\mathbf{k}}(z) - ik\frac{c_0^2\alpha_P}{\gamma}\tilde{T}_{\mathbf{k}}(z) = v_{\mathbf{k}}^{\parallel}(0), \tag{10.64}$$

$$-z\frac{c_0^2\alpha_P}{\rho_0\gamma}\tilde{\rho}_{\mathbf{k}}(z) + \frac{c_\rho}{T_0}(z + \gamma\chi k^2)\tilde{T}_{\mathbf{k}}(z) = -\frac{c_0^2\alpha_P}{\rho_0\gamma}\rho_{\mathbf{k}}(0) + \frac{\tilde{c}_\rho}{T_0}T_{\mathbf{k}}(0), \tag{10.65}$$

and

$$(z + \nu_t k^2)\tilde{\mathbf{v}}_{\mathbf{k}}^{\perp}(z) = \mathbf{v}_{\mathbf{k}}^{\perp}(0). \tag{10.66}$$

Solving the linearized hydrodynamic equations is now simply a matter of doing some algebra. Since the transverse modes completely decouple from the longitudinal modes, we will consider them separately below.

10.C.2. Transverse Hydrodynamic Modes

Let us assume that the Fourier components of the transverse velocity at time $t = 0$ are known to be $\mathbf{v}_{\mathbf{k}}^{\perp}(0)$. Then from Eq. (10.66) we have

$$\tilde{\mathbf{v}}_{\mathbf{k}}^{\perp}(z) = \frac{\mathbf{v}_{\mathbf{k}}^{\perp}(0)}{z + \nu_t k^2}. \tag{10.67}$$

The Fourier components of the transverse velocity at time t are then

$$\mathbf{v}_{\mathbf{k}}^{\perp}(t) = \frac{1}{2\pi i}\int_{\delta - i\infty}^{\delta + i\infty} dz \frac{\mathbf{v}_{\mathbf{k}}^{\perp}(0)e^{zt}}{z + \nu_t k^2} = \mathbf{v}_{\mathbf{k}}^{\perp}(0)e^{-\nu_t k^2 t}. \tag{10.68}$$

In order to obtain the final result in Eq. (10.68), we have changed the integration along the line $z = \delta + iy$ (with y varying from $-\infty$ to $+\infty$) to a contour integration with the contour shown in Fig. 10.1. We see that any transverse velocity variations in the fluid decay in time and cannot propagate. The short-wavelength disturbances decay faster than the long-wavelength disturbances. This wavelength dependence of the decay time is the signature of a hydrodynamic mode.

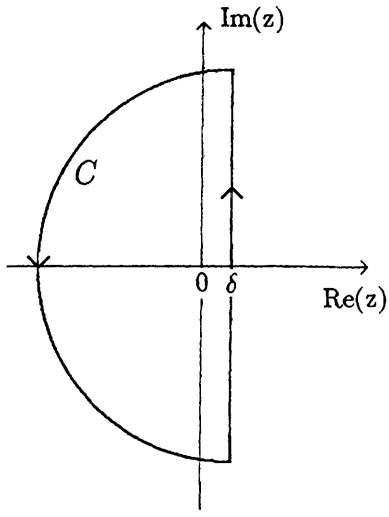


Fig. 10.1. The contour, C, used to integrate Eq. (10.68).

10.C.3. Longitudinal Hydrodynamic Modes

The time evolution of the longitudinal modes can be determined from Eqs. (10.63)–(10.65). Let us first write them in the following matrix from:

$$\begin{pmatrix} z & -i\rho_0 k & 0 \\ -\frac{ikc_0^2}{\gamma\rho_0} & [z+\nu_l k^2] & -\frac{ikc_0^2\alpha_P}{\gamma} \\ -z\frac{c_0^2\alpha_P}{\rho_0\gamma} & 0 & \frac{\tilde{c}_\rho}{T_0}[z+\gamma\chi k^2] \end{pmatrix} \begin{pmatrix} \tilde{\rho}_{\mathbf{k}}(z) \\ \tilde{v}_{\mathbf{k}}^{\parallel}(z) \\ \tilde{T}_{\mathbf{k}}(z) \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ -\frac{c_0^2\alpha_P}{\rho_0\gamma} & 0 & \frac{c_\rho}{T_0} \end{pmatrix} \begin{pmatrix} \Delta\rho_{\mathbf{k}}(0) \\ v_{\mathbf{k}}^{\parallel}(0) \\ \Delta T_{\mathbf{k}}(0) \end{pmatrix}. \tag{10.69}$$

If we multiply by the inverse of the matrix on the left in Eq. (10.69), we obtain

$$\begin{pmatrix} \tilde{\rho}_{\mathbf{k}}(z) \\ \tilde{v}_{\mathbf{k}}^{\parallel}(z) \\ \tilde{T}_{\mathbf{k}}(z) \end{pmatrix} = \frac{\bar{\mathbf{M}}}{D(\mathbf{k},z)} \begin{pmatrix} \Delta\rho_{\mathbf{k}}(0) \\ v_{\mathbf{k}}(0) \\ -\frac{c_0^2\alpha_P}{\rho_0\gamma}\Delta\rho_{\mathbf{k}}(0) + \frac{\tilde{c}_\rho}{T_0}\Delta T_{\mathbf{k}}(0) \end{pmatrix}, \tag{10.70}$$

where $D(\mathbf{k},z)$ is the determinant of the 3×3 matrix on the left in Eq. (10.69), and $\bar{\mathbf{M}}/D(\mathbf{k},z)$ is its inverse. The determinant $D(\mathbf{k},z)$, can be written

$$D(\mathbf{k},z) = \frac{\tilde{c}_\rho}{T_0}[z^3 + z^2(\nu_l+\gamma\chi)k^2 + z(\gamma\chi\nu_l k^4 + c_0^2 k^2) + c_0^2\chi k^4]. \tag{10.71}$$

The matrix, $\bar{\mathbf{M}}$, which appears in Eq. (10.70) can be written

$$\bar{\mathbf{M}} = \begin{pmatrix} \frac{\tilde{c}_\rho}{T_0}(z+\nu_l k^2)(z+\gamma\chi k^2) & \frac{ik\rho_0\tilde{c}_\rho}{T_0}(z+\gamma\chi k^2) & -\rho_0\alpha_P c_0^2 k^2/\gamma \\ \frac{ik\tilde{c}_\rho c_0^2}{\rho_0 T_0}(z+\chi k^2) & \frac{\tilde{c}_\rho}{T_0}z(z+\gamma\chi k^2) & ikz\alpha_P c_0^2/\gamma \\ \frac{c_0^2\alpha_P}{\rho_0\gamma}z(z+\nu_l k^2) & ikz\frac{c_0^2\alpha_P}{\gamma} & z^2+z\nu_l k^2+k^2\frac{c_0^2}{\gamma} \end{pmatrix}. \tag{10.72}$$

Before we use Eqs.(10.70) and (10.72) to solve the equations of motion, it is useful to look more closely at the determinant, Eq. (10.71).

To second order in k, the three roots of the equation $D(\mathbf{k}, z) = 0$, are given by $z_1 = -\chi k^2$ and $z_\pm = \pm ic_0 k - \frac{1}{2}k^2[\nu_l + \chi(\gamma - 1)]$. Therefore, for long-wavelength disturbances (small k), $D(\mathbf{k}, z)$ is approximately given by

$$D(\mathbf{k}, z) \approx \frac{\tilde{c}_\rho}{T_0}(z+\chi k^2)(z+ikc_0+\Gamma k^2)(z-ikc_0+\Gamma k^2), \tag{10.73}$$

where $\Gamma = \frac{1}{2}[\nu_l + \chi(\gamma - 1)]$ and we have neglected terms of higher order in k. This approximate expression for the roots of the equation $D(\mathbf{k}, z) = 0$ must be used with care. There are cases when the exact expressions for the roots must be kept.

The dissipative fluid has three longitudinal normal modes. The time evolution of the density, longitudinal velocity, and temperature variations each contain contributions from all three longitudinal normal modes. One normal mode is primarily a heat mode and has a decay rate given by z_1. The other two normal modes are primarily damped sound modes. The sound modes can propagate but eventually will be damped out by dissipative processes in the fluid, both viscous and thermal.

The time evolution of the density, longitudinal velocity, and temperature variations can be obtained by performing the following integration:

$$\begin{pmatrix} \rho_{\mathbf{k}}(t) \\ v_{\mathbf{k}}^{\parallel}(t) \\ T_k(t) \end{pmatrix} = \frac{1}{2\pi i}\int_{\varepsilon-i\infty}^{\varepsilon+i\infty} dz e^{zt} \begin{pmatrix} \rho_{\mathbf{k}}(z) \\ v_{\mathbf{k}}^{\parallel}(z) \\ T_{\mathbf{k}}(z) \end{pmatrix}. \tag{10.74}$$

In Exercise 10.3 we obtain the time dependence of Fourier components of the density under special conditions.

■ **EXERCISE 10.3.** Compute $\rho_{\mathbf{k}}(t)$ assuming that at time $t = 0$ we have $\rho_{\mathbf{k}}(0) \neq 0$, $v_{\mathbf{k}}^{\parallel}(0) = 0$, and $T_{\mathbf{k}}(0) = 0$. Write the amplitude of the evolution to lowest order in k.

Answer: From Section 10.C.3 we can write

$$\tilde{\rho}_{\mathbf{k}}(z) = \left(\frac{[z + \nu_l k^2][z + \gamma\chi k^2] + c_0^2 k^2 (\gamma - 1)/\gamma}{[z + \nu_l k^2][z + ic_0 k + \Gamma k^2][z - ic_0 k + \Gamma k^2]} \right) \rho_{\mathbf{k}}(0). \tag{1}$$

The density at time t is

$$\rho_{\mathbf{k}}(t) = \frac{1}{2\pi i} \int_{\delta - i\infty}^{\delta + i\infty} dz \tilde{\rho}_{\mathbf{k}}(z) e^{zt}. \tag{2}$$

If we retain terms in the amplitudes to zeroth order in k, Eq. (2) reduces to

$$\rho_{\mathbf{k}}(t) \approx \left[\left(1 - \frac{1}{\gamma} \right) e^{-\chi k^2 t} + \frac{1}{\gamma} e^{-\Gamma k^2 t} \cos(c_0 k t) \right] \rho_{\mathbf{k}}(0). \tag{3}$$

Thus, the initial disturbance in the density is eventually damped out. The long-wavelength components are the last to go.

10.D. DYNAMIC EQUILIBRIUM FLUCTUATIONS AND TRANSPORT PROCESSES

Because matter is discrete, systems in equilibrium will undergo fluctuations about their equilibrium states. The hydrodynamic equations govern the dynamics of the long-wavelength and low-frequency components of those fluctuations, and they determine the behavior of dynamic equilibrium correlation functions and dynamic structure factors. Onsager was able to use this fact, along with the reversibility of dynamical laws on the microscopic level, to show that certain relations exist between transport coefficients describing coupled transport processes. Hydrodynamic equations (equations which describe the long-wavelength, low-frequency dynamics) can be obtained for a large variety of systems, including dilute gases, liquids, solids, liquid crystals, superfluids, and chemically reacting systems. For complicated systems, transport processes are often coupled. For example, in a multicomponent system, it is possible to have a temperature gradient drive a particle current and a concentration gradient drive a heat current. Some complicated systems can have as many as 10 or 20 (or more) transport coefficients to describe the decay to equilibrium from the hydrodynamic regime. Onsagar's relations are of immense importance because they enable us to link seemingly independent transport processes and thereby reduce the number of experiments that must be performed in order to measure all the transport coefficients.

Once an expression has been obtained for the dynamic correlation function of an equillibrium system, we can use the Weiner–Khintchine theorem to derive the dynamic structure function which gives the power spectrum of the

equilibrium fluctuations. The power spectrum is the quantity which is most often measured in experiments.

10.D.1. Onsager's Relations [6, 7]

Systems which are out of equilibrium generally return to the equilibrium state through a variety of transport processes which may or may not be coupled to one another. Onsagar, without any reference to a particular physical system, was able to derive relations between the transport coefficients for coupled transport processes. These relations are a general consequence of the invariance under time reversal of Hamiltonian dynamic. There are essentially two aspects of the proof: (a) It uses the time-reversal invariance of mechanical equations of motion at the microscopic level (Newtons's equations) to determine properties of time-dependent correlation functions, and (b) it assumes that fluctuations about the equilibrium state decay, on the average, according to the same laws that govern the decay of macroscopic deviations from equilibrium—that is, the hydrodynamic equations.

10.D.1.1. Microscopic Reversibility

The first step in deriving Onsager's relations is to show that the time-reversal in variance of Hamiltonian dynamics requires that the time-dependent correlation functions of macroscopic fluctuations, $\boldsymbol{\alpha} = (\alpha_1, \alpha_2, \ldots, \alpha_n)$, obey the relations

$$\langle \alpha_i \alpha_j(\tau) \rangle = \langle \alpha_i(\tau) \alpha_j \rangle. \tag{10.75}$$

The quantities $\alpha_i = A_i - A_i^0$ and $\alpha_j = A_j - A_j^0$ are the fluctuations about the equilibrium values of the state variables A_i and A_j (cf. Section 7.C). Equation (10.75) tells us that the correlation between a fluctuation α_i at time $t = 0$ and a fluctuation α_j at time $t = \tau$ is the same as that of a fluctuation α_j at time $t = 0$ and a fluctuation α_i at time $t = \tau$. The quantities α_i and α_j can correspond to fluctuations in the same state variables at different points in space. Thus, Eq. (10.75) can also be turned into an equation relating correlations between space- and time-dependent fluctuations.

To establish Eq. (10.75), we note that the correlation matrix $\langle \boldsymbol{\alpha}\boldsymbol{\alpha}(\tau) \rangle$ can be written

$$\langle \boldsymbol{\alpha}\boldsymbol{\alpha}(\tau) \rangle \equiv \int\int d\boldsymbol{\alpha} d\boldsymbol{\alpha}' \boldsymbol{\alpha}\boldsymbol{\alpha}' f(\boldsymbol{\alpha}) P(\boldsymbol{\alpha}|\boldsymbol{\alpha}', \tau) \tag{10.76}$$

where $P(\boldsymbol{\alpha}|\boldsymbol{\alpha}', \tau)$ is the conditional probability that the fluctuation has value $\boldsymbol{\alpha}'$ at time $t = \tau$, given that it had value $\boldsymbol{\alpha}$ at time $t = 0$ (we are now using the notation of Section 5.B).

For a closed isolated system, $f(\boldsymbol{\alpha})$ can be written

$$f(\boldsymbol{\alpha}) = \left(\frac{\bar{g}}{(2\pi k_B)^n} \right)^{1/2} e^{-\bar{\mathbf{g}}:\boldsymbol{\alpha}\boldsymbol{\alpha}/2k_B} \tag{10.77}$$

[cf. Eq. (7.24)], and the change in entropy which results from these fluctuations is

$$\Delta S = -\frac{1}{2}\bar{\mathbf{g}} : \boldsymbol{\alpha}\boldsymbol{\alpha}. \tag{10.78}$$

It is useful to introduce a generalized force, χ, which is defined as

$$\chi = \bar{\mathbf{g}} \cdot \boldsymbol{\alpha} = -\left(\frac{\partial \Delta S}{\partial \boldsymbol{\alpha}}\right), \tag{10.79}$$

and a generalized current, $\mathcal{J}$, defined as

$$\mathcal{J} = \frac{d\boldsymbol{\alpha}}{dt}. \tag{10.80}$$

Then the time rate of change of the entropy due to fluctuations is

$$\frac{d\Delta S}{dt} = -\mathcal{J} \cdot \chi. \tag{10.81}$$

For a resistor held at constant temperature, where $\mathcal{J}$ is the electric current and χ is the applied electric field, Eq. (10.81) is proportional to the rate at which energy is dissipated through Joule heating.

We must now remember that $\boldsymbol{\alpha}$ is a macroscopic variable. Thus, for each value of $\boldsymbol{\alpha}$ there are many possible microscopic states of the system. We can relate the joint probability distribution $f(\boldsymbol{\alpha})P(\boldsymbol{\alpha}|\boldsymbol{\alpha}', \tau)$ for fluctuations $\boldsymbol{\alpha}$ and $\boldsymbol{\alpha}'$ to the microscopic probability density in the density in the following way:

$$\begin{aligned} f(\boldsymbol{\alpha})P(\boldsymbol{\alpha}|\boldsymbol{\alpha}', \tau) = \frac{1}{\Omega_{\Delta E}(E)} \iint\limits_{\substack{(\boldsymbol{\alpha} \to \boldsymbol{\alpha} + d\boldsymbol{\alpha}) \\ (E \to E + \Delta E)}} d\mathbf{q}^N d\mathbf{p}^N \\ \times \iint\limits_{(\boldsymbol{\alpha}' \to \boldsymbol{\alpha}' + d\boldsymbol{\alpha}')} d\mathbf{q}'^N d\mathbf{p}'^N P(\mathbf{p}^N, \mathbf{q}^N | \mathbf{p}'^N, \mathbf{q}'^N, \tau). \end{aligned} \tag{10.82}$$

In Eq. (10.82) we have used the fact that $\rho(\mathbf{p}^N, \mathbf{q}^N) = \Omega_{\Delta E}(E)^{-1}$ for a closed isolated system ($\Omega_{\Delta E}(E)$ is the volume of the energy shell). The phase space integrations are restricted to the energy shell and to trajectories with values of $\boldsymbol{\alpha}$ and $\boldsymbol{\alpha}'$ appearing in the left-hand side of Eq. (10.82); $P(\mathbf{p}^N, \mathbf{q}^N | \mathbf{p}'^N, \mathbf{q}'^N, \tau)$ is the conditional probability that a system be in a state $(\mathbf{p}'^N, \mathbf{q}'^N)$ at time $t = \tau$, given that it was in the state $(\mathbf{p}^N, \mathbf{q}^N)$ at time $t = 0$. Since classical systems are completely deterministic, we must have

$$\begin{aligned} P(\mathbf{p}^N, \mathbf{q}^N | \mathbf{p}'^N, \mathbf{q}'^N, \tau) = \delta(\mathbf{q}'^N - \mathbf{q}^N - \Delta\mathbf{q}^N(\mathbf{p}^N, \mathbf{q}^N, \tau)) \\ \times \delta(\mathbf{p}'^N - \mathbf{p}^N - \Delta\mathbf{p}^N(\mathbf{p}^N, \mathbf{q}^N, \tau)), \end{aligned} \tag{10.83}$$

where $\Delta\mathbf{q}^N$ and $\Delta\mathbf{p}^N$ are uniquely determined from Hamilton's equations.

Because Hamilton's equations are causal and time-reversal invariant, reversal of all momenta in the system will cause the system to retrace its steps. This implies that

$$P(\mathbf{q}^N, \mathbf{p}^N | \mathbf{q}'^N, \mathbf{p}'^N, \tau) = P(\mathbf{q}'^N, -\mathbf{p}'^N | \mathbf{q}^N, -\mathbf{p}^N, \tau). \tag{10.84}$$

Since α and α' are even functions of momentum, we can combine Eqs. (10.82)–(10.84) to obtain microscopic detailed balance

$$f(\alpha)P(\alpha|\alpha', \tau) = f(\alpha')P(\alpha'|\alpha, \tau). \tag{10.85}$$

From Eq. (10.85), Eq (10.75) follows easily.

10.D.1.2. Regression of Fluctuations

Equation (10.75) is important because we can use it to find relations between various transport coefficients. Let us first introduce the conditional average $\langle \alpha(t) \rangle_{\alpha_0}$, which is the average value of α at time t, given that the initial value of α was α_0. We then can write

$$\langle \alpha(t) \rangle_{\alpha_0} \equiv \int d\alpha \alpha P(\alpha_0 | \alpha, t) \tag{10.86}$$

for the conditional average.

Onsagar assumed that, on the average, the fluctuations decay according to the same linear laws (hydrodynamic equations) that govern the decay to equilibrium of systems which are macroscopically out of equilibrium. Thus, the average fluctuation, $\langle \alpha(t) \rangle_{\alpha_0}$, obeys an equation of the form

$$\frac{d}{dt} \langle \alpha(t) \rangle_{\alpha_0} = -\bar{\mathbf{M}} \cdot \langle \alpha(t) \rangle_{\alpha_0}. \tag{10.87}$$

Equation (10.87) has the solution

$$\langle \alpha(t) \rangle_{\alpha_0} = e^{-\bar{\mathbf{M}}t} \cdot \alpha_0. \tag{10.88}$$

The time derivative in Eq. (10.87) must be used with caution. It is defined in the following sense:

$$\frac{d\langle \alpha(t) \rangle_{\alpha_0}}{dt} \equiv \frac{\langle \alpha(t+\tau) \rangle_{\alpha_0} - \langle \alpha(t) \rangle_{\alpha_0}}{\tau}, \tag{10.89}$$

where τ is a small time interval whose values are bounded by inequalities,

$$T_0 \ll \tau \ll T. \tag{10.90}$$

T_0 is the time between collisions, and T is the time it takes the fluctuation to decay to equilibrium. The limitation in Eq. (10.90) rules out fluctuations which are too small—that is, fluctuations which decay to equilibrium in a few collision times. Similarly, Eq. (10.90) is not valid when the fluctuation has just been created. It takes a few collision times for it to settle down to a hydrodynamic decay.

Equation (10.75) imposes a condition on the matrix $\bar{\mathbf{M}}$. If we expand Eq. (10.88) for short times,

$$\langle \boldsymbol{\alpha}(t) \rangle_{\boldsymbol{\alpha}_0} = \boldsymbol{\alpha}_0 - t\bar{\mathbf{M}} \cdot \boldsymbol{\alpha}_0 + O(t^2), \tag{10.91}$$

and substitute it into Eq. (10.75), we obtain

$$\langle \boldsymbol{\alpha}_0 \bar{\mathbf{M}} \cdot \boldsymbol{\alpha}_0 \rangle = \langle \bar{\mathbf{M}} \cdot \boldsymbol{\alpha}_0 \boldsymbol{\alpha}_0 \rangle. \tag{10.92}$$

If we now use the fact that $\bar{\mathbf{M}} \cdot \boldsymbol{\alpha} = \boldsymbol{\alpha}^T \cdot \bar{\mathbf{M}}^T$ and use Eq. (7.27) for the variance in the fluctuations, we obtain

$$\bar{\mathbf{g}}^{-1} \cdot \bar{\mathbf{M}}^T = \bar{\mathbf{M}} \cdot \bar{\mathbf{g}}^{-1}, \tag{10.93}$$

where T denotes the transpose. We can define a new tensor

$$\bar{\mathbf{L}} \equiv \bar{\mathbf{M}} \cdot \bar{\mathbf{g}}^{-1}; \tag{10.94}$$

then Eq. (10.93) becomes

$$\bar{\mathbf{L}} = \bar{\mathbf{L}}^T \quad \text{or} \quad L_{ij} = L_{ji}. \tag{10.95}$$

Equations (10.95) are called *Onsagar's relations*. If we make use of the generalized force $\boldsymbol{\chi}$ [cf. Eq. (10.79)], the time rate of change of the fluctuation can be written

$$\frac{d}{dt} \langle \boldsymbol{\alpha}(t) \rangle_{\boldsymbol{\alpha}_0} = -\bar{\mathbf{L}} \cdot \langle \boldsymbol{\chi}(t) \rangle_{\boldsymbol{\alpha}_0}. \tag{10.96}$$

Equation (10.96) has the same form as the linearized hydrodynamic equations (cf. Section 10.C). Eq. (10.95) is so useful that Onsagar received a Nobel prize for deriving it. The matrix $\bar{\mathbf{L}}$ is a matrix of transport coefficients. Equation (10.96) tells us that a force resulting from a fluctuation α_i can cause a flux of A_j, and a force arising from a fluctuation α_j can cause a flux of A_i. Eq. (10.95) tells us that the transport coefficients for the two processes are the same. For example, a particle concentration gradient can derive a heat current, and a temperature gradient can drive a particle current. The transport coefficients for the two processes are the same although the processes physically appear to be very different.

10.D.2. Weiner–Khintchine Theorem [3, 8, 9]

The Wiener–Khintchine theorem enables us to obtain a relation between the correlation matrix for time-dependent fluctuations and the spectral density matrix of fluctuations for ergodic systems with stationary distribution functions. We shall first derive some properties of time-dependent correlation matrices and then derive the Wiener–Khintchine theorem.

Let us consider the time-dependent correlation matrix, $\langle \boldsymbol{\alpha}(\tau)\boldsymbol{\alpha}(0)\rangle$, for a system governed by a stationary distribution function (such as a system in equilibrium). The correlation matrix has the property

$$\bar{\mathbf{C}}_{\alpha\alpha}(\tau) \equiv \langle \boldsymbol{\alpha}(\tau)\boldsymbol{\alpha}\rangle = \langle \boldsymbol{\alpha}(t+\tau)\boldsymbol{\alpha}(t)\rangle = \langle \boldsymbol{\alpha}(-\tau)\boldsymbol{\alpha}\rangle^T = \bar{\mathbf{C}}_{\alpha\alpha}(-\tau)^T, \quad (10.97)$$

where we have let $t = -\tau$ and T denotes the transpose of the correlation matrix. From the condition of microscopic reversibility, we know that $\langle \boldsymbol{\alpha}(\tau)\boldsymbol{\alpha}\rangle = \langle \boldsymbol{\alpha}\boldsymbol{\alpha}(\tau)\rangle$ and, therefore,

$$\bar{\mathbf{C}}_{\alpha\alpha}(\tau) = \bar{\mathbf{C}}_{\alpha\alpha}(\tau)^T. \quad (10.98)$$

Furthermore, from Section 7.C we have

$$\bar{\mathbf{C}}_{\alpha\alpha}(0) = \langle \boldsymbol{\alpha}\boldsymbol{\alpha}\rangle = k_B\bar{\mathbf{g}}^{-1} \quad (10.99)$$

where $\bar{\mathbf{g}}^{-1}$ depends on the thermodynamic response functions. From Eqs. (10.88) and (10.97) the correlation matrix can be written

$$\bar{\mathbf{C}}_{\alpha\alpha}(\tau) = \int d\boldsymbol{\alpha}_0 f(\boldsymbol{\alpha}_0)\boldsymbol{\alpha}_0\langle \boldsymbol{\alpha}(\tau)\rangle_{\boldsymbol{\alpha}_0} = k_B\bar{\mathbf{g}}^{-1}\cdot e^{-\bar{\mathbf{M}}|\tau|} \quad (10.100)$$

since $\bar{\mathbf{M}}$ is a self-adjoint matrix ($|\tau|$ indicates the absolute value of τ).

We now will introduce the spectral density matrix of fluctuations and show that it is the Fourier transform of the correlation matrix. Let us introduce a slight modification of the state variable $\boldsymbol{\alpha}(t)$ as follows:

$$\boldsymbol{\alpha}(t;T) \equiv \begin{cases} \boldsymbol{\alpha}(t) & |t| < T, \\ 0 & |t| > T \end{cases} \quad (10.101)$$

such that

$$\lim_{T\to\infty} \boldsymbol{\alpha}(t;T) = \boldsymbol{\alpha}(t). \quad (10.102)$$

We next introduce the Fourier transform of $\boldsymbol{\alpha}(t;T)$:

$$\boldsymbol{\alpha}(\omega;T) = \int_{-\infty}^{\infty} dt\boldsymbol{\alpha}(t;T)e^{i\omega t} = \int_{-T}^{T} dt\boldsymbol{\alpha}(t;T)e^{i\omega t}. \quad (10.103)$$

Since the fluctuations, $\boldsymbol{\alpha}(t)$, are real, we find

$$\boldsymbol{\alpha}^*(\omega; T) = \boldsymbol{\alpha}(-\omega; T) \tag{10.104}$$

(* denotes complex conjugate).

The spectral density matrix is defined as

$$\bar{\mathbf{S}}_{\alpha\alpha}(\omega) = \lim_{T\to\infty} \frac{1}{T} \boldsymbol{\alpha}^*(\omega; T)\boldsymbol{\alpha}(\omega; T) \tag{10.105}$$

(cf. Section 5.E.2). Combining Eqs. (10.102) and (10.104) we can write

$$\bar{\mathbf{S}}_{\alpha\alpha}(\omega) = \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \lim_{T\to\infty} \frac{1}{T} \int_{-\infty}^{\infty} dt \boldsymbol{\alpha}(t; T)\boldsymbol{\alpha}(t+\tau; T). \tag{10.106}$$

If we now invoke the ergodic theorem (cf. Section 6.C), we can equate the time average in Eq. (10.106) to the phase average of the fluctuations:

$$\begin{aligned} \langle \boldsymbol{\alpha}\boldsymbol{\alpha}(\tau)\rangle &= \lim_{T\to\infty} \frac{1}{T} \int_{-T}^{T} \boldsymbol{\alpha}(t)\boldsymbol{\alpha}(t+\tau)dt \\ &= \lim_{T\to\infty} \frac{1}{T} \int_{-\infty}^{\infty} \boldsymbol{\alpha}(t; T)\boldsymbol{\alpha}(t+\tau; T)dt. \end{aligned} \tag{10.107}$$

Then Eqs. (10.106) and (10.107) lead to the relation

$$\bar{\mathbf{S}}_{\alpha\alpha}(\omega) = \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \langle \boldsymbol{\alpha}\boldsymbol{\alpha}(\tau)\rangle = \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \bar{\mathbf{C}}_{\alpha\alpha}(\tau). \tag{10.108}$$

Thus, the spectral density matrix is the Fourier transform of the correlation matrix. Equation (10.108) is called the *Wiener–Khintchine theorem.*

We can now derive some general properties for the spectral density matrix. From Eq. (10.97) we find that the spectral density matrix is Hermitian,

$$\bar{\mathbf{S}}_{\alpha\alpha}(\omega) = \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \bar{\mathbf{C}}_{\alpha\alpha}(-\tau)^T = \bar{\mathbf{S}}^{*T}_{\alpha\alpha}(\omega), \tag{10.109}$$

where we have let $\tau \to -\tau$ to obtain the last term. Furthermore, since $\bar{\mathbf{C}}_{\alpha\alpha}(\tau)$ is real, we have

$$\bar{\mathbf{S}}^{*}_{\alpha\alpha}(\omega) = \int_{-\infty}^{\infty} d\tau e^{-i\omega\tau} \bar{\mathbf{C}}_{\alpha\alpha}(-\tau) = \bar{\mathbf{S}}_{\alpha\alpha}(-\omega), \tag{10.110}$$

It is useful to divide $\bar{\mathbf{S}}_{\alpha\alpha}(\omega)$ into its real and imaginary parts, $\bar{\mathbf{R}}_{\alpha\alpha}(\omega)$ and $\bar{\mathbf{I}}_{\alpha\alpha}(\omega)$,

respectively:

$$\bar{\mathbf{S}}_{\alpha\alpha}(\omega) = \bar{\mathbf{R}}_{\alpha\alpha}(\omega) + i\bar{\mathbf{I}}_{\alpha\alpha}(\omega). \tag{10.111}$$

Then from Eqs. (10.109) and (10.110) we find that $\bar{\mathbf{R}}_{\alpha\alpha}(\omega)$ is a real, symmetric matrix and an even functin of ω ($\bar{\mathbf{R}}_{\alpha\alpha}(\omega) = \bar{\mathbf{R}}_{\alpha\alpha}(\omega)^T = \bar{\mathbf{R}}_{\alpha\alpha}(-\omega)$), while $\bar{\mathbf{I}}_{\alpha\alpha}(\omega)$ is a real, antisymmetric matrix and an odd function of ω ($\bar{\mathbf{I}}_{\alpha\alpha}(\omega) = -\bar{\mathbf{I}}_{\alpha\alpha}(\omega)^T = -\bar{\mathbf{I}}_{\alpha\alpha}(-\omega)$). Furthermore, we find that $\bar{\mathbf{S}}_{\alpha\alpha}(\omega) = \bar{\mathbf{S}}_{\alpha\alpha}(\omega)^\dagger$. Thus, $\bar{\mathbf{I}}_{\alpha\alpha}(\omega) = -\bar{\mathbf{I}}_{\alpha\alpha}(\omega) = 0$, and the spectral density matrix is a real, symmetric matrix and an even function of ω. We therefore can write the correlation matrix in the form

$$\bar{\mathbf{C}}_{\alpha\alpha}(\tau) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega e^{-i\omega\tau}\bar{\mathbf{S}}_{\alpha\alpha}(-\omega) = \frac{1}{\pi}\int_{0}^{\infty} d\omega \bar{\mathbf{R}}_{\alpha\alpha}(\omega)\cos(\omega\tau). \tag{10.112}$$

If a magnetic field is present or the system is rotating, Eq. (10.112) must be generalized to take into account the behavior of the magnetic field or angular velocity under time reversal [3]. This is done in Section S10.A. In Exercise 10.4, we compute the power spectrum of density fluctuations in an isotropic fluid.

■ **EXERCISE 10.4.** The dynamic density correlation function for a fluid in a box of volume V may be written

$$C_{nn}(\boldsymbol{\rho}, \tau) = \frac{1}{N}\int d\mathbf{r}\langle n(\mathbf{r}+\boldsymbol{\rho}, \tau)n(\mathbf{r}, 0),$$

where N is the total number of particles. The dynamic structure factor is given by

$$S_{nn}(\mathbf{k}, \Omega) = \int d\boldsymbol{\rho}\int_{-\infty}^{\infty} d\tau C_{nn}(\boldsymbol{\rho}, \tau)e^{i\mathbf{k}\cdot\boldsymbol{\rho}}e^{-i\Omega\tau}.$$

Compute both $C_{nn}(\boldsymbol{\rho}, \tau)$ and $S_{nn}(\mathbf{k}, \Omega)$ for a fluid of point particles in equilibrium. For such a fluid, the average, $\langle\rangle$, is taken over the equilibrium distribution of fluctuations. Assume that fluctuations in the average velocity are independent of temperature and density fluctuations.

Answer:

(a) Let us first write the density variations as $n(\mathbf{r}, t) = n_0 + \Delta n(\mathbf{r}, t)$, where $n_0 = \langle n(\mathbf{r}, t)\rangle = N/V$, is the equilibrium density and $\Delta n(\mathbf{r}, t)$ describes fluctuations about equilibrium such that $\langle \Delta n(\mathbf{r}, t)\rangle = 0$

If we substitute into the expression for the correlation function, we obtain

$$C_{nn}(\boldsymbol{\rho},\tau) = \frac{1}{N}\int d\mathbf{r}\langle n(\mathbf{r}+\boldsymbol{\rho},t)n(\mathbf{r},0)\rangle, \\ = n_0 + \frac{1}{N}\int d\mathbf{r}\langle \Delta n(\mathbf{r}+\boldsymbol{\rho},t)\Delta n(\mathbf{r},0)\rangle. \tag{1}$$

Let us introduce the Fourier series expansion of the density

$$\Delta n(\mathbf{r},t) = \frac{1}{V}\sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot r} n_{\mathbf{k}}(t) \quad \text{with} \quad n_{\mathbf{k}}(t) = \int d\mathbf{r} e^{i\mathbf{k}\cdot r}\Delta n(\mathbf{r},t), \tag{2}$$

and of the correlation function

$$C_{nn}(\mathbf{k},\tau) = \int d\boldsymbol{\rho} e^{i\mathbf{k}\cdot\boldsymbol{\rho}} C_{nn}(\boldsymbol{\rho},\tau) = N\delta_{\mathbf{k},0} + \frac{1}{N}\langle n_{\mathbf{k}}(t)n_{-\mathbf{k}}(0)\rangle. \tag{3}$$

To obtain the last term in Eq. (3), we have substituted the Fourier expansion of the density, Eq. (2), into Eq. (1) and have used the identity

$$\frac{1}{V}\int d\mathbf{r} e^{ik\cdot r} = \delta_{\mathbf{k},0}, \tag{4}$$

where $\delta_{\mathbf{k},0}$ is the Kronecker delta function. From Einstein fluctuation theory (Section 7.C) we know that temperature and density fluctuations are statistically independent. Therefore, $\langle \Delta n_{\mathbf{k}}(0)\Delta T_{-\mathbf{k}}(0)\rangle = 0$. Also, we will assume that velocity fluctuations are statistically independent of density fluctuations. Therefore, any contributions to the density at time t, due to fluctuations in velocity or temperature at time $t = 0$, will disappear when the average, $\langle\rangle$, is taken. As a result, we can use the solution for the density, $\rho_{\mathbf{k}}(t) \equiv mn_{\mathbf{k}}(t)$, obtained in Exercise 10.3. to determine the time evolution of the density correlation function. We can write

$$C_{nn}(\mathbf{k},t) = N\delta_{\mathbf{k},0} + \frac{1}{m^2N}\langle n_{\mathbf{k}}(0)n_{-\mathbf{k}}(0)\rangle \\ \times \left[\left(1-\frac{1}{\gamma}\right)e^{-\chi k^2|t|} + \frac{1}{\gamma}e^{-\Gamma k^2|t|}\cos(c_0 kt)\right], \tag{5}$$

where $\gamma = \tilde{c}_P/c_\rho$, $\tilde{c}_0$ is the speed of sound, $\Gamma = \frac{1}{2}[\nu_l + \chi(\gamma-1)]$, ν_l is the longitudinal kinetic viscosity, and χ is the thermal diffusivity. The absolute value of the time appears in Eq. (5) because it is the correlation function for a stationary process. We must remember that

Eq. (5) is an approximate expression for the density correlation function. Some terms proportional to the wave vector have been neglected. We shall leave it as a homework problem to determine the size of these neglected terms.

(**b**) Let us now consider the spectral density function (also called the dynamic structure factor),

$$S_{nn}(\mathbf{k}, \Omega) = \int d\boldsymbol{\rho} \int_{-\infty}^{\infty} dt C_{nn}(\boldsymbol{\rho}, t) e^{i\mathbf{k}\cdot\boldsymbol{\rho}} e^{-i\Omega t}. \tag{6}$$

If we substitute Eq. (1) into Eq. (6) and made use of Eqs. (3) and (5), we find

$$S_{nn}(\mathbf{k}, \Omega) = 2\pi N \delta(\Omega)\delta_{\mathbf{k},0} + \frac{1}{m^2 N} \langle n_{\mathbf{k}}(0) n_{-\mathbf{k}}(0) \rangle \left[\left(1 - \frac{1}{\gamma}\right) \frac{2\chi k^2}{\Omega^2 + \chi^2 k^4} + \frac{1}{\gamma} \left(\frac{\Gamma k^2}{(\Omega - c_0 k)^2 + \Gamma^2 k^4} + \frac{\Gamma k^2}{(\Omega + c_0 k)^2 + \Gamma^2 k^4} \right) \right], \tag{7}$$

where we have used the fact that $(1/2\pi) \int_{-\infty}^{\infty} dt e^{i\Omega t} = \delta(\Omega)$. Away from the critical point, the correlation function, $\langle n_{\mathbf{k}}(0) n_{-\mathbf{k}}(0) \rangle$, is independent of $\mathbf{k}$ and proportional to the compressibility. Near the critical point it behaves like $(C + k^2)^{-1}$, where $C \sim (T - T_c)$ [cf. Eq. (8.21)]. The dynamic structure factor for an isotropic fluid has three terms of the form

$$f(\Omega) = \frac{2\Delta}{\Delta^2 + (\Omega - \Omega')^2}, \tag{8}$$

where $f(\Omega)$ is a Lorentzian centered at frequency, Ω', with half-width at one-half maximum given by Δ. Therefore, the dynamic structure factor, as a function of frequency, has three peaks. One is centered at $\Omega = 0$ with width χk^2 and is due to the thermal hydrodynamic mode. This is called the *Rayleigh peak*. The other two are centered at $\Omega = \pm c_0 k$ with width, Γk^2. They are called the *Brillouin peaks*.

10.E LINEAR RESPONSE THEORY AND THE FLUCTUATION–DISSIPATION THEOREM [3]

Fluctuations in an equilibrium system decay, *on the average*, according to the same linear macroscopic laws (in a fluid system the hydrodynamic equations) that describe the decay of the system from a nonequilibrium state to the equilibrium state. If we can probe the equilibrium fluctuations, we have a means

of probing the transport processes in the system. The fluctuation–dissipation theorem shows that it is possible to probe the equilibrium fluctuations by applying a weak external field which couples to particles in the medium but yet is too weak to affect the medium. The system will respond to the field and absorb energy from the field in a manner which depends entirely on the spectrum of the equilibrium fluctuations. According to the fluctuation–dissipation theorem, the spectrum of the equilibrium fluctuations and the rate of absorption of energy from the external field can be expressed in terms of a response matrix which is related to the correlation matrix for equilibrium fluctuations.

In this section we derive the fluctuation–dissipation theorem. We first introduce linear response theory and use the assumption of causality to obtain a relation between the real and imaginary parts of the dynamic susceptibility matrix, which is the Fourier transform of the response matrix. We then obtain a relation between the dynamic susceptibility matrix and the correlation matrix, and we obtain an expression for power absorption in terms of the dynamic susceptibility matrix. This gives us a relation between the fluctuations in an equilibrium system and energy absorbed by that system when an external field is applied.

10.E.1. The Response Matrix

Let us assume that external forces, $\mathbf{F} = (F_1, F_2, \ldots, F_n)$, are applied to a system and that these forces couple to the state variables, $A_1, A_2, \ldots, A_n$, causing them to deviate from their equilibrium values. We shall assume that the deviations from equilibrium of the state variables, $A_1, A_2, \ldots, A_n$, depend linearly on the applied forces (linear response). Then we can write

$$\langle \boldsymbol{\alpha}(t) \rangle_F = \int_{-\infty}^{\infty} dt' \bar{\mathbf{K}}(t - t') \cdot \mathbf{F}(t') = \int_{-\infty}^{\infty} \bar{\mathbf{K}}(\tau) \cdot \mathbf{F}(t - \tau) d\tau. \tag{10.113}$$

The matrix $\bar{\mathbf{K}}(t - t')$ is real and is called the *response matrix*. Since the response must be causal (the response cannot precede the force which causes it), $\bar{\mathbf{K}}(t - t')$ must satisfy the causality condition,

$$\bar{\mathbf{K}}(t - t') = 0, \quad t - t' < 0, \tag{10.114}$$

Since Eq. (10.113) is linear in the force, its Fourier transform has a very simple form. If we note that

$$\langle \boldsymbol{\alpha}(t) \rangle_{\mathbf{F}} = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle \tilde{\boldsymbol{\alpha}}(\omega) \rangle_{\mathbf{F}} e^{-i\omega t} d\omega \tag{10.115}$$

and use similar expressions relating $\mathbf{F}(\tau)$ to $\tilde{\mathbf{F}}(\omega)$ and $\bar{\mathbf{K}}(\tau)$ to $\bar{\chi}(\omega)$, we obtain

$$\langle \tilde{\boldsymbol{\alpha}}(\omega) \rangle_F = \bar{\chi}(\omega) \cdot \tilde{\mathbf{F}}(\omega), \tag{10.116}$$

where

$$\bar{\chi}(\omega)) = \int_{-\infty}^{\infty} \bar{\mathbf{K}}(t) e^{i\omega t}\, dt \tag{10.117}$$

is the dynamic susceptibility. We have also used the definition for the delta function, $\delta(t) = (1/2\pi)\int_{-\infty}^{\infty} d\omega\, e^{-i\omega t}$.

Thus, a force of a given frequency can only excite a response of the same frequency. This will not be true if the response function depends on the force (nonlinear response).

10.E.2. Causality

Let us now study the restrictions imposed on the response matrix by causality. We shall assume that the response matrix relaxes fast enough that the integral

$$\int_0^{\infty} \bar{\mathbf{K}}(t)\, dt < \infty \tag{10.118}$$

is finite. Physically, this means that a finite force must give rise to a finite response. It is convenient to continue the frequency dependence of $\bar{\chi}(\omega)$ into the complex plane by writing

$$\bar{\chi}(z) = \int_0^{\infty} dt \bar{\mathbf{K}}(t)\, e^{izt}, \tag{10.119}$$

where $z = \omega + i\varepsilon$ (ε positive). If $\bar{\chi}(\omega)$ is well-behaved (nonsingular), then $\bar{\chi}(z)$ will be well-behaved since the extra factor $e^{-\varepsilon t}$ introduced simply makes the integral fall off faster. The function $\bar{\chi}(z)$ is not singular (has no poles) for z in the upper-half complex plane, but we can say nothing about its behavior in the lower-half complex plane. Note also that $\bar{\chi}(z) \to 0$ as $\varepsilon \to \infty$.

The matrix $\bar{\chi}(\omega)$ is complex ($\bar{\chi}^*(\omega) = \bar{\chi}(-\omega)$), but causality enables us to obtain a relation between its real and imaginary parts. We do this by introducting the following trick. Define a new matrix

$$\bar{\mathbf{f}}(z) = \frac{\bar{\chi}(z)}{z - u} \tag{10.120}$$

and integrate it over a contour C' (cf. Fig. 10.2) so that C' encloses no poles of $\bar{\mathbf{f}}(z)$. (Note that u is real.) Then

$$\oint_C \bar{\mathbf{f}}(z)\, dz = 0 = \oint_{C'} \frac{\bar{\chi}(z)}{z - u}\, dz. \tag{10.121}$$

Since $\bar{\chi}(z) \to 0$ as $\varepsilon \to \infty$ there will be no contribution from the semicircle at

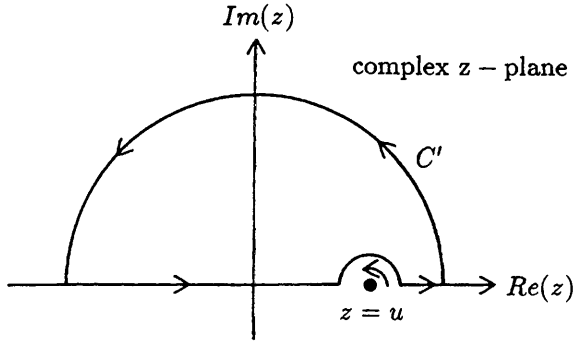


Fig. 10.2. Integration contour used to obtain the Kramers–Kronig relations.

infinity. Thus,

$$\oint_{C'} \frac{\bar{\chi}(z)}{z-u}\,dz = \int_{-\infty}^{u-r} \frac{\bar{\chi}(\omega)}{\omega-u}\,d\omega + \int_{u+r}^{\infty} d\omega \frac{\bar{\chi}(\omega)}{\omega-u} + \int_{\pi}^{0} d\phi i r e^{i\phi} \frac{\bar{\chi}(u+re^{i\phi})}{u+re^{i\phi}-u} = 0. \tag{10.122}$$

It is useful to introduce the Cauchy principal part,

$$P\int_{-\infty}^{\infty} d\omega \frac{\bar{\chi}(\omega)}{\omega-u} \equiv \lim_{r\to 0}\left[\int_{-\infty}^{u-r} d\omega \frac{\bar{\chi}(\omega)}{\omega-u} + \int_{u+r}^{\infty} d\omega \frac{\bar{\chi}(\omega)}{\omega-u}\right]. \tag{10.123}$$

Equation (10.122) then gives

$$P\int_{-\infty}^{\infty} d\omega \frac{\bar{\chi}(\omega)}{\omega-u} = -\lim_{r\to 0}\int_{\pi}^{0} i\,d\phi \bar{\chi}(u+re^{i\phi}) = i\pi\bar{\chi}(u). \tag{10.124}$$

or

$$\bar{\chi}(u) = \frac{1}{\pi i} P\int_{-\infty}^{\infty} \frac{\bar{\chi}(\omega)d\omega}{\omega-u}. \tag{10.125}$$

Equation (10.125) is a consequence of causality and allows us to relate the real part, $\bar{\chi}'(\omega)$, and the imaginary part, $\bar{\chi}''(\omega)$, of the dynamic susceptibility matrix. Let us write

$$\bar{\chi}(\omega) = \bar{\chi}'(\omega) + i\bar{\chi}''(\omega) \tag{10.126}$$

and make us of Eq. (10.125). We then obtain the following relations between

$\bar{\chi}'(\omega)$ and $\bar{\chi}''(\omega)$:

$$\bar{\chi}'(u) = \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\bar{\chi}''(\omega)}{\omega - u} d\omega \tag{10.127}$$

and

$$\bar{\chi}''(u) = -\frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\bar{\chi}'(\omega)}{\omega - u} d\omega. \tag{10.128}$$

Equations (10.127) and (10.128) are called the *Kramers–Kronig relations* and enable us to compute the real part of $\bar{\chi}(\omega)$ if we know the imaginary part and vice versa. As we shall see, the imaginary part of $\bar{\chi}(\omega)$ can be obtained from experiment.

The Kramers–Kronig relations give us a relation between the real and imaginary parts of the dynamic susceptibility matrix. Therefore, it is only necessary to find one or the other to determine the response, $\langle \alpha(t) \rangle$. We can show this explicitly as follows. The Kramers–Kronig relations allow us to rewrite the dynamic susceptibility matrix, $\bar{\chi}(\omega)$, as

$$\bar{\chi}(\omega) = \lim_{\eta \to 0} \int \frac{d\omega'}{\pi} \frac{\bar{\chi}''(\omega')}{\omega' - \omega - i\eta}, \tag{10.129}$$

where we have used the identity

$$\lim_{\eta \to 0} \frac{1}{\omega' - \omega \mp i\eta} = P\left(\frac{1}{\omega' - \omega}\right) \pm i\pi \delta(\omega' - \omega). \tag{10.130}$$

The response $\langle \alpha(t) \rangle$ then becomes

$$\begin{aligned} \langle \alpha(t) \rangle &= \frac{1}{2\pi} \int d\omega\, e^{-i\omega t} \bar{\chi}(\omega) \cdot \mathbf{F}(\omega) \\ &= \lim_{\eta \to 0} \frac{2}{(2\pi)^2} \int_{-\infty}^{\infty} dt' \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} d\omega' \frac{e^{-i\omega(t-t')}}{\omega' - \omega - i\eta} \bar{\chi}''(\omega') \cdot \mathbf{F}(t'). \end{aligned} \tag{10.131}$$

In Eq. 10.131, we have used Eq. (10.129) and have Fourier transformed $\tilde{\mathbf{F}}(\omega)$. If we now make a change of variables $\omega'' = \omega - \omega'$ and introduce the following spectral representation of the Heaviside function,

$$\theta(t - t') = -\lim_{\eta \to 0} \int_{-\infty}^{\infty} \frac{d\omega}{(2\pi i)} \frac{e^{-i\omega(t-t')}}{\omega + i\eta}, \tag{10.132}$$

we obtain

$$\langle \alpha(t) \rangle = 2i \int_{-\infty}^{t} dt' \bar{\mathbf{K}}''(t - t') \cdot \mathbf{F}(t'), \tag{10.133}$$

where $\bar{\mathbf{K}}''(t - t')$ is the Fourier transform of $\bar{\mathbf{K}}''(\omega)$. Thus, we have succeeded in writing the response entirely in terms of the imaginary part of the dynamic susceptibility matrix. The expression for the linear response given in Eq. (10.133) is the one most commonly seen in the literature.

Everything we have done to this point is completely general. Let us now obtain an explicit expression for the response for the case of a constant force which acts for an infinite length of time and then is abruptly shut off. The force we consider has the form

$$\mathbf{F}(t) = \begin{cases} \mathbf{F} & \text{for } t < 0 \\ 0 & \text{for } t > 0. \end{cases} \tag{10.134}$$

The Fourier transform of the force is

$$\begin{aligned} \tilde{\mathbf{F}}(\omega) &= \mathbf{F} \int_{-\infty}^{0} e^{i\omega t}\, dt = \lim_{\varepsilon \to 0} \mathbf{F} \int_{-\infty}^{0} e^{izt}\, dt \\ &= \lim_{\varepsilon \to 0} \mathbf{F} \frac{1}{iz} = (-i) \lim_{\varepsilon \to 0} \mathbf{F} \left[\frac{\omega}{\omega^2 + \varepsilon^2} + \frac{i\varepsilon}{\omega^2 + \varepsilon^2} \right]. \end{aligned} \tag{10.135}$$

If we now use the following definitions for the Cauchy principal part

$$P\left(\frac{1}{\omega}\right) = \lim_{\varepsilon \to 0} \frac{\omega}{\omega^2 + \varepsilon^2} \tag{10.136}$$

and the Dirac delta function

$$\delta(\omega) = \lim_{\varepsilon \to 0} \frac{\varepsilon}{\omega^2 + \varepsilon^2}, \tag{10.137}$$

we obtain

$$\tilde{\mathbf{F}}(\omega) = \mathbf{F} \left[P\left(\frac{1}{i\omega}\right) + \pi \delta(\omega) \right]. \tag{10.138}$$

From Eqs. (10.113) and (10.116) the response can be written in the form

$$\langle \alpha(t) \rangle_F = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega\, e^{-i\omega t} \bar{\chi}(\omega) \cdot \tilde{\mathbf{F}}(\omega). \tag{10.139}$$

It is useful to write the response in a slightly different form. To do this we must generalize Eq. (10.125). Let us introduce the matrices

$$\bar{\mathbf{f}}_+(z, t) = \frac{e^{izt}\bar{\boldsymbol{\chi}}(z)}{z - u}, \qquad t > 0 \tag{10.140}$$

and

$$\bar{\mathbf{f}}_-(z, t) = \frac{e^{-izt}\bar{\boldsymbol{\chi}}(z)}{z - u}, \qquad t < 0 \tag{10.141}$$

With our choice of sign in the exponential factors, the functions $\bar{\mathbf{f}}_\pm(z, t)$ will still go to zero as $\varepsilon \to \infty$. From Eq. (10.125) we obtain

$$e^{iut}\bar{\boldsymbol{\chi}}(u) = \frac{1}{i\pi} P \int_{-\infty}^{\infty} \frac{e^{i\omega t}\bar{\boldsymbol{\chi}}(\omega)d\omega}{\omega - u}, \qquad t > 0 \tag{10.142}$$

and

$$e^{-iut}\bar{\boldsymbol{\chi}}(u) = \frac{1}{i\pi} P \int_{-\infty}^{\infty} \frac{e^{-i\omega t}\bar{\boldsymbol{\chi}}(\omega)d\omega}{\omega - u}, \qquad t < 0 \tag{10.143}$$

Then, for $t < 0$, Eq. (10.143) yields the expression

$$\bar{\boldsymbol{\chi}}(0) = \frac{1}{i\pi} P \int_{-\infty}^{\infty} d\omega \frac{e^{-i\omega t}\bar{\boldsymbol{\chi}}(\omega)}{\omega}, \tag{10.144}$$

and, for $t > 0$, Eq. (10.142) yields the expression

$$\bar{\boldsymbol{\chi}}(0) = \frac{1}{i\pi} P \int_{-\infty}^{\infty} d\omega \frac{e^{i\omega t}\bar{\boldsymbol{\chi}}(\omega)}{\omega}. \tag{10.145}$$

If we combine Eqs. (10.138), (10.139), and (10.145), the response for $t < 0$ is

$$\langle \boldsymbol{\alpha}(t) \rangle_F = \bar{\boldsymbol{\chi}}(0) \cdot \mathbf{F} \tag{10.146}$$

and for $t > 0$

$$\langle \boldsymbol{\alpha}(t) \rangle_F = \frac{1}{i\pi} P \int_{-\infty}^{\infty} d\omega \frac{\bar{\boldsymbol{\chi}}(\omega) \cdot \mathbf{F}}{\omega} \cos(\omega t). \tag{10.147}$$

Thus, while the force is turned on, the response is constant. When it is turned off, the response becomes time dependent. The variables $A_1, \ldots, A_n$ begin to decay back to their equilibrium values.

10.E.3. The Fluctuation–Dissipation Theorem

The fluctuation–dissipation theorem is extremely important because it relates the response matrix to the correlation matrix for equilibrium fluctuations. As a result, the external field can be used as a probe of equilibrium fluctuations.

To derive the fluctuation–dissipation theorem, let us consider a system to which a constant force is applied from $t = -\infty$ to $t = 0$ and switched off at $t = 0$. We first write the response, $\langle \boldsymbol{\alpha}(t) \rangle_{\mathbf{F}}$, for times $t \geq 0$ in terms of the conditional average $\langle \boldsymbol{\alpha}(t) \rangle_{\boldsymbol{\alpha}_0}$,

$$\langle \boldsymbol{\alpha}(t) \rangle_{\mathbf{F}} = \int d\boldsymbol{\alpha}_0 f(\boldsymbol{\alpha}_0, \mathbf{F}) \langle \boldsymbol{\alpha}(t) \rangle_{\boldsymbol{\alpha}_0} \qquad \text{for } t \geq 0, \tag{10.148}$$

where $f(\boldsymbol{\alpha}_0, \mathbf{F})$ is the distribution for fluctuations $\boldsymbol{\alpha}_0$ at time $t = 0$ in the presence of a constant external field, $\mathbf{F}$. For times $t > 0$, the field is no longer turned on and we can write

$$\langle \boldsymbol{\alpha}(t) \rangle_{\boldsymbol{\alpha}_0} = e^{-\bar{\mathbf{M}}t} \cdot \boldsymbol{\alpha}_0 \qquad \text{for } t \geq 0 \tag{10.149}$$

[cf. Eq. (10.88)]. Combining Eqs. (10.148) and (10.149), we obtain

$$\begin{aligned} \langle \boldsymbol{\alpha}(t) \rangle_F &= e^{-\bar{\mathbf{M}}t} \cdot \int d\boldsymbol{\alpha}_0 f(\boldsymbol{\alpha}_0, \mathbf{F}) \boldsymbol{\alpha}_0 = e^{-\bar{\mathbf{M}}t} \cdot \langle \boldsymbol{\alpha}(0) \rangle_{\mathbf{F}} \\ &= e^{-\bar{\mathbf{M}}t} \cdot \bar{\boldsymbol{\chi}}(0) \cdot \mathbf{F} = \frac{1}{i\pi} P \int_{-\infty}^{\infty} d\omega \cos(\omega t) \frac{\bar{\boldsymbol{\chi}}(\omega)}{\omega} \cdot \mathbf{F}, \end{aligned} \tag{10.150}$$

where we have used Eqs. (10.146) and (10.147). Thus, we find

$$e^{-\bar{\mathbf{M}}t} \cdot \bar{\boldsymbol{\chi}}(0) = \frac{1}{i\pi} P \int_{-\infty}^{\infty} d\omega \cos(\omega t) \frac{\bar{\boldsymbol{\chi}}(\omega)}{\omega}. \tag{10.151}$$

If we remember that

$$\bar{\mathbf{C}}_{\alpha\alpha}(t) = \langle \boldsymbol{\alpha}(t) \boldsymbol{\alpha} \rangle = k_B e^{-\bar{\mathbf{M}}|t|} \cdot \bar{\mathbf{g}}^{-1}, \tag{10.152}$$

[cf. Eq. (10.100)] we may combine Eqs. (10.150) and (10.151) to obtain

$$\bar{\mathbf{C}}_{\alpha\alpha}(t) = \frac{k_B}{i\pi} P \int_{-\infty}^{\infty} d\omega \cos(\omega t) \frac{\bar{\boldsymbol{\chi}}(\omega)}{\omega} \cdot \bar{\boldsymbol{\chi}}^{-1}(0) \cdot \bar{\mathbf{g}}^{-1} \tag{10.153}$$

for $t > 0$. Thus, we have obtained a relation between the dynamic susceptibility matrix, $\bar{\boldsymbol{\chi}}(\omega)$, and the equilibrium correlation function for fluctuations. In Exercise 10.5 we show that $\bar{\boldsymbol{\chi}}(0) = \bar{\mathbf{g}}^{-1}/T$. Therefore, we finally obtain

$$\bar{\mathbf{C}}_{\alpha\alpha}(t) = \frac{k_B T}{i\pi} P \int_{-\infty}^{\infty} d\omega \frac{\bar{\boldsymbol{\chi}}(\omega)}{\omega} \cos(\omega t). \tag{10.154}$$

Equation (10.154) is the famous *fluctuation–dissipation theorem.* It gives a relation between the linear response function and the correlation function for equilibrium fluctuations.

■ **EXERCISE 10.5.** Prove that $\bar{\chi}(0) = \bar{\mathbf{g}}^{-1}/T$, where $\mathbf{g}$ is the matrix whose matrix element is $g_{ij} = (\partial^2 S/\partial\alpha_i\partial\alpha_j)_U$.

Answer: The external field, $\mathbf{F}$, does work on the system and increases its internal energy by an amount

$$dU = \mathbf{F} \cdot d\boldsymbol{\alpha}. \tag{1}$$

We can expand the differential of the entropy dS and use internal energy and state variables $\boldsymbol{\alpha}$ as independent variables,

$$dS = \left(\frac{\partial S}{\partial U}\right)_{\alpha} dU + \left(\frac{\partial S}{\partial \boldsymbol{\alpha}}\right)_U \cdot d\alpha. \tag{2}$$

But $(\partial S/\partial U)_{\alpha} = 1/T$ and $(\partial S/\partial\boldsymbol{\alpha})_U = -\bar{\mathbf{g}} \cdot \boldsymbol{\alpha}$. Therefore, we can rewrite dS as

$$dS = \left(\frac{\mathbf{F}}{T} - \bar{\mathbf{g}} \cdot \boldsymbol{\alpha}\right) \cdot d\boldsymbol{\alpha} \tag{3}$$

For a constant force, $\langle\boldsymbol{\alpha}\rangle = \bar{\chi}(0) \cdot \mathbf{F}$ is the expectation value of $\langle\boldsymbol{\alpha}\rangle$ rather than zero, and the entropy will have its maximum for $\boldsymbol{\alpha} = \bar{\chi}(0) \cdot \mathbf{F}$. Thus, from Eq. (3) we have

$$\left(\frac{\partial S}{\partial \boldsymbol{\alpha}}\right) = \left(\frac{\mathbf{F}}{T} - \bar{\mathbf{g}} \cdot \boldsymbol{\alpha}\right), \tag{4}$$

and the condition that entropy be maximum at $\boldsymbol{\alpha} = \bar{\chi}(0) \cdot \mathbf{F}$ yields

$$\left(\frac{\partial S}{\partial \boldsymbol{\alpha}}\right)_{\boldsymbol{\alpha}=\bar{\chi}(0)\cdot\mathbf{F}} = \frac{1}{T}\mathbf{F} - \bar{\mathbf{g}} \cdot \bar{\chi}(0) \cdot \mathbf{F} = 0 \tag{5}$$

or

$$\bar{\chi}(0) = \frac{1}{T}\bar{\mathbf{g}}^{-1}. \tag{6}$$

10.E.4. Power Absorption

The work done by an external force $\mathbf{F}$ to change $\boldsymbol{\alpha}$ by an amount $d\boldsymbol{\alpha}$ is

$$đW = -\mathbf{F} \cdot d\boldsymbol{\alpha} \tag{10.155}$$

(this is work done on the medium). The average rate at which work is done on the medium is just the power $P(t)$ absorbed by the medium:

$$P(t) = \left\langle \frac{đW}{dt} \right\rangle_{\mathbf{F}} = -\mathbf{F}(t) \cdot \langle \dot{\boldsymbol{\alpha}}(t) \rangle_{\mathbf{F}} = -\mathbf{F}(t) \cdot \frac{d}{dt} \int_{-\infty}^{\infty} dt' \bar{\mathbf{K}}(t-t') \cdot \mathbf{F}(t'). \tag{10.156}$$

If we write the right-hand side in terms of Fourier transforms $\bar{\boldsymbol{\chi}}(\omega)$ and $\tilde{\mathbf{F}}(\omega)$, we obtain

$$P(t) = i\left(\frac{1}{2\pi}\right)^2 \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} d\omega' \, \omega' \tilde{\mathbf{F}}(\omega) \cdot \bar{\boldsymbol{\chi}}(\omega') \cdot \tilde{\mathbf{F}}(\omega') e^{-i(\omega+\omega')t}. \tag{10.157}$$

We can now compute the power absorbed and the total energy absorbed for various types of external forces.

10.E.4.1. Delta Function Force

Let us assume that at time $t = 0$ a delta function force is applied. Then,

$$\mathbf{F}(t) = \mathbf{F}\delta(t) \quad \text{and} \quad \tilde{\mathbf{F}}(\omega) = \mathbf{F}. \tag{10.158}$$

Substituting into Eq. (10.157), we obtain

$$P(t) = i\left(\frac{1}{2\pi}\right)^2 \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} d\omega' \, \omega' \bar{\boldsymbol{\chi}}(\omega') : \mathbf{FF} \, e^{-(\omega+\omega')t}. \tag{10.159}$$

(*Note*: $\mathbf{F} \cdot \bar{\boldsymbol{\chi}}(\omega) \cdot \mathbf{F} = \bar{\boldsymbol{\chi}}(\omega) : \mathbf{FF}$.) We can find the total energy absorbed by integrating over all times:

$$W_{\text{abs}} = \int_{-\infty}^{\infty} P(t)\, dt = -\left(\frac{1}{2\pi}\right) \int_{-\infty}^{\infty} d\omega \, \omega \bar{\boldsymbol{\chi}}''(\omega) : \mathbf{FF}, \tag{10.160}$$

where $\bar{\boldsymbol{\chi}}''(\omega)$ is the imaginary part of the dynamic susceptibility matrix. Since the total energy absorbed must be a real quantity, only the imaginary part of $\bar{\boldsymbol{\chi}}(\omega)$ contributes.

10.E.4.2. Oscillating Force

Now let us consider a monochromatic oscillating force of the form

$$\mathbf{F}(t) = \mathbf{F} \cos \omega_0 t = \tfrac{1}{2}\mathbf{F}\,(e^{i\omega_0 t} + e^{-i\omega_0 t}). \tag{10.161}$$

Then

$$\tilde{\mathbf{F}}(\omega) = \pi\mathbf{F}(\delta(\omega + \omega_0) + \delta(\omega - \omega_0)). \tag{10.162}$$

From Eqs. (10.157) and (10.162), the power absorbed can be written

$$P(t) = -\tfrac{1}{4}[(-i\omega_0)\,(e^{-i2\omega_0 t} + 1)\bar{\boldsymbol{\chi}}(\omega_0) + (i\omega_0)(e^{i2\omega_0 t} + 1)\bar{\boldsymbol{\chi}}(-\omega_0)] : \mathbf{FF} \tag{10.163}$$

As we can see, the instantaneous power absorption oscillates in time. We can find the average power absorbed by taking the time average of Eq. (10.163) over one period of oscillation:

$$\langle \mathbf{P}(t) \rangle = \frac{\omega_0}{\pi} \int_0^{\pi/\omega_0} dt P(t) = \frac{i\omega_0}{4}[\bar{\boldsymbol{\chi}}(\omega_0) - \bar{\boldsymbol{\chi}}(-\omega_0)] : \mathbf{FF} = \frac{\omega_0}{2}\bar{\boldsymbol{\chi}}''(\omega_0) : \mathbf{FF}, \tag{10.164}$$

where $\bar{\boldsymbol{\chi}}''(\omega_0)$ is the imaginary part of $\bar{\boldsymbol{\chi}}(\omega_0)$. Again we see that the average power absorbed depends on the imaginary part of the response matrix. In principle, the average power absorbed can be measured, and therefore $\bar{\boldsymbol{\chi}}''(\omega_0)$ can be measured for all ω_0. The Kramers–Kronig relations allow us to obtain the real part of $\bar{\boldsymbol{\chi}}(\omega_0)$ once we know $\bar{\boldsymbol{\chi}}''(\omega_0)$. The fluctuation–dissipation theorem relates $\bar{\boldsymbol{\chi}}(\omega)$ to the correlation matrix $\bar{\mathbf{C}}_{\alpha\alpha}(\tau)$ for equilibrium fluctuations and therefore also relates $\bar{\boldsymbol{\chi}}(\omega)$ to the spectral density matrix, $\bar{\mathbf{S}}_{\alpha\alpha}(\omega)$, of equilibrium fluctuations. Thus, by applying a weak external field to a system, we can probe the equilibrium fluctuations.

■ **EXERCISE 10.6.** A Brownian particle of mass m is attached to a harmonic spring with force constant, k, and is driven by an external force, $F(t)$. The particle is constrained to move in one dimension. The Langevin equation is

$$m\frac{d^2x(t)}{dt^2} + \gamma\frac{dx(t)}{dt} + m\omega_0^2 x(t) = \xi(t) + F(t),$$

where $\omega_0^2 = (k/m)$, γ is the friction constant, and $\xi(t)$ is a Gaussian white noise with zero mean. Then equation of motion of the average position, $\langle x(t)\rangle_F$, in the presence of the external force, $F(t)$, is

$$m\frac{d^2\langle x(t)\rangle_F}{dt^2} + \gamma\frac{d\langle x(t)\rangle_F}{dt} + m\omega_0^2\langle x(t)\rangle_F = F(t).$$

(a) Compute and plot the linear response function, $K(t)$, where $\langle x(t)\rangle_F = \int_{-\infty}^{\infty} K(t - t')F(t')dt'$. (b) Compute the total energy absorbed for the case of a driving force, $F(t) = F_0\delta(t)$ [10].

Answer:

(a) From the condition of causality we know that $K(t-t') \neq 0$ for $t > t'$ and $K(t-t') = 0$ for $t < t'$. Also, the linear response function is independent of the type of force we apply. Therefore, we can use the simplest force to obtain an expression for the linear response function. If we apply a delta-function driving force, $F(t) = F_0\delta(t)$ at time $t = 0$, then for times $t > 0$ the response is

$$\langle x(t)\rangle_F = K(t)F_0. \tag{1}$$

Given that the average, $\langle x(t)\rangle_F$, obeys the equation

$$m\frac{d^2\langle x(t)\rangle_F}{dt^2} + \gamma\frac{d\langle x(t)\rangle_F}{dt} + m\omega_0^2\langle x(t)\rangle_F = F(t), \tag{2}$$

we obtain the following equation for the response function

$$m\frac{d^2K(t)}{dt^2} + \gamma\frac{dK(t)}{dt} + m\omega_0^2K(t) = F(t). \tag{3}$$

If we take the Fourier transform of Eq. (3), we obtain

$$-m\omega^2\chi(\omega) - i\omega\gamma\chi(\omega) + m\omega_0^2\chi(\omega) = 1, \tag{4}$$

where $\chi(\omega)$ is the susceptibility function. Therefore,

$$\chi(\omega) = \frac{1}{-m\omega^2 + m\omega_0^2 - i\gamma\omega}. \tag{5}$$

We can divide the susceptibility function into its real part, $\chi'(\omega)$, and imaginary part, $\chi''(\omega)$, so that

$$\chi(\omega) = \chi'(\omega) + i\chi''(\omega). \tag{6}$$

Then we find

$$\chi'(\omega) = \frac{m(\omega_0^2 - \omega^2)}{m^2(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2} \tag{7}$$

and

$$\chi''(\omega) = \frac{\gamma\omega}{m^2(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2}. \tag{8}$$

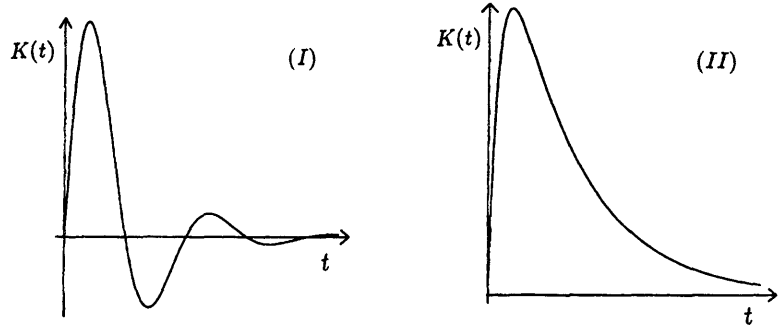
The response function is given by

$$K(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega\, \chi(\omega)\, e^{-i\omega t} = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega\, \frac{e^{-i\omega t}}{-m\omega^2 + m\omega_0^2 - i\gamma\omega}. \tag{9}$$

Notice that the poles of $\chi(\omega)$ occur at $\omega = -i(\gamma/2m) \pm \sqrt{\omega_0^2 - (\gamma^2/4m^2)}$, which is in the lower half-plane. $\chi(\omega)$ has no poles in the upper half-plane. For $t > 0$ we can write Eq. (9) as a contour integral, but we must close the contour in the lower half-plane so that the integral will be convergent. There are two poles in the lower half plane, so we get a nonzero result. For $t < 0$ we must close the contour in the upper half-plane, but since there are no poles there, we get zero. Therefore we find

$$K(t) = \frac{\theta(t) e^{-\gamma t/2m} \sin\left[\sqrt{\omega_0^2 - \gamma^2/4m^2}\, t\right]}{m\sqrt{\omega_0^2 - \gamma^2/4m^2}}, \tag{10}$$

where $\theta(t)$ is the Heaviside function ($\theta(t) = 1$ for $t > 0$ and $\theta(t) = 0$ for $t < 0$). A plot of the response function is shown below for the (I) underdamped case where $\omega_0 > \gamma/2m (\omega_0 = 3, (\gamma/2m) = 1, m = 1)$ and for the (II) overdamped case where $\omega_0 < \gamma/2m (\omega_0 = 2, (\gamma/2m) = 3, m = 1)$. If we hit the Brownian oscillator with a delta function force, it is displaced from equilibrium and slowly decays back to its equilibrium value.



(b) The total energy absorbed by the harmonic oscillator for the case of the delta function force can be obtained from Eq. (10.160) and Eq. (8) above. We find

$$W_{abs} = -\frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega\, \frac{\gamma\omega^2 F_0^2}{m^2(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2} = -\frac{F_0^2}{2m}. \tag{8}$$

Since the absorbed energy is negative, this is actually energy which is dissipated by the oscillator due to friction.

10.F. TRANSPORT PROPERTIES OF MIXTURES [3, 11, 12]

Hydrodynamic processes are a consequence of both (a) symmetries at work in fundamental interactions and (b) entropy producing decay processes caused by interactions and internal changes in the constituents of a hydrodynamic system. In Sections 10.B and 10.C we derived the full set of hydrodynamic equations for a single-component classical fluid of point particles. Most of the interesting behavior in such a system occurs in the macroscopic flow processes. Indeed, three transport coefficients characterized the decay to equilibrium of such a system, thermal conductivity, shear viscosity, and bulk viscosity. Both the shear and bulk viscosity characterize decay processes in the macroscopic flow of the fluid. Only the thermal diffusion would remain if the fluid were at rest. In this section we will consider a multicomponent fluid of particles that can interact and undergo chemical reactions, but we will assume that, while constituent particles may move relative to one another, the fluid as a whole does not move. Under these conditions, there will be no viscosity but there will be various kinds of diffusion processes at work. In Section 10.F.1 we will derive a general expression for the entropy production in such systems, since this is the starting of any transport theory. In Sections S10.D and S10.E we will study some examples of transport processes in multicomponent fluids and membranes.

10.F.1. Entropy Production in Multicomponent Systems

Let us imagine a large system containing N different kinds of molecules undergoing r different chemical reactions. We will focus on a small sub-volume, V, within that system and assume that the small subvolume can exchange energy and matter with the larger system it is embedded in. The combined first and second laws describe the thermodynamic behavior of the material inside the subvolume, V. They can be written $TdS = dU + PdV - \sum_{j=1}^{N} \tilde{\mu}_j dm_j$ and the fundamental equation can be written $TS = U + PV - \sum_{j=1}^{N} \tilde{\mu}_j m_j$, where m_j is the mass of particles of type j. The mass, m_j, can be written $m_j = M_j n_j$, where M_j is the molecular mass (grams/mole) of particles, j, and n_j is the number of moles. It is useful to rewrite the combined first and second laws in terms of densities. We will let $s = S/V, u = U/V$, and $\rho_j = m_j/V$, where ρ_j is the mass density of particles of type j. Then we find

$$Tds - du + \sum_{j=1}^{N} \tilde{\mu}_j d\rho_j = 0 \tag{10.165}$$

for a subsystem with variable volume, V.

Let us now return to the first law, $dU = đQ - PdV + \sum_{j=1}^{N} \tilde{\mu}_j dm_j$, which keeps track of energy exchange. We can divide the heat transfer, $đQ$, into a contribution from pure heat exchange and a contribution due to transport of matter. This is easy to see for reversible processes where we can write

$$đQ \equiv TdS = T[dS]_{\{m_j\}} + T \sum_{j=1}^{N} \tilde{s}_j dm_j. \tag{10.166}$$

where $\tilde{s}_j = (\partial S/\partial m_j)_{T,P,\{m_{i\neq j}\}}$ is a partial specific entropy. If we further note that $\tilde{s}_j T = \tilde{h}_j - \tilde{\mu}_j$, where $\tilde{h}_j = (\partial H/\partial m_j)_{T,P,\{m_{i\neq j}\}}$ is a partial specific enthalpy and $\tilde{\mu}_j$ is a partial specific Gibbs free energy (the chemical potential of species, j), then Eq. (10.166) takes the form

$$đQ = TdS = T[dS]_{\{m_j\}} + \sum_{j=1}^{N} (\tilde{h}_j - \tilde{\mu}_j) dm_j. \tag{10.167}$$

The first term, $[dS]_{\{m_j\}}$, is the change in the heat content of the system due to mechanical and thermal heat exchange with the outside environment. It does not include the change in heat content due to flow of particles into or out of the system. For a system out of equilibrium, where $đQ < TdS$, we can write $đQ = đQ' + \sum_{j=1}^{N} (\tilde{h}_i - \tilde{\mu}_i) dm_j$, where $đQ'$ represents pure heat exchange with the environment, minus contributions due to particle exchange. When written in terms of $đQ'$, the first law takes the form

$$dU = đQ' - PdV + \sum_{j=1}^{N} \tilde{h}_j dm_j. \tag{10.168}$$

We will now write Eq. (10.168) for densities. We again define $s = S/V$, $u = U/V$, and $\rho_j = m_j/V$, but we also introduce the heat exchange per unit volume, $đq' = đQ'/V$. The Eq. (10.168) can be written

$$V\left(du - đq' - \sum_{j=1}^{N} \tilde{h}_j d\rho_j\right) = dV\left(-u - P + \sum_{j=1}^{N} \tilde{h}_j \rho_j\right). \tag{10.169}$$

However, $u + P = H/V$ and $\sum_{j=1}^{N} \tilde{h}_j \rho_j = H/V$. Therefore, the term on the right is identically zero and we obtain

$$du = đq' + \sum_{j=1}^{N} \tilde{h}_j d\rho_j \equiv dq, \tag{10.170}$$

where dq is the total amount of heat transfered per unit volume. If we substitute Eq. (10.170) into Eq. (10.165), we can write the following expression for the

entropy change in our open system

$$Tds = dq - \sum_{j=1}^{N} \tilde{\mu}_j d\rho_j. \tag{10.171}$$

We can now use Eq. (10.171) to compute the entropy production in open systems.

We will neglect convection of fluid in our small volume, V. That is, we assume that the baryocentric velocity of the fluid, $\mathbf{v} = \sum_{j=1}^{N} \rho_j \mathbf{v}_j / \rho = 0$, where $\rho = \sum_{j=1}^{N} \rho_j$ is the total mass density. If $\tilde{\mathbf{J}}_j = \rho_j \mathbf{v}_j$ is the mass flux (grams/area · second) of particles of type j, this gives the additional condition, $\sum_{j=1}^{N} \tilde{\mathbf{J}}_j = 0$. The time rate of change of thermodynamic quantities inside the volume are related through Eq. (10.171). Since $\mathbf{v} = 0$, we can write

$$T \frac{\partial s}{\partial t} = \frac{\partial q}{\partial t} - \sum_{j=1}^{N} \tilde{\mu}_j \frac{\partial \rho_j}{\partial t}. \tag{10.172}$$

Changes inside the volume, V, are due to flows across the boundary and sources inside the volume. We can therefore introduce the following balance equations for the entropy density,

$$\frac{\partial s}{\partial t} = -\nabla_{\mathbf{r}} \cdot \mathbf{J}_S + \sigma, \tag{10.173}$$

the mass density of particles of type j,

$$\frac{\partial \rho_j}{\partial t} = -\nabla_{\mathbf{r}} \cdot \tilde{\mathbf{J}}_j + \sum_{\alpha=1}^{r} \tilde{\nu}_{j,\alpha} J_\alpha^c, \tag{10.174}$$

and heat density,

$$\frac{\partial q}{\partial t} = -\nabla_{\mathbf{r}} \cdot \mathbf{J}_q. \tag{10.175}$$

In Eq. (10.173), σ is the entropy source term and is the quantity we wish to find. In Eq. (10.174), $\tilde{\mathbf{J}}_j$ is the mass flux of particles of type j across the boundaries, and $\tilde{\nu}_{j,\alpha} = M_j \nu_{j,\alpha}$, where $\nu_{j,\alpha}$ is the stoichiometric coefficient for the jth particle in the αth chemical reaction. The αth chemical reaction acts as a source (or sink) of particles of type j, and the "source" term, $J_\alpha^c = (1/V)(d\xi_\alpha/dt)$, represents this contribution (ξ_α is the degree of reaction for the αth chemical reaction). In Eq. (10.175), $\mathbf{J}_q$ is the total heat flow across the boundaries. If we substitute these equations into Eq. (10.173), we find

$$-\nabla_{\mathbf{r}} \cdot \mathbf{J}_S + \sigma = -\frac{1}{T} \nabla_{\mathbf{r}} \cdot \mathbf{J}_q - \sum_{j=1}^{N} \frac{\tilde{\mu}_j}{T} \left[-\nabla_{\mathbf{r}} \cdot \tilde{\mathbf{J}}_j + \sum_{\alpha=1}^{r} \tilde{\nu}_{j,\alpha} J_\alpha^c \right]. \tag{10.176}$$

If we now rearrange terms we obtain

$$-\nabla_{\mathbf{r}} \cdot \mathbf{J}_S + \sigma = -\nabla_{\mathbf{r}} \cdot \left[\frac{\mathbf{J}_q - \sum_{j=1}^{N} \tilde{\mu}_j \tilde{\mathbf{J}}_j}{T} \right] + \mathbf{J}_q \cdot \nabla_{\mathbf{r}} \left(\frac{1}{T} \right) - \sum_{j=1}^{N} \tilde{\mathbf{J}}_j \cdot \nabla_{\mathbf{r}} \left(\frac{\tilde{\mu}_j}{T} \right) + \sum_{\alpha=1}^{r} J_\alpha^c \frac{A_\alpha}{T}, \tag{10.177}$$

where $A_\alpha = \sum_{j=1}^{N} \tilde{\nu}_{j,\alpha} \tilde{\mu}_j$ is the affinity of the αth chemical reaction. Thus, the entropy current is

$$\mathbf{J}_S = \frac{\mathbf{J}_q - \sum_{j=1}^{N} \tilde{\mu}_j \tilde{\mathbf{J}}_j}{T}, \tag{10.178}$$

and the entropy source is

$$\begin{aligned} \sigma &= \mathbf{J}_q \cdot \nabla_{\mathbf{r}} \left(\frac{1}{T} \right) - \sum_{j=1}^{N} \tilde{\mathbf{J}}_j \cdot \nabla_{\mathbf{r}} \left(\frac{\tilde{\mu}_j}{T} \right) - \sum_{\alpha=1}^{r} J_\alpha^c \frac{A_\alpha}{T} \\ &= -\mathbf{J}_S \cdot \nabla_{\mathbf{r}} T - \frac{1}{T} \sum_{j=1}^{N} \tilde{\mathbf{J}}_j \cdot \nabla_{\mathbf{r}} \tilde{\mu}_j - \sum_{\alpha=1}^{r} J_\alpha^c \frac{A_\alpha}{T}. \end{aligned} \tag{10.179}$$

The entropy source term is again written as a product of a current and an affinity or force (the two words are often used interchangeably). Gradients in the temperature and chemical potentials of the various constituent particles act as forces driving the heat current, $\mathbf{J}_q$, and the particle mass current, $\tilde{\mathbf{J}}_j$. The chemical affinity, A_α, is the force driving the αth chemical reaction.

It is sometimes useful to write Eq. (10.179) in a slightly different form. Let us note that $d(\tilde{\mu}_j/T) = [d\tilde{\mu}_j]_T/T + [(\partial/\partial T)(\tilde{\mu}_j/T)]_{P,\{m_i\}}$. But $[(\partial/\partial T)(\tilde{\mu}_j/T)]_{P,\{m_i\}} = -(1/T^2)(\tilde{\mu}_j - \tilde{s}_j T) = -\tilde{h}_j/T^2$, where $\tilde{s}_j = (\partial S/\partial m_j)_{T,P,\{m_{i\neq j}\}} = -(\partial \tilde{\mu}_j/\partial T)_{P,\{m_i\}}$. We finally obtain $d(\tilde{\mu}_j/T) = [d\tilde{\mu}_j]_T/T - (\tilde{h}T^2)dT$. This in turn leads to the relation $\nabla_{\mathbf{r}}(\tilde{\mu}_j/T) = [\nabla_{\mathbf{r}}\tilde{\mu}_j]_T/T - (\tilde{h}_j/T^2)\nabla_{\mathbf{r}}T$. If we substitute into Eq. (10.179), we obtain

$$T\sigma = -\frac{1}{T}\mathbf{J}_q' \cdot \nabla_{\mathbf{r}} T - \sum_{j=1}^{N} \tilde{\mathbf{J}}_j \cdot [\nabla_{\mathbf{r}} \tilde{\mu}_j]_T - \sum_{\alpha=1}^{r} J_\alpha^c A_\alpha, \tag{10.180}$$

where $\mathbf{J}_q' = \mathbf{J}_q - \sum_j \tilde{h}_j \tilde{\mathbf{J}}_j$ is the heat current minus the contribution due to diffusion. Notice that the entropy production is again written in terms of products of affinities (forces) and currents. The affinity driving the heat current is a temperature gradient. The affinity driving a mass current of particles of type

j is a gradient in the chemical potential of particles of type j. The affinity driving the αth nonequilibrium chemical reaction is just the chemical affinity, A_α.

It is interesting that even in a completely homogeneous system, chemical reactions out of chemical equilibrium create entropy. A chemical reaction is a spontaneous, random event which, if the system is out of chemical equilibrium, causes a discrete change in the chemical composition of the system. It is the prototype of a spontaneous process. As we show in Exercise 10.7, chemical reactions also provide a simple example of how the underlying microscopic reversibility of a system in equilibrium (the principle of detailed balance) leads to Onsager's relations between cross-transport coefficients (cf. Section 10.D.1).

■ **EXERCISE 10.7.** The cyclic set of chemical reactions

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B, \qquad B \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C, \qquad C \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} A,$$

provides a "textbook" example of the use of Onsager's relations. When the reactions are out of equilibrium they produce an amount of entropy/volume $\cdot$time, σ, where $T\sigma = J_1A_1 + J_2A_2 + J_3A_3, J_\alpha = (1/V)(d\xi_\alpha/dt)$ is the current for the αth reaction, and A_α is the affinity for the αth reaction. Assume that the chemical potential is that of an ideal gas mixture of molecules, A, B, and C. (a) Show that near equilibrium, $J_1 - J_3 = L_{11}A_1 + L_{12}A_2$ and find L_{11}, L_{12}, L_{21}, L_{22} and $J_2 - J_3 = L_{21}A_1 + L_{22}A_2$. (b) Show that $L_{12} = L_{21}$.

Answer: The degree of reaction, $d\xi_\alpha$, of the αth reaction (for $\alpha = 1, 2$, and 3) is

$$d\xi_1 = \frac{dn_A}{\nu_{A1}} = \frac{dn_B}{\nu_{B1}}, \qquad d\xi_2 = \frac{dn_B}{\nu_{B2}} = \frac{dn_C}{\nu_{C2}}, \quad \text{and} \quad d\xi_3 = \frac{dn_C}{\nu_{C3}} = \frac{dn_A}{\nu_{A3}}, \tag{1}$$

where $\nu_{A1} = \nu_{B2} = \nu_{C3} = -1$ and $\nu_{B1} = \nu_{C2} = \nu_{A3} = +1$. The time rate of change in the number of moles, n_A, of molecule A due to reaction $\alpha = 1$ is $dn_A/dt = k_{-1}n_B - k_1n_A$. The time rate of change of the number of moles of molecule B due to reaction $\alpha = 2$ is $dn_B/dt = k_{-2}n_C - k_2n_B$, and the time rate of change in the number of moles of molecule C due to reaction $\alpha = 3$ is $dn_C/dt = k_{-3}n_A - k_3n_C$. The affinities for reactions $\alpha = 1, 2$, and 3 are

$$A_1 = \mu_A - \mu_B, \qquad A_2 = \mu_B - \mu_C, \qquad \text{and} \quad A_3 = \mu_C - \mu_A, \tag{2}$$

respectively, where $\mu_j = M_j\tilde{\mu}_j$. Since $A_3 = -(A_1 + A_2)$, the rate of entropy production per unit volume, σ, due to the chemical reactions can be written

$$T\sigma = (J_1 - J_3)A_1 + (J_2 - J_3)A_2. \tag{3}$$

Therefore, the generalized Ohm's law takes the form

$$J_1 - J_3 = L_{11}A_1 + L_{12}A_2 \quad \text{and} \quad J_2 - J_3 = L_{21}A_1 + L_{22}A_2. \tag{4}$$

Now we must find explicit expressions for the Onsager coefficients, L_{11}, L_{12}, L_{21}, and L_{22}.

From the rate of change of mole numbers, we can write the currents as

$$J_1 = k_1 c_A - k_{-1} c_B, \qquad J_2 = k_2 c_B - k_{-2} c_C, \quad \text{and} \quad J_3 = k_3 c_C - k_{-3} c_A, \tag{5}$$

where $c_i = n_i/V$ is the molar concentration of molecules of type i. At equilibrium these currents are zero. If we denote the equilibrium molar densities as $\bar{c}_A, \bar{c}_B$, and $\bar{c}_C$, then we find the equilibrium conditions

$$\frac{\bar{c}_B}{\bar{c}_A} = \frac{k_1}{k_{-1}}, \qquad \frac{\bar{c}_C}{\bar{c}_B} = \frac{k_2}{k_{-2}}, \quad \text{and} \quad \frac{\bar{c}_A}{\bar{c}_C} = \frac{k_3}{k_{-3}}. \tag{6}$$

We can also write the affinities. Let us approximate the Gibbs free energy of the system by that of an ideal gas mixture of molecules A, B, and C,

$$\begin{aligned} G(P, T, n_A, n_B, n_C) = & G^{(0)} - nRT \ln\left(\frac{T^{(5/2)}}{P}\right) + n_A RT \ln(x_A) \\ & + n_B RT \ln(x_B) + n_C RT \ln(x_C), \end{aligned} \tag{7}$$

where $G^{(0)}$ is a constant and x_i is the mole fraction of molecules of type i. The chemical potentials are partial Gibbs free energies and are given by

$$\begin{aligned} \mu_A &= -RT \ln\left(\frac{T^{5/2}}{P}\right) + RT \ln(x_A), \\ \mu_B &= -RT \ln\left(\frac{T^{5/2}}{P}\right) + RT \ln(x_B), \quad \text{and} \\ \mu_C &= -RT \ln\left(\frac{T^{5/2}}{P}\right) + RT \ln(x_C). \end{aligned} \tag{8}$$

The affinities are therefore

$$\begin{aligned} A_1 &= -RT \ln\left(\frac{x_B}{x_A}\right) = -RT \ln\left(\frac{c_B}{c_A}\right), \\ A_2 &= -RT \ln\left(\frac{c_C}{c_B}\right), \quad \text{and} \\ A_3 &= -RT \ln\left(\frac{c_A}{c_C}\right). \end{aligned} \tag{9}$$

We now want to approximate the currents and affinities by their values close to equilibrium. Let us expand the molar densities about their equilibrium values, $c_A = \bar{c}_A + \alpha_A, c_B = \bar{c}_B + \alpha_B$, and $c_C = \bar{c}_C + \alpha_C$, where α_A, α_B, and α_C are small deviations from equilibrium. Then we find

$$J_1 = \frac{k_1 \bar{c}_A}{RT} A_1, \qquad J_2 = \frac{k_2 \bar{c}_B}{RT} A_2, \quad \text{and} \quad J_3 = \frac{k_3 \bar{c}_C}{RT}(A_1 + A_2). \tag{10}$$

Thus, we finally obtain

$$J_1 - J_3 = \frac{k_1 \bar{c}_A + k_3 \bar{c}_C}{RT} A_1 + \frac{k_3 \bar{c}_C}{RT} A_2 \tag{11}$$

and

$$J_2 - J_3 = \frac{k_3 \bar{c}_C}{RT} A_1 + \frac{k_2 \bar{c}_B + k_3 \bar{c}_C}{RT} A_2. \tag{12}$$

We therefore find $L_{11} = (1/RT)(k_1 \bar{c}_A + k_3 \bar{c}_C), L_{12} = L_{21} = (k_3 \bar{c}_C / RT)$, and $L_{22} = (1/RT)(k_2 \bar{c}_B + k_3 \bar{c}_C)$ so that Onsager's relations are satisfied for this cyclic set of chemical reactions.

10.F.2. Fick's Law for Diffusion

In order to develop some intuition about these equations it is useful to consider Brownian motion. Let us imagine that we have a very dilute mixture of a solvent (which we will choose to be water) and a solute (which we will leave variable). Let ρ_w (ρ_s) be the density of water (solute) and let $\rho = \rho_s + \rho_w$ be the total density. We will assume that the mass density of solute is much smaller than the mass density of water, so that $\tilde{x} = (\rho_s / \rho_w) \ll 1$. Also, we shall assume that the pressure, P, and temperature, T, are uniform throughout the fluid. From Eq. (10.180) the entropy production, σ, is given by

$$T\sigma = -\tilde{\mathbf{J}}_w \cdot [\nabla_{\mathbf{r}} \tilde{\mu}_w]_T - \tilde{\mathbf{J}}_s \cdot [\nabla_{\mathbf{r}} \tilde{\mu}_s]_T. \tag{10.181}$$

From the Gibbs–Duhem equation (2.62), for constant temperature and pressure, we find $\rho_s [\nabla_{\mathbf{r}} \tilde{\mu}_s]_{T,P} + \rho_w [\nabla_{\mathbf{r}} \tilde{\mu}_w]_{T,P} = 0$. Also, $\tilde{\mathbf{J}}_s + \tilde{\mathbf{J}}_w = 0$ since the baryocentric velocity is assumed to be zero. Therefore, the entropy production can be written

$$T\sigma = -\left(\tilde{\mathbf{J}}_s - \frac{\rho_s}{\rho_w} \tilde{\mathbf{J}}_w\right) \cdot [\nabla_{\mathbf{r}} \tilde{\mu}_s]_{T,P}. \tag{10.182}$$

The current that appears in Eq. (10.182) is the diffusion current, $\tilde{\mathbf{J}}_s^D = \tilde{\mathbf{J}}_s - (\rho_s / \rho_w) \tilde{\mathbf{J}}_w = \tilde{\mathbf{J}}_s (1 + \rho_s / \rho_w)$, of solute relative to water. This is easy

to see. Since $\tilde{\mathbf{J}}_s \equiv \rho_s \mathbf{v}_s$ is the current of solute relative to the walls and $\tilde{\mathbf{J}}_w \equiv \rho_w \mathbf{v}_w$ is the current of water relative to the walls, $\tilde{\mathbf{J}}_s^D = \tilde{\mathbf{J}}_s - (\rho_s/\rho_w)$, $\tilde{\mathbf{J}}_w = \rho_s(\mathbf{v}_s - \mathbf{v}_w)$ is the current of solute relative to water. It is this current that must be nonzero to have diffusion of solute relative to water. In terms of the diffusion current, the entropy production takes the form

$$\sigma = -\tilde{\mathbf{J}}_s^D \cdot [\nabla_{\mathbf{r}} \tilde{\mu}_s]_{T,P}. \tag{10.183}$$

We can write a generalized Ohm's law for this process. Since for a binary mixture, $\mu_s = \mu_s(T, P, x_s)$, where x_s is the mole fraction of solute, we have

$$\tilde{\mathbf{J}}_s^D = -\tilde{L}_s[\nabla_{\mathbf{r}} \tilde{\mu}_s]_{T,P} = -\tilde{L}_s \left(\frac{\partial \tilde{\mu}_s}{\partial x_s}\right)_{P,T} \nabla_{\mathbf{r}} x_s. \tag{10.184}$$

If we treat the mixture as an ideal mixture, then $\tilde{\mu}_s = \tilde{\mu}_s^0 + (RT/M_s)\ln(x_s)$ and $(\partial \tilde{\mu}_s/\partial x_s)_{PT} = RT/x_s M_s$. Also note that $\nabla_{\mathbf{r}} x_s = (c_w/c^2)\nabla c_s - (c_s/c^2)\nabla c_w$, where $c_i = n_i/V$ is the concentration (moles/volume) of molecules of type i. However, since $c_s \ll c_w$, to lowest order in c_s/c_w, we can write the particle flux, $\tilde{\mathbf{J}}_s^D$ (moles/area · second), as

$$\mathbf{J}_s^D = \frac{\tilde{\mathbf{J}}_s^D}{M_s} = -\tilde{L}_s \frac{RT}{M_s^2 c_s} \nabla_{\mathbf{r}} c_s \equiv -D \nabla_{\mathbf{r}} c_s. \tag{10.185}$$

The equation $\mathbf{J}_s^D = -D\nabla_{\mathbf{r}} c_s$ is *Fick's law* for diffusion, and $D = \tilde{L}_s RT/M_s^2 c_s$ is the diffusion coefficient. If we equate the diffusion coefficient, D, to the Einstein diffusion coefficient for Brownian motion, $D = RT/(N_A 6\pi\eta a)$, then we find $\tilde{L}_s = c_s M_s^2/N_A 6\pi\eta a$, where η is the coefficient of viscosity for water, a is the radius of the solute molecule, and N_A is Avogadro's number. We can obtain a numerical estimate for these quantities. At $T = 25\,^\circ\text{C} = 298.15\,\text{K}$, the viscosity of water is $\eta \approx 0.9 \times 10^{-3}\,\text{P} \cdot \text{sec}$ (Pascal-seconds). For solute molecules with a radius of 4Å, the Einstein diffusion coefficient is $D \approx 0.61 \times 10^{-5}\,\text{cm}^2/\text{sec}$. We can compare this with actual measurements of the diffusion coefficient, given in Table 10.1, for very dilute aqueous solutions. The value given by the Einstein diffusion coefficient is of the correct order of magnitude. It is also interesting to see how the diffusion coefficient depends on

TABLE 10.1. Diffusion Coefficients for Some Typical Substances in the Limit of Infinitely Dilute Aqueous Solution ($T = 25°C$) [14]

Solute	Formula	D (10^{-5} cm^2 sec^{-1})
Acetone	C_3H_6O	1.28
Benzene	C_6H_6	1.02
Ethanol	C_2H_6O	1.24
Methane	CH_4	1.49
Ethylbenzene	C_8H_{10}	0.8

TABLE 10.2. Diffusion Coefficient, D, of Benzene in Some Typical Solvents in the Limit of Infinitely Dilute Solution ($T = 25°C$). η is the Viscosity of the Solvent [14]

Solvent	Formula	$D(10^{-5}\text{cm}^2\text{sec}^{-1})$	$\eta(10^{-3}$ Pa-sec)
1-Butanol	$C_4H_{10}O$	1.00	2.544
Cyclohexane	C_6H_{12}	1.41	0.894
Ethanol	C_2H_6O	1.81	1.074
Heptane	C_7H_{16}	3.91	0.387
Toluene	C_7H_8	2.54	0.560

the solvent. In Table 10.2 we give the diffusion coefficient for some infinitely dilute solutions of benzene in various solvents.

10.F.3. Thermal Diffusion

If a temperature gradient exists in a mixture of molecules, it can drive diffusion processes. Also, if a concentration gradient exists in a mixture, it can induce a temperature gradient. Diffusion induced by a temperature gradient is called *thermal diffusion.* The parameter that measures its strength is called the *Soret coefficient.*

Let us again consider a binary mixture consisting of water (the solvent) and a solute. We shall assume that the pressure, P, is uniform throughout the mixture. From Eq. (10.180) the entropy production, σ, is given by

$$\begin{aligned} T\sigma &= -\frac{1}{T}\mathbf{J}'_q \cdot \nabla_{\mathbf{r}} T - \tilde{\mathbf{J}}_s \cdot [\nabla_{\mathbf{r}} \tilde{\mu}_s]_T - \tilde{\mathbf{J}}_w \cdot [\nabla_{\mathbf{r}} \tilde{\mu}_w]_T \\ &= -\frac{1}{T}\mathbf{J}'_q \cdot \nabla_{\mathbf{r}} T - \tilde{\mathbf{J}}^D_s \cdot [\nabla_{\mathbf{r}} \tilde{\mu}_s]_{T,P}, \end{aligned} \tag{10.186}$$

where $\tilde{\mathbf{J}}^D_s$ is the mass current of solute relative to water. The generalized Ohm's law for this system can be written

$$\begin{aligned} \tilde{\mathbf{J}}^D_s &= -\tilde{L}_{ss}[\nabla_{\mathbf{r}} \tilde{\mu}_s]_{T,P} - \tilde{L}_{sq} \nabla_{\mathbf{r}} T, \\ \mathbf{J}'_q &= -\tilde{L}_{qs}[\nabla_{\mathbf{r}} \tilde{\mu}_s]_{T,P} - L_{qq} \nabla_{\mathbf{r}} T. \end{aligned} \tag{10.187}$$

where L_{ss}, L_{sq}, L_{sq}, and L_{qq} are the transport coefficients associated with this process. Let us again assume that we have a dilute mixture of solute in water so that $[\nabla_{\mathbf{r}} \tilde{\mu}_s]_{T,P} \approx (\partial \tilde{\mu}_s / \partial c_s)_{T,P} \nabla_{\mathbf{r}} c_s$. Then Eqs. (10.187) take the form

$$\begin{aligned} \tilde{\mathbf{J}}^D_s &= -\tilde{L}_{ss}\left(\frac{\partial \tilde{\mu}_s}{\partial c_s}\right)_{T,P} \nabla_{\mathbf{r}} c_s - \tilde{L}_{sq} \nabla_{\mathbf{r}} T \\ \mathbf{J}'_q &= -\tilde{L}_{qs}\left(\frac{\partial \tilde{\mu}_s}{\partial c_s}\right)_{T,P} \nabla_{\mathbf{r}} c_s - L_{qq} \nabla_{\mathbf{r}} T. \end{aligned} \tag{10.188}$$

The diffusion coefficient is then $D = (\tilde{L}_{ss}/M_s)(\partial\tilde{\mu}_s/\partial c_s)_{T,P}$. The coefficient of thermal conductivity is $K = L_{qq}$. In experiments it is found that the coefficient L_{sq} is linearly proportional to the solute concentration. Therefore, a *coefficient of thermal diffusion*, D^T, is introduced and is defined so $\tilde{L}_{sq} = M_s c_s D^T$. The solute particle flux, $\mathbf{J}_s^D = \tilde{\mathbf{J}}_s^D/M_s$, then takes the form

$$\mathbf{J}_s^D = -D\nabla_{\mathbf{r}} c_s - c_s D^T \nabla_{\mathbf{r}} T. \tag{10.189}$$

The *Soret coefficient*, S_T, is defined as $S_T = D^T/D = \tilde{L}_{sq}/(M_s c_s D)$. The Soret coefficient is a measure of the concentration gradient that is set up as the result of a temperature gradient for a system in its steady state. The steady state is defined so that $\mathbf{J}_s^D = 0$ and $\nabla_{\mathbf{r}} T$ =constant. Therefore, if we set $\mathbf{J}_s^D = 0$, the Soret coefficient can also be written $S_T = -\nabla_{\mathbf{r}} \ln(c_s)/\nabla_{\mathbf{r}} T$. The effect of thermal diffusion is generally small with $D^T \approx 10^{-2} D$ or $D^T \approx 10^{-3} D$. However, it has been used as a basis to separate isotopes (Kr^{84} from Kr^{86} and HCl^{35} from HCl^{37}) in the gaseous phase [13].

10.F.4. Electrical Conductivity and Diffusion in Fluids [12]

Electrical conductivity of charged particles in a fluid and the diffusion of those particles are closely related phenomena, because in both cases the process is governed by how the particles interact with the medium around them. Let us imagine a fluid consisting of a dilute solution of charged solute particles (ions), with charge $z_s e$, in water. We can place electrodes in the solution and create an electric field, $\mathbf{E} = -\nabla_{\mathbf{r}}\phi$, in the fluid. There may also be a gradient in the concentration solute particles. Under such conditions there will be a transport of solute particles from one region of the fluid to another. For simplicity we shall assume the temperature, T, and pressure, P, are uniform thoughout the fluid. However, we shall assume that there are gradients in the chemical potentials of the ions and the water and an electric potential gradient in the fluid. The entropy production, σ, is given by

$$T\sigma = -\mathbf{J}_s \cdot \nabla_{\mathbf{r}} \tilde{\mu}_s^e - \mathbf{J}_w \cdot \nabla_{\mathbf{r}} \tilde{\mu}_w, \tag{10.190}$$

where $\tilde{\mu}_s^e$ is the electrochemical potential of the ions. From the Gibbs–Duheim equation we know that for constant T and P, $\rho_s \nabla_{\mathbf{r}} \tilde{\mu}_s^e + \rho_w \nabla_{\mathbf{r}} \tilde{\mu}_w = 0$. Therefore, we can rewrite the entropy production as

$$T\sigma = -\mathbf{J}_s^D \cdot \nabla_{\mathbf{r}} \tilde{\mu}_s^e, \tag{10.191}$$

where $\mathbf{J}_s^D = \mathbf{J}_s - (\rho_s/\rho_w)\mathbf{J}_w$ is the ion current (relative to the water) induced by the electrochemical potential gradient. For a very dilute solution, $\rho_s \ll \rho_w$ and $\mathbf{J}_s^D \approx \mathbf{J}_s$. The generalized Ohm's law for this system can be written

$$\mathbf{J}_s^D = -L\nabla_{\mathbf{r}} \tilde{\mu}_s^e. \tag{10.192}$$

Equation (10.192) contains information about both diffusion and electric conduction processes.

If no electric potential gradient exists in the fluid and if the solution is sufficiently dilute that the interaction between ions can be neglected, then the ions diffuse in a fairly normal manner. The generalized Ohm's law takes the form

$$\mathbf{J}_s^D = -L\frac{RT}{M_s c_s}\nabla_{\mathbf{r}} c_s \equiv -D\nabla_{\mathbf{r}} c_s, \tag{10.193}$$

and the diffusion coefficient is $D = LRT/M_s c_s$, where M_s is the molecular weight of the ion (grams/mole) and c_s is its concentration (moles/volume).

Let us now consider the case in which the concentration of ions and water are uniform, but a constant electric field is imposed across the fluid. Then the ion current takes the form

$$\mathbf{J}_s^D = -L\nabla_{\mathbf{r}}\tilde{\mu}_s^e = -L\frac{z_s \mathrm{F}}{M_s}\nabla_{\mathbf{r}}\phi = L\frac{z_s \mathrm{F}}{M_s}\mathbf{E}. \tag{10.194}$$

where F is the Faraday constant (cf. Exercise 2.7).

In the limit of very dilute concentration of ions, $\mathbf{J}_s^D \approx \mathbf{J}_s$, where $\mathbf{J}_s$ gives the ion flux (moles/area · time). The electric current, I, carried by these ions is

$$I = z_s \mathrm{F}\mathbf{J}_s^D = L\frac{z_s^2 \mathrm{F}^2}{M_s}E. \tag{10.195}$$

The electrical conductivity of the fluid is $\kappa = I/E$. Therefore,

$$\kappa = L\frac{z_s^2 \mathrm{F}^2}{M_s} = \frac{c_s z_s^2 \mathrm{F}^2}{RT}D \equiv z_s c_s \lambda, \tag{10.196}$$

where λ is the *equivalent conductance*. Thus we have related the diffusion coefficient for an ion to its electrical conductivity. In Table 10.3 we give the

TABLE 10.3. The Diffusion Coefficient, D, and Equivalent Conductance, λ, for Some Ions in the Limit of Infinitely Dilute Aqueous Solution ($T = 25°$ C) [14]

Ion	$D(10^{-5}\,\mathrm{cm^2 sec^{-1}})$	$\lambda(10^{-4}\mathrm{m^2 S\,mol^{-1}})$
H^+	9.311	349.65
K^+	1.957	73.48
Na^+	1.334	50.08
Cl^-	2.032	76.31
F^-	1.475	55.4

diffusion coefficients for some commonly found ions in the limit of infinitely dilute aqueous solution.

■ **EXERCISE 10.8.** Consider a very dilute solution of salt, which we denote $A^-_{\nu_a}C^+_{\nu_c}$, which dissociates as

$$A^-_{\nu_a}C^+_{\nu_c} \rightleftharpoons \nu_a A^- + \nu_c C^+,$$

where ν_a and ν_c are the stoichiometric coefficients for the dissociation. Compute the diffusion coefficient for the salt in terms of the diffusion coefficients of the ions in the limit of an infinitely dilute solution. (Assume uniform temperature and pressure throughout the system).

Answer: Let us assume that there are no external electric fields present, so the mass current is driven only by gradients in the chemical potentials of the ions. The entropy production, σ, is given by

$$T\sigma = -\tilde{\mathbf{J}}_a \cdot \nabla\tilde{\mu}_a - \tilde{\mathbf{J}}_c \cdot \nabla\tilde{\mu}_c - \tilde{\mathbf{J}}_w \cdot \nabla\tilde{\mu}_w, \tag{1}$$

where $\tilde{\mathbf{J}}$ is the mass flux of particle of type $i(i = a, c, w)$. From the Gibbs–Duhem equation we know that for constant T and $P, \rho_a\nabla_{\mathbf{r}}\tilde{\mu}_a + \rho_c\nabla_{\mathbf{r}}\tilde{\mu}_c + \rho_w\nabla_{\mathbf{r}}\tilde{\mu}_w = 0$. Therefore, we can rewrite the entropy production as

$$T\sigma = -\tilde{\mathbf{J}}^D_a \cdot \nabla_{\mathbf{r}}\tilde{\mu}_a - \tilde{\mathbf{J}}^D_c \cdot \nabla_{\mathbf{r}}\tilde{\mu}_c, \tag{2}$$

where $\tilde{\mathbf{J}}^D_i = \tilde{\mathbf{J}}_i - (\rho_i/\rho_w)\tilde{\mathbf{J}}_w (i = a, c)$ is the diffusion mass current of ion i. In the limit of infinitely dilute solutions, we can neglect the effect contributions to the current of cations due to gradients in the chemical potential of anions, and vice versa. Therefore, in this limit the generalized Ohm's law for this system can be written in the simple form

$$\tilde{\mathbf{J}}^D_a = -\tilde{L}_a\nabla_{\mathbf{r}}\tilde{\mu}_a \quad \text{and} \quad \tilde{\mathbf{J}}^D_c = -\tilde{L}_c\nabla_{\mathbf{r}}\tilde{\mu}_c. \tag{3}$$

We can restrict ourselves to the case when the total electric current is zero so that

$$z_a\mathbf{J}^D_a + z_c\mathbf{J}^D_c = z_a\tilde{\mathbf{J}}^D_a/M_a + z_c\tilde{\mathbf{J}}^D_c/M_c = -\frac{z_a}{M_a}\tilde{L}_a\nabla_{\mathbf{r}}\tilde{\mu}_a - \frac{z_c}{M_c}\tilde{L}_c\nabla_{\mathbf{r}}\tilde{\mu}_c = 0, \tag{4}$$

where $\mathbf{J}_i (i = a, c)$ is the flux of ions of type i. From Eq. (4) we obtain

$$\nabla_{\mathbf{r}}\tilde{\mu}_a = -\frac{z_c\tilde{L}_c M_a}{z_a\tilde{L}_a M_c}\nabla_{\mathbf{r}}\tilde{\mu}_c. \tag{5}$$

The condition for chemical equilibrium of the dissociation of salt into ions is given by

$$M_s \nabla_{\mathbf{r}} \tilde{\mu}_s = \nu_a M_a \nabla_{\mathbf{r}} \tilde{\mu}_a + \nu_c M_c \nabla_{\mathbf{r}} \tilde{\mu}_c. \tag{6}$$

If we combine Eqs. (5) and (6), we can write

$$\nabla_{\mathbf{r}} \tilde{\mu}_c = \left(\frac{z_a \tilde{L}_a M_c}{\nu_c M_c^2 z_a \tilde{L}_a - \nu_a M_a^2 z_c \tilde{L}_c} \right) M_s \nabla_{\mathbf{r}} \tilde{\mu}_s, \tag{7}$$

and

$$\nabla_{\mathbf{r}} \tilde{\mu}_a = \left(\frac{z_c \tilde{L}_c M_a}{\nu_a M_a^2 z_c \tilde{L}_c - \nu_c M_c^2 z_a \tilde{L}_a} \right) M_s \nabla_{\mathbf{r}} \tilde{\mu}_s, \tag{8}$$

The particle flux of salt molecules is given by

$$J_s^D = J_a^D + J_c^D = -\frac{\tilde{L}_a}{M_a} \nabla_{\mathbf{r}} \tilde{\mu}_a - \frac{\tilde{L}_c}{M_c} \nabla_{\mathbf{r}} \tilde{\mu}_c. \tag{9}$$

We can now substitute Eqs. (7) and (8) into Eq. (9) to compute the particle flux of salt molecules. Let us first note that $\tilde{L}_a = D_a M_a^2 c_a / RT$ and $\tilde{L}_c = D_c M_c^2 c_c / RT$, where D_i is the diffusion coefficient for ions of type i. Let us also note that $c_a = \nu_a c_s$, $c_c = \nu_c c_s$, and $\nabla_{\mathbf{r}} \tilde{\mu}_s = (RT/M_s c_s) \nabla_{\mathbf{r}} c_s$. If we make use of these relations, we find $\mathbf{J}_s = -D_s \nabla_{\mathbf{r}} c_s$, where

$$D_s = \frac{(z_c + |z_a|) D_a D_c}{z_c D_c + |z_a| D_a} \tag{10}$$

is the diffusion coefficient for a very dilute aqueous solution of salt molecules.

▶ SPECIAL TOPICS

▶ S10.A. Onsager's Relations When a Magnetic Field is Present [3]

When a magnetic field, $\mathbf{B}$, is present or when we consider a system in a rotating container where Coriolis forces are present, the Onsager relations must be generalized. When we reverse the time and velocities in the equations of motion, we must also reverse the magnetic field, $\mathbf{B}$, in order to keep the equations of motion invariant, since the magnetic force on particles with velocity $\mathbf{v}$ and charge q is $\mathbf{F} = q\mathbf{v} \times \mathbf{B}$. If we have a rotating container, we must

reverse both the velocity of the particles and the angular velocity $\boldsymbol{\omega}$ of the container to keep the Coriolis force $\mathbf{F} = 2m\mathbf{v} \times \boldsymbol{\omega}$ from changing sign.

In the presence of a magnetic field and fluctuations β (the fluctuations β change sign under time reversal), the distribution function must satisfy the relation

$$f(\boldsymbol{\alpha}, \boldsymbol{\beta}, \mathbf{B}) = f(\boldsymbol{\alpha}, -\boldsymbol{\beta}, -\mathbf{B}) \tag{10.197}$$

under time reversal [here $\boldsymbol{\alpha} = (\alpha_1, \alpha_2, \ldots, \alpha_n)$ and $\boldsymbol{\beta} = (\beta_1, \ldots, \beta_m)$]. This is easily understood if we write $f(\boldsymbol{\alpha}, \boldsymbol{\beta}, \mathbf{B})$ in terms of microscopic states:

$$f(\boldsymbol{\alpha}, \boldsymbol{\beta}, \mathbf{B}) = \frac{1}{\Omega_{\Delta E}(E)} \int_{\substack{\boldsymbol{\alpha} \to \boldsymbol{\alpha} + d\boldsymbol{\alpha} \\ \boldsymbol{\beta} \to \boldsymbol{\beta} + d\boldsymbol{\beta} \\ E \to E + \Delta E}} \cdots \int d\mathbf{r}^N d\mathbf{p}^N. \tag{10.198}$$

For both classical and quantum systems, energy is an even function of the momentum and the magnetic field. Therefore, if we reverse time and the magnetic field in Eq. (10.198), the integral does not change and Eq. (10.197) follows immediately.

When a magnetic field and fluctuations β are present, we can write the distribution function in the more general form:

$$f(\boldsymbol{\alpha}, \boldsymbol{\beta}, \mathbf{B}) = C \exp\left(-\frac{1}{2k_B}(\bar{\mathbf{g}} : \boldsymbol{\alpha}\boldsymbol{\alpha} + \bar{\mathbf{m}} : \boldsymbol{\alpha}\boldsymbol{\beta} + \bar{\mathbf{n}} : \boldsymbol{\beta}\boldsymbol{\alpha} + \bar{\mathbf{h}} : \boldsymbol{\beta}\boldsymbol{\beta})\right), \tag{10.199}$$

where C is the normalization constant and the tensors $\bar{\mathbf{m}}$ and $\bar{\mathbf{n}}$ can be represented by $m \times n$ rectangular matrices. The tensors $\bar{\mathbf{g}}$, $\bar{\mathbf{m}}$, $\bar{\mathbf{n}}$, and $\bar{\mathbf{h}}$ may now depend on the magnetic field. In order to satisfy Eq. (10.197), they must have the following behavior when the magnetic field is reversed:

$$\bar{\mathbf{g}}(\mathbf{B}) = \bar{\mathbf{g}}(-\mathbf{B}), \qquad \bar{\mathbf{h}}(\mathbf{B}) = \bar{\mathbf{h}}(-\mathbf{B}) \tag{10.200}$$

and

$$\bar{\mathbf{m}}(\mathbf{B}) = -\bar{\mathbf{m}}(-\mathbf{B}), \qquad \bar{\mathbf{n}}(\mathbf{B}) = -\bar{\mathbf{n}}(-\mathbf{B}). \tag{10.201}$$

Note that when $\mathbf{B} = 0$ we have $\bar{\mathbf{m}} = \bar{\mathbf{n}} = 0$. The matrix $\bar{\mathbf{m}}$ is simply the transpose of $\bar{\mathbf{n}}$:

$$\bar{\mathbf{m}} = \bar{\mathbf{n}}^T. \tag{10.202}$$

The change in the entropy due to fluctuations in the presence of a magnetic field is

$$\Delta S = -\tfrac{1}{2}(\bar{\mathbf{g}} : \boldsymbol{\alpha}\boldsymbol{\alpha} + \bar{\mathbf{m}} : \boldsymbol{\alpha}\boldsymbol{\beta} + \bar{\mathbf{n}} : \boldsymbol{\beta}\boldsymbol{\alpha} + \bar{\mathbf{h}} : \boldsymbol{\beta}\boldsymbol{\beta}), \tag{10.203}$$

and we must introduce two generalized forces:

$$\mathbf{X} = -\frac{\partial \Delta S}{\partial \boldsymbol{\alpha}} = \bar{\mathbf{g}} \cdot \boldsymbol{\alpha} + \tfrac{1}{2}\boldsymbol{\beta} \cdot \bar{\mathbf{m}} + \tfrac{1}{2}\bar{\mathbf{n}} \cdot \boldsymbol{\beta} = \bar{\mathbf{g}} \cdot \boldsymbol{\alpha} + \bar{\mathbf{n}} \cdot \boldsymbol{\beta} \tag{10.204}$$

and

$$\mathbf{Y} = -\frac{\partial \Delta S}{\partial \boldsymbol{\beta}} = \bar{\mathbf{h}} \cdot \boldsymbol{\beta} + \bar{\mathbf{m}} \cdot \boldsymbol{\alpha}. \tag{10.205}$$

[Note that in Eqs. (10.204) and (10.205) we have used Eq. (10.202)]. The various time-independent correlation functions take the form

$$\langle \boldsymbol{\alpha}\boldsymbol{\alpha} \rangle = k_B(\bar{\mathbf{g}} - \mathbf{n} \cdot \bar{\mathbf{h}}^{-1} \cdot \bar{\mathbf{m}})^{-1}, \tag{10.206}$$

$$\langle \boldsymbol{\alpha}\boldsymbol{\beta} \rangle = -k_B(\bar{\mathbf{g}} - \bar{\mathbf{n}} \cdot \bar{\mathbf{h}}^{-1} \cdot \bar{\mathbf{m}})^{-1} \cdot \bar{\mathbf{n}} \cdot \bar{\mathbf{h}}^{-1}, \tag{10.207}$$

$$\langle \boldsymbol{\beta}\boldsymbol{\alpha} \rangle = -k_B(\bar{\mathbf{h}} - \bar{\mathbf{m}} \cdot \bar{\mathbf{g}}^{-1} \cdot \bar{\mathbf{n}})^{-1} \cdot \bar{\mathbf{m}} \cdot \bar{\mathbf{g}}^{-1}, \tag{10.208}$$

and

$$\langle \boldsymbol{\beta}\boldsymbol{\beta} \rangle = k_B(\bar{\mathbf{h}} - \bar{\mathbf{m}} \cdot \bar{\mathbf{g}}^{-1} \cdot \bar{\mathbf{n}})^{-1}. \tag{10.209}$$

In the presence of a magnetic field, Eq. (10.84) is generalized to the form

$$P(\mathbf{q}^N, \mathbf{p}^N | \mathbf{q}'^N \mathbf{p}'^N; \tau, \mathbf{B}) = P(\mathbf{q}'^N, -\mathbf{p}'^N | \mathbf{q}^N - \mathbf{p}^N; \tau, -\mathbf{B}), \tag{10.210}$$

and the joint probability density for fluctuations is generalized to the form

$$f(\boldsymbol{\alpha}, \boldsymbol{\beta}, \mathbf{B}) P(\boldsymbol{\alpha}, \boldsymbol{\beta} | \boldsymbol{\alpha}', \boldsymbol{\beta}', \tau, \mathbf{B}) = f(\boldsymbol{\alpha}', -\boldsymbol{\beta}', -\mathbf{B}) P(\boldsymbol{\alpha}', -\boldsymbol{\beta}' | \boldsymbol{\alpha}, -\boldsymbol{\beta}, \tau, -\mathbf{B}). \tag{10.211}$$

From Eq. (10.210) it follows that the time-dependent correlation functions given by expressions analogous to Eq. (10.76) satisfy the following relations:

$$\langle \boldsymbol{\alpha}\boldsymbol{\alpha}(\tau); \mathbf{B} \rangle = \langle \boldsymbol{\alpha}(\tau)\boldsymbol{\alpha}; -\mathbf{B} \rangle, \tag{10.212}$$

$$\langle \boldsymbol{\alpha}\boldsymbol{\beta}(\tau); \mathbf{B} \rangle = -\langle \boldsymbol{\alpha}(\tau)\boldsymbol{\beta}; -\mathbf{B} \rangle, \tag{10.213}$$

$$\langle \boldsymbol{\beta}\boldsymbol{\alpha}(\tau); \mathbf{B} \rangle = -\langle \boldsymbol{\beta}(\tau)\boldsymbol{\alpha}; -\mathbf{B} \rangle, \tag{10.214}$$

and

$$\langle \boldsymbol{\beta}\boldsymbol{\beta}(\tau); \mathbf{B} \rangle = \langle \boldsymbol{\beta}(\tau)\boldsymbol{\beta}; -\mathbf{B} \rangle \tag{10.215}$$

under time reversal.

The equations describing the regression of fluctuations can be written as in Eq. (10.87) except that now the matrix $\mathbb{M}$ depends on the magnetic field. Thus,

$$\frac{d}{dt}\begin{pmatrix}\langle \boldsymbol{\alpha}(t)\rangle_{\alpha_0\beta_0}\\ \langle \boldsymbol{\beta}(t)\rangle_{\alpha_0\beta_0}\end{pmatrix} = -\bar{\mathbf{M}}(\mathbf{B})\cdot\begin{pmatrix}\langle \boldsymbol{\alpha}(t)\rangle_{\alpha_0\beta_0}\\ \langle \boldsymbol{\beta}(t)\rangle_{\alpha_0\beta_0}\end{pmatrix}, \tag{10.216}$$

where

$$\bar{\mathbf{M}}\mathbf{B} = \begin{pmatrix}\bar{\mathbf{M}}^{\alpha\alpha}(\mathbf{B}) & \bar{\mathbf{M}}^{\alpha\beta}(\mathbf{B})\\ \bar{\mathbf{M}}^{\beta\alpha}(\mathbf{B}) & \bar{\mathbf{M}}^{\beta\beta}(\mathbf{B})\end{pmatrix} \tag{10.217}$$

or

$$\frac{d}{dt}\begin{pmatrix}\langle \boldsymbol{\alpha}(t)\rangle_{\alpha_0\beta_0}\\ \langle \boldsymbol{\beta}(t)\rangle_{\alpha_0\beta_0}\end{pmatrix} = -\bar{\mathbf{L}}(\mathbf{B})\cdot\begin{pmatrix}\langle \mathbf{X}(t)\rangle_{\alpha_0\beta_0}\\ \langle \mathbf{Y}(t)\rangle_{\alpha_0\beta_0}\end{pmatrix}. \tag{10.218}$$

If we use arguments similar to those in Section 10.D, Onsager's relations take the form

$$\bar{\mathbf{L}}^{\alpha\alpha}(-\mathbf{B})^T = \bar{\mathbf{L}}^{\alpha\alpha}(\mathbf{B}), \tag{10.219}$$

$$\bar{\mathbf{L}}^{\beta\alpha}(-\mathbf{B})^T = -\bar{\mathbf{L}}^{\alpha\beta}(\mathbf{B}), \tag{10.220}$$

$$\bar{\mathbf{L}}^{\alpha\beta}(-\mathbf{B})^T = -\bar{\mathbf{L}}^{\beta\alpha}(\mathbf{B}), \tag{10.221}$$

and

$$\bar{\mathbf{L}}^{\beta\beta}(-\mathbf{B})^T = \bar{\mathbf{L}}^{\beta\beta}(\mathbf{B}). \tag{10.222}$$

Equations (10.219)–(10.222) give the general form of Onsager's relations. If we were considering a rotating system, then we would replace the magnetic field, $\mathbf{B}$, by the angular velocity, ω.

▶ S10.B. Microscopic Linear Response Theory [15]

Kubo was the first to show that it is possible to derive the linear response matrix directly from microscopic theory. Let us consider a system to which we apply an external field, $F_j(\mathbf{r}, t)$, which couples to microscopic densities, $\hat{a}_j(\mathbf{r})$. The total Hamiltonian of the system in the presence of the external field is

$$\hat{H}(t) = \hat{H}_0 + \Delta\hat{H}(t), \tag{10.223}$$

where $\hat{H}_0$ is the Hamiltonian of the system in the absence of the field and

$$\Delta\hat{H}(t) = -\int d\mathbf{r}\hat{\mathbf{a}}(\mathbf{r})\cdot\mathbf{F}(\mathbf{r}, t) \tag{10.224}$$

is the contribution to the Hamiltonian due to the external field. We assume that the external field is turned on at time $t = -\infty$. The total density operator, $\hat{\rho}(t)$, in the presence of the field satisfies the equation of motion

$$i\hbar \frac{\partial \hat{\rho}(t)}{\partial t} = [\hat{H}(t), \hat{\rho}(t)], \tag{10.225}$$

Let us write the total density operator in the form

$$\hat{\rho}(t) = \hat{\rho}_{eq} + \Delta\hat{\rho}(t), \tag{10.226}$$

where $\Delta\hat{\rho}(t)$ is the change in the state of the system due to the perturbation and $\hat{\rho}_{eq} = e^{-\beta\hat{H}_0}/\mathrm{Tr}\,[e^{-\beta\hat{H}_0}]$ is the equilibrium density operator. Since $[\hat{H}_0, \hat{\rho}_{eq}] = 0$, we find

$$i\hbar \frac{\partial \hat{\rho}(t)}{\partial t} = [\Delta\hat{H}(t), \hat{\rho}_{eq}] + [\hat{H}_0, \Delta\hat{\rho}(t)] + [\Delta\hat{H}(t), \Delta\hat{\rho}(t)]. \tag{10.227}$$

To obtain an expression for $\Delta\hat{\rho}(t)$ which is linear in the applied field, we will neglect the nonlinear term, $[\Delta\hat{H}(t), \Delta\hat{\rho}(t)]$, and write

$$i\hbar \frac{\partial \Delta\hat{\rho}(t)}{\partial t} = [\Delta\hat{H}(t), \hat{\rho}_{eq}] + [\hat{H}_0, \Delta\hat{\rho}(t)]. \tag{10.228}$$

It is now possible to solve Eq. (10.228) for $\Delta\hat{\rho}(t)$.

The solution to Eq. (10.228) is straightforward. First write

$$\Delta\hat{\rho}(t) = e^{-i\hat{H}_0 t/\hbar}\Delta\hat{\rho}_I(t)e^{i\hat{H}_0 t/\hbar}$$

and plug this expression into Eq. (10.228). Then the equation for $\Delta\hat{\rho}_I(t)$ is

$$i\hbar \frac{\partial \Delta\hat{\rho}_I(t)}{\partial t} = [e^{i\hat{H}_0 t/\hbar}\Delta\hat{H}(t)e^{-i\hat{H}_0 t/\hbar}, \hat{\rho}_{eq}]. \tag{10.229}$$

We can integrate Eq. (10.229). If we assume $\Delta\hat{\rho}_I(-\infty) = 0$, we find

$$\Delta\hat{\rho}_I(t) = \frac{1}{i\hbar}\int_{-\infty}^{t} dt' [e^{i\hat{H}_0 t'/\hbar}\Delta\hat{H}(t')e^{-i\hat{H}_0 t'/\hbar}, \hat{\rho}_{eq}]. \tag{10.230}$$

The equation for $\Delta\hat{\rho}(t)$ is then

$$\Delta\hat{\rho}(t) = \frac{1}{i\hbar}\int_{-\infty}^{t} dt' [e^{-i\hat{H}_0(t-t')/\hbar}\Delta\hat{H}(t')e^{i\hat{H}_0(t-t')/\hbar}, \hat{\rho}_{eq}]. \tag{10.231}$$

We can use Eqs. (10.226) and (10.231) to find the average value of any desired quantity.

Let us first compute the average value of the operator, $\hat{a}_i(\mathbf{r})$, at time t. Let us assume that $\mathrm{Tr}[\hat{a}_i(\mathbf{r})\hat{\rho}_{eq}] = 0$, although this not always the case. Then we find

$$\langle \hat{a}_i(\mathbf{r},t)\rangle = \mathrm{Tr}\,[\hat{a}_i(\mathbf{r})\Delta\hat{\rho}(t)] = -\frac{1}{i\hbar}\int_{-\infty}^{t} dt' \int d\mathbf{r}'\, \langle [\hat{a}_i(\mathbf{r},t), \hat{a}_j(\mathbf{r}',t')]\rangle_{eq} F_j(\mathbf{r}',t'), \tag{10.232}$$

where

$$\langle [\hat{a}_i(\mathbf{r},t), \hat{a}_j(\mathbf{r}',t')]\rangle_{eq} = \mathrm{Tr}(\hat{\rho}_{eq}[\hat{a}_i(\mathbf{r},t), \hat{a}_j(\mathbf{r}',t')]) \tag{10.233}$$

and

$$\hat{a}_i(\mathbf{r},t) = e^{i\hat{H}_0 t/\hbar}\hat{a}_i(\mathbf{r})e^{-i\hat{H}_0 t/\hbar}. \tag{10.234}$$

To obtain Eq. (10.232), we have cyclically permuted operators under the trace and have assumed that $\langle \hat{a}_i(\mathbf{r})\rangle_{eq} = 0$. If we compare Eqs. (10.133) and (10.232), we can write the response as

$$\langle \hat{a}_i(\mathbf{r},t)\rangle = 2i\int_{-\infty}^{t} dt' \int d\mathbf{r}'\, K''_{a_i,a_j}(\mathbf{r},\mathbf{r}';t-t')F_j(\mathbf{r}',t'), \tag{10.235}$$

where we use the notation of Section (10.E) and

$$K''_{a_i,a_j}(\mathbf{r},\mathbf{r}';t-t') = \frac{1}{2\hbar}\langle [\hat{a}_i(\mathbf{r},t), \hat{a}_j(\mathbf{r}',t')]\rangle_{eq}. \tag{10.236}$$

Thus, from microscopic linear response theory we obtain the result that the dissipative part of the response matrix is given by the equilibrium average of the commutator of the relevant operators at different times and positions in space.

We can also obtain the fluctuation–dissipation theorem from microscopic linear response theory. The position-dependent correlation function in a translationally invariant stationary system can be written

$$C_{a_i a_j}(\mathbf{r}-\mathbf{r}';\tau) = \langle \hat{a}_i(\mathbf{r},\tau)\hat{a}_j(\mathbf{r}')\rangle_{eq}, \tag{10.237}$$

where we have assumed that $\langle \hat{a}_i(\mathbf{r})\rangle_{eq} = 0$. Write the Fourier transform is

$$\begin{aligned} G_{a_i,a_j}(\mathbf{k},\tau) &= \int d(\mathbf{r}-\mathbf{r}')e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}\langle \hat{a}_i(\mathbf{r},\tau)\hat{a}_j(\mathbf{r}')\rangle_{eq} \\ &= \frac{1}{V}\int\int d\mathbf{r}\, d\mathbf{r}' e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}\langle \hat{a}_i(\mathbf{r},\tau)\hat{a}_j(\mathbf{r}')\rangle_{eq} \\ &= \frac{1}{V}\langle \hat{a}_i(-\mathbf{k},\tau)\hat{a}_j(\mathbf{k})\rangle_{eq} = \frac{1}{V}\langle \hat{a}_i^*(\mathbf{k},\tau)\hat{a}_j(\mathbf{k})\rangle_{eq}. \end{aligned} \tag{10.238}$$

In Eq. (10.238), we have used the definition, $\hat{a}_j(\mathbf{k}) = \int d\mathbf{r}\, e^{+i\mathbf{k}\cdot\mathbf{r}}\, \hat{a}_j(\mathbf{r})$. From Eq. (10.236), the momentum-dependent response matrix can be written

$$K''_{a_i,a_j}(\mathbf{k},\tau) = \frac{1}{2\hbar}\frac{1}{V}\langle[\hat{a}_i^*(\mathbf{k},\tau),\, \hat{a}_j(\mathbf{k})]\rangle_{eq}. \tag{10.239}$$

However,

$$\langle\hat{a}_j\hat{a}_i(\tau)\rangle_{eq} = \langle\hat{a}_i(\tau - i\hbar\beta)\hat{a}_j\rangle_{eq} = e^{-i\beta\hbar(\partial/\partial\tau)}\langle\hat{a}_i(\tau)\hat{a}_j\rangle_{eq}, \tag{10.240}$$

where $\hat{a}_i(-i\hbar\beta) \equiv e^{\beta\hat{H}_0}\hat{a}_i e^{-\beta\hat{H}_0}$. Therefore

$$K''_{a_i,a_j}(\mathbf{k},\tau) = \frac{1}{2\hbar}(1 - e^{-i\beta\hbar(\partial/\partial\tau)})G_{a_i,a_j}(\mathbf{k},\tau). \tag{10.241}$$

The Fourier transform of Eq. (10.241) takes the form

$$\chi''_{a_i,a_j}(\mathbf{k},\omega) = \frac{1}{2\hbar}(1 - e^{-\beta\hbar\omega})S_{a_i,a_j}(\mathbf{k},\omega), \tag{10.242}$$

where $S_{a_i,a_j}(\mathbf{k},\omega)$ is the spectral density matrix. Equations (10.240) and (10.242) were first derived by Kubo [15] and are the form of the fluctuation–dissipation theorem that results from microscopic linear response theory. We see that the imaginary part of the response matrix is expressed directly in terms of the equilibrium correlation function. The dynamic susceptibility can be expressed directly in terms of $S_{a_i,a_j}(\mathbf{k},\omega)$ and is given by

$$\chi_{a_i,a_j}(\mathbf{k},\omega) = \lim_{\eta\to 0}\int\frac{d\omega'}{2\pi\hbar}\frac{(1 - e^{-\beta\hbar\omega'})S_{a_i,a_j}(\mathbf{k},\omega')}{\omega' - \omega - i\eta}, \tag{10.243}$$

where we have made use of the Kramers–Kronig relations.

▶ S10.C. Light Scattering [16–19]

The use of light scattering as a probe of the structure of matter began a little more than 100 years ago. The incident light polarizes a medium, and the medium then reemits the light in a manner which depends on the dynamics of the medium. Light scattering as a tool to study the internal dynamics of systems has developed in three stages. From the late 1800s until 1928, light scattering experiments involved measurement of the *intensity* of scattered light as a function of angle with respect to the incident direction. However, in 1928, Raman measured the *spectrum* of light inelastically scattered from gases, and he found frequency shifts in the scattered light due to internal degrees of freedom of the molecules. From then on, most light scattering experiments focused on

observation of the spectrum of inelastically scattered light from various media. However, such experiments depended on conventional light sources and with conventional light sources, it is impossible to obtain monochromatic light. One of the sharpest conventional light sources is the 6438 Å line of cadmium. But it has a line width of order 6×10^8 Hz which swamps the details of the spectrum of the inelastically scattered light. Also, conventional light sources are very weak so experiments often last 10–12 hours. A revolution in the subject occurred in the early 1960s with the development of lasers. The neon–helium laser had a monochromatic light source with a line width of order 1 Hz and a very high power. Light scattering experiments can now measure dynamical events on time scales ranging from 10^{-1} sec to 10^{-15} sec.

The equilibrium fluctuations in a fluid can be probed with light or with neutrons. Since equilibrium fluctuations in a fluid decay, on the average, according to the laws of hydrodynamics, we should be able to obtain information about transport coefficients simply by scattering light or particles off of fluctuations in a fluid at equilibrium. The fact that this could be done was established by Landau and Placzek [20] and by van Hove [21]. In 1934, Landau and Placzek showed that it is possible to obtain the time dependence of the density autocorrelation function for a fluid from the hydrodynamic equations. Later, van Hove, in a very important paper, was able to relate the differential cross section for scattering of neutrons from a fluid to the density autocorrelation function of the fluid, thus establishing the connection. In this section we shall obtain an expression for the intensity of light scattered from a fluid in terms of the hydrodynamic modes.

A light wave incident on a simple fluid induces oscillating dipoles in the particles of the fluid. These oscillating dipoles reemit spherical light waves. If the medium is homogeneous, all scattered light waves cancel except those in the forward direction. However, if density fluctuations exist in the fluid, light will be scattered in directions other than the forward direction.

Density fluctuations are both thermal and mechanical in origin. Thermal density fluctuations result from damped temperature or entropy waves, while mechanical density fluctuations result from sound waves in the fluid. Light which scatters from density fluctuations will be unshifted in frequency, while light which scatters from the sound waves will undergo a frequency shift (Doppler shift).

In general, there will be sound waves with a wide range of wavevectors and frequencies in the fluid. However, for a given scattering angle, θ, only selected sound modes will contribute to the scattering. Light will scatter from the wave-fronts of the sound waves and must satisfy the Bragg condition (cf. Fig. 10.3)

$$2\lambda_s \sin \frac{\theta}{2} = \lambda_0 \tag{10.244}$$

where λ_s is the wavelength of the sound and λ_0 is the wavelength of the incident

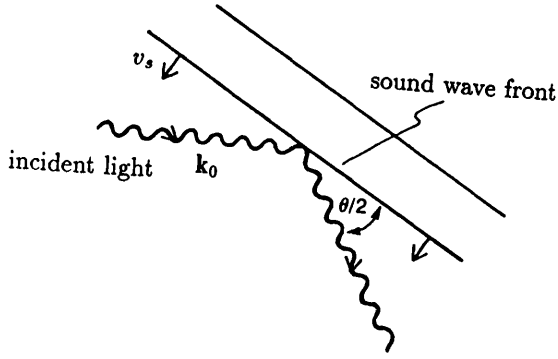


Fig. 10.3. Light scattered from a sound wavefront.

light. The wavevector of the light wave will be shifted by an amount

$$\Delta k = 2k_0 \sin\frac{\theta}{2}, \tag{10.245}$$

where $k_0 = (2\pi/\lambda_0)$. The frequency of the scattered light will be Doppler-shifted by

$$\Omega = \omega - \omega_0 = \pm\frac{2\omega_0 v_s}{c}\sin\frac{\theta}{2} = \pm v_s \Delta k, \tag{10.246}$$

where $\omega_0 = ck_0$, v_s is the speed of sound in the fluid, and c is the speed of light.

We will now derive these results. We will first find an expression relating the intensity of scattered light to the correlation function for density fluctuations in the fluid. Then we will find an expression for the density correlation function from the hydrodynamic equations.

▶ S10.C.1. Scattered Electric Field [22, 23]

We wish to find an expression for the intensity of light scattered from a simple fluid of identical particles. We shall assume that a monochromatic light wave,

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}_0 e^{i(\mathbf{k}_0 \cdot \mathbf{r} - \omega_0 t)}, \tag{10.247}$$

impinges on the fluid, and that the fluid particles have a polarizability α. The induced polarization gives rise to a dipole moment density,

$$\mathbf{P}(\mathbf{r}, t) = \alpha \mathbf{E}(\mathbf{r}, t) \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{q}_i(t)), \tag{10.248}$$

($\mathbf{q}_i(t)$ is the position of the ith particle at time t), which enables the external field to couple to the particles in the fluid. In writing in Eq. (10.248) we have neglected multiple scattering effects because we are assuming the polarization is induced entirely by the external field.

The easiest way to obtain the amplitude of the scattered light is to introduce the Hertz potential $\mathbf{Z}(\mathbf{r}, t)$. This is done in the following way. The electric field $\mathbf{E}(\mathbf{r}, t)$ is defined in terms of the usual scalar potential $\phi(\mathbf{r}, t)$ and vector potential $\mathbf{A}(\mathbf{r}, t)$ as

$$\mathbf{E} = -\nabla_{\mathbf{r}}\phi - \frac{\partial \mathbf{A}}{\partial t}. \tag{10.249}$$

In the Lorentz gauge, the scalar and vector potentials satisfy the equations

$$\nabla_{\mathbf{r}}^2\mathbf{A} - \varepsilon\mu\frac{\partial^2\mathbf{A}}{\partial t^2} = -\mu\mathbf{J} = -\varepsilon\mu\frac{\partial \mathbf{P}}{\partial t}, \tag{10.250}$$

where μ is the permeability of the medium and ε is the permitivity of the medium, and

$$\nabla_{\mathbf{r}}^2\phi - \varepsilon\mu\frac{\partial^2\phi}{\partial t^2} = -\frac{\rho}{\varepsilon} = \nabla_{\mathbf{r}}\cdot\mathbf{P}, \tag{10.251}$$

where $\mathbf{J}$ is the electric current and ρ is the electric charge density. For the system we are considering, the source of electric current and electric charge is the dipole moment density, $\mathbf{P}(\mathbf{r}, t)$. We now introduce the Hertz potential, $\mathbf{Z}(\mathbf{r}, t)$ [22] by means of the equations

$$\mathbf{A} = \varepsilon\mu\frac{\partial \mathbf{Z}}{\partial t} \tag{10.252}$$

and

$$\phi = -\nabla_{\mathbf{r}}\cdot\mathbf{Z}. \tag{10.253}$$

Comparing Eqs. (10.250)–(10.253) we find that $\mathbf{Z}(\mathbf{r}, t)$ satisfies the following equation:

$$\nabla_{\mathbf{r}}^2\mathbf{Z} - \varepsilon\mu\frac{\partial^2\mathbf{Z}}{\partial t^2} = -\mathbf{P}. \tag{10.254}$$

Thus, we have an equation of motion for the Hertz potential in which the polarization acts as a source.

Given Eq. (10.254) we now find the Hertz potential for the scattered light wave. The retarded solution to Eq. (10.254) is given by

$$\mathbf{Z}(\mathbf{r}, t) = \frac{1}{4\pi}\int d\mathbf{r}'\int_{-\infty}^{\infty} dt'\frac{\mathbf{P}(\mathbf{r}', t')}{|\mathbf{r}' - \mathbf{r}|}\delta\left(t' - t + \frac{|\mathbf{r}' - \mathbf{r}|}{c}\right) \tag{10.255}$$

(cf. Ref. 23). We next introduce the Fourier expansion of the delta function and obtain

$$\mathbf{Z}(\mathbf{r},t)=\frac{1}{2}\left(\frac{1}{2\pi}\right)^2\int d\mathbf{r}'\int_{-\infty}^{\infty}dt'\int_{-\infty}^{\infty}d\omega'\frac{\mathbf{P}(\mathbf{r}',t')}{|\mathbf{r}'-\mathbf{r}|}\exp\left\{i\omega'\left(t'-t+\frac{|\mathbf{r}'-\mathbf{r}|}{c}\right)\right\} \tag{10.256}$$

for the outgoing wave. The outgoing electric field is related to $\mathbf{Z}(\mathbf{r},t)$ through the expression

$$\mathbf{E}'(\mathbf{r},t)=\nabla_r(\nabla_r\cdot\mathbf{Z})-\varepsilon\mu\frac{\partial^2\mathbf{Z}}{\partial t^2} \tag{10.257}$$

[cf. Eqs. (10.249), (10.251), (10.252)].

We only need an expression for the scattered light far from the source. If we remember that $\mathbf{r}'$ is restricted to the region of the dipoles and $\mathbf{r}$ is the coordinate of the observer, we can make the following approximation:

$$|\mathbf{r}-\mathbf{r}'|\approx r-\hat{\mathbf{r}}\cdot\mathbf{r}'+\cdots, \tag{10.258}$$

where $\hat{\mathbf{r}}$ is the unit vector $\hat{\mathbf{r}}=\mathbf{r}/|\mathbf{r}|$. If we substitute Eqs. (10.248) and (10.258) into Eq. (10.256), we obtain

$$Z(\mathbf{r},t)\approx\frac{1}{2}\left(\frac{1}{2\pi}\right)^2\frac{\alpha\mathbf{E}_0}{r}\int d\mathbf{r}'\int_{-\infty}^{\infty}dt'\int_{-\infty}^{\infty}d\omega' e^{i(\mathbf{k}_0\cdot\mathbf{r}'-\omega_0t')}\sum_{i=1}^{N}\delta(\mathbf{r}'-\mathbf{q}_i(t'))$$
$$\times\exp\left\{i\omega'\left(t'-t+\frac{r}{c}-\frac{\hat{\mathbf{r}}\cdot\mathbf{r}'}{c}\right)\right\}. \tag{10.259}$$

We next substitute Eq. (10.259) into Eq. (10.257) and neglect terms of order r'/r and smaller. We then obtain the following expression for the scattered electric field:

$$\mathbf{E}'(\mathbf{r},t)=\frac{1}{2}\left(\frac{1}{2\pi}\right)^2\frac{\alpha}{c^2r}(\mathbf{E}_0-\hat{\mathbf{r}}(\hat{\mathbf{r}}\cdot\mathbf{E}_0))\int d\mathbf{r}'\int_{-\infty}^{\infty}dt'\int_{-\infty}^{\infty}d\omega'\omega'^2$$
$$\times\exp\{i(\mathbf{k}_0\cdot\mathbf{r}'-\omega_0t')\}\exp\left\{i\omega'\left(t'-t+\frac{r}{c}-\frac{1}{c}\hat{\mathbf{r}}\cdot\mathbf{r}'\right)\right\}n(\mathbf{r}',t'), \tag{10.260}$$

where

$$n(\mathbf{r}',t')\equiv\sum_{i=1}^{N}\delta(\mathbf{r}'-\mathbf{q}_i(t')) \tag{10.261}$$

is the microscopic density of particles in the medium and we remember that $c^2 = \varepsilon_0\mu_0$ in free space.

▶ S10.C.2. Intensity of Scattered Light

The spectral intensity of scattered light is defined as [cf. Eq. (5.87)]

$$I(\mathbf{r},\omega) \equiv \lim_{T\to\infty} \frac{1}{2T}\sqrt{\frac{\varepsilon_0}{\mu_0}}\,\mathbf{E}'(\mathbf{r},\omega;T)\cdot\mathbf{E}'^{*}(\mathbf{r},\omega;T), \tag{10.262}$$

where

$$\mathbf{E}'(\mathbf{r},\omega;T) = \int_{-\infty}^{\infty} dt\, e^{i\omega t}\mathbf{E}'(\mathbf{r},t)\theta(T-|t|) \tag{10.263}$$

and $\theta(T-|t|)$ is a Heaviside function. If we assume the system is ergodic, we can combine Eqs. (10.262) and (10.263) to obtain

$$\begin{aligned} I(\mathbf{r},\omega) &= \lim_{T\to\infty}\frac{1}{2T}\sqrt{\frac{\varepsilon_0}{\mu_0}}\int_{-\infty}^{\infty}dt\int_{-\infty}^{\infty}dt' \\ &\quad\times e^{i\omega(t-t')}\mathbf{E}'(\mathbf{r},t)\cdot\mathbf{E}'^{*}(\mathbf{r},t')\theta(T-|t|)\theta(T-|t'|) \\ &= \frac{1}{2}\sqrt{\frac{\varepsilon_0}{\mu_0}}\int_{-\infty}^{\infty}d\tau\, e^{i\omega\tau}\lim_{T\to\infty}\frac{1}{T}\int_{-T}^{T}dt'\,\mathbf{E}'(\mathbf{r},t'+\tau)\cdot\mathbf{E}'^{*}(\mathbf{r},t') \\ &= \frac{1}{2}\sqrt{\frac{\varepsilon_0}{\mu_0}}\int_{-\infty}^{\infty}d\tau\, e^{i\omega\tau}\langle\mathbf{E}'(\mathbf{r},\tau)\cdot\mathbf{E}'^{*}(\mathbf{r},0)\rangle. \end{aligned} \tag{10.264}$$

The average in Eq. (10.264) is taken with respect to a stationary equilibrium ensemble. If we now substitute Eq. (10.260) into Eq. (10.264), we obtain

$$\begin{aligned} I(\mathbf{r},\omega) &= \frac{1}{8}\sqrt{\frac{\varepsilon_0}{\mu_0}}\left(\frac{\alpha}{(2\pi)^2c^2r}\right)^2 E_0^2\sin^2(\phi)\int d\mathbf{r}'\int d\mathbf{r}''\int_{-\infty}^{\infty}dt'\int_{-\infty}^{\infty}dt''\int_{-\infty}^{\infty}d\omega' \\ &\quad\times\int_{-\infty}^{\infty}d\omega''\int_{-\infty}^{\infty}d\tau\,\omega'^2\omega''^2 e^{i\omega\tau}\,e^{i(\mathbf{k}_0\cdot\mathbf{r}'-\omega_0t')}e^{-i(\mathbf{k}_0\cdot\mathbf{r}''-\omega_0t'')} \\ &\quad\times\exp\left\{i\omega'\left(t'-\tau+\frac{r}{c}-\frac{1}{c}\,\hat{\mathbf{r}}\cdot\mathbf{r}'\right)\right\}\exp\left\{-i\omega''\left(t''+\frac{r}{c}-\frac{1}{c}\,\hat{\mathbf{r}}\cdot\mathbf{r}''\right)\right\} \\ &\quad\times\langle n(\mathbf{r}',t')n(\mathbf{r}'',t'')\rangle, \end{aligned} \tag{10.265}$$

where we have let $\hat{\mathbf{r}} \cdot \mathbf{E}_0 \cos\phi$. We next integrate over τ and ω'. This gives us

$$I(\mathbf{r},\omega)=\frac{1}{16}\sqrt{\frac{\varepsilon_0}{\mu_0}}\left(\frac{\alpha}{2\pi c^2 r}\right)^2 E_0^2 \sin^2(\phi)\int d\mathbf{r}'\int d\mathbf{r}''\int_{-\infty}^{\infty} dt'\int_{-\infty}^{\infty} dt''\int_{-\infty}^{\infty} d\omega''\omega''^2\omega^2$$
$$\times e^{i(\mathbf{k}_0\cdot\mathbf{r}'-\omega_0 t')}e^{-i(\mathbf{k}_0\cdot\mathbf{r}''-\omega_0 t'')}\exp\left\{i\omega\left(t'+\frac{r}{c}-\frac{1}{c}\hat{\mathbf{r}}\cdot\mathbf{r}'\right)\right\}$$
$$\times\exp\left\{-i\omega''\left(t''+\frac{r}{c}-\frac{1}{c}\hat{\mathbf{r}}\cdot\mathbf{r}''\right)\right\}\langle n(\mathbf{r}',t')n(\mathbf{r}'',t'')\rangle. \tag{10.266}$$

We now make the change of variables $\tau = t' - t''$ and note that $\langle n(\mathbf{r}',t')n(\mathbf{r}'',t'')\rangle$ can only depend on the difference $\tau' = t' - t''$. We then can write Eq. (10.266) in the following form:

$$I(\mathbf{r},\omega)=\frac{1}{8}\sqrt{\frac{\varepsilon_0}{\mu_0}}\left(\frac{\alpha}{2\pi r c^2}\right)^2 E_0^2\sin^2(\phi)\int d\mathbf{r}'\int d\mathbf{r}''\int_{-\infty}^{\infty} d\tau\omega^4 e^{-i(\omega_0-\omega)\tau}$$
$$\times\exp\left\{i\left(\mathbf{k}_0 - i\frac{\omega}{c}\hat{\mathbf{r}}\right)\cdot(\mathbf{r}'-\mathbf{r}'')\right\}\langle n(\mathbf{r}',\tau)n(\mathbf{r}'')\rangle; \tag{10.267}$$

or with the change of variables $\boldsymbol{\rho} = \mathbf{r}' - \mathbf{r}''$ we find

$$I(\mathbf{r},\omega)=\frac{1}{8}\sqrt{\frac{\varepsilon_0}{\mu_0}}\left(\frac{\alpha}{2\pi r c^2}\right)^2 E_0^2\sin^2(\phi)\int d\boldsymbol{\rho}\int d\mathbf{r}''\int_{-\infty}^{\infty} d\tau\omega^4$$
$$\times e^{-i(\omega_0-\omega)\tau}\exp\left\{i\left(\mathbf{k}_0 - i\frac{\omega}{c}\hat{\mathbf{r}}\right)\cdot\boldsymbol{\rho}\right\}\langle n(\mathbf{r}''+\boldsymbol{\rho},\tau)n(\mathbf{r}'')\rangle. \tag{10.268}$$

We next introduce the dynamic density correlation function

$$C(\boldsymbol{\rho},\tau)\equiv\frac{1}{N}\int d\mathbf{r}'\langle n(\mathbf{r}'+\boldsymbol{\rho},\tau)n(\mathbf{r}',0)\rangle, \tag{10.269}$$

where N is the number of particles in the fluid, and the spectral density function (dynamic structure factor),

$$S(\mathbf{k},\Omega)=\int d\boldsymbol{\rho}\int_{-\infty}^{\infty} d\tau C(\boldsymbol{\rho},\tau)e^{+i\mathbf{k}\cdot\boldsymbol{\rho}}e^{-i\Omega\tau}. \tag{10.270}$$

In terms of these quantities, the intensity may be written

$$I(\mathbf{r},\omega) = \frac{1}{4} I_0 \omega^4 \left(\frac{\alpha}{2\pi c^2 r}\right)^2 N \sin^2(\phi) \int d\boldsymbol{\rho} \int d\tau C(\boldsymbol{\rho},\tau) \times \exp\left\{i\left(\mathbf{k}_0 - \frac{\omega_0}{c}\hat{\mathbf{r}}\right)\cdot\boldsymbol{\rho}\right\} e^{-i(\omega_0-\omega)\tau} = \frac{1}{4} I_0 \omega^4 \left(\frac{\alpha}{2\pi c^2 r}\right)^2 N \sin^2(\phi) S(\mathbf{k},\Omega), \tag{10.271}$$

where $I_0 = \frac{1}{2}\sqrt{(\varepsilon_0/\mu_0)}\, E_0^2$, $\mathbf{k} = \mathbf{k}_0 - (\omega_0/c)\,\hat{\mathbf{r}}$ and $\Omega = \omega_0 - \omega$.

An expression for the spectral density function, $S_{nn}(\mathbf{k},\Omega)$, for an isotropic fluid was obtained in Exercise 10.4, Eq. (7). If we use that result, we find that the intensity of scattered light for an isotropic fluid can be written

$$I(\mathbf{r},\omega) = \frac{1}{4} I_0 \omega^4 \left(\frac{\alpha}{2\pi c^2 r}\right)^2 \sin^2(\phi) \left\{ 2\pi N^2 \delta(\Omega)\delta_{k,0} + \frac{1}{m^2}\langle n_{\mathbf{k}}(0) n_{-\mathbf{k}}(0)\rangle \left[\left(1 - \frac{1}{\gamma}\right) \frac{2\chi k^2}{\Omega^2 + \chi^2 k^4} + \frac{1}{\gamma}\left(\frac{\Gamma k^2}{(\Omega - c_0 k)^2 + \Gamma^2 k^4} + \frac{\Gamma k^2}{(\Omega + c_0 k)^2 + \Gamma^2 k^4} \right) \right] \right\}, \tag{10.272}$$

where $\gamma = (c_P/c_\rho)$, χ is the thermal diffusivity, $\Gamma = \frac{1}{2}[\nu_l + \chi(\gamma - 1)]$, and ν_l is the longitudinal kinetic viscosity. In a typical light scattering experiment for a simple liquid, $c_0 \approx 10^5$ cm/sec, $k \approx 10^5\,\text{cm}^{-1}$, $\chi k/c_0 \approx 10^{-2} - 10^{-3}$, and $\nu_l k/c_0 \approx 10^{-2} - 10^{-3}$.

Thus we see that the scattered light spectral intensity will have peaks at frequencies $\Omega = \omega_0$ and $\Omega = \omega_0 \pm c_0 k$. As we discussed in Exercise 10.4, the central peak ($\Omega = \omega_0$) is due to scattering off of thermal density fluctuations. It is called the *Rayleigh peak*. The two side peaks ($\Omega = \omega_0 \pm c_0 k$) are due to scattering of light off of mechanical density fluctuations (sound waves) in the fluid. They are called *Brillioun peaks.*

The ratio of the intensity, I_{th}, of light scattered from thermal density fluctuations to the intensity, I_{mech}, of light scattered off of mechanical density fluctuations is given by

$$\frac{I_{th}}{I_{mech}} = \frac{c_P - c_\rho}{c_\rho} = \frac{\kappa_T - \kappa_S}{\kappa_S}, \tag{10.273}$$

where κ_T is the isothermal compressibility and κ_S is the adiabatic compressibility. Since $c_P \to \infty$ and $\kappa_T \to \infty$ as we approach the critical point, we expect the Rayleigh peak to become very large compared to the Brillioun peaks. In Fig. 10.4, we show experimental plots for the intensity of light

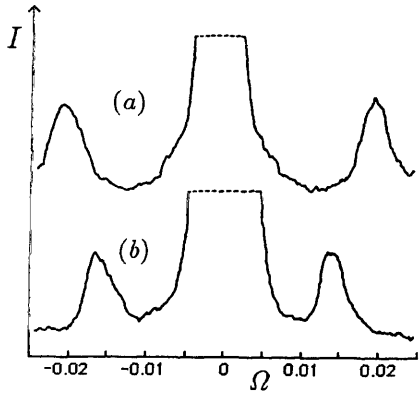


Fig. 10.4. Intensity of light scattered from CO_2 at an angle of 90° from the incident direction, shown as a function of frequency shift, Ω. The CO_2 is 2.7 °C below the critical point. (a) Light scattered from CO_2 liquid. (b) Light scattered from CO_2 vapor. Reprinted, by permission, from H. Z. Cummins, Inter. School of Physics, "E. Fermi", vol. XLII, edition R. Glauber Varenna, 1967.

scattered from CO_2 at an angle of 90° with respect to the incident direction. The CO_2 is at a temperature 2.7 °C below the critical temperature. Note that the Rayleigh peak is very wide and high (not all of it is shown) compared to the Brillioun peaks. This is because the system is close to the critical point.

▶ S10.D. Thermoelectricity [3, 12, 24, 25]

In 1822, Seebeck found that if two different metals (copper and iron, for example) are joined to form a closed circuit and if the metal junctions are kept at different temperatures, an electric current will flow in the circuit. The presence of the current means that the temperature difference has created an electromotive force (EMC) in the circuit. This EMF is now known to be microscopic in origin. The electrons in the two different metals occupy different energy states. When the metals are placed in contact, electrons from the metal in which higher energy states are occupied will flow into the metal in which lower-energy states are occupied, thus creating a potential difference at the junction. This is called a *contact potential* and is a source of EMF for the circuit. For a closed circuit with two such junctions at the same temperature, these contact potentials just balance and no current flows. However, when the junctions have different temperatures, the occupied energy levels are changed, and the contact potentials in the two junctions become unbalanced allowing a current to flow in the circuit. The effect in metals is small. For example, a copper–iron junction gives rise to an EMF of about 1.6×10^{-4} volts for each 1 °C temperature difference between the junctions. Such a device is called a *thermocouple*. Because the effect is small, thermocouples made from metals are not useful for generating electricity, but they are useful in measuring temperatures or rapid temperature changes.

In 1834, Peltier found another effect. If the metal junctions are kept at the same temperature, but a battery is connected to the circuit and an electric current is passed through circuit, one junction will become hotter (absorb

heat) and the other junction will become colder (emit heat). Finally, in 1854, Thomson (Lord Kelvin) found a third effect. He found that if a temperature gradient is set up along a wire, heat will be absorbed (or emitted depending on the direction of the electric current) along the length of the wire. Below we will analyze these effects and verify Onsager's relations for this system.

One may view a metal wire as an electrically neutral binary system consisting of positively charged metal ions at rest and negatively charged electrons which are free to move through the metal. (Although the carriers of current are negatively charged, we follow the usual convention of depicting the direction of electric current flow to be that of positive charges.) A flux of electrons can carry both a charge current, $I = -FJ_{\text{el}}$, where F is Faraday's constant and J_{el} is electron current (moles/area-time), and an entropy current, J_S, (or heat current TJ_S). We will assume that the electrons have uniform spatial density since the system is electrically neutral and density of positive metal ions is fixed. Therefore, the electrochemical potential of the electrons can be written in the form $\mu^e_{\text{el}} = \mu_{\text{el}}(T) - F\phi$, where $\mu_{\text{el}}(T)$ is the chemical potential of the electrons, F is Faraday's constant, and ϕ is the electric potential. The entropy production, σ, which results from the flow of electrons in the metal can be written

$$T\sigma = -J_S \nabla T - J_{\text{el}} \nabla \mu^e_{\text{el}}. \tag{10.274}$$

The generalized Ohm's law takes the form

$$J_S = -L_{SS}\nabla T - L_{SE}\nabla \mu^e_{\text{el}}, \tag{10.275}$$

$$J_{\text{el}} = -L_{ES}\nabla T - L_{EE}\nabla \mu^e_{\text{el}}, \tag{10.276}$$

As we shall show below, Onsager's relation, $L_{SE} = L_{ES}$, is well verified for this system. Let us now consider the the Peltier Effect, the Seebeck Effect, and the Thomson Effect in that order.

▶ S10.D.1. The Peltier Effect

If two distinct metals, A and B, are placed in contact and kept at uniform temperature, and an electric current is passed through the metal junction, an amount of heat, $\dot{Q} \equiv \bar{\pi} I$, ($\dot{Q}$ has units Joule/area · time) will be absorbed or emitted (depending on the types of metal at the junction and the direction of current flow). The amount of heat absorbed per unit area per unit time per unit electric current is called the *Peltier heat*, $\bar{\pi}$, and is written

$$\bar{\pi} = \left(\frac{\dot{Q}}{I}\right)_{\nabla T = 0}. \tag{10.277}$$

The electric current, I, will be continuous at the junction, but the entropy

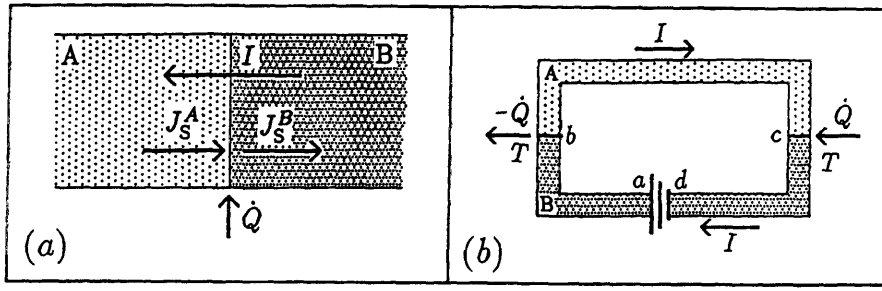


Fig. 10.5. The Peltier effect. (a) If an electric current, I, flows through the junction of two metals, A and B, held at uniform temperature, $Q \equiv \bar{\pi} I$ will be absorbed (or emitted). (b) A circuit at uniform temperature, consisting of two wires, one of metal A and the other of metal B, joined together. A battery is inserted between points a and d, and an electric current, I, is induced in the circuit. At one metal junction, an amount of heat/time, $\dot{Q}$, is absorbed; and at the other metal function, $-\dot{Q}$ is absorbed (emitted).

current will be discontinuous due to the absorption or emission of heat. As we show in Fig. 10.5.a, the relation between the entropy current in metal A and in metal B is given by

$$TJ_S^B = TJ_S^A - \bar{\pi} I. \tag{10.278}$$

It is useful to consider a specific example. In Fig. (10.5.b), if metal A is iron and B is copper then junction b cools and junction c becomes hotter. If the current is reversed, then junction c is cooled and junction b becomes hotter. The absorption or emission of heat depends on both the types of metal and the direction of the current. Therefore, the Peltier heat is not a Joule heat since Joule heat depends on the square of the current. Peltier heat is due to the contact potential in the junction. When an electron must "climb" a potential hill in crossing a junction, it will absorb energy, thus causing the junction to cool. When the electron "decends" a potential hill in crossing a junction, it will emit energy, thus causing the junction to heat.

Let us now consider the circuit in Fig. (10.5.b) which contains two junctions between metals A and B (cf. Fig. 10.5b). We assume that the entire circuit is kept at temperature T. We connect a battery between points a and d and drive a current, I, in the circuit. If Eqs. (10.275) and (10.276) correctly describe the system, then the electrical current, I, will be accompanied by an entropy current, J_S^A (J_S^B), in metal A (B). We can define an *entropy transport parameter*, S_i^*, for metal i, such that

$$S_i^* = \left(\frac{J_S^i}{J_{\text{el}}^i}\right)_{\nabla T=0} = \frac{L_{SE}^i}{L_{EE}^i}, \qquad \text{where } i = \text{A,B}. \tag{10.279}$$

S_i^* is a measure of the amount of entropy carried along with the electron current when the temperature in the circuit is uniform. Measurement of the entropy transport parameter enables us to determine the ratio of phenomenological coefficients (L_{SE}/L_{EE}), for each metal.

The Peltier heat, $\bar{\pi}$, can be expressed in terms of the entropy transport parameters, S_A^* and S_B^*. Since from Eq. (10.279) we have $[J_S^i]_{\nabla T=0} = S_i^*[J_{el}^i]_{\nabla T=0} = -S_i^* I/\mathrm{F}$, we can use Eq. (10.278) to obtain

$$\bar{\pi} = \frac{T}{\mathrm{F}}(S_B^* - S_A^*). \tag{10.280}$$

Thus the change in entropy carried by the electrons across the junction has been connected to the heat absorbed at the junction.

▶ S10.D.2. The Seebeck Effect

Two wires made of different metals, A and B, are connected to form a circuit, as for the Peltier effect. However, now the junctions are maintained at different temperatures, T, and $T + \Delta T$, and a potentiometer is inserted at points a and d, rather than a battery. Also, the points a and d, and the potentiometer are all maintained at a common temperature, T_0, which lies between T and $T + \Delta T$ (cf. Fig. 10.6). For this arrangement there will be no electric current flow so $I = 0$. When $\Delta T \neq 0$, a potential difference, $\Delta\phi_{ad} = \phi_a - \phi_d$, is measured between points a and d. From Eq. (10.276), $J_{el} = -L_{ES}\nabla_{\mathbf{r}}T - L_{EE}\nabla_{\mathbf{r}}\mu_{el}^e = 0$ so that

$$[\nabla_{\mathbf{r}}\mu_{eli}^e]_{J_{el}=0} = -\frac{L_{ES}^i}{L_{EE}^i}\nabla_{\mathbf{r}}T = -\frac{L_{SE}^i}{L_{EE}^i}\nabla_{\mathbf{r}}T = -S_i^*\nabla_{\mathbf{r}}T, \tag{10.281}$$

where we have made use of Onsager's relation, $L_{SE}^i = L_{ES}^i$.

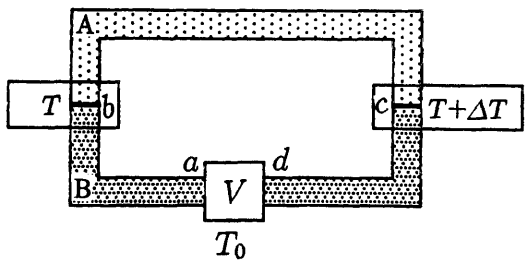


Fig. 10.6. The Seebeck effect. A circuit consisting of two wires, one of metal A and the other of metal B, are joined together and the junctions are held at different temperatures, T and $T + \Delta T$. A potentiometer is inserted between points a and d, and a potential difference, $\Delta\phi_{ad} = \phi_a - \phi_d$, is measured.

We can now obtain a relation between the temperature difference, ΔT, and the potential difference, $\Delta\phi_{ad} = \phi_a - \phi_d$, measured by the potentiometer. Let x denote the spatial coordinate along the wire. We can integrate Eq. (10.281) along the wire, but it must be done in segments. In Fig. (10.6) we have marked points a, b, c, and d. The change in electrochemical potential as we go from point d to point c is

$$(\Delta\mu^e_{\rm el})_{cd} = -\int_{T_0}^{T+\Delta T} S^*_B dT. \tag{10.282}$$

Similarly,

$$(\Delta\mu^e_{\rm el})_{bc} = -\int_{T+\Delta T}^{T} S^*_A dT, \tag{10.283}$$

$$(\Delta\mu^e_{\rm el})_{ab} = -\int_{T}^{T_0} S^*_B dT. \tag{10.284}$$

But the change in electrochemical potential from d to a is

$$(\Delta\mu^e_{\rm el})_{da} = -(\Delta\mu^e_{\rm el})_{cd} - (\Delta\mu^e_{\rm el})_{bc} - (\Delta\mu^e_{\rm el})_{ab} = \int_{T}^{T+\Delta T} (S^*_B - S^*_A)\, dT. \tag{10.285}$$

Since points a and d are at the same temperature, we obtain $(\Delta\mu^e_{\rm el})_{da} = -\mathrm{F}\Delta\phi_{da}$ and

$$\Delta\phi_{ad} = \phi_a - \phi_d = \frac{1}{\mathrm{F}} \int_{T}^{T+\Delta T} (S^*_B - S^*_A)\, dT. \tag{10.286}$$

The potential difference depends only on properties of the metal wires and the temperature difference between the junctions. For very small temperature differences, we can write

$$\frac{d\phi_{ad}}{dT} = \frac{S^*_B - S^*_A}{F} = \frac{\bar{\pi}}{T}. \tag{10.287}$$

The quantity $(d\phi_{ad}/dT)$ is the relative thermoelectric power of metal A against metal B. In order to obtain Eq. (10.287), we had to use Onsager's relation, $L^i_{SE} = L^i_{ES}$. Therefore, the validity of Eq. (10.287) provides a test of Onsager's relations. In Table 10.4, we compare measured values of $(d\phi_{ad}/dT)$ and $(\bar{\pi}/T)$ over a range of temperatures for two different thermocouples. We see that the agreement is quite good.

TABLE 10.4. Test of Equation, $d\phi_{ad}/dT = \bar{\pi}/T$ [24, 25]

Thermocouple	$T(K)$	$\frac{\bar{\pi}}{T}\left(\frac{\mu V}{K}\right)$	$\frac{d\phi_{ad}}{dT}\left(\frac{\mu V}{K}\right)$
Cu–Ni	273	18.6	20.39
	302	22.3	21.7
	373	24.4	24.9
Fe–Hg	292	16.7	16.66
	373	15.6	15.42
	456	13.9	13.74

▶ S10.D.3. Thomson Heat

A temperature gradient can be induced in a metal wire by placing opposite ends of the wire in contact with thermal reservoirs at different temperatures. If the wire is connected to a battery, an electric current, I, will flow in the wire. Thomson found that in the presence of the electric current, the original temperature gradient (in the absence of current) can only be maintained if heat, called *Thomson heat*, is absorbed (or emitted depending on the direction of current flow) along the wire. Thomson heat is distinct from Joule heat. Thomson showed that in order to maintain the original temperature gradient in a wire made of metal A, one must add or subtract an amount of heat, $dQ = \sigma_A(T)IdT$, for each incremental change in temperature, dT, along a wire of metal A. The quantity

$$\sigma_A = \frac{1}{I}\frac{dQ}{dT} \tag{10.288}$$

is called the *Thomson heat*. Thomson heat depends both on the type of metal and the magnitude and direction of the electric current, I.

▶ S10.E. Entropy Production in Discontinuous Systems

From Eq. (10.179), we see that entropy is produced when gradients in the temperature and in the chemical potential of constituent molecules induce spontaneous flows in a system. There are many cases in which these gradients are non-negligible only over very short distances. Such a situation occurs, for example, when a membrane separates two regions with different chemical compositions but which are well-stirred. Another case might be a boundary separating two regions maintained at different temperature by external reservoirs. For such cases it is useful to compute the rate of entropy production

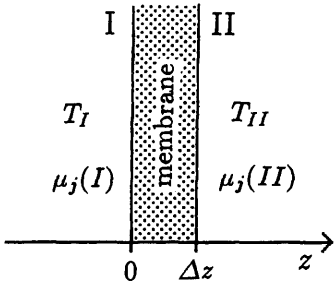


Fig. 10.7. The spontaneous flow of heat or particles due to a gradient of temperature of chemical potential across a boundary or membrane leads to a production of entropy at the boundary.

per unit area rather than per unit volume. Consider Fig. 10.7, which shows a membrane of width Δz separating two regions with different temperature and chemical potential. We assume that a steady state is set up so that the flux of heat and of particles is constant. At the boundary, the chemical potential and temperature must be continuous. If they were not, then their gradients, which are the generalized forces driving the heat and particle fluxes, would be infinite at the discontinuity, and this cannot occur. Gradients in the temperature and chemical potential, however, need not be continuous. Inside the membrane, there will be a gradient in the temperature of order $(\Delta T/\Delta z)$. There will also be a gradient in the chemical potential of contituent i of order $(\Delta\mu_i/\Delta z)$. Then the entropy/area · time, produced by flows across the membrane, is given by

$$\begin{aligned}\sigma_A &\equiv \int_0^{\Delta z} \sigma dz = J_q \cdot \int_0^{\Delta z} \frac{d}{dz}\left(\frac{1}{T}\right) dz - \sum_{j=1}^{N} \tilde{J}_j \cdot \int_0^{\Delta z} \frac{d}{dz}\left(\frac{\tilde{\mu}_j}{T}\right) dz \\ &= J_q \Delta\left(\frac{1}{T}\right) - \sum_{j=1}^{N} \tilde{J}_j \Delta\left(\frac{\tilde{\mu}_j}{T}\right) = -\frac{1}{T}\tilde{J}_S \Delta T - \frac{1}{T}\sum_j \tilde{J}_j \Delta\tilde{\mu}_j\end{aligned} \tag{10.289}$$

and

$$T\sigma_A = -\tilde{J}_S \Delta T - \sum_j \tilde{J}_j \Delta\tilde{\mu}_j, \tag{10.290}$$

where $\tilde{J}_S$ is the entropy current. The quantities ΔT and $\Delta\tilde{\mu}_j$ are differences in temperature and chemical potential, respectively, across the membrane.

▶ S10.E.1. Volume Flow Across a Membrane

Let us consider the transport of a solution consisting of water and an uncharged solute (such as a sugar) across a membrane which is permeable to both water and solute. The mechanisms by which water molecules and solute molecules cross the membrane might be quite different. For example, the water molecules may be able to move through small pores in the membrane while the solute

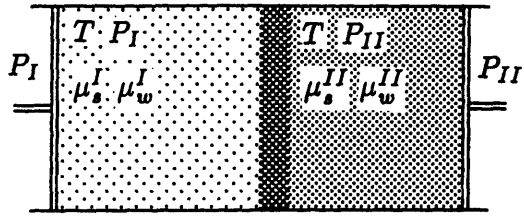


Fig. 10.8. A membrane separates two compartments containing different concentrations of an aqueous solution of uncharged solutes. The compartments are held at different pressure, but have the same temperature.

molecules have to diffuse through the substance the membrane is made of. We will consider a system containing two compartments separated by the membrane, and we will assume that the compartments are held at different pressures and have different concentrations of solute, but that the temperature is uniform through out the system (cf. Fig. 10.8). The chemical potentials of the water and solute will be different in the two compartments. This will cause a flow of water and solute across the membrane. The entropy per unit area produced by this flow can be written

$$T\sigma_A = -\tilde{J}_s \Delta\tilde{\mu}_s - \tilde{J}_w \Delta\tilde{\mu}_w = -J_s \Delta\mu_s - J_w \Delta\mu_w. \tag{10.291}$$

In this section we will work with molar densities rather than mass densities. To evaluate the entropy production, we need expressions for the chemical potentials of water and the solute. We shall assume the solute concentration is fairly low in both compartments.

Differential changes in the chemical potential of the water and solute can be written

$$d\mu_i = \left(\frac{\partial \mu_i}{\partial T}\right)_{P,x_i} dT + \left(\frac{\partial \mu_i}{\partial P}\right)_{T,x_i} dP + \left(\frac{\partial \mu_i}{\partial x_i}\right)_{T,P} dx_s, \tag{10.292}$$

where $i = w, s$ and x_s in the mole fraction of solute. Since we assume that the temperature is uniform throughout the system, we set $dT = 0$. Also $(\partial\mu_i/\partial P)_{T,x_i} = (\partial V/\partial n_i)_{T,P,n_{j\neq i}} = \bar{v}_i$, where $\bar{v}_i$ is the partial molar volume of constituent i. Because water is highly incompressible, the partial volumes, $\bar{v}_i$, can be taken as constant for small changes in pressure. The chemical potentials of the water and solute can then be written $\mu_w = \mu_w^0(T) + \bar{v}_w P + RT\ln(x_w)$ and $\mu_s = \mu_s^0(T) + \bar{v}_s P + RT\ln(x_s)$, respectively. We can use these expressions to compute the difference in chemical potential of the two components.

For the water, the difference in chemical potential is

$$\Delta\mu_w = \mu_w^{II} - \mu_w^I = \bar{v}_w(P^{II} - P^I) + RT\ln\left(\frac{x_w^{II}}{x_w^I}\right). \tag{10.293}$$

But $\ln(x_w) = -\ln(1 + n_s/n_w) \approx -n_s/n_w = -(n_s/V)/(n_w/V) = -\bar{v}_w c_s$. Therefore

$$\Delta\mu_w = \bar{v}_w [\Delta P - RT\,\Delta c_s] = \bar{v}_w [\Delta P - \Delta\pi], \tag{10.294}$$

where $\Delta\pi = RT\Delta c_s$ is the osmotic pressure difference that results from the difference in concentrations in the two compartments.

For the solute, the difference in chemical potential is

$$\Delta\mu_s = \mu_s^{II} - \mu_s^I = \bar{v}_s(P^{II} - P^I) + RT \ln\left(\frac{x_s^{II}}{x_s^I}\right). \tag{10.295}$$

If we denote $\Delta x_s = x_s^{II} - x_s^I$, we can write

$$\begin{aligned}\frac{\Delta x_s}{\ln\left[\frac{x_s^{II}}{x_s^I}\right]} &= \frac{\Delta x_s}{\ln\left[1 + \frac{\Delta x_s}{x_s^I}\right]} \approx \frac{\Delta x_s}{\left[\frac{\Delta x_s}{x_s^I} - \frac{1}{2}\left(\frac{\Delta x_s}{x_s^I}\right)^2 + \cdots\right]} \approx \frac{x_s^I}{\left[1 - \frac{\Delta x_s}{2x_s^I} + \cdots\right]} \\ &= x_s^I\left[1 + \frac{\Delta x_s}{2x_s^I} + \cdots\right] = \frac{1}{2}(x_s^{II} + x_s^I) \equiv \bar{x}_s,\end{aligned} \tag{10.296}$$

where $\bar{x}_s$ is the mean mole fraction of solute in the two compartments. If we now note that $x_s = n_s/(n_s + n_w) \approx n_s/n_w$ so $\Delta x_s/\bar{x}_s = \Delta c_s/\bar{c}_s$, then

$$\Delta\mu_w \approx \bar{v}_s\Delta P + RT\frac{\Delta c_s}{\bar{c}_s} = \bar{v}_w\Delta P + \frac{\Delta\pi}{\bar{c}_s} \tag{10.297}$$

is the approximate difference in solute chemical potential across the membrane.

Let us again consider the entropy production. It can now be written

$$\begin{aligned}T\sigma_A &= -J_s\Delta\mu_s - J_w\Delta\mu_w = -J_w\bar{v}_w(\Delta P - \Delta\pi) - J_s\left(\bar{v}_s\Delta P + \frac{\Delta\pi}{\bar{c}_s}\right) \\ &= -(J_s\bar{v}_s + J_w\bar{v}_w)\Delta P - (J_s/\bar{c}_s - J_w\bar{v}_w)\Delta\pi = -J_V\Delta P - J_D\Delta\pi.\end{aligned} \tag{10.298}$$

The current, $J_V \equiv J_s\bar{v}_s + J_w\bar{v}_w$, is the total flux of fluid volume (the volume current) across the membrane. It has units (volume/area-time). The current $J_D = J_s/\bar{c}_s - J_w\bar{v}_w$ is the volume exchange current. It can also be thought of as the relative velocity of solvent to solute, since $J_D = \mathbf{v}_s - \mathbf{v}_w$ where $\mathbf{v}_s = J_s/\bar{c}_s$ and $\mathbf{v}_w = J_w\bar{v}_w$ have units of velocity. J_D is like a diffusion current.

We can now write the generalized Ohm's laws for this system:

$$J_V = -L_{PP}\Delta P - L_{PD}\Delta\pi, \tag{10.299}$$

$$J_D = -L_{DP}\Delta P - L_{DD}\Delta\pi. \tag{10.300}$$

Microscopic reversibility gives us Onsager's relation, $L_{PD} = L_{DP}$.

We can explore the implications of these equations. If the concentrations on the two sides are the same so $\Delta c_s = 0$, the osmotic pressure will be zero but the hydrostatic pressure imbalance still drives a volume of solution through the membrane. The volume current is $[J_V]_{\Delta\pi=0} = -L_{PP}\Delta P$ and the coefficient L_{PP} is called the *hydraulic conductance*. Even if the osmotic pressure is zero, there can still be a diffusion current, $[J_D]_{\Delta\pi=0} = -L_{DP}\Delta P$, through the membrane, driven by the hydrostatic pressure difference. This diffusion current arises because the mechanisms by which the solvent and solute can cross the membrane are different. This movement of solvent relative to solute is called *ultrafiltration*, and the coefficient L_{DP} is a measure of the ultrafiltration capabilities of a given membrane.

Now assume that the solute concentrations are nonzero and different in the two compartments, so the osmotic pressure difference, $\Delta\pi$, does not equal to zero but the hydrostatic pressure difference, ΔP, is zero. There will be a diffusion current, $[J_D]_{\Delta P=0} = -L_{DD}\Delta\pi$, where L_{DD} is the diffusional mobility of the membrane. There will also be a volume flow, $[J_V]_{\Delta P=0} = -L_{PD}\Delta\pi$, called *osmotic flow*, and the coefficient L_{PD}, is a measure of this osmotic flow.

Osmotic flow and ultrafiltration are related through Onsager's relation, $L_{PD} = L_{DP}$. Both of them are measures of the permeability of the membrane to the solute. We can see this if we express the solute current, J_s, in terms of ΔP and $\Delta\pi$. It is easy to show that

$$J_v + J_D = J_s\left(\bar{v}_s + \frac{1}{\bar{c}_s}\right) = -(L_{PP} + L_{DP})\Delta P - (L_{PD} + L_{DD})\Delta\pi. \tag{10.301}$$

The condition that a membrane be semipermeable (i.e., totally block passage of solute molecules) is that $J_s = 0$ for any value of ΔP and $\Delta\pi$. This, in turn, leads to the condition that for a semipermeable membrane, $L_{PP} = L_{DD} = -L_{PD}$. We can now introduce a *refection coefficient*, σ, for the membrane which is defined as $\sigma = -(L_{PD}/L_{PP})$. For a semipermeable membrane, $\sigma = 1$ and solute molecules are totally "reflected" from the membrane (i.e., cannot pass through). All real membranes will have a reflection coefficient $0 < \sigma < 1$. The measured value of the reflection coefficient will depend both on the membrane and on the solute. For example, in aqueous solution, toad skin has values $\sigma = 0.89$ for solute *acetamide* and $\sigma = 0.50$ for solute *methanol*. The human red blood cell has values $\sigma = 0.62$ for solute *urea* and $\sigma = 0.82$ for solute *malonamide*. Dupont "wet gel" has values $\sigma = 0.0016$ for solute *urea* and $\sigma = 0.036$ for solute *sucrose*.

▶ S10.E.2. Ion Transport Across a Membrane

Let us consider a dilute aqueous salt solution which is separated into two compartments by a membrane. We assume that there are equal concentrations of the salt molecules in the two compartments. The salt molecules dissociate into cations and anions. Assume that the membrane is permeable to water and to the ions. The two compartments are held at different pressure and an electric potential difference is induced across the membrane by inserting electrodes in the system (cf. Fig. 10.9). We assume that the temperature is uniform throughout. We can write the entropy production due to flow across the membrane as

$$T\sigma_A = -J_c\Delta\mu_c^e - J_a\Delta\mu_a^e - J_w\Delta\mu_w, \tag{10.302}$$

where J_c, J_a, and J_w denote the fluxes of cations, anions, and water, respectively and $\Delta\mu_c^e$, $\Delta\mu_a^e$, and $\Delta\mu_w$ are their respective differences in electrochemical potential across the membrane.

The *electrochemical* potentials of the anions and cations, respectively, can be written $\Delta\mu_a^e = \Delta\mu_a + z_a\mathrm{F}\phi$ and $\Delta\mu_c^e = \Delta\mu_c + z_c\mathrm{F}\phi$, where $\Delta\mu_a$ and $\Delta\mu_c$ are the *chemical* potentials of the anions and cations. Therefore, the entropy production takes the form

$$T\sigma_A = -J_c\Delta\mu_c - J_a\Delta\mu_a - J_w\Delta\mu_w - (J_cz_c\mathrm{F} + J_az_a\mathrm{F})\Delta\phi. \tag{10.303}$$

We can further simplify Eq. (10.303) if we note that the ion currents are related to the salt current, J_s, since $J_a = \nu_aJ_s$ and $J_c = \nu_cJ_s$, where ν_a and ν_c are the stoichiometric coefficients for the dissociation (cf. Exercise 10.8). The chemical potential of the salt, μ_s, is related to the chemical potentials of the ions through the relation $\mu_s = \nu_a\Delta\mu_a + \nu_c\Delta\mu_c$. The electric current across the membrane is given by $I = z_a\mathrm{F}J_a + z_c\mathrm{F}J_c$. In terms of these quantities, the entropy production

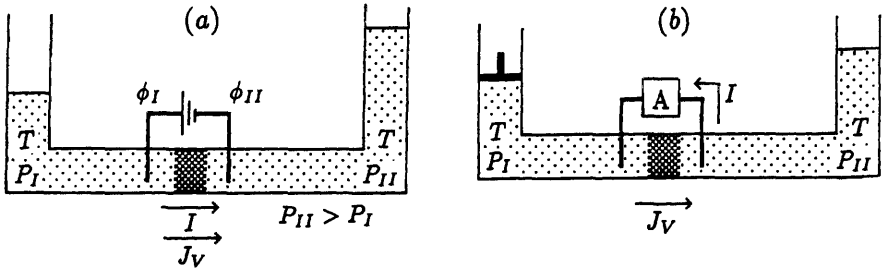


Fig. 10.9. An applied electric potential difference induces an electric current and a volume current across the membrane, and a pressure difference induces *electroosmotic pressure* between the two compartments. (b) An induced volume flow creates an electric *streaming current* in the circuit.

takes the form

$$T\sigma_A = -J_s\Delta\mu_s - J_w\Delta\mu_w - I\Delta\phi, \tag{10.304}$$

and we have written it in a form that does not explicitly separate the anion and cation contributions.

Let us now consider the difference in the chemical potentials of water and salt across the membrane. Since the concentrations are the same on the two sides and the temperatures are the same, the change in the chemical potential across the membrane is entirely due to the pressure difference and we can write $\Delta\mu_s = \bar{v}_s\Delta P$ and $\Delta\mu_w = \bar{v}_w\Delta P$. The entropy production then can be written in the form

$$T\sigma_A = -J_V\Delta P - I\Delta\phi, \tag{10.305}$$

where $J_V = \bar{v}_sJ_s + \bar{v}_wJ_w$ is the volume flux of the solution.

Let us now write the generalized Ohm's laws for the system. They are

$$J_V = -L_{PP}\Delta P - L_{PE}\Delta\phi \tag{10.306}$$

$$I = -L_{EP}\Delta P - L_{EE}\Delta\phi. \tag{10.307}$$

Onsager's argument of microscopic reversibility predicts that $L_{PE} = L_{EP}$. There is a fair amount of experimental data which allows us to check this prediction. Two measurements, one of the *electroosmotic pressure* and the other of the *streaming current*, will give us the information we need.

If we induce an electric potential drop across the membrane, an electric current, I, and a volume current, J_V, occur across the membrane. These currents continue until a pressure difference is built up, and the system reaches a steady state in which the volume current, J_V equals zero. The volume current induced by the electric potential difference across the membrane is called *electro-osmosis*. The electroosmotic pressure, EOP, is defined as

$$\text{EOP} = \left(\frac{\Delta P}{\Delta\phi}\right)_{J_V=0} = -\frac{L_{PE}}{L_{PP}} \tag{10.308}$$

(cf. Fig. 10.9a).

Let us next consider the same fluid and membrane, but replace the battery by an ammeter to measure current flow for the case when the induced potential drop across the membrane is zero, $\Delta\phi = 0$. We force fluid through the membrane with a piston. An electric current, I, is measured in the ammeter. We can define the streaming current, SC, as

$$\text{SC} = \left(\frac{I}{J_V}\right)_{\Delta\phi=0} = \frac{L_{EP}}{L_{PP}}, \tag{10.309}$$

(cf. Fig. 10.9b).

TABLE 10.5. Measurements of the EOP and SC for Aqueous Solutions Using a clay Plug as the Membrane [24]. Two different experiments with the same concentration are shown.

Percent Concentration	$-1/\mathrm{SC}\,(\mathrm{cm}^{3/2}\,\mathrm{g}^{1/2})$	$1/\mathrm{EOP}\,(\mathrm{cm}^{3/2}\mathrm{g}^{1/2})$	$-\mathrm{EOP}/\mathrm{SC} = L_{PE}/L_{EP}$
0.75% $ZnSO_4$	0.386	0.388	0.99
0.75% $ZnSO_4$	0.3776	0.377	1.00
1.0% $CuSO_4$	0.392	0.380	1.03
1.0% $CuSO_4$	0.385	0.389	0.99
1.0% $CdSO_4$	0.532	0.567	0.94
1.0% $CdSO_4$	0.116	0.115	1.01

The ratio of the EOP and the SC allow us the check the Onsager relation since $(\mathrm{EOP/SC}) = (L_{PE}/L_{EP})$. In Table 10.5 we give experimental values for this ratio. All the measurements were done using a clay plug as the membrane. Since one clay plug will differ from another, care must be taken to use the same clay plug in a given set of experiments. Also care must be take not to alter the properties of the clay plug in the course of the experiment. The data given in Table 10.5 show that Onsager's relation is well-satisfied for this system.

▶ S10.F. Stochastic Hydrodynamics [1]

The hydrodynamic equations describe the average motion of conserved quantities in the fluid. They do not include detailed information about the other 10^{23} degrees of freedom in the fluid. When we derived the hydrodynamic equations in Section (10.B), we used a generalization of Ohm's law to obtain approximate phenomenological expressions for the dissipative heat current and the dissipative momentum current (stress tensor) in terms of spatial gradients of the temperature and velocity, respectively. We will now add a random contribution, $\mathbf{g}(\mathbf{r},t)$, to the heat current and add a random contribution, $\bar{\mathbf{S}}(\mathbf{r},t)$, to the stress tensor. In this way we can, to some extent, incorporate the effect of the very rapid nonhydrodynamic fluctuations in the other 10^{23} degrees of freedom. When these random currents are added, the entropy current takes the form

$$\mathbf{J}_s(\mathbf{r},t) = -\frac{K}{T}\nabla_{\mathbf{r}}T(\mathbf{r},t) + \frac{1}{T}\mathbf{g}(\mathbf{r},t), \tag{10.310}$$

and the stress tensor takes the form

$$\bar{\Pi}(\mathbf{r},t) = -2\eta[\nabla_{\mathbf{r}}\mathbf{v}(\mathbf{r},t)]^s - \zeta\bar{\mathbf{U}}\nabla_{\mathbf{r}}\cdot\mathbf{v}(\mathbf{r},t) + \bar{\mathbf{S}}(\mathbf{r},t). \tag{10.311}$$

The random heat current is a vector with components $g_i(\mathbf{r},t)$, where $i = x,y,z$.

The random stress tensor is a second-order tensor with components $S_{ij}(\mathbf{r},t)$. Below we will include these random currents into the hydrodynamic equations and use properties of equilibrium correlation functions to obtain expressions for correlation functions for the random currents.

▶ S10.F.1. Stochastic Hydrodynamic Equations

When the random heat current and the random stress tensor are incorporated into the hydrodynamic equations, the linearized hydrodynamic equations take the form

$$\frac{\partial \Delta\rho}{\partial t} + \rho_0 \nabla_{\mathbf{r}} \cdot \mathbf{v} = 0, \tag{10.312}$$

$$\rho_0 \frac{\partial \mathbf{v}}{\partial t} = -\left(\frac{\partial P}{\partial \rho}\right)_T^0 \nabla_{\mathbf{r}} \Delta\rho - \left(\frac{\partial P}{\partial T}\right)_\rho^0 \nabla_{\mathbf{r}} \Delta T + \eta \nabla_{\mathbf{r}}^2 \mathbf{v} + \left(\zeta + \frac{1}{3}\eta\right) \nabla_{\mathbf{r}} (\nabla_{\mathbf{r}} \cdot \mathbf{v}) - \nabla \cdot \bar{\mathbf{S}}, \tag{10.313}$$

and

$$\rho_0 \left(\frac{\partial s}{\partial \rho}\right)_T^0 \frac{\partial \Delta\rho}{\partial t} + \rho_0 \left(\frac{\partial s}{\partial T}\right)_\rho^0 \frac{\partial \Delta T}{\partial t} = \frac{K}{T_0} \nabla_{\mathbf{r}}^2 \Delta T - \frac{1}{T_0} \nabla \cdot \mathbf{g}. \tag{10.314}$$

With the inclusion of random terms, the hydrodynamic equations become stochastic equations. As we will show below, we can use the properties of the equilibrium correlation functions, $\langle \Delta\rho(\mathbf{r}_1,t_1)\Delta\rho(\mathbf{r}_2,t_2)\rangle$, $\langle \mathbf{v}(\mathbf{r}_1,t_1)\mathbf{v}(\mathbf{r}_2,t_2)\rangle$, and $\langle \Delta T(\mathbf{r}_1,t_1)\Delta T(\mathbf{r}_2,t_2)\rangle$, to determine the correlation funtion, $\langle \mathbf{g}(\mathbf{r}_1,t_1)\mathbf{g}(\mathbf{r}_2,t_2)\rangle$, for the heat current and $\langle \bar{\mathbf{S}}(\mathbf{r}_1,t_1)\bar{\mathbf{S}}(\mathbf{r}_2,t_2)\rangle$ for the stress tensor.

It is useful to rewrite the hydrodynamic equations in terms of the response functions and the kinetic viscosities and thermal diffusivity given in Eqs. (10.61) and (10.62). If we also Fourier transform the space dependence and separate the equations into their longitudinal and transverse parts, we obtain

$$\frac{\partial \rho_{\mathbf{k}}(t)}{\partial t} - i\rho_0 k v_{\mathbf{k}}^{\parallel}(t) = 0, \tag{10.315}$$

$$\frac{\partial v_{\mathbf{k}}^{\parallel}(t)}{\partial t} = +ik\frac{c_0^2}{\rho_0\gamma}\rho_{\mathbf{k}}(t) + ik\frac{c_0^2\alpha_P}{\gamma}T_{\mathbf{k}}(t) - \nu_l k^2 v_{\mathbf{k}}^{\parallel}(t) + \frac{ik}{\rho_0}S_{\mathbf{k}}^{\parallel}(t), \tag{10.316}$$

$$-\frac{T_0 c_0^2 \alpha_P}{\rho_0 \tilde{c}_\rho \gamma}\frac{\partial \rho_{\mathbf{k}}(t)}{\partial t} + \frac{\partial T_{\mathbf{k}}(t)}{\partial t} = -\gamma\chi k^2 T_{\mathbf{k}}(t) + \frac{ik}{\rho_0 \tilde{c}_\rho} g_{\mathbf{k}}(t) \tag{10.317}$$

$$\frac{\partial v_{\mathbf{k}}^{I}(t)}{\partial t} = -\nu_t k^2 v_{\mathbf{k}}^{I}(t) + \frac{ik}{\rho_0} S_{\mathbf{k}}^{I}(t). \tag{10.318}$$

and

$$\frac{\partial v_{\mathbf{k}}^{II}(t)}{\partial t} = -\nu_t k^2 v_{\mathbf{k}}^{II}(t) + \frac{ik}{\rho_0} S_{\mathbf{k}}^{II}(t). \tag{10.319}$$

In above equations, we have broken the velocity vector, $\mathbf{v}_{\mathbf{k}}(t)$, into its longitudinal part, $v_{\mathbf{k}}^{\|}(t)$, and its transverse parts, $v_{\mathbf{k}}^{I}(t)$ and $v_{\mathbf{k}}^{II}(t)$, where

$$\mathbf{v}_k(t) = v_{\mathbf{k}}^{\|}(t)\hat{\mathbf{k}} + v_{\mathbf{k}}^{I}(t)\hat{\mathbf{t}}_I + v_{\mathbf{k}}^{II}(t)\hat{\mathbf{t}}_{II}. \tag{10.320}$$

The unit vectors, $\hat{\mathbf{t}}_I$ and $\hat{\mathbf{t}}_{II}$, are orthogonal to $\mathbf{k}$ and are orthogonal to each other. We have also broken the random momentum current into a longitudinal part, $S_{\mathbf{k}}^{\|}(t)$, and transverse parts, $S_{\mathbf{k}}^{I}(t)$ and $S_{\mathbf{k}}^{II}(t)$, where

$$\mathbf{k} \cdot \bar{\mathbf{S}}_{\mathbf{k}}(t) = kS_{\mathbf{k}}^{\|}(t)\hat{\mathbf{k}} + kS_{\mathbf{k}}^{I}(t)\hat{\mathbf{t}}_I + kS_{\mathbf{k}}^{II}(t)\hat{\mathbf{t}}_{II}. \tag{10.321}$$

Note also that only the longitudinal component of the random heat current affects the hydrodynamics.

The procedure for computing the random current correlation functions in volves two steps. First we compute the correlation functions for velocity fluctuations and temperature fluctuations for a fluid in equilibrium. Then we can use these to compute the random current correlation functions. In the remainder of this section, we shall consider fluids in which the thermal expansivity, α_P, is so small that it can be neglected. That is, we shall set $\alpha_P = 0$ in Eqs. (10.315)–(10.319). From Eq. (10.269), we can write $\gamma(\gamma - 1) = c_0^2 \alpha_P^2 T_0 / \tilde{c}_\rho$, so we can also set $\gamma = 1$.

▶ S10.F.2. Properties of Equilibrium Correlation Functions

Equilibrium correlation functions must satisfy certain conditions which then determine the form of the correlation functions for the random currents. Let us consider the correlation function, $\langle \Delta T(\mathbf{r}_1, t_1) \Delta T(\mathbf{r}_2, t_2) \rangle$, for the temperature fluctuations. From Section 5.B we know that it must be stationary. Therefore, $\langle \Delta T(\mathbf{r}_1, t_1) \Delta T(\mathbf{r}_2, t_2) \rangle = \langle \Delta T(\mathbf{r}_1, t_1 - t_2) \Delta T(\mathbf{r}_2, 0) \rangle$. Furthermore, for systems with very large volume, where we can neglect the boundaries (and if no spatially varying external fields are present), the correlation function depends only on the relative displacement, $\mathbf{r}_1 - \mathbf{r}_2$. Thus, we can write

$$C_{TT}(\mathbf{r}_1 - \mathbf{r}_2, t_1 - t_2) = \langle \Delta T(\mathbf{r}_1, t_1) \Delta T(\mathbf{r}_2, t_2) \rangle \tag{10.322}$$

for a system in equilibrium. That is, the correlation function, $\langle \Delta T(\mathbf{r}_1, t_1) \Delta T(\mathbf{r}_2, t_2) \rangle$, only depends on the differences, $\mathbf{r}_1 - \mathbf{r}_2$ and $t_1 - t_2$.

Let us now consider the Fourier transform

$$\langle \tilde{T}_{\mathbf{k}_1}(\omega_1)\tilde{T}_{\mathbf{k}_2}(\omega_2)\rangle = \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \int_V d\mathbf{r}_1 \int_V d\mathbf{r}_2 e^{-i\omega_1 t_1} e^{-i\omega_2 t_2} e^{i\mathbf{k}_1\cdot\mathbf{r}_1} e^{i\mathbf{k}_2\cdot\mathbf{r}_2} \times \langle \Delta T(\mathbf{r}_1, t_1)\Delta T(\mathbf{r}_2, t_2)\rangle, \tag{10.323}$$

where the spatial integral is taken over the volume, V, of the hydrodynamic system. We assume periodic boundary conditions. Let us make a change of coordinates, $\mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2), \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2, T = \frac{1}{2}(t_1 + t_2)$, and $\tau = t_1 - t_2$. Then,

$$\begin{aligned}\langle \tilde{T}_{\mathbf{k}_1}(\omega_1)\tilde{T}_{\mathbf{k}_2}(\omega_2)\rangle &= \int_{-\infty}^{\infty} dT \int_{-\infty}^{\infty} d\tau \int_V d\mathbf{R} \int_V d\mathbf{r} e^{-i(\omega_1+\omega_2)T} e^{-i(\omega_1-\omega_2)\tau/2} \\ &\quad \times e^{i(\mathbf{k}_1-\mathbf{k}_2)\cdot\mathbf{r}/2} e^{i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{R}} \langle \Delta T(\mathbf{r}_1, t_1)\Delta T(\mathbf{r}_2, t_2)\rangle \\ &= 2\pi V \delta(\mathbf{k}_1 + \mathbf{k}_2)\delta(\omega_1 + \omega_2) \int_{-\infty}^{\infty} d\tau e^{-i\omega_1\tau} \langle T_{\mathbf{k}_1}(\tau) T_{-\mathbf{k}_1}(0)\rangle.\end{aligned} \tag{10.324}$$

We must now define what we mean by these correlations functions. In Section 5.E, where we introduced the theory of Brownian motion, we had to introduce two different averages. The "random average," $\langle\rangle_\xi$, was an average taken using the probability distribution of realizations of the random force. The "thermal average", $\langle\rangle_T$, was a thermal average over possible values of the much more slowly varying conserved degree of freedom. We shall use these two types of averages to compute hydrodynamic correlation functions. The correlation, $\langle T_{\mathbf{k}_1}(\tau) T_{-\mathbf{k}_1}(0)\rangle$, that appears in Eq. (10.324), is defined

$$\langle T_{\mathbf{k}_1}(\tau) T_{-\mathbf{k}_1}(0)\rangle \equiv \langle \langle T_{\mathbf{k}_1}(\tau)\rangle_\xi T_{-\mathbf{k}_1}(0)\rangle_T. \tag{10.325}$$

We shall assume that the random currents have zero mean so that $\langle S_{ij}(\mathbf{r}, t)\rangle_\xi = 0$ and $\langle g_i(\mathbf{r}, t)\rangle_\xi = 0$.

In order to fully determine the correlation function, $\langle \tilde{T}_{\mathbf{k}_1}(\omega_1)\tilde{T}_{\mathbf{k}_2}(\omega_2)\rangle$, we must know the expressions for the stationary correlation functions $\langle \rho_{\mathbf{k}}(0) T_{-\mathbf{k}}(0)\rangle$, $\langle v_{\mathbf{k}}^{\parallel}(0) T_{-\mathbf{k}}(0)\rangle$, and $\langle |T_{\mathbf{k}}(0)|^2\rangle$ [note that $T_{-\mathbf{k}}(0) = T_{\mathbf{k}}^*(0)$]. As we showed in Section 8.B for the magnetization correlation function, in the limit where $\mathbf{k} \to 0$, these correlation functions can be obtained from Einstein fluctuation theory (Section 7.C). Einstein fluctuation theory, introduced in Section 7.C, allows us to determine thermal averages. It is valid in equilibrium and far from a critical point so that flutuations are small. Under these conditions, it tells us that temperature and density fluctuations are statistically independent of one another. We can also assume that velocity fluctuations are statistically independent of density and temperature flutuations.

Then we obtain

$$\lim_{\mathbf{k}\to 0}\langle|T_{\mathbf{k}}(0)|^2\rangle_T = \frac{k_B T^2}{\rho_0 \tilde{c}_\rho V}, \qquad \lim_{\mathbf{k}\to 0}\langle|v_{\mathbf{k}}^{\parallel}(0)|^2\rangle_T = \lim_{\mathbf{k}\to 0}\langle|v_{\mathbf{k}}^{I}(0)|^2\rangle_T = \frac{k_B T}{\rho_0 V},$$
$$\lim_{\mathbf{k}\to 0}\langle\rho_{\mathbf{k}}(0)T_{-\mathbf{k}}(0)\rangle_T = \lim_{\mathbf{k}\to 0}\langle v_{\mathbf{k}}^{\parallel}(0)T_{-\mathbf{k}}(0)\rangle_T = \lim_{\mathbf{k}\to 0}\langle v_{\mathbf{k}}^{\parallel}(0)v_{-\mathbf{k}}^{I}(0)\rangle_T = 0, \tag{10.326}$$

where $\tilde{c}_\rho$ is the specific heat. The temperature correlation function in Eq. (10.326) was obtained in Section 7.C, and the velocity correlation function is given by equipartition [cf. Sect. 5.E].

We can now obtain expressions for the time dependence of the temperature and velocity correlation functions. We first must find the time dependence of the averages, $\langle T_{\mathbf{k}}(t)\rangle_\xi \langle v_{\mathbf{k}}^{\parallel}(t)\rangle_\xi$, $\langle v_{\mathbf{k}}^{I}(t)\rangle_\xi$, and $\langle v_{\mathbf{k}}^{II}(t)\rangle_\xi$. Let us return to Eqs. (10.315)–(10.319) and take the "random average," $\langle\rangle_\xi$, of those equations. Let us also set $\alpha_P = 0$ and $\gamma = 1$ and take the Laplace transform of the time dependence, as we did in Section 10.C. For the case when $\alpha_P = 0$, we then find

$$\langle\tilde{T}_{\mathbf{k}}(z)\rangle_\xi = \frac{T_{\mathbf{k}}(0)}{z+\chi k^2}, \tag{10.327}$$

$$\langle\tilde{v}_{\mathbf{k}}^{\parallel}(z)\rangle_\xi = \frac{zv_{\mathbf{k}}^{\parallel}(0) + ik(c_0^2/\rho_0)\rho_{\mathbf{k}}(0)}{z^2 + z\nu_l k^2 + c_0^2 k^2}, \tag{10.328}$$

$$\langle\tilde{v}_{\mathbf{k}}^{I}(z)\rangle_\xi = \frac{v_{\mathbf{k}}^{I}(0)}{z+\nu_t k^2} \quad \text{and} \quad \langle\tilde{v}_{\mathbf{k}}^{II}(z)\rangle_\xi = \frac{v_{\mathbf{k}}^{II}(0)}{z+\nu_t k^2} \tag{10.329}$$

The time dependence is now easily found. For the temperature, we obtain

$$\langle T_{\mathbf{k}}(t)\rangle_\xi = \frac{1}{2\pi i}\int_{\delta-i\infty}^{\delta+i\infty} dz \frac{T_{\mathbf{k}}(0)}{z+\chi k^2} = T_{\mathbf{k}}(0)e^{-\chi k^2 t}. \tag{10.330}$$

For the longitudinal velocity, we obtain

$$\langle v_{\mathbf{k}}^{\parallel}(t)\rangle_\xi = v_{\mathbf{k}}^{\parallel}(0)\left(e^{-\Delta t}\cos(c_k kt) - \frac{\Delta}{c_k k}\sin(c_k kt)\right) + R_{v\rho}(t)\rho_{\mathbf{k}}(0), \tag{10.331}$$

where $\Delta = \frac{\nu_l k^2}{2}$, $c_k = c_0\sqrt{1-\Delta^2/(c_0^2 k^2)}$, and $R_{v\rho}(t)$ is a time-dependent term that we won't write here. Since $\lim_{\mathbf{k}\to 0}\langle v_{\mathbf{k}}^{\parallel}(0)\rho_{-\mathbf{k}}(0)\rangle_T = 0$, it does not contribute to the equilibrium velocity correlation function. We should note also that we have solved Eq. (10.331) exactly given equation (10.328). We have not just kept terms up to order, k^2, in the denominator as was done in Eq. (10.73). It is necessary to keep the full k dependence of Eq. (10.331) in order to obtain the correct expression for the random current correlation functions. For

the transverse velocities we find

$$\langle v_{\mathbf{k}}^{I}(t)\rangle_{\xi} = v_{\mathbf{k}}^{I}(0)e^{-\nu_t k^2 t} \quad \text{and} \quad \langle v_{\mathbf{k}}^{II}(t)\rangle_{\xi} = v_{\mathbf{k}}^{II}(0)e^{-\nu_t k^2 t}. \tag{10.332}$$

If we now substitute Eq. (10.330) into Eq. (10.324), we obtain

$$\langle \tilde{T}_{\mathbf{k}_1}(\omega_1)\tilde{T}_{\mathbf{k}_2}(\omega_2)\rangle = 2\pi V\delta(\mathbf{k}_1+\mathbf{k}_2)\delta(\omega_1+\omega_2)\langle |T_{\mathbf{k}_1}(0)|^2\rangle_T \frac{2\chi k_1^2}{\omega_1^2+\chi^2 k_1^4}. \tag{10.333}$$

Similarly, we obtain the following expression for the correlation function for the longitudinal component of velocity:

$$\langle \tilde{v}_{\mathbf{k}_1}^{\parallel}(\omega_1)\tilde{v}_{\mathbf{k}_2}^{\parallel}(\omega_2)\rangle = 2\pi V\delta(\mathbf{k}_1+\mathbf{k}_2)\delta(\omega_1+\omega_2)\langle |v_{\mathbf{k}_1}^{\parallel}(0)|^2\rangle_T \times \left[\frac{\omega_1\Delta_1/(c_{k_1}k_1)}{(\omega_1-c_{k_1}k_1)^2+\Delta_1^2} - \frac{\omega_1\Delta_1/(c_{k_1}k_1)}{(\omega_1-c_{k_1}k_1)^2+\Delta_1^2}\right]. \tag{10.334}$$

For the transverse velocity fluctuations we obtain

$$\langle \tilde{v}_{\mathbf{k}_1}^{I}(\omega_1)\tilde{v}_{\mathbf{k}_2}^{I}(\omega_2)\rangle = 2\pi V\delta(\mathbf{k}_1+\mathbf{k}_2)\delta(\omega_1+\omega_2)\langle |v_{\mathbf{k}_1}^{I}(0)|^2\rangle_T \left(\frac{2\nu_t k_1^2}{\omega_1^2+\nu_t^2 k_1^4}\right), \tag{10.335}$$

with a similar expression for $\langle \tilde{v}_{\mathbf{k}_1}^{II}(\omega_1)\tilde{v}_{\mathbf{k}_2}^{II}(\omega_2)\rangle$. Equations (10.333) and (10.334) apply to an equilibrium fluid in which thermal expansivity can be neglected so that $\alpha_P = 0$. With the information given in Eqs. (10.333)–(10.335), we can obtain the correlation functions for the random currents.

▶ S10.F.3. Random Current Correlation Functions

We now will obtain expressions for the random current correlation functions for the case when $\alpha_P \approx 0$. From Eqs. (10.316)–(10.319) we obtain the following expressions for the random currents:

$$\tilde{S}_{\mathbf{k}}^{\parallel}(\omega) = \frac{\rho_0}{k}\left(\omega - \frac{c_0^2 k^2}{\omega} - i\nu_l k^2\right)\tilde{v}_{\mathbf{k}}^{\parallel}(\omega), \tag{10.336}$$

$$\tilde{g}_{\mathbf{k}}(\omega) = \frac{\rho_0\tilde{c}_\rho}{k}(\omega - i\chi k^2)\tilde{T}_{\mathbf{k}}(\omega), \tag{10.337}$$

$$\tilde{S}_{\mathbf{k}}^{I}(\omega) = \frac{\rho_0}{k}(\omega - i\nu_t k^2)\tilde{v}_{\mathbf{k}}^{I}(\omega), \tag{10.338}$$

and

$$\tilde{S}^{II}_{\mathbf{k}}(\omega) = \frac{\rho_0}{k}(\omega - i\nu_t k^2)\tilde{v}^{II}_{\mathbf{k}}(\omega). \tag{10.339}$$

From these equations we obtain the following correlation function:

$$\langle \tilde{S}^{\parallel}_{\mathbf{k}_1}(\omega_1)\tilde{S}^{\parallel}_{\mathbf{k}_2}(\omega_2)\rangle = \frac{\rho_0^2}{k_1 k_2}\left(\omega_1 - \frac{c_0^2 k_1^2}{\omega_1} - i\nu_l k_1^2\right)\left(\omega_2 - \frac{c_0^2 k_2^2}{\omega_2} - i\nu_l k_2^2\right) \times \langle \tilde{v}^{\parallel}_{\mathbf{k}_1}(\omega_1)\tilde{v}^{\parallel}_{\mathbf{k}_2}(\omega_2)\rangle, \tag{10.340}$$

$$\langle \tilde{g}_{\mathbf{k}_1}(\omega_1)\tilde{g}_{\mathbf{k}_2}(\omega_2)\rangle = \frac{\rho_0^2 \tilde{c}^2_\rho}{k_1 k_2}(\omega_1 - i\chi k_1^2)(\omega_2 - i\chi k_2^2)\langle \tilde{T}_{\mathbf{k}_1}(\omega_1)\tilde{T}_{\mathbf{k}_2}(\omega_2)\rangle, \tag{10.341}$$

and

$$\langle \tilde{S}^{I}_{\mathbf{k}_1}(\omega_1)\tilde{S}^{I}_{\mathbf{k}_2}(\omega_1)\rangle = \frac{\rho_0^2}{k_1 k_2}[-\omega_1 + i\nu_t k_1^2][-\omega_2 + i\nu_t k_2^2]\langle \tilde{v}^{I}_{\mathbf{k}_1}(\omega_1)\tilde{v}^{I}_{\mathbf{k}_2}(\omega_2)\rangle. \tag{10.342}$$

The expression for $\langle \tilde{S}^{II}_{\mathbf{k}_1}(\omega_1)\tilde{S}^{II}_{\mathbf{k}_2}(\omega_2)\rangle$ is the same as Eq. (10.340), but with $\tilde{v}^{I}$ replaced by $\tilde{v}^{II}$

Let us now substitute Eqs. (10.333)–(10.335) into Eqs. (10.340)–(10.342). We then obtain

$$\langle \tilde{S}^{\parallel}_{\mathbf{k}_1}(\omega_1)\tilde{S}^{\parallel}_{\mathbf{k}_2}(\omega_2)\rangle = 4\pi k_B T \rho_0 \nu_l \delta(\mathbf{k}_1 + \mathbf{k}_2)\delta(\omega_1 + \omega_2), \tag{10.343}$$

$$\langle \tilde{S}^{I}_{\mathbf{k}_1}(\omega_1)\tilde{S}^{I}_{\mathbf{k}_2}(\omega_2)\rangle = 4\pi k_B T \rho_0 \nu_t \delta(\mathbf{k}_1 + \mathbf{k}_2)\delta(\omega_1 + \omega_2), \tag{10.344}$$

and

$$\langle \tilde{g}_{\mathbf{k}_1}(\omega_1)\tilde{g}_{\mathbf{k}_2}(\omega_2)\rangle = 4\pi k_B T^2 K \delta(\mathbf{k}_1 + \mathbf{k}_2)\delta(\omega_1 + \omega_2). \tag{10.345}$$

Equations (10.343)–(10.345) are an expression of the fluctuation–dissipation theorem for fluids in equilibrium. We have written the correlation functions for random current fluctuations in terms of the transport coefficients which are measures of internal friction or dissipation in the fluid.

We need to obtain expressions for correlation functions of arbitrary components of the random heat current $g_i(\mathbf{r}, t)$, and of the random stress tensor, $S_{ij}(\mathbf{r}, t)$. Let us first consider their Fourier transforms, $\tilde{g}_i(\mathbf{k}, \omega)$ and

$\tilde{S}_{ij}(\mathbf{k},\omega)$, respectively. For an isotropic fluid, such as we are considering, the correlation functions $\langle \tilde{g}_i(\mathbf{k}_1,\omega_1)\tilde{g}_j(\mathbf{k}_2,\omega_2)\rangle$ and $\langle \tilde{S}_{ij}(\mathbf{k}_1,\omega_1)\tilde{S}_{kl}(\mathbf{k}_2,\omega_2)\rangle$ must be invariant under rotation of coordinates. This restricts the correlation function for the random stress tensor to depend on terms with tensor character, $\delta_{ij}\delta_{kl}$, $\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk}$, and $\delta_{ik}\delta_{jl}-\delta_{il}\delta_{jk}$. However, the random stress tensor cannot ontain an antisymmetric part for a fluid of point particles (which we are considering here). Therefore, the correlation function $\langle \tilde{S}_{ij}(\mathbf{k}_1,\omega_1)\tilde{S}_{kl}(\mathbf{k}_2,\omega_2)\rangle$ must have the form

$$\begin{aligned}\langle \tilde{S}_{ij}(\mathbf{k}_1,\omega_1)\tilde{S}_{kl}(\mathbf{k}_2,\omega_2)\rangle &= 4\pi k_B T\rho_0[A(\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk})+B(\delta_{ij}\delta_{kl})]\\ &\quad\times\delta(\mathbf{k}_1+\mathbf{k}_2)\delta(\omega_1+\omega_2),\end{aligned}\tag{10.346}$$

where A and B are constants to be determined. Let us now consider the special case in which the wavevector, $\mathbf{k}$, lies in the z direction. Then $\hat{\mathbf{t}}_1=\hat{\mathbf{x}}$, $\hat{\mathbf{t}}_2=\hat{\mathbf{y}}$, and $\hat{\mathbf{k}}=\hat{\mathbf{z}}$, and we find

$$\begin{aligned}\langle \tilde{S}_{33}(\mathbf{k}_1,\omega_1)\tilde{S}_{33}(\mathbf{k}_2,\omega_2)\rangle &= \langle \tilde{S}^{\parallel}_{\mathbf{k}_1}(\omega_1)\tilde{S}^{\parallel}_{\mathbf{k}_2}(\omega_2)\rangle\\ &= 4\pi k_B T\rho_0(2A+B)\delta(\mathbf{k}_1+\mathbf{k}_2)\delta(\omega_1+\omega_2)\end{aligned}\tag{10.347}$$

and

$$\begin{aligned}\langle \tilde{S}_{31}(\mathbf{k}_1,\omega_1)\tilde{S}_{31}(\mathbf{k}_2,\omega_2)\rangle &= \langle \tilde{S}^{I}_{\mathbf{k}_1}(\omega_1)\tilde{S}^{I}_{\mathbf{k}_2}(\omega_2)\rangle\\ &= 4\pi k_B T\rho_0 A\delta(\mathbf{k}_1+\mathbf{k}_2)\delta(\omega_1+\omega_2).\end{aligned}\tag{10.348}$$

If we now compare Eqs. (10.347) and (10.348) with Eqs. (10.343) and (10.344), we find that $A=\nu_t$ and $B=\nu_l-2\nu_t$. Thus we finally obtain

$$\begin{aligned}\langle \tilde{S}_{ij}(\mathbf{k}_1,\omega_1)\tilde{S}_{kl}(\mathbf{k}_2,\omega_2)\rangle &= 4\pi k_B T[\eta(\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk})+(\zeta-\tfrac{2}{3}\eta)(\delta_{ij}\delta_{kl})]\\ &\quad\times\delta(\mathbf{k}_1+\mathbf{k}_2)\delta(\omega_1+\omega_2).\end{aligned}\tag{10.349}$$

Similarly, in order to be invariant under rotation of coordinates, the random heat current correlation function, $\langle \tilde{g}_i(\mathbf{k}_1,\omega_1)\tilde{g}_j(\mathbf{k}_2,\omega_2)\rangle$, can only depend on δ_{ij}. Therefore, we find

$$\langle \tilde{g}_i(\mathbf{k}_1,\omega_1)\tilde{g}_j(\mathbf{k}_2,\omega_2)\rangle = 4\pi k_B T^2\delta_{ij}K\delta(\mathbf{k}_1+\mathbf{k}_2)\delta(\omega_1+\omega_2).\tag{10.350}$$

Since thermal fluctuations are statistically independent of velocity fluctuations, we also have $\langle \tilde{g}_i(\mathbf{k}_1,\omega_1)\tilde{S}_{kl}(\mathbf{k}_2,\omega_2)\rangle=0$.

We can also find the space and time dependence of these correlation functions. If we Fourier transform them, we obtain

$$\begin{aligned}\langle \tilde{S}_{ij}(\mathbf{r}_1,t_1)\tilde{S}_{kl}(\mathbf{r}_2,t_2)\rangle &= \frac{2k_BT}{V}[\eta(\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk})+(\zeta-\tfrac{2}{3}\eta)(\delta_{ij}\delta_{kl})]\\ &\quad\times\delta(\mathbf{r}_1-\mathbf{r}_2)\delta(t_1-t_2)\end{aligned}\tag{10.351}$$

and

$$\langle \tilde{g}_i(\mathbf{r}_1, t_1)\tilde{g}_j(\mathbf{r}_2, t_2)\rangle = \frac{2k_B T^2}{V}\delta_{ij}K\delta(\mathbf{r}_1 - \mathbf{r}_2)\delta(t_1 - t_2). \qquad (10.352)$$

These equations give the random current correlation functions for an isotropic fluid of point particles in which the thermal expansivity, α_P equals zero. Notice that they are "delta-correlated.' That is, they have extremely short range. This is a reflection of the fact that these fluctuations occur on a much faster time scale and over much shorter spatial distances than do those of conserved quantities. For a discussion of the effect of noise on a broad class of systems see Ref. 26.

▶ S10.G. Long-Time Tails [27–36]

In Section 5.E we reviewed the traditional theory of Brownian motion in which a Brownian particle of radius R is assumed to move under the influence of a constant friction force (the Stokes friction, $6\pi\eta R$) and a random white noise, both due to the medium in which the Brownian particle moves. Under such conditions, the velocity autocorrelation function of the Brownian particle decays exponentially with time [cf. Eq. (5.84)]. However, in the 1960s, molecular dynamics computer simulations by Rahman [27] of liquid Argon showed significant deviations from exponential behavior in the velocity autocorrelations function of Argon atoms. His results are shown in Fig. 10.10.

Alder and Wainwright [29] used computer simulations to compute the velocity autocorrelation of hard-sphere particles in a hard-sphere gas. They also

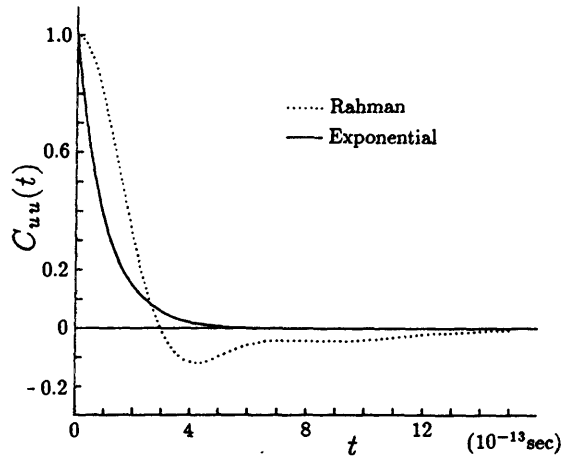


Fig. 10.10. The velocity autocorrelation function for argon atoms in liquid argon. The dotted line is from numerical simulation of Rahman. The solid line is the exponential decay predicted by traditional Brownian motion. Reprinted, by permission, from R. Zwanzig and M. Bixon, *Phys. Rev.* **A2**, 2005 (1970).

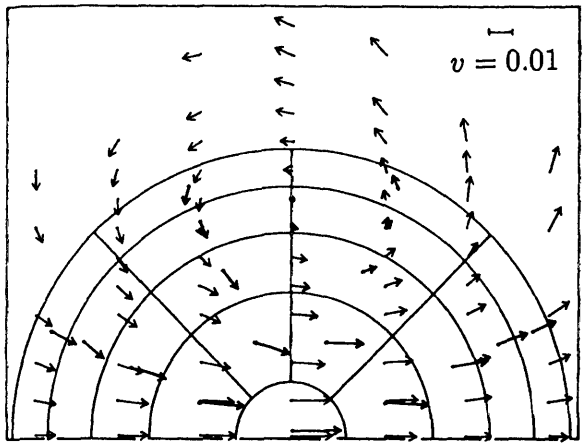


Fig. 10.11. The flow pattern around a hard-sphere particle in a hard-sphere gas. Reprinted, by permission, from B. J. Alder and T. E. Wainwright, *Phys. Rev.* **A1**, 18 (1970).

found deviations from exponential behavior. One of the more striking features they found was the long-time tail in the velocity autocorrelation function. In the long-time limit, the velocity autocorrelation function decayed as $t^{-3/2}$ rather than exponentially with time. They observed vortices in the flow pattern around the Brownian particle (cf. Fig. 10.11). As the Brownian particle moved through the fluid, it left a memory of its motion which could influence its later movement. This complicated flow around the Brownian particle is a direct consequence of hydrodynamics. In the sections below, we shall whos how the long-time tails emerge as a natural consequence of hydrodynamics.

▶ S10.G.1. Fluid Flow Around the Brownian Particle

The linearized hydrodynamic equations were given in Eqs. (10.36)–(10.38). If the Fourier transform their time dependence, we can write Eqs. (10.36) and (10.38) as

$$-i\omega\rho_\omega(\mathbf{r}) + \rho_0\nabla_\mathbf{r}\cdot\mathbf{v}_\omega(\mathbf{r}) = 0, \tag{10.353}$$

$$-i\omega\rho_0\mathbf{v}_\omega(\mathbf{r}) = -\nabla_\mathbf{r}P_\omega(\mathbf{r}) - \eta\nabla_\mathbf{r}\times(\nabla_\mathbf{r}\times\mathbf{v}_\omega(\mathbf{r})) + (\zeta+\tfrac{4}{3}\eta)\nabla_\mathbf{r}(\nabla_\mathbf{r}\cdot\mathbf{v}_\omega(\mathbf{r})), \tag{10.354}$$

where we have used the vector identity, $\nabla_\mathbf{r}^2\mathbf{v} = \nabla_\mathbf{r}(\nabla_\mathbf{r}\cdot\mathbf{v}) - \nabla_\mathbf{r}\times(\nabla_\mathbf{r}\times\mathbf{v})$.

Let us now assume that a spherical Brownian particle of radius R moves through the fluid with velocity $\mathbf{u}(t) = u(t)\hat{\mathbf{z}}$. Let us also assume that the surface of the Brownian particle is very rough so the fluid sticks to its surface. Then at

the surface the velocity of the fluid equals the velocity of the surface. To find the force exerted on the Brownian particle by the fluid, we must first find the velocity distribution of the fluid in the presence of the moving Brownian particle. With that solution, we can construct the pressure tensor, $\bar{\mathbf{P}}$ (cf. Section 10.B). Then the force on the Brownian particle is given By

$$\mathbf{F} = \oint d\mathbf{S} \cdot \bar{\mathbf{P}} = \oint dS\, \hat{\mathbf{r}} \cdot \bar{\mathbf{P}}. \tag{10.355}$$

Below we will solve the hydrodynamic equations for the velocity of the fluid in the presence of the Brownian particle subject to "stick" boundary conditions. We shall assume that the fluid has velocity $\mathbf{v}_\omega(\mathbf{r}) = \mathbf{u}_\omega$ at $r = R$ [$\mathbf{u}_\omega$ is the Fourier transform of $\mathbf{u}(t)$], and it has velocity $\mathbf{v}_\omega(\mathbf{r}, t) = 0$ when $r = \infty$. Also at $r = \infty$, all derivatives of the velocity are zero.

For simplicity, we will consider an incompressible fluid so that $\nabla_\mathbf{r} \cdot \mathbf{v}_\omega = 0$. The equation for the velocity flow reduces to

$$-i\omega\rho_0 \mathbf{v}_\omega(\mathbf{r}) = -\nabla_\mathbf{r} P_\omega(\mathbf{r}) - \eta \nabla_\mathbf{r} \times (\nabla_\mathbf{r} \times \mathbf{v}_\omega(\mathbf{r})). \tag{10.356}$$

The velocity, $\mathbf{v}_\omega$, can be written $\mathbf{v}_\omega = \nabla_\mathbf{r} \times \mathbf{A}_\omega$, where $\mathbf{A}_\omega$ is a velocity "vector potential." Let us note that $\mathbf{v}_\omega$ is a polar vector. In order for the combination $\nabla_\mathbf{r} \times \mathbf{A}_\omega$ to form a polar vector, $\mathbf{A}_\omega$ must be an axial vector. There are two vectors in the problem from which we can build this axial vector. They are the radial vector, $\mathbf{r}$, and the velocity, $\mathbf{u}_\omega = u_\omega \hat{\mathbf{z}}$. Let us write $\mathbf{A}_\omega = (\partial g(r)/\partial r)\hat{\mathbf{r}} \times \mathbf{u}_\omega$, where $\partial g(r)/\partial r$ is a function of the distance, r, from the center of the Brownian particle. It must be determined from boundary conditions. If we note that $[\partial g(r)/\partial r]\,\hat{\mathbf{r}} = \nabla_\mathbf{r} g(r)$, then the velocity vector potential takes the form $\mathbf{A}_\omega = (\nabla_\mathbf{r} g(r)) \times \mathbf{u}_\omega = \nabla \times (g(r)\mathbf{u}_\omega)$ and the fluid velocity can be written

$$\mathbf{v}_\omega = \nabla_\mathbf{r} \times \nabla_\mathbf{r} \times (g(r)\mathbf{u}_\omega). \tag{10.357}$$

Let us now take the curl of Eq. (10.356). We find

$$-i\omega\rho_0 \nabla_\mathbf{r} \times \mathbf{v}_\omega = -\eta \nabla_\mathbf{r} \times \nabla_\mathbf{r} \times (\nabla_\mathbf{r} \times \mathbf{v}_\omega) = \eta \nabla_\mathbf{r}^2 (\nabla_\mathbf{r} \times \mathbf{v}_\omega) \tag{10.358}$$

where

$$\nabla_\mathbf{r} \times \mathbf{v}_\omega(\mathbf{r}) = -\nabla_\mathbf{r}^2 (\nabla_\mathbf{r} \times g(r)\mathbf{u}_\omega) = 0, \tag{10.359}$$

Equation (10.358) then reduces to

$$(k^2 \nabla_\mathbf{r}^2 \nabla g(r) + \nabla_\mathbf{r}^4 \nabla g(r)) \times \mathbf{u}_\omega, \tag{10.360}$$

where $k^2 = i\omega\rho_0/\eta$ and $k = \sqrt{\omega\rho_0/2\eta}\,(1 + i)$. Thus, we must solve the

equation

$$\nabla_{\mathbf{r}}[\nabla_{\mathbf{r}}^4 g(r) + k^2 \nabla_{\mathbf{r}}^2 g(r)] = 0, \tag{10.361}$$

subject to the boundary conditions of the problem. If we integrate Eq. (10.361) once, we obtain

$$\nabla_{\mathbf{r}}^4 g(r) + k^2 \nabla_{\mathbf{r}}^2 g(r) = C, \tag{10.362}$$

where C is an integration constant. Since all derivatives of the velocity must be zero at $r = \infty$, we must have $C = 0$. We must find a solution to Eq. (10.362) such that $\nabla_{\mathbf{r}}^2 g(r)$ and all derivatives of $\nabla_{\mathbf{r}}^2 g(r)$ go to zero at $r = \infty$. These conditions are satisfied by the solution

$$\nabla_{\mathbf{r}}^2 g(r) = \frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial g}{\partial r} = \frac{c_1}{r} e^{ikr}, \tag{10.363}$$

where c_1 is a constant.

Let us now integrate Eq. (10.363) once to find

$$\frac{\partial g}{\partial r} = \frac{1}{r^2}\left[c_1 e^{ikr}\left(r + \frac{1}{ik}\right) + c_2\right]. \tag{10.364}$$

From Eq. (10.357), the fluid velocity can be written

$$\mathbf{v}_\omega(\mathbf{r}) = -\hat{\mathbf{r}}\frac{2u_\omega \cos(\theta)}{r}\frac{\partial g}{\partial r} + \hat{\boldsymbol{\theta}}\frac{u_\omega \sin(\theta)}{r}\left(\frac{\partial g}{\partial r} + r\frac{\partial^2 g}{\partial r^2}\right). \tag{10.365}$$

The constants c_1 and c_2 in Eq. (10.364) can be found from the "stick" boundary condition at the surface of the Brownian particle, $\mathbf{v}_\omega(R, \theta) = \mathbf{u}_\omega$. This boundary condition, together with Eqs. (10.364) and (10.365), yields

$$c_1 = \frac{3R}{2ik} e^{-ikR} \quad \text{and} \quad c_2 = \frac{R^3}{2}\left(-1 - \frac{3}{ikR} + \frac{3}{k^2R^2}\right). \tag{10.366}$$

We now are in a position to find the drag force on the Brownian particle due to its movement through the fluid.

▶ S10.G.2. Drag Force on the Brownian Particle

To find the drag force on the Brownian particle, we must perform the integration in Eq. (10.355). The first step is to write the pressure tensor. Eq. (10.356) can be written

$$\nabla_{\mathbf{r}} P_\omega(\mathbf{r}) = i\omega\rho_0 \mathbf{v}_\omega(\mathbf{r}) - \eta \nabla_{\mathbf{r}} \times (\nabla_{\mathbf{r}} \times \mathbf{v}_\omega(\mathbf{r})). \tag{10.367}$$

If we use the results from Eqs. (10.364)–(10.366), we find the following expression for the pressure

$$P = \eta u_\omega \cos(\theta)\left(\frac{3R}{2r^2} - \frac{3ikR^2}{2r^2} - \frac{k^2R^3}{2r^2}\right). \tag{10.368}$$

From Eq. (10.355), the drag force on the Brownian particle is given by

$$\mathbf{F} = R^2 \int_0^\pi \sin(\theta) d\theta \int_0^{2\pi} d\phi \, (P_{rr}\hat{\mathbf{r}} + P_{r\theta}\hat{\boldsymbol{\theta}} + P_{r\phi}\hat{\boldsymbol{\varphi}}), \tag{10.369}$$

where components P_{rr} and $P_{r\theta}$ of the pressure tensor are given by

$$P_{rr} = P - 2\eta \frac{\partial v_r}{\partial r} \quad \text{and} \quad P_{r\theta} = -\eta\left(\frac{1}{r}\frac{\partial v_r}{\partial \theta} + \frac{\partial v_\theta}{\partial r} - \frac{v_\theta}{r}\right). \tag{10.370}$$

Due to the geometry of the problem, there is no contribution from $P_{r\phi}$. On the surface of the Brownian particle we find that $(\partial v_r/\partial r)_{r=R} = 0$, so

$$P_{rr} = \eta u_\omega \cos(\theta)\left(\frac{3}{2R} - \frac{3ik}{2} - \frac{k^2R}{2}\right) \quad \text{and} \quad P_{r\theta} = -\eta u_\omega \sin(\theta)\left(\frac{3}{2R} - \frac{3ik}{2}\right) \tag{10.371}$$

on the surface.

We can now substitute these results into Eq. (10.369) and integrate. However, before we do the integration we must expand the unit vectors $\hat{\mathbf{r}}$ and $\hat{\boldsymbol{\theta}}$ in terms of Cartesian unit vectors. The directions of $\hat{\mathbf{r}}$ and $\hat{\boldsymbol{\theta}}$ vary over the surface while the Cartesian unit vectors do not. Note that $\hat{\mathbf{r}} = \sin(\theta)\cos(\phi)\hat{\mathbf{x}} + \sin(\theta)\sin(\phi)\hat{\mathbf{y}} + \cos(\theta)\hat{\mathbf{z}}$ and $\hat{\boldsymbol{\theta}} = \cos(\theta)\cos(\phi)\hat{\mathbf{x}} + \cos(\theta)\sin(\phi)\hat{\mathbf{y}} - \sin(\theta)\hat{\mathbf{z}}$. If we perform the integration in Eq. (10.369), we obtain

$$\mathbf{F} = 6\pi\eta u_\omega R\hat{\mathbf{z}}\left(1 - ikR - \frac{k^2R^2}{9}\right). \tag{10.372}$$

In the frequency limit $\omega \to 0$, the drag force reduces to the usual Stokes friction force, namely, $\mathbf{F} = 6\pi\eta u R\hat{\mathbf{z}}$. The Stokes friction can only be used to describe Brownian particles which are moving very slowly. Below we will compute the velocity autocorrelation function for a Brownian particle which is bouncing around rather rapidly. Then frequency-dependent terms cannot be neglected.

▶ S10.G.3. Velocity Autocorrelation Function

As we can see from Eq. (10.372), the friction force for a Brownian particle in a fluid depends on the frequency. This means that it has memory. The equation of

motion for the Brownian particle can be written

$$m\frac{du(t)}{dt}+\int_{-\infty}^{\infty}\alpha(t-t')u(t')dt'=F_{rand}(t), \tag{10.373}$$

where $\alpha(t)$ is a memory-dependent friction coefficient whose Fourier transform is given by Eq. (10.372). Namely,

$$\alpha(\omega)=\int_{-\infty}^{\infty}dt\,\alpha(t)e^{i\omega t}=6\pi\eta R\left(1-ikR-\frac{k^2R^2}{9}\right). \tag{10.374}$$

The friction force is assumed to be causal so that $\alpha(t)=0$ for $t<0$ and $\alpha(t)\neq 0$ for $t>0$. In Eq. (10.373), $F_{rand}(t)$ is the random fluctuation force of the medium on the Brownian particle. We assume that the random force has zero average value, $\langle F_{rand}(t)\rangle_F=0$, where $\langle\rangle_F$ is an average over realizations of the random force. Because there is memory, the random force will not be "white."

If we make use of Eq. (10.374), the Fourier transform of Eq. (10.373) can be written

$$-im'\omega\tilde{u}(\omega)+\zeta\tilde{u}(\omega)-\zeta\Delta i\sqrt{-i\omega}\tilde{u}(\omega)=\tilde{F}_{rand}(\omega), \tag{10.375}$$

where $\Delta=\sqrt{(R^2\rho_0/\eta)}$, $m'=m+\frac{2}{3}M$, $\zeta=6\pi\eta R$, and $M=\frac{4}{3}\pi\rho_0R^3$ is the mass of the displaced fluid. If we take the inverse Fourier transform of Eq. (10.375), we find

$$m'\frac{du(t)}{dt}+\zeta u(t)+\frac{\zeta\Delta}{\sqrt{\pi}}\int_{-\infty}^{t}ds\,\frac{1}{\sqrt{t-s}}\frac{du}{ds}=F_{rand}(t). \tag{10.376}$$

Equation (10.376) is the Langevin equation for a Brownian particle of radius R in an incompressible fluid assuming "stick" boundary conditions. There are two interesting features. First, the particle has a memory-dependent friction coefficient as a result of the complicated flows around the particle. Second, and somewhat unexpectedly, there is a dressing of the mass of the Brownian particle. We will talk more about that below.

Let us now construct the velocity autocorrelation function for the Brownian particle. We first average Eq. (10.376) over the random force and obtain

$$m'\frac{d\langle u(t)\rangle_F}{dt}+\zeta\langle u(t)\rangle_F+\frac{\zeta\Delta}{\sqrt{\pi}}\int_{-\infty}^{t}ds\,\frac{1}{\sqrt{t-s}}\frac{d\langle u(s)\rangle_F}{ds}=0. \tag{10.377}$$

The velocity autocorrelation function is defined as

$$C_{uu}(t)\equiv\langle\langle u(t)\rangle_F u(0)\rangle_T, \tag{10.378}$$

where $\langle\rangle_T$ denotes a thermal average over the initial conditions. Therefore, in order to compute the velocity autocorrelation function, we must find $\langle u(t)\rangle_F$ for a given initial condition, $u(0)$. This can be done by means of a Laplace transform. In Exercise 10.9, we take the Laplace transform of Eq. (10.377). We then find

$$C_{uu}(t) = \frac{1}{2\pi i}\int_{\delta-i\infty}^{\delta+i\infty} dz\, e^{zt}\, \frac{m'\langle|u(0)|^2\rangle_T}{m'z+\zeta+\zeta\Delta\sqrt{z}}. \tag{10.379}$$

■ **EXERCISE 10.9.** Take the Laplace transform of the equation

$$m'\frac{df(t)}{dt} + \zeta f(t) + \frac{\zeta\Delta}{\sqrt{\pi}}\int_{-\infty}^{t} ds\, \frac{1}{\sqrt{t-s}}\frac{df(s)}{ds} = 0.$$

Answer: Let us first note that

$$f(t) = \frac{1}{2\pi i}\int_{\delta-i\infty}^{\delta+i\infty} dz\, e^{zt}\tilde{f}(z) \quad \text{and} \quad \tilde{f}(z) = \int_0^\infty dt\, e^{-zt} f(t). \tag{1}$$

and

$$\int_0^\infty dt\, e^{-zt}\frac{df(t)}{dt} = z\tilde{f}(z) - f(0) \quad \text{and} \quad \frac{df(t)}{dt} = \frac{1}{2\pi i}\int_{\delta-i\infty}^{\delta+i\infty} dz\, e^{zt} z\tilde{f}(z). \tag{2}$$

Also, we need to find the Laplace transform $I(t) = \int_{-\infty}^{t} ds\,(1/\sqrt{t-s})\,[df(s)/ds]$. We can write

$$\begin{aligned}\tilde{I}(z) &= \int_0^\infty dt e^{-zt} I(t) = \int_0^\infty dt e^{-zt}\int_{-\infty}^{t} ds\,\frac{1}{\sqrt{t-s}}\frac{df(s)}{ds} \\ &= \frac{1}{2\pi i}\int_{\delta-i\infty}^{\delta+i\infty} dz'\int_0^\infty dt\, e^{-t(z-z')}\int_{-\infty}^{t}\frac{ds}{\sqrt{t-s}}\, e^{-z'(t-s)}\, z'\tilde{f}(z').\end{aligned} \tag{3}$$

Let us note that

$$\int_{-\infty}^{t}\frac{ds}{\sqrt{t-s}}\, e^{-z'(t-s)} = \int_0^\infty \frac{dx}{\sqrt{x}}\, e^{-z'x} = \sqrt{\frac{\pi}{z'}}, \tag{4}$$

where $x = t - s$. Equation (3) then takes the form

$$\tilde{I}(z) = \frac{1}{2\pi i} \int_{\delta - i\infty}^{\delta + i\infty} dz' \int_0^\infty dt\, e^{-t(z-z')} \sqrt{\frac{\pi}{z'}} z' \tilde{f}(z'). \tag{5}$$

This expression for $\tilde{I}(z)$ is well-behaved provided that $\mathrm{Re}(z) > \mathrm{Re}(z')$. Then we can perform the integration over time to obtain

$$\tilde{I}(z) = \frac{1}{2\pi i} \int_{\delta - i\infty}^{\delta + i\infty} dz' \frac{1}{z - z'} \sqrt{\frac{\pi}{z'}} z' \tilde{f}(z'). \tag{6}$$

Let us now consider the contours in Fig. 10.12. The integrand in Eq. (6) has a pole at $z' = z$ which is to the right of the contour C_1. Therefore, to perform the integration, we close the contour to the right and pick up the contribution from that pole. We then find

$$\tilde{I}(z) = \sqrt{\pi z}\, \tilde{f}(z). \tag{7}$$

If we now combine the above results, we obtain

$$\tilde{f}(z) = \frac{m' f(0)}{m' z + \zeta + \zeta \Delta \sqrt{z}}. \tag{8}$$

To obtain the final expression for the velocity autocorrelation function, we must compute the thermal average, $\langle |u(0)|^2 \rangle_T$. First note that the mass, m', of the Brownian particle is now a "dressed mass." In order to obtain the correct

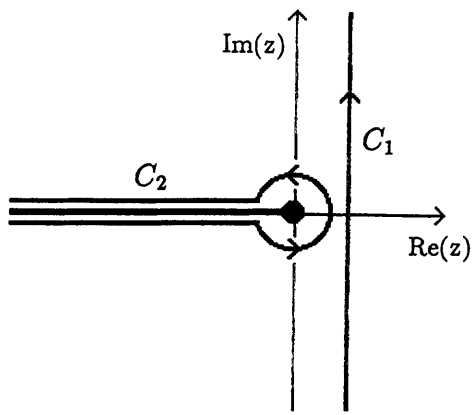


Fig. 10.12. Branch cut and integration contours. C_1 is the Bromwich contour.

diffusion coefficient, D, we must use the dressed mass, m', when defining the thermal average. We write $\langle |u(0)|^2 \rangle_T = (k_B T/m')$. The velocity autocorrelation function then becomes

$$C_{uu}(t) = \frac{k_B T}{2\pi i} \int_{\delta - i\infty}^{\delta + i\infty} dz\, e^{zt} \frac{1}{m'z + \zeta + \zeta\Delta\sqrt{z}}. \tag{10.380}$$

The Laplace transform of the velocity autocorrelation function is given by

$$\tilde{C}_{uu}(z) = \frac{k_B T}{m'z + \zeta + \zeta\Delta\sqrt{z}}. \tag{10.381}$$

It has the property that $\lim_{z\to 0} \tilde{C}_{uu}(z) = D = k_B T/\zeta$, where D is the Einstein diffusion coefficient.

Let us now evaluate the integral, Eq. (10.380). The integrand has a branch point at $z = 0$. We draw the branch cut along the negative real axis as shown in Fig. (10.12). Then we integrate along the contour C_2. The contribution from the small semicircle at the origin is zero because there is no pole at the origin. The correlation function is then found to be

$$C_{uu}(t) = \frac{k_B T}{\pi} \int_0^\infty dx\, e^{-x|t|} \left(\frac{\zeta\Delta\sqrt{x}}{(\zeta - m'x)^2 + \zeta^2\Delta^2 x} \right). \tag{10.382}$$

This integral must be evaluated numerically. However, some limiting cases can be obtained analytically.

We can obtain an analytic expression for the long-time behavior of the velocity autocorrelation function. The long-time behaviour is determined by small values of x since contributions for large x are exponentially small. Thus we can obtain the long-time behavior by expanding the integrand in powers of $\sqrt{x}$. We find [29–34]

$$C_{uu}(t) = \frac{k_B T \delta}{\pi\zeta} \int_0^\infty dx\, \sqrt{x}\, e^{-x|t|} + \cdots = \frac{D\Delta}{2\sqrt{\pi}|t|^{3/2}} + \cdots, \tag{10.383}$$

where $D = k_B T/6\pi\eta R$ is the Einstein diffusion coefficient. Notice that the velocity autocorrelation function for the Brownian particle does not die off exponentially, but has a long-time tail. It decays with time as $t^{-3/2}$.

We can also compute the variance of the Brownian particle. Let us remember that $x(t) - x(0) = \int_0^t dt'\, v(t')$. Then for a Brownian particle in equilibrium with

the surrounding fluid, we obtain

$$\langle \Delta x^2(t) \rangle = \langle (x(t) - x(0))^2 \rangle = \int_0^t dt_1 \int_0^t dt_2 \, \langle u(t_1) u(t_2) \rangle$$

$$= \left(\int_{t/2}^{t} dT \int_{2(T-t)}^{2(t-T)} d\tau + \int_0^{t/2} dT \int_{-2T}^{2T} d\tau \right) C_{uu}(\tau)$$

$$= 2 \int_0^t d\tau \int_{\tau/2}^{t-\tau/2} dT \, C_{uu}(\tau) = 2 \int_0^t d\tau (t - \tau) C_{uu}(\tau). \quad (10.384)$$

In the fourth term we have made the change of variables, $\tau = t_2 - t_1$ and $T = \frac{1}{2}(t_1 + t_2)$. In the fifth term, we have changed the order of integration. For example, $\int_{t/2}^{t} dT \int_0^{2(t-T)} d\tau = \int_0^t d\tau \int_{t/2}^{t-\tau/2} dT$. For long times the variance takes the form

$$\langle \Delta x^2(t) \rangle = 2Dt - \frac{4D\Delta}{\sqrt{\pi}} t^{1/2} + \cdots. \quad (10.385)$$

Thus, in the very long time limit it approaches the expected value.

It is also useful to define a "time-dependent diffusion coefficient" given by

$$D(t) \equiv \frac{1}{2} \frac{d\langle \Delta x^2(t) \rangle}{dt} = \int_0^t d\tau \, C_{uu}(\tau). \quad (10.386)$$

For long times, the time-dependent diffusion coefficient has the form

$$D(t) = D - \frac{D\Delta}{\pi} \sqrt{\frac{\pi}{t}} + \cdots. \quad (10.387)$$

The long-time tail in the velocity autocorrelation function for a Brownian particle with radius $R = 1.7$ microns in water has been measured in light scattering experiments by Paul and Pusey [36]. The light scattering experiments actually measure the variance, $\langle \Delta x^2(t) \rangle$, because the correlation function for the intensity of the scattered light, $\langle I(t) I(0) \rangle$, can be related directly to the variance through a relation of the form $\langle I(t) I(0) \rangle \approx 1 + C \exp(-K^2 \langle \Delta x^2(t) \rangle)$, where C and K are constants which depend on the medium [36]. We show the results in Fig. 10.13. Curve A is the result for the case when the friction coefficient, $\alpha = 6\pi\eta R$, has no memory. Curve B is the prediction of Eq. (10.385). The black dots are the result of experiment. While the results of experiment qualitatively follow the theoretical predictions, they differ by a systematic quantitative amount. One possible source [4, 1982] for these deviations is the rotational degrees of freedom of water. The deviations between theory and experiment in Fig. 10.13 have been used to estimate the rotational transport coefficients in water.

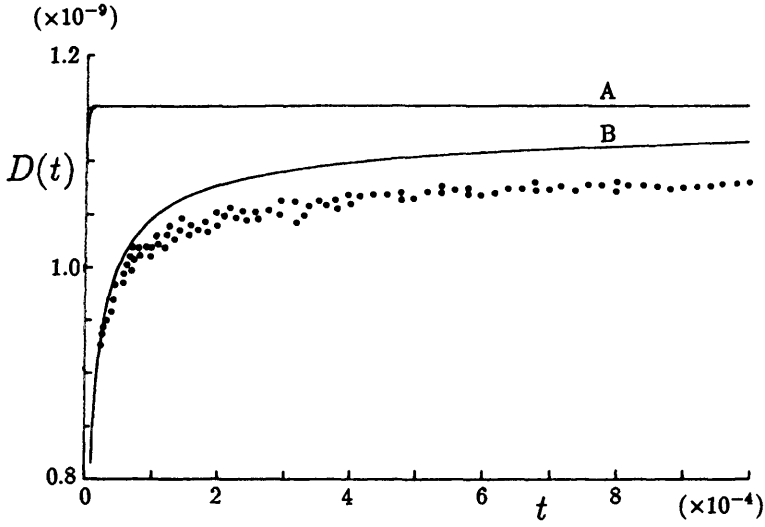


Fig. 10.13. Measurements of the time-dependent diffusion coefficient, $D(t)$ (in units of $cm^2\ sec^{-1}$), versus time (in seconds). Curve A is the predicted result using the constant Stokes friction coefficent, $\alpha = 6\pi\eta R$. Curve B is the prediction of theory if memory effects are included. The black dots are measurements for a Brownian particle in water. Reprinted, by permission, from G. L. Paul and P. N. Pusey, *J. Phys. A: Math. Gen.* **14**, 3301 (1981).

As we mentioned at the beginning of Section S10.G, the deviations from exponential behaviour observed by Rahman [27] for the velocity autocorrelation function of argon atoms moving in argon have been reproduced theoretically by Zwanzig and Bixon [28] using the hydrodynamic equations to compute the time evolution of the velocity autocorrelation function, assuming that the Brownian particle is an argon atom. For argon atoms in argon, there will be very high-frequency components to the Brownian motion. Zwanzig and Bixon therefore included effects due to the compressibility of the fluid. They also included viscoelastic effects. For high-frequency motion, the liquid begins to take on some of the rigidity of a solid. Some of this rigidity can be accounted for by including frequency-dependent contributions to the viscosity. The calculation of the memory terms in the friction coefficient then proceeds in the same manner as described above. Zwanzig and Bixon, however, used slightly different boundary conditions. For Brownian particles as small as atoms, they used "slip" boundary conditions, rather than the "stick" boundary conditions that we used above. Slip boundary conditions mean that no torques can act on the Brownian particle. Also, for the case of a hard sphere, the normal component of the velocity of the fluid at the surface of the sphere is equal to the normal component of velocity of the sphere (no fluid can flow into or out of the sphere). A comparison of the results of the Zwanzig and Bixon with Rahman's numerical experiments is shown in Fig. 10.14. The qualitative agreement is quite impressive. This shows that even on the molecular scale, the conservation

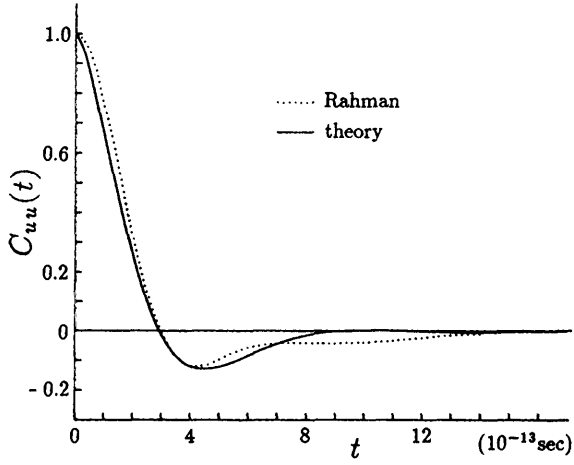


Fig. 10.14. The velocity autocorrelation function normalized to unity at the initial time. The dotted curve is Rahman's data. The solid curve is theory. Reprinted, by permission, from R. Zwanzig and M. Bixon, *Phys. Rev.* **A2**, 2005 (1970).

laws which give rise to hydrodynamic behavior play a fundamental role. A systematic study of the effects of compressibility and viscoelasticity on rotational and translational Brownian motion is given in Ref. 37. The effect of hydrodynamic memory on the dielectric response of a Brownian particle in a nonpolar fluid was studied in Ref. 38.

▶ S10.H Superfluid Hydrodynamics [1, 39–43]

In this section we shall derive the hydrodynamic equations describing He(II)—that is, liquid He^4 below the λ line (cf. Sections 3.D and 3.F). We assume that He(II) is composed of two interpenetrating fluids: (1) a normal fluid which behaves somewhat like a classical fluid and has velocity $\mathbf{v}_n$ in the laboratory frame and (2) a superfluid which carries no entropy and has velocity $\mathbf{v}_s$ in the laboratory frame. We shall first obtain the hydrodynamic equations for the system and then obtain dispersion relations for first and second sound in the superfluid.

▶ S10.H1. Superfluid Hydrodynamic Equations

It is useful to first write the balance equations for He(II). The mass balance (mass conservation) equation is given by

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{J} = 0, \tag{10.388}$$

where ρ is the total mass density and $\mathbf{J}$ is the total momentum density of the fluid. The total mass density can be written $\rho = \rho_n + \rho_s$, where ρ_n is the mass density of the normal fluid and ρ_s is the mass density of the superfluid. The momentum density of the fluid can be written $\mathbf{J} = \rho_n \mathbf{v}_n + \rho_s \mathbf{v}_s$, where $\mathbf{v}_n$ is the normal fluid velocity and $\mathbf{v}_s$ is the superfluid velocity. It is important to note that the superfluid and normal fluid phases cannot be separated in real space. The superfluid phase results from the condensation of part of the substance into a single quantum state.

The momentum balance equation is

$$\frac{\partial \mathbf{J}}{\partial t} + \nabla P + \nabla \cdot \bar{\mathbf{\Pi}}^R + \nabla \cdot \bar{\mathbf{\Pi}}^D = 0, \tag{10.389}$$

where P is the hydrostatic pressure, $\bar{\mathbf{\Pi}}^R$ is the reversible stress tensor (momentum current), and $\bar{\mathbf{\Pi}}^D$ is the dissipative stress tensor.

The energy balance equation is

$$\frac{\partial \mathbf{U}}{\partial t} + \nabla \cdot (\mathbf{J}_E^R + \mathbf{J}_E^D) = 0, \tag{10.390}$$

where $\mathbf{J}_E^R$ and $\mathbf{J}_E^D$ are the reversible and dissipative energy currents.

The entropy balance equation is

$$\frac{\partial \rho s}{\partial t} + \nabla \cdot (\rho s \mathbf{v}_n + \mathbf{J}_S^D) = \sigma, \tag{10.391}$$

where s is the specific entropy, $\rho s \mathbf{v}_n$ is the reversible entropy current, $\mathbf{J}_S^D$ is the dissipative entropy current, and σ is the entropy production. The reversible entropy current only depends on the normal fluid velocity, $\mathbf{v}_n$, because the superfluid does not carry entropy.

In Section S3.B we found that the superfluid velocity is driven by gradients in the chemical potential. Thus we write

$$\frac{d\mathbf{v}_s}{dt} = \frac{\partial \mathbf{v}_s}{\partial t} + (\mathbf{v}_s \cdot \nabla)\mathbf{v}_s = -\nabla(\mu^R + \mu^D), \tag{10.392}$$

where $d\mathbf{v}_s/dt$ is the convective time derivative of the superfluid, and μ^R and μ^D are reversible and dissipative contributions to the chemical potential.

It is useful to consider the fluid in the rest frame of the superfluid. Let E_0 denote the energy in the superfluid rest frame. Then differential changes in the energy are given by

$$dE_0 = \mu d\rho + T d(\rho s) + \mathbf{w} d\mathbf{J}_0, \tag{10.393}$$

where $\mathbf{J}_0 = \mathbf{J} - \rho \mathbf{v}_s$ is the momentum density of the fluid in the superfluid rest frame and $\mathbf{J}$ is the momentum density in the laboratory frame of reference. The

chemical potential is $\mu = (\partial E_0/\partial\rho)_{\rho s,\mathbf{J}_0}$. The temperature is $T = (\partial E_0/\partial \rho s)_{\rho,\mathbf{J}_0}$. The new quantity, $\mathbf{w}$, is a velocity which is defined $\mathbf{w} = (\partial E_0/\partial \mathbf{J}_0)_{\rho,\rho s}$.

The total energy, E, in the laboratory frame is related to the energy, E_0, in the rest frame of the fluid by a Galilean transformation

$$E = E_0 + \mathbf{v}_s \cdot \mathbf{J}_0 + \tfrac{1}{2}\rho v_s^2 = E_0 + \mathbf{v}_s \cdot (\mathbf{J} - \rho \mathbf{v}_s) + \tfrac{1}{2}\rho v_s^2. \tag{10.394}$$

In the discussion below, we shall consider the fluid to be a function of the variables, $\rho, \rho s, \mathbf{J}$, and $\mathbf{v}_s$. From Eqs. (10.393) and (10.394), a differential change in energy, E, can be written

$$dE = (\mu - \mathbf{w}\cdot\mathbf{v}_s - \tfrac{1}{2}v_s^2)d\rho + Td(\rho s) + (\mathbf{w} + \mathbf{v}_s)\cdot d\mathbf{J} + (\mathbf{J} - \rho(\mathbf{w} + \mathbf{v}_s))\cdot d\mathbf{v}_s. \tag{10.395}$$

It is found experimentally that if the velocities of the fluid are too great the superfluid phase can be destroyed. Therefore the superfluid equations are only useful for low velocities and we can neglect convective contributions to the hydrodynamic equations. As a first step we will reexpress Eq. (10.395) in terms of partial time derivatives rather than total time derivatives since total time derivatives contain contributions due to convection. Thus we write

$$\frac{\partial E}{\partial t} = (\mu - \mathbf{w}\cdot\mathbf{v}_s - \tfrac{1}{2}v_s^2)\frac{\partial \rho}{\partial t} + T\frac{\partial \rho_s}{\partial t} + (\mathbf{w} + \mathbf{v}_s)\cdot\frac{\partial \mathbf{J}}{\partial t} + (\mathbf{J} - \rho(\mathbf{w} + \mathbf{v}_s))\cdot\frac{\partial \mathbf{v}_s}{\partial t}. \tag{10.396}$$

As a next step we will substitute the balance equations, (10.388)–(10.392), into Eq. (10.396) and eliminate terms which are cubic in the velocity. This gives

$$\begin{aligned} T\frac{\partial \rho s}{\partial t} = &-\nabla_{\mathbf{r}}\cdot(\mathbf{J}_E^R + \mathbf{J}_E^D) + \mu\nabla_{\mathbf{r}}\cdot\mathbf{J} + (\mathbf{w} + \mathbf{v}_s)\cdot\nabla_{\mathbf{r}}P + (\mathbf{w} + \mathbf{v}_s)\cdot(\nabla_{\mathbf{r}}\cdot\bar{\mathbf{\Pi}}^D) \\ &+ (\mathbf{J} - \rho(\mathbf{v} + \mathbf{w}))\cdot\nabla_{\mathbf{r}}(\mu^R + \mu^D). \end{aligned} \tag{10.397}$$

The reversible stress tensor does not appear in Eq. (10.397) because it is a momentum current which is explicitly quadratic in the velocity and therefore leads to contributions in Eq. (10.397) which are cubic in the velocity.

Let us now write the Gibbs–Duhem equation in the superfluid rest frame,

$$dP = \rho d\tilde{\mu} + \rho s dT + \mathbf{J}_0 \cdot d\mathbf{w}. \tag{10.398}$$

If we substitute the Gibbs–Duhem equation (10.398) into Eq. (10.397) and neglect terms cubic in the velocity, we obtain

$$\begin{aligned} T\frac{\partial \rho s}{\partial t} = &-\nabla_{\mathbf{r}}\cdot[\mathbf{J}_E^R + \mathbf{J}_E^D - \mu\mathbf{J} - (\mathbf{w} + \mathbf{v}_s)\cdot\bar{\mathbf{\Pi}}^D] + (\mathbf{J} - \rho(\mathbf{v}_s + \mathbf{w})\cdot\nabla_{\mathbf{r}}(\mu^R - \tilde{\mu}) \\ &+ (\mathbf{J} - \rho(\mathbf{v}_s + \mathbf{w}))\cdot\nabla_{\mathbf{r}}\mu^D + \rho s(\mathbf{v}_s + \mathbf{w})\cdot\nabla_{\mathbf{r}}T - \bar{\mathbf{\Pi}}^D : \nabla_{\mathbf{r}}(\mathbf{v}_s + \mathbf{w}). \end{aligned} \tag{10.399}$$

There is one final step necessary to put the entropy balance equation into the form Eq. (10.391). If we divide Eq. (10.399) by T and rearrange terms, we find

$$\frac{\partial \rho s}{\partial t} = -\nabla_{\mathbf{r}} \cdot \left[\frac{(\mathbf{J}_E^R + \mathbf{J}_E^D - \mu \mathbf{J} - (\mathbf{w} + \mathbf{v}_s) \cdot \bar{\mathbf{\Pi}}^D - \mu^D \boldsymbol{\lambda})}{T} \right] + [\mathbf{J}_E^R + \mathbf{J}_E^D - \tilde{\mu} \mathbf{J} - (\mathbf{w} + \mathbf{v}_s) \cdot \bar{\mathbf{\Pi}}^D - \rho s T (\mathbf{w} + \mathbf{v}_s) - \mu^D \boldsymbol{\lambda}] \cdot \nabla_{\mathbf{r}} \left(\frac{1}{T} \right) + \frac{1}{T} \boldsymbol{\lambda} \cdot \nabla_{\mathbf{r}} (\mu^R - \tilde{\mu}) - \frac{\mu^D}{T} \nabla_{\mathbf{r}} \cdot \lambda - \frac{1}{T} \bar{\mathbf{\Pi}}^D : \nabla_{\mathbf{r}} (\mathbf{w} + \mathbf{v}_s). \tag{10.400}$$

To obtain Eq. (10.400), we have used the fact that

$$\frac{1}{T} (\mathbf{J} - \rho(\mathbf{v}_s + \mathbf{w})) \cdot \nabla_{\mathbf{r}} \mu^D = \nabla_{\mathbf{r}} \cdot \left(\frac{\mu^D \boldsymbol{\lambda}}{T} \right) - \frac{\mu^D}{T} \nabla_{\mathbf{r}} \cdot \boldsymbol{\lambda} - \mu^D \boldsymbol{\lambda} \cdot \nabla_{\mathbf{r}} \left(\frac{1}{T} \right), \tag{10.401}$$

where $\boldsymbol{\lambda} = \mathbf{J} - \rho(\mathbf{v}_s + \mathbf{w})$. Equation (10.400) can be simplified further if we first consider the case of a reversible fluid. The fact that the entropy production must be zero for a reversible fluid allows us to give a more precise definition of the reversible currents.

In a reversible fluid, all the dissipative contributions in Eq. (10.400) are zero. The equation for a reversible fluid is then

$$\frac{\partial \rho s}{\partial t} = -\nabla_{\mathbf{r}} \cdot \left[\frac{(\mathbf{J}_E^R - \tilde{\mu} \mathbf{J})}{T} \right] + [\mathbf{J}_E^R - \mu \mathbf{J} - \rho s T (\mathbf{w} + \mathbf{v}_s)] \cdot \nabla_{\mathbf{r}} \left(\frac{1}{T} \right) + \frac{1}{T} \boldsymbol{\lambda} \cdot \nabla_{\mathbf{r}} (\mu^R - \tilde{\mu}). \tag{10.402}$$

A reversible fluid, by definition, has no entropy production. This, in turn, means that the reversible energy current must be given by

$$\mathbf{J}_E^R = \tilde{\mu} \mathbf{J} + \rho s T (\mathbf{w} + \mathbf{v}_s), \tag{10.403}$$

and the reversible entropy current is given by

$$\mathbf{J}_S^R = \frac{1}{T} (\mathbf{J}_E^R - \tilde{\mu} \mathbf{J}) = \rho s (\mathbf{w} + \mathbf{v}_s). \tag{10.404}$$

However, the superfluid can't carry entropy so we must have $\mathbf{J}_S^R = \rho s \mathbf{v}_n$, and this in turn means that

$$\mathbf{w} = \mathbf{v}_n - \mathbf{v}_s. \tag{10.405}$$

Also, $\mu^R = \tilde{\mu}$, so the reversible part of the chemical potential is just the

thermodynamic chemical potential. The quantity μ^D is a contribution to the chemical potential due to dissipative processes. We can write the equation for the dissipative fluid as

$$\frac{\partial \rho s}{\partial t} = -\nabla_{\mathbf{r}} \cdot (\rho s \mathbf{v}_n + \mathbf{J}_S^D) - \frac{1}{T}\mathbf{J}_S^D \cdot \nabla_{\mathbf{r}} T - \frac{\mu^D}{T}\nabla_{\mathbf{r}} \cdot \boldsymbol{\lambda} - \frac{1}{T}\bar{\boldsymbol{\Pi}}^D : \nabla_{\mathbf{r}} \mathbf{v}_s, \quad (10.406)$$

where $\mathbf{J}_S^D = \mathbf{J}_E^D - \mathbf{v}_n \cdot \bar{\boldsymbol{\Pi}}^D - \mu^D \boldsymbol{\lambda}$ and $\boldsymbol{\lambda} = \mathbf{J} - \rho \mathbf{v}_n$.

Let us now write the generalized Ohm's laws for superfluid. There are two scalar forces, namely, $\nabla_{\mathbf{r}} \cdot \boldsymbol{\lambda}$ and $\nabla_{\mathbf{r}} \cdot \mathbf{v}_n$. There is one vector force, $\nabla_{\mathbf{r}} T$, and one symmetric tensor force, $(\nabla_{\mathbf{r}} \mathbf{v}_n)^s$. We therefore can write

$$\Pi^D = -\zeta_1 \nabla_{\mathbf{r}} \cdot \boldsymbol{\lambda} - \zeta_1 \nabla_{\mathbf{r}} \cdot \mathbf{v}_n, \quad (10.407)$$

$$\mu^D = -\zeta_3 \nabla_{\mathbf{r}} \cdot \boldsymbol{\lambda} - \zeta_4 \nabla_{\mathbf{r}} \cdot \mathbf{v}_n, \quad (10.408)$$

$$\mathbf{J}_S^D = -\frac{K}{T}\nabla_{\mathbf{r}} T, \quad (10.409)$$

and

$$(\bar{\boldsymbol{\Pi}}^D)^s = -\eta (\nabla_{\mathbf{r}} \mathbf{v}_n)^s. \quad (10.410)$$

The superfluid has six transport coefficients. From Onsager's relations we have $\zeta_1 = \zeta_4$.

▶ S10.H.2. Sound Modes

In this section we will obtain dispersion relations for the various types of sound modes in the absence of dissipation. To obtain sound modes in the nondissipative case, we set all dissipative currents to zero in Eqs. (10.388), (10.389), (10.391), and (10.392) and we linearize about absolute equilibrium. We shall write $\rho = \rho_0 + \Delta\rho, s = s_0 + \Delta s, P = P_0 + \Delta P$, where ρ_0, s_0, and P_0 denote the equilibrium density, entropy, and pressure, respectively, and $\Delta\rho = \Delta\rho(\mathbf{r}, t), \Delta s = \Delta s(\mathbf{r}, t)$, and $\Delta P = \Delta P(\mathbf{r}, t)$ denote their deviations from equilibrium. We also neglect all terms to second order in the velocities, $\mathbf{v}_n$ and $\mathbf{v}_s$. The hydrodynamic equations then take the form

$$\frac{\partial \Delta\rho}{\partial t} + \rho_n^0 \nabla_{\mathbf{r}} \cdot \mathbf{v}_n + \rho_s^0 \nabla_{\mathbf{r}} \cdot \mathbf{v}_s = 0, \quad (10.411)$$

$$\rho_n^0 \frac{\partial \mathbf{v}_n}{\partial t} + \rho_s^0 \frac{\partial \mathbf{v}_s}{\partial t} + \nabla_{\mathbf{r}} \Delta P = 0, \quad (10.412)$$

$$\rho^0 \frac{\partial \Delta s}{\partial t} + s^0 \frac{\partial \Delta\rho}{\partial t} + \rho^0 s^0 \nabla_{\mathbf{r}} \cdot \mathbf{v}_n = 0, \quad (10.413)$$

and

$$\frac{\partial \mathbf{v}_s}{\partial t} + \nabla_{\mathbf{r}} \Delta\mu = 0. \tag{10.414}$$

Let us now choose the density and temperature to be our independent thermodynamic variables. Equations (10.411)–(10.414) then become

$$\frac{\partial \Delta\rho}{\partial t} + \rho_n^0 \nabla_{\mathbf{r}} \cdot \mathbf{v}_n + \rho_s^0 \nabla_{\mathbf{r}} \cdot \mathbf{v}_s = 0, \tag{10.415}$$

$$\rho_n^0 \frac{\partial \mathbf{v}_n}{\partial t} + \rho_s^0 \frac{\partial \mathbf{v}_s}{\partial t} + \frac{1}{\rho\kappa_T} \nabla_{\mathbf{r}} \Delta\rho + \left(\frac{\partial P}{\partial T}\right)_\rho^0 \nabla_{\mathbf{r}} \Delta T = 0, \tag{10.416}$$

$$\left[s^0 - \frac{1}{\rho^0}\left(\frac{\partial P}{\partial T}\right)_\rho^0\right] \frac{\partial \Delta\rho}{\partial t} + \frac{\rho^0 \tilde{c}_\rho}{T^0} \frac{\partial \Delta T}{\partial t} + \rho^0 s^0 \nabla_{\mathbf{r}} \cdot \mathbf{v}_n = 0, \tag{10.417}$$

and

$$\frac{\partial \mathbf{v}_s}{\partial t} + \frac{1}{(\rho^0)^2 \kappa_T} \nabla \Delta\rho - \left[s^0 - \frac{1}{\rho}\left(\frac{\partial P}{\partial T}\right)_\rho^0\right] \nabla \Delta T = 0. \tag{10.418}$$

In Eqs. (10.415)–(10.418) we have used the fact that the isothermal compressibility is defined as $\kappa_T = (1/\rho)(\partial\rho/\partial P)_T$ and the specific heat is defined $\tilde{c}_\rho = T(\partial s/\partial T)_\rho$. Also $s = -(\partial\tilde{\mu}/\partial T)_P$ and $1/\rho = (\partial\tilde{\mu}/\partial P)_T$, so that $(\partial\tilde{\mu}/\partial T)_\rho = (\partial\tilde{\mu}/\partial T)_P + (\partial\tilde{\mu}/\partial P)_T (\partial P/\partial T)_\rho$ and $(\partial\tilde{\mu}/\partial\rho)_T = (\partial\tilde{\mu}/\partial P)_T (\partial P/\partial\rho)_T = 1/(\rho^2\kappa_T)$.

Equations (10.411)–(10.414) enable us to obtain the dispersion relations for the various types of sound that can exist in an ideal superfluid system. Let us now Laplace transform the time-dependent part of the above equations and Fourier transform the space-dependent part. It we note that all contributions from the normal and superfluid velocities are longitudinal, we can write the Fourier–Laplace transform of Eqs. (10.411)–(10.414) in the following matrix form:

$$\begin{pmatrix} z & 0 & -ik\rho_n^0 & -ik\rho_s^0 \\ z\left[s^0 - \frac{1}{\rho^0}\left(\frac{\partial P}{\partial T}\right)_\rho^0\right] & z\frac{\rho^0\tilde{c}_\rho}{T^0} & -ik\rho^0 s^0 & 0 \\ -\frac{ik}{\rho^0\kappa_T} & -ik\left(\frac{\partial P}{\partial T}\right)_\rho^0 & \rho_n^0 z & \rho_s^0 z \\ -i\frac{k}{(\rho^0)^2\kappa_T} & ik\left[s^0 - \frac{1}{\rho^0}\left(\frac{\partial P}{\partial T}\right)_\rho^0\right] & 0 & z \end{pmatrix} \begin{pmatrix} \tilde{\rho}(\mathbf{k}, z) \\ \tilde{v}_n(\mathbf{k}, z) \\ \tilde{T}(\mathbf{k}, z) \\ \tilde{v}_s(\mathbf{k}, z) \end{pmatrix}$$

$$= \begin{pmatrix} 1 & 0 & 0 & 0 \\ \left[s^0 - \frac{1}{\rho^0}\left(\frac{\partial P}{\partial T}\right)_\rho^0\right] & 0 & \frac{\rho^0\tilde{c}_\rho}{T} & 0 \\ 0 & \rho_n^0 & 0 & \rho_s^0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \Delta\rho(\mathbf{k}, 0) \\ v_n(\mathbf{k}, 0) \\ \Delta T(\mathbf{k}, 0) \\ v_s(\mathbf{k}, 0) \end{pmatrix}. \tag{10.419}$$

The determinant of the 4×4 matrix,

$$\bar{\mathbf{S}}(\mathbf{k}, z) = \begin{pmatrix} z & 0 & -ik\rho_n^0 & -ik\rho_s^0 \\ z\left[s^0 - \frac{1}{\rho^0}\left(\frac{\partial P}{\partial T}\right)_\rho^0\right] & z\frac{\rho^0 \tilde{c}_\rho}{T^0} & -ik\rho^0 s^0 & 0 \\ -\frac{ik}{\rho^0 \kappa_T} & -ik\left(\frac{\partial P}{\partial T}\right)_\rho^0 & \rho_n^0 z & \rho_n^0 z \\ -\frac{k}{(\rho^0)^2 \kappa_T} & ik\left[s^0 - \frac{1}{\rho^0}\left(\frac{\partial P}{\partial T}\right)_\rho^0\right] & 0 & z \end{pmatrix}, \tag{10.420}$$

gives the dispersion relation for sound modes in the fluid. The sound frequencies occur at values of z which satisfy the equation

$$\mathrm{Det}[\bar{\mathbf{S}}(\mathbf{k}, z)] = -\frac{\rho^0 \rho_n^0 \tilde{c}_\rho}{T^0}\left\{z^4 + \left(\frac{1}{\rho^0 \kappa_T} + \frac{T^0 (s^0)^2 \rho_s^0}{\tilde{c}_\rho \rho_n^0} + \frac{T^0}{\tilde{c}_\rho (\rho^0)^2}\left[\left(\frac{\partial P}{\partial T}\right)_\rho^0\right]^2\right) k^2 z^2 + \frac{T^0 \rho_s^0 (s^0)^2}{\rho^0 \rho_n^0 \tilde{c}_\rho \kappa_T} k^4\right\} = 0. \tag{10.421}$$

We can simplify the dispersion relation somewhat because the thermal expansivity, α_P, for He(II) is very small, at least for temperatures well below the transition temperature. This can also be seen in Fig. 3.20. For low enough temperature, the slope, $(\partial P/\partial T)_\rho$ is approximately zero. Thus, to good approximation we can set

$$\alpha_P = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P = \kappa_T \left(\frac{\partial P}{\partial T}\right)_\rho \approx 0. \tag{10.422}$$

The dispersion relation then simplifies to

$$\begin{aligned} \mathrm{Det}[\bar{\mathbf{S}}(\mathbf{k}, z)] &\approx -\frac{\rho^0 \rho_n^0 \tilde{c}_\rho}{T^0}\left\{z^4 + \left(\frac{1}{\rho^0 \kappa_T} + \frac{T^0 (s^0)^2 \rho_s^0}{\tilde{c}_\rho \rho_n^0}\right) k^2 z^2 + \frac{T^0 \rho_s^0 (s^0)^2}{\rho^0 \rho_n^0 \tilde{c}_\rho \kappa_T} k^4\right\} \\ &= -\frac{\rho^0 \rho_n^0 \tilde{c}_\rho}{T^0}\left(z^2 + \frac{1}{\rho^0 \kappa_T} k^2\right)\left(z^2 + \frac{T^0 \rho_s^0 (s^0)^2}{\rho_n^0 \tilde{c}_\rho} k^2\right) = 0. \end{aligned} \tag{10.423}$$

We see from Eq. (10.423) that there are two different types of propagating sound modes in He(II). They are called *first sound* and *second sound*, respectively.

First sound has a dispersion relation, $z = \pm i c_1 k$, and propagates with speed

$$c_1 = \sqrt{1/\rho^0 \kappa_T}. \tag{10.424}$$

First sound consists of density waves in He(II), similar to sound modes in classical fluids, with one difference. The speed of first sound depends on the isothermal compressibility, while the speed of ordinary sound in classical fluids depends on the adiabatic compressibility. Note that Eq. (10.424) assumes that $(\partial P/\partial T)_\rho \approx 0$.

Second sound has a dispersion relation $z - \pm ic_2 k$ and propagates with a speed

$$c_2 = \sqrt{\frac{\rho_s^0 (s^0)^2 T^0}{\tilde{c}_\rho \rho_n^0}}. \tag{10.425}$$

Second sound consists of temperature waves which can propagate across the fluid. It was first measured by Peshkov [43], who used an oscillating heat source to set up standing waves in a tube. A plot of the speed of second sound as a function of temperature is given in Fig. 10.15. We see that the velocity first peaks at 20.36 m/sec at $T = 1.65K$ and decreases slightly as we lower the temperature, but then increases again and reaches a limiting value of about 150 m/sec at $T = 0$ K.

Measurements of the speed of second sound enable us to obtain a value of the ratio ρ_n^0/ρ^0. If we remember that $\rho = \rho_n^0 + \rho_s^0$, then Eq. (10.425) takes the form

$$\frac{\rho_n^0}{\rho^0} = \frac{T^0 (s^0)^2}{\tilde{c}_\rho c_2^2 + T^0 (s^0)^2}. \tag{10.426}$$

From Eq. (10.426), estimates of the hydrodynamic density of the normal fluid can be obtained. Another form for sound occurs when He(II) flows through a porous material. It is called *fourth sound.* Derivation of the dispersion relation of fourth sound is left as a homework problem.

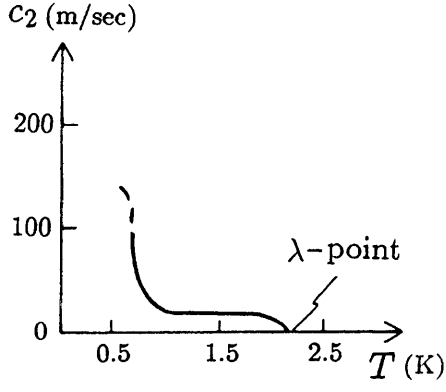


Fig. 10.15. Speed of second sound. (Based on Ref. 44.)

In Eq. (10.414) we have postulated the existence of an additional hydrodynamic equation for He(II). Its origin is not the microscopic conservation laws, but broken gauge symmetry in the fluid. We shall consider the hydrodynamics of symmetry broken systems in the next section and obtain a deeper understanding of the origin of Eq. (10.414).

▶ S10.I. General Definition of Hydrodynamic Modes [45]

The most commonly observed quantities in physical systems are the correlation functions or their Fourier–Laplace transforms, the spectral density functions. The behavior of these quantities gives essential information about the dominant underlying dynamics of a system. In many-body systems, as we shall show below, when correlation functions show hydrodynamic behavior, it can orginate from two different sources, either conserved quantities or broken symmetries.

Let us consider the microscopic densities, $\hat{a}_i(\mathbf{r})$, which may represent the number density, momentum density, spin density, or any other density we might be interested in. The equilibrium dynamic correlation function may be written

$$C_{ij}(\mathbf{r}_1, t_1; \mathbf{r}_2, t_2) = \mathrm{Tr}[e^{-\beta\hat{H}}\hat{a}_i(\mathbf{r}_1, t_1)\hat{a}_j(\mathbf{r}_2, t_2)]. \tag{10.427}$$

According to Eq. (6.53), the microscopic density evolves in time as $\hat{a}_i(\mathbf{r}_1, t_1) = e^{i\hat{L}t_1}\hat{a}_i(\mathbf{r}_1)$, where $\hat{L}$ is the Liouville operator. Because we are looking at an equilibrium correlation function, the correlation function depends only on the time difference, $t_1 - t_2$. This is easy to see. The trace of a product of operators is invariant under cyclic permutation of the operators. Also, the Liouville operator, $\hat{L}$, commutes with the Hamiltonian, $\hat{H}$. Therefore the dynamic correlation function can be written in the form

$$C_{ij}(\mathbf{r}_1, \mathbf{r}_2 : t_1 - t_2) = \mathrm{Tr}[e^{-\beta\hat{H}}\hat{a}_i(\mathbf{r}_1)e^{-i\hat{L}(t_1-t_2)}\,\hat{a}_j(\mathbf{r}_2)]. \tag{10.428}$$

Let us now introduce the Fourier–Laplace transform of the correlation function,

$$S_{ij}(\mathbf{k}_1, \mathbf{k}_2; z) = \int d\mathbf{r}_1 e^{+i\mathbf{k}_1\cdot\mathbf{r}_1} \int d\mathbf{r}_2 e^{+i\mathbf{k}_2\cdot\mathbf{r}_2} \int_0^\infty d(t_1 - t_2) e^{-z(t_1-t_2)} C_{ij}(\mathbf{r}_1, \mathbf{r}_2; t_1 - t_2). \tag{10.429}$$

In the absence of any spatially varying external fields, the correlation function can only depend on the relative displacement, $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$. Therefore, the spectral density function can be written

$$S_{ij}(\mathbf{k}_1, \mathbf{k}_2; z) = V\delta(\mathbf{k}_1 + \mathbf{k}_2)S_{ij}(\mathbf{k}_2, z), \tag{10.430}$$

where

$$S_{ij}(\mathbf{k},z)=\mathrm{Tr}\left[e^{-\beta\hat{H}}\hat{a}_i(-\mathbf{k})\frac{1}{z+i\hat{L}}\hat{a}_j(\mathbf{k})\right], \tag{10.431}$$

(cf. Section S10.F). In the discussion below, it will be useful to think of the spectral density matrix, $S_{ij}(\mathbf{k},z)$, as a matrix elements with respect to the states, $|a_i(\mathbf{k})\rangle$. Then we can write it

$$S_{ij}(\mathbf{k},z)=\left\langle a_i(\mathbf{k})\left|\frac{1}{z+i\hat{L}}\right|a_j(\mathbf{k})\right\rangle\equiv\mathrm{Tr}\left[e^{-\beta\hat{H}}\hat{a}_i^*(\mathbf{k})\frac{1}{z+i\hat{L}}\hat{a}_j(\mathbf{k})\right], \tag{10.432}$$

where $a_i(-\mathbf{k})=a_i^*(\mathbf{k})$. We shall limit ourselves to small amplitude fluctuations (not too close to a phase transition) so that coupling between modes of different wavelength can be neglected. Also, we shall choose our modes so they are statistically independent (cf. Section 7.C). Then

$$\langle a_i(\mathbf{k})|a_j(\mathbf{k}')\rangle=\delta_{i,j}\delta_{\mathbf{k},\mathbf{k}'}\langle a_i(\mathbf{k})|a_i(\mathbf{k})\rangle. \tag{10.433}$$

As we saw in Section 10.C, the dynamics is determined by the spectrum of the spectral density matrix in the complex z plane. In order to determine the behavior of this spectrum, it is useful to introduce projection operators.

▶ S10.I.1. Projection Operators [45]

Projection operators allow us to decompose the system into one space which contains the hydrodynamic densities and another space orthogonal to it. They also allow us to generalize the concept of a hydrodynamic mode to include modes which arise not only from conserved quantities, but from broken symmetries as well. Projection operators provide a very powerful means of analyzing systems. They were first used in statistical mechanics by Zwanzig [46], although the idea of projecting onto the macroscopic modes of a system was first used by Mori [47]. Projection operators have also played an important role in the microscopic theory of irreversible processes developed by Prigogine et al. [48]. They can be used to study stochastic processes [49]. In this section we shall only be interested in projectors onto the macroscopic modes of the system. Our discussion follows closely the presentation of Forster [45].

We introduce the projection operator;

$$\hat{P}_k=\sum_i|a_i(\mathbf{k})\rangle\frac{1}{\langle a_i(\mathbf{k})|a_i(\mathbf{k})\rangle}\langle a_i(\mathbf{k})|, \tag{10.434}$$

and an orthogonal projection operator, $\hat{Q}_\mathbf{k}$, such that $\hat{P}_\mathbf{k}+\hat{Q}_\mathbf{k}=\hat{I}$, $\hat{P}_\mathbf{k}$ and $\hat{Q}_\mathbf{k}$ are orthogonal projection operators because they satisfy the conditions

$\hat{P}_{\mathbf{k}}^2 = \hat{P}_{\mathbf{k}}, \hat{Q}_{\mathbf{k}}^2 = \hat{Q}_{\mathbf{k}}$, and $\hat{P}_{\mathbf{k}}\hat{Q}_{\mathbf{k}} = \hat{Q}_{\mathbf{k}}\hat{P}_{\mathbf{k}} = 0$. $\hat{Q}_{\mathbf{k}}$ removes all modes, $\{\hat{a}_i(\mathbf{k}\}$, from any object that it acts on. The orthogonal space defined by $\hat{Q}_{\mathbf{k}}$ acts as a bath or reservoir that influences the behavior of the collection of modes, $\{\hat{a}_i(\mathbf{k})\}$.

We will now use the projection operators to rewrite the spectral density matrix in a more revealing form. Let us first note that

$$\frac{1}{z+i\hat{L}} = \frac{1}{z+i\hat{L}\hat{P}_{\mathbf{k}}+i\hat{L}\hat{Q}_{\mathbf{k}}} = \frac{1}{z+i\hat{L}\hat{Q}_{\mathbf{k}}} - \frac{1}{z+i\hat{L}\hat{Q}_{\mathbf{k}}} i\hat{L}\hat{P}_{\mathbf{k}} \frac{1}{z+i\hat{L}}$$

and

$$\frac{1}{z+i\hat{L}\hat{Q}_{\mathbf{k}}} = \frac{1}{z}\left[1 - \frac{i\hat{L}\hat{Q}_{\mathbf{k}}}{z+i\hat{L}\hat{Q}_{\mathbf{k}}}\right].$$

Then

$$\frac{1}{z+i\hat{L}} = \frac{1}{z+i\hat{L}\hat{Q}_{\mathbf{k}}} - \frac{1}{z} i\hat{L}\hat{P}_{\mathbf{k}} \frac{1}{z+i\hat{L}} + \frac{1}{z} i\hat{L}Q_{\mathbf{k}} \frac{1}{Z+i\hat{L}\hat{Q}_{\mathbf{k}}} i\hat{L}\hat{P}_{\mathbf{k}} \frac{1}{z+i\hat{L}}. \tag{10.435}$$

The spectral density matrix can then be written

$$\begin{aligned} S_{ij}(\mathbf{k},z) &= \left\langle a_i(\mathbf{k}) \left| \frac{1}{z+i\hat{L}} \right| a_j(\mathbf{k}) \right\rangle \\ &= \frac{1}{z}\langle a_i(\mathbf{k})\rangle - \frac{1}{z}\sum \langle a_i(\mathbf{k})|i\hat{L}|a_l(\mathbf{k})\rangle \\ &\quad \times \frac{1}{\langle a_l(\mathbf{k})|a_l(\mathbf{k})\rangle} \left\langle a_l(\mathbf{k}) \left| \frac{1}{z+i\hat{L}} \right| a_j(\mathbf{k}) \right\rangle \\ &\quad + \frac{1}{z}\sum_l \left\langle a_i(\mathbf{k}) \left| i\hat{L}\hat{Q}_{\mathbf{k}} \frac{1}{z+i\hat{L}\hat{Q}_{\mathbf{k}}} i\hat{L} \right| a_l(\mathbf{k}) \right\rangle \\ &\quad \times \frac{1}{\langle a_l(\mathbf{k})|a_l(\mathbf{k})\rangle} \left\langle a_l(\mathbf{k}) \left| \frac{1}{z+i\hat{L}} \right| a_j(\mathbf{k}) \right\rangle. \end{aligned} \tag{10.436}$$

Equation (S10.I.10) can be simplified. Let us remember that $\partial\hat{a}_i(\mathbf{k})/\partial t = i\hat{L}\hat{a}_i(\mathbf{k})$ so $\partial|a_i(\mathbf{k})\rangle/\partial t = i\hat{L}|a_i(\mathbf{k})\rangle$. We can denote $\partial|a_i(\mathbf{k})\rangle/\partial t = |\dot{a}_i(\mathbf{k})\rangle = i\hat{L}|\hat{a}_i(\mathbf{k})\rangle$. Now define a frequency

$$\omega_{ij} \equiv \langle a_i(\mathbf{k})|\hat{L}|a_j(\mathbf{k})\rangle. \tag{10.437}$$

Then

$$\langle a_i(\mathbf{k})|\dot{a}_j(\mathbf{k})\rangle = -\langle \dot{a}_i(\mathbf{k})|a_j(\mathbf{k})\rangle = -i\omega_{ij}. \tag{10.438}$$

We also introduce the so-called memory function, $M_{ij}(\mathbf{k}, z)$, which is defined as

$$\begin{aligned} M_{ij}(\mathbf{k}, z) &= \langle a_i(\mathbf{k}) | i\hat{L}\hat{Q}_{\mathbf{k}} \frac{1}{z + i\hat{L}\hat{Q}_{\mathbf{k}}} i\hat{L} | a_j(\mathbf{k}) \rangle \\ &= -\langle \dot{a}_i(\mathbf{k}) | \hat{Q}_{\mathbf{k}} \frac{1}{z + i\hat{L}\hat{Q}_{\mathbf{k}}} | \dot{a}_j(\mathbf{k}) \rangle. \end{aligned} \tag{10.439}$$

Then the equation for the spectral density matrix takes the form

$$z\bar{\mathbf{I}} \cdot \bar{\mathbf{S}}(\mathbf{k}, z) + i\bar{\boldsymbol{\omega}}(\mathbf{k}) \cdot \bar{\mathbf{G}}^{-1}(\mathbf{k}) \cdot \bar{\mathbf{S}}(\mathbf{k}, z) + \bar{\mathbf{M}}(\mathbf{k}, z) \cdot \bar{\mathbf{G}}^{-1}(\mathbf{k}) \cdot \bar{\mathbf{S}}(\mathbf{k}, z) = \bar{\mathbf{G}}(\mathbf{k}), \tag{10.440}$$

where $G_{ij}(\mathbf{k}) = \langle a_i(\mathbf{k}) | a_j(\mathbf{k}) \rangle \delta_{ij}$. For the case of two modes, Eq. (10.440) takes the form

$$\begin{aligned} &\left[\begin{pmatrix} z & 0 \\ 0 & z \end{pmatrix} + i \begin{pmatrix} \omega_{11} & \omega_{12} \\ \omega_{21} & \omega_{22} \end{pmatrix} \begin{pmatrix} G_{11}^{-1} & 0 \\ 0 & G_{22}^{-1} \end{pmatrix} \right. \\ &\quad \left. + \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \begin{pmatrix} G_{11}^{-1} & 0 \\ 0 & G_{22}^{-1} \end{pmatrix} \right] \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} = \begin{pmatrix} G_{11} & 0 \\ 0 & G_{22} \end{pmatrix}. \end{aligned} \tag{10.441}$$

Let us now look more carefully at the structure of this equation. We first consider the case of conserved densities and then consider the case of broken symmetries.

▶ S10.I.2. Conserved Quantities

For simplicity, let us consider a system with two hydrodynamic modes, whose microscopic operators are given by $\hat{a}_1(\mathbf{r})$ and $\hat{a}_2(\mathbf{r})$. We consider the case when $\langle \dot{a}_1 | a_2 \rangle = \langle a_1 | \dot{a}_2 \rangle = 0$ so there are no propagating (sound) modes. From the linearized hydrodynamic equations, the average values of these quantities evolve according to the phenomenological equations

$$\frac{\partial \langle a_1(\mathbf{r}, t) \rangle}{\partial t} = \eta_{11} \nabla^2 \langle a_1(\mathbf{r}, t) \rangle + \eta_{12} \nabla^2 \langle a_2(\mathbf{r}, t) \rangle \tag{10.442}$$

and

$$\frac{\partial \langle a_2(\mathbf{r}, t) \rangle}{\partial t} = \eta_{21} \nabla^2 \langle a_1(\mathbf{r}, t) \rangle + \eta_{22} \nabla^2 \langle a_2(\mathbf{r}, t) \rangle, \tag{10.443}$$

where η_{ij} are transport coefficients. From these equations we can write the equations of motion for the correlation functions (cf. Ex. 10.4)

$$\frac{\partial}{\partial t}\begin{pmatrix} C_{11}(\mathbf{r},t) & C_{12}(\mathbf{r},t) \\ C_{21}(\mathbf{r},t) & C_{22}(\mathbf{r},t) \end{pmatrix} = \begin{pmatrix} \eta_{11} & \eta_{12} \\ \eta_{21} & \eta_{22} \end{pmatrix} \nabla_{\mathbf{r}}^2 \begin{pmatrix} C_{11}(\mathbf{r},t) & C_{12}(\mathbf{r},t) \\ C_{21}(\mathbf{r},t) & C_{22}(\mathbf{r},t) \end{pmatrix}, \tag{10.444}$$

where $C_{ij}(\mathbf{r}_1 - \mathbf{r}_2, t_1 - t_2) = \mathrm{Tr}[e^{-\beta\hat{H}}\hat{a}_1(\mathbf{r}_1,t)\hat{a}_2(\mathbf{r}_2,t_2)]$. If we take the Fourier–Laplace transform of Eq. (10.444), the equation for the spectral density matrix takes the form

$$\left[\begin{pmatrix} z & 0 \\ 0 & z \end{pmatrix} - k^2 \begin{pmatrix} \eta_{11} & \eta_{12} \\ \eta_{21} & \eta_{22} \end{pmatrix}\right] \begin{pmatrix} S_{11}(\mathbf{k},z) & S_{12}(\mathbf{k},z) \\ S_{21}(\mathbf{k},z) & S_{22}(\mathbf{k},z) \end{pmatrix} = \begin{pmatrix} G_{11}(\mathbf{k}) & 0 \\ 0 & G_{22}(\mathbf{k}) \end{pmatrix}. \tag{10.445}$$

Comparison with Eq. (10.441) yields the following identification:

$$\eta_{ij} = \lim_{z\to 0}\lim_{k\to 0}\left\{\frac{1}{k^2} M_{ij}(\mathbf{k},z) G_{jj}^{-1}(\mathbf{k})\right\}. \tag{10.446}$$

Thus the transport coefficients are given by a specific limit of the memory function.

It is useful to examine the memory function, $M_{ij}(\mathbf{k},z)$, a little more closely. Following a derivation similar to that used to obtain Eq. (10.445), we can write

$$\frac{1}{z+i\hat{L}} = \frac{1}{z+i\hat{Q}_{\mathbf{k}}\hat{L}} - \frac{1}{z}\hat{P}_{\mathbf{k}} i\hat{L} \frac{1}{z+i\hat{L}} + \frac{1}{z}\frac{1}{z+i\hat{Q}_{\mathbf{k}}\hat{L}} \hat{Q}_{\mathbf{k}} i\hat{L}\hat{P}_{\mathbf{k}} i\hat{L} \frac{1}{z+i\hat{L}}. \tag{10.447}$$

We then can write

$$\begin{aligned} \left\langle \dot{a}_i \middle| \frac{1}{z+i\hat{L}} \middle| \dot{a}_j \right\rangle &= \left\langle \dot{a}_i \middle| \frac{1}{z+i\hat{Q}_{\mathbf{k}}\hat{L}} \middle| \dot{a}_j \right\rangle \\ &\quad - \frac{1}{z}\sum_l \left\langle \dot{a}_i \middle| \frac{1}{z+i\hat{Q}_{\mathbf{k}}\hat{L}} \middle| \dot{a}_l \right\rangle \frac{1}{\langle a_l | a_l \rangle} \left\langle \dot{a}_l \middle| \frac{1}{z+i\hat{L}} \middle| \dot{a}_j \right\rangle, \end{aligned} \tag{10.448}$$

where we have used the fact that $\langle \dot{a}_l | \hat{P}_{\mathbf{k}} = 0$. We can rewrite Eq. (10.448) in matrix form to obtain

$$\begin{aligned} &\begin{pmatrix} \langle \dot{a}_1 | \frac{1}{z+i\hat{L}} | \dot{a}_1 \rangle & \langle \dot{a}_1 | \frac{1}{z+i\hat{L}} | \dot{a}_2 \rangle \\ \langle \dot{a}_2 | \frac{1}{z+i\hat{L}} | \dot{a}_1 \rangle & \langle \dot{a}_2 | \frac{1}{z+i\hat{L}} | \dot{a}_2 \rangle \end{pmatrix} \\ &\quad = \left[\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \frac{1}{z}\begin{pmatrix} M_{11}G_{11}^{-1} & M_{12}G_{22}^{-1} \\ M_{21}G_{11}^{-1} & M_{22}G_{22}^{-1} \end{pmatrix}\right]^{-1} \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix}. \end{aligned} \tag{10.449}$$

In Section 6.D.3 we found that if the quantity, $\hat{a}_i(\mathbf{r},t)$ is conserved microscopically, then it satisfies a microscopic balance equation of the form

$$\frac{\partial \hat{a}_i}{\partial t} = -\nabla_{\mathbf{r}} \cdot \hat{\mathbf{J}}_{a_i}(\mathbf{r},t). \tag{10.450}$$

Therefore, $|\hat{a}_i(\mathbf{k})\rangle = i|\mathbf{k}\cdot\mathbf{J}_{a_i}(\mathbf{k})\rangle$ and M_{ij} is of order k^2. Therefore, to lowest order in k^2, we can write $M_{ij} \approx \langle \dot{a}_i|1/(z+i\hat{L})|\dot{a}_j\rangle$. The transport coefficient, η_{ij}, takes the form

$$\begin{aligned}\eta_{ij} &= -\lim_{z\to 0}\lim_{k\to 0}\left\{\left\langle \hat{\mathbf{k}}\cdot\mathbf{J}_i \left| \frac{1}{z+i\hat{L}} \right| \hat{\mathbf{k}}\cdot\mathbf{J}_j \right\rangle G_{jj}^{-1}(\mathbf{k})\right\} \\ &= -\lim_{z\to 0}\lim_{k\to 0}\int_0^\infty dt\left\{\langle \hat{\mathbf{k}}\cdot\mathbf{J}_i|e^{-(z+i\hat{L})t}|\hat{\mathbf{k}}\cdot\mathbf{J}_j\rangle G_{jj}^{-1}(\mathbf{k})\right\},\end{aligned} \tag{10.451}$$

where $\hat{\mathbf{k}}$ is the unit vector in the direction of $\mathbf{k}$. In Eq. (10.451), we have written the transport coefficient, η_{ij}, in terms of a current correlation function. This is a form commonly seen in the literature.

▶ S10.I.3. Hydrodynamic Modes Due to Broken Symmetry [45]

In this section we wish to find the origin of hydrodynamic modes which arise due to broken symmetries. However, it is useful first to consider how the spectral density function for a quantity which is not conserved on the microscopic level behaves. Let us consider a microscopic quantity, $\hat{B}$, which has a density, $\hat{b}(\mathbf{k},t)$, which is not conserved during collisions and does not commute with the Hamiltonian. One such quantity might be the orientation of the molecules in the system. It will satisfy a microscopic balance equation of the form

$$\frac{\partial \hat{b}(\mathbf{k},t)}{\partial t} + i\mathbf{k}\cdot\hat{\mathbf{J}}_b(\mathbf{k},t) = \sigma_b(\mathbf{k},t), \tag{10.452}$$

where $\hat{\sigma}_b(\mathbf{k},t)$ is an operator which acts as a source of the quantity $\hat{B}$ and satisfies the condition $\lim_{k\to 0}\sigma_b(\mathbf{k},t) = \sigma_b(t) = \int d\mathbf{r}\sigma_b(\mathbf{r},t) \neq 0$, Thus, $(d/dt)\int d\mathbf{r}\hat{b}(\mathbf{r},t) = \sigma_b(t) \neq 0$. For simplicity, let us assume $\langle \dot{b}(\mathbf{k})|b(\mathbf{k})\rangle = 0$. Then

$$\lim_{k\to 0}\langle \dot{b}(\mathbf{k})|\hat{Q}_{\mathbf{k}}\frac{1}{z+i\hat{L}\hat{Q}_{\mathbf{k}}}\hat{Q}_{\mathbf{k}}|\dot{b}(\mathbf{k})\rangle = \langle \sigma_b|\hat{Q}_{\mathbf{o}}\frac{1}{z+i\hat{L}\hat{Q}_{\mathbf{o}}}\hat{Q}_{\mathbf{o}}|\sigma_b\rangle$$

and the memory function does not go to zero as $\mathbf{k}\to\mathbf{0}$. Thus, to lowest order in $\mathbf{k}$ the spectral density has a pole independent of $\mathbf{k}$ and we can write

$$\lim_{k\to 0} S_{bb}(\mathbf{k},z) = \frac{G_{bb}(0)}{z+\tau_b^{-1}}, \tag{10.453}$$

where the relaxation time, τ_b is independent of k and can be expressed in terms of the memory function. This is definitely not hydrodynamic behavior.

Let us now consider what happens when a symmetry is broken. Let $\hat{Q}$ be the generator of a symmetry transformation. It is a constant of the motion and therefore commutes with the Hamiltonian so $[\hat{Q}, \hat{H}] = 0$. The density, $\hat{q}(\mathbf{r})$, of $\hat{Q}$ will satisfy the microscopic balance equation

$$\frac{\partial \hat{q}}{\partial t} + \nabla_r \cdot \mathbf{J}_q = 0. \tag{10.454}$$

Let us now consider two other densities, $\hat{a}$ and $\hat{b}$, such that $(1/i\hbar)[\hat{Q}, \hat{a}(\mathbf{r})] = \hat{b}(\mathbf{r})$. The densities, $\hat{a}$ and $\hat{b}$, may or may not be conserved quantities. If we take the equilibrium expectation value of the commutator, $[\hat{Q}, \hat{a}(\mathbf{r})]$, we find

$$\begin{aligned} \frac{1}{i\hbar}\mathrm{Tr}\left[\hat{\rho}_{eq}[\hat{Q}, \hat{a}(\mathbf{r}')]\right] &= \frac{1}{i\hbar}\int d\mathbf{r}\mathrm{Tr}\left[\hat{\rho}_{eq}[\hat{q}(\mathbf{r}), \hat{a}(\mathbf{r}')]\right] \\ &= \frac{1}{i\hbar}\int d\mathbf{r}\mathrm{Tr}\left[\hat{a}(\mathbf{r}')[\hat{\rho}_{eq}, \hat{q}(\mathbf{r})]\right] = \langle \hat{b}(\mathbf{r}')\rangle, \end{aligned} \tag{10.455}$$

where $\hat{\rho}_{eq}$ is the equilibrium state of the system. Notice that $\langle \hat{b}(\mathbf{r}')\rangle \neq 0$ only if $[\hat{\rho}, \hat{q}(\mathbf{r})] \neq 0$. Thus even though $\hat{Q}$ commutes with the Hamiltonian, it may not commute with the state of the system. When this happens, the symmetry generated by $\hat{Q}$ has been broken. The quantity, $\langle \hat{b}(\mathbf{r})\rangle$ is the order parameter for this broken symmetry. For a translationally invariant system we have $\langle \hat{b}(\mathbf{r}) = b_0$, where b_0 is a constant.

As we shall now show, the fact that $\langle \hat{b}(\mathbf{r})\rangle \neq 0$ means that there will be hydrodynamic waves in the density, $\langle \hat{a}(\mathbf{r}, t)\rangle$. These waves are called *Goldstone bosons*. To see this, let us rewrite Eq. (10.455) as

$$\frac{1}{i\hbar}\int d\mathbf{r}\mathrm{Tr}\left[\hat{\rho}_{eq}[\hat{q}(\mathbf{r}, t), \hat{a}(\mathbf{r}')]\right] = b_0. \tag{10.456}$$

Then from microscopic linear response theory [cf. Eq. (10.239)], we have

$$\int d\mathbf{r} K''_{qa}(\mathbf{r} - \mathbf{r}', t) = K''_{qa}(\mathbf{k} = 0, t) = \frac{i}{2} b_0. \tag{10.457}$$

But since $\hat{Q}$ is a conserved quantity, $K''_{qa}(\mathbf{r} - \mathbf{r}, t)$ must be independent of time. The Fourier transform of Eq. (10.457) then yields

$$\chi''_{qa}(\mathbf{k} = 0, \omega) = i\pi b_0 \delta(\omega). \tag{10.458}$$

Now let us assume that the limit in Eq. (10.458) is uniform. {*A function, $f(\mathbf{k})$, is uniform at* $\mathbf{k} = 0$ *if* $f(\mathbf{r})$ *falls off rapidly enough so that* $\int d\mathbf{r} f(\mathbf{r}) < \infty$. *Then,*

$\lim_{k\to 0} f(\mathbf{k}) = f(\mathbf{k}=0) = \int d\mathbf{r} f(\mathbf{r}).\}$ The limit in Eq. (10.458) is uniform: $\lim_{k\to 0}\chi''_{qa}(\mathbf{k},\omega) = \chi''_{qa}(\mathbf{k}=0,\omega)$ if $\chi''_{qa}(\mathbf{r}-\mathbf{r}',\omega) = (i/\hbar)\langle[\hat{q}(\mathbf{r}),\hat{a}(\mathbf{r}')]\rangle$ vanishes rapidly enough as $\mathbf{r}-\mathbf{r}' \to \infty$. This will be true if $\hat{q}(\mathbf{r})$ and $\hat{a}(\mathbf{r})$ are local densities—that is, depend on field operators in the neighborhood of $\mathbf{r}$ and $\mathbf{r}'$. This will be true for systems with short-range interactions. The fact that $\chi''_{qa}(\mathbf{r},\omega)$ decays rapidly need not mean that $\chi_{qa}(\mathbf{r},\omega)$ decays rapidly.

If $\hat{q}(\mathbf{r})$ and $\hat{a}(\mathbf{r})$ are local operators, we can write

$$\lim_{k\to 0}\chi''_{qa}(\mathbf{k},\omega) = i\pi b_0\delta(\omega). \tag{10.459}$$

Thus, there is a mode whose energy goes to zero as $\mathbf{k}\to 0$. Let us assume that this is true. Then

$$\chi''_{qa}(\mathbf{k},\omega) = i\pi b_0\delta(\omega-\omega(\mathbf{k})), \tag{10.460}$$

where $\lim_{k\to 0}\omega(\mathbf{k}) = 0$. The mode with frequency, $\omega(\mathbf{r})$, is the Goldstone boson.

The spectral density function for the modes, $\hat{a}(\mathbf{k})$, can be written

$$S_{aa}(\mathbf{k},z) = \frac{G_{aa}(\mathbf{k})}{z + M_{aa}(\mathbf{k},z)G_{aa}^{-1}(\mathbf{k})} \tag{10.461}$$

if we assume that $\langle\dot{a}(\mathbf{k})|a(\mathbf{k})\rangle = 0$. Since $\hat{a}(\mathbf{k})$ is not a conserved quantity, we will have

$$\lim_{k\to 0}\left\langle \dot{a}(\mathbf{k}) \left| \hat{Q}_{\mathbf{k}} \frac{1}{z + i\hat{L}\hat{Q}_{\mathbf{k}}} \right| \dot{a}(\mathbf{k}) \right\rangle = \sigma_a, \tag{10.462}$$

where σ_a is a constant. The only possibility of obtaining a pole which goes to zero as $\mathbf{k}\to 0$ lies in the quantity $G_{aa}(\mathbf{k})$. Thus, we must determine how $G_{aa}(\mathbf{k})$ depends on $\mathbf{k}$. We first use the Schwartz inequality to write

$$\langle a(\mathbf{k})|a(\mathbf{k})\rangle\langle\dot{q}(\mathbf{k})|\dot{q}(\mathbf{k})\rangle \geq |\langle a(\mathbf{k})|\dot{q}(\mathbf{k})\rangle|^2. \tag{10.463}$$

Let us next use Eq. (10.129) and Exercise 10.5 to write

$$G_{aa}(\mathbf{k}) = \langle a(\mathbf{k})|a(\mathbf{k})\rangle = \frac{1}{\beta}\chi_{aa}(\mathbf{k},\omega=0) = \frac{1}{\beta}\int\frac{d\omega}{\pi}\frac{\chi''_{aa}(\mathbf{k},\omega)}{\omega}. \tag{10.464}$$

Equations (10.463) and (10.464) yield the so-called Bogoliubov inequality,

$$\int\frac{d\omega}{\pi}\frac{\chi''_{aa}(\mathbf{k},\omega)}{\omega}\int\frac{d\omega}{\pi}\frac{\chi''_{\dot{q}\dot{q}}(\mathbf{k},\omega)}{\omega} \geq \left|\int\frac{d\omega}{\pi}\frac{\chi''_{a\dot{q}}(\mathbf{k},\omega)}{\omega}\right|^2. \tag{10.465}$$

Let us now note that since $\hat{\mathrm{q}}$ is a conserved quantity, $\dot{\mathrm{q}} = i\omega \mathrm{q}$ and $\dot{\mathrm{q}} = ik\hat{\mathbf{k}} \cdot \mathbf{J}_{\mathrm{q}}$. Thus,

$$\left| \int \frac{d\omega}{\pi} \frac{\chi''_{a\dot{\mathrm{q}}}(\mathbf{k}, \omega)}{\omega} \right|^2 = \left| \int \frac{d\omega}{\pi} \chi''_{a\mathrm{q}}(\mathbf{k}, \omega) \right|^2 = b_0^2 \tag{10.466}$$

(see Eq. (10.458)) and

$$\int \frac{d\omega}{\pi} \frac{\chi''_{\dot{\mathrm{q}}\dot{\mathrm{q}}}(\mathbf{k}, \omega)}{\omega} = k^2 \int \frac{d\omega}{\pi} \frac{\chi''_{\hat{\mathbf{k}}\cdot\mathbf{J}_{\mathrm{q}}\hat{\mathbf{k}}\cdot\mathbf{J}_{\mathrm{q}}}(\mathbf{k}, \omega)}{\omega}. \tag{10.467}$$

Thus, the Bogoliubov inequality yields

$$G_{aa}(\mathbf{k}) = \frac{b_0^2}{k^2 R_a}, \tag{10.468}$$

where

$$R_a \leq \beta \lim_{k \to 0} \int \frac{d\omega}{\pi} \frac{\chi''_{\hat{\mathbf{k}}\cdot\mathbf{J}_{\mathrm{q}}\hat{\mathbf{k}}\cdot\mathbf{J}_{\mathrm{q}}}(\mathbf{k}, \omega)}{\omega} \tag{10.469}$$

is called the *stiffness constant*. A broken symmetry can give rise to a k^{-2} dependence in $G_{aa}(\mathbf{k})$, and the spectral density function for mode $\hat{a}(\mathbf{k})$ takes the form

$$S_{aa}(\mathbf{k}, z) = \frac{G_{aa}(\mathbf{k})}{z + k^2 R_a \sigma_a b_0^{-2}}. \tag{10.470}$$

Thus, $\hat{a}(\mathbf{k})$ is a hydrodynamic mode even though it is not a conserved quantity.

As a consequence of this broken symmetry, the state is not described by the density matrix $\hat{\rho}_{eq} = e^{-\beta \hat{H}}$, where $[\hat{H}, \hat{\mathrm{Q}}] = 0$. Instead it is described by a new density matrix for which $[\hat{\rho}_{eq}, \hat{\mathrm{Q}}] \neq 0$. We have already seen this in several examples in Chapter 7. In fact, one way to determine if a system has undergone a phase transition is to include the order parameter in the density matrix in a physically meaningful way. For example, apply an external field that couples to the order parameter. Then find a temperature-dependent equation for the order parameter. Above the transition temperature, the stable solution is the one for which the order parameter is zero when the external field is set to zero. Below the transition temperature, the stable solution is one with a nonzero order parameter when the external field is set to zero.

■ **EXERCISE S10.10.** A spin system has Hamiltonian $\hat{H} = -\frac{1}{2}\sum_{\alpha \neq \beta} J(|\mathbf{r}_\alpha - \mathbf{r}_\beta|)\hat{\mathbf{S}}_\alpha \hat{\mathbf{S}}_\beta$, where α and β denote lattice sites, the coupling constant, $J(|\mathbf{r}_\alpha - \mathbf{r}_\beta|)$, depends only on the magnitude of the displacement, $\mathbf{r}_\alpha - \mathbf{r}_\beta$, between sites α and β, and $\hat{\mathbf{S}}_\alpha$ and $\hat{\mathbf{S}}_\alpha$ are the spin operators associated with sites α and β. The total spin, $\hat{\mathbf{S}}_{tot} = \sum_\alpha \hat{\mathbf{S}}_\alpha$,

commutes with the Hamiltonian so $[\hat{H}, \hat{\mathbf{S}}_{tot}] = 0$. Show that if $\langle \hat{S}_{z,tot} \rangle = M_0$ and $\langle \hat{S}_{x,tot} \rangle = \langle \hat{S}_{y,tot} \rangle = 0$, the rotational symmetry of the system about the z axis is preserved but about the x and y axes it is broken (rotational symmetry about axis i is preserved if $[\hat{\rho}_{eq}, \hat{S}_{i,tot}] = 0$).

Answer: First note that at a given site the spin operators satisfy commutation relation, $[\hat{S}_{i,\alpha}, \hat{S}_{j,\alpha}] = i\hbar\varepsilon_{ijk}\hat{S}_{k,\alpha}$, $\varepsilon_{xyz} = \varepsilon_{yzx} = \varepsilon_{zxy} = 1$, $\varepsilon_{xzy} = \varepsilon_{zyx} = \varepsilon_{yxz} = -1$, and $\varepsilon_{ijk} = 0$ otherwise. Spin operators belonging to different lattice sites commute. Note also that $[\hat{S}_{x,tot}, \hat{S}_{y,tot}] = i\hbar\hat{S}_{z,tot}$. Thus,

$$\begin{aligned} M_0 &= \mathrm{Tr}[\hat{\rho}_{eq}, \hat{S}_{z,tot}] = \mathrm{Tr}[\hat{\rho}_{eq}, [\hat{S}_{x,tot}, \hat{S}_{y,tot}]] \\ &= \frac{1}{i\hbar}\mathrm{Tr}[[\hat{\rho}_{eq}, \hat{S}_{x,tot}]\hat{S}_{y,tot}] = -\frac{1}{i\hbar}\mathrm{Tr}[[\hat{\rho}_{eq}, \hat{S}_{y,tot}]\hat{S}_{x,tot}]. \end{aligned} \tag{1}$$

Thus, if M_0 is nonzero, then $[\hat{\rho}_{eq}, \hat{S}_{x,tot}] \neq 0$ and $[\hat{\rho}_{eq}, \hat{S}_{y,tot}] \neq 0$. By a similar argument we can show that $[\hat{\rho}_{eq}, \hat{S}_{z,tot}] = 0$. Thus, the z-component of the total spin operator commutes with the state of the system and rotational symmetry of the state of the system about the z- axis is preserved. However, it is broken about the x and y axes. This means that the state of the system remains unchanged by rotating all spins about the z axis through the same angle. This will not be true if all spins are rotated about the x or y axis. (Note that we have neglected all the structure of the lattice that supports these spins.)

■ **EXERCISE S10.11.** At the λ-transition in He^4, gauge symmetry is broken. The generator of a gauge transformation is the number operator, $\hat{N} = \int d\mathbf{r}\hat{\psi}^\dagger(\mathbf{r})\hat{\psi}(\mathbf{r})$, where $\hat{\psi}^\dagger(\mathbf{r})$ and $\hat{\psi}(\mathbf{r})$ are boson field operators which create and destroy particles, respectively, at point $\mathbf{r}$ (cf. Appendix B). Show that if $[\hat{\rho}_{eq}, \hat{N}] \neq 0$ so that gauge symmetry of the system is broken (where $\hat{\rho}_{eq}$ is the equilibrium state of the system), then $\langle \hat{\psi}(\mathbf{r}) \rangle = \mathrm{Tr}[\hat{\rho}_{eq}\hat{\psi}(\mathbf{r})]$ is the order parameter.

Answer: First note that the commutation relations for boson field operators are given by

$$[\psi(\mathbf{r}), \hat{\psi}^\dagger(\mathbf{r}')] = \delta(\mathbf{r} - \mathbf{r}'), \qquad [\psi(\mathbf{r}), \hat{\psi}(\mathbf{r}')] = 0, \quad \text{and} \quad [\hat{\psi}(\mathbf{r}), \hat{\psi}^\dagger(\mathbf{r}')] = 0. \tag{1}$$

The commutation relations of the field operators with the number operator are given by

$$[\hat{N}, \hat{\psi}(\mathbf{r})] = -\hat{\psi}(\mathbf{r}) \quad \text{and} \quad [\hat{N}, \hat{\psi}^\dagger(\mathbf{r})] = \hat{\psi}^\dagger(\mathbf{r}). \tag{2}$$

Therefore, we can write

$$\langle\hat{\psi}(\mathbf{r})\rangle = \mathrm{Tr}[\hat{\rho}_{eq}\hat{\psi}(\mathbf{r})] = -\mathrm{Tr}[\hat{\rho}_{eq}[\hat{N}, \hat{\psi}(\mathbf{r})]] = \mathrm{Tr}[[\hat{\rho}_{eq}, \hat{N}]\hat{\psi}(\mathbf{r})]. \quad (3)$$

Thus, when the gauge symmetry of the state of the system is broken, then $\langle\hat{\psi}(\mathbf{r})\rangle$ is the order parameter.

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PROBLEMS

Problem 10.1. Assume that a viscous fluid flows in a pipe with a circular cross section of radius a. Choose the z axis to be the direction of motion of the fluid. Assume that the density of the fluid is constant and that the flow is steady. Starting from the hydrodynamic equations, find the equation relating pressure gradients to velocity

gradients in the fluid. Describe what is happening in the pipe. (*Note:* For steady flow, the velocity is independent of time, but can vary in space. At the walls the velocity is zero due to friction.)

Problem 10.2. Consider an ideal fluid. Assume that at time $t = 0$ the Fourier amplitudes of the density, velocity, and temperature variations are given by $\rho_{\mathbf{k}}(0)$, $\mathbf{v}_{\mathbf{k}}(0)$, and $T_{\mathbf{k}}(0)$, respectively. Compute $\rho_{\mathbf{k}}(t)$, $\mathbf{v}_{\mathbf{k}}(t)$, and $T_{\mathbf{k}}(t)$.

Problem 10.3. Consider a fluid of point particles. Assume that at time $t = 0$ the Fourier amplitudes of the coupled longitudinal density, velocity, and temperature variations are given by $\rho_{\mathbf{k}}(0)$, $v_{\mathbf{k}}^{\parallel}(0)$, and $T_{\mathbf{k}}(0)$. Compute $\rho_{\mathbf{k}}(t)$, $v_{\mathbf{k}}^{\parallel}(t)$, and $T_{\mathbf{k}}(t)$, but only keep terms in the amplitudes which are zeroth order in the wavevector, k.

Problem 10.4. Consider an isotropic fluid whose deviation from equilibrium can be described by the linearized Navier–Stokes equations. Assume that at time $t = 0$ the velocity is $\mathbf{v}(\mathbf{r}, 0) = v_0 e^{-ar^2}\hat{\mathbf{z}}$. Compute $\mathbf{v}_{\mathbf{k}}^{\perp}(t)$, where $\mathbf{v}_{\mathbf{k}}^{\perp}(t) = \mathbf{v}_{\mathbf{k}}(t) - \hat{\mathbf{k}}v_{\mathbf{k}}^{\parallel}(t)$ and $\mathbf{v}_{\mathbf{k}}(t)$ is the Fourier transform of $\mathbf{v}(\mathbf{r}, t)$.

Problem 10.5. Consider an isotropic fluid contained in a rectangular box with sides of length $L_x = L, L_y = 2L$, and $L_z = 3L$. Assume that the temperature of the fluid at time $t = 0$ has a distribution $T(\mathbf{r}, 0)$, but the fluid is initially at rest. Assume that the thermal expansivity of the fluid is very small so that coupling to pressure variations can be neglected. (a) Show that under these conditions the temperature variations satisfy the heat equation, $\partial T(\mathbf{r}, t)/\partial t = -\kappa \nabla^2 T(\mathbf{r}, t)$. What is κ? (b) If the walls of the box conduct heat and are maintained at temperature, T_0, approximatlely how long does it take for the system to reach equilibrium. (c) If the walls of the box are insulators, approximately how long does it take for the system to reach equilibrium? (*Hint*: No heat currents flow through the walls of insulators.)

Problem 10.6. Consider an isotropic fluid of point particles. (a) Write the dyatic, $\nabla_{\mathbf{r}}\mathbf{v}$, in spherical coordinates. (b) Use your results in (a) to write the stress tensor in spherical coordinates.

Problem 10.7. A Brownian particle of mass m is attached to a harmonic spring with force constant, k, and is driven by an external force, $F(t)$. The particle is constrained to move in one dimension. The Langevin equation is

$$m\frac{d^2x(t)}{dt^2} + \gamma\frac{dx(t)}{dt} + m\omega_0^2 x(t) = \xi(t) + F(t),$$

where $\omega_0 = k/m, \gamma$ is the friction constant, and $\xi(t)$ is a Gaussian white noise with zero mean, $\langle \xi(t) \rangle_{\xi} = 0$. Here $\langle \rangle_{\xi}$ denotes the average over values of the random force. (a) Compute the equilibrium correlation function, $\langle x(t)x(0) \rangle$, starting from the Langevin equation above with $F(t) = 0$. Let $\langle \rangle_T$ denote the thermal average over the initial position and velocity of the Brownian particle. Assume that $\langle x(0)v(0) \rangle_T = 0$ and $\langle x(0)^2 \rangle_T = k_B T/m\omega_0^2$ (cf. Exercise (5.5)). (b) The dynamic susceptibility for the Brownian oscillator is $\chi(\omega) = (-m\omega^2 + m\omega_0^2 - i\gamma\omega)^{-1}$ (cf. Exercise (10.6)). Use the fluctuation–dissipation theorem,

$$\langle x(t)x(0) \rangle = \frac{k_B T}{i\pi} P \int_{-\infty}^{\infty} \frac{1}{\omega}\chi(\omega)\cos(\omega t),$$

to compute the equilibrium correlation function. Do your results in (a) and (b) agree?

Problem 10.8. A paramagnetic system sits in a constant external field, $H_0\hat{\mathbf{z}}$, and therefore has constant magnetization, $M_0\hat{\mathbf{z}}$. Assume that this is the equilibrium configuration of the system and that a small uniform time-dependent magnetic field, $H_1(t) = H_1\cos(\omega_0 t)\hat{\mathbf{x}}$ is applied to the system. The magnetization then becomes time-dependent. Its equation of motion can be written

$$\frac{d\langle\mathbf{M}\rangle}{dt} = -\gamma\langle\mathbf{M}\rangle \times \mathbf{H}(t) - D(\langle\mathbf{M}\rangle)$$

(these are called Bloch equations), where $\langle\mathbf{M}\rangle = \mathrm{Tr}(\hat{\rho}\mathbf{M}) = M_x(t)\hat{\mathbf{x}} + M_y(t)\hat{\mathbf{y}} + (M_0 - M_z(t)\hat{\mathbf{z}}, \mathbf{H}(t) = H_0\hat{\mathbf{z}} + H_1(t)\hat{\mathbf{x}}$, and $D(\langle\mathbf{M}\rangle)$ is a damping term due to interactions between particles in the medium. The constant γ equals $g\mu/\hbar$, where g is the Lande g-factor and μ is the magnetic moment of particles in the system. (a) Write the equations of motion for $M_x(t), M_y(t)$, and $M_z(t)$, assuming $D_x = M_x/T_2, D_y = M_y/T_2$, and $D_z = M_z/T_1$. The equations you derive will be nonlinear functions of H_1, M_x, M_y, and M_z. (b) Assume that H_1, M_x, M_y, and M_z are small, so the equations can be linearized. If we define the response matrix, $\bar{\mathbf{K}}(t)$, from the equation $\langle\mathbf{M}(t)\rangle = \int_{-\infty}^{\infty} dt'\bar{\mathbf{K}}(t-t')\cdot\mathbf{H}(t')$, find $\chi_{xx}(\omega)$ and $K_{xx}(t)$. Write the expression for $\chi_{xx}(\omega)$ in the limits $1/T_1 \to 0$ and $1/T_2 \to 0$. (c) Compute the average power absorbed during the period $T = 2\pi/\omega_0$. (Note that $\hat{\mathbf{x}}, \hat{\mathbf{y}}$, and $\hat{\mathbf{z}}$ are unit vectors in the x, y, and z directions, respectively.)

Problem 10.9. Consider a casual function, $g(t)$, such that $g(t) = 0$ for $t < 0$ and $g(t) \neq 0$ for $t > 0$. Let $\tilde{g}_L(z) = \int_0^{\infty} dt\, e^{-zt} g(t)$ be the Laplace transform. Let $\tilde{g}_F(\omega) = \int_{-\infty}^{\infty} dt\, e^{i\omega t} g(t)$ be the Fourier transform. Show that

$$\tilde{g}_L(z) = \int_{\infty}^{\infty} \frac{d\omega}{2\pi}\left(\frac{\tilde{g}_F(\omega)}{z + i\omega}\right) = \tilde{g}_F(iz),$$

and show that the inverse transforms give the correct behavior for $g(t)$.

Problem 10.10. Consider an aqueous solution of salt, $A^-_{\nu_a}C^+_{\nu_c}$, which dissociates as $A^-_{\nu_a}C^+_{\nu_c} \rightleftharpoons \nu_a A^- + \nu_c C^+$, where ν_a and ν_c are the stoichiometric coefficients for the dissociation. The generalized Ohm's laws for the diffusion currents are

$$\tilde{\mathbf{J}}^D_a = -\tilde{L}_{aa}\nabla\tilde{\mu}^e_a - \tilde{L}_{cc}\nabla\tilde{\mu}^e_c, \quad \text{and} \quad \tilde{\mathbf{J}}^D_c = -\tilde{L}_{ca}\nabla\tilde{\mu}^e_a - \tilde{L}_{cc}\nabla\tilde{\mu}^e_c,$$

where $\tilde{L}_{aa}, \tilde{L}_{cc}, \tilde{L}_{ac}$ and $\tilde{L}_{ca}$ are Onsager coefficients. Since $\tilde{L}_{ac} = \tilde{L}_{ca}$, only three are independent. Three independent transport coefficients can be measured experimentally for this system, and their values can be used to obtain values for the Onsager coefficients. The measurable quantities are the electric conductivity, $\kappa = I/E$, the diffusion coefficient, D_s, for the salt, and the Hittorf transference number, $\tau_a = z_a F\tilde{J}^D_a/IM_a$, which is the fraction of the current carried by one of the ions. Find expressions for (a) κ, (b) τ_a, and (c) D_s in terms of the three Onsager coefficients. (Assume uniform temperature and pressure throughout the system.)

Problem S10.1. Compute corrections of order k to the spectral density function of an isotropic fluid of point particles. Estimate the size of these corrections relative to the dominant terms in a light scattering experiment.

Problem S10.2. Consider a rough hard sphere of radius R immersed in an incompressible fluid of point particles. Assume the sphere is free to rotate about its

diameter but cannot translate. Also, assume that the sphere has angular velocity, $\Omega(t) = \Omega_0(t)\hat{\mathbf{z}}$. (a) What is the velocity distribution of the fluid? (b) Let $\tau(t)$ be the torque on the sphere due to friction between the sphere and the medium, and let $\tilde{\tau}(\omega)$ be its Fourier transform. Show that

$$\tilde{\tau}(\omega) = -8\pi\Omega_\omega \eta R^3 \hat{\mathbf{z}}\left(1 - \frac{k^2R^2}{3(1+ikR)}\right),$$

where Ω_ω is the Fourier transform of $\Omega(t)$. [*Hint*: The velocity is a polar vector and $\Omega(t)$ is an axial vector, so assume the velocity has the form $\mathbf{v} = \nabla \times (g(r)\Omega_0\hat{\mathbf{z}})$, where $g(r)$ is to be determined by solving Eq. (10.391). Assume stick boundary conditions on the surface of the sphere and assume the fluid velocity and all its derivatives go to zero at infinity.]

Problem S10.3. Consider a particle undergoing rotational Brownian motion. Write an expression for the angular velocity autocorrelation function for the rotating Brownian particle. Show that for long times it depends on time t as follows:

$$C_{\Omega\Omega}(t) \approx \frac{\pi I}{\rho_0}\left(\frac{\rho_0}{4\pi\eta t}\right)^{5/2} \langle|\Omega(0)|^2\rangle_T,$$

where ρ_0 is the fluid density, η is the shear viscosity, I is the moment of inertia of the sphere, and $\langle|\Omega(0)|^2\rangle_T$ is the initial mean square angular velocity. (*Hint*: Use the result of Problem S10.2 for the friction coefficient.)

Problem S10.4. Consider a membrane of thickness Δx which separates two regions containing dilute aqueous solutions of ions. One particular ion, i, with charge z_i can diffuse through the membrane. It has diffusion coefficient, D, inside the membrane. A constant electric field, E, directed perpendicular to the membrane surface exists inside the membrane. Assume that a steady current, J_i, of ions diffuses across the membrane. The phenomenological equation relating the current to the gradient of the electrochemical potential of the ion inside the membrane is $J_i = L(\partial\mu_i^e/\partial x)$, where L is the phenomenological coefficient, $L = Dc_i/RT$, and c_i is the concentration of ion i. For dilute solutions, the gradient of the electrochemical potential of the ion is $\mu_i^e = (RT/c_i)(dc_i/dx) + z_i\mathrm{F}(d\phi/dx)$, where ϕ is the electric potential, F is Faraday's constant, and $E = -(d\phi/dx)$. Show that the ion current inside the membrane can be written

$$J_i = -\frac{Dz_i\mathrm{F}\Delta\phi}{RT\Delta x}\frac{(c_i^L - c_i^R\exp(z_i\mathrm{F}\Delta\phi/RT))}{(1-\exp(z_i\mathrm{F}\Delta\phi/RT))},$$

where c_i^L and c_i^R are the ion concentrations on the inside left and right surfaces of the membrane, respectively, and $\Delta\phi = \phi_R - \phi_L$ is the difference in electric potential on the inside left and right surfaces of the membrane.

Problem S10.5. The entropy production, σ, in a thermocouple can be written

$$T\sigma = -\mathbf{J}_S \cdot \nabla_\mathbf{r} T - \mathbf{I} \cdot \left(\nabla_\mathbf{r}\left(\frac{\mu_{el}}{\mathrm{F}}\right) - \mathrm{F}\mathbf{E}\right),$$

where $\mathbf{J_S}$ is the entropy current, $\mathbf{I}$ is the current carried by the electrons, F is Faraday's constant, $\mathbf{E}$ is the electric field in the metal wires, and μ_{el} is the chemical potential of the electrons. The balance equation for the entropy/volume, s, is $\partial s/\partial t = -\nabla \cdot \mathbf{J}_S + \sigma$. The

generalized Ohm's laws can be written

$$\mathbf{J}_S = -\frac{\lambda}{T}\nabla_{\mathbf{r}}T + \frac{\Gamma}{T}\mathbf{I} \quad \text{and} \quad \left(\mathbf{E} - \nabla_{\mathbf{r}}\left(\frac{\mu_{\text{el}}}{F}\right)\right) = -\zeta\nabla_{\mathbf{r}}T + R\mathbf{I},$$

where λ is the coefficient of thermal conductivity at zero electrical current, R is the isothermal electrical resistance, ζ is the differential thermoelectric power, and Γ/T is the entropy transported per unit electric current. (a) Show that the Onsager relation, $L_{SE} = L_{ES}$, implies that $\Gamma = T\zeta$. (b) Show that the entropy balance equation can be written $\partial s/\partial t = (\lambda/T)\nabla_{\mathbf{r}}^2(T) - \nabla_{\mathbf{r}} \cdot (\Gamma\mathbf{I}/T) + RI^2/T$. The first term on the right is the entropy production due to thermal conductivity. The third term on the right is the entropy production due to Joule heating. The second term on the right is the entropy production due to the Peltier and Thomson effects.

Problem S10.6. Consider the thermocouple shown in Fig. (10.4). Replace the potentiometer with a capacitor held at temperature T_0 with wire of metal B attached at points a and d. Show that

$$\frac{\Delta\phi_{ad}}{\Delta T} = \zeta_A - \zeta_B,$$

where $\Delta\phi_{ad} = \phi_a - \phi_d$ is the potential difference across the capacitor and ζ_A and ζ_B are the differential thermoelectric powers in the two metals (cf. Problem S10.5). Note that in this circuit, there is no electric current.

Problem S10.7. The junction between two metal wires, A and B, in a thermocouple has a circular cross-sectional area, $\pi\rho^2$, where ρ is the radius of the wires. Assume that the transition between the two metals takes place smoothly over a distance, ΔL, so the transition region (the junction) has a volume, $\pi\rho^2\Delta L$. Assume that the temperature is uniform throughout the junction and that an electric current, $\mathbf{I}$, is flowing through the junction. From Problem S10.5 the entropy production, σ (entropy/volume · time), is given by

$$\sigma = -\nabla \cdot \left(\frac{\Gamma\mathbf{I}}{T}\right) + \frac{RI^2}{T}.$$

In the limit $\Delta L \to 0$, show that the Peltier heat, $\bar{\pi}$ which is just the entropy/(area · time · current) produced (or lost) in the junction, is given by $\bar{\pi} = (\Gamma_B - \Gamma_A)$.

Problem S10.8. Consider the flow of He(II) through a porous material. Only the superfluid can flow so $\mathbf{v}_n = 0$. Also, the porous material exchanges momentum with fluid so that momentum is not conserved and the momentum balance equation cannot be used. Use the linearized nondissipative superfluid hydrodynamic equations to determine the dispersion relation for density oscillations (fourth sound). Show that fourth sound has a speed $c_4 = \sqrt{(\rho_n/\rho)c_2^2 + (\rho_s/\rho)c_1^2}$ where c_1 and c_2 are the speeds of first and second sound, respectively. Assume that $(\partial P/\partial T)_\rho = 0$.

Problem S10.9. Derive the wave equations for first sound and second sound in a nondissipative superfluid for the case when $(\partial P/\partial T)_\rho = 0$ Show that only second sound propagates when the momentum density is zero. Show that only first sound propagates when the super fluids and normal fluids move in phase so $\mathbf{v}_n = \mathbf{v}_s$.

Problem S10.10. Consider a magnetic crystal whose magnetic interactions are governed by the Hamiltonian, $\hat{H} = -\frac{1}{2}\sum_{\alpha\neq\beta} J(|\mathbf{r}_\alpha - \mathbf{r}_\beta|)\hat{\mathbf{S}}_\alpha \cdot \hat{\mathbf{S}}_\beta$, where α and β denote lattice

sites and the coupling constant, $J(|\mathbf{r}_\alpha - \mathbf{r}_\beta|)$, depends only on the magnitude of the displacement, $\mathbf{r}_\alpha - \mathbf{r}_\beta$, between sites α and β. The i^{th} component $(i = x, y, z)$ of the magnetization operator is $M_i(\mathbf{r}) = \sum_\alpha \hat{S}_{i,\alpha}\delta(\mathbf{r} - \mathbf{r}_\alpha)$, where $\mathbf{r}_\alpha$ is the position operator for the α^{th} lattice site and $\hat{S}_{i,\alpha}$ is the i^{th} component of the spin operator for that site. The total spin of the lattice can be written $\hat{S}_{i,tot} = \int d\,\mathbf{r}\hat{M}_i(\mathbf{r})$. The total spin operator commutes with the Hamiltonian, so the spin density (the magnetization operator) satisfies the balance equation

$$\frac{\partial \hat{M}_i(\mathbf{r}, t)}{\partial t} + \sum_j \nabla_{\mathbf{r}} \cdot J_{ij}(\mathbf{r}, t) = 0,$$

where $J_{ij}(\mathbf{r}, t)$ is a magnetization current. Consider only long-wavelength modes so the discreteness of the lattice can be neglected. Assume that $\langle \hat{S}_{z,tot} \rangle = M_0$ and $\langle \hat{S}_{x,tot} \rangle = \langle \hat{S}_{x,tot} \rangle = 0$. Compute the spectral density matrix

$$\begin{pmatrix} S_{M_x M_x}(\mathbf{k}, z) & S_{M_x M_y}(\mathbf{k}, z) \\ S_{M_y M_x}(\mathbf{k}, z) & S_{M_y M_y}(\mathbf{k}, z) \end{pmatrix}$$

and determine its poles to lowest nonzero order in k. Describe the hydrodynamic excitations in this system. What is unusual about them?

11

TRANSPORT THEORY

11.A. INTRODUCTION

In this chapter we will consider the microscopic theory of dilute gases which are close to equilibrium. We assume that all disturbances are slowly varying in space and have small amplitude. Thus, in any small region the system will be in equilibrium and its state in that region can be specified by thermodynamic state variables. However, the values of thermodynamic variables can vary from one region to another in the fluid.

When a system is disturbed from its equilibrium state, all quantities which are not conserved during collisions decay rapidly to their equilibrium values. After a few collision times, only quantities which are conserved during the collisions remain out of equilibrium. The densities of conserved quantities entirely characterize the nonequilibrium behavior of the fluid after long times. The equations of motion for the densities of conserved quantities are called the *hydrodynamic equations*. Examples of conserved quantities are the number of particles, the total momentum of the particles, and the total kinetic energy of the particles (for elastic collisions). If there are inhomogeneities in the densities of these quantities, then particles, momentum, or kinetic energy must be transported from one part of the fluid to another to achieve equilibrium. The rate at which a fluid returns to its equilibrium state is determined by the transport coefficients. They are the constants of proportionality between the gradients in the densities of conserved quantities and the currents that result from those density gradients and lead the system back to equilibrium. The aim of transport theory is to compute the transport coefficients in terms of the microscopic properties of the fluid.

In order to build intuition concerning the nature of transport processes, we will first derive expressions for the coefficients of self-diffusion, shear viscosity, and thermal conductivity using the simplest possible mean free path arguments. The expressions we obtain make it possible to estimate the order of magnitude of the transport coefficients by simple "back of the envelope" calculations.

To obtain a deeper understanding of transport phenomena, we must derive the transport coefficients from a more rigorous microscopic theory. That is, we must derive expressions for them starting from the kinetic equation for the fluid

(cf. Section 6.C). However, we are then faced with one of the fundamental dilemmas of statistical physics. The exact kinetic equation derived in Chapter 6 is reversible, whereas transport processes are irreversible or dissipative. Boltzmann was the first to derive an irreversible kinetic equation to describe relaxation processes in fluid. He did it by using probabilistic arguments. Thus, his equation is not based rigorously on the properties of the underlying dynamics of the system. However, the Boltzmann equation works extremely well in providing numerical values for the transport coefficients in dilute fluids and to this day remains one of the great milestones in the history of statistical physics. Much of this chapter is devoted to a study of the Boltzmann equation. We will derive it using arguments similar to Boltzmann's original arguments, and we will indicate its irreversible nature by proving the famous Boltzmann H theorem. From the H theorem, Boltzmann was able to obtain a microscopic expression for the entropy of a system near equilibrium which has the proper behavior as the system approaches the equilibrium state.

We will apply Boltzmann's equation to the case of dilute two-component gas of particles which have different identity but are dynamically the same. For this system, we derive microscopic expressions for the coefficients of self-diffusion, shear viscosity, and thermal conductivity. The method we use to derive the transport coefficients is very simple and elegant and was first introduced by Resibois. We first derive the hydrodynamic equations from the Boltzmann equation, introducing into them the transport coefficients, and we then find the normal mode frequencies of the hydrodynamic equations in terms of the transport coefficients. We next find the hydrodynamic eigenfrequencies of the Boltzmann equation and match these to the normal mode frequencies of the hydrodynamic equations. This gives us the desired microscopic expressions for the transport coefficients.

11.B. ELEMENTARY TRANSPORT THEORY [1, 2]

Before we discuss the full microscopic theory of transport processes based ont he Boltzmann equation, it is useful to derive the transport coefficients using very simple mean free part arguments and kinetic theory. These arguments are entirely probabilistic and are independent of the form of the interparticle potential, although they do assume that the interaction is very short-ranged compared to the average interparticle spacing. As we will see, the same type of arguments can be used to obtain microscopic expression for the reaction rates in chemical systems.

11.B.1. The Maxwell–Boltzmann Distribution

Let us consider a dilute gas of N particles contained in a volume V. We assume that the gas is in equilibrium and that the interaction energy between particles is negligible compared to the kinetic energy of the particles. The probability

density of finding the particles with phase space coordinates in the interval $\mathbf{p}^N \to \mathbf{p}^N + d\mathbf{p}^N$ and $\mathbf{q}^N \to \mathbf{q}^N + d\mathbf{q}^N$ is

$$\rho(\mathbf{p}^N, \mathbf{q}^N) = \frac{\exp\left(-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m}\right)}{\int d\mathbf{p}^N \int d\mathbf{q}^N \exp\left(-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m}\right)}, \tag{11.1}$$

where $d\mathbf{p}^N d\mathbf{q}^N = d\mathbf{p}_1 \times \cdots \times d\mathbf{p}_N d\mathbf{q}_1 \times \cdots \times d\mathbf{q}_N$. The probability density, $\rho_1(\mathbf{p}_1)$, that particle 1 has momentum, in the interval, $\mathbf{p}_1 \to \mathbf{p}_1 + d\mathbf{p}_1$, is obtained by integrating over all position variables, $\mathbf{q}_1, \ldots \mathbf{q}_N$, and the momentum variables, $\mathbf{p}_2, \ldots \mathbf{p}_N$,

$$\begin{aligned} \rho_1(\mathbf{p}_1) &= \int \ldots \int d\mathbf{p}_2 \times \cdots \times d\mathbf{p}_N d\mathbf{q}_1 \times \cdots \times d\mathbf{q}_N \rho(\mathbf{p}^N, \mathbf{q}^N) \\ &= \left(\frac{\beta}{2\pi m}\right)^{3/2} \exp\left(-\frac{\beta p_i^2}{2m}\right). \end{aligned} \tag{11.2}$$

Similarly, we can write an expression for the normalized probability density, $F(\mathbf{v}_1)$, of finding a particle with velocity, $\mathbf{v}_1 \to \mathbf{v}_1 + d\mathbf{v}_1$, where $\mathbf{v}_1 = \mathbf{p}_1/m$. It is given by

$$F(\mathbf{v}_1) = \left(\frac{m\beta}{2\pi}\right)^{3/2} \exp\left(\frac{-\beta m v_1^2}{2}\right) \tag{11.3}$$

and is normalized to one when we integrate over $\mathbf{v}_1$. Equation (11.3) is called *the Maxwell–Boltzmann distribution.*

11.B.2. The Mean Free Path

The mean free path, λ, of a particle is the average distance it travels between collisions. We shall assume that collisions occur at random in a gas. We wish to find the probability that a particle can travel a distance r without collision. Because the collisions occur at random, a particle has the same chance of collision in any interval $r \to r + dr$. If the average number of collisions per unit length is $1/\lambda$, then the probability that a collision occurs in an interval dr is dr/λ.

Let $P_o(r)$ denote the probability that no collision occurs in an interval of length r. Then the probability that no collision occurs in interval of length $r + dr$ is

$$P_o(r + dr) = P_o(r)\left(1 - \frac{dr}{\lambda}\right). \tag{11.4}$$

The factor $(1 - (dr/\lambda))$ is the probability that no collision occurs in interval dr.

We multiply $P_o(r)$ and $(1 - (dr/\lambda))$ together because the events "collision in length r" and "collision in length dr" are independent. If we expand the left-hand side of Eq. (11.4) in a Taylor series, we obtain

$$\frac{d}{dr}P_o(r) = -P_0(r)\frac{1}{\lambda} \tag{11.5}$$

and therefore

$$P_o(r) = e^{-r/\lambda}. \tag{11.6}$$

The probability of no collision in length of path r is a Poisson distribution. The probability that a particle suffers its first collision in an interval $r \to r + dr$ is $P_o(r)(dr/\lambda)$. The average distance traveled between collisions is

$$\langle r \rangle = \int_0^\infty rP_0(r)\frac{dr}{\lambda} = \lambda, \tag{11.7}$$

which is just our original definition of the mean free path.

11.B.3. The Collision Frequency

Let us consider a fluid containing several types of particles A, B, C, ... and so on. Let us assume that particles A have mass m_A, a diameter d_A, and a number density n_A; particles B have a mass m_B, a diameter d_B, and a number density n_B; and so on. Let us further assume that the particles are distributed at random in the fluid and that each type of particle is distributed in the fluid according to the Maxwell–Boltzmann distribution [cf. Eq. (11.3)].

We will find the collision frequency between particles A and B. The radius of the sphere of influence between A and B is

$$d_{AB} = \frac{d_A + d_B}{2} \tag{11.8}$$

(cf. Fig. 11.1). The average relative speed between particles A and B is given by

$$\langle v_r \rangle_{AB} \equiv \int d\mathbf{v}_A \int d\mathbf{v}_B F(\mathbf{v}_A)F(\mathbf{v}_B)|\mathbf{v}_A - \mathbf{v}_B|. \tag{11.9}$$

The center-of-mass velocity of particles A and B is

$$\mathbf{V}_{cm} = \frac{m_A\mathbf{v}_A + m_B\mathbf{v}_B}{m_A + m_B} \tag{11.10}$$

and the relative velocity is

$$\mathbf{v}_r = \mathbf{v}_A - \mathbf{v}_B. \tag{11.11}$$

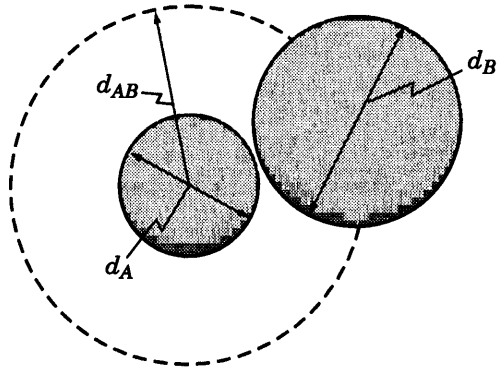


Fig. 11.1. The circle of radius d_{AB} is the sphere of influence for particles A and B.

The Jacobian of the transformation from coordinates $\mathbf{v}_A$ and $\mathbf{v}_B$ to coordinates $\mathbf{v}_r$ and $\mathbf{V}_{cm}$ is equal to one. Thus, $\langle v_r \rangle_{AB}$ can be rewritten

$$\langle v_r \rangle_{AB} = \left(\frac{\beta M_{AB}}{2\pi}\right)^{3/2} \left(\frac{\beta \mu_{AB}}{2\pi}\right)^{3/2} \int\int d\mathbf{v}_r \, d\mathbf{V}_{cm} v_r e^{-(\beta/2)(M_{AB}V_{cm}^2 + \mu_{AB}v_r^2)}, \quad (11.12)$$

where $M_{AB} = m_A + m_B$ is the total mass and $\mu_{AB} = m_A m_B/(m_A + m_B)$ is the reduced mass. If we perform the integrations in Eq (11.12), we obtain

$$\langle v_r \rangle_{AB} = \left(\frac{8k_BT}{\pi \mu_{AB}}\right)^{1/2} \quad (11.13)$$

for the average relative speed of particles A and B.

Let us now assume that all particles of mass m_B in the fluid are at rest and a particle of mass m_A moves through the gas with a speed $\langle v_r \rangle_{AB}$. Particle A sweeps out a collision cylinder of radius d_{AB} (radius of the sphere of influence) and volume $\pi d_{AB}^2 \langle v_r \rangle_{AB} t$ in time t. The number of particles B that particle A collides with in time t is $f_{AB}t$, where f_{AB} is the collision frequency

$$f_{AB} = n_B \pi d_{AB}^2 \langle v_r \rangle_{AB}. \quad (11.14)$$

Therefore, the total number of collisions per unit volume per second, ν_{AB}, between particles of type A and of type B is

$$\nu_{AB} = n_A n_B \pi d_{AB}^2 \langle v_r \rangle_{AB} = n_A n_B \pi d_{AB}^2 \left(\frac{8k_BT}{\pi \mu_{AB}}\right)^{1/2}. \quad (11.15)$$

From Eq. (11.15) we can easily write down the collision frequency ν_{AA} between

identical particles:

$$\nu_{AA} = \tfrac{1}{2} n_A^2 \pi d_{AA}^2 \langle v_r \rangle_{AA} = \tfrac{1}{2} n_A{}^2 \pi d_{AA}^2 \left(\frac{16 k_B T}{\pi m_A} \right)^{1/2}. \tag{11.16}$$

The extra factor of $\frac{1}{2}$ enters because the particles colliding are identical and it is needed to prevent overcounting.

If we consider a gas of identical particles, then the mean free path, λ, the collision frequency for a single particle, f_{AA}, and the average speed, $\langle v \rangle$, are simply related by the equation

$$\lambda = \frac{\langle v \rangle}{f_{AA}} = \langle v \rangle \tau = \frac{1}{\sqrt{2} n_A \pi d_{AA}^2}, \tag{11.17}$$

where τ is the collision time (the time between collisions), and the average speed, $\langle v \rangle$, is related to the relative speed by the relation $\langle v_{\text{rel}} \rangle = \sqrt{2} \langle v \rangle$.

11.B.4. Self-Diffusion

We can now use the above ideas to obtain an expression for the coefficient of self-diffusion, D. Let us consider a gas of particles which are identical in every way except that a small fraction of the particles have a radioactive tracer attached (or they might have different color or different spin). Self-diffusion involves the transport of tracer particles through a gas of otherwise identical particles. If initially there is an uneven distribution of tracer particles in the gas, the distribution will even out and become uniform through the diffusion process. The rate at which inhomogeneities in the density of tracer particles become smoothed out is determined by the value of the coefficient of self-diffusion, D.

We shall assume that the density of tracer particles, $n_T(z)$, varies in the z direction, while the total particle density, n, is held constant. As a first step in obtaining the coefficient of self-diffusion, we draw an imaginary wall in the fluid at $z = 0$ and find the net flux of particles across the wall.

Let us first find the number of particles which hit the wall from above. We will look at a segment of the wall, dS, and choose the origin of coordinates to be at the center of dS. We next consider a volume element, dV, of the gas located at position r, θ, ϕ above the wall (cf. Fig 11.2). The average number of tracer particles undergoing collisions in dV per unit time is $f n_T(z) dV = (\langle v \rangle / \lambda) n_T(z) dV$, where f is the collision frequency. Particles in dV leave in random directions (any direction is equally likely). The fraction of particles that move towards dS is $d\Omega/4\pi$, where $d\Omega$ is the solid angle subtended by dS and $d\Omega = dS|\cos\theta|/r^2$. Not all particles particles leaving dV in the direction of dS reach dS. The probability that a tracer particle will reach dS is $e^{-r/\lambda}$ (the probability that it will not undergo a collision). Combining the above results, we obtain the following expression for the number of tracer particles, $dn_T(\mathbf{r})$,

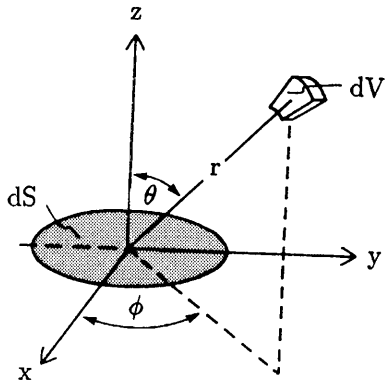


Fig. 11.2. Only a fraction of the particles in volume element, dV, reach the surface area element, dS, without undergoing a collision en route.

which collide in dV, leave directed toward dS, and reach dS without another collision:

$$dn_T(\mathbf{r}) = \left(\frac{\langle v\rangle n_T(z)dV}{\lambda}\right)\left(\frac{dS\,|\cos\theta|}{4\pi r^2}\right)e^{-r/\lambda}. \tag{11.18}$$

The total number hitting a unit area of wall per unit time from above, $\dot{N}_+$, is found by integrating over the entire volume for $z > 0$:

$$\dot{N}_+ = \frac{\langle v\rangle}{4\pi\lambda}\int_0^\infty r^2 dr \int_0^{\pi/2} \sin\theta d\theta \int_0^{2\pi} d\phi n_T(z)\cos\theta \frac{e^{-r/\lambda}}{r^2}. \tag{11.19}$$

For the case in which the tracer particles are distributed uniformly throughout the gas—that is, $n(z) = \text{constant}$, —Eq. (11.19) reduces to $\dot{N}_+ = n\langle v\rangle/4$.

For small variations in tracer density we may expand $n_T(z)$ in a Taylor series about the origin,

$$n_T(z) = n_T(0) + z\left(\frac{\partial n_T}{\partial z}\right)_0 + \frac{z^2}{2}\left(\frac{\partial^2 n_T}{\partial z^2}\right)_0 + \cdots. \tag{11.20}$$

If $n_T(z)$ is a slowly varying function of z, then higher-order derivatives $(\partial^2 n_T/\partial z^2)_0$, $(\partial^3 n_T/\partial z^3)_0$, and so on, will be small. Because of the factor $e^{-r/\lambda}$ in the integral in Eq. (11.19), only small values of z (values of $z \approx \lambda$) will contribute. Therefore, we can terminate the expansion at $(z^2/2)(\partial^2 n_T/\partial z^2)_0$.

The net transport of tracer particles in the negative z direction across a unit area of the wall per unit time is given by $(\dot{N}_+ - \dot{N}_-)$, where $\dot{N}_-$ is the number crossing a unit area per unit time in the positive z direction. The expression for $\dot{N}_-$ is the same as for $\dot{N}_+$ except that θ is integrated from $\theta = (\pi/2) \to \pi$ and $|\cos\theta|$ is changed to $-\cos\theta$. Therefore,

$$(\dot{N}_+ - \dot{N}_-) = \frac{\langle v\rangle}{4\pi\lambda}\int_0^\infty dr r^2 \int_0^{\pi} \sin\theta\, d\theta \int_0^{2\pi} d\phi n_T(z)\cos\theta \frac{e^{-r/\lambda}}{\mathbf{r}^2}. \tag{11.21}$$

If we substitute Eq. (11.20) into Eq. (11.21), the first and third terms are identically zero and we obtain

$$(\dot{N}_+ - \dot{N}_-) = \frac{\langle v \rangle \lambda}{3} \left(\frac{\partial n_T}{\partial z} \right)_0 . \tag{11.22}$$

If the density increases in the z direction, then $(\partial n_T/\partial z)_0 > 0$ and $(\dot{N}_+ - \dot{N}_-) > 0$. Therefore, there will be a net transport of particles in the negative z direction.

If we let $J_D(z)$ denote the number of tracer particles crossing a unit area at z in unit time in the positive z direction [$J_D(z)$ is the particle flux or current], then

$$J_D(z) = -D \frac{\partial n_T(z)}{dz}, \tag{11.23}$$

where

$$D = \frac{\langle v \rangle \lambda}{3} \tag{11.24}$$

is the coefficient of self-diffusion. If the density is a slowly varying function of x, y, and z, then we can write the current as in the more general form

$$\mathbf{J}_D(\mathbf{r}) = -D \nabla_{\mathbf{r}} n_T(\mathbf{r}), \tag{11.25}$$

where $\nabla_{\mathbf{r}}$ denotes the spatial gradient. Equation (11.25) is called *Fick's law.*

Let us now consider diffusive flow which is changing in time. We assume that $n_T = n_T(z,t)$ and $J_D = J_D(z,t)$ and consider a region in the fluid bounded by two fixed planes, one at z and the other at $z + dz$. The net increase in the number of particles per unit area per unit time between the planes is

$$J_D(z+dz,t) - J_D(z,t) = \left(\frac{\partial J_D}{\partial z} \right) dz = -\frac{\partial}{\partial z} \left(D \frac{\partial n_T}{\partial z} \right) dz. \tag{11.26}$$

If there are no sources or sinks of particles between the planes (particles are conserved), then Eq. (11.26) must equal the rate of increase of number of tracer particles between the planes. Thus,

$$\frac{\partial n_T}{\partial t} = D \frac{\partial^2 n_T}{\partial z^2}. \tag{11.27}$$

We would obtain the same equation if we assumed that the particles performed a random walk through the gas (cf. Chapters 4 and 5). For variations in three dimensions, Eq. (11.27) can be written

$$\frac{\partial n_T(\mathbf{r},t)}{\partial t} = D \nabla_{\mathbf{r}}^2 n_T(\mathbf{r},t). \tag{11.28}$$

Thus, using kinetic theory, we have derived again the diffusion equation and we have obtained an expression for the diffusion coefficient in terms of the mean free path. We can now use these results to find an expression for the coefficients of viscosity and thermal conductivity.

11.B.5. The Coefficients of Viscosity and Thermal Conductivity

In addition to self-diffusion, other types of transport can occur in a fluid. If a fluid is stirred so that one part moves relative to another part (that is, if the average velocity of particles is a function of position $\langle \mathbf{v} \rangle = \langle \mathbf{v}(\mathbf{r}) \rangle$), then "friction" (viscosity) between the moving parts will bring them to equilibrium and the average velocity of the particles will become uniform throughout the gas. The quantity that is transported is the average velocity of the particles. The rate at which the average velocity is transported is determined by the coefficient of viscosity.

If one part of the fluid is hotter than another part, the particles in the hot region will have a greater average kinetic energy than particles in the cooler region. Transport processes will equalize the average kinetic energy (temperature) in the two regions. The quantity transported is the average kinetic energy and the process which brings the gas to equilibrium is called *heat conduction.* The rate at which the temperatures in different parts of the gas are equalized is determined by the coefficient of thermal conductivity, K.

It is possible to treat all these transport processes in a unified manner. Let us assume that $A = A(z)$ is the *molecular property* to be transported and that it varies in the z direction. Let us draw an imaginary plane in the gas at $z = z_0$. When a particle crosses the plane, it transports the value of A it obtained in its last collision and transfers it to another particle in its next collision.

Let $A(z_0 + \Delta z)$ be the value of A transported in the negative z direction across the plane; $\Delta z = a\lambda$ is the distance above the plane where the particle had its last collision (cf. Fig. 11.3; λ is the mean free path, and a is a proportionality constant). The average number of particles crossing the plane per unit area per unit time is $n\langle v \rangle$. The net amount of A transported in the positive z direction per unit area per unit time is

$$n\langle v \rangle [A(z_0 - \Delta z) - A(z_0 + \Delta z)] = -2n\langle v \rangle \Delta z \frac{dA}{dz} = -2an\langle v \rangle \lambda \frac{dA}{dz}. \quad (11.29)$$

Let us denote the net amount of A per unit area per unit time (the current) by J_A. Then

$$J_A(z) = -b_A n\langle v \rangle \lambda \frac{dA}{dz}, \quad (11.30)$$

where b_A is a proportionality constant. We can determine b_A from our expression for the coefficient of self-diffusion in Eq. (11.24). Let us now apply Eq. (11.30) to the cases of self-diffusion, viscosity, and heat conductivity.

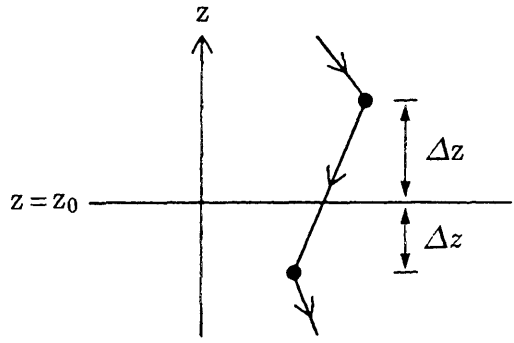


Fig. 11.3. A particle has a collision a distance Δz above the plan and transports property A to another particle a distance Δz below the plane.

11.B.5.1. Self-Diffusion

Let us again consider the system in Section 11.B.4. The concentration of tracer particles per particle is $A = n_T(z)/n$. If the density of tracer particles varies in the z direction, then there will be a concentration gradient $(1/n)(dn_T/dz) = dA/dz$ causing them to diffuse through space. If we let $J_A = J_D$, where J_D is the tracer particle current, then from Eq. (11.30) we obtain

$$J_D(z) = -b_A\langle v\rangle\lambda\frac{dn_T}{dz} = -D\frac{dn_T}{dz} \tag{11.31}$$

and the coefficient of self-diffusion is given by $D = \langle v\rangle\lambda/3$, if we let $b_A = \frac{1}{3}$.

11.B.5.2. Viscosity

If a gas is stirred, one part will move relative to another part. Let us assume that the y component of the average velocity varies in the z direction. Then $A(z) = m\langle v_y(z)\rangle$ and $J_A = J_{zy}$, where J_{zy} is the net flux of y component of momentum per unit area per unit time in the z direction. From Eq. (11.30) we have

$$J_{zy} = -\frac{1}{3}nm\langle v\rangle\lambda\frac{d\langle v_y(z)\rangle}{dz} = -\eta\frac{d\langle v_y(z)\rangle}{dz} \tag{11.32}$$

where

$$\eta = \frac{1}{3}nm\langle v\rangle\lambda \tag{11.33}$$

is the coefficient of viscosity. From Eq. (11.17) we know that $\lambda = [\sqrt{2}n\pi d^2]^{-1}$ for hard spheres of diameter d. Therefore,

$$\eta = \frac{m\langle v\rangle}{3\sqrt{2}\pi d^2} \tag{11.34}$$

and the coefficient of viscosity is independent of density—a somewhat surprising result that is verified by experiment.

11.B.5.3. Heat Conduction

If the temperature of the gas varies in the z direction then

$$A(z) = \tfrac{1}{2}m\langle v^2(z)\rangle = \tfrac{3}{2}k_B T(z) \tag{11.35}$$

and $J_A = J_Q$ is the heat current (the net flux of thermal energy per unit area per unit time). Since $b_A = \frac{1}{3}$, Eq. (11.30) gives

$$J_Q = -K\frac{dT}{dz}, \tag{11.36}$$

where

$$K = \frac{n\langle v\rangle \lambda k_B}{2} \tag{11.37}$$

is the coefficient of thermal conductivity.

The coefficient of thermal conductivity can be put in another form. The change in average internal energy per particle as a function of z can be written $\Delta u(z) = m\tilde{c}_v T(z)$, where $\tilde{c}_v$ is the specific heat. Then

$$K = \frac{nm\langle v\rangle \lambda \tilde{c}_v}{3}. \tag{11.38}$$

If we compare Eqs. (11.33) and (11.38), we obtain the following simple relation between the coefficients of viscosity and heat conductivity and the specific heat:

$$\frac{K}{\eta} \approx \tilde{c}_v. \tag{11.39}$$

The above expressions for the transport coefficients have been derived by very simple arguments, but they do describe fairly well the observed qualitative behavior of transport coefficients in dilute gases.

11.B.6. The Rate of Reaction [3]

We are often interested in transport processes in systems in which chemical reactions can occur. We can use elementary kinetic theory to obtain a qualitative expression for the rate of the reactions. We cannot simply equate the number of collisions between various molecules to the rate at which they undergo chemical reactions. A simple example will illustrate this. Let us consider the reaction $2HI \rightarrow H_2 + I_2$. The radius of the sphere of influence may be obtained

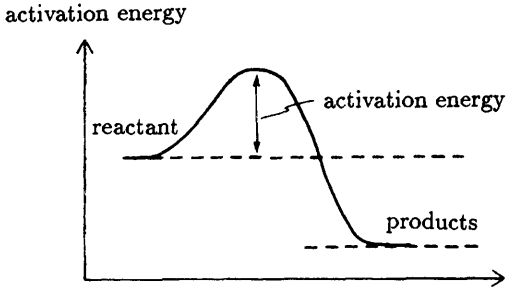


Fig. 11.4. There is an energy barrier that must be surmounted before a chemical reaction can occur.

from viscosity data on HI gas ($d = 4 \times 10^{-8}$ cm). At a temperature $T = 700$K, pressure $P = 1$ atm, the collision frequency is easily computed and yields $\nu_{(HI)^2} = 1.3 \times 10^{28}$/sec. If every collision between HI molecules contributed to the reaction, then for a gas containing 10^{23} molecules the reaction would be completed in a fraction of a second. However, experimentally one finds that it takes a much longer time to complete the reaction, the reason being that not all collisions lead to a reaction.

In order to cause a reaction of the type $A + B \rightarrow C + D$, a certain amount of the kinetic energy of A and B must be absorbed during the collision. A and B first form an intermediate state (AB), which then can decay into the products C and D. The intermediate state (AB) is called an *activated complex* and A and B are called the *reactants*. The amount of energy which must be absorbed in order to form the activated complex is called the *activation energy* (cf. Fig. 11.4).

All of the energy which goes into exciting the activated complex must come from the energy of relative motion of the reactants. Energy in the center-of-mass motion cannot contribute. If ε is the activation energy of the activated complex, then a reaction between A and B can occur only if the relative velocity of A and B is such that

$$\tfrac{1}{2}\mu_{AB}v_r^2 > \varepsilon. \tag{11.40}$$

Therefore, to find the rate at which reactions between A and B can take place, we must multiply the collison frequency between A and B by the probability that A and B have a relative velocity greater than $\sqrt{2\varepsilon/\mu_{AB}}$.

The probability that the molecules A and B have center-of-mass velocity in the range $\mathbf{V}_{cm} \rightarrow \mathbf{V}_{cm} + d\mathbf{V}_{cm}$ and a relative velocity in the range $\mathbf{v}_r \rightarrow \mathbf{v}_r + d\mathbf{v}_r$ is given by

$$P(\mathbf{V}_{cm}, \mathbf{v}_r)d\mathbf{V}_{cm}d\mathbf{v}_r = \left(\frac{\beta M_{AB}}{2\pi}\right)^{3/2}\left(\frac{\beta\mu_{AB}}{2\pi}\right)e^{-(\beta/2)(M_{AB}V_{cm}^2+\mu_{AB}v_r^2)}d\mathbf{V}_{cm}\,d\mathbf{v}_r. \tag{11.41}$$

The probability that A and B have a relaive velocity in the range $\mathbf{v}_r \to \mathbf{v}_r + d\mathbf{v}_r$ is found by integrating Eq. (11.41) over the center-of-mass velocity. We then find

$$P(\mathbf{v}_r)d\mathbf{v}_r = \left(\frac{\beta\mu_{AB}}{2\pi}\right)^{3/2} e^{-(\beta/2)(\mu_{AB}v_r^2)} d\mathbf{v}_r. \tag{11.42}$$

The probability that A and B have a relative velocity $v_r > \sqrt{2\varepsilon/\mu_{AB}}$ is found by integrating Eq. (11.42) from $v_r = \sqrt{2\varepsilon/\mu_{AB}}$ to $v_r = \infty$ and integrating over all angles. Thus,

$$\begin{aligned} \text{Prob}\left(v_r > \sqrt{\frac{2\varepsilon}{\mu_{AB}}}\right) &= \left(\frac{\beta\mu_{AB}}{2\pi}\right)^{3/2} \int_0^{\pi} d\theta \int_0^{2\pi} d\phi \int_{\sqrt{2\varepsilon/\mu_{AB}}}^{\infty} dv_r v_r^2 \sin\theta \\ &\quad \times e^{-(\beta/2)(\mu_{AB}v_r^2)} \\ &= f(\beta,\varepsilon)e^{-\beta\varepsilon}. \end{aligned} \tag{11.43}$$

The probability that a reaction takes place depends exponentially on the activation energy. The quantity $f(\beta\varepsilon)$ is a function of temperture and activation energy. Its form is not important here.

We can now write the following qualitative expression for the rate of reaction of A and B. The number of reacting molecules, $\dot{N}_R$, per second per unit volume is

$$\dot{N}_R = K(\beta\varepsilon)\nu_{AB}e^{-\beta\varepsilon}, \tag{11.44}$$

where ν_{AB} is the collision frequency between molecules A and B, and the coefficient $K(\beta\varepsilon)$ depends on activation energy and temperature and may also depend on the geometry of the interacting molecules A and B. We may rewrite Eq. (11.44) in the form of a rate equation. If we let n_A denote the number of moles of A per unit volume and use Eq. (11.15), we can write

$$\frac{dn_A}{dt} = -K'(\varepsilon,\beta,\mu_{AB})d_{AB}^2 e^{-\beta\varepsilon} n_A n_B \equiv -k_{AB}n_A n_B. \tag{11.45}$$

In Eq. (11.45), $K'(\varepsilon\beta\mu_{AB})$ is a function of ε, β, and μ_{AB} and may depend on the geometry of A and B. The quantity k_{AB} is called the rate constant for the reaction. It depends exponentially on the activation energy. We see that the activation energy is the most important quantity in determining the rate of a chemical reaction, since a small change in ε can cause a large change in k_{AB}. Equation (11.45) gives the rate of decrease of A in the fluid due to the reaction $A + B \to C + D$. It is a second-order rate equation because it depends on the square of the molar density of species in the fluid. It is the simplest form of rate equation one can have because the rate of change in the concentration of A is

determined by only one reaction. There will often be a number of competing reactions taking place in the fluid which determine the rate of change in the concentration of a given type of molecule. Then the rate equation for a given reaction can be a more complicated function of the concentrations.

In general, the expression describing a given chemical reaction is written in the form

$$-\nu_A A - \nu_B B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \nu_C C + \nu_D D \tag{11.46}$$

where ν_i are the stoichiometric coefficients and tell us how many molecules of each species must combine to enable the reaction to take place. By convention, the stoichiometric coefficients on the left-hand side are negative and those on the right-hand side are positive. The constant k_1 is the rate constant for the forward reaction and k_2 is the rate constant for the backward reaction. The rate of change of A can, in general, be written

$$\frac{dn_A}{dt} = -k_1 n_A^{|\nu_A|} n_B^{|\nu_B|} + k_2 n_C^{\nu_c} n_D^{\nu_c} \tag{11.47}$$

where $|\nu_A|$ denotes the absolute value of ν_A.

When more than one reaction contributes to the rate of change of a given species, the rate equations can become more complicated. For example, the simple process $A \rightarrow B + C$ cannot be explained using collision theory. One must introduce an intermediate in the process. Consider the following two reactions:

$$2A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A + A^* \tag{11.48}$$

and

$$A^* \xrightarrow{k_3} B + C. \tag{11.49}$$

Two molecules, A, collide to form one A an an excited A^*. A^* then decays into B and C. The rate equations for this process may be written

$$\frac{dn_A}{dt} = -k_1 n_A^2 + k_2 n_A n_{A^*}, \tag{11.50}$$

$$\frac{dn_{A^*}}{dt} = k_1 n_A^2 - k_2 n_A n_{A^*} - k_3 n_{A^*}, \tag{11.51}$$

and

$$\frac{dn_B}{dt} = k_3 n_{A^*}. \tag{11.52}$$

We can solve Eqs. (11.50)–(11.52) if we make the assumption that the concentration of A^* is roughly constant—that is, that the rate of formation of A^* is equal to the rate of decay of A^*. Then

$$\frac{dn_{A^*}}{dt} = 0 \Rightarrow n_{A^*} = \frac{k_1 n_A^2}{k_3 + k_2 n_A}. \tag{11.53}$$

With Eq. (11.53), we obtain the following equation for the rate of increase of n_B:

$$\frac{dn_B}{dt} = \frac{k_1 k_3 n_A^2}{k_3 + k_2 n_A}. \tag{11.54}$$

If $k_3 \gg k_2 n_A$, then $dn_B/dt \approx k_1 n_A^2$ and the rate of formation of B looks as if it were governed by the process $2A \xrightarrow{k_1} B + C$. If $k_2 n_A \gg k_3$, then $dn_B/dt = (k_1 k_3/k_2) n_A$ and the rate of formation of B looks as if it were governed by the process $A \xrightarrow{k'} B + C$, where $k' = k_1 k_3/k_2$.

In general, more than one chemical reaction will contribute to the rate of formation or depletion of a given molecule. As we can see from the above example, experimental measurement of the rate equations is not always sufficient for determining the type of chemical processes which are occurring in a fluid.

Now that we have built some intuition about the transport coefficients, we will derive microscopic expressions for them based on a more rigorous microscopic theory—that is, one based on the Boltzmann equation.

11.C. THE BOLTZMANN EQUATION [4–8]

Until now, we have treated transport processes from a phenomenological point of view and we have obtained very simple expressions for the transport coefficients which are independent of the detailed form of the interaction. Most of the rest of this chapter will be devoted to a derivation of the transport coefficients starting from a kinetic equation similar to that in Eq. (6.75), which is an exact equation for the one-body reduced probability density. However, Eq. (6.75) cannot be solved exactly. In practice, we try to obtain an approximation to it which contains the important physical features of the system we are considering. In subsequent sections, we shall be interested in one of the simplest types of nonequilibrium systems—a dilute gas of particles which interacts via a short-range, spherically symmetric interaction potential. We shall assume that inhomogeneities in the gas are slowly varying. The form of the kinetic equation which gives the time evolution of the probability density of such a system is called the Boltzmann equation. Although it can be derived directly from Eq. (6.75) the arguments are rather long and tedious. In this

section, we shall derive the Boltzmann equation from simple physical arguments.

Let us consider a dilute gas of particles of mass, m, which interact via a spherically symmetric potential $\phi(|\mathbf{q}_i - \mathbf{q}_j|)$. We shall assume that the time a particle spends between collisions is very much longer than the duration of a collision. We shall describe the behavior of the system in terms of a number density $f(\mathbf{p}, \mathbf{q}, t)$ rather than a probability density. The distribution function, $f(\mathbf{p}, \mathbf{q}, t)$, gives the number of particles in the six-dimensional phase space volume element $\mathbf{p} \to \mathbf{p} + d\mathbf{p}$, $\mathbf{q} \to \mathbf{q} + d\mathbf{q}$. It is related to the reduced probability density $\rho_1(\mathbf{p}, \mathbf{q}, t)$ and the distribution function $F_1(\mathbf{p}, \mathbf{q}, t)$ through the relation

$$f(\mathbf{p}, \mathbf{q}, t) \equiv N\rho_1(\mathbf{p}, \mathbf{q}, t) = \frac{N}{V} F_1(\mathbf{p}, \mathbf{q}, t) \tag{11.54}$$

($\rho_1(\mathbf{p}, \mathbf{q}, t)$) and $F_1(\mathbf{p}, \mathbf{q}, t)$ are defined in Section S6.A).

Let us now consider a volume element, $\Delta V_1 = d\mathbf{p}_1 \Delta\mathbf{r}$, lying in the region $\mathbf{p}_1 \to \mathbf{p}_1 + d\mathbf{p}_1$, $\mathbf{r} \to \mathbf{r} + \Delta\mathbf{r}$ of the six-dimensional phase space. We shall assume the volume element $\Delta\mathbf{r}$ is large enough to contain many particles and small enough that the distribution function $f(\mathbf{p}, \mathbf{r}, t)$ does not vary appreciably over $\Delta\mathbf{r}$. We wish to find an equation for the rate of change of number of particles in ΔV_1. This change will be due to free streaming of particles into (and out of) ΔV_1 and to scattering of particles into (and out of) ΔV_1 because of collisions. The rate of change of $f(\mathbf{p}_1, \mathbf{r}, t)$ may be written in the form

$$\frac{\partial f_1}{\partial t} = -\dot{\mathbf{q}}_1 \cdot \frac{\partial f_1}{\partial \mathbf{q}_1} + \left.\frac{\partial f_1}{\partial t}\right|_{\text{collisions}}. \tag{11.55}$$

The first term on the right is the contribution due to streaming (flow through the surface of ΔV_1), and the second term is the contribution due to collisions. If an external field were present, then an additional streaming term of the form $-\dot{\mathbf{p}}_1 \cdot \partial f_1 / \partial \mathbf{p}_1$ would be present on the right.

We shall assume that the gas is dilute enough that only two-body collisions need be considered. Furthermore, we shall assume that all collisions are elastic. Before we can write an expression for $\partial f / \partial t|_{\text{coll}}$, we must review some aspects of two-body scattering theory.

11.C.1. Two-Body Scattering [9]

In this section we shall review those aspects of two-body scattering theory necessary to derive the Boltzmann equation. We first discuss the dynamics of the scattering process and then derive an expression for the scattering cross section. We shall restrict ourselves to elastic scattering processes.

11.C.1.1. Dynamics of the Scattering Process

We consider two particles, one with mass m_1 and displacement $\mathbf{r}_1(t)$ at time. t, and another with mass m_2 and displacement $\mathbf{r}_2(t)$ at time t. The particles interact via a short-range interaction, $V(|\mathbf{r}_2 - \mathbf{r}_1|)$. It is useful to introduce the relative displacement, $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$, and the center-of-mass displacement, $\mathbf{R} = (m_1/M)\mathbf{r}_1 + (m_2/M)\mathbf{r}_2$, where $M = m_1 + m_2$ is the total mass. They are related through the equations (cf. Fig. 11.5)

$$\mathbf{r}_1 = \mathbf{R} - \frac{m_2}{M}\mathbf{r} \quad \text{and} \quad \mathbf{r}_2 = \mathbf{R} + \frac{m_1}{M}\mathbf{r}. \tag{11.56}$$

The momenta of particles 1 and 2 are $\mathbf{P}_1$ and $\mathbf{P}_2$, respectively. The center of mass momentum is $\mathbf{P} = \mathbf{p} + \mathbf{p}_2$. The relative momentum is $\mathbf{p} = (m_1/M)\mathbf{p}_2 - (m_2/M)\mathbf{p}_1$.

The total Hamiltonian for the system can be written

$$H_{tot} = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V(|\mathbf{r}_2 - \mathbf{r}_1|) = \frac{P^2}{2M} + \frac{p^2}{2\mu} + V(|\mathbf{r}|) = E_{tot}. \tag{11.57}$$

The Hamiltonian decomposes into a part that depends only on the center-of-mass coordinates, $H_{cm} = P^2/2M = E_{cm}$, and a part that depends only on the relative coordinates, $H = p^2/2\mu + V(r) = E$, so $H_{tot} = H_{cm} + H$. Therefore, the center-of-mass motion evolves independently from the relative motion. From Hamilton's equation, $\dot{\mathbf{P}} = -\partial H_{tot}/\partial \mathbf{R} = 0$, so the center-of-mass momentum, $\mathbf{P} = \mathbf{p}_1 + \mathbf{p}_2$, is a constant of the motion.

We will assume that the scattering is elastic, so the total kinetic energy, $p_1^2/2m_1 + p_2^2/2m_2$, is conserved. Because the potential, $V(|\mathbf{r}_2 - \mathbf{r}_1|)$, is sphericlly symmetric (it depends only on the distance, $|\mathbf{r}_2 - \mathbf{r}_1|$), the total angular momentum vector, $\mathbf{L} = \mathbf{r}_1 \times \mathbf{p}_1 + \mathbf{r}_2 \times \mathbf{p}_2$, is a constant of the motion.

Let us assume that initially the particles are far apart and free but approach one another with momenta, $\mathbf{p}_1$ and $\mathbf{p}_2$, in the lab frame. Once they approach close enough to feel the interaction, the scattering process begins and their momenta will be altered. After the collision process is finished, they fly apart

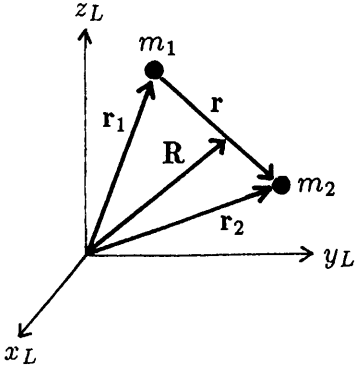


Fig. 11.5. Relation between lab frame coordinates and center-of-mass and relative coordinates.

with final momenta, $\mathbf{p}_1'$ and $\mathbf{p}_2'$. Conservation of momentum and of kinetic energy (for elastic processes) then gives

$$\mathbf{P}_{cm} = \mathbf{p}_1 + \mathbf{p}_2 = \mathbf{p}_1' + \mathbf{p}_2' \tag{11.58}$$

and

$$\frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} = \frac{p_1'^2}{2m_1} + \frac{p_2'^2}{2m_2}, \tag{11.59}$$

respectively. One can combine Eqs. (11.58) and (11.59) to show that for elastic collisions, the *magnitude* of the relative velocity, $|\mathbf{v}_2 - \mathbf{v}_1|$, is unchanged by the collision. The relative velocities *before* and *after* the collision are $\mathbf{g} = \mathbf{v}_2 - \mathbf{v}_1$ and $\mathbf{g}' = \mathbf{v}_2' - \mathbf{v}_1'$, respectively. Then for elastic collisions

$$g = |\mathbf{g}| = |\mathbf{g}'|, \tag{11.60}$$

where g is the magnitude of the relative velocity before and after the collision.

Because angular momentum is conserved, the scattering process occurs in a plane perpendicular to the angular momentum vector. We can choose the z axis to lie along the angular momentum vector. Then, the scattering process takes place in the x–y plane. If we introduce polar coordinates $x = r\cos(\phi)$ and $y = r\sin(\phi)$, the relative Hamiltonian can be written

$$H = p^2/2\mu + V(r) = \frac{1}{2\mu}\left(p_r^2 + \frac{p_\phi^2}{r^2}\right) + V(r) = E, \tag{11.61}$$

where $p_r = \mu\dot{r}$ and $p_\phi = \mu r^2\dot{\phi}$. Hamilton's equation take the form

$$\begin{aligned} \frac{dp_r}{dt} &= -\frac{\partial H}{\partial r} = \frac{p_\phi^2}{\mu r^3} - \frac{\partial V}{\partial r}, & \frac{dr}{dt} &= \frac{\partial H}{\partial p_r} = \frac{p_r}{\mu}, \\ \frac{dp_\phi}{dt} &= -\frac{\partial H}{\partial \phi} = 0, & \frac{d\phi}{dt} &= \frac{\partial H}{\partial p_\phi} = \frac{p_\phi}{\mu r^2}. \end{aligned} \tag{11.62}$$

Since $dp_\phi/dt = 0$, the magnitude of angular momentum, p_ϕ, is a constant of the motion. We therefore set $p_\phi = l$, where l is a constant. Since $d\phi/dt = l/\mu r^2$, we can write

$$d\phi = \frac{l}{\mu r^2}dt = \frac{l}{r^2}\frac{dr}{p_r} = \frac{(l/r^2)dr}{\sqrt{2\mu(E - V(r)) - l^2/r^2}}. \tag{11.63}$$

Equation (11.63) relates the polar angle, ϕ, to the distance between the particles at any time during the scattering process.

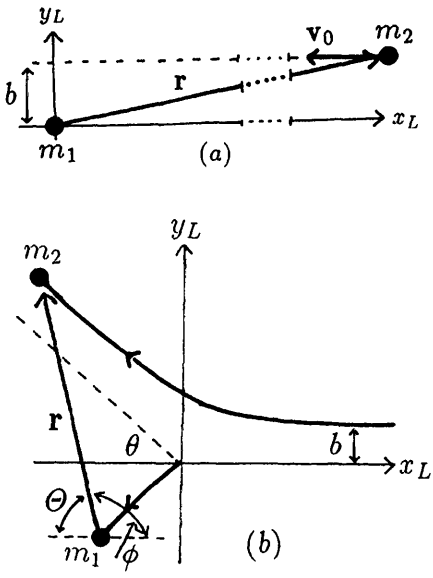


Fig. 11.6. Scattering in the lab frame. (a) $t = -\infty$. (b) $t = +\infty$.

Let us now consider the scattering process in more detail. Let us assume that at time $t = -\infty$, mass m_1 is at rest at the origin and mass m_2 has coordinates $x = +\infty$ and $y = b$ and is moving parallel to the x axis in the negative x direction with a velocity $\mathbf{v}_2 = \mathbf{v}_0 = -v_0\hat{\mathbf{x}}$. The quantity b is the *impact parameter.* Thus, at time $t = -\infty$ we have $(\mathbf{r}_1 = 0, \mathbf{v}_1 = 0, \mathbf{r}_2 = \infty\hat{\mathbf{x}} + b\,\hat{\mathbf{y}}, \mathbf{v}_2 = -v_0\hat{\mathbf{x}})$ (cf. Fig. 11.6a). The center-of-mass velocity is $\mathbf{V}_{cm} = m_2\mathbf{v}_0/M = \mu\mathbf{v}_0/m_1$ and the relative velocity is $\mathbf{v} = -v_0\hat{\mathbf{x}}$. The total angular momentum is $\mathbf{L} = \mathbf{r}_1 \times \mathbf{p}_1 + \mathbf{r}_2 \times \mathbf{p}_2 = -m_2 v_0 b\hat{\mathbf{z}}$. The angular momentum can also be divided into center-of-mass angular momentum, $\mathbf{L}_{cm} = M\mathbf{R} \times \mathbf{V}_{cm}$, and relative angular momentum, $\mathbf{L}_{rel} = \mu\mathbf{r} \times \mathbf{v} = \mu b v_0\hat{\mathbf{z}}$, so that $\mathbf{L} = \mathbf{L}_{cm} + \mathbf{L}_{rel}$. Since the magnitude of the relative velocity, $g = v_0$, is unchanged by the collision, the impact parameter, b, is the same before and after the collision. Therefore, g and b are intrinsic parameters of the elastic collision processes.

At the end of the scattering event, the particles move apart with constant relative velocity. At time $t = -\infty$ we have $\phi = 0$. At time $t = +\infty$ we have $\phi = \phi_f$. The angle, Θ, between the incident relative velocity and the final relative velocity is called the *scattering angle* and it satisfies the relation $\Theta = \pi - \phi_f$ (cf. Fig. 11.6).

It is useful to view the scattering process from the center-of-mass frame of reference, which is the reference frame in which the origin of coordinates is fixed to the center of mass and moves with it. In the center-of-mass frame, the displacement of m_1 is $\mathbf{r}_{1,c} = -m_2\mathbf{r}/M$ and the displacement of m_2 is $\mathbf{r}_{2,c} = m_1\mathbf{r}/M$. Similarly, their velocities are $\mathbf{v}_{1,c} = -m_2\mathbf{v}/M$ and $\mathbf{v}_{2,c} = m_1\mathbf{v}/M$, respectively. The relation between the final velocities, $\mathbf{v}_2'$ and $\mathbf{v}_{2,c}' = m_1\mathbf{g}'/M$, of mass m_2 in the lab frame and center-of-mass frames,

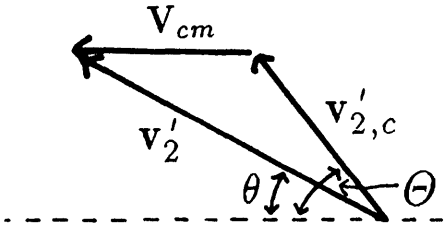


Fig. 11.7. Relation between lab frame velocity, v_2', and center-of-mass frame velocity, $v_{2,c}'$, of mass m_2.

respectively, is shown in Fig. 11.7. From this figure we can relate the scattering angles, θ and Θ, as seen from the lab and center-of-mass frames, respectively. Equating components of the vectors in Figure 11.7, we find

$$v_{2,c}'\sin(\Theta) = v_2'\sin(\theta), \tag{11.64}$$

and

$$v_{2,c}'\cos(\Theta) + V_{cm} = v_2'\cos(\theta). \tag{11.65}$$

We can combine these equations to obtain

$$\cos(\theta) = \frac{\xi + \cos(\Theta)}{\sqrt{1 + \xi^2 + 2\xi\cos(\Theta)}}, \tag{11.66}$$

where $\xi = V_{cm}/v_{2,c}'$. The magnitude of the center-of-mass velocity is $V_{cm} = \mu v_0/m_1$. Also, for elastic collisions we have $v_{2,c}' = m_1 v_0/M$ and $\xi = m_2/m_1$. It is useful now to introduce the concept of scattering cross section.

11.C.2.2. The Scattering Cross Section

The scattering problem may be viewed in the lab frame as that of a beam of particles of mass, m_2, incident on a mass, m_1, which is at rest. Let I be the intensity of the incident beam (number of incident particles/time-area). Consider a circular area element of the incident beam consisting of those particles with impact parameter in the interval $b \to b + db$ and azimuthal angle element $d\alpha$ (cf. Fig. 11.8). These particles are scattered into the solid angle $d\omega = \sin(\theta)d\theta d\alpha$ in the lab frame and into the solid angle $d\Omega = \sin(\Theta)d\Theta d\alpha$ in the center-of-mass frame. The angle, α, is the same in the two frames. The number of particles/time, $d\dot{N}$, scattered into the solid angle $d\omega = \sin(\theta)d\theta d\alpha$ in the lab frame and into the solid angle $d\Omega = \sin(\Theta)d\Theta d\alpha$ in the center-of-mass frame is given by (α is the azimuthal angle)

$$d\dot{N} = Ibdbd\alpha = I\sigma_{lab}\sin(\theta)d\theta d\alpha = I\sigma_{cm}\sin(\Theta)d\Theta d\alpha, \tag{11.67}$$

where $\sigma_{lab} = \sigma_{lab}(g, b)$ and $\sigma_{cm} = \sigma_{cm}(g, b)$ are the differential scattering cross setions in the lab and center-of-mass frames, respectively. Equation (11.67)

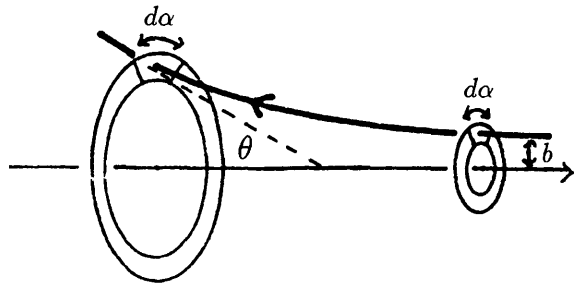


Fig. 11.8. Relation between the impact parameter and the scattering angle in the lab frame.

gives the relation between the impact parameter, b, and either the lab frame differential cross section, σ_{lab}, or the center-of-mass differential cross section, σ_{cm}:

$$\sigma_{lab} = \left| \frac{bdb}{\sin(\theta)d\theta} \right| \quad \text{and} \quad \sigma_{cm} = \left| \frac{bdb}{\sin(\Theta)d\Theta} \right|. \tag{11.68}$$

The differential scattering cross section is independent of α because of the spherical symmetry of the potential. As b increases, θ and Θ decrease. The absolute value signs in Eq. (11.68) are necessary for positive cross sections.

The total scattering cross section, σ_{tot}, is given by

$$\sigma_{tot} = \int_0^{\pi} \sin(\Theta)d\Theta \int_0^{2\pi} d\alpha \sigma_{cm}(b,g) = \int_0^{\pi} \sin(\theta)d\theta \int_0^{2\pi} d\alpha \sigma_{lab}(b,g). \tag{11.69}$$

The scattering cross section can be thought of as the effective area cutout of the incident beam by the scattering process. This is clear in Exercise 11.1, where we compute the cross section for an incident beam of hard-sphere particles colliding with a fixed hard sphere.

From Eqs. (11.66) and (11.68), the relation between the differential scattering cross sections in the center of mass and the lab frames is given by

$$\sigma_{lab} = \frac{\sigma_{cm}[1 + \xi^2 + 2\xi\cos(\Theta)]^{3/2}}{(1 + \xi\cos(\Theta))}. \tag{11.70}$$

In Fig. 11.9 we picture the scattering process in the center-of-mass frame of reference. In the center-of-mass frame, the scattering event, $(\mathbf{p}_1, \mathbf{p}_2) \rightarrow (\mathbf{p}_1', \mathbf{p}_2')$, and the reverse scattering event, $(\mathbf{p}_1', \mathbf{p}_2') \rightarrow (\mathbf{p}_1, \mathbf{p}_2)$, are identical except that the directions of the particles are reversed. Therefore, $\sigma_{cm}(b,g)$ is the differential scattering cross section for both the forward and the reverse scattering events in the center-of-mass frame.

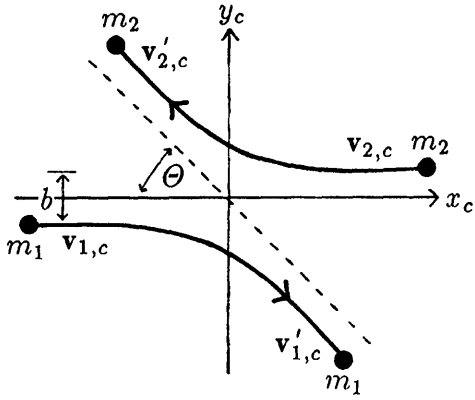
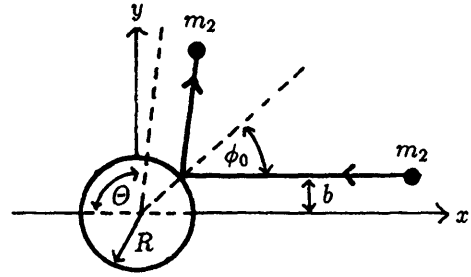


Fig. 11.9. Scattering process as viewed from the center-of-mass frame. Here $\mathbf{v}_{1,c} = -m_2\mathbf{g}/M$, $\mathbf{v}'_{1,c} = -m_2\mathbf{g}'/M$, $\mathbf{v}_{2,c} = m_1\mathbf{g}/M$, and $\mathbf{v}'_{2,c} = m_1\mathbf{g}'/M$.

■ **EXERCISE 11.1.** Compute the total scattering cross section for elastic scattering of a point particle of mass m off of a hard sphere of radius R which is fixed in position. Assume that the incident particle has velocity $\mathbf{v}_0$ and impact parameter b.

Answer: The fact that the hard sphere is fixed in position means that it, in effect, has an infinite mass and $\mathbf{v}_1 = 0$. If we let $m_2 = m$ and $m_1 = \infty$, we find $V_{cm} = 0$. Therefore, $\xi = 0$ and the scattering angles in the center-of-mass and lab frames are equal, $\cos(\theta) = \cos(\Theta)$. Also the collision cross sections in the center-of-mass and lab frames are equal, $\sigma_{lab} = \sigma_{cm}$.

The collision process is shown in the accompanying figure.



Let ϕ_0 be the angle of closest approach. Then the scattering angle is given by $\Theta = \pi - 2\phi_0$. The impact parameter is $b = R\sin(\phi_0) = R\cos(\Theta/2)$ so that, $db = -(R/2)\sin(\Theta/2)d\Theta$ and $bdb = -(R^2/2)\sin(\Theta/2)\cos(\Theta/2)d\Theta = -(R^2/4)\sin(\Theta)d\Theta$. Therefore

$$\sigma_{cm}(b,g) = \left|\frac{b}{\sin(\Theta)}\frac{db}{d\Theta}\right| = \frac{R^2}{4}. \tag{1}$$

For this special case, the differential scattering cross section is independent of angle. The scattering is isotropic. The total cross section, σ_{tot}, is given by

$$\sigma_{tot} = \int_0^{\pi} \sigma_{cm}(b, g) 2\pi \sin(\Theta) d\Theta = \pi R^2. \tag{2}$$

Thus, the total cross section is just the area of the fixed scatterer as seen by the incoming beam.

■ **EXERCISE 11.2.** Compute the differential scattering cross section, σ_{cm}, for two particles of mass m_1 and m_2 which interact via a repulsive Coulomb force with potential $V(r) = \frac{\kappa}{r}$, where κ is a positive coupling constant. Assume that the incident particle has velocity $\mathbf{v}_0$ and impact parameter b.

Answer: For this scattering process, the angular momentum is a constant of the motion. Assume that the scattering process occurs in x–y plane. The Hamiltonian for relative motion, in polar coordinates, is

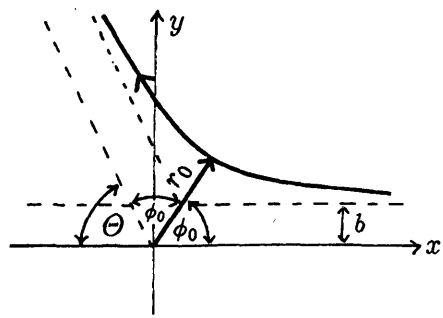
$$H = \frac{p_r^2}{2\mu} + \frac{l^2}{2\mu r^2} + \frac{\kappa}{r} = E, \tag{1}$$

where $\mu = m_1 m_2/(m_1 + m_2)$ is the reduced mass, p_r is the radial component of momentum, and $p_\phi = l$ is the magnitude of the angular momentum. We will assume that m_1 is initially at rest, and m_2 is incident from infinity with velocity $\mathbf{v}_0 = -v_0\hat{\mathbf{x}}$ and impact parameter b. The magnitude of p_r^2 can be written

$$p_r^2 = 2\mu E - \frac{2\mu\kappa}{r} - \frac{l^2}{r^2} = \frac{2\mu E}{r^2}\left[r^2 - \frac{l^2}{2\mu E} - \frac{\kappa r}{E}\right]. \tag{2}$$

The particles must climb a potential hill. The greater the initial kinetic energy, the closer they can get before the repulsive force causes them to move apart. The distance of closest approach, r_0, is the value of r for which $p_r = 0$. This is also called the *turning point*. From Eq. (2) we find $r_0 = (\kappa/2E)(1 + \sqrt{1 + 2l^2E/\mu\kappa})$.

The scattering process is shown in the accompanying figure.



The scattering process is symmetric about the point of closest approach. Let us make use of the relation, $d\phi = ldr/p_r r^2$ and integrate the relative distance from $r = \infty$ to $r = r_0$. Then we find

$$\phi_0 = \int_0^{\phi_0} d\phi = \int_\infty^{r_0} \frac{dr}{r\sqrt{2\mu E r^2 - 2\mu\kappa r - l^2}} = \sin^{-1}\left(\frac{1}{e}\right) - \frac{\pi}{2}, \tag{3}$$

where $e = \sqrt{1 + 2l^2E/\mu\kappa^2}$. The scattering angle, Θ, is related to the angle ϕ_0 through the relation $\Theta + 2\phi_0 = \pi$. From Eq. (3) we find $1/e = \sin(\Theta/2)$. This in turn leads to $\cot(\Theta/2) = \sqrt{e^2 - 1} = \sqrt{2El^2/\mu\kappa^2}$. However, the relative angular momentum is $l = \mu v_0 b = b\sqrt{2\mu E}$, so that $\cot(\Theta/2) = 2Eb/\kappa$. Thus, we find

$$b = \frac{\kappa}{2E}\cot\left(\frac{\Theta}{2}\right). \tag{4}$$

Equation (4) gives us a relation between the scattering angle, Θ, and the impact parameter, b, from which we can compute the differential scattering cross section. We find

$$\sigma_{cm} = \left|\frac{bdb}{\sin(\Theta)d\Theta}\right| = \frac{1}{4}\left(\frac{\kappa}{2E}\right)^2 \frac{1}{\sin^4(\Theta/2)}. \tag{5}$$

Equation (5) is the Rutherford formula for repulsive scattering between two electrically charged particles. The Coulomb force is too long-ranged for the arguments leading to the derivation of the Boltzmann equation to apply. An interaction potential is considered short-ranged if it falls off faster than $1/r^2$.

11.C.2. Derivation of the Boltzmann Equation

Let us denote the rate of particles scattered out of ΔV_1 by $(\partial f_-/\partial t)\Delta\mathbf{r}d\mathbf{p}_1$. The number of particles in ΔV_1 at time t with coordinates $\mathbf{p}_1 \to \mathbf{p}_1 + d\mathbf{p}_1$ and $\mathbf{r} \to \mathbf{r} + \Delta\mathbf{r}$ is $f(\mathbf{p}_1, \mathbf{r}, t)\Delta\mathbf{r}d\mathbf{p}_1$. All particles of momentum $\mathbf{p}_2$ lying within a cylinder of volume $d\mathbf{q}_2 = 2\pi bdbgdt$ collide with particles $\mathbf{p}_1$ in time dt. The number of such particles is $f(\mathbf{p}_2, \mathbf{r}, t)2\pi bdbgdtd\mathbf{p}_2$. The total number of collisions, $N(\mathbf{p}_1\mathbf{p}_2 \to \mathbf{p}_1'\mathbf{p}_2')$, per unit volume in time dt between particles of momentum $\mathbf{p}_1$ and particles of momentum $\mathbf{p}_2$ resulting in new momenta $\mathbf{p}_1'$ and $\mathbf{p}_2'$ is given by

$$N(\mathbf{p}_1\mathbf{p}_2 \to \mathbf{p}_1'\mathbf{p}_2') = 2\pi gb\, db\, dt\, f(\mathbf{p}_2, \mathbf{r}, t)f(\mathbf{p}_1, \mathbf{r}, t)d\mathbf{p}_1 d\mathbf{p}_2. \tag{11.71}$$

In Eq. (11.71) we have assumed that the distribution functions do not change appreciably in position space for the volume element ΔV_1 we are considering.

Also, we have assumed that the particles $\mathbf{p}_1$ and $\mathbf{p}_2$ are completely uncorrelated. This assumption is called *molecular chaos*, or *Stosszahl-Ansatz*.

In analogy to Eq. (11.71) we may write for the inverse scattering process

$$N(\mathbf{p}_1', \mathbf{p}_2' \rightarrow \mathbf{p}_1, \mathbf{p}_2) = 2\pi g b \, db \, dt \, f(\mathbf{p}_1', \mathbf{r}, t) f(\mathbf{p}_2', \mathbf{r}, t) d\mathbf{p}_1' d\mathbf{p}_2'. \tag{11.72}$$

For elastic collisions, $d\mathbf{p}_1 d\mathbf{p}_2 = d\mathbf{p}_1' d\mathbf{p}_2'$. (This is easily proved if we note that $d\mathbf{p}_1 d\mathbf{p}_2 = d\mathbf{P} d\mathbf{p}$ and $d\mathbf{p}_1' d\mathbf{p}_2' = d\mathbf{P}' d\mathbf{p}'$. Furthermore, for elastic collisions, $d\mathbf{P} = d\mathbf{P}'$ and $p^2 dp = p'^2 dp'$. Therefore, $d\mathbf{p}_1 d\mathbf{p}_2 = d\mathbf{p}_1' d\mathbf{p}_2'$.) We may now combine Eqs. (11.67), (11.71) and (11.72) to obtain the following expression for the net increase, $(\partial f_1/\partial t)_{\text{coll}} d\mathbf{p}_1$, in number of particles with momentum $\mathbf{p}_1 \rightarrow \mathbf{p}_1 + d\mathbf{p}_1$ per unit volume per unit time:

$$\left(\frac{\partial f_1}{\partial t}\right)_{\text{coll}} d\mathbf{p}_1 = d\mathbf{p}_1 \int d\mathbf{p}_2 \int d\Omega g \sigma_{cm}(b, g) \times \left(f(\mathbf{p}_1', \mathbf{r}, t) f(\mathbf{p}_2', \mathbf{r}, t) - f(\mathbf{p}_1, \mathbf{r}, t) f(\mathbf{p}_2, \mathbf{r}, t)\right), \tag{11.73}$$

where $d\Omega = \sin(\Theta) d\Theta d\alpha$, and σ_{cm} is the center-of-mass collision cross section. If we now combine Eqs. (11.55) and (11.73), we obtain

$$\frac{df_1}{\partial t} + \dot{\mathbf{q}}_1 \cdot \frac{\partial f_1}{\partial \mathbf{r}} = \int d\mathbf{p}_2 \int d\Omega g \sigma_{cm}(b, g)(f_{1'} f_{2'} - f_1 f_2), \tag{11.74}$$

where $f_i = f(\mathbf{p}_i, \mathbf{r}, t)$. Equation (11.74) is *the Boltzmann equation*. Note that we have written the second term with $\partial f_1/\partial \mathbf{r}$ rather than $\partial f_1/\partial \mathbf{q}_1$ (cf. Eq. 11.55) to indicate that Eq. (11.74) is valid for long wavelength disturbances. Since $f(\mathbf{p}, \mathbf{q}, t) = (N/V) F_1(\mathbf{p}, \mathbf{q}, t)$, the Boltzmann equation has the same form as the exact kinetic equation (6.75) except that the right-hand side is expressed entirely in terms of the one-particle distribution function, $f(\mathbf{p}_i, \mathbf{r}, t)$. The Boltzmann equation is a nonlinear integrodifferential equation for $f(\mathbf{p}_i, \mathbf{r}, t)$.

11.C.3. Boltzmann's *H* Theorem [4]

Boltzmann's equation describes the time evolution of the distribution of particles in six-dimensional phase space for a dilute gas with inhomogeneities which are slowly varying in position space. If no external fields drive the system, it should decay to equilibrium after a long time. Boltzmann's equation describes such behavior. To show this, Boltzmann introduced a function $H(t)$ which he defined as

$$H(t) = \int\int d\mathbf{q}_1 d\mathbf{p}_1 f(\mathbf{p}_1, \mathbf{q}_1, t) \ln f(\mathbf{p}_1, \mathbf{q}_1, t). \tag{11.75}$$

He then showed that if $f(\mathbf{p}_1, \mathbf{q}_1, t)$ satisfies the Boltzmann equation, $H(t)$ always decreases because of the effect of collisions. The proof goes as follows. We first

take the derivative of $H(t)$:

$$\frac{\partial H}{\partial t} = \int\int d\mathbf{p}_1, d\mathbf{q}_1 \frac{\partial f_1}{\partial t}[\ln f_1 + 1] \tag{11.76}$$

and then substitute Eq. (11.74) into Eq. (11.76). This gives

$$\begin{aligned}\frac{\partial H}{\partial t} = &- \int\int d\mathbf{p}_1, d\mathbf{q}_1 \left(\dot{\mathbf{q}}_1 \cdot \frac{\partial f_1}{\partial \mathbf{q}_1}\right)[\ln f_1 + 1] \\ &+ \int d\mathbf{q}_1 \int d\mathbf{p}_1 \int d\mathbf{p}_2 \int d\Omega g \sigma_{cm}(b, g)(f_{1'} f_{2'} - f_1 f_2)[\ln f_1 + 1].\end{aligned} \tag{11.77}$$

We next change the first term on the right-hand side into a surface integral and assume that for large $\mathbf{p}_1$ and $\mathbf{q}_1$ we have $f(\mathbf{p}_1, \mathbf{q}_1, t) \to 0$. With this assumption the first term on the right-hand side gives no contribution and we have

$$\frac{\partial H}{\partial t} = \int d\mathbf{q}_1 \int d\mathbf{p}_1 \int d\mathbf{p}_2 \int d\Omega g \sigma_{cm}(b, g)(f_{1'} f_{2'} - f_1 f_2)[\ln f_1 + 1]. \tag{11.78}$$

We now can rewrite Eq. (11.78). If we interchange coordinates $\mathbf{p}_1$ and $\mathbf{p}_2$ we obtain

$$\frac{\partial H}{\partial t} = \int d\mathbf{q}_1 \int d\mathbf{p}_1 \int d\mathbf{p}_2 \int d\Omega g \sigma_{cm}(b, g)(f_{1'} f_{2'} - f_1 f_2)[\ln f_2 + 1]. \tag{11.79}$$

We next add Eqs. (11.78) and (11.79) and divide by two to obtain

$$\frac{\partial H}{\partial t} = \frac{1}{2}\int d\mathbf{q}_1 \int d\mathbf{p}_1 \int d\mathbf{p}_2 \int d\Omega g \sigma_{cm}(b, g)(f_{1'} f_{2'} - f_1 f_2)[\ln f_1 + \ln f_2 + 2]. \tag{11.80}$$

As a final step, we make a change of dummy variables $\mathbf{p}_1 \leftrightarrow \mathbf{p}_1'$ and $\mathbf{p}_2 \leftrightarrow \mathbf{p}_2'$ in Eq. (11.80), add the result to Eq. (11.80) and divide by two. If we remember that $d\mathbf{p}_1 d\mathbf{p}_2 = d\mathbf{p}_1' d\mathbf{p}_2'$, we find

$$\frac{\partial H}{\partial t} = \frac{1}{4}\int d\mathbf{q}_1 \int d\mathbf{p}_1 \int d\mathbf{p}_2 \int d\Omega g \sigma_{cm}(b, g)(f_{1'} f_{2'} - f_1 f_2)\ln\frac{f_1 f_2}{f_{1'} f_{2'}} \leqslant 0. \tag{11.81}$$

Equation (11.81) is always less than or equal to zero since a function of the form $(y - x)\ln x/y$ is always less than or equal to zero.

The derivative $\partial H/\partial t$ will be zero only if $f_{1'} f_{2'} = f_1 f_2$ for all collisions. This is the condition of *detailed balance* and is the equilibrium condition for the gas. It can also be written in the form

$$\ln f_1 + \ln f_2 = \ln f_{1'} + \ln f_{2'}. \tag{11.82}$$

At equilibrium, the single particle distribution must be independent of absolute position in the gas. Thus, Eq. (11.82) is a condition which must be satisfied by some function of the momentum of particles before and after collisions. The only microscopic quantities that are conserved in a collision are the total momentum, the kinetic energy, and a constant (particle number). Therefore, in equilibrium $\ln f_1$ must be of the form

$$\ln f_1 = A + \mathbf{B} \cdot \mathbf{p}_1 + C\frac{p_1^2}{2m} \tag{11.83}$$

and f_1 reduces to

$$f_1(\mathbf{p}_1) \sim e^{A+\mathbf{B}\cdot\mathbf{p}_1+Cp_1^2/2m},$$

where A, $\mathbf{B}$, and C are constant. This is the general form of the Maxwell-Boltzmann distribution for a gas whose average momentum is not necessarily zero, and it is a stationary solution of the Boltzmann equation.

Since $H(t)$ always decreases with time, the negative of $H(t)$ will always increase with time. Boltzmann identified the following quantity as the nonequilibrium entropy $S(t)$:

$$S(t) = -k_B H(t) = -k_B \int\int d\mathbf{q}_1\, d\mathbf{p}_1\, f(\mathbf{p}_1, \mathbf{q}_1, t) \ln f(\mathbf{p}_1, \mathbf{q}_1, t). \tag{11.84}$$

This entropy differs from the Gibbs entropy in that it depends only on a reduced distribution function and not on the full distribution function as does the Gibbs entropy (cf. Section 7.A).

11.D. LINEARIZED BOLTZMANN AND LORENTZ–BOLTZMANN EQUATIONS

We wish to obtain microscopic expressions for the coefficient of self-diffusion, D, thermal conductivity, K, and shear viscosity, η for a two-component system whose distribution function varies in time and space according to the Boltzmann equation.

11.D.1. Kinetic Equations for a Two-Component Gas

Let us consider a dilute gas of identical particles and place a radioactive tracer on half of the particles but not change their properties in any other way. Then the dynamics of the two kinds of particles and the collision cross sections will be identical. The Boltzmann equation for the normal particles can be

written

$$\frac{\partial f_{1,N}}{\partial t} + \dot{\mathbf{q}}_1 \cdot \frac{\partial f_{1,N}}{\partial \mathbf{r}} = \sum_{\alpha,\beta,\gamma} \int d\mathbf{p}_2 \int d\Omega g \sigma(b,g)_{\alpha\beta:N\gamma} (f_{1',\alpha} f_{2',\beta} - f_{1,N} f_{2,\gamma}), \tag{11.85}$$

and for the tracer particles it can be written

$$\frac{\partial f_{1,T}}{\partial t} + \dot{\mathbf{q}}_1 \cdot \frac{\partial f_{1,T}}{\partial \mathbf{r}} = \sum_{\alpha,\beta,\gamma} \int d\mathbf{p}_2 \int d\Omega g \sigma(b,g)_{\alpha\beta:T\gamma} (f_{1',\alpha} f_{2',\beta} - f_{1,T} f_{2,\gamma}), \tag{11.86}$$

where the summations over α, β, and γ are over normal and tracer particles and we have used the notations $f_{1,N} = f_N(\mathbf{p}_1, \mathbf{r}, t)$ and $f_{1,T} = f_T(\mathbf{p}_1, \mathbf{r}, t)$. The number of tracer and normal particles is conserved during collisions. Thus, only the cross sections $\sigma_{NN:NN} = \sigma_{NT:NT} = \sigma_{TN:TN} = \sigma_{TT:TT} = \sigma$ are nonzero. Note that these are center-of-mass cross sections.

When we compute transport coefficients, it is sufficient to consider systems with small-amplitude disturbance from equilibrium. We then expand the normal and tracer particle distributions about absolute equilibrium. If we denote the normal particle equilibrium distribution by $f_N^0(\mathbf{p}_1)$ and the tracer particle equilibrium distribution by $f_T^0(\mathbf{p}_1)$, we have

$$f^0(\mathbf{p}_1) = f_N^0(\mathbf{p}_1) = f_T^0(\mathbf{p}_1) = \frac{n_0}{2} \left(\frac{\beta}{2\pi m}\right)^{3/2} e^{-\beta p_1^2/2m}. \tag{11.87}$$

We have assumed that there are $N/2$ tracer and $N/2$ normal particles in the system and have let $n_0 = N/V$.

As a first step in linearizing the Boltzmann equation, we can write

$$f_N(\mathbf{p}_1, \mathbf{r}, t) = f^0(\mathbf{p}_1)[1 + h_N(\mathbf{p}_1, \mathbf{r}, t)] \tag{11.88}$$

and

$$f_T(\mathbf{p}_1, \mathbf{r}, t) = f^0(\mathbf{p}_1)[1 + h_T(\mathbf{p}_1, \mathbf{r}, t)], \tag{11.89}$$

where $h_N(\mathbf{p}_1, \mathbf{r}, t)$ and $h_T(\mathbf{p}_1, \mathbf{r}, t)$ denote small amplitude disturbances in the normal particle and tracer particle distributions, respectively.

If we substitute Eqs. (11.88) and (11.89) into Eqs. (11.85) and (11.86), respectively, and neglect terms of second order or higher in $h_{N(T)}(\mathbf{p}_1, \mathbf{r}, t)$, we obtain

$$\left(\frac{\partial h_{1,N}}{\partial t} + \dot{\mathbf{q}}_1 \cdot \frac{\partial h_{1,N}}{\partial \mathbf{r}}\right) = \sum_{\alpha,\beta,\gamma} \int d\mathbf{p}_2 \int d\Omega g \sigma(b,g)_{\alpha\beta:N\gamma} f^0(\mathbf{p}_2) \times (h_{1',\alpha} + h_{2',\beta} - h_{1,N} - h_{2,\gamma}) \tag{11.90}$$

and

$$\left(\frac{\partial h_{1,T}}{\partial t} + \dot{\mathbf{q}}_1 \cdot \frac{\partial h_{1,T}}{\partial \mathbf{r}}\right) = \sum_{\alpha,\beta,\gamma} \int d\mathbf{p}_2 \int d\Omega g \sigma(b,g)_{\alpha\beta:T\gamma} f^0(\mathbf{p}_2) \times (h_{1',\alpha} + h_{2',\beta} - h_{1,T} - h_{2,\gamma}). \tag{11.91}$$

In Eqs. (11.90) and (11.91), we have used kinetic energy conservation to write $f^0(\mathbf{p}_1')f^0(\mathbf{p}_2') = f^0(\mathbf{p}_1)f^0(\mathbf{p}_2)$. Equations (11.90) and (11.91) are the linearized Boltzmann equations for the normal and tracer components, respectively.

We can now decouple diffusion effects from viscous and thermal effects. Let us define the total distribution function as

$$h^+(\mathbf{p}_1, \mathbf{r}, t) = h_N(\mathbf{p}_1, \mathbf{r}, t) + h_T(\mathbf{p}_1, \mathbf{r}, t) \tag{11.92}$$

and the distribution function for the difference in normal and tracer distribution as

$$h^-(\mathbf{p}_1, \mathbf{r}, t) = h_N(\mathbf{p}_1, \mathbf{r}, t) - h_T(\mathbf{p}_1, \mathbf{r}, t). \tag{11.93}$$

As long as $h^-(\mathbf{p}_1, \mathbf{r}, t)$ is nonzero, diffusion will occur in the field.

The equations of motion for the total distribution, $h^+(\mathbf{p}_1, \mathbf{r}, t)$, and for the difference distribution, $h^-(\mathbf{p}_1, \mathbf{r}, t)$, decouple. If we add Eqs. (11.90) and (11.91) we find

$$\frac{\partial h_1^+}{\partial t} + \dot{\mathbf{q}}_1 \cdot \frac{\partial h_1^+}{\partial \mathbf{r}} = 2 \int d\mathbf{p}_2 \int d\Omega g \sigma(b,g) f^0(\mathbf{p}_2)(h_{1'}^+ + h_{2'}^+ - h_1^+ - h_2^+), \tag{11.94}$$

which is just the *Boltzmann equation* for the total particle distribution. If we subtract Eq. (11.91) from (11.90), we find

$$\frac{\partial h_1^-}{\partial t} + \dot{\mathbf{q}}_1 \cdot \frac{\partial h_1^-}{\partial \mathbf{r}} = 2 \int d\mathbf{p}_2 \int d\Omega g \sigma(b,g) f^0(\mathbf{p}_2)(h_{1'}^- - h_1^-). \tag{11.95}$$

Equation (11.95) is called the *Lorentz–Boltzmann equation* and is the kinetic equation describing diffusion.

11.D.2. Collision Operators

It is convenient to introduce the concept of a linearized collision operator. Let us consider Eq. (11.94). We write it as

$$\frac{\partial h_1^+}{\partial t} + \dot{\mathbf{q}}_1 \cdot \frac{\partial h_1^+}{\partial \mathbf{r}} = \hat{C}_1^+ h_1^+, \tag{11.96}$$

where $\hat{C}_1^+$ is the *Boltzmann collision operator*, which, when acting on some arbitrary function $g(\mathbf{p}_1)$, yields

$$\hat{C}_1^+ g(\mathbf{p}_1) = 2\int d\mathbf{p}_2 \int d\Omega g\sigma(b,g) f^0(\mathbf{p}_2)(g_{1'} + g_{2'} - g_1 - g_2). \quad (11.97)$$

Let us now introduce a scalar product of two functions $\phi(\mathbf{p}_1)$ and $\chi(\mathbf{p}_1)$:

$$\langle \phi, \chi \rangle \equiv \left(\frac{\beta}{2\pi m}\right)^{3/2} \int d\mathbf{p}_1 e^{-\beta p_1^2/2m} \phi(\mathbf{p}_1)\chi(\mathbf{p}_1). \quad (11.98)$$

Using Eq. (11.98) it is easy to show that $\hat{C}^+$ is self-adjoint:

$$\langle \Phi, \hat{C}^+ \chi \rangle = \langle \hat{C}^+ \Phi, \chi \rangle \quad (11.99)$$

(we leave it as a homework problem).

If we write the eigenvalue equation for $\hat{C}^+$ in the form

$$\hat{C}_{\mathbf{p}}^+ \Psi(\mathbf{p}) = \lambda \Psi(\mathbf{p}), \quad (11.100)$$

we can show there are five eigenfunctions of $\hat{C}_{\mathbf{p}}^+$ with eigenvalue zero. They are the five additive constants of the motion: 1, $\mathbf{p}$, and $p^2/2m$. All other eigenvalues of $\hat{C}_{\mathbf{p}}^+$ are negative. We prove this by writing the expectation value of $\hat{C}_{\mathbf{p}}^+$ in the form

$$\langle \Phi, \hat{C}_{\mathbf{p}}^+ \Phi \rangle = -\frac{1}{4}\frac{N}{V}\left(\frac{\beta}{2\pi m}\right)^3 \int\int d\mathbf{p}_1 d\mathbf{p}_2 \int d\Omega e^{-(\beta/2m)(p_1^2+p_2^2)} \times g\sigma(b,g)(\Phi_{1'} + \Phi_{2'} - \Phi_1 - \Phi_2)^2. \quad (11.101)$$

Thus, $\langle \Phi, \hat{C}_{\mathbf{p}}^+ \Phi \rangle$ is less than or equal to zero for an arbitrary function $\Phi(\mathbf{p})$. It will be equal to zero only if $(\Phi_{1'} + \Phi_{2'} - \Phi_1 - \Phi_2) = 0$—that is, if $\Phi(\mathbf{p})$ is a linear combination of the five additive constants of motion 1, $\mathbf{p}$, and $p^2/2m$. Therefore, $\hat{C}_{\mathbf{p}}^+$ is a negative semidefinite operator with a nonpositive spectrum of eigenvalues.

The linearized collision operator $\hat{C}_{\mathbf{p}}^+$ has one other interesting property. It behaves as a scalar operator with respect to rotations in momentum space. That is, $\hat{C}_{\mathbf{p}}^+ h(\mathbf{p})$ transforms in the same way under rotation in momentum space as does $h(\mathbf{p})$. Therefore, eigenfunctions of $\hat{C}_{\mathbf{p}}^+$ have the form

$$\Psi_{r,l,m}(\mathbf{p}) = R_{r,l}(p) Y_{l,m}(\mathbf{p}/|\mathbf{p}|), \quad (11.102)$$

where $Y_{l,m}(\mathbf{p}/|\mathbf{p}|)$ are spherical harmonics.

Let us now consider a simple example. Let us solve the linearized Boltzmann equation (11.94) for the case of a spatially homogeneous system.

Equation (11.94) then becomes

$$\frac{\partial h_1^+}{\partial t} = \hat{C}_1^+ h_1^+ = 2\int d\mathbf{p}_2 \int d\Omega g\sigma(b,g) f_2^0 [h_{1'} + h_{2'} - h_1 - h_2], \qquad (11.103)$$

where $h_1^+ = h^+(\mathbf{p}_1, t)$, and so on. If we assume that $h_1^+(\mathbf{p}_1, 0) = \sum_{r,l,m} A_{r,l,m} \Psi_{r,l,m}(\mathbf{p}_1)$, we may write the solution in the form

$$h_1^+(\mathbf{p}_1, t) = \sum_{r,l,m} e^{\lambda_{r,l} t} A_{r,l,m} \Psi_{r,l,m}(\mathbf{p}_1). \qquad (11.104)$$

The fact that the eigenvalues $\lambda_{r,l}$ must all be negative or zero means that $h_1^+(\mathbf{p}_1, t)$ will decay to a time-independent quantity after long enough time and the system relaxes to equilibrium.

The *Lorentz–Boltzmann collision operator*, $\hat{C}_1^-$, appearing in the equation for the difference distribution has simpler structure than the Boltzmann collision operator. If we write

$$\frac{\partial h_1^-}{\partial t} + \dot{\mathbf{q}}_1 \cdot \frac{\partial h_1^-}{\partial \mathbf{r}} = \hat{C}_1^- h_1^-, \qquad (11.105)$$

the collision operator $\hat{C}_1^-$, when acting on an arbitrary function $\Phi(\mathbf{p}_1)$ of $\mathbf{p}_1$, yields

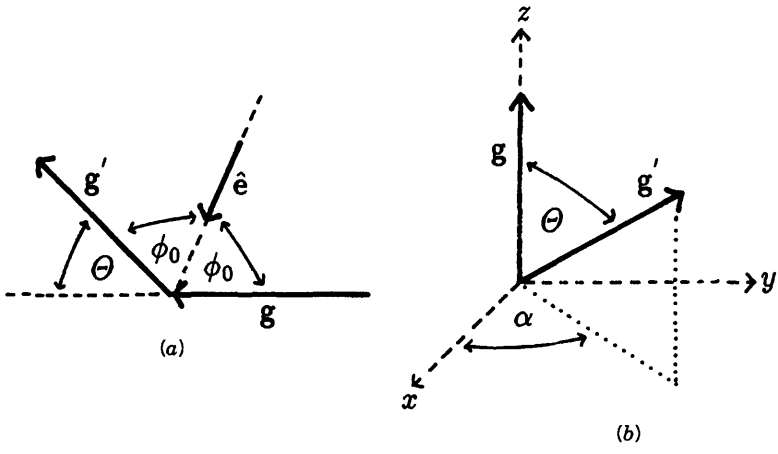
$$\hat{C}_1^- \Phi(\mathbf{p}_1) = 2\int d\mathbf{p}_2 \int d\Omega g\sigma(b,g) f_2^0 (\Phi_{1'} - \Phi_1). \qquad (11.106)$$

The Lorentz–Boltzman collision operator $\hat{C}_1^-$ differs from $\hat{C}_1^+$ in that it has only one zero eigenvalue, a constant, while the Boltzmann collision operator, $\hat{C}_1^+$, has a five fold degenerate zero eigenvalue.

We can use the Boltzmann and Lorentz–Boltzmann equations to obtain microscopic expressions for the coefficients of self-diffusion, viscosity, and thermal conductivity.

■ **EXERCISE 11.3.** Write $\langle \chi, \hat{C}^+ \chi \rangle$ in a form that makes explicit the conservation of kinetic energy and momentum during the collision process.

Answer: The relative velocity before the collision is $\mathbf{g} = \mathbf{v}_2 - \mathbf{v}_1$, and after the collision it is $\mathbf{g}' = \mathbf{v}_2' - \mathbf{v}_1'$, where $|\mathbf{g}| = |\mathbf{g}'| = g$. Let us introduce a unit vector, $\hat{\mathbf{e}}$, which lies in the scattering plane and on the symmetry line between the initial and final directions of the relative velocity, as is shown in Fig. (a).



Using $\hat{\mathbf{e}}$, we can write

$$\mathbf{g}' = \mathbf{g} - 2\hat{\mathbf{e}}(\hat{\mathbf{e}} \cdot \mathbf{g}) \quad \text{and} \quad \mathbf{g}' \cdot \mathbf{g} = g^2 \cos(\Theta) = g^2(1 - 2\cos^2(\phi_0)), \tag{1}$$

where the scattering angle, Θ, satisfies the condition, $\Theta = \pi - 2\phi_0$. In Fig. (b) we draw the scattering plane in three-dimensional space, with the initial relative velocity vector, $\mathbf{g}$, lying along the z axis. If we note that $d\Omega = d(\cos(\Theta))d\alpha$, we can write

$$\begin{aligned} g d\Omega &= \int g' dg' d\Omega \delta(g' - g) = \int g' dg' d\Omega \delta(g' - g) \int d\mathbf{V}'_{cm} \delta(\mathbf{V}'_{cm} - \mathbf{V}_{cm}) \\ &= \frac{m}{2} \int\int d\mathbf{V}'_{cm}\, d\mathbf{g}' \delta(E' - E) \delta(\mathbf{V}'_{cm} - \mathbf{V}_{cm}), \end{aligned} \tag{2}$$

where $d\mathbf{g}' = g'^2 dg' d\Omega$. We have used the fact that the total kinetic energy can be written

$$E = \frac{m}{2}(v_1^2 + v_1^2) = m(V_{cm}^2 + \tfrac{1}{4}g^2) = m(V_{cm}'^2 + \tfrac{1}{4}g'^2). \tag{3}$$

Note that $\delta(E' - E)\delta(\mathbf{V}'_{cm} - \mathbf{V}_{cm}) = \delta((m/4)(g'^2 - g^2))\delta(\mathbf{V}'_{cm} - \mathbf{V}_{cm})$ and $\delta((m/4)(g'^2 - g^2)) = \frac{2}{mg}\delta(g' - g)$. We can also write Eq. (2) as

$$g d\Omega = \frac{8}{m} \int\int d\mathbf{p}'_1 d\mathbf{p}'_2 \delta(p_1'^2 + p_2'^2 - p_1^2 - p_2^2) \delta(\mathbf{p}'_1 + \mathbf{p}'_2 - \mathbf{p}_1 - \mathbf{p}_2), \tag{4}$$

where we have used the fact that $m^6\, d\mathbf{V}'_{cm} d\mathbf{g}' = d\mathbf{p}'_1 d\mathbf{p}'_2$ and $\delta(E' - E)$ $\delta(\mathbf{V}'_{cm} - \mathbf{V}_{cm}) = 16m^4 \delta(p_1^2 + p_2^2 - p_1'^2 - p_2'^2)\, \delta(\mathbf{p}_1 + \mathbf{p}_2 - \mathbf{p}'_1 - \mathbf{p}'_2)$.

We can now use the above results to write the Boltzmann collision operator in the form

$$\hat{C}^{+}_{\mathbf{p}_1}\chi(\mathbf{p}_1) = \frac{8}{m}\frac{N}{V}\left(\frac{\beta}{2\pi m}\right)^{3/2}\int d\mathbf{p}_2 \int d\mathbf{p}_1' \int d\mathbf{p}_2' \sigma(g,\Theta)\delta(p_1^2 + p_2^2 - p_1'^2 - p_2'^2)$$
$$\times \delta(\mathbf{p}_1 + \mathbf{p}_2 - \mathbf{p}_1' - \mathbf{p}_2') e^{-\beta p_2^2/2m}(\chi(\mathbf{p}_1') + \chi(\mathbf{p}_2') - \chi(\mathbf{p}_1) - \chi(\mathbf{p}_2)). \tag{5}$$

In Eq. (5), we have written the scattering cross section as a function of scatering angle, Θ, rather than impact parameter, b. Using Eq. (5), we can write $\langle \chi, \hat{C}^{+}\chi\rangle$ in a form which shows explicitly the conservation of momentum and energy. We find

$$\langle \chi, \hat{C}^{+}\chi\rangle = -\frac{2}{m}\frac{N}{V}\left(\frac{\beta}{2\pi m}\right)^{3}\int d\mathbf{p}_1 \int d\mathbf{p}_2 \int d\mathbf{p}_1' \int d\mathbf{p}_2' \sigma(g,\Theta)$$
$$\times \delta(p_1^2 + p_2^2 - p_1'^2 - p_2'^2)\delta(\mathbf{p}_1 + \mathbf{p}_2 - \mathbf{p}_1' - \mathbf{p}_2') \tag{6}$$
$$\times e^{-(\beta/2m)(p_1^2 + p_2^2)}(\chi(\mathbf{p}_1') + \chi(\mathbf{p}_2') - \chi(\mathbf{p}_1) - \chi(\mathbf{p}_2))^2.$$

11.E. COEFFICIENT OF SELF-DIFFUSION

We shall begin with a derivation of the coefficient of self-diffusion because it is the easiest to obtain. The method we use is due to Resibois [10] and consists of two steps. In the first step, we derive the linearized hydrodynamic equation from the Lorentz–Boltzman equation and introduce the self-diffusion coefficient into the hydrodynamic equation using Fick's law. We then can find the dispersion relation for the hydrodynamic diffusion mode. In the second step we use Rayleigh–Schrödinger perturbation theory to obtain the hydrodynamic eigenvalues of the Lorentz–Boltzmann equation. We then match the eigenvalue of the hydrodynamic equation to that of the Lorentz–Boltzmann equation and thereby obtain a microscopic expression for the self-diffusion coefficient.

11.E.1. Derivation of the Diffusion Equation

The difference in tracer and normal particle densities at some point $\mathbf{r}$ is given by

$$m(\mathbf{r},t) = n_N(\mathbf{r},t) - n_T(\mathbf{r},t) = \int d\mathbf{p}_1 f^0(\mathbf{p}_1) h^{-}(\mathbf{p}_1,\mathbf{r},t) \tag{11.107}$$

(at equilibrium this difference is zero). If we multiply the Lorentz–Boltzmann

equation by $f^0(\mathbf{p}_1)$ and integrate over $\mathbf{p}_1$, we obtain

$$\frac{\partial}{\partial t} m(\mathbf{r}, t) + \nabla_{\mathbf{r}} \cdot \mathbf{J}^D(\mathbf{r}, t) = 0, \tag{11.108}$$

where $\mathbf{J}^D(\mathbf{r}, t)$ is the diffusion current and is defined microscopically as

$$\mathbf{J}^D(\mathbf{r}, t) = \int d\mathbf{p}_1 \frac{\mathbf{p}_1}{m} f^0(\mathbf{p}_1) h^-(\mathbf{p}_1, \mathbf{r}, t). \tag{11.109}$$

The contribution from the collision term is identically zero because $C_{\mathbf{p}}^{(-)} 1 = 0$. We now introduce the self-diffusion coefficient using Fick's law:

$$\mathbf{J}^D(\mathbf{r}, t) = -D \nabla_{\mathbf{r}} m(\mathbf{r}, t). \tag{11.110}$$

If we combine Eqs. (11.108) and (11.110), we obtain the following hydrodynamic equation for the self-diffusion process:

$$\frac{\partial}{\partial t} m(\mathbf{r}, t) = D \nabla_{\mathbf{r}}^2 m(\mathbf{r}, t). \tag{11.111}$$

To find the dispersion relation for hydrodynamic modes we define the Fourier transform

$$m(\mathbf{r}, t) = \frac{1}{(2\pi)^4} \int d\mathbf{k} \int d\omega \bar{m}(\mathbf{k}, \omega) e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)}, \tag{11.112}$$

which allows us to study each Fourier component of the diffusion equation separately. If we substitute Eq. (11.112) into Eq. (11.111) we obtain

$$-i\omega \bar{m}(\mathbf{k}, \omega) + Dk^2 \bar{m}(\mathbf{k}, \omega) = 0 \tag{11.113}$$

(different Fourier components do not couple, because the hydrodynamic equation is linear). From Eq. (11.113) we obtain the following dispersion relation for the self-diffusion mode:

$$\omega = -iDk^2. \tag{11.114}$$

The diffusion frequency is imaginary, which means that the contribution to the density $m(\mathbf{r}, t)$ with wavevector k dies out in a time which depends on the diffusion coefficient and the wavevector k:

$$m(\mathbf{r}, t) \sim e^{i\mathbf{k} \cdot \mathbf{r}} e^{-Dk^2 t}. \tag{11.115}$$

Thus, very-long-wavelength disturbances take a long time to decay away. This

is the characteristic behavior of a hydrodynamic mode. Since the identity of the particles is preserved in each collision, the only way to cause difference in the density of normal and tracer particles to disappear is to physically transport particles from one part of the fluid to another. For very-long-wavelength disturbances the equalization takes a long time since the particles must be transported over long distances.

11.E.2. Eigenfrequencies of the Lorentz–Boltzmann Equation

We can obtain the hydrodynamic eigenfrequencies of the Lorentz–Boltzmann equation in terms of a perturbation expansion in powers of the wavevector k by using the Rayleigh–Schrödinger perturbation theory [11]. After this has been done we can equate the eigenfrequency of the hydrodynamic equation to the hydrodynamic eigenfrequency of the Lorentz–Boltzmann equation and thereby obtain a microscopic expression for the coefficient of self-diffusion.

Since Eq. (11.105) is a linear equation for $h^-(\mathbf{p}_1, \mathbf{r}, t)$, we can consider each Fourier component separately and write

$$h^-(\mathbf{p}, \mathbf{r}, t) = |\Psi_n(\mathbf{p}, \mathbf{k})\rangle_- e^{i\mathbf{k}\cdot\mathbf{r}} e^{-i\omega_n t}; \tag{11.116}$$

we obtain the following eigenvalue equation for $|\Psi_n(\mathbf{p}, \mathbf{k})\rangle_-$:

$$\left(\hat{C}_p^- - ik\boldsymbol{\kappa}\cdot\frac{\mathbf{p}}{m}\right)|\Psi_n(\mathbf{p}, \mathbf{k})\rangle_- = -i\omega_n^-|\Psi_n(\mathbf{p}, \mathbf{k})\rangle_- \tag{11.117}$$

where $\boldsymbol{\kappa} = \mathbf{k}/|\mathbf{k}|$ and the eigenfunctions, $|\Psi_n(\mathbf{q}, \mathbf{k})\rangle_-$, are assumed to be orthonormal. For long-wavelength hydrodynamic disturbances, k will be a small parameter. Thus, we can use Rayleigh–Schrödinger perturbation theory to obtain a perturbation expansion for ω_n in powers of k.

Let us assume that both ω_n^- and $|\Psi_n(\mathbf{q}, \mathbf{k})\rangle_-$ can be expanded in powers of k. Then

$$\omega_n = \omega_n^{(0)} + k\omega_n^{(1)} + k^2\omega_n^{(2)} + \cdots \tag{11.118}$$

and

$$|\Psi_n\rangle_- = |\Psi_n^{(0)}\rangle_- + k|\Psi_n^{(1)}\rangle_- + k^2|\Psi_n^{(2)}\rangle_- + \cdots. \tag{11.119}$$

If we substitute Eqs. (11.118) and (11.119) into Eq. (11.117), we obtain the following expression for frequencies $\omega_n^{(0)}, \omega_n^{(1)}$ and $\omega_n^{(2)}$:

$$\omega_n^{(0)} = i_-\langle\Psi_n^{(0)}|\hat{C}_\mathbf{p}^-|\Psi_n^{(0)}\rangle_-, \tag{11.120}$$

$$\omega_n^{(1)} = {}_-\langle\Psi_n^{(0)}|\boldsymbol{\kappa}\cdot\frac{\mathbf{p}}{m}|\Psi_n^{(0)}\rangle_-, \tag{11.121}$$

and

$$\omega_n^{(2)} = -\langle \Psi_n^{(0)} | \left(\boldsymbol{\kappa} \cdot \frac{\mathbf{p}}{m} - \omega_n^{(1)} \right) \left(\frac{-1}{i\hat{C}_{\mathbf{p}}^- + \omega_n^{(0)}} \right) \left(\boldsymbol{\kappa} \cdot \frac{\mathbf{p}}{m} - \omega_n^{(1)} \right) | \Psi_n^{(0)} \rangle_-, \tag{11.122}$$

where the matrix elements are defined as in Eq (11.98) and $\langle \Psi_{n'}^0 | \Psi_n^0 \rangle \equiv \delta_{n,n'}$. At this point we shall restrict our attention to the eigenvalue which reduces to zero when $k \to 0$. This corresponds to the hydrodynamic mode. There will be only one such eigenvalue of $\hat{C}_{\mathbf{p}}^-$ since there is only one zero eigenfunction of $\hat{C}_{\mathbf{p}}^-$, namely a constant.

We will let $|\Psi_1^{(0)}\rangle_-$ denote the zero eigenfunction of $\hat{C}_{\mathbf{p}}^-$ and we will normalize it using the scalar product in Eq. (11.98). Thus,

$$|\Psi_1^{(0)}\rangle_- = 1 \tag{11.123}$$

and we find

$$\omega_1^{(0)} = 0, \tag{11.124}$$

$$\omega_1^{(1)} = \frac{1}{m} \left(\frac{\beta}{2\pi m} \right)^{3/2} \int d\mathbf{p}_1 e^{-\beta p_1^2/2m} \boldsymbol{\kappa} \cdot \mathbf{p}_1 \equiv 0, \tag{11.125}$$

and

$$\omega_1^{(2)} = -\frac{1}{m^2} \left(\frac{\beta}{2\pi m} \right)^{3/2} \int d\mathbf{p}_1 e^{-\beta p_1^2/2m} \boldsymbol{\kappa} \cdot \mathbf{p}_1 \frac{1}{i\hat{C}_{\mathbf{p}}^-} \boldsymbol{\kappa} \cdot \mathbf{p}_1. \tag{11.126}$$

The hydrodynamic eigenfrequency, ω_1, has the correct hydrodynamic behavior. If we now equate Eqs. (11.114) and (11.118) and use Eqs. (11.124)–(11.126), we find

$$D = -\frac{1}{m^2} \left(\frac{\beta}{2\pi m} \right)^{3/2} \int d\mathbf{p}_1 e^{-\beta p_1^2/2m} \boldsymbol{\kappa} \cdot \mathbf{p}_1 \frac{1}{\hat{C}_{\mathbf{p}}^-} \boldsymbol{\kappa} \cdot \mathbf{p}_1. \tag{11.127}$$

Thus, we have obtained a microscopic expression for the self-diffusion coefficient, D. In Section 11.G we will discuss how to evaluate the integral in Eq. (11.127).

11.F. COEFFICIENTS OF VISCOSITY AND THERMAL CONDUCTIVITY

The Boltzmann collision operator, $\hat{C}_{\mathbf{p}}^{(+)}$, has five zero eigenvalues (it is fivefold degenerate) and therefore we can derive from the linearized Boltzmann

equation five linearized hydrodynamic equations: one equation for the total particle density, $n(\mathbf{r},t) = n_N(\mathbf{r},t) + n_T(\mathbf{r},t)$; three equations for the three components of the momentum density, $mn(\mathbf{r},t)\mathbf{v}(\mathbf{r},t)$, where $\mathbf{v}(\mathbf{r},t)$ is the average velocity; and one equation for the average internal energy density. To find the hydrodynamic eigenfrequencies (which will be expressed in terms of the coefficients of viscosity and thermal conductivity), we must find the normal modes of the system of five hydrodynamic equations. We then use the Rayleigh–Schrödinger perturbation theory to find the five *microscopic* hydrodynamic frequencies of the Boltzmann equation. Once they are found we can match them to the five normal mode frequencies of the hydrodynamic equations and thereby obtain microscopic expressions for the coeffcients of viscosity and thermal conductivity.

11.F.1. Derivation of the Hydrodynamic Equations [12]

The average particle density is defined by

$$n(\mathbf{r},t) = \int d\mathbf{p} f^0(\mathbf{p})[1 + h^+(\mathbf{p},\mathbf{r},t)]. \tag{11.128}$$

If we multiply Eq. (11.94) by $f^0(\mathbf{p}_1)$, integrate over $\mathbf{p}_1$, and make use of the fact that $\hat{C}_{\mathrm{p}}^{(+)}1 = 0$, we obtain

$$\frac{\partial}{\partial t} n(\mathbf{r},t) + \nabla_{\mathbf{r}} \cdot \mathbf{J}^n(\mathbf{r},t) = 0, \tag{11.129}$$

where $\mathbf{J}^n(\mathbf{r},t)$ is the average particle current and is defined as

$$\mathbf{J}^n(\mathbf{r},t) = \int d\mathbf{p} \frac{\mathbf{p}}{m} f^0(\mathbf{p}) h^+(\mathbf{p},\mathbf{r},t). \tag{11.130}$$

It is useful to decompose $\mathbf{J}^n(\mathbf{r}, t)$ into the product $\mathbf{J}^n(\mathbf{r}, t) = n(\mathbf{n}, t)\mathbf{v}(\mathbf{r}, t)$. In the linear regime, $\mathbf{J}^n(\mathbf{r},t) \approx n_0 \mathbf{v}(\mathbf{r},t)$, where n_0 is the equilibrium particle density. Eq. (11.129) then becomes

$$\frac{\partial}{\partial t} n(\mathbf{r},t) + n_0 \nabla_{\mathbf{r}} \cdot \mathbf{v}(\mathbf{r},t) = 0. \tag{11.131}$$

Equation (11.131) is the linearized continuity equation and describes the conservation of total particle number. The continuity equation is entirely reactive. If we reverse time in Eq. (11.131), we do not change the form of the equation. Thus, the continuity equation contains no irreversible effects. These must come from the other hydrodynamic equations.

If we multiply Eq. (11.94) by $\mathbf{p}_1 f^0(\mathbf{p}_1)$, integrate over $\mathbf{p}_1$, and use the fact that $\hat{C}_{\mathbf{p}}^{(+)}\mathbf{p} \equiv 0$, we obtain

$$m\frac{\partial}{\partial t}\mathbf{J}^n(\mathbf{r},t) = -\nabla_{\mathbf{r}} \cdot \bar{P}(\mathbf{r},t), \tag{11.132}$$

where $\bar{P}(\mathbf{r},t)$ is the pressure tensor and is defined

$$\bar{P}(\mathbf{r},t) = \frac{1}{m}\int d\mathbf{p}\, f^0(\mathbf{p})\mathbf{p}\mathbf{p}h^+(\mathbf{p},\mathbf{r},t) \tag{11.133}$$

(we have let $\dot{\mathbf{q}} = \mathbf{p}/m$). The pressure tensor describes the momentum flux, or current, in the system and contains an irreversible part due to viscous effects.

To obtain the equation for the internal energy density, we must take the average of the thermal kinetic energy $(1/2m)(\mathbf{p} - m\mathbf{v}(\mathbf{r},t))^2$. However, in the linear approximation, $\mathbf{v}(\mathbf{r},t)$ does not contribute. Thus, to find the hydrodynamic equation for the internal energy density, we can multiply Eq. (11.96) by $p_1^2/2m$ and integrate over $\mathbf{p}_1$. If we use the fact that $\hat{C}_{\mathbf{p}}^{(+)}p^2 \equiv 0$, we obtain

$$\frac{\partial}{\partial t}u(\mathbf{r},t) = -\nabla_{\mathbf{r}} \cdot \mathbf{J}^u(\mathbf{r},t), \tag{11.134}$$

where $u(r,t)$ is the internal energy per unit volume,

$$u(\mathbf{r},t) = \int d\mathbf{p}\frac{p^2}{2m} f^0(\mathbf{p})h^+(\mathbf{p},\mathbf{r},t), \tag{11.135}$$

and $\mathbf{J}^u(\mathbf{r},t)$ is the internal energy current,

$$\mathbf{J}^u(\mathbf{r},t) = \int d\mathbf{p}\frac{p^2}{2m}\frac{\mathbf{p}}{m} f^0(\mathbf{p})h^+(\mathbf{p},\mathbf{r},t). \tag{11.136}$$

We can write the internal energy density in the form $u(\mathbf{r},t) = n(\mathbf{r},t)e(\mathbf{r},t)$, where $e(\mathbf{r},t)$ is the internal energy per particle. In the linear approximation we find $u(\mathbf{r},t) = n_0 e(\mathbf{r},t) + e_0 n(\mathbf{r},t)$, and Eq. (11.134) takes the form

$$n_0\frac{\partial}{\partial t}e(\mathbf{r},t) + e_0\frac{\partial}{\partial t}n(\mathbf{r},t) = -\nabla_{\mathbf{r}} \cdot \mathbf{J}^u(\mathbf{r},t), \tag{11.137}$$

where e_0 is the equilibrium internal energy per particle. The current $\mathbf{J}^u(\mathbf{r},t)$ will contain an irreversible part due to thermal conduction.

Equations (11.131), (11.132), and (11.137) are the linearized equations of motion for the average particle density, $n(\mathbf{r},t)$, the momentum density, $m\mathbf{J}^n(\mathbf{r},t)$, and the internal energy density, $u(\mathbf{r},t)$. They govern the variation in time and space of these quantities. However, they cannot yet be solved because

they contain too many unknowns. As a next step we must write expressions for the pressure tensor, $\bar{P}(\mathbf{r},t)$, and the energy current, $\mathbf{J}^u(\mathbf{r},t)$. The form that these two quantities must take was already discussed in Section 10.B. From Eqs. (10.7), (10.30), and (10.31), we can write the pressure tensor in the form

$$P_{ij}(\mathbf{r},t) = P(\mathbf{r},t)\delta_{ij} - \zeta\delta_{ij}(\nabla_{\mathbf{r}}\cdot\mathbf{v}) - \eta\left(\frac{\partial v_i}{\partial x_j}+\frac{\partial v_j}{\partial x_i}-\frac{2}{3}\delta_{ij}\nabla_{\mathbf{r}}\cdot\mathbf{v}\right), \quad (11.138)$$

where $P(\mathbf{r},t)$ is the hydrostatic pressure, ζ is the coefficient of bulk viscosity, and η is the coefficient of shear viscosity. If we substitute Eq. (11.138) into Eq. (11.132) we obtain, after some rearrangement,

$$mn_0\frac{\partial}{\partial t}\mathbf{v}(\mathbf{r},t) = -\nabla_{\mathbf{r}}P(\mathbf{r},t) + \eta\nabla_{\mathbf{r}}^2\mathbf{v}(\mathbf{r},t) + (\zeta+\tfrac{1}{3}\eta)\nabla_{\mathbf{r}}(\nabla_{\mathbf{r}}\cdot\mathbf{v}(\mathbf{r},t)). \quad (11.139)$$

The contribution from the hydrostatic pressure term is reactive [it has the same dependence under time reversal as the left-hand side of Eq. (11.139)], whereas the viscous contribution is dissipative (it changes sign relative to the left-hand side). All terms in Eq. (11.139) are linear in deviations from equilibrium and depend only on first-order gradients. Thus, we have assumed that all spatial variations have very long wavelengths and higher-order gradients can be neglected.

Let us now consider the energy equation, Eq. (11.137). The energy current will have a contribution from the convection of internal energy, a contribution involving the pressure which comes from work done in compression or expansion of regions in the fluid, and a contribution from heat conduction [cf. Eq. (10.25)]. Thus in the linear approximation we can write

$$\mathbf{J}^u(\mathbf{r},t) = n_0e_0\mathbf{v}(\mathbf{r},t) + P_0\mathbf{v}(\mathbf{r},t) - K\nabla_{\mathbf{r}}T(\mathbf{r},t), \quad (11.140)$$

where P_0 is the equilibrium pressure, K is the coefficient of thermal conductivity, and $T(\mathbf{r},t)$ is the temperature. If we substitute Eq. (11.140) into Eq. (11.137) and make use of Eq. (11.131), we find

$$n_0\frac{\partial}{\partial t}e(\mathbf{r},t) = -P_0\nabla_{\mathbf{r}}\cdot\mathbf{v}(\mathbf{r},t) + K\nabla_{\mathbf{r}}^2T(\mathbf{r},t). \quad (11.141)$$

Equation (11.141) simplifies when we write it in terms of the local entropy. If we use the thermodynamic relation $de = Tds + (P/n^2)dn$, we can write

$$\frac{\partial e}{\partial t} = T\frac{\partial s}{\partial t} + \frac{P}{n^2}\frac{\partial n}{\partial t}. \quad (11.142)$$

If we combine Eqs. (11.141) and (11.142) and again use Eq. (11.131), we obtain

$$n_0 T_0 \frac{\partial}{\partial t} s(\mathbf{r}, t) = K \nabla_{\mathbf{r}}^2 T(\mathbf{r}, t) \tag{11.143}$$

where T_0 is the equilibrium temperature and $s(\mathbf{r}, t)$ is the local entropy per particle.

The hydrodynamic Eqs. (11.131), (11.139), and (11.143), which have been derived from the Boltzmann equation with the help of thermodynamic relations, are identical to Eqs. (10.36)–(10.38). If we choose the density, $n(\mathbf{r}, t)$, and the temperature, $T(\mathbf{r}, t)$, to be the independent variables, the hydrodynamic equations take the form

$$\frac{\partial n}{\partial t} + n_0 \nabla_{\mathbf{r}} \cdot \mathbf{v} = 0, \tag{11.144}$$

$$mn_0 \frac{\partial \mathbf{v}}{\partial t} = -\left(\frac{\partial P}{\partial n}\right)_T^0 \nabla_{\mathbf{r}} n - \left(\frac{\partial P}{\partial T}\right)_n^0 \nabla_{\mathbf{r}} T + \eta \nabla_{\mathbf{r}}^2 \mathbf{v} + (\zeta + \frac{1}{3}\eta) \nabla_{\mathbf{r}} (\nabla_{\mathbf{r}} \cdot \mathbf{v}), \tag{11.145}$$

and

$$mn_0 \left(\frac{\partial s}{\partial n}\right)_T^0 \frac{\partial n}{\partial t} + mn_0 \left(\frac{\partial s}{\partial T}\right)_\rho^0 \frac{\partial T}{\partial t} = \frac{K}{T_0} \nabla_{\mathbf{r}}^2 T. \tag{11.146}$$

Equations (11.144)–(11.146) are coupled equations for variations in average density, velocity, and temperature. We now must find normal mode solutions. Since the equations are linear, each Fourier component will propagate independently. Thus, we only need to consider a single Fourier component. We will write

$$n(\mathbf{r}, t) = n_{\mathbf{k}}(\omega) e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{11.147}$$

$$\mathbf{v}(\mathbf{r}, t) = \mathbf{v}_{\mathbf{k}}(\omega) e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{11.148}$$

and

$$T(\mathbf{r}, t) = T_{\mathbf{k}}(\omega) e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{11.149}$$

We will also separate the average velocity, $\mathbf{v}_{\mathbf{k}}$, into a longitudinal part, $\mathbf{v}^{\parallel} = v^{\parallel}\hat{\mathbf{k}}$, and a transverse part, $\mathbf{v}^{\perp}$ (cf. Section 10.C).

The hydrodynamic equation for the transverse velocity, which describes the propagation of shear waves, takes the form

$$(-i\omega + \nu_t k^2) \tilde{\mathbf{v}}_{\mathbf{k}}^{\perp}(\omega) = 0, \tag{11.150}$$

where $\nu_t = \eta/mn_0$ denotes the transverse kinetic viscosity. The dispersion relation for the transverse mode is given by Eq. (11.150). It is

$$\omega = -i\nu_t k^2. \tag{11.151}$$

There are two shear modes with this frequency. Thus, we find that the shear waves behave very much like the diffusion waves in Section 11.E. Any shear disturbance will be damped out.

The longitudinal modes satisfy the equation

$$\begin{pmatrix} i\omega & -i\rho_o k & 0 \\ -\dfrac{ikc_0^2}{\gamma\rho_0} & [i\omega + \nu_l k^2] & -\dfrac{ikc_0^2\alpha_P}{\gamma} \\ -i\omega\dfrac{c_0^2\alpha_P}{\rho_0\gamma} & 0 & \dfrac{c_\rho}{T_0}[i\omega + \gamma\chi k^2] \end{pmatrix} \begin{pmatrix} \tilde{\rho}_{\mathbf{k}}(\omega) \\ \tilde{v}_{\mathbf{k}}^{\parallel}(\omega) \\ \tilde{T}_{\mathbf{k}}(\omega) \end{pmatrix} = 0, \tag{11.152}$$

where $c_0 = \sqrt{(\partial P/\partial mn)_s}$ is the speed of sound, $\alpha_P = -(1/n_0)(\partial n/\partial T)_P$ is the thermal expansivity, $\gamma = c_P/c_{mn}$, $\nu_l = (1/\rho_0)(\zeta + \frac{4}{3}\eta)$ is the longitudinal kinetic viscosity and $\chi = K/mn_0c_P$ (cf. Section 10.C). The dispersion relations for the longitudinal modes can be found by setting the determinant of the matrix in Eq. (11.151) to zero and solving for ω. To second order in wavevector k, we find

$$\omega_1 = -i\left[\frac{Kk^2}{n_0c_P}\right] \tag{11.153}$$

and

$$\omega_\pm = \pm c_0 k - \frac{ik^2}{2mn_0}\left[\frac{4}{3}\eta + \zeta + mK\left(\frac{1}{c_v} - \frac{1}{c_P}\right)\right]. \tag{11.154}$$

The first solution [Eq. (11.153)] is purely imaginary and the second two [Eq. (11.154)] are complex. (Small k means long-wavelength disturbances.)
The wave of frequency ω_1 corresponds predominantly to an entropy (or heat) wave. It is damped out exponentially with time.

The waves of frequency $\omega_\pm$ (waves going in opposite directions) correspond to pressure or longitudinal velocity waves (sound waves). These waves propagate, but in the presence of transport processes they eventually get damped out. Thus, at long wavelengths there are two shear modes: one heat mode, and two sound modes in the fluid. The frequencies in Eqs. (11.151), (11.153), and (11.154) are the normal mode frequencies of the system. These five frequencies, together with the diffusion frequency, Eq. (11.114), give the six normal mode frequencies of this two-component, dilute gas of dynamically identical particles.

11.F.2. Eigenfrequencies of the Boltzmann Equation [10, 13]

The second step in deriving microscopic expression for the thermal conductivity and shear viscosity is to obtain the hydrodynamic eigenfrequencies of the linerized Boltzmann equation. Just as in Section 11.E we only need to consider one Fourier component of the linearized Boltzmann equation. If we let

$$h^+(\mathbf{p}, \mathbf{r}, t) = |\Psi_n(\mathbf{p}, \mathbf{k})\rangle_+ e^{i\mathbf{k}\cdot\mathbf{r}} e^{-i\omega_n t}, \tag{11.155}$$

we obtain the following eigenvalue equation for the eigenvectors:

$$(\hat{C}^+_{\mathbf{p}} - ik\kappa \cdot \mathbf{p}/m)|\Psi_n(\mathbf{p}, \mathbf{k})\rangle_+ = -i\omega_n|\Psi_n(\mathbf{p}, \mathbf{k})\rangle_+. \tag{11.156}$$

To obtain a perturbation expression for ω_n in powers of k, we must first look at the eigenvalue problem for the unperturbed operator $\hat{C}^+_{\mathbf{p}}$. We will denote the eigenfunctions of $\hat{C}^+_{\mathbf{p}}$ by $|\phi_n\rangle$. Then

$$\hat{C}^+_{\mathbf{p}}|\phi_n\rangle = -i\omega^0_n|\phi_n\rangle. \tag{11.157}$$

We know that $\hat{C}^+_{\mathbf{p}}$ has five zero eigenvalues and, therefore, five degenerate eigenfunctions. Orthonormalized eigenfunctions with eigenvalue zero are given by

$$|\phi_1\rangle = 1, \tag{11.158}$$

$$|\phi_2\rangle = \sqrt{\frac{\beta}{m}} p_x. \tag{11.159}$$

$$|\phi_3\rangle = \sqrt{\frac{\beta}{m}} p_y, \tag{11.160}$$

$$|\phi_4\rangle = \sqrt{\frac{\beta}{m}} p_z, \tag{11.161}$$

and

$$|\phi_5\rangle = \sqrt{\frac{2}{3}}\left(-\frac{3}{2} + \frac{\beta}{2m} p^2\right). \tag{11.162}$$

We shall denote the five eigenfunctions collectively as $|\phi_\alpha\rangle$, where $\alpha = 1, 2, 3, 4$, and 5. All other eigenfunctions will be denoted collectively as $|\phi_\beta\rangle$ where $\beta = 6, \ldots, \infty$. The eigenfunctions $|\phi_n\rangle$ are assumed orthonormal with respect to the scalar product in Eq. (11.98).

Since the eigenfunctions $|\phi_\alpha\rangle$ are degenerate, we must first find the proper linear combination of them to use for the zero-order approximation to the exact

eigenfunctions $|\Psi_\alpha\rangle_+$. That is, we must find some $|\Psi_\alpha^{(0)}\rangle_+$ such that

$$|\Psi_\alpha\rangle_+ = |\Psi_\alpha^{(0)}\rangle_+ + k|\Psi_\alpha^{(1)}\rangle_+ + k^2|\Psi_\alpha^{(2)}\rangle_+ + \cdots, \tag{11.163}$$

where

$$|\Psi_\alpha^{(0)}\rangle_+ = \sum_{\alpha'} c_{\alpha\alpha'}|\phi_{\alpha'}\rangle. \tag{11.164}$$

The process of determining of the coefficients $c_{\alpha\alpha'}$ will also give us the first-order term, $\omega_\alpha^{(1)}$, in the perturbation expansion of ω_α:

$$\omega_\alpha = \omega_\alpha^{(0)} + k\omega_\alpha^{(1)} + k^2\omega_\alpha^{(2)} + \cdots. \tag{11.165}$$

To find the coefficients $c_{\alpha\alpha'}$ and $\omega_\alpha^{(1)}$, let us first insert the expansions in Eqs. (11.158)–(11.162) and (11.165) into Eq. (11.156) and equate coefficients of order k. We then obtain

$$\hat{C}_{\mathbf{p}}^+ |\Psi_\alpha^{(1)}\rangle_+ = i\left(-\omega_\alpha^{(1)} + \frac{\boldsymbol{\kappa}\cdot\mathbf{p}}{m}\right)|\Psi_\alpha^{(0)}\rangle_+. \tag{11.166}$$

If we multiply Eq. (11.166) by $\langle\phi_{\alpha''}|$, we obtain

$$\omega_\alpha^{(1)}\langle\phi_{\alpha''},\, \Psi_\alpha^{(0)}\rangle_+ = \langle\phi_{\alpha''},\, (\boldsymbol{\kappa}\cdot\mathbf{p}/m)\,\Psi_\alpha^{(0)}\rangle_+ \tag{11.167}$$

(note that since $\hat{C}_{\mathbf{p}}^{(+)}$ is self-adjoint, $\langle\phi_{\alpha''}|$ is the same as its dual vector $|\phi_{\alpha''}\rangle$), or, using Eq. (11.164), we obtain

$$\omega_\alpha^{(1)}\, c_{\alpha\alpha''} = \sum_{\alpha'} W_{\alpha''\alpha'} c_{\alpha\alpha'}, \tag{11.168}$$

where

$$\begin{aligned} W_{\alpha''\alpha'} &= \left\langle \phi_{\alpha''} \frac{\boldsymbol{\kappa}\cdot\mathbf{p}}{m}\, \phi_{\alpha'} \right\rangle \\ &= \left(\frac{\beta}{2\pi m}\right)^{3/2} \int d\mathbf{p}\, e^{-\beta p^2/2m}\, \phi_{\alpha''}(\mathbf{p})\, \frac{\boldsymbol{\kappa}\cdot\mathbf{p}}{m}\, \phi_{\alpha'}(\mathbf{p}). \end{aligned} \tag{11.169}$$

If we use the expressions for $|\phi_\alpha\rangle$ $(\alpha = 1, \ldots, 5)$ appearing in Eqs. (11.158)–(11.162) and assume that $\mathbf{k}$ lies along the x axis so that $\mathbf{p}\cdot\boldsymbol{\kappa} = p_x$, we find by explicit calculation that

$$W_{12} = W_{21} = \left(\frac{1}{m\beta}\right)^{1/2} \tag{11.170}$$

and

$$W_{25} = W_{52} = \left(\frac{2}{3}\right)^{1/2} \left(\frac{1}{m\beta}\right)^{1/2}. \tag{11.171}$$

For all other α'' and α', $W_{\alpha''\alpha'} \equiv 0$.

We may obtain values for $\omega_\alpha^{(1)}$ from Eq. (11.168). We first write it in matrix form and set the determinant of the matrix to zero:

$$\det(\bar{\mathbf{W}} - \omega^{(1)}\bar{\mathbf{I}}) = 0. \tag{11.172}$$

If we evaluate the above determinant, we obtain the following equation for $\omega_\alpha^{(1)}$:

$$(-\omega^{(1)})^3 \left[(\omega^{(1)})^2 - \frac{5}{3}\frac{1}{m\beta}\right] = 0. \tag{11.173}$$

From Eq. (11.173) we obtain the following first-order corrections to ω_α:

$$\omega_1^{(1)} = -\omega_2^{(1)} = \left(\frac{5}{3}\frac{1}{m\beta}\right)^{1/2} = c_0 \tag{11.174}$$

and

$$\omega_3^{(1)} = \omega_4^{(1)} = \omega_5^{(1)} = 0. \tag{11.175}$$

In Eq. (11.174), $c_0 = (\frac{5}{3}(1/m\beta))^{1/2}$ is the velocity of sound of an ideal gas. Notice that we have lifted the degeneracy of only two of the states $|\Psi_\alpha\rangle_+$. We have to go to higher orders in the perturbation expansion to lift the degeneracy in the rest of the states.

Now that we have expressions for $\omega_\alpha^{(1)}$ and $W_{\alpha\alpha'}$, we can use Eq. (11.168) and the condition that the states $|\Psi_\alpha^{(0)}\rangle_+$ must be orthogonal to obtain expressions for $c_{\alpha\alpha'}$ and, therefore, for $|\Psi_\alpha^{(0)}\rangle_+$. Substitution of Eqs. (11.170), (11.171), (11.174), and (11.175) into Eq. (11.168) gives the following results: $c_{13} = c_{14} = c_{23} = c_{24} = c_{32} = c_{42} = c_{52} = 0$, $c_{15} = (\frac{2}{5})^{1/2} c_{12} = (\frac{2}{3})^{1/2} c_{11}$, $c_{25} = -(\frac{2}{5})^{1/2} c_{22} = (\frac{2}{3})^{1/2} c_{21}, c_{35} = -(\frac{3}{2})^{1/2} c_{31}, c_{45} = -(\frac{3}{2})^{1/2} c_{41}$, and $c_{51} = -(\frac{2}{3})^{1/2} c_{55}$. The condition of orthonormality of $|\Psi_\alpha^{(0)}\rangle_+$ gives us $c_{12} = c_{22} = (2)^{-1/2}$, $c_{55} = (\frac{3}{5})^{1/2}$, and $c_{31} = c_{34} = c_{41} = c_{43} = c_{53} = c_{54} = 0$. We therefore obtain the following expressions for the wave functions $|\Psi_\alpha^{(0)}\rangle_+$:

$$|\Psi_1^{(0)}\rangle_+ = \frac{1}{\sqrt{2}}[(\tfrac{3}{5})^{1/2}|\phi_1\rangle + |\phi_2\rangle + (\tfrac{2}{5})^{1/2}|\phi_5\rangle], \tag{11.176}$$

$$|\Psi_2^{(0)}\rangle_+ = \frac{1}{\sqrt{2}}[(\tfrac{3}{5})^{1/2}|\phi_1\rangle - |\phi_2\rangle + (\tfrac{2}{5})^{1/2}|\phi_5\rangle], \tag{11.177}$$

$$|\Psi_3^{(0)}\rangle_+ = |\phi_3\rangle, \tag{11.178}$$

$$|\Psi_4^{(0)}\rangle_+ = |\phi_4\rangle, \tag{11.179}$$

and

$$|\Psi_5^{(0)}\rangle_+ = \sqrt{\tfrac{2}{5}}[-|\phi_1\rangle + (\tfrac{3}{2})^{1/2}|\phi_5\rangle]. \tag{11.180}$$

We will use the state $|\Psi_\alpha^{(0)}\rangle_+$ as the basis states for the perturbation theory. The general expression for $\omega_n^{(2)}$ has been given in Eq. (11.122). We thus find the following expressions for the five hydrodynamic frequencies:

$$\omega_1 = c_0 k + ik^2 {}_+\left\langle \Psi_1^{(0)} \right| \left(\frac{p_x}{m} - c_0\right) \frac{1}{\hat{C}_{\mathbf{p}}^+} \left(\frac{p_x}{m} - c_0\right) \left| \Psi_1^{(0)} \right\rangle_+, \tag{11.181}$$

$$\omega_2 = -c_0 k + ik^2 {}_+\left\langle \Psi_1^{(0)} \right| \left(\frac{p_x}{m} + c_0\right) \frac{1}{\hat{C}_{\mathbf{p}}^+} \left(\frac{p_x}{m} + c_0\right) \left| \Psi_1^{(0)} \right\rangle_+, \tag{11.182}$$

$$\omega_3 = ik^2 {}_+\left\langle \Psi_3^{(0)} \right| \frac{p_x}{m} \frac{1}{\hat{C}_{\mathbf{p}}^+} \frac{p_x}{m} \left| \Psi_3^{(0)} \right\rangle_+, \tag{11.183}$$

$$\omega_4 = ik^2 {}_+\left\langle \Psi_4^{(0)} \right| \frac{p_x}{m} \frac{1}{\hat{C}_{\mathbf{p}}^+} \frac{p_x}{m} \left| \Psi_4^{(0)} \right\rangle_+, \tag{11.184}$$

and

$$\omega_5 = ik^2 {}_+\left\langle \Psi_5^{(0)} \right| \frac{p_x}{m} \frac{1}{\hat{C}_{\mathbf{p}}^+} \frac{p_x}{m} \left| \Psi_5^{(0)} \right\rangle_+. \tag{11.185}$$

The frequencies ω_1 and ω_2 may be identified with sound modes, frequencies ω_3 and ω_4 may be identified with shear modes, and frequency ω_5 may be identified with the heat mode.

11.F.3. Shear Viscosity and Thermal Conductivity

Given the microscopic expressions for the hydrodynamic frequencies in Eqs. (11.181)–(11.185), we can match them to the frequencies obtained from the linearized, hydrodynamic equations and obtain microscopic expressions for the transport coefficients. If we equate Eqs. (11.151) and (11.183), we find for the shear viscosity

$$\eta = -\frac{n_0 \beta}{m^2} \left(\frac{\beta}{2\pi m}\right)^{3/2} \int d\mathbf{p}\, e^{-\beta p^2/2m} p_y p_x \frac{1}{\hat{C}_{\mathbf{p}}^+} p_y p_x. \tag{11.186}$$

If we equate Eqs. (11.153) and (11.185), we obtain for the thermal conductivity

$$K = -\frac{2 n_0 c_P}{5m^2} \left(\frac{\beta}{2\pi m}\right)^{3/2} \int d\mathbf{p}\, e^{-\beta p^2/2m} \left[\frac{p^2\beta}{2m} - \frac{5}{2}\right] \times p_x \frac{1}{\hat{C}_{\mathbf{p}}^+} p_x \left[\frac{p^2\beta}{2m} - \frac{5}{2}\right]. \tag{11.187}$$

Note that the shear viscosity is expressed in the form of a momentum current correlation function and the thermal conductivity is expressed in the form of an enthalpy current correlation function.

The expression of the transport coefficients in terms of correlation functions can be made still more explicit. Let us consider the viscosity. We can write Eq. (11.186) in the form

$$\eta = n_0\beta\left(\frac{\beta}{2\pi m}\right)^{3/2}\int d\mathbf{p}\, e^{-\beta p^2/2m}\int_0^\infty d\tau\, J_{xy}e^{\hat{C}_p\tau}J_{xy}, \tag{11.188}$$

where $J_{xy} = p_x p_y/m = p_x v_y$ is a microscopic current, or flux, of x component of momentum in the y direction. If we denote

$$J_{xy}(\tau) = e^{\hat{C}_p\tau}J_{xy}, \tag{11.189}$$

the viscosity becomes

$$\eta = n_0\beta\int_0^\infty d\tau\,\langle J_{xy}J_{xy}(\tau)\rangle_{eq}. \tag{11.190}$$

Equation (11.190) clearly expresses the viscosity in terms of a momentum current correlation function. We found in Chapter 10 that this is quite a general result.

11.G. COMPUTATION OF TRANSPORT COEFFICIENTS [6]

The coefficients of self-diffusion, D, thermal conductivity, K, and shear viscosity, η, may be written in the form

$$D = -\frac{1}{m^2}\left(\frac{\beta}{2\pi m}\right)^{3/2}\int d\mathbf{p}\, e^{-\beta p^2/2m}p_x\Delta_x, \tag{11.191}$$

$$K = -\frac{n_0 k_B}{m^2}\left(\frac{\beta}{2\pi m}\right)^{3/2}\int d\mathbf{p}\, e^{-\beta p^2/2m}\left[\frac{\beta p^2}{2m}-\frac{5}{2}\right]p_x A_x, \tag{11.192}$$

and

$$\eta = -\frac{n_0\beta}{m^2}\left(\frac{\beta}{2\pi m}\right)^{3/2}\int d\mathbf{p}\, e^{-\beta p^2/2m}p_x p_y B_{xy}, \tag{11.193}$$

respectively, where we have used the ideal gas expression for the heat capacity per particle, $c_P = \frac{5}{2}k_B$. The functions D_x, A_x, and B_{xy} satisfy the

equations

$$\hat{C}_{\mathbf{p}}^{-}\Delta_x = p_x, \tag{11.194}$$

$$\hat{C}_{\mathbf{p}}^{+}A_x = \left[\frac{\beta p^2}{2m} - \frac{5}{2}\right] p_x. \tag{11.195}$$

and

$$\hat{C}_{\mathbf{p}}^{+}B_{xy} = p_x p_y, \tag{11.196}$$

These results are identical to the results obtained using the more traditional Chapman–Enskog procedure [6]. In order to obtain numerical values for the transport coefficients, we must expand the unknown functions Δ_x, A_x, and B_{xy} in terms of a set of orthogonal functions, $S_m^n(x)$, called *Sonine polynomials*, which are closely related to Leguerre polynomials. We describe these polynomials below.

11.G.1. Sonine Polynomials

The Sonine polynomials form a complete set of orthogonal polynomials which may be used to obtain approximate expressions for the transport coefficients. The Sonine polynomials are defined as

$$S_q^n(x) = \sum_{l=0}^{n} (-1)^l \frac{\Gamma(q+n+1)x^l}{\Gamma(q+l+1)\,(n-l)!(l!)}, \tag{11.197}$$

where x and q are real numbers, n is an integer, and $\Gamma(q+n+1)$ is a gamma function. The two cases of the gamma function we shall be concerned about are

$$\Gamma\left(n+\frac{1}{2}\right) = \frac{1\cdot 3\cdot 5\cdots(2n-3)\,(2n-1)\sqrt{\pi}}{2^n}, \tag{11.198}$$

and $\Gamma(n+1) = n!$. The Sonine polynomials for $n = 0$ and $n = 1$ are easily found to be

$$S_q^0(x) = 1 \tag{11.199}$$

and

$$S_q^1(x) = q + 1 - x. \tag{11.200}$$

The Sonine polynomials have the orthogonality property

$$\int_0^\infty dx\, e^{-x} x^q S_q^n(x) S_q^{n'}(x) = \frac{\Gamma(q+n+1)}{n!}\,\delta_{n,n'}. \tag{11.201}$$

Below we use the Sonine polynomials to obtain approximate expressions for the transport coefficients. We consider them one at a time below.

11.G.2. Diffusion Coefficient

In Eq. (11.191) the diffusion coefficient is expanded in terms of an unknown quantity, Δ_x, Let us expand Δ_x in terms of Sonine polynomials, $S^l_{3/2}(\beta p^2/2m)$, so that

$$\Delta_x = \sum_{l=0}^{\infty} \mathrm{d}_l p_x S^l_{3/2}\left(\frac{\beta p^2}{2m}\right), \tag{11.202}$$

We use these particular Sonine polynomials because in terms of them the diffusion coefficient becomes particularly simple. Let us substitute the expansion, (11.202), into Eq. (11.191) and perform the integration. Then

$$\begin{aligned} D &= -\frac{1}{m^2}\left(\frac{\beta}{2\pi m}\right)^{3/2} \sum_{l=0}^{\infty} \mathrm{d}_l \int \mathbf{dp}\, e^{-\beta p^2/2m} p_x^2 S^l_{3/2}\left(\frac{\beta p^2}{2m}\right) \\ &= -\frac{1}{m^2}\left(\frac{\beta}{2\pi m}\right)^{3/2} \sum_{l=0}^{\infty} \mathrm{d}_l \int_0^{\infty} p^4 dp\, e^{-\beta p^2/2m} S^l_{3/2}\left(\frac{\beta p^2}{2m}\right) \\ &\quad \times \int_{-1}^{1} d\cos(\theta)\, \sin^2(\theta) \int_0^{2\pi} d\phi\, \cos^2(\phi) = -\frac{d_0}{m\beta}. \end{aligned} \tag{11.203}$$

Thus, the self-diffusion coefficient depends only on the coefficient d_0.

We now must find an approximate expression for d_0. Let us substitute Eq. (11.202) into Eq. (11.194), multiply the resulting expression by $(\beta/2\pi m)^{3/2} e^{-\beta p^2/2m} S^{l'}_{3/2}(\beta p^2/2m)\, p_x$ and integrate over $\mathbf{p}$. Equation (11.194) then takes the form

$$\sum_{l=0}^{\infty} \mathrm{D}_{l',l}\mathrm{d}_l = \frac{m}{\beta}\delta_{l',0}, \tag{11.204}$$

where

$$D_{l',l} = \left(\frac{\beta}{2\pi m}\right)^{3/2} \int d\mathbf{p}\, e^{-\beta p^2/2m} S^{l'}_{3/2}\left(\frac{\beta p^2}{2m}\right) p_x \hat{C}^-_{\mathbf{p}} S^l_{3/2}\left(\frac{\beta p^2}{2m}\right) p_x, \tag{11.205}$$

Equation (11.204) is actually an infinite set of equations which determines all the coefficients, d_l.

The self-diffusion coefficient only depends on d_0. We can obtain an approximate expression for the self-diffusion coefficient if we use a truncated version of Eq. (11.204). Let us retain only the first $\nu + 1$ terms in the sum and

write

$$\sum_{l=0}^{\nu} D_{l',l}^{(\nu)} d_l^{(\nu)} = \frac{m}{\beta}\,\delta_{l',0} \quad \text{for} \quad l' = 0, 1, \ldots, \nu. \tag{11.206}$$

The set of coefficients $D_{l',l}^{(\nu)}$ form a $(\nu+1) \times (\nu+1)$ matrix. The coefficient $d_0^{(\nu)}$ is given by

$$d_0^{(\nu)} = \frac{m}{\beta}\,([D^{(\nu)}]^{-1})_{0,0}, \tag{11.207}$$

where $([D^{(\nu)}]^{-1})_{0,0}$ is the $(0,0)$ matrix element of the inverse of matrix, $D^{(\nu)}$. The coefficient of self-diffusion now becomes

$$D = -\frac{1}{\beta^2} \lim_{\nu\to\infty} ([D^{(\nu)}]^{-1})_{0,0}. \tag{11.208}$$

When the matrix is truncated to lowest order, the self-diffusion coefficient is given by

$$D = -\frac{1}{\beta^2}\frac{1}{D_{00}} = -\frac{1}{\beta^2}\frac{1}{\langle p_x \hat{C}_{\mathbf{p}}^{+} p_x\rangle}. \tag{11.209}$$

To second order it is

$$D = -\frac{1}{\beta^2}\frac{1}{D_{00}}\left[1 - \frac{D_{01}D_{10}}{D_{00}D_{11}}\right]^{-1}, \tag{11.210}$$

and so on.

The self-diffusion coefficient is straightforward to compute for a hard sphere gas (see Exercise 11.4). For hard spheres of radius R it is

$$D = -\frac{1}{\beta^2}\frac{1}{\langle p_x \hat{C}_{\mathbf{p}}^{+} p_x\rangle} = \frac{3}{32}\frac{1}{n_0 R^2}\sqrt{\frac{k_B T}{m\pi}}. \tag{11.211}$$

In practice it is found that higher-order corrections only change Eq. (11.211) by a few percent (cf. Ref. 6, page 168).

11.G.3. Thermal Conductivity

In Eq. (11.192) the thermal conductivity is written in terms of an unknown quantity, A_x. Let us expand A_x in terms of Sonine polynomials, $S_{3/2}^{l}(\beta p^2/2m)$, so that

$$A_x = \sum_{l=0}^{\infty} a_l p_x S_{3/2}^{l}\left(\frac{\beta p^2}{2m}\right). \tag{11.212}$$

If we substitute the expansion, Eq. (11.212), into Eq. (11.192) and perform the

integration, we find

$$K = -\frac{n_0 k_B}{m^2}\left(\frac{\beta}{2\pi m}\right)^{3/2}\sum_{l=0}^{\infty} a_l \int d\mathbf{p}\, e^{-\beta p^2/2m}\left[\frac{\beta p^2}{2m}-\frac{5}{2}\right] p_x^2 S^l_{3/2}\left(\frac{\beta p^2}{2m}\right)$$

$$= +\frac{n_0 k_B}{m^2}\left(\frac{\beta}{2\pi m}\right)^{3/2}\sum_{l=0}^{\infty} a_l \int_0^{\infty} p^4 dp\, e^{-\beta p^2/2m} S^1_{3/2}\left(\frac{\beta p^2}{2m}\right) S^l_{3/2}\left(\frac{\beta p^2}{2m}\right)$$

$$\times \int_{-1}^{1} d\cos(\theta)\sin^2(\theta)\int_0^{2\pi} d\phi \cos^2(\phi) = \frac{5 n_0 k_B}{2m\beta} a_1. \tag{11.213}$$

The thermal conductivity depends only on a_1.

Let us next determine a_1. In Eq. (11.195) expand A_x in Sonine polynomials, then multiply by $(\beta/2\pi m)^{3/2} e^{-\beta p^2/2m} S^{l'}_{3/2}(\beta p^2/2m) p_x$ and integrate over $\mathbf{p}$. Equation (11.195) then takes the form

$$\sum_{l=0}^{\infty} \mathrm{M}_{l',l} a_l = -\frac{5}{2}\frac{m}{\beta}\delta_{l',1}, \tag{11.214}$$

where

$$\mathrm{M}_{l',l} = \left(\frac{\beta}{2\pi m}\right)^{3/2}\int d\mathbf{p}\, e^{-\beta p^2/2m} S^{l'}_{3/2}\left(\frac{\beta p^2}{2m}\right) p_x \hat{C}^+_{\mathbf{p}} S^l_{3/2}\left(\frac{\beta p^2}{2m}\right) p_x. \tag{11.215}$$

In evaluating the integral on the righthand side of Eq. (11.214), we have used the orthogonality of the Sonine polynomials. Note that since the collision operator, $\hat{C}^+_{\mathbf{p}}$, conserves momentum we have $\hat{C}^+_{\mathbf{p}} p_x = 0$. Therefore, $\mathrm{M}_{l',0} = 0$ and $\mathrm{M}_{0,l} = 0$. Equation (11.214) becomes

$$\sum_{l=1}^{\infty} \mathrm{M}_{l',l} a_l = -\frac{5}{2}\frac{m}{\beta}\delta_{l',1} \qquad \text{for} \quad l' \geqslant 1. \tag{11.216}$$

Using a similar approximation as in Eq. (11.209), we write the coefficient of thermal conductivity as

$$K = -\frac{25}{4}\frac{n_0 k_B}{\beta^2}\frac{1}{\mathrm{M}_{11}} = -\frac{25}{4}\frac{n_0 k_B}{\beta^2}\frac{1}{\langle S^1_{3/2} p_x \hat{C}^+_{\mathbf{p}} S^1_{3/2} p_x\rangle}. \tag{11.217}$$

In Exercise 11.4 we compute the thermal conductivity for a gas of hard spheres of radius R. We find

$$K = \frac{75}{256 R^2}\sqrt{\frac{k_B^3 T}{m\pi}}. \tag{11.218}$$

TABLE 11.1. Thermal Conductivity, K, in Units of 10^{-3} W/m.K. for Some Monatomic Gases at Pressure $P = 10^5$ Pa. [14]

Gas	K(200 K)	K (300 K)	K (400 K)
Argon (Ar)	12.4	17.9	22.6
Helium (He)	119.3	156.7	190.6
Krypton (Kr)	6.4	9.5	12.3
Neon (Ne)	37.6	49.8	60.3
Xenon (Xe)	3.6	5.5	7.3

Equation (11.218) is obtained by truncating Eq. (11.216) to lowest order. However, it is good to within a few percent (Ref. 6, page 168). Values of the thermal conductivity for some simple monatomic gases are given in Table 11.1.

■ **EXERCISE 11.4.** The coefficient of thermal conductivity can be written

$$K = -\frac{n_0 k_B}{m^2}\left(\frac{\beta}{2\pi m}\right)^{3/2}\int d\mathbf{p} e^{-\beta p^2/2m}\left[\frac{\beta p^2}{2m}-\frac{5}{2}\right]p_x A_x,$$

where $A_x = \sum_{l=1}^{\infty} a_l p_x S_{3/2}^l(\beta p^2/2m)$. Compute the coefficient of thermal conductivity, K, for a gas of hard-sphere particles of radius R, keeping only the lowest order term ($l = 1$) in the expansion for A_x.

Answer: First note that

$$\begin{aligned} K &= -\frac{n_0 k_B}{m^2}\left(\frac{\beta}{2\pi m}\right)^{3/2}\int d\mathbf{p}\, e^{-\beta p^2/2m}\left[\frac{\beta p^2}{2m}-\frac{5}{2}\right]p_x A_x \\ &= +\frac{n_0 k_B}{m^2}\, a_1\left(\frac{\beta}{2\pi m}\right)^{3/2}\int d\mathbf{p}\, p_x^2\, e^{-\beta p^2/2m}\left[S_{3/2}^1\left(\frac{\beta p^2}{2m}\right)\right]^2 \qquad (1) \\ &= \frac{5}{2}\frac{n_0 k_B}{m\beta}\, a_1, \end{aligned}$$

so the thermal conductivity depends only on a_1. Since the coefficient of thermal conductivity can be written

$$K = -\frac{n_0 k_B}{m^2}\left(\frac{\beta}{2\pi m}\right)^{3/2}\int d\mathbf{p} e^{-\beta p^2/2m}\left[\frac{\beta p^2}{2m}-\frac{5}{2}\right]p_x \frac{1}{\hat{C}_{\mathbf{p}}^{+}}\left[\frac{\beta p^2}{2m}-\frac{5}{2}\right]p_x, \quad (2)$$

we have that

$$\hat{C}_{\mathbf{p}}^{+} A_x = \left[\frac{\beta p^2}{2m} - \frac{5}{2}\right] p_x. \tag{3}$$

If we multiply by $(\beta/2\pi m)^{3/2} \int d\mathbf{p}\, e^{-\beta p^2/2m} S_{3/2}^{1} (\beta p^2/2m) p_x$ and keep only the lowest order term in the expansion of A_x, Eq. (3) takes the form

$$\mathrm{M}_{11} \mathrm{a}_1 = -\frac{5}{2} \frac{m}{\beta}, \tag{4}$$

where

$$\begin{aligned} \mathrm{M}_{11} &= \langle S_{3/2}^{1} p_x \hat{C}_{\mathbf{p}}^{+} S_{3/2}^{1} p_x \rangle \\ &= \left(\frac{\beta}{2\pi m}\right)^{3/2} \int d\mathbf{p}\, e^{-\beta p^2/2m} S_{3/2}^{1} \left(\frac{\beta p^2}{2m}\right) p_x \hat{C}_{\mathbf{p}}^{+} S_{3/2}^{1} \left(\frac{\beta p^2}{2m}\right) p_x. \end{aligned} \tag{5}$$

We can use the fact that momentum is conserved during the collisions so $\hat{C}_{\mathbf{p}}^{+} p_x = 0$. Therefore M_{11} becomes

$$\begin{aligned} \mathrm{M}_{11} &= \left(\frac{\beta m}{2}\right)^2 \langle p^2 p_x \hat{C}_{\mathbf{p}}^{+} p^2 p_x \rangle \\ &= -\frac{1}{4} \frac{N}{V} \frac{\beta^2}{4} m^{10} \left(\frac{\beta}{2\pi m}\right)^3 \iint d\mathbf{v}_1\, d\mathbf{v}_2 e^{-\beta m(v_1^2 + v_2^2)/2} \\ &\quad \times \int d(\cos(\Theta)) d\alpha g \sigma(\Theta, g) \\ &\quad \times (v_{1',x} v_{1'}^2 + v_{2',x} v_{2'}^2 - v_{1,x} v_1^2 - v_{2,x} v_2^2)^2. \end{aligned} \tag{6}$$

In order to evaluate the integral in Eq. (6), we introduce the center-of-mass velocity, $\mathbf{V}_{cm} = \frac{1}{2}(\mathbf{v}_1 + \mathbf{v}_2)$, and the relative velocity, $\mathbf{g} = \mathbf{v}_2 - \mathbf{v}_1$, so that $\mathbf{v}_1 = \mathbf{V}_{cm} - \frac{1}{2}\mathbf{g}$, $\mathbf{v}_2 = \mathbf{V}_{cm} + \frac{1}{2}\mathbf{g}$, $\mathbf{v}_{1'} = \mathbf{V}_{cm} - \frac{1}{2}\mathbf{g}'$, and $\mathbf{v}_{2'} = \mathbf{V}_{cm} + \frac{1}{2}\mathbf{g}'$. Then after some algebra we find

$$v_{1',x} v_1^2 + v_{2',x} v_{2'}^2 - v_{1,x} v_1^2 - v_{2,x} v_2^2 = g_x' (\mathbf{g}' \cdot \mathbf{V}_{cm}) - g_x (\mathbf{g} \cdot \mathbf{V}_{cm}) \tag{7}$$

and

$$\begin{aligned} \mathrm{M}_{11} &= -\frac{1}{4} \frac{N}{V} \frac{\beta^2}{4} m^{10} \left(\frac{\beta}{2\pi m}\right)^3 \iint d\mathbf{V}_{cm} d\mathbf{g}\, e^{-\beta m(V_{cm}^2 + g^2/4)} \\ &\quad \times \int d(\cos(\Theta)) d\alpha\, g\, \sigma(\Theta, g) \\ &\quad \times [(g_x')^2 (\mathbf{g}' \cdot \mathbf{V}_{cm})^2 - 2 g_x' g_x (\mathbf{g}' \cdot \mathbf{V}_{cm}) (\mathbf{g} \cdot \mathbf{V}_{cm}) + g_x^2 (\mathbf{g} \cdot \mathbf{V}_{cm})^2]. \end{aligned} \tag{8}$$

The collision cross section for hard spheres of radius R is $\sigma(\Theta, g) = (2R)^2/4 = R^2$. Let $V_{cm,i}$ $(i = x, y, z)$ denote the ith component of the center-of-mass velocity. Then

$$\int d\mathbf{V}_{cm}\, e^{-\beta m V_{cm}^2} V_{cm,i} V_{cm,j} = \frac{1}{2m\beta}\left(\frac{\pi}{m\beta}\right)^{3/2} \delta_{ij}. \tag{9}$$

If we integrate over the center-of-mass velocity, we find

$$\begin{aligned} \mathrm{M}_{11} &= -\frac{1}{4}\frac{N}{V}\frac{\beta^2}{4} m^{10}\left(\frac{\beta}{2\pi m}\right)^3 \frac{1}{2m\beta}\left(\frac{\pi}{m\beta}\right)^{3/2} R^2 \int d\mathbf{g}\, g\, e^{-\beta m g^2/4} \\ &\quad \times \int d(\cos(\Theta)) d\alpha [g_x'^2 g'^2 - 2g_x' g_x (\mathbf{g}' \cdot \mathbf{g}) + g_x^2 g^2] \\ &= -\frac{2}{3}\frac{N}{4V}\frac{\beta^2}{4} m^{10}\left(\frac{\beta}{2\pi m}\right)^3 \frac{1}{2m\beta}\left(\frac{\pi}{m\beta}\right)^{3/2} R^2 \int d\mathbf{g}\, g\, e^{-\beta m g^2/4} \\ &\quad \times \int d(\cos(\Theta)) d\alpha\, [g^4 - (\mathbf{g}' \cdot \mathbf{g})^2]. \end{aligned} \tag{10}$$

In Eq. (10), we have let $g_x^2 \to \frac{1}{3} g^2$ inside the integral, since by symmetry $\langle S^1_{3/2} p_x \hat{C}^+_{\mathbf{p}} S^1_{3/2} p_x \rangle = \langle S^1_{3/2} p_y \hat{C}^+_{\mathbf{p}} S^1_{3/2} p_y \rangle = \langle S^1_{3/2} p_z \hat{C}^+_{\mathbf{p}} S^1_{3/2} p_z \rangle$. Now choose the z-axis to lie along $\mathbf{g}$. Then $g_x' = g \sin(\Theta) \cos(\alpha)$, $g_y' = g \sin(\Theta) \sin(\alpha)$, $g_z' = g \cos(\Theta)$ and $\mathbf{g}' \cdot \mathbf{g} = g^2 \cos(\Theta)$. First integrate over $d(\cos(\Theta))\, d\alpha$. Then integrate over $d\mathbf{g}$. We finally obtain

$$\mathrm{M}_{11} = -\frac{64}{3}\frac{n_0 R^2 \sqrt{m\pi}}{\beta^{3/2}}, \tag{11}$$

and coefficient of thermal conductivity is given by

$$K = \frac{75}{256 R^2}\sqrt{\frac{k_B^3 T}{m\pi}}. \tag{12}$$

11.G.4. Shear Viscosity

In Eq. (11.193), the shear viscosity is written in terms of an unknown quantity, B_{xy}. Let us expand B_{xy} in terms of Sonine polynomials, $S^l_{5/2}(\beta p^2/2m)$, so that

$$B_{xy} = \sum_{l=0}^{\infty} \mathrm{b}_l p_x p_y S^l_{5/2}\left(\frac{\beta p^2}{2m}\right), \tag{11.219}$$

Let us substitute the expansion, Eq. (11.219), into Eq. (11.193) and perform the

integration. Then

$$\eta = -\frac{n_0\beta}{m^2}\left(\frac{\beta}{2\pi m}\right)^{3/2}\sum_{l=0}^{\infty} \mathrm{b}_l \int d\mathbf{p} e^{-\beta p^2/2m} p_x^2 p_y^2 S_{5/2}^l\left(\frac{\beta p^2}{2m}\right)$$

$$= -\frac{n_0\beta}{m^2}\left(\frac{\beta}{2\pi m}\right)^{3/2}\sum_{l=0}^{\infty} \mathrm{b}_l \int_0^{\infty} p^6 dp e^{-\beta p^2/2m} S_{5/2}^l\left(\frac{\beta p^2}{2m}\right) \tag{11.220}$$

$$\times \int_{-1}^{1} d\cos(\theta)\sin^4(\theta)\int_0^{2\pi} d\phi \sin^2(\phi)\cos^2(\phi) = -\frac{n_0 \mathrm{b}_0}{\beta}.$$

Thus, the shear viscosity depends only on b_0.

In order to determine b_0, substitute the expansion Eq. (11.219) for B_{xy} into Eq. (11.196). Then multiply by $(\beta/2\pi m)^{3/2} e^{-\beta p^2/2m} S_{5/2}^{l'}(\beta p^2/2m) p_x p_y$ and integrate over $\mathbf{p}$. Equation (11.196) then takes the form

$$\sum_{l=0}^{\infty} \mathrm{N}_{l',l}\,\mathrm{b}_l = \frac{m^2}{\beta^2}\,\delta_{l',0}, \tag{11.221}$$

where

$$\mathrm{N}_{l',l} = \left(\frac{\beta}{2\pi m}\right)^{3/2}\int d\mathbf{p} e^{-\beta p^2/2m} S_{5/2}^{l'}\left(\frac{\beta p^2}{2m}\right) p_x p_y \hat{C}_{\mathbf{p}}^{+} S_{5/2}^{l}\left(\frac{\beta p^2}{2m}\right) p_x p_y. \tag{11.222}$$

If we truncate Eq. (11.221) to lowest order, we can write the shear viscosity as

$$\eta = -\frac{n_0 m^2}{\beta^3}\frac{1}{\mathrm{N}_{00}} = -\frac{m_0 m^2}{\beta^3}\frac{1}{\langle p_x p_y \hat{C}_{\mathbf{p}}^{+} p_x p_y\rangle}. \tag{11.223}$$

For a gas of hard spheres of radius R, Eq. (11.223) yields for the shear viscosity

$$\eta = \frac{5}{64R^2}\sqrt{\frac{mk_BT}{\pi}}. \tag{11.224}$$

TABLE 11.2. Viscosity, η, in Units of 10^{-5} poise for Some Monatomic gases at Pressure $P = 10^5$ Pa. [14]

Gas	η (200 K)	η (300 K)	η (400 K)
Argon (Ar)	15.9	22.9	38.8
Helium (He)	15.3	20.0	24.4
Krypton (Kr)	17.1	25.6	33.1
Neon (Ne)	24.3	32.1	38.9
Xenon (Xe)	15.4	23.2	30.7

This expression is correct to within a few percent (cf. Ref. 6, page 168). Values of the viscosity for some monatomic gases are given in Table 11.2.

It is interesting to compare the viscosity and thermal conductivity. If we take the ratio we find $K/\eta = 15k_B/4m = \frac{5}{2}c_V$, where $c_V = 3k_B/2m$ is the specific heat of an ideal monatomic gas. The ratio $K/\eta c_V = \frac{5}{2}$ is called the *Euken number*. One can check to see if this relation is satisfied by the monatomic gases in Tables 11.1 and 11.2.

▶ SPECIAL TOPICS

▶ S11.A. Beyond the Boltzmann Equation

Computer experiments and a careful study of correlation functions have shown that the picture of transport phenomena given by Boltzmann is not completely correct. It is now realized that many-body processes play a very important role in determining of the long-time behavior of the correlation functions, and, at best, Boltzmann's equation can only describe short-time processes. The Boltzmann equation predicts exponential decay of the correlation functions, but simple hydrodynamic arguments give a decay of the form, $t^{-d/2}$ (long-time tail), where d is the dimension of the system. These long-time tails have been observed in computer experiments and are now well-established theoretically. Long-time tails in the velocity autocorrelations function of a Brownian particle were derived in Section (S10.G).

The many-body processes which give rise to the long-time tails have forced a change in our analysis of linear hydrodynamics. It was long thought that corrections to the Navier–Stokes equations could be obtained by expanding the macroscopic currents in terms of higher-order gradients, thereby introducing new transport coefficients to account for shorter-wavelength effects. However, this is now known to be incorrect. Microscopic calculations have shown that the transport coefficients in the so-called Burnett order (coefficients of the fourth-order gradients) and higher order are infinite. Therefore, a simple power series expansion of the hydrodynamic frequencies in terms of the wavevector will not work. The hydrodynamic frequencies are nonanalytic functions of the wave vectors.

Transport coefficients can be computed by integrating the appropriate time dependent current correlation functions over an infinite time interval, from $t = 0$ to $t = \infty$ [cf. Eq. (11.190)]. Therefore, if the transport coefficients are to be finite, the correlation functions must decay sufficiently rapidly in time. For a long time it was a common view that the correlation functions would decay exponentially since this is what is predicted by the Boltzmann equation. However, in 1967, Alder and Wainwright [15], in a computer calculation of the velocity autocorrelation function for a gas of hard spheres, found that the decay of the autocorrelation function was exponential only for a few mean free times and that after a longer time the decay went as $t^{-3/2}$ (in three dimensions). In

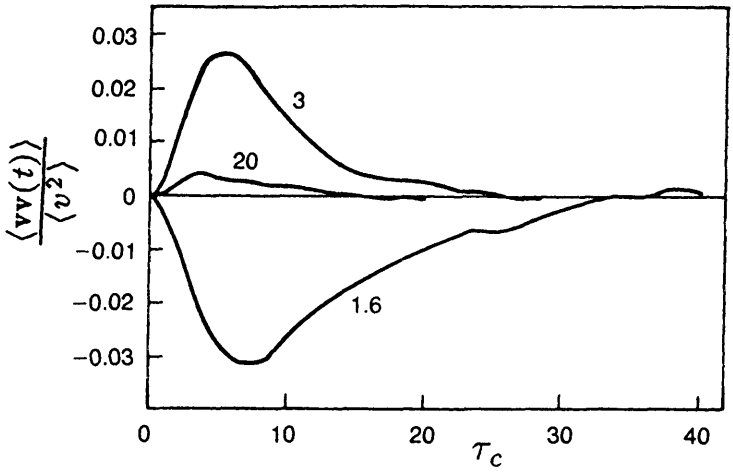


Fig. 11.10. A plot of the difference between the velocity autocorrelation function obtained from molecular dynamics calculations for hard spheres and that given by Boltzmann theory. The correlation function is plotted as a function of mean collision times for 108 particles at $V/V_0 = 1.6$, 3, and 20 (based on Ref. [15]).

other words, it had a long-time tail. In Fig. 11.10 we give their results for various densities. The figure gives the difference between the exact velocity autocorrelation function for a hard-sphere gas and that computed using the Boltzmann equation. Both are plotted as a function of the number of collisions that have occurred. The different curves correspond to different particle densities (V_0 is the close-packed volume). We see that after many collisions have occurred, the correlation functions decay away very slowly, as $t^{3/2}$. The long-time tails are now known to be due to the long-lived hydrodynamic modes of the fluid. This can be shown using hydrodynamic arguments [16] (see Section S10.G).

Expressions for transport coefficients obtained using the Boltzmann equation are limited to systems with very low density. If we wish to obtain expressions for the transport coefficients at higher densities using microscopic theory, we must begin by writing them in terms of a virial expansion (expansion in powers of the density). The first attempt in this direction was made by Bogoliubov [17], who gave a prescription for obtaining a virial expansion for the transport coefficients, but the first actual calculation was done by Choh and Uhlenbeck [18]. The Boltzmann equation includes only effects of two-body collisions. Choh and Uhlenbeck computed the contribution to the transport coefficients due to three-body processes. Their result was well-behaved. Somewhat later, a number of authors attempted to extend calculations of the transport coefficients to higher order in density. In so doing, they found that all higher-order terms are infinite, and therefore the expansion of the transport coefficients in powers of the density is divergent and ill-defined. The divergences in the virial expansion come from secular effects. Resummation of divergent terms [19] leads to well-

defined expressions for the transport coefficients but introduces a nonanalytic density expansion for them. The divergences are related to the appearance of long-time tails in the correlation functions. One of the simplest correlation functions we can compute, and the one measured in the molecular dynamics calculations of Alder and Wainwright, is the velocity autocorrelation function. We will discuss briefly how a virial expansion for this quantity is introduced.

If we consider a classical system of N particles which interact via a spherically symmetric potential, the Hamiltonian has the form

$$H^N(\mathbf{X}^N) = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i<j} V(|\mathbf{q}_i - \mathbf{q}_j|), \tag{11.225}$$

and the Liouville operator has the form

$$\mathrm{L}^N(\mathbf{X}^N) = \sum_{i=1}^{N} \frac{\mathbf{p}_i}{m} \cdot \frac{\partial}{\partial \mathbf{q}_i} - \sum_{i<j} \frac{\partial V_{ij}}{\partial \mathbf{q}_i} \cdot \left(\frac{\partial}{\partial \mathbf{p}_i} - \frac{\partial}{\partial \mathbf{p}_j} \right). \tag{11.226}$$

If we tag particle 1, the probability density of finding particle 1 at point $\mathbf{r}$ at time t is

$$\rho_1(\mathbf{r}, t) = \langle \delta(\mathbf{q}_1(t) - \mathbf{r}) \rangle = \int \cdots \int d\mathbf{X}_1 \cdots d\mathbf{X}_N \, \rho_{eq}(\mathbf{X}^N) \, e^{t\mathrm{L}^N} \, \delta(\mathbf{q}_1 - \mathbf{r}), \tag{11.227}$$

where $\mathbf{q}_1$ is the position of particle 1 at time $t = 0$, and $\rho_{eq}(\mathbf{X}^N)$ is the equilibrium probability density

$$\rho_{eq}(\mathbf{X}^N) = \frac{e^{-\beta H^N}}{\int \cdots \int d\mathbf{X}_1 \cdots d\mathbf{X}_N \, e^{-\beta H^N}}. \tag{11.228}$$

The velocity autocorrelation function is given by

$$\begin{aligned} C_{\mathrm{vv}} &= \langle \mathbf{v}(\mathbf{0}, 0) \mathbf{v}(\mathbf{r}, t) \rangle = \frac{1}{m^2} \langle \mathbf{p}_1 \delta(\mathbf{q}_1) \mathbf{p}_1(t) \delta(\mathbf{q}_1(t) - \mathbf{r}) \rangle \\ &= \frac{1}{m^2} \int \cdots \int d\mathbf{X}_1 \cdots d\mathbf{X}_N \, \rho_{eq}(\mathbf{X}^N) \mathbf{p}_1 \delta(\mathbf{q}_1) \, e^{t\mathrm{L}^N} \, \mathbf{p}_1 \delta(\mathbf{q}_1 - \mathbf{r}). \end{aligned} \tag{11.229}$$

It is most convenient to work with the Fourier–Laplace transform

$$S_{\mathrm{vv}}(\mathbf{k}, z) = \int_0^\infty dt e^{-zt} \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \, C_{\mathrm{vv}}(\mathbf{r}, t). \tag{11.230}$$

If we expand in the time evolution operator, $e^{t\mathrm{L}^N}$, in a power series, integrate

each term by parts, and resum it, we obtain an expression in which the time evolution operator acts on the phase function to the left. We then find, after some simplification,

$$S_{vv}(\mathbf{k},z) = \frac{1}{m^2}\frac{1}{V}\int_0^\infty dt\, e^{-zt} \sum_{\mathbf{k}_1} \int \cdots \int d\mathbf{X}_1 \cdots d\mathbf{X}_N \times \mathbf{p}_1 e^{i\mathbf{k}\cdot\mathbf{q}_1} e^{-tL^N} \rho_{eq}(\mathbf{X}^N) e^{-i\mathbf{k}_1\cdot\mathbf{q}_1}\mathbf{p}_1, \tag{11.231}$$

where the minus sign on the evolution operator comes from the integration by parts.

Let us now rewrite $S_{vv}(\mathbf{k},z)$ in the form

$$S_{vv}(\mathbf{k},z) = \frac{1}{m^2}\int d\mathbf{p}_1\mathbf{p}_1\chi(\mathbf{p}_1;\mathbf{k},z)\mathbf{p}_1, \tag{11.232}$$

where

$$\chi(\mathbf{p}_1;\mathbf{k},z) = \frac{1}{V}\int_0^\infty dt e^{-zt} \sum_{\mathbf{k}_1} \int d\mathbf{q}_1 \int d\mathbf{X}_2 \cdots \int d\mathbf{X}_N \times e^{i\mathbf{k}\cdot\mathbf{q}_1} e^{-tL^N} \rho_{eq}(\mathbf{X}^N)\, e^{-i\mathbf{k}\cdot\mathbf{q}_1}. \tag{11.233}$$

We can write the operator, $\chi(\mathbf{p}_1;\mathbf{k},z)$, as a virial expansion:

$$\chi(\mathbf{p}_1;\mathbf{k},z) = \sum_{l=0}^{\infty} n^l \chi_l(\mathbf{p}_1;\mathbf{k},z). \tag{11.234}$$

To find a microscopic expression for the virial coefficients, $\chi_l(\mathbf{p}_1;\mathbf{k},z)$, we first introduce a cumulant expansion for the evolution operator,

$$e^{-tL^N} \equiv S_t(1,,N) = \exp\left(\sum_{l=1}^{\infty} \mathrm{U}_t(1,\ldots,1)\right), \tag{11.235}$$

where $U_t(1,\ldots,l)$ is an l-body cluster operator. The cluster operators can be expressed in terms of the evolution operator through the following hierarchy of equations:

$$U_t(1) = S_t(1), \tag{11.236}$$

$$U_t(1,2) = S_t(1,2) - S_t(1)S_t(2), \tag{11.237}$$

$$U_t(1,2,3) = S_t(1,2,3) - \sum_{p}^{(3)} S_t(1)S_t(2,3) + 2!\prod_{i=1}^{3} S_t(i), \tag{11.238}$$

and so on, where $\sum_p^{(j)}$ denotes the sum over all j distinct permutations of the particles. If we isolate those cluster operators which depend on the coordinates of particle 1, we can write the evolution operator in terms of the following hierarchy:

$$S_t(1) = U_t(1), \tag{11.239}$$

$$S_t(1,2) = U_t(1)S_t(2) + U_t(1,2), \tag{11.240}$$

$$S_t(1,2,3) = U_t(1)S_t(2,3) + \sum_p^{(2)'} U_t(1,2)S_t(3) + U_t(1,2,3), \tag{11.241}$$

and so on. The prime the summation, $\sum_p^{(j)'}$, means that particle 1 is not to be included in the j distinct permutations.

We now substitute Eqs. (11.239)–(11.241) for the case of N particles into Eq. (11.233) and we obtain

$$\begin{aligned}\chi(\mathbf{p}_1;\mathbf{k},z) = \frac{1}{V}\sum_{\mathbf{k}_1}{}' \int_0^\infty dt e^{-zt} \int d\mathbf{q}_1 \int d\mathbf{X}_2 \cdots \int d\mathbf{X}_N \\ \times e^{i\mathbf{k}\cdot\mathbf{q}_1}\left\{ U_t(1)\, S_t(2,\ldots,N) + \sum_p^{(N-1)'} U_t(1,2)S_t(3,\ldots,N) \right. \\ \left. + \sum_p^{(N-1)(N-2)/2'} U_t(1,2,3)S_t(4,\ldots,N) + \cdots \right\} \rho_{eq}(\mathbf{X}^N) e^{-i\mathbf{k}_1\cdot\mathbf{q}_1}.\end{aligned} \tag{11.242}$$

Equation (11.242) simplifies somewhat if we note that

$$\frac{1}{V}\phi(1) \equiv \int\cdots\int d\mathbf{X}_2 \cdots d\mathbf{X}_N\, S_t(2,\ldots,N)\rho_{eq}(\mathbf{X}^N) = \frac{1}{V}\left(\frac{\beta}{2\pi m}\right)^{3/2} e^{-\beta p_1^2/2m}. \tag{11.243}$$

Let us now use Eq. (11.243) and take the thermodynamic limit in Eq. (11.242). That is, we let $N \to \infty$ and $V \to \infty$ so $n = N/V$ is finite. Also, $(1/V)\sum_{\mathbf{k}_1} \to [1/(2\pi)^3] \int d\mathbf{k}_1$. We can then write Eq. (11.242) in the form

$$\begin{aligned}\chi(\mathbf{p}_1;\mathbf{k},z) = \frac{1}{(2\pi)^3}\int d\mathbf{k}_1 \int_0^\infty dt\, e^{-zt} \int d\mathbf{q}_1 \left\{ e^{i\mathbf{k}\cdot\mathbf{q}_1} U_t(1) e^{-i\mathbf{k}_1\cdot\mathbf{q}_1}\, \phi(1) \right. \\ + n\int d\mathbf{X}_2\, e^{i\mathbf{k}\cdot\mathbf{q}_1} U_t(1,2) e^{-i\mathbf{k}_1\cdot\mathbf{q}_1} \phi(1)\phi(2) \\ \left. + \frac{n^2}{2!}\int d\mathbf{X}_2 \int d\mathbf{X}_3\, e^{i\mathbf{k}\cdot\mathbf{q}_1}\, U_t(1,2,3) e^{-i\mathbf{k}_1\cdot\mathbf{q}_1}\, \phi(1)\phi(2)\phi(3) + \cdots \right\}.\end{aligned} \tag{11.244}$$

Let us next note that

$$\frac{1}{(2\pi)^3}\int d\mathbf{k}_1 \int_0^\infty dt\, e^{-zt} \int d\mathbf{q}_1 e^{i\mathbf{k}\cdot\mathbf{q}_1} U_t(1) e^{-i\mathbf{k}_1\cdot\mathbf{q}_1} = \frac{1}{z - i\mathbf{k}\cdot\mathbf{p}_1/m}. \quad (11.245)$$

Then the equation for $\chi(\mathbf{p}_1;\mathbf{k},z)$ takes the form of a virial expansion,

$$\chi(\mathbf{p}_1;\mathbf{k},z)\phi^{-1}(1) = \frac{1}{z - i\mathbf{k}\cdot\mathbf{p}_1/m} + \sum_{l=1}^{\infty} n^l \chi_l(\mathbf{p}_1;\mathbf{k},z)\phi^{-1}(1), \quad (11.246)$$

with virial coefficients,

$$\chi_1(\mathbf{p}_1;\mathbf{k},z) = \frac{1}{(2\pi)^3}\int d\mathbf{k}_1 \int_0^\infty dt\, e^{-zt} \int d\mathbf{q}_1 \int d\mathbf{X}_2 \times e^{i\mathbf{k}\cdot\mathbf{q}_1} U_t(1,2) e^{-i\mathbf{k}_1\cdot\mathbf{q}_1} \phi(1)\phi(2), \quad (11.247)$$

$$\chi_2(\mathbf{p}_1;\mathbf{k},z) = \frac{1}{2!}\frac{1}{(2\pi)^3}\int d\mathbf{k}_1 \int_0^\infty dt e^{-zt} \int d\mathbf{q}_1 \int d\mathbf{X}_2 \int d\mathbf{X}_3 \times e^{i\mathbf{k}\cdot\mathbf{q}_1} U_t(1,2,3) e^{-i\mathbf{k}_1\cdot\mathbf{q}_1} \phi(1)\phi(2)\phi(3), \quad (11.248)$$

and so on.

As a final step we can use a resummation procedure introduced by Zwanzig [20] and write $\chi(\mathbf{p}_1;\mathbf{k},z)$ in the form

$$\chi(\mathbf{p}_1;\mathbf{k},z)\phi^{-1}(1) = \frac{1}{z - i\mathbf{k}\cdot\mathbf{p}_1/m + \sum_{l=1}^{\infty} n^l B_l(\mathbf{p}_1;\mathbf{k},z)}, \quad (11.249)$$

where

$$B_1(\mathbf{p}_1;\mathbf{k},z) = \left(z - \frac{i}{m}\mathbf{k}\cdot\mathbf{p}_1\right)\chi_1(\mathbf{p}_1;\mathbf{k},z)\left(z - \frac{i}{m}\mathbf{k}\cdot\mathbf{p}_1\right)\phi^{-1}(1), \quad (11.250)$$

$$B_2(\mathbf{p}_1;\mathbf{k},z) = \left(z - \frac{i}{m}\mathbf{k}\cdot\mathbf{p}_1\right)\chi_2(\mathbf{p}_1;\mathbf{k},z)\left(z - \frac{i}{m}\mathbf{k}\cdot\mathbf{p}_1\right)\phi^{-1}(1) - \left(z - \frac{i}{m}\mathbf{k}\cdot\mathbf{p}_1\right)\chi_1(\mathbf{p}_1;\mathbf{k},z)\left(z - \frac{i}{m}\mathbf{k}\cdot\mathbf{p}_1\right) \times \chi_1(\mathbf{p}_1;\mathbf{k},z)\left(z - \frac{i}{m}\mathbf{k}\cdot\mathbf{p}_1\right)\phi^{-1}(1), \quad (11.251)$$

and so on. Note that $\mathbf{p}_1$ and $\chi(\mathbf{p}_1;\mathbf{k},z)$ do not commute. We can now combine Eqs. (11.232) and (11.249) and write the velocity autocorrelation function in the

form

$$S_{vv}(\mathbf{k},z)=\frac{1}{m^2}\int d\mathbf{p}_1\mathbf{p}_1\left(\frac{1}{z-i\mathbf{k}\cdot\mathbf{p}_1/m+\sum_{l=1}^{\infty}n^lB_l(\mathbf{p}_1;\mathbf{k},z)}\right)\mathbf{p}_1\phi(1). \tag{11.252}$$

The long-time hydrodynamic behavior of the correlation function is determined by the behaviour of $B_l(\mathbf{p}_1;\mathbf{k},z)$ in the limit $z\to 0$ and $\mathbf{k}\to 0$. Microscopic expressions for $B_l(\mathbf{p}_1;\mathbf{k},z)$ have been obtained by several authors using a binary collision expansion. We will not attempt to repeat their results but only describe the essential features.

The first-order term, $B_1(\mathbf{p}_1;\mathbf{k},z)$, is well-behaved in the limit $z\to 0$ and $\mathbf{k}\to 0$ and, in fact, reduces to the Lorentz–Boltzmann collision operator. Higher-order contributions were studied by Zwanzig [21] and Kawasaki and Oppenheim [19]. Zwanzig found that in three dimensions, $B_2(\mathbf{p}_1;\mathbf{k},z)$ is well-defined as $z\to 0$. Kawasaki and Oppenheim found that $B_2(\mathbf{p}_1;\mathbf{k},z)$ is well-defined for three dimensions and diverges as $\ln(z)$ for two dimensions:

$$B_2(\mathbf{p}_1,z)\sim\begin{cases}\text{well-behaved} & \text{(3 dimensions)}\\ \ln(z) & \text{(2 dimensions)..}\end{cases} \tag{11.253}$$

For all higher powers they found that the most divergent terms behave as

$$B_l(\mathbf{p}_1,z)\sim\begin{cases}\dfrac{1}{z^l} & \text{(3 dimensions)}\\[2ex] \dfrac{1}{z^{l-1}} & \text{(2 dimensions).}\end{cases} \tag{11.254}$$

Kawasaki and Oppenheim showed that these most divergent terms in each order of the density expansion result from repeated collisions in the binary collision expansion of $B_l(\mathbf{p}_1,z)$. These repeated collisions can last a very long time and therefore lead to secular terms in the correlation function which diverge in the limit $t\to\infty$.

The relation between the divergences in the viral expansion of the transport coefficients and the long-time tails found by Alder and Wainwright [15] has been shown by Dorfmann and Cohen [21] and by Dufty [22]. The Boltzmann equation is unable to account for the long-time tails observed in the correlation functions. They, in fact, result from long-wavelength hydrodynamic effects in the system. When the most divergent terms in the virial expansion of the transport coefficients are summed together, they give contributions to the current–current correlation functions which decay as $t^{-d/2}$ (where d is the number of dimensions) even for low density. To obtain this result it is necessary to retain contributions from collision processes involving all possible numbers of particles, even for low density. In practice, at very low density the many-

body effects give only a very small contribution to the transport coefficients and the Boltzmann equation is adequate. But in principle they are there and become more important as the density is raised.

The fact that we must include many-body effects in our expressions for the time correlation function has important consequences for hydrodynamics. Until now we have only discussed the Navier–Stokes limit of the hydrodynamic equations. That is, we have kept terms to order k^2 in the linearized hydrodynamic equations. However, it is also of interest to go to higher orders in k and by so doing introduce new transport coefficients. For example, we may wish to write the diffusion equation in the form

$$\frac{\partial n}{\partial t} = Dk^2 n + D_2 k^4 n + \cdots . \tag{11.255}$$

Corrections of this type were first introduced by Burnett [23] for the linearized hydrodynamic equations. By including contributions to the correlation function from higher powers in the density, Dufty and McLennan [24] have shown for diffusion processes that the transport coefficient, D_2, does not exist (is infinite) and that simple corrections of the linearized hydrodynamic equations involving higher-order gradients are not possible. Similar results have been obtained by Ernst and Dorfmann [25] for the corrections to the Navier–Stokes equations. Thus, and k-dependent corrections to the Navier–Stokes equations appear to be nonanalytic in k, and simple corrections in terms of higher-order gradients are not possible.

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PROBLEMS

Problem 11.1. A dilute gas of density n is contained in a cubic box and is in equilibrium with the walls at temperature T. Find the number of particles per unit area per unit time which collide with the walls and have magnitude of velocity greater than v_0.

Problem 11.2. Estimate the value of the coefficient of viscosity of argon gas at 25 °C and 1 atm pressure. Compare your estimate with the experimentally observed value of $\eta = 2.27 \times 10^{-4}\text{g} \cdot \text{cm}^{-1} \cdot \text{sec}^{-1}$. Argon has an atomic weight of 39.9 and at low temperature forms a closely packed solid with density $\rho = 1.65\,\text{g/cm}^3$.

Problem 11.3. The number density in phase space of an ideal gas can be written

$$f(\mathbf{p}, \mathbf{r}) = \frac{N}{V}\left(\frac{\beta}{2\pi m}\right)^{3/2} e^{-\beta p^2/2m}\,(1 + \varepsilon \sin(\theta)\cos(\theta)),$$

where θ and ϕ are the polar and azimuthal angles, respectively, of the momentum, $\mathbf{p}$, measured with respect to the z axis.

(**a**) Compute the *net* number of particles, per unit area per unit time, that pass through the y–z plane.
(**b**) Compute the *net* number of particles, per unit area per unit time, that pass through the x–z plane.

Problem 11.4. The electrons in a cubic sample of metallic solid of volume L^3 and temperature T may be considered to be a highly degenerate ideal Fermi–Dirac gas. Assume the surface of the cube forms a potential energy barrier which is infinitely high,

and assume that the electrons have spin $s = \frac{1}{2}$, mass m, and charge e. (a) What is the number of electrons in the velocity interval, $\mathbf{v} \to \mathbf{v} + d\mathbf{v}$? (b) Assume that an electrode is attached to the surface which lowers the potential energy to a large but finite value, W, in a small area, A, of the surface. Those electrons which have enough kinetic energy to overcome the barrier can escape the solid. How many electrons per second escape through the area, A? Assume that $W \gg 0$ and use this fact to make simplifying approximations to any integrals you might need to do.

Problem 11.5. Find the differential scattering cross section, in the lab frame, for two identical hard spheres of diameter D and mass m.

Problem 11.6. (a) Prove that the linearized Boltzmann and Lorentz–Boltzmann collision operators, $\hat{C}_{\mathbf{p}}^{+}$ and $\hat{C}_{\mathbf{p}}^{-}$, respectively, are self-adjoint. (b) Prove that the scalar products, $\langle \Phi, \hat{C}^{+}\Phi \rangle$ and $\langle \Phi, \hat{C}^{-}\Phi \rangle$, are always less than or equal to zero for arbitrary functions, $\Phi = \Phi(\mathbf{p})$.

Problem 11.7. An approximate expression for the Boltzmann collision operator, $\hat{C}$, is

$$\hat{C} = -\gamma \hat{1} + \gamma \sum_{i=1}^{5} |\phi_i\rangle\langle\phi_i|,$$

where $|\phi_i\rangle$ are the five orthonormal eigenfunctions of $\hat{C}$ with eigenvalue equal to zero. The five eigenfunctions are $|\phi_1\rangle = |1\rangle$, $|\phi_2\rangle = |p_x\rangle$, $|\phi_3\rangle = |p_y\rangle$, $|\phi_4\rangle = |p_z\rangle$, and $|\phi_5\rangle = |\frac{5}{2} - (\beta p^2/2m)\rangle$. They are orthonormal with respect to the scalar product,

$$\langle \phi(\mathbf{p}) | \chi(\mathbf{p}) \rangle = \left(\frac{\beta}{2\pi m}\right)^{3/2} \int d\mathbf{p} e^{-\beta p^2/2m} \phi(\mathbf{p}) \chi(\mathbf{p}).$$

(a) Compute the coefficient of shear viscosity

$$\eta = -\lim_{\varepsilon \to 0} \frac{n\beta}{m^2} \langle p_x p_y | \frac{1}{\hat{C} + \varepsilon} p_x p_y \rangle,$$

and the coefficient thermal conductivity,

$$K = -\lim_{\varepsilon \to 0} \frac{nk_B}{m^2} \left\langle \left(\frac{\beta p^2}{2m} - \frac{5}{2}\right) p_x | \frac{1}{\hat{C} + \varepsilon} p_x \left(\frac{\beta p^2}{2m} - \frac{5}{2}\right) \right\rangle,$$

where n is the number density of particles in the gas described by $\hat{C}$ and m is the mass of the particles.

(b) What are the units of γ? What are the units of η?

Problem 11.8. The coefficient of diffusion can written in the form

$$D = -\lim_{\varepsilon \to 0} \frac{1}{m^2} \left(\frac{\beta}{2\pi m}\right)^{3/2} \int d\mathbf{p}\, e^{-\beta p^2/2m} p_x \frac{1}{(\hat{C}_{\mathbf{p}}^{(-)} + \varepsilon)} p_x,$$

where $\hat{C}_{\mathbf{p}}^{(-)}$ is the Lorentz–Boltzmann collision operator. Replace $\hat{C}_{\mathbf{p}}^{(-)}$ by an effective collision operator, $\hat{J}_{\mathbf{p}}^{(-)}$, where $\hat{J}_{\mathbf{p}}^{(-)}$ acting on an arbitrary function, $h(\mathbf{p}, \mathbf{r}, t)$, has the form

$$\hat{J}_{\mathbf{p}}^{(-)} h(\mathbf{p}, \mathbf{r}, t) = -\gamma h(\mathbf{p}, \mathbf{r}, t) + \gamma \left(\frac{\beta}{2\pi m}\right)^{3/2} \int d\mathbf{p}'\, e^{-\beta p'^2/2m} h(\mathbf{p}', \mathbf{r}, t).$$

(a) Show that $\hat{J}_{\mathbf{p}}^{(-)}$ is self-adjoint and negative semidefinite and has one eigenfunction with eigenvalue zero.
(b) Use $\hat{J}_{\mathbf{p}}^{(-)}$ to obtain an explicit expression for the diffusion coefficient (do all the integrals).
(c) What are the units of γ?

Problem 11.9. Write the linearized Boltzmann equation for a dilute gas of interacting particles.

(a) Starting from this linearized Boltzmann equation, derive five linearized hydrodynamic equations.
(b) From the information in part (a), write a microscopic expression for the momentum current.

Problem 11.10. The coefficient of self-duffusion can be written

$$D = -\frac{1}{m^2}\left(\frac{\beta}{2\pi m}\right)^{3/2}\int d\mathbf{p} e^{-\beta p^2/2m} p_x \Delta_x,$$

where $\Delta_x = \sum_{l=0}^{\infty} \mathrm{d}_l p_x S_{3/2}^l(\beta p^2/2m)$. Compute the coefficient of self-diffusion, D, for a gas of hard-sphere particles of radius R, keeping only the lowest-order term ($l = 0$) in the expansion for Δ_x.

Problem 11.11. The coefficient of shear viscosity can be written

$$\eta = -\frac{n_0\beta}{m^2}\left(\frac{\beta}{2\pi m}\right)^{3/2}\int d\mathbf{p} e^{-\beta p^2/2m} p_x p_y B_{xy},$$

where $B_{xy} = \sum_{l=0}^{\infty} \mathrm{b}_l p_x p_y S_{5/2}^l(\beta p^2/2m)$. Compute the coefficient of shear viscosity, η, for a gas of hard-sphere particles of radius R, keeping only the lowest-order term ($l = 0$) in the expansion for B_{xy}.

12

NONEQUILIBRIUM PHASE TRANSITIONS

12.A. INTRODUCTION

In previous chapters we considered phase transitions that occur in systems in thermodynamic equilibrium. In this chapter we will give examples of phase transitions which can occur in chemical and hydrodynamic systems far from absolute thermodynamic equilibrium. The systems we will consider are locally in thermodynamic equilibrium, so the state of the system can be described in terms of thermodynamic densities which vary in space. However, they are far enough from absolute equilibrium that nonlinear effects must be included in the chemical rate equations or hydrodynamic equations. As we shall see, nonlinear effects open a whole new world of behavior for such systems. Nonlinear equations allow the possibility of multiple solutions, each with different regions of stability. Thus, as we change the parameters of a nonlinear system, it can exhibit phase transitions from one state to another.

Prigogine was first to show that near equilibrium (in the linear regime), if one of the thermodynamic forces is held fixed, the stable state of the system is a steady state characterized by a minimum entropy production and it is unique. This state is said to lie on the thermodynamic branch. However, as we move away from the linear regime, nonlinearities in the hydrodynamic equations or chemical rate equations become more important and at some point the thermodynamic branch becomes unstable and a nonequilibrium phase transition occurs. The system then changes to a new state which is characterized by an order parameter. Often the change is dramatic. Even if the boundary is held fixed and the steady state in the linear regime is homogeneous or has constant gradients, the new state that appears in the nonlinear regime can oscillate in space and/or in time and often exhibits nonlinear wave motion. Thus, the symmetry of such systems in space and/or in time is broken at the phase transition, and the new stable nonequilibrium state exhibits much more structure than the state on the thermodynamic branch or the state of thermodynamic equilibrium. These structured states (called *dissipative structures* by

Prigogine) require a flow of energy and sometimes a flow of matter and, therefore, a production of entropy to maintain them.

In this chapter we will illustrate nonequilibrium phase transitions with some classic examples taken from hydrodynamics and chemistry. Before we begin to consider examples, we will discuss how equilibrium stability arguments determine the stability of systems far from equilibrium. We will then consider two important nonlinear chemical reactions. In the first, the Schlögl model, we show that chemical systems can exhibit nonequilibrium phase transitions similar to the first-order transitions in the van der Waals system. That is, abrupt transitions in the concentration of one of the chemicals can occur. As a second example, we discuss the Brusselator chemical model introduced by Prigogine and Lefever. This is the simplest chemical model that can exhibit spatial and temporal *dissipative structures*—that is, oscillations in space and in time maintained by the flow of chemicals through the system. (It is interesting to note that many of the ideas of nonlinear chemistry can also be applied to population dynamics and ecological systems because, much like chemical systems, individuals continually interact and are changed by their interactions, thus causing dynamical evolution of the populations. Unfortunately, we do not have space to explore this fascinating subject here.)

As a final example, we consider a purely hydrodynamic system and show that the nonlinearities in the Navier–Stokes equations can lead to instabilities in fluid flow. Turbulence is one example of such an instability. The example we shall consider is called the *Rayleigh–Benard instability*, and it occurs in a fluid layer in the presence of gravity when the layer is heated from below. When the temperature gradient becomes great enough, the fluid undergoes a transition from an isotropic stationary state to a state whose macroscopic behavior is dominated by stationary spatially periodic convection cells. The hydrodynamic equations can predict the parameter values at which this instability occurs.

In the *special topics* section, we study the behavior of fluctuations in the neighbourhood of some instabilities in the Brusselator and Rayleigh–Benard systems. Near the critical point, but in the isotropic phase, it is possible to isolate an order parameter for the nonequilibrium phase transition. The order parameter corresponds to a mode in the nonequilibrium system which exhibits *critical slowing down*. One can then use this 'critical' mode to write a time-dependent Ginzburg–Landau equation which describes the dominant behavior close to the critical point. In this way one obtains a description of nonequilibrium phase transitions which has some analogies to the description of equilibrium phase transitions.

12.B. NONEQUILIBRIUM STABILITY CRITERIA [1–3]

Nonequilibrium systems are dissipative because of transport processes and chemical reactions which lead to an increase in their entropy. Prigogine [1] showed that there are stability conditions associated with the rate at which

entropy increases in a nonequilibrium system. In this section we will discuss these stability criteria, first for systems near equilibrium and then for systems far from equilibrium.

Let us consider the entropy balance equation for a closed isolated system of constant volume. For such a system no heat or matter can be transported through the walls. We can integrate the entropy balance equation [cf. Eqs. (10.10), (10.24), and (10.179)] over the volume, V, of the system and find the following equation for the total time rate of change of the entropy:

$$\begin{aligned}\frac{dS}{dt} &= \int_V \frac{\partial \rho s}{\partial t} dV = -\int_V \nabla_{\mathbf{r}} \cdot (\rho s \mathbf{v} + \mathbf{J}_s^D) dV + \int_V \sigma_s dV \\ &= -\int_S (\rho s \mathbf{v} + \mathbf{J}_s^D) \cdot d\mathbf{S} + \int_V \sigma_s dV,\end{aligned} \tag{12.1}$$

where $\int_S$ denotes integration over the surface of volume, V. Since no energy or matter can flow through the surface, the contribution from the surface integral is zero. Thus

$$\frac{dS}{dt} = \int_V \sigma_s dV \tag{12.2}$$

is the rate of entropy production due to spontaneous processes in the system. The second law of thermodynamics tells us that for reversible processes the entropy of the system does not change, but for irreversible or spontaneous processes it must increase. Therefore,

$$\frac{dS}{dt} = \int_V \sigma_s dV \geq 0 \tag{12.3}$$

and the local entropy production, σ_s (time rate of change of entropy per unit volume), must be positive. The local entropy production can be written in the form

$$\sigma_s = -\sum_i \mathscr{J}_i \chi_i \geq 0, \tag{12.4}$$

where $\mathscr{J}_i$ is a local current, or flux, and χ_j is a local force [cf. Eqs. (10.26) and (10.179). We will now examine the behavior of this quantity both near equilibrium and far from equilibrium.

12.B.1. Stability Conditions Near Equilibrium

As we have seen in Chapter 10, near equilibrium the currents, $\mathscr{J}_i$, may be approximated by a linear relation of the form

$$\mathscr{J}_i = -\sum_j L_{ij} \chi_j, \tag{12.5}$$

where L_{ij} is a symmetric matrix, $L_{ij} = L_{ji}$ (Onsager's relation). If we substitute Eq. (12.5) into Eq. (12.4), we find in the linear regime

$$\sigma_s = \sum_i \sum_i L_{ij}\chi_i\chi_j \geq 0 \tag{12.6}$$

[cf. Eq. (12.4)]. Therefore, for a system in which spontaneous processes take place, the phenomenological coefficients form a symmetric positive definite matrix (cf. Section 2.H).

We can now ask under what conditions the entropy production will be minimum. For simplicity, let us first consider the case with two currents and two forces:

$$\sigma_s = \sum_{i=1}^{2} \sum_{i=1}^{2} L_{ij}\chi_i\chi_j > 0, \tag{12.7}$$

where we have taken the forces to be independent variables. The fluxes are then dependent. If we allow the forces to vary freely, the condition for minimum entropy production is given by the equations

$$\left(\frac{\partial\sigma_s}{\partial\chi_1}\right)_{\chi_2} = 2L_{11}\chi_1 + 2L_{12}\chi_2 \equiv -2\mathcal{J}_1 = 0 \tag{12.8}$$

and

$$\left(\frac{\partial\sigma_s}{\partial\chi_2}\right)_{\chi_1} = 2L_{22}\chi_2 + 2L_{21}\chi_1 \equiv -2\mathcal{J}_2 = 0 \tag{12.9}$$

(Note that we have assumed that L_{ij} is constant.) When there are no constraints on the forces, the state of minimum entropy production is the equilibrium state. The entropy production will be minimum (zero) when all forces and fluxes vanish.

Let us now hold one force fixed. That is, we let $\chi_1 =$ constant (this could be the case of a system with a constant temperature gradient maintained across it). Then the condition for minimum entropy production becomes simply

$$\left(\frac{\partial\sigma_s}{\partial\chi_2}\right)_{\chi_1} = 2L_{22}\chi_2 + 2L_{21}\chi_1 \equiv -2\mathcal{J}_2 = 0 \tag{12.10}$$

If we hold $\chi_1 =$ constant, then $\mathcal{J}_2$ will be zero in a state of minimum entropy production, but $\mathcal{J}_1$ will be nonzero and constant. Thus, the state of minimum entropy production will be a stationary state. This fact was first established by Prigogine [1].

We can generalize this result to an arbitrary number of forces and currents. Let us consider a system with n independent forces $\chi_i (i = 1, \ldots, n)$. The entropy production is

$$\sigma_s = \sum_{i,j=1}^{n} L_{ij} \chi_i \chi_j. \tag{12.11}$$

Let us now hold the forces $\chi_i (i = 1, \ldots, k)$ constant. The condition for minimum entropy production becomes

$$\left(\frac{\partial \sigma_s}{\partial \chi_i}\right)_{\{\chi_j \neq \chi_i\}} = \sum_{j=1}^{n} (L_{ij} + L_{ji}) \chi_j = 0 \tag{12.12}$$

$(i = k+1, \ldots, n)$. Using Onsager's relations, Eq. (12.5) becomes

$$2\mathcal{J}_i = 0 \tag{12.13}$$

for $(i = k+1, \ldots, n)$. In other words, if we hold $\chi_i (i = 1, \ldots, k)$ fixed, then $\mathcal{J}_i \equiv 0 (i = k+1, \ldots, n)$ when the system is in a state of minimum entropy production, and the currents $\mathcal{J}_i (i = 1, \ldots, k)$ will be constant. Such a state is a kth-order stationary state.

In the linear regime, the stationary states are always stable. That is, fluctuations cannot drive a system away from the stationary state. (This is no longer true in the nonlinear regime.) Let us consider a system specified by n independent forces. We will hold forces $\chi_1, \ldots, \chi_k$ fixed and allow fluctuations to occur in forces $\chi_{k+1}, \ldots, \chi_n$. Thus, we consider the entropy production to be a function of the forces $\chi_{k+1}, \ldots, \chi_n$. We will let $\chi_{k+1}^0, \ldots, \chi_n^0$ denote the values of the forces $\chi_{k+1}, \ldots, \chi_n$ in the steady state. The entropy production near the steady state can be expanded in a Taylor series of the form

$$\begin{aligned}
\sigma_s(\chi_{k+1}, \ldots, \chi_n) &= \sigma_s(\chi_{k+1}^0, \ldots, \chi_n^0) + \sum_{i=k+1}^{n} \left(\frac{\partial \sigma_s}{\partial \chi_i}\right)_{\{\chi_j \neq \chi_i\}}^{0} \delta\chi_i \\
&\quad + \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} \left[\frac{\partial}{\partial \chi_i} \left(\frac{\partial \sigma_s}{\partial \chi_j}\right)_{\{\chi_k \neq \chi_j\}}^{0}\right]_{\{\chi_l \neq \chi_i\}}^{0} \delta\chi_i \delta\chi_j + \cdots \\
&= \sigma_s(\chi_{k+1}^0, \ldots, \chi_n^0) + \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} L_{ij} \delta\chi_i \delta\chi_j + \cdots.
\end{aligned} \tag{12.14}$$

The quantity

$$\Delta P = \frac{1}{2} \int dV \sum_{i,j=k+1}^{n} L_{ij} \delta\chi_i \delta\chi_j > 0 \tag{12.15}$$

is called the excess entropy production and is always positive since the coefficients L_{ij} form a positive definite symmetric matrix. Since the stationary state is a state of minimum entropy production, we also have

$$\frac{d\Delta P}{dt} = -\int_V dV \sum_{j=k+1}^{N} \delta \mathscr{J}_j \frac{d\delta\chi_j}{dt} = -\int_V dV \sum_{j=k+1}^{N} g_{ij}\delta\mathscr{J}_i\delta\mathscr{J}_j \leq 0, \qquad (12.16)$$

where we have used the fact that $\delta\boldsymbol{\chi} = \bar{\mathbf{L}}^{-1}\cdot\bar{\mathbf{M}}\cdot\delta\boldsymbol{\alpha} = \bar{\mathbf{g}}\cdot\delta\boldsymbol{\alpha}$ and $\delta\boldsymbol{\mathscr{J}} = d\delta\boldsymbol{\alpha}/dt$ (cf. Section 10.D). Thus, the excess entropy function, ΔP, is a Liapounov function (cf. Appendix C).

Equations (12.15) and (12.16) guarantee the stability of stationary states in the linear regime. In the nonlinear regime, Eqs. (12.15) and (12.16) need not be satisfied and we have the possibility of forming unstable stationary states as various parameters are changed and of having phase transitions far from equilibrium.

12.B.2. Stability Conditions Far From Equilibrium

As we have seen above, it is possible to create a nonequilibrium steady state by holding some thermodynamic forces, such as the affinity or gradients of various densities, fixed. In the linear regime, the steady state which results is a state of minimum entropy production and is always stable. In the nonlinear regime, we can no longer write the currents as linear functions of the forces and it is no longer possible to prove that the steady state will continue to be stable in the nonlinear regime. Thus, we have the possibility of creating nonequilibrium steady states which become unstable as we vary certain parameters of the system, and the system can evolve to a new state which does not exist in the linear regime. That is, it can undergo a nonequilibrium phase transition.

12.B.2.1. General Arguments

A thermodynamic stability theory for systems far from equilibrium has been developed by Glansdorff and Prigogine [2]. When we consider systems for which the linear approximation is no longer valid, we can no longer show that the time rate of change of the entropy production has a definite sign, but we can show that part of it has a definite sign. If we write the entropy production in the form

$$P = -\int dV \sum_i \mathscr{J}_i\chi_i, \qquad (12.17)$$

its time derivative can be written

$$\frac{\partial P}{\partial t} = -\int dV \sum_i \left(\frac{\partial \mathscr{J}_i}{\partial t}\chi_i + \mathscr{J}_i\frac{\partial\chi_i}{\partial t}\right). \qquad (12.18)$$

In the linear regime we know that

$$\int dV \sum_i \frac{\partial \mathscr{J}_i}{\partial t} \chi_i = \int dV \sum_i \mathscr{J}_i \frac{\partial \chi_i}{\partial t} = \frac{1}{2} \frac{\partial P}{\partial t} \leq 0. \tag{12.19}$$

In the nonlinear regime for systems in local equilibrium, it is possible to prove that the relation

$$\frac{\partial_x P}{\partial t} \equiv - \int dV \sum_i \mathscr{J}_i \frac{\partial \chi_i}{\partial t} \leq 0 \tag{12.20}$$

is always true because of thermodynamic stability relations which hold in each small region of the system, but it is not in general possible to say anything about the sign of $\partial P_J / \partial t$, where

$$\frac{\partial_J P}{\partial t} \equiv - \int dV \sum_i \frac{\partial \mathscr{J}_i}{\partial t} \chi_i \tag{12.21}$$

However, under certain conditions, if we can establish one additional property for the system, Equation (12.20) enables us to say something about the stability of a nonequilibrium steady state.

In order to illustrate the use of thermodynamic stability theory for nonequilibrium steady states, we shall consider the case of a chemically reacting system of N types of molecules which is held far from equilibrium (it has large affinity). We shall assume that the effects of diffusion, viscosity, and thermal conductivity can be neglected and that the pressure and temperature are uniform throughout the system. The entropy production for such a system can be written

$$P = - \frac{1}{T} \int dV \sum_{\alpha=1}^{r} J_\alpha^c A_\alpha \tag{12.22}$$

[cf. Eq. (10.179)], where r is the number of reactions. Therefore,

$$\frac{\partial_x P}{\partial t} = - \frac{1}{T} \int dV \sum_{\alpha=1}^{r} J_\alpha^c \frac{\partial A_\alpha}{\partial t}. \tag{12.23}$$

From Eq. (10.179), we can write the balance equation for the jth molecular component in the form

$$\frac{\partial c_j}{\partial t} = \sum_{\alpha=1}^{r} \nu_{j\alpha} J_\alpha^c. \tag{12.24}$$

If we now use the definition of the affinity, $A_\alpha = \sum_{j=1}^{N} \nu_{j\alpha}\mu_j$, of the αth reaction, we find

$$\frac{\partial_x P}{\partial t} = -\frac{1}{T}\int dV \sum_{j=1}^{N} \frac{\partial c_j}{\partial t}\frac{\partial \mu_j}{\partial t}. \tag{12.25}$$

Let us next note that since pressure and temperature are held constant

$$\frac{\partial \mu_j}{\partial t} = \sum_{j}^{N} \left(\frac{\partial \mu_j}{\partial c_i}\right)_{P,T,\{c_k \neq c_i\}} \frac{\partial c_i}{\partial t} \tag{12.26}$$

and Eq. (12.25) becomes

$$\frac{\partial_x P}{\partial t} = -\frac{1}{T}\int dV \sum_{i=1}^{N}\sum_{j=1}^{N} \left(\frac{\partial \mu_j}{\partial c_i}\right)_{P,T,\{c_k \neq c_i\}} \frac{\partial c_j}{\partial t}\frac{\partial c_j}{\partial t} \leq 0. \tag{12.27}$$

To establish the inequality we have used the stability condition in Eq. (2.179). Since we assume that the system is in local equilibrium, equilibrium stability conditions ensure that $\partial_x P/\partial t$ always has a well-defined sign.

12.B.2.2. Stability of Nonlinear Chemical Reactions

Thermodynamic stability theory for systems undergoing nonlinear chemical reactions is of considerable interest because of the importance of such reactions in biological systems. The approximation in which the rates of reaction, J_α^c, are driven by terms linear in the affinities is true only near equilibrium. If we wish to examine the behavior of chemically reacting systems far from equilibrium, we must first find the exact dependence of reaction rates on the affinities. This can be done as follows. Let us consider a general chemical reaction of the form

$$-\nu_1 A_1 - \nu_2 A_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \nu_3 A_3 + \nu_4 A_4. \tag{12.28}$$

The rate equation can then be written

$$\begin{aligned}\frac{\partial c_3}{\partial t} &= k_1 c_1^{|\nu_1|} c_2^{|\nu_2|} - k_2 c_3^{|\nu_3|} c_4^{|\nu_4|} \\ &= k_1 c_1^{|\nu_1|} c_2^{|\nu_2|}\left[1 - \frac{k_2 c_3^{|\nu_3|} c_4^{|\nu_4|}}{k_1 c_1^{|\nu_1|} c_2^{|\nu_2|}}\right],\end{aligned} \tag{12.29}$$

where $c_i = n_i/V$ is the molar density. The rate of reaction, J^c, is determined from $J^c = (1/\nu)(\delta c_i/\partial t)$ [cf. Eq. (12.24)]. For system of ideal gases, we can

write the affinity in the form

$$A = RT \ln \left[K(T,P) \frac{c_3^{\nu_3} c_4^{\nu_4}}{c_1^{|\nu_1|} c_2^{|\nu_2|}} \right] \tag{12.30}$$

[cf. Eq. (2.244)], where $K(T,P)$ is a function of temperature and pressure only. At equilibrium, $A = 0$ and $\partial c_i/\partial t = 0$. If we compare Eqs. (12.29) and (12.30), we see that $K(T,P) = k_2/k_1$ and

$$\frac{\partial c_3}{\partial t} = \nu_3 J^c = k_1 c_1^{|\nu_1|} c_2^{|\nu_2|} [1 - e^{A/RT}]. \tag{12.31}$$

Thus, Eq. (12.31) relates the reaction rate, J^c, to the affinity, A. In general, J^c is a nonlinear function of A. For small A, J^c becomes linear in A.

Let us now look at the stability problem for a case in which only chemical reactions take place. To determine the stability of a given steady state we can expand the local entropy around that steady state. The result, schematically, is of the form

$$S_{local} = S^0_{local} + \delta S_{local} + \delta^2 S_{local} + \cdots. \tag{12.32}$$

The various terms in Eq. (12.32) are identical in *form* to those obtained for the Taylor expansion about absolute equilibrium. However, Eq. (12.32) differs from the equilibrium case because we expand about a nonequilibrium steady state where entropy is produced at a constant rate rather than about the absolute equilibrium state for which entropy has fixed value. The second-order term is of the form

$$\delta^2 S_{local} = -\frac{1}{2T} \sum_{i=1}^{N} \sum_{j=1}^{N} \left(\frac{\partial \mu_i}{\partial c_j} \right)^0_{P,T,\{c_k \neq c_j\}} \delta c_i \delta c_j \leq 0. \tag{12.33}$$

Since we assume that the system is in local equilibrium, the equilibrium stability conditions tell us that $\delta^2 S_{local}$ will be negative or zero at each point.

We can now find the time rate of change of the local entropy due to terms which are quadratic in the local fluctuations about the steady state. If we take the derivative of Eq. (12.33), we find

$$\frac{\partial}{\partial t} \delta^2 S_{\text{local}} = -\int dV \left[\frac{1}{T} \sum_{i=1}^{N} \sum_{j=1}^{N} \left(\frac{\partial \mu_i}{\partial c_j} \right)^0_{P,T,\{c_k \neq c_j\}} \delta c_i \frac{\partial \delta c_j}{\partial t} \right], \tag{12.34}$$

where we have used Maxwell's relation, Eq. (2.115). We can use Eq. (12.23) to write

$$\frac{\partial \delta c_i}{\partial t} = \sum_{\alpha=1}^{r} \nu_{i\alpha} \delta J^c_\alpha. \tag{12.35}$$

Furthermore, if we note that

$$\delta\mu_i = \sum_{j=1}^{N} \left(\frac{\partial \mu_i}{\partial c_j}\right)^0_{P,T,\{c_k \neq c_j\}} \delta c_j \tag{12.36}$$

(pressure and temperature are assumed to be fixed) and that

$$\delta A_\alpha = \sum_{i=1}^{N} \nu_{i\alpha} \delta\mu_i, \tag{12.37}$$

we obtain

$$\frac{\partial \delta^2 S_{\text{local}}}{\partial t} = -\int dV \left[\frac{1}{T} \sum_{\alpha=1}^{r} \delta J_\alpha^c \delta A_\alpha\right]. \tag{12.38}$$

Thus, the time variation of the second-order contribution to the entropy production due to fluctuations about the nonequilibrium steady state is given by a product of fluctuations in the current and forces. The function, $\delta^2 S_{local}$, may be viewed as a Lyapounov function (cf. Appendix C). If we can show that $\delta^2 S_{local} \leq 0$ and $\partial \delta^2 S_{local}/\partial t > 0$, then the steady state we are considering is stable. Since the condition $\delta^2 S_{local} \leq 0$ is always true, the condition that must be established is $\partial \delta^2 S_{local}/\partial t > 0$.

Let us now compare Eq. (12.38) with the excess entropy production, $\delta_x P$. The entropy production itself is given by

$$P = -\int dV \left[\frac{1}{T} \sum_{\alpha=1}^{r} J_\alpha^c A_\alpha\right]. \tag{12.39}$$

and the contribution to the entropy production due to fluctuations of the independent forces about their equilibrium value is

$$\delta_x P = -\int dV \left[\frac{1}{T} \sum_{\alpha=1}^{r} J_\alpha^c \delta A_\alpha\right]. \tag{12.40}$$

In the steady state, currents corresponding to the independent (unconstrained) forces vanish. Therefore, we can make the following expansion of J_α^c about the steady state,

$$J_\alpha^c = 0 + \delta J_\alpha^c + \delta^2 J_\alpha^c + \cdots. \tag{12.41}$$

For very small deviations from the steady state, Eq. (12.40) becomes

$$\delta_x P = -\int dV \left[\frac{1}{T} \sum_{\alpha=1}^{r} \delta J_\alpha^c \delta A_\alpha\right] = \frac{\partial \delta^2 S_{tot}}{\partial t}. \tag{12.42}$$

If the steady state is to be stable with respect to small fluctuations, then the fluctuations must cause the entropy production to increase since the entropy production for a stable steady state is minimum. An example of how these criteria are used is given in Exercise 12.1.

■ **EXERCISE 12.1.** Consider the autocatalytic nonlinear chemical reaction

$$B + X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2X.$$

The affinity can be written $A = RT\ln(k_1 c_X^2/k_2 c_B c_X)$, where c_B (c_X) is the molar density of chemical $B(X)$. (a) When the molar densities are allowed to vary freely, what steady states can occur? Are they stable? What is the state of thermodynamic equilibrium? (b) Hold the molar density of B fixed at $\bar{c}_B^0$ by allowing molecules of B to flow in and out of the system. Determine if the steady states are stable.

Answer:

(a) This chemical reaction is nonlinear because it requires X to produce X. The rate of the reaction is

$$J^c = \frac{dc_X}{dt} = k_1 c_B c_X - k_2 c_X^2. \tag{1}$$

Steady states, $c_X = \bar{c}_X$ and $c_B = \bar{c}_B$, occur when $dc_X/dt = 0$. Therefore there are two possible steady states. They are $\bar{c}_X = k_1\bar{c}_B/k_2$ and $\bar{c}_X = \bar{c}_B = 0$. The second steady state is uninteresting since there are no chemicals in the system. The first steady state, $\bar{c}_X = k_1\bar{c}_B/k_2$, is a state for which the affinity, $A = 0$. Therefore, it is a state of thermodynamic equilibrium.

(b) Hold the molar density of B fixed at $c_B = c_B^0$, by allowing B to flow in and out of the system. The steady states are then $\bar{c}_X = k_1 c_B^0/k_2$ and $\bar{c}_X = 0$. To determine which is stable, consider a small fluctuation, δc_X, about the steady state so $c_x = \bar{c}_X + \delta c_X$. The fluctuation in the rate of reaction (to lowest order in δc_X) is $\delta J = (k_1 c_B^0 - 2k_2\bar{c}_X)\delta c_X$. The fluctuation in the affinity is $\delta A = RT\delta c_X/\bar{c}_X$. Therefore, the excess entropy production is

$$d_X P = \frac{1}{P}\delta J^c \delta A = -\frac{R}{\bar{c}_X}(k_1 c_B^0 - 2k_2\bar{c}_X)(\delta c_X)^2. \tag{2}$$

Since $d_X P > 0$ for steady state, $\bar{c}_X = k_1 c_B^0/k_2$, this steady state is stable. Since $d_X P < 0$ for steady state, $\bar{c}_X = 0$, it is unstable. This

reaction is a little too simple to be very interesting, but it illustrates the point that nonlinear chemical reactions can have multiple steady states when held out of equilibrium.

In general, as we increase the affinity of a chemical system in which autocatalytic (nonlinear) chemical reactions occur, the system will undergo a series of phase transitions. The first transition occurs from the near equilibrium steady state to a new state which cannot exist near equilibrium. Then, in general, there will be transitions between a whole series of states, each of which becomes stable and then unstable as the parameters of the system are changed.

The possibility of having phase transitions to more ordered states far from equilibrium opened a new field of research in the chemical and biological sciences. For example, living systems may be thought of as chemical systems (although of *huge* complexity) maintained far from equilibrium. There is now some evidence that the formation and maintenance of ordered states far from equilibrium in such systems is important for the maintenance of life processes. In 1977, Ilya Prigogine received the Nobel prize in chemistry for laying the foundations of this field of chemistry and for his many contributions to its development.

In the subsequent sections we shall consider some more interesting chemical reactions than those which were considered here. We will generally use the linear stability theory discussed in Appendix C, because it is simpler to apply than the Lyapounov approach discussed in this section and it is sufficient for the purposes of this chapter. However, stability conditions for the reactions discussed in the next two sections can be obtained using the methods of this section and therefore can be fitted into the framework of thermodynamics.

12.C. THE SCHLOGL MODEL [4]

The first nonlinear chemical reaction we will consider was introduced by Schlogl [4] and exhibits a phase transition which is analogous to the first-order phase transition predicted by the van der Waals equation. The Schlogl model is given by the nonlinear reaction scheme

$$A + 2X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 3X \quad \text{and} \quad X \underset{k_4}{\overset{k_3}{\rightleftharpoons}} B. \tag{12.43}$$

Thermodynamic equilibrium occurs when

$$k_1 c_A^{eq} (c_X^{eq})^2 = k_2 (c_X^{eq})^3 \quad \text{and} \quad k_3 c_X^{eq} = k_4 c_B^{eq}, \tag{12.44}$$

where c_A^{eq}, c_B^{eq}, and c_X^{eq} are the equilibrium molar densities of molecules A, B, and X, respectively. At thermodynamic equilibrium, the ratio of the equilibrium

densities, c_A^{eq} and c_B^{eq}, is fixed,

$$R_{eq} = \frac{c_A^{eq}}{c_B^{eq}} = \frac{k_4 k_2}{k_3 k_1}, \tag{12.45}$$

and is determined by the rate constants.

If we now hold c_A and c_B fixed at some nonequilibrium values, $c_A = c_A^0$ and $c_B = c_B^0$, and allow c_X to vary, the rate equation for c_X can be written

$$\frac{dc_X}{dt} = k_1 c_A^0 c_X^2 - k_2 c_X^3 - k_3 c_X + k_4 c_B^0. \tag{12.46}$$

The steady states occur when $dc_X/dt = 0$ and therefore for values molar density, $c_X = c_X$, which satisfy the equation

$$c_X^3 - a c_X^2 + \kappa c_X - b = 0, \tag{12.47}$$

where $a = k_1 c_A^0/k_2, b = k_4 c_B^0/k_2$, and $\kappa = k_3/k_2$. If we fix the ratio $R = c_A^0/c_B^0 \neq R_{eq}$, the steady state, $\bar{c}_X$, need not be a state of thermodynamic equilibrium.

Equation (12.47) is a cubic equation, as is the van der Waals equation, and has similar properties. In Fig. 12.1 we *sketch* $\bar{c}_X$ as a function of b for fixed values of a and κ. In the parameter range $b_- \leq b \leq b_+$, three steady-state solutions exist (they can be realized in nature, only if they are stable). The values, b_- and b_+ are easily found. They are the extrema of the curve, $b = b(\bar{c}_X)$, and are obtained from the roots of the equation

$$\frac{db}{d\bar{c}_X} = 3\bar{c}_X^2 - 2a\bar{c}_X + \kappa = 0. \tag{12.48}$$

The two roots, $c_X^{\pm}$, of Eq. (12.48) are given by

$$\bar{c}_X^{\pm} = \frac{1}{3}(a \pm \sqrt{a^2 - 3\kappa}). \tag{12.49}$$

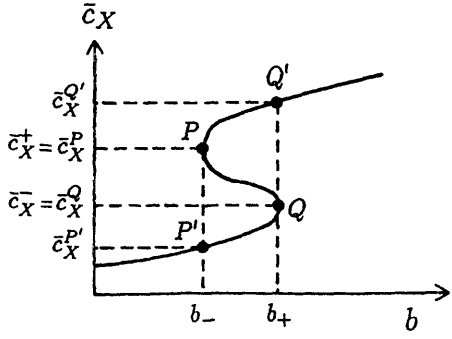

Fig. 12.1. A sketch of the line of steady-state solutions for the Schlogl model.

The values, $b_{\pm} = b(\bar{c}_X^{\pm})$, can be found from Eq. (12.47). For $a > \sqrt{3\kappa}$, there is a range of values of $b(b_- \leq b \leq b_+)$ for which the system can have three different steady states. For $a < \sqrt{3\kappa}$, it can have only one steady state for each value of b.

From linear stability theory (cf. Appendix C) it is possible to show that the region QP in Fig. 12.1 is unstable while regions $P'Q$ and PQ' are stable. We can let $c_X(t) = \bar{c}_X + \delta c_X(t)$, where $\delta c_X(t)$ is a small fluctuation about the steady state, $\bar{c}_X$. If we then substitute $c_X(t)$ into Eq. (12.47) and keep only terms first order in $\delta c_X(t)$, we obtain a linearized equation for $\delta c_X(t)$. We can solve this linearized equation and find that $\delta c_X(t)$ decays exponentially in regions $P'Q$ and PQ' in Fig. (12.1), and it grows exponentially in regions PQ. Since fluctuations are always present, the system will be driven away from the steady state in the region PQ and it cannot be found in nature.

Let us consider Fig. 12.1 again and move along the steady state from point P' to point Q by increasing b. When the state of the system reaches Q, it must jump from a steady state with molar density, $\bar{c}_X^Q$, to a steady state with molar density, $\bar{c}_X^{Q'}$, for values of $b > b_+$. Thus the chemical system appears to undergo an abrupt transition at the value $b = b_+$. The system also exhibits hysteresis behavior. As we decrease b, we remain on the curve PQ' until we reach the value $b = b_-$. Then the system undergoes an abrupt transition from a steady state with molar density, $\bar{c}_X^P$, to a steady state with molar density, $\bar{c}_X^{P'}$. In Fig. 12.2 we have plotted the hysteresis region as a function of a and b. Such behavior has been used as a model for explosive reactions.

The rate equation (12.47) is a macroscopic equation for the molar density of the molecular species X. It is possible to do a stochastic analysis of this reaction and to obtain some of the critical exponents of the reaction [5].

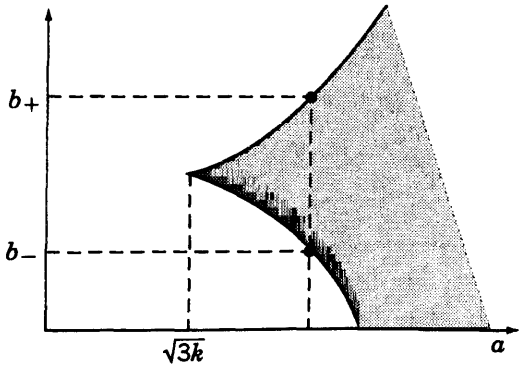

Fig. 12.2. Hysteresis region for the Schlogl model plotted as a function of a and b.

12.D. THE BRUSSELATOR [2, 3, 6–8]

Chemical systems which are locally in thermodynamic equilibrium but held far from chemical equilibrium (constrained to have a large affinity) can undergo phase transitions to new stable states with striking behavior. The new stable states may be steady states in which the relative concentrations of the constituents vary in space, or they may be spatially homogeneous states in which the concentrations of some constituents vary in time (chemical clocks), or they may be states with nonlinear traveling waves in the concentrations of some constituents. The classic example of such behavior is the Belousov [9]–Zhabotinski [10] reaction. This reaction, which is too complicated to discuss in detail here (cf. Ref. 11), involves the cerium ion catalyzed oxidation of malonic acid by bromate in a sulfuric acid medium. The reaction is nonlinear because it contains autocatalytic steps. The system, when it is well-stirred, can behave like a chemical clock. That is, there is a periodic change in the concentration of Br^- and of the relative concentration Ce^{4+}/Ce^{3+}. The system oscillates between red and blue color with a period of the order of a minute. Perhaps the most fascinating behavior of this system is the traveling waves in the concentration of Br^- and the relative concentration Ce^{4+}/Ce^{3+} which are observed in shallow unstirred dishes (cf. Fig. 12.3).

The Belousov–Zhabotinski reaction appears to be well-described by a model which contains three variable intermediates. This model is called the Oregonator and was first introduced by Field and Noyes [11, 12]. However, the qualitative behavior of the type appearing in the Belousov–Zhabotinski reaction also occurs in a simpler model called the Brusselator, first introduced

Fig. 12.3. Traveling waves in the chemical concentrations for the Belousov–Zhabotinski reaction. Reprinted, by permission, from A. T. Winfree, *The Timing of Biological Clocks* (Scientific American Books, 1987).

by Prigogine and Lefever [6], which contains two variable intermediates. In this section we shall discuss some properties of the Brusselator, using linear stability theory (cf. Appendix C).

12.D.1. The Brusselator—A Nonlinear Chemical Model

The Brusselator is one of the simplest models of a nonlinear chemical system for which the relative concentration of the constituents can oscillate in time, or can exhibit nonlinear waves. It has six different components, four of which are held fixed and two others whose concentrations can vary in space and time. The chemical reaction takes place in four steps and is held far from equilibrium by allowing the reactions to go in one direction only. The four steps are

$$\begin{aligned} A &\xrightarrow{k_1} X \\ B + X &\xrightarrow{k_2} Y + D, \\ 2X + Y &\xrightarrow{k_3} 3X, \end{aligned} \tag{12.50}$$

and

$$X \xrightarrow{k_4} E.$$

In practice, A and B are present in excess and D and E are removed as soon as they appear. The rate equations for X and Y can be written

$$\frac{dc_X}{dt'} = k_1 c_A - (k_2 c_B + k_4) c_X + k_3 c_X^2 c_Y + D_1' \nabla_{\mathbf{r}}^2 c_X \tag{12.51}$$

and

$$\frac{dc_Y}{dt'} = k_2 c_B c_X - k_3 c_X^2 c_Y + D_2' \nabla_{\mathbf{r}}^2 c_Y. \tag{12.52}$$

We have allowed the densities to vary in space and have allowed for the possibility of diffusion (D_1' and D_2' are the coefficients of diffusion). If we now introduce a change of variables, $t = k_2 t'$, $X = \sqrt{k_3/k_4}\, c_X$, $Y = \sqrt{k_3/k_4}\, c_Y$, $A = \sqrt{k_1^2 k_3/k_4^3}\, c_A$, $B = (k_2/k_4)\, c_B$, and $D_i = D_i'/k_4$, then Eqs. (12.51) and (12.52) take the form

$$\frac{dX}{dt} = A - (B+1)X + X^2 Y + D_1 \nabla_{\mathbf{r}}^2 X \tag{12.53}$$

and

$$\frac{dY}{dt} = BX - X^2 Y + D_2 \nabla_{\mathbf{r}}^2 Y. \tag{12.54}$$

Equations (12.53) and (12.54) have a spatially uniform steady-state solution of the form

$$X_0 = A \quad \text{and} \quad Y_0 = B/A, \tag{12.55}$$

which is the continuation far from equilibrium of the steady-state solution which occurs at chemical equilibrium when the reverse reactions in Eq. (12.50) are allowed to occur. That is, the steady state [Eq. (12.55)] lies on the "thermodynamic branch" of steady-state solutions. We wish to look for conditions under which the thermodynamic branch becomes unstable and a bifurcation (nonequilibrium phase transition) occurs to a state which may oscillate in space or time.

We can use linear stability theory (cf. Appendix C) to look for instabilities in the steady-state homogeneous solution to Eq. (12.55). We write X and Y as

$$X(\mathbf{r}, t) = A + \delta x(\mathbf{r}, t) \tag{12.56}$$

and

$$Y(\mathbf{r}, t) = \frac{B}{A} + \delta y(\mathbf{r}, t), \tag{12.57}$$

where δx and δy are small space and time-dependent perturbations. We shall introduce Eqs. (12.56) and (12.57) into Eqs. (12.53) and (12.54) and linearize them with respect to $\delta x(\mathbf{r}, t)$ and $\delta y(\mathbf{r}, t)$. We then obtain

$$\frac{d\delta x}{dt} = (B - 1 + D_x \nabla_{\mathbf{r}}^2)\, \delta x + A^2\, \delta y \tag{12.58}$$

and

$$\frac{d\delta y}{dt} = -B\delta x + (-A^2 + D_y \nabla_{\mathbf{r}}^2)\, \delta y. \tag{12.59}$$

Since Eqs. (12.58) and (12.59) are linear, it is sufficient to consider one Fourier component of $\delta x(\mathbf{r}, t)$ and $\delta y(\mathbf{r}, t)$. Before we proceed further, we must specify both the shape of container in which the reaction takes place and the boundary conditions on the walls of the container.

12.D.2. Boundary Conditions

For simplicity, we shall assume that the reaction takes place in a rectangular container with sides of length L_x, L_y, and L_z. We shall consider two different types of boundary conditions. For Case I, we will hold the concentrations, X and Y, constant on the boundaries. For Case II, we will assume there is no flux of X and Y through the boundaries. Let us consider these two cases separately below.

Case I Boundary Conditions: Let us assume the concentrations, X and Y are constant on the boundaries and take on the values

$$X_{bound} = A \quad \text{and} \quad Y_{bound} = B/A$$

on the boundaries. These boundary conditions can be maintained by allowing a flow of X and Y through the boundaries. A given Fourier component of $\delta x(\mathbf{r}, t)$ and $\delta y(\mathbf{r}, t)$ can be written

$$\delta x(\mathbf{r}, t) = \tilde{x}(\mathbf{k}, \omega) \sin(k_x x) \sin(k_y y) \sin(k_z z)\, e^{\omega(\mathbf{k})t} \tag{12.60}$$

and

$$\delta y(\mathbf{r}, t) = \tilde{y}(\mathbf{k}, \omega) \sin(k_x x) \sin(k_y y) \sin(k_z z)\, e^{\omega(\mathbf{k})t}, \tag{12.61}$$

where

$$\mathbf{k} = \frac{n_x \pi}{L_x}\hat{\mathbf{x}} + \frac{n_y \pi}{L_y}\hat{\mathbf{y}} + \frac{n_z \pi}{L_z}\hat{\mathbf{z}},$$

and n_x, n_y, and n_z can each have values $1, 2, \ldots, \infty$.

Case II Boundary Conditions: Let us assume there is no flux of X and Y perpendicular to the boundary surfaces so

$$\hat{\mathbf{n}} \cdot \nabla_{\mathbf{r}} X = \hat{\mathbf{n}} \cdot \nabla_{\mathbf{r}} Y = 0$$

on the boundaries, where $\hat{\mathbf{n}}$ is normal to the boundaries. A given Fourier component of $\delta x(\mathbf{r}, t)$ and $\delta y(\mathbf{r}, t)$ can now be written

$$\delta x(\mathbf{r}, t) = \tilde{x}(\mathbf{k}, \omega) \cos(k_x x) \cos(k_y y) \cos(k_z z)\, e^{\omega(\mathbf{k})t}, \tag{12.62}$$

and

$$\delta y(\mathbf{r}, t) = \tilde{y}(\mathbf{k}, \omega) \cos(k_x x) \cos(k_y y) \cos(k_z z)\, e^{\omega(\mathbf{k})t}, \tag{12.63}$$

where the wavevector $\mathbf{k}$ is defined as in Case I and n_x, n_y, and n_z can each have values $0, 1, 2, \ldots, \infty$.

If we substitute either of the solutions—Eqs. (12.60) and (12.61) or Eqs. (12.62) and (12.63)—into Eqs. (12.58) and (12.59), we obtain the following matrix equation

$$\begin{pmatrix} \omega - B + 1 + D_x k^2 & -A^2 \\ B & \omega + A^2 + D_y k^2 \end{pmatrix} \begin{pmatrix} \tilde{x} \\ \tilde{y} \end{pmatrix} = 0. \tag{12.64}$$

An equation for $\omega(\mathbf{k})$ is found by setting the determinant of the 2×2 matrix on the left equal to zero. We then have

$$\omega(\mathbf{k})^2 + (C_1 - C_2)\,\omega(\mathbf{k}) + A^2B - C_1C_2 = 0, \tag{12.65}$$

where

$$C_1 = B - 1 - k^2D_1 \quad \text{and} \quad C_2 = A^2 + k^2D_2. \tag{12.66}$$

Equation (12.65) has two solutions:

$$\omega^{\pm}(\mathbf{k}) = \tfrac{1}{2}\{C_1 - C_2 \pm \sqrt{(C_1 + C_2)^2 - 4A^2B}\}. \tag{12.67}$$

From Eq. (12.67), it is easy to see that, depending on the variables D_1, D_2, A, and B, the frequency $\omega(\mathbf{k})$ can be either complex or real and the real part can be either positive or negative. Below we will consider the cases of real frequency and complex frequency separately.

12.D.3. Linear Stability Analysis

To determine if a given mode is unstable, we must substitute the solutions—Eqs. (12.60) and (12.61) or Eqs. (12.62) and (12.63)—into Eqs. (12.58) and (12.59) and find an equation for the frequency $\omega(\mathbf{k})$. In general, $\omega(\mathbf{k})$ can be complex. If it is complex, the component of the perturbation $\delta x(\mathbf{r}, t)$ and $\delta y(\mathbf{r}, t)$ with wavevector $\mathbf{k}$ and frequency $\omega(\mathbf{k})$ will oscillate about the steady state (12.55) with frequency given by the imaginary part of $\omega(\mathbf{k})$. The real part of $\omega(\mathbf{k})$ determines if the steady state is stable with respect to the perturbation. If the real part of $\omega(\mathbf{k})$ is negative, then the perturbation will decay away and the steady state is stable with respect to fluctuations with wavevector $\mathbf{k}$ and frequency $\omega(\mathbf{k})$. However, if the real part of $\omega(\mathbf{k})$ is positive, the perturbation $\delta x(\mathbf{r}, t)$ and $\delta y(\mathbf{r}, t)$ grow exponentially. Thus, when the real part of $\omega(\mathbf{k})$ is positive, a bifurcation or phase transition occurs. Linear stability analysis cannot tell us the form of the new state, but it can tell us where the bifurcation occurs.

12.D.2.1. Real Frequency $\omega(\mathbf{k})$

The frequency $\omega(\mathbf{k})$ is real when

$$(C_1 + C_2)^2 - 4A^2B > 0 \tag{12.68}$$

[cf. Eq. (12.67)] and $\omega(\mathbf{k})$ is positive if

$$C_1C_2 - A^2B > 0 \tag{12.69}$$

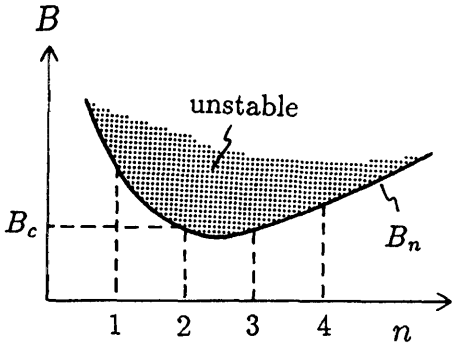

Fig. 12.4. Linear stability diagram for the onset of a time-independent dissipative structure. For the case pictured here, as B increases, the first bifurcation occurs at $n = 2$. (Based on Ref. 3.)

or

$$B > B_n = 1 + \frac{D_1}{D_2} A^2 + \frac{A^2}{D_2 n^2 \pi^2} L^2 + \frac{D_1 n^2 \pi^2}{L^2}. \tag{12.70}$$

In this case, there will be no oscillations in time but only in space. The linear stability diagram for the onset of time-independent spatial oscillations of the concentrations of X and Y is given in Fig. 12.4. The curved line is B_n. The bifurcation first occurs for $B = B_c$, where B_c is the lowest value of B corresponding to an integer value of n. Linear stability analysis can only tell us that a bifurcation to a new spatially oscillating steady state is possible for a particular set of values for the parameters A, B, D_1, D_2, and L. It cannot give us information about the form of the new state. However, for the Brusselator the spatially varying states can be obtained numerically. In Fig. 12.5 we give an example for a one-dimensional system for the following values of the parameters: $B = 4.6, A = 2, L = 1, D_1 = 1.6 \times 10^{-3}$, $D_2 = 6.0 \times 10^{-3}$, and fixed boundary conditions $X_{\text{bound}} = A$ and $Y_{\text{bound}} = B/A$. The figure shows a state with oscillations in the concentration of X as a function of position.

12.D.2.1. Complex Frequency $\omega(\mathbf{k})$

The frequency $\omega(\mathbf{k})$ is real when

$$(C_1 + C_2)^2 - 4A^2 B > 0 \tag{12.71}$$

[cf. Eq. (12.67)]. From Eq. (12.71), we can show that $\omega(\mathbf{k})$ will be complex if

$$D_2 - D_1 \leq \frac{L^2}{n^2 \pi^2}. \tag{12.72}$$

In addition, $\omega(\mathbf{k})$ will have a positive real part if $C_1 - C_2 > 0$ or if

$$B > A^2 + 1 + \frac{n^2 \pi^2}{L^2} (D_1 + D_2). \tag{12.73}$$

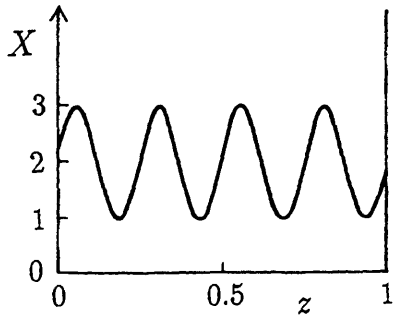

Fig. 12.5. A steady-state spatial dissipative structure for $B = 4.6$, $A = 2$, $L = 1$, $D_1 = 1.6 \times 10^{-3}$, and $D_2 = 6.0 \times 10^{-3}$. The boundary conditions are fixed at $X = A$ and $Y = B/A$. (Based on Ref. 3.)

Thus, the curve

$$B_n = A^2 + 1 + \frac{n^2\pi^2}{L^2}(D_1 + D_2) \tag{12.74}$$

denotes the boundary between the region where the steady state [Eq. (12.55)] is stable and where it is unstable as a function of n.

We note that for the Case II boundary conditions we can have $n = 0$ and, therefore, the possibility of spatially homogeneous oscillations in time of the relative conentrations of X and Y—that is, a chemical clock. For all finite values of n, we have the possibility of a new state which varies in both space and time and therefore may exhibit wave motion. The linear stability diagram for the transition to time-dependent states is given in Fig. 12.6. In Fig. 12.7 we give the results of a computer simulation, of a one-dimensional system, for a state which oscillates in space and time. The solution is reminiscent of a standing wave on a string, but, due to the nonlinearities, it has a much more complicated structure. In two dimensions, computer simulations have shown that traveling waves can exist which are similar to the waves shown in the Belousov–Zhabotinski reaction [Fig. 12.3 (cf. Ref. 3)].

Spatially varying steady states, temporally oscillating homogeneous states, and nonlinear traveling waves have been observed in chemical systems. These

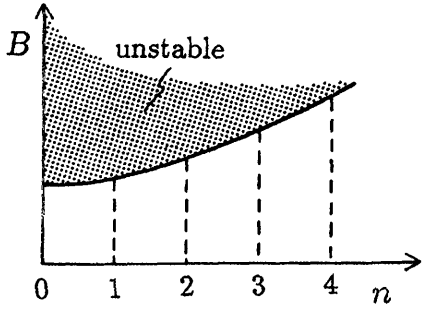

Fig. 12.6. Linear stability diagram for the onset of time-dependent dissipative structures. As B is increased, the first bifurcation occurs at $n = 0$ and yields a spatially homogeneous chemical clock. (Based on Ref. 3.)

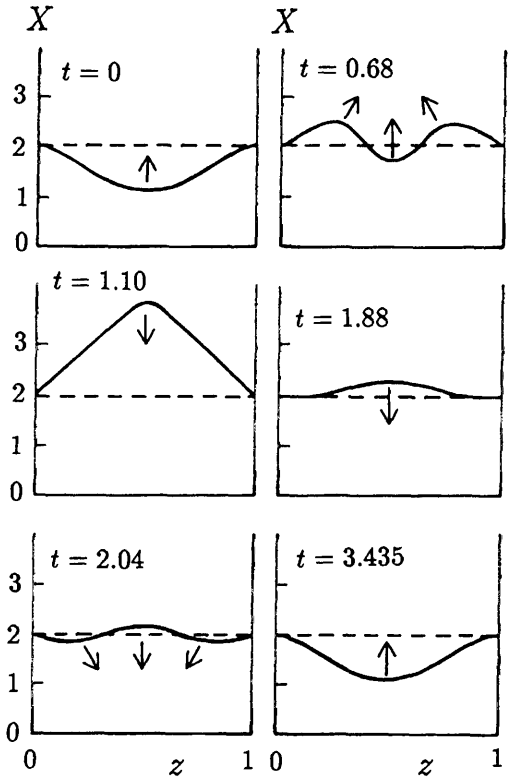

Fig. 12.7. Successive time steps for a dissipative structure with fixed concentrations on the boundary which exhibits oscillations in both space and time. The parameters used are $L = 1$, $A = 2$, $B = 5.45$, $D_1 = 8 \times 10^{-3}$, and $D_2 = 4 \times 10^{-3}$. (Based on Ref. 3.)

states, which only become stable far from equilibrium, have been called "dissipative structures" by I. Prigogine [2, 3] because their very existence depends upon dissipative processes, such as chemical reactions far from equilibrium or diffusion (if spatial structures occur). As we have seen in Section 12.B, they are maintained by production of entropy and by a related flow of energy and matter from the world. It is curious that the type of autocatalytic reactions which produce them are abundant in living systems and yet are rare in nonliving systems. It is possible that dissipative structures in living systems play an important role in the maintenance of life processes [14].

12.E. THE RAYLEIGH–BÉNARD INSTABILITY [15–19]

Nonequilibrium phase transitions are abundant in hydrodynamic systems because they are governed by nonlinear equations. For example, if we let fluid flow in a pipe, we find for low velocities or high viscosities that the flow is

smooth and steady. However, as we increase the velocity or decrease the viscosity, we get a transition to turbulent flow. The smooth steady state becomes unstable and a turbulent state becomes favored. As another example, let us consider a fluid at rest and place it between horizontal parallel plates in the gravitational field. If we put a temperature gradient across the plates (with the hottest plate below) and slowly increase the temperature gradient, we find that at some point the rest state becomes unstable and the fluid breaks into convective flow cells which occur periodically in space. In each cell, fluid rises in one part of the cell and descends in another part. The circulation of fluid repeats itself in each cell. This instability is called the *Rayleigh–Bénard instability* and is the one we shall study in this section. We will follow closely the classic presentation of Chandrasekhar [15].

12.E.1. Hydrodynamic Equations and Boundary Conditions

Let us first write the hydrodynamic equations in a form which will be useful to us. The full nonlinear Navier–Stokes equations can be written

$$\frac{\partial \rho}{\partial t} + \nabla_{\mathbf{r}} \cdot \rho \mathbf{v} = 0, \tag{12.75}$$

$$\frac{\partial \rho \mathbf{v}}{\partial t} + \nabla_{\mathbf{r}} \cdot (\rho \mathbf{v}\mathbf{v}) = -\nabla_{\mathbf{r}} P + \rho \mathbf{F} + \eta \nabla_{\mathbf{r}}^2 \mathbf{v} + (\zeta + \tfrac{1}{3}\eta) \nabla_{\mathbf{r}} (\nabla_{\mathbf{r}} \cdot \mathbf{v}), \tag{12.76}$$

and

$$\frac{\partial \rho s}{\partial t} + \nabla_{\mathbf{r}} \cdot \left(\rho s \mathbf{v} - \frac{K}{T} \nabla_{\mathbf{r}} T \right) = \bar{\bar{\Pi}} : \nabla_{\mathbf{r}} \mathbf{v}, \tag{12.77}$$

where ρ is the mass/volume, s is the entropy/mass, and the remaining quantities have been defined in Section 10.B. We will consider the case of a fluid at rest constrained to lie between two infinitely large parallel plates which extend in the x- and y directions. The distance between the plates is d. We will put a temperature gradient across the plates so that the temperature of the bottom plate is greater than that of the top, and we will assume that a gravitational field acts in the negative z direction (cf. Fig. 12.8). If we have a thin enough fluid layer, any density variations in the system will be due primarily to the temperature gradient (as opposed to gravity) and we can write

$$\rho = \rho_0 [1 + \alpha_P (T_0 - T)], \tag{12.78}$$

where $\alpha_P = -(1/\rho)(\partial \rho / \partial T)_P$ is the thermal expansivity. Heating the bottom more than the top causes the fluid at the top to be denser and heavier and creates the possibility for an instability to occur.

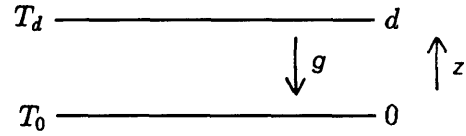

Fig. 12.8. Geometical configuration for the Bénard problem.

Let us now write the equations for the steady state in the absence of any macroscopic flow; that is, $\mathbf{v} = 0$. We obtain

$$\nabla_{\mathbf{r}} \cdot \rho \mathbf{v} = 0, \tag{12.79}$$

$$\nabla_{\mathbf{r}} P = -\rho g \hat{\mathbf{z}}, \tag{12.80}$$

and

$$\nabla_{\mathbf{r}}^2 T = 0, \tag{12.81}$$

where we have let $\mathbf{F} = -g\hat{\mathbf{z}}$ and g is the acceleration of gravity. If we note the boundary conditions $T(0) = T_0$ and $T(d) = T_d$, we can solve Eqs. (12.80) and (12.81) to obtain the steady-state solutions. We find

$$T(z) = T_0 - az, \tag{12.82}$$

$$\rho(z) = \rho_0 [1 + \alpha_P (T_0 - T)] = \rho_0 [1 + \alpha_P az], \tag{12.83}$$

and

$$P(z) = P_0 - g\rho_0 [z + \tfrac{1}{2} \alpha_P a z^2], \tag{12.84}$$

where a is the temperature gradient, $a = (T_0 - T_d)/d$, and P_0 is the pressure at $z = 0$.

Equations (12.82)–(12.84) are the steady-state solutions in the absence of flow. We wish to determine conditions for which they are stable. As usual, we will perturb the steady state solutions slightly and study the linearized equations for the perturbations. Thus, we write $T(\mathbf{r}, t) = T(z) + \delta T(\mathbf{r}, t)$, $P(\mathbf{r}, t) = P(z) + \delta P(\mathbf{r}, t)$, and $\rho(\mathbf{r}, t) = \rho(z) + \delta\rho(\mathbf{r}, t)$. The velocity, $\mathbf{v}(\mathbf{r}, t)$, is a first-order perturbation from equilibrium. Let us further note that the dominant contribution to entropy variations will come from temperature variations. Thus, we write $\delta s = (\tilde{c}_\rho / T)\, \delta T$, where $\tilde{c}_\rho$ is the constant density specific heat, and we have neglected terms proportional to α_P. If we substitute these expressions into the hydrodynamic equations, and linearize Eqs. (12.75)–(12.77) in the perturbations δT, δP, $\delta\rho$, and $\mathbf{v}$, we find

$$\frac{\partial}{\partial t} \delta\rho = -\nabla_{\mathbf{r}} \cdot (\rho(z)\mathbf{v}), \tag{12.85}$$

$$\frac{\partial}{\partial t} \rho(z)\mathbf{v} = -\nabla_{\mathbf{r}}(P(z) + \delta P) - \rho g \hat{\mathbf{z}} + \eta \nabla_{\mathbf{r}}^2 \mathbf{v} + (\zeta + \tfrac{1}{3}\eta)\, \nabla_{\mathbf{r}}(\nabla_{\mathbf{r}} \cdot \mathbf{v}), \tag{12.86}$$

and

$$\frac{\partial}{\partial t}(\rho(z)\tilde{c}_\rho \delta T) = -\nabla_{\mathbf{r}} \cdot [\rho(z)\tilde{c}_\rho T(z)\mathbf{v} - K\nabla_{\mathbf{r}}(T(z) + \delta T)]. \tag{12.87}$$

Let us now note that

$$\delta\rho(\mathbf{r}, t) = -\rho_0 \alpha_P \, \delta T(\mathbf{r}, t) \tag{12.88}$$

[cf. Eq. (12.78)]. Then from Eq. (12.85) we have $\nabla_{\mathbf{r}} \cdot \mathbf{v} \approx \alpha_P$. If we now neglect all terms which depend on α_P except those that appear in the term involving the external field, we obtain

$$\nabla_{\mathbf{r}} \cdot \mathbf{v} = 0, \tag{12.89}$$

$$\rho_0 \frac{\partial \mathbf{v}}{\partial t} = -\nabla_{\mathbf{r}} \, \delta P + \rho_0 \alpha_P \, \delta T g \hat{\mathbf{z}} + \eta \nabla_{\mathbf{r}}^2 \mathbf{v}, \tag{12.90}$$

and

$$\frac{\partial}{\partial t} \delta T = a v_z + \frac{K}{\rho_0 \tilde{c}_\rho} \nabla_{\mathbf{r}}^2 \, \delta T. \tag{12.91}$$

The above approximation is called the *Boussinesq approximation.* The consistency of the Boussinesq approximation has been demonstrated by Mihaljan [18]. Equations (12.89)–(12.91) form the starting point of our linear stability analysis.

We can simplify these equations somewhat through the following steps. We first take the curl of Eq. (12.90) to obtain

$$\frac{\partial \nabla_{\mathbf{r}} \times \mathbf{v}}{\partial t} = g\alpha_P \nabla_{\mathbf{r}} \times (\delta T \hat{\mathbf{z}}) + \nu_t \nabla_{\mathbf{r}}^2 (\nabla_{\mathbf{r}} \times \mathbf{v}), \tag{12.92}$$

where $\nu_t = \eta/\rho_0$. We next take the curl of Eq. (12.92) and note that $\nabla_{\mathbf{r}} \times (\nabla_{\mathbf{r}} \times \mathbf{v}) = \nabla_{\mathbf{r}}(\nabla_{\mathbf{r}} \cdot \mathbf{v})) - \nabla_{\mathbf{r}}^2 \mathbf{v}$. Using Eq. (12.89), we then find

$$\frac{\partial}{\partial t} \nabla_{\mathbf{r}}^2 \mathbf{v} = -g\alpha_P \nabla_{\mathbf{r}} \left(\frac{\partial \delta T}{\partial z} \right) + g \, \alpha_P \nabla_{\mathbf{r}}^2 (\delta T \hat{\mathbf{z}}) + \nu \nabla_{\mathbf{r}}^4 \mathbf{v}. \tag{12.93}$$

In our stability analysis, we shall be interested in instabilities in the z components of velocity. The equation of motion for the z component of velocity is given by

$$\frac{\partial}{\partial t} \nabla_{\mathbf{r}}^2 v_z = g\alpha_P \left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} \right) \delta T + \nu \nabla^4 v_z. \tag{12.94}$$

If an instability occurs in which flow develops in the z-direction, then $v_z\hat{\mathbf{z}}$ must change sign as we move in the x- or y-direction (what goes up must come down).

As for the case of the Brusselator, we must specify boundary conditions before we apply the stability analysis. We first note the general boundary conditions that

$$\delta T(x, y, 0; t) = \delta T(x, y, d; t) = 0 \tag{12.95}$$

and

$$v_z(x, y, 0; t) = v_z(x, y, d; t) = 0. \tag{12.96}$$

In addition to the above general boundary conditions, we have additional constraints on the surfaces at $z = 0$ and $z = d$. We can have either rigid surfaces for which there can be no tangential components of velocity or smooth surfaces where we can have a tangential flow.

Case I: For a rigid surface we have the boundary conditions

$$\mathbf{v}(x, y, 0; t) = \mathbf{v}(x, y, d; t) = 0. \tag{12.97}$$

Since $\mathbf{v} = 0$ for all x and y, we find $dv_x/dx = dv_y/dy = 0$, and thus from Eq. (12.89) we have the additional condition $dv_z\, dz = 0$.

Case II: On a smooth surface there can be horizontal flow but no transport of the horizontal components of velocity in the z direction. Thus, the components of the stress tensor satisfy the condition

$$\pi_{xz}(x, y, 0; t) = \pi_{xz}(x, y, d; t) = \pi_{yz}(x, y, 0; t) = \pi_{yz}(x, y, d; t) = 0 \tag{12.98}$$

or

$$\left(\frac{\partial v_x}{\partial z} + \frac{\partial v_z}{\partial x}\right)_{\text{bound}} = 0 \tag{12.99}$$

and

$$\left(\frac{\partial v_y}{\partial z} + \frac{\partial v_z}{\partial y}\right)_{\text{bound}} = 0 \tag{12.100}$$

Since $v_z = 0$ for all x and y on the surface, we have

$$\left(\frac{\partial v_z}{\partial x}\right)_{\text{bound}} = \left(\frac{\partial v_z}{\partial y}\right)_{\text{bound}} = 0 \quad \text{and} \quad \left(\frac{\partial v_x}{\partial z}\right)_{\text{bound}} = \left(\frac{\partial v_y}{\partial z}\right)_{\text{bound}} = 0 \tag{12.101}$$

on the smooth surface.

12.E.2. Linear Stability Analysis

We shall now look for instabilities in v_z, as well as for fluctuations in T which vary in space in the x and y directions. Since in the linear stability analysis we work with linearized equations, we only need to consider one Fourier component. Thus, we shall write

$$v_z(\mathbf{r},t) = \tilde{V}_z(z)e^{i(k_x x+k_y y)}\, e^{\omega t} \tag{12.102}$$

and

$$T(\mathbf{r},t) = \tilde{T}(z)e^{i(k_x x+k_y y)}\, e^{\omega t}, \tag{12.103}$$

where $\tilde{V}_z(z)$ and $\tilde{T}(z)$ are assumed to depend on $\mathbf{k} = k_x\hat{\mathbf{i}} + k_y\hat{\mathbf{j}}$ and on ω. Substitution into Eqs. (12.91) and (12.94) yields

$$\omega\tilde{T} = a\tilde{V}_z + \frac{K}{\rho_0\tilde{c}_\rho}\left(\frac{d^2}{dz^2} - k^2\right)\tilde{T} \tag{12.104}$$

and

$$\omega\left(\frac{d^2}{dz^2} - k^2\right)\tilde{V}_z = -g\alpha_P k^2\tilde{T} + \nu\left(\frac{d^2}{dz^2} - k^2\right)^2\tilde{V}_z. \tag{12.105}$$

From the general boundary conditions we must have $\tilde{T}(0) = \tilde{T}(d) = 0$ and $\tilde{V}_z(0) = \tilde{V}_z(d) = 0$. On a rigid surface we have

$$\left.\frac{d\tilde{V}_z}{dz}\right|_{z=0} = \left.\frac{d\tilde{V}_z}{dz}\right|_{z=d} = 0.$$

On a smooth surface we have

$$\left.\frac{d^2\tilde{V}_z}{dz^2}\right|_{z=0} = \left.\frac{d^2\tilde{V}_z}{dz^2}\right|_{z=d} = 0.$$

It is convenient to introduce a change of length scale. We will let $\mathscr{Z} = z/d$, $s = \omega d^2/\nu$, $\alpha = kd$, and $\mathrm{P} = \nu\rho_0\tilde{c}_\rho/K$ (P is the Prandl number). Then Eqs. (12.104) and (12.105) can be combined and written

$$\left(\frac{\partial^2}{\partial\mathscr{Z}^2} - \alpha^2\right)\left(\frac{\partial^2}{\partial\mathscr{Z}^2} - \alpha^2 - s\right)\left(\frac{\partial^2}{\partial\mathscr{Z}^2} - \alpha^2 - \mathrm{P}s\right)\tilde{V}_z(z) = -\mathrm{R}\alpha^2\tilde{V}_z(z) \tag{12.106}$$

and an identical equation holds for $\tilde{T}(z)$. In Eq. (12.106),

$$\mathrm{R} = \frac{g a \rho_0 \tilde{c}_\rho \alpha_P d^4}{\nu K} \tag{12.107}$$

is the *Rayleigh number.* In Exercise 12.2 we show that for the Rayleigh–Bénard system the rescaled frequency, s, must be real.

■ **EXERCISE 12.2.** Show that s, the rescaled frequency, must be real.

Answer: We first define two functions, $G(\mathscr{Z})$ and $F(\mathscr{Z})$, such that

$$G(\mathscr{Z}) = \left(\frac{\partial^2}{\partial \mathscr{Z}^2} - \alpha^2\right) \tilde{V}_z(\mathscr{Z}) \tag{1}$$

and

$$F(\mathscr{Z}) = \left(\frac{\partial^2}{\partial \mathscr{Z}^2} - \alpha^2 - s\right) G(\mathscr{Z}) = \left(\frac{\partial^2}{\partial \mathscr{Z}^2} - \alpha^2 - s\right)\left(\frac{\partial^2}{\partial \mathscr{Z}^2} - \alpha^2\right) \tilde{V}_z(\mathscr{Z}). \tag{2}$$

Then Eq. (12.106) can be written

$$\left(\frac{\partial^2}{\partial \mathscr{Z}^2} - \alpha^2 - \mathrm{P}s\right) F(\mathscr{Z}) = -\mathrm{R}\alpha^2 \tilde{V}_z(\mathscr{Z}). \tag{3}$$

We next multiply by the complex conjugate of $F(\mathscr{Z})$ and integrate $\mathscr{Z}$ from 0 to 1:

$$\int_0^1 F^*\left(\frac{\partial^2}{\partial \mathscr{Z}^2} - \alpha^2 - \mathrm{P}s\right) F \, d\mathscr{Z} = -\mathrm{R}\alpha^2 \int_0^1 F^* \hat{V}_z d\mathscr{Z}. \tag{4}$$

An integration by parts, together with the boundary conditions in Eqs. (12.95) and (12.96), yields for the first term on the left

$$\int_0^1 F^* \frac{\partial^2}{\partial \mathscr{Z}^2} F \, d\mathscr{Z} = -\int_0^1 \left|\frac{\partial F}{\partial \mathscr{Z}}\right|^2 d\mathscr{Z}. \tag{5}$$

If we now use the definition of $F^*(\mathscr{Z})$ obtained from Eq. (2) and integrate by parts to rearrange the right-hand side of Eq. (4), we find, after some

algebra,

$$\int_0^1 \left\{ \left| \frac{\partial F}{\partial \mathscr{Z}} \right|^2 + \alpha^2 |F|^2 + \mathrm{P}s|F|^2 \right\} d\mathscr{Z} = \mathrm{R}\alpha^2 \int_0^1 \left\{ |G|^2 + s^* \left[\left| \frac{\partial V_z}{\partial \mathscr{Z}} \right|^2 + \alpha^2 |V_z|^2 \right] \right\} d\mathscr{Z}. \tag{6}$$

The real and imaginary parts of Eq. (6) must vanish separately. Thus, we find

$$\mathrm{Im}\,(s) \left[\int_0^1 \mathrm{P}|F|^2 \, d\mathscr{Z} + \mathrm{R}\alpha^2 \int_0^1 \left(\left| \frac{\partial V_z}{\partial \mathscr{Z}} \right|^2 + \alpha^2 |V_z| \right) d\mathscr{Z} \right] = 0, \tag{7}$$

where Im (s) is the imaginary part of s. Since the term in square brackets in Eq. (7) is positive and finite, the imaginary part of s must vanish. Thus, s is a real frequency as long as R and P are positive numbers (R and P must be positive from thermodynamic stability considerations).

The transition from the steady state in Eqs. (12.82)–(12.84) to a new steady state (often called a "soft mode" transition when the frequency is real and no temporal oscillations are allowed) occurs when $s = 0$. For $s < 0$, fluctuations are damped. For $s > 0$, they can grow. To find conditions under which the transition occurs, we set $s = 0$ in Eq. (12.106) and find values of R which satisfy the equation

$$\left(\frac{\partial^2}{\partial \mathscr{Z}^2} - \alpha^2 \right)^3 \tilde{V}_z(\mathscr{Z}) = -\mathrm{R}\alpha^2 \tilde{V}_z(\mathscr{Z}). \tag{12.108}$$

Thus the whole problem has been reduced to an eigenvalue problem. In Exercise 12.3 we solve this eigenvalue problem for smooth boundary conditions. We find that a *nonequilibrium phase transition* first occurs, as Rayleigh number is increased, at Rayleigh number $\mathrm{R} = \mathrm{R}_c = 27\pi^4/4$. At this Rayleigh number a mode emerges which has wavevector $\mathbf{q} = k_x\hat{\mathbf{x}} + k_y\hat{\mathbf{y}}$ with magnitude $q^2 = q_c^2 = \pi^2/(2d^2)$.

■ **EXERCISE 12.3.** Consider a Rayleigh–Bénard system with smooth boundary conditions. Compute the lowest value of the Rayleigh number for which an instability can occur.

Answer: Boundary conditions for two smooth boundaries are such that

$$\left(\frac{\partial^{2n}}{\partial \mathscr{Z}^{2n}} \tilde{V}_z(\mathscr{Z})\right)_{\text{bound}} = 0 \tag{1}$$

for all integer n. Thus, $\tilde{V}_z(\mathscr{Z})$ must have the form

$$\tilde{V}_z(\mathscr{Z}) = A \sin n\pi\mathscr{Z}, \tag{2}$$

where $n = 1, 2, \ldots, \infty$. Substitution into Eq. 12.108 leads to the eigenvalue equation

$$\mathrm{R} = \frac{(n^2\pi^2 + \alpha^2)^3}{\alpha^2}. \tag{3}$$

The smallest value of R for which an instability can occur is for $n = 1$ or

$$\mathrm{R} = \frac{(\pi^2 + \alpha^2)^3}{\alpha^2}. \tag{4}$$

If we plot R as a function of α, we find a critical value of α (α is related to the size of cells in the x and y directions) for which R takes on its lowest value. To find it analytically we must find the position to the minimum of R. Thus, we set

$$\frac{\partial \mathrm{R}}{\partial \alpha^2} = 3\,\frac{(\pi^2 + \alpha^2)^2}{\alpha^2} - \frac{(\pi^2 + \alpha^2)^3}{\alpha^4} = 0 \tag{5}$$

and obtain

$$\alpha_c = \frac{\pi}{\sqrt{2}} = 2.22. \tag{6}$$

The critical wavelength (the distance across a cell in the x–y plane) for the onset of instabilities is

$$\lambda_c = \frac{2\pi d}{\alpha} = 2^{3/2}\, d \tag{7}$$

and the critical Rayleigh number is

$$\mathrm{R}_c = \frac{27}{4}\pi^4 = 657.51. \tag{8}$$

Note that the critical wavelength depends on the size of the container.

The case of two smooth surfaces, while easy to analyze (cf. Exercise 12.3), is difficult to realize in experiments. Generally, in experiments one has one smooth surface and one rigid surface, or two rigid surfaces. For these more realistic boundary conditions the analysis preceeds along similar lines but is slightly more complicated [15] and will not be discussed here. For the case of one rigid and one free surface, one finds $R_c = 1100.65$ and $\alpha_c = 2.68$. For the case of two rigid boundaries, one finds $R_c = 1707.76$ and $\alpha_c = 3.12$.

Let us now summarize our results. For the region in which the steady state in Eqs. (12.82)–(12.84) is stable, the system is homogeneous in the x and y directions. However, at the transition point, convection begins and the system breaks into cells in the x and y directions. The cells will have a periodicity in the x and y directions which is proportional to d, the distance between the plates. We expect the cell walls to be vertical and that at the cell walls the normal gradient of velocity $v_z(\mathbf{r}, t)$ is zero. Thus, at the cell walls we have

$$(\hat{\mathbf{n}} \cdot \nabla_{\mathbf{r}_\perp} v_z(\mathbf{r}, t)) = 0, \tag{12.109}$$

where $\nabla_{\mathbf{r}_\perp} = \hat{\mathbf{i}}(\partial/\partial x) + \hat{\mathbf{j}}(\partial/\partial y)$ and $\hat{\mathbf{n}}$ is normal to the walls of the cell.

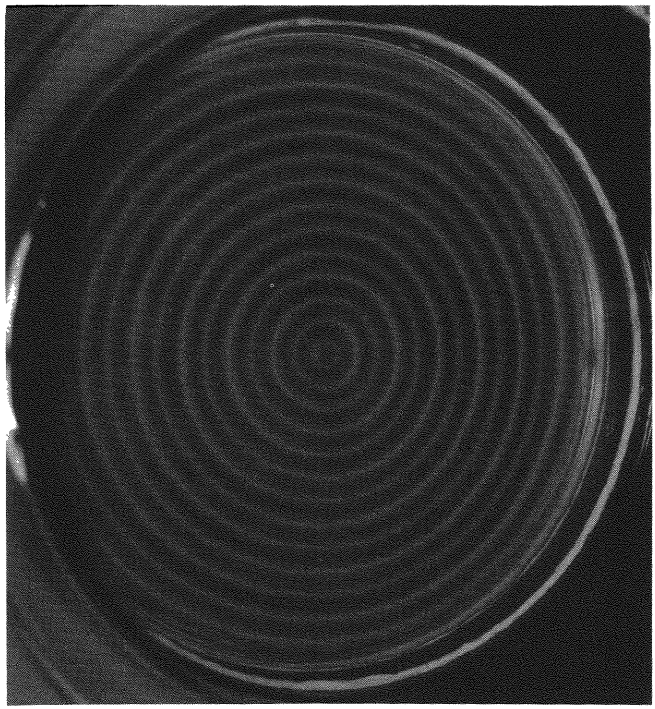

Fig. 12.9. Bénard instability. In a circular covered container, rolls usually form. The bright areas represent horizontal motion and the fine white lines are settled aluminum powder. (Reprinted, by permission, from E. L. Koschmeider, *Adv. Chem. Phys.* **26**, 177 (1974).)

The simplest type of cell pattern that can develop is that of a roll—that is, a cell pattern which depends only on one horizontal coordinate, say x. Then we have

$$v_z(\mathbf{r}, t) = \tilde{V}_z(z) \cos kx, \tag{12.110}$$

where k is the wavevector of the rolls.

The theory we have developed here assumes that the planes are of infinite extent in the x and y directions. In practice, the experiments must be done in finite containers. Then the cell pattern that emerges is strongly dependent on the shape of the container. For rectangular containers and circular covered containers, rolls usually form. Square cells can be formed in square containers. In uncovered circular containers, where the effects of surface tension are important, hexagonal cells usually form [19]. In Figs. 12.9 and 12.10 we give some examples of rolls and hexagons, respectively, which have been observed experimentally. This transition has also been observed in molecular dynamics experiments on a two-dimensional Rayleigh–Bénard system [20, 21]. In the *special topics* section we describe the behavior of fluctuations in the neighborhood of the transition point.

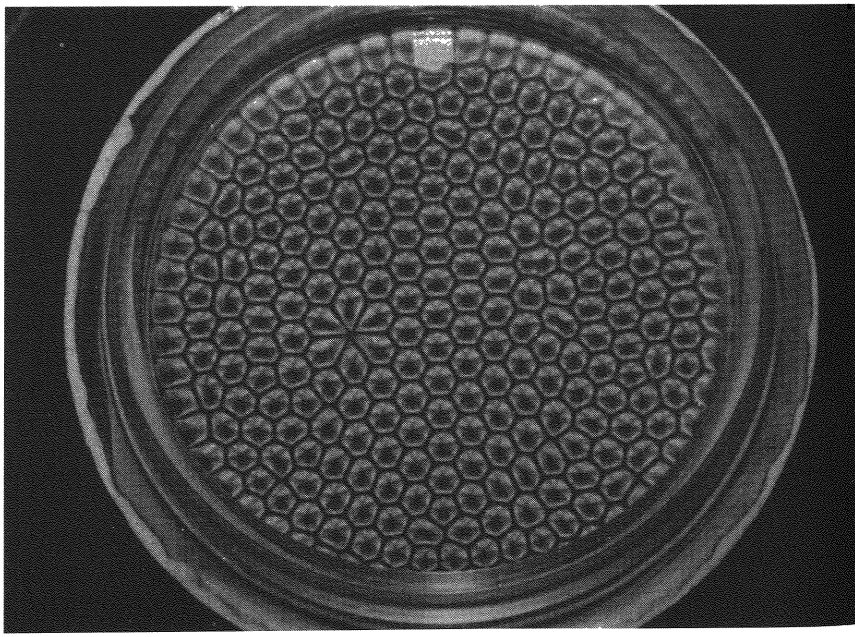

Fig. 12.10. Bénard instability. In an opened container where the effects of surface tension are important hexagonal cells usually form. The dark lines indicate vertical motion, and the bright lines indicate predominantly horizontal motion. (Reprinted, by permission, from E. L. Koschmeider, *Adv. Chem. Phys.* **26**, 177 (1974).)

▶ SPECIAL TOPICS

▶ S12.A. Fluctuations Near a Nonequilibrium Phase Transition

In both chemical and hydrodynamic systems, as we move away from equilibrium, new macroscopic modes (dissipative structures) can suddenly appear in a system, leading to dramatic new macroscopic behavior. In the Brusselator, chemical clocks, chemical waves, and chemical "crystals" (stationary spatially varying chemical concentrations) can emerge far from chemical equilibrium. A picture of chemical waves in the Belousov–Zhabotinski reaction was shown in Fig. 12.3.

In the Rayleigh–Bénard system, stationary convective spatial structures can form. These dissipative structures appear at a critical Rayleigh number in the form of a stationary convective mode which dominates the macroscopic behavior of the fluid as the Rayleigh number is increased. Some examples of such modes were shown in Figs. 12.9 and 12.10.

Ginzburg–Landau theory has proven to be a very useful tool for the analysis of nonequilibrium structures. The reason is that in the neighborhood of the critical point, the new modes exist on much slower time scales than order modes. Their behavior can be isolated and analyzed independently of the other degrees of freedom. Below we will show how this may be done for the lowest mode in the Rayleigh–Bénard system and for the onset of stationary spatial structures in the Brusselator.

▶ S12.A.1. Fluctuations in the Rayleigh–Bénard System [22–24]

In the Rayleigh–Bénard system, the lowest nonequilibrium mode for the case of smooth boundary conditions on the horizontal planes at $z = 0$ and $z = d$ was identified in Exercise (12.3). From linear stability analysis we found that this mode had a horizontal velocity variation of the form

$$v_z(\mathbf{k}, t) = A \sin\left(\frac{\pi z}{d}\right) e^{i(k_x x + k_y y)}, \tag{12.111}$$

where A is a constant. It appears at a critical Rayleigh number, $\mathrm{R}_c = 27\pi^4/4$. The critical wavevector in the vertical direction is $(k_z)_c \equiv p_c = \pi/d$. If we denote $q^2 \equiv k_x^2 + k_y^2$, then the critical wavevector in the horizontal (x, y) direction is given by $q_c^2 = \pi^2/2d^2$. One can also introduce a critical total wavevector, $k_c^2 = q_c^2 + p_c^2 = 3\pi^2/2d^2$.

In the isotropic system, near the critical point, it is possible to obtain an expression for the correlation function for the mode that will appear at the critical point. We will consider a system with Rayleigh number, $\mathrm{R} < \mathrm{R}_c$, just below the critical value. Even though the system is isotropic, the mode that appears at $\mathrm{R} = \mathrm{R}_c$ will begin to dominate the fluctuation spectrum because it

experiences *critical slowing down* near $R = R_c$. If it is excited, it takes a relatively long time to decay away. This fact allows us to isolate the new mode and treat the many degrees of freedom of the background fluid as a rapidly oscillating noise acting on the new mode. Since fluctuations in the background fluid oscillate very rapidly in time, we can use the expressions for hydrodynamic random noise correlation functions introduced in Section S10.F. The use of the equilibrium noise correlation functions to describe nonequilibrium hydrodynamic phenomena has been found to give good agreement with numerical simulations of nonequilibrium hydrodynamic systems [25].

▶ *S12.A.1.1. Equations of Motion*

Let us write the linearized equations for the temperature and velocity variations obtained in Section 12.E, but now include the random background contributions to the stress tensor and heat current which were introduced in Section S10.F. From Eqs. 10.311 and 12.90, we find

$$\rho_0 \frac{\partial \mathbf{v}}{\partial t} = -\nabla_{\mathbf{r}} \delta P + \rho_0 \alpha_P g \delta T \hat{\mathbf{z}} + \eta \nabla_{\mathbf{r}}^2 \mathbf{v} - \nabla_{\mathbf{r}} \cdot \bar{\mathbf{S}}. \tag{12.112}$$

From Eqs. (10.310) and (12.91) we find

$$\rho_0 \tilde{c}_\rho \frac{\partial \delta T}{\partial t} = \rho_0 \tilde{c}_\rho a v_z + K \nabla_{\mathbf{r}}^2 \delta T - \nabla_{\mathbf{r}} \cdot \mathbf{g}_s. \tag{12.113}$$

We are interested in how the z component of velocity varies in the (x, y) direction. Let us take the curl of Eq. (12.112) twice and use the vector identity, $\nabla_{\mathbf{r}} \times (\nabla_{\mathbf{r}} \times \mathbf{v}) = -\nabla_{\mathbf{r}}^2 \mathbf{v} + \nabla_{\mathbf{r}}(\nabla_{\mathbf{r}} \cdot \mathbf{v})$. Then the equation for $v_z(\mathbf{r}, t)$ takes the form

$$\begin{aligned} \rho_0 \frac{\partial}{\partial t} \nabla_{\mathbf{r}}^2 v_z = \rho_0 \alpha_P g \nabla_{\mathbf{r}}^2 (\delta T) - \rho_0 \alpha_P g \frac{\partial^2 \delta T}{\partial z^2} + \eta \nabla_{\mathbf{r}}^4 v_z \\ + \hat{\mathbf{z}} \cdot (\nabla_{\mathbf{r}} \times (\nabla_{\mathbf{r}} \times (\nabla_{\mathbf{r}} \cdot \bar{\mathbf{S}}))), \end{aligned} \tag{12.114}$$

Since Eqs. (12.113) and (12.114) are linear equations for δT and v_z, we can study each Fourier component separately. Therefore, we let

$$\begin{aligned} v_z(\mathbf{r}, t) &= \tilde{V}_z(\mathbf{k}, \omega) e^{i\mathbf{q}\cdot\mathbf{r}} e^{-i\omega t} \sin(k_z z), \\ \delta T(\mathbf{r}, t) &= \tilde{T}(\mathbf{k}, \omega)\, e^{i\mathbf{q}\cdot\mathbf{r}}\, e^{-i\omega t} \sin(k_z z), \\ \bar{\mathbf{S}}(\mathbf{r}, t) &= (\tilde{\mathbf{S}}_+ e^{ip_z z} + \tilde{\mathbf{S}}_- e^{-ip_z z})\, e^{i\mathbf{q}\cdot\mathbf{r}_\perp}\, e^{-i\omega t}, \\ \text{and } \mathbf{g}_s(\mathbf{r}, t) &= (\tilde{\mathbf{g}}_+ e^{ip_z z} + \tilde{\mathbf{g}}_- e^{-ip_z z}) e^{i\mathbf{q}\cdot\mathbf{r}_\perp}\, e^{-i\omega t}, \end{aligned} \tag{12.115}$$

where $\mathbf{r}_\perp = x\hat{\mathbf{x}} + y\hat{\mathbf{y}}$, $\tilde{\mathbf{S}}_\pm = \tilde{\mathbf{S}}(\mathbf{k}^\pm, \omega)$, $\tilde{\mathbf{g}}_\pm = \tilde{\mathbf{g}}(\mathbf{k}^\pm, \omega)$, and $\mathbf{k}^\pm = \mathbf{q} \pm p_z \hat{\mathbf{z}}$. We will imagine our system confined to a volume $V = 8dL^2$ (length $2L$ in the x

and y directions and $2d$ in the z direction) with periodic boundary conditions. The temperature and z component of velocity must be zero at $z = 0$ and $z = d$.

Equations (12.113) and (12.114) can be combined and take the form

$$\omega \begin{pmatrix} \tilde{V}_z \\ \tilde{T} \end{pmatrix} + i \begin{pmatrix} \nu_t k^2 & -\dfrac{g\alpha_P q^2}{k^2} \\ -a & \dfrac{Kk^2}{\rho_0 \tilde{c}_\rho} \end{pmatrix} \begin{pmatrix} \tilde{V}_z \\ \tilde{T} \end{pmatrix}$$
$$= \begin{pmatrix} -\dfrac{i}{\rho_0 k^2} \left[\hat{\mathbf{z}} \cdot (\mathbf{k}^+ \times (\mathbf{k}^+ \times (\mathbf{k}^+ \cdot \tilde{\mathbf{S}}_+))) - \hat{\mathbf{z}} \cdot (\mathbf{k}^- \times (\mathbf{k}^- \times (\mathbf{k}^- \cdot \tilde{\mathbf{S}}_-))) \right] \\ \dfrac{i}{\rho_0 \tilde{c}_\rho} \left[\mathbf{k}^+ \cdot \tilde{\mathbf{g}}_+ - \mathbf{k}^- \cdot \tilde{\mathbf{g}}_- \right] \end{pmatrix}, \tag{12.116}$$

where on the right-hand side we have used the expansion $\sin(x) = (1/2i)(e^x - e^{-x})$. The nature of the macroscopic mode that emerges at the critical point is determined by the eigenvalues and eigenvectors of the matrix on the left-hand side of Eq. (12.116). We will determine these below.

▶ *S12.A.1.2. The Critical Eigenmode*

Let us find the eigenvalues and eigenvectors of the matrix,

$$\bar{\mathbf{M}} = \begin{pmatrix} \nu_t k^2 & -\dfrac{g\alpha_P q^2}{k^2} \\ -a & \dfrac{Kk^2}{\rho_0 \tilde{c}_\rho} \end{pmatrix} = \begin{pmatrix} \nu_t k^2 & -\dfrac{g\alpha_P q^2}{k^2} \\ -a & \dfrac{ag\alpha_P d^4 k^2}{\nu \mathrm{R}} \end{pmatrix}, \tag{12.117}$$

where $\mathrm{R} = ag\alpha_P \rho_0 \tilde{c}_\rho d^4/\nu K$ is the Rayleigh number. It is instructive first to write this matrix at the critical point where $\mathrm{R} = \mathrm{R}_c = 27\pi^4/4$, $q^2 = q_c^2 = \pi^2/2d^2$, and $k^2 = k_c^2 = 3\pi^2/2d^2$. Then

$$\bar{\mathbf{M}}_c = \begin{pmatrix} \dfrac{3\nu_t \pi^2}{2d^2} & -\dfrac{g\alpha_P}{3} \\ -a & \dfrac{2ag\alpha_P d^2}{9\pi^2 \nu_t} \end{pmatrix}. \tag{12.118}$$

The matrix $\bar{\mathbf{M}}_c$ has eigenvalues

$$\lambda_s^c = 0 \quad \text{and} \quad \lambda_f^c = -\frac{4ag\alpha_P d^4 + 27\nu_t^2 \pi^4}{18\, d^2 \nu_t \pi^2}, \tag{12.119}$$

where λ_s^c denotes the eigenvalue of the slow mode at the critical point and λ_f^c

denotes the eigenvalue of the fast mode at the critical point. The mode with eigenvalue $\lambda_s^c = 0$ at the critical point is the mode which emerges and becomes macroscopic as the Rayleigh number is increased further. This happens because the eigenvalue λ_s changes from negative to positive at the critical point and for $R > R_c$ this particular mode can grow exponentially.

The matrix $\bar{\mathbf{M}}_c$ is not self-adjoint. Therefore, its left eigenvectors differ from its right eigenvectors. The left and right eigenvectors are easy to find. At the critical point, the orthonormalized left and right eigenvectors for the mode with eigenvalue λ_s^c are given by

$$\chi_s^c = A\left(1, \frac{3\nu_t\pi^2}{2ad^2}\right) \quad \text{and} \quad \psi_s^c = A\begin{pmatrix} \frac{g\alpha_P}{3} \\ \frac{3\nu_t\pi^2}{2ad^2} \end{pmatrix}, \tag{12.120}$$

respectively, where the normalization constant is given by

$$A = \frac{2ad^2}{\sqrt{\frac{4ag\alpha_P d^4}{3} + 9\nu_t^2\pi^4}}. \tag{12.121}$$

The left and right eigenvectors of the mode with eigenvalue λ_f^c can also be found, but since we won't need them, we won't write them.

We can also obtain the eigenvalues and eigenvectors of $\bar{\mathbf{M}}$ near the critical point but with $R < R_c$. We will focus on the mode with wavevector $k_z = p_z = \pi/d$. Therefore, we set $k_z = \pi/d$ in the matrix $\bar{\mathbf{M}}$. We then find the eigenvalues and eigenvectors for noncritical values of q^2 and R. Once we have them, we expand about the critical point. That is, we set $q^2 = (\pi^2/2d^2)(1 + \delta q)$ and $R = (27\pi^2/4)(1 - \delta R)$ and expand in powers of δq and δR. To lowest nonzero order in δq and δR, we find

$$\lambda_s = \frac{\nu_t k_c^2}{1+P}\left(\frac{R_c - R}{R_c} + \frac{(q^2 - q_c^2)^2}{k_c^2 q_c^2}\right) + \cdots, \tag{12.122}$$

where $P = \nu_t\rho_0\tilde{c}_\rho/K$ is the Prandl number. To lowest order in δq and δR, we approximate the left and right eigenvectors by their values at the critical point. These were given in Eq. (12.120).

▶ *S12.A.1.3. Correlation Function for the Macroscopic Mode*

Let us now isolate the critical eigenmode from the equations of motion. If we multiply Eq. (12.116) by the left eigenvector, χ_s^c, we find

$$(\omega + i\lambda_s(q, R))\,\tilde{u}_{\mathbf{q}}(\omega) = -i\frac{1}{\rho_0 k^2}(S^+ - S^-) - \frac{\nu k_c^2}{a\rho_0\tilde{c}_\rho}(G^+ - G^-), \tag{12.123}$$

where $S^{\pm} = \hat{\mathbf{z}} \cdot (\mathbf{k}^{\pm} \times (\mathbf{k}^{\pm} \times (\mathbf{k}^{\pm} \cdot \tilde{\mathbf{S}}(\mathbf{k}^{\pm}, \omega))))$, $G^{\pm} = \mathbf{k}^{\pm} \cdot \tilde{\mathbf{g}}_s(\mathbf{k}^{\pm}, \omega)$, and

$$\tilde{u}_{\mathbf{q}}(\omega) = \tilde{V}_z(\mathbf{k}, \omega) + \frac{\nu_t k_c^2}{a} \tilde{T}(\mathbf{k}, \omega) \tag{12.124}$$

is the critical eigenmode. The correlation function for the critical eigenmode can be written

$$\begin{aligned} \langle \tilde{u}_{\mathbf{q}_1}(\omega_1) \tilde{u}_{\mathbf{q}_2}(\omega_2) \rangle = & \frac{-1}{(\omega_1 + i\lambda_{s1})(\omega_2 + i\lambda_{s2})} \\ & \times \left[\frac{\nu_t^2 k_c^4}{a^2 \rho_0^2 \tilde{c}_\rho^2} \langle (G_1^+ - G_1^-)(G_2^+ - G_2^-) \rangle \right. \\ & \left. + \frac{1}{\rho_0^2 k_1^2 k_2^2} \langle (S_1^+ - S_1^-)(S_2^+ - S_2^-) \rangle \right]. \end{aligned} \tag{12.125}$$

From Eq. (10.349), we find

$$\begin{aligned} & \langle \hat{\mathbf{z}} \cdot (\mathbf{k}_1 \times (\mathbf{k}_1 \times (\mathbf{k}_1 \cdot \tilde{\mathbf{S}}(\mathbf{k}_1, \omega_1)))) \hat{\mathbf{z}} \cdot (\mathbf{k}_2 \times (\mathbf{k}_2 \times (\mathbf{k}_2 \cdot \tilde{\mathbf{S}}(\mathbf{k}_2, \omega_2))))) \rangle \\ & = \sum_{i=1}^{3} \sum_{j=1}^{3} \sum_{m=1}^{3} \sum_{n=1}^{3} k_{1i} (k_{1z} k_{1j} - \delta_{j,z} k_1^2) k_{2m} (k_{2z} k_{2n} - \delta_{n,z} k_2^2) \\ & \quad \times \langle \tilde{S}_{ij}(\mathbf{k}_1, \omega_1) \tilde{S}_{mn}(\mathbf{k}_2, \omega_2) \rangle \\ & = -4\pi k_B T \eta \, \delta(\mathbf{k}_1 + \mathbf{k}_2) \delta(\omega_1 + \omega_2) k_1^4 (k_1^2 - k_{1z}^2). \end{aligned} \tag{12.126}$$

Similarly, from Eq. (10.350), we obtain

$$\begin{aligned} \langle \mathbf{k}_1 \cdot \mathbf{g}_s(\mathbf{k}_1, \omega_1) \mathbf{k}_2 \cdot \mathbf{g}_s(\mathbf{k}_2, \omega_2) \rangle &= \sum_{i=1}^{3} \sum_{j=1}^{3} k_{1i} k_{2j} \langle g_{si}(\mathbf{k}_1, \omega_1) \langle g_{sj}(\mathbf{k}_2, \omega_2) \rangle \\ &= -4\pi k_B T^2 K k_1^2 \delta(\mathbf{k}_1 + \mathbf{k}_2) \delta(\omega_1 + \omega_2). \end{aligned} \tag{12.127}$$

Note that $\langle G_1^+ G_2^+ \rangle = \langle G_1^- G_2^- \rangle = 0$ because $\delta(\mathbf{k}_1^{\pm} + \mathbf{k}_2^{\pm}) = 0$ since the argument $\mathbf{k}_1^{\pm} + \mathbf{k}_2^{\pm}$ cannot be zero. Similarly, $\langle S_1^+ S_2^+ \rangle = \langle S_1^- S_2^- \rangle$. Therefore, the mode correlation function reduces to

$$\begin{aligned} \langle \tilde{u}_{\mathbf{q}_1}(\omega_1) \tilde{u}_{\mathbf{q}_2}(\omega_2) \rangle = & \frac{1}{(\omega_1 + i\lambda_{s1})(\omega_2 + i\lambda_{s2})} \\ & \times \left[\frac{\nu_t^2 k_c^4}{a^2 \rho_0^2 \tilde{c}_\rho^2} (\langle G_1^+ G_2^- \rangle + \langle G_1^- G_2^+ \rangle) \right. \\ & \left. + \frac{1}{\rho_0^2 k_1^2 k_2^2} (\langle S_1^+ S_2^- \rangle + \langle S_1^- S_2^+ \rangle) \right]. \end{aligned} \tag{12.128}$$

Use of Eqs. (12.126) and (12.127), then give us the following expression for the correlation function for the macroscopic mode for Rayleigh number just below the critical Rayleigh number,

$$\langle \tilde{u}_{\mathbf{q}_1}(\omega_1)\tilde{u}_{\mathbf{q}_2}(\omega_2)\rangle = \frac{A_c\delta(\mathbf{q}_1+\mathbf{q}_2)\delta(\omega_1+\omega_2)}{(\omega_1^2+\lambda_{s1}^2)}, \tag{12.129}$$

and

$$A_c = \frac{8\pi k_B T\nu q_c^2}{\rho_0}\left[1+\frac{3k_c^2\nu^2 T}{a^2\tilde{c}_\rho P}\right]. \tag{12.130}$$

Comparision of Eqs. (12.129) and (10.324) shows that

$$\int_{-\infty}^{\infty} dt e^{-i\omega t}\langle u_{\mathbf{q}_1}(t)u_{-\mathbf{q}_1}(0)\rangle = \frac{A_c}{2\pi V\lambda_{s1}}\left(\frac{\lambda_{s1}}{\omega^2+\lambda_{s1}^2}\right). \tag{12.131}$$

If we take the inverse Fourier transform of Eq. (12.131), we find

$$\langle u_{\mathbf{q}_1}(t)u_{-\mathbf{q}_1}(0)\rangle = \frac{A_c}{4\pi^2 V\lambda_{s1}}\int_{-\infty}^{\infty} d\omega e^{i\omega t}\left(\frac{\lambda_{s1}}{\omega^2+\lambda_{s1}^2}\right) = \frac{A_c}{4\pi\lambda_{s1}}e^{-\lambda_{s1}t}. \tag{12.132}$$

There are several things to notice about Eq. (12.132). First, as we approach the critical point, the fluctuations in this mode take longer and longer to die away. However, something else happens. This correlation function begins to diverge because of the dependence on λ_{s1} in the denonimator. Near the critical point the linear theory we have been considering breaks down and nonlinear effects must be included.

In Exercise 12.4 we show that a time-dependent Ginzberg–Landau equation with a Gaussian free energy can reproduce the correlation function obtained in Eq. (12.132). Fluctuations in the unstable mode can be assumed to satisfy a time-dependent Ginzburg–Landau equation,

$$\frac{\partial u_{\mathbf{q}}(t)}{\partial t} = -\frac{\delta F}{\delta u_{-\mathbf{q}}(t)} + \eta_{\mathbf{q}}(t), \tag{12.133}$$

where

$$\langle \tilde{\eta}_{\mathbf{q}}(\omega)\tilde{\eta}_{-\mathbf{q}}(-\omega)\rangle = \frac{A_c}{2\pi}, \tag{12.134}$$

and the free energy is $F = \frac{1}{2}\int d\mathbf{q}\lambda_s(\mathbf{q})|u_{\mathbf{q}}(t)|^2$.

If we wish to study behavior of the Rayleigh–Bénard system very near the critical point, we must include nonlinear terms for the slow mode in the free energy [23, 24]. The form of the non-Gaussian corrections to the free energy that must be included are determined by the nonlinear terms in the

hydrodynamic equations. Inclusion of nonlinear terms in the Ginzburg–Landau free energy also is necessary to determine the symmetry properties of the emerging convective structures—that is, whether they are hexagons, rolls, and so on [26]. Linear stability theory has only given us the *magnitude* of the critical wavevector, q_c, but says nothing about its *direction*. At the level of linear stability theory, there is a continuous degeneracy in the direction of $\mathbf{q}$. One needs to (a) include nonlinear corrections to the equations of motion in order to remove this degeneracy and (b) determine the spatial symmetry of the emerging modes.

■ **EXERCISE 12.4.** The Fourier amplitude, $u_{\mathbf{k}}(t) = \frac{1}{V}\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}\, u(\mathbf{r}, t)$, of a fluctuating mode, $u(\mathbf{r}, t)$, in a nonequilibrium system (V is the volume) is assumed to satisfy a time-dependent Ginzburg–Landau equation

$$\frac{du_{\mathbf{k}}(t)}{dt} = -\frac{\delta F(t)}{\delta u_{-\mathbf{k}}(t))} + \eta_{\mathbf{k}}(t),$$

where $\mathbf{k}$ is a wavevector, F is a free energy functional, and $\eta_{\mathbf{k}}(t)$ is a random noise. In the Gaussian approximation, the free energy functional can be written $F(t) = \int d\mathbf{k}\, \lambda_{\mathbf{k}} u_{\mathbf{k}}(t) u_{-\mathbf{k}}(t)$, where $\lambda_{\mathbf{k}}$ is a function of $\mathbf{k}$ and other relevant parameters of the system. The random noise satisfies the conditions

$$\langle \eta_{\mathbf{k}}(t)\rangle_\eta = 0 \quad \text{and} \quad \langle \eta_{\mathbf{k}_1}(t)\eta_{\mathbf{k}_2}(t)\rangle_\eta = 2\pi V \Gamma_{\mathbf{k}}\, \delta(\mathbf{k}_1 + \mathbf{k}_2)\, \delta(\omega_1 + \omega_2).$$

The variational derivative is $(\delta u_{\mathbf{k}_1}(t)/\delta u_{\mathbf{k}_2}(t)) = \delta(\mathbf{k}_1 - \mathbf{k}_2)$. Assume that the medium is isotropic and that the correlation functions are time translation invariant but not time reversal invariant (since we are far from equilibrium). What is the strength, $\Gamma_{\mathbf{k}}$, of the random noise [27]?

Answer: The equations of motion for $u_{\mathbf{k}}(t)$ and $u_{-\mathbf{k}}(t)$ are

$$\frac{du_{\mathbf{k}}(t)}{dt} = -\lambda_{\mathbf{k}}\, u_{\mathbf{k}}(t) + \eta_{\mathbf{k}}(t) \quad \text{and} \quad \frac{du_{-\mathbf{k}}(t)}{dt} = -\lambda_{-\mathbf{k}}\, u_{-\mathbf{k}}(t) + \eta_{-\mathbf{k}}(t), \quad (1)$$

respectively. The averages evolve as

$$\langle u_{\mathbf{k}}(t)\rangle_\eta = e^{-\lambda_{\mathbf{k}} t}\, u_{\mathbf{k}}(0) \quad \text{and} \quad \langle u_{-\mathbf{k}}(t)\rangle_\eta = e^{-\lambda_{-\mathbf{k}} t} u_{-\mathbf{k}}(0). \quad (2)$$

Since the system is assumed isotropic and stationary, the correlation function has the property $\langle u(\mathbf{r}_1, t_1)\, u(\mathbf{r}_2, t_2)\rangle = C_{uu}(\mathbf{r}_1 - \mathbf{r}_2,\, t_1 - t_2)$, and therefore

$$\langle \tilde{u}_{\mathbf{k}_1}(\omega_1)\tilde{u}_{\mathbf{k}_2}(\omega_2)\rangle = 2\pi V \delta(\mathbf{k}_1 + \mathbf{k}_2)\delta(\omega_1 + \omega_2) \int_{-\infty}^{\infty} dt e^{-i\omega_1 t} \langle u_{\mathbf{k}_1}(t) u_{-\mathbf{k}_1}(0)\rangle. \quad (3)$$

Let $C_{uu}(\mathbf{k},t) \equiv \langle u_{\mathbf{k}}(t)u_{-\mathbf{k}}(0)\rangle$. Then under time translation invariance we obtain

$$C_{uu}(\mathbf{k},t) \equiv \langle u_{\mathbf{k}}(t)u_{-\mathbf{k}}(0)\rangle = \langle u_{\mathbf{k}}(0)u_{-\mathbf{k}}(-t)\rangle = C_{uu}(-\mathbf{k},-t). \tag{4}$$

The correlation functions can be written

$$C_{uu}(\mathbf{k},t) = e^{-\lambda_{\mathbf{k}}t}\langle u_{\mathbf{k}}(0)u_{-\mathbf{k}}(0)\rangle \quad \text{and} \quad C_{uu}(-\mathbf{k},t) = e^{-\lambda_{-\mathbf{k}}t}\langle u_{-\mathbf{k}}(0)u_{\mathbf{k}}(0)\rangle. \tag{5}$$

Now take the Fourier transform of $C_{uu}(\mathbf{k},t)$:

$$\begin{aligned}\tilde{C}_{uu}(\mathbf{k},\omega) &= \int_{-\infty}^{\infty} dt\, C_{uu}(\mathbf{k},t)\, e^{-i\omega t} \\ &= \int_0^{\infty} dt C_{uu}(\mathbf{k},t)\, e^{-i\omega t} + \int_0^{\infty} dt C_{uu}(\mathbf{k},-t)\, e^{+i\omega t} \\ &= \int_0^{\infty} dt C_{uu}(\mathbf{k},t)\, e^{-i\omega t} + \int_0^{\infty} dt C_{uu}(-\mathbf{k},t)\, e^{+i\omega t},\end{aligned} \tag{6}$$

where in the last term we have used Eq. (4). Next use Eqs. (5) and perform the integrations in Eq. (6). We obtain

$$\tilde{C}_{uu}(\mathbf{k},\omega) = \frac{C_{uu}(\mathbf{k},0)}{i\omega + \lambda_{\mathbf{k}}} + \frac{C_{uu}(-\mathbf{k},0)}{-i\omega + \lambda_{-\mathbf{k}}}. \tag{7}$$

If we Fourier transform the time dependence in Eqs. (1), we can write the following noise correlation function

$$\begin{aligned}\langle \tilde{\eta}_{\mathbf{k}}(\omega)\tilde{\eta}_{-\mathbf{k}}(-\omega)\rangle &= (i\omega + \lambda_{\mathbf{k}})(-i\omega + \lambda_{-\mathbf{k}})\langle \tilde{u}_{\mathbf{k}}(\omega)\tilde{u}_{-\mathbf{k}}(-\omega)\rangle \\ &= (\lambda_{\mathbf{k}} + \lambda_{-\mathbf{k}})C_{uu}(\mathbf{k},0),\end{aligned} \tag{8}$$

since $C_{uu}(\mathbf{k},0) = C_{uu}(-\mathbf{k},0)$. Thus, the noise strength is

$$\Gamma_{\mathbf{k}} = (\lambda_{\mathbf{k}} + \lambda_{-\mathbf{k}})C_{uu}(\mathbf{k},0). \tag{9}$$

▶ S12.A.2. Fluctuations in the Brusselator [28, 29]

Chemical clocks and chemical waves have been realized in the Belousov–Zhabotinski reaction (cf. Section 12.D) and have been seen in other autocatalytic chemical reactions as well (see, for example, Refs. 30 and 31). Chemical "crystals" have been more difficult to achieve experimentally. They were first proposed by A. Turing [32] in 1952 and were finally realized in the

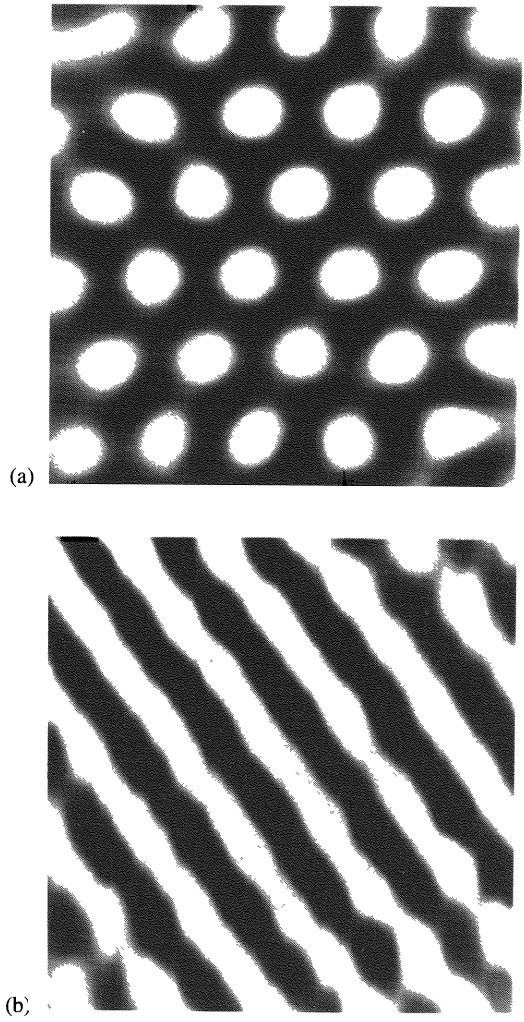

Fig. 12.11. Two-dimensional Turing structures produced with the CIMA chemical reaction in a two-dimensional gel. (a) Stripes, (b) hexagons. (Reprinted with permission from *Nature* (Q. Quyang and H. L. Swinney, **352**, 610 (1991), MacMillan Magazines Limited.)

laboratory for the first time in 1990 [33]. Chemical "crystals" or *Turing structures*, as they are now generally called, are stationary chemical concentration patterns (dissipative structures) which can emerge far from chemical equilibrium in nonlinear reaction–diffusion proceses. The reason they proved difficult to realize in the laboratory is that they generally require that the diffusion coefficients governing the reaction be very different in value [34]. This was first achieved using the so-called CIMA reaction (a chlorite–malonic acid reaction [30])) in a two-dimensional gel. It has now been well-studied and can be made to undergo a transitions to a variety of spatial structures [35]. Two such

structures are shown in Fig. 12.11. The Brusselator chemical model discussed in Section 12.D can reproduce these structures. Therefore we shall focus on it below.

▶ *S12.A.2.1. Equations of Motion and Stability Analysis*

Let us examine the chemical fluctuations that occur near the critical point for the onset of stationary chemical patterns. We will expand Eqs. (12.53) and (12.54) about the equilibrium stationary state so $X(\mathbf{r},t) = A + \delta x(\mathbf{r},t)$ and $Y(\mathbf{r},t) = B/A + \delta y(\mathbf{r},t)$. If we keep all nonlinear terms in Eqs. (12.53) and (12.54) and, in addition, if we add random chemical noise contributions, $\xi_x(\mathbf{r},t)$ and $\xi_y(\mathbf{r},t)$, to the equations for concentration fluctuations, we obtain

$$\frac{\partial \delta x}{\partial t} = (B-1)\delta x + A^2 \delta y + \frac{B}{A}(\delta x)^2 + 2A\delta x\delta y + (\delta x)^2\delta y + D_x\nabla_{\mathbf{r}}^2\delta x + \xi_x, \tag{12.135}$$

and

$$\frac{\partial \delta y}{\partial t} = -B\delta x - A^2\delta y - \frac{B}{A}(\delta x)^2 - 2A\delta x\delta y - (\delta x)^2\delta y + D_y\nabla_{\mathbf{r}}^2\delta x + \xi_y, \tag{12.136}$$

It is the linear part of Eqs. (12.135) and (12.136) that determines the critical point. If we Fourier transform both the space and time dependence of Eqs. (12.135) and (12.136) and keep only the linear terms, we obtain

$$i\omega\begin{pmatrix}\tilde{x}_{\mathbf{k}}(\omega)\\ \tilde{y}_{\mathbf{k}}(\omega)\end{pmatrix} - \begin{pmatrix}(B-1-k^2D_x) & A^2\\ -B & -A^2-k^2D_y\end{pmatrix}\begin{pmatrix}\tilde{x}_{\mathbf{k}}(\omega)\\ \tilde{y}_{\mathbf{k}}(\omega)\end{pmatrix} = \begin{pmatrix}\tilde{\xi}_x(\mathbf{k},\omega)\\ \tilde{\xi}_y(\mathbf{k},\omega)\end{pmatrix}. \tag{12.137}$$

The matrix

$$\bar{\mathbf{M}} = \begin{pmatrix}(B-1-k^2D_x) & A^2\\ -B & -A^2-k^2D_y\end{pmatrix} \tag{12.138}$$

determines whether there are any modes which become critical. In fact a critical point occurs for $B = B_c = (1 + A\sqrt{D_x/D_y})^2$ and $k^2 = k_c^2 = A/\sqrt{D_xD_y}$. Then for these values of B and k^2, the matrix $\bar{\mathbf{M}}$ has eigenvalues

$$\lambda_s(k_c,B_c) = 0 \quad \text{and} \quad \lambda_f(k_c,B_c) = A\left(\sqrt{\frac{D_x}{D_y}} + A\frac{D_x}{D_y} - A - \sqrt{\frac{D_y}{D_x}}\right), \tag{12.139}$$

where $\lambda_s(k,B)$ is the eigenvalue of the slow mode and $\lambda_f(k,B)$ is the eigenvalue of the fast mode. Note that if $D_x \approx D_y$, then $\lambda_f \approx 0$ and no separation of time

scales occurs. This is part of the reason why Turing structures took so long to observe. For chemical reactions in fluids, all the diffusion coefficients generally are of the same order of magnitude. By placing the CIMA reaction in a gel, the diffusion coefficients could be changed and separated in value.

The left eigenstate of the slow mode for $B = B_c$ and $k = k_c$ is given by

$$\chi_S(k_c, B_c) = \sqrt{\frac{D_x}{D_x - D_y}}\left(1 + \frac{1}{k_c^2 D_x}, 1\right). \tag{12.140}$$

We can also obtain the eigenvalue of the slow mode near the critical point. It is given by

$$\lambda_s(k, B) \approx 2A\sqrt{\frac{D_y}{D_x}}(B - B_c) + 2D_x D_y(k^2 - k_c^2)^2. \tag{12.141}$$

With this information, we can now separate the slow mode from the equations of motion and obtain its correlation function near the critical point.

▶ *S12.A.2.3. Correlation Function for the Critical Eigenmode*

If we multiply Eq. (12.137) by the eigenvector, Eq. (12.140), we find

$$(i\omega - \lambda_s(k, B))\,\tilde{u}_{\mathbf{k}}(\omega) = \tilde{\eta}_{\mathbf{k}}(\omega), \tag{12.142}$$

where $\tilde{u}_{\mathbf{k}}(\omega)$ is the amplitude of the critical eigenmode,

$$\tilde{u}_{\mathbf{k}}(\omega) = \left(1 + \frac{1}{k_c^2 D_x}\right)\tilde{x}_{\mathbf{k}}(\omega) + \tilde{y}_{\mathbf{k}}(\omega), \tag{12.143}$$

and $\tilde{\eta}_{\mathbf{k}}(\omega)$ is the chemical noise it experiences,

$$\tilde{\eta}_{\mathbf{k}}(\omega) = \left(1 + \frac{1}{k_c^2 D_x}\right)\tilde{\xi}_x(\mathbf{k}, \omega) + \tilde{\xi}_y(\mathbf{k}, \omega). \tag{12.144}$$

From Exercise (12.4) the noise satisfies the correlation function

$$\langle \tilde{\eta}_{\mathbf{k}}(\omega)\tilde{\eta}_{-\mathbf{k}}(-\omega)\rangle = 2\lambda_s(k, B)\langle u_{\mathbf{k}}(0)u_{-\mathbf{k}}(0)\rangle. \tag{12.145}$$

We see that the equation of motion of the critical eigenmode can we written in terms of a time-dependent Ginzburg–Landau equation with a Gaussian free energy (cf. Exercise 12.4) with a structure similar to that in Eq. (12.133), but with a noise strength given by Eq. (12.145).

In order to determine the spatial symmetry of the Turing patterns that emerge as parameters are varied, it is necessary to go beyond the Gaussian approximation to the Ginzburg–Landau free energy and include higher-order

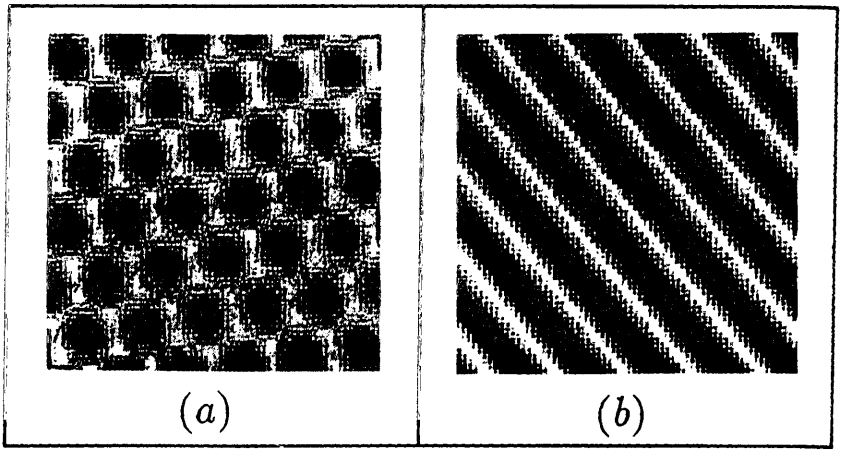

Fig. 12.12. Numerical simulation of Turing structures using the Brusselator chemical model and parameters of the CIMA reaction in a gel. Note the excellent agreement with experimental results in Fig. 12.11. (Reprinted from G. Dewel, et. al. *Physica* **A213,** 181 (1995) with kind permission from Elsevier Science – NL, Sara Burgerhart Straat 25, 1055 KV Amsterdam, The Netherlands.)

terms in the free energy. The nature of these higher-order terms is determined by the type of nonlinearities that occur in the reaction diffusion equations that describe the chemical reaction process. A detailed discussion for the case of the Brusselator chemical model can be found in Refs. 28 and 29 (see Fig. 12.12).

The study of autocatalytic chemical reactions in media such as gels, which can change the diffusion coefficients, is an area of growing interest. One of the more intriguing recent discoveries was the possibility of forming self-replicating spots in such systems [36]. These are circular spots of chemical concentration which grow and then subdivide and produce multiple spots.

▶ S12.A.3. The Time-Dependent Ginzburg–Landau Equation

The time-dependent Ginzburg–Landau equation has proven to be a very powerful tool for studying the dynamical behavior of systems near their critical points, both in equilibrium [37] and out of equilibrium. In this book we have focused on its applications to nonequilibrium phase transitions because they are more easily visualized. The use of the Ginzburg–Landau equation in both cases is based on the fact that at a critical point an unstable mode, $u(\mathbf{r}, t)$, emerges which has a time scale much slower that those of the rest of the fluid and plays the role of an order parameter [in the sections above we have worked with the spatial Fourier transform of $u(\mathbf{r}, t)$]. Fluctuations in this unstable mode near the critical point obey a Ginzburg–Landau equation such as in Eq. (12.133). The

simplest non-Gaussian free energy one might encounter can be written

$$F = \int d\mathbf{r} \left[\frac{1}{2} \left(\frac{a_c - a}{a_c} \right) u^2(\mathbf{r}) + \frac{1}{4} b u^4(\mathbf{r}) + \frac{1}{2} c (\nabla u(\mathbf{r}))^2 \right], \tag{12.146}$$

where a, b, and c are parameters determined by the physics of the problem. The parameter a is an externally controlled parameter which plays the role of the temperature. When $b = 0$, the free energy reduces to the Gaussian approximation. As one nears the critical point, order parameter fluctuations begin to exhibit *critical slowing down* and correlation functions begin to exhibit long-range spatial order, similar to the mean field behavior discribed in Section 8.B. However, very near the critical point, the Gaussian approximation and therefore mean field theory breaks down and higher-order contributions ($b \neq 0$) to the Ginzburg–Landau free energy begin to play a dominant role in the behavior of the system. One of the few exceptions to this is the equilibrium superconducting phase transition which is well-described by mean field theory. Time-dependent Ginzburg–Landau equations have also been used to describe instabilities in the electromagnetic modes of lasers [23]. The detailed form of the nonlinear corrections to the Gaussian free energy is determined by the nonlinear contributions to the dynamical equations which governs the problem at hand. For electromagnetic modes of a laser [23] and for the lowest mode of the Rayleigh–Bénard system [24], Eq. (12.146) has been used. For the Brusselator chemical model, cubic terms must also be added to the free energy [28]. Variations of Ginzburg–Landau theory have also been used to study problems of phase separation [38]. While we can't go into all these applications here, we hope to have conveyed the fact that it is, indeed, a fascinating field of study.

The Rayleigh-Benard instability is just one of several instabilities that emerge in Navier-Stokes fluids out of equilibrium. Flowing fluids exhibit a series of transitions which can lead to fully developed turbulence in these systems [3].

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PROBLEMS

Problem 12.1. Use linear stability theory to locate the stable and unstable steady-state solutions for the Schlogl chemical model.

Problem 12.2. For the Schlogl chemical model, show that multiple steady states can only occur far from thermodynamic equilibrium.

Problem 12.3. A one-dimensional chemically reacting system has variable constituent, X, whose rate equation is linear,

$$\frac{\partial c_X}{\partial t} = kc_X - D\nabla_{\mathbf{r}}^2 c_X.$$

Assume that the concentration, c_X, is held fixed on the boundaries with values $c_X = c_0$. Find the steady-state value of c_X as a function of position (D is the diffusion coefficient). Sketch the steady-state solution as a function of position.

Problem 12.4. Write the rate equations for the Brusselator near equilibrium and find the equilibrium values of c_X and c_Y. Find the steady-state solutions for the system near equilibrium (assume it is spatially homogeneous) and show that far from equilibrium (A and B large and D and E eliminated as soon as they are produced) they reduce to the expressions $X_0 = A$ and $Y_0 = B/A$.

Problem 12.5. Show that the Brusselator admits traveling wave solutions, $c_X(r\theta \pm vt)$ and $c_Y(r\theta \pm vt)$, for linear motion on a circle, assuming periodic boundary conditions. Find the condition for a bifurcation from the thermodynamic branch to a travelling wave solution using linear stability theory. Show that the velocity, v, of the waves is a decreasing function of the wave number.

Problem 12.6. A fluid is constrained between two smooth surfaces a distance d apart in a gravitational field with a temperature gradient across the fluid. If a Bénard instability develops, show that it is possible to have square cells. Find the horizontal width of the cells in terms of d. Find an expression for the velocity, $\mathbf{v}$, of the fluid and sketch the flow in each cell. Assume that at the cell walls the fluid flows upward and has its maximum speed.

Problem S12.1. Locate the critical point in the Schlogl chemical reaction. Compute the correlation function for concentration fluctuations, just "below" the critical point and in the Gaussian approximation. Compute the correlation function for the chemical noise.

APPENDIX A

BALANCE EQUATIONS

A.1. GENERAL FLUID FLOW

Let us consider a continuous medium which moves with velocity $\mathbf{v}(\mathbf{x}, t)$ at time t and position $\mathbf{x}$. The position $\mathbf{x}$ is measured with respect to a fixed frame of reference whose origin lies at $O_{\mathbf{x}}$. In addition, it is convenient to introduce a second coordinate system whose origin lies at $O_{\mathbf{z}}$ and which moves with the fluid. We assume that at time $t = 0$ the two coordinate systems coincide; and at time $t = 0$ we select a given fluid "particle" (small volume element of the fluid) which has position $\mathbf{x}(0)$ with respect to frame $O_{\mathbf{x}}$ and position $\mathbf{z}$ with respect to frame $O_{\mathbf{z}}$. Because the coordinate systems coincide at time $t = 0$, $\mathbf{z} = \mathbf{x}(0)$.

Let us assume that both the frame $O_{\mathbf{z}}$ and the fluid particle move freely with the fluid and that the fluid particle always has position $\mathbf{z}$ with respect to the frame $O_{\mathbf{z}}$. The position of the fluid particle with respect to the frame $O_{\mathbf{x}}$ at time t is

$$\mathbf{x}(t) = \mathbf{x}(\mathbf{z}, t), \tag{A.1}$$

where $\mathbf{z} = \mathbf{x}(0)$ is the initial position of the particle. Equation (A.1) relates the coordinates of the fluid particle as seen by observers in the two frames (cf. Fig. A.1).

We now introduce a density $\mathscr{D}(\mathbf{x}, t)$, where $\mathscr{D}(\mathbf{x}, t)$ could be a probability per unit volume, internal energy per unit volume, mass per unit volume, angular momentum per unit volume, and so on. At time $t = 0$, an observer in frame $O_{\mathbf{x}}$ sees a density $\mathscr{D}(\mathbf{x}(0), 0)$ and an observer in frame $O_{\mathbf{z}}$ sees a density $\mathscr{D}'(\mathbf{z}, 0)$ in the neighborhood of the fluid particle, where $\mathscr{D}(\mathbf{x}(0), 0) = \mathscr{D}'(\mathbf{z}, 0)$. At time t, an observer in $O_{\mathbf{x}}$ sees a density $\mathscr{D}(\mathbf{x}(\mathbf{z}, t), t)$ and an observer in $O_{\mathbf{z}}$ sees a density $\mathscr{D}'(\mathbf{z}, t)$ in the neighborhood of the fluid particle, where $\mathscr{D}(\mathbf{x}(\mathbf{z}, t), t) = \mathscr{D}'(\mathbf{z}, t)$. [Once the density is given in one coordinate system, it can be found in the other using Eq. (A.1)].

We shall denote the total time rate of change of the density in the neighborhood of the fluid particle by $d\mathscr{D}/dt$. Then

$$\frac{d\mathscr{D}}{dt} = \left(\frac{\partial \mathscr{D}'}{\partial t}\right)_{\mathbf{z}} = \left(\frac{\partial \mathscr{D}}{\partial t}\right)_{\mathbf{x}} + \left(\frac{\partial \mathscr{D}}{\partial \mathbf{x}}\right)_{\mathbf{t}} \left(\frac{\partial \mathbf{x}}{\partial t}\right)_{\mathbf{z}}. \tag{A.2}$$

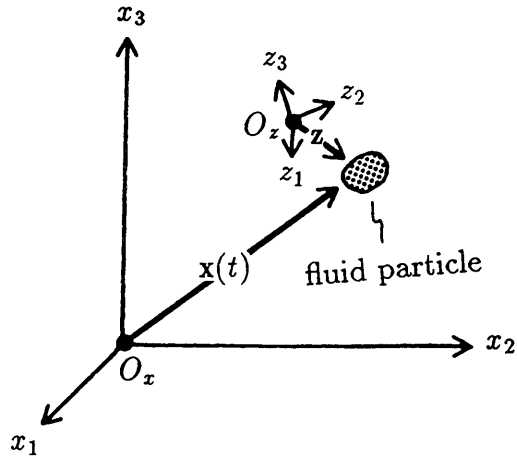

Fig. A.1. Coordinates of a fluid particle at time t.

However, $(\partial \mathbf{x}/\partial t)_{\mathbf{z}}$ is the velocity of the fluid particle:

$$\mathbf{v} \equiv \frac{d\mathbf{x}}{dt} = \left(\frac{\partial \mathbf{x}}{\partial t}\right)_{\mathbf{z}}. \tag{A.3}$$

From Eq. (A.2), we see that $d\mathscr{D}/dt = (\partial \mathscr{D}'/\partial t)_{\mathbf{z}}$ is the time rate of change of the density as seen by an observer moving with the fluid particle, and $(\partial \mathscr{D}/\partial t)_{\mathbf{x}}$ is the time rate of change of the density at a fixed point in space (not moving with the fluid). Combining Eqs. (A.2) and (A.3), we may write the total derivative d/dt in the form

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}}. \tag{A.4}$$

Equation (A.4) is often called the *convective time derivative*. It allows one to find the time rate of change at a moving point in terms of coordinates which are fixed in space.

Let us now consider a given set of fluid particles contained in a volume element dV_0 at time $t = 0$. We wish to follow the same set of fluid particles with time and see how their volume changes with time. If we remember that $\mathbf{x}(0) = \mathbf{z}$, we may write

$$dV_t = \mathscr{J}\begin{pmatrix} x_1, x_2, x_3 \\ z_1, z_2, z_3 \end{pmatrix} dV_0, \tag{A.5}$$

where

$$dV_0 = d\mathbf{z} = d\mathbf{x}(0) \tag{A.6}$$

and

$$dV_t = d\mathbf{x}(t). \tag{A.7}$$

In Eq. (A.5), x_1, x_2, and x_3 are the components of the vector $\mathbf{x}(t)$, and z_1, z_2, and z_3 are the components of the vector $\mathbf{z}$. The Jacobian is defined as

$$\mathscr{J}\begin{pmatrix} x_1 & x_2 & x_3 \\ z_1 & z_2 & z_3 \end{pmatrix} = \det \begin{vmatrix} \dfrac{\partial x_1}{\partial z_1} & \dfrac{\partial x_1}{\partial z_2} & \dfrac{\partial x_1}{\partial z_3} \\ \dfrac{\partial x_2}{\partial z_1} & \dfrac{\partial x_2}{\partial z_2} & \dfrac{\partial x_2}{\partial z_3} \\ \dfrac{\partial x_3}{\partial z_1} & \dfrac{\partial x_3}{\partial z_2} & \dfrac{\partial x_3}{\partial z_3} \end{vmatrix} \tag{A.8}$$

and may be evaluated from Eq. (A.1). From Eq. (A.5) we see that the Jacobian is a measure of the amount by which the volume of a given set of fluid particles changes as a function of time. The change in the Jacobian with time, as seen by an observer moving with the volume element, is $d\mathscr{J}/dt$. If we note that

$$\frac{d}{dt}\frac{\partial x_i}{\partial z_j} = \frac{\partial}{\partial z_j}\frac{dx_i}{dt} = \frac{\partial v_i}{\partial z_j} \tag{A.9}$$

($\mathbf{z}$ is held constant when the differentiation d/dt is carried out), we may write

$$\frac{d\mathscr{J}}{dt} = \det \begin{vmatrix} \dfrac{\partial v_1}{\partial z_1} & \dfrac{\partial v_1}{\partial z_2} & \dfrac{\partial v_1}{\partial z_3} \\ \dfrac{\partial x_2}{\partial z_1} & \dfrac{\partial x_2}{\partial z_2} & \dfrac{\partial x_2}{\partial z_3} \\ \dfrac{\partial x_3}{\partial z_1} & \dfrac{\partial x_3}{\partial z_2} & \dfrac{\partial x_3}{\partial z_3} \end{vmatrix} + \det \begin{vmatrix} \dfrac{\partial x_1}{\partial z_1} & \dfrac{\partial x_1}{\partial z_2} & \dfrac{\partial x_1}{\partial z_3} \\ \dfrac{\partial v_2}{\partial z_1} & \dfrac{\partial v_2}{\partial z_2} & \dfrac{\partial v_2}{\partial z_3} \\ \dfrac{\partial x_3}{\partial z_1} & \dfrac{\partial x_3}{\partial z_2} & \dfrac{\partial x_3}{\partial z_3} \end{vmatrix} + \det \begin{vmatrix} \dfrac{\partial x_1}{\partial z_1} & \dfrac{\partial x_1}{\partial z_2} & \dfrac{\partial x_1}{\partial z_3} \\ \dfrac{\partial x_2}{\partial z_1} & \dfrac{\partial x_2}{\partial z_2} & \dfrac{\partial x_2}{\partial z_3} \\ \dfrac{\partial v_3}{\partial z_1} & \dfrac{\partial v_3}{\partial z_2} & \dfrac{\partial v_3}{\partial z_3} \end{vmatrix}. \tag{A.10}$$

However,

$$\frac{\partial v_i}{\partial z_j} = \sum_{k=1}^{3} \frac{\partial v_i}{\partial x_k}\frac{\partial x_k}{\partial z_j}. \tag{A.11}$$

If we substitute Eq. (A.11) into Eq. (A.10), then, in the first determinant on the right-hand side, only the term in the sum with $k = 1$ is nonzero, because for $k = 2$ or 3 two rows of the determinant become identical and therefore give zero. The second and third determinants are only nonzero for $k = 2$ and 3, respectively, We therefore obtain

$$\frac{d\mathscr{J}}{dt} = \left(\frac{\partial v_1}{\partial x_1} + \frac{\partial v_2}{\partial x_2} + \frac{\partial v_3}{\partial x_3}\right)\mathscr{J} = \nabla_{\mathbf{x}} \cdot \mathbf{v}\mathscr{J}. \tag{A.12}$$

If $\nabla_{\mathbf{x}} \cdot \mathbf{v} = 0$, then $d\mathscr{J}/dt = 0$ and the size of the volume element remains constant with time; that is, the fluid is incompressible. If $\nabla_{\mathbf{x}} \cdot \mathbf{v} \neq 0$, the volume element may expand and contract with time.

A.2. GENERAL BALANCE EQUATION

We now wish to find the equation of motion for an arbitrary density $\mathscr{D}(\mathbf{x}, t)$. Let us consider a finite volume element V_0 at time $t = 0$ containing a given set of fluid particles. At time t, that same set of fluid particles will occupy a volume $V(t)$. The total amount of quantity D contained in $V(t)$ is found by integrating $\mathscr{D}(\mathbf{x}, t)$ over the volume $V(t)$:

$$D(t) = \int\int\int_{V(t)} \mathscr{D}(\mathbf{x}, t) dV_t. \tag{A.13}$$

The rate of change of the amount of D in $V(t)$ as seen by an observer moving with $V(t)$ is given by

$$\frac{dD}{dt} = \frac{d}{dt} \int\int\int_{V(t)} \mathscr{D}(\mathbf{x}, t)\, dV_t. \tag{A.14}$$

Since the limits of integration depend on time, the derivative cannot be taken inside the integral. However, if we write the integral in terms of coordinates at time $t = 0$, we can take the derivative inside:

$$\frac{dD}{dt} = \frac{d}{dt} \int\int\int_{V_0} \mathscr{D}(\mathbf{x}, t) \mathscr{J}\, dV_0 = \int\int\int_{V_0} \left(\frac{d\mathscr{D}}{dt}\, \mathscr{J} + \mathscr{D}\, \frac{d\mathscr{J}}{dt} \right) dV_0. \tag{A.15}$$

In Eq. (A.15), $\mathscr{J}$ is the Jacobian. Using Eq. (A.12), we obtain

$$\frac{dD}{dt} = \int\int\int_{V_0} \left(\frac{d\mathscr{D}}{dt} + \mathscr{D} \nabla_{\mathbf{x}} \cdot \mathbf{v} \right) \mathscr{J}\, dV_0 = \int\int\int_{V(t)} \left(\frac{d\mathscr{D}}{dt} + \mathscr{D} \nabla_{\mathbf{x}} \cdot \mathbf{v} \right) dV_t. \tag{A.16}$$

The total amount of the quantity D in $V(t)$ can change if there is a flow of D through the sides of $V(t)$ or a source of D in $V(t)$. We can imagine a flow of D through the sides. An example would be the case when $\mathscr{D}(\mathbf{x}, t)$ is the heat density at position $\mathbf{x}$ and time t, and the surrounding medium is at a different temperature. If we let $\mathbf{J}_D$ represent a current of D through the sides of $V(t)$ and

σ_D represent a source of D inside $V(t)$, then we can write

$$\frac{dD}{dt} = \int\int\int_{V(t)} \left(\frac{d\mathscr{D}}{dt} + \mathscr{D}\nabla_{\mathbf{x}} \cdot \mathbf{v} \right) dV_t = \int\int\int_{V(t)} \sigma_D dV_t - \int\int_{S(t)} \mathbf{J}_D \cdot d\mathbf{S}_t. \quad \text{(A.17)}$$

(The surface area element $d\mathbf{S}_t$ is assumed to point out of $V(t)$.) If we first change the surface integral to a volume integral ($\int\int_{s(t)} \mathbf{J}_D \cdot d\mathbf{S}_t = \int\int\int_{V(t)} \nabla_{\mathbf{x}} \cdot \mathbf{J}_D \, dV_t$), then, since $V(t)$ is arbitrary, we may equate integrands to obtain

$$\frac{d\mathscr{D}}{dt} = -\mathscr{D}\nabla_{\mathbf{x}} \cdot \mathbf{v} + \sigma_D - \nabla_{\mathbf{x}} \cdot \mathbf{J}_D. \quad \text{(A.18)}$$

Equation (A.18) is one form of the *balance equation*. If we use the definition of the convective time derivative given in Eq. (A.4), we may write the balance equation in the more usual form:

$$\frac{\partial \mathscr{D}}{\partial t} = -\nabla_{\mathbf{x}} \cdot (\mathscr{D}\mathbf{v} + \mathbf{J}_D) + \sigma_D. \quad \text{(A.19)}$$

The quantity $\mathscr{D}\mathbf{v}$ is a convective current of D. It is a current which occurs simply because the fluid is in motion. Equation (A.18) gives the time rate of change of the density in the neighborhood of a point moving with the fluid. Equation (A.19) gives the time rate of change of the density at a fixed point in the fluid.

We can get a better understanding of the meaning of various terms in Eq. (A.19) if we integrate it over a fixed volume, V_f, in the fluid. Then

$$\int\int\int_{V_f} \frac{\partial \mathscr{D}}{\partial t} \, dV_f = -\int\int\int_{V_f} \nabla_{\mathbf{x}} \cdot (\mathscr{D}\mathbf{v} + \mathbf{J}_D) \, dV_f + \int\int\int \sigma_D \, dV_f. \quad \text{(A.20)}$$

Since the volume V_f is fixed, the limits of integration are time independent and the time derivative on the left-hand side can be taken outside the integral. Also, we can use Stokes' theorem to change the volume integral of the divergence on the right-hand side to a surface integral. We then obtain

$$\frac{\partial}{\partial t} \int\int\int_{V_f} \mathscr{D} \, dV_f = -\int\int_{S_f} (\mathscr{D}\mathbf{v} + \mathbf{J}_D) \cdot d\mathbf{S}_f + \int\int\int_{V_f} \sigma_D \, dV_f, \quad \text{(A.21)}$$

where S_f is the surface of V_f and $d\mathbf{S}_f$ is an infinitesimal surface area segment whose direction is along the outward normal to the surface S_f. From Eq. (A.21),

we see that the rate of change of the amount of D in V_f is due, in part, to a flow of D through the surface and to the creation of D in the fluid.

REFERENCE

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APPENDIX B

SYSTEMS OF IDENTICAL PARTICLES

The indistinguishability of a system of N identical particles lies in the fact that the Hamiltonian and all other physical observables are invariant under permutation of their dynamical variables [1]. This symmetry property of the Hamiltonian leads to a decomposition of the eigenstates of the Hamiltonian and all other states of the system into two types, either symmetric or antisymmetric under permutation of the N particles. Particles with symmetric eigenstates are bosons. Particles with antisymmetric eigenstates are fermions. Experiment shows that systems of particles with integral spin (photons, He^4, etc.) are bosons. Systems of particles with half-integral spin (electrons, protons, He^3, etc.) are fermions.

In this book, we often consider systems of N identical particles with spin, confined to a finite or an infinite volume. We will usually consider Hamiltonians which can be decomposed into a kinetic energy and a potential energy,

$$\hat{H}_N = \sum_{i=1}^{N} \frac{\hat{\mathbf{p}}_i^2}{2m} + \sum_{i<j=1}^{(\frac{1}{2})N(N-1)} V(\hat{\mathbf{q}}_i, \hat{\mathbf{q}}_j, \hat{\mathbf{s}}_i \hat{\mathbf{s}}_j), \tag{B.1}$$

where m is the mass of a particle, $\hat{\mathbf{p}}_i$ and $\hat{\mathbf{q}}_i$ are the momentum and position operators, respectively, for the i^{th} particle, and $\hat{\mathbf{s}}_i$ is the spin operator for the i^{th} particle. If a particle has spin, then we must specify not only its momentum or position, but also the component of its spin along some direction in space (we choose the z direction). We will be interested in evaluating traces and expectation values in terms of complete sets of symmetized position and momentum eigenstates, and we will be interested in the relation between these states and the "number" basis. Therefore, in Section B.1 we construct complete sets of symmetrized momentum and position eigenstates and show how to use them. In Section B.2 we show the connection between symmetrized position and momentum eigenstates and field operators.

B.1. POSITION AND MOMENTUM EIGENSTATES

In this section we derive expressions for the position and momentum eigenstates of a free particle and for a particle confined to a box with periodic boundary conditions.

B.1.1. Free Particle

Let the ket, $|\mathbf{r}\rangle$, denote the right eigenstate of the position operator, $\hat{\mathbf{q}}$, and let the ket, $|\mathbf{p}\rangle$, denote the right eigenstate of the momentum operator, $\hat{\mathbf{p}}$, so that $\hat{\mathbf{q}}|\mathbf{r}\rangle = \mathbf{r}|\mathbf{r}\rangle$ and $\hat{\mathbf{p}}|\mathbf{p}\rangle = \mathbf{p}|\mathbf{p}\rangle$. It is often useful to write the momentum operator as $\hbar\mathbf{k}$, where $\hat{\mathbf{k}}$ is the wavevector. Then $\hat{\mathbf{p}}|\mathbf{k}\rangle = \hbar\hat{\mathbf{k}}|\mathbf{k}\rangle$. The left eigenstates of the position and momentum operators are found by taking the Hermitian adjoint (denoted by †) of these equations (note that $(\hat{\mathbf{q}}|\mathbf{r}\rangle)^\dagger = \langle\mathbf{r}|\hat{\mathbf{q}}^\dagger = \langle\mathbf{r}|\hat{\mathbf{q}}$, since the position operator is Hermitian, $\hat{\mathbf{q}}^\dagger = \hat{\mathbf{q}}$). Thus, the left eigenvalue problem can be written $\langle\mathbf{r}|\hat{\mathbf{q}} = \langle\mathbf{r}|\mathbf{r}$ and $\langle\mathbf{p}|\hat{\mathbf{p}} = \langle\mathbf{p}|\mathbf{p}$. The left and right eigenvectors are orthonormal $\langle\mathbf{r}'|\mathbf{r}\rangle = \delta(\mathbf{r}' - \mathbf{r}) = \delta(x' - x)\delta(y' - y)\delta(z' - z)$ and $\langle\mathbf{p}'|\mathbf{p}\rangle = \delta(\mathbf{p}' - \mathbf{p}) = \delta(p'_x - p_x)\ \delta(p'_y - p_y)\delta(p'_z - p_z)$ or $\langle\mathbf{k}'|\mathbf{k}\rangle = \delta(\mathbf{k}' - \mathbf{k}) = \delta(k'_x - k_x)\delta(k'_y - k_y)\delta(k'_z - k_z)$. The left and right eigenvectors form complete sets

$$\int d\mathbf{r}|\mathbf{r}\rangle\langle\mathbf{r}| = \hat{\mathbf{1}} \quad \text{and} \quad \int d\mathbf{p}|\mathbf{p}\rangle\langle\mathbf{p}| = \hat{\mathbf{1}} \quad \text{or} \quad \int d\mathbf{k}|\mathbf{k}\rangle\langle\mathbf{k}| = \hat{\mathbf{1}}, \tag{B.2}$$

where the integrations are taken over the entire allowed range of $\mathbf{r}, \mathbf{p}$, and $\mathbf{k}$, respectively. For a free particle, this is $-\infty < x < \infty$, $-\infty < y < \infty$, and $-\infty < z < \infty$. Also, $-\infty < p_x < \infty$, $-\infty < p_y < \infty$, and $-\infty < p_z < \infty$ and similarly for $\mathbf{k}$. The momentum operator in the position basis is defined as

$$\langle\mathbf{r}'|\hat{\mathbf{p}}|\mathbf{r}\rangle = \delta(\mathbf{r}' - \mathbf{r})\frac{\hbar}{i}\nabla_{\mathbf{r}}, \tag{B.3}$$

and a function of the momentum operator in the position basis is defined as

$$\langle\mathbf{r}'|f(\hat{\mathbf{p}})|\mathbf{r}\rangle = \delta(\mathbf{r}' - \mathbf{r})f\left(\frac{\hbar}{i}\nabla_{\mathbf{r}}\right). \tag{B.4}$$

Similarly, the position operator in the momentum basis is defined as

$$\langle\mathbf{p}'|\hat{\mathbf{q}}|\mathbf{p}\rangle = \delta(\mathbf{p}' - \mathbf{p})\frac{-\hbar}{i}\nabla_{\mathbf{p}}. \tag{B.5}$$

and a function of the position operator in the momentum basis is defined as

$$\langle\mathbf{p}'|f(\hat{\mathbf{r}})|\mathbf{p}\rangle = \delta(\mathbf{p}' - \mathbf{p})f\left(\frac{-\hbar}{i}\nabla_{\mathbf{p}}\right), \tag{B.6}$$

We can compute the momentum eigenstate in the position basis, $\phi_{\mathbf{p}}(\mathbf{r}) \equiv \langle\mathbf{r}|\mathbf{p}\rangle$ and $\phi_{\mathbf{k}}(\mathbf{r}) \equiv \langle\mathbf{r}|\mathbf{k}\rangle$. It is the solution to the equation

$$\langle\mathbf{r}|\hat{\mathbf{p}}|\mathbf{p}\rangle = \mathbf{p}\langle\mathbf{r}|\mathbf{p}\rangle \quad \text{or} \quad \frac{\hbar}{i}\nabla_{\mathbf{r}}\langle\mathbf{r}|\mathbf{p}\rangle = \mathbf{p}\langle\mathbf{r}|\mathbf{p}\rangle. \tag{B.7}$$

The orthonormalized solution to Eq. (B.7) is

$$\langle \mathbf{r}|\mathbf{p}\rangle = \phi_{\mathbf{p}}(\mathbf{r}) = \left(\frac{1}{2\pi\hbar}\right)^{3/2} \exp\left(\frac{i\mathbf{p}\cdot\mathbf{r}}{\hbar}\right) \quad \text{or} \quad \langle \mathbf{r}|\mathbf{k}\rangle = \phi_{\mathbf{k}}(\mathbf{r}) = \left(\frac{1}{2\pi}\right)^{3/2} e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{B.8}$$

The normalized momentum eigenstate in the momentum basis is

$$\langle \mathbf{p}'|\mathbf{p}\rangle = \phi_{\mathbf{p}}(\mathbf{p}') = \delta(\mathbf{p}-\mathbf{p}') \quad \text{or} \quad \langle \mathbf{k}'|\mathbf{k}\rangle = \phi_{\mathbf{k}}(\mathbf{k}') = \delta(\mathbf{k}-\mathbf{k}'). \tag{B.9}$$

Similarly, the normalized position eigenstate in the momentum basis is

$$\begin{aligned} \langle \mathbf{p}|\mathbf{r}\rangle = \phi_{\mathbf{r}}(\mathbf{p}) &= \left(\frac{1}{2\pi\hbar}\right)^{3/2} \exp\left(\frac{-i\mathbf{p}\cdot\mathbf{r}}{\hbar}\right) \\ \text{or} \quad \langle \mathbf{k}|\mathbf{r}\rangle = \phi_{\mathbf{r}}(\mathbf{k}) &= \left(\frac{1}{2\pi}\right)^{3/2} e^{-i\mathbf{k}\cdot\mathbf{r}}. \end{aligned} \tag{B.10}$$

and the normalized position eigenstate in the position basis is

$$\langle \mathbf{r}'|\mathbf{r}\rangle = \phi_{\mathbf{r}}(\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}'). \tag{B.11}$$

B.1.2. Particle in a Box

Let us now assume that the particle is confined to a cubic box of volume $V = L^3$, and let us assume that the position eigenstates satisfy periodic boundary conditions $\phi_{\mathbf{k}}(\mathbf{r}) = \phi_{\mathbf{k}}(x,y,z) = \phi_{\mathbf{k}}(x+n_xL, y+n_yL, z+n_zL)$, where n_x, n_y, and n_z are integers ranging from $-\infty$ to ∞ (we will just consider the wavevector basis here). This will be true if the momentum operator is written $\hat{\mathbf{p}} = \hbar\hat{\mathbf{k}}$, and the wavevector $\hat{\mathbf{k}}$ takes on discrete values

$$\mathbf{k} = \frac{2\pi}{L}(n_x\mathbf{i} + n_y\mathbf{j} + n_z\mathbf{k}). \tag{B.12}$$

We denote the complete set of orthonormal eigenvectors of $\hat{\mathbf{k}}$ by $|\mathbf{k}\rangle$. They obey the orthogonality condition $\langle \mathbf{k}|\mathbf{k}'\rangle = \delta^{Kr}_{\mathbf{k},\mathbf{k}'}$, where $\delta^{Kr}_{\mathbf{k},\mathbf{k}'}$, is the Kronecker delta function. Completenes of the states $|\mathbf{r}\rangle$ and $|\mathbf{k}\rangle$ gives

$$\int_0^L dx \int_0^L dy \int_0^L dz\, |\mathbf{r}\rangle\langle\mathbf{r}| = 1 \quad \text{and} \quad \sum_{n_x=-\infty}^{\infty} \sum_{n_y=-\infty}^{\infty} \sum_{n_z=-\infty}^{\infty} |\mathbf{k}\rangle\langle\mathbf{k}| = 1. \tag{B.13}$$

The wavevector eigenstate in the position basis is then

$$\langle \mathbf{r}|\mathbf{k}\rangle = \phi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{L^{3/2}}\, e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{B.14}$$

The position eigenstate in the wavevector basis, $\langle \mathbf{k}|\mathbf{r}\rangle$, is just the Hermitian adjoint of $\langle \mathbf{r}|\mathbf{k}\rangle$.

B.2. SYMMETRIZED N-PARTICLE POSITION AND MOMENTUM EIGENSTATES [2, 3]

We will let $|r\rangle = |\mathbf{r}, s_z\rangle = |\mathbf{r}\rangle|s_z\rangle$ denote the eigenstates of both the position operator $\hat{\mathbf{q}}$ and the z component of spin, $\hat{\mathbf{s}}_z$, and we will let $|k\rangle = |\mathbf{k}, s_z\rangle$ denote the eigenstate of both the wavevector $\hat{\mathbf{k}}$ and the z component of spin. We shall often refer to $|k\rangle$ as a "momentum" eigenstate.

The position eigenstates of the N-body system may be written as the direct product of the position eigenstates of the constituent particles,

$$|r_a, r_b, \ldots, r_l\rangle \equiv |r_a\rangle_1 |r_b\rangle_2 \times \cdots \times |r_l\rangle_N. \tag{B.15}$$

On the left-hand side of Eq. (B.15), we use the convention that the positions of the particles labeled from 1 to N are ordered from left to right from 1 to N. Thus, particle 1 has position r_a, particle 2 has position $r_b, \ldots$, and particle N has position r_l. On the right-hand side of Eq. (B.15), the ket, $|r_a\rangle_i$, is a position eigenstate of particle i. (When we say "position" we include spin if the particle has spin.) A "momentum" (and spin) eigenstate of the N-body system is written

$$|k_a, k_b, \ldots, k_l\rangle \equiv |k_a\rangle_1 |k_b\rangle_2 \times \cdots \times |k_l\rangle_N. \tag{B.16}$$

where particle 1 has momentum k_a, particle 2 has position k_b, and so on.

In the position representation, the Hamiltonian takes the form

$$\begin{aligned} H(r_1, \ldots, r_N) &= \langle r_1, \ldots, r_N|\hat{H}_N|r_1, \ldots, r_N\rangle \\ &= \sum_{i=1}^{N} \frac{-\hbar^2}{2m}\, \nabla_{\mathbf{r}_i}^2 + \sum_{i<j=1}^{N(N-1)/2} V(\mathbf{r}_i, \mathbf{r}_j, \mathbf{s}_i, \mathbf{s}_j). \end{aligned} \tag{B.17}$$

For the case when the Hamiltonian (and the other dynamical variables) are symmetric under interchange of particles, we must use only symmetric or antisymmetric combinations of position or momentum eigenstates when computing expectation values. We will describe these states for the cases of Bose–Einstein and Fermi–Dirac particles separately.

B.2.1. Symmeterized Momentum Eigenstates for Bose–Einstein Particles

By definition, any wave function describing the state of a system containing N identical Bose–Einstein particles must be symmetric under interchange of coordinates of any two particles. Furthermore, any number of bosons can have the same quantum numbers.

Let us first introduce a permutation operator, P_{ij}, such that P_{ij} interchanges the momenta of particles i and j:

$$P_{ij}|k_1, k_2, \ldots, k_i, k_j, \ldots, K_N\rangle = |k_1, k_2, \ldots, k_j, k_i, \ldots, k_N\rangle. \tag{B.18}$$

We shall use the following notation for the sum of all possible permutations:

$$\sum_P P|k_1, k_2, \ldots, k_N\rangle \equiv \sum (\text{all } N! \text{ permutations of momenta in } |k_1, k_2, \ldots, k_N\rangle). \tag{B.19}$$

For example

$$\begin{aligned}\sum_P P|k_1, k_2, k_3\rangle = \{&|k_1, k_2, k_3\rangle + |k_2, k_1, k_3\rangle + |k_1, k_3, k_2\rangle \\ &+ |k_3, k_2, k_1\rangle + |k_3, k_1, k_2\rangle + |k_2, k_3, k_1\rangle\}.\end{aligned} \tag{B.20}$$

Note that in $|k_2, k_3, k_1\rangle$, particle 1 has momentum k_2, particle 2 has momentum k_3, and particle 3 has momentum k_1.

If in the ket $|k_1, k_2, \ldots, k_N\rangle$ there are n_1 particles with momentum k_1, n_2 particles with momentum k_2, n_3 particles with momentum k_3, and so on, then $\sum_P P|k_1, k_2, k_3\rangle$ contains $N!$ terms, but only $N!/\prod_{\alpha=1}^{\infty} n_\alpha!$ of them are different. In $\sum_P P|k_1, k_2, k_3\rangle$ each term is repeated $\prod_{\alpha=1}^{\infty} n_\alpha!$ times. If we now use the orthonormality of momentum states,

$$\langle k_a, k_b, \ldots, k_l|k'_a, k'_b, \ldots, k'_l\rangle = \delta_{k_a,k'_a}\delta_{k_b,k'_b} \times \cdots \times \delta_{k_l,k'_l}, \tag{B.21}$$

we find that

$$|k_1, k_2, \ldots, k_N\rangle^{(S)} = \frac{1}{\sqrt{N!\prod_{\alpha=1}^{\infty} n_\alpha!}} \sum_P P|k_1, \ldots, k_N\rangle \tag{B.22}$$

is a symmetrized orthonormal N-body momentum eigenstate. The symmetrized states have the normalization

$${}^{(S)}\langle k_1, k_2, \ldots, k_N|k_1, k_2, \ldots, k_N\rangle^{(S)} = 1 \tag{B.23}$$

and satisfy the completeness relation

$$\hat{1}^{(S)} = \frac{1}{N!} \sum_{k_1,\ldots,k_N} \left(\prod_{\alpha=1}^{\infty} n_\alpha! \right) |k_1, k_2, \ldots, k_N\rangle^{(S)\,(S)}\langle k_1, k_2, \ldots, k_N|. \tag{B.24}$$

The factor $\prod_{\alpha=1}^{\infty} n_\alpha!/N!$ in the summation comes from the fact that the summation produces $N!/\prod_{\alpha=1}^{\infty} n_\alpha!$ copies of each term.

B.2.2. Antisymmetrized Momentum Eigenstates for Fermi–Dirac Particles

Any wave function describing the state of a system containing N identical Fermi–Dirac particles must be antisymmetric under interchange of coordinates of any two particles. Because of the Pauli exclusion principle, no more than one fermion can have a given set of quantum numbers.

An antisymmetrized momentum eigenstate may be written

$$|k_1, k_2, \ldots, k_N\rangle^{(A)} = \frac{1}{\sqrt{N!}} \sum_P (-1)^P P|k_1, \ldots, k_N\rangle, \tag{B.25}$$

where $(-1)^P = +1$ for an even number of permutations and $(-1)^P = -1$ for an odd number of permutations. For example,

$$\begin{aligned} \sum_P (-1)^P P|k_1, k_2, k_3\rangle = \{&|k_1, k_2, k_3\rangle - |k_2, k_1, k_3\rangle - |k_1, k_3, k_2\rangle \\ &- |k_3, k_2, k_1\rangle + |k_3, k_1, k_2\rangle + |k_2, k_3, k_1\rangle\}. \end{aligned} \tag{B.26}$$

The antisymmetrized states have the normalization

$$^{(A)}\langle k_1, k_2, \ldots, k_N|k_1, k_2, \ldots, k_N\rangle^{(A)} = 1 \tag{B.27}$$

and satisfy the completeness relation

$$\hat{1}^{(A)} = \frac{1}{N!} \sum_{k_1,\ldots,k_N} |k_1, k_2, \ldots, k_N\rangle^{(A)\,(A)}\langle k_1, k_2, \ldots, k_N|. \tag{B.28}$$

Note that if any two particles have the same momentum and spin, then the state $|k_1, k_2, \ldots, k_N\rangle^{(A)}$ is identically zero. For example, $|k_1, k_1, \ldots, k_N\rangle^{(A)} \equiv 0$.

The wave function $\langle r_1, r_2, \ldots, r_N|k_1, k_2, \ldots, k_N\rangle^{(A)}$ can be written in the form of a determinant,

$$\langle r_1, r_2, \ldots, r_N|k_1, k_2, \ldots, k_N\rangle^{(A)} = \frac{1}{\sqrt{N}} \begin{pmatrix} \langle r_1|k_1\rangle & \langle r_1|k_2\rangle & \cdots & \langle r_1|k_N\rangle \\ \langle r_2|k_1\rangle & \langle r_2|k_2\rangle & \cdots & \langle r_2|k_N\rangle \\ \vdots & \vdots & \ddots & \vdots \\ \langle r_N|k_1\rangle & \langle r_N|k_2\rangle & \cdots & \langle r_N|k_N\rangle \end{pmatrix}, \tag{B.29}$$

known as the *Slater determinant.*

B.2.3. Partition Functions and Expectation Values

When evaluating the properties of many-body systems, we must compute partition functions and expectation values. Some of these quantities can be simplified as we shall show here.

The trace for an N–particle boson system can be written

$$\begin{aligned}\mathrm{Tr}\,(\hat{\rho}_N) &= \frac{1}{N!}\sum_{k_1,\ldots,k_N}\left(\prod_{\alpha=1}^{\infty} n_\alpha!\right)\,{}^{(S)}\langle k_1,k_2,\ldots,k_N|\hat{\rho}_N|k_1,k_2,\ldots,k_N\rangle^{(S)} \\ &= \left(\frac{1}{N!}\right)^2\sum_{k_1,\ldots,k_N}{}^{(+)}\langle k_1,k_2,\ldots,k_N|\hat{\rho}_N|k_1,k_2,\ldots,k_N\rangle^{(+)} \\ &= \frac{1}{N!}\sum_{k_1,\ldots,k_N}\langle k_1,k_2,\ldots,k_N|\hat{\rho}_N|k_1,k_2,\ldots,k_N\rangle^{(+)},\end{aligned} \tag{B.30}$$

where

$$|k_1,k_2,\ldots,k_N\rangle^{(+)} \equiv \sum_P P|k_1,k_2,\ldots,k_N\rangle. \tag{B.31}$$

Similarly, for an N-particle fermion system we have

$$\begin{aligned}\mathrm{Tr}(\hat{\rho}_N) &= \frac{1}{N!}\sum_{k_1,\ldots,k_N}{}^{(A)}\langle k_1,k_2,\ldots,k_N|\hat{\rho}_N|k_1,k_2,\ldots,k_N\rangle^{(A)} \\ &= \frac{1}{N!}\sum_{k_1,\ldots,k_N}\langle k_1,k_2,\ldots,k_N|\hat{\rho}_N|k_1,k_2,\ldots,k_N\rangle^{(-)},\end{aligned} \tag{B.32}$$

where

$$|k_1,k_2,\ldots,k_N\rangle^{(-)} \equiv \sum_P (-1)^P P|k_1,k_2,\ldots,k_N\rangle. \tag{B.33}$$

It is useful also to look at expectation values. Let consider the N-particle one-body operator

$$\hat{O}_N^{(1)} \equiv \sum_{i=1}^{N}\hat{O}_i, \tag{B.34}$$

where $\hat{O}_i$ depends only on momentum and coordinate operators for particle i. The kinetic energy is an example of such an operator. The expectation value of

a one-body operator for a system of N bosons can be written

$$\begin{aligned}\langle \hat{O}^{(1)} \rangle &= \mathrm{Tr}_N (\hat{O}_N^{(1)} \hat{\rho}_N) = \frac{1}{N!} \sum_{k_1,\ldots,k_N} \left(\prod_{\alpha=1}^{\infty} n_\alpha! \right) \\ &\quad \times {}^{(S)}\langle k_1, k_2, \ldots, k_N | \hat{O}_N^{(1)} \hat{\rho}_N | k_1, k_2, \ldots, k_N \rangle^{(S)} \\ &= \left(\frac{1}{N!} \right)^4 \sum_{k_1,\ldots,k_N} \sum_{k'_1,\ldots,k'_N} \sum_{i=1}^{N} {}^{(+)}\langle k_1, \ldots, k_N | \hat{O}_i | k'_1, \ldots, k'_N \rangle^{(+)} \\ &\quad \times {}^{(+)}\langle k'_1, \ldots, k'_N | \hat{\rho}_N | k_1, \ldots, k_N \rangle^{(+)} \\ &= N \left(\frac{1}{N!} \right)^2 \sum_{k_1,\ldots,k_N} \sum_{k'_1,\ldots,k'_N} \langle k_1, \ldots, k_N | \hat{O}_1 | k'_1, \ldots, k'_N \rangle^{(+)} \\ &\quad \times \langle k'_1, \ldots, k'_N | \hat{\rho}_N | k_1, \ldots, k_N \rangle^{(+)} \\ &= \frac{1}{(N-1)!} \sum_{k'_1} \sum_{k_1,\ldots,k_N} \langle k_1 | \hat{O}_1 | k'_1 \rangle \, {}^{(+)}\langle k'_1, k_2, \ldots, k_N | \hat{\rho}_N | k_1, \ldots, k_N \rangle. \end{aligned} \tag{B.35}$$

We can rewrite $\langle \hat{O}^{(1)} \rangle$ in terms of the reduced probability density $\langle k'_1 | \hat{\rho}_{(1)} | k_1 \rangle$:

$$\langle \hat{O}^{(1)} \rangle = \sum_{k'_1} \sum_{k_1} \langle k_1 | \hat{O}_1 | k'_1 \rangle \, \langle k'_1 | \hat{\rho}_{(1)} | k_1 \rangle \tag{B.36}$$

For bosons, the reduced one-body probability density, $\langle k'_1 | \hat{\rho}_{(1)} | k_1 \rangle$, is defined as

$$\langle k'_1 | \hat{\rho}_{(1)} | k_1 \rangle = \frac{1}{(N-1)!} \sum_{k_2,\ldots,k_N} {}^{(+)}\langle k'_1, k_2, \ldots, k_N | \hat{\rho}_N | k_1, \ldots, k_N \rangle. \tag{B.37}$$

For fermions, the reduced one-body probability density is defined as

$$\langle k'_1 | \hat{\rho}_{(1)} | k_1 \rangle = \frac{1}{(N-1)!} \sum_{k_2,\ldots,k_N} {}^{(-)}\langle k'_1, k_2, \ldots, k_N | \hat{\rho}_N | k_1, \ldots, k_N \rangle. \tag{B.38}$$

Analogous expressions can be written for two-body operators, but we will leave that as an exercise.

B.3. THE NUMBER REPRESENTATION

The wavefunctions $|k_1, \ldots, k_N\rangle$ tell us which momentum state each particle is in. However, the states $|k_1, \ldots, k_N\rangle^{(S)(A)}$ contain no such information because

they contain permutations of particles among all momentum states listed in the ket. Also, they can be clumsy to work with. Therefore, it is convenient to change representations from one which tells the momentum state of each particle (the momentum representation) to one which tells us the number of particles in each momentum state (the number representation).

B.3.1. The Number Representation for Bosons

The basis states in the number representation are written $|n_1, n_2, \ldots, n_\infty\rangle$, where n_α is the number of particles in the state of momentum and spin k_α. Operators in the number representation are written $\hat{a}_k^+$ and $\hat{a}_k$ and are called creation and annihilation operators, respectively. They are Hermitian conjugates of one another.

The states and operators of the number representation are related to the N-particle states $|k_1, \ldots, k_m\rangle^{(S)}$ as follows:

$$\begin{aligned} |k_1, \ldots, k_m\rangle^{(S)} &= |0, \ldots, n_1, \ldots, n_m,\ 0 \to 0\rangle \\ &\equiv \frac{1}{\sqrt{\prod_{\alpha=1}^{\infty} n_\alpha!}} (\hat{a}_{k_1}^+)^{n_1} (\hat{a}_{k_2}^+)^{n_2} \times \cdots \times (\hat{a}_{k_m}^+)^{n_m} |0\rangle, \end{aligned} \tag{B.39}$$

where $\sum_{i=1}^m n_i = N$. We have labeled the momenta in $|k_1, \ldots, k_m\rangle^{(S)}$ from 1 to m. However, it is understood that there are N positions in the ket. Several particles may have the same momentum. The notation $0 \to 0$ means that all occupation numbers after n_m are zero. Note that zeros may be interspersed between occupation numbers $n_1, \ldots, n_m$. If we interchange momenta of two particles, the wavefunction should not change:

$$\begin{aligned} |k_1, k_2, \ldots, k_m\rangle^{(S)} &= |k_2, k_1, \ldots, k_m\rangle^{(S)} \\ &= \frac{1}{\sqrt{\prod_{\alpha}^{\infty} n_\alpha!}} (\hat{a}_{k_1}^+)^{n_1} (\hat{a}_{k_2}^+)^{n_2} \times \cdots \times (\hat{a}_{k_m}^+)^{n_m} |0\rangle \\ &= \frac{1}{\sqrt{\prod_{\alpha}^{\infty} n_\alpha!}} (\hat{a}_{k_1}^+)^{n_1 - 1} \hat{a}_{k_2}^+ \hat{a}_{k_1}^+ (\hat{a}_{k_2}^+)^{n_2 - 1} \times \cdots \times (\hat{a}_{k_m}^+)^{n_m} |0\rangle. \end{aligned} \tag{B.40}$$

Thus, we find that symmetrization of the wavefunctions gives

$$\hat{a}_{k_1}^+ \hat{a}_{k_2}^+ = \hat{a}_{k_2}^+ \hat{a}_{k_1}^+, \tag{B.41}$$

and, therefore, creation operators commute. If we take the Hermitian adjoint of Eq. (B.40), we find

$$
\begin{aligned}
{}^{(S)}\langle k_1, k_2, \ldots, k_m| &= {}^{(S)}\langle k_2, k_1, \ldots, k_m| \\
&= \frac{1}{\sqrt{\prod_{\alpha}^{\infty} n_\alpha!}} \langle 0|(\hat{a}_{k_m})^{n_m} \times \cdots \times (\hat{a}_{k_2})^{n_2} (\hat{a}_{k_1})^{n_1} \\
&= \frac{1}{\sqrt{\prod_{\alpha}^{\infty} n_\alpha!}} \langle 0|(\hat{a}_{k_m})^{n_m} \times \cdots \times (\hat{a}_{k_2})^{n_2-1} \hat{a}_{k_1} \hat{a}_{k_2} (\hat{a}_{k_1})^{n_1-1}.
\end{aligned}
\tag{B.42}
$$

Thus, annihilation operators also commute:

$$
\hat{a}_{k_1} \hat{a}_{k_2} = \hat{a}_{k_2} \hat{a}_{k_1}. \tag{B.43}
$$

The wavefunctions must satisfy the following condition:

$$
\begin{aligned}
&{}^{(S)}\langle k_1, k_2, \ldots, k_m | k'_1, k'_2, \ldots, k'_m \rangle^{(S)} \\
&\quad \equiv \frac{1}{\prod_{\alpha}^{\infty} n_\alpha!} \langle 0|\hat{a}_{k_m} \times \cdots \times \hat{a}_{k_1} \hat{a}^{+}_{k'_1} \times \cdots \times \hat{a}^{+}_{k'_m}|0\rangle \qquad \text{(B.44)} \\
&\quad = \begin{cases} 0 & \text{if the sets } [k_1, \ldots k_m] \text{ and } [k'_1, \ldots k'_m] \text{ are not the same.} \\ 1 & \text{if the sets } [k_1, \ldots k_m] \text{ and } [k'_1, \ldots k'_m] \text{ are the same.} \end{cases}
\end{aligned}
$$

Equation (B.44) will be satisfied if the state $|0\rangle$ and the creation and annihilation operators have the following properties:

$$
\langle 0|0\rangle = 1, \tag{B.45}
$$

$$
\hat{a}_k|0\rangle = 0 \qquad \text{for all } k, \tag{B.46}
$$

and

$$
[\hat{a}_k, \hat{a}^{+}_{k'}]_- = \hat{a}_k \hat{a}^{+}_{k'} - \hat{a}^{+}_{k'} \hat{a}_k = \delta_{k,k'}. \tag{B.47}
$$

One can easily show that Eq. (B.44) follows from Eqs. (B.45)–(B.47) by doing some examples. One simply commutes each annihilation operator to the right using Eqs. (B.45)–(B.47) as they are needed. The result is Eq. (B.44).

Again, by using Eqs. (B.39), (B.46), and (B.47), we can show that

$$
\hat{a}_{k_j}|n_1, \ldots, n_j, \ldots, n_\infty\rangle = \sqrt{n_j}|n_1, \ldots, n_j - 1, \ldots, n_\infty\rangle, \tag{B.48}
$$

$$
\hat{a}^{+}_{k_j}|n_1, \ldots, n_j, \ldots, n_\infty\rangle = \sqrt{n_j + 1}|n_1, \ldots, n_j + 1, \ldots, n_\infty\rangle, \tag{B.49}
$$

and

$$\langle n_1, \ldots, n_j, \ldots, n_\infty | \hat{a}_{k_j}^+ \hat{a}_{k_j} | n_1, \ldots, n_j, \ldots, n_\infty \rangle = n_j. \tag{B.50}$$

Equation (B.50) follows from the normalization of the states:

$$\langle n_1, \ldots, n_j, \ldots, n_\infty | n_1, \ldots, n_j, \ldots, n_\infty \rangle = 1. \tag{B.51}$$

When working with N-body systems, we commonly must evaluate one-body operators of the type

$$\hat{O}_{(1)}^N = \sum_{i=1}^N O_i(\hat{\mathbf{q}}_i, \hat{\mathbf{p}}_i, \hat{\boldsymbol{\sigma}}_i). \tag{B.52}$$

(Note that these operators are symmetric under interchange of particle labels.) Some examples are the kinetic energy, the number density, and the particle current. We wish to express these operators in the number representation.

The correspondence between $\hat{O}_{(1)}^N$ and its analog in the number representation is

$$\hat{O}_{(1)}^N \to \hat{O}_{(1)}^{nb} = \sum_{k_a k_b} \langle k_a | \hat{O}_1(\hat{\mathbf{q}}_1, \hat{\mathbf{p}}_1, \hat{\boldsymbol{\sigma}}_i) | k_b \rangle \hat{a}_{k_a}^+ \hat{a}_{k_b}. \tag{B.53}$$

To show that Eq. (B.53) is correct, we must show that

$$\begin{aligned} &{}^{(S)}\langle k_1, \ldots, k_m | \hat{O}_{(1)}^N | k_1', \ldots, k_m' \rangle^{(S)} \\ &\quad = \langle 0, \ldots, n_1, \ldots, n_m, 0 \to 0 | \hat{O}_{(1)}^{nb} | 0, \ldots, n_1', \ldots, n_m', 0 \to 0 \rangle. \end{aligned} \tag{B.54}$$

We leave this as an exercise.

In going from the momentum representation to the number representation, we thus make the correspondence

$$|k_1, k_2, \ldots, k_m\rangle^{(S)} \to 0, \ldots, n_1, n_2, \ldots, n_m, 0 \to 0\rangle \tag{B.55}$$

and

$$\sum_{i=1}^N O_i(\hat{\mathbf{q}}_i, \hat{\mathbf{p}}_i, \hat{\boldsymbol{\sigma}}_i) \to \sum_{k_a, k_b} \langle k_a | O_1(\hat{\mathbf{q}}_1, \hat{\mathbf{p}}_1, \hat{\boldsymbol{\sigma}}_1) | k_b \rangle \hat{a}_{k_a}^+ \hat{a}_{k_b}. \tag{B.56}$$

In practice, the only other type of N-body operators we encounter are two-body operators of the form

$$\hat{O}_{(2)}^N = \sum_{i<j}^{(1/2)N(N-1)} O_{ij}(\hat{\mathbf{q}}_i, \hat{\mathbf{q}}_j, \hat{\mathbf{p}}_i, \hat{\mathbf{p}}_j, \hat{\boldsymbol{\sigma}}_i, \hat{\boldsymbol{\sigma}}_j). \tag{B.57}$$

Some examples are the potential energy and the momentum currents (stress tensor). Similarly, we can show that

$$\sum_{i<j}^{(1/2)N(N-1)} O_{ij}(\hat{\mathbf{q}}_i, \hat{\mathbf{q}}_j, \hat{\mathbf{p}}_i, \hat{\mathbf{p}}_j, \hat{\boldsymbol{\sigma}}_i, \hat{\boldsymbol{\sigma}}_j) \rightarrow \frac{1}{2} \sum_{k_a k_b k'_a k'_b} \langle k_a k_b | O_{12}(\hat{\mathbf{q}}_1 \hat{\mathbf{q}}_2 \hat{\mathbf{p}}_1 \hat{\mathbf{p}}_2 \hat{\boldsymbol{\sigma}}_1 \hat{\boldsymbol{\sigma}}_2) | k'_a k'_b \rangle \times \hat{a}^+_{k_a} \hat{a}^+_{k_b} \hat{a}_{k'_b} \hat{a}_{k'_a} \tag{B.58}$$

when going from the coordinate to number representation.

B.3.2. The Number Representation for Fermions

The basis states for fermions are also written $|n_1, n_2, \ldots, n_\infty\rangle$, but because of the Pauli exclusion principle the occupation numbers take on values $n_\alpha = 0$ or 1 only. We also introduce creation and annihilation operators $\hat{a}^+_k$ and $\hat{a}_k$, respectively. But they obey different commutation relations.

The correspondence between states in the number representation and antisymmetrized momentum states is

$$\begin{aligned} |0, \ldots, 1_1, 1_2, \ldots, 1_N, 0 \rightarrow 0\rangle &\equiv \hat{a}^+_{k_1} \hat{a}^+_{k_2} \times \cdots \times \hat{a}^+_{k_N} |0\rangle \\ &= |k_1, k_2, \ldots, k_N\rangle^{(A)}, \end{aligned} \tag{B.59}$$

where we have used the convention $n_\alpha = 1_\alpha$ when the state k_α is filled and zero otherwise. In general, there will be zeros interspersed between the occupation numbers $1_1, 1_2, \ldots, 1_N$ on the left-hand side of Eq. (B.59). If we interchange momenta of two particles, the states must change sign:

$$\begin{aligned} |k_1, k_2, \ldots, k_N\rangle^{(A)} &= -|k_2, k_1, \ldots, k_N\rangle^{(A)} \\ &= \hat{a}^+_{k_1} \hat{a}^+_{k_2} \times \cdots \times \hat{a}^+_{k_N} |0\rangle = -\hat{a}^+_{k_2} \hat{a}^+_{k_1} \times \cdots \times \hat{a}^+_{k_N} |0\rangle. \end{aligned} \tag{B.60}$$

Thus, the creation operators anticommute,

$$\hat{a}^+_{k_1} \hat{a}^+_{k_2} = -\hat{a}^+_{k_2} \hat{a}^+_{k_1}. \tag{B.61}$$

If we take the Hermitian adjoint of Eq. (B.60), we find

$$\hat{a}_{k_2} \hat{a}_{k_1} = -\hat{a}_{k_1} \hat{a}_{k_2}. \tag{B.62}$$

The annihilation operators also anticommute.

The wave functions must satisfy the condition

$$
\begin{aligned}
&{}^{(A)}\langle k_1, k_2, \ldots, k_N | k'_1, k'_2, \ldots, k'_N \rangle^{(A)} \\
&\quad \equiv \langle 0 | \hat{a}_{k_N} \times \cdots \times \hat{a}_{k_1} \hat{a}^+_{k'_1} \times \cdots \times \hat{a}^+_{k'_N} | 0 \rangle \\
&\quad = \begin{cases} 0 & \text{if the sets } \{k_i\} \text{ and } \{k'_i\} \text{ differ,} \\ +1 & \text{if the sets } \{k_i\} \text{ and } \{k'_i\} \text{ are the same but differ by an even permutation,} \\ -1 & \text{if the sets } \{k_i\} \text{ and } \{k'_i\} \text{ are the same but differ by an odd permutation.} \end{cases}
\end{aligned}
\tag{B.63}
$$

Equation (B.63) will be satisfied if

$$\langle 0 | 0 \rangle = 1, \tag{B.64}$$

$$\hat{a}_k | 0 \rangle = 0 \qquad \text{for all } k, \tag{B.65}$$

and

$$[\hat{a}_k, \hat{a}^+_k]_+ \equiv \hat{a}_k \hat{a}^+_{k'} + \hat{a}^+_{k'} \hat{a}_k = \delta_{k,k'}. \tag{B.66}$$

To show Eq. (B.63) for the case of identical states, we use Eq. (B.61) to permute operators until

$$\hat{a}^+_{k'_1} \times \cdots \times \hat{a}^+_{k'_N} = \pm \hat{a}^+_{k_1} \times \cdots \times \hat{a}^+_{k_N}. \tag{B.67}$$

There will be a plus sign if an even number of permutations are needed, and there will be a minus sign if an odd number are needed. One can then show that

$$\langle 0 | \hat{a}_{k_N} \times \cdots \times \hat{a}_{k_1} \hat{a}^+_{k_1} \times \cdots \times a^+_{k_N} | 0 \rangle = 1 \tag{B.68}$$

by permuting each annihilation operator all the way to the right using Eqs. (B.65) and (B.66).

For Fermi systems there can be ambiguity in the overall sign of the states. Therefore, *one uses the convention that in the states* $|n_1, n_2, \ldots, n_\infty\rangle$ *the occupation numbers are ordered from left to right in order of increasing energy.* We then find that

$$\hat{a}_{k_j} | n_1, n_2, \ldots, n_j, \ldots, n_\infty \rangle = (-1)^{\Sigma_j} \sqrt{n_j}\, | n_1, n_2, \ldots, (1 - n_j), \ldots, n_\infty \rangle, \tag{B.69}$$

$$\hat{a}^+_{k_j} | n_1, n_2, \ldots, n_j, \ldots, n_\infty \rangle = (-1)^{\Sigma_j} \sqrt{1 - n_j}\, | n_1, n_2, \ldots, (1 + n_j), \ldots, n_\infty \rangle, \tag{B.70}$$

where $\sum_j \equiv \sum_{l=1}^{j-1} n_l$ and we have used Eqs. (B.61), (B.62), and (B.64)–(B.66). In Eqs. (B.69)–(B.71), the occupation numbers may equal 0 or 1.

For systems of identical fermions, the same correspondence holds between operators in the coordinate representation and number representation (cf. Eqs. (B.56) and (B.57) as was found to hold for systems of identical bosons. However, for fermions the creation and annihilation operators anticommute and for bosons they commute.

To establish this correspondence, we must show that

$$
\begin{aligned}
&{}^{(A)}\langle k_1, \ldots, k_N | \hat{O}^N_{(1)} | k'_1, \ldots, k'_N \rangle^{(A)} \\
&\qquad = \langle 0, \ldots, 1_1, \ldots, 1_N, 0 \to 0 | \hat{O}^{nb}_{(1)} | 0, \ldots, 1_1, \ldots, 1_N, 0 \to 0 \rangle.
\end{aligned}
\tag{B.72}
$$

In Eq. (B.72) we have used the ordering convention discussed above. We will assume that the occupation numbers and momenta are labeled in order of increasing energy, and that the states, $k_1, \ldots, k_N$ are all filled. We leave this as an exercise.

A similar correspondence holds for the operator $O^N_{(2)}$. However, we must make a brief comment about sign conventions. The correspondence is

$$
\begin{aligned}
\hat{O}^N_{(2)} &= \sum_{i<j}^{(1/2)N(N-1)} O_{ij}(\hat{\mathbf{q}}_i \hat{\mathbf{q}}_j \hat{\mathbf{p}}_i \hat{\mathbf{p}}_j \hat{\boldsymbol{\sigma}}_i \hat{\boldsymbol{\sigma}}_j) \\
&\to \frac{1}{2} \sum_{k_a k_b k'_a k'_b} \langle k_a, k_b | O_{12}(\hat{\mathbf{q}}_1 \hat{\mathbf{q}}_2 \hat{\mathbf{p}}_1 \hat{\mathbf{p}}_2 \hat{\boldsymbol{\sigma}}_1 \hat{\boldsymbol{\sigma}}_2) | k'_a, k'_b \rangle \hat{a}^+_{k_a} \hat{a}^+_{k_b} \hat{a}_{k'_b} \hat{a}_{k'_a}.
\end{aligned}
\tag{B.73}
$$

Note that the order of the operators $\hat{a}_{k'_a}$ and $\hat{a}_{k'_b}$ is opposite to the order of k'_a and k'_b in the ket $|k'_a k'_b\rangle$. The reason is most easily seen by evaluating a matrix element of the operator on the right-hand side of Eq. (B.73) with respect to a state containing only two particles. We find

$$
\begin{aligned}
&\langle 0, \ldots, 0, 1_2, 0, \ldots, 1_1, 0, \ldots | \hat{a}^+_{k_a} \hat{a}^+_{k_b} \hat{a}_{k'_b} \hat{a}_{k'_b} | 0, \ldots, 0, 1_3, \ldots, 1_4, \ldots, 0 \rangle \\
&\quad = \langle 0 | \hat{a}_{k_2} \hat{a}_{k_1} \hat{a}^+_{k_4} \hat{a}^+_{k_b} \hat{a}^+_{k'_b} \hat{a}^+_{k'_a} \hat{a}^+_{k_3} \hat{a}^+_{k_4} | 0 \rangle \\
&\quad = +\delta_{1,a}\delta_{2,b}\delta_{3,a'}\delta_{4,ba'} - \delta_{2,a}\delta_{1,b}\delta_{4,a'}\delta_{3,b'} - \delta_{1,a}\delta_{2,b}\delta_{4,a'}\delta_{3,b'} \\
&\qquad + \delta_{2,a}\delta_{1,b}\delta_{3,a'}\delta_{4,b'}
\end{aligned}
$$

and, hence,

$$
\begin{aligned}
&\langle 0, \ldots, 0, 1_2, 0, \ldots, 1_1, 0, \ldots | \hat{O}^{nb}_{(2)} | 0, \ldots, 0, 1_3, \ldots, 1_4, \ldots, 0 \rangle \\
&\quad = \langle k_1 k_2 | \hat{O}_{12} | k_3 k_4 \rangle - \langle k_1 k_2 | \hat{O}_{12} | k_4 k_3 \rangle.
\end{aligned}
$$

Thus, with this convention, the matrix elements whose momenta appear in the same order (of increasing or decreasing energy) on each side have a positive sign.

B.3.3. Field Operators

In Sections D.3.1 and D.3.2, we have written general one- and two-body operators in the number representation using momentum and spin as coordinates. We can also write them using position and spin as coordinates.

Let us first consider the single-particle operators in Eq. (B.52). If we insert a complete set of position (and spin) states $|r\rangle$ into the matrix element, we find

$$\begin{aligned}\hat{O}^{nb}_{(1)} &= \sum_{k_a k_b} \langle k_a | O(\hat{\mathbf{q}}, \hat{\mathbf{p}}, \hat{\boldsymbol{\sigma}}) | k_b \rangle \hat{a}^+_{k_a} \hat{a}_{k_b} \\ &= \int\int dr_1\, dr_2 \langle r_1 | O(\hat{\mathbf{q}}, \hat{\mathbf{p}}, \hat{\boldsymbol{\sigma}}) | r_2 \rangle \hat{\psi}^+(r_1) \hat{\psi}(r_2)\end{aligned} \tag{B.74}$$

where

$$\hat{\psi}(r) = \sum_k \langle r|k\rangle \hat{a}_k \tag{B.75}$$

and

$$\hat{\psi}^+(r) = \sum_k \langle k|r\rangle \hat{a}^+_k. \tag{B.76}$$

Similarly, for two-particle operators we find

$$\begin{aligned}\hat{O}^{nb}_{(2)} &= \frac{1}{2} \sum_{k_a k_b k_c k_d} \langle k_a, k_b | O(\hat{\mathbf{q}}_1, \hat{\mathbf{q}}_2, \hat{\mathbf{p}}_1, \hat{\mathbf{p}}_2, \hat{\boldsymbol{\sigma}}_1, \hat{\boldsymbol{\sigma}}_2) | k_c, k_a \rangle \hat{a}^+_{k_a} \hat{a}^+_{k_b} \hat{a}_{k_d} \hat{a}_{k_c} \\ &= \frac{1}{2} \int \cdots \int dr_1 \cdots dr_4 \\ &\quad \times \langle r_1 r_2 | O(\hat{\mathbf{q}}_1, \hat{\mathbf{q}}_2, \hat{\mathbf{p}}_1, \hat{\mathbf{p}}_2, \hat{\boldsymbol{\sigma}}_1, \hat{\boldsymbol{\sigma}}_2) | r_3 r_4 \rangle \hat{\psi}^+(r_1) \hat{\psi}^+(r_2) \hat{\psi}(r_4) \hat{\psi}(r_3).\end{aligned} \tag{B.77}$$

It is easy to show that the momentum-dependent commutation relations

$$[\hat{a}_{\mathbf{k},\lambda}, \hat{a}^+_{\mathbf{k}',\lambda'}]_\pm = \delta_{\mathbf{k},\mathbf{k}'} \delta_{\lambda,\lambda'} \tag{B.78}$$

are equivalent to position-dependent commutation relations

$$[\hat{\psi}_\lambda(\mathbf{r}), \hat{\psi}^+_{\lambda'}(\mathbf{r}')]_\pm = \delta(\mathbf{r} - \mathbf{r}') \delta_{\lambda,\lambda'} \tag{B.79}$$

for bosons and fermions (+ for fermions and − for bosons).

It is worthwhile to give a few examples of commonly used operators. The number operator may be written

$$N^N = \sum_{i=1}^{N} 1_i \rightarrow \hat{N}_{nb} = \sum_{\lambda} \int d\mathbf{r} \psi_\lambda^+(\mathbf{r}) \psi_\lambda(\mathbf{r}) = \sum_{\lambda} \sum_{\mathbf{k}} \hat{a}_{\mathbf{k},\lambda}^+ \hat{a}_{\mathbf{k},\lambda}. \tag{B.80}$$

The number density operator may be written

$$\begin{aligned} \hat{n}^N(\hat{\mathbf{q}}_1, \ldots, \hat{\mathbf{q}}_N; \mathbf{R}) &= \sum_{i=1}^{N} \delta(\hat{\mathbf{q}}_i - \mathbf{R}) \rightarrow \hat{n}_{nb}(\mathbf{R}) = \sum_{\lambda} \hat{\psi}_\lambda^+(\mathbf{R}) \psi_\lambda(\mathbf{R}) \\ &= \frac{1}{V} \sum_{\lambda} \sum_{\mathbf{k}_1 \mathbf{k}_2} e^{-i\mathbf{R}\cdot(\mathbf{k}_1 - \mathbf{k}_2)} \hat{a}_{\mathbf{k}_1,\lambda}^+ \hat{a}_{\mathbf{k}_2,\lambda}. \end{aligned} \tag{B.81}$$

The spin density operator is given by

$$\begin{aligned} \hat{\mathbf{S}}^N(\hat{\mathbf{q}}_1, \ldots, \hat{\mathbf{q}}_N; \hat{\boldsymbol{\sigma}}_1, \ldots, \hat{\boldsymbol{\sigma}}_N; \mathbf{R}) &= \sum_{i=1}^{N} \boldsymbol{\sigma}_i \, \delta(\hat{\mathbf{q}}_1 - \mathbf{R}) \\ \rightarrow \hat{\mathbf{S}}_{nb}(\mathbf{R}) &= \sum_{\lambda_1 \lambda_2} \langle \lambda_1 | \boldsymbol{\sigma} | \lambda_2 \rangle \hat{\psi}_{\lambda_1}^+(\mathbf{R}) \psi_{\lambda_2}(\mathbf{R}) \\ &= \frac{1}{V} \sum_{\lambda_1 \lambda_2} \sum_{\mathbf{k}_1, \mathbf{k}_2} \langle \lambda_1 | \boldsymbol{\sigma} | \lambda_2 \rangle \, e^{-i\mathbf{R}\cdot(\mathbf{k}_1 - \mathbf{k}_2)} \hat{a}_{\mathbf{k}_1,\lambda_1} \hat{a}_{\mathbf{k}_2,\lambda_2}^+. \end{aligned} \tag{B.82}$$

The kinetic energy operator is written

$$\begin{aligned} \hat{T}^N &= \sum_{i=1}^{N} \frac{\hbar^2 k_i^2}{2m} \rightarrow \hat{T}_{nb} = \sum_{\lambda} \sum_{\mathbf{k}} \frac{\hbar^2 \mathbf{k}^2}{2m} \hat{a}_{\mathbf{k}\lambda}^+ \hat{a}_{\mathbf{k},\lambda} \\ &= \sum_{\lambda} \int d\mathbf{r} \hat{\psi}_\lambda^+(\mathbf{r}) \left(\frac{-\hbar^2 \nabla_{\mathbf{r}}^2}{2m} \right) \hat{\psi}_\lambda(\mathbf{r}). \end{aligned} \tag{B.83}$$

The potential energy operator takes the form

$$\begin{aligned} V^N &= \sum_{i<j=1}^{(1/2)N(N-1)} V_{ij} \rightarrow \hat{V}_{nb} \\ &= \frac{1}{2} \sum_{\lambda_1, \ldots, \lambda_4} \iint d\mathbf{r}_1 d\mathbf{r}_2 \langle \mathbf{r}_1, \lambda_1; \mathbf{r}_2 \lambda_2 | V_{12} | \mathbf{r}_1, \lambda_3; \mathbf{r}_2, \lambda_4 \rangle \\ &\quad \times \hat{\psi}_{\lambda_1}^+(\mathbf{r}_1) \hat{\psi}_{\lambda_2}^+(\mathbf{r}_2) \hat{\psi}_{\lambda_4}(\mathbf{r}_2) \hat{\psi}_{\lambda_3}(\mathbf{r}_1) \\ &= \frac{1}{2} \sum_{\substack{\mathbf{k}_1, \ldots, \mathbf{k}_4 \\ \lambda_1, \ldots, \lambda_4}} \langle \mathbf{k}_1, \lambda_1; \mathbf{k}_2, \lambda_2 | V | \mathbf{k}_3, \lambda_3; \mathbf{k}_4, \lambda_4 \rangle \hat{a}_{\mathbf{k}_1,\lambda_1}^+ \hat{a}_{\mathbf{k}_2,\lambda_2}^+ \hat{a}_{\mathbf{k}_4,\lambda_4}^+ \hat{a}_{\mathbf{k}_3,\lambda_3}^+. \end{aligned} \tag{B.84}$$

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APPENDIX C

STABILITY OF SOLUTIONS TO NONLINEAR EQUATIONS

C.1. LINEAR STABILITY THEORY [1–3]

Any set of nonlinear differential equations of arbitrary order can be reduced to a larger number of first-order nonlinear differential equations. Therefore, to study the stability of a system, it is sufficient to study the stability of the set of first-order nonlinear equations governing the behavior of the system.

For simplicity, we will consider a system of two nonlinear first-order differential equations:

$$\frac{dy_1}{dt} \equiv \dot{y}_1 = f_1(y_1, y_2) \tag{C.1}$$

and

$$\frac{dy_2}{dt} = \dot{y}_2 = f_2(y_1, y_2). \tag{C.2}$$

If there exist positive numbers k and δ such that for given values of coordinates y_1^0 and y_2^0 the functions $f_i(y_1, y_2)$ satisfy the condition

$$|f_i(y_1^0, y_2^0) - f_i(y_1, y_2)| \leqslant k \sum_{j=1}^{2} |y_j^0 - y_j|$$

for $|y_j^0 - y_j| < \delta$, and if the partial derivatives of $f_i(y_1, y_2)$ exist and are continuous, then the functions $f_i(y_1, y_2)$ satisfy Lipschitz conditions and the differential equations (C.1) and (C.2) have unique solutions in the neighborhood y_1^0, y_2^0. We shall always assume that the above conditions are satisfied.

In general, the set of Eqs. (C.1) and (C.2) will have a number of steady state solutions (which are often called fixed or singular or critical points). These are solutions $\bar{y}, \bar{y}_2$ which satisfy the conditions

$$\dot{\bar{y}}_1 = f_1(\bar{y}_1, \bar{y}_2) = 0 \tag{C.3}$$

and

$$\dot{\bar{y}}_2 = f_2(\bar{y}_1, \bar{y}_2) = 0. \tag{C.4}$$

We may plot the solutions of Eqs. (C.1) and (C.2) in a two-dimensional phase plane. The time-independent steady-state solutions correspond to points in the phase plane which do not change their position with time. The time-dependent solutions form trajectories in the phase plane. The equation for the trajectories can be found by dividing Eq. (C.1) by Eq. (C.2):

$$\frac{dy_1}{dy_2} = \frac{f_1(y_1, y_2)}{f_2(y_1, y_2)}. \tag{C.5}$$

Equation (C.5) uniquely relates y_1 to y_2 for a given value of y_2.

In general, a given steady state solution will occur at some point $\bar{y}_1 = A$ and $\bar{y}_2 = B$ in the phase plane. It can always be moved to the origin by the change of variables $y_1' = y_1 - A$ and $y_2' = y_2 - B$. We therefore wish to study the stability of a given steady state solution to Eqs. (C.1) and (C.2) which occurs at the origin.

Consider a system which is described by Eqs. (C.1) and (C.2) and which is in the steady state $\bar{y}_1$, $\bar{y}_2$. We often want to know how the system behaves under the influence of a small perturbation. Will the system leave the steady state and move to a different state? Will it decay back to the steady state? Or will the system remain in the neighborhood of the steady state and not decay back?

With linear stability theory, we can say something about the stability of a very small neighborhood of the steady state. We can say nothing about the global stability of the phase space. To examine the stability of solutions in the neighborhood of the steady state, let us expand y_1 and y_2 about the steady state,

$$y_1 = \bar{y}_1 + x_1 \tag{C.6}$$

and

$$y_2 = \bar{y}_2 + x_2, \tag{C.7}$$

and let us expand both sides of Eqs. (C.1) and (C.2) about the steady state. We then find

$$\dot{x}_1 = \frac{dx_1}{dt} = \left(\frac{\partial f_1}{\partial y_1}\right)_{\bar{y}_1, \bar{y}_2} x_1 + \left(\frac{\partial f_1}{\partial f_2}\right)_{\bar{y}_1, \bar{y}_2} x_2 + O(x^2) \tag{C.8}$$

and

$$\dot{x}_2 = \frac{dx_2}{dt} = \left(\frac{\partial f_2}{\partial y_1}\right)_{\bar{y}_1, \bar{y}_2} x_1 + \left(\frac{\partial f_1}{\partial y_2}\right)_{\bar{y}_1, \bar{y}_2} x_2 + O(x^2). \tag{C.9}$$

For very small values of x_i (for solutions very close to the steady state), we can linearize Eqs. (C.8) and (C.9) and obtain

$$\begin{pmatrix} \dot{x}_1 \\ \dot{x}_2 \end{pmatrix} = \bar{\mathbf{A}} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix}, \tag{C.10}$$

where

$$\bar{\mathbf{A}} = \begin{pmatrix} a & b \\ c & d \end{pmatrix} \tag{C.11}$$

and

$$a = \left(\frac{\partial f_1}{\partial y_1}\right)_{\bar{y}_1, \bar{y}_2}, \quad b = \left(\frac{\partial f_1}{\partial y_2}\right)_{\bar{y}_1, \bar{y}_2}, \quad c = \left(\frac{\partial f_2}{\partial y_1}\right)_{\bar{y}_1, \bar{y}_2}, \quad \text{and} \quad d = \left(\frac{\partial f_2}{\partial y_2}\right)_{\bar{y}_1, \bar{y}_2}.$$

We next transform to normal coordinates of Eq. (C.10). If we find the eigenvalues of $\bar{\mathbf{A}}$ and expand Eq. (C.10) in terms of the right eigenvectors of $\bar{\mathbf{A}}$, which we denote z_1 and z_2 (cf. Section 6.C), Eq. (C.10) then takes the form

$$\begin{pmatrix} \dot{z}_1 \\ \dot{z}_2 \end{pmatrix} = \begin{pmatrix} \lambda_+ & 0 \\ 0 & \lambda_- \end{pmatrix} \begin{pmatrix} z_1 \\ z_2 \end{pmatrix}, \tag{C.12}$$

where the eigenvalues are determined by the condition that

$$\det \begin{vmatrix} a - \lambda & b \\ c & d - \lambda \end{vmatrix} = 0 \tag{C.13}$$

or

$$\lambda_\pm = \tfrac{1}{2}\{(a+d) \pm \sqrt{(a+d)^2 - 4(ad - bc)}\}. \tag{C.14}$$

For a conservative system, which is area-preserving, Eq. (C.14) simplifies because $\det |\bar{\mathbf{A}}| = ad - cb = 1$. If the coordinates initially have values z_1^0 and z_2^0, at a later time they will have values

$$z_1(t) = e^{\lambda_+ t} z_1^0 \quad \text{and} \quad z_2(t) = e^{\lambda_- t} z_2^0. \tag{C.15}$$

The eigenvalues, in general, are complex. We can consider several cases which can occur depending on values of the real and imaginary parts of λ_+ and λ_-:

(**a**) Fig. C.1a: Both λ_+ and λ_- are real and $\lambda_- < \lambda_+ < 0$. This is a completely stable case. A solution displaced from the steady state will decay back to the state, exponentially.

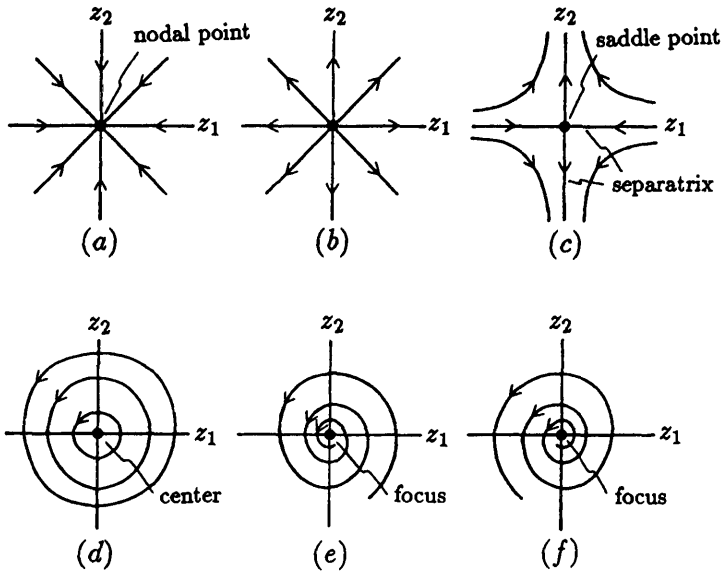


Fig. C.1. Different types of fixed points: (a) Both λ_+ and λ_- are real and $\lambda_- < \lambda_+ < 0$; (b) both λ_+ and λ_- are real and $0 < \lambda_- < \lambda_+$; (c) both λ_+ and λ_- are real and $\lambda_- < 0 < \lambda_+$; (d) both λ_+ and λ_- are pure imaginary with $\lambda_+ = i\beta$ and $\lambda_- = -i\beta$ ($z_+ = \zeta_- + i\zeta_+$ and $z_- = \zeta_+ - i\zeta_-$); (e) both λ_+ and λ_- are complex, $\lambda_+ = \alpha + i\beta, \lambda_- = \alpha - i\beta$, and $\alpha < 0$; (f) both λ_+ and λ_- are complex, $\lambda_+ = \alpha + i\beta$, $\lambda_- = \alpha = -i\beta$, and $\alpha > 0$.

(**b**) Fig. C.1b: Both λ_+ and λ_- are real and $0 < \lambda_- < \lambda_+$. This is a completely unstable case. A solution displaced from the steady state will move away exponentially.

(**c**) Fig. C.1c: Both λ_+ and λ_- are real and $\lambda_- < 0 < \lambda_+$. This is an unstable case. A solution which starts with a nonzero value of z_2 will move away from the steady state. (Note that the trajectories moving along the z_1 axis never reach the steady state. It is a separate solution.)

(**d**) Fig. C.1d: Both λ_+ and λ_- are pure imaginary; that is, $\lambda_+ = i\beta$ and $\lambda_- = -i\beta$. To find the stability in this case, one must consider nonlinear terms. The solution neither decays nor moves away from the steady state. It simply oscillates around it. In Fig. C.1 *d* we have let $z_1 = \zeta_1 + i\zeta_2$ and $z_2 = \zeta_1 - i\zeta_2$; therefore,

$$\begin{pmatrix} \dot{\zeta}_1 \\ \dot{\zeta}_2 \end{pmatrix} = \begin{pmatrix} \cos\beta & \sin\beta \\ -\sin\beta & \cos\beta \end{pmatrix} \begin{pmatrix} \zeta_1 \\ \zeta_2 \end{pmatrix}$$

(this is a case of marginal stability). For this case, the fixed point is often called a *center.*

(e) Fig. C.1e: Both λ_+ and λ_- are complex, so $\lambda_+ = \alpha + i\beta$ and $\lambda_- = \alpha - i\beta$ where $\alpha < 0$. This is a stable case in which the solution spirals toward the steady state (which is called a focus).

(f) Fig. C.1f: Both λ_+ and λ_- are complex, so that $\lambda_+ = \alpha + i\beta$ and $\lambda_- = \alpha - i\beta$ and $\alpha > 0$. This is an unstable case in which the solution spirals away from the steady state.

The linear stability analysis provides a very simple tool for studying the stability of a steady state. For example, if the real parts of λ_+ and λ_- are both negative, the steady state is stable. It can be shown that the nonlinear terms which were neglected in the stability analysis do not change this fact (Ref. 1, p. 32). Similarly, if at least one of the eigenvalues has a positive real part, the steady state will be unstable. Inclusion of the nonlinear terms cannot make it stable.

When linear stability analysis reveals a center (d), then one must look at the effect of nonlinear terms on the stability. They will, usually (but not always), change the center to a stable or unstable focus.

C.2. LIMIT CYCLES

In Section C.1 we studied conditions under which steady-state solutions might be stable. We found that if a steady-state solution was stable, then all states in the neighborhood of the steady state would decay to it after long times.

For nonconservative nonlinear equations, it is also possible to find stable *periodic* solutions. Such solutions are called *limit cycles*. If a periodic solution is stable, then all solutions in its neighborhood will decay to it after long times.

EXERCISE C.1. Show that the set of equations

$$\frac{dy_1}{dt} = y_2 + \frac{y_1(1 - y_1^2 - y_2^2)}{\sqrt{y_1^2 + y_2^2}} \quad \text{and} \quad \frac{dy_2}{dt} = -y_1 + \frac{y_2(1 - y_1^2 - y_2^2)}{\sqrt{y_1^2 + y_2^2}},$$

admit a limit cycle.

Answer: If we change to polar coordinates, $y_1 = r\cos(\theta)$ and $y_2 = r\sin(\theta)$ these equations become

$$\frac{dr}{dt} = 1 - r^2 \quad \text{and} \quad \frac{d\theta}{dt} = 1. \tag{1}$$

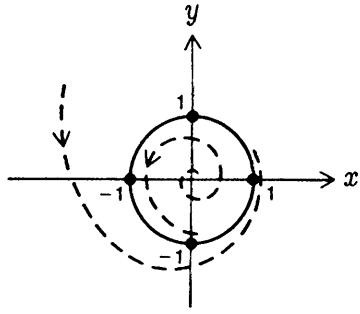
If we integrate the first of Eqs. (1), we find

$$\int_{R_0}^{R(t)} \frac{dr}{1 - r^2} = \int_0^t dt = t = \frac{1}{2} \ln\left(\frac{1 + r}{1 - r}\right)\Bigg|_{R_0}^{R}, \tag{2}$$

or

$$R(t) = \frac{Ae^{2t} - 1}{Ae^{2t} + 1}, \tag{3}$$

where $A = (1 + R_0)/(1 - R_0)$. From Eq. (3) we see that regardless of the value of R_0 (unless $R_0 = 1$), we have $R(t) \to 1$. If $R_0 = 1$, the $R(t) = 1$ for all time t. Therefore, Eqs. (a) and (b) admit a periodic solution with radius $R = 1$, and all trajectories decay to it after long times. If a solution starts with $R_0 = 1$, then it will keep that value for all times (see the accompanying figure). Not all limit cycles are stable. One can find limit cycles for which the neighboring trajectories move away in time.



Not all limit cycles are stable. One can find limit cycles for which the neighboring trajectories move away in time.

C.3. LIAPOUNOV FUNCTIONS AND GLOBAL STABILITY

In Section C.1, we discussed methods for determining the infinitesimal stability of stationary solutions. Liapounov introduced a means of determining the stability of a finite region of the phase space surrounding a stationary state.

Let us again consider Eqs. (C. 1) and (C. 2) and assume that a steady state occurs at $\bar{y}_1 = \bar{y}_2 = 0$. If we can find a function $V(y_1, y_2)$ such that for a region of space $(D : |y_1| < h, |y_2| < h)$ around the steady state, $V(y_1, y_2) > 0$ (assume $V(0, 0) = 0$) and $dV/dt \leqslant 0$), then the steady state will be stable. In other words, if $V > 0$ (except at the origin) and $dV/dt \leqslant 0$, a trajectory which starts in D remains in D for all time.

The region D forms a square with sides $2h$ centered at the origin. Consider two more squares with sides 2ε and 2δ in D such that $\delta < \varepsilon < h$ (cf. Fig. C.2). Let B^h denote the boundary of square $2h$, B^ε the boundary of square 2ε, and B^δ the boundary of square 2δ. We now let α denote the lower bound of $V(y_1, y_2)$ on B^ε. Thus on B^ε, $V \geqslant \alpha > 0$.

Let us next consider a point $y_0 = (y_1(t_0), y_2(t_0))$ contained in the square B^δ. at time t_0 and let us follow its motion with time. At time t, the point will have

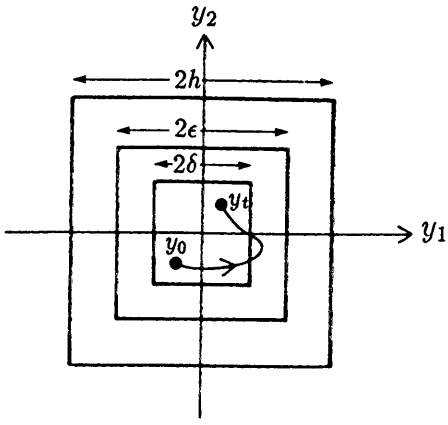


Fig. C.2. Regions of phase space used to prove stability of the steady state if Liapounov's criteria are satisfied.

coordinates $y_t = (y_1(t), y_2(t))$. We shall choose B^δ so that $V(y_1(t_0), y_2(t_0)) < \alpha$. Then since $dV/dt \leqslant 0$ we must have

$$V(y_1(t), y_2(t)) \leqslant V(y_1(t_0), y(t_0)) < \alpha.$$

Therefore, for all times $t > t_0$, the point $y_t = (y_1(t), y_2(t))$ must remain inside the boundary B^ϵ and the steady state is stable.

An identical argument can be made if $V(y_1, y_2) < 0$ in D and $dV/dt \geqslant 0$. If such a function can be found, then again, the steady state in stable.

■ **EXERCISE C.2.** Consider a damped harmonic oscillator whose equation of motion is $d^2y_1/dt^2 + \alpha(dy_1/dt) + \omega_0^2 y_1 = 0$. (a) Show that the total energy, $\frac{1}{2}\dot{y}_1^2 + \frac{1}{2}y_1^2 = E$, can be used as a Liapounov function for this problem. (b) Locate and classify the steady states for the cases $\alpha > 0$ and $\alpha = 0$

Answer:

(a) Introduce the variable y_2, where $dy_2/dt = -\omega_0^2 y_1$. Then the equation for the dampled harmonic oscillator can be written as two first order equations

$$\frac{dy_1}{dt} = y_2 - \alpha y_1 \quad \text{and} \quad \frac{dy^2}{dt} = -\omega_0^2 y_1. \tag{1}$$

(Note that for this example, the exact equations of motion are linear.) We may now introduce the Liapounov function

$$F(y_1, y_2) = \tfrac{1}{2}y_2^2 + \tfrac{1}{2}\omega_0^2 y_1^2 > 0 \tag{2}$$

for all y_1 and y_2. The time rate of change of the Liapounov function is

$$\frac{dF}{dt} = \frac{\partial F}{\partial y_1}\frac{dy_1}{dt} + \frac{\partial F}{\partial y_2}\frac{dy_2}{dt} = -\alpha\omega_0^2 y_1^2. \tag{3}$$

(**b**) The steady state occurs at $y_1 = 0$ and $y_2 = 0$. Since $F(y_1, y_2) > 0$ for all the space around it and since for $\alpha > 0$, $dF/dt < 0$ in all the space around it, then for $\alpha > 0$ the steady state is stable. In fact it is a *stable focus*. When $\alpha = 0$, the steady state is a *center*. It is marginally stable.

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