Unit 1: Classical Thermodynamics

Classical thermodynamics deals with physical systems where the number of degrees of freedom are huge – typically of order 10^{23}. The goal is to describe the average behavior of *macroscopic* properties, rather than the microscopic details of each and every particle or degree of freedom.

For example, consider a classical ideal gas of 10^{23} particles. The particles move according to Newton's equations of motion, traveling at constant velocity until they hit either another particle or a wall, and then they bounce off. Suppose one was able to make an exact solution giving all the trajectories of the 10^{23} particles as a function of time (never mind that it is impossible to do so). What would one have learned? Not necessarily much! We are not really interested in where each and every particle is at any moment of time. Rather we are interested in macroscopic properties of the gas – what is its temperature? its pressure?

Classical thermodynamics, the subject of Unit 1, proposes to show how one can determine the relations between such macroscopic properties, if one accepts a few fundamental postulates about the behavior of such large degree of freedom systems. These postulates, inferred from experiments, are regarded as fundamental to classical thermodynamics, just as Newton's laws are the underlying postulates behind classical mechanics. The main concepts behind classical thermodynamics are the notions of *equilibrium* and *entropy*.

Kinetic theory tries to connect classical thermodynamics to classical mechanics, showing how to use Newton's equations of motion to compute thermodynamic quantities. We will touch on kinetic theory only briefly. The main concept in kinetic theory is the *Boltzmann equation*, which seeks to compute the probability distribution for degrees of freedom to have particular values.

Ensemble theory is the more modern way to connect classical thermodynamics to mechanics (classical or quantum). Ensemble theory seeks to compute fundamental thermodynamic properties, such as entropy, from knowledge of the Hamiltonian that governs the dynamics of the system. The main concept in ensemble theory is the *partition function*. The correctness of ensemble theory is based on the *ergodic hypothesis* which, except for very simple systems, cannot be proven but must be accepted on faith because of the agreement with experiments that it gives. In Unit 2 we will be discussing ensemble theory for classical systems, while in Unit 3 we will discuss ensemble theory for quantum systems. In Unit 4 we will discuss ensemble theory as applied to phase transitions.

Unit 1-1: Postulates and Variables of Classical Thermodynamics (from Callen Chapters 1 and 2)

We assume that there exists a set of macroscopic variables, in terms of which the macroscopic behavior of the system is completely described. For example, for a gas of identical point particles, these macroscopic variables are:

$$\begin{array}{ll} E & \text{the total internal energy} \\ V & \text{the volume of the gas} \\ N & \text{the total number of particles} \end{array} \tag{1.1.1}$$

These are all *extensive* variables, meaning that they grow proportional to the size of the system. If we double the size of the system, keeping everything else the same, then E, V and N all double.

For another system, there might be additional variables. For example, for a ferromagnetic material the macroscopic variables are E, V, N, and also $\mathbf{M}$ the total magnetization of the material. For a ferroelectric material the macroscopic variables are E, V, N, and also $\mathbf{P}$ the total electric dipole moment of the material.

The first step in starting a thermodynamic description of a system is always to correctly identify what are the relevant macroscopic variables. This is not always easy.

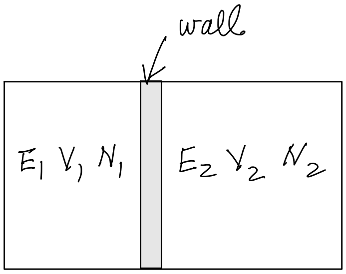
Classical thermodynamics can be reduced to a set of postulates, from which all other results can be derived. We do not seek to prove these postulates from other physical theories. Rather we claim that these postulates give results that are consistent with experimental observations, so we accept them on that basis. You may have heard of the *first law of thermodynamics*, the *second law of thermodynamics*, etc. We will not discuss those. Rather we will take our set of postulates to be those described in the text by Callen.

Postulate I - Equilibrium

We assert that for a thermodynamic system there exist *equilibrium states* that are characterized completely by the set of macroscopic variables. We will think of a gas of particles as the example in terms of which we will phrase our discussion. In this case the macroscopic variables are E, V, and N.

The criteria for an equilibrium state is that its macroscopic variables stay constant in time, and it does not depend in any way on the history by which the system arrived in this state. In classical thermodynamics we are interested *only* in equilibrium states.

The basic question of thermodynamics that we seek to answer can be phrased in terms of the following simple example.

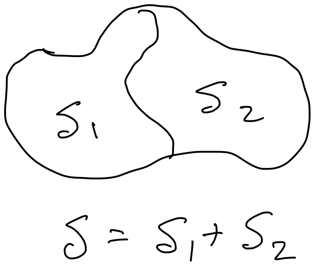


Consider two systems, each in equilibrium, separated by a wall (the wall is a *constraint*). What will happen if the wall is removed (the constraint is *relaxed*). What will be the new equilibrium state of the system?

Postulate II - Entropy

There exists a function of the extensive macroscopic variables called the *entropy* S. The value of S is *maximized* whenever a constraint is removed. This will allow us to answer the basic thermodynamic question posed above.

Postulate III - Entropy is Additive



The entropy S is *additive* over subsystems. S is a continuous and differentiable and increasing function of the total internal energy E.

Entropy $S(E,V,N)$ with $\left(\dfrac{\partial S}{\partial E}\right)_{V,N} > 0$ monotonic increasing in E.

Note, the subscripts V,N on the above derivate means that we differentiate with respect to E holding V and N constant.

The property of additivity of the entropy is only strictly valid in the limit of large system sizes, and only when the interactions between the degrees of freedom are short ranged, so that the total internal energy will satisfy, $E = E_1 + E_2$.

More generally, if we have two systems, we might expect $E = E_1 + E_2 + E_{12}$, where E_{12} is the interaction energy between the two systems. But E is extensive, so $E_1 \sim V_1$ and $E_2 \sim V_2$, while if the interaction is short ranged, then $E_{12} \sim A$, where A is the area of the interface separating the two subsystems. So then

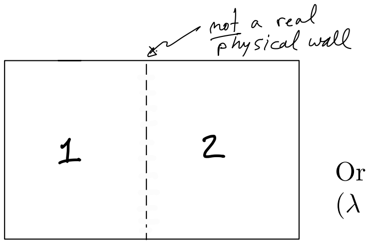
$$\frac{E_{12}}{E} \sim \frac{A}{V} \to 0 \quad \text{as } V \to \infty, \text{ and so energy is additive.} \tag{1.1.2}$$

When this assumption of additivity fails, then the $V \to \infty$ limit, which is called the *thermodynamic limit*, may depend on the shape of the container enclosing the system.

When the entropy is additive, then the total entropy of two subsystems 1 and 2 can be written as,

$$S(E,V,N) = S_1(E_1,V_1,N_1) + S_2(E_2,V_2,N_2) \tag{1.1.3}$$

Suppose our system is a gas in a box of total volume V. We can consider it conceptually to be divided into two subsystems 1 and 2 which are the left and right halves of the box. That is, there is no physical wall separating the two subsystems, the interface between them is just in our "mind's eye." Since the two halves 1 and 2 each have half the total system energy, volume, and number of particles, we can then write for the entropy,



$$S(E,V,N) = 2S\left(\frac{E}{2},\frac{V}{2},\frac{N}{2}\right) \quad \text{or} \quad \frac{1}{2}S\left(E,V,N\right) = S\left(\frac{E}{2},\frac{V}{2},\frac{N}{2}\right) \tag{1.1.4}$$

Or, more generally, if we considered the system to be divided into $1/\lambda$ equal subsystems ($\lambda = 1/2$ in the above example), then we have,

$$\lambda S(E,V,N) = S(\lambda E, \lambda V, \lambda N) \tag{1.1.5}$$

Any function that obeys this property is said to be a *homogeneous function of the 1st order.* So, in the thermodynamic limit where entropy is additive, the entropy is a 1st order homogeneous function of its extensive variables.

Now let $\lambda = 1/N$, with N the total number of particles. The above then gives,

$$S(E,V,N) = NS\left(\frac{E}{N},\frac{V}{N},1\right) = Ns(u,v) \qquad \text{where} \qquad s(u,v) \equiv S\left(\frac{E}{N},\frac{V}{N},1\right) \tag{1.1.6}$$

Here

$$\begin{aligned} u &= \frac{E}{N} \quad \text{is the energy per particle} \\ v &= \frac{V}{N} \quad \text{is the volume per particle, also called the } \textit{specific volume} \\ s &= \frac{S}{N} \quad \text{is the entropy per particle} \end{aligned} \tag{1.1.7}$$

S, E, V, N are *extensive* variables – they grow proportional to the system size as V increases.
s, u, v are *intensive* variables – they become constant as we take the thermodynamic limit.

Postulate IV

The states for which $\left(\frac{\partial E}{\partial S}\right)_{N,V} = 0$ have zero entropy, $S = 0$. This will turn out to correspond to $T = 0$. This postulate holds only when the system has a unique ground state.

This rule is often referred to as Planck's extension of Nernst's 3rd law of thermodynamics.

Energy as the basic thermodynamic function - T, p, and μ

Since, by postulate III, S is a monotonic increasing function of E, we can always invert to get E as a function of S, i.e. we can write,

$$E = E(S,V,N) \tag{1.1.8}$$

If we now consider $E(S,V,N)$ as the basic thermodynamic function (or also called the thermodynamic *potential*), we can define (i.e., we name) its partial derivatives as follows:

$$\begin{aligned} \left(\frac{\partial E}{\partial S}\right)_{V,N} &\equiv T \qquad \text{temperature} \\ -\left(\frac{\partial E}{\partial V}\right)_{S,N} &\equiv p \qquad \text{pressure} \\ \left(\frac{\partial E}{\partial N}\right)_{S,V} &\equiv \mu \qquad \text{chemical potential} \end{aligned} \tag{1.1.9}$$

T, p, μ are *intensive* variables since they are the derivatives of the extensive quantity E with respect to the extensive variables S, V, N.

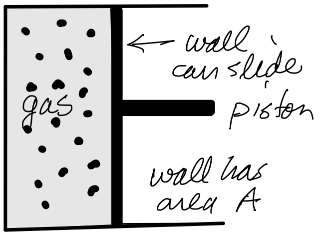
From the chain rule for differentiation, we can then write,

$$dE = \left(\frac{\partial E}{\partial S}\right)_{V,N} dS + \left(\frac{\partial E}{\partial V}\right)_{S,N} dV + \left(\frac{\partial E}{\partial N}\right)_{S,V} dN \tag{1.1.10}$$

or

$$\boxed{dE = TdS - pdV + \mu dN} \tag{1.1.11}$$

This definition of pressure agrees with the mechanical notion that pressure is the force per unit area. Consider a gas confined in the chamber of a piston – one wall can slide back and forth, so that the volume can change. The wall has area A.



If the chamber is thermally insulating, so that no heat is added or taken out of the chamber, and the gas is allowed to expand by moving the piston wall a distance Δx, then the work done *by* the gas *on* the wall is

$$F^{\text{total}} \Delta x = pA\,\Delta x = p\Delta V \tag{1.1.12}$$

where $\Delta V = A\Delta x$ is the change in volume. Since the gas is not heated (chamber is thermally insulating) and it does mechanical work, the energy of the gas must decrease by the work done, so,

$$\Delta E = -p\Delta V \quad \Rightarrow \quad \left(\frac{\partial E}{\partial V}\right)_{S,N} = -p \quad \text{as defined above.} \tag{1.1.13}$$

Note, keeping S constant as we differentiate with respect to V means that no heat is exchanged between the gas and the external world (see below).

When $dN = 0$, as is the case for a gas confined to a box, then Eq. (1.1.11) simplifies to

$$dE = TdS - pdV \tag{1.1.14}$$

Since we just showed that pdV is the mechanical work done *by* the gas, then

$$TdS \equiv \text{đ}Q \tag{1.1.15}$$

is the heat absorbed by the gas. We denote the heat as $\text{đ}Q$, with a slash through the d, to denote that this is an *imperfect* differential, i.e. it may depend on the path one takes in going from the initial to the final state. Similarly we can write for the work done by the gas, $\text{đ}W = pdV$. The work done $\text{đ}W$ and the heat absorbed $\text{đ}Q$ may depend on the details of the process that takes one from the initial to the final state, but their difference $dE = \text{đ}Q - \text{đ}W = TdS - pdV$ depends only on the end points, i.e. the initial and final states.

The above Eq. (1.1.14) thus has the interpretation of energy conservation,

$$\text{(change in energy)} = \text{(heat absorbed) - (mechanical work done)} \tag{1.1.16}$$

where we have introduced a new form of energy, the *thermal* energy or *heat*, that is associated with changes in entropy.

$$\begin{array}{ccccc} \text{heat absorbed} & \Rightarrow & \text{entropy increases} & & \\ (\text{đ}Q > 0) & \Rightarrow & (TdS) > 0 & \Rightarrow & dS > 0 \end{array} \tag{1.1.17}$$

In the last step we used that $T = \left(\frac{\partial E}{\partial S}\right)_{V,N} > 0$ since E is a monotonic increasing function of S by postulate III.

Entropy as the basic thermodynamic function

The above discussion regarded $E(S, V, N)$ as the basic thermodynamic function. But we could also, if we prefer, treat $S(E, V, N)$ as the basic thermodynamic function. From Eq. (1.1.11) we then have,

$$dE = TdS - pdV + \mu dN \quad \Rightarrow \quad TdS = dE + pdV - \mu dN \quad \Rightarrow \quad \boxed{dS = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN} \qquad (1.1.18)$$

from which we conclude,

$$\begin{aligned} \left(\frac{\partial S}{\partial E}\right)_{V,N} &= \frac{1}{T} \\ \left(\frac{\partial S}{\partial V}\right)_{E,N} &= \frac{p}{T} \\ \left(\frac{\partial S}{\partial N}\right)_{E,V} &= -\frac{\mu}{T} \end{aligned} \qquad (1.1.19)$$

In remembering thermodynamic rules such as Eq. (1.1.11) and (1.1.18) it is always a problem to remember which is the term that has the $(-)$ minus sign. The key is to remember that, when regarding E as the basic thermodynamic function, it is the pdV term that enters with the minus sign. If you remember that, so as to get Eq. (1.1.11) correct, then you can always reproduce Eq. (1.1.18) correctly to conclude that, when regarding S as the basic thermodynamic function, it is the $(\mu/T)dN$ term that enters with the minus sign.