How the mass movement of trillions of atoms changed the world

Einstein, Sutherland, Atoms, and Brownian motion

Bruce H J McKellar
15th July 2005

Thanks to David Jamieson, Rod Holme, Hector Giacomini

Please feel this cup of coffee, and remember how hot it is

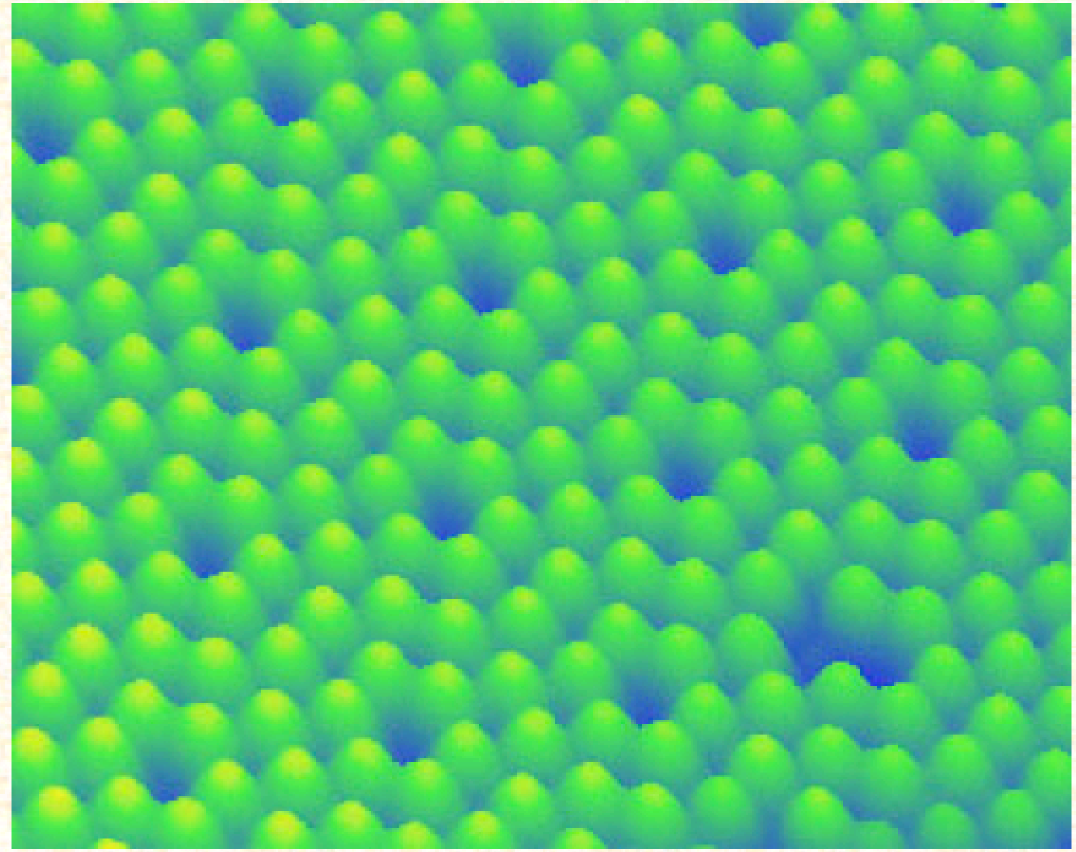
1905 Citation Count

(World of Science, Dec. 2004)

A. Einstein, Annalen der Physik 17, 132 (1905)	Photoelectric Effect	325
A. Einstein, Annalen der Physik 17, 549 (1905)	Brownian Motion	1368
A. Einstein, Annalen der Physik 17, 891 (1905)	Special Relativity	664
A. Einstein, Annalen der Physik 18, 639 (1905)	$E = mc^2$	91
A. Einstein, Annalen der Physik 19, 289 (1906) Thesis Work	Molecular Size (Einstein's thesis)	1447

Einstein's thesis is his most cited paper!!
Brownian motion is next

We know that matter is made of atoms, and we can see them



But 100 years ago there were still important reasons to doubt the existence of atoms

This is an image of silicon atoms arranged on a face of a crystal. It is impossible to "see" atoms this way using ordinary light. The image was made by a Scanning Tunneling Microscope, a device that "feels" the cloud of electrons that form the outer surface of atoms, rather as a phonograph needle feels the grooves in a record.

http://www.aip.org/history/einstein/atoms.htm22/6/2005 01:33:19

The philosophical reasoning

- Solids, fluids, particulates, ...

The Chemists

200 years ago Dalton had shown that atoms allowed an improved understanding of chemical reactions — these ideas were further developed and enhanced in the 19th Century. By 1905 most chemists thought atoms were very convenient, but they could have done without them if necessary.

John Dalton
http://library.thinkquest.org/15567/bio/dalton.html

Amadeo Avogadro
http://www.chemheritage.org/EducationalServices/chemach/ppt/aa.html

Dmitriy Mendeleev
http://www.chem.msu.su/eng/misc/mendeleev/welcome.html

The Physicists

270 years ago Daniel Bernoulli showed how to understand Boyle's gas law (ie gas pressure) in terms of atoms, and by 1865 James Clerk Maxwell had calculated the specific heats of gases assuming they were made of molecules. He got some of them right

Daniel Bernoulli

http://www-groups.dcs.st-and.ac.uk/~history/PictDisplay/Bernoulli_Daniel.html

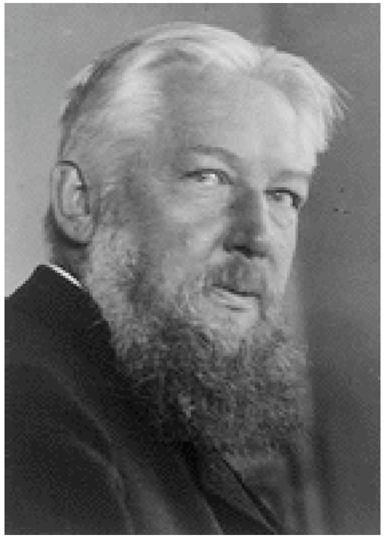
James Clerk Maxwell

http://www-groups.dcs.st-and.ac.uk/~history/PictDisplay/Maxwell.html

The Doubts

But there was a big problem which caused some influential physicists (Mach, Ostwald) to reject atoms in the late 19th Century. An atomic explanation of the Second Law of Thermodynamics was lacking, and even thought to be impossible

Ernst Mach
Public domain



Wilhelm Ostwald
http://nobelprize.org/chemistry/laureates/1909/ostwald-bio.html

The first and second law of thermodynamics

Michael Flanders

Donald Swan

First and Second Law
from
At the drop of another hat, 1964

http://www.nyanko.pwp.blueyonder.co.uk/fas/

Let's check the coffee

it is colder, and no one is surprised — but why not? The total energy in the room is about 10 thousand times more than the coffee, so why can't it force it's way in?

The 2nd Law is a one way street, incompatible with Newton

- Planck (1883) *The consistent interpretation of the second law is incompatible with the existence of finite atoms.*
- Ostwald (1895) *The proposition that all natural phenomena can ultimately be reduced to mechanical ones ... is simply a mistake. This mistake is most clearly revealed by the following fact. .. theoretically perfect mechanical processes can develop equally well forward and backward in time... an old man could turn into a child, no explanation is given for the fact that this does not happen. The irreversibility of natural phenomena thus proves the existence of processes that cannot be described by mechanical equations*

Einstein enters

In 1903 this was one of the central questions in Physics. The resolution of it was every bit as important as resolving the incompatability of Maxwell's equations for light and electromagnetic waves, and Newtons Laws, or the meaning of Planck's quantisation. Many of the great physicists of the day worried about one or two of these questions. Einstein, in his nights and weekends, worried about all three while he was working by day in the patent office in Berne, as a technical officer class III.

Einstein's house, Bern

http://www.berninfo.com/fr/navpage.cfm?category=CultureBET&subcat=MuseumsBET&id=34392

Einstein's approach to the problem of atoms

He looked for ways to count the atoms — we would now say to determine Avagadro's number N_0 — the number of atoms in a mole of substance. Einstein's idea was that a number of different determinations of N_0, all of which gave the same answer, would be convincing evidence of the existence of atoms.

Einstein in the patent office

Einstein in the Bern patent office. "A practical profession is a salvation for a man of my type; an academic career compels a young man to scientific production, and only strong characters can resist the temptation of superficial analysis."

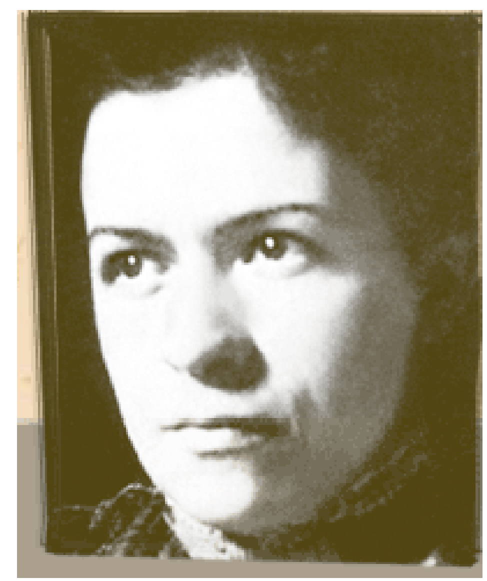
http://www.aip.org/history/einstein/great1.htm

Einstein’s way of working

Einstein's way of working was to discuss various ideas, and to study various papers, with his friends Marcel Grossman and Michele Besso, and his wife, Mileva Maric. They called themselves “the Academy”. Some of the discussions were in correspondence, so we know what was being studied

Marcel Grossman
http://www.icra.it/MG/Marcel%20Grossmann%20cv.htm

Michele Besso
http://www.aip.org/history/einstein/ae11.htm



Mileva Maric
http://www.pbs.org/opb/einsteinswife

Enter Sutherland

One paper discussed by Einstein and Besso was by William Sutherland (of Melbourne):

Ionization, ionic velocities, and atomic sizes. *Philosophical Magazine*, S.6, 3 (1902), 161-177.

It contains the quote *“Now this simple theory must have been written down by many a physicist and found to be wanting”*

But it contains the important idea that one can use Stokes’ Law to determine the size of large molecules

William Sutherland

William Sutherland, was born in Scotland in 1859, and emigrated with his parents to Australia in 1864. He graduated with a BA from Melbourne University in 1879, and with a BSc, with first class honours (and first place) in Experimental Physics from University College of London University in 1881. His attachment to his family, and to Australia, was strong, and he returned to Melbourne. In 1885 his first paper appeared in the Philosophical Magazine, to be immediately followed by one in Nature. He never held a permanent University position, but made a little money as a tutor, conducting examinations and writing for *The Age* and *The Argus* newspapers.

William Sutherland in his 20th year

Sutherland's papers
The ANZAAS paper

Sutherland then turned his attention to large neutral molecules with success, and presented the paper:

The measurement of large molecular masses. *Australasian Association for the Advancement of Science. Report of Meeting.*, 10 (Dunedin, 1904), 117 -121.

The conference was in January 1904, and the proceedings appeared in early 1905

Sutherland's papers
The *Phil Mag* paper

LXXV. *A Dynamical Theory of Diffusion for Non-Electrolytes and the Molecular Mass of Albumin.* *By* WILLIAM SUTHERLAND ‡.

IN a paper communicated to the Australian Association for the Advancement of Science at Dunedin, 1904, on the Measurement of Large Molecular Masses, a purely dynamical theory of diffusion was outlined, with the aim of getting a formula for calculating from the data of diffusion those large molecular masses for which the ordinary methods fail. The formula obtained made the velocity of diffusion of

A dynamical theory of diffusion for non-electrolytes and the molecular mass of albumin. *Philosophical Magazine*, S.6, 9 (1905), 781-785.

Mailed to London in March 1905, and published in June 1905

Einstein’s thesis

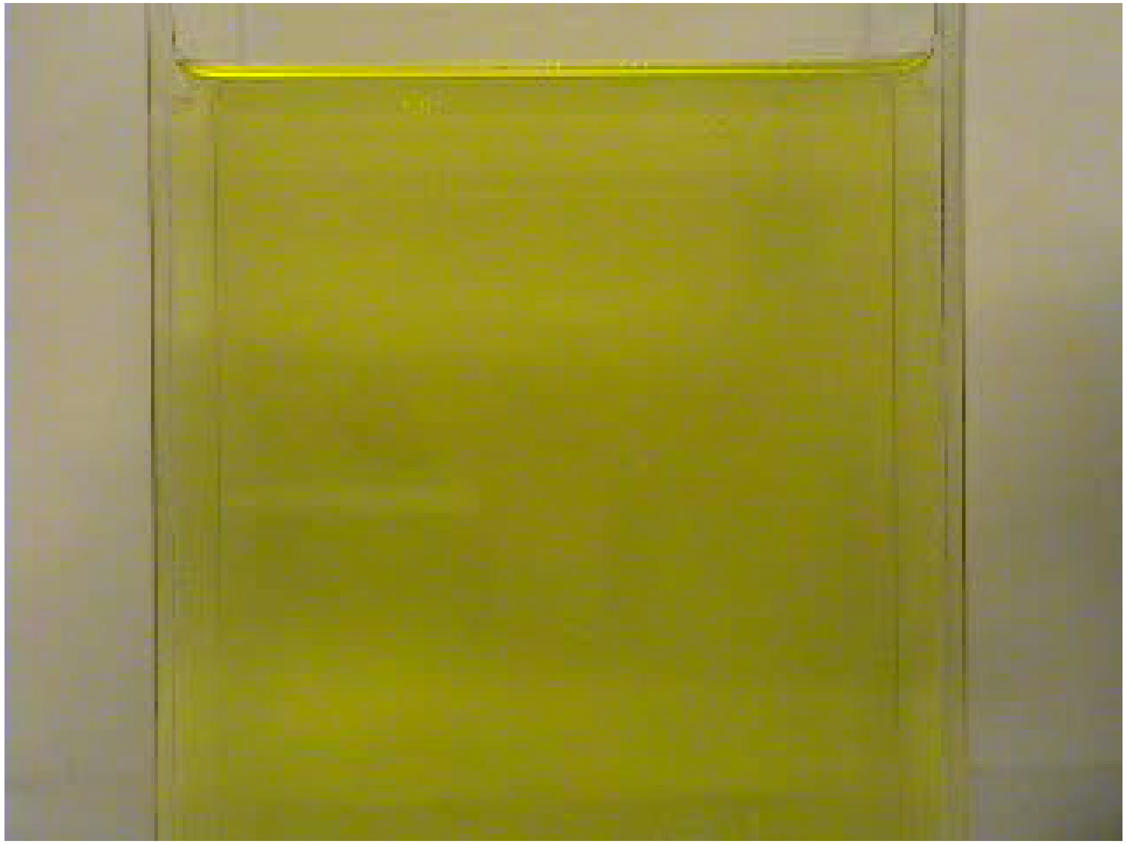
On 30th April 1905 Einstein completed his thesis, *“A new estimate of molecular dimensions”*, which was submitted 20th July, accepted 24th July, and published in *Annalen der Physik*, Jan 1906 (vol 19, p 289)

(There was an error in one of the calculations, not discovered and corrected until 1911)

What did Sutherland and Einstein do?

- Use Stokes' Law for the viscous force on a sphere
- Combine this with the gas law (as used for osmotic pressure in liquids)
- Thus relate the diffusion coefficient, viscosity, molecular size, and Avagadro's number

Stokes' Law



Stokes' Law

$$F = 6\pi\eta a v$$

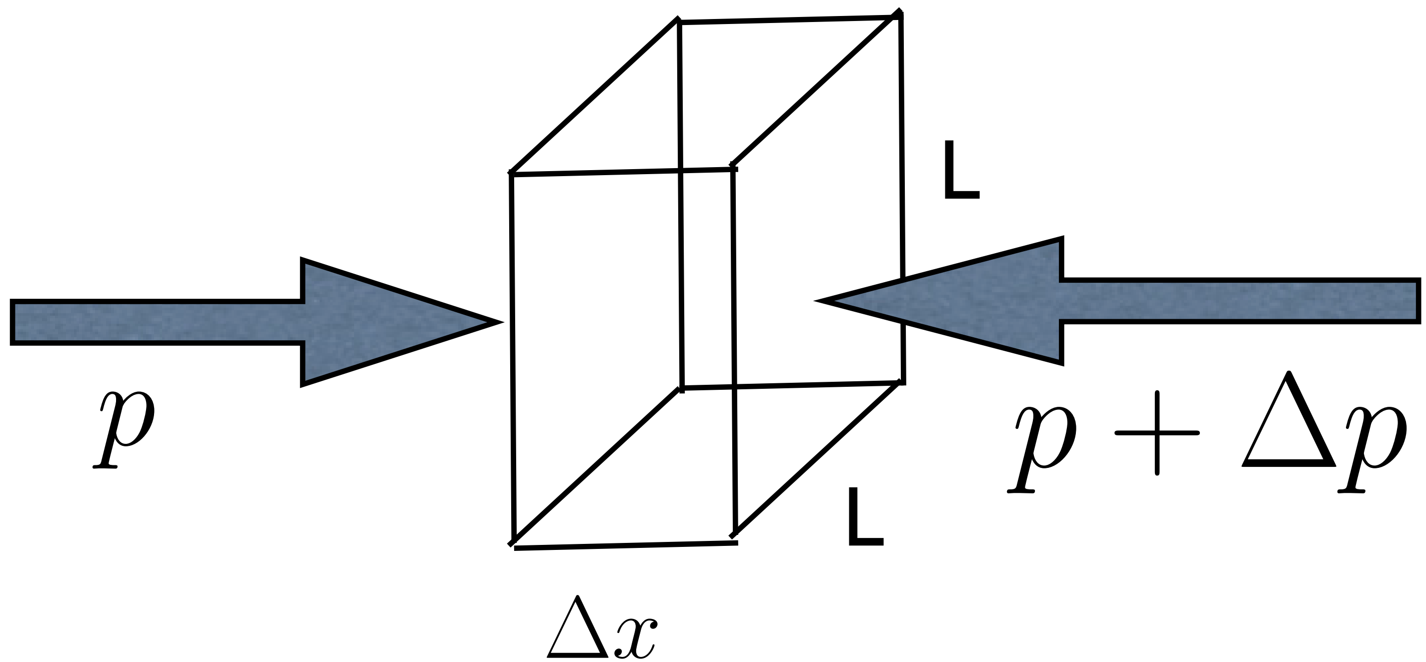
In equilibrium

$$mg = 6\pi\eta a v$$

or

$$v = \frac{mg}{6\pi\eta a} \propto a^2$$

Force due to pressure difference



$$
\begin{aligned}
\text{Net force} &= L^2 \Delta p \\
\text{Number of particles per unit volume} &= n \\
\text{Total number of particles} &= n L^2 \Delta x \\
\text{Pressure force per particle} &= \frac{\text{Net force}}{\text{Total number of particles}} \\
&= \frac{1}{n} \frac{\Delta p}{\Delta x}
\end{aligned}
$$

Now use the gas law

Write the gas law as

$$p = n \frac{R}{N_0} T$$

so

$$\frac{\Delta p}{\Delta x} = \frac{R}{N_0} T \frac{\Delta n}{\Delta x}$$

Balance the forces

In equilibrium

Pressure force per particle = Stokes law force on the particle

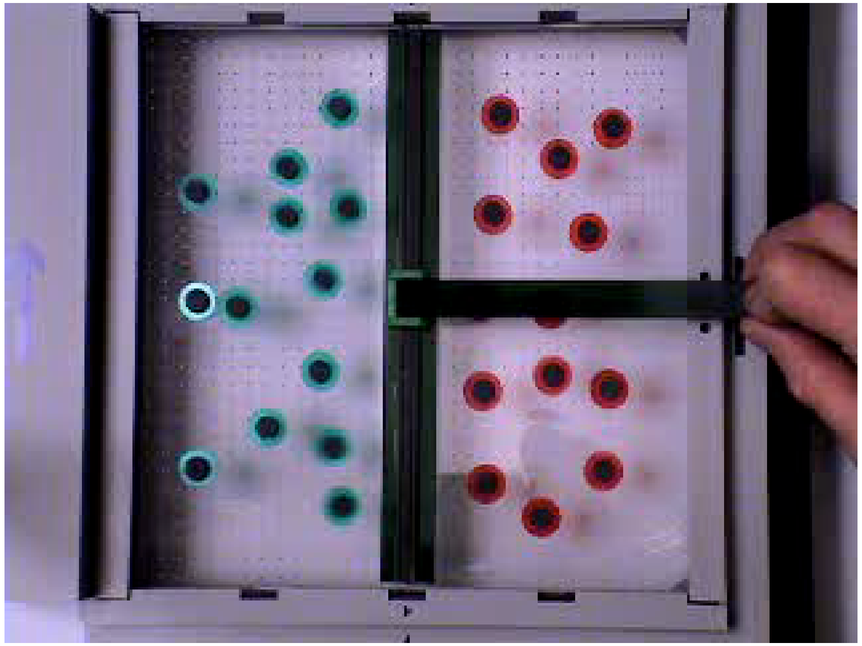
or

$$\frac{1}{n}\frac{R}{N_0}T\frac{\Delta n}{\Delta x} = 6\pi\eta a v$$

whence, with a little algebra

$$nv = \frac{R}{N_0}\frac{T}{6\pi\eta a}\frac{\Delta n}{\Delta x}$$

Diffusion



Diffusion

But nv is the number of particles crossing unit area per second, and the definition of the diffusion coefficient $\mathcal{D}$ is

$$nv = \mathcal{D}\frac{\Delta n}{\Delta x}$$

So

$$\mathcal{D} = \frac{R}{N_0}\frac{T}{6\pi\eta a}$$

The Sutherland-Einstein Equation

Sutherland's application $\mathcal{D} = \frac{R}{N_0}\frac{T}{6\pi\eta a}$

In a fluid, the molecules are close packed, and the molecular radius should be proportional to the cube root of the molar volume $\mathcal{B}$ (the volume occupied by Avagrdro's number of particles)

As

$$a\mathcal{D} = \text{constant}$$

it follows that

$$\mathcal{B}^{1/3}\mathcal{D} = \text{constant}$$

Sutherland estimated the constant as 21/1000000, and then from the diffusion constant for albumin, he could obtain its molar volume and thus get an estimate of the molecular weight of albumin as 32814.

Einstein's application

The Sutherland-Einstein equation gives

$$N_0 a = \frac{RT}{6\pi\eta\mathcal{D}}$$

Einstein found another relation between N_0 and a. He showed that the flow of a set of hard spheres suspended in a fluid was approximately given by changing the viscosity η to an effective viscosity η^*

$$\eta^* = \eta(1 + \frac{5}{2}\frac{4\pi}{3}N_0 n a^3)$$

The omission of the 5/2 factor was the mistake.

From data on sugar solutions, for η^* and $\mathcal{D}$ he could obtain

$$N_0 = 6.6 \times 10^{23}$$

Why did Einstein and not Sutherland get to be famous?

- Einstein addressed a fundamental problem of the time, the existence of atoms, and counting them
- Sutherland had worked assuming the existence of atoms, and attacked a practical question. While that is what everyone now uses the Sutherland-Einstein equation for, it was not much interest at the time.

The Sutherland-Einstein Equation was the birth of nanotechnology

Abstract for an Invited Paper for the MAR05 Meeting of
The American Physical Society

Einstein's thesis revisited: the size, geometry, and interactions of nanoparticles a basis for NEMS

ALEX ZETTL, University of California, Berkeley

Many of the physics problems of interest to Einstein throughout his career had and continue to have relevance to solid state physics. Einstein's doctoral thesis work, submitted in April 1905, in fact concerned the size, geometry, and interactions of nanoscale particles. These topics are of fundamental relevance to the design, creation, and operation of next-generation nanoelectromechanical systems. I will highlight some interesting problems which, 100 years later, have come full circle.

Some recent articles referencing Einstein's thesis:

Diffusion of epidermal growth factor in rat brain extracellular space measured by integrative optical imaging

JOURNAL OF NEUROPHYSIOLOGY

A generalized mixture rule for estimating the viscosity of solid-liquid suspensions and mechanical properties of polyphase rocks and composite materials

JOURNAL OF GEOPHYSICAL RESEARCH

Constitutive model for stretch-induced softening of the stress-stretch behavior of elastomeric materials

JOURNAL OF THE MECHANICS AND PHYSICS OF SOLIDS

Tribological behavior of ceramics at high sliding speeds in steam

TRIBOLOGY LETTERS

Rheological properties of coarse food suspensions in tube flow at high temperatures

JOURNAL OF FOOD ENGINEERING

In a Norwegian plant physiology dictionary

Botanisk og plantefysiologisk leksikon

Einstein-Sutherland ligningen - Viser sammenhengen mellom Brownske bevegelser og diffusjon

$$D = \frac{R \cdot T}{N \cdot f}$$

hvor D er diffusjonskoeffisienten, R er gasskonstanten, T er absolutt temperatur, N er Avogadros tall og f er friksjonskoeffisienten.

http://biologi.uio.no/plfys/haa/leks/e/einstein.htm

And the most recent reference to the Sutherland-Einstein Equation

Journal of Cellular and Comparative Physiology, 4 Feb 2005, pp 271-291

T C Nelson

Sexual Competence in Escherichia Coli

Brownian Motion

While he had his thesis his desk, Einstein wrote up and submitted a paper to Annalen "*On the motion required by the molecular kinetic theory of heat of particles suspended in fluids at rest.*"

Which is what we call Brownian Motion

Robert Brown

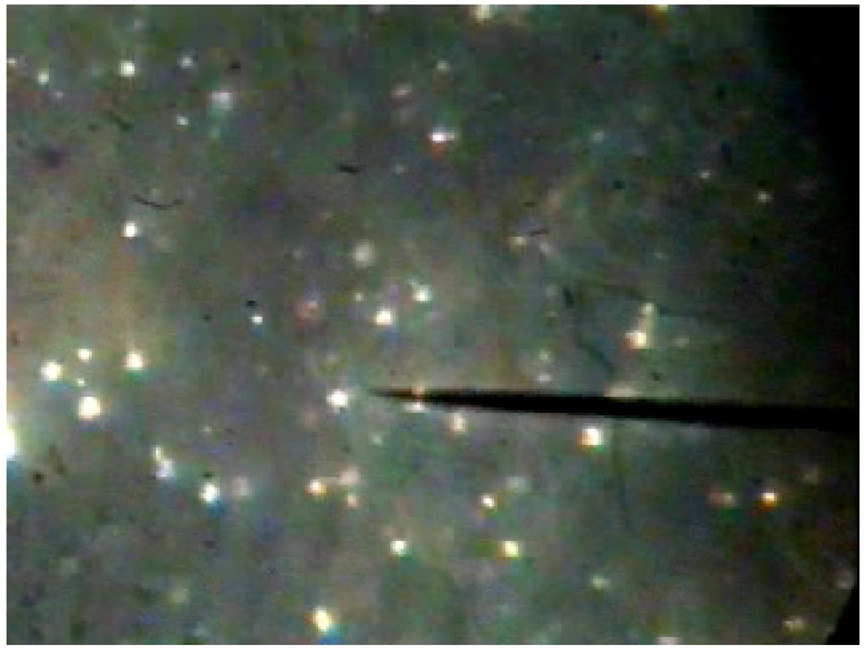
- Robert Brown was the botanist on the *Investigator* during Flinder's circumnavigation of Australia
- The leading botanist to collect in Australia in the early 19th century

Text

- He observed Brownian motion in 1827, just after the introduction nof the first achromatic objectives for microscopes

Robert Brown
http://www.anbg.gov.au/banksia/brown.robert.biog.html

What Brown saw

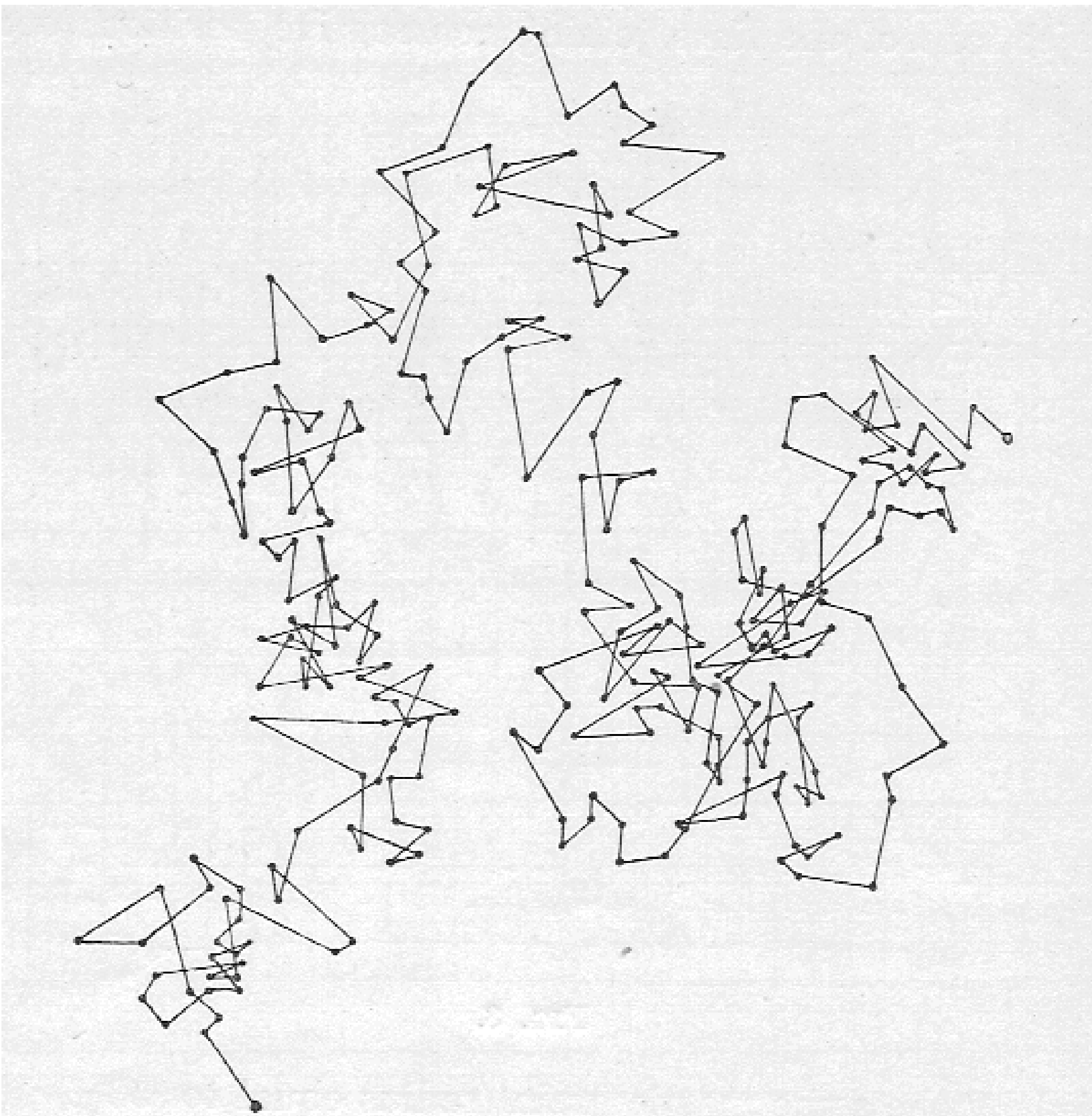


We now see under our eyes heat changed into motion. This is contrary to the Second Law of Thermodynamics. — Poincaré, 1900 http://galileo.phys.virginia.edu/classes/109N/more_stuff/Applets/brownian/brownian.html

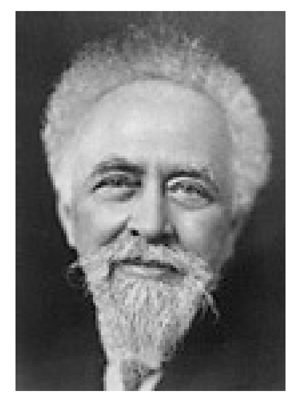
Einstein’s insight

The motion of the Brownian particle was driven by the molecular impacts on the particle, which produce a randomly fluctuating force on it. By taking averages we can make some progress in understanding.

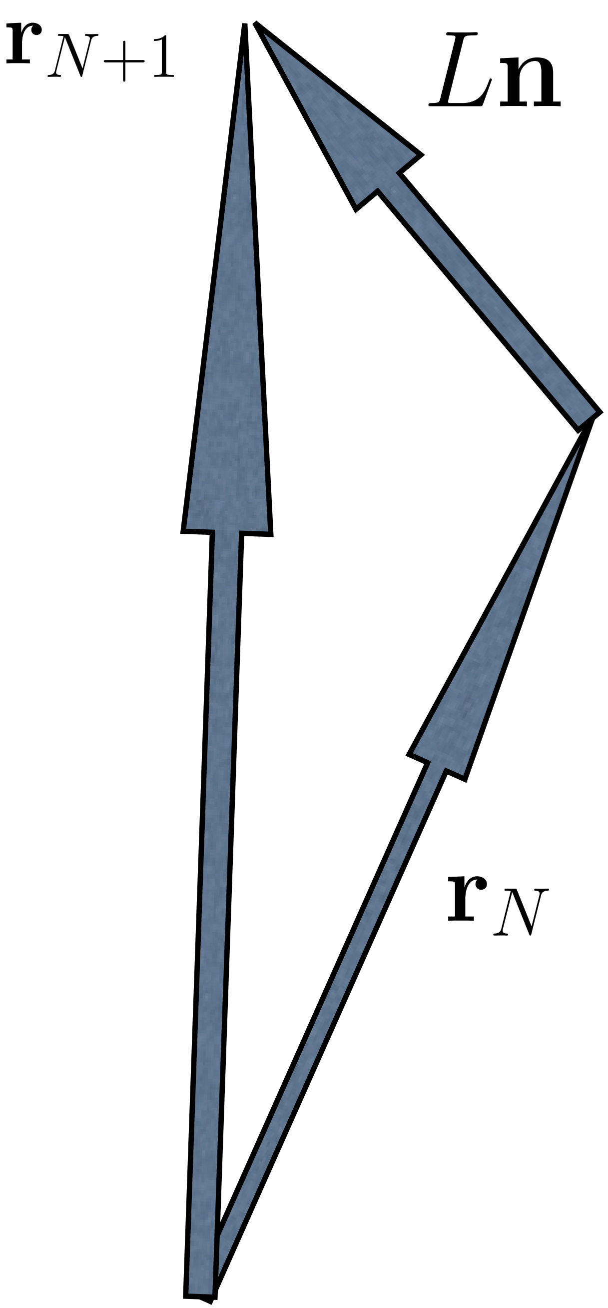
A random walk



The trajectory of a 0.53 micron particle
J. Perrin "Atoms" 1916



Jean Perrin
http://nobelprize.org/physics/laureates/1926



Major assumption — each step is of a fixed length in a random direction, independent of the previous steps.

$$\mathbf{r}_{N+1} = \mathbf{r}_N + L\mathbf{n}$$

where $\mathbf{n}$ is a unit vector pointing in a random direction.

Square

$$\mathbf{r}_{N+1}^2 = \mathbf{r}_N^2 + L^2 + 2L\mathbf{n} \cdot \mathbf{r}_N$$

Average, remembering that as $\mathbf{n}$ is randomly directed, it will average to zero

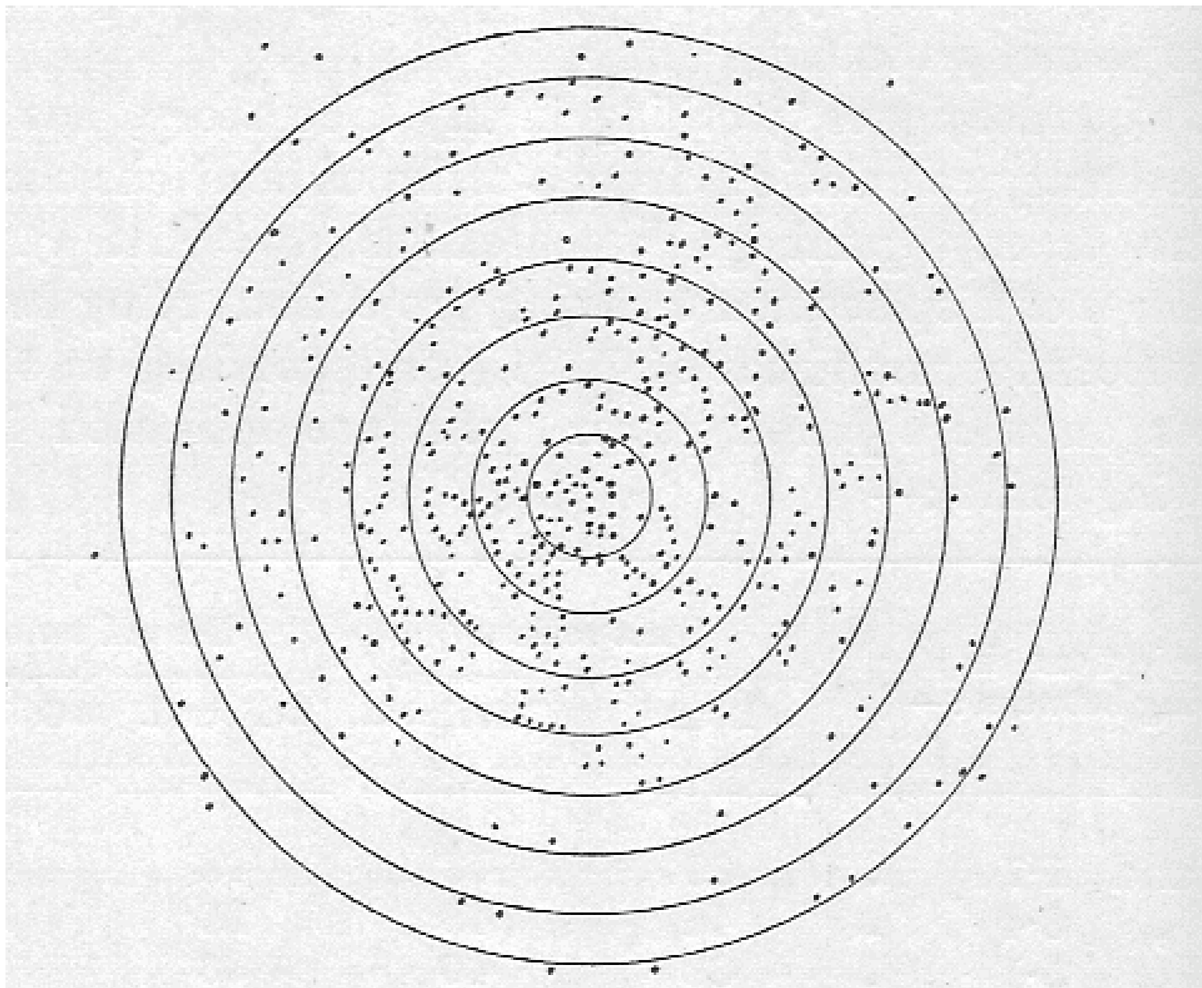
$$\overline{\mathbf{r}_{N+1}^2} = \overline{\mathbf{r}_N^2} + L^2$$

which gives

$$\overline{\mathbf{r}_N^2} = NL^2$$

On average, the mean square distance travelled is proportional to the number of steps, or the root-mean-square distance travelled is proportional to the square root of the number of steps, or the time taken.

Perrin's results



The numbers

Displacement between :—	P for each ring.	n Calculated.	n Found.
0 and $\frac{e}{4}$ . .	·063	32	34
$\frac{e}{4}$,, $2\frac{e}{4}$ . .	·167	83	78
$2\frac{e}{4}$,, $3\frac{e}{4}$ . .	·214	107	106
$3\frac{e}{4}$,, $4\frac{e}{4}$ . .	·210	105	103
$4\frac{e}{4}$,, $5\frac{e}{4}$ . .	·150	75	75
$5\frac{e}{4}$,, $6\frac{e}{4}$ . .	·100	50	49
$6\frac{e}{4}$,, $7\frac{e}{4}$ . .	·054	27	30
$7\frac{e}{4}$,, $8\frac{e}{4}$ . .	·028	14	17
$8\frac{e}{4}$,, $9\frac{e}{4}$ . .	·014	7	9

Theory

Einstein related the mean square displacement (X^2) at the time t to the diffusion coefficient:

$$\mathcal{D} = \frac{1}{2}\frac{X^2}{t}$$

But from his thesis he know that

$$\mathcal{D} = \frac{R}{N_0}\frac{T}{6\pi\eta a}$$

so measurements of X^2/t give us yet another way of getting at N_0

Further developments

- Einstein revisited Brownian motion several times, including relating it to noise in electrical circuits
- He and Smoluchowski related the random fluctuations to critical opalescence and the blue of the sky
- Einstein's Brownian motion analysis contained the first example of a fluctuation-dissipation theorem, relating a dissipation coefficient (the diffusion coefficient), to the fluctuations (X^2).

The triumph of Atoms

Phenomena observed.		$\frac{N}{10^{22}}$.
Viscosity of gases (van der Waal's equation)		62
Brownian movement	Distribution of grains	68·3
	Displacements	68·8
	Rotations	65
	Diffusion	69
Irregular molecular distribution	Critical opalescence	75
	The blue of the sky	60 (?)
Black body spectrum		64
Charged spheres (in a gas)		68
Radioactivity	Charges produced	62·5
	Helium engendered	64
	Radium lost	71
	Energy radiated	60

Perrin's 1916 results on N_0 — *that the numbers agree amongst themselves, without discrepency, for all the methods employed, the real existence of the molecule is given a probability bordering on certainty*

What of the second law?

- Boltzmann had shown that the second law was not absolute, the coffee cup cooling down was simply overwhelming the most likely possibility
- Einstein (1917): *"Because of the understanding of the essence of Brownian motion, suddenly all doubts vanished about the correctness of Boltzmann's interpretation of the thermodynamic laws"*

Ostwald's magnanimous concession

- 1908 — Ostwald refers to the Brownian motion results and says they *"entitle even the cautious scientist to speak of the experimental proof for the atomistic constitution of space-filled matter"*
- 1910 — Ostwald nominates Einstein for the Nobel Prize (for special relativity)

Perrin's restatement of the second law

On the scale of magnitudes that are of practical interest to us, perpetual motion of the second kind is in general so insignificant that it would be foolish to take it into consideration

Later developments

- Brownian motion led us to understand fluctuations and noise
- Modern applications to astrophysics, condensed matter physics, electronics, finance, economics, ...

A 2005 Journal issue on the subject

Peter Hänggi *et al* 2005 *New J. Phys.* **7**

EDITORIAL

Focus on Brownian Motion and Diffusion in the 21st Century

Without doubt, the problem of Brownian motion has played a guiding role in the development for both the foundations of thermodynamics and the dynamical aspects of statistical physics. The development of the phenomenon of Brownian motion based on the molecular-kinetic theory of heat provides a link between the microscopic dynamics and the macroscopic phenomena such as diffusion and fluctuation phenomena. It has also provided a first link between the macroscopic response and the equilibrium fluctuation characteristics via an early form of the ubiquitous fluctuation-dissipation theorem: the Einstein relation that relates the mobility to the diffusion strength.

The topic of Brownian motion has likewise inspired many scientists to deploy a consistent treatment of phenomena far from thermal equilibrium via such concepts as the Fokker–Planck or master equation descriptions of noisy nonlinear dynamics in such diverse areas as soft matter physics, surface science, solid state physics and chemical kinetics. In recent years this theme has also increasingly impacted upon the life sciences and even extends to areas such as cosmology, astrophysics and econophysics.

This celebratory Focus Issue in *New Journal of Physics* is not only timely but also circumstantiates that this research topic is very much alive and indeed multifaceted. As Guest Editors we share the confident belief that the contributions by leading practitioners from a diverse range of backgrounds will together provide a fair and accurate snapshot of the current state of this rich and interdisciplinary research field. Last but not least, we hope that this issue will stimulate readers into pursuing research of their own in the exciting areas represented.

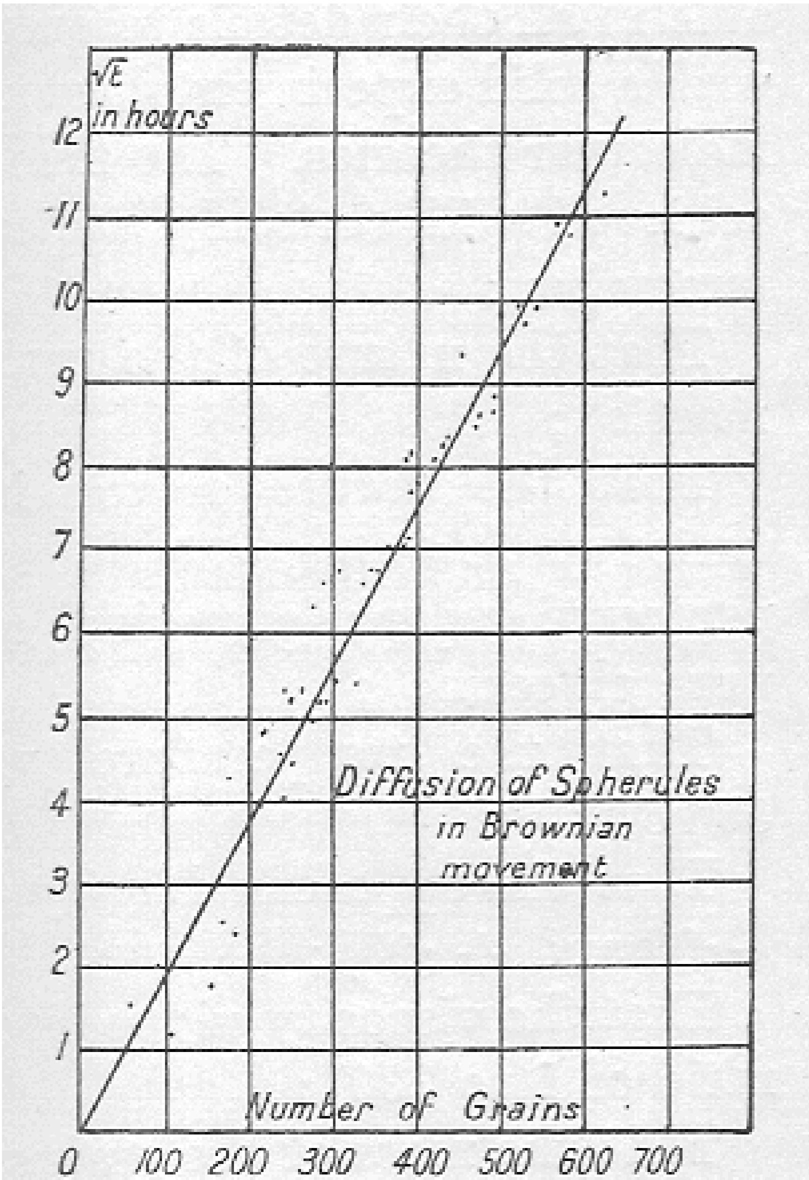
Brownian Motion

The Research Goes On ...

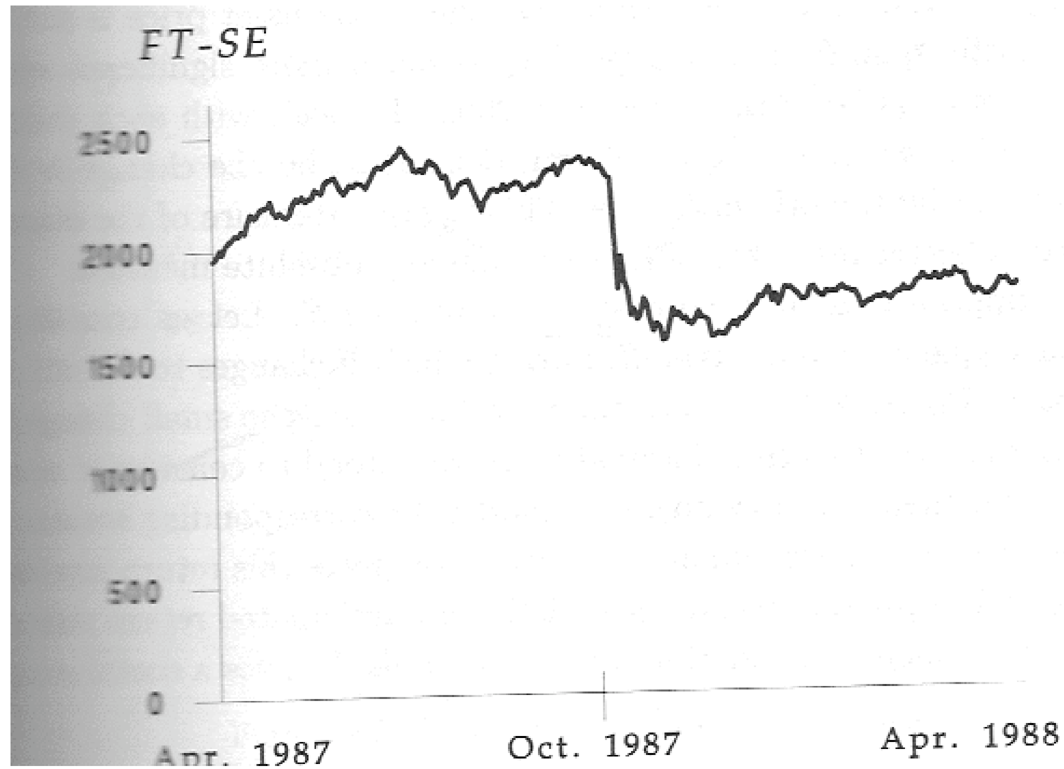
by Y.K.Lee and Kelvin Hoon

Applications in Medical Imaging
Brownian Motion In Robotics
Estimation of Extreme Floods and Droughts
Applications of Brownian Motion to Market Analysis
Applications of Brownian Motion in Manufacturing
Brownian Motion in Decision Making
Brownian Motion of Aerosol Particles
Aerosol transport phenomena
Particle disposition on the human nose and mouth
Laser evaporation of Copper Aerosol

http://www.doc.ic.ac.uk/~nd/surprise_95/journal/vol4/ykl/report.html



Perrin's results



The London Stock Market

But Einstein wasn’t first

Louis Bachelier published his thesis *“Théorie de la Speculation”* in 1900, applying Brownian motion techniques to the Paris stock market. He was Poincaré’s student, and his thesis received excellent marks, his career was interrupted by the war, and an unfortunate disagreement with Paul Lévy, and he retreated to provincial France to become regarded as the *tragic hero of financial economics.* The thesis was translated under the title *“Random Character of Stock Market Prices”*

In the mathematical literature, the basic process is called the Weiner process, or in some cases the Bachelier-Weiner process

Conclusion

- It is remarkable that three papers published in 1905 by Einstein and Sutherland laid such a foundation for science that they lie at the base of our understanding of nanostructures, are useful to biologists, are essential to professional investors. It is certainly a centenary worth celebrating!