Brownian Motion
and
The Atomic Theory

Albert Einstein
Annus Mirabilis
Centenary Lecture

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Founders’ Day
1. **What phenomenon did Einstein explain?**

   (a) Random motion of particles in liquid  
   (b) Dependence on temperature  
   (c) Dependence on viscosity of the liquid  
   (d) Dependence on the size of the particles

2. **How did he explain it?**

   (a) Statistical Theory of Heat  
   (b) Ideal Gases  
   (c) Treat Microscopic and Macroscopic Objects Uniformly

3. **Why was it important?**

   (a) Universal Validity of Statistical Mechanics  
   (b) Reality of Atoms and Molecules
In 1827 Robert Brown, a Scottish botanist and curator of the British Museum, observed that pollen grains suspended in water, instead of remaining stationary or falling downwards, would trace out a random zig-zagging pattern. This process, which could be observed easily with a microscope, gained the name of **Brownian motion**.
It is discovered that no matter how long the particles are left in the liquid in a sealed container, they never come to rest or even slow down. The experimenters observed a system of pollen motes in a sealed volume of liquid over a period of one year, and Brown’s zig-zagging effect continued undiminished.
It is discovered that the speed with which the pollen motes disperse was slower in more viscous liquid and faster in less viscous liquid.
It is discovered that the zig-zagging gets faster as the temperature of the water is raised; also, that the motion becomes slower as the size of the particles is made larger.
By 1905, Einstein had begun to think about Brownian motion in the context of the young science of **statistical mechanics**.

Statistical mechanics aims to understand the **thermal behavior** of macroscopic matter in terms of the **average behavior** of microscopic constituents under the influence of **mechanical forces**.
The theory originated in an attempt to solve the puzzle of energy conservation.

**Heat as energy**

Both are forms of mechanical energy.

- Potential energy (depends on position)
- Kinetic energy (depends on speed)

**MECHANICAL ENERGY**

**NOT** conserved here
Development of the theory

Sometimes mechanical energy is conserved; sometimes it is partially or completely converted to heat.

1842-1847: Conservation of Energy

Several scientists (including Mayer, Helmholtz, and Joule) proposed that a modified law of conservation of energy would hold for all processes, when heat was appropriately taken into account as a form of energy:

\[ dU = dQ - dW \]

which means that

mechanical energy + thermal energy = constant over time

in a closed system. This is the First Law of Thermodynamics.
1850-1898: Kinetic theory of Gases

From studies of the behavior of gases, an understanding of thermodynamics began to emerge:

- Matter is made up of microscopic molecular constituents.

- The molecules of matter are constantly in motion, even for matter which appears to be at rest. The macroscopic momentum of matter is only an average momentum of its constituents.

- The speed of the molecular constituents much higher at ordinary temperatures than the typical speed of the matter in bulk.

- Most importantly: thermal energy of macroscopic matter is identical with the mechanical energy of its constituents.

This last idea gives a simple explanation for the First Law of thermodynamics: on molecular scales, there is only mechanical energy, and it is absolutely conserved!
Scientists studying gas behavior introduced the concept of an ideal gas – a gas whose molecules’ energy was purely kinetic. An ideal gas is a tiny set of billiard balls, which move in straight lines, occasionally colliding and exchanging momentum.

Ludwig Boltzmann then proved that in the limit of a large number of such billiard balls, the collection of balls would approach thermal equilibrium – a condition of uniform temperature and density, macroscopically a gas at rest, with thermal energy stored as kinetic energy of the billiards.
An ideal gas satisfies the law

\[ pV = n R T, \]

where \( p = \text{pressure}, \ T = \text{temperature}, \ V \) is the \text{volume of the container}, and \( R \) is the \text{universal gas constant},

\[ R = 8.315 \text{ Joule/degree centigrade}. \]

\( n \) is the \text{number of molecules} divided by \text{Avogadro’s number} \( N_A \), the number of \text{atoms} in a \text{gram of hydrogen}.

As a physical theory, the ideal gas law was \text{extraordinarily successful}, correctly describing the behavior of many \text{actual gases} over a wide range of \text{temperatures and pressures}.
One weakness of the kinetic theory of gases was that it only dealt with ratios of numbers of atoms or molecules. So atoms took on a certain abstract quality. If you imagined an alternate universe in which the number of atoms per unit weight was multiplied by a thousand, the behavior of gases (and thus actual gases) would be completely unaffected!

So if the absolute scale of an atom was never important, should they be considered real at all? Or were they ultimately like Leibnitz’s infinitesimals – just mathematical devices to model the behavior of gases, without any robust reality?

This is the question Einstein was to settle conclusively with his paper on Brownian motion.

To see this, let us set the stage with two more ideas from statistical mechanics.
Thermal Equilibrium

The most basic axiom of thermodynamics states that two systems interacting with one another will eventually approach the same temperature after a sufficiently long time has passed. Boltzmann showed that this principle could be derived from statistical mechanics under broad conditions.

Principle of Equipartition

This principle refers to a gas in which the molecules have internal degrees of freedom – internal structures which can move, oscillate, or vibrate according to mechanical forces within the molecule.

The principle of equipartition states that for a gas in thermal equilibrium, the average energy stored in each available degree of freedom will be equal to the overall kinetic energy of the molecule’s center of mass.

With these two ideas, we can understand Einstein’s theory of Brownian motion.
Einstein’s Idea: Brownian motion comes from collision of macroscopic particles with microscopic ones.

Is it true?
How do you make it quantitative?
What are the observable consequences?
Einstein asked himself, “What happens if you treat large, complicated objects like grains of pollen as if they were large, round gas molecules with an enormous mass and many, many degrees of freedom? “ That is, treat the dissolved pollen like a gas of extremely complicated spherical molecules – in thermal equilibrium with the ambient water. With only this input, he could make a quantitative prediction about the average motion of the grains.
Let us consider the motion for the pollen grain in the $x$ direction, under the influence of the surrounding water. We are going to write an equation for the time derivative of the quantity $x \dot{x}$. Its time derivative will have two pieces – a **macroscopic piece**, which we obtain an expression for by thinking of the sphere as a **classical object moving in continuous water**, and a **microscopic piece**, which we obtain by thinking of the sphere as a **complicated molecule, in thermal equilibrium with the water**.

\[
\frac{d}{dt} [x \dot{x}] = \dot{x}^2 + x \ddot{x}
\]

In order to evaluate these quantities with confidence, average the equation over a time scale of **many molecular collisions**, so that the energy of the molecule can be **continuous trajectory**.
Since the sphere is in thermal equilibrium with the water, the average kinetic energy of its center of mass must be $\frac{1}{2}RT/N_A$, in accordance with the principle of equipartition.

So the first term on the right hand side is given by

$$\dot{x}^2 = \frac{RT}{mN_A}$$

where $m$ is the mass of the pollen grain.

Here we have just used the ideal gas law, the equipartition principle, and the classical formula for the kinetic energy: $E = \frac{1}{2}mv^2$. 
To evaluate the second term, $x\ddot{x}$, we switch points of view and think of the pollen grain as a macroscopic sphere, travelling at some speed through a viscous liquid.

By 1905, there was a well-known hydrodynamic formula for the force on a sphere due to viscous drag from a fluid. For a sphere of radius $r$, the force is proportional to the velocity of the sphere and the viscosity of the fluid, and given by $F = m\ddot{x} = -6\pi \eta r \dot{x}$. So the macroscopic term in the time derivative of $x\ddot{x}$ is

$$x\ddot{x} = -\frac{6\pi \eta r}{m} \dot{x} \dddot{x}$$

Here $\eta$ is the dynamical viscosity coefficient.
Solving for the sphere’s motion

So we have the following differential equation for $x\dot{x}$:

$$\frac{d}{dt} [x\dot{x}] = \frac{RT}{mN_A} - \frac{6\pi \eta r}{m} [x\dot{x}]$$

to which the solution (assuming $x = 0$ at $t = 0$) is:

$$x\dot{x} = \frac{1}{2} \frac{d}{dt} [x^2] \frac{RT}{6\pi \eta r N_A} \left(1 - \exp \left\{ -\frac{t}{t_0} \right\} \right)$$

with $t_0$ defined as the characteristic time scale $t_0 = \frac{m}{6\pi \eta r}$.

Remember, we have used the equipartition formula for $\dot{x}^2$, so this equation holds only in an average sense. Without knowledge of the state of every water molecule in the system, the actual behavior of the grains appears random rather than deterministic.
Features of the solution

At times longer than $t_0$, we can drop the exponential term, to obtain

$$\Delta(t) \equiv \sqrt{x^2 + y^2 + z^2} = \sqrt{3|x|} \sim \sqrt{\frac{RT}{\pi \eta r N_A}} \sqrt{t}$$

The middle equality is again an average, since motions of the particle in the three spatial dimensions should be statistically uncorrelated. We have obtained an expression for the average distance from the origin due to Brownian motion after a time $t$.

Note this behavior has the following desirable features.

- The motion increases with temperature $T$;
- it decreases with increasing viscosity;
- it also decreases with the size of the particles.

All these behaviors agree with the previously observed behavior of Brownian motion.
Notice that the magnitude of the motion directly senses the discreteness of the molecules in the liquid; that is, it is inversely proportional to Avogadro’s number $N_A$.

In the approximation where the number of molecules in a gram of water is infinite, Brownian motion does not occur at all! Einstein’s direct demonstration of the finiteness of $N_A$ disposed permanently of the empiricists’ objection to the molecular theory of heat – that molecules were merely mathematical book-keeping devices.
Conclusion:

means = HAPPY ANNIVERSARY, ALBERT!
Figure 1: Random trajectory of a pollen mote moving by Brownian motion in a liquid at room temperature.
Figure 2: In the statistical theory of liquids, water molecules move with random speeds in random directions. If a macroscopic object like a pollen mote is suspended in the water, some of the water molecules will occasionally hit it, and change its momentum.
Figure 3: Random trajectories of three pollen motes moving by Brownian motion in water at room temperature.
Figure 4: A second random trajectory of a pollen mote moving by Brownian motion in a liquid at room temperature.