

The Brownian Movement and The experimental determination of Boltzmann's constant



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1. Brownian Movement

The Brownian movement was discovered in 1827 by the botanist Robert Brown. While he was studying microscopic life, he noticed little particles of plant pollen jiggling around in the liquid, he was looking at in the microscope. He was experienced enough to realize, that these were not living, but rather small pieces of dirt moving around in the water.

To ascertain that the motion of the particles was not due to organic life, he found a quartz crystal in which there was embedded some small drops of water. Since the crystal was probably several millions years old, it was excluded that any form of life could be inside the water drops.

But inside in the water drops, he could observe the same jiggling of pollen particles.

Since Dalton's (chemical) atomic theory, was first published in 1808, Robert Brown had himself no conceptual foundation to link the movements of the pollen particles to the thermal vibrations of the molecules, which were described theoretically by Ludvig Boltzmann in the late 19'th century.

According to the equipartition principle the average kinetic energy of an atom is given by Boltzmann's formula.

$$(1.1) \quad \langle \frac{1}{2}mv^2 \rangle = \frac{3}{2}kT$$

Where m is the mass of the atom, $k = 1.38110^{-23} J / K$ is Boltzmann's constant, and T is the Kelvin temperature.

This gives a velocity of some hundred meters per second for molecules at room temperature.

Actually Boltzmann's formula holds for any object in thermal equilibrium, so the speed will be very slow even for a object, which is an micron (10^{-6}) in diameter. What we can observe is, however, how far it moves in a longer period of time.

To estimate this, we shall apply a mechanical model of the collision of a tiny pollen and the molecules in the liquid.

2. The random walk

The classical example to introduce the random walk is the drunken sailor problem. The sailor is standing in the middle of a street. He takes a series of N steps at random directions.

Where he will end, no one can say, of course, but we should like to know the mean distance he has reached after the N steps.

For several reasons the mean distance $\langle R \rangle$ is not a practical statistical measurement, so instead we shall calculate the mean of the square of the distance $\langle R^2 \rangle$.

Let \vec{R}_N be the position after N steps, and let \vec{d} be a step, where the length of the step d is constant.

We thus have:

$$(2.1) \quad \vec{R}_N = \vec{R}_{N-1} + \vec{d} \quad \text{and} \quad \vec{R}_N \cdot \vec{R}_N = R_N^2 = (\vec{R}_{N-1} + \vec{d})^2 = R_{N-1}^2 + 2\vec{R}_{N-1} \cdot \vec{d} + d^2$$

If we take the mean we find: $\langle R_N^2 \rangle = \langle R_{N-1}^2 \rangle + d^2$ since the two vectors \vec{R}_{N-1} and \vec{d} are at a random angles to each other, and therefore their scalar product must average to zero.

Since each step has the same numeric size, we have by induction:

$$(2.2) \quad \langle R_N^2 \rangle = Nd^2$$

So the average of the square of the distance to the N 'th position is proportional to the number of steps. Taking the square root, we get:

$$(2.3) \quad \sqrt{\langle R_N^2 \rangle} = \sqrt{Nd}d$$

Statistically this is not the same as $\langle R_N \rangle$. We have namely for any stochastic variable.

$$(2.4) \quad \begin{aligned} \sigma^2(X) &= E(X^2) - E(X)^2 \Rightarrow E(X)^2 = E(X^2) - \sigma^2(X) \Rightarrow \\ E(X) &= \sqrt{E(X^2) - \sigma^2(X)} \neq \sqrt{E(X^2)} \end{aligned}$$

Since each step is taken with the same time interval, the mean square distance proportional to N must also be proportional to the time t .

$$(2.5) \quad \langle R_N^2 \rangle = Nd^2 = \alpha t$$

Our objective is then to find an expression for α based on the kinetic theory of molecules.

3. A Mechanical model for the Brownian movement

We shall first establish the equation of motion for a particle moving in a liquid due to an external force.

When moving in a liquid, there is always a drag force, which for moderate velocities, is directed opposite to the velocity and proportional to the speed.

First consider a motion in one dimension: From Newton's law we have:

$$(2.1) \quad m \frac{d^2x}{dt^2} + \mu \frac{dx}{dt} = F_{ext}$$

μ is the drag coefficient for the liquid in question. It can however be determined experimentally, for example by letting a body sink in the liquid.

Our intention is to apply the same formula when the force is not external, but equal to the irregular forces of the Brownian movement. We shall then try to determine the mean square distance the object goes.

Instead of taking the distances in three dimensions, we shall do the analysis in one dimension.

Clearly, we must have: $\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle$, and therefore the mean square distance is just three times $\langle x^2 \rangle$. The x -component of an irregular force is just as irregular as any other component. So what is the rate of change of x^2 . It is $d(x^2)/dt = 2x(dx/dt)$, so what we have to do is to find the average of the position times the velocity. We shall show that this is a constant.

To do so, we multiply equation (2.1) by x , and take the average.

$$mx \frac{d^2x}{dt^2} + \mu x \frac{dx}{dt} = xF_x$$

The time average of x times the force $\langle xF_x \rangle$ must be zero, since the force from the collisions with the molecules is completely irregular. In the one dimensional case the force is along or opposite directed to x with equal probabilities.

We shall make the following rewriting of the first term in the equation:

$$mx \frac{d^2x}{dt^2} = m \frac{d(x(dx/dt))}{dt} - m \left(\frac{dx}{dt} \right)^2$$

The average of x times the velocity does not change with time, since when it gets to some position it has no longer any remembrance of where it was before, and therefore the rate of change in first term on the left side is zero. Taking the average of the equation, we then find:

$$\begin{aligned} \left\langle m \frac{d(x(dx/dt))}{dt} \right\rangle - \left\langle m \left(\frac{dx}{dt} \right)^2 \right\rangle + \left\langle \mu x \frac{dx}{dt} \right\rangle &= \langle xF_x \rangle \\ - \left\langle m \left(\frac{dx}{dt} \right)^2 \right\rangle + \left\langle \mu x \frac{dx}{dt} \right\rangle &= 0 \\ - m \left\langle \left(\frac{dx}{dt} \right)^2 \right\rangle + \frac{1}{2} \mu \left\langle \frac{dx^2}{dt} \right\rangle &= 0 \\ - \langle mv^2 \rangle + \frac{1}{2} \mu \left\langle \frac{dx^2}{dt} \right\rangle &= 0 \end{aligned}$$

From the kinetic theory of gasses, we know, however, that:

$$\langle \frac{1}{2} mv^2 \rangle = \frac{1}{2} kT \quad (\text{for a one dimensional motion})$$

From which we find:

$$\frac{d\langle x^2 \rangle}{dt} = 2 \frac{kT}{\mu} \quad \text{or} \quad \langle x^2 \rangle = 2 \frac{kT}{\mu} t$$

If we compare this to (2.5): $\langle R_N^2 \rangle = Nd^2 = \alpha t$, we see that $\alpha = 2 \frac{kT}{\mu}$.

Since we have in three dimensions: $\langle \frac{1}{2} mv^2 \rangle = \frac{3}{2} kT$, we find:

$$\langle R^2 \rangle = 6 \frac{kT}{\mu} t$$

This formula was first discovered by Einstein. And it is vitally important because it allows for an experimental value of Boltzmann's constant.

The equation of state of gasses reads: $PV = n_M RT$ n_M = number of moles, and R is the gas constant. The gas constant can easily be determined experimentally. $k = \frac{R}{N_A}$, where N_A is Avogadro's number, which was also unknown in the beginning of the 20'th century.

But by watching the movement of tiny pollen particles in a microscope, one was in fact able to determine Boltzmann's constant, and thereby the hitherto unknown Avogadro's number.

$$N_A = 6.023 \cdot 10^{23} \text{ mol}^{-1}$$