Tracking Brownian Motion Through Video Microscopy

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Date: December 01, 2018

Boltzmann’s constant $k_B$ was measured by observing the Brownian motion of polystyrene spheres in water. An inexpensive monochrome CCD camera and video card were used to create a video of the spheres’ motion. After preprocessing the images, custom routines were used to examine the video and to identify and track the particles from one frame to the next. From the mean squared displacement of the particles versus time, we extracted the value of $k_B$ from the slope, assuming that the drag force on an individual sphere is well modeled by Stokes’ law. By averaging over $N$ even particles, we obtained $k_B = (1.49 \pm 0.07) \times 10^{-23} \text{J/K}$.

I. INTRODUCTION

Brownian motion is the random motion of particles suspended in a fluid (a liquid or a gas) resulting from their collision with the fast-moving molecules in the fluid.[1] This pattern describes a fluid at thermal equilibrium, defined by a given temperature. Within such a fluid there exists no preferential direction of flow as in transport phenomena. More specifically the fluid’s overall linear and angular momenta remain null over time. It is important also to note that the kinetic energies of the molecular Brownian motions, together with those of molecular rotations and vibrations sum up to the calorico component of a fluid’s internal energy.

This motion is named after the botanist Robert Brown, who was the most eminent microscopist of his time. In 1827, while looking through a microscope at pollen of the plant Clarksia pulchella immersed in water, the triangular shaped pollen burst at the corners, emitting particles which he noted jiggled around in the water in random fashion. He was not able to determine the mechanisms that caused this motion. Atoms and molecules had long been theorized as the constituents of matter, and Albert Einstein published a paper in 1905 that explained in precise detail how the motion that Brown had observed was a result of the pollen being moved by individual water molecules, making one of his first big contributions to science. This explanation of Brownian motion served as convincing evidence that atoms and molecules exist, and was further verified experimentally by Jean Perrin in 1908. The direction of the force of atomic bombardment is constantly changing, and at different times the particle is hit more on one side than another, leading to the seemingly random nature of the motion.

II. THEORY

There are two parts of theory: the first part consists in the formulation of a diffusion equation for Brownian particles, in which the diffusion coefficient is related to the mean squared displacement of a Brownian particle, while the second part consists in relating the diffusion coefficient to measurable physical quantities.[2]

Classical mechanics is unable to determine this distance because of the enormous number of bombardments a Brownian particle will undergo, roughly of the order of $10^{14}$ collisions per second. Einstein regarded the increment of particle positions in time $\tau$ in a one-dimensional $(x)$ space (with the coordinates chosen so that the origin lies at the initial position of the particle) as a random variable $(x'\tau)$ with some probability density function $\varphi(x')$. Further, assuming conservation of particle number, he expanded the density (number of particles per unit volume) at time $t+\tau$ in a Taylor series,

$$\rho(x,t)\tau + \frac{\partial \rho(x)}{\partial t} + \cdots = \rho(x,t+\tau)$$

(1)

$$\int_{-\infty}^{+\infty} \rho(x-x',t) \cdot \varphi(x') dx' = E_{x'}[\rho(x,t+\tau)]$$

(2)

$$\int_{-\infty}^{+\infty} \rho(x,t) \cdot \varphi(x') dx' - \frac{\partial \rho}{\partial x} \int_{-\infty}^{+\infty} x' \cdot \varphi(x') dx'$$

(3)

$$\varphi(x')\int_{-\infty}^{+\infty} \frac{x'^2}{2} \cdot \varphi(x') dx' + \cdots$$

(4)

here the Eq 2. is by definition of $\varphi$. The integral in the first term is equal to one by the definition of probability, and the second and other even terms (i.e. first and other odd moments) vanish because of space symmetry. What is left gives rise to the following relation:

$$\frac{\partial \rho}{\partial t} = \frac{\partial^2 \rho}{\partial x^2} \int_{-\infty}^{+\infty} \frac{x'^2}{2\tau} \cdot \varphi(x') dx' + \text{higher-order moments}$$

(5)

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Where the coefficient before the Laplacian, the second moment of probability of displacement \( x^2 \), is interpreted as mass diffusivity \( D \):

\[
D = \int_{-\infty}^{\infty} \frac{2}{\pi} \int_{0}^{\infty} \frac{r}{x^2} e^{-r^2/x^2} \, dr \, dx.
\]

Then the density of Brownian particles \( \rho \) at point \( x \) at time \( t \) satisfies the diffusion equation:

\[
\frac{\partial \rho}{\partial t} = D \frac{\partial^2 \rho}{\partial x^2},
\]

assuming that \( N \) particles start from the origin at the initial time \( t = 0 \), the diffusion equation has the solution

\[
\rho(x, t) = \frac{N}{\sqrt{4\pi D t}} e^{-x^2/(4Dt)}.
\]

This expression (which is a normal distribution with the mean \( \mu = 0 \) and variance \( \sigma^2 = 2Dt \) usually called Brownian motion \( B_t \)) allowed Einstein to calculate the moments directly. The first moment is seen to vanish, meaning that the Brownian particle is equally likely to move to the left as it is to move to the right. The second moment is, however, non-vanishing, being given by

\[
\langle x^2 \rangle = 2Dt.
\]

We can also write the mean squared displacement in two dimensions,

\[
\langle x^2 \rangle = 4Dt.
\]

This expresses the mean squared displacement in terms of the time elapsed and the diffusivity. From this expression Einstein argued that the displacement of a Brownian particle is not proportional to the elapsed time, but rather to its square root. His argument is based on a conceptual switch from the "ensemble" of Brownian particles to the "single" Brownian particle. We can speak of the relative number of particles at a single instant just as well as of the time it takes a Brownian particle to reach a given point. The second part of theory relates the diffusion constant to physically measurable quantities, such as the mean squared displacement of a particle in a given time interval. This result enables the experimental determination of Avogadro's number. Einstein analyzed a dynamic equilibrium being established between opposing forces. The beauty of his argument is that the final result does not depend upon which forces are involved in setting up the dynamic equilibrium.

Consider, for instance, particles suspended in a viscous fluid in a gravitational field. Gravity tends to make the particles settle, whereas diffusion acts to homogenize them, driving them into regions of smaller concentration. Under the action of gravity, a particle acquires a downward speed of \( v = \mu mg \), where \( m \) is the mass of the particle, \( g \) is the acceleration due to gravity, and \( \mu \) is the particle's mobility in the fluid. George Stokes had shown that the mobility for a spherical particle with radius \( r \) is \( \mu = 1/6\pi \eta r \), where \( \eta \) is the dynamic viscosity of the fluid. In a state of dynamic equilibrium, and under the hypothesis of isothermal fluid, the particles are distributed according to the barometric distribution

\[
\rho = \rho_0 e^{-\frac{\rho}{\rho_0}},
\]

where \( \rho_0 \) is the difference in density of particles separated by a height difference of \( h \). The Boltzmann constant \( k_B \) is Boltzmann's constant (namely, the ratio of the universal gas constant, \( R \), to Avogadro's number, \( N_A \)), and \( T \) is the absolute temperature. Avogadro's number is to be determined. Dynamic equilibrium is established because the more that particles are pulled down by gravity, the greater the tendency for the particles to migrate to regions of lower concentration. The flux is given by Fick's law,

\[
J = -D \frac{\partial \rho}{\partial h},
\]

where \( J = \rho v \). Introducing the formula for \( \rho \), we find that

\[
v = \frac{Dr\rho_0}{k_B T}.
\]

In a state of dynamical equilibrium, this speed must also be equal to \( v = \mu mg \). Notice that both expressions for \( v \) are proportional to \( mg \), reflecting that the derivation is independent of the type of forces considered. Similarly, one can derive an equivalent formula for identical charged particles of charge \( q \) in a uniform electric field of magnitude \( E \), where \( mg \) is replaced with the electrostatic force \( qE \). Equating these two expressions yields a formula for the diffusivity, independent of \( mg \) or \( qE \) or other such forces:

\[
\frac{\langle x^2 \rangle}{4t} = D = \frac{\mu k_B T}{N} = \frac{\mu RT}{6\pi \eta r N_A}.
\]

Here the first equality follows from the first part of the theory, the third equality follows from the definition of Boltzmann's constant \( \mu k_B = R/N_A \), and the fourth equality follows from Stokes's formula for the mobility. By measuring the mean squared displacement over a time interval along with the universal gas constant \( R \), the temperature \( T \), the viscosity \( \eta \), and the particle radius \( r \), Avogadro's number \( N_A \) can be determined.

**III. EXPERIMENTAL SETUP**

We used an inexpensive American Optical Spencer Microscope. The image from the objective lens is directly imaged onto the CCD. We calibrated the image using a Motic calibrating slide and obtained values of 0.207101 \( \mu m/\mu m \) horizontal and 0.208550 \( \mu m/\mu m \) vertical. To observe Brownian motion, we used 0.75 \( \mu m \) diameter polystyrene micro-spheres. One drop of the microsphere solution was placed on a cover slip and the cover
IV. RESULTS AND DISCUSSION

To obtain Boltzmann's constant, we need to plot the mean squared displacement versus time. From the calculations performed in section VII of our manuscript, we have

\[ \Delta x^2 = \frac{8}{3} k_B T \frac{t}{m} \]

\[ \Delta y^2 = \frac{8}{3} k_B T \frac{t}{m} \]

We can use these equations to calculate the value of \( k_B \) for each temperature and viscosity.

The most difficult aspect of determining \( k_B \) is solving for the time at which the mean squared displacement is at its maximum. This value can be approximated using Equation (1). The square of the displacement is therefore

\[ (\Delta x^2)^2 = \left( \frac{8}{3} k_B T \frac{t}{m} \right)^2 \]

\[ (\Delta y^2)^2 = \left( \frac{8}{3} k_B T \frac{t}{m} \right)^2 \]

At the end of a successful run, the script will leave some variables (\( k_B \), \( N \), and \( D \)) in the main workspace.
$D = (7.1 \pm 0.3) \times 10^{-13} \text{ m}^2 \text{s}^{-1}$.

Some care must be taken when calculating the sphere's self-diffusivity $D$, due to the effects of the walls. For a sphere far from two parallel walls, the modified self-diffusivity is given by \cite{4}

$$D' = D \left[ 1 - \frac{9r}{16} \left( \frac{1}{x_1} + \frac{1}{x_2} \right) \right]$$  \hspace{1cm} (16)

where $x_1$ and $x_2$\cite{10} are the distances from the sphere to the two walls. The distance $d$ between the wall is $d = 0.11 \pm 0.01 \text{ mm}$ (by measuring the width of tape which is used between cover slip and glass slide measured by Screw gauge) and $d = 0.116 \text{ mm}$ (measured using fine focusing knob of Microscope)\cite{11} Applying Eq. (16) yields a wall-corrected value which is 0.95% smaller:

$$D' = (6.99 \pm 0.30) \times 10^{-13} \text{ m}^2 \text{s}^{-1}$$

which also gives us the corrected value of $k_b$ as:

$$k_b = (1.49 \pm 0.07) \times 10^{-23} \text{ J/K}.$$  \hspace{1cm} (17)

Error in the value of Boltzmann's constant is 8% which is good in agreement with the sensitivity of our experimentation.

\[\text{Conclude} \] Conclusion is missing.