Diffusion and Boltzmann's constant

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We'll use modern microscopy techniques to measure Boltzmann's constant by looking at the diffusion of microspheres suspended in fluid and by looking at the diffusion of quantum dots attached to PE lipids in supported membranes. We will follow the methodology from [NALS03]. The paper is pretty good, and we'll do both types of analysis mentioned in the article, meaning that we'll want to use both equation (3) and equation (5) from the paper. Here's where those come from. This treatment is known as Stokes-Einstein diffusion.

1 The Langevin Equation

We've spent a lot of the class so far learning the lesson of statistical physics: we can determine an enormous amount of physics related to "large" systems by looking at average properties. Here, we apply the same thinking to dynamics. If we want to describe the motion of a grain of pollen floating on a pond (or a microsphere in solution, or a lipid in a membrane), we know that we'll need some sort of differential equation. The statistical physics trick is that we'll want a *stochastic* differential equation. That is, we'll want our differential equation to have a *random* term representing the interaction of our pollen with the water. The specific type of differential equation we'll want is called a Langevin equation. Don Lemons has written a fantastic introduction to stochastic processes [LL02] and MacDonald [Mac62] has a wonderful small book as well if this topic catches your interest. Reif [RR65] also has a nice derivation starting in §15.5 and we follow it below.

We'll treat a one-dimensional system, and the first goal is to get the Langevin equation

$$m\frac{dv}{dt} = -\zeta v + \eta(t) \tag{1}$$

In looking at (1), the two terms on the right hand side are new to us. The first of these a) slows us down and b) is proportional to velocity, and so is known as a "velocity-dependent drag force" and ζ is called the "drag coefficient". Although we won't use it here, the quantity $1/\zeta$ is called the "mobility" and is typically written as μ. The second is our stochastic, or "noise" term, a rapidly fluctuating force due to the environmental water molecules (the Greek letter eta is chosen because η looks like the "n" from "noise").

In general, we start with Newton's second law:

$$m\frac{d^2x}{dt^2} = m\frac{dv}{dt} = F \tag{2}$$

and we will try to say some smart things about F that will let us write (2) as (1).

On the statistical side, if F is the force on our microsphere due to the surrounding waters, we'd like to consider the average of a large number N of identically prepared systems, finding the average force at a specific time t_1 on our particle as

$$\langle F(t_1)\rangle \equiv \frac{1}{N}\sum_{n=1}^{N} F^{(n)}(t_1) \tag{3}$$

where n indexes the identically prepared systems. If we assume that $F(t)$ is rapidly fluctuating, it must then be true that v is also rapidly fluctuating.

The physical insight here is that we can then break v up into two pieces:

$$v = \langle v\rangle + \tilde{v} \tag{4}$$

where $\langle v\rangle$ is the (slowly varying) ensemble average velocity, and $\tilde{v}$ a rapidly fluctuating term with mean zero. The key thing here is that, if we want the long-time behavior of our particle, the relative *magnitudes* of $\langle v\rangle$ and $\tilde{v}$ don't matter. In fact, the microscopic world is turbulent and extremely violent. Living in the macroscopic world, we don't usually think about such things, but the forces bombarding very small objects result in $\tilde{v}$'s that are typically much larger than $\langle v\rangle$'s.

We can use the same sort of physical insight to the force acting on the particle:

$$F = \langle F\rangle + \tilde{F} \equiv \langle F\rangle + \eta \tag{5}$$

We're almost done at this point, so take a quick look back at (1) and (2). We have the rapidly-varying part, but we need to be a little more detailed in our treatment of the slowly-varying part. We don't usually talk about force as a function of velocity, but there's no reason not to. In fact, (2) makes it quite clear that it's reasonable to do so.

If $\langle F\rangle$ is the slowly-varying part of F, it must be a function of the slowly-varying part of v, $\langle v\rangle$. We know this because, in equilibrium, if $\langle v\rangle$ is zero, must find $\langle F\rangle = 0$. Being Physicists, we immediately think to expand $\langle F(\langle v\rangle)\rangle$ (for the next equation, we'll use overbars to represent averages, because $\overline{F}(\bar{v})$ looks much clearer than $\langle F(\langle v\rangle)\rangle$) in a power series:

$$\overline{F}(\bar{v}) = \sum_{k=0}^{\infty} a_0 + a_1\bar{v} + a_2\bar{v}^2 + a_3\bar{v}^3 + ... \tag{6}$$

If we assume that our system is unbiased (that is, that the constant term in (6) is zero), our first non-zero term is the linear term. Renaming a_1 to be $-\zeta$ where the explicit minus sign indicates that our environmental forces will tend to slow an object down, we have our velocity-dependent drag force[1]:

$$\langle F\rangle = -\zeta\langle v\rangle \tag{7}$$

Plugging 7 into the right hand side of 5, and plugging the result into the right hand side of 2, we get

$$m\frac{d^2x}{dt^2} = m\frac{dv}{dt} = F = \langle F\rangle + \eta = -\zeta\langle v\rangle + \eta$$

which, looking at the 2nd and 5th parts, is the Langevin equation that we wanted!

In the presence of an external force, this becomes

[1]Actually, the derivation here is sweeping some things under the rug. Langevin's 1908 derivation just *assumed* that one could model the average force from the environment as a velocity-dependent drag. That's a perfectly physical reasonable assumption on its own. More rigorously, one can derive the generalized Langevin equation (GLE, see, for example, [Tuc08]), and from it the Langevin equation used here.

$$m\frac{dv}{dt} = F_{ext} - \zeta v + \eta(t) \tag{8}$$

and the slowly-varying part becomes

$$m\frac{d\langle v\rangle}{dt} = F_{ext} - \zeta \langle v\rangle \tag{9}$$

2 Mean-square displacement

As with the previous section, this follows [RR65] §15.6. So, after having derived the equation of motion for our particle

$$m\frac{dv}{dt} = -\zeta v + \eta(t)$$

what sorts of quantities can we calculate? In absence of an external force, it seems pretty clear that $\langle x\rangle = 0$ in thermal equilibrium, so we'd better turn towards higher moments. The most commonly useful of these is the mean-square displacement, $\langle x^2\rangle$.

The key insight we'll need in order to find $\langle x^2\rangle$ is that we already know something about average values! In particular, the equipartition theorem tells us that the kinetic energy, $\frac{1}{2}mv^2$, ought to have average value $\frac{1}{2}kT$. If we write v as $\dot{x}$ and multiply both of those by two, and hope that for our sanity mass does not fluctuate, we have

$$m\left\langle \dot{x}^2\right\rangle = kT \tag{10}$$

If you haven't recently taken a probability/statistics class, two reminders are in order. First, we need to be careful with averages, as $\langle x\rangle^2 \neq \langle x^2\rangle$. Second, we often use the product rule to do things like multiply both sides of

$$m\frac{d\dot{x}}{dt} = -\zeta\dot{x} + \eta(t) \tag{11}$$

by x specifically so that we can get an equation involving $\dot{x}^2$:

$$mx\frac{d\dot{x}}{dt} = m\left[\frac{d}{dt}(x\dot{x}) - \dot{x}^2\right] = -\zeta x\dot{x} + x\eta(t) \tag{12}$$

We're now in a position to take the ensemble average of both sides of this equation. OK, a third reminder: the ensemble average of the sum of two quantities is the sum of their respective ensemble averages. If two quantities are independent, the ensemble average of their product is the product of their ensemble averages. In particular, looking at the right hand side of our equation,

$$\langle -\zeta x\dot{x} + x\eta(t)\rangle = \langle -\zeta x\dot{x}\rangle + \langle x\eta(t)\rangle = -\zeta\langle x\dot{x}\rangle + \langle x\rangle\langle\eta(t)\rangle = -\zeta\langle x\dot{x}\rangle \tag{13}$$

where the last equality comes from the fact that the expectation value of our randomly fluctuating force is, by definition, zero. If we rearrange (12) as

$$m\frac{d}{dt}(x\dot{x}) = m\dot{x}^2 - \zeta x\dot{x} + x\eta(t) \tag{14}$$

we can take ensemble averages and use (10) to write[2]

$$\begin{aligned}
\left\langle m\frac{d}{dt}(x\dot{x})\right\rangle &= \left\langle m\dot{x}^2 - \zeta x\dot{x} + x\eta(t)\right\rangle & (15)\\
m\frac{d}{dt}\langle x\dot{x}\rangle &= m\left\langle \dot{x}^2\right\rangle - \zeta\langle x\dot{x}\rangle \\
m\frac{d}{dt}\langle x\dot{x}\rangle &= kT - \zeta\langle x\dot{x}\rangle \\
\frac{d}{dt}\langle x\dot{x}\rangle &= \frac{kT}{m} - \frac{\zeta}{m}\langle x\dot{x}\rangle & (16)
\end{aligned}$$

That last line may look a little funny, but it's just an ODE in $\langle x\dot{x}\rangle$, which is something we surely know how to solve:

$$\langle x\dot{x}\rangle = Ce^{-\frac{\zeta}{m}t} + \frac{kT}{m}\frac{m}{\zeta} \equiv Ce^{-\frac{1}{\tau}t} + \frac{kT}{\zeta} \tag{17}$$

where C is a constant of integration, and $\tau = \frac{m}{\zeta}$ is the characteristic time. Before we plug in some initial conditions, note that $\langle x\dot{x}\rangle$ isn't a completely foreign quantity:

$$\frac{1}{2}\frac{d\left\langle x^2\right\rangle}{dt} = \langle x\dot{x}\rangle \tag{18}$$

Now, as far as our initial conditions go, we want $\left\langle x^2\right\rangle$ to be the mean-square displacement of a particle, so it makes sense to set $x(t=0)=0$. Plugging that into (17) gives

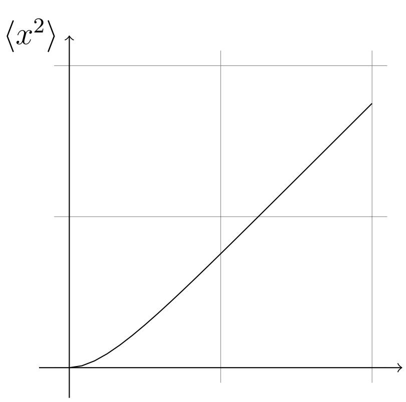
$$0 = C + \frac{kT}{\zeta} \tag{19}$$

so we know $C = -\frac{kT}{\zeta}$ and we can rewrite (17) as

$$\langle x\dot{x}\rangle = \frac{1}{2}\frac{d\left\langle x^2\right\rangle}{dt} = \frac{kT}{\zeta}(1 - e^{-\frac{1}{\tau}t}) \tag{20}$$

and we can finally get an equation for $\left\langle x^2\right\rangle$ by integrating once:

$$\left\langle x^2\right\rangle = \frac{2kT}{\zeta}\left[t - \tau(1 - e^{-\frac{1}{\tau}t})\right] \tag{21}$$



[2]OK, fine, a fourth thing to remember: you can commute the time derivative inside an ensemble average. To prove this to yourself, write the average out as an explicit sum and note that taking the derivative of the sum is just taking the sum of the derivatives of the individual terms.

At short time scales, that looks parabolic, and is called "ballistic" diffusion. At long time scales, that looks linear, and is called "normal" diffusion. If we plotted this on a loglog scale, we would indeed see two linear regions with slopes 2 and 1 respectively.

We can see this explicitly. If $t < \tau$, we can expand

$$e^{-\frac{1}{\tau}t} = 1 - \frac{1}{\tau}t + \frac{1}{2}\frac{1}{\tau^2}t^2 + ... \tag{22}$$

and we make our "short" time scale explicit as $t \ll \tau$, where we can truncate the series as above and (21) becomes

$$\langle x^2 \rangle \approx \frac{2kT}{\zeta}\left[t - \tau(1 - 1 + \frac{1}{\tau}t - \frac{1}{2}\frac{1}{\tau^2}t^2\right] = kT\frac{1}{\tau\zeta}t^2 = \frac{kT}{m}t^2 \tag{23}$$

We can now see why this regime is called "ballistic": the particle behaves as a free particle with constant velocity $v = \sqrt{kT/m}$. Meanwhile, on long time scales $t \gg \tau$, the exponential term in (21) tends towards zero, yielding

$$\langle x^2 \rangle = \frac{2kT}{\zeta}\left[t - \tau\right] \approx \frac{2kT}{\zeta}t \tag{24}$$

From your statistics classes, you should recognize this as the exact same equation as a particle performing a random walk. Indeed, we expect a random walker to diffuse with

$$\langle x^2 \rangle = 2Dt \tag{25}$$

in one dimension, so we've found an equation for our diffusion constant,

$$D = \frac{kT}{\zeta} \tag{26}$$

The "Stokes" part of the picture involves classical *macroscopic* hydrodynamics showing that, for a sphere of radius a in a medium of viscosity η,

$$\zeta = 6\pi\eta a \tag{27}$$

so we can write (24) as

$$\langle x^2 \rangle = \frac{kT}{3\pi\eta a}t \tag{28}$$

and we're finally ready to analyze some data! We take experimental data, look at a plot of mean-square displacement vs. time, and extract the diffusion constant from the slope. Knowing the viscosity of our media and the temperature of the experiments then allows us to determine Boltzmann's constant, all from watching grains of pollen diffuse in water as Perrin did in his famous 1910 work.

3 Potential projects

If this sort of thing strikes your fancy, you could certainly do an independent project on related matters. Specific topics might include

- The generalized Langevin equation
- Fluctuation-dissipation theorems
- Fokker-Planck equations
- Green-Kubo functions
- Einstein's 1905 paper and Langevin's 1908 paper
- Computer simulations of diffusion
- Diffusion as a function of probability distributions

4 Thanks

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References

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