

DIFFUSION AND BROWNIAN MOTION

Microscopically, nothing is ever still. Molecules of perfume from an open bottle will slowly **diffuse** across a room. Chemicals will spread through your cells. As Robert Brown observed over a century ago, microscopic particles in pollen grains and particles of dust in a cup of water will jitter endlessly, subject to what we now call Brownian motion. Diffusion and Brownian Motion are some of the most ubiquitous processes in physics, chemistry, and biology; conceptual extensions to other “random” processes are also found throughout mathematics and economics. We’ll examine the properties of diffusion. Much of this discussion, especially on the Einstein-Smoluchowski relation, follows Berg’s excellent book [1].

Random Walks

As I walk down the street, the distance, x , I travel is linearly proportional to the number of steps, N , that I take; x is also proportional to the time, t , that I spend walking. This is not the case, however, for a microscopic object – e.g. a perfume molecule in the air, or a microparticle in a dish of water. These objects are constantly buffeted by the molecules around them, a consequence of the molecular nature of matter and also of finite temperature (as we’ll see below). They exhibit random walks, where each “step” is in a random direction relative to the one that preceded it. (Of course, we can have both random and directed motion – for example if gravity pulls in one direction, “biasing” our random walk. We’ll consider here unbiased random walks, however.) How are x and t related for a random walker?

The canonical random walker, always invoked as an example, is the “drunken sailor” who starts at a lamppost at position $x = 0$ and, every τ seconds¹, randomly moves left or right by one step of size δ . (We’re considering a one-dimensional walk, for simplicity. The 2D and 3D cases are very similar.) After many (N) steps, where does the sailor end up?

¹ Throughout this document, the symbol τ will refer to this time step, **not** the temperature. None of our “final” relations will refer to τ , so we needn’t retain this as a symbol that we’ll make use of. We’ll write $k_B T$ for the temperature, using Boltzmann’s constant and the conventional temperature, T .

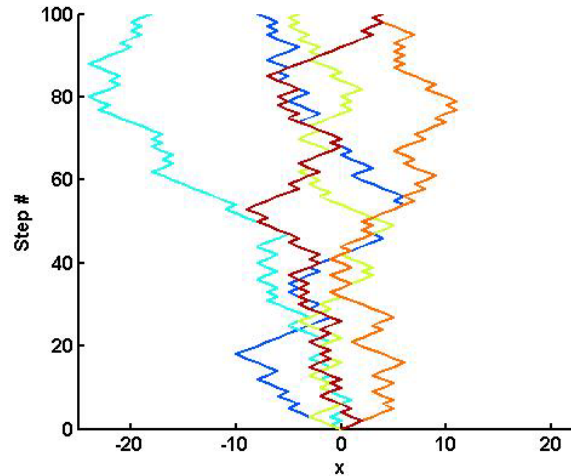


Figure 1. Five random walks. The walker's position is plotted versus step number, for $N = 100$ steps.

The answer, as for all these sorts of statistical questions like this, is that we don't know where the sailor ends up – it's a random process! (See Figure 1 for a few random walk trajectories.) We can, however, examine the **probabilities** of ending up in various places. We can consider lots of random walkers, and take the average of all of their trajectories to get at “average” properties.

On average, our sailor will get nowhere ($x = 0$), being equally likely to take leftward as rightward steps. So $\langle x \rangle = 0$, where “ $\langle \ \rangle$ ” indicates the average over many walks. See Figure 2 for plots of many random walks, as well as a histogram of the final positions – note that the distribution is peaked at $x = 0$.

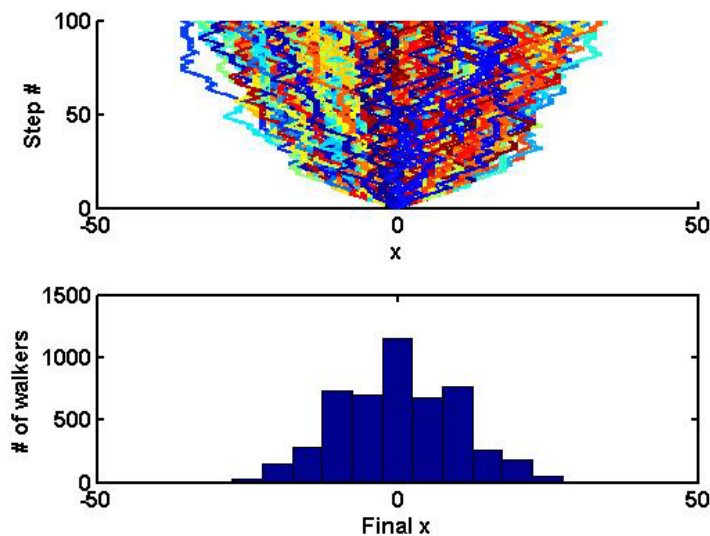


Figure 2. Five thousand random walks, and a histogram of the walkers' final positions. The distribution (for a large number of walkers) is Gaussian in form, and is centered at zero – $x = 0$ is the most probable destination. The distribution has a finite width, however, that is an indicator of the distance traveled during a “typical” random walk.

But the sailor does move and is certainly more likely to cover more and more ground as time goes on. How can we characterize this? Let's ask what the average value of $x^2(N)$ – the mean distance-squared from the lamppost after N steps – is. Since $x(N) = x(N-1) \pm \delta$,

$$x^2(N) = [x(N-1) \pm \delta]^2 = x^2(N-1) \pm 2\delta x(N-1) + \delta^2. \text{ The average value:}$$

$\langle x^2(N) \rangle = \langle x^2(N-1) \rangle \pm 2\delta \langle x(N-1) \rangle + \delta^2$. The middle term is zero, as we noted above, so $\langle x^2(N) \rangle = \langle x^2(N-1) \rangle + \delta^2$. At each step, the mean-squared-displacement increases by **one** step-squared. Since $\langle x^2(0) \rangle = 0$, $\langle x^2(1) \rangle = \delta^2$, $\langle x^2(2) \rangle = 2\delta^2$, etc. We find that

$$\boxed{\langle x^2(N) \rangle = N\delta^2}.$$

The characteristic distance traveled is $\langle x^2(N) \rangle^{1/2}$: We see that

$$\boxed{\langle x^2(N) \rangle^{1/2} \propto N^{1/2}}.$$

Each step takes some amount of time, τ ; the total time $t = N\tau$, so:

$$\boxed{\langle x^2(t) \rangle = \left(\frac{\delta^2}{\tau}\right)t}, \text{ and } \boxed{\langle x^2(t) \rangle^{1/2} \propto t^{1/2}}.$$

Rather than increasing linearly with time, the characteristic distance our random walker travels increases as the square root of time. To go twice as far, the walker needs to take four times as many steps. This is the key characteristic of Brownian motion!

There are other issues we won't go into – questions like, if there's a cliff 100δ away from the lamppost, what are the odds the sailor will tumble over it after N steps? (As you might guess, this is important for the “capture” of diffusive molecules, as well as the survival of drunken sailors.)

We'll define a diffusion coefficient, $D \equiv \frac{\delta^2}{2\tau}$, and therefore write:

$$\boxed{\langle x^2(t) \rangle = 2Dt} \text{ for a 1D random walk.}$$

In two and three dimensions, one can show (quite easily) that

$$\boxed{\langle r^2(t) \rangle = 4Dt} \text{ [2D random walk; } r^2 = x^2 + y^2 \text{]}$$

$$\boxed{\langle r^2(t) \rangle = 6Dt} \text{ [3D random walk; } r^2 = x^2 + y^2 + z^2 \text{]}$$

A small molecule in room-temperature water has $D \approx 10^{-3} \text{ mm}^2/\text{s}$, and so will diffuse about $10 \mu\text{m}$ (10×10^{-6}), a typical diameter of one of your cells, in about 20 ms. The same molecule would diffuse 10 mm in 20,000 s (5 hours). Since time scales as distance squared, long “trips” take a very long time!

Diffusion and Temperature

We've discussed our random walker, and related the diffusion coefficient D to the length (δ) and time (τ) required for a step. How can we connect this to the environment experienced by microscopic objects? And what does this have to do with temperature? These questions take us to Switzerland, in 1905.

Einstein published three groundbreaking papers in 1905. In one, certainly the most famous among non-physicists, he invented / discovered special relativity. In another, he explained the photoelectric effect by invoking the quantum nature of photons – for this, he received the Nobel Prize. In the third, he explained the molecular underpinnings of Brownian Motion, one of the most important feats in statistical mechanics. Remember that at the time, the very existence of “molecules” was still controversial!

We'll take a brief look at the nature of the diffusion coefficient. Consider a particle of mass m in a fluid. Every τ seconds it takes a step (let's say one-dimensionally) with velocity $\pm v_x = \pm \delta / \tau$ – i.e. it performs a random walk as above. This velocity, v_x , is determined by the temperature of the fluid – a fundamental result from statistical mechanics that we'll derive later in the course. The fact that the object is in thermal equilibrium with the molecules of the fluid means that the kinetic energy of its motion in the x -direction, $\frac{1}{2}mv_x^2$, equals $\frac{1}{2}k_B T$, where k_B is Boltzmann's constant and T is the absolute temperature (e.g. measured in Kelvin). Thus $mv_x^2 = k_B T$.

Let's say the particle is subject to some externally applied force, F_x , acting in the x direction. The force leads to an acceleration $a = F_x / m$. The particle undergoes its random walk, and in time τ moves a distance $\delta_+ = v_x \tau + \frac{1}{2}a\tau^2$ or $\delta_- = -v_x \tau + \frac{1}{2}a\tau^2$. Each is equally probable, so the particle drifts with velocity $v_d = \frac{1}{2} \frac{(\delta_+ + \delta_-)}{\tau} = \frac{1}{2}a\tau = \frac{1}{2} \frac{F_x}{m} \tau$. The drift velocity is linearly proportional to the force – as we noted last quarter, this is characteristic of highly damped motion – which is the case anyway for small objects in fluids. We write $F_x = bv_d$, where b is the drag coefficient. With the symbols above, $b = \frac{2m}{\tau}$.

Recalling from above that $D = \frac{\delta^2}{2\tau}$, we combine the four boxed expressions above to give

$$b = \frac{k_B T}{D}, \text{ or } D = \frac{k_B T}{b}.$$

This is known as the **Einstein-Smoluchowski relation**. It is remarkably general, and does not depend on nature of the particle or details of the forces acting on it. In deriving it, we “made up” discrete steps of size δ and duration τ , and also made up an external force about which we knew nothing. All of these parameters, however, drop out of the analysis! The Einstein-Smoluchowski relation combines a macroscopic thermodynamic quantity (the temperature, T) and a “mechanical” quantity (the drag coefficient, b) to give the diffusion coefficient.

For a sphere of radius a in a fluid of viscosity η , the drag coefficient $b = 6\pi\eta a$. (This might look familiar from last quarter.) Therefore $D = \frac{k_B T}{6\pi\eta a}$. As Einstein wrote in 1905 [2]: “The coefficient of diffusion of the suspended substance therefore depends (except for universal constants and the absolute temperature) only on the coefficient of viscosity of the liquid and on the size of the suspended particles.”

Some numbers: A microsphere of radius $1\mu\text{m}$ (around the size of a bacterium) in water at room temperature has $D \approx 2 \times 10^{-7} \text{ mm}^2/\text{s} = 2 \times 10^{-1} \mu\text{m}^2/\text{s}$. It would take around a minute to diffuse $10 \mu\text{m}$.

The Einstein-Smoluchowski equation is a special case of “fluctuation-dissipation relations” that are very important in physics, revealing relationships between parameters that characterize fluctuations (here, D) and the dissipation of energy (here, b).

References

- [1] Berg, Howard C., *Random Walks in Biology* (Princeton University Press, Princeton NJ, 1993).
- [2] Einstein, Albert, *Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen*, or *On the Motion—Required by the Molecular Kinetic Theory of Heat—of Small Particles Suspended in Stationary Liquid*, *Annalen der Physik* **17**, 549, (1905).