

Random Walks, Friction, and Diffusion

It behoves us always to remember that in physics it has taken great minds to discover simple things. They are very great names indeed which we couple with the explanation of the path of a stone, the droop of a chain, the tints of a bubble, the shadows in a cup.

— D'Arcy Thompson, 1917

Section 3.2.5 argued that the origin of friction was the conversion of organized motion to disordered motion by collisions with a surrounding, disordered medium. In this picture, the First Law of thermodynamics is just a restatement of the conservation of energy. To justify such a unifying conclusion, we'll continue to look for nontrivial, testable, quantitative predictions from the model.

This process is not just an exercise in retracing others' historical footsteps. Once we understand the origin of friction, a wide variety of other **dissipative processes**—those that irreversibly turn order into disorder—will make sense, too:

- The diffusion of ink molecules in water erases order; for example, any pattern initially present disappears (Section 4.4.2).
- Friction erases order in the initial directed *motion* of an object (Section 4.1.4).
- Electrical resistance runs down your flashlight batteries, making heat (Section 4.6.4).
- The conduction of heat erases the initial separation into hot and cold regions (Section 4.4.2').

In every case just listed, organized kinetic or potential energy gets degraded into disorganized motion, by collisions with a large, random environment. The paradigm we will study for all these processes will be the physics of the random walk (Section 4.1.2).

None of the dissipative processes listed in the preceding paragraph matters much for the Newtonian questions of celestial mechanics. But all will turn out to be of supreme importance in understanding the physical world of cells. The difference is that, in cells, the key actors are single molecules or perhaps structures of at most a few thousand molecules. In this nanoworld, the tiny energy $k_B T_r$ is *not* so tiny; the randomizing kicks of neighboring molecules can quickly degrade any concerted motion. For example,

- Diffusion turns out to be the dominant form of material transport on submicrometer scales (Section 4.4.1).
- The mathematics of random walks is also the appropriate language to understand the conformations of many biological macromolecules (Section 4.3.1).
- Diffusion ideas will give us a quantitative account of the permeability of bilayer membranes (Section 4.6.1) and the electrical potentials across them (Section 4.6.3), two topics of great importance in cell physiology.

The Focus Question for this chapter is

Biological question: If everything is so random in the nanoworld of cells, how can we say anything predictive about what's going on there?

Physical idea: The collective activity of many randomly moving actors can be effectively predictable, even if the individual motions are not.

4.1 BROWNIAN MOTION

4.1.1 Just a little more history

Even up to the end of the nineteenth century, influential scientists were criticizing, even ridiculing, the hypothesis that matter consisted of discrete, unchangeable, real particles. The idea seemed to them philosophically repugnant. Many physicists, however, had by this time long concluded that the atomic hypothesis was indispensable for explaining the ideal gas law and a host of other phenomena. Nevertheless, doubts and controversies swirled. For one thing, the ideal gas law doesn't actually tell us how big molecules are. We can take 2 g of molecular hydrogen (one mole) and measure its pressure, volume, and temperature, but all we get from the gas law is the product $k_B N_{\text{mole}}$, not the separate values of k_B and N_{mole} ; thus we don't actually find how *many* molecules were in that mole. Similarly, in Section 3.2 on page 78, the decrease of atmospheric density on Mt. Everest told us that $mg \times 10 \text{ km} \approx \frac{1}{2}mv^2$, but we can't use this to find the mass m of a single molecule— m drops out.

If only it were possible to *see* molecules and their motion! But this dream seemed hopeless. The many improved estimates of Avogadro's number deduced in the century since Franklin all pointed to an impossibly small size for molecules, far below what could ever be seen with a microscope. But there was one ray of hope.

In 1828, a botanist named Robert Brown had noticed that pollen grains suspended in water do a peculiar incessant dance, visible with his microscope. At roughly $1 \mu\text{m}$ in diameter, pollen grains seem tiny to us. But they're enormous on the scale of atoms, and big enough to see under the microscopes of Brown's time (the wavelength of visible light is around half a micrometer). We will generically call such objects **colloidal particles**. Brown naturally assumed that what he was observing was some life process, but being a careful observer, he proceeded to check this assumption. What he found was that:

- The motion of the pollen never stopped, even after the grains were kept for a long time in a sealed container. If the motion were a life process, the grains would run out of food eventually and stop moving. They didn't.

- Totally lifeless particles do exactly the same thing. Brown tried using soot (“deposited in such Quantities on all Bodies, especially in London”) and other materials, eventually getting to the most exotic material available in his day: ground-up bits of the Sphinx. The motion was always the same for similar-size particles in water at the same temperature.

Brown reluctantly concluded that his phenomenon had nothing to do with life.

By the 1860s several people had proposed that the dance Brown observed was caused by the constant collisions between the pollen grains and the molecules of water agitated by their thermal motion. Experiments by several scientists confirmed that this **Brownian motion** was more vigorous at higher temperature, as expected from the relation (average kinetic energy) = $\frac{3}{2}k_B T$ (Idea 3.21). (Other experiments had ruled out other, more prosaic, explanations for the motion, such as convection currents.) It looked as though Brownian motion could be the long-awaited missing link between the macroscopic world of bicycle pumps (the ideal gas law) and the nanoworld (individual molecules). Missing from these proposals, however, was any precise quantitative test.

But the molecular-motion explanation of Brownian motion seems, on the face of it, absurd, as others were quick to point out. The critique hinged on two points:

1. If molecules are tiny, then how can a molecular collision with a comparatively enormous pollen grain make the grain move appreciably? The grain takes steps that are visible in light microscopy and hence are enormous relative to the size of a molecule.
2. Section 3.2 argued that molecules are moving at high speeds, around 10^3 m s^{-1} . If water molecules are about a nanometer in size and closely packed, then each one moves less than a nanometer before colliding with a neighbor. The collision rate is then at least $(10^3 \text{ m s}^{-1})/(10^{-9} \text{ m})$, or about 10^{12} collisions per second. Our eyes can resolve events at rates no faster than 30 s^{-1} . How could we see these hypothetical dance steps?

This is where matters stood when a graduate student was finishing his thesis in 1905. The student was Albert Einstein. The thesis kept getting delayed because Einstein had other things on his mind that year. But everything turned out all right in the end. One of Einstein’s distractions was Brownian motion.

4.1.2 Random walks lead to diffusive behavior

Random walks Einstein’s beautiful resolution to the two paradoxes just mentioned was that *the two problems cancel each other*. To understand his logic, imagine moving a marker on the sidewalk below a skyscraper. Once per second, you toss a coin. Each time you get heads, you move the marker one step to the east; for tails, one step to the west. You have a friend looking down from the top of the building. She cannot resolve the individual squares on the sidewalk; they are too distant for that. Nevertheless, *once*

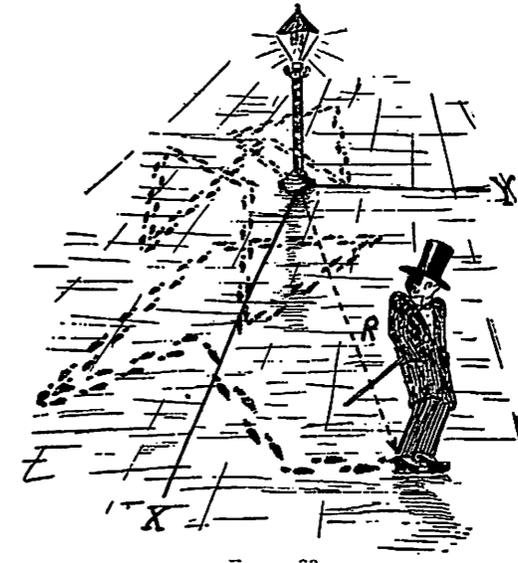


Figure 4.1: (Metaphor.) A random (or “drunkard’s”) walk. [Cartoon by George Gamow, from Gamow, 1961.]

afar. Certainly such events are rare; your friend can check up on your game only every hour or so and still not miss them.

In just the same way, Einstein said, although we cannot see the small, rapid jerks of the pollen grain due to individual molecular collisions, still we can and will see the rare large displacements.¹

The fact that rare large displacements exist is sometimes expressed by the statement that *a random walk has structure on all length scales*, not just on the scale of a single step. Moreover, studying only the rare large displacements will not only confirm that the picture is correct but will also tell us something quantitative about the invisible molecular motion (namely, the value of the Boltzmann constant). The motion of pollen grains may not seem to be very significant for biology, but Section 4.4.1 will argue that thermal motion becomes more and more important as we look at smaller objects—and biological macromolecules are much smaller than pollen grains.

It’s easy to adapt this logic to more realistic motions, in two or three dimensions. For two dimensions, place the marker on a checkerboard and flip *two* coins each second, a penny and a nickel. Use the penny to move the marker east/west as before. Use the nickel to move the marker north/south. The path traced by the marker is then a two-dimensional **random walk** (Figures 4.1 and 4.2); each step is a diagonal across a square of the checkerboard. We can similarly extend our procedure to three dimensions. But to keep the formulas simple, the rest of this section will only discuss the one-dimensional case.

¹ **T₂** What follows is a simplified version of Einstein’s argument. Track-2 readers will have little difficulty

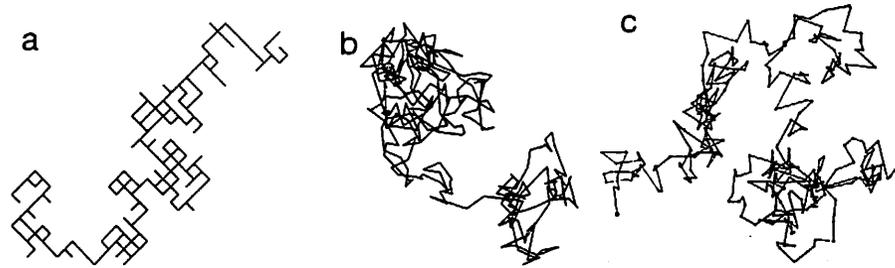


Figure 4.2: (Mathematical functions; experimental data.) (a) Computer simulation of a two-dimensional random walk with 300 steps. Each step lies on a diagonal as discussed in the text. (b) The same with 7500 steps, each 1/5 the size of the steps in (a). The walk has been sampled every 25 steps, giving a mean step size similar to that in (a). The figure has both fine detail and an overall structure: We say there is structure on all length scales. (c) Jean Perrin's actual experimental data from 1908. Perrin periodically observed the location of a single particle, then plotted these locations joined by straight lines, a procedure similar to the periodic sampling used to generate the mathematical graph (b). The field of view is about 75 μm wide. [Simulations kindly supplied by P. Biancaniello; experimental data from Perrin, 1948.]

Suppose our friend looks away for 10 000 s (about three hours). When she looks back, it's quite unlikely that our marker will be exactly where it was originally. For that to happen, we would have to have taken exactly 5000 steps right and 5000 steps left. Just how improbable is this outcome? For a walk of *two* steps, there are two possible outcomes that end where we started (HT and TH), out of a total of $2^2 = 4$ possibilities; thus the probability to return to the starting point is $P_0 = 2/2^2$ or 0.5. For a walk of four steps, there are six ways to end at the starting point, so $P_0 = 6/2^4 = 0.375$. For a walk of 10 000 steps, we again need to find M_0 , the number of different outcomes that land us at the starting point, then divide by $M = 2^{10\,000}$.

Example: Finish the calculation.

Solution: Of the M possible outcomes, we can describe the ones with exactly 5000 heads as follows: To describe a particular sequence of coin tosses, we make a list of which tosses came out heads. This list contains 5000 different integers, (n_1, \dots, n_{5000}) , each less than 10 000. We want to know how many such distinct lists there are.

We can take n_1 to be any number between 1 and 10 000, n_2 to be any of the 9999 remaining choices, and so on, for a total of $10\,000 \times 9999 \times \dots \times 5001$ lists. We can rewrite this quantity as $(10\,000!)/(5000!)$, where the exclamation point denotes the factorial function. But any two lists differing by exchange (or permutation) of the n_i 's are not really different, so we must divide our answer by the total number of possible permutations, which is $5000 \times 4999 \times \dots \times 1$. Altogether, then, we have

$$M_0 = \frac{10\,000!}{5000! \times 5000!} \quad (4.1)$$

distinct lists

Dividing by the total number of possible outcomes gives the probability of landing exactly where you started as $P_0 = M_0/M \approx 0.008$. It's less than a 1% chance.

The probability distribution found in the Example is called the **binomial distribution**. (Some authors abbreviate Equation 4.1 as $M_0 = \binom{10\,000}{5000}$, pronounced "ten thousand choose five thousand.")

Your Turn 4A

You can't do the preceding calculation on a calculator. You could do it with a computer-algebra package, but now is a good time to learn a handy tool: **Stirling's formula** gives an approximation for the factorial $M!$ of a large number M as

$$\ln M! \approx M \ln M - M + \frac{1}{2} \ln(2\pi M). \quad (4.2)$$

Work out for yourself the result for P_0 just quoted, using this formula.

The preceding discussion shows that it's quite unlikely that you will end up exactly where you started. But you're even less likely to end up 10 000 steps to the left of your starting point, a movement requiring that you flip 10 000 consecutive tails, with $P \approx 5 \cdot 10^{-3011}$. Instead, you're likely to end up somewhere in the middle. Figure 4.3 illustrates these ideas with some shorter walks.

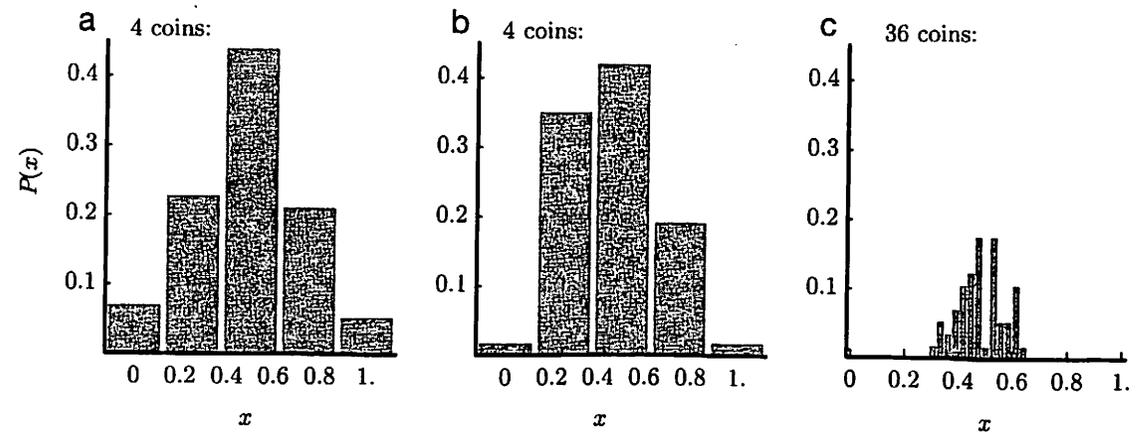


Figure 4.3: (Experimental data.) Behavior of the binomial distribution. (a) Four coins were tossed, and the fraction x that came up heads was recorded. The histogram shows the result for a sample of 57 such trials. Because this is a discrete distribution, the bars have been normalized so that the sum of their heights equals 1. (b) Another sample of 57 tosses of 4 coins. (c) This time, 36 coins were tossed, again 57 times. The resulting distribution is much narrower than (a,b); we can say with greater certainty that "about half" our coin tosses will come up heads if the total number of tosses is large. The bars are not as tall as in (a,b) because the same number of tosses (57) is now being divided among a larger number of bins (37 rather than 5). [Data kindly supplied by P. Nelson.]

The diffusion law One way to find how far you're likely to go in a random walk would be to list explicitly all the possible outcomes for a 10 000-toss sequence, then find the average over all outcomes of $(x_{10\,000})^2$, the mean-square position after step 10 000. Luckily, there is an easier way.

Suppose each step is of length L . Thus the displacement of step j is $k_j L$, where k_j is equally likely to be ± 1 . Call the position after j steps x_j ; the initial position is $x_0 = 0$ (see Figure 4.4a). Then $x_1 = k_1 L$, and similarly the position after j steps is $x_j = x_{j-1} + k_j L$.

We can't say anything about x_j because each walk is random. We *can*, however, make definite statements about the *average* of x_j over many different trials: For example, Figure 4.4b shows that $\langle x_3 \rangle = 0$. The diagram makes it clear why we got this result: In the average over all possible outcomes, those with net displacement to the left will cancel the contributions of their equally likely analogs with net displacement to the right.

Thus the mean displacement of a random walk is zero. But this doesn't imply we won't go anywhere! The preceding Example showed that the probability of ending right where we started is *small* for large N . To get a meaningful result, recall the discussion in Section 3.2.1: For an ideal gas, $\langle v_x \rangle = 0$ but $\langle v_x^2 \rangle \neq 0$. Following that hint, let's compute $\langle x_N^2 \rangle$ in our problem. Figure 4.4 shows such a computation, yielding $\langle x_3^2 \rangle = 3L^2$.

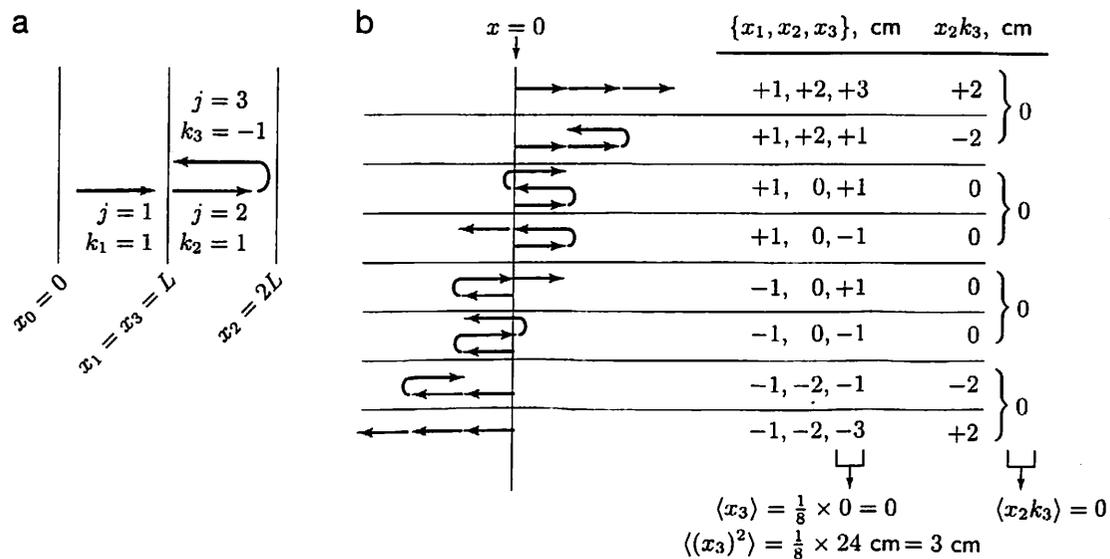


Figure 4.4: (Diagram.) (a) Anatomy of a random walk. Three steps, labeled $j = 1, 2, 3$, are shown. Step j makes a displacement of $k_j = \pm 1$. (b) Complete list of the eight distinct 3-step walks, with step length $L = 1$ cm. Each of these outcomes is equally probable in our simplest model.

Your Turn 4B

Repeat this calculation for a walk of four steps, just to make sure you understand how it works.

Admittedly, the math gets tedious. Instead of exhaustively listing all possible outcomes, though, we can note that

$$\langle (x_N)^2 \rangle = \langle (x_{N-1} + k_N L)^2 \rangle = \langle (x_{N-1})^2 \rangle + 2L \langle x_{N-1} k_N \rangle + L^2 \langle (k_N)^2 \rangle. \quad (4.3)$$

In the last expression, the final term just equals L^2 , because $(\pm 1)^2 = 1$. For the middle term, note that we can group all 2^N possible walks into pairs (see the last column of Figure 4.4). Each pair consists of two equally probable walks with the same x_{N-1} , differing only in their last step, so each pair contributes zero to the average of $x_{N-1} k_N$. Think about how this step implicitly makes use of the multiplication rule for probabilities (see page 75) and the assumption that every step was independent of the previous ones.

Thus, Equation 4.3 says that a walk of N steps has mean-square displacement bigger by L^2 than a walk of $N - 1$ steps, which in turn is L^2 bigger than a walk of $N - 2$ steps, and so on. Carrying this logic to its end, we find

$$\langle (x_N)^2 \rangle = NL^2. \quad (4.4)$$

We can now apply our result to our original problem of moving a marker in one dimension, once per second. If we wait a total time t , the marker makes $N = t/\Delta t$ random steps, where $\Delta t = 1$ s. Define the **diffusion constant** of the process as $D = L^2/(2\Delta t)$. Then,²

- The mean-square displacement in a one-dimensional random walk increases linearly in time: $\langle (x_N)^2 \rangle = 2Dt$, where
- The constant D equals $L^2/(2\Delta t)$.

The first part of Idea 4.5 is called the one-dimensional **diffusion law**. In our example, the time between steps is $\Delta t = 1$ s; so if the marker makes 1 cm steps, we get $D = 0.5 \text{ cm}^2 \text{ s}^{-1}$. Figure 4.5 illustrates the fact that the averaging symbol in Idea 4.5a must be taken seriously—any *individual* walk will not conform to the diffusion law, even approximately.

Idea 4.5a makes our expectations about random walks precise. For example, we will observe excursions of any size X , even if X is much longer than the elementary step length L , as long as we are prepared to wait a time on the order of $X^2/(2D)$.

Returning to the physics of Brownian motion, our result means that, even if we cannot see the elementary steps in our microscope, we can nevertheless confirm Idea 4.5a and measure D experimentally: Simply note the initial position of a colloidal particle, wait a time t , note the final position, and calculate $x^2/(2t)$. Repeat the

²The definition of D in Idea 4.5b contains a factor of 1/2. We can define D any way we like, as long as we're consistent; the definition we chose results in a compensating factor of 2 in the diffusion law, Idea 4.5a. This convention will be convenient when we derive the diffusion equation in Section 4.4.2.

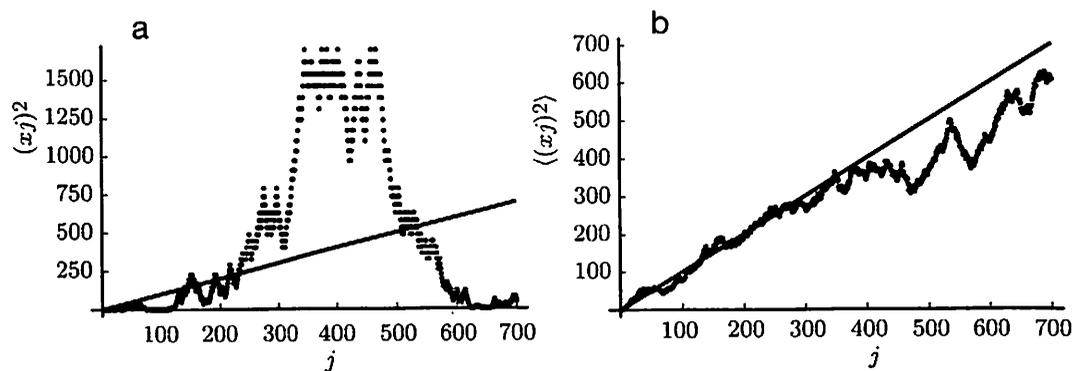


Figure 4.5: (Mathematical functions.) (a) Squared deviation $(x_j)^2$ for a single, one-dimensional random walk of 700 steps. Each step is one unit long. The solid line shows j itself; the graph shows that $(x_j)^2$ is not at all the same as j . (b) Here the dots represent the average $\langle (x_j)^2 \rangle$ for 30 walks, each having 700 steps. Again the solid line shows j . This time $\langle (x_j)^2 \rangle$ does resemble the idealized diffusion law (Equation 4.4).

observation many times; the average of $x^2/2t$ gives D . The content of Idea 4.5a is that the value of D thus found will not depend on the elapsed time t .

We can extend all these ideas to two or more dimensions (Figure 4.2). For a walk on a two-dimensional checkerboard with squares of side L , we still define $D = L^2/(2\Delta t)$. Now, however, each step is a diagonal and hence has length $L\sqrt{2}$. Also, the position \mathbf{r}_N is a vector, with two components x_N and y_N . Thus $\langle (\mathbf{r}_N)^2 \rangle = \langle (x_N)^2 \rangle + \langle (y_N)^2 \rangle = 4Dt$ is twice as large as before, because each term on the right separately obeys Idea 4.5a. Similarly, in three dimensions, we find

$$\langle (\mathbf{r}_N)^2 \rangle = 6Dt. \quad \text{diffusion in three dimensions} \quad (4.6)$$

It may seem confusing to keep track of all these different cases. But the important features about the diffusion law are simple: In any number of dimensions, mean-square displacement increases linearly with time, so the constant of proportionality D has dimensions $\mathbb{L}^2\mathbb{T}^{-1}$. Remember this, and many other formulas will be easy to remember.

From macro to micro Section 4.1.1 introduced a puzzle: How can we learn things about the molecular-scale (or “microscopic”) world, when we can’t see molecules? This section has explored the idea that Brownian motion supplies the link between the microscopic world and the “macroscopic” world (things we can see with light). Ultimately, we’d like to find that observations of Brownian motion, a macroscopic phenomenon, not only support the molecular theory of heat qualitatively but also test some quantitative prediction of that theory. We’re not ready to get this prediction yet (it’s Equation 4.16). But at least we have found one relation between the microscopic parameters of Brownian motion (the step size L and step time Δt) and a quantity observable in macroscopic experiments (the diffusion constant D), namely, Idea 4.5b.

Unfortunately, we cannot solve one equation for two unknowns: Just measuring D is not enough to find specific values for either one of these parameters. We need a second formula relating L and Δt to some macroscopic observation, so that we can solve two equations for the two unknowns. Section 4.1.4 will provide the required additional formula.

4.1.3 The diffusion law is model independent

Our mathematical treatment of the random walk made some drastic simplifying assumptions. One might well worry that our simple result, Idea 4.5, may not survive in a more realistic model. This subsection will show that, on the contrary, *the diffusion law is universal*—it’s independent of the model, as long as we have some distribution of random, independent steps.

For simplicity, we’ll continue to work in one dimension. (Besides being mathematically simpler than three dimensions, the one-dimensional case will be of great interest in Section 10.4.4.) Suppose that our marker makes steps of various lengths. We are given a set of numbers P_k , the probabilities of taking steps of length kL , where k is an integer. The length k_j of step j can be positive or negative, for forward or backward steps. We assume that the relative probabilities of the various step sizes are all the same for each step (that is, each value of j). Let u be the mean value of k_j :

$$u = \langle k_j \rangle = \sum_k kP_k. \quad (4.7)$$

u describes average drift motion superimposed on the random walk. (The analysis of the preceding subsection corresponds to the special case $P_{\pm 1} = \frac{1}{2}$, with all the other $P_k = 0$. For that case, $u = 0$.)

The mean position of the walker is now

$$\langle x_N \rangle = \langle x_{N-1} \rangle + L\langle k_N \rangle = \langle x_{N-1} \rangle + uL = NuL. \quad (4.8)$$

To get the last equality, we noticed that a walk of N steps can be built one step at a time; after each step, the mean displacement grows by uL .

The mean displacement is not the whole story: We know from our earlier experience that diffusion concerns the *fluctuations* about the mean. Accordingly, let’s now compute the variance (or mean-square deviation, Equation 3.11) of the actual position about its mean. Repeating the analysis leading to Equation 4.3 gives

$$\begin{aligned} \text{variance}(x_N) &\equiv \langle (x_N - \langle x_N \rangle)^2 \rangle = \langle (x_{N-1} + k_N L - NuL)^2 \rangle \\ &= \langle ((x_{N-1} - u(N-1)L) + (k_N L - uL))^2 \rangle \\ &= \langle (x_{N-1} - u(N-1)L)^2 \rangle + 2\langle (x_{N-1} - u(N-1)L)(k_N L - uL) \rangle \\ &\quad + L^2 \langle (k_N - u)^2 \rangle. \end{aligned} \quad (4.9)$$

As before, we now recall that kL , the length of the N th step, was assumed to be a random variable, statistically independent of all the previous steps. Thus the middle term of the last formula becomes $2L\langle x_{N-1} - u(N-1)L \rangle \langle k_N - u \rangle$, which is zero by

the definition of u (Equation 4.7). Thus Equation 4.9 says that the variance of x_N increases by a fixed amount on every step, or

$$\begin{aligned}\text{variance}(x_N) &= \langle (x_{N-1} - \langle x_{N-1} \rangle)^2 \rangle + L^2 \langle (k_N - \langle k_N \rangle)^2 \rangle \\ &= \text{variance}(x_{N-1}) + L^2 \times \text{variance}(k).\end{aligned}$$

After N steps, the variance is then $NL^2 \times \text{variance}(k)$. Suppose the steps come every Δt , so that $N = t/\Delta t$. Then

$$\text{variance}(x_N) = 2Dt, \quad \text{where } D = \frac{L^2}{2\Delta t} \times \text{variance}(k). \quad (4.10)$$

In the special case where $u = 0$ (no drift), Equation 4.10 just reduces to our earlier result, Idea 4.5a!

Thus the diffusion law (Idea 4.5a) is model independent. Only the detailed formula for the diffusion constant depends on the microscopic details of the model (compare Idea 4.5b to Equation 4.10).³ Such universality, whenever we find it, gives a result great power and wide applicability.

4.1.4 Friction is quantitatively related to diffusion

Diffusion is essentially a question of random fluctuations: Knowing where a particle is now, we seek the spread in its expected position at a later time t . Section 3.2.5 argued qualitatively that the *same* random collisions responsible for this spread also give rise to friction. So we should be able to relate the microscopic quantities L and Δt to friction, another experimentally measurable, macroscopic quantity. As usual, we'll make some simplifications to get to the point quickly. For example, we again consider an imaginary world where everything moves only in one dimension.

To study friction, we want to consider a particle pulled by a constant external force f in the \hat{x} direction. For example, f could be the force mg of gravity, or the artificial gravity inside a centrifuge. We want to know the average motion of each particle as it falls in the direction of the force. In first-year physics, you probably learned that a falling body eventually comes to a "terminal velocity" determined by friction. Let's investigate the origin of friction, in the case of a small body suspended in fluid.

In the same spirit as Section 4.1.2, suppose that the collisions occur exactly once per Δt (although really there is a distribution of times between collisions). In between kicks, the particle is free of random influences, so it is subject to Newton's Law of motion, $dv_x/dt = f/m$; its velocity accordingly changes with time as $v_x(t) = v_{0,x} + ft/m$, where $v_{0,x}$ is the starting value just after a kick and m is the mass of the particle. The resulting uniformly accelerated motion of the particle is then

$$\Delta x = v_{0,x}\Delta t + \frac{1}{2} \frac{f}{m} (\Delta t)^2. \quad (4.11)$$

³ [T₂] Section 9.2.2' on page 389 will show that, similarly, the structure of the three-dimensional diffusion law (Equation 4.6) does not change if we replace our simple model (diagonal steps on a cubic lattice) by something more realistic (steps in any direction).

Following Section 4.1.1, we assume that each collision obliterates all memory of the previous step. Thus, after each step, $v_{0,x}$ is randomly pointing left or right, so its average value, $\langle v_{0,x} \rangle$, equals zero. Taking the average of Equation 4.11 thus gives $\langle \Delta x \rangle = (f/2m)(\Delta t)^2$. In other words, the particle, although buffeted about by random collisions, nevertheless acquires a net **drift velocity** equal to $\langle \Delta x \rangle / \Delta t$, or

$$v_{\text{drift}} = f/\zeta, \quad (4.12)$$

where

$$\zeta = 2m/\Delta t. \quad (4.13)$$

Equation 4.12 shows that, under the assumptions made, a particle under a constant force indeed comes to a terminal velocity proportional to the force. The **viscous friction coefficient** ζ , like the diffusion constant, is experimentally measurable—we just look through a microscope and see how fast a particle settles under the influence of gravity, for example.

Recovering the familiar friction law (Equation 4.12) strengthens the idea that friction originates in randomizing collisions of a body with the thermally disorganized surrounding fluid. Our result goes well beyond the motion of Robert Brown's pollen grains: *Any* macromolecule, small dissolved solute molecule, or even the molecules of water itself are subject to Equations 4.12 and 4.13. Each type of particle, in each type of solvent, has its own characteristic values of D and ζ .

Returning to colloidal particles, in practice it's often not necessary to measure ζ directly. The viscous friction coefficient for a spherical object is related to its *size* by a simple relation:

$$\zeta = 6\pi\eta R. \quad \text{Stokes formula} \quad (4.14)$$

In this expression, R is the radius of the particle and η is a constant called the viscosity of the fluid. Chapter 5 will discuss viscosity in greater detail; for now, we only need to know that the viscosity of water at room temperature is about $10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$. Equation 4.14 gives us ζ once we measure the size of a colloidal particle (for example, by looking at it). If we also know the density of the particle (for example, by weighing a bulk sample of soot), then knowing its size also lets us determine its mass m .

Summarizing, we have found that ζ and m are experimentally measurable properties of a macroscopic colloidal particle. Equation 4.13 connects them to a molecular-scale quantity, the collision time Δt . We can also substitute this value back into Idea 4.5b and use the particle's diffusion constant D to find another molecular-scale quantity, the effective step size L .

Unfortunately, however, our theory has *not* made a falsifiable, quantitative prediction yet. It lets us compute the molecular-scale parameters L and Δt of the random walk's steps, but these are unobservable! To test the idea that diffusion and friction are merely two faces of thermal motion, we must take one further step.

Einstein noticed that there's a *third* relation involving L and Δt . To find it, note that $(L/\Delta t)^2 = (\nu_{0,x})^2$. Our discussion leading to the ideal gas law concluded that

$$\langle (\nu_{0,x})^2 \rangle = k_B T/m. \quad (4.15)$$

(Unlike Idea 3.21 on page 80, there's no factor of 3: We need only one component of the velocity.)

Combining Equation 4.15 with our earlier results (Idea 4.5b and Equation 4.13) overdetermines L and Δt . That is, these three relations in two unknowns can only hold if D and ζ themselves satisfy a particular relation. This relation between experimentally measurable quantities is the prediction we were seeking. To find it, consider the product ζD .

**Your
Turn
4C**

Put all the pieces together: Use Equations 4.5b and 4.13 to express ζD in terms of m , L , and Δt . Then use the definition $\nu_{0,x} = L/\Delta t$, and Equation 4.15, to show that

$$\zeta D = k_B T. \quad \text{Einstein relation} \quad (4.16)$$

Equation 4.16 is Einstein's 1905 result. It states that the *fluctuations* in a particle's position are linked to the *dissipation* (or frictional drag) that it is subject to.

The Einstein relation is remarkable in a number of ways. For one thing, it tells us how to find k_B by making macroscopic measurements. Einstein was then able to find Avogadro's number by dividing the ideal gas law constant, $N_{\text{mole}} k_B$, by k_B . That is, he found how many molecules are in a mole, and hence how small molecules are—without seeing molecules.

The Einstein relation is quantitative and *universal*: It always yields the same value for $k_B T$, no matter what sort of particle and solvent we study. For example, the right-hand side of Equation 4.16 does not depend on the mass m of the particle. Smaller particles will feel less drag (smaller ζ), but will diffuse more readily (bigger D), in such a way that all particles obey Equation 4.16. Also, although both ζ and D generally depend on temperature in a complicated way, Equation 4.16 says their *product* depends on T in a very simple way.

The universality of ζD is a falsifiable prediction of the hypothesis that heat is disordered molecular motion: We can check whether various kinds of particles, of various sizes, at various temperatures, all give the same value of k_B . (They do; you'll see one example in Problem 4.5.)

Einstein also checked whether the experiment he was proposing was *actually doable*. He reasoned that, to see a measurable displacement of a single $1 \mu\text{m}$ colloidal particle, we'd have to wait until it had moved several micrometers. If the waiting time for such a motion were impracticably long, then the experiment itself would be impractical. Using existing estimates of k_B , Einstein estimated that a $1 \mu\text{m}$ sphere in water would take about a minute, a convenient waiting time, to wander a mean-

square distance of $5 \mu\text{m}$. Einstein concluded that colloidal particles occupy a window of experimental opportunity: They are large enough to resolve optically, yet not so large as to render their Brownian motion unobservably sluggish. Very soon after his prediction, Jean Perrin and others did the experiments and confirmed the predictions. As Einstein put it later, "Suddenly all doubts vanished about the foundations of Boltzmann's theory [of heat]."

T₂ Section 4.1.4' on page 147 mentions several finer points about random walks.

4.2 EXCURSION: EINSTEIN'S ROLE

Einstein was not the first to suggest that the origin of Brownian motion was thermal agitation. What did he do that was so great?

First of all, Einstein had exquisite taste in realizing what problems were important. At a time when others were pottering with acoustics and such, he realized that the pressing questions of the day were the reality of molecules, the structure of Maxwell's theory of light, the apparent breakdown of statistical physics in the radiation of hot bodies, and radioactivity. His three articles from 1905 practically form a syllabus for all of twentieth-century physics.

Einstein's interests were also interdisciplinary. Most scientists at that time could hardly comprehend that these problems even belonged to the same field of inquiry, and certainly no one guessed that they would all interlock as they did in Einstein's hands.

Third, Einstein grasped that the way to take the molecular theory out of its disreputable state was to find new, testable, quantitative predictions. Thus Section 4.1.4 discussed how the study of Brownian motion gives a numerical value for the constant k_B , and hence, for N_{mole} . The molecular theory of heat says that the value obtained in this way should agree with earlier, approximate, determinations—and it did.

Nor did Einstein stop there. His doctoral thesis gave yet another independent determination of N_{mole} (and hence of k_B), again making use of Equation 4.16. Over the next few years, he published *four more* independent determinations of N_{mole} ! Einstein was making a point: If molecules are real, then they have a real, finite size, which manifests itself in many different ways. If they were not real, it would be an absurd coincidence that all these independent measurements pointed to the *same* size scale.

These theoretical results had technological implications. Einstein's thesis work, on the viscosity of suspensions, remains his most heavily cited work today. At the same time, Einstein was also sharpening his tools for a bigger project: Showing that matter consisted of discrete particles prepared his mind to show that *light* does as well (see Section 1.5.3 on page 26). It is no accident that the Brownian motion work immediately preceded the light-quantum paper.

T₂ Section 4.2' on page 148 views some of Einstein's other early work in the light of the preceding discussion.

cross section A is $R = \ell/(A\kappa)$, where κ is the conductivity of the material. In our simplified model, each ion species contributes $Dq^2c/k_B T$ to κ (Section 4.6.4).

- *Diffusion from an initial sharp point:* Suppose N molecules all begin at the same location in three-dimensional space at time zero. Later the concentration is

$$c(\mathbf{r}, t) = \frac{N}{(4\pi Dt)^{3/2}} e^{-r^2/(4Dt)}$$

(Equation 4.28).

FURTHER READING

Semipopular:

Historical: Pais, 1982, §5.

Finance: Malkiel, 1996.

Intermediate:

General: Berg, 1993; Tinoco et al., 2001.

Polymers: Grosberg & Khokhlov, 1997.

Better derivations of the Einstein relation: Benedek & Villars, 2000b, §2.5A–C; Feynman et al., 1963a, §43.

Technical:

Einstein's original discussion: Einstein, 1956.

T₂

4.1.4' Track 2

Some fine points:

1. Sections 4.1.2 and 4.1.4 made a number of idealizations, so Equations 4.5b and 4.13 should not be taken too literally. Nevertheless, it turns out that the Einstein relation (Equation 4.16) is both general and accurate. This broad applicability must mean that it actually rests on a more general, although more abstract, argument than the one given here. Indeed, Einstein gave such an argument in his original 1905 paper (Einstein, 1956).

For example, introducing a realistic distribution of times between collisions does not change our main results, Equations 4.12 and 4.16. See Feynman et al., 1963a, §43 for the analysis of this more detailed model. In it, Equation 4.13 for the viscous friction coefficient ζ expressed in terms of microscopic quantities becomes instead $\zeta = m/\tau$, where τ is the mean time between collisions.

2. The assumption that each collision wipes out all memory of the previous step is also not always valid. A bullet fired into water does not lose all memory of its initial motion after the first molecular collision! Strictly speaking, the derivation given here applies to the case where the particle of interest starts out with momentum comparable to that transferred in each collision, that is, not too far from equilibrium. We must also require that the momentum *imparted* by the external force in each step not be bigger than that transferred in molecular collisions, or, in other words, that the applied force is not too large. Chapter 5 will explore how great the applied force may be before “low Reynolds-number” formulas like Equation 4.12 become invalid, concluding that the results of this chapter are indeed applicable in the world of the cell. Even in this world, however, our analysis can certainly be made more rigorous: Again see Feynman et al., 1963a, §43.
3. Cautious readers may worry that we have applied a result obtained for the case of low-density gases (Idea 3.21, that the mean-square velocity is $\langle(v_x)^2\rangle = k_B T/m$), to a dense *liquid*, namely, water. But our working hypothesis, the Boltzmann distribution (Equation 3.26 on page 85) assigns probabilities on the basis of the total system energy. This energy contains a complicated potential energy term, plus a simple kinetic energy term, so the probability distribution factors into the product of a complicated function of the positions, times a simple function of the velocities. But we don't care about the positional correlations. Hence we may simply integrate the complicated factor over $d^3x_1 \cdots d^3x_N$, leaving behind a constant times the *same* simple probability distribution function of velocities (Equation 3.25 on page 84) as the one for an ideal gas. Taking the mean-square velocity then leads again to Idea 3.21.

Thus, in particular, the average kinetic energy of a colloidal particle is the same as that of the water molecules, just as argued in Section 3.2.1 for the different kinds of gas molecule in a mixture. We implicitly used this equality in arriving at Equation 4.16.
4. The Einstein relation, Equation 4.16, was the first of many similar relations between fluctuations and dissipation. In other contexts such relations are generically called fluctuation–dissipation theorems.