

# Pollen Grains, Random Walks and Einstein

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I work on soft condensed matter and statistical physics. My current interests include the physics of biomembranes with pumps, the flow of soft materials such as colloidal crystals and liquid crystals, and sedimentation.

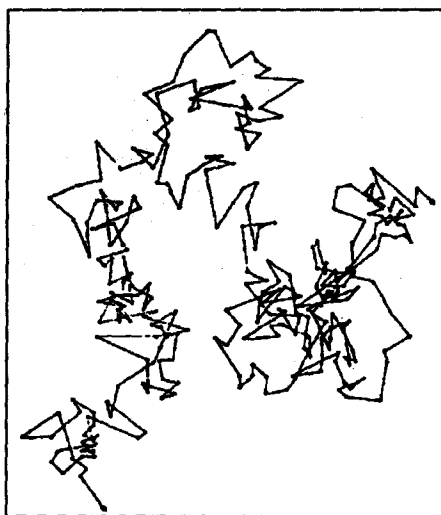
This article reviews the history of the phenomenon of Brownian motion, how it confirmed the molecular view of matter, and how it led to the invention of nonequilibrium statistical mechanics.

## 1. Introduction

### 1.1. What is Brownian Motion?

Look through a microscope at very still dirty water or curdled milk, and you'll see tiny particles in a state of constant, rapid, erratic motion<sup>1</sup>. *Figure 1* is the trajectory of such a particle, as seen in the 1916 experiments of the French physicist Jean Perrin [1].

In 1828, a botanist named Robert Brown saw this movement in pollen grains dispersed in water, and achieved permanent fame, because it has been known as Brownian motion ever since. What he observed, to be precise, was that pollen, dropped into water, disintegrated into a very large number of tiny particles, a few  $\mu\text{m}$  in size,



**Figure 1.** The random walk of a resin particle, from *ATOMS*, by J Perrin [1].



which were seen to be dancing about ceaselessly. He thought at first that the movement was a sign of life, and that the tiny particles were the fundamental constituents of living matter, since pollen came from plants. He later found that inorganic materials did this as well, and so speculated that all matter was made of these 'primitive molecules'. People seem to have realised quite soon that these tiny but visible particles weren't molecules, just finely divided matter, and the focus shifted to what was making them dance around like that. Many explanations were offered: perhaps the particles were being carried around by flows produced by small temperature differences in the water; maybe illuminating the material was itself causing the movement; maybe electrical forces were involved; and so forth. Experiments and speculations on the phenomenon continued through the 1880s. A particularly careful set of experiments by Gouy showed that the fluctuations became more rapid if the viscosity of the fluid was decreased, and that neither changes in the intensity of the light source used to illuminate the sample nor large electromagnetic fields affected the movement. He was thus convinced of the view that some others had by then begun to express: the molecules of the liquid were moving around rapidly simply because the liquid had a temperature and the pollen grains were being kicked here and there by repeated collisions with these molecules.

Einstein had been wondering about ways to find direct evidence for the existence of discrete molecules. Since there were already estimates of their sizes (of the order of  $10^{-10}$  m; see section 2) which made it clear that they were too small to see through a microscope, he took a different approach. Unaware initially of the observations of Brown and the work that followed, he argued that a small particle suspended in a fluid should be agitated by collisions with molecules, and constructed a detailed quantitative theory of the motion of such a par-

<sup>1</sup> You are likely to be misled by much slower processes with larger amplitudes: the effects of convection currents, particles being carried aloft by rising air bubbles, or others settling under gravity. But it's worth persisting, eliminating all these stray effects and looking for the real thing. It's easier said than done, but it can be done. Another way to see it is to point a low-power laser (a hand-held laser pointer should do) at a test-tube of milk and look at the reflected spot on a screen. The 'speckle pattern' will change (why?) constantly and delicately as a result of Brownian motion (of what?).



ticle. His calculations showed that the resulting motion, for particles the size of pollen grains, should be seen easily through a microscope. He suggested cautiously that the movement he was predicting might be the same as the Brownian movement, which he had by then learnt about. As we shall see, the importance of his work was that it provided a decisive test for the kinetic theory and hence for the very existence of molecules.

The developments that followed Einstein's theory of Brownian motion show us how the most profound physics and mathematics can emerge from simple, direct observation of natural phenomena. Ideas related to Brownian motion and random walks appear today in mathematics, all the natural sciences, engineering, linguistics, finance, economics, and even the social sciences. Accordingly, I think an acquaintance with the fundamentals of this phenomenon should be required of all scientists and engineers, at the very least. Brownian motion is visible evidence for the existence of molecules. Careful studies of this motion made it possible, as we shall see by and by, to count the number of atoms in a given mass of gas (i.e., to obtain Avogadro's number <sup>2</sup>), therefore to infer the mass of a proton, and lastly to estimate the sizes of molecules, all using an ordinary light microscope!

<sup>2</sup> I shall assume that the readers of this article are all familiar with the idea of a *mole* or gram molecular weight of a substance, since the concept is taught in the X or XI standard. Moles of hydrogen, oxygen and water, respectively weigh 2, 32 and 18 grams, and  $N_A$ , the number of molecules in one mole, named in honour of Avogadro, is about  $6 \times 10^{23}$ . In particular, note that measuring  $N_A$  tells us that one hydrogen atom (and hence one *proton*) weighs about  $1.7 \times 10^{-24}$  gram.

This article discusses the *physics* and a bit of the mathematics of Brownian motion. I've tried to use only 'plus-two' and B Sc physics and mathematics (the ideal gas law, partial pressures, elementary kinetic theory, terminal velocity, combinations and permutations, vector calculus), so that science and engineering undergraduates should, in principle, be able to understand all of it if they stretch themselves a bit. The interested standard XI or XII student should be able to follow a fair fraction of the article, and readers with other backgrounds should get the general idea.



## 1.2 Einstein's Key Result

How would you count the number of molecules in a mole (or any other quantity) of gas? Let's start with high school physics: it is an experimental fact that the pressure  $p$ , volume  $V$ , and temperature  $T$  of  $\mu$  moles of a dilute gas obey

$$pV = \mu RT, \quad (1)$$

where  $R$  has the same value for all gases. The kinetic theory of gases, about which I will say more below, explains this observation and tells us that the constant

$$R = N_A k_B \quad (2)$$

where Avogadro's number  $N_A$  is the number of molecules in one mole of any ideal gas, and  $k_B$  is known as Boltzmann's constant. Now remember where  $k_B$  comes from: kinetic theory tells you that temperature is just molecular kinetic energy, i.e., that the molecules in a gas at temperature  $T$  have mean kinetic energy  $(3/2)k_B T$ , where  $k_B$  is simply an unknown constant of proportionality. This is because we measure temperature using a rather arbitrary scale: whereas the absolute *zero* of temperature is uniquely defined, the *unit* of temperature is not. From kinetic theory we know that if we double the absolute temperature we have doubled the kinetic energy of the molecules, but thermometers do not tell us the actual value of the kinetic energy in Joules. Thus the ideal gas law allows us to measure  $N_A k_B$ , but not  $N_A$  by itself. If we could measure  $k_B$  independently, we would then have succeeded in counting the number of molecules in a mole.

What Einstein showed was that a particle of radius  $a$  executing Brownian motion in a fluid with viscosity  $\eta$  and temperature  $T$  would wander, in a time  $t$ , a distance<sup>3</sup>  $R(t) \sim \sqrt{Dt}$ , with the 'diffusion constant'  $D$  determined entirely by  $k_B$  and the known quantities  $T$ ,  $\eta$ , and  $a$ . A measurement of  $R(t)$  through a microscope would thus

<sup>3</sup> I will frequently make estimates of this sort where the  $\sim$  symbol means that I have left out purely numerical factors of order unity, but have included the dependence on all physical parameters.

yield a value for  $k_B$  and hence, as argued above, for Avogadro's number  $N_A$ . Einstein extracted  $N_A$  by applying his theory to the motion of sugar molecules in solution. Now you can't see a sugar molecule through a microscope, so the properties of its Brownian motion had to be inferred by measuring the diffusion or spread of the concentration of sugar through unstirred water. Perrin got  $N_A$  by applying Einstein's theory to infer  $k_B$  from the vertical distribution of heavier-than-water micron-sized resin particles, as well as from direct measurements of their Brownian motion. The resulting values for  $N_A$  and the size of molecules agreed wonderfully with those due to Clausius and Maxwell (see section 2) – a triumph for the kinetic theory.

### 1.3 *Structure of the Article*

The rest of this article is organised as follows: In the next section, we recall why molecules were postulated to begin with, and how the kinetic theory extracts one set of estimates of  $N_A$  and molecular sizes from macroscopic experiments. In section 3, we present and solve a mathematical model for the motion of a Brownian particle, and use it to show that the particle wanders a distance proportional to the square-root of the time. We then reconstruct the remarkable connection that Einstein established between diffusion and viscous friction, which allows us to infer Boltzmann's constant from experiment. We show in addition how a direct consideration of the equilibrium between gravity and Brownian motion when the particles are less dense than the fluid in which they are suspended gave Einstein an independent and direct route to Boltzmann's constant. We also discuss briefly the experiments of Perrin. The article concludes in section 4.

## 2. Molecules and Kinetic Theory

By the late 19th century it was generally agreed that matter was made of discrete bits called atoms or mole-



cules. As you learnt in the 11th or 12th standard, the first hints in this direction came from chemistry: gases reacted in simple proportions by volume; the masses of oxygen which react with a given mass of nitrogen to form its various oxides are again in simple integer ratios; and so forth. Simple but striking chemical facts such as these were accounted for nicely by two crucial ideas: (i) that chemical reactions involved the combination of fixed numbers of atoms; and (ii) Avogadro's hypothesis that different gases of the same volume, and at the same temperature and pressure contained the same number of molecules. As a result, it became possible to estimate the *ratios* of the masses of molecules, but not the values of the masses themselves. Of course, no one then knew why Avogadro's hypothesis should be true. It was not until the success of the molecular-kinetic theory of heat, or simply *kinetic theory*, that the existence of molecules was firmly established. The kinetic theory accounted for the observed properties of gases which you've studied in school, such as the gas equation (1), in terms of a picture of an enormous number of molecules flying around at random and bouncing elastically off the walls of the container, provided one *defined* temperature  $T$  by the statement that the average kinetic energy per molecule is equal to  $(3/2)k_B T$ . Using this theory, Clausius and Maxwell were able to express measurable macroscopic properties of gases in terms of molecular parameters like the size  $d$  of a molecule, the number  $n$  of molecules per unit volume of gas, and the average speed  $\bar{v}$  of the molecules. They found what really mattered was the *mean free path*  $\ell$ , i.e., the mean distance a molecule travels before it collides with another molecule.

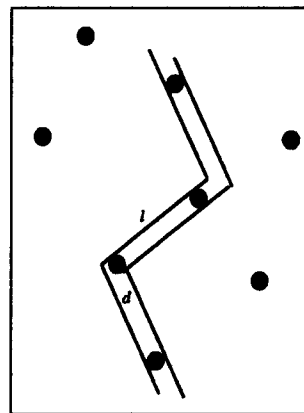
From Figure 2 it is easy to convince yourself that

$$\ell \sim 1/(nd^2). \quad (3)$$

They found that the kinematic viscosity was

$$\nu \sim \bar{v}\ell \quad (4)$$

**Figure 2.** A cylinder with diameter equal to the molecular size  $d$  and length equal to one mean free path  $\ell$  contains on average one molecule. This defines  $\ell$  and shows that  $\ell \sim 1/(nd^2)$ .



which you could have guessed using dimensional analysis since the units of  $\nu$  are  $\text{length}^2 \text{ time}^{-1}$ , and that the speed of sound in a gas was

$$c_s \sim \bar{v}. \quad (5)$$

Straightforward measurements of  $c_s$  and  $\nu$  thus yield the combination  $\ell \sim \nu d^2$ . The measured mass density of a gas gives us  $nm$ , where  $m$  is the (unknown) mass of a molecule. Knowing the mass density of the liquid or solid phase of the same material gives us  $md^{-3}$  if we assume that in that phase the molecules are closely packed (one molecule per  $d^3$ ). Put together, these considerations yield values for  $n$ ,  $m$ , and  $d$ . For air at room pressure and temperature we find  $\nu \simeq 2 \times 10^{-5} \text{ m}^2\text{s}^{-1}$  and  $c_s \simeq 300 \text{ m/s}$ . In its liquid phase, the mass density is  $\sim 1000 \text{ kg/m}^3$ . This leads to answers which we now know to be quite reasonable:  $d \sim 10^{-10} \text{ m}$  and  $n \sim 3 \times 10^{25}$  molecules per  $\text{m}^3$ , i.e., about  $6 \times 10^{23}$  molecules in a mole.

## 2.1 The Need for an Independent Test

Clearly, a crucial test of the kinetic theory would be to see if the above estimates agreed with those from an entirely independent experiment. In this context, note that although kinetic theory was based on a molecular description, its successes at the time lay in its ability to account for macroscopic phenomena, averaged over a large number of molecules. How much more satisfying it would be to have direct evidence for molecules, in the form of events caused by the impact of a small number of them! Taking the kinetic theory seriously, if you looked at a tiny region in a gas or liquid for a tiny instant of time, then sometimes you'd see a molecule going one way, sometimes another, and sometimes maybe you'd see no molecule at all. Although on average the molecules you saw would be as likely to be going in any direction as in any other, there would be *fluctuations* about this average behaviour. It is an important



principle of statistics that if the number of impacts on the particle is small their effect won't average out instantaneously. So if the particle were itself small or if it were floating around in a partially evacuated chamber so the number density of molecules was small, these fluctuations could become large and deliver an appreciable kick to the particle, in a direction which would vary randomly from one kick to the next. The resulting movement is what we see as Brownian motion. This was Einstein's idea. In the next section we model the trajectory of the Brownian particle by a 'random walk' whose properties will lead us along one path to our final result.

### 3. Random Walks

#### 3.1 *Brownian Particles are Just Big Molecules*

A notable feature of the theory of Brownian motion is that it requires no understanding of the detailed nature of the collisions between the molecules and the Brownian particles, of how many collisions take place per second, and at what angle of incidence, and so forth. All one does is to treat the Brownian particle as just another molecule, only larger than the rest. Kinetic theory then tells us, crucially, that a Brownian particle of mass  $M$  has the same mean kinetic energy  $(3/2)k_B T$  as any other molecule in the system, and hence a randomly directed mean speed

$$\bar{V} = \sqrt{\frac{3k_B T}{M}}. \quad (6)$$

The collisions with the molecule enter in one other way: they damp out the instantaneous velocity of the Brownian particle in a time  $\tau$  determined by a macroscopic property of the fluid, namely its viscosity. We can imagine that the Brownian particle then abruptly acquires a speed  $\bar{V}$  again through collisions, once again in a random direction. Physically it is clear that this is not a very rapid way for the particle to get around, since the

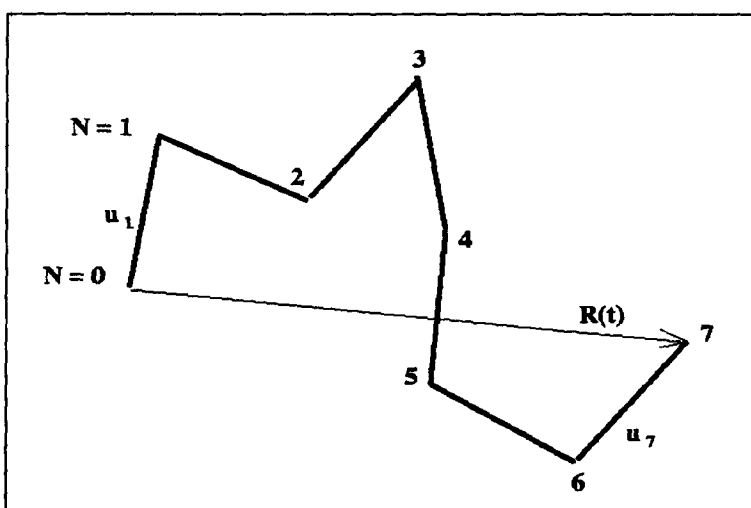


random direction of the velocity will take the particle as often in one direction as in the opposite direction. The product  $\bar{V}^2\tau$  has units of  $\text{length}^2 \text{ time}^{-1}$ , as does the diffusion coefficient  $D$  defined later in equation (14); if you therefore guessed that the ‘random walk’ defined above in fact leads to a particle ‘diffusing’ a typical distance  $\sim (Dt)^{1/2}$  with  $D \sim \bar{V}^2\tau$ , you’d be right. Let us make these ideas mathematically precise, as Einstein did. My presentation is equivalent to his, although not identical in detail.

### 3.2 How Far does a Brownian Particle Travel?

Assume that the trajectory of the Brownian particle is a sequence of discrete steps of length  $b$  in a completely random direction. Each step takes a time  $\tau$ , which means that during the step the particle has a speed  $\bar{V} = b/\tau$ . Let the direction of the  $j$ th step be given by the unit vector  $\mathbf{u}_j$ , which can point in any direction with equal probability. The  $\mathbf{u}_j$ s for different  $j$  are statistically independent. After a time  $t \equiv N\tau$ , a particle which started from the origin would be at a point (see *Figure 3*)

$$\mathbf{R}(t) = b \sum_{j=1}^N \mathbf{u}_j. \quad (7)$$



**Figure 3.** A random walk reaching a point  $\mathbf{R}(t)$  after  $N$  steps.



Each  $\mathbf{u}_j$  has mean zero, since it is distributed uniformly over all possible directions, so that the average displacement

$$\langle \mathbf{R}(t) \rangle = b \sum_{j=1}^N \langle \mathbf{u}_j \rangle = 0. \quad (8)$$

This average tells you nothing about how far from the origin the particle is likely to be. The average vanishes only because there is no preferred direction in which the particle is likely to be found. We could look instead at the average of the absolute value  $|\mathbf{R}(t)|$ ; it turns out to be easier to calculate the mean-squared displacement, i.e., the variance of  $\mathbf{R}(t)$  which, from (7), is

$$\begin{aligned} \Delta^2(t) &\equiv \langle \mathbf{R}(t) \cdot \mathbf{R}(t) \rangle \\ &= b^2 \sum_{i=1}^N \sum_{j=1}^N \langle \mathbf{u}_i \cdot \mathbf{u}_j \rangle. \end{aligned} \quad (9)$$

This sum is easy to do: the  $\mathbf{u}_i$  for distinct  $i$  are statistically independent, so that for  $i \neq j$   $\langle \mathbf{u}_i \cdot \mathbf{u}_j \rangle = \langle \mathbf{u}_i \rangle \cdot \langle \mathbf{u}_j \rangle = 0$ ; and for  $i = j$   $\langle \mathbf{u}_i \cdot \mathbf{u}_j \rangle = 1$  since they're unit vectors, so we see that the root-mean-square displacement is

$$\Delta(t) = b\sqrt{N} = \sqrt{\bar{V}^2 \tau t} \quad (10)$$

with  $\bar{V}$  and  $t$  as defined above.

The above result is probably familiar to you in its one-dimensional form: if you add  $N$  numbers each of which is equally likely to be  $+1$  or  $-1$ , the resulting sum has mean zero and standard deviation  $\sqrt{N}$ . In fact, for a one-dimensional random walk, you can quite easily get the entire probability distribution, and use this to solve immediately the problem in any number of dimensions. For instance: simple counting arguments, using the ideas of combinations and permutations you learnt in school, tell you that the probability that a random walk in one dimension (step length  $\delta$ , step duration  $\tau$ ) achieves a nett displacement  $k\delta$  (where  $k$  can be positive

Another way of seeing why this average is zero:  $u_i u_j = \cos \theta$  where  $\theta$  is the angle between the two vectors.  $\theta$  &  $180^\circ - \theta$  are equally probable since the two vectors are independent. These make contributions to  $\langle \cos \theta \rangle$  which cancel.



or negative) after  $N$  steps is

$$P_N(k) = \frac{N!}{[(N+k)/2]![(N-k)/2]!} 2^{-N}. \quad (11)$$

For  $N \gg k$

$$P_N(k) \simeq \sqrt{\frac{2}{\pi N}} e^{-k^2/2N} \quad (12)$$

asymptotically (think about how you might prove this), as you can convince yourself by plotting  $P_N(k)$  versus  $k$  for a reasonably large value of  $N$ , say 20. For large  $N$  it's convenient to work in terms of the coordinate  $x = k\delta$  and the time  $t = N\tau$ , treated as continuous rather than discrete variables. Then the probability  $P(x, t)dx$  of finding the particle between  $x$  and  $x + dx$  at time  $t$  is given by

$$P(x, t) = \frac{e^{-x^2/4Dt}}{\sqrt{4\pi Dt}} \quad (13)$$

where the 'diffusion coefficient'

$$D = \frac{\delta^2}{2\tau}. \quad (14)$$

For a walk in  $q$  dimensions, since the displacements along the coordinate axes are statistically independent, we can make the random elementary step of length  $b$  by adding vectorially  $q$  elementary random steps of length  $\delta$  in the coordinate directions. Thus  $b = \sqrt{q}\delta$ , and the distribution is just the product of  $q$  distributions of the form (13):

$$P(\mathbf{R}, t) = \frac{e^{-R^2/4Dt}}{(4\pi Dt)^{q/2}}, \quad (15)$$

and

$$D = \frac{b^2}{2q\tau} = \frac{\bar{V}^2\tau}{2q}, \quad (16)$$

so that the root-mean-square displacement of equation (10) is

$$\Delta(t) = \sqrt{2qDt} \quad (17)$$



with  $D$  as in (16). So measuring the diffusion coefficient  $D$  will give us  $\bar{V}^2\tau$ . If we can relate  $\tau$  to an independently measurable physical quantity, we can then find  $k_B$  using (6).

Let's do this qualitatively first. Macroscopically, our Brownian particle is just a particle moving through a viscous fluid. The effect of the fluid is put in simply as a force  $f = -\Gamma v$  proportional to the particle velocity  $v$ , with a coefficient  $\Gamma$  of viscous friction. The equation of motion for the particle velocity in one dimension is

$$M \frac{dv}{dt} = -\Gamma v. \quad (18)$$

You all have probably solved an equation like (18), with an additional constant force on the right-hand side, when you studied 'terminal velocity'. We see from (18) that our particle, starting from any initial speed (say  $\bar{V}$ ), will effectively lose this speed in a time of order  $M/\Gamma$ . In other words,

$$\tau \sim \frac{M}{\Gamma} \quad (19)$$

so that, from (6), (16), and (19),

$$D \sim \frac{k_B T}{\Gamma}. \quad (20)$$

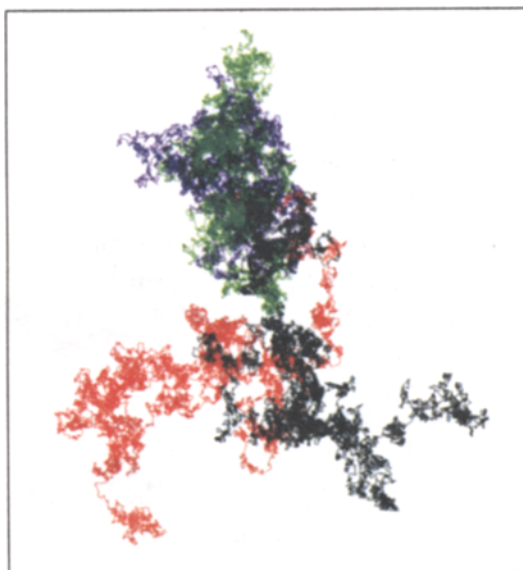
This turns out to be exactly correct, i.e.,  $D$  is *precisely*  $k_B T/\Gamma$ , as we'll see shortly.  $\Gamma$ , moreover, can be obtained independently, as we shall see below. We'll return to the complete solution of the problem after two short digressions. One of these is on 'noisy' differential equations, the other on numerical simulations of random walks.

**3.2.1. Langevin Equations:** One way to model Brownian motion is to include the kicks of the molecules in Newton's second law of motion (18) for the Brownian particle in the form of a 'noise'. This is done by adding to the



right-hand side a function  $f(t)$  defined only by its statistical properties. The resulting object is called a ‘stochastic differential equation’ (often a ‘Langevin equation’ after the man who invented it in 1908) and can be solved using techniques [2] which are now standard. This approach is now the method of choice for solving problems in the dynamics of statistical systems. The noise, while random, is not arbitrary: just as (20) connects diffusion and friction, there is a strict relation between  $\Gamma$  and the statistical properties of the noise. This sort of approach is now widely used even for systems where the noise comes not from equilibrium thermal fluctuations but from other sources such as chaos. In such truly nonequilibrium situations there is no general relation between the noise statistics and the damping coefficients in the problem. I will say no more about this here: the interested reader can look at the ‘Suggested Reading’ at the end of this article.

**3.2.2 Random Walks through Simulations and Coin-tosses:** Try generating random walks on a PC and measuring their properties. It’s not too difficult and it is very instructive. *Figure 4* shows the results of such a study.



**Figure 4. Four random walks in two dimensions, shown in different colours, from a numerical simulation by Ashwin Pande.**



To test our predictions (10), (11) or (12), you'll have to generate a large number of walks, each starting from the origin, and extract the probability of finding the particle at various locations. It's fun to do the same thing by tossing a coin: a head means a step to the right, a tail to the left. A hundred tosses divided into groups of ten give you ten short random walks. You could even use it to check if the coin is biased. Try it!

### 3.3 Viscosity and Diffusion : the Stokes-Einstein Relation

Returning to the main narrative, recall that we're trying to use Brownian motion to obtain a value for Boltzmann's constant  $k_B$ . I presented qualitative arguments for this which I will now make quantitative and complete, by expressing  $D$  in terms of the viscosity of the fluid.

To do this, note first, as you can and should check explicitly, that the distribution (15) obeys the 'diffusion equation'

$$\frac{\partial P(\mathbf{R}, t)}{\partial t} = D \nabla^2 P. \quad (21)$$

This means that if we now take a collection of  $\mathcal{N}$  independent random walkers (pollen grains), not interacting with each other, and start them all out at the origin, then the mean number of grains we'd find per unit volume at a point  $\mathbf{R}$  at time  $t$  would be given (why?) by  $n(\mathbf{R}, t) = \mathcal{N}P(\mathbf{R}, t)$ . Thus  $n(\mathbf{R}, t)$  would also obey the diffusion equation (21). A useful way of writing this assuming, for simplicity, variation only along the  $z$  direction, is

$$\frac{\partial n}{\partial t} = -\frac{\partial j}{\partial z} \quad (22)$$

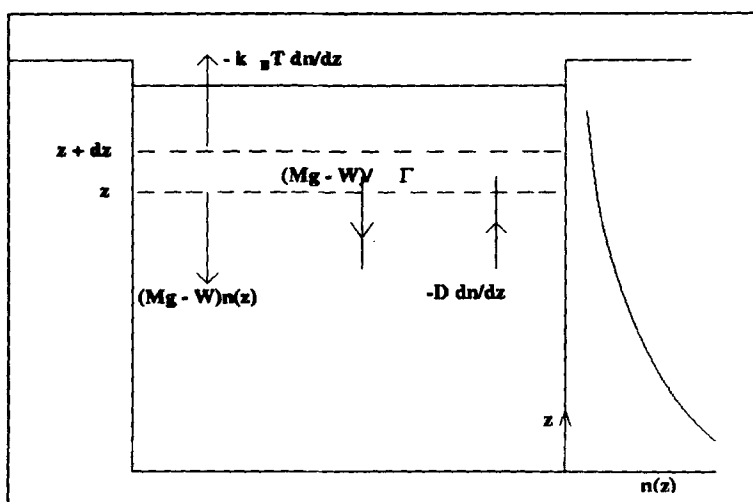
where the particle *current*, that is the number of particles crossing unit area normal to the  $z$  axis in unit time is

$$j(z, t) = -D \frac{\partial n}{\partial z} \equiv j_{\text{diff}}. \quad (23)$$

Now imagine imposing, along the  $-z$  axis, a constant force  $F$  on the particles. In the typical experiment this force is gravity, in which case  $F = Mg - W$ , where  $M$  is the mass of a Brownian particle,  $g$  the acceleration due to gravity, and  $W$  the weight of water displaced by the Brownian particle. In the absence of Brownian motion and walls this would cause each particle to drift downwards with a terminal speed  $F/\Gamma$  where  $\Gamma$  is the friction coefficient opposing the motion of the particles as a result of the viscosity of the fluid. For spherical particles of radius  $a$  much larger than molecular dimensions, moving slowly through a fluid with viscosity  $\eta$ , with the condition that the fluid in contact with the particle is at rest with respect to the particle, G G Stokes showed in 1851 that  $\Gamma = 6\pi\eta a$ . The resulting current due to the force  $F$  would then be  $j_F = -n(z)F/\Gamma = -n(z)(Mg - W)/\Gamma \equiv j_{\text{grav}}$  for gravity. At equilibrium, when Brownian motion is included,  $j_{\text{diff}}$  from (23) and  $j_F$  should balance, i.e.,

$$\frac{nF}{\Gamma} = -D \frac{dn}{dz}, \quad (24)$$

giving a steady,  $z$ -dependent profile for the concentration (see *Figure 5*).



**Figure 5.** An atmosphere in a test-tube: gravitational and osmotic forces balance, as do the corresponding currents.



We can derive an almost identical condition in a rather different way, without ever looking at the underlying dynamical processes; and this will finally give us the vital relation between  $D$  and the friction  $\Gamma$ . Instead of balancing currents, let us balance the forces on the Brownian particles in the steady state arising from the interplay of gravity and Brownian motion. Treat the combined system of Brownian particles and molecules as a mixture of gases. Then the partial pressure<sup>4</sup> of the Brownian particles (known as the osmotic pressure), now a function of the vertical coordinate  $z$ , is simply  $p_{\text{osm}}(z) = n(z)k_{\text{B}}T$ . Since the osmotic pressure varies with depth, the difference between the osmotic pressures at the top and the bottom of a layer of particles at height  $z$  and thickness  $dz$  results in a force  $-(dp_{\text{osm}}/dz)dz = -k_{\text{B}}T(dn/dz)dz$  on the layer. Thus the ‘osmotic force’ per unit volume is  $f_{\text{osm}} = -k_{\text{B}}Tdn/dz$ . This is balanced by the gravitational force per unit volume, giving

$$n(z)F = n(z)(Mg - W) = -k_{\text{B}}T \frac{dn}{dz}. \quad (25)$$

Comparing (24) and (25) leads us to Einstein’s famous result

$$D = \frac{k_{\text{B}}T}{\Gamma} = \frac{k_{\text{B}}T}{6\pi\eta a} \quad (26)$$

where the second equality comes from using Stokes’ estimate for the friction. This is the result promised in section 1.2, which lets us extract  $k_{\text{B}}$  from a measurement of diffusion.

Comparing (24) to our earlier expression (16) for  $D$  with dimension  $q = 3$ , the step time  $\tau$  turns out to  $M/3\pi\eta a$  for a Brownian particle with mass  $M$ . For particles with  $a = 1\mu\text{m}$  in water, and with a density comparable to that of water, this yields  $\tau \simeq 0.4\mu\text{s}$ . This makes it amply clear that you can’t measure the instantaneous speed of the Brownian particle by observations through a microscope, a fact unclear to some early workers<sup>5</sup>.

<sup>4</sup> A concept that you have seen in B Sc physics, if not earlier.

<sup>5</sup> This prompted Perrin to remark in ch. IV of his book [1] that the paths of Brownian particles are like the continuous but nowhere differentiable functions that mathematicians discuss and that this means that such objects are far from being mere mathematical curiosities. In the preface to his book, he makes similar remarks about the surfaces of aggregates of colloidal particles. These ideas are clearly the precursors of the notion of a fractal [4].





The Stokes–Einstein relation (26) connects  $D$ , a property of fluctuations, to the viscosity, a measure of friction or dissipation. If you go on to study statistical physics you will find many such ‘fluctuation-dissipation’ relations. The physics underlying all these is the same: friction and thermal fluctuations are engendered by the same processes, at least in systems at thermal equilibrium.

### 3.4 A Test-tube Atmosphere

Einstein also used the relation (25) directly to get  $k_B$ . Solving (25) gives a depth-dependent concentration

$$n(z) = n(0)e^{-Fz/k_BT}. \quad (27)$$

Thus the concentration of suspended particles in a test-tube (see *Figure 5*), provided the particles have a higher mass density than the fluid, obeys the same law as the density of air in the atmosphere (neglecting the variation of gravity with height).

### 3.5 Experiments

Einstein used his theory along with existing data on the diffusion (the spread of an initially concentrated region of sugar) in water to get a value for  $k_B$ . Since he couldn’t see the sugar molecules, he needed one more piece of information from which he could infer their size. This he did by combining measurements of the diffusivity with those of the viscosity of the solution as a function of concentration. For this he had to calculate the change in viscosity of a fluid when small particles were added to it. He found that the fractional change, to first order in the concentration, was 2.5 times the volume fraction of particles added, a result still used by chemical engineers. The trouble with using this approach for the diffusion of molecules is that the Stokes result and Einstein’s calculation of the excess viscosity are for a particle large enough that the fluid can be treated as a continuum around it, an assumption not obviously valid for the



flow of water around sugar. Although on dimensional grounds a law like (26) might hold, there is no reason to trust the  $6\pi$ . In fact, if we assume the fluid slips a bit around the particles, smaller numbers such as  $3\pi$  are possible, which might explain why Einstein's estimate for Avogadro's number from this approach is small by a factor of two.

Perrin observed the concentration as a function of height in a suspension of resin particles, by actually counting the number of particles seen in a small reference volume at various heights and verified the law (27). He also measured the diffusion coefficient and used it to give  $k_B$  using the Stokes–Einstein relation. The values he got by the two methods were quite consistent with each other and with modern values. They agreed, moreover, with those obtained from the kinetic theory estimates I mentioned earlier. The existence of molecules was thus firmly established.

#### 4. Conclusion

This article was meant not only to communicate a classic piece of physics but to make the point that physics is about the things we see around us. I hope I've convinced the reader of the importance of keeping one's eyes open – especially when looking through a microscope.

Meanwhile, the subject that Einstein invented before he got so busy with relativity and quantum mechanics lives on, in colloid science – the world of particles much bigger than a molecule but much smaller than a mustard seed, statistical physics, mathematics, finance, the working of motor proteins in cells, the analysis of DNA sequences, and so forth. The random walk is the simplest model for a polymer chain, and the physics of rubber elasticity can be understood from such a model. The mathematics of random walks is at the base of one formulation of quantum mechanics. The bibliography at the end of this article consists mainly of classic treatments of the



subject. To learn more about what people are doing with Brownian motion today, try searching for it on the Web and then looking at some of the sites in detail. My attempt, through a popular search engine, turned up 4732 sites! Some of these were for physics courses, but many were from wildly diverse areas, which will give you an idea of the extraordinary reach of the subject.

## 5. Acknowledgements

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## Suggested Reading

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*Our experience ... justifies us in believing that nature is the realisation of the simplest conceivable mathematical ideas.*

*Albert Einstein*