2 The Brownian motion

- Einstein advanced the first satisfactory theory of Brownian motion—the jiggling motion of suspended particles in a liquid as seen under a microscope. It provides us with direct visual evidence for the existence of the point-like structure of matter. The theory suggests that we can see with our own eyes the molecular thermal motion.
- The Brownian motion paper may be viewed as part of Einstein's doctoral dissertation work on the atomic structure of matter; it continues his pursuit of the idea that particles suspended in a fluid behave like molecules in solution. The motion of a Brownian particle is governed by the diffusion equation.
- Einstein was the first to provide a statistical derivation of the diffusion equation. From its solution one can calculate its variance, showing diffusion as fluctuations of a discrete system, like the prototype case of random walks. The mean-square displacement of a Brownian particle is related to the diffusion coefficient as $\langle x^2 \rangle = 2Dt$.
- The Einstein–Smoluchowski relation (already discussed in the previous chapter) between diffusion and viscosity, $D = k_B T/(6\pi \eta P)$ with η being the viscosity coefficient, is the first fluctuation–dissipation relation ever noted. This theory not only illuminates diffusion but also explains friction by showing that they both spring from the same underlying thermal process.
- Verification of Einstein's theory came about through the painstaking experimental work of Jean Perrin. This work provided another means to measure the molecular size P and Avogadro's number N_A. It finally convinced everyone, even the skeptics, of the reality of molecules.

Eleven days after Einstein completed his thesis on April 20, 1905, he submitted this "Brownian motion paper" to *Annalen der Physik* (Einstein 1905c). This paper can be regarded as part of Einstein's dissertation research and it represents the culmination of his study of atomic structure of matter (extending back at least to 1901) by explaining the Brownian motion. To many of us, before the advent of (field-ion) "atomic" microscopes in the 1960s, the most direct visual evidence for atoms' existence was viewing the jiggling motion of suspended particles (e.g. pollen) in a liquid, as seen under a microscope. This

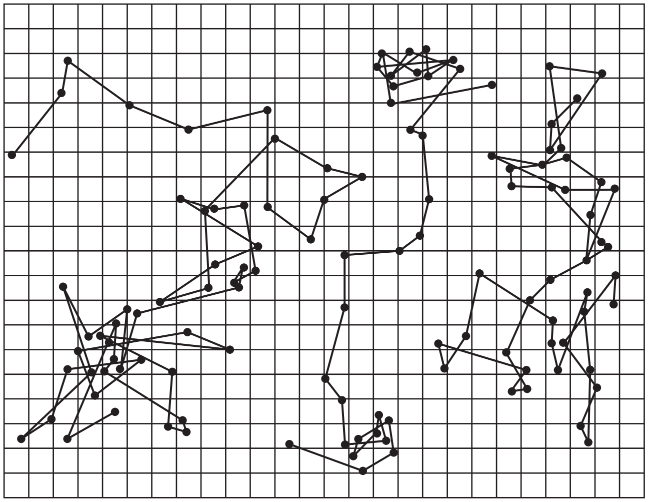

Fig. 2.1 The zigzag motion of Brownian particles as sketched by Perrin, at 30-second intervals. The grid size is 3.2μ and the radius of the particle is 0.53μ. Reproduction of Fig. 6 in Perrin (1909).

"Brownian motion" was originally discussed in 1827 by botanist Robert Brown (1773–1858). Although it was suggested soon afterwards that such Brownian motion is an outward manifestation of the molecular motion postulated by the kinetic theory of matter, it was not until 1905 that Einstein was finally able to advance a satisfactory theory.

Einstein pioneered several research directions in his Brownian motion paper. In particular he argued that, while thermal forces change the direction and magnitude of the velocity of a suspended particle on such a small time-scale that it cannot be measured, the mean-square displacement (the overall drift) of such a particle is an observable quantity, and can be calculated in terms of molecular dimensions. One cannot but be amazed by the fact that Einstein found a physics result so that a careful measurement of this zigzag motion (see Fig. 2.1) through a simple microscope would allow us to deduce Avogadro's number!

It is also interesting to note that the words "Brownian motion" did not appear in the title of Einstein's paper (Einstein 1905c), even though he conjectured that the motion he predicted was the same as Brownian motion. He was prevented from being more definitive because he had no access then to any literature on Brownian motion. One should remember that in 1905 Albert Einstein was a patent office clerk in Bern and did not have ready access to an academic library and other research tools typically associated with a university.

2.1 Diffusion and Brownian motion

Einstein argued that the suspended particles in a liquid, differing in their statistical and thermal behavior from molecules only in their sizes, should obey the same diffusion equation that describes the chaotic thermal motion of the liquid's constituent molecules. Here we follow Einstein in his derivation of the Brownian motion equation and show that it is just the diffusion equation.

2.1.1 Einstein's statistical derivation of the diffusion equation

Einstein assumed that each individual particle executes a motion that is independent of the motions of all the other particles; the motions of the same particle in different time intervals are also mutually independent processes, so long as these time intervals are chosen not to be too small. For simplicity of presentation, we will work in a one-dimensional (1D) model. One is interested in the displacement $x(t)$ after the particle makes a large number (N) of discrete displacement steps of size Δ in a time interval τ. The probability density $f_\tau(\Delta)$ is introduced as

$$f_\tau(\Delta)d\Delta = \frac{dN}{N}, \quad \text{or} \quad dN = Nf_\tau(\Delta)d\Delta. \tag{2.1}$$

The probability should clearly be the same whether the step is taken in the forward or backward direction: $f_\tau(\Delta) = f_\tau(-\Delta)$.

Let $\rho(x,t)$ be the number of particles per unit volume. One can then calculate the distribution at time $t+\tau$ from the distribution at time t. The change of particle density at the spatial interval $(x, x+dx)$ is due to particles flowing in from both directions (hence the $\pm\infty$ limits),

$$\rho(x, t+\tau) = \int_{-\infty}^{+\infty} \rho(x+\Delta, t) f_\tau(\Delta)d\Delta. \tag{2.2}$$

One then makes Taylor series expansions on both sides of this equation, the LHS being

$$\rho(x, t+\tau) = \rho(x,t) + \tau\frac{\partial\rho(x,t)}{\partial t} + \cdots \tag{2.3}$$

and the RHS being

$$\begin{aligned} &\int_{-\infty}^{+\infty}\left[\rho(x,t) + \Delta\frac{\partial\rho(x,t)}{\partial x} + \frac{\Delta^2}{2!}\frac{\partial^2\rho(x,t)}{\partial x^2} + \cdots\right] f_\tau(\Delta)d\Delta \\ &\quad = \rho(x,t) + \left[\int_{-\infty}^{+\infty}\frac{\Delta^2}{2}f_\tau(\Delta)d\Delta\right]\frac{\partial^2\rho(x,t)}{\partial x^2} + \cdots \end{aligned} \tag{2.4}$$

where we have used the conditions that the probability must add to unity and $f_\tau(\Delta)$ is an even function of Δ:

$$\int_{-\infty}^{+\infty} f_\tau(\Delta)d\Delta = 1, \quad \text{and} \quad \int_{-\infty}^{+\infty}\Delta f_\tau(\Delta)d\Delta = 0. \tag{2.5}$$

Equating the leading terms of both the LHS and RHS, we obtain the diffusion equation

$$\frac{\partial\rho}{\partial t} = D\frac{\partial^2\rho}{\partial x^2}, \tag{2.6}$$

with the diffusion coefficient being related to the probability density as

$$D = \frac{1}{2\tau}\int_{-\infty}^{+\infty}\Delta^2 f_\tau(\Delta)d\Delta. \tag{2.7}$$

In practice D can be obtained from experiment. We should remark that the fundamental assumption in this derivation is that $f_\tau(\Delta)$ depends only on Δ, not on previous history. Such a process we now call "Markovian" in the study of random processes. Einstein's Brownian investigation is one of the pioneering papers laying the foundation for a formal theory of stochastic processes.

In Chapter 1 we defined the diffusion coefficient D through (1.23) as opposed to its introduction in Eq. (2.6). Their equivalence can be demonstrated by taking the gradient of both terms in Fick's first law (1.23) and turning the equation into (2.6), sometimes called Fick's second law, by using the equation of continuity (written in 1D form again for simplicity[1])

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho v}{\partial x} = 0. \tag{2.8}$$

[1] Just as the continuity equation in 3D is written as $\partial_t \rho + \nabla \cdot \rho \mathbf{v} = 0$, Fick's second law has the 3D form of $\partial_t \rho = D\nabla^2 \rho$.

2.1.2 The solution of the diffusion equation and the mean-square displacement

The solution to the diffusion equation (2.6) is a Gaussian distribution (*Exercise*: check that this is the case)

$$\rho(x,t) = \frac{1}{\sqrt{4\pi Dt}} e^{-x^2/4Dt} \tag{2.9}$$

which is a bell-shaped curve, peaked at $x = 0$. Initially ($t = 0$) the density function is a Dirac delta function $\rho(x) = \delta(x = 0)$; as t increases, the height of this peak, still centered around $x = 0$, shrinks but the area under the curve remains unchanged. In other words, the probability of finding the particle away from the origin (as given by the density ρ) increases with time. There is, on the average, a drift motion away from the origin (cf. Fig. 2.2). One can easily check that it is properly normalized using the familiar result of Gaussian integrals (cf. Appendix A.2).

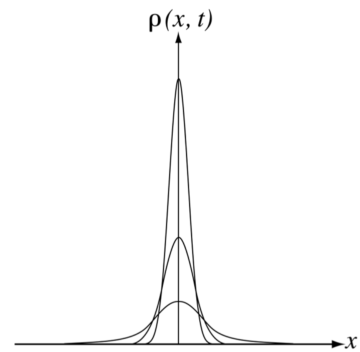

Fig. 2.2 Density distribution plotted for various values of t. At $t = 0$ it is a delta function at $x = 0$; as t increases, the distribution becomes broader and spreads out.

Clearly the curve in Fig. 2.2 is symmetric with respect to $\pm x$. This implies a vanishing average displacement $\langle x \rangle = 0$. But we have a nonzero mean-square displacement (the variance) that monotonically increases with time [cf. Eq. (A.44)]:

$$\left\langle x^2 \right\rangle = \int_{-\infty}^{\infty} x^2 \rho dx = 2Dt. \tag{2.10}$$

We note that $\left\langle x^2 \right\rangle$ is just the width of the Gaussian distribution. Thus the broadening of the bell-shaped curve with time (as shown in Fig. 2.2) just reflects the increase of the mean-square displacement.

The basic point is that while the fluid density represents the overall coarse (i.e. averaged) description of the underlying molecular motion, still, once the density function is known, the fluid fluctuation of such motion, like the root-mean-square (i.e. the variance) displacement, can then be calculated. Such a fluctuation property shows up as an observable drift motion of the immersed Brownian particles.

2.2 Fluctuations of a particle system

To substantiate the claim that Brownian motion is evidence of the point-like structure of matter, we now directly connect this Gaussian distribution (2.9) and the mean-square displacement (2.10) to the fluctuations of a particle system.[2] Random walks being the prototype of a discrete system, we first discuss the fluctuation phenomenon associated with this system.

[2]This is to be contrasted with the fluctuation of a system of waves to be discussed in Section 6.5.

2.2.1 Random walk

Consider a particle moving in one dimension at regular time intervals in steps of equal size. At each instance it moves forward and backward at random. Let a walk of N steps end at k steps from the initial point. F is the number of forward steps and B the backward steps. Thus $F + B = N$ and $F - B = k$. After a large number of such walks (each ends at a different position), one is interested in the distribution of the end-point positions. Namely, we seek the probability $p(k, N)$ of finding the particle at k steps from the origin after making N steps. Since at each step one makes a two-valued choice, there are a total 2^N possible outcomes; the probability is evidently

$$p(k,N) = \frac{N!/F!B!}{2^N} = \frac{2^{-N}N!}{\left(\frac{N+k}{2}\right)!\left(\frac{N-k}{2}\right)!}. \tag{2.11}$$

Since we expect the result to have the form of an exponential, we proceed by first taking the logarithm of this expression,

$$\ln p = -N\ln 2 + \ln N! - \ln\left(\frac{N+k}{2}\right)! - \ln\left(\frac{N-k}{2}\right)!.$$

Using Stirling's formula[3] of $\ln X! \simeq X\ln X - X$ for large X, we have

[3]See Section A.3 for a proof of Stirling's formula.

$$\begin{aligned}\ln p &= -N\ln 2 + N\ln N - N - \left(\frac{N+k}{2}\right)\ln\left(\frac{N+k}{2}\right) + \left(\frac{N+k}{2}\right) \\ &\quad - \left(\frac{N-k}{2}\right)\ln\left(\frac{N-k}{2}\right) + \left(\frac{N-k}{2}\right) \\ &= -\frac{N}{2}\left[\left(1+\frac{k}{N}\right)\ln\left(1+\frac{k}{N}\right) + \left(1-\frac{k}{N}\right)\ln\left(1-\frac{k}{N}\right)\right].\end{aligned}$$

In the limit of small k/N, the logarithm can be approximated by $\ln(1+\epsilon) \simeq \epsilon - \epsilon^2/2$. The probability logarithm becomes $\ln p \simeq -k^2/2N$, which can be inverted and normalized (by a standard Gaussian integration) to yield

$$p(k,N) = \frac{1}{\sqrt{2\pi N}}e^{-k^2/2N}. \tag{2.12}$$

Similarly using the Gaussian integral we also have

$$\left\langle k^2\right\rangle = \int k^2 p(k,N)dk = N, \tag{2.13}$$

which is the variance $\langle \Delta k^2 \rangle = \langle k^2 \rangle - \langle k \rangle^2$ because for our case $\langle k \rangle = 0$. In particular one often uses the fractional variance to characterize the fluctuation from the mean, leading to the well-known result

$$\frac{\sqrt{\langle \Delta k^2 \rangle}}{N} = \frac{1}{\sqrt{N}}. \tag{2.14}$$

This is the characteristic of fluctuations in a discrete system.

2.2.2 Brownian motion as a random walk

So far in this calculation no scales have been introduced. For the problem of calculating the displacement of a random walker, we will denote a displacement step by λ and the time interval by τ so that $x = k\lambda$ and $t = N\tau$. This allows us to translate the above probability density into the number density $p(k, N) \to \rho(x, t)$ with

$$\rho(x,t) = \frac{1}{\sqrt{4\pi Dt}} e^{-x^2/4Dt} \qquad \text{with } D = \frac{\lambda^2}{2\tau}. \tag{2.15}$$

Thus we can interpret the solution (2.9) of the diffusion equation as representing, at some small scale, a Brownian particle executing a random walk. This exercise in random walks emphasizes the discrete nature of the molecular process underlying the diffusion phenomenon. We shall have occasion (in Section 6.1) to use this connection in the discussion of Einstein's proposal for a discrete basis of radiation—the quanta of light.

2.3 The Einstein–Smoluchowski relation

In the previous chapter on Einstein's doctoral thesis (Einstein 1905b) we derived this relation between the diffusion coefficient D and the viscosity η:

$$D = \frac{k_{\mathrm{B}} T}{6\pi \eta P} \tag{2.16}$$

with P being the radius of the suspended particle, T the absolute temperature, and k_{B} Boltzmann's constant, related to the gas constant and Avogadro's number as $k_{\mathrm{B}} = R/N_{\mathrm{A}}$. This relation was also obtained by the Polish physicist Marian Smoluchowski (1872–1917) in his independent work on Brownian motion (Smoluchowski 1906). Hence, it is often referred to as the Einstein–Smoluchowski relation. Einstein in his Brownian motion paper (Einstein 1905c) rederived it and improved its theoretical reasoning in two aspects:

1. In his thesis paper, for the osmotic pressure $F_{\mathrm{os}} = -n^{-1}\partial p/\partial x$ as shown in Eq. (1.24), Einstein assumed the validity of the **van't Hoff analogy**—the behavior of solute molecules in a dilute solution are similar to those of an ideal gas, and used the ideal gas law (1.25) to relate the pressure to mass density, obtaining the result:

$$F_{\mathrm{os}} = -\frac{RT}{\rho N_{\mathrm{A}}} \frac{\partial \rho}{\partial x}. \tag{2.17}$$

In the Brownian motion paper, he justified the applicability of this result on more general thermodynamical grounds. Consider a cylindrical volume with unit cross-sectional area and length $x = l$. Under an arbitrary virtual displacement δx, the change of internal energy is given by

$$\delta U = -\int_0^l F_{\mathrm{os}} \rho \delta x dx \tag{2.18}$$

and the change of entropy by[4]

$$\delta S = \int_0^l \frac{R}{N_{\mathrm{A}}} \rho \frac{\partial \delta x}{\partial x} dx = -\frac{R}{N_{\mathrm{A}}} \int_0^l \frac{\partial \rho}{\partial x} \delta x dx. \tag{2.19}$$

[4]One may be more familiar with the entropy change under an isothermal expansion when written $\delta S = N k_{\mathrm{B}} \delta V / V = \rho k_{\mathrm{B}} \delta V$. In the case here we have $\delta V = \delta x$ because of unit cross-sectional area.

We have performed an integration by parts in reaching the last expression. The relation (2.17) then follows from the observation that the free energy of a system of suspended particles vanishes for such a displacement, $\delta F = \delta U - T \delta S = 0$.

2. In his thesis paper, Einstein arrived at the result (2.16) by the balance of the osmotic force and the frictional drag force (described by Stokes' law) $F_{\mathrm{os}} = F_{\mathrm{dg}}$ on a single molecule. In the Brownian motion paper this would be obtained by a more general thermodynamical argument. Consider the flow of particles that encounters the viscous drag force F_{dg} reaching the terminal velocity ω. The mobility parameter μ is defined by $\omega = \mu F_{\mathrm{dg}} = -\mu \partial U / \partial x$. The drift current density $j = \rho \omega$ produces a density gradient which in turn produces a counteracting diffusion current. This current is related to the diffusion coefficient by the diffusion equation in the form of Fick's first law (1.23)

$$D \frac{\partial \rho}{\partial x} = \rho \omega = -\rho \mu \frac{\partial U}{\partial x}. \tag{2.20}$$

On the other hand, at equilibrium we must have the Boltzmann distribution

$$\rho(x) = \rho(0) e^{-U(x)/k_{\mathrm{B}} T} \tag{2.21}$$

so that

$$\frac{\partial \rho}{\partial x} = -\frac{\rho}{k_{\mathrm{B}} T} \frac{\partial U}{\partial x}. \tag{2.22}$$

Substituting this into (2.20),

$$D \frac{\rho}{k_{\mathrm{B}} T} \frac{\partial U}{\partial x} = \rho \mu \frac{\partial U}{\partial x}, \tag{2.23}$$

we have

$$D = \mu k_{\mathrm{B}} T, \tag{2.24}$$

which is the Einstein–Smoluchowski relation (2.16), upon using the Stokes' law of $\mu = (6\pi \eta P)^{-1}$ as derived in (1.29).

2.3.1 Fluctuation and dissipation

The Einstein–Smoluchowski relation (2.16) is historically the first example of a fluctuation–dissipation theorem, which would turn into a powerful tool in statistical physics for predicting the behavior of nonequilibrium thermodynamical systems. These systems involve the irreversible dissipation of energy into heat from their reversible thermal fluctuations at thermodynamic equilibrium.

As illustrated in our discussion of the Einstein–Smoluchowski relation the fluctuation–dissipation theorem relies on the assumption that the response of a system in thermodynamic equilibrium to a small applied force is the same as its response to a spontaneous fluctuation. Thus Browning motion theory not only illuminates diffusion but also explains friction by showing that they spring from the same underlying thermal process.

2.3.2 Mean-square displacement and molecular dimensions

Having demonstrated that the observable root-mean-square displacement of the Brownian particle was related to the diffusion coefficient D, as shown in (2.10), which in turn can be expressed in terms of molecular dimensions (molecular size P and Avogadro number N_A) through the Einstein–Smoluchowski relation (2.16), Einstein derived the final result of

$$x_{\mathrm{rms}} = \sqrt{\langle x^2 \rangle} = \sqrt{2Dt} = \sqrt{\frac{2RT}{N_A}\frac{t}{6\pi\eta P}}. \tag{2.25}$$

This is what we meant earlier when we said "a careful measurement of this zigzag motion through a simple microscope would allow us to deduce the Avogadro number!"

2.4 Perrin's experimental verification

Precise observations of Brownian motion were difficult at that time. The results obtained during the first few years after 1905 were inconclusive. Einstein was skeptical about the possibility of obtaining sufficiently accurate data for such a comparison with theory.

But in 1908 Jean Perrin (1870–1942) entered the field and came up with an ingenious combination of techniques for preparing emulsions with precisely controllable particle sizes,[5] and for measuring particle numbers and displacements. For this series of meticulously carried out brilliant experiments (and other related work) Perrin received the Nobel Prize in physics in 1926. The Brownian motion work was summed up masterfully in his 1909 paper (Perrin 1909) from which we extracted Figs. 2.1 and 2.3.

[5] Recall that Einstein's calculation assumed equal size P for all suspended particles.

In particular we have Fig. 2.3 in which Perrin translated 365 projected Brownian paths to a common origin. The end-position of each path is then projected onto a common plane, call it the x-y plane. The radial distance on this plane (labelled by σ) is marked by a series of rings with various σ values. The 3D version of the solution (2.9) of the diffusion equation reads as

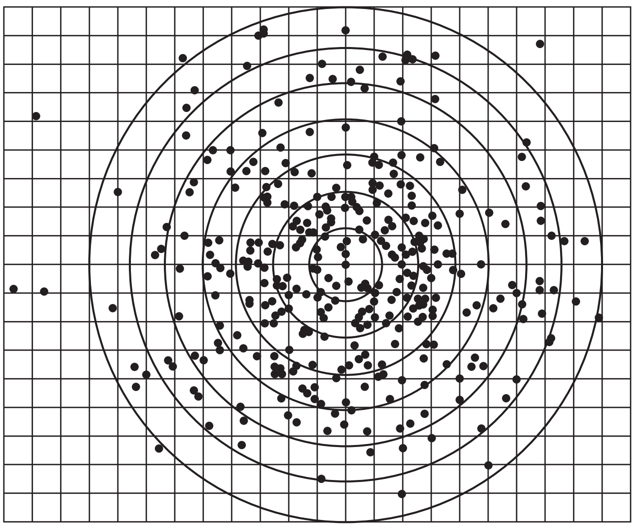

Fig. 2.3 In order to check the diffusion law, Jean Perrin parallel-transported 365 Brownian paths to a common origin. The end-position of each path is then projected onto a common plane. Reproduction of Fig. 7 in Perrin (1909).

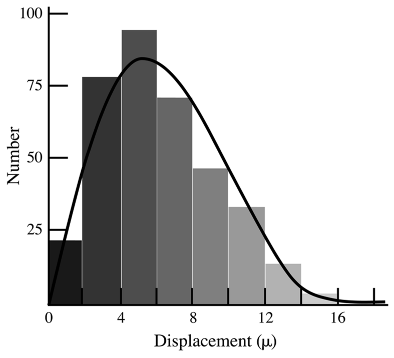

Fig. 2.4 Verification of the diffusion law in Brownian motion. The solid line is the theoretical curve. Each bar in the histogram represents the total number of paths with endpoints at given plane-radial distance (σ) from the origin according to the data as shown in Fig. 2.3.

$$\rho(x,t) = \frac{1}{(4\pi Dt)^{3/2}} e^{-r^2/4Dt} \tag{2.26}$$

where r is the 3D radial distance from the origin $r^2 = \sigma^2 + z^2$. As an infinitesimal ring-shaped volume is $2\pi\sigma d\sigma dz$, one can calculate the number of particles within each of the rings in Fig. 2.3 by a simple integration over the vertical distance

$$\Delta N = \frac{2\pi\sigma\Delta\sigma}{(4\pi Dt)^{3/2}} \int_{-\infty}^{+\infty} e^{-(\sigma^2+z^2)/4Dt} dz. \tag{2.27}$$

A simple Gaussian integration yields

$$\Delta N = \frac{\sigma\Delta\sigma}{2Dt} e^{-\sigma^2/4Dt}, \tag{2.28}$$

which is the theoretical curve plotted in Fig. 2.4.

Thus experiments were able to confirm in detail the theoretical predictions by Einstein and Smoluchowski. This work finally convinced everyone, even the skeptics, of the reality of molecules.