

Lecture 8: Brownian motion in liquids

8.1 Historical Overview

The notion of random motion has been a topic of great philosophical and scientific discourse throughout the history of humanity. As one of the earliest proponents of this idea, a Roman poet and philosopher Lucretius in his scientific poem “On the Nature of Things” wrote the following about the behaviour of dust particles:

“And thus they flit around in all directions,
At random all and every way, and fill
The hidden nooks of things with a seething whirl.”

An idea he proposed to reinforce the atomistic models in Roman philosophy bears a gross resemblance to the nature of the random motion of particles suspended in a fluid. However, the first true discovery of random motion of particles in a fluid is credited to the botanist Robert Brown. In 1827, during a study on the suspension of pollen grains in water, he observed numerous particles ejected by pollen grains performing zig-zag motion. Through a series of observations on different materials, Brown noted that this motion was not related to life, but rather a physical phenomenon which had no biological origin. After Brown’s notable work, very little progress was taken in understanding the physical principles of this process.

In the second half of the 19th century, the framework of the molecular kinetic theory of gases was making significant strides, particularly pioneered by Maxwell, Boltzmann and Gibbs. This instilled Gouy to suggest that the nature of Brownian motion could be linked to molecular kinetic theory. However, a more quantitative formalism of this relationship between kinetic theory and Brownian motion was developed by Einstein in 1905. Simultaneously, around the same period, Smoluchowski and Sutherland also made similar observations about the nature of Brownian motion.

8.2 Einstein’s model of Brownian motion

In his groundbreaking 1905 paper, Einstein built upon the progress in molecular kinetic theory, primarily pioneered by the efforts of Boltzmann, Maxwell, and Gibbs. By employing these fundamental principles, Einstein addressed the phenomenon of Brownian motion, elucidating the molecular or atomic underpinnings of the persistent and irregular motion displayed by microscopic particles suspended in a stationary fluid.

Owing to the probabilistic nature of particle dynamics, a probability distribution function (PDF), $P(x, t)$, characterizing the probability of finding the particle at some position x at a time t , is considered along with certain initial conditions $P(x, 0)$. In Einstein’s model, the Brownian motion of particles is propagated by making small displacements of length Δ . These displacements occur due to random molecular collisions on the particle and are characterized by a probability

distribution, $f(\Delta)$. An equation governing the time–evolution of the PDF $P(x, t + \tau)$ can then be written as

$$P(x, t + \tau) = \int_{-\infty}^{\infty} d\Delta f(\Delta) P(x - \Delta, t), \quad (8.2.1)$$

where τ is a small time increment. The above equation quantitatively relates the probability of detecting particles at position x at time $t + \tau$ to two factors: (i) the likelihood of encountering the particle at $x - \Delta$ at time t and (ii) the probability of the particle undergoing a displacement of length Δ . It is crucial to emphasize several key assumptions that form the foundation of Eq. (8.2.1). Foremost among these assumptions is that it considers the occurrence of a single displacement within the time interval τ . Additionally, the equation assumes that the probability of the jump’s magnitude remains unaffected by the displacements at an earlier time. These assumptions align naturally with the meaningful scales inherent to the time interval τ . This interval is considerably small when compared to the macroscopic time frame of experimental measurements, a factor that allows it to be treated as a single displacement. However, it retains a reasonably large magnitude when compared to the average time–interval between molecular collisions, thereby maintaining the assumption of independence between consecutive jumps.

To obtain a rate equation governing the probability density $P(x, t)$, we expand the right–hand side of Eq. (8.2.1) in powers of Δ and τ . Keeping terms up to second order yields

$$P(x, t) + \tau \frac{\partial P(x, t)}{\partial t} + \mathcal{O}(\tau^2) = \int_{-\infty}^{\infty} d\Delta f(\Delta) \left[P(x, t) - \Delta \frac{\partial P}{\partial x} + \frac{\Delta^2}{2} \frac{\partial^2 P}{\partial x^2} + \dots \right]. \quad (8.2.2)$$

The zeroth–order terms on both sides cancel owing to the normalization of $f(\Delta)$. Isotropic collisions enforce a zero mean jump length, $\langle \Delta \rangle = 0$. Retaining only the lowest nonzero term in the series, we obtain

$$\frac{\partial P(x, t)}{\partial t} = \frac{\langle \Delta^2 \rangle}{2\tau} \frac{\partial^2 P(x, t)}{\partial x^2}, \quad (8.2.3)$$

which is recognized as the diffusion equation with diffusivity $D = \langle \Delta^2 \rangle / (2\tau)$. Writing D explicitly gives

$$\frac{\partial P(x, t)}{\partial t} = D \frac{\partial^2 P(x, t)}{\partial x^2}. \quad (8.2.4)$$

8.2.1 Solutions to the diffusion equation

The diffusion equation may be solved by Fourier transformation. Defining the characteristic function (the Fourier transform of P) as

$$\tilde{P}(k, t) = \int_{-\infty}^{\infty} e^{-ikx} P(x, t) dx, \quad (8.2.5)$$

the diffusion equation transforms into

$$\frac{d\tilde{P}(k, t)}{dt} = -Dk^2 \tilde{P}(k, t), \quad (8.2.6)$$

whose solution is

$$\tilde{P}(k, t) = \tilde{P}(k, 0) \exp[-Dk^2 t]. \quad (8.2.7)$$

Taking the inverse Fourier transform yields the solution of the diffusion equation for an arbitrary initial condition $P_0(x)$:

$$P(x, t) = \left(\frac{1}{\sqrt{4\pi Dt}} e^{-x^2/(4Dt)} \right) \otimes P_0(x), \quad (8.2.8)$$

where \otimes denotes convolution. For the trivial initial condition $P_0(x) = \delta(x)$, Eq. (8.2.8) reduces to

$$P(x, t) = \frac{1}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right). \quad (8.2.9)$$

8.2.2 Moments and cumulants of the displacement distribution

Because the characteristic function is known, all moments and cumulants of the displacement distribution can be derived. Defining the cumulant generating function $K(k, t) = \ln \tilde{P}(k, t)$, it follows from Eq. (8.2.7) that

$$K(k, t) = \ln \tilde{P}(k, 0) - Dk^2 t. \quad (8.2.10)$$

The n th cumulant is given by

$$\kappa_n(t) = \frac{(-1)^n}{i^n} \left. \frac{d^n K(k, t)}{dk^n} \right|_{k=0}. \quad (8.2.11)$$

For Brownian motion the mean displacement $\kappa_1(t)$ is zero by symmetry. The variance of the displacement reads

$$\Delta x^2(t) = \langle x^2(t) \rangle - \langle x(t) \rangle^2 = 2Dt + x_0^2, \quad (8.2.12)$$

where x_0^2 arises from the second derivative of $\ln \tilde{P}(k, 0)$. Thus the mean-squared displacement (MSD) grows linearly with time,

$$\langle x^2(t) \rangle = 2Dt. \quad (8.2.13)$$

The square-root time-dependence of the displacement, $\sqrt{\langle x^2(t) \rangle} \propto \sqrt{t}$, is one of the hallmarks of Brownian motion.

8.2.3 Connection to viscosity: the Stokes–Einstein relation

Diffusive flux in 1D (Fick’s law):

$$j_{\text{diff}}(x) = -D \frac{\partial c(x)}{\partial x}$$

where $c(x)$ is the particle concentration.

Drift flux under a constant force F :

If each particle experiences a force F , and responds with a steady drift velocity $v_d = \mu F$, then

$$j_{\text{drift}}(x) = c(x) \mu F$$

Equilibrium (no net current):

$$j_{\text{total}} = j_{\text{diff}} + j_{\text{drift}} = 0 \implies -D \frac{\partial c}{\partial x} + \mu F c = 0$$

Assuming $F = -\frac{\partial U(x)}{\partial x}$, and thermal equilibrium so that

$$c(x) \propto \exp\left[-\frac{U(x)}{k_B T}\right],$$

we get

$$\frac{\partial c}{c} = -\frac{1}{k_B T} \frac{\partial U}{\partial x} \implies \frac{\mu F}{D} = \frac{1}{k_B T} \implies \boxed{D = \mu k_B T.}$$

Thus the diffusion constant D , characterizing spontaneous fluctuations, is linked to the mobility μ , i.e. the response to a force — the 1D version of the Einstein (fluctuation–dissipation) relation.

Although the diffusion equation and its solutions describe how probability spreads in time and space, it is also instructive to relate the diffusion coefficient D to a macroscopic property of the solvent. Einstein accomplished this by equating the diffusive flux to the drift that arises when a constant external force F acts on a suspended particle. In steady state the particle moves with velocity v , and Stokes’ law for a sphere of radius a in a fluid of viscosity η gives a frictional force

$$F_{\text{fric}} = 6\pi\eta a v. \tag{8.2.14}$$

On the other hand, a small external force produces a drift current density $J_{\text{drift}} = vP(x, t)$, while diffusion produces a current density $J_{\text{diff}} = -D \partial P / \partial x$. At equilibrium these two contributions balance (no net current), leading to $D = \mu k_B T$, where $\mu = 1/(6\pi\eta a)$ is the mobility and $k_B T$ is the thermal energy. One therefore obtains the celebrated Stokes–Einstein relation

$$D = \frac{k_B T}{6\pi\eta a}, \tag{8.2.15}$$

which connects the microscopic diffusion coefficient to the macroscopic viscosity of the solvent.

This relation implies that measuring D not only characterizes the stochastic motion but also provides a route to determine the hydrodynamic radius of the diffusing particle or the viscosity of the medium.

8.3 Random walk \rightarrow Diffusion equation

The diffusion equation can also be derived from a simple one-dimensional random walk by considering the probability distribution of a particle moving in discrete time steps and then taking the continuum limit. Consider a particle performing a random walk on a one-dimensional lattice with lattice spacing Δx . At each time step Δt , the particle can move to the left or right with equal probability $1/2$. Let $P(x, t)$ denote the probability of finding the particle at position x at time t .

The transition probabilities for the particle are given by

$$P(x, t + \Delta t) = \frac{1}{2}P(x + \Delta x, t) + \frac{1}{2}P(x - \Delta x, t). \quad (8.3.1)$$

To proceed, we expand $P(x \pm \Delta x, t)$ in a Taylor series about the point x :

$$P(x \pm \Delta x, t) \approx P(x, t) \pm \Delta x \frac{\partial P(x, t)}{\partial x} + \frac{(\Delta x)^2}{2} \frac{\partial^2 P(x, t)}{\partial x^2} + \dots \quad (8.3.2)$$

Substituting these expansions into the transition equation and collecting terms, we find to leading order that

$$P(x, t + \Delta t) \approx P(x, t) + \frac{(\Delta x)^2}{2} \frac{\partial^2 P(x, t)}{\partial x^2}. \quad (8.3.3)$$

Rearranging and dividing by Δt yields

$$\frac{P(x, t + \Delta t) - P(x, t)}{\Delta t} \approx \frac{(\Delta x)^2}{2\Delta t} \frac{\partial^2 P(x, t)}{\partial x^2}. \quad (8.3.4)$$

Taking the continuum limit $\Delta x \rightarrow 0$ and $\Delta t \rightarrow 0$ such that the ratio $D = (\Delta x)^2/(2\Delta t)$ remains finite leads to the diffusion equation

$$\frac{\partial P(x, t)}{\partial t} = D \frac{\partial^2 P(x, t)}{\partial x^2}. \quad (8.3.5)$$

8.3.1 Introducing drift in the random walk

To introduce drift, the probabilities for stepping right and left are taken to be unequal (p to the right and $q = 1 - p$ to the left). The discrete evolution equation is then

$$P(x, t + \Delta t) = p P(x - \Delta x, t) + q P(x + \Delta x, t). \quad (8.3.6)$$

Expanding $P(x \pm \Delta x, t)$ in a Taylor series about x gives

$$P(x \pm \Delta x, t) \approx P(x, t) \pm \Delta x \frac{\partial P}{\partial x} + \frac{(\Delta x)^2}{2} \frac{\partial^2 P}{\partial x^2} + \dots \quad (8.3.7)$$

Substituting these series into the transition equation and keeping terms up to second order leads to

$$P(x, t + \Delta t) \approx P(x, t) + (q - p)\Delta x \frac{\partial P(x, t)}{\partial x} + \frac{(\Delta x)^2}{2} \frac{\partial^2 P(x, t)}{\partial x^2}. \quad (8.3.8)$$

Subtracting $P(x, t)$ from both sides, dividing by Δt , and taking the continuum limit $\Delta x, \Delta t \rightarrow 0$ with

$$D = \frac{(\Delta x)^2}{2\Delta t}, \quad v = \frac{(q - p)\Delta x}{\Delta t}, \quad (8.3.9)$$

held constant yields the diffusion equation with drift,

$$\frac{\partial P(x, t)}{\partial t} = -v \frac{\partial P(x, t)}{\partial x} + D \frac{\partial^2 P(x, t)}{\partial x^2}. \quad (8.3.10)$$

Here v is the drift velocity and D is the diffusivity. Equation (8.3.10) is the general form of the one-dimensional Fokker–Planck equation for advection and diffusion.

8.4 Protein diffusion and quasielastic neutron scattering

The diffusive solutions derived above are not merely of abstract interest— they underlie the interpretation of neutron-scattering experiments that probe the dynamics of complex molecules. In particular, *quasielastic neutron scattering* (QENS) is a powerful technique for studying translational diffusion of proteins in solution. Because hydrogen has a large incoherent scattering cross-section, the neutron signal from a protein solution is dominated by the self-correlations of hydrogen atoms, effectively measuring the single-particle dynamics of the protein molecules in the solvent.

8.4.1 Intermediate scattering function and dynamic structure factor

In neutron scattering the quantity measured in the time domain is the intermediate scattering function $F(k, t)$, which is the spatial Fourier transform of the van Hove self-correlation function $G_s(r, t)$. The self part of the van Hove function is nothing other than the probability density function for the displacement vector \mathbf{r} : for isotropic diffusion the motion along each Cartesian axis is independent, so the three-dimensional distribution factorizes as $P(\mathbf{r}, t) = P(x, t)P(y, t)P(z, t)$, with the one-dimensional Gaussian $P(x, t)$ given by Eq. (8.2.9). Multiplying the three factors yields the familiar three-dimensional Gaussian form,

$$G_s(r, t) = \frac{1}{(4\pi Dt)^{3/2}} \exp(-r^2/(4Dt)). \quad (8.4.1)$$

Taking the spatial Fourier transform yields

$$F(k, t) = \exp(-Dk^2 t), \quad (8.4.2)$$

where $k = |\mathbf{k}|$ is the magnitude of the scattering vector and D is the translational diffusion coefficient. This simple exponential decay is the analogue of Eq. (8.2.9) in reciprocal space.

The dynamic structure factor $S(k, \omega)$ is defined as the temporal Fourier transform of $F(k, t)$,

$$S(k, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} F(k, t) dt. \quad (8.4.3)$$

In the present case $F(k, t) = \exp[-Dk^2 t]$ for $t \geq 0$ and is extended symmetrically to negative times as $F(k, t) = \exp[-Dk^2 |t|]$. Introducing $a = Dk^2$ one may rewrite the integral as

$$S(k, \omega) = \frac{1}{2\pi} \left[\int_0^{\infty} e^{-(a-i\omega)t} dt + \int_0^{\infty} e^{-(a+i\omega)t} dt \right]. \quad (8.4.4)$$

Each exponential integral can be evaluated directly by observing that the antiderivative of $e^{-(a \mp i\omega)t}$ is $-e^{-(a \mp i\omega)t}/(a \mp i\omega)$. Evaluating at the limits $t = 0$ and $t \rightarrow \infty$ gives $\int_0^\infty e^{-(a \mp i\omega)t} dt = 1/(a \mp i\omega)$. Summing the two contributions yields

$$S(k, \omega) = \frac{1}{2\pi} \left[\frac{1}{a - i\omega} + \frac{1}{a + i\omega} \right] = \frac{1}{\pi} \frac{a}{a^2 + \omega^2}. \quad (8.4.5)$$

Recognizing $\Gamma(k) = Dk^2 = a$, one obtains the Lorentzian line shape

$$S(k, \omega) = \frac{1}{\pi} \frac{\Gamma(k)}{\Gamma(k)^2 + \omega^2}, \quad (8.4.6)$$

which is centred at zero energy transfer with half-width at half-maximum (HWHM) $\Gamma(k) = Dk^2$. The relation $\Gamma(k) = Dk^2$ expresses Fickian diffusion in reciprocal space and follows directly from the mean-squared displacement $\langle r^2(t) \rangle = 6Dt$ (the three-dimensional analogue of Eq. (8.2.13)). By measuring the energy broadening Γ as a function of k^2 , one can extract the diffusion coefficient from the slope.

8.4.2 Application to protein diffusion: example of BSA

Quasielastic neutron backscattering. As a concrete illustration, consider bovine serum albumin (BSA), a globular protein of hydrodynamic radius of a few nanometres. Quasielastic neutron scattering experiments on BSA solutions analyse the spectra $S(k, \omega)$ at various scattering vectors k . For small k (typically $k^2 \lesssim 1.5 \text{ \AA}^{-2}$) the quasielastic peak can be described by a sum of Lorentzian components: a broad component associated with internal vibrational dynamics and a narrow component arising from translational diffusion of the whole protein. The narrow width γ of this component varies linearly with k^2 , $\gamma = Dk^2$, in direct agreement with Eq. (8.4.6). The diffusion coefficient is obtained from the slope of γ versus k^2 ; for dilute BSA at $T \approx 280 \text{ K}$ one finds $D \approx 3 \times 10^{-11} \text{ m}^2/\text{s}$, while the coefficient decreases with increasing concentration owing to hydrodynamic and direct intermolecular interactions. This example demonstrates how the simple diffusion solutions derived earlier translate into the analysis of real protein motion.

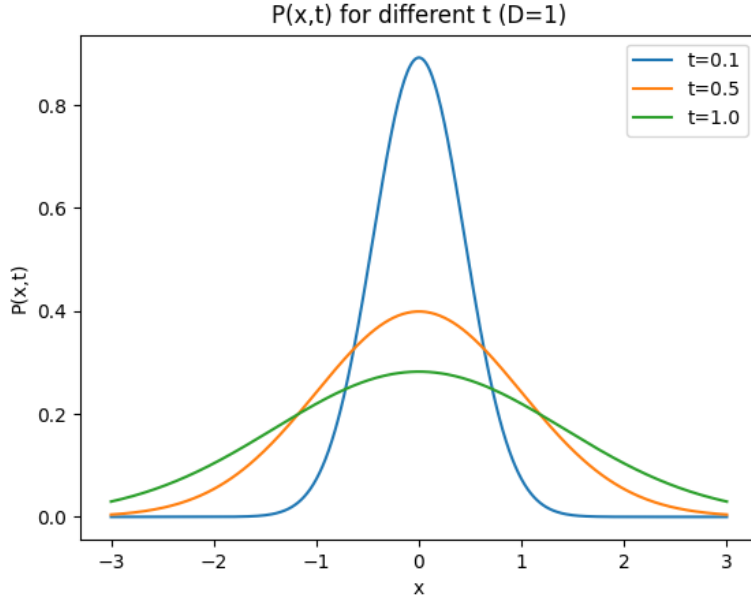


Figure 1: Time evolution of the one-dimensional probability density $P(x, t)$ for several times ($D = 1$). The diffusion peak broadens as time increases.

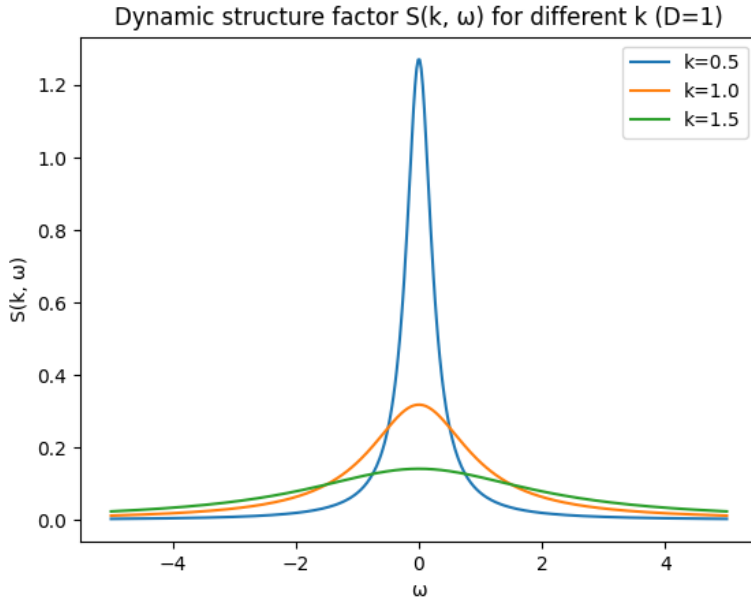


Figure 2: Dynamic structure factor $S(k, \omega)$ for several values of the momentum transfer k ($D = 1$). At larger k the quasielastic peak broadens ($\Gamma = Dk^2$).

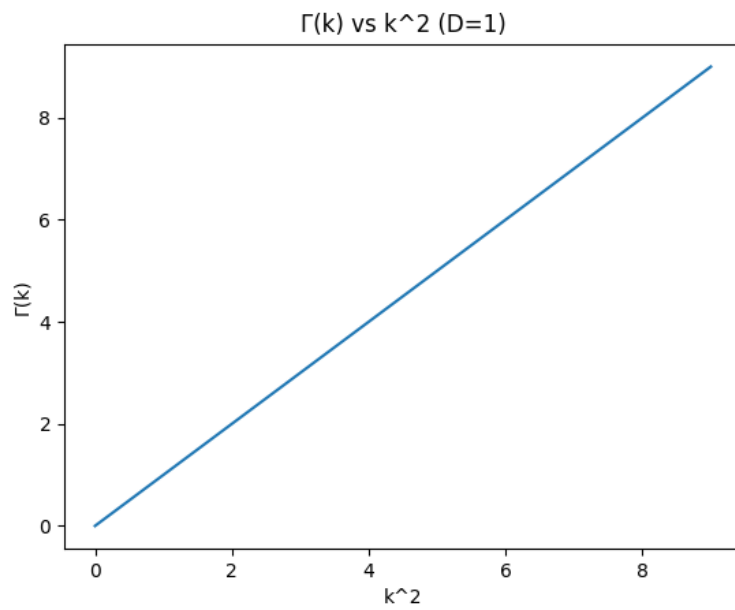


Figure 3: Width $\Gamma(k)$ of the Lorentzian quasielastic line as a function of k^2 . The linear dependence $\Gamma = Dk^2$ (with slope $D = 1$ in this example) allows the diffusion coefficient to be extracted from quasielastic scattering data.