Physics of Complex Systems

Brownian Motion

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Abstract. These notes correspond to a short lesson of a course on the Physics of Complex Systems within the Degree on Physics of University of Granada (4th year). In this chapter we review the phenomenon of Brownian motion, and its description from different points of view.

Keywords: Statistical physics, complex systems, probability and statistics, stochastic differential equations, Langevin equation, Fokker-Planck equation, molecular dynamics.

References and sources

After a brief historical account, we describe Einstein theory on Brownian motion, which led via Perrin’s experiment to the verification of the molecular hypothesis. We also describe Langevin’s approach in terms of a random force, and how the comparison of both approaches leads to Stokes-Einstein relation. Langevin’s theory allows us to introduce the concept of stochastic differential equations, and its equivalent description in terms of Fokker-Planck equations. Finally, we discuss the Random Walk model as a microscopic approach to Brownian motion. This last approach allows us to introduce the concept of large deviations and rare event statistics.
1. A brief historical perspective on Brownian motion

- **Brownian motion** is the random motion of particles suspended in a fluid (a liquid or a gas).

- This transport phenomenon is named after the botanist Robert Brown. In 1827, while looking through a microscope at particles trapped in cavities inside pollen grains in water, he noted that the particles moved chaotically through the water.

- What did Robert Brown observe through the microscope?
  
  Brownian motion 1
  Brownian motion 2
  Brownian motion 3

- However, Brown was not able to determine the mechanisms that caused this motion. He investigated whether this motion could be a consequence of the fact that pollen grains were collected from living plants.

- He repeated his experiments with particles derived not only from dead plants but also from "rocks of all ages, ...a fragment of the Sphinx ...volcanic ashes, and meteorites from various localities" From these experiments he concluded, "extremely minute particles of solid matter, whether obtained from organic or inorganic substances, when suspended in pure water, or in some other aqueous fluids, exhibit motions for which I am unable to account ..."

- By the time he completed these investigations, Brown no longer believed the random motions to be signatures of life.
Following Brown’s work, several other investigators studied Brownian motion in further detail. All these investigations helped in narrowing down the plausible cause(s) of the incessant motion of the Brownian particles. For example, temperature gradients, capillary actions, convection currents, etc. could be ruled out.

Did Brown really discover the phenomenon which is named after him? No. In fact, Brown himself did not claim to have discovered it. Brownian motion had been observed as early as in the seventeenth century by Antony van Leeuwenhoek under simple optical microscope. It was reported by Jan Ingenhousz in the eighteenth century. In fact, Brown himself critically reviewed the works of several of his predecessors.

Even the Roman Lucretius’s scientific poem 'On the Nature of Things' (c. 60 BC!!) has a remarkable description of Brownian motion of dust particles in verses 113–140 from Book II. He uses this as a proof of the existence of atoms:

"Observe what happens when sunbeams are admitted into a building and shed light on its shadowy places. You will see a multitude of tiny particles mingling in a multitude of ways... their dancing is an actual indication of underlying movements of matter that are hidden from our sight... It originates with the atoms which move of themselves..."

Nevertheless, this phenomenon was named after Brown; this reminds us of Stigler’s law of eponymy:

'No scientific discovery is named after its original discoverer'.

But what is the physical origin of this phenomenon? Brownian motion results from the collision of the mesoscopic particles suspended in a fluid with the fast-moving atoms or molecules in the gas or liquid.

The direction of the force of atomic bombardment is constantly changing, and at different times the particle is hit more on one side than another, leading to the seemingly random nature of the motion. A computer simulation may help in visualizing this phenomenon:

Simulation of Brownian motion
Atoms and molecules had long been theorized as the constituents of matter. For example, Greek philosophers like Democritus and Leucippus assumed discrete constituents of matter, John Dalton postulated the existence of atoms and, by the end of the nineteenth century a molecular kinetic theory of gases was developed by Clausius, Maxwell and Boltzmann.

Yet, the existence of atoms and molecules was not universally accepted, and many people didn’t believe in their existence at the beginning of the XX century. For example, physicist-philosopher Ernst Mach believed that atoms have only a didactic utility, while they themselves are purely fictitious. The great chemist Wilhelm Ostwald also believed atoms were not real.

And yet one man, at that critical turn of the century, stood up for the reality of atoms on fundamental grounds of theory. He was Ludwig Boltzmann. It is not so well known that Boltzmann knew as early as 1896 the reason.

‡ In fact, a most famous biography of Boltzmann is titled "Ludwig Boltzmann: the man who trusted atoms", by Carlo Cercignani.
for the erratic Brownian movement when he wrote "... very small particles in a gas execute motions which result from the fact that the pressure on the surface of the particles may fluctuate."

- However, the world had to wait up to 1905, when Albert Einstein published a paper\textsuperscript{1} that explained in precise detail how the motion that Brown had observed was a result of the pollen being moved by individual water molecules.

- Marian Smoluchowski, some time before Einstein, developed a similar theoretical explanation of Brownian motion in terms of molecular collisions. However he did not publish his results, waiting for experimental results. He finally published his theory in 1906, shortly after Einstein. An additional, more mesoscopic explanation in terms of random forces was introduced by Paul Langevin in 1908.

- The main result of Einstein 1905 paper states that the mean square displacement $\langle r^2(t) \rangle$ of a spherical Brownian particle grows linearly with time, with an amplitude inversely proportional to the number of molecules in the fluid.

- In 1908 Jean Perrin, together with his students and collaborators embarked on the experimental testing of Einsteins theoretical predictions. They studied in the microscope a colloidal suspension with dispersed particles of appropriate size (they used gamboge, a gum extrac).

- With the samples thus prepared, Perrin not only confirmed that the root-mean-square displacement of the dispersed particles grow linearly with time $t$ as predicted, but also made a good estimate of the Avogadro number.

\textsuperscript{†} This is one of the four famous papers during Einstein "\textit{annus mirabilis}", 1905. The other three papers were on the theory of special relativity, which showed that space and time are parts of the same entity, spacetime, the explanation of the photoelectric effect, which triggered the development of the quantum theory, and the equivalence between mass and energy, which led to the atomic bomb.
Einstein’s explanation of Brownian motion, together with the outstanding experimental verification of Perrin’s experiments, served as convincing evidence that atoms and molecules exist. Perrin was awarded the Nobel Prize in Physics in 1926 "for his work on the discontinuous structure of matter".

It is an irony of fate that, just when atomic doctrine was on the verge of intellectual victory, Ludwig Boltzmann felt defeated and committed suicide in 1906.

Brownian motion plays an important role not only in a wide variety of systems studied within the traditional disciplinary boundaries of physical sciences but also in systems that are subjects of investigation in earth and environmental sciences, life sciences as well as in engineering and technology.

However the greatest importance of Einstein’s theory of Brownian motion lies in the fact that experimental verification of his theory silenced all skeptics who did not believe in the existence of atoms.

Mathematically, Brownian motion is among the simplest of the continuous-time stochastic (or probabilistic) processes, and it is a limit of both simpler and more complicated stochastic processes (e.g. the random walk). This universality is closely related to the universality of the normal distribution (central limit theorem).
Figure 1. A historical sketch on Brownian motion [Source: http://radhakrishna.typepad.com/.a/6a00d83453194569e20162f35a1d1970d-600wi]
2. Einstein theory

- A. Einstein in 1905 successfully introduced the first mathematical treatment of the erratic movement of the Brownian particles. Rather than focusing on the (complicated) trajectory of a single particle, Einstein introduced a probabilistic description valid for an ensemble of Brownian particles.

- First, Einstein introduced the concept of a coarse-grained description defined by a time \( \tau \) such that different parts of the trajectory separated by a time \( \tau \) or larger can be considered independent. No attempt is made to characterize the dynamics at a timescale smaller than this coarse-grain time \( \tau \). Instead, we consider snapshots of the system taken at time intervals \( \tau \) (see right panel of Fig. 3).

- The second concept, probabilistic in nature, introduced by Einstein is that of the probability density function (or pdf) \( f(\Delta) \), for the three-dimensional distance \( \Delta = (\Delta_x, \Delta_y, \Delta_z) \) traveled by the Brownian particle in a fixed time interval \( \tau \).
The only assumption one needs to make about the function $f(\Delta)$ (besides the general condition of nonnegativity and normalization) comes from the fact that the collisions of the fluid molecules and the Brownian particle occur with the same probability in any direction$^1$. The absence of preferred directions translates to a symmetry condition for $f(\Delta)$, as
\[ f(-\Delta) = f(\Delta), \quad \forall \Delta \in \mathbb{R}^3. \] (1)

The third step in this description is to consider an ensemble of $N$ Brownian particles in a large enough system. Also, we focus on large spatial scales, much larger than the size of a Brownian particle, so that we can define a density of the particles $n(\mathbf{x},t)$ such that $n(\mathbf{x},t) \, d\mathbf{x}$ is the number of particles in the interval $(\mathbf{x}, \mathbf{x} + d\mathbf{x})$ at time $t$.

From the assumption that the parts of the trajectories separated a time interval $\tau$ are statistically independent and the conservation of particle number, it follows that the number of particles at location $\mathbf{x}$ at time $t + \tau$ will be given by the number of particles at location $\mathbf{x} - \Delta$ at time $t$ multiplied by the probability that the particle jumps from $\mathbf{x} - \Delta$ to $\mathbf{x}$ in an elementary time step $\tau$, which is $f(\Delta)$, and integrated for all the possible $\Delta$ values, i.e.
\[ n(\mathbf{x}, t + \tau) = \int_{\mathbb{R}^3} n(\mathbf{x} - \Delta, t) \, f(\Delta) \, d\Delta. \] (2)

This is the basic evolution equation for the number density $n(\mathbf{x}, t)$. From the technical point of view, it is a continuity equation expressing particle conservation, i.e. that Brownian particles can neither be created, nor can they disappear as a result of the collisions with the fluid molecules.

$^1$ We also disregard the effect of gravity in the Brownian particle, which would lead to a preferred direction in the movement.
By Taylor expansion of the above expression

\[ n(x,t + \tau) \approx n(x,t) + \tau \frac{\partial n(x,t)}{\partial t}, \]

\[ n(x - \Delta,t) \approx n(x,t) - \Delta \cdot \nabla n(x,t) + \frac{\Delta^2}{2} \nabla^2 n(x,t). \]

Therefore

\[ \int_{\mathbb{R}^3} n(x - \Delta,t) f(\Delta) d\Delta \approx n(x,t) \int_{\mathbb{R}^3} f(\Delta) d\Delta - \nabla n(x,t) \cdot \int_{\mathbb{R}^3} \Delta f(\Delta) d\Delta + \frac{1}{2} \nabla^2 n(x,t) \int_{\mathbb{R}^3} \Delta^2 f(\Delta) d\Delta, \]

and making use of the normalization of the pdf \( f(\Delta) \) and the symmetry relation \( f(-\Delta) = f(\Delta) \), we simplify the first term in the right-hand side of this equation and get rid of the second one. Hence we finally obtain the diffusion equation for the particle density field as

\[ \frac{\partial n(x,t)}{\partial t} = D \nabla^2 n(x,t), \]

where the diffusion coefficient \( D \) is given in terms of the pdf \( f(\Delta) \) as

\[ D = \frac{1}{2\tau} \int_{\mathbb{R}^3} \Delta^2 f(\Delta) d\Delta = \frac{\langle \Delta^2 \rangle}{2\tau}. \]

To solve this partial differential equation, we first need an initial condition. If initially all Brownian particles are located at the origin, we thus have \( n(x,0) = N\delta(x) \). The diffusion equation can be solved via different methods. One of the most common is via Fourier transform of the particle density field. In particular, we define

\[ n(k,t) = \int_{\mathbb{R}^3} e^{ik \cdot x} n(x,t) dx, \]
and derive it with respect to time to obtain (after integrating by parts twice and neglecting boundary terms at $\infty$)

$$\frac{\partial n(k, t)}{\partial t} = -Dk^2 n(k, t) \quad \Rightarrow \quad n(k, t) = Ne^{-Dk^2 t},$$

(9)

where we have already used the initial condition mentioned above. Notice that $n(k, t)$ is a Gaussian curve, so its inverse Fourier transform is also a Gaussian, namely

$$n(x, t) = \frac{N}{(4\pi Dt)^{3/2}} e^{-x^2/4Dt}.$$  

(10)

- Another, very instructive way of solving the diffusion equation is via dimensional analysis. For that, first note that the $n(x, t)$ is a particle density field so it has units of inverse volume, $[n(x, t)] = L^{-d}$ in dimension $d$, with $L$ the unit of length. Moreover, the diffusion constant $D$ defined above has units $[D] = L^2 / T$, with $T$ the unit of time, and obviously $[t] = T$. The only nontrivial quantity that can be defined with units of length in the problem is $\sqrt{Dt}$, so $(Dt)^{d/2}n(x, t)$ is a dimensionless quantity which should depend only on other dimensionless quantities. From variables $x$, $t$, $D$ we can form a single dimensionless quantity $x / \sqrt{Dt}$. Therefore the most general dependence of the density field on the basic variables that is allowed by dimensional analysis is

$$n(x, t) = \frac{1}{(Dt)^{d/2}} \rho(\zeta), \quad \zeta = \frac{x}{\sqrt{Dt}}.$$  

(11)

- The density depends on a single scaling variable rather than on two basic variables $x$ and $t$. This remarkable feature greatly simplifies analysis of the typical partial differential equations that describe nonequilibrium systems. Equation (11) is often referred to as the scaling ansatz. Finding the right scaling ansatz for a physical problem often represents a large step toward a solution. For the diffusion equation, substituting in the ansatz (11) reduces this partial differential equation to

$$2 \nabla^2 \rho(\zeta) + \zeta \cdot \nabla \rho(\zeta) + d \rho(\zeta) = 0.$$  

(12)
Figure 3. Time evolution of the density field for an initially localized ensemble of Brownian particles. It is a Gaussian curve whose variance grows linearly with time, see Eq. (10). [Wikipedia. Source author: Bernard H. Lavenda]

Invoking both the normalization condition and the symmetry of $\rho(\zeta)$ around $\zeta = 0$, so that $\rho(\zeta) = \rho(-\zeta)$, and integrating twice the above equation, we obtain $\rho(\zeta) = (4\pi)^{-d/2} e^{-\zeta^2/4}$ for arbitrary dimension $d$, and using that $\zeta = x/\sqrt{Dt}$ we recover the Gaussian solution for $n(x, t)$ described above.

- Whatever the solution method, from the Gaussian solution $n(x, t)$ it follows that the average position of the Brownian particle is $\langle x(t) \rangle = 0$ and that the average square position increases linearly with time, namely $\langle x(t)^2 \rangle = 6Dt$ in $d = 3$ dimensions. As mentioned above, this prediction was successfully confirmed in Perrin’s experiments and contributed decisively to the acceptance of the atomic/molecular theory of matter.
3. Langevin theory, Stokes-Einstein relation and Green-Kubo formula

- However successful Einstein’s approach was, it is very phenomenological and cannot yield, for instance, an explicit expression for the diffusion coefficient in terms of microscopic quantities.

- Paul Langevin (1908) initiated a different approach which, in some ways, can be considered complementary to the previous one. In his approach, Langevin focused on the trajectory of a single Brownian particle and wrote down Newton’s equation $\text{Force} = \text{mass} \times \text{acceleration}$.

- The trajectory of the Brownian particle is highly erratic and therefore its description would demand a peculiar kind of force. Langevin considered two types of forces acting on the Brownian particle: the usual friction forces which, according to Stokes law, would be proportional to the velocity, and a sort of "fluctuating" force $\xi(t)$, which represents the "erratic" force that comes from the action of the fluid molecules on the Brownian particle.

- The equation of motion for the Brownian particle becomes then

$$m \frac{d\mathbf{v}}{dt} = -6\pi \eta a \mathbf{v} + \xi,$$

where $\eta$ is the viscosity coefficient and $a$ is the radius of the Brownian particle (which is assumed to be spherical). Multiplying both sides of by $\mathbf{x}$, and noting that $\mathbf{v} = \frac{d\mathbf{x}}{dt}$, one gets

$$\frac{m d^2 \mathbf{x}}{2 dt^2} - m \left( \frac{d\mathbf{x}}{dt} \right)^2 = -3\pi \eta a \frac{d\mathbf{x}^2}{dt} + \mathbf{x} \cdot \xi.$$
Langevin made two assumptions about the fluctuating force $\xi(t)$: that it has mean 0 (collisions do not push the Brownian particle in any preferred direction) and that it is uncorrelated to the actual position of the Brownian particle (the action of the molecules of fluid on the Brownian particle is the same no matter the location of the Brownian particle), that is

$$\langle \xi(t) \rangle = 0 ; \quad \langle \mathbf{x} \cdot \xi(t) \rangle = \langle \mathbf{x} \rangle \cdot \langle \xi(t) \rangle = 0. \quad (15)$$

Taking the averages with respect to all realizations of the random force $\xi(t)$ in the above differential equation and using the previous conditions on the statistics of $\xi(t)$, one gets

$$\frac{m}{2} \frac{d^2}{dt^2} \langle \mathbf{x}^2 \rangle = m \langle \mathbf{v}^2 \rangle - 3\pi \eta a \frac{d}{dt} \langle \mathbf{x}^2 \rangle , \quad (16)$$

which is an equation for the average square position of the Brownian particle.

Langevin assumed that we are now in a regime in which thermal equilibrium between the Brownian particle and the surrounding fluid has been reached. In particular, this implies that, according to the equipartition theorem, the average kinetic energy of the Brownian particle is $\langle m\mathbf{v}^2/2 \rangle = 3kT/2$ ($k$ is Boltzmann’s constant and $T$ is the fluid temperature).

One can now solve the previous equation and find that, after some transient time, the asymptotic mean square displacement is given

$$\langle \mathbf{x}^2(t) \rangle = \frac{kT}{\pi \eta a} t. \quad (17)$$

This is nothing but Einstein’s diffusion law, $\langle \mathbf{x}(t)^2 \rangle = 6Dt$, but now we have an explicit expression for the diffusion coefficient in terms of other macroscopic variables

$$D = \frac{kT}{6\pi \eta a} = \frac{RT}{6\pi \eta a N_A}, \quad (18)$$
where we have used in the last equality the definition of Boltzmann’s constant $k$ in terms of the ideal gas constant $R$ and Avogadro’s number $N_{\text{Av}}$, i.e. $k = R/N_{\text{Av}}$. This last equation is known as Stokes-Einstein relation.

- In this way, by measuring the Brownian particle diffusion coefficient and the fluid’s viscosity (two macroscopic observables) we can obtain an indirect measurement of the size $a$ of the fluid’s molecules or equivalently of Avogadro’s number!

3.1. A simple example of Green-Kubo formula for transport coefficients

- In this section we will derive a simple relation between the diffusion constant and the integral of the equilibrium time-correlation function of the velocity of a Brownian particle. This is a particular (and very illustrative) example of the Green-Kubo formulae relating transport coefficients and equilibrium time-correlation functions, a main result of nonequilibrium statistical mechanics.

- Let’s consider the net displacement of the Brownian particle’s position during the interval from 0 to $t$. This can be written as

$$\mathbf{x}(t) = \int_0^t ds \, \mathbf{v}(s), \quad (19)$$

where $\mathbf{v}(s)$ is the velocity of the particle at time $s$.

- The ensemble average of the mean squared displacement is

$$\langle |\mathbf{x}(t)|^2 \rangle = \left\langle \int_0^t ds_1 \int_0^t ds_2 \, \mathbf{v}(s_1) \cdot \mathbf{v}(s_2) \right\rangle = \int_0^t ds_1 \int_0^t ds_2 \left\langle \mathbf{v}(s_1) \cdot \mathbf{v}(s_2) \right\rangle \quad (20)$$

Note that the integral contains the time-correlation function of the velocity at times $s_1$ and $s_2$.

- We now take the time derivative and combine two equivalent terms on the right-hand side,

$$\frac{d}{dt} \langle |\mathbf{x}(t)|^2 \rangle = 2 \int_0^t ds \, \langle \mathbf{v}(t) \cdot \mathbf{v}(s) \rangle \quad (21)$$
• The velocity correlation function is an equilibrium average and cannot depend on any arbitrary origin of the time axis. It can depend only on the time difference $t - s = u$, so that

$$\frac{d}{dt} \langle \mathbf{x}(t)^2 \rangle = 2 \int_0^t ds \langle \mathbf{v}(t - s) \cdot \mathbf{v}(0) \rangle = 2 \int_0^t du \langle \mathbf{v}(u) \cdot \mathbf{v}(0) \rangle$$

(22)

• The velocity correlation function generally decays to zero in a short time; in simple liquids, this may be of the order of picoseconds. On the other hand, the diffusion equation is expected to be valid only at times much longer than a molecular time.

• In the limit of large $t t$, according to Einstein’s theory $\langle \mathbf{x}(t)^2 \rangle = 6Dt$, so the left-hand side of the above equation approaches $6D$. In the same regime, the right-hand side approaches a time integral from zero to infinity.

• Therefore we have derived the simplest example of the Green-Kubo relation of a transport coefficient to a time correlation function,

$$D = \frac{1}{3} \int_0^\infty du \langle \mathbf{v}(u) \cdot \mathbf{v}(0) \rangle$$

(23)
4. Stochastic differential equations and Fokker-Planck equations

- Langevin’s equation is an example of stochastic differential equation, and Langevin’s random force $\xi(t)$ is an illustration of a stochastic process. The natural language to understand both concepts is that of probability theory.

4.1. Stochastic differential equations

- A stochastic differential equation is a differential equation that contains a stochastic process $\hat{\eta}(t)$: that is, an equation of the form
  \[
  \frac{d\hat{x}(t)}{dt} = G\left(\hat{x}(t), t, \hat{\eta}(t)\right)
  \]
  (24)
  where $G$ is a given function that depends, in general, on the variable $x(t)$, on the time $t$, and on the stochastic process $\hat{\eta}(t)$.

- A stochastic process is a family $\hat{x}(t)$ of random variables depending on some continuous, real parameter $t$. In most applications, $t$ is a physical time and the stochastic process can be thought as performing multiple probabilistic experiments one at each time instant.

- Stochastic processes (as well as random variables) are usually denoted in the mathematical literature with a "hat"-symbol, $\hat{x}(t)$, to distinguish them from a particular realization of the stochastic process, i.e. from a particular realization or trajectory of the set of probabilistic experiments which give rise to a stochastic process. The stochastic process can be seen as the collection of all these possible trajectories.

- A stochastic differential equation can be seen as a family of ordinary differential equations, one for each outcome of all the successive probabilistic experiments associated with the stochastic process $\hat{\eta}(t)$. As a consequence, for any given initial condition $x_0$ at time $t_0$, one has a family of possible trajectories.
Therefore, \( \hat{x}(t) \), which is the collection of all these possible trajectories, has to be viewed also as a stochastic process and this is why we label it with the 'hat' symbol. However, \( \hat{x}(t) \) is not an arbitrary stochastic process, rather it depends on \( \hat{\eta}(t) \) in a specific manner determined by the stochastic differential equation, and, as a consequence, the statistical properties of \( \hat{x}(t) \) depend on the statistical properties of \( \hat{\eta}(t) \).

Strictly speaking, "solving the stochastic differential equation" means to provide the complete characterization of the stochastic process \( \hat{x}(t) \), namely to give all the \( m \)-times probability density functions (pdfs) \( f(x_1, \ldots, x_m; t_1, \ldots, t_m) \), in terms of the statistical properties of \( \hat{\eta}(t) \). However, one has to understand that a complete characterization of a general stochastic process implies the knowledge of a function of an arbitrary number of parameters and is very difficult to carry out in practice.

On many occasions, one is happy if one can give just the one-time pdf \( f(x; t) \) and the two-times pdf \( f(x_1, x_2; t_1, t_2) \). In terms of those, it is possible to compute the trajectory averages

\[
\langle \hat{x}(t)^n \rangle = \int_{-\infty}^{\infty} dx \, x^n f(x; t)
\]

and the time correlations

\[
\langle \hat{x}(t_1)^n \hat{x}(t_2)^m \rangle = \int_{-\infty}^{\infty} dx \, x_1^n x_2^m f(x_1, x_2; t_1, t_2).
\]

In general, the function \( G \) can depend on the stochastic process \( \hat{\eta}(t) \) in an arbitrary way. However, many systems of interest can be described by stochastic differential equations in which \( \hat{\eta}(t) \) appears linearly, namely

\[
\frac{d\hat{x}(t)}{dt} = q(\hat{x}(t)) + g(\hat{x}(t)) \hat{\eta}(t).
\]

This kind of stochastic differential equations are called Langevin equations in honor of one of the first scientists to use them to describe a physical phenomenon.
• In this case (Langevin equations), the independent stochastic process $\hat{\eta}(t)$ is usually referred to as noise, a notation that comes from the early days of radio broadcasting when the random fluctuations in the electrical signals taking place in the emitter during the propagation in the atmosphere or at the receiver device led to noises that were actually heard on top of the radio emission.

• Terminology: Following this notation, the term $g(\hat{x}(t)) \hat{\eta}(t)$ in Eq. (27) is referred to as the noise term or diffusion term whereas $q(\hat{x}(t))$ is the deterministic term or drift term. One distinguishes the case in which the function $g(\hat{x}(t))$ is a constant, in which case the noise is said to be additive. Otherwise, the noise is said to be multiplicative.

• For the sake of simplicity in the notation, from now on we will drop the "hats" from the stochastic process and therefore we write the Langevin differential equation as

$$\frac{dx(t)}{dt} = q(x(t)) + g(x(t)) \eta(t). \quad (28)$$

4.2. Fokker-Planck equations

• So far, we have focused on trajectories to describe stochastic processes following the initial Langevin approach for Brownian motion.

• An alternative approach introduced by Einstein focuses on probabilities rather than in trajectories and, as it happens with the Langevin approach, it can be extended way beyond the Brownian motion.

• In what follows, we are going to determine an equation for one-time probability distribution for a stochastic process described by a Langevin equation with Gaussian white noise. This is called the Fokker-Planck equation and it is a generalization of the diffusion equation obtained by Einstein to describe the Brownian process.
To be more precise, we want to find an equation for the one-time probability distribution function $f(x, t)$ for a stochastic process $x(t)$ which arises as a solution of a stochastic differential equation with a Gaussian white noise $\xi(t)$, defined such that $\langle \xi(t) \rangle = 0$ and $\langle \xi(t)\xi(t') \rangle = \delta(t - t')$, i.e.

$$\frac{dx(t)}{dt} = q(x(t)) + g(x(t))\xi(t).$$

(29)

To obtain this equation, we have to average over all possible initial conditions and all realizations of the stochastic process $\xi(t)$. The derivation, which lies outside the scope of the present discussion (see however the appendix), leads to the so-called Fokker-Planck equation for the probability density function:

$$\frac{\partial f(x; t)}{\partial t} = -\frac{\partial}{\partial x} [q(x)f(x; t)] + \frac{1}{2} \frac{\partial}{\partial x} \left[ g(x) \frac{\partial}{\partial x} [g(x)f(x; t)] \right].$$

(30)

This framework can be extended to the case of Langevin equations for multidimensional variables, and even to field-theoretic Langevin equations which emerge in the description of equilibrium and nonequilibrium critical phenomena, nonequilibrium dynamics, transport problems, etc.
5. The random walk model

- Arguably, the most well-known example of a stochastic process is that of the random walk. Moreover, the continuum (large scale) limit of a (3-dimensional) random walk offers a good description of Brownian motion. It also serves as a simple model to understand the physics of polymers, motion in cells, financial markets, etc.

- Here for simplicity we will focus on the one-dimensional random walk, though all results can be easily generalized to arbitrary dimensions.

- The probabilistic experiment is now a series of binary results representing, for instance, the outcome of repeatedly tossing a coin:

  \[ \chi \equiv (-1, -1, +1, +1, -1, +1, -1, -1, +1, +1, -1, ..., ...) = \{ \chi_k, k = 1, 2, \ldots \} \tag{31} \]

  where +1 means "heads" and −1 means "tails".

- Consider that the tossing takes place at given times 0, τ, 2τ, ... To the outcome of this set of probabilistic experiments, we associate a one-dimensional function \( x(t) \) which starts at \( x(0) = 0 \) and that moves to the right (left) at time \( k\tau \) an amount +\( a \) (−\( a \)) if the \( k \)-th result of the tossed coin was +1 (−1).

- In the intermediate times between two consecutive tossings, namely in the times between \( k \) and \( (k + 1) \), the system just remains in the same location. Fig. 4 shows a typical trajectory.

- The random walk constitutes an example of a Markov process, as the probability of having a particular value of the position at time \( (k + 1)\tau \) depends only on the particle’s location at time \( k\tau \) and not on the way it got to this location.
Figure 4. Example of a random walk trajectory. We have taken $\tau = a = 1$ and plotted the resulting trajectory after a large number of steps ($10^5$). In the inset, we see the fine detail with the discrete jumps occurring at times which are multiples of $\tau$.

- Starting at $x = 0$ at time $t = 0$, the location of the random walker after tossing the coin $n$ times is given by the number of steps $n_+$ increasing $x$ (number of 'heads') minus the number of steps decreasing $x$, $n_- = n - n_+$ (number of 'tails'),
  \[
  x(n\tau) = (n_+ - n_-)a = (2n_+ - n)a.
  \]
  \(32\)

- The probability of having $n_+$ 'heads' after $n$ throws is given by a binomial distribution with probability $p = 1/2$
  \[
  P(n_+) = \binom{n}{n_+}2^{-n} = \frac{n!}{n_+!(n-n_+)!}2^{-n}.
  \]
  \(33\)
In general, a binomial distribution with probability $p$ has the form

$$f_{\hat{N}_B}(n_+) = \binom{n}{n_+} p^{n_+} (1 - p)^{n-n_+}.$$  \hfill (34)

We denote as $\hat{N}_B(p, n)$ a random variable obeying a binomial distribution with probability $p$ and number of repetitions $n$. Its mean value and variance are given by

$$\langle \hat{N}_B \rangle = np,$$
$$\sigma^2[\hat{N}_B] = \langle \hat{N}_B^2 \rangle - \langle \hat{N}_B \rangle^2 = np(1 - p).$$  \hfill (35, 36)

- In this way, the probability that the walker is at a location $x = ra$ after a time $t = n\tau$ is

$$P(x(n\tau) = ra) = \left(\frac{n}{\frac{n+r}{2}}\right)^2 2^{-n}.$$  \hfill (37)

- Using now the binomial distribution properties, in particular the first two central moments, we find that

$$\langle x(n\tau) \rangle = (2\langle n_+ \rangle - n)a = 0,$$
$$\langle x(n\tau)^2 \rangle = (4\langle n_+^2 \rangle - 4\langle n_+ \rangle n + n^2)a^2 = na^2 = n\tau \frac{a^2}{\tau},$$  \hfill (38, 39)

where we have used that $\langle n_+ \rangle = \frac{n}{2}$ and $\langle n_+^2 \rangle = \frac{n(n+1)}{4}$. The last expression is strongly reminiscent of the mean squared displacement formula for Brownian motion.

- It can be easily probed that in the limit $n \gg 1$ the binomial distribution can be well approximated by a Gaussian distribution (of mean $np$ and variance $np(1 - p)$ for a $\hat{N}_B(p, n)$ variable).
If we now take the continuum limit $n \to \infty$, $\tau \to 0$, $r \to \infty$, $a \to 0$ while preserving a finite value for $t = n\tau$, $x = ra$, and $D = a^2/\tau$, it can be shown that the random walk process converges to the so-called Wiener process $W(t)$, characterized by a Gaussian probability distribution function with zero mean and variance $Dt$, namely

$$f(x; t) = \frac{1}{\sqrt{2\pi Dt}} \exp \left( -\frac{x^2}{2Dt} \right).$$

This is exactly the solution of the diffusion equation in Einstein’s theory of Brownian motion in one dimension.

5.1. A glimpse at rare events and large deviations

- The previous discussion referred to the probability distribution for finding the random walker at some position at a given time, $f(x; t)$.
- We now turn our attention to the sample average position of the random walker. Consider the following average

$$S_n(\chi) = \frac{1}{n} \sum_{k=1}^{n} \chi_k = \frac{1}{n} (n_+ - n_-) = \frac{1}{n} (2n_+ - n)$$

In this way, for a given trajectory $\chi$, the time-averaged position of the random walker is $\bar{x}_n(\chi) = S_n(\chi)a$.
- What is the probability of observing a sample average position $sa$ after $n$ steps? This is nothing but the probability that $S_n(\chi) = s$, or equivalently the probability of obtaining $n_+ = n(1+s)/2$ "heads" after $n$ throws, i.e.

$$P(S_n = s) = \left( \frac{n}{2n_+} \right) 2^{-n}$$

Intuitively, the sample average position of the random walker should converge for large enough $n$ to the actual average position of the random walker, which is just 0.
• For large $n$, we may use now Stirling approximation $n! \approx n^n e^{-n}$ so
\[
P(S_n = s) \approx \frac{n^n e^{-n}}{\left[ \frac{n}{2} (1 + s) \right]^{\frac{n}{2}(1+s)} e^{-\frac{n}{2}(1+s)} \left[ \frac{n}{2} (1 - s) \right]^{\frac{n}{2}(1-s)} e^{-\frac{n}{2}(1-s)} 2^{-n}} = \left[ (1 + s)^{\frac{n}{2}(1+s)} (1 - s)^{\frac{n}{2}(1-s)} \right]^{-n}.
\] (43)

• In this way, the probability that the sample average position $S_n$ of a random walker takes a given value obeys a large deviation principle for large $n$
\[
P(S_n = s) \approx e^{-nI(s)},
\] (44)
with $I(s)$ a large deviation function of the form
\[
I(s) = \frac{1}{2} \left[ (1 + s) \ln(1 + s) + (1 - s) \ln(1 - s) \right].
\] (45)

• The large deviation function measures the rate at which the sample mean $S_n$ concentrates around the average value of the distribution ($s = 0$ in this case) as the sample size $n$ grows.

• The above large deviation principle means that sample averages differing appreciable from the true average are exponentially unlikely with $n$, the sample size.

• The large deviation function quantifies the probability of both typical and rare events for a given stochastic process.

• Large deviation functions (LDFs) as the one here introduced play a crucial role in equilibrium and nonequilibrium statistical physics. In equilibrium systems, the thermodynamic potentials associated to the different ensembles (canonical, micro- and macro-canonical, etc.) can be seen as large deviation functions associated to the different conserved observables. In nonequilibrium systems LDFs play the role of thermodynamic-like potentials, even though we do not have yet a suitable macroscopic theory for systems out of equilibrium.
6. Appendix: Derivation of Fokker-Planck equation

- So far, we have focused on trajectories to describe stochastic processes following the initial Langevin approach for Brownian motion.

- The alternative approach introduced by Einstein focuses on probabilities rather than in trajectories and, as it happens with the Langevin approach, it can be extended way beyond the Brownian motion.

- In what follows, we are going to determine an equation for one-time probability distribution for a stochastic process described by a Langevin equation with white noise. This is called the Fokker-Planck equation and it is a generalization of the diffusion equation obtained by Einstein to describe the Brownian process.

- To be more precise, we want to find an equation for the one-time probability distribution function $f(x, t)$ for a stochastic process $x(t)$ which arises as a solution of a stochastic differential equation with a Gaussian white noise $\xi(t)$, defined such that $\langle \xi(t) \rangle = 0$ and $\langle \xi(t)\xi(t') \rangle = \delta(t - t')$, i.e.

$$
\frac{dx(t)}{dt} = q(x(t)) + g(x(t))\xi(t).
$$

This is to be understood in the Stratonovich interpretation.

6.1. Deterministic dynamics and sampling over initial conditions

- Let us consider first the corresponding deterministic equation

$$
\frac{dx(t)}{dt} = q(x(t)), \quad x(t = 0) = x_0.
$$

The solution of this equation is a (deterministic) function $x(t) = F(t, x_0)$. Nevertheless, for our purposes, we can see $x(t)$ as a random variable whose probability density function $\rho(x; t)$ gives the probability to find the system
at a given location \( x \) in phase space at a time \( t \). As the trajectory followed by the system is uniquely determined once the initial condition is given, this probability is zero everywhere except at the location \( x = F(t, x_0) \). Therefore, the probability density function is a delta function, given by
\[
\rho(x; t) = \delta(x - F(t, x_0)).
\] (48)

- We can now transform \( x(t) \) into a stochastic process by simply letting the initial condition \( x_0 \) to become a random variable. We have now an ensemble of trajectories, each one starting from a different initial condition \( x_0 \). In this case, the probability density function \( \rho(x, t) \) is obtained by averaging the above pdf over the distribution of the initial conditions
\[
\rho(x; t) = \langle \delta(x - F(t, x_0)) \rangle_{x_0}.
\] (49)

In fact, \( \rho(x, t) \) can be seen as a density function.

- To visualize it, we assume that at time \( t = 0 \) we have unleashed a large number of particles \( N \) with one particle at each of the initial conditions we are considering in our ensemble. We let the particles evolve according to the dynamics and, after a time \( t \), \( \rho(x, t)dx \) measures the fraction of particles located in the interval \((x, x + dx)\)
\[
\rho(x, t)dx = \frac{\# \text{ particles in } (x, x + dx) \text{ at time } t}{\text{total } \# \text{ of particles}} = \frac{n(x, t)}{N} dx.
\] (50)

- Assuming there are no sinks nor sources of particles, then the number of particles at a given location changes as a result of the number of particles crossing the borders. Let \( J(x, t) \) be the flux of particles:
\[
J(x, t)dx = \frac{\# \text{ particles that cross the point } x \text{ in the interval } (t, t + dt)}{N}.
\] (51)

\( J \) has a direction. For convenience, we consider \( J > 0 \) if the particle moves to the right. Then
\[
\rho(x; t + dt)dx - \rho(x; t)dx = J(x, t)dt - J(x + dx, t)dt.
\] (52)
• The first term on the left-hand side (LHS) is the final number of particles at \( x \), whereas the second is the initial one. Thus, the LHS corresponds to the variation of the number of particles at \( x \) from time \( t \) to time \( t + dt \). On the right-hand side (RHS), the first term is the number of particles that have entered or left during the interval \((t, t + dt)\) through the left boundary, whereas the second term measures the number of particles that crossed the right boundary.

• Therefore, one has

\[
\frac{\rho(x; t + dt) - \rho(x; t)}{dt} = \frac{J(x, t) - J(x + dx, t)}{dx}
\] (53)

which in the continuous limit corresponds to

\[
\frac{\partial \rho(x; t)}{\partial t} = -\frac{\partial J(x, t)}{\partial x}
\] (54)

which is nothing but the continuity equation.

• As particles move following a deterministic dynamics given by \( \frac{dx(t)}{dt} = q(x(t)) \), trajectories cannot cross and therefore in a one-dimensional system they cannot advance from one to the other. The particles that will cross the point \( x \) in the interval \((t, t + dt)\) are all those located in the interval \( dx = q(x)dt \). Therefore,

\[
J(x, t) = \frac{n(x, t)}{N} \frac{dx}{dt} = \rho(x; t)q(x). \tag{55}
\]

Replacing this in the above continuity equation, one gets the Liouville equation

\[
\frac{\partial \rho(x; t)}{\partial t} = -\frac{\partial}{\partial x} [q(x)\rho(x; t)] . \tag{56}
\]
6.2. Full stochastic dynamics

• We consider now the full stochastic differential equation

\[
\frac{dx(t)}{dt} = q(x(t)) + g(x(t))\xi(t).
\]  

(57)

• We can repeat the above argument for a given realization of the noise term. The probability density function \( f(x; t) \) will be the average of \( \rho(x; t) \) with respect to the noise distribution:

\[
f(x; t) = \langle \rho(x; t) \rangle_{\xi} = \langle \delta(x - x(t, x_0)) \rangle_{x_0, \xi}.
\]  

(58)

• \( \rho(x; t) \) satisfies the continuity equation. Now the current is given by

\[
J(x, t) = \rho(x; t) \frac{dx(t)}{dt} = \rho(x; t) [q(x(t)) + g(x(t))\xi(t)].
\]  

(59)

Therefore

\[
\frac{\partial \rho(x; t)}{\partial t} = - \frac{\partial}{\partial x} \left[ (q(x) + g(x(t))\xi(t))\rho(x; t) \right].
\]  

(60)

• Taking now the average over the noise term, we get

\[
\frac{\partial f(x; t)}{\partial t} = \left\langle \frac{\partial \rho(x; t)}{\partial t} \right\rangle_{\xi} = - \frac{\partial}{\partial x} \left[ (q(x) + g(x(t))\xi(t))\rho(x; t) \right]_{\xi} \\
= - \frac{\partial}{\partial x} [q(x)\langle \rho(x; t) \rangle_{\xi}] - \frac{\partial}{\partial x} [g(x(t))\langle \xi(t)\rho(x; t) \rangle_{\xi}].
\]  

(61)

The averages on the first term of the right-hand side (RHS) can be easily performed, \( \langle \rho(x; t) \rangle = f(x; t) \).
However, averages on the second term of the RHS are more cumbersome, since one has to keep in mind that the density distribution $\rho$ depends on $x(t)$, which itself depends functionally on the noise through the Langevin dynamics.

In fact, to be precise, the average on the second term of the RHS should be written as $\langle \xi(t)\rho(x[\xi(t)]; t) \rangle$. This average can be obtained by using Novikov’s theorem, which establishes that, for any Gaussian stochastic process $\xi_G(t)$ with zero mean, $\langle \xi_G(t) \rangle = 0$, and for any functional of the noise $F[\xi_G(t)]$ one has

$$\langle \xi_G(t)F[\xi_G(t)] \rangle_{\xi_G} = \int_0^t ds \langle \xi_G(t)\xi_G(s) \rangle_{\xi_G} \left( \frac{\delta F}{\delta \xi_G(s)} \right)_{\xi_G},$$

where the last term is the functional derivative of $F[\xi_G(t)]$ with respect to $\xi_G(s)$. We note that Novikov’s theorem is quite general; it only requires the noise to be Gaussian but does not require it to be white, namely, the noise correlations need not be a delta function.

In our case, we have a Gaussian white noise, for which the correlation is a delta function. This allows us to evaluate the integral easily:

$$\langle \xi(t)\rho(x[\xi(t)]; t) \rangle = \int_0^t ds \delta(t - s) \left( \frac{\delta \rho(x[\xi(t)]; t)}{\delta \xi(s)} \right)_{\xi} = \frac{1}{2} \left( \frac{\delta \rho(x[\xi(t)]; t)}{\delta \xi(s)} \right)_{s=t},$$

where we have used the Stratonovich convention to perform the integral over the $\delta$-function. By using the chain rule in functional calculus, this can be computed as follows

$$\left( \frac{\delta \rho(x[\xi(t)]; t)}{\delta \xi(s)} \right)_{s=t} = \left( \frac{\delta x(t)}{\delta \xi(s)} \frac{\partial \rho(x; t)}{\partial x(t)} \right)_{\xi} = -\frac{\partial}{\partial x} \left( \frac{\delta x(t)}{\delta \xi(s)} \right)_{s=t} \rho(x; t)_{\xi}.$$
To evaluate the functional derivative of the stochastic process \( x(t) \) with respect to the noise, we use a formal solution of the Langevin stochastic differential equation, namely

\[
x(t) = x_0 + \int_0^t ds \, q(x(s)) + \int_0^t ds \, g(x(s)) \xi(s).
\]

(65)

Then

\[
\frac{\delta x(t)}{\delta \xi(s)} \bigg|_{s=t} = g(x(t))
\]

(66)

and

\[
\left\langle \frac{\delta \rho(x[\xi(t)]; t)}{\delta \xi(s)} \bigg|_{s=t} \right\rangle = -\frac{\partial}{\partial x} \left[ g(x(t)) \left\langle \rho(x(t)) \right\rangle \xi \right] = -\frac{\partial}{\partial x} \left[ g(x(t)) f(x; t) \right].
\]

(67)

Using this result in Eq. (61) above, we finally get the Fokker-Planck equation for the probability density function:

\[
\frac{\partial f(x; t)}{\partial t} = -\frac{\partial}{\partial x} \left[ q(x) f(x; t) \right] + \frac{1}{2} \frac{\partial}{\partial x} \left[ g(x) \frac{\partial}{\partial x} [g(x) f(x; t)] \right].
\]

(68)

The procedure we have used to derive the Fokker-Planck equation for a single variable can be extended to the case of several variables. Consider a set of stochastic variables \( \mathbf{x} = (x_1, x_2, \ldots, x_N) \) whose dynamics is given by the set of Langevin equations to be considered in the Stratonovich interpretation

\[
\frac{dx_i}{dt} = q_i(\mathbf{x}, t) + \sum_{j=1}^N g_{ij}(\mathbf{x}, t) \xi_j(t) \quad i = 1, \ldots, N
\]

(69)

where we allow for the drift terms \( q_i(\mathbf{x}, t) \) and diffusion terms \( g_{ij}(\mathbf{x}, t) \) to explicitly depend on the time. \( \xi_j(t) \) are uncorrelated Gaussian white noises with zero mean, that is

\[
\left\langle \xi_i(t) \right\rangle = 0 \quad ; \quad \left\langle \xi_i(t) \xi_j(s) \right\rangle = \delta_{ij} \delta(t - s) \quad \forall i, j \in [1, N]
\]

(70)
• By using a straightforward extension of the method used for one variable, one can prove that the one-time probability density function $f(\mathbf{x}; t)$ satisfies the following multivariate Fokker-Planck equation

$$\frac{\partial f(\mathbf{x}; t)}{\partial t} = -\sum_{i=1}^{N} \frac{\partial}{\partial x_i} [q_i(\mathbf{x}, t)f(\mathbf{x}; t)] + \frac{1}{2} \sum_{i,j,k=1}^{N} \frac{\partial}{\partial x_i} \left[ g_{ik}(\mathbf{x}, t) \frac{\partial}{\partial x_j} [g_{jk}(\mathbf{x}, t)f(\mathbf{x}; t)] \right].$$  \hspace{1cm} (71)

• It can also be written in the form of a continuity equation

$$\frac{\partial f(\mathbf{x}; t)}{\partial t} + \sum_{i=1}^{N} \frac{\partial}{\partial x_i} J_i(\mathbf{x}, t) = 0,$$

where the probability currents $J_i(\mathbf{x}, t)$ are given by

$$J_i(\mathbf{x}, t) = q_i(\mathbf{x}, t)f(\mathbf{x}; t) - \frac{1}{2} \sum_{j,k=1}^{N} \left[ g_{ik}(\mathbf{x}, t) \frac{\partial}{\partial x_j} [g_{jk}(\mathbf{x}, t)f(\mathbf{x}; t)] \right].$$  \hspace{1cm} (73)

• If $q_i(\mathbf{x}, t)$ and $g_{ij}(\mathbf{x}, t)$ do not depend explicitly on time, i.e. $q_i(\mathbf{x}, t) = q_i(\mathbf{x})$ and $g_{ij}(\mathbf{x}, t) = g_{ij}(\mathbf{x})$, then the Fokker-Planck equation is called *homogeneous*. 