Stochastic processes in statistical mechanics

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0.1 Brownian motion

In 1827, the botanic R. Brown observed with a microscope the never-ending and strongly irregular motion of the small particles of pool in suspension with water. During the whole 19th century this behaviour was not understood and at given point even the presence of some "vital force" specific of biological objects was considered. This hypothesis was later discarded when the same phenomenon was observed also for small mineral particles.

The first theoretical explanation of the Brownian motion was given by A. Einstein in 1905 who had the idea to look a the problem from a probabilistic point of view by discarding all the microscopic details. He interpreted the Brownian motion as coming from the motion of a *mesoscopic* particle that continuously experiences collisions with the (much smaller) particles of the surrounding fluid. Since then the Brownian Motion has become the paradigm of a large class of stochastic processes and more generally to the statistical mechanics of non-equilibrium.

0.2 The Einstein solution

In the Einstein solution of the Brownian Motion two are the major points to be considered:

1. As the solution considered is very diluted, the motion of the mesoscopic particle is mainly due to the (very frequent) collisions it experience with the molecules of the surrounding fluid (ensemble of mesoscopic particles that do not interact with one another).

2. The motion of the molecules is so complicated that their effect on the motion of the mesoscopic particle cannot be fully described in terms of classical equations of motion but can be treated only in a *probabilistic sense*, i.e. by considering the result of several, statistically independent, collisions.

We will focuss on a one dimensional motion. Following the last consideration one can then introduce a time interval τ which is small with respect to the observation time scale but sufficiently large that the motion of the mesoscopic particles between two intervals in τ can be considered as *independent events* (**two time scales hypothesis**). Let N be the number of mesoscopic particles suspended in the fluid and suppose we know the x-coordinates of all the meso-particles at times t and $t + \tau$. In a given interval τ the x-coordinates of the particles will vary of a small quantity Δ whose value depends on the particle (i.e. the first meso-particle will experience a shift of Δ_1, the second a shift of Δ_2 and so on). Half of these shifts will be in average positive and half negative. Of course we cannot compute all the shifts particle by particle because of the large number of solvent molecules colliding to them. We can just follow a *probabilistic approach* and say that after the time τ the number of particles dN who will experience a shift with a span from Δ to $\Delta + d\Delta$ will be given by:

$$dN = N\Phi(\Delta)d\Delta, \tag{1}$$

where $\Phi(\Delta)d\Delta$ is the fraction of particles that have experienced a shift with a span between Δ and $\Delta + d\Delta$ and

$$\int_{\mathbb{R}} \Phi(\Delta)d\Delta = 1. \tag{2}$$

In this picture the shift Δ is regarded as a stochastic variable and $\Phi(\Delta)$ is the associated probability density. By the plus minus symmetry mentioned before $\Phi(-\Delta) = \Phi(\Delta)$.

In order to write an evolution equation let us call $f(x, t + \tau)dx$ be the number of particles for unit volume that are, at time $t + \tau$, within the interval $[x, x + dx]$. This number is obtained by two terms. The first is related to the number of particles that at time t were within the interval $[x + \Delta, x + dx + \Delta]$ multiplied by the fraction of particles $\Phi(-\Delta)d\Delta$ that have experienced (because of collisions) a shift of $-\Delta$ with $\Delta > 0$. The second is determined by the number of particles that at time t were within the interval $[x - \Delta, x + dx - \Delta]$ multiplied by the fraction of particles $\Phi(\Delta)d\Delta$ that have experienced a shift of Δ ($\Delta > 0$). By integrating over all possible positive values of Δ one has:

$$f(x, t + \tau)dx = dx \left(\int_{\mathbb{R}^+} f(x + \Delta, t)\Phi(-\Delta)d\Delta + \int_{\mathbb{R}^+} f(x - \Delta, t)\Phi(\Delta)d\Delta \right), \tag{3}$$

that can be written (remember that $\Phi(-\Delta) = \Phi(\Delta)$) as

$$f(x, t + \tau)dx = dx \int_{\mathbb{R}} f(x + \Delta, t)\Phi(\Delta)d\Delta. \tag{4}$$

Note. We will see later that Eq. (4) is a particular form of the so called Chapman-Kolmogorov equation for Markov processes. We can indeed rephrase eq. (4) as follow: The probability of a particle to be in x at time $t + \tau$ is given by the probability of being in $x + \Delta$ at time t times the probability of experiencing a shift $-\Delta$ when it was in $x + \Delta$.

Since by hypothesis τ is much smaller then the observation time scale we can expand $f(x, t+\tau)$ for small τ giving:

$$f(x, t + \tau) = f(x, t) + \tau \frac{\partial f}{\partial t} \tag{5}$$

We can also expand $f(x + \Delta, t)$ in terms of Δ obtaining (see later the Kramers Moyal expansion for the Chapmann-Kolmogorov equation)

$$f(x + \Delta, t) = f(x, t) + \Delta \frac{\partial f}{\partial x} + \frac{\Delta^2}{2} \frac{\partial^2 f(x, t)}{\partial x^2} + O(\Delta^3). \tag{6}$$

By plugging together the two sides we have

$$\begin{aligned} f(x, t) + \tau \frac{\partial f}{\partial t} &= f(x, t) \int_{\mathbb{R}} \Phi(\Delta)d\Delta + \frac{\partial f}{\partial x} \int_{\mathbb{R}} \Delta\Phi(\Delta)d\Delta \\ &+ \frac{\partial^2 f(x, t)}{\partial x^2} \int_{\mathbb{R}} \frac{\Delta^2}{2}\Phi(\Delta)d\Delta + O\left(\int_{\mathbb{R}} \frac{\Delta^3}{6}\Phi(\Delta)d\Delta \right). \end{aligned} \tag{7}$$

As one can see the right hand side of the equation is a sum of terms that contain the moments of the distribution function $\Phi(\Delta)$. Since $\Phi(-\Delta) = \Phi(\Delta)$ the odd moments are zero and one can assume that the higher order even moments can be neglected(see later for a rigorous theorem on that assumption). We then have:

$$\frac{\partial f(x, t)}{\partial t} = D \frac{\partial^2 f(x, t)}{\partial x^2} \tag{8}$$

where

$$D \equiv \frac{1}{\tau} \int_{\mathbb{R}} \frac{\Delta^2}{2}\Phi(\Delta)d\Delta. \tag{9}$$

Eq. (8) is known as *diffusion equation* with *diffusion coefficient D*.

Note. The diffusion coefficient D is related to the second moment of the distribution function $\Phi(\Delta)$ of the shifts and is inversely proportional to the time interval between sets of collisions.
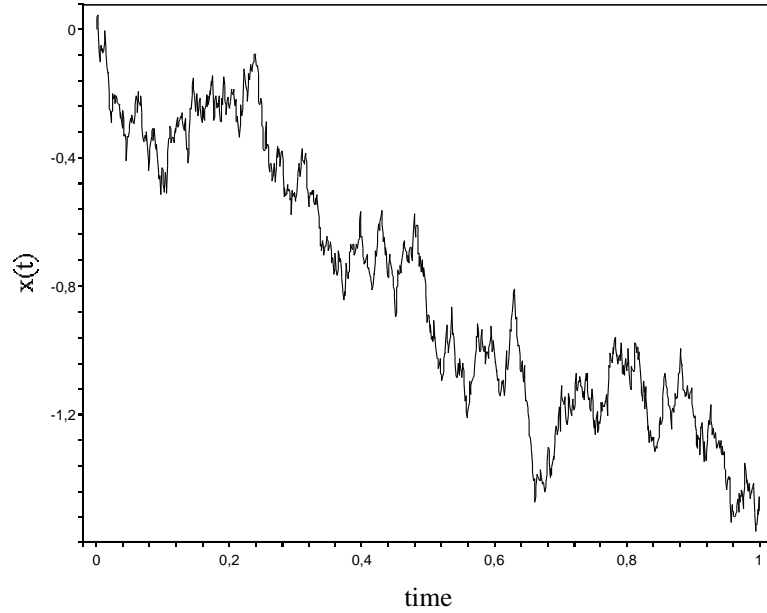
1D Brownian Motion

Figure 1: Time evolution of the position (distance from the origin) for a 1D Brownian motion.

From the solution of the diffusion equation when then have

$$f(x,t) = \frac{1}{\sqrt{4\pi Dt}} e^{-\frac{x^2}{4Dt}} \tag{10}$$

The number of particles per unit volume (concentration) at time t and within the interval $[x, x+dx]$ follows a Gaussian distribution with variance σ^2 which depends on time t as $\sigma^2(t) = 2Dt$. Notice that the average squared distance $\langle x^2 \rangle$ is

$$\langle x^2 \rangle = \int_{\mathbb{R}} x^2 f(x,t) dx = 2Dt \tag{11}$$

giving the scaling law

$$\sqrt{\langle x^2 \rangle} \simeq \sqrt{t} \tag{12}$$

Einstein adds that for diffusion in three dimension $\langle x^2 \rangle\rangle = 6Dt$ and consequently it should be $\langle x^2 \rangle = 4Dt$ in two dimension.

0.3 Kinematic of Brownian motion

Before we start to study how the interactions particle-molecules can generate such an erratic motion (dynamic of the Brownian motion) we will try to describe the motion itself from a statistical point of view. For simplicity let us focus on the 1D motion of a single particle. In figure 1) we show the time evolution of the position of a single Brownian particle in 1D. The position of the particle is unbounded and as t increases it will go far away from the initial point (origin) In figure 2 we show the square of the position as a function of time. As one can see the function is quite irregular but has fluctuations that increase as time increases. From classical kinematics, in order to obtain the distance covered by the particle from the origin we integrate its velocity over time

$$x(t) = x_0 + \int_0^t v(s) ds \tag{13}$$
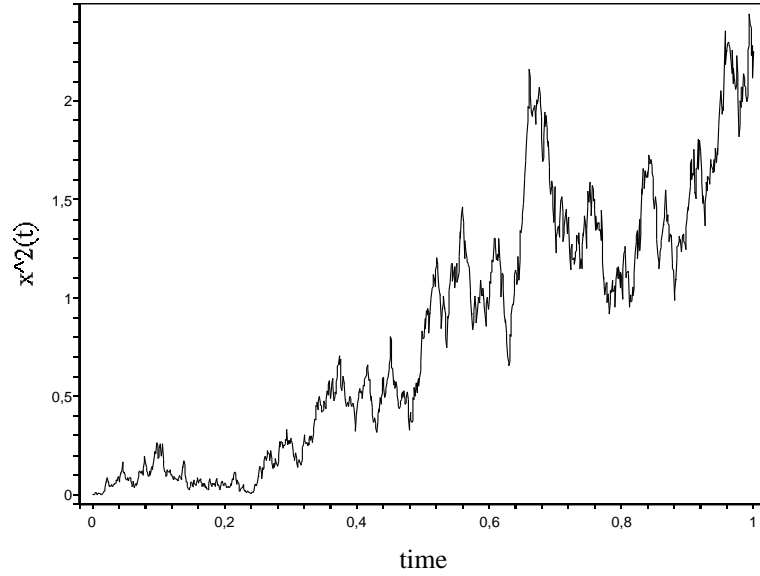
1D Brownian Motion

Figure 2: Time evolution of the squared of the position for the path presented in figure 1.

The square of the distance is then

$$
\begin{aligned}
x^2(t) & = x_0^2 + 2x_0 \int_0^t v(s)ds + \left[\int_0^t v(s)ds \right]^2 \\
& = x_0^2 + 2x_0(x - x_0) + \int_0^t ds_1 v(s_1) \int_0^t ds_2 v(s_2).
\end{aligned}
\tag{14}
$$

Hence

$$
(x(t) - x_0)^2 = \int_0^t ds_1 \int_0^t ds_2 v(s_1) v(s_2),
\tag{15}
$$

and, by taking the average one gets

$$
\left\langle (x(t) - x_0)^2 \right\rangle = \int_0^t ds_1 \int_0^t ds_2 \left\langle v(s_1) v(s_2) \right\rangle.
\tag{16}
$$

In other words the mean squared distance covered by the particle in a time t can be computed from the autocorrelation function of the velocities

$$
C_v(s_1, s_2) \equiv \langle v(s_1) v(s_2) \rangle.
\tag{17}
$$

In stationary states the correlation function depends only on the time difference $s_1 - s_2$ and one can write

$$
\left\langle (x(t) - x_0)^2 \right\rangle = \int_0^t ds_1 \int_0^t ds_2 C_v(s_1 - s_2).
\tag{18}
$$

By putting $\tau = s_1 - s_2$ and $T = s_1 + s_2$ and by integrating over T one obtains (**Exercise**)

$$
\boxed{\left\langle (x(t) - x_0)^2 \right\rangle = 2 \int_0^t d\tau (t - \tau) C_v(\tau).}
\tag{19}
$$

In order to perform integral (19) a functional form of the correlation function is needed. This will be obtained later when we will consider the Langevin approach to the Brownian motion. One can however make the following considerations. In general

$$C_v(t) \simeq e^{-t/\tau_v} \tag{20}$$

and is natural to consider as the important time scale of the process the correlation time τ_v. This is indeed the time such that for $t << \tau_v$ $C_v(t)$ is practically constant whereas for $t >> \tau_v$ $C_v(t)$ is essentially zero.

Definition (Autocorrelation time τ_v.). The autocorrelation time τ_v is the time such that

$$
\begin{aligned}
C_v(t) &\simeq C_v(0) & t << \tau_v \\
C_v(t) &\simeq 0 & t >> \tau_v
\end{aligned}
\tag{21}
$$

Note. τ_v is a rough measure of the width of the correlation function. An estimate of τ_v can be obtained by computing the area below the curve. A very rough estimate of such area consists in measuring the height of $C_v(t)$ i.e. its initial value $C_v(0)$, times a rough measure of its width i.e.

$$\int_0^\infty C_v(t)dt = \tau_v C_v(0), \tag{22}$$

giving

$$\boxed{\frac{1}{C_v(0)} \int_0^\infty C_v(t)dt}. \tag{23}$$

One can then consider the two limits of large and small time scales as follows:

Short time scale limit If $t << \tau_v$, it is reasonable to substitute $C_v(t)$ with $C_v(0)$ in the integral for $\left\langle (x(t) - x_0)^2 \right\rangle$ obtaining

$$
\begin{aligned}
\left\langle (x(t) - x_0)^2 \right\rangle &= 2C_v(0) \int_0^t (t - \tau)d\tau \tag{24} \\
&= 2C_v(0) \left[t^2 - t^2/2 \right] = C_v(0)t^2 \tag{25}
\end{aligned}
$$

On the other hand $C_v(0) = \langle v^2 \rangle$ and we get

$$\left\langle (x(t) - x_0)^2 \right\rangle = \langle v^2 \rangle t^2 \tag{26}$$

This is similar to free motion and in this regime the Brownian particle is essentially non interacting with the environment. This regime is known as *ballistic regime*.

Large time scale limit For $t >> \tau_v$ $C_v(t) \simeq 0$ and one can extend to ∞ the upper limit in the integral expression for $\langle x^2 \rangle$ giving:

$$\left\langle (x(t) - x_0)^2 \right\rangle = 2t \int_0^\infty C_v(\tau)d\tau - 2 \int_0^\infty \tau C_v(\tau)d\tau. \tag{27}$$

The second term does not depend on time and it will be small if compared to the first one for t big enough. Hence

$$\left\langle (x(t) - x_0)^2 \right\rangle \simeq 2t \int_0^\infty C_v(\tau)d\tau. \tag{28}$$

Notice that in this regime the mean squared distance is proportional to t (instead then t^2). This regime is known as *diffusive regime*. Indeed the solution of the 1D diffusion equation gives

$$\left\langle (x(t) - x_0)^2 \right\rangle = 2Dt \tag{29}$$

where D is the diffusion coefficient. This interpretation will allow then to make the following identification

$$D = \int_0^\infty \langle v(0)v(\tau) \rangle d\tau. \tag{30}$$

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