Brownian Motion. Diffusion

A direct application of the Central Limiting Theorem in Statistical Mechanics is the theory of Brownian motion. This theory is the first of the three remarkable Einstein’s works published in 1905 (visit the site www.einsteinyear.org/facts for historical details).

Suppose we have a one-dimensional Brownian particle in some medium localized at the initial time moment \( t_0 \) at some point \( x_0 \) (for the sake of briefness, we set \( t_0 = 0 \) and \( x_0 = 0 \)). What is the probability density to find the particle at the point \( x \) at time \( t \)? One may argue that the answer depends on particular details of the interactions of the particle with the medium—and this is indeed the case, but it is crucial that all these details are absorbed by just one parameter—diffusion coefficient, the evolution picture being absolutely universal.

We consider a 1D case; the generalization to any dimensions is straightforward. Let us measure the coordinate of the particle with some time intervals \( \Delta t \): the \( n \)-th measurement corresponds to the time moment \( t_n = n\Delta t \). We get the coordinates \( x_n = x(t_n) \). Now we introduce the displacement during the \( n \)-th time interval

\[
s_n = x_n - x_{n-1}
\]

and write

\[
x_n = s_1 + s_2 + \ldots + s_n .
\]

Mathematically, Eqs. (1)-(2) look like a trivial rewriting. There is, however, a deep physical idea behind (2), provided the interval \( \Delta t \) is large enough: the displacements \( \{s_n\} \) can be treated as independent random numbers. Indeed, if \( \Delta t \) is large enough, then during this time interval the Brownian particle experiences a large number of kicks from the particles of the medium and completely forgets about its previous state. Hence, in the limit of \( n \to \infty \) we can apply the Central Limiting Theorem to the variable \( x_n \) and find the probability density

\[
W_n(x_n) = \frac{e^{-x_n^2/2n\sigma^2}}{\sqrt{2\pi n \sigma}},
\]

where \( \sigma \) is the dispersion of \( s_j \) (it is \( j \)-independent because all time intervals are equal). We also take into account that by symmetry of the problem \( \bar{s}_j = 0 \), and thus \( \bar{x}_n = 0 \). Instead of \( n \) we can simply use time, since \( n = t/\Delta t \). From now on we omit the subscript \( n \) from \( x, t, \) and \( W \). Introducing the parameter (the factor of 2 in denominator is for further convenience)

\[
D = \frac{\sigma^2}{2\Delta t} ,
\]

we write

\[
W(x,t) = \frac{e^{-x^2/4Dt}}{2\sqrt{\pi Dt}} .
\]

We make the final step by noticing that the parameter \( D \) is actually independent of \( \Delta t \). Indeed, let us increase \( \Delta t \) by a factor of 2 by introducing \( \Delta t' = 2\Delta t \). This means that now we are dealing with displacements \( \bar{s}_n = s_{2n-1} + s_{2n} \). Correspondingly \( \bar{\sigma}^2 = 2\sigma^2 \), and the ratio (4) remains the same. Hence, Eq. (5) contains no \( \Delta t \) dependence and is valid at any time moment, provided \( t \) is large enough. The parameter \( D \) is called diffusion coefficient. Its specific value depends on the microscopic details of the process. An order-of-magnitude estimate for \( D \) follows from the above consideration: Is the square of the mean free path of the Brownian particle over the typical interval between its collisions with the particles of the medium. The diffusion coefficient describes the rate at which the dispersion of \( x \) grows with time: \( \Delta x = \sqrt{2Dt} \).
Eq. (5) implies that we start at \( t = 0 \) and place the particle at \( x = 0 \). If we start at \( t = t_0 \) and \( x(t_0) = x_0 \), then we just need to modify (5) by \( t \to t - t_0 \), \( x \to x - x_0 \).

**Problem 12.** Consider the following random walker—a simple model of a Brownian motion. Each time moment \( t_n = nt \), we toss a coin and with equal probabilities shift our particle either right or left by a distance \( l \). Find the diffusion coefficient.

We are in a position to generalize our result to the case when the initial coordinate \( x_0 \) is also a random number distributed as

\[
Q_0(x) \, dx_0.
\]

This is a diffusion problem, when we have a lot of independent particles (random walkers) distributed with one and the same probability density. In this case, the probability density \( Q_0(x) \) is nothing else than the concentration (=number density) of particles divided by their total number. Hence, single-particle probability density and particle concentration are proportional to each other quantities, and we will not distinguish between them. Given initial distribution of concentration, we are interested in its evolution with time. The solution is readily obtained if we use our result (5) in combination with the ideas of conditional probability. We denote the distribution at the time moment \( t \) as \( Q(x,t) \), that is \( Q(x,t_0) \equiv Q_0(x) \). Now we note that the probability \( dP = Q(x,t) \, dx \) of finding our particle at the time moment \( t \) in some interval \( dx \) at the point \( x \) can be decomposed into an integral over the probabilities of mutually exclusive events corresponding to different starting points \( x_0 \):

\[
dP = \int_{x_0} \, dP_{x_0 \to x}.
\]

The precise meaning of \( dP_{x_0 \to x} \) is as follows. It is the probability of the event when at time moment \( t_0 \) the particle is in the interval \( dx_0 \) at the point \( x_0 \) AND at time moment \( t \) the particle is in the interval \( dx \) at the point \( x \). According to conditional probabilities, \( dP_{x_0 \to x} \) is a product of probability (6) for the given initial state and the probability \( W(x - x_0, t - t_0) \, dx \) for getting to the point \( x \) from this particular initial state. Plugging

\[
dP_{x_0 \to x} = Q_0(x_0) \, dx_0 \cdot W(x - x_0, t - t_0) \, dx
\]

into (7), we get

\[
dP = \int_{x_0} Q_0(x_0) \, dx_0 \cdot W(x - x_0, t - t_0) \, dx = dx \int Q_0(x_0) W(x - x_0, t - t_0) \, dx_0.
\]

We see that the law of evolution of \( Q \) is

\[
Q(x,t) = \int Q(x_0,t_0) W(x - x_0, t - t_0) \, dx_0.
\]

Mathematically, evolution is equivalent to acting on the initial distribution with some linear operator. The function \( W \), Eq. (5), plays the role of the kernel of this operator. In this context it is called *Green’s function* or *propagator*.

The evolution of \( Q \) can be also found from a partial-derivative equation known as diffusion equation:

\[
\frac{\partial Q}{\partial t} = D \frac{\partial^2 Q}{\partial x^2}.
\]

To arrive at (10), we first rewrite it in the form

\[
\mathcal{L} Q = 0,
\]

where

\[
\mathcal{L} = \frac{\partial}{\partial t} - D \frac{\partial^2}{\partial x^2},
\]

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is a linear—this is important—differential operator. Then we explicitly check that

$$\mathcal{L}W = 0$$  \hspace{1cm} (13)$$

and act with the operator $\mathcal{L}$ on both sides of Eq. (9), observing that the operation $\mathcal{L}$ in the right-hand side can be done under the sign of integral.

**Problem 13.** Perform this procedure step by step, starting from checking Eq. (13).

This derivation is easily generalized to any dimensions by an observation that displacements with respect to different coordinates are independent at large $\Delta t$. This means that each coordinate should be treated independently and leads to the following expressions (below $d$ is the space dimension).

$$W(r, t) = e^{-r^2/4Dt}/(4\pi Dt)^{d/2} \ .$$  \hspace{1cm} (14)$$

$$Q(r, t) = \int Q(r_0, t_0) W(r - r_0, t - t_0) \, dr_0 \ .$$  \hspace{1cm} (15)$$

[Here $dr = dr_1 \, dr_2 \, \ldots \, dr_d$ is the element of the $d$-dimensional volume.] We also have the diffusion equation in the form equivalent to (11) and (13), where the differential operator now is given by

$$\mathcal{L} = \frac{\partial}{\partial t} - D \left( \frac{\partial^2}{\partial r_1^2} + \ldots + \frac{\partial^2}{\partial r_d^2} \right) \ .$$  \hspace{1cm} (16)$$

Note that up to a dimensional coefficient the spatial part of the operator $\mathcal{L}$ is the Laplace operator, $\nabla^2$. The diffusion equation thus can be written as

$$\frac{\partial Q}{\partial t} = D \nabla^2 Q \ .$$  \hspace{1cm} (17)$$