

Lecture 20: (Physical) Brownian Motion

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1 Overview and simple models

When we talk about Brownian motion, we're interested in the motion of a large particle in a gas or liquid in equilibrium, which is roughly approximated by a random walk. You might imagine something like this:

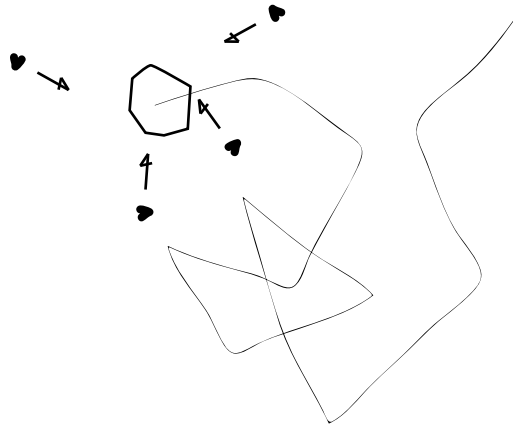


Figure 1: A large particle undergoing Brownian motion due to collision with smaller particles from a liquid or gas.

Brownian motion is named for Robert Brown, who published a paper on his observations of pollen particles.¹ Prof. Bazant recommends looking at this web applet of a molecular dynamics simulation of Brownian motion: <http://www.phy.ntnu.edu.tw/java/gas2d/gas2d.html>

¹Robert Brown's original 1827 paper on his light microscope observations of pollen grains is available online (<http://sciweb.nybg.org/science2/pdfs/dws/Brownian.pdf>). Interestingly, one of Brown's tasks was to make sure that the motion continued even after plant death: "Having found motion in the particles of the pollen of all the living plants which I had examined, I was led next to inquire whether this property continued after the death of the plant, and for what length of time it was retained." He goes on to show the existence of the motion in inorganic substances and in organic substances after burning over a fire and thus concludes these "Active Molecules" are "readily obtained from all bodies".

Simplest models

1. Discrete RW with IID steps.

As mentioned in the first lecture, the simplest model of Brownian motion is a random walk where the “steps” are random displacements, assumed to be IID random variables, between nearly instantaneous collisions. The constant time step represents the mean time between collisions, which is usually well defined near equilibrium, except in very small systems or very low densities, where the mean free path is comparable to the system size. (We will discuss this exotic regime of “low Knudsen number” gases later in the class.)

2. Continuous Wiener process.

This is the limit of infinitesimal displacements in the discrete random walk with IID steps, first given a rigorous mathematical definition by MIT mathematician, Norbert Wiener, in the 1920s. We will discuss the Wiener process and its connection to discrete random walks later in the class.

Mathematicians have come to call this formal construction “Brownian motion”, even though it is only a crude approximation of the physical phenomenon of Brownian motion. Therefore, the Wiener process is sometimes referred to as “mathematical Brownian motion”.

One curious feature of this limit, emphasized by Wiener, is that the particle has an infinite velocity at all times² It is easy to see this heuristically, assuming that the infinitesimal displacement dx (stochastic differential) is a Gaussian random variable with mean zero and variance $2D dt$, where $D = \lim_{dt \rightarrow 0} \langle dx^2 \rangle / 2 dt$ is the diffusivity. The typical displacement in time dt has size $\sqrt{2D dt}$, which implies a divergent instantaneous velocity $v = \sqrt{2D/dt} \rightarrow \infty$.

Both of these models have the attractive feature of mathematical simplicity, but each fails to describe various important features of *physical* Brownian motion:

1. **Inertia.** Momentum is conserved after collisions, so a particle will recoil after a collision with a bias in the previous direction of motion. This causes correlations in time, between successive steps.
2. **Ballistic motion.** In a physical Brownian motion, there is in fact a well defined instantaneous velocity, which varies around some typical value. A more complete microscopic theory of Brownian motion would account for the ballistic motion of a particle between collisions (in a gas) or the gradual “turning of the steering wheel” when collision events are not well separated in time (in a liquid).
3. **Interactions between particles.** Each particle, whether large or small, collides and interacts with all of its neighbors, so it is not always possible to focus on just one independent random walker interacting with a source of “noise”, although that is a reasonable first approximation.

Today, we will focus models addressing the first two problems.

NOTE: The material below is covered in more detail in lectures 9 –11 from 2003.

²The trajectory of Brownian motion is thus an example of a curve which is continuous and yet nowhere differentiable. This shows that stochastic calculus is markedly different from the more familiar continuous calculus.

2 Random walk with correlated steps

Consider unbiased ($\langle \Delta x \rangle = 0$) identically distributed steps with $\langle \Delta x \rangle = \sigma^2$ which are not independent. In this case, if the correlations between steps are not too strong, the CLT still holds, but with a modified diffusion coefficient.

$$X_N = \sum_{n=1}^N \Delta x_n \quad (1)$$

$$\langle X_N^2 \rangle = \sum_n \sum_m \langle \Delta x_n \cdot \Delta x_m \rangle \quad (2)$$

$$= \sum_n \sum_m C_{n,m} \quad (3)$$

Consider translation invariance in time, so that

$$C_{n,m} = C(|n - m|) \quad \text{Note: } C(0) = \sigma^2 \quad (4)$$

We have $C_{n,m}$ symmetric with values decaying away from the diagonal. Since the correlations are between times that are close together, then we expect the near diagonal entries to have greater (magnitude) values than those further away from the diagonal. Of course, the diagonal terms $C(0)$ will all be σ^2 .

$$\langle X_N^2 \rangle = N\sigma^2 + 2 \sum_{n'=1}^N (N - n') C(n') \quad \text{where } n' = n - m \quad (5)$$

In the continuum limit:

$$N = \frac{t_n}{\tau}, \quad \tau \rightarrow 0, \quad N \rightarrow \infty$$

with t fixed

$$\frac{\Delta t_n}{\tau} = V(t_n) \quad V = \text{velocity}$$

$$\frac{C_{n,m}}{\tau^2} = \langle V(t_n) \cdot V(t_m) \rangle$$

$$D_o = \frac{\sigma^2}{2\tau} \quad (6)$$

$$\langle X(t)^2 \rangle = 2Dt + \int_0^t \langle V(0) \cdot V(t') \rangle (t - t') dt'$$

$$D \equiv \lim \frac{1}{2} \frac{d}{dt} \langle X(t)^2 \rangle = D_o + \int_0^\infty \langle V(0) \cdot V(t) \rangle_{t>0} dt$$

We have D_o as the standard diffusion constant without any correlation and the additional expectation to be taken $t > 0$. Note: It is common to introduce a delta function in $\langle V(0) \cdot V(t) \rangle_{t>0} = f(t) + \delta_{t>0}(t)D_o$. The first term $f(t)$ is the memory of the past and the delta function is simply an autocorrelation.

This is called the Green-Kubo relationship:

$$\int_0^{\infty} \langle V(0) \cdot V(t) \rangle_{t>0} dt \quad (7)$$

It is useful in molecular dynamics simulations because you always know the velocity of every particle at every time and thus can easily plug-in to get D . There exists a whole family of Green-Kubo equations that relate transport coefficients (for mass, energy, momentum, etc.) to time integrals of autocorrelation functions.

In the discrete case:

$$D = \lim_{N \rightarrow \infty} \frac{\langle X_N^2 \rangle}{2N\tau} \quad (8)$$

Note:

1. D is finite (maybe $\neq D_o$) if C is short ranged (and not oscillating too fast). We get $\sqrt{\langle X^2 \rangle} \sim \sqrt{2Dt}$.
2. $D \rightarrow 0$, C oscillates. We get $\sqrt{\langle X^2 \rangle} \propto t^\nu$ with $0 \leq \nu < \frac{1}{2}$. **Subdiffusion.**
3. $D \rightarrow \infty$, C is long ranged. We get $\sqrt{\langle X^2 \rangle} \propto t^\nu$ with $\frac{1}{2} < \nu \leq 1$. **Superdiffusion.**

3 Exponentially decaying correlations

Now, we will look at what happens when there is a direct correlation of p with the previous step (lecture 9, 2003). When $p > 0$ this implies a tendency to keep going in the same direction after a collision, sometimes called “persistence”, which approximates the effect of inertia in Brownian motion. The “persistent random walk” can be traced back at least to 1921, in an early model of G. I. Taylor for tracer motion in a turbulent fluid flow. ($-1 < p < 1$)

$$\Delta x_n = p\Delta x_{n-1} + \sqrt{(1-p^2)}\Delta x'_n \quad (9)$$

This linear combination, illustrated in the figure on a circle, ensures that if the variables $\{\Delta x'_n\}_{n=1}^N$ are IID with zero mean and variance σ^2 , then the variables $\{\Delta x_n\}_{n=1}^N$ are dependent, with correlation p between successive steps and the same variance σ^2 . We have

$$C(1) = \langle \Delta x_n \cdot \Delta x_{n-1} \rangle = p\sigma^2 \quad (\text{by construction}) \quad (10)$$

$$\text{because } \langle \Delta x'_n \cdot \Delta x'_m \rangle = \sigma^2 \delta_{n,m} \quad (\langle \Delta x'_n \rangle = 0) \quad (11)$$

$$C(2) = \langle \Delta x_n \cdot \Delta x_{n-2} \rangle = p^2 \sigma^2 \quad (12)$$

$$C(m) = \langle \Delta x_n \cdot \Delta x_{n-m} \rangle = p^m \sigma^2 \quad (13)$$

$$\left. \begin{aligned} C(m) &= \sigma^2 e^{\frac{-2m}{n_c}} \\ n_c &= \frac{-2}{\log p} \end{aligned} \right\} \quad (14)$$

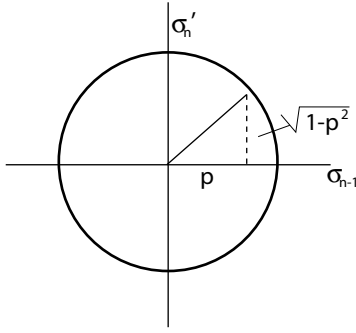


Figure 2: A geometrical construction for the “mixing” of a new random variable with the previous random displacement to create a dependent random displacement, with correlation coefficient p .

$$\frac{\langle X_N^2 \rangle}{N\sigma^2} = 1 + \frac{2}{N} \underbrace{\sum_{n=1}^N p^n (N-n)}_{\text{geometric series}} \tag{15}$$

$$= \frac{1+p}{1-p} + \frac{2}{N} \frac{p(1-p^N)}{(1-p)^2} \tag{16}$$

Long-time scaling:

$$\frac{D}{D_o} = \frac{1+p}{1-p} \quad N \rightarrow \infty \tag{17}$$

Recall from last lecture that $p = 1/3$ for a tetrahedral polymer chain.

Now, consider $p \rightarrow 1$.

$$p = 1 - \epsilon \tag{18}$$

$$n_c = \frac{-2}{\log p} \sim \frac{2}{\epsilon} \tag{19}$$

$$\frac{1+p}{1-p} \sim \frac{2}{\epsilon} = n_c \tag{20}$$

Rescale with dimensionless variables

$$\tilde{N} = \frac{N}{n_c}, \quad \tilde{X}_N = \frac{X_N}{n_c\sigma}$$

$$\langle \tilde{X}_N^2 \rangle \sim \lim_{\epsilon \rightarrow 0} \tilde{N} + \frac{1}{2} (e^{-2\tilde{N}} - 1) \tag{21}$$

$$\sim \begin{cases} \tilde{N}^2 & \tilde{N} \ll 1 & \text{Ballistic motion at constant velocity} \\ \tilde{N} & \tilde{N} \gg 1 & \text{Diffusion} \end{cases} \tag{22}$$

With strong, exponentially decaying correlation ($p = 1 - \epsilon$), the correlated random walk is equivalent at long times ($N \gg n_c$) to an uncorrelated random walk with IID steps with size $n_c\sigma$ and time step $n_c = \tau/\epsilon$.

Historic moment³

Continuum limit

The persistent random walk in one dimension has an interesting continuum limit (see also lecture 10, 2003). Some definitions:

$$\tau_c = \tau/\epsilon \quad , \quad c = \sigma/\tau \quad (23)$$

$$p = 1 - \epsilon \quad (24)$$

Now, we will be taking the following limits

$$\epsilon \rightarrow 0 \quad (25)$$

$$\tau \rightarrow 0 \quad (26)$$

$$\sigma \rightarrow 0 \quad (27)$$

τ_c is fixed and c is fixed (ie. ballistic regime). We have P as the PDF for position under these assumptions:

$$\boxed{\frac{\partial^2 P}{\partial t^2} + \frac{1}{\tau_c} \frac{\partial P}{\partial t} = c^2 \frac{\partial^2 P}{\partial x^2}} \quad (28)$$

$$\begin{array}{ll} t \ll \tau_c & \text{Wave equation} \quad \frac{\partial^2 P}{\partial t^2} \sim c^2 \frac{\partial^2 P}{\partial x^2} \\ t \gg \tau_c & \text{Diffusion equation} \quad \frac{\partial P}{\partial t} \sim D \frac{\partial^2 P}{\partial x^2} \quad D = \sigma^2 \tau_c \end{array} \quad (29)$$

The fundamental solution (Green function) for a localized initial condition at rest consists of two delta function pulses moving in either direction (as in the wave equation), with decreasing amplitude, to represent walkers undergoing ballistic motion before their first collision. Between these pulses is a smooth distribution of walkers who have had at least one collision, which eventually tends to a Gaussian shape (solving the diffusion equation) due to the long-time independence of steps which implies the CLT. The variance takes the simple form

$$\langle x(t)^2 \rangle = \frac{2e^2}{\gamma^2} (\gamma t + e^{-\gamma t} - 1) \quad (30)$$

³At this point in the lecture, Prof. Bazant received the important phone call that would, less than 12 hours later, culminate in the birth of Isabella Rose Bazant. If there was ever a good reason to answer a cell phone in class, this is it. Congratulations! (Note also that Prof. Bazant continued for an additional 15 minutes to actually derive the continuum limit before going to the hospital. Impressive.)

showing a transition from ballistic to diffusive scaling at a time scale γ^{-1} . In the next lecture, we will relate this parameter to the mass of the particle and the system temperature, by starting from Newton's laws of mechanics in a more complete stochastic theory of Brownian motion.

Note: a good reference for “physical Brownian motion” and continuous stochastic processes is *The Fokker-Planck Equation* by Risken.