Lecture 2: Continuum Approximations of Random Walks

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February 8, 2001

1 Summary of the Previous Lecture

In Lecture 1, we discussed the problem of finding the concentration $c(x,t)$ of a large number of independent walkers taking random steps at regular intervals of time τ time. If the individual step displacements y are independent, identically distributed ("iid") random variables with probability density function ("PDF") $p_\tau(y)$, i.e. $p_\tau(y)dy$ is the probability that a step displacement falls between y and $y+dy$, then the concentration satisfies the following exact recursion

$$C(x,t+\tau) = \int p_\tau(x-x')C(x',t)dx'$$

due to Bachelier (1900). Assuming that after long times the concentration varies very slowly on the scale of typical displacements, we obtained the diffusion equation from Bachelier's equation through Taylor expansion

$$\frac{\partial C}{\partial t} + v\frac{\partial C}{\partial x} = D\frac{\partial^2 C}{\partial x^2} + O(\tau^{\frac{1}{2}}),$$

with v, D defined as

$$\begin{aligned} v &= \lim_{\tau\to 0}\frac{\langle y\rangle_\tau}{\tau} = \lim_{\tau\to 0}\frac{1}{\tau}\int y p_\tau(y)dy, \\ D &= \lim_{\tau\to 0}\frac{\langle y^2\rangle_\tau}{2\tau} = \lim_{\tau\to 0}\frac{1}{2\tau}\int y^2 p_\tau(y)dy. \end{aligned}$$

Approximating the long-time behavior of the random walk using the diffusion equation clearly requires the first and the second moments of distribution $p_\tau(y)$ and the above two limits exist. (Strictly speaking, in this derivation all higher moments must also exist, but later we will see that the existence of higher moments is not required.) It is also clear that the natural length scale for diffusion part, which is the standard deviation of the random displacement, decreases as $\sqrt{\tau}$

$$\sqrt{\langle y^2\rangle_\tau} \sim \sqrt{2D\tau}$$

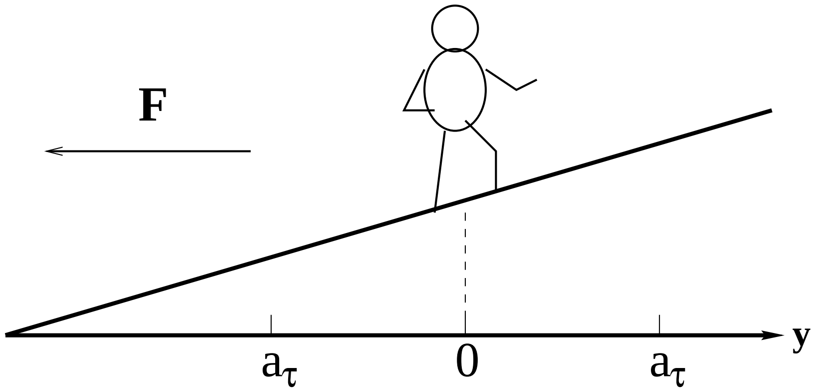

Figure 1: Illustration of the biased random walk

while the drift part decreases as τ,

$$\langle y \rangle_\tau \sim v\tau$$

as $\tau \to 0$. Therefore, intuitively, diffusion "wins" in the short time-step regime ($t = O(\tau)$), although drift "wins" in the long time regime ($t \gg \tau$). In other words fluctuations dominate at short times, while deterministic net flow dominates at large times. Since $\sqrt{2D\tau}$ is the dominant length scale of the transition PDF at small τ, and important consequence is that the nth moment scales like

$$\langle y^n \rangle_\tau \propto \tau^{n/2}$$

a fact which allows us to ignore higher terms in the moment expansion above in the long-time limit (leaving us with the simple diffusion equation). This point will be elucidated further in subsequent lectures.

2 The Einstein Relation

Now consider the case of biased random walk. As shown in Fig. 1, the energy bias is given by the product of force bias and the distance,

$$E_\pm = \pm F \cdot a_\tau,$$

and the force is the negative of the gradient of potential,

$$F = -\frac{\partial \phi}{\partial y}.$$

If assuming local thermal equilibrium, $k_B T$ can be naturally treated as the energy scale for microscopic fluctuations, where T is the absolute temperature and k_B is the Boltzmann constant. In a discret fashion, the probability to either direction is modulated by the energy bias in the following way,

$$\begin{aligned} P_+ &= \frac{1}{2} - \frac{E_+}{4k_B T}, \\ P_- &= \frac{1}{2} - \frac{E_-}{4k_B T}. \end{aligned}$$

Given that the spatial step size is a_τ, and the force field F is biased toward the negative y axis direction,

$$\begin{aligned} v &\sim \frac{\langle y\rangle}{\tau} = \frac{a_\tau(P_+ - P_-)}{\tau} = \frac{a_\tau}{\tau}\frac{Fa_\tau}{2k_BT} \\ D &\sim \frac{\langle y^2\rangle}{\tau}\frac{a_\tau^2(P_+ + P_-)}{\tau} = \frac{a_\tau^2}{2\tau}. \end{aligned}$$

So it leads to

$$\frac{v}{D} = \frac{F}{k_BT} \quad \text{or} \quad \mu = \frac{D}{k_BT}$$

where $\mu = v/F$ is the mobility or drag. This relation is sometimes also called Smoluchowski relation. For spherical objects, $\mu = 1/(6\pi\eta a)$ given by Stokes Law. η ccharacterizes the viscosity of the fluid medium. The above relations lead directly to the famous Einstein's relation

$$D = \frac{k_BT}{6\pi\eta a}.$$

Considering that the viscosity actually leads to energy dissipation while the diffusion process characterizes energy fluctuation, the above relation is also called **Fluctuation-Dissipation Theorem**.

3 Einstein ("Kramers-Moyal") Expansion

In this section we present a derivation closer to that of Einstein's, based on what is now sometimes called the Kramers-Moyal expansion (essentially a moment expansion). Consider the space and time transition probability $P(x,t|x',t')$ as the probability to transit from (x,t) to (x',t'), the concentration of Brownian particles is controlled by the following equation

$$C(x,t+\tau) = \int p(x,t+\tau|x',t')C(x',t')dx',$$

Kramers-Moyal expansion of which (homework problem) leads to

$$\frac{\partial C}{\partial t} + \sum_{n=2}^{\infty}\frac{\tau^{n-1}}{n!}\frac{\partial^n C}{\partial t^n} = \sum_{n=1}^{\infty}\frac{(-1)^n}{n!}\frac{\partial^n}{\partial x^n}[\frac{M_n(x,t,\tau)}{\tau}C(x,t)],$$

where $M_n(x,t,\tau) = \int p(x+y,t+\tau|x,t)y^n dy$ is the n-th moment of the transition probability. Let

$$D_n(x,t,\tau) = \frac{M_n(x,t,\tau)}{n!\tau} \overset{\tau\to 0}{\Rightarrow} D_n(x,t),$$

The expansion can be simplified as

$$\frac{\partial C}{\partial t} + \sum_{n=2}^{\infty}\frac{\tau^{n-1}}{n!}\frac{\partial^n C}{\partial t^n} = \sum_{n=1}^{\infty}(-\frac{\partial}{\partial x})^n[D_n(x,t,\tau)C(x,t)].$$

In the case that

$$D_n(x,t,\tau) \to 0, \quad \text{for} \;\; n > 2,$$

the Fokker-Planck equation can be obtained from the above expansion,

$$\frac{\partial C}{\partial t} + \frac{\partial}{\partial x}[D_1(x,t)C(x,t)] = \frac{\partial^2}{\partial x^2}[D_2(x,t)C(x,t)]$$

The flux density function, defined as

$$S(x,t) = D_1(x,t)C(x,t) - \frac{\partial}{\partial x}[D_2(x,t)C(x,t)],$$

leads to the conservation law of the total number of Brownian particles,

$$\begin{aligned} \frac{\partial C}{\partial t} + \frac{\partial S}{\partial x} &= 0, \\ \frac{\partial}{\partial t}\int_{x_{in}}^{x_{out}} C(x,t)dx &= -\int_{x_{in}}^{x_{out}} \frac{\partial S}{\partial x} = S_{in} - S_{out}. \end{aligned}$$

In the steady state, the drift part

$$D_1(x,t) \to v(x) = \mu F(x) = -\mu \frac{\partial \phi(x)}{\partial x},$$

because the force is the negative of the gradient of potential $\phi(x)$. Assuming

$$D_2(x,t) = D \equiv \text{const},$$

from the steady state condition $S(x) = 0$, we conclude that

$$-\mu \frac{\partial \phi(x)}{\partial x} C(x) - D\frac{\partial}{\partial x}C(x) = 0.$$

Therefore the equilibrium concentration of Brownian particles is controlled by

$$C(x) = C_0 e^{-\frac{\mu}{D}\phi(x)}.$$

Einstein said the above equation must be consistent with the well known Boltzmann distribution

$$C(x,t) = C_0 e^{-\frac{\phi(x)}{k_B T}},$$

thus leads the Einstein relation

$$\frac{\mu}{D} = \frac{1}{k_B T}.$$

But in the previous discussion, we got the same expression directly from microscopic details of random walk. In some sense, in the simple argument above we assumed microscopic equilibrium and reached the equivalent conclusion as Einstein while he proved the relation from the point of view of macroscopic distribution.