Stat. Phys. IV: Lecture 1

Spring 2025

Brownian motion: Einstein's derivation [1]

Chapman - Kolmogorov equation (Markov process)

$$f(x,t+\tau)dx = dx \int_{-\infty}^{\infty} \Phi(\Delta) f(x+\Delta,t)d\Delta$$

Taylor expanding:

$$f(x,t) + \frac{\partial f}{\partial t}\tau = f \underbrace{\int_{-\infty}^{\infty} \Phi(\Delta)d\Delta}_{\text{unity}} + \frac{\partial f}{\partial x} \underbrace{\int_{-\infty}^{\infty} \Delta\Phi(\Delta)d\Delta}_{=0 \text{ for a symmetric random walk}} + \frac{\partial^2 f}{\partial x^2} \int_{-\infty}^{\infty} \frac{\Delta^2}{2}\Phi(\Delta)d\Delta$$

Diffusion equation

$$\Rightarrow \frac{\partial f}{\partial t} = D\frac{\partial^2 f}{\partial x^2} \; ; \; D \equiv \frac{1}{T} \int_{-\infty}^{\infty} \frac{\Delta^2}{2}\Phi(\Delta)d\Delta^{a}$$

[a] later we will see that $D = \frac{k_B T}{m\gamma}$, where γ is the friction coefficient associated with the friction force $m\gamma v$

Properties ($p(x,t) = f(x,t)/n$, where n is the number of particles in the system):

$p(x,t) > 0$ $\qquad$ $\int_{-\infty}^{\infty} p(x,t)dx = 1$ $\qquad$ $\lim_{t\to 0} p(x,t) = \delta(x)$

[1] A. Einstein (1905). "Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen". Annalen der Physik. 322 (8): 549–560.

Langevin treatment (microscopic treatment)[3]

Langevin equation

$$m\frac{d^2x}{dt^2} = -6\pi\eta a\frac{dx}{dt} + \delta F(t)$$

$\delta F(t)$ is a fluctuating force causing the random motion ("Langevin force").
KEY INSIGHT: $\langle \delta F(t) \cdot x(t) \rangle = 0$[2]

$$\Leftrightarrow \frac{d}{dt}\left\langle x^2 \right\rangle = \frac{k_\mathrm{B}T}{3\pi\eta a} + c\exp\left(-\frac{6\pi\eta a}{m}t\right) \ , \ c \in \mathbb{R}$$

So for $t \to \infty$:

$$\left\langle x^2 \right\rangle - \left\langle x_0^2 \right\rangle = \frac{k_\mathrm{B}T}{3\pi\eta a}t \ ,$$

and we recover the same diffusive behaviour as with Einstein i.e. $\left\langle x^2 \right\rangle \propto t$. Here:

$$D = \frac{k_\mathrm{B}T}{3\pi\eta a}$$

[2] Important: $\langle \delta F(t) v(t) \rangle$ is NOT generally zero.

[3] "Sur la théorie du mouvement brownien", C. R. Acad. Sci. (Paris) 146, 530–533 (1908)

Solution to the diffusion equation[4]

Define the probability of finding a particle at position x at time t when the position x_0 at time t_0 is known, as: $P(x_0, t_0; x, t)$.

The diffusion equation tells us:

$$P(x_0, t_0; x, t)\Big|_{t=t_0} = \delta(x - x_0) \ ,$$

Transition probability

$$P(x_0, t_0; x, t) = \frac{1}{\sqrt{4\pi D(t-t_0)}} \exp\left(-\frac{(x-x_0)^2}{4D(t-t_0)}\right) \ .$$

Which leads to the following in one dimension:

Probability distribution

$$P(x, t) = \int_{\mathbb{R}} dx_0 \underbrace{W(x_0, t_0)}_{\text{initial statistical distribution}} P(x_0, t_0; x, t) \ .$$

[4] c.f. Script P. Martin, Chapter 1.

Alternative: master equation derivation

Consider a discrete random walk in 1D of step size Δ, where a step is taken every τ seconds. The probability of finding the particle at $n\Delta$ at time $k\tau$ is given by $P(n\Delta, k\tau)$. The probability of jumping to the right is given by p, to the left by $q = 1 - p$.

Detailed balance

$$P(n\Delta, (k+1)\tau) = p \cdot P((n-1)\Delta, k\tau) + q \cdot P((n+1)\Delta, k\tau) \tag{1}$$

Set now $p = q = \frac{1}{2}$ and rearrange (defining $t = k\tau$ and $x = n\Delta$) to obtain

$$\frac{P(x, t+\tau) - P(x,t)}{\tau} = \underbrace{\frac{\Delta^2}{\tau}}_{\equiv D} \frac{P(x+\Delta, t) - 2P(x,t) + P(x-\Delta, t)}{\Delta^2}.$$

Taking the limit $\tau, \Delta \to 0$ we obtain the diffusion equation:

Diffusion equation

$$\frac{\partial P(x,t)}{\partial t} = D \frac{\partial^2 P(x,t)}{\partial x^2}$$

Smoluchowski equation

How do you describe Brownian motion in a force field with the master equation approach? Force field $\Leftrightarrow p \neq q$.

$$p = \frac{1}{2} + \alpha\Delta \; ; \; q = \frac{1}{2} - \alpha\Delta$$

We can further assume that Brownian motion is spatially varying (e.g. in a gravitational field) so that $\alpha = \alpha(n\Delta)$. Equation (1) becomes:

$$P(n\Delta, (k+1)\tau) = p((n-1)\Delta) \cdot P((n-1)\Delta, k\tau) + q((n+1)\Delta) \cdot P((n+1)\Delta, k\tau) \; .$$

Rearranging and taking the limit $\tau, \Delta \to 0$ we obtain the Smoluchowski equation:

Smoluchowski equation

$$\frac{\partial}{\partial t} P(x,t) = -\frac{1}{m\gamma} \frac{\partial}{\partial x} (F(x) P(x,t)) + D \frac{\partial^2}{\partial x^2} P(x,t)$$

For dimensional reasons $4D\alpha(x) = \frac{F(x)}{m\gamma}$

Derivation of the diffusion constant

Consider n particles in a gravitational field $\vec{g}$. Define $n(x,t) = Np(x,t)$ and $j_D(x,t) = -D\frac{\partial}{\partial x}n(x,t)$ - the particle current. The diffusion equation reads:

Diffusion equation

$\frac{\partial}{\partial t}n(x,t) = -\frac{\partial}{\partial x}j_D(x,t)$; which is also a continuity equation.

Equation of motion for the gas particles: $m\frac{d}{dt}v(t) = -mg - m\gamma v(t)$. From the stationary solution we get $v = -g/\gamma$ and we define the current due to the gravitational force by $j_{\text{grav}} = -gn(x,t)/\gamma$. Statistical mechanics predicts (V is the potential):

$$n(x,t) = n(x_0)\exp\left(-\frac{V(x-x_0)}{k_\text{B}T}\right) = n(x_0)\exp\left(-\frac{mg(x-x_0)}{k_\text{B}T}\right)$$

Require $j_{\text{tot}} = j_D + j_{\text{grav}} = 0$ (steady state condition), to obtain the familiar expression

Diffusion constant (Stokes–Einstein–Sutherland equation)

$$D = \frac{k_\text{B}T}{m\gamma}$$

Example of harmonic potential

We can solve the Smoluchowski equation in the case of a harmonic potential $V(x) = \frac{1}{2}m\omega^2 x^2$.

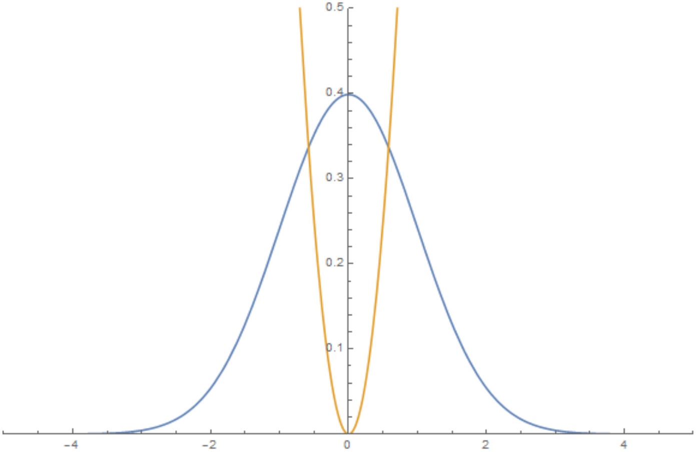


Figure: In orange the harmonic potential and in blue the (gaussian) particle distribution.

Langevin force correlator

Langevin equation ($\delta F_L(t)$ is the Langevin force):

$$\frac{dv}{dt} = -\gamma v(t) + \frac{\delta F_L(t)}{m}$$

Langevin made two hypotheses:

1. $\langle \delta F_L(t) \rangle = 0$,
2. $\langle \delta F_L(t_1) \delta F_L(t_2) \rangle = c \cdot \delta(t_1 - t_2)$, $c \in \mathbb{R}$.

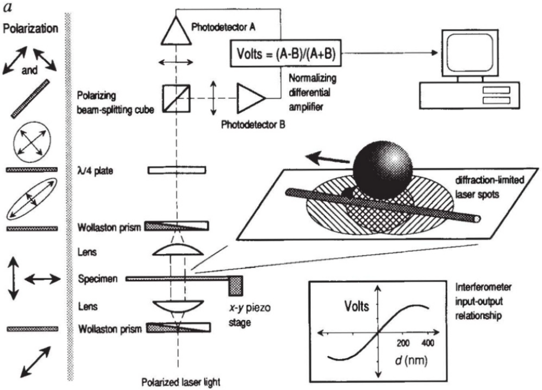
What is the value of c?

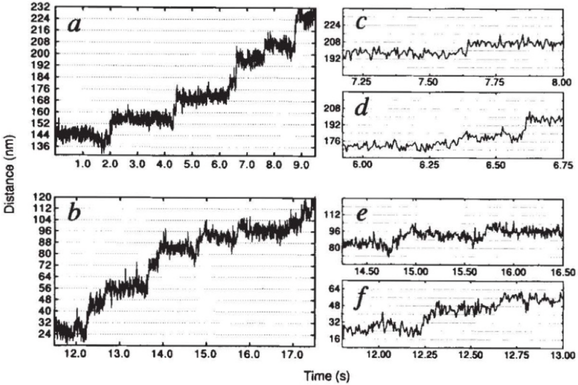
By studying the velocity correlations we can obtain:

$$\langle \delta F_L(t_1) \delta F_L(t_2) \rangle = 2 m \gamma k_{\mathrm{B}} T \cdot \delta(t_1 - t_2)$$

Paper for next week's presentation

Direct observation of kinesin stepping by optical trapping interferometry:





Questions for the paper

- Why do they use kinesin to monitor the random motion of a particle, and what is the minimal step length that can be resolved in this experiment?
- Explain the experimental setup they used to trap and monitor the kinesin.
- Explain the calibration procedure for the optical tweezers trapping force vs the laser intensity(Fig. 1b) and of the detector noise (Fig. 1c).
- Explain the concept of noise power spectral density, and how it is obtained from the voltage signal experimentally?
- What is the requirement for the acquisition rate and trace length to obtain the shown spectrum
- What is the effect of the ATP load?