Lecture 14: Applications in Statistical Mechanics

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OUTLINE

1. Physical model: Brownian motion with a bias proportional to the force field

2. Biased discrete Bernoulli random walk leads to the Einstein relation

3. Biased continuous stochastic process provides the definition of temperature

4. Diffusion in a harmonic potential

   (a) Continuous case: Ornstein-Uhlenbeck process
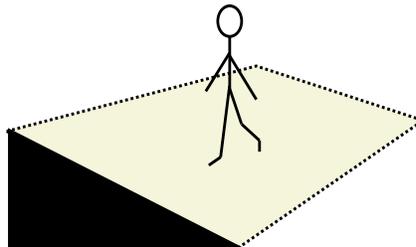   (b) Discrete case and paradoxes of classical mechanics

Figure 1: The idea of a random walker on an inclined plane illustrates the physics discussed in todays lecture

PHYSICAL MODEL

Statistical mechanics is conserned with systems of many interacting particles or more general bodies. Experimental observation of Brownian motion suggest a very simple model of the interactions. Specifically, collisions between molecules or small particles make the motion of each appear to be a random walk.

It is also very useful to consider such systems in externally imposed potential. In this case, we will generally assume that the forces due to random collisions exactly balance the force of the external field on any given particle. This is a physically accurate when the inertial force on a particle of interest is much smaller than the dissipative (the friction force due to random collisions) and the external force. In this case, the particle will have a steady average drift velocity.

BIASED BERNOULLI WALK

Consider one-dimensional motion of a Brownian particle. Suppose it makes discrete jumps of a typical length a at each time step τ. The change in the position of the particle, x, at every step is given by the PDF:

$$
\begin{align}
P(\Delta x = +a) &= p \tag{1} \\
P(\Delta x = -a) &= q = 1 - p \tag{2}
\end{align}
$$

The particle then moves with the average velocity, u_{drift},

$$
u_{drift} = \frac{\langle \Delta x \rangle}{\tau} = \frac{(p-q)a}{\tau}
$$

We can also define the diffusion coefficient of this particle as

$$
\begin{align}
D &= \frac{var(\Delta x)}{2\tau} \\
&= \frac{1}{2\tau}\big(\langle \Delta x^2 \rangle - \langle \Delta x \rangle^2\big) = \frac{1}{2\tau}a^2\big(1 - (p-q)^2\big) \\
&= \frac{1}{2\tau}a^2\big((p+q)^2 - (p-q)^2\big) = \frac{1}{2\tau}4\,p\,q\,a^2 \quad \Rightarrow \\
D &= \frac{2pqa^2}{\tau}
\end{align}
$$

Now, suppose there is a force F on this particle. The bias in the velocity should depend on the imposed force. Notice, that the effect of the random collisions on a given particle is to exert a friction force on it. From the study of macroscopic objects in flow, we know under a wide range of conditions the friction forces is proportional and opposite in direction to the velocity of the body in a fluid. Invoking Newton's law of motion and neglecting the inertial effects, we obtain

$$
\sum F = ma = 0 = -u_{drift}A + F_{imposed}
$$

where A is a friction coefficient. With this motivation, we assume that the bias for the walk proportional to the force

$$
p - q = \frac{a}{2k_BT}F
$$

We will show that the k_BT in the proportionality constant is the Boltzmann constant multiplied by the temperature, but for not it is just a constant required for this equality hold. We can now

express the drift velocity and the diffusion coefficient in terms of F:

$$D = \frac{a^2}{2\tau}\left[1 - \left(\frac{aF}{2k_BT}\right)^2\right]$$

$$u_{drift} = \frac{F}{k_BT}\frac{a^2}{2\tau}$$

$$= \frac{F}{k_BT}\left(D + \frac{u_{drift}^2\tau}{2}\right)$$

Suppose now that D and u_{drift} may be assumed constant as $\tau \to 0$. Then from the above expression we get

$$u_{drift} \approx \frac{FD}{k_BT}$$

We then define *mobility*, μ, as the drift velocity induced by a given force,

$$\mu \equiv \frac{u_{drift}}{F} = \frac{D}{k_BT}$$

and finally state what is known as the *Einstein relation*

$$\boxed{D = \mu k_BT = \frac{u_{drift}}{F}k_BT}$$

Notice that this equation relates the result of an equilibrium measurement of $\langle \Delta x^2 \rangle$ to the result of a non-equilibrium measurement of the drag on the particle as it is dragged through its medium by force F.

Einstein (1905) made a Nobel prize winning assumption here that μ of a spherical Brownian particle with the diameter equal to the step size a is given by the Stokes drag. Stokes drag is the value of μ obtained by solving the Navier-Stokes momentum conservation equations in the limit of the Reynolds number going to 0, that is, for very viscous fluids, small velocities and small sphere dimensions. These conditions are observed when inertial forces (mass times acceleration) on the fluid is negligible. For a fluid of viscosity η,

$$F = (6\pi\eta a)u_{drift}$$

$$\mu = \frac{1}{6\pi\eta a}$$

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

Notice, that if k_BT is indeed the thermodynamic temperature, by measuring the self-diffusion coefficient of a dilute gas, we may obtain an independent measure of the gas temperature. With pressure and volume easily measured as well, the ideal gas equation then yields the value of the actual number of atoms in a given volume of gas, and thus Avogadro's number: $N = PV/k_BT$. This measurement has been performed by Perrin in another Nobel prize winning work. [1] The ability to measure the actual number of molecules in a box was a crucial piece of evidence for molecular nature of matter.

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[1] Jean Baptiste Perrin published this in paper *"Réalité moléculaire"* (Molecular reality), *Ann. Phys.*, in 1909. The

BIASED CONTINUOUS STOCHASTIC PROCESS

One way to establish that $k_B T$ is indeed the thermodynamic temperature is by treating the motion of a particle as a continuous stochastic process. In other words, we will take the limit of $\tau \to 0$ assuming that the third and higher moments of Δx are $O(\tau)$ or greater. The particle position is then given by the following stochastic differential equation

$$\mathrm{d}x \;\; = \;\; \mu F \mathrm{d}t + \sqrt{2D}\mathrm{d}W$$

Thus, x drifts with a velocity μF, combining the drift with an unbiased random walk with the average step size of $\sqrt{2D\mathrm{d}t}$. Expressing the force as a derivative of a potential ϕ, we obtain the corresponding Fokker-Planck equation for the PDF of finding the Brownian particle at x at time t, as we did in Lecture 13:

$$\frac{\partial \rho}{\partial t} = \mu \frac{\partial}{\partial x}\left(\phi'(x)\rho\right) + D\frac{\partial^2 \rho}{\partial x^2}$$

In the context of Brownian motion, this is called the *Smoluchowski* equation. It is convenient to write this equation in terms of the *probability current*, S

$$\frac{\partial \rho}{\partial t} \;\; + \;\; \frac{\partial S}{\partial x} = 0$$

$$S \;\; = \;\; -\mu\phi'(x)\rho - D\frac{\partial \rho}{\partial x} \quad \text{(and, using the Einstein relation)}$$

$$\;\; = \;\; -D\exp\left(-\frac{\phi}{k_B T}\right)\frac{\partial}{\partial x}\left[\exp\left(\frac{\phi}{k_B T}\right)\rho\right]$$

Suppose a steady state exists for this distribution, *i.e.* consider thermal equilibrium. This state would exists when diffusion is exactly balanced by the imposed force field, that is, when $S = 0$. Hence, in equilibrium we obtain

$$\rho(x) = \rho_0 \exp\left(-\frac{\phi(x)}{k_B T}\right)$$

This is simply the Boltzmann formula known from statistical mechanics. This implies that $k_B T$ used in the previous section to obtain the Einstein relation is indeed the thermodynamic temperature.

DIFFUSION IN A HARMONIC POTENTIAL

We consider an important special case of harmonic potential, generally valid for all small x:

$$\phi(x) = \frac{1}{2}kx^2 \quad \Rightarrow \quad F = -kx$$

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measurement was performed on colloids rather than gas, with the version of the ideal gas law for the osmotic pressure. Perrin received the Nobel price in physics "for his work on the discontinuous structure of matter, and especially for his discovery of sedimentation equilibrium". Source: `http://www.nobelprize.org` The text of Perrin's Nobel prize acceptance lecture is also found there. Perrin credits Langevin with informing him of Einstein's work, as well as Einstein and Smoluchowski with having a verifiable kinetic theory of matter to check. In the same lecture, he states that the Avogadro's constant is $6.4 \; 10^{23}$ – a very decent estimate.
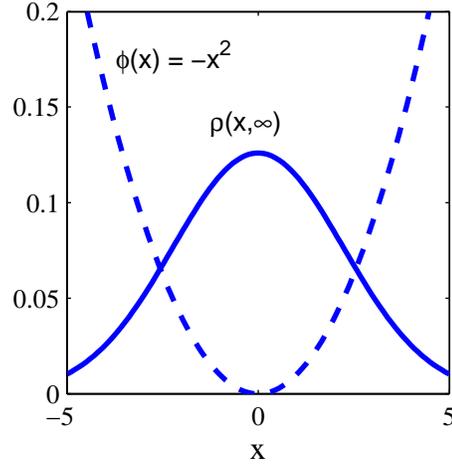
Figure 2: Steady state solution for the Ornstein-Uhlenbeck process

Continuous case: Ornstein-Uhlenbeck Process

The continuous version of this random walk (with "Central Limit Theorem scaling"), known as the Ornstein-Uhlenbeck process, given by the stochastic PDE,

$$\mathrm{d}x = -\mu k x \,\mathrm{d}t + \sqrt{2D}\mathrm{d}W$$

The corresponding Fokker-Planck equation is simply

$$\frac{\partial \rho}{\partial t} = -\gamma \frac{\partial}{\partial x}\left(\phi'(x)\rho\right) + D\frac{\partial^2 \rho}{\partial x^2}$$

where $\gamma = \mu k$. In the appendix, we solve the equation for a delta function initial condition $\rho(x, t = 0) = \delta(x - x_0)$ using the method of characteristics, and we derive the same time-dependent solution directly from the SDE. The steady state solution is just the expected Boltzmann relation (see Figure 2)

$$\rho(x, t \to \infty) = \sqrt{\frac{\gamma}{2\pi D}}\exp\left(-\frac{1}{2D}\gamma x^2\right) = \sqrt{\frac{k}{2\pi k_B T}}\exp\left(-\frac{k\,x^2}{k_B T}\right)$$

 That is, the distribution is Gaussian that widens with growing temperature and narrows with increasing spring constant, k. Notice also that the time scale in the problem is $1/\gamma$. Using the Einstein relation, we can check that

$$\tau \sim \frac{1}{\gamma} = \frac{k_B}{kD}$$

Discrete case: Ehrenfest's Model

Physicists at the end of 19th century believed in both Newton's laws of mechanics and classical thermodynamics. This led to two apparent paradoxes:

1. *Loschmidt's paradox* Newton's equations are unchanged by the reversal of time direction (sign), yet classical thermodynamics claims that all real processes are irreversible. Thus there is a definite direction to time.

2. *Zermelo's paradox* Poincaré proved that any initial state of Newton's equations will recur with any precision infinitely often, again suggesting that there are not really irreversible processes.

A simple statistical model to resolve these paradoxes was proposed by Paul and Tatyana Ehrenfest and is based on the discrete version of a random walk in a harmonic potential. The model considers a system composed of $2N$ balls distributed between two bins. Each ball could represent a particle or a quantity of heat energy, separated into two large reservoirs in thermal contact. Every time τ we make a "step" by picking a ball at random and moving it from its current bin to the other. Suppose there are $N + n$ balls in the first bin, and $N - n$ in the other. The probability p that n increases by one is simply the probability of picking a ball from the second bin:

$$p = \frac{N - n}{2N} = \frac{1}{2}\left(1 - \frac{n}{N}\right)$$

Comparing this to the case of the biased Bernoulli walk we considered at the beginning of the lecture, the drift in the random variable $x = n/N$ is

$$p - q = -\frac{n}{N} = -x$$

That is, there's an effective spring "force" with the spring constant $k = 1$ acting on x. In the limit of $N \to \infty$ when x is appoximately continuous and $n/N << 1$ so that $D \sim pq \approx const$, we see that x is the Ornstein-Uhlenbeck process we considered before. Therefore, this classical system on average always relaxes in one direction: towards $x = 0$, simply illustrating the fact that thermodynamic irreversibility is only a reflection of how unlikely something is to happen rather than whether it may happen.

A direct resolution of Loschmidt's paradox from Ehrenfest's model comes from the following elementary results for the position n of the walk after m steps, starting from position n_0

$$\langle n \rangle = n_0 \left(1 - \frac{1}{N}\right)^m$$

This shows that there is a "direction of time" as the system relaxes toward equilibrium. In the "thermodynamic limit", with $(N\tau)^1 \to \gamma$, and $m\tau = t$, we recover the analogous result for the Ornstein-Uhlenbeck process, which in this context corresponds to "Newton's Law of Cooling":

$$\langle n \rangle \sim n_0 e^{-gammat}$$

The resolution of Zermelo's paradox via Ehrenfests' model was clearly demonstrated by Mark Kač, who discovered the exact solution to the discrete problem in 1946. Kač proved the analog of Poincaré's theorem – that the random walk is recurrent with a probabilty one of returning to any given state – and calculated the expected recurrence time from an arbitrary position $-N \leq n_0 \leq N$:

$$\tau_r(n_0, N) = \tau 2^{2N} \left(\begin{array}{c} 2N \\ N + n_0 \end{array}\right)^{-1}$$

He noted that this time is enormous for any significant departure from equilibrium, e.g. for $\tau = 1$ sec, $\tau_r(10000, 10000) \approx 10^{6000}$ years, while recurrence is frequent close to equilibrium, e.g. $\tau_r(0, 100000) \approx 100\sqrt{\pi}$ sec ≈ 175 sec using Stirling's formula. He also attributes to Smoluchowski the original argument that a long recurrence time makes a recurrent random process appear to be irreversible.

For more historical notes an early reviews of random walks and diffusion in physics and engineering, see the outstanding collection, *Selected Papers on Noise and Stochastic Processes*, edited by Nelson Wax (Dover, 1954).

A   PDF of the Ornstein-Uhlenbeck process

A.1   Method of characteristics applied to the Fokker-Planck equation

$$\frac{\partial \rho}{\partial t} = -\gamma \frac{\partial}{\partial x} (x\rho) + D \frac{\partial^2 \rho}{\partial x^2}$$

$$\rho(x, t = 0) = \delta(x - x_0)$$

First, we transform the FPE in the x space:

$$\hat{\rho} = \int e^{-ikx} \rho(x) \mathrm{d}x$$

$$\frac{\partial \hat{\rho}}{\partial t} + \gamma k \frac{\partial \hat{\rho}}{\partial x} = -Dk^2 \hat{\rho}$$

With the Fourier transformed initial condition, $\rho(x, 0) = \delta(x - x_0)$ given by

$$\hat{\rho}_0 = e^{-ikx_0}$$

Now use the method of characteristics. Suppose

$$\frac{\mathrm{d}\hat{\rho}}{\mathrm{d}t} = \frac{\partial \hat{\rho}}{\partial t} + \frac{\partial \hat{\rho}}{\partial x} \frac{\partial x}{\partial t} = \frac{\partial \hat{\rho}}{\partial t} + \gamma k \partial x \frac{\partial x}{\partial t}$$

$$\Rightarrow \frac{\mathrm{d}k}{\mathrm{d}t} = \gamma k \quad \Rightarrow \quad k = k_0 e^{\gamma t}$$

In other words, the left hand side of the FPE is the total time derivative along each of the curves $k(t, k_0)$. On this curve, then

$$\frac{\mathrm{d}\hat{\rho}}{\mathrm{d}t} = -Dk^2 \hat{\rho} = -Dk_0^2 e^{2\gamma t} \hat{\rho} \quad \Rightarrow$$

$$\hat{\rho} = \exp \left[-\frac{Dk_0^2}{2\gamma} \left(e^{2\gamma t} - 1 \right) \right] \hat{\rho}_0$$

$$\begin{aligned}
\hat{\rho} &= \exp \left[-ik_0 x_0 - \frac{Dk_0^2}{2\gamma} \left(e^{2\gamma t} - 1 \right) \right] \\
&= \exp \left[-ix_0 k e^{-\gamma t} - \frac{Dk^2}{2\gamma} \left(1 - e^{-2\gamma t} \right) \right] \\
&= \exp \left[-ikM(t) - \frac{k^2}{2} \sigma^2(t) \right]
\end{aligned}$$

This is just the Fourier transform of a Gaussian with a mean $M(t)$ and a standard deviation σ

$$\boxed{\rho(x, t) = \frac{1}{\sqrt{2\pi\sigma(t)^2}} \exp \left[-\frac{\left(x - M(t) \right)^2}{2\sigma(t)^2} \right]}$$

where

$$\sigma^2 = \frac{D}{\gamma} \left(1 - e^{-2\gamma t} \right)$$

$$M(t) = x_0 e^{-\gamma t}$$

The position x, on average, relaxes to zero with a time constant $1/\gamma$.

A.2 Derivation from the stochastic differential equation

(by Geraint Jones, 3/30/05)

If we start with the Fokker-Planck equation for the density of the OU process:

$$\frac{\partial \rho}{\partial t} = \gamma \frac{\partial}{\partial x}(x\rho) + D \frac{\partial^2}{\partial x^2}\rho$$

Then the associated SDE is

$$dx = -\gamma x dt + \sqrt{2D} dz$$

But we can solve this explicitly with an integrating factor:

$$d\left(e^{\gamma t}x\right) = \sqrt{2D}e^{\gamma t}dz \implies x_t = x_0 e^{-\gamma t} + e^{-\gamma t}\sqrt{2D}\int_0^t e^{\gamma s}dz_s$$

This is a stochastic integral, but because the integrand is deterministic it has a particularly simple form - in particular it is basically a weighted sum of normal increments, so x_t is a normal random variable, and to characterize it we just need to know the mean and variance.

The mean is immediate becase $E_0 \int_0^t e^{\gamma s}dz_s = 0 \implies E_0 x_t = x_0 e^{-\gamma t}$

The variance is derived as

$$E_0 \left(x_t - E_0 x_t\right)^2 = E_0 \left[e^{-\gamma t}\sqrt{2D}\int_0^t e^{\gamma s}dz_s\right]^2$$
$$= 2De^{-2\gamma t}E_0 \left[\int_0^t e^{\gamma s}dz_s\right]^2$$
$$= 2De^{-2\gamma t}\left[\int_0^t e^{2\gamma s}ds\right]$$
$$= 2De^{-2\gamma t}\frac{1}{2\gamma}\left(e^{2\gamma t} - 1\right) = \frac{D}{\gamma}\left(1 - e^{-2\gamma t}\right)$$