Lecture 15: Motion of Brownian particles in energy landscapes
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The topics we will cover today include:

1. uniform force
2. escape from a trap (kramers)
3. motion in a periodic potential
4. "pumping" of particles in asymmetric potentials

This lecture will have more of a physics perspective than mathematical perspective. The lecturer's interests are in polymers, liquid crystals, separation of DNA, and microfluidics.

The objects of interest are small particles in a viscous environment, size of a few nanometers or microns, floating in some solution. Motion is due to thermal agitation, and the randomness is usually referred to as Brownian motion.

1 Motion in constant force

Recall Prof. Bazant's lecture last time, where we still consider the 1D case (but most problems are 3D). The force F and potential $\phi(x)$ are defined

$$F \rightarrow \phi(x) = -Fx \tag{1}$$

and $F = -d\phi/dx$. The conservation law, associated with the Smoluchowski equation, from the previous lecture is,

$$\frac{\partial p}{\partial t} + \frac{\partial S}{\partial t} = 0 \tag{2}$$

where S is the probability current and

$$S = -\mu\phi^{'}(x)p - D\frac{\partial \phi}{\partial x} \tag{3}$$

where the first term is associated with migration, with drift due to force $\phi^{'}$, and the second term is diffusion, as in Fick's law.

Here we change notation slightly (Prof. Bazant used S notation for probability current but physicists more frequently use J) and have

$$\frac{\partial p(x,t)}{\partial t} + \frac{\partial J}{\partial x} = 0$$
$$J = -D\frac{\partial \phi}{\partial x} + \mu F p(x,t)$$

where $p(x,t)$ is the particle distribution, D is diffusion coefficient, μF is drift velocity due to force F, and μ is mobility. We have a bath at temperature T, and kT is inducing shaking in the system.

Remarks.

1. Equilibrium thermodynamics. If closed system, from statistical mechanics

$$p = p_0 \exp[\frac{-\phi(x)}{k_B T}] \tag{4}$$

the Boltzmann equation, and the Einstein relation is $D = k_B T \mu$. In viscous, sluggish medium, the mobility μ is very small.

2. In general, physicists don't just follow one particle in an experiment, but many particles. Therefore, $c(x,t)$ is concentration of particles, where assumption is noninteracting particles.

$$c(x,t) = Np(x,t) \tag{5}$$

If we let go of particles at $t = 0$, since drift velocity $v = \mu F$, vt is the distance travelled, so exact solution is

$$c(x,t) = \frac{1}{(4\pi Dt)^{1/2}} \exp(\frac{(x-vt)^2}{4Dt}) \tag{6}$$

2 Escape from a trap (Kramers formula)

This formula is used in many areas of physics.
Suppose there is a difference in potential ϕ between a well with bottom at x_W, and a barrier with maximum at x_B. The difference in potential between the well and barrier, $\phi(x_B) - \phi(x_W) = \Delta\phi$, where $\Delta\phi >> k_B T$.
Here we are waiting for something improbable, i.e. very rare events. Like in chemistry, an example is transition rates from closed to open angles. In "activated escape", temperature plays a role.

Approximate derivation (found in many books) Assume steady-state concentration
$c(x,t) = c(x) \rightarrow J =$ constant.

$$\therefore J = -D\frac{dc}{dx} + \mu c(-\frac{d\phi}{dx}) \tag{7}$$

Using the Einstein relation, equivalently

$$J = -De^{-\frac{\phi}{kT}} \frac{d}{dx}[ce^{\frac{\phi}{kT}}] \tag{8}$$

Rearranging,

$$\frac{-J}{D} e^{\frac{\phi}{kT}} = \frac{d}{dx}[ce^{\frac{\phi}{kT}}] \tag{9}$$

Remembering that J is constant, we integrate from x_w to ∞.

$$-\frac{J}{D}\int_{x_W}^{\infty}\exp(\frac{\phi(x)}{kT})dx = [ce^{\phi}kT]_{x_w}^{+\infty} \tag{10}$$

$$= c(x\to\infty)e^{\phi(x\to\infty)/kT} - c(x_w)e^{\frac{\phi(x_w)}{kT}} \tag{11}$$

An approximation is made, that there is no probability in coming back (i.e. the first term on right hand side is zero. We have J, $c(x_w)$ and

$$J = \frac{N}{\tau} \tag{12}$$

where N is number of particles in well, at steady-state, and τ = the rate of escape $(1/\tau)$.

Approximation: well

$$c(x) \simeq c(x_w)\exp(-\frac{\phi(x)-\phi(x_w)}{k_BT}) \tag{13}$$

which is a nonquantified approximation and is Boltzmann "thermal equilibrium."In some sense, saying leak is rather small.

$$N \approx \int_{\text{well}} dxc(x) = c(x_w)\int_{\text{well}} dx\exp(-\frac{\phi(x)-\phi(x_w)}{k_BT}) \tag{14}$$

where "well" is loose notation.
The value of this integral only weakly depends on position. The contribution is negligible far away from the well.

$$\frac{1}{\tau} = D(\int_{\text{well}} e^{-\frac{\phi(x)-\phi(x_w)}{k_BT}})^{-1}(\int dxe^{\frac{\phi(x)}{kT}})^{-1}e^{\frac{\phi(x_w)}{kT}} \tag{15}$$

$$\frac{1}{\tau} = \frac{De^{-\frac{\phi(x_B)-\phi(x_w)}{kT}}}{(\int_{\text{well}} dxe^{-\frac{\phi(x)-\phi(x_w)}{kT}})(\int_{x_w}^{\infty} dxe^{-\frac{\phi(x_B)-\phi(x)}{kT}})} \tag{16}$$

A more common way to write this equation, considering the two integrals in the denominator as length scales, is

$$\frac{1}{\tau} = \frac{De^{-\frac{\Delta\phi}{k_BT}}}{l_wl_B} \tag{17}$$

which is called **Kramers formula**.
The length scale l_w has to do with the length of the well (storage) and the length scale l_B has to do with the width of the barrier amplitude. A wider barrier, such as a mesa-like flat hill, (l_B large) leads to a decrease in rate of escape. These two ingredients (l_w and l_B) are what is important, and there is almost no dependence on the region in between the well and the barrier.

3 Motion in a periodic potential

In applications such as separation and chromatography, we engineer environments, at the micron, cm or larger scale where *the structure is repeated.* The periodic potential imposed by the structure creates a situation where particles are more happy at some places, and less happy at other places.

For example, consider a positive/negative comb-like structure where an electron is attracted to positive combs but repelled by negative combs. The difference in potential between combs $\Delta\phi >> k_BT$ and the spacing between minimum potentials is L.

$$W_{\text{struct}}(x) - Fx = \phi(x) \tag{18}$$

The probability of hop to right, $\tau_{\rightarrow}$, and the probability of hop to left, $\tau_{\leftarrow}$, can be obtained from Kramers formula. This can be considered a random walk, with step size L, i.e. at the large scale it is an effective random walk.
Now apply an (additional) "external force" F. What is the motion? Kramers formula

$$\tau_{\rightarrow} = \tau_0 \exp(+\frac{\Delta\phi_{\rightarrow}}{k_BT}) \tag{19}$$

$$\approx \tau_0 \exp(\frac{\Delta w - FL/2}{k_BT}) \tag{20}$$

and

$$\tau_{\leftarrow} = \tau_0 \exp(-\frac{\Delta\phi_{\leftarrow}}{k_BT}) \tag{21}$$

$$\approx \tau_0 \exp(\frac{\Delta w + FL/2}{k_BT}) \tag{22}$$

Assume small force $\rightarrow$ linearize,

$$v_{\text{drift}} = +L\frac{1}{\tau_{\rightarrow}} - L\frac{1}{\tau_{\leftarrow}} = \frac{L}{\tau_0 \exp(\frac{\Delta w}{kT})}(\frac{FL}{k_BT}) \tag{23}$$

$$\mu_{\text{eff}} = \frac{L^2}{\tau_0 k_BT} \exp(-\frac{\Delta w}{k_BT}) \tag{24}$$

where $v_{\text{drift}} = \mu_{\text{eff}} F$.

Remarks.

1. For $F = 0$ (don't bias structure)
$$< x^2(t) >= 2D_{\text{eff}}\tau \tag{25}$$
which is normal diffusive spreading, unbiased. Check that $D_{\text{eff}} = k_BT\mu_{\text{eff}}$.
2. Selectivity of structure. One of the reasons why is sensitivity to particle type.
The last topic deals with personal research he's been working on.

4 Asymmetric structures

Suppose we have situation where now the barriers are close to the well. There is now a short arm distance a, of the "sawtooth" potential function and L is as before, the spacing between minimum potentials. Left/right symmetry is broken.
If we have only one temperature, a 19th century statement is that we can't make a motor with one temperature. However, if we heat right part of the wells, biased to move to the right, and it favors hops to right.

The asymmetry is created by switching potential V on and off. The potential starts at $V = V_0$ or "on". Then we shut the switch, $V = 0$ or "off." This causes spreading as in diffusion, as we have constant potential. The switch is then turned back on and $V = V_0$.
We assume that the particle either ends up at the same well or in the well to the right. We have created a biased random walk. This involves **local symmetry breaking not global**. The cycling of potential on and off is described by

$$\tau_{\text{on}} + \tau_{\text{off}} = \tau_{\text{cycle}} \tag{26}$$

and we have

$$v_{\text{drift}} = p\frac{L}{\tau_{\text{cycle}}} \tag{27}$$

This is like a Bernoulli walk (but move +1 or stay at same place.)

$$D_{eff} = \frac{1}{2}p(1-p)\frac{L^2}{\tau_{\text{cycle}}} \tag{28}$$

where $p = 0$ or 1. This is like sorting powders or sands. A question was asked, that we have neglected these possibilities (+2,-1). We have

$$p_n = \int_{(n-1)La}^{nL+a} \frac{e^{-\frac{x^2}{4D\tau_{\text{off}}}}}{\sqrt{4\pi D\tau_{\text{off}}}}dx \tag{29}$$

There are several conditions ASSUMED–required for "OPTIMAL" RW. These are

1. $\rightarrow \tau_{off}$

$$D\tau_{\text{off}} \simeq a^2 \tag{30}$$

$$D\tau_{\text{off}} < b^2 \tag{31}$$

where $b = L - a$ and

2. $\rightarrow \tau_{\text{on}}$
Want to be on long enough.

$$\tau_{\text{on}} > \frac{b}{v_{\text{drift}}} = \frac{b}{\mu\frac{\Delta w}{b}} \tag{32}$$

Another question was asked that in the case of electrons, they interact in that they repel each other. There is a more complicated description in that case.
Note: Armand Ajdari's website is http://hogarth.pct.espci.fr/ armand/ at Physico-Chimie Theorique, ESPCI, Paris.