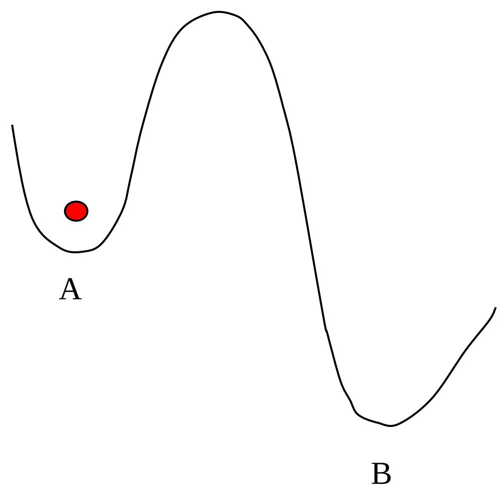
IP326. Lecture 27. Thursday, April 4, 2019

● <u>The first passage time formalism</u>

Another approach to the calculation of barrier crossing rates is based on the notion of first passage times. The first passage time refers in general to the time it takes some random event to happen for the first time. Consider, for example, a particle moving stochastically in the double well potential of the previous section under the action of thermal fluctuations, as in the figure below



The very first time the particle reaches the top of the barrier is when a chemical reaction can be said to occur. The time it takes for this to happen – the first passage time, as it is called – is a random variable, since the particle will in general follow different trajectories to reach the barrier top from even the same initial starting point. Because the first passage time is a random variable, its possible values are spread across a distribution, which is referred to as the first passage time distribution. The first moment of this distribution – its average, in other words – is referred to as the mean first passage time (MFPT), and its reciprocal provides a measure of the average rate of the reaction (again, assuming that the reaction occurs as soon as the summit of the barrier is reached). In this section, we'll calculate the MFPT for a particle moving in the above potential in the presence of white noise and in the high friction (i.e., overdamped) limit, and compare the results to Kramers theory in the same high friction limit.

The equation of motion for a particle moving in one dimension under these conditions is

$$\zeta \dot{x}(t) = -\frac{\partial U(x)}{\partial x} + \theta(t) \qquad (1)$$

Here, $\langle\theta(t)\rangle = 0$ and $\langle\theta(t)\theta(t')\rangle = 2\zeta k_B T\delta(t-t')$. At time t, the distribution of the particle's position, $P(x,t)$, is defined as

$$P(x,t) = \langle\delta(x - x(t))\rangle \tag{2}$$

so

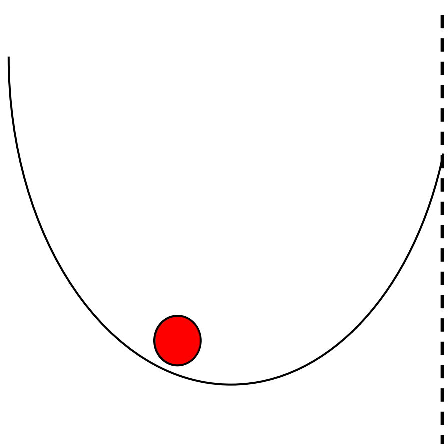
$$\frac{\partial P(x,t)}{\partial t} = -\frac{\partial}{\partial x}\left\langle \delta(x-x(t))\left\{-\frac{1}{\zeta}\frac{\partial U(x(t))}{\partial x(t)} + \frac{1}{\zeta}\theta(t)\right\}\right\rangle$$

$$= \frac{1}{\zeta}\frac{\partial}{\partial x}U'(x)P(x,t) - \frac{1}{\zeta}\frac{\partial}{\partial x}\langle\delta(x-x(t))\theta(t)\rangle$$

$$= \frac{1}{\zeta}\frac{\partial}{\partial x}U'(x)P(x,t) + D\frac{\partial^2}{\partial x^2}P(x,t) \tag{3}$$

where $D = k_B T/\zeta$ and $U'(x) = \partial U(x)/\partial x$.

To model a chemical reaction, we introduce an absorbing boundary at the top of the barrier. As soon as the particle reaches this boundary during the course of its random motion along the potential energy surface, it is removed from the system, and a chemical reaction can be said to have taken place. Schematically, the situation is as depicted below:



Absorbing boundary
($x = b$)

In this scenario, the particle will be located between $-\infty$ and b for some time before eventually disappearing. The probability that the particle is at the point x in this region at time t given that it started out from the point x_0 at time t_0 can be denoted $P(x,t\,|\,x_0,t_0)$. This probability is the solution to Eq. (3) under the initial condition

$$P(x,t\,|\,x_0,t_0) = \delta(x - x_0) \tag{4}$$

The probability that the particle is *somewhere* between $-\infty$ and b at time t, having started off at x_0, can be interpreted as the probability that it *survives* till that time without being absorbed. Denoting this probability as $S(t;x_0)$, with t_0 chosen to be 0, we can write

$$S(t;x_0) = \int_{-\infty}^{b} dx P(x,t\,|\,x_0) \tag{5}$$

$S(t;x_0)$ can also be interpreted as the *fraction* of particles in an ensemble that start out from x_0 at the same time and survive up to time t. In the same way, $S(t+dt;x_0)$ can be interpreted as the fraction of such particles that survive up to time $t+dt$. This means that $S(t;x_0) - S(t+dt;x_0)$ represents the fraction of particles that have been absorbed in the interval between t and $t+dt$. If dt is sufficiently small, this difference can be approximated as

$$S(t;x_0) - S(t+dt;x_0) = -\frac{\partial S(t;x_0)}{\partial t} dt \tag{6}$$

The derivative $f(t;x_0) \equiv -\partial S(t;x_0)/\partial t$ can therefore be thought of as the fraction of particles per unit of time that have the survival time t. In other words, $f(t;x_0)$ is the <u>first passage time distribution</u>. This in turn means that it's now possible to define a <u>mean first passage time</u>, or MFPT, as

$$\langle t(x_0) \rangle = \int_0^{\infty} dt\, t\, f(t;x_0)$$

$$= -\int_0^{\infty} dt\, t \frac{\partial S(t;x_0)}{\partial t} \tag{7}$$

By partial integration, Eq. (7) can be rewritten as

$$\langle t(x_0) \rangle = -\left[tS(t;x_0)\Big|_0^{\infty} - \int_0^{\infty} dt\, S(t;x_0) \right] \tag{8}$$

Now, at long times, we expect that all particles in the ensemble will have been absorbed, and so $S(\infty;x_0)$ can be set to 0. At $t=0$, on the other hand, we expect that no particles will have been absorbed, and so $S(0;x_0)=1$. Thus, in Eq. (8) the contribution of the surface terms to $\langle t(x_0)\rangle$ is 0, and the equation reduces to

$$\langle t(x_0)\rangle = \int_0^\infty dt\, S(t;x_0) \tag{9}$$

Replacing $S(t;x_0)$ in the above expression by its definition in terms of $P(x,t\,|\,x_0)$ [see Eq. (5)], we can rewrite Eq. (9) as

$$\langle t(x_0)\rangle = \int_0^\infty dt \int_{-\infty}^{b} dx P(x,t\,|\,x_0) \tag{10}$$

So, in general, in order to calculate the MFPT we need the solution to a diffusion (i.e., Fokker-Planck) equation. But it turns out that for certain special kinds of stochastic processes, the MFPT can be calculated without actually having to first find $P(x,t\,|\,x_0)$. The kinds of processes for which $P(x,t\,|\,x_0)$ is not needed when calculating $\langle t(x_0)\rangle$ are known as Markov processes. The distinguishing property of a Markov process is that it satisfies the so-called Chapman-Kolmogorov equation, which is defined by the relation

$$P(x,t\,|\,x_0,t_0) = \int dy P(x,t\,|\,y,s)P(y,s\,|\,x_0,t_0) \tag{11}$$

This is a very special restriction that holds only if the stochastic process is such that the probability that some property of the process has a certain value in the future is solely determined by the corresponding probability at the present time, and not by the probabilities at any earlier times.

If a stochastic process satisfies the Chapman-Kolmogorov equation (and is therefore Markovian), it will satisfy another equation called the backward Fokker-Planck equation. This latter equation can be used to derive an equation for the MFPT itself, which will make it possible to sidestep the problem of having to calculate $P(x,t\,|\,x_0)$ separately.

So let's assume that we're dealing with a Markov process. Equation (11) therefore holds. Now the LHS of this equation is independent of s, so if we differentiate both sides of the equation with respect to s, we get

$$0 = \int dy P(y,s\,|\,x_0,t_0)\frac{\partial}{\partial s}P(x,t\,|\,y,s) + \int dy P(x,t\,|\,y,s)\frac{\partial}{\partial s}P(y,s\,|\,x_0,t_0) \tag{12}$$

In the second term on the RHS, we can use a diffusion equation (i.e., a Fokker-Planck equation) to substitute for the factor of $\partial P/\partial s$. Now in its most general form, this diffusion equation can be written as

$$\frac{\partial}{\partial t}P(x,t\,|\,x_0,t_0)=\frac{\partial}{\partial x}A(x)P(x,t\,|\,x_0,t_0)+\frac{\partial^2}{\partial x^2}B(x)P(x,t\,|\,x_0,t_0) \qquad (13)$$

Substituting this form of the equation in Eq. (12), we get

$$0=\int dyP(y,s\,|\,x_0,t_0)\frac{\partial}{\partial s}P(x,t\,|\,y,s)+\int dyP(x,t\,|\,y,s)\left\{\frac{\partial}{\partial y}A(y)P(y,s\,|\,x_0,t_0)+\right.$$

$$\left.+\frac{\partial^2}{\partial y^2}B(y)P(y,s\,|\,x_0,t_0)\right\} \qquad (14)$$

If the second and third terms on the RHS of Eq. (14) are integrated by parts, the result is

$$0=\int dyP(y,s\,|\,x_0,t_0)\frac{\partial}{\partial s}P(x,t\,|\,y,s)+\int dy\left\{-A(y)P(y,s\,|\,x_0,t_0)\frac{\partial}{\partial y}P(x,t\,|\,y,s)+\right.$$

$$\left.+B(y)P(y,s\,|\,x_0,t_0)\frac{\partial^2}{\partial y^2}P(x,t\,|\,y,s)\right\} \qquad (15)$$

There are no contributions from the surface terms because the probability distributions have been assumed to be well-behaved at the extremes of the variable *y*.

Equation (15) can now be rearranged to

$$\int dyP(y,s\,|\,x_0,t_0)\left\{\frac{\partial}{\partial s}P(x,t\,|\,y,s)-A(y)\frac{\partial}{\partial y}P(x,t\,|\,y,s)+B(y)\frac{\partial^2}{\partial y^2}P(x,t\,|\,y,s)\right\}=0$$

(16)

which can hold only if

$$\frac{\partial}{\partial s}P(x,t\,|\,y,s)=A(y)\frac{\partial}{\partial y}P(x,t\,|\,y,s)-B(y)\frac{\partial^2}{\partial y^2}P(x,t\,|\,y,s) \qquad (17)$$

Equation (17) is the backward Fokker-Planck equation alluded to above. The term backward refers to the fact that the evolution of the distribution function is in respect of the *initial* position and time, the final position and time being kept fixed.

From here, we determine the MFPT as follows: First, let’s assume that the probability distribution in Eq. (17) is *time homogeneous*, meaning it depends only on the difference of two times, not on their separate values. (This is not too restrictive an assumption.) Under this assumption, and taking *t* to be greater than *s*, we can rewrite Eq. (17) as

$$\frac{\partial}{\partial s}P(x,0\,|\,y,-(t-s)) = A(y)\frac{\partial}{\partial y}P(x,0\,|\,y,-(t-s)) - B(y)\frac{\partial^2}{\partial y^2}P(x,0\,|\,y,-(t-s)) \qquad (18)$$

If we now change variables from s to τ, where τ is defined as $\tau = -s + t$, Eq. (18) becomes

$$-\frac{\partial}{\partial \tau}P(x,0\,|\,y,-\tau) = A(y)\frac{\partial}{\partial y}P(x,0\,|\,y,-\tau) - B(y)\frac{\partial^2}{\partial y^2}P(x,0\,|\,y,-\tau) \qquad (19)$$

A second application of time homogeneity leads to

$$\frac{\partial}{\partial \tau}P(x,\tau\,|\,y,0) = -A(y)\frac{\partial}{\partial y}P(x,\tau\,|\,y,0) + B(y)\frac{\partial^2}{\partial y^2}P(x,\tau\,|\,y,0) \qquad (20)$$

Relabelling τ as t and y as x_0, we see that Eq. (20) is equivalent to

$$\frac{\partial}{\partial t}P(x,t\,|\,x_0,0) = -A(x_0)\frac{\partial}{\partial x_0}P(x,t\,|\,x_0,0) + B(x_0)\frac{\partial^2}{\partial x_0^2}P(x,t\,|\,x_0,0) \qquad (21)$$

At this point, we can particularize to the problem we were considering, where the relevant Fokker-Planck/diffusion equation is given by Eq. (3). Comparing that equation with Eq. (13), we can make the identifications

$$A(x_0) = \frac{1}{\zeta}U'(x_0) \qquad \text{and} \qquad B(x_0) = D$$

With these identifications, Eq. (21) becomes

$$\frac{\partial}{\partial t}P(x,t\,|\,x_0,0) = -\frac{1}{\zeta}U'(x_0)\frac{\partial}{\partial x_0}P(x,t\,|\,x_0,0) + D\frac{\partial^2}{\partial x_0^2}P(x,t\,|\,x_0,0) \qquad (22)$$

If we now integrate both sides of this equation with respect to x from $-\infty$ to b, and introduce the definition $S(t;x_0) = \int_{-\infty}^{b} dxP(x,t\,|\,x_0,0)$, we can transform Eq. (22) to

$$\frac{\partial}{\partial t}S(t;x_0) = -\frac{1}{\zeta}U'(x_0)\frac{\partial}{\partial x_0}S(t;x_0) + D\frac{\partial^2}{\partial x_0^2}S(t;x_0) \qquad (23)$$

Recalling the definition of $\langle t(x_0)\rangle$ from Eq. (9), we next integrate both sides of Eq. (23) with respect to t from 0 to ∞, obtaining thereby

$$-1 = -\frac{1}{\zeta} U'(x_0) \frac{\partial}{\partial x_0} \langle t; x_0 \rangle + D \frac{\partial^2}{\partial x_0^2} \langle t; x_0 \rangle \tag{24}$$

where we have made use of the fact that $S(\infty; x_0) = 0$ and $S(0; x_0) = 1$. We have now derived an equation for just $\langle t(x_0) \rangle$ itself.

As you should be able to confirm, Eq. (24) can be rewritten identically as

$$De^{\beta U(x_0)} \frac{\partial}{\partial x_0} e^{-\beta U(x_0)} \frac{\partial}{\partial x_0} \langle t(x_0) \rangle = -1 \tag{25}$$

This equation must be solved subject to the condition that there is an absorbing boundary at the point *b*. The solution is found by first dividing Eq. (25) by $D \exp \beta U(x_0)$, and then integrating both sides of the equation over x_0 from $-\infty$ to some point *x*; the result is

$$e^{-\beta U(x)} \frac{\partial}{\partial x} \langle t(x) \rangle = -\frac{1}{D} \int_{-\infty}^{x} dx_0 e^{-\beta U(x_0)}$$

or equivalently,

$$\frac{\partial}{\partial z} \langle t(z) \rangle = -\frac{1}{D} e^{\beta U(z)} \int_{-\infty}^{z} dy e^{-\beta U(y)} \tag{26}$$

Integrating this equation over *z* from *x* to *b*, we get

$$\langle t(b) \rangle - \langle t(x) \rangle = -\frac{1}{D} \int_{x}^{b} dz e^{\beta U(z)} \int_{-\infty}^{z} dy e^{-\beta U(y)} \tag{27}$$

That is,

$$\langle t(x) \rangle = \frac{1}{D} \int_{x}^{b} dz e^{\beta U(z)} \int_{-\infty}^{z} dy e^{-\beta U(y)} \tag{28}$$

Now the first integral in this expression (over *z*) is dominated by the largest values of *U*, which are at the barrier top. So to a reasonable approximation, we can replace *U* in the first integral by

$$U(z) \approx E_B - \frac{1}{2} m \omega_B^2 (z - x_B)^2 \tag{29}$$

The second integral, on the other hand, (over y), is dominated by the smallest values of U, which are near the potential minimum. So here, the potential can be approximated as

$$U(y) \approx E_0 + \frac{1}{2} m\omega_0^2 (y - x_0)^2 \tag{30}$$

Plugging Eqs. (29) and (30) back into Eq. (28), we see that

$$\langle t(x) \rangle = \frac{1}{D} e^{\beta(E_B - E_0)} \int_x^b dz e^{-\beta m\omega_B^2 (z - x_B)^2/2} \int_{-\infty}^{z} dy e^{-\beta m\omega_0^2 (y - x_0)^2/2} \tag{31}$$

Given the rapid decay of the Gaussian functions around their mean values in the above equation, very little error is introduced by letting the integration variables z and y range from $-\infty$ to $+\infty$. This makes it possible to evaluate both integrals in closed form. The result is

$$\langle t(x) \rangle = \frac{1}{D} e^{\beta(E_B - E_0)} \sqrt{\frac{2\pi k_B T}{m\omega_B^2}} \sqrt{\frac{2\pi k_B T}{m\omega_0^2}}$$

$$= \frac{2\pi\zeta e^{\beta(E_B - E_0)}}{m\omega_B \omega_0} \tag{32}$$

Assuming that the rate constant k can be identified with the reciprocal of the mean first passage time, we finally arrive at the result

$$k = \frac{m\omega_B \omega_0}{2\pi\zeta} e^{-\beta(E_B - E_0)} \tag{33}$$

which is exactly the result derived by Kramers in the high friction limit.