18.366 Random Walks and Diffusion, Spring 2005
10.95/18.325 Mathematical Modeling of Electrochemical Systems, Spring 2009

Escape from a Symmetric Trap

Notes by MIT Student (and MZB)

Problem Statement. (Exam 2, 18.366, 2005) Consider a diffusing particle which feels a conservative force, $f(x) = -\phi'(x)$, in a smooth, symmetric potential, $\phi(x) = \phi(-x)$, causing a drift velocity, $v(x) = bf(x)$, where $b = D/kT$ is the mobility and D is the diffusion constant. If the particle starts at the origin, then PDF of the position, $P(x,t)$, satisfies the Fokker-Planck equation,

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

with $P(x,0) = \delta(x)$. Suppose that the potential has a minimum $\phi = 0$ at $x = 0$ with $\phi''(0) = K_0 > 0$ and two equal maxima $\phi = E > 0$ at $x = \pm x_1$ with $\phi''(x_1) = -K_1 < 0$. Let τ be the mean first passage time to reach one of the barriers at $x = \pm x_1$ (and then escape from the well with probability 1/2).

1. Derive the general formula

$$\tau = \frac{1}{D}\int_0^{x_1} dx\, e^{\phi(x)/kT} \int_0^{x} dy\, e^{-\phi(y)/kT}$$

2. In the low temperature limit, $kT/E \to 0$, calculate the leading-order asymptotics of the escape rate, $R = 1/2\tau \sim R_0(T)$, using the saddle-point method. Verify the classical result of Kramers: $R_0(T) \propto e^{-E/kT}$.

3. Calculate the first correction to the Kramers escape rate:

$$R(T) \sim R_0(T)\left(1 + a\,\frac{kT}{E}\right).$$

SOLUTION

1. Mean escape time. We have:

$$\frac{\partial P}{\partial t} = D\frac{\partial^2 P}{\partial x^2} + \frac{D}{kT}\frac{\partial}{\partial x}\left(\phi'(x)P(x,t)\right)$$

where $P(x,t) = p(x,t|0,0)$ within initial condition at the bottom of the well, $P(x,0) = \delta(x)$, and absorbing boundary conditions at the exit points, $P(\pm x_1, t) = 0$. We can write:

$$\frac{\partial P}{\partial t} = \mathcal{L}_x P \tag{1}$$

where the spatial operator L_x can be simplified using an integrating factor:

$$\mathcal{L}_x = D\frac{\partial}{\partial x}\left[e^{-\phi(x)/kT}\frac{\partial}{\partial x}\left(e^{\phi(x)/kT}\quad\right)\right] \tag{2}$$

The probability $S(t)$ of realization which have started at $x = 0$ and which have not yet reached $x = \pm x_1$ up to time t is given by:

$$S(t) = \int_{-x_1}^{x_1} p(x,t|0,0)\mathrm{d}x = \int_{-x_1}^{x_1} P(x,t)\mathrm{d}x$$

The distribution function $f(t)$ for the first passage time is then given by:

$$f(t) = \frac{\partial}{\partial t} \; 1 - S(t) \; = -\frac{\partial S}{\partial t} = -\int_{-x_1}^{x_1} \frac{\partial P}{\partial t}\mathrm{d}x$$

The mean escape time is then given by[1]:

$$\tau = \int_0^\infty t f(t)\mathrm{d}t = \int_{-x_1}^{x_1} g_1(x)\mathrm{d}x \quad \text{with} \quad g_1(x) = -\int_0^\infty t\frac{\partial P}{\partial t}\mathrm{d}t$$

Performing an integration by parts (assuming that $P(x,t)$ decays quickly enough in time that $\lim_{t\to\infty} tP(x,t) = 0$) gives:

$$g_1(x) = \int_0^\infty P(x,t)\mathrm{d}t$$

By applying the operator $\mathcal{L}_x$ on both sides of this relation, we get:

$$\mathcal{L}_x g_1(x) = \int_0^\infty \mathcal{L}_x P(x,t)\mathrm{d}t = \int_0^\infty \frac{\partial P}{\partial t}\mathrm{d}t = -P(x,0) = -\delta(x)$$

where we have used (1). Using the expression (2) for $\mathcal{L}_x$, it is easy to solve:

$$g_1(x) = \frac{e^{-\phi(x)/kT}}{D} \int_x^{x_1} e^{\phi(y)/kT} \left[\int_0^y \delta(z)\mathrm{d}z \right] \mathrm{d}y$$

Now we can express the mean escape time:

$$\begin{aligned} \tau &= \int_{-x_1}^{x_1} g_1(x)\mathrm{d}x = 2\int_0^{x_1} g_1(x)\mathrm{d}x \\ &= \frac{1}{D}\int_0^{x_1} e^{-\phi(x)/kT} \left[\int_x^{x_1} e^{\phi(y)/kT}\mathrm{d}y \right] \mathrm{d}x \end{aligned}$$

Switch the order of integration, to get finally:

$$\boxed{\tau = \frac{1}{D}\int_0^{x_1} \mathrm{d}x\, e^{\phi(x)/kT} \int_0^x \mathrm{d}y\, e^{-\phi(y)/kT}}$$

2. Kramers Mean Escape Rate. We use the saddle-point asymptotics (just Laplace's method on the real axis, in this case) to evaluate the integrals as $kT \to 0$. Factors of $1/2$ arise since the maximum and minimum occur at the endpoints.

$$\int_0^x e^{-\phi(y)/kT}\mathrm{d}y \sim \frac{1}{2}\sqrt{\frac{2\pi kT}{\phi''(0)}}e^{-\phi(0)/kT} = \sqrt{\frac{\pi kT}{2K_0}}$$

So that:

$$\int_0^{x_1} \mathrm{d}x\; e^{\phi(x)/kT} \int_0^x \mathrm{d}y\; e^{-\phi(y)/kT} \sim \sqrt{\frac{\pi kT}{2K_0}} \int_0^{x_1} e^{\phi(x)/kT}\mathrm{d}x$$

with:

$$\int_0^{x_1} e^{\phi(x)/kT}\mathrm{d}x \sim \frac{1}{2}\sqrt{-\frac{2\pi kT}{\phi''(x_1)}}e^{\phi(x_1)/kT} = \sqrt{\frac{\pi kT}{2K_1}}e^{E/kT}$$

Escape occurs with probability $1/2$ from either of 2 activation barriers, so

$$\boxed{R = 2\frac{1}{2}\frac{1}{\tau} = \frac{1}{\tau} \sim R_0(T) = \frac{2D\sqrt{K_0K_1}}{\pi kT}e^{-E/kT} \propto e^{-E/kT}}$$

[1] The function $g_1(x)$ from 10.95 Lecture 11 is denoted $g_0(x)$ in 18.366 Lecture 18 from 2005, and some of this derivation can also be found in both sets of scribe notes.

3. First Correction to the Kramers Escape Rate. In the next derivation, we will use the following relation:

$$\begin{aligned}\int_{-\infty}^{+\infty} e^{-ax^2+bx^3+cx^4}\mathrm{d}x &\sim \int_{-\infty}^{+\infty}\left(1+bx^3+cx^4+\frac{b^2x^6}{2}\right)e^{-ax^2}\mathrm{d}x\\ &= \sqrt{\frac{\pi}{a}}\left(1+\frac{3}{4}\frac{c}{a^2}+\frac{15}{16}\frac{b^2}{a^3}\right)\end{aligned}$$

Using saddle-point asymptotics with the previous formula:

$$\int_0^x e^{-\phi(y)/kT}\mathrm{d}y \sim \frac{1}{2}\sqrt{\frac{2\pi kT}{\phi''(0)}}\left(1-\frac{kT}{8}\frac{\phi^{(4)}(0)}{\left[\phi''(0)\right]^2}+\frac{5kT}{24}\frac{\left[\phi^{(3)}(0)\right]^2}{\left[\phi''(0)\right]^3}\right)e^{-\phi(0)/kT}$$

Since the well is symmetric, $\phi^{(3)}(0)=0$, we end up with:

$$\int_0^x e^{-\phi(y)/kT}\mathrm{d}y \sim \sqrt{\frac{\pi kT}{2K_0}}\left(1-\frac{kT}{8}\frac{M_0}{K_0^2}\right)$$

with $M_0=\phi^{(4)}(0)$. The same way:

$$\int_0^{x_1} e^{\phi(x)/kT}\mathrm{d}x \sim \frac{1}{2}\sqrt{-\frac{2\pi kT}{\phi''(x_1)}}\left(1+\frac{kT}{8}\frac{\phi^{(4)}(x_1)}{\left[\phi''(x_1)\right]^2}-\frac{5kT}{24}\frac{\left[\phi^{(3)}(x_1)\right]^2}{\left[\phi''(x_1)\right]^3}\right)e^{\phi(x_1)/kT}$$

that we write:

$$\int_0^{x_1} e^{\phi(x)/kT}\mathrm{d}x \sim \sqrt{\frac{\pi kT}{2K_1}}\left(1+\frac{kT}{8}\frac{M_1}{K_1^2}-\frac{5kT}{24}\frac{L_1^2}{K_1^3}\right)e^{E/kT}$$

with $L_1=\phi^{(3)}(x_1)$ and $M_1=\phi^{(4)}(x_1)$. We write then:

$$\begin{aligned}\tau &\sim \frac{1}{R_0(T)}\left(1-\frac{kT}{8}\frac{M_0}{K_0^2}\right)\left(1+\frac{kT}{8}\frac{M_1}{K_1^2}-\frac{5kT}{24}\frac{L_1^2}{K_1^3}\right)\\ &\sim \frac{1}{R_0(T)}\left[1+\frac{kT}{8}\left(\frac{M_1}{K_1^2}-\frac{M_0}{K_0^2}-\frac{5}{3}\frac{L_1^2}{K_1^3}\right)\right]\end{aligned}$$

that is:

$$\boxed{R(T)\sim R_0(T)\left[1-\frac{kT}{8}\left(\frac{M_1}{K_1^2}-\frac{M_0}{K_0^2}-\frac{5}{3}\frac{L_1^2}{K_1^3}\right)\right]}$$

with:

$$K_0=\phi''(0) \qquad L_1=\phi^{(3)}(x_1) \qquad M_0=\phi^{(4)}(0)$$
$$K_1=-\phi''(x_1) \qquad M_1=\phi^{(4)}(x_1)$$

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