Lecture 11: Kramers Escape Problem

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1 General Theory of First Passage Processes

1.1 Defining the Problem

We continue our discussion of first passage processes, noting that we are interested in systems that will produce probability distributions satisfying the Fokker-Planck Equation (sometimes called the Drift-Diffusion Equation). At present, we consider only drifts caused by conservative force fields. Recall from previous lectures that the Fokker-Planck Equation is a partial differential equation, which can be expressed using an operator $\mathcal{L}$.

$$\frac{\partial P}{\partial t} = \mathcal{L}P = D\frac{\partial^2 P}{\partial x^2} - \frac{\partial}{\partial x}(\mathbf{v}P)$$

Here, $P(x,t)$ is the probability distribution function (PDF) for our stochastic process of interest. We want to find $f(t)$, the PDF for the first passage time starting from $x = x_0$ at $t = 0$. More generally, this can represent the PDF for reaching the a point x in the target **set** $\mathbb{S}_T$ starting from the initial set $\mathbb{S}_0$ at $t = 0$. This process is illustrated schematically in Figure 1.

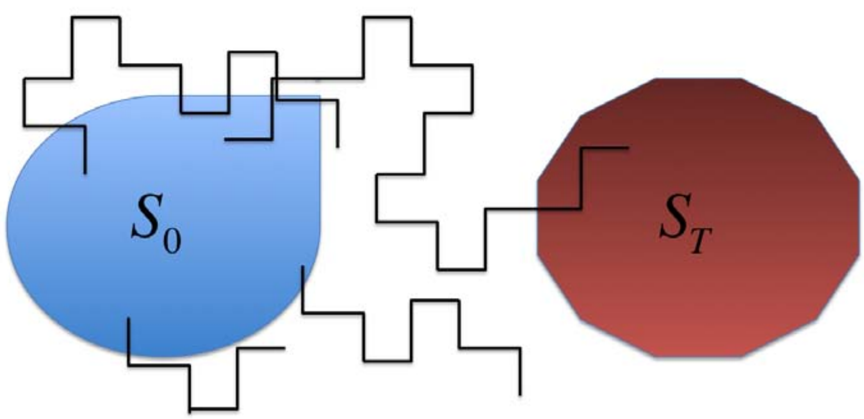

Figure 1: Schematic of a random walk starting in $\mathbb{S}_0$ reaching the target set $\mathbb{S}_T$

To obtain $f(t)$, we first solve the Fokker-Planck equation with initial conditions

$$P(x,0) = \delta(x - x_1) = P_o(x)$$

and with “absorbing” boundary condition

$$P = 0 \text{ for } x \in \mathbb{S}_T$$

which eliminates all trajectories that have reached the target set. This ensures that we only count first passages.

Next, we note that the survival probability $S(t)$ is the probability that random walkers have not yet reached the target set $\mathbb{S}_T$. Formally, we define $S(t)$ as

$$S(t) = \int P(x,t)\mathrm{d}x$$

$$S(t) = \int_{\tau}^{\infty} f(\tau')\mathrm{d}\tau'$$

which provides us the convenient relationship

$$f(\tau) = -S'(\tau)$$

This means that if we can obtain $S(t)$, we have $f(t)$ as well, and we can calculate quantities related to $f(t)$, for instance the moments of $f(t)$. Here, we also note the following relationships for the first passage time PDF $f(t)$:

$$f(t) = -\int \frac{\partial P}{\partial t}\mathrm{d}x = -\int \mathcal{L}P\mathrm{d}x$$

1.2 Calculating Moments of the First Passage Time

But perhaps we are only interested in the moments of the first passage time, rather than the PDF. The n-th moment is defined as

$$\langle \tau^n \rangle = \int_0^{\infty} t^n f(t)\mathrm{d}t = -\int_0^{\infty}\int t^n \frac{\partial P}{\partial t}\mathrm{d}x\mathrm{d}t$$

$$\langle \tau^n \rangle = -\int_0^{\infty} t^n \frac{\partial}{\partial t}\left[\int P(x,t)\mathrm{d}x\right]\mathrm{d}t$$

1.3 Mean First Passage Time

To make this all more tangible, we consider the specific case of the mean first passage time (the first moment of $f(t)$). Calculation of the variance (second moment) is left for Problem Set 2. Letting $n = 1$ in the preceding formula, we see that the mean first passage time is given by

$$\langle \tau \rangle = -\int_0^{\infty} t \frac{\partial}{\partial t}\left[\int P(x,t)\mathrm{d}x\right]\mathrm{d}t$$

We evaluate the outer integral by parts, obtaining

$$\langle \tau \rangle = -t\left[\int P(x,t)\mathrm{d}x\right]_0^{\infty} + \int_0^{\infty}\int P(x,t)\mathrm{d}x\mathrm{d}t$$

Here, we argue that the first term is zero. This amounts to arguing that as $t \to \infty$ the probability density becomes vanishingly small at any single position x. The $t = 0$ limit clearly evaluates to zero. This leaves

$$\langle \tau \rangle = \int_0^\infty \int P(x,t) \mathrm{d}x \mathrm{d}t$$

Now, we switch the order of integration, obtaining

$$\langle \tau \rangle = \int \left(\int_0^\infty P(x,t) \mathrm{d}t \right) \mathrm{d}x$$

and we define the inner integral as the function $g_1(x)$

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

Here, we see that we have reduced the problem of calculating $\langle \tau \rangle$ to the problem of finding $g_1(x)$. To find $g_1(x)$, we use the following trick: we apply the Fokker-Planck operator, $\mathcal{L}$, to both sides of the equation defining $g_1(x)$. Assuming we can take $\mathcal{L}$ inside the integral, we have

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

Recall that

$$\mathcal{L} P = \frac{\partial P}{\partial t}$$

Making this substitution, we have

$$\mathcal{L} g_1(x) = \int_0^\infty \frac{\partial P(x,t)}{\partial t} \mathrm{d}t = P(x,t)|_0^\infty = -P(x,0)$$

Noting our initial condition, we find

$$\mathcal{L} g_1(x) = -\delta(x)$$

Now, we can also evaluate $\mathcal{L} g_1(x)$ by applying the definition of the operator $\mathcal{L}$. Assuming we have a conservative force field, $F = -\frac{\partial U(x)}{\partial x}$, we have

$$\mathcal{L} g_1(x) = D \left[\frac{\partial^2 g_1}{\partial x^2} + \frac{1}{kT} \frac{\partial}{\partial x} \left(U'(x) g_1 \right) \right]$$

which can be rearranged as

$$\mathcal{L} g_1(x) = D \frac{\partial}{\partial x} \left[\frac{\partial g_1}{\partial x} + g_1 \frac{\partial \left(\frac{U'(x)}{kT} \right)}{\partial x} \right]$$

Using an integrating factor, we can further simplify this expression to

$$\mathcal{L}g_1(x) = D\frac{\partial}{\partial x}\left[e^{\frac{-U}{kT}}\frac{\partial}{\partial x}\left(e^{\frac{U}{kT}}g_1\right.\right]$$

Now we see that we have obtained the relationship

$$D\frac{\partial}{\partial x}\left[e^{\frac{-U}{kT}}\frac{\partial}{\partial x}\left(e^{\frac{U}{kT}}g_1\right.\right] = -\delta(x)$$

Using the Fundamental Theorem of Calculus, we can unravel these successive derivatives to invert the expression and obtain $g_1(x)$. Doing so, we find

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

Where y and x_A are chosen to satisfy the boundary conditions of the problem at hand. Also, note that the integral over "half" of a delta function evaluates to $\frac{1}{2}$. This expression also corrects the sign error from lecture.

2 Kramers Escape Problem

Now we come to the problem at hand: escape from a symmetric one-dimensional potential well due to a random walk caused by thermal fluctuations. The shape of the well is shown schematically in Figure 2 below.

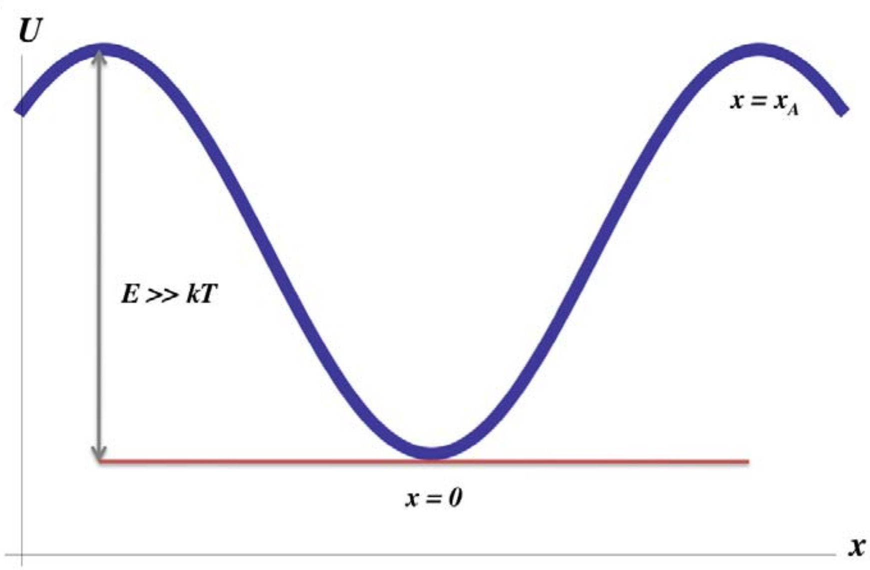

Figure 2: Schematic of our symmetric potential well

The relevant boundary condition is

$$P(x_A, t) = 0$$

which implies

$$g_1(x_A) = 0$$

To solve for the mean first passage time, we need $g_1(x)$ for $|x| < x_A$ so that we can evaluate the integral

$$\langle \tau \rangle = \int g_1(x) \mathrm{d}x$$

Using the expression we obtained for $g_1(x)$, we have

$$\langle \tau \rangle = \frac{1}{2D} \int_{-x_A}^{x_A} e^{-U(x)/kT} \int_{x}^{x_A} e^{U(y)/kT} \mathrm{d}y \mathrm{d}x$$

Noting the symmetry of the well, we can split the domain of the outer integration

$$\langle \tau \rangle = \frac{1}{D} \int_{0}^{x_A} e^{-U(x)/kT} \int_{x}^{x_A} e^{U(y)/kT} \mathrm{d}y \mathrm{d}x$$

Finally, we can remove dimensions from the problem by normalizing the barrier height, defining

$$\tilde{U} = \frac{U}{E}$$

Which leaves us with

$$\langle \tau \rangle = \frac{1}{D} \int_{0}^{x_A} e^{-(E/kT)\tilde{U}(x)} \int_{x}^{x_A} e^{(E/kT)\tilde{U}(y)} \mathrm{d}y \mathrm{d}x$$

We end here, but note that we will be interested in considering the limit $\frac{E}{kT} \to \infty$.

References

[1] M.Z. Bazant. 18.366 exam 2, problem 3. 2005.

[2] J.F. 18.366 lecture 15: Motion of brownian particles in energy landscapes. 2005.

[3] Kenny Kamrin. 18.366 lecture 17: Return and first passage on a lattice. 2005.

[4] Mustafa Sabri Kilic. 18.366 lecture 16: First passage in the continuum limit. 2005.

[5] Kirill Titievsky. 18.366 lecture 18: First passage in higher dimensions. 2005.

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