AM216 Stochastic Differential Equations

Lecture 13

List of topics in this lecture

- Exit problem: reflecting boundary condition for the average exit time $T(x)$
- Escape of a Brownian particle from a potential well: Langevin equation, Smoluchowski-Kramers approximation, over-damped Langevin equation
- Non-dimensionalization, exact integral solution of $T(x)$
- Escape from a deep potential well, Kramers' approximate solution of $T(x)$

Recap

Stochastic differential equation:

$$dX = b(X)dt + \sqrt{a(X)}\,dW$$

The associated backward equation:

$$u_t = L_x[u], \qquad L_x \equiv b(x)\frac{\partial \bullet}{\partial x} + \frac{1}{2}a(x)\frac{\partial^2 \bullet}{\partial x^2}$$

Meaning of $u(x, t)$

$u(x, t)$ = average reward at end time T given $X(T-t) = x$

Absorbing boundary at $x = L$: $\quad u(x,t)\big|_{x=L} = 0$

Reflecting boundary at $x = L$: $\quad \left.\dfrac{\partial u(x,t)}{\partial x}\right|_{x=L} = 0$

The associated forward equation:

$$p_t = L_x^*[p], \qquad L_x^* \equiv \text{adjoint of } L_x = -\frac{\partial\big(b(x)\bullet\big)}{\partial x} + \frac{1}{2}\frac{\partial^2\big(a(x)\bullet\big)}{\partial x^2}$$

Meaning of $p(x, t)$

$p(x, t)$ = mass density at time t.

Absorbing boundary at $x = L$: $\quad p(x,t)\big|_{x=L} = 0$

Reflecting boundary at $x = L$: $\quad J(x,t)\big|_{x=L} = 0, \quad J(x,t) \equiv b(x)p - \tfrac{1}{2}\big(a(x)p\big)_x$

Exit problem of $dX = b(X)dt + \sqrt{a(X)}\, dW$

$T(x)$ = E(time until exit | $X(0) = x$)

Governing equation: $\quad \frac{1}{2}a(x)T_{xx} + b(x)T_x = -1$

Exit problem: boundary conditions for $T(x)$

Absorbing boundary at $x = 0$

By definition, we have $\quad T(0) = 0$

Reflecting boundary at $x = 0$

We look at what happens when X starts with $X(0) = 0$.

$$E\left(dX \middle| X(0)=0\right) = E\left(\left|b(0)dt + \sqrt{a(0)}\, dW\right|\right)$$

$$= E\left(\sqrt{a(0)}\,|dW| + O(dt)\right) = O(\sqrt{dt})$$

We write $T(0)$ as

$$T(0) = E(T(dX)) + dt = E\left(T(0) + T'(0)dX + O(dt)\right) + dt$$

$$= T(0) + T'(0)E(dX) + O(dt)$$

==> $\quad 0 = T'(0)E(dX) + O(dt)$

==> $\quad T'(0) = \frac{O(dt)}{E(dX)} = \frac{O(dt)}{O(\sqrt{dt})} = O(\sqrt{dt}) \to 0 \quad \text{as } dt \to 0$

Conclusion: at reflecting boundary $x = 0$, $T(x)$ satisfies

$$T'(0) = 0$$

In comparison, $u(x, t)$, the probability of exiting by time t, satisfies

$$\left.\frac{\partial u(x,t)}{\partial x}\right|_{x=0} = 0$$

Example:

Suppose X is governed by $dX = b(X)dt + \sqrt{a(X)}\, dW$ with

$a(x) = 1, \quad b(x) = b$

Note: When $a(x) \equiv$ const, Ito = Stratonovich

We consider the escape from [L_1, L_2] where

L_1 is a reflecting boundary and

L_2 is an absorbing boundary.

Draw a slope over [L_1, L_2], tilted either downward ($b > 0$) or upward ($b < 0$), with an exit at L_2 and a dead end at L_1.

The boundary value problem (BVP) for $T(x)$ is

$$\begin{cases} T_{xx} + 2bT_x = -2 \\ T'(L_1) = 0, \quad T(L_2) = 0 \end{cases}$$

We follow the procedure below to solve the BVP.

*) find a particular solution of the nonhomogeneous equation;

*) find a general solution of the homogeneous equation;

*) superpose the two and enforce boundary conditions; ...

The solution for a reflecting boundary at L_1

$$T(x) = \frac{1}{b}(L_2 - x) - \frac{1}{2b^2} \cdot \frac{\exp(2b(L_2 - x)) - 1}{\exp(2b(L_2 - L_1))} \qquad \text{(homework problem)}$$

We discuss 3 cases.

Case 1: $b > 0$; L_1 = negative and large.

Taking the limit as $L_1 \to -\infty$, we have

$$T(x) \to \frac{1}{b}(L_2 - x) \quad \text{as } L_1 \to -\infty$$

Remark: when the bias is driving X toward the exit and the other end of the region is far away, $T(x)$ is affected by i) how far x is from the exit and ii) the bias. $T(x)$ is not affected by the size of the region ($L_2 - L_1$).

Case 2: $b = 0$; [L_1, L_2] stays finite.

We can solve the BVP directly or we can take the limit as $b \to 0$.

We first expand $e^{bz} - 1$ and e^{-bw} as $b \to 0$

$$e^{bz} - 1 = 1 + bz + \frac{1}{2}b^2z^2 + O(b^3) - 1 = bz\left(1 + \frac{1}{2}bz + O(b^2)\right)$$

$$e^{-bw} = \left(1 - bw + O(b^2)\right)$$

$$\frac{e^{bz}-1}{e^{bw}}=(e^{bz}-1)e^{-bw}=bz\left(1+\frac{1}{2}bz+O(b^2)\right)\left(1-bw+O(b^2)\right)$$

$$=bz\left(1+b(\frac{1}{2}z-w)+O(b^2)\right)$$

Apply the expansion to the analytical solution, we obtain

$$T(x)=\frac{1}{b}(L_2-x)-\frac{1}{2b^2}\cdot\frac{\exp(2b(L_2-x))-1}{\exp(2b(L_2-L_1))}$$

$$=\frac{1}{b}(L_2-x)-\frac{1}{2b^2}2b(L_2-x)\left(1+b\left((L_2-x)-2(L_2-L_1)\right)+O(b^2)\right)$$

$$=(L_2-x)\left(2(L_2-L_1)-(L_2-x)+O(b)\right)$$

For $b = 0$, the solution is

$$T(x)=(L_2-x)\left(2(L_2-L_1)-(L_2-x)\right)$$

<u>Remark:</u> when the bias is zero, $T(x)$ is affected by i) how far x is from the exit and ii) the size of the region (L_2-L_1).

<u>Case 3:</u> $b = -k < 0$ (where $k > 0$).

We rewrite $T(x)$ in terms of parameter $k > 0$.

$$T(x)=\frac{1}{b}(L_2-x)-\frac{1}{2b^2}\left(\exp(2b(L_2-x))-1\right)\exp(-2b(L_2-L_1))$$

$$=\frac{-1}{k}(L_2-x)+\frac{1}{2k^2}\left(1-\exp(-2k(L_2-x))\right)\exp(2k(L_2-L_1))$$

(pulling out the dominant factor)

$$=\frac{1}{2k^2}\exp(2k(L_2-L_1))\left[1-\exp(-2k(L_2-x))-2k(L_2-x)\exp(-2k(L_2-L_1))\right]$$

When $2k(L_2-x)$ is moderately large, for example, $2k(L_2-x) \geq 5$, we have

$$\exp(-2k(L_2-x))<<1$$

$$2k(L_2-x)\exp(-2k(L_2-L_1))<<1$$

It follows that $T(x)$ is approximately (in the sense of small relative error)

$$T(x)\approx\frac{1}{2k^2}\exp(2k(L_2-L_1))=\underbrace{(L_2-L_1)}_{\text{width}}{}^2\frac{1}{2\left(k(L_2-L_1)\right)^2}\exp(2\underbrace{k(L_2-L_1)}_{\text{depth}})$$

Remark: when the bias $b = -k$ is driving X away from exit and when the depth of slope, $k(L_2-L_1)$, is moderately large, $T(x)$ has two properties

- $T(x)$ is independent of x as long as x is not too close to the exit.
- $T(x)$ is exponentially large, depending on the depth and the width of slope.

In this example, we derived the two properties based on the analytical solution. We will see that these two properties are generally valid when the bias is against the exit.

Escape of a Brownian particle from a potential well

Model equations

Consider a particle undergoes Brownian motion in a potential well $V(x)$. The potential exerts a position-dependent conservative force $-V'(x)$ on the particle.

We consider the problem of a Brownian particle escaping from a potential well. This problem serves as a model for a wide spectrum of application problems, for example, breaking of a molecular bond, activation in a chemical reaction, …

The stochastic motion of the particle is governed by Newton's second law.

$$dX = Y\,dt$$

$$m\,dY = -\underbrace{bY\,dt}_{\text{Viscous drag}} - \underbrace{V'(X)dt}_{\text{Force from potential}} + \underbrace{\sqrt{2k_B T b}\,dW}_{\text{Brownian force}}$$

X: position

Y: velocity

m: mass

b: drag coefficient

This equation is called Langevin equation (named after Paul Langevin).

In the limit of small particle (i.e., particle size converging to zero), we have

$$0 = -bY\,dt - V'(X)dt + \sqrt{2k_B T b}\,dW$$

(The derivation is more complicated than setting $m = 0$!)

The small particle limit is called the Smoluchowski-Kramers approximation (named after Marian Smoluchowski and Hans Kramers), which we will discuss separately.

Writing (Ydt) as dX, we obtain an equation for X.

$$0 = -b\,dX - V'(X)dt + \sqrt{2k_B T b}\,dW$$

$$\Longrightarrow \quad dX = -\frac{1}{b}V'(X)dt + \sqrt{2\frac{k_B T}{b}}\,dW$$

We write it in terms of the diffusion coefficient, $D = k_B T/b$.

$$dX = -D\frac{V'(X)}{k_B T}dt + \sqrt{2D}\,dW$$

This equation is called the over-damped Langevin equation.

The physical (dimensional) exit problem

Suppose a particle is governed by the over-damped Langevin equation. We consider the problem of the particle escaping from $[0, L]$ where

$x = 0$ is a reflecting boundary and

$x = L$ is an absorbing boundary.

Draw a potential over $[0, L]$.

Scales for non-dimensionalization

At room temperature (~295K),

$k_B T \approx 4.1\ pN\cdot\text{nm} = 4.1\times 10^{-21}\ N\cdot m$ (Joule)

- $k_B T$ serves as the energy scale for normalizing potential $V(x)$.

  $[\,k_B T\,]$ = Energy

- L (the width of the region) serves as the length scale for normalizing X.

  $[\,L\,]$ = Length

- Diffusion coefficient D has the dimension

  $$[\,D\,] = \frac{(\text{Length})^2}{\text{Time}}$$

- We construct a time scale from L and D.

  $$\left[\frac{L^2}{D}\right] = \text{Time}$$

Non-dimensional variables

We define

$$X_{new} = \frac{X_{old}}{L} \qquad ==> \qquad X_{old} = L X_{new}$$

$$t_{new} = \frac{D}{L^2}t_{old} \qquad ==> \qquad t_{old} = \frac{L^2}{D}t_{new}$$

$$V_{new}(X_{new}) = \frac{1}{k_B T} V_{old}(X_{old}) \qquad ==> \qquad V_{old}(X_{old}) = k_B T\, V_{new}(X_{new})$$

Non-dimensional SDE:

We start with the physical SDE:

$$dX = -D \cdot \frac{V'(X)}{k_B T} dt + \sqrt{2D}\, dW .$$

We write all old variables in terms of new variables.

$$dX_{old} = L dX_{new}, \qquad dt_{old} = \frac{L^2}{D} dt_{new}$$

$$\frac{1}{k_B T} V_{old}{}'(X_{old}) = \frac{dV_{new}}{dX_{old}} = \frac{dV_{new}}{dX_{new}} \cdot \frac{dX_{new}}{dX_{old}} = V_{new}{}'(X_{new}) \frac{1}{L}$$

$$dW(t_{old}) = \sqrt{dt_{old}} \underbrace{\frac{dW(t_{old})}{\sqrt{dt_{old}}}}_{\sim N(0,1)} = \sqrt{\frac{L^2}{D} dt_{new}} \frac{dW(t_{new})}{\sqrt{dt_{new}}} = \sqrt{\frac{L^2}{D}}\, dW(t_{new})$$

Substituting these terms into the equation, we obtain

$$\underbrace{L dX_{new}}_{dX_{old}} = -D \cdot \underbrace{V_{new}{}'(X_{new}) \frac{1}{L}}_{\frac{1}{k_B T} V_{old}{}'(X_{old})} \cdot \underbrace{\frac{L^2}{D} dt_{new}}_{dt_{old}} + \sqrt{2D} \underbrace{\sqrt{\frac{L^2}{D}}\, dW(t_{new})}_{dW(t_{old})}$$

$$==> \qquad dX_{new} = -V_{new}{}'(X_{new}) dt_{new} + \sqrt{2}\, dW(t_{new})$$

For conciseness, we recycle the simple notion and write the equation as

$$dX = -V'(X) dt + \sqrt{2}\, dW$$

Now all quantities in the equation are dimensionless.

Exact solution of the dimensionless average escape time

Let $T(x)$ be the dimensionless average escape time.

Recall that for $dX = b(X)dt + \sqrt{a(X)}\, dW$, the governing equation for $T(x)$ is

$$\frac{1}{2} a(x) T_{xx} + b(x) T_x = -1$$

Substituting $a(x) = 2$ and $b(x) = -V'(x)$, we write out the BVP for $T(x)$

$$\begin{cases} T_{xx} - V'(x)T_x = -1 \\ T'(0) = 0\,, \quad T(1) = 0 \end{cases} \qquad \text{(T\_BVP1)}$$

Theorem:

The solution of (T_BVP1) is

$$\boxed{T(x) = \int_x^1 dy \exp(V(y)) \int_0^y ds \exp(-V(s))} \qquad \text{(T\_SOL1)}$$

Derivation:

We use the method of integrating factor.

Multiplying $T_{xx} - V'(x)\, T_x = -1$ by $\exp(-V(x))$, we write the ODE as

$$\exp(-V(x))T_{xx} - \exp(-V(x))V'(x)T_x = -\exp(-V(x))$$

$$\Longrightarrow \quad \left(\exp(-V(x))T_x\right)_x = -\exp(-V(x))$$

Integrating from 0 to y, and using $T_x(0) = 0$, we obtain

$$\exp(-V(y))T_x(y) = -\int_0^y ds \exp(-V(s))$$

$$\Longrightarrow \quad T_x(y) = -\exp(V(y)) \int_0^y ds \exp(-V(s))$$

Integrating from x to 1, and using $T(1) = 0$, we arrive at

$$T(x) = \int_x^1 dy \exp(V(y)) \int_0^y ds \exp(-V(s))$$

End of derivation

(T_SOL1) is the exact solution of (T_BVP1). It does not have any approximation error.

Next, we find an approximation to (T_SOL1) when the potential well is deep.

Escape from a deep potential well: an approximate solution

We consider the potential shown. Specifically,

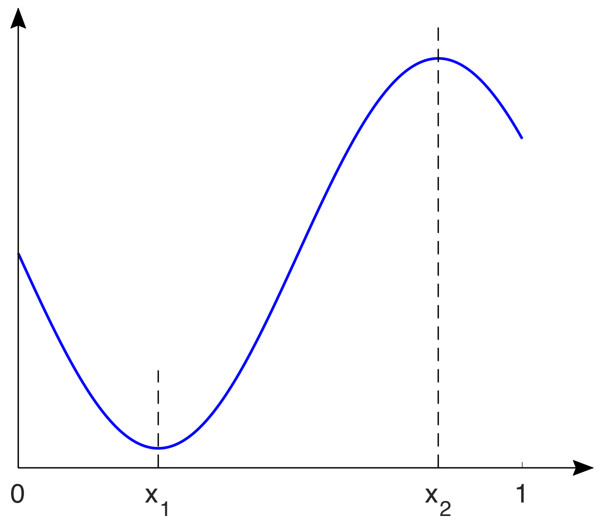
- $V(x)$ decreases monotonically in $(0, x_1)$;
- $V(x)$ attains the only minimum at $x_1 > 0$;
- $V(x)$ increases monotonically in (x_1, x_2);
- $V(x)$ attains the only maximum at $x_2 > x_1$; and
- $V(x)$ decreases monotonically in $(x_2, 1)$.

The depth of the potential well is defined as the height from bottom to top.

$\Delta G \equiv V(x_2) - V(x_1)$

We consider the case of moderately large ΔG, for example, $\Delta G \geq 10$.

Goal: Find an approximate solution for $T(x)$.



Writing the potential in terms of its depth

Since only $V'(x)$ appears in the stochastic differential equation, we shift $V(x)$ by a constant to make $V(x_1) = 0$. We write potential $V(x)$ as

$$V(x) = \Delta G \cdot \phi(x)$$

where $\phi(x)$ satisfies i) $\phi(x) \geq 0$ for $x \in (0, 1)$, ii) $\phi(x_1) = 0$ and iii) $\phi(x_2) = 1$.

Case 1: $\phi''(x) \neq 0$ at both of the two extrema.

Writing the exact solution in terms of ΔG and $\phi(x)$, we have

$$T(x) = \int_x^1 dy \exp(\Delta G \cdot \phi(y)) \int_0^y ds \exp(-\Delta G \cdot \phi(s))$$

In the inner integral $\int_0^y ds$, the dominant contribution comes from near $s = x_1$. When s gets away from x_1, $\phi(s)$ is positive and the integrand $\exp(-\Delta G\, \phi(s))$ is exponentially small. As a result, we only need to capture the integrand approximately near $s = x_1$.

We expand $\phi(s)$ near $s = x_1$.

$$\phi(s) = \underbrace{\phi(x_1)}_{=0} + \underbrace{\phi'(x_1)}_{=0}(s - x_1) + \frac{1}{2}\underbrace{\phi''(x_1)}_{>0}(s - x_1)^2 + \cdots$$

For $y > x_1$, the inner integral is

$$\int_0^y ds \exp(-\Delta G \cdot \phi(s)) \approx \int_0^y ds \exp\left(-\Delta G \cdot \frac{1}{2}\phi''(x_1)(s-x_1)^2\right)$$

$$\approx \int_{-\infty}^{+\infty} ds \exp\left(\frac{-1}{2}\Delta G \cdot \phi''(x_1)(s-x_1)^2\right) = \underbrace{\sqrt{\frac{2\pi}{\Delta G \cdot \phi''(x_1)}}}_{\text{independent of } y} \qquad \text{for } y > x_1$$

Here we used the integration formula

$$\int_{-\infty}^{+\infty} \exp\left(\frac{-1}{2}\alpha u^2\right) du = \sqrt{\frac{2\pi}{\alpha}} \int_{-\infty}^{+\infty} \underbrace{\frac{1}{\sqrt{2\pi\alpha^{-1}}} \exp\left(\frac{-u^2}{2\alpha^{-1}}\right)}_{\text{Normal distribution}} du = \sqrt{\frac{2\pi}{\alpha}}$$

For $y < x_1$, the inner integral is negligible relative to its value for $y > x_1$.

Summary of the inner integral:

For $y > x_1$, $\quad \int_0^y ds \exp(-\Delta G \cdot \phi(s)) \approx$ high constant, independent of y.

For $y < x_1$, $\quad \int_0^y ds \exp(-\Delta G \cdot \phi(s)) \approx 0$.

In the outer integral $\int_x^1 dy$, the factor $\exp(\Delta G \cdot \phi(y))$ attains its maximum at $y = x_2$ where $\phi(x_2) = 1$. When y gets away from x_2, $\exp(\Delta G \cdot \phi(y))$ decreases rapidly relative to its maximum at $y = x_2$. Also for y near x_2, the inner integral takes its high constant value. Thus, in the outer integral, the dominant contribution comes from near $y = x_2$, we only need to capture the integrand approximately near $y = x_2$. We expand $\phi(y)$ near $y = x_2$.

$$\phi(y) = \underbrace{\phi(x_2)}_{=1} + \underbrace{\phi'(x_2)}_{=0}(y-x_2) + \frac{1}{2}\underbrace{\phi''(x_2)}_{<0}(y-x_2)^2 + \cdots$$

For $x < x_2$, (i.e., the starting point is inside the potential well), $T(x)$ is

$$T(x) \approx \int_x^1 dy \underbrace{\exp(\Delta G \cdot \phi(y))}_{\text{focus on near } y=x_2} \underbrace{\int_0^y ds \exp(-\Delta G \cdot \phi(s))}_{=\text{ high constant value}}$$

$$\approx \int_x^1 dy \exp\left(\Delta G + \Delta G \cdot \frac{1}{2}\phi''(x_2)(y-x_2)^2\right)\sqrt{\frac{2\pi}{\Delta G \cdot \phi''(x_1)}}$$

$$\approx \exp(\Delta G)\cdot\sqrt{\frac{2\pi}{\Delta G\cdot\phi''(x_1)}}\int_{-\infty}^{+\infty} dy \exp\left(\frac{-1}{2}\Delta G\underbrace{(-\phi''(x_2))}_{>0}(y-x_2)^2\right)$$

$$=\exp(\Delta G)\cdot\underbrace{\sqrt{\frac{2\pi}{\Delta G\cdot\phi''(x_1)}}\sqrt{\frac{2\pi}{\Delta G\cdot(-\phi''(x_2))}}}_{\text{independent of } x} \qquad \text{for } x<x_2$$

Kramers' approximate solution for $T(x)$:

When the potential height ΔG is moderately large and the starting point x is inside the potential well, $T(x)$ is approximately (in the sense of small relative error)

$$T(x)\approx \exp(\Delta G)\cdot\frac{1}{\Delta G}\underbrace{\sqrt{\frac{(2\pi)^2}{\phi''(x_1)\cdot(-\phi''(x_2))}}}_{\text{independent of } x} \qquad \text{for } x<x_2$$

This is part of Kramers' theory of reaction kinetics.

Remarks:

1. Q: Why do we want an approximate solution?
   A: It gives us a clear picture on the behaviors of $T(x)$.
2. When ΔG is moderately large, $T(x)$ has two properties:
   - $T(x)$ is independent of x as long x is inside the potential well.
   - $T(x)$ is exponentially large.

   We will look at the dependence on the width and the height of potential when we go back to the physical average exit time T_{phy}.

Case 2: $\phi''(x_1) > 0$ at x_1; $\phi''(x_2) = 0$ and $\phi^{(4)}(x_2) < 0$ at x_2 (skip)

We expand $\phi(y)$ near $y = x_2$.

$$\phi(y)=\frac{1}{4!}\phi^{(4)}(x_2)(y-x_1)^4+\cdots$$

For $x < x_2$, we have

$$T(x)\approx \exp(\Delta G)\cdot\sqrt{\frac{2\pi}{\Delta G\cdot\phi''(x_1)}}\int_{-\infty}^{+\infty} dy \exp\left(\frac{-1}{4!}\Delta G(-\phi^{(4)}(x_2))(y-x_2)^4\right)$$

$$= \exp(\Delta G) \cdot \sqrt{\frac{2\pi}{\Delta G \cdot \phi''(x_1)}} \frac{(3/2)^{1/4}\Gamma(1/4)}{\left(\Delta G(-\phi^{(4)}(x_2))\right)^{1/4}} \qquad \text{for } x < x_2$$

Here we used the integral formula

$$\int_{-\infty}^{+\infty} \exp(-bu^4)du = 2\int_0^{+\infty} \exp(-bu^4)du$$

(change of variables $bu^4 = w$)

$$= \frac{1}{2b^{1/4}} \int_0^{+\infty} \exp(-w) w^{-3/4} dw = \frac{1}{2b^{1/4}} \Gamma(1/4), \qquad \Gamma(1/4) \approx 3.6256$$

Kramers' approximate solution for $T(x)$:

When the potential height ΔG is moderately large and the starting point x is inside the potential well, $T(x)$ is approximately (in the sense of small relative error)

$$T(x) \approx \exp(\Delta G) \cdot \frac{1}{(\Delta G)^{3/4}} \underbrace{\sqrt{\frac{2\pi}{\phi''(x_1)}} \cdot \frac{(3/2)^{1/4}\Gamma(1/4)}{(-\phi^{(4)}(x_2))^{1/4}}}_{\text{independent of } x} \qquad \text{for } x < x_2$$