AM216 Stochastic Differential Equations

Lecture 13
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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 solution for $T(x)$
- Escape from a deep potential well, approximate solution for $T(x)$

Review (a big picture view)

Stochastic differential equation

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

The associated backward equation:

$$q_t = L_z[q], \qquad L_z \equiv b(z)\frac{\partial \bullet}{\partial z} + \frac{1}{2}a(z)\frac{\partial^2 \bullet}{\partial z^2}$$

Meaning:

$q(z, t)$ = average reward at real time T given $X(T-t) = z$

The associated forward equation:

$$p_t = L_x^*[p], \qquad L_x^* \equiv \text{adjoint operator of } L_x$$

Meaning:

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

Clarification: ensemble density vs probability density

City of Santa Cruz has 12.74 sq mi land and 60,000 population.

Assuming the population is uniformly distributed.

Ensemble density = 5,478 per sq mi

Probability density = 0.0785 per sq mi (fraction of population)

Exit time:

Average exit time

$T(x) = E(\text{time until exit} \mid X(0) = x)$

Governing quation:

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

End of review

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

Absorbing boundary at $x = 0$

We encountered this in the gambler's ruin problem. By definition, we have

$T(L) = 0$

Reflecting boundary at $x = 0$

To figure out the boundary condition for $T(x)$ at $x = 0$, we look at what happens when X starts with $X(0) = 0$. If X exits the region $[0, L]$ at $x = 0$, it will be put back in.

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

$$\Longrightarrow \quad E(dX) = O(\sqrt{dt})$$

We write $T(0)$ as

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

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

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

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

Conclusion:

The condition on average exit time $T(x)$ at reflecting boundary $x = 0$ is

$$T'(0) = 0$$

Similarly for $u(x, t)$, the probability of exiting by time t, the condition on $u(x, t)$ at reflecting boundary $x = 0$ is

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

Example:

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

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

We consider the escape from $[L_1, L_2]$ where L_2 is absorbing and L_1 is reflecting.

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 is

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

(The derivation is in your homework.)

We discuss 3 cases.

<u>Case 1:</u> $b > 0$

For L_1 negative and large, we have

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

This is the same as in the case of absorbing boundary at $x = L_1$.

When the bias is driving the system toward one exit door and the other end is far away, the boundary condition at the other end (reflecting or absorbing) does not matter.

<u>Case 2:</u> $b = 0$

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

As $b \to 0$, we have

$$\begin{aligned} \exp(2b(L_2 - x)) - 1 &= 2b(L_2 - x) + \frac{1}{2}(2b)^2 (L_2 - x)^2 + O(b^3) \\ &= 2b(L_2 - x)\left(1 + b(L_2 - x) + O(b^2)\right) \end{aligned}$$

$$\exp(-2b(L_2 - L_1)) = 1 - 2b(L_2 - L_1) + O(b^2)$$

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

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

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

$$=(L_2-L_1)^2-(L_1-x)^2+O(b)$$

For $b = 0$, the solution is

$$T(x)=(L_2-L_1)^2-(L_1-x)^2$$

Case 3: $b = -k < 0$ where $k > 0$

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

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

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

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

When $k(L_2-x)$ is moderately large, for example, $k(L_2-x) \geq 3$, 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

$$T(x)\approx\frac{1}{2k^2}\exp(2k(L_2-L_1))$$

Remark:

In the case of $b = -k < 0$, the average escape time has two properties

- $T(x)$ is independent of x as long x is not too close to L_2 (the exit door).
- $T(x)$ is exponentially large.

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 system bias is against the escape.

Escape of a Brownian particle from a potential well

Model equations

We consider the situation where a particle undergoes Brownian motion in a potential well $V(x)$. The potential exerts a position-dependent conservative force $-V'(x)$.

The problem of a Brownian particle escaping from a potential well 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.

$$dX = Y\,dt$$

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

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 not as simple as 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.

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

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

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 exit problem

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

$x = 0$ is a reflecting boundary and

$x = L$ is an absorbing boundary.

We carry out non-dimensionalization.

Scales for non-dimensionalization

We examine various scales in the over-damped Langevin equation.

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

At room temperature (~295K),

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

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

  $[\, k_B T \,] = \text{Energy}$

- L serves as the length scale for normalizing X.

  $[\, L \,] = \text{Length}$

- 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 quantities/variables

We define

$$X_{new} = \frac{1}{L} X_{old} \qquad \Longrightarrow \qquad X_{old} = L X_{new}$$

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

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

Non-dimensional equation

We write out various terms in the over-damped Langevin equation

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

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

$$dW(t_{old}) = \sqrt{dt_{old}}\underbrace{\frac{dW(t_{old})}{\sqrt{dt_{old}}}}_{\text{Independent of } t_{old}} = \sqrt{\frac{L^2}{D}dt_{new}}\,\frac{dW(t_{new})}{\sqrt{dt_{new}}} = \sqrt{\frac{L^2}{D}}\,dW(t_{new})$$

Substituting these terms into the over-damped Langevin equation, we obtain

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

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

We revert back to the simple notion and write the equation as

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

Now all quantities in the equation are dimensionless.

<u>Exact solution of the dimensionless problem</u>

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

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

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

<u>Theorem:</u>

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 start with the differential equation

$$T_{xx} - V'(x)\, T_x = -1.$$

Multiplying the differential equation by $\exp(-V(x))$, we write it as

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

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

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

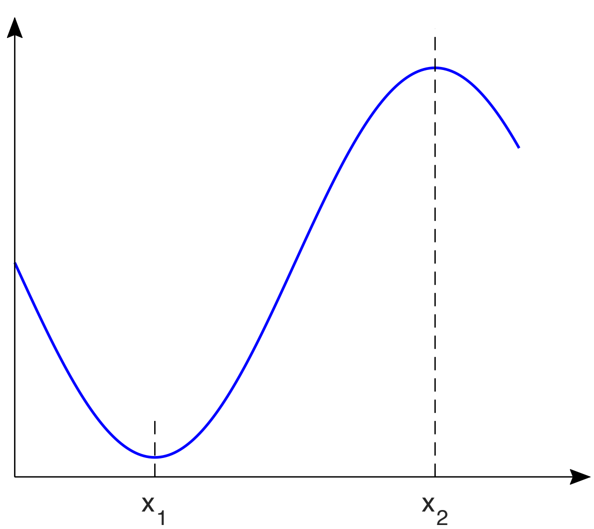
End of derivation

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

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

Escape from a deep potential well

We consider the situation where $V(x)$ attains the only minimum at $x = x_1 > 0$ and attains the only maximum at $x = x_2 > x_1$, as shown below.



Specifically,

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

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

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

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

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 $\phi(x) \geq 0$ for $x \in (0, 1)$, $\phi(x_1) = 0$ and $\phi(x_2) = 1$.

<u>Case 1:</u> $\phi''(x) \neq 0$ at the two extrema.

Expressing $T(x)$ in terms of ΔG and $\phi(x)$, we have

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

<u>In the inner integral</u> $\int_0^y ds$, 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 $s = x_1$.

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

When $y > x_1$, the inner integral is

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

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

which is valid for $y > x_1$ and is independent of y.

Here we used the integral formula

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

When $y < x_1$, we have $\phi(s) \geq \phi(y) > 0$ for $s \in [0, y]$. The inner integral for $y < x_1$ is

$$\int_0^y ds \exp(-\Delta G \cdot \phi(s)) \leq \int_0^y ds \exp(-\Delta G \cdot \phi(y)) = y \cdot \exp(-\Delta G \cdot \phi(y))$$

which is negligible relative to its value for $y > x_1$.

<u>In the outer integral</u> $\int_x^1 dy$, 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, we $\exp(\Delta G \cdot \phi(y))$ decreases rapidly relative to its maximum at $y = x_2$.

$$\exp(\Delta G \cdot \phi(y)) = \exp\Big(\Delta G \cdot \big(\phi(y) - \phi(x_2)\big)\Big) \underbrace{\exp\big(\Delta G \cdot \phi(x_2)\big)}_{\text{Maximum at } x_2}$$

As we discussed above, for y near x_2, the inner integral $\int_0^y ds$ contains its dominant contribution from near $s = x_1 < x_2$. Thus, in the outer integral, the dominant contribution comes from near $y = x_2$.

We consider the situation of $x < x_2$, which means the starting point is <u>inside</u> the potential well. For $x < x_2$, the outer integral $\int_x^1 dy$ contains the dominant contribution from near $y = x_2$ and we only need to capture the integrand approximately near $y = x_2$. We expand $\phi(y)$ near $y = x_2$.

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

For $x < x_2$, we have

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

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

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

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

which is valid for $x < x_2$ and is independent of x.

Here again we used $\int_{-\infty}^{+\infty} \exp\left(\frac{-1}{2}au^2\right)du = \sqrt{\frac{2\pi}{a}}$

Therefore, we conclude that when the starting point is inside the potential well, and the potential height is moderately large, the dimensionless escape time $T(x)$ is approximately

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

This is part of Kramers' theory of reaction kinetics.

<u>Remark:</u>

When ΔG is moderately large, dimensionless $T(x)$ has two properties:

- $T(x)$ is independent of x as long x is inside the potential well.
- $T(x)$ is exponentially large.

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

...

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

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

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

Here we used the integral formula

$$\int_{-\infty}^{+\infty} \exp(-bu^4)du = 2\int_{0}^{+\infty} \exp(-bu^4)du \qquad \text{change of variables } bu^4 = w$$

$$= \frac{1}{2b^{1/4}} \int_{0}^{+\infty} \exp(-w)w^{-3/4}\,dw = \frac{1}{2b^{1/4}}\Gamma(1/4), \qquad \Gamma(1/4) \approx 3.6256$$

For $x < x_2$, the dimensionless escape time $T(x)$ is approximately

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

which is valid for $x > x_2$ and is independent of y.