AM216 Stochastic Differential Equations

Lecture 14
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List of topics in this lecture

- Kramers' theory of reaction kinetics, physical escape time, effects of potential width, diffusion coefficient, and energy barrier
- Memoryless property of average escape time, exponential distribution, escape rate
- Application of Kramers' theory: a simplified model of ignition
- Feynman-Kac formula, fatality rate, path integral $u(x, t, T)$, interpretation of path integral as relative population size, governing equation of $u(x, t, T)$

Review

Exit time: reflecting boundary condition for $T(x)$

$$T'(L_1) = 0$$

Escape of a Brownian particle from a potential well

Langevin equation → Smoluchowski-Kramers approximation in the limit of small particle → over-damped Langevin equation

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

Dimensionless equation

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

Exact solution for $T(x)$

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

Deep potential well

$V(x) = \Delta G\, \phi(x)$ $\qquad$ ΔG is moderately large

Approximate solution for $T(x)$

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

$T(x)$ is independent of starting position x when x is inside the potential well.

End of review

Kramers' theory of reaction kinetics

Physical escape time in terms of physical quantities

Recall the non-dimensionalization.

$$t = \frac{D}{L^2} t_{\text{phy}}, \qquad T(x) = \frac{D}{L^2} T_{\text{phy}}(x_{\text{phy}}), \qquad \Delta G = \frac{1}{(k_B T)} \Delta G_{\text{phy}}$$

Substituting these into the expression of $T(x)$, we get

$$\frac{D}{L^2} T_{phy}(x_{phy}) = \exp\left(\frac{\Delta G_{phy}}{k_B T}\right) \cdot \frac{k_B T}{\Delta G_{phy}} \sqrt{\frac{(2\pi)^2}{\phi''(x_1)\cdot(-\phi''(x_2))}}$$

Caution on the notation:

T in $(k_B T)$ is the temperature.

$T(x)$ is the average exit time.

The physical escape time has the expression

$$T_{phy}(x_{phy}) = \underbrace{\frac{L^2}{D}}_{\text{Effect of mobility}} \cdot \underbrace{\exp\left(\frac{\Delta G_{phy}}{k_B T}\right) \frac{k_B T}{\Delta G_{phy}}}_{\text{Effect of energy barrier}} \underbrace{\sqrt{\frac{(2\pi)^2}{\phi''(x_1)\cdot(-\phi''(x_2))}}}_{\text{Effect of geometric factors}}$$

We can see how the physical escape time scales with other physical quantities.

- When the width of potential L is doubled, T_{phy} is increased by a factor of 4. It is more difficulty to escape from a wide potential well.
- When the diffusion coefficient D is doubled, T_{phy} is halved. It is easier for a smaller particle to escape.
- T_{phy} increases exponentially with the energy barrier ΔG_{phy}. When ΔG_{phy} is increased by $2.3 k_B T$, T_{phy} is approximately multiplied by a factor of 10. By far, the energy barrier ΔG_{phy} has the dominant influence on T_{phy}.

An example:

Consider the escape of a 1-nm (diameter) particle from a potential well of width 0.5nm.

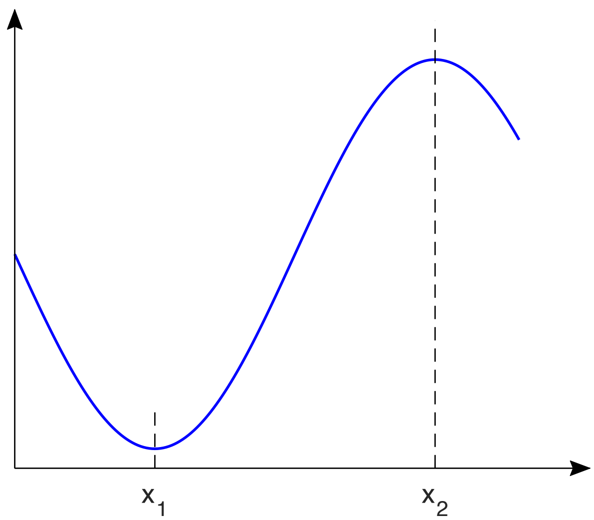
L = 0.5nm; ΔG_{phy} is left as a variable;

a (particle radius) = 0.5nm; η (viscosity of water) = 0.01 $\text{g(cm)}^{-1}\text{s}^{-1}$;

D is calculated below.

$$D = \frac{k_B T}{6\pi\eta a} = 4.350\times 10^{8}\,\text{nm}^2\text{s}^{-1}$$

We use the function shown below for $\phi(x)$, the non-dimensionalized and normalized potential with min $\phi(x) = 0$, max $\phi(x) = 1$, $0 \le x \le 1$.



Mathematically, function $\phi(x)$ has the expression

$$\phi(x) = \frac{1}{2} + \frac{1}{2}\sin\big((1.8x - 1.0)\pi\big)$$

$$x_1 = \arg\min \phi(x) = \frac{5}{18}, \qquad x_2 = \arg\max \phi(x) = \frac{15}{18}$$

$$\phi''(x_1) = \frac{1}{2}(1.8\pi)^2, \qquad \phi''(x_2) = \frac{-1}{2}(1.8\pi)^2$$

Substituting these quantities into the expression of T_{phy}, we obtain

$$T_{phy}(x_{phy}) = \exp\left(\frac{\Delta G_{phy}}{k_B T}\right)\frac{k_B T}{\Delta G_{phy}}\left(2.258\times 10^{-10}\,\text{s}\right)$$

- $\Delta G_{\text{phy}} = 10\ k_B T$ ==> $T_{\text{phy}} = 4.974\times10^{-7}$ s = 0.497 μs
- $\Delta G_{\text{phy}} = 15\ k_B T$ ==> $T_{\text{phy}} = 4.922\times10^{-5}$ s = 49.2 μs
- $\Delta G_{\text{phy}} = 20\ k_B T$ ==> $T_{\text{phy}} = 5.478\times10^{-3}$ s = 5.48 ms

Distribution of the random escape time

Let $Y(\omega)$ denote the random exit time. In the above, we derived an expression for

$T(x) \equiv E(Y(\omega)|X(0) = x)$

Question:

What can we say about the distribution of the random exit time?

Answer:

For a deep potential well, the escape process is (approximately) memoryless.

Specifically, the solution of $T(x)$ tells us

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

That is, the average exit time is memoryless. Mathematically, it gives us

$$E(Y - t_0 \big| Y > t_0) = E(Y) \qquad \text{independent of } t_0$$

Let $\rho(t)$ be the probability density of Y. Based on this memoryless property of the average exit time, we derive density $\rho(t)$.

In terms of $\rho(t)$, the memoryless property above becomes

$$\frac{1}{\int_{t_0}^{\infty} \rho(t)\,dt} \int_{t_0}^{\infty} (t - t_0)\rho(t)\,dt = E(Y) \qquad \text{independent of } t_0$$

We write $\rho(t) = -G'(t)$ where $G(t) \equiv \int_t^{\infty} \rho(s)\,ds$. Carrying out integration by parts in the numerator and multiplying by the denominator, we write the equation as

$$\int_{t_0}^{\infty} G(t)\,dt = E(Y)G(t_0)$$

Differentiating with respect to t_0, we arrive at

$$\frac{-1}{E(Y)} G(t_0) = G'(t_0)$$

(This is the same ODE as you obtained previously.)

...

We conclude that $Y(\omega)$ has the exponential distribution:

$$\rho(t) = r\exp(-rt)\,, \qquad r = \frac{1}{E(Y)} = \frac{1}{T(x)}$$

where r is called the escape rate and has the meaning of probability per time:

$$r = \frac{1}{\Delta t} \Pr\Big(\text{escaping in } (t_0, t_0 + \Delta t) \,\Big|\, \text{has not escaped by } t_0\Big)$$

The physical escape rate has the expression

$$r_{phy} = \frac{1}{T_{phy}(x_{phy})} = \underbrace{\frac{D}{L^2}}_{\substack{\text{Effect of}\\ \text{mobility}}} \cdot \underbrace{\exp\left(\frac{-\Delta G_{phy}}{k_B T}\right)\frac{\Delta G_{phy}}{k_B T}}_{\substack{\text{Effect of}\\ \text{energy barrier}}} \underbrace{\sqrt{\frac{\phi''(x_1)\cdot(-\phi''(x_2))}{(2\pi)^2}}}_{\substack{\text{Effect of}\\ \text{geometric factors}}}$$

This is the Kramers theory of reaction kinetics (named after Hans Kramers).

Remarks:

- The chemical reaction between molecules A and B requires activation, which means crossing over an energy barrier. The energy barrier, for example, may be that molecule A has to fluctuate to an energetically unfavorable configuration.
- The process of crossing over an energy barrier is mathematically an escape process.
- The escape process is memoryless and is described by a reaction rate.
- The reaction rate has a strong dependence on the temperature.

$$r_{phy} \sim \exp\left(\frac{-\Delta G_{phy}}{k_B T}\right)$$

- Another aspect of the chemical reaction is the probability of encounter between molecules A and B, which is affected by concentrations and the temperature.

A simplified model of ignition

Let T_0 = temperature of the environment.

$T(t)$ = spot temperature at time t at an interface of gasoline and air

(where locally there is a mix of gasoline and air)

$T(t)$ is governed by Newton's law of cooling

$$\frac{dT(t)}{dt} = \underbrace{-\mu(T(t)-T_0)}_{\text{cooling}} + \underbrace{\alpha \exp\left(\frac{-\Delta G}{T(t)}\right)}_{\substack{\text{heat generated}\\ \text{by reaction}}}$$

Let $y(t) \equiv (T(t)-T_0)/T_0$, the normalized temperature increase.

We expand the non-linear term in the ODE for small y.

$T(t) = T_0(1+y)$

$$\frac{-\Delta G}{T(t)} = \frac{-\Delta G}{T_0(1+y)} = \frac{-\Delta G}{T_0}(1-y+\cdots) = \frac{-\Delta G}{T_0} + \frac{\Delta G}{T_0}y + \cdots$$

$$\exp\left(\frac{-\Delta G}{T(t)}\right) = \exp\left(\frac{-\Delta G}{T_0}\right)\exp\left(\frac{\Delta G}{T_0}y+\cdots\right) = \exp\left(\frac{-\Delta G}{T_0}\right)\left(1+\frac{\Delta G}{T_0}y+\cdots\right)$$

Substituting the expansion in the ODE yields

$$T_0\frac{dy}{dt} = \underbrace{-\mu T_0 y}_{\text{cooling}} + \underbrace{\alpha\exp\left(\frac{-\Delta G}{T_0}\right)\left(1+\frac{\Delta G}{T_0}y+\cdots\right)}_{\substack{\text{heat generated}\\ \text{by reaction}}}$$

Governing equation for y

Dividing by T_0 and neglecting higher order terms, we obtain

$$\frac{dy}{dt} = \underbrace{\left(\frac{\alpha\Delta G}{T_0^2}\exp\left(\frac{-\Delta G}{T_0}\right)-\mu\right)}_{\equiv\lambda(T_0)}y + \underbrace{\frac{\alpha}{T_0}\exp\left(\frac{-\Delta G}{T_0}\right)}_{q}$$

Initial condition

$y(0) = 0$

Behavior of the IVP

$$\begin{cases} y' = \lambda y + q \\ y(0) = 0 \end{cases}$$

Exact solution: $\quad y(t) = \left(e^{\lambda t}-1\right)\dfrac{q}{\lambda}$

Case of $\lambda < 0$:

As t increases, $y(t) \to \dfrac{q}{(-\lambda)} > 0$

Temperature stabilizes at a finite value. No ignition.

Case of $\lambda > 0$:

As t increases, $y(t) \to +\infty$

Temperature increases unbounded. Ignition.

Ignition temperature:

We examine how $\lambda(T_0)$ varies with T_0.

$$\lambda(T_0) \equiv \frac{\alpha\Delta G}{T_0^2}\exp\left(\frac{-\Delta G}{T_0}\right)-\mu$$

$$\Longrightarrow \quad \frac{d\lambda}{dT_0} = \frac{\alpha\Delta G}{T_0^3}\exp\left(\frac{-\Delta G}{T_0}\right)\left(\frac{\Delta G}{T_0}-2\right)$$

$\lambda(T_0)$ is an increasing function of ambient temperature T_0 when $\Delta G/T_0 > 2$ (when the energy barrier of the reaction is significant).

The ignition temperature T_0^* is defined as $\lambda(T_0^*)=0$.

For ambient temperature $T_0 > T_0^*$, spot temperature $T(t)$ increases unbounded, making the reaction at the spot faster and faster (combustion).

Feynman-Kac formula

Consider the Ito interpretation of

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

The moments of dX are

$$E\left(dX \middle| X(t)=x\right) = b(x,t)dt + o(dt)$$

$$E\left((dX)^2 \middle| X(t)=x\right) = a(x,t)dt + o(dt)$$

$$E\left((dX)^n \middle| X(t)=x\right) = o(dt) \quad \text{for } n \ge 3$$

<u>Definition of</u> $u(x, t, T)$

Consider function $u(x, t, T)$ defined as

$$u(x,t,T) = E\left(\exp\left(-\int_t^T \psi(X(s),s)ds\right) \middle| X(t)=x\right)$$

<u>Meaning of</u> $u(x, t, T)$

For $\psi(z, s)>0$, we view $\psi(z, s)$ is the fatality rate at position z at time s.

Fatality rate = fatality probability per time

= Pr(fatality in $[s, s+\Delta s]$) / Δs

==> Pr(fatality in $[s, s+\Delta s]$) = (fatality rate) × Δs

Let us follow one <u>particular path $x(s)$</u> from time t to T.

We discretize the path on a time grid

$$\Delta s = \frac{T-t}{N}, \qquad s_j = t + j\Delta s, \quad s_0 = t, \quad s_N = T$$

Probability of surviving from time s_j to s_{j+1} along the given path $x(s)$ is approximately

$$1 - \underbrace{\psi(x(s_j), s_j)\Delta s}_{\Pr(\text{fatality in } [s_j, s_{j+1}]} \approx \exp\left(-\psi(x(s_j), s_j)\Delta s\right)$$

Probability of surviving from time t to T along the given path $x(s)$ is

$$\prod_{j=0}^{N-1}\left(1-\psi(x(s_j),s_j)\Delta s\right)\approx\prod_{j=0}^{N-1}\exp\left(-\psi(x(s_j),s_j)\Delta s\right)$$

$$=\exp\left(-\sum_{j=0}^{N-1}\psi(x(s_j),s_j)\Delta s\right)$$

$$\to\exp\left(-\int_t^T\psi(x(s),s)ds\right)\qquad\text{as } N\to\infty$$

We average the surviving probability over all paths starting at $X(t) = x$.

$$u(x,t,T)\equiv E\left(\exp\left(-\int_t^T\psi(X(s),s)ds\right)\middle|X(t)=x\right)$$

= probability of surviving from time t to time T,

averaged over all paths starting at $X(t) = x$.

For the case of negative fatality rate $\psi(z, s) < 0$, we can interpret $[-\psi(z, s)]>0$ as the growth rate at position z at time s.

For the general case ($\psi(z, s)$ may be positive or negative),

$u(x, t, T)$ = population size at time T <u>relative to that at time t</u>,

averaged over all paths starting at $X(t) = x$.

The interpretation of $u(x, t, T)$ as the relative population size is more general; it is valid for both positive and negative $\psi(z, s)$.

Examples:

$X(s)$ = temperature at time s

u = size of a bacteria population at time = T relative to that at time t

$X(s)$ = <u>collective population</u> size of <u>all predators</u> at time s

u = size of <u>a prey population</u> at time = T relative to that at time t

$X(s)$ = <u>collective population</u> size of all <u>preys</u> at time s

u = size of <u>a predator population</u> at time = T relative to that at time t

$X(s)$ = oil price at time s.

u = stock price of an oil company at time T relative to that at time t.

<u>Governing equation</u> for $u(x, t, T)$

Now we derive the partial differential equation gverning $u(x, t, T)$.

We use the backward view for $u(x, t, T)$:

$[\, t \to T\,]$ is divided into $[t \to t+\Delta t\,]$ and $[\, t+\Delta t \to T\,]$.

$$\exp\left(-\int_t^T \psi(X(s),s)ds\right)$$

$$=\exp\left(-\int_t^{t+dt} \psi(X(s),s)ds\right)\exp\left(-\int_{t+dt}^T \psi(X(s),s)ds\right)$$

$$=\exp\left(-\psi(x,t)dt+o(dt)\right)\exp\left(-\int_{t+dt}^T \psi(X(s),s)ds\right)$$

$$=\underbrace{\left(1-\psi(x,t)dt\right)}_{\text{independent of path}}\exp\left(-\int_{t+dt}^T \psi(X(s),s)ds\right)+o(dt)$$

We average $\exp\left(-\int_{t+dt}^T \quad\right)$ over <u>all paths</u> starting at $X(t) = x$.

We use the law of total expectation to write the average over $\{X(s),\, t \le s \le T\}$ as

$$E_{\{X(s),t\le s\le T\}}\left(*\,\middle|\, X(t)=x\right)=E_{dX}\left(E_{\{X(s),t+\Delta t\le s\le T\}}\left(*\,\middle|\,X(t+dt)=x+dX\right)\right)$$

The average of $\exp\left(-\int_{t+dt}^T \quad\right)$ over all paths starting at $X(t) = x$ has the expression

$$E\left(\exp\left(-\int_{t+dt}^T \psi(X(s),s)ds\right)\middle|X(t)=x\right)$$

Law of total expectation

$$=E_{dX}\left(E_{\{X(s),t+dt\le s\le T\}}\left(\exp\left(-\int_{t+dt}^T \psi(X(s),s)ds\right)\middle|X(t+dt)=x+dX\right)\right)$$

Definition of $u(x, t, T)$

$$=E_{dX}\left(u(x+dX,t+dt,T)\right)$$

Taylor expansion

$$=E_{dX}\left(u(x,t,T)+u_t dt+u_x dX+\frac{1}{2}u_{xx}(dX)^2\right)+o(dt)$$

Using moments of dX

$$=u(x,t,T)+u_t dt+u_x b(x,t)dt+\frac{1}{2}u_{xx}a(x,t)dt+o(dt)$$

Using this result, we write $u(x, t, T)$ as

$$u(x,t,T)=E\left(\exp\left(-\int_t^T \psi(X(s),s)ds\right)\middle| X(t)=x\right)$$

$$=\underbrace{(1-\psi(x,t)dt)}_{\text{independent of path}}E\left(\exp\left(-\int_{t+dt}^T \psi(X(s),s)ds\right)\right)+o(dt)$$

$$=(1-\psi(x,t)dt)\left(u(x,t,T)+u_t dt+u_x b(x,t)dt+\frac{1}{2}u_{xx}a(x,t)dt\right)+o(dt)$$

$$=u(x,t,T)+u_t dt+u_x b(x,t)dt+\frac{1}{2}u_{xx}a(x,t)dt-\psi(x,t)u\,dt+o(dt)$$

Dividing by dt and taking the limit at $dt \to 0$, we obtain the governing equation

$$0=u_t+b(x,t)u_x+\frac{1}{2}a(x,t)u_{xx}-\psi(x,t)u$$

It is the backward equation with a fatality/growth term.

The End/final condition

$$u(x, t, T)|_{t=T} = 1$$

We consider the FVP

$$\begin{cases} 0=u_t+b(x,t)u_x+\frac{1}{2}a(x,t)u_{xx}-\psi(x,t)u \\ u(x,t,T)\big|_{t=T}=1 \end{cases}$$

The solution of the FVP has the path integral expression

$$u(x,t,T)=E\left(\exp\left(-\int_t^T \psi(X(s),s)ds\right)\middle| X(t)=x\right)$$

This is called the Feynman-Kac formula for the backward equation (named after Richard Feynman and Mark Kac).

A more general case

Consider the function

$$u(x,t,T)=E\left(\exp\left(-\int_t^T \psi(X(s),s)ds\right)f(X(T))\middle| X(t)=x\right)$$

Meaning of $u(x, t, T)$

$\psi(z, s)$ is the fatality/growth rate at position z at time s.

$f(z)$ is the reward for surviving and reaching position z at final time T.

$u(x, t, T)$ = reward at final time T per population at time t,

averaged over all paths starting at $X(t) = x$

Governing equation for $u(x, t, T)$

The governing equation is not affected by function $f(z)$.

$$0 = u_t + b(x,t)u_x + \frac{1}{2}a(x,t)u_{xx} - \psi(x,t)u$$

which is the same as in the special case of $f(z) \equiv 1$.

The end/final condition

$u(x, t, T)|_{t=T} = f(x)$

The effect of $f(z)$ is contained in the end/final condition.

Remarks:

- If we know the PDE, we can solve the PDE for solution $u(x, t, T)$.
- If we don't know PDE but we are given a set of sample paths, we can calculate $u(x, t, T)$ using Feynman-Kac formula, and use $u(x, t, T)$ to learn about the PDE.

Feynman-Kac formula for the forward equation

Definition of $u(x, t)$

Consider the function

$$u(x,t) = E\left(\delta\big(X(t) - x\big)\exp\left(-\int_0^t \psi(X(s),s)ds\right)\right)$$

where $\psi(x, t)$ is the fatality/growth rate at position x at time t.

Items of the discussion:

1) We need to explain the δ function in the average.
2) We need to derive the governing equation for $u(x, t)$.
3) We need to explain the meaning of $u(x, t)$ and discuss the distribution of $X(0)$.

Item #1: We first explain the δ function in the average.

Definition #1:

Let $I_{[x,x+\Delta x]}(z)$ be the indicator function defined as

$$I_{[x,x+\Delta x]}(z) = \begin{cases} 1, & x \le z \le x + \Delta x \\ 0, & \text{otherwise} \end{cases}$$

$u(x, t)$ can be viewed as

$$u(x,t) = \lim_{\Delta x \to 0} \frac{1}{\Delta x} E\left(I_{[x,x+\Delta x]}(X(t)) \exp\left(-\int_0^t \psi(X(s),s)ds \right) \right)$$

Definition #2: Method of test function

$$\int h(x)u(x,t)dx = E\left(\left(\int h(x)\delta(X(t)-x)dx \right) \exp\left(-\int_0^t \psi(X(s),s)ds \right) \right)$$

which leads to

$$\boxed{\int h(x)u(x,t)dx = E\left(h(X(t)) \exp\left(-\int_0^t \psi(X(s),s)ds \right) \right)}$$

Here $h(x)$ is any smooth function that decays to zero rapidly as $|x| \to \infty$.

The two definitions are equivalent to each other. We are going to use definition #2 in the derivation of the governing equation for $u(x, t)$.