Formulas in Lecture 13

Escape of a Brownian particle from a potential well

Smoluchowski-Kramers approximation in the limit of small particle

$$\underbrace{m\,dY = -bY\,dt - V'(X)dt + \sqrt{2k_B T b}\,dW}_{\text{Langevin equation}}$$

==> $$\underbrace{dX = -\frac{D}{k_B T}V'(X)dt + \sqrt{2D}\,dW}_{\text{over-damped Langevin equation}}$$

Dimensionless SDE

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

BVP for the average exit time $T(x)$

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

Exact integral solution of $T(x)$

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

Deep potential well

$V(x) = \Delta G\ \phi(x)$, $\min \phi(x) = \phi(x_1) = 0$, $\max \phi(x) = \phi(x_2) = 1$,

ΔG is moderately large.

Kramers' approximate solution of $T(x)$

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

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

Formulas in Lecture 14

Kramers' theory of reaction kinetics

Physical escape time in terms of physical quantities

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

Exponential distribution of the random exit time

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

The physical escape rate

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

Feynman-Kac formula for the backward equation

Consider the Ito interpretation of SDE

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

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

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

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 to time T and reaching position z at time T.

$u(x, t, T)$ = expected reward at final time T per unit population at time t | $X(t) = x$.

Each cell of the population gets its own reward. The growth increases the population size and increases the reward for the population.

Governing equation for $u(x, t, T)$ (not affected by function $f(z)$)

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

The final value problem (FVP)

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

The solution is given by the Feynman-Kac path integral formula

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