Lecture 20 Rare Events: II *

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1 Computing Transition Paths

The characterization of the MEP yields a natural methodology to compute the optimal transition path connecting metastable states A and B for the Brownian dynamics by a pseuso-steepest descent flow

$$\partial_t \boldsymbol{\varphi}(\alpha, t) = -(\nabla U(\boldsymbol{\varphi}))^{\perp} + r\hat{\boldsymbol{\tau}}, \qquad \boldsymbol{\varphi}(0) = A, \boldsymbol{\varphi}(1) = B \tag{1}$$

where $\boldsymbol{\varphi}(\alpha, t)$ is parametric curve of $\alpha \in (0, 1)$, $\hat{\boldsymbol{\tau}} = \boldsymbol{\varphi}_\alpha / |\boldsymbol{\varphi}_\alpha|$, and

$$(\nabla U(\boldsymbol{\varphi}))^{\perp} = \nabla U(\boldsymbol{\varphi}) - (\hat{\boldsymbol{\tau}} \otimes \hat{\boldsymbol{\tau}}) \cdot \nabla U(\boldsymbol{\varphi}).$$

The function r is just a Lagrange multiplier to ensure the equi-arclength parameterization

$$(|\boldsymbol{\varphi}_\alpha|)_\alpha = 0.$$

Note that the term $r\hat{\boldsymbol{\tau}}$ is not necessary for the evolution of a continuous path $\boldsymbol{\varphi}$, and the equi-arclength parameterization can be also replaced by other choices. They are taken in (1) for reason of numerics since otherwise the discretization points will collapse into state A or B after long time computations. This is called *string method* [1] in the literature.

The real implementation of (1) can be performed with the following simplified two-step iterations.

Step 1. Evolution of the steepest descent dynamics. For example, one can simply apply the

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forward Euler scheme

$$\tilde{\boldsymbol{\varphi}}_i^{n+1} = \boldsymbol{\varphi}_i^n - \Delta t \nabla U(\boldsymbol{\varphi}_i^n)$$

or Runge-Kutta type schemes for one or several steps.

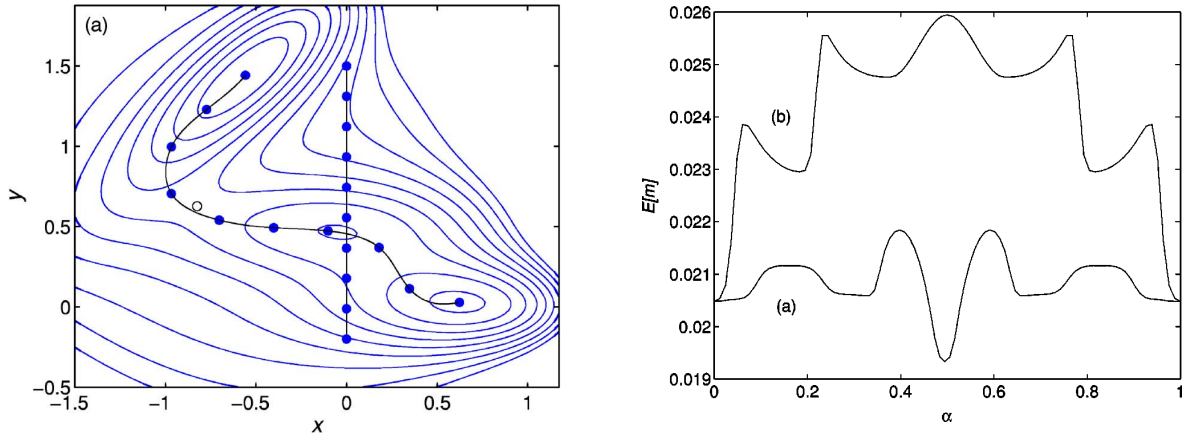
Step 2. Reparameterization of the string. One can redistribute the points $\{\tilde{\boldsymbol{\varphi}}_i^{n+1}\}$ according to equi-arclength or other weighted parameterizations. The positions of new points can be obtained by suitable interpolation as below.

a). Define $s_0 = 0$, $s_i = s_{i-1} + |\tilde{\boldsymbol{\varphi}}_i^n - \tilde{\boldsymbol{\varphi}}_{i-1}^n|$ for $i = 1, \ldots, N$, and $\tilde{\alpha}_i = s_i / s_N$.

b). Interpolate $\boldsymbol{\varphi}_i^{n+1}$ at $s_i = i/N$ from $\{\tilde{\alpha}_i, \tilde{\boldsymbol{\varphi}}_i^{n+1}\}$.

With such implementation, the boundary states can be chosen close to A and B instead of knowing their exact locations.

A simple illustration of the application of string method to the Mueller potential and micromagnetic switching is shown in Figure 1.



(a) Transition path in Mueller potential. (b) Magnetic energy along two transition paths.

Figure 1: Illustration of the performance of string method for 2D Mueller potential [3] and micromagnetic switching [2]. Left panel: The calculated MEP and initial string (the vertical straight line). Right panel: Magnetic energy along two transition paths found by string method with different initial values. The path (a) costs lower action than path (b).

2 Transition Rates

Let us quantify the difficulty of transitions in terms of mean first exit times from metastable states. Consider the one-dimensional diffusion process associated with the Brownian dynamics

$$dX_t = -\partial_x U(X_t)dt + \sqrt{2\varepsilon}dW_t. \tag{2}$$

We assume that $U(x)$ has two local minima at $x_A = -1$, $x_B = 1$ and a local maximum, which in this case is also a saddle point, at $x_C = 0$. We are interested in estimating the mean first passage time from x_A to x_B.

To do this, let us consider a diffusion process X_t in the domain $D = [a, b]$ with reflecting and absorbing boundary conditions at a and b, respectively. Denote the first passage time to b by

$$\tau_b := \inf\{t \geq 0 : X_t = b\}$$

and the mean first passage time starting from x by

$$\tau(x) = \mathbb{E}^x \tau_b.$$

Then the probability remaining in $[a, b)$ at time t has the form

$$R(x,t) = \mathbb{P}^x(X_t \in [a,b)) = \int_a^b p(y,t|x,0)dy = \mathbb{P}^x(\tau_b \geq t).$$

We have

$$\tau(x) = \mathbb{E}^x \tau_b = -\int_0^\infty t\partial_t R(x,t)dt = \int_0^\infty R(x,t)dt \tag{3}$$

under the assumption that $tR(x,t) \to 0$ as $t \to \infty$. Applying $\mathcal{L}$ to both sides of (3) we get

$$\begin{aligned}\mathcal{L}\tau(x) &= \int_0^\infty \mathcal{L}R(x,t)dt = \int_0^\infty \int_a^b \partial_t p(y,t|x,0)dydt \\ &= \int_a^b p|_{t=\infty} - p|_{t=0}dy = -\int_a^b \delta(x-y)dy = -1\end{aligned} \tag{4}$$

From the boundary conditions for the backward equation, we have $R(x,t)|_{x=b} = 0$ and $\partial_x R(x,t)|_{x=a} =$

0, which implies the boundary conditions for $\tau(x)$

$$\partial_x \tau(x)|_{x=a} = 0, \quad \tau(x)|_{x=b} = 0. \tag{5}$$

For our problem, we have

$$\mathcal{A}\tau(x) = -U'(x)\tau'(x) + \varepsilon\tau''(x) = -1 \ \text{ for } x \in (a,b) \quad \text{ and } \tau|_{x=b} = 0, \ \tau'|_{x=a} = 0. \tag{6}$$

The solution to this problem is given simply by

$$\tau(x) = \frac{1}{\epsilon}\int_x^b e^{\frac{U(y)}{\varepsilon}} \int_a^y e^{-\frac{U(z)}{\varepsilon}} dzdy. \tag{7}$$

Now let us take $a \to -\infty$, $b \to x_B$ and $x = x_A$, thus obtain

$$\tau(x_A) = \frac{1}{\epsilon}\int_{x_A}^{x_B} \int_{-\infty}^y e^{\frac{U(y)-U(z)}{\varepsilon}} dzdy. \tag{8}$$

Define the function $F(y,z) = U(y) - U(z)$ on the domain

$$S = \Big\{(y,z) : y \in [x_A, x_B] \text{ and } z \in (-\infty, y] \text{ for any } y\Big\}.$$

We have

$$\max_{(y,z)\in S} F(y,z) = \Delta U_{AB} = U(x_C) - U(x_A)$$

at $(y,z) = (x_C, x_A)$. With Laplace asymptotics in the 2D domain S, we have in the leading order

$$\tau(x) \approx \tau(x_A) \sim \frac{2\pi}{\sqrt{|U''(x_C)|U''(x_A)}} e^{\frac{\Delta U_{AB}}{\varepsilon}} \tag{9}$$

for any $x \le x_C - \delta_0$, where δ_0 is a positive constant. Here we implicitly require the condition that $U''(x_A)$ and $|U''(x_C)|$ are positive.

The formula (9) tells us that the transition time is exponentially large in $O(\Delta U_{AB}/\varepsilon)$, which is a typical result in rare event study. The derivations also tell that the length of transition times does not heavily depends on where the particle starts from. Even when the starting point x is close to

x_C, mostly it will relax to the neighborhood of x_A at first, then transit to x_B. The choice of the first passage point does not affect the final result very much. As long as x_b is beyond x_C in a nonzero distance, the transition time asymptotics remains the same.

In the considered case, we naturally define the transition rate

$$k_{AB} = \frac{1}{\tau(x_A)} = \frac{\sqrt{|U''(x_C)|U''(x_A)}}{2\pi} \exp\left(-\frac{\Delta U_{AB}}{\varepsilon}\right). \tag{10}$$

This is the celebrated Kramers reaction rate formula in the Brownian dynamics case, which is also called Arrhenius's law of reaction rates. In the multi-dimensional case with index-one saddle point x_C, one can also derive the reaction rate asymptotics

$$k_{AB} = \frac{\sqrt{|\lambda_s|}}{2\pi} \sqrt{\frac{\det H_A}{\det H_C^{\perp}}} \exp\left(-\frac{\Delta U_{AB}}{\varepsilon}\right). \tag{11}$$

for the Brownian dynamics, where $\lambda_s < 0$ is the unique negative eigenvalue of the Hessian $H_C = \nabla^2 U(\boldsymbol{x}_C)$, $H_A = \nabla^2 U(\boldsymbol{x}_A)$, $H_C^{\perp}$ is the restriction of H_C on the $(d-1)$-dimensional stable manifold at $\boldsymbol{x}_C$. The readers can be referred to [4, 5] for more details.

References

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