Lecture 10: Minimal energy paths and string method

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1.1 Transition events

We consider the Brownian dynamics in $\mathbb{R}^d$

$$dX_t = -\nabla V(X_t)\,dt + \sqrt{2\varepsilon}dB_t, \quad t \geq 0\,, \tag{1.1}$$

where $V : \mathbb{R}^d \to \mathbb{R}$ is a smooth potential function, B_t is a d-dimensional Brownian motion, and $\varepsilon > 0$ is a constant.

We know from previous lectures that, under certain conditions, the dynamics of X_t is ergodic and the invariant distribution of X_t is the Boltzmann distribution, whose probability density is $\pi(x) = \frac{1}{Z}\mathrm{e}^{-\frac{1}{\varepsilon}V(x)}$, for $x \in \mathbb{R}^d$, where $Z = \int_{\mathbb{R}^d} \mathrm{e}^{-\frac{1}{\varepsilon}V(x)}dx$ is a normalizing constant.

We introduce the basin of attraction associated to a local minimum point of V as follows.

Definition 1 (Basin of attraction)**.** Let $a \in \mathbb{R}^d$ be a local minimum point of V. The basin of attraction associated to a, denoted by $\Omega(a)$, is the set of states that converge to a under the flow map $X(t;x) : [0,+\infty) \times \mathbb{R}^d \to \mathbb{R}^d$ of the ODE

$$\frac{dX(t;x)}{dt} = -\nabla V(X(t;x))\,,\ t \geq 0\,, \quad X(0;x) = x\,. \tag{1.2}$$

Precisely,

$$\Omega(a) = \Big\{x \in \mathbb{R}^d \,\Big|\, \lim_{t\to+\infty} X(t;x) = a\Big\}. \tag{1.3}$$

We are interested in the case where ε is small. In this case, the perturbation of the noise in (1.1) is weak and the process X_t follows largely the negative gradient direction of the potential V. Once the process enters the basin of attraction associated to a local minimal point, say a, it will be attracted to the vicinity of a and will stay there for a relatively long time, before it can leave the basin of attraction $\Omega(a)$ under the perturbation of the noise.

Let $a, b \in \mathbb{R}^d$ be two local minimum points of V such that the *separatrix* $\partial\Omega(a) \cap \partial\Omega(b) \neq \emptyset$. When ε is small, numerical simulations of the transition of the process X_t from $\Omega(a)$ to $\Omega(b)$ become computationally challenging due to their rare occurances. Our goal is to characterize such transition events, e.g. to identify the most probable transition pathways.

1.2 Minimal energy path

Given two local minimum points a and b, we want to identify the most probable transition pathways of the process X_t (1.1) from a to b, as $\varepsilon \to 0$.

To this end, we apply the Wentzell-Freidlin theory [4] (also the large deviation theory in probability), which characterizes the probability of a path using the so-called action functional. Given $T > 0$, we define the space of all continuous transition paths from a to b as

$$\mathbf{P}_T = \Big\{\varphi \,\Big|\, \varphi \in C([0,T],\mathbb{R}^d),\, \varphi(0) = a,\, \varphi(T) = b\Big\}.$$

Then, the Wentzell-Freidlin theory states that

$$\lim_{\varepsilon\to 0} \varepsilon \ln P(B) = -\min_{\varphi\in B} I_T(\varphi)\,, \tag{1.4}$$

for any measurable subset $B \subset \mathbf{P}_T$, where I_T, the action functional associated to the dynamics (1.1), is defined as

$$I_T(\varphi) = \frac{1}{4}\int_0^T \left|\dot\varphi(t) + \nabla V(\varphi(t))\right|^2 dt\,. \tag{1.5}$$

Similarly, on a time interval $[T_1, T_2]$, where $-\infty < T_1 < T_2 < +\infty$, the action functional is

$$I_{[T_1,T_2]}(\varphi) = \frac{1}{4}\int_{T_1}^{T_2} \left|\dot\varphi(t) + \nabla V(\varphi(t))\right|^2 dt\,, \tag{1.6}$$

among all paths which satisfy

$$\varphi(T_1) = a, \quad \varphi(T_2) = b\,. \tag{1.7}$$

Now, we consider the lower bound of the action in (1.6). Recall that $\Omega(a)$ and $\Omega(b)$ are the basins of attraction associated to a and b, respectively, and that the separatrix $\partial\Omega(a)\cap\partial\Omega(b)$ is non-empty. For a path φ that satisfies (1.7), we assume that φ intersects with the separatrix at time T^*, where $T_* \in (T_1, T_2)$. We can derive

$$\begin{aligned}
I_{[T_1,T_2]}(\varphi) =& \frac{1}{4}\int_{T_1}^{T^*} \left|\dot\varphi(t) + \nabla V(\varphi(t))\right|^2 dt + \frac{1}{4}\int_{T^*}^{T_2} \left|\dot\varphi(t) + \nabla V(\varphi(t))\right|^2 dt \\
=& \frac{1}{4}\int_{T_1}^{T^*} \left|\dot\varphi(t) - \nabla V(\varphi(t))\right|^2 dt + \frac{1}{4}\int_{T^*}^{T_2} \left|\dot\varphi(t) + \nabla V(\varphi(t))\right|^2 dt \\
&+ \int_{T_1}^{T^*} \dot\varphi(t)\cdot\nabla V(\varphi(t))\,dt \\
\geq& \int_{T_1}^{T^*} \dot\varphi(t)\cdot\nabla V(\varphi(t))dt \\
=& V(\varphi(T^*)) - V(\varphi(T_1)) \\
\geq& V(c) - V(a) =: \Delta V,
\end{aligned} \tag{1.8}$$

where c is the state on $\Omega(a)\cap\partial\Omega(b)$ with the minimal potential, i.e.

$$c = \operatorname*{arg\,min}_{x\in\partial\Omega(a)\cap\partial\Omega(b)} V(x)\,. \tag{1.9}$$

On the other hand, there exists a path φ, called the minimal energy path, which satisfies that

$$\begin{aligned}
&\varphi(T_1) = a, \quad \varphi(T^*) = c, \quad \varphi(T_2) = b, \\
&\dot\varphi(t) = \begin{cases} \nabla V(\varphi(t)), & T_1 < t < T^*\,, \\ -\nabla V(\varphi(t)), & T^* < t < T_2, \end{cases}
\end{aligned} \tag{1.10}$$

for $T_1 \to -\infty, T_2 \to +\infty$. The lower bound of the action in (1.8) will be achieved by this path. Therefore, the limit in (1.4) implies that the minimal energy path is the most probable transition path when $\varepsilon \to 0$.

Intuitively, the transition happens in two stages. The first stage corresponds to the time $[T_1, T^*]$, during which the system follows the gradient direction of the potential V until it reaches the point c on the separatrix. In this stage, the system has to overcome the potential barrier and the system's potential increases from $V(a)$ to $V(c)$. The second stage corresponds to the time interval $[T^*, T_2]$, during which the system enters the basin of attraction associated to b and approaches to b following the negative gradient direction of V. In this stage, the system's potential decreases from $V(c)$ to $V(b)$.

Note that the minimal energy path in (1.10) can also be characterized as

$$\dot{\varphi}(t) \parallel \nabla V(\varphi(t)), \quad \text{or} \quad \nabla V^{\perp}(\varphi(t)) = 0, \tag{1.11}$$

where $\nabla V^{\perp}$ denotes the component of ∇V that is orthogonal to the path.

1.3 String method

String method is a numerical method for computing the minimal energy path (1.11) connecting two local minimum points a and b [1, 2]. Different from the parametrization of the path by time t adopted in the previous section, in the following we consider a geometric parametrization of the path by a parameter $s \in [0, 1]$.

Given an initial path $\varphi(s)$ such that $\varphi(0) = a$ and $\varphi(1) = b$, the string method evolves each state $\varphi(s)$ along the path according to the ODE

$$\frac{dX_t}{dt} = -\nabla V(X_t), \tag{1.12}$$

while keeping the magnitude of the tangent vector $|\dot{\varphi}(s)|$ to be uniform, that is, $|\dot{\varphi}(s)| \equiv C$ for $s \in [0, 1]$, where $C > 0$.

The dynamics of the path under the string method can be rather complicated. Assume that the path converges to a limiting path, which we again denote by φ. The convergence indicates that the path φ is invariant under the ODE (1.12), although each state $\varphi(s)$ may move along the path φ. This in turn implies that the gradient $\nabla V(\varphi(s))$ is parallel to the tangent direction $\dot{\varphi}(s)$. In other words, φ is a minimal energy path satisfying the characterization (1.11).

In practice, the path φ is discretized into N states $\varphi_0, \varphi_1, \ldots, \varphi_N \in \mathbb{R}^d$, where $\varphi_0 = a$ and $\varphi_N = b$. The string method updates these discrete states iteratively until certain convergence criteria is met. Let $\varphi_0^k, \varphi_1^k, \ldots, \varphi_N^k \in \mathbb{R}^d$ denote the discrete states at kth iteration, where $k \geq 0$. Each iteration consists of the following two steps.

1. Update:
$$\varphi_i^* = -\tau \nabla V(\varphi_i^k) + \varphi_i^k, \quad i = 0, 1, 2, \cdots, N,$$
where τ is the step-size.

2. Reparameterization. For $i = 1, \ldots, N-1$, the new state φ_i^{k+1} is obtained by linear interpolation between φ_j^* and φ_{j+1}^*:
$$\varphi_i^{k+1} = \frac{L_{j+1}^* - L_i}{L_{j+1}^* - L_j^*} \varphi_j^* + \frac{L_i - L_j^*}{L_{j+1}^* - L_j^*} \varphi_{j+1}^*,$$

where j is an index satisfying $L_j^* < L_i \le L_{j+1}^*$, and the lengths L_i^*, L_i are defined as

$$L_0^* = L_0 = 0\,,$$
$$L_i^* = \frac{\sum_{j=0}^{i-1} |\varphi_{j+1}^* - \varphi_j^*|}{\sum_{j=0}^{N-1} |\varphi_{j+1}^* - \varphi_j^*|}\,, \quad L_i = \frac{i}{N}, \quad i = 1, \cdots, N\,.$$

1.4 Computing saddle point

Let φ be the minimal energy path parametrized by $s \in [0,1]$ such that $\varphi(0) = a$, $\varphi(1) = b$ and $\varphi(s^*) = c$, where $s^* \in (0,1)$ and c is the state given in (1.9).

From the discussion above, we know that c is the state on the path φ with the highest potential V. At the same time, c is defined in (1.9) as the state on the separatrix (a manifold of dimension $d-1$) with the lowest potential. Combining these two facts, we know that c is an index-1 critical point of potential V. In particular, it satisfies

1. $\nabla V(c) = 0$.
2. The Hessian of V at c, denoted by $H = \mathrm{Hess}V(c) \in \mathbb{R}^{d\times d}$, has $d-1$ positive eigenvalues and one negative eigenvalue.

Tangent direction of φ at saddle point. It turns out that the tangent vector $\dot\varphi(s^*)$ is the eigenvector of H corresponding to its unique negative eigenvalue. To see this, notice that the minimal energy path satisfies (see (1.10))

$$\dot\varphi(s) = -C(s)\nabla V(\varphi(s))\,, \quad s \in (0,1)\,, \tag{1.13}$$

where $C(s)$ is some scalar quantity, such that $C(s) > 0$ for $s \in (s^*, 1)$ and $C(s) < 0$ for $s \in (0, s^*)$. Expanding ∇V at $c = \varphi(s^*)$ and utilizing the condition $\nabla V(c) = 0$, we obtain

$$\dot\varphi(s) = -C(s)\Delta s H \frac{\varphi(s) - \varphi(s^*)}{\Delta s} + O(|\varphi(s) - \varphi(s^*)|^2), \tag{1.14}$$

where $\Delta s = s - s^*$. Letting $s > s^*$ and $s \to s^*$, since

$$\lim_{s\to s^*} \frac{\varphi(s) - \varphi(s^*)}{\Delta s} = \dot\varphi(s^*),$$

from (1.14) we see that $C(s)\Delta s$ converges and

$$H\dot\varphi(s^*) = \mu\dot\varphi(s^*), \tag{1.15}$$

for some $\mu < 0$, which implies that μ is the unique negative eigenvalue of H and $\dot\varphi(s^*)$ is the corresponding eigenvector.

In practice, the minimal energy path computed by the string method is represented by finite discrete states. Among these discrete states, the state that has the highest potential V provides an approximation of the saddle point c. In the following, we discuss two numerical methods that yield accurate estimation of the saddle point.

1. Climbing image method [5].

   Due to the existence of the negative eigenvalue μ of $H = \mathrm{Hess}V(c)$, the saddle point c is an unstable stationary state under the dynamics (1.2), and the analysis above implies that the unique unstable direction (the eigenvector corresponding to μ) is

   $$\tau = \frac{\dot{\varphi}(s^*)}{|\dot{\varphi}(s^*)|}\,. \tag{1.16}$$

   Based on this observation, we can compute the saddle point c by updating an initial guess ϕ_0 of c using the dynamics

   $$\dot{\phi}_t = -\nabla V(\phi_t) + 2\langle \nabla V(\phi_t), \tau_0\rangle \tau_0\,, \quad t \geq 0\,, \tag{1.17}$$

   where τ_0 is an approximation of the normalized unstable direction τ. Intuitively, in (1.17), the vector field is modified so that the unstable direction at c becomes a stable direction. In fact, because $\nabla V(c) = 0$, it is clear that c is a stationary state under (1.17). Moreover, the Jacobian of the vector field of (1.17) at c is $-(I - 2\tau_0\tau_0^\top)H$, whose eigenvalues have negative real parts, provided that τ_0 is close to τ. This analysis shows that the saddle point c becomes a stable stationary state under (1.17). Therefore, as long as the initial state ϕ_0 is close to c and τ_0 is a good approximation of the unstable direction τ, the dynamics ϕ_t will converge to c as $t \to +\infty$.

   In practice, once the minimal energy path φ is identified by string method, one can choose the state with the highest potential as an initial guess of the saddle point, and obtain an approximation of the unstable direction (1.16) using finite difference method. After that, one can numerically compute the saddle point by simulating the dynamics (1.17).

2. Gentlest Ascent Dynamics (GAD) [3].

   The second method employs the following dynamics

   $$\begin{aligned} \dot{\phi}_t &= -\nabla V(\phi_t) + 2\frac{\langle \nabla V(\phi_t), \tau_t\rangle}{\langle \tau_t, \tau_t\rangle}\tau_t, \\ \dot{\tau}_t &= -\nabla^2 V(\phi_t)\tau_t + \frac{\langle \tau_t, \nabla^2 V(\phi_t)\tau_t\rangle}{\langle \tau_t, \tau_t\rangle}\tau_t, \end{aligned} \tag{1.18}$$

   in order to find an index-1 critical point of V. In contrast to the previous method, where the vector τ_0 approximating the unstable direction is fixed in (1.17), this method searches the saddle point and at the same time updates the approximation of the unstable direction. Note that simulating (1.18) requires computing the Hessian of V, whereas simulating (1.17) does not.

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