Transition path theory

July 09, 2025

Reminder

1. **Exercises**: solve 8 – 10 questions. Submission deadline: **23.07.2025**

2. **Course project**: Select one topic to conduct numerical experiment, and write a short report. Submission deadline: **27.07.2025**

3. give a 10-15 min **presentation**. Date: 11.07.2025 or 18.07.2025.

Part 1: Transition paths in the zero-temperature limit

Brownian dynamics

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1. Brownian dynamics in $\mathbb{R}^d$

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

where $\epsilon > 0$ is a constant.

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where $\epsilon > 0$ is a constant.

2. Invariant probability density is

$$\pi(x) = \frac{1}{Z}\mathrm{e}^{-\frac{1}{\epsilon}V(x)}\,, \quad \text{where } Z = \int_{\mathbb{R}^d} \mathrm{e}^{-\frac{1}{\epsilon}V(x)}dx.$$

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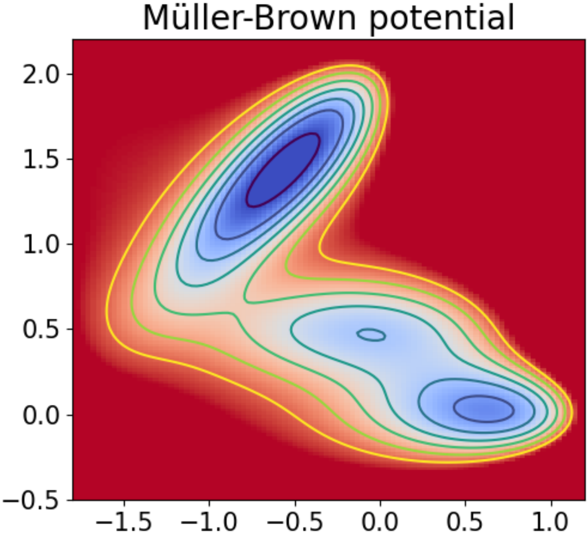
3. Assume that V has multiple local minima.

Example



Wentzell-Freidlin theory and minimal energy path

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1. For a subset B in path space, we have

$$\lim_{\epsilon \to 0} \epsilon \ln P(B) = -\min_{\varphi \in B} I_T(\varphi) \iff P(B) \approx \exp\Big(-\frac{1}{\epsilon}\min_{\varphi \in B} I_T(\varphi)\Big)\,.$$

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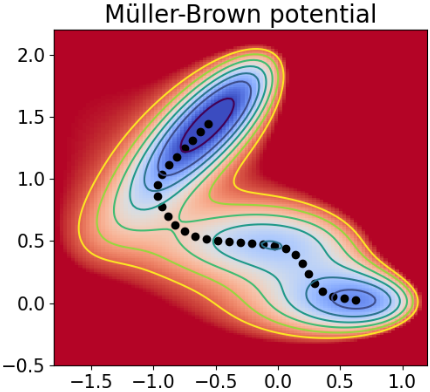
3. Minimizing action $\implies$ Minimal energy path (MEP):

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

Lower bound of action is achieved as $T_1 \to -\infty$, $T_2 \to +\infty$.

Example of MEP



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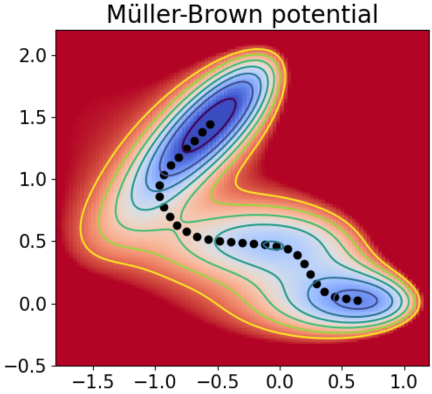

At low temperature, transition paths concentrate on a single path (MEP).

Part 2: Committor

Brownian dynamics

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3. Infinitesimal generator:

$$\mathcal{L}f = -\nabla V \cdot \nabla f + \frac{1}{\beta}\Delta f\,.$$

Sets A and B

Two disjoint closed subsets $A, B \subset \mathbb{R}^d$, such that $(A \cup B)^c \neq \emptyset$.

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Goal: to study the transition of X_t from A to B.

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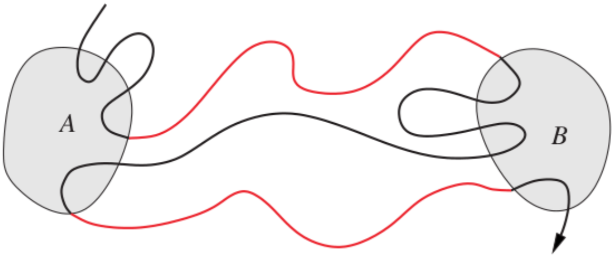
2. Committor: the probability that X_t will hit B before it hits A.

Definition (Forward committor)

$$q(x) = P(\tau_{B,x} < \tau_{A,x}), \quad x \in \mathbb{R}^d.$$

Illustration



Committor equation

Proposition

The committor $q(x) = P(\tau_{B,x} < \tau_{A,x})$ *solves*

$$\mathcal{L}q = 0, \quad \text{on } (A \cup B)^c$$
$$q|_{\partial A} = 0, \quad q|_{\partial B} = 1\,,$$

where $\mathcal{L} = -\nabla V \cdot \nabla + \frac{1}{\beta}\Delta$ *is the generator.*

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Proof.

1. Applying Ito's formula and taking expectation

$$\Longrightarrow \quad \mathbb{E}\big(q(X_t)\,\big|\,X_0 = x\big) = q(x) + \int_0^t \mathbb{E}\Big(\mathcal{L}q(X_s)\Big|X_0 = x\Big)ds\,.$$

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□

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\begin{aligned}
&\frac{1}{\beta} \int_{(A\cup B)^c} |\nabla f(x)|^2 \pi(x) dx \\
=&\frac{1}{\beta} \int_{(A\cup B)^c} |\nabla q(x)|^2 \pi(x) dx + \frac{1}{\beta} \int_{(A\cup B)^c} |\nabla (f-q)(x)|^2 \pi(x) dx \,.
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Therefore, q solves the minimization problem

$$\min_f \Big(\frac{1}{\beta} \int_{(A\cup B)^c} |\nabla f(x)|^2 \pi(x) dx \Big)$$

among all C^1-smooth $f : (A \cup B)^c \to \mathbb{R}$ such that $f|_{\partial A} = 0$ and $f|_{\partial B} = 1$.

Part 3: Transition path theory (TPT)

Random times

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3. $$\sigma_A^{(k)} = \sup\left\{t \,|\, \tau_A^{(k)} < t < \tau_B^{(k)},\, X_t \in A\right\}, \quad k \geq 1\,.$$

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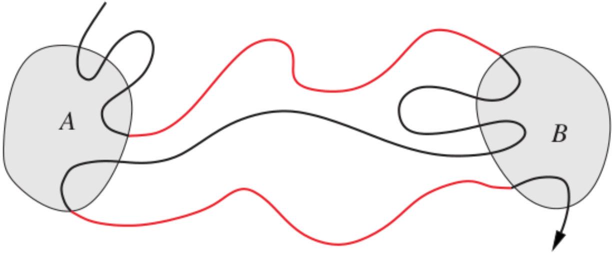
2. $[t_1, t_2]$ corresponds to a reactive segment, if and only if

$$X_{t_1} \in A, \quad X_{t_2} \in B, \quad \text{and } X_t \in (A \cup B)^c,\ \forall\ t_1 < t < t_2 .$$

Illustration



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Definition (Mean reaction time)

$$t_{AB}^R = \lim_{T\to+\infty} \frac{\sum_{k=1}^{M_T} (\tau_B^{(k)} - \sigma_A^{(k)})}{M_T}.$$

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1. q^- is the forward committor for the time-reversal of X_t from B to A.
2. For Brownian dynamics, $q^-(x) = 1 - q(x)$.

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$$Z_{AB} = \int_{(A\cup B)^c} \pi(x)q^-(x)q(x)dx = \lim_{T\to+\infty} \frac{\sum_{k=1}^{M_T}(\tau_B^{(k)} - \sigma_A^{(k)})}{T}.$$

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   $$q^- = 1 - q \quad \Longrightarrow \quad \pi^R(x) = Z_{AB}^{-1}\pi(x)(1 - q(x))q(x).$$

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$$k_{AB} = \lim_{T \to +\infty} \frac{M_T}{T},$$

where M_T is the total number of reactive segments within time $[0, T]$.

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Lemma

$k_{AB} = k_{BA}$.

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among all C^1-smooth $f : (A\cup B)^c \to \mathbb{R}$ such that $f|_{\partial A} = 0$ and $f|_{\partial B} = 1$.

Loss function for learning committor

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$$\begin{aligned}\mathrm{Loss}(q) =& \frac{1}{\beta N}\sum_{n=1}^{N} |\nabla q(X_n)|^2 \mathbb{1}_{(A\cup B)^c}(X_n) \\ & + \frac{\lambda_1}{N}\sum_{n=1}^{N}\left(|q(X_n)|^2 \mathbb{1}_A(X_n)\right) + \frac{\lambda_2}{N}\sum_{n=1}^{N}\left(|q(X_n)-1|^2 \mathbb{1}_B(X_n)\right).\end{aligned}$$

where $\lambda_1, \lambda_2 > 0$ are tunable parameters.

Part 4: Committor for Markov chains

Markov chains

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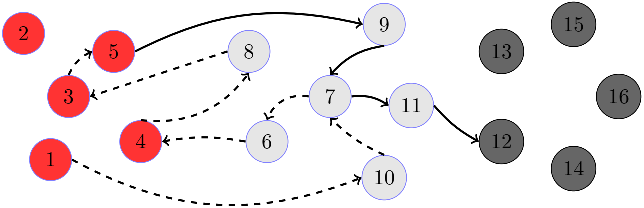
Proposition

The committor q solves

$$\begin{cases} \sum_{j=1}^{m} P_{ij} q_j = q_i, & i \in (A \cup B)^c\,, \\ q_i = 0, & i \in A\,, \\ q_i = 1, & i \in B\,. \end{cases}$$

Example



Example