L24. Transition Paths III.

Transition Path Path Sampling

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- How can we collect the TSE?

- “Answer”: collect (real-time) transition trajectories (paths) under the relevant condition
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Seems HARD! “Throw ropes between rough mountain passes in the dark”
In contrast to diffusive processes, which also take a long time to be “productive”
Transition Path Sampling (TPS): basic idea

- **Reactive** trajectories (transition paths) are rare to sample but they are **SHORT**

- **Importance** (Monte Carlo) sampling in the **reactive** trajectory space

- Need to sample trajectories with proper (relative) **weights** to gain meaningful insights and compute properties (e.g., rate constant)
Define the Transition Path ensemble

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\text{Trajectory of length } T
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Specifically for a **transition path**

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\mathcal{P}_{AB}[\mathbf{x}(T)] = h_A(\mathbf{x}_0) \mathcal{P}[\mathbf{x}(T)] h_B(\mathbf{x}_T) / Z_{AB}(T)
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Statistical weight for a general traj.\[
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1: \( x_0 \in A \)
0: \( x_0 \not\in A \)
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\[ Z_{AB}(T) = \int D\mathbf{x}(T) h_A(x_0) P[\mathbf{x}(T)] h_B(x_T) \]

normalization
Monte Carlo Sampling

Just like the MC approach we talked about earlier, we want to satisfy detailed balance - such that the sampling would produce the desired distribution.
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Substituting this in, rearrange - follow once again the standard MC recipe, we get the following Metropolis acceptance rule:

\[ P_{acc}[\mathbf{x}^{(o)}(T) \rightarrow \mathbf{x}^{(n)}(T)] = \min \left[ 1, \frac{P_{AB}[\mathbf{x}^{(n)}(T)] P_{gen}[\mathbf{x}^{(n)}(T) \rightarrow \mathbf{x}^{(o)}(T)]}{P_{AB}[\mathbf{x}^{(o)}(T)] P_{gen}[\mathbf{x}^{(o)}(T) \rightarrow \mathbf{x}^{(n)}(T)]} \right] \]
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which can be re-written as,

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P_{acc}[x^{(o)}(T) \rightarrow x^{(n)}(T)] = h_A[x^{(n)}_0] h_B[x^{(n)}_T] \times \min \left[ 1, \frac{P[x^{(n)}(T)] P_{gen}[x^{(n)}(T) \rightarrow x^{(o)}(T)]}{P[x^{(o)}(T)] P_{gen}[x^{(o)}(T) \rightarrow x^{(n)}(T)]} \right]
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A simple procedure

1. Generate a new pathway $x^{(n)}(T)$ from the existing one, $x^{(o)}(T)$, with generation probability $P_{\text{gen}}(x^{(o)}(T) \rightarrow x^{(n)}(T))$.

2. Accept or reject the new pathway according to a Metropolis acceptance criterion obeying detailed balance with respect to the transition path ensemble $\mathcal{P}_{AB}[x(T)]$.

3. If the new trajectory is accepted, it becomes the current one. Otherwise the old trajectory is retained as the current trajectory again.

4. Repeat starting from 1.

**Need:** 1. Move type and the corresponding generation probability. 2. Explicit expression for the acceptance probability.
A simple procedure

1. Given
2. Accept $V(x)$
3. If true
4. Repeat

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A simple procedure

1. Generate type and the corresponding generation probability.
2. Explicit expression for the
   acceptance probability.
3. If trajectory $V(x)$
4. Repeat one, $x^{(o)}(T)$,

In this way, we sample the transition paths with LARGE statistical weights!
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2. Accept or reject the new pathway according to a Metropolis acceptance criterion obeying detailed balance with respect to the transition path ensemble \( \mathcal{P}_{AB}[x(T)] \).

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In this way, we sample the transition paths with **LARGE** statistical weights!
Example: Shooting move

\[ P_{\text{gen}}[x^{(o)}(\mathcal{T}) \rightarrow x^{(n)}(\mathcal{T})] = p_{\text{gen}}[x^{(o)}_{t'} \rightarrow x^{(n)}_{t'}] \prod_{i=t'/\Delta t}^{\mathcal{T}/\Delta t-1} p(x^{(n)}_{i\Delta t} \rightarrow x^{(n)}_{(i+1)\Delta t}) \]

\[ \times \prod_{i=t'/\Delta t}^{t'/\Delta t} \bar{p}(x^{(n)}_{i\Delta t} \rightarrow x^{(n)}_{(i-1)\Delta t}) \cdot \]

\[ P_{\text{acc}}[x^{(o)}(\mathcal{T}) \rightarrow x^{(n)}(\mathcal{T})] = h_A[x^{(n)}_0] h_B[x^{(n)}_{\mathcal{T}}] \times \min \left[ 1, \frac{P[x^{(n)}(\mathcal{T})]}{P[x^{(o)}(\mathcal{T})]} \frac{P_{\text{gen}}[x^{(n)}(\mathcal{T}) \rightarrow x^{(o)}(\mathcal{T})]}{P_{\text{gen}}[x^{(o)}(\mathcal{T}) \rightarrow x^{(n)}(\mathcal{T})]} \right] \]
Example: Shooting move

Under specific conditions (reversible integration, stationary state, initial condition in equilibrium, symmetric generation probability) one can show that the acceptance probability is simplified:

\[
P_{\text{gen}}[x^{(o)}(T) \to x^{(n)}(T)] = p_{\text{gen}}[x^{(o)}_{t'} \to x^{(n)}_{t'}] \prod_{i=t'/\Delta t}^{T/\Delta t-1} p \left( x^{(n)}_{i\Delta t} \to x^{(n)}_{(i+1)\Delta t} \right) \\
\times \prod_{i=1}^{t'/\Delta t} \tilde{p} \left( x^{(n)}_{i\Delta t} \to x^{(n)}_{(i-1)\Delta t} \right).
\]
Example: Shooting move

\[ P_{\text{gen}}[x^{(o)}(\mathcal{T}) \rightarrow x^{(n)}(\mathcal{T})] = P_{\text{gen}}[x_{t'}^{(o)} \rightarrow x_{t'}^{(n)}] \prod_{i=t'/\Delta t}^{\mathcal{T}/\Delta t - 1} p(x_{i\Delta t}^{(n)} \rightarrow x_{(i+1)\Delta t}^{(n)}) \]

\[ \times \prod_{i=1}^{t'/\Delta t} \bar{p} \left(x_{i\Delta t}^{(n)} \rightarrow x_{(i-1)\Delta t}^{(n)} \right). \]

Under specific conditions (reversible integration, stationary state, initial condition in equilibrium, symmetric generation probability) one can show that the acceptance probability is simplified:

\[ P_{\text{acc}}[x^{(o)}(\mathcal{T}) \rightarrow x^{(n)}(\mathcal{T})] = h_A[x_0^{(n)}] h_B[x_T^{(n)}] \min \left[ 1, \frac{\rho(x_{t'}^{(n)})}{\rho(x_{t'}^{(o)})} \right] \]
The efficiency of sampling depends on the magnitude of perturbation - or, acceptance ratio. Model studies indicate that acceptance ratio of 40% is reasonable.

\[
P_{\text{acc}}[x^{(o)}(\mathcal{T}) \rightarrow x^{(n)}(\mathcal{T})] = h_A[x^{(n)}_0] h_B[x^{(n)}_\mathcal{T}] \min \left[ 1, \frac{\rho(x^{(n)}_t)}{\rho(x^{(o)}_t)} \right]
\]

1. Randomly select a time slice \( x^{(o)}_t \) on a existing trajectory \( x^{(o)}(\mathcal{T}) \).

2. Modify the selected time slice by adding a random displacement: \( x^{(n)}_t = x^{(o)}_t + \delta x \). The random displacement must be consistent with the ensemble of initial conditions and should be symmetric with respect to the reverse move.

3. Accept the new shooting point with probability \( \min[1, \rho(x^{(n)}_t)/\rho(x^{(o)}_t)] \). Abort the trial move if the shooting point is rejected.

4. If the shooting point is accepted, integrate the equations of motion forward to time \( \mathcal{T} \) starting from \( x^{(n)}_t \).

5. Abort the trial move if the final point of the path segment, \( x^{(n)}_{\mathcal{T}} \), is not in \( B \) and continue otherwise.

6. Integrate the equations of motion backward to time \( 0 \) starting from \( x^{(n)}_t \).

7. Accept the new trajectory if its initial point \( x^{(n)}_0 \) is in \( A \) and reject it otherwise.

8. In case of a rejection the old trajectory is counted again in the calculation of path averages. Otherwise the new trajectory is used as the current one.
A few other practical issues

- Other move types (e.g., shift etc.), sampling tricks (parallel-T)
- Definition for the A/B basin
- The first trajectory (high-T/steering, then equilibrate)
- Length of trajectories $T$ (larger than the max. transition time)
- Analysis of the results

$$\mathcal{P}_{AB}[x(T)] = h_A(x_0)\mathcal{P}[x(T)]h_B(x_T)/Z_{AB}(T)$$

Only need a good order parameter and range for TPS

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![Diagram](image.png)
Example: Water autoionization

Reac. region

30fs

60fs

Prod. region

TS region

Key: coincidence of rare & collective solvent fluctuations (ionization & H-bond rearrangement)


Real-time: 10 hrs. TPS time: 200 fs (CPMD) Order-parameter: $l=0$ (neutral) $l \geq 3$ (ionic)
Critical solvent fluctuations

A

B

C

$E - E_{\text{neut}} \ (\text{kcal/mol})$

$q$

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