March 16 2011
Speaker: Maria Cameron
Transitions between metastable states in gradient systems.
Continuous-time Markov chains.
Transition Path Theory.

1. Gradient systems.

\[ dx = -V(x) dt + \sqrt{2\rho} dW, \quad x \in \mathbb{R}^n \]

 Wentzell-Freidlin Action Functional:

\[ S_T^*(\phi) = \frac{1}{2} \int_0^T |\dot{\phi} + \nabla V(x)|^2 dt, \quad \phi = \text{path}, \quad T = \text{time} \]

- Note: if \( \dot{\phi} = -V(\phi) \) on \([t_1, t_2]\), the contribution into this functional is zero on \([t_1, t_2]\).

- Now suppose that \( x_a \) is a minimum of \( V(x) \).
Let us relate the potential \( V(x) \) and the quasipotential.

A region surrounding the minimum \( x_a \) and containing no other points with \( \nabla V = 0 \).

\[ U^*_{x_a}(x) = \min_{\phi, \text{path}} \left\{ S_T^*(\phi) \mid \phi(0) = x_a, \phi(T) = x \right\} \]

\[ 1a^2 + 1b^2 \geq 2a + b \]

\[ a = 1, b = -1 \]

We can always choose \( 1\dot{\phi} = ||\nabla V|| \).

\[ S_T^*(\phi) = \frac{1}{2} \int_0^T (\dot{\phi}, \dot{V}) + (\nabla V, \nabla V) dt \geq \frac{1}{2} \int_0^T 2||\dot{\phi}||^2 + 2(\dot{\phi}, \nabla V) dt = (V(x) - V(x_a)) + \int_0^T ||\nabla V|| dt \]

\( \int_0^T ||\nabla V|| dt \) is independent of the parameterization of the path \( \phi \).

Therefore \( S_T^*(\phi) \geq (V(x) - V(x_a)) + \int_0^T ||\nabla V|| dt \).
The integral $\int_{s_0}^{s_1} \langle \mathbf{y}_s \cdot \mathbf{v} \rangle ds = V(x) - V(x_A)$, 

"\(=\)" is achieved if \(s_0 \neq s_1\) for \(\mathbf{v}\).

Thus, \(\min_{s_T} S_T(x) = 2(V(x) - V(x_A))\),

\[ U(x) = 2(V(x) - V(x_A)) \]

- Two minima separated by a single mountain pass.

\[ \begin{array}{|c|c|}
\hline
T_A & \text{time spent in } \mathcal{D}_A, \\
\hline
n_{AB} & \# \text{ of transitions from } A \text{ to } B \\
\hline
\end{array} \]

\[ U(x_s) = \min_{s_T} S_T(x_s) = 2(V(x_s) - V(x_A)) \]

Note also, \(\min_{s_T} S_T(x_B) = \min_{s_T} S_T(x_s)\), and this minimum is achieved on the path \(\mathcal{P}\) going directly uphill from \(x_A\) to \(x_s\), and directly downhill from \(x_s\) to \(x_B\), on \(T = +\infty\).

Such a path is called a "Minimum Energy Path" or "MEP." (This name is historical.)

**Def.** Let \(x_A\) and \(x_B\) be two minima of \(V(x)\). Then any path satisfying

\[ \mathcal{P}(t) = x_A, \quad \mathcal{P}(\infty) = x_B \]

is called a minimum energy path.

We actually are interested in such curves rather than paths.
Is the global minimum of the W-F action the right measure of the transition rate?

Not always!

**Example 1**  A three-well potential (symmetric)

For simplicity, let

\[ V(x_A) = V(x_B) = 0 \]
\[ V(x_{AB}) = 3 \]
\[ V(x_{AC}) = V(x_{BC}) = 2 \]

Then

\[ \min_{\phi, T} S_T = 2(V(x_{AB}) - V(x_A)) = 2V(x_{AB}) \]

\[ \min_{\phi, T} S_T = 2(V(x_{AC}) - V(x_A)) = 2V(x_{AC}) \]

\[ \min_{\phi, T} S_T = 2(V(x_{CB}) - V(x_C)) \]

Note: there are two MEP's from \( x_A \) to \( x_B \)

Continuous-time Markov chain

If \( V_C = V(x_C) = 1 \),

\[ S(T_{\infty}) \]

\[ S(T_{\infty}) \]
The generator matrix \( Q \) of the size \((\# \text{ of states}) \times (\# \text{ of states})\) is defined by the following properties:

\[
(i) \quad 0 \leq -q_{ii} < \infty \quad \forall i \\
(ii) \quad q_{ij} \geq 0 \quad \forall i \neq j \\
(iii) \quad \sum_j q_{ij} = 0 \quad \forall i
\]

For the Markov chain \((\text{A})\)

\[
Q = \begin{pmatrix}
-3\beta & e^{-3\beta} & e^{-2\beta} \\
-e^{-3\beta} & -3\beta & e^{-2\beta} \\
e^{-(\beta/2) - \beta} & e^{-(\beta/2) + \beta} & -2e^{-(\beta/2) - \beta}
\end{pmatrix}
\]

The continuous-time Markov Chain \((\text{A})\) can be reduced to a discrete time Markov Chain. For this, we need to calculate the jump (or transition) matrix \( \Pi \) by the following rules:

\[
\Pi_{ij} = \begin{cases} 
\frac{q_{ij}}{q_i} & \text{if } i \neq j \text{ and } q_i > 0 \\
0 & \text{if } j = i \text{ and } q_i > 0 \\
\end{cases}
\]

The rate of escape \( \boxed{q_i = -q_{ii}} \) from the state \( i \).

The rate of transition \( \boxed{\Pi_{ij} = \text{probability to jump from state } i \text{ to state } j} \).
For the Markov Chain (A) the jump matrix $\Pi$ is

$$
\Pi = \begin{pmatrix}
0 & \frac{e^{-\beta}}{1 + e^{-\beta}} & \frac{1}{1 + e^{-\beta}} \\
\frac{e^{-\beta}}{1 + e^{-\beta}} & 0 & \frac{1}{1 + e^{-\beta}} \\
\frac{1}{2} & \frac{1}{2} & 0
\end{pmatrix}
$$

In the limit of $\beta \to \infty$, $\Pi$ becomes

$$
\Pi = \begin{pmatrix}
0 & 0 & 1 \\
0 & 0 & 1 \\
\frac{1}{2} & \frac{1}{2} & 0
\end{pmatrix}
$$

that corresponds to the discrete time Markov chain [A:A]

The Markov chain (A:A) shows that, despite for $V_c < 1$ the Wentzell-Freidlin action is smaller for MEP1, the dominant mechanism of transition from $x_A$ to $x_B$ is via MEP2 that is through $x_c$.

The transition rate from $x_A$ to $x_B$ is exponentially equivalent to the minimum of the rates from $x_A$ to $x_c$ and from $x_c$ to $x_B$, i.e.

$$
\Gamma_{AB} \approx \min \{ e^{-\beta}, e^{-\beta(2-V_c)} \}
$$

Therefore, the transition rate from $x_A$ to $x_B$ is not necessarily determined by the minimal value of the Wentzell-Freidlin action
Example 2 An asymmetric three-well potential.

![Diagram](image)

Continuous-time Markov chain:

\[
Q = \begin{pmatrix}
-1 + e^{-3\beta} & e^{-2\beta} & e^{-3\beta} \\
e^{-3\beta} & -1 + e^{-3\beta} & e^{-3\beta/2} \\
e^{-3\beta/2} & e^{-3\beta/2} & -1 + e^{-3\beta/2}
\end{pmatrix}
\]

Jump matrix \( \Pi \):

\[
\Pi = \begin{pmatrix}
1 & 0 & 0 \\
\frac{1}{1 + e^{-3\beta}} & 0 & 1 \\
\frac{1}{1 + e^{-3\beta/2}} & 1 & 0
\end{pmatrix}
\]

\( \beta \to \infty \): \( \Pi \approx \begin{pmatrix}
0 & 0 & 1 \\
0 & 0 & 1 \\
0 & 1 & 0
\end{pmatrix}
\]

In this chain, state A is transient.
Since the state A is transient, we need to continue the process of reduction of the original gradient system to a reduced continuous-time Markov chain where we want to leave only the dominant mechanisms of transition between any pair of states.

For now, we have obtained the B ⇔ C cycle. We can treat B ⇔ C as a macrostate.

We are interested in the exit times and channels from this macrostate B ⇔ C.

The exit time from the state B in the cycle B ⇔ C is
\[ t_B = e^{\frac{3\beta}{2}} \]

The exit time from the state C in the cycle B ⇔ C is
\[ t_C = e^{\beta} \]

Given that the system is in the B ⇔ C cycle, the probability to find it in B:
\[ P_B = \frac{e^{\frac{3\beta}{2}}}{1 + e^{\frac{3\beta}{2}}} = \frac{1}{1 + e^{-\frac{3\beta}{2}}} \]

...to find it in C:
\[ P_C = \frac{e^{\beta}}{1 + e^{\frac{3\beta}{2}}} = \frac{e^{-\frac{3\beta}{2}}}{1 + e^{-\frac{3\beta}{2}}} \]

The exit rate from the cycle B ⇔ C through the state B is
\[ P \cdot r_{BA} = \frac{e^{-\frac{3\beta}{2}}}{1 + e^{-\frac{3\beta}{2}}} \]

The exit rate from the cycle B ⇔ C through the state C is
\[ P \cdot r_{CA} = \frac{e^{\beta} \cdot e^{-\frac{3\beta}{2}}}{1 + e^{\frac{3\beta}{2}}} = \frac{e^{-2\beta}}{1 + e^{\frac{3\beta}{2}}} \]
Now we define a quasimatrix $Q_4$ that is obtained from the matrix $Q$ by replacing the rates $r_{AA}$ and $r_{CA}$ with the corrected rates, and replacing transition rates from the cycle $B \leftrightarrow C$ with a single number, the exit rate from the cycle $B \leftrightarrow C$.

$$Q_4 = \begin{pmatrix}
-e^{3\beta} & e^{3\beta} & e^{-2\beta} \\
\frac{e^{-3\beta}}{1+e^{-\beta}} & \frac{1}{1+e^{\beta}} & -e^{-2\beta} \\
\frac{-2\beta}{1+e^{\beta}} & \frac{e^{-3\beta} + e^{-2\beta}}{1+e^{-\beta}} & \frac{1}{1+e^{\beta}}
\end{pmatrix}$$

Jump quasimatrix $\Pi_4 = \begin{pmatrix}
0 & \frac{e^{-\beta}}{1+e^{-\beta}} & \frac{1}{1+e^{\beta}} \\
\frac{e^{-\beta}}{1+e^{-\beta}} & \frac{1}{1+e^{\beta}} & 0 \\
\frac{1}{1+e^{\beta}} & 0 & 0
\end{pmatrix}$

$\beta \to \infty: \quad \Pi_4 \to \begin{pmatrix}
0 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 0
\end{pmatrix}$

Q: What is wrong with this approach?

A: Suppose we are interested in transitions between metastable states $x_A$ and $x_B$. It is hard to identify all of the intermediate minima and compute the minimal W.F. action for every pair of them.