LDT of Rare Events

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When we discussed Markov chain models of materials we assumed that the transition rates were obtained by some means, and then focused on the resulting chain. But how to obtain transition rates from the underlying microscopic dynamics?

Large Deviation theory gives the exponent of exponentially unlikely (rare) events

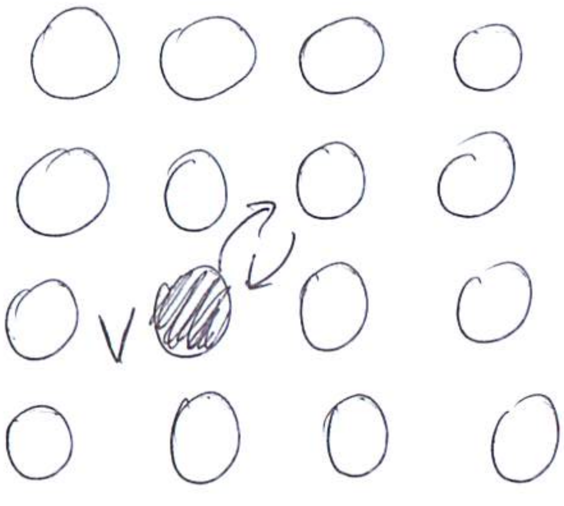
As an example, we consider the Freidlin-Wentzell theory for rare events in weakly perturbed dynamical systems.

Let

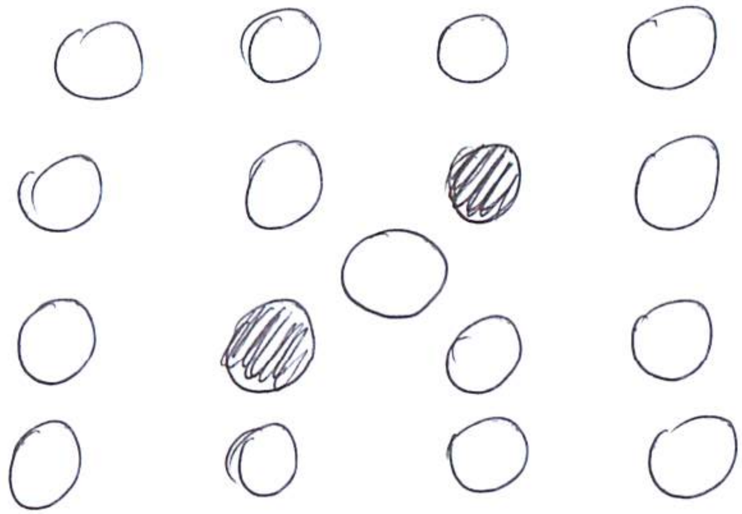
$$dx_\varepsilon(t) = b(x_\varepsilon)\,dt + \sqrt{\varepsilon}\,dB(t)$$

and consider how unlikely it is to see a trajectory that transitions (visits) two states A & B which would never happen in the deterministic system.

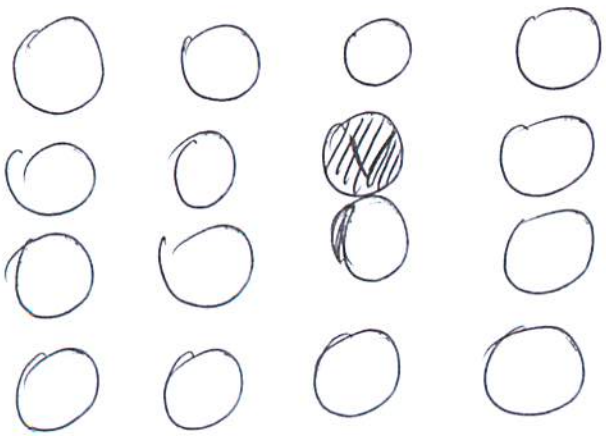
Think of a vacancy in the crystal lattice of a metal jumping from one site to another.



Initial



Transition state



(unlikely and requires a push from the noise)

If the crystal lattice is stable, zero temperature dynamics would not transition

$\ddot{x} = F(x) = -\nabla U(x)$ will remain near $x(0)$ forever if $x(0)$ is close to a minimum of $U(x)$.

If you give enough momentum you can melt the crystal, of course, but if below the melting temperature the vacancy can still diffuse with help from the momenta of sufficiently many particles. We approximate this here with white noise $\sqrt{\varepsilon = k_B T}\ \dot{W}(t)$ for simplicity (but also not a bad approximation)

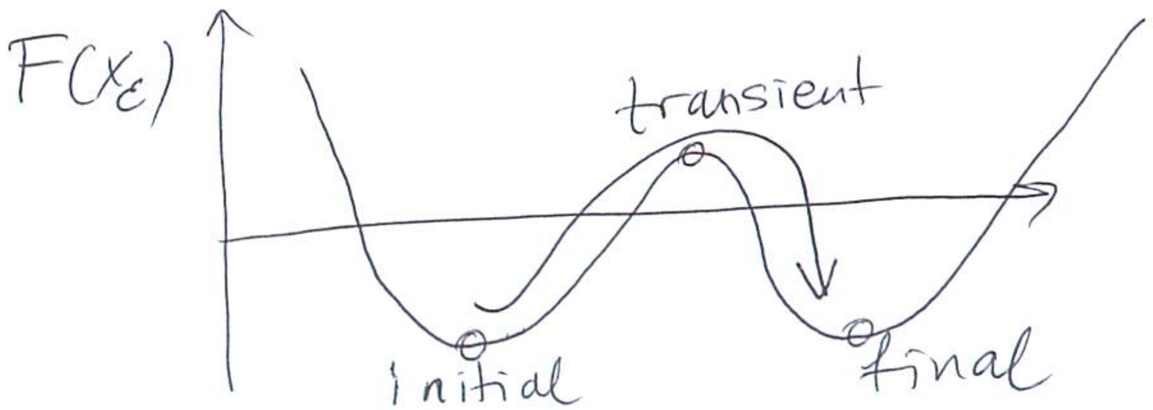
Think of using the vacancy position as a coarse-grained DOF and writing a Langevin equation:

$$\begin{bmatrix} q(t) \\ \dot{q}(t) \end{bmatrix} = -N(X_\varepsilon)\cdot\underbrace{\nabla F(X_\varepsilon)}_{\text{free energy}} + \sqrt{2k_B T}\; B(X_\varepsilon)\, W(t)$$

vacancy only

$$\begin{bmatrix} q(t) \\ \dot{q}(t) \end{bmatrix} \equiv X_\varepsilon$$

where $BB^* = \dfrac{N+N^*}{2}$



How often does the transition happen?

Go back to general

$$\dot{X}_\varepsilon = b(X_\varepsilon) + \sqrt{\varepsilon}\, W(t)$$

Consider the probability of a path

$P[X_\varepsilon(t)]$ – path <u>functional</u>, $t \in [0, \tau]$

This obeys an LD principle

$$\boxed{\begin{aligned} &\lim_{\varepsilon \to 0} \varepsilon \ln \left[P\left(\sup_{0 \le t \le \tau} |X_\varepsilon(t) - X(t)| < \delta \right) \right] \\ &= -J[X(t)] = -\frac{1}{2} \int_0^\tau [\dot{X} - b(X)]^2 \, dt \\ &\text{for any } \delta > 0, \text{ small} \end{aligned}}$$

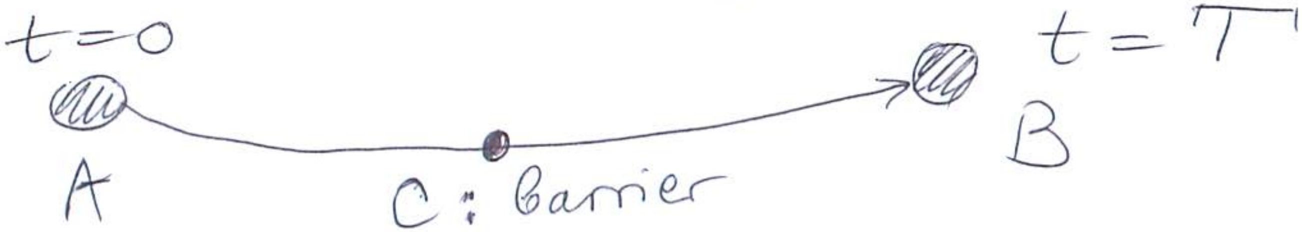
So we write in short-hand

$$P_\varepsilon[x] \asymp e^{-\mathcal{J}[x]/k_B T}$$

action functional or entropy of path

Note that $\mathcal{J}[x]$ has a unique zero corresponding to the deterministic path $\dot{x}_{det} = b(x_{det})$.

Deviations from the deterministic path are exponentially unlikely



The most likely transition path (8)
from $A \to B$ is the solution of

$$\boxed{J^* = \inf_{T} \inf_{x(t):\, x(0)=A,\, x(T)=B} J[x(t)]}$$

i.e. the minimum action path.

Take $b(x) = -\nabla U(x)$ [gradient flow]

$$J[x(t)] = \frac{1}{2}\int_0^T [\dot{x} + \nabla u(x)]^2 \, dt =$$

$$= \frac{1}{2}\int_0^T (\dot{x} - \nabla u)^2 \, dt + 2\int_0^T \dot{x}\cdot\nabla u \, dt$$

$$\geq 2 \int \dot{u} \, dt = 2\left(u(x(T)) - u(x(0))\right)$$

If $\dot{x} = \nabla U$ (uphill) ⑨

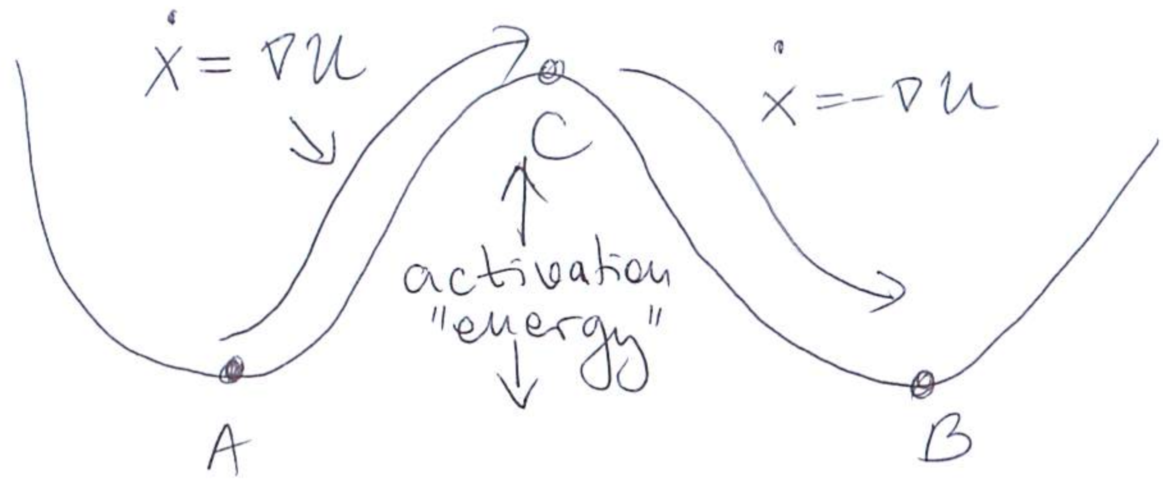
$$J[x] = \frac{1}{2}\int_0^T 2^2 \dot{x}(\nabla U)\,dt = 2\int_0^T \dot{u}\,dt$$

so this path achieves the minimum.

Down $\left\{\begin{array}{l} \text{So if } U(x(0)) > U(x(T)) \\ \text{then } J^* = 0 \text{ and } \underset{\text{downhill}}{\boxed{\dot{x} = -\nabla U(x)}} \end{array}\right.$

Up $\left\{\begin{array}{l} \text{and if } U(x(0)) < U(x(T)) \\ \text{then } J^* = 2\Delta U \text{ and } \underset{\text{uphill}}{\boxed{\dot{x} = \nabla U}} \end{array}\right.$

Note that the infimum is $\boxed{T = \infty}$

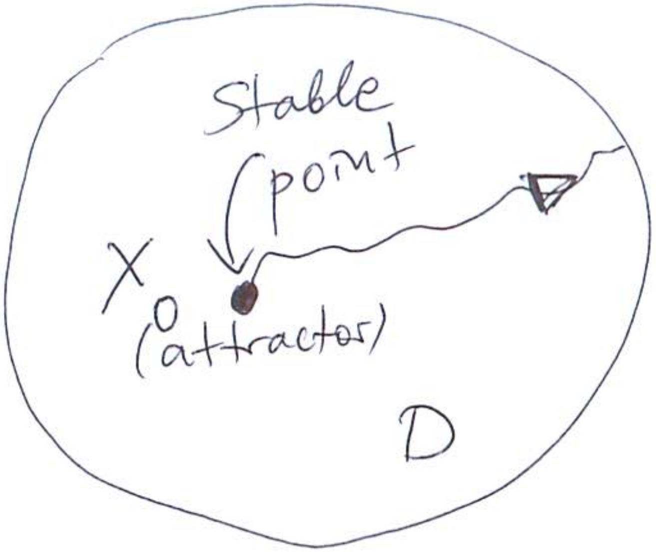


Arrhenius scaling

$$P\big(x(T) = B \mid x(0) = A \big) \asymp e^{-\frac{(U(C) - U(A))}{k_B T}}$$

where C is the point that has the lowest lying energy over all possible transition paths. btw $A \to B$.

[How long does it take for the transition to occur at finite but small ε? This is a <u>rate</u> for KMC.



Let $\overline{\tau}_\varepsilon$ be the escape time from a region D around a stable point of the deterministic dynamics.

Friedlin–Wentzell:

$$\boxed{\overline{\tau}_\varepsilon \longrightarrow e^{V^*/\varepsilon}}$$

i.e.

$$\lim_{\varepsilon \to 0} \varepsilon \ln \overline{\tau}_\varepsilon = V^*$$

$$V^* = \inf_{\underline{\overline{x}} \in \partial D} \; \inf_{t \geq 0} \; \inf_{\substack{x(t):\, x(0)=x_0 \\ x(t) = \underline{\overline{x}}}} J[x(t)]$$

KMC transition rate

$$\boxed{\Gamma \sim e^{-\Delta U_a / k_B T}}$$

Arrhenius

Note that LDT only gives the exponent, i.e., the scaling as $k_B T \to 0$ (or $\Delta U_a \gg k_B T$) and does not give the prefactor. <u>Transition State</u> and <u>Transition Path</u> theory provides more detailed information (see E. Vanden-Eijnden)

<u>Multidimensional</u>: generalization:

$$dx_\varepsilon = b(x_\varepsilon)\,dt + \sqrt{\varepsilon}\,\sigma(x_\varepsilon)\,dw$$

$$J[x(t)] = \frac{1}{2}\int_0^\tau [\dot{x} - b(x(t))]^T A^{-1} [\dot{x} - b(x(t))]\,dt$$

where $A = \sigma\sigma^T$ (covariance of noise)