

Molecular Dynamics and Accelerated Molecular Dynamics

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Lecture 3

Tutorial Lecture Series
Institute for Pure and Applied Mathematics (IPAM)
UCLA
September 13-16, 2005

Acknowledgment: DOE/BES

Overall Outline

Day 1: Molecular dynamics methods

Day 2: Molecular dynamics methods

Day 3: (accuracy of MD), Infrequent events, transition state theory, saddle finding, etc.

Day 4: Accelerated molecular dynamics methods

Trajectory Accuracy

Hamiltonian systems, with very few exceptions, are chaotic.

Two trajectories differing initially by an infinitesimal amount (Δx) will diverge exponentially in time -- Lyapunov instability:

$$\Delta x(t) = \Delta x(0)\exp(\lambda t)$$

Thus, any imperfect integrator (and all are imperfect) introduces errors that guarantee the trajectory diverges from the true trajectory.

---> How can we know that we are generating the correct results in MD?

Example of chaotic divergence

“cos” potential:
$$V_{cos}(x, y) = \cos(2\pi x)(1 + d_1 y) + d_2 \frac{(2\pi)^2}{2} y^2$$

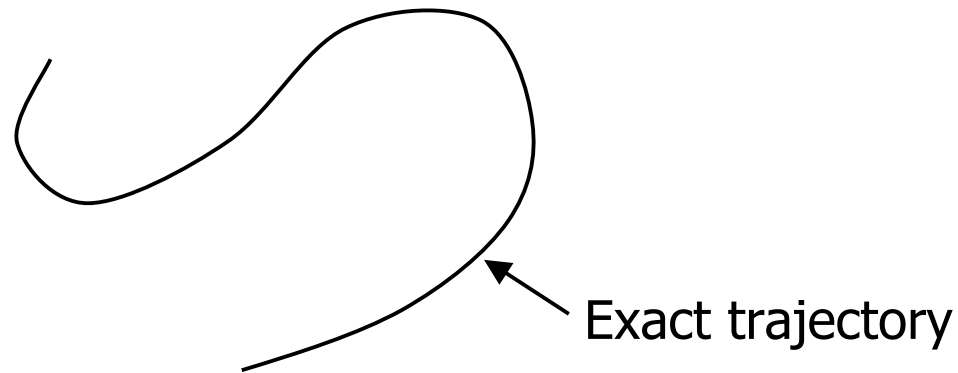
Trajectory Accuracy

How can we know that we are generating the correct results in MD?

Answer: We can't know for sure, but there is hope...

Shadow Orbits

In some cases, there is actually a “shadow orbit” that closely follows the integrated trajectory.



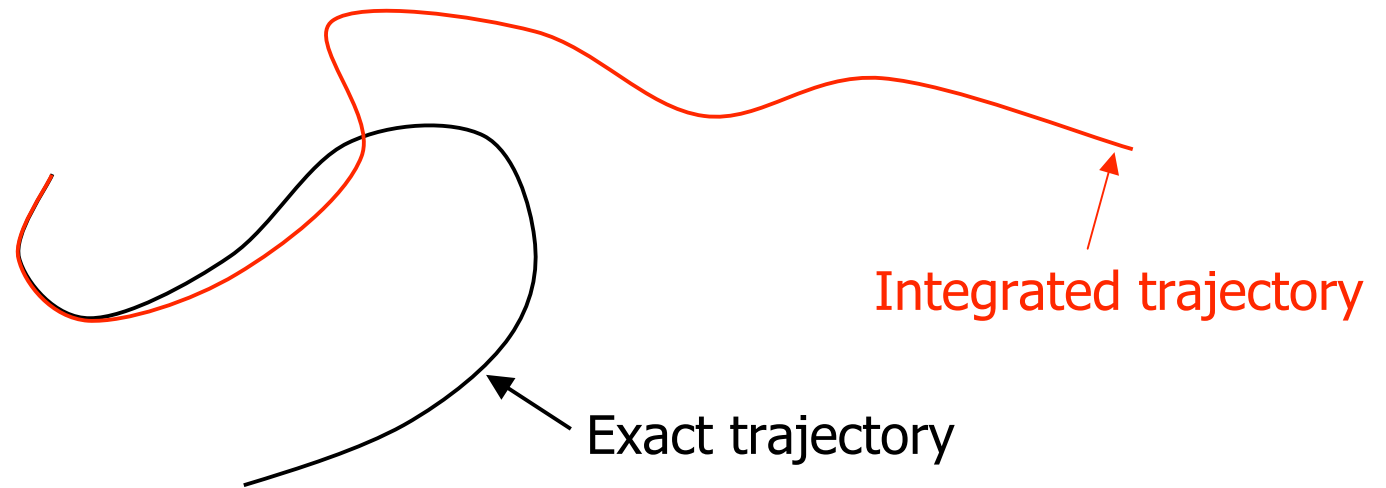
The shadow orbit is an *exact* trajectory for the system, but one that starts from a slightly displaced initial point.

These are known to exist for hyperbolic systems.

Can sometimes be shown to exist, for long times, for more general systems [e.g., see Quinlan and Tremaine, *Mon. Not. R. Astron. Soc.* **259**, 5050 (1992)].

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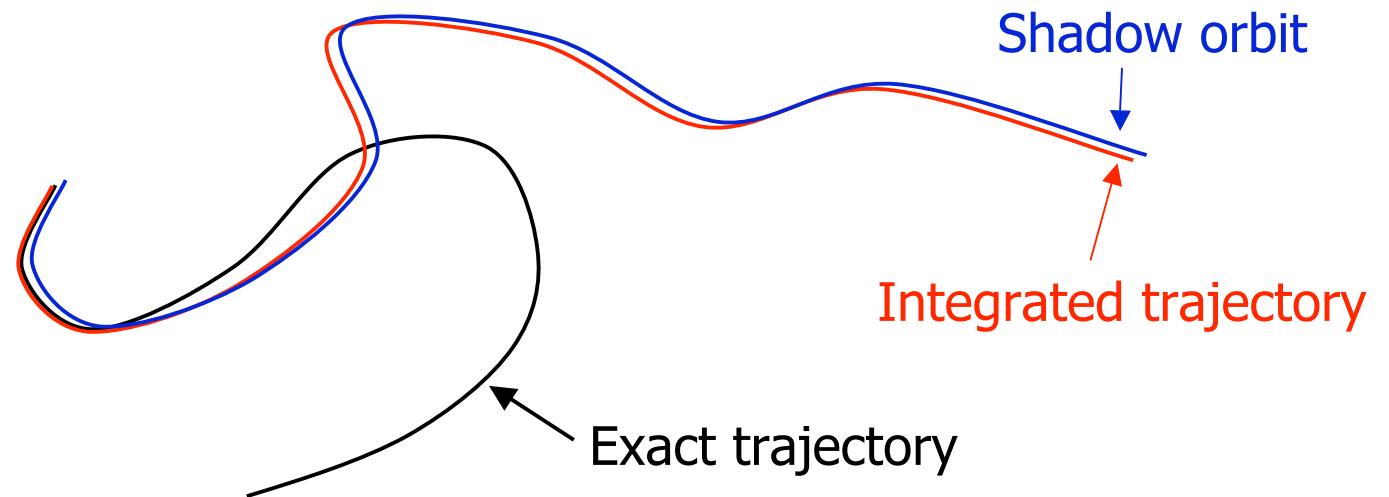
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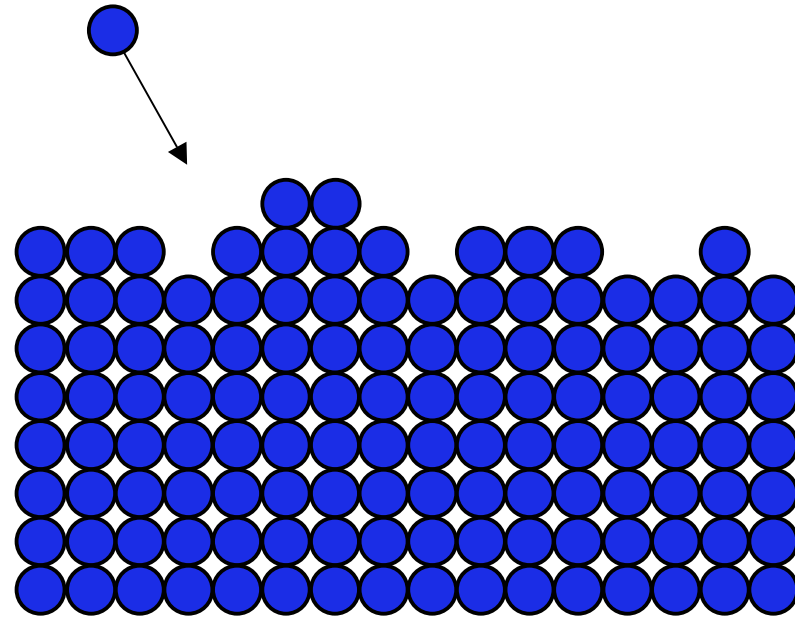
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Day 3: Infrequent events, transition state theory, saddle finding, etc.

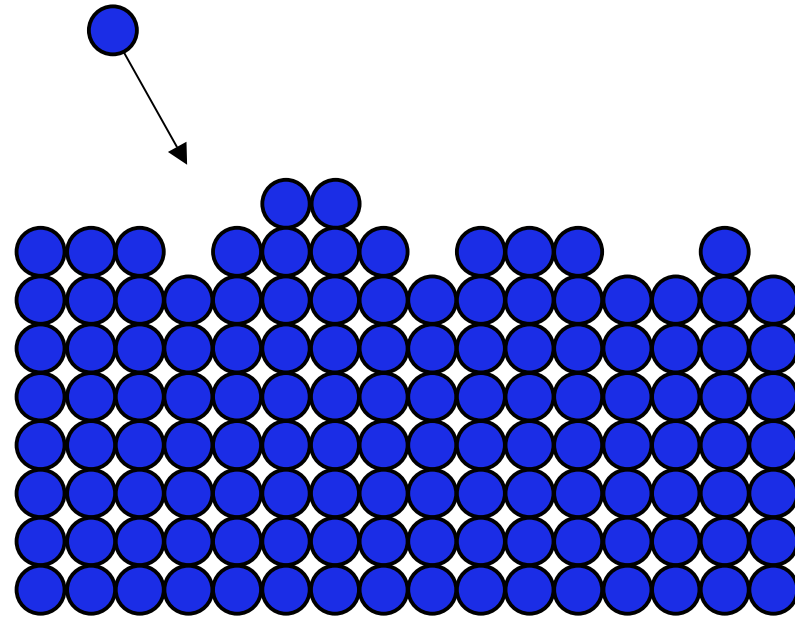
Day 4: Accelerated molecular dynamics methods

Film or Crystal Growth



Deposition event takes ~ 2 ps
– use molecular dynamics (can reach ns)

Film or Crystal Growth



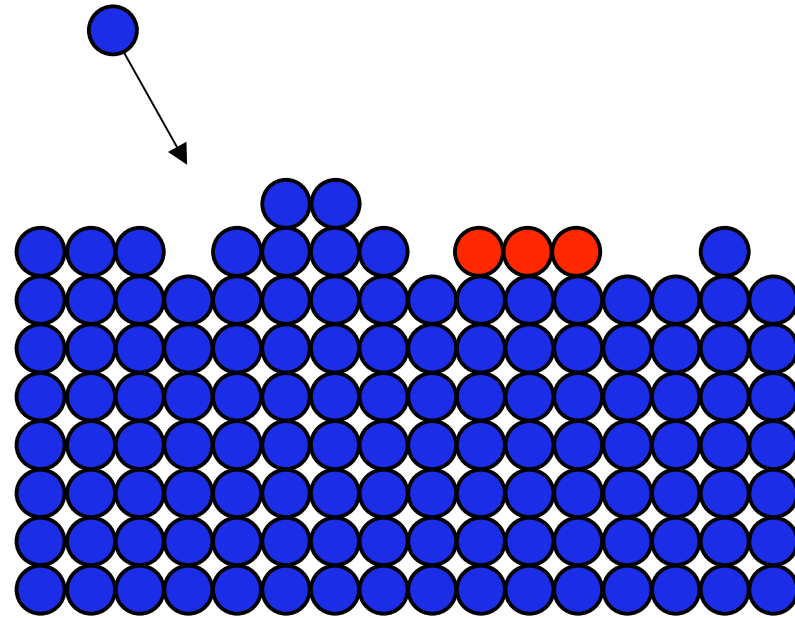
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Time to next deposition is ~ 1 s

- diffusion events affect the film morphology
- mechanisms can be surprisingly complex
- > need another approach to treat these

Film or Crystal Growth



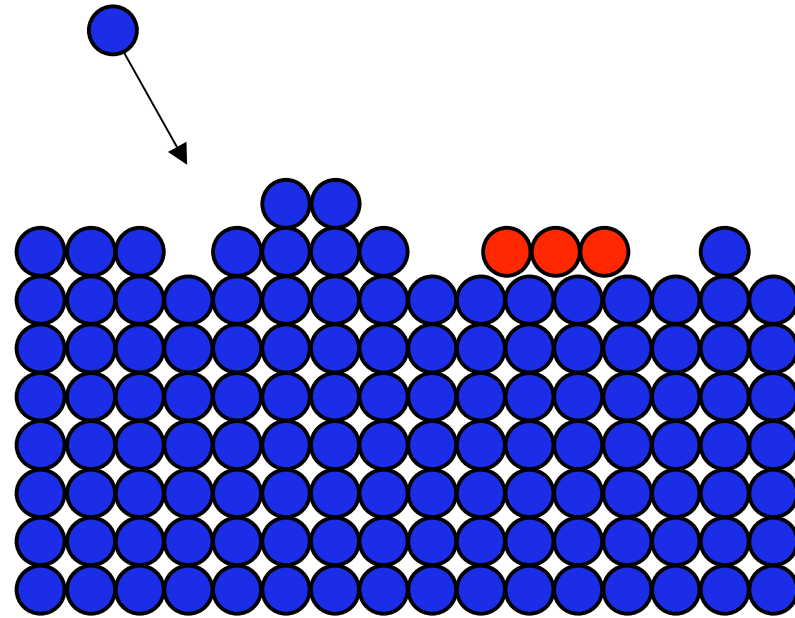
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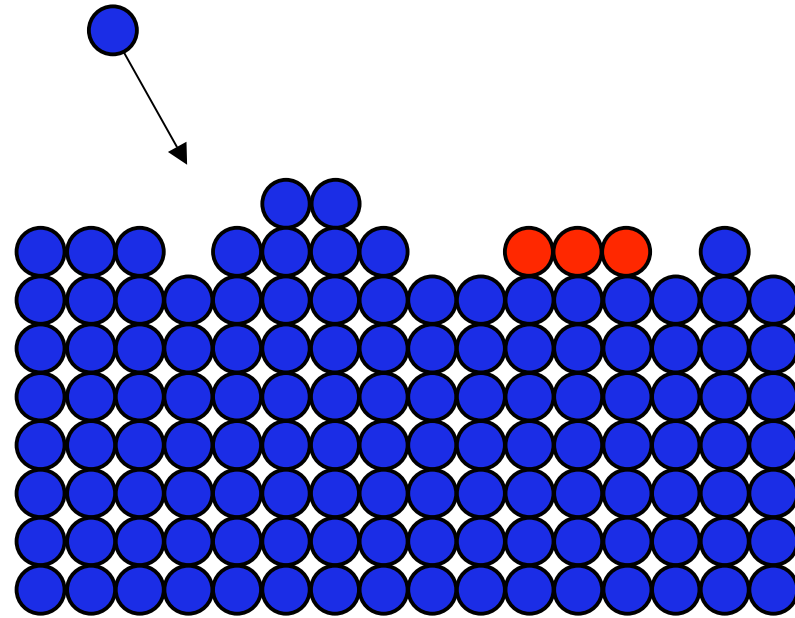
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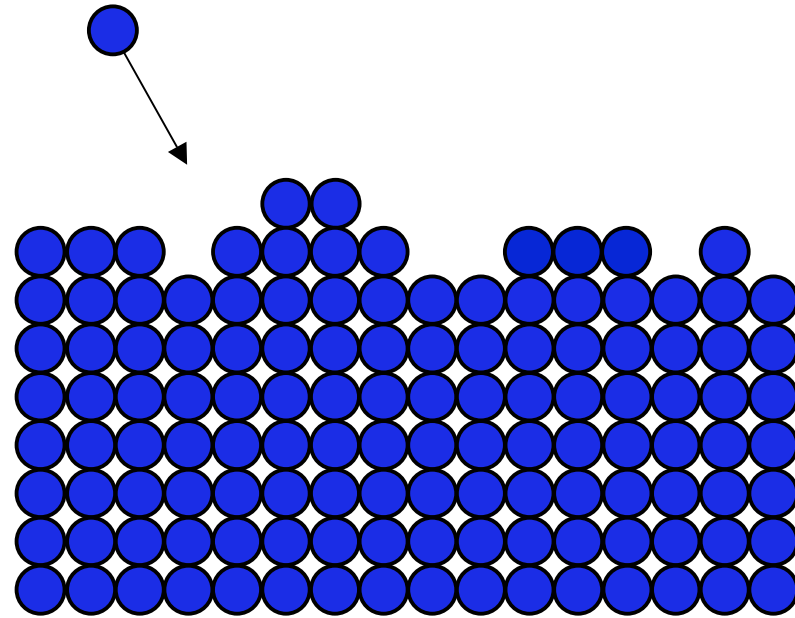
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Direct MD example: Ag/Ag(100)

T=300K

MD for 1 ps shown

Time to next hop event = 9 μ s

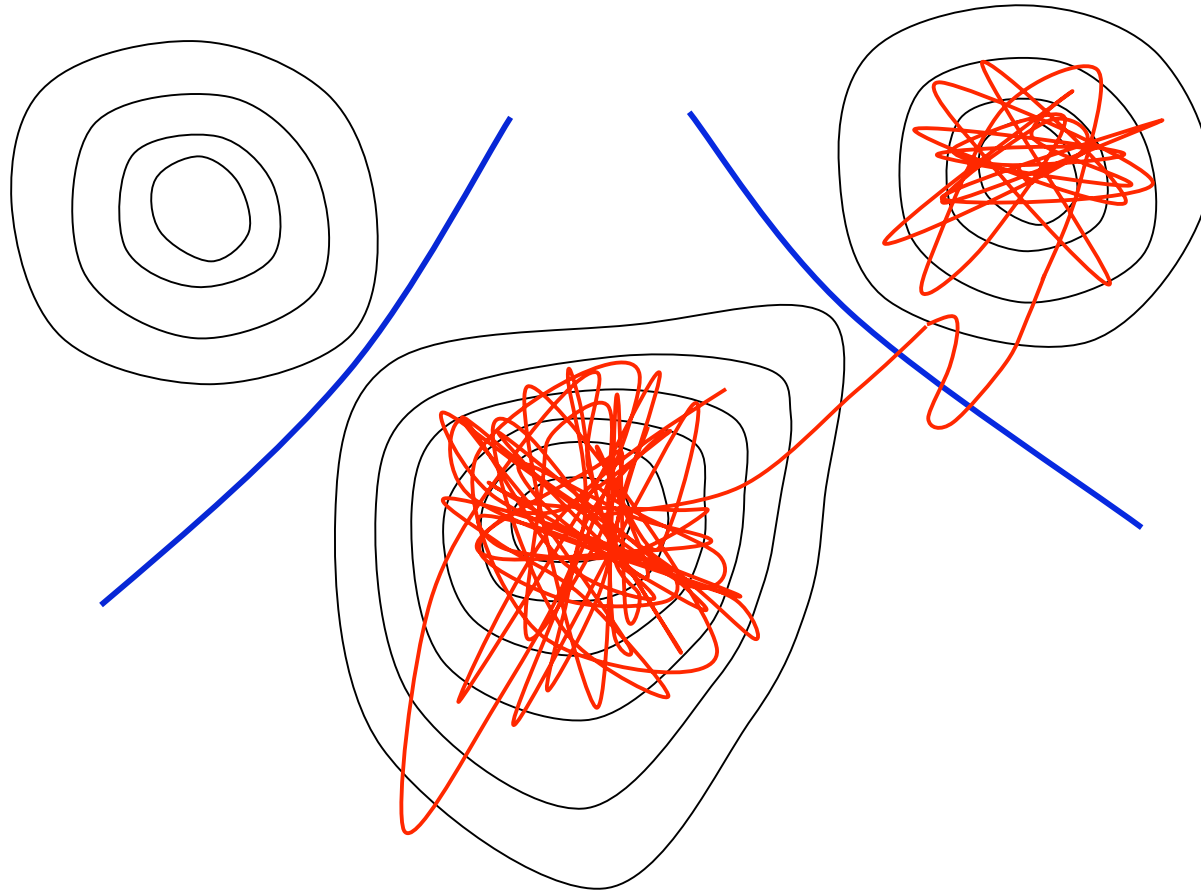
(weeks of CPU time for this very
small system)

Ag/Ag(100), EAM potential

55 moving atoms

Langevin thermostat

Infrequent Event System



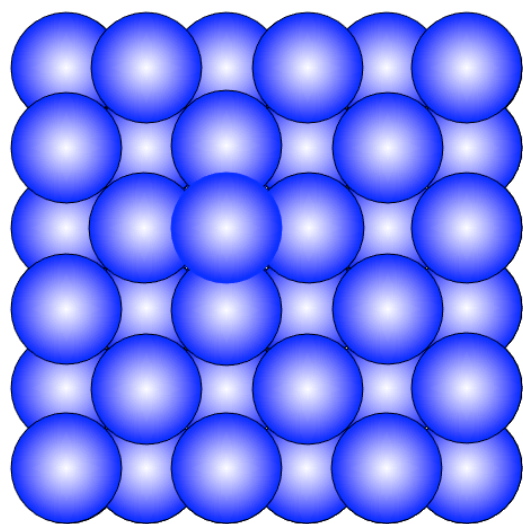
The system vibrates in $3N$ -dimensional basin.

Occasionally it escapes, crossing through a dividing surface to a new basin.

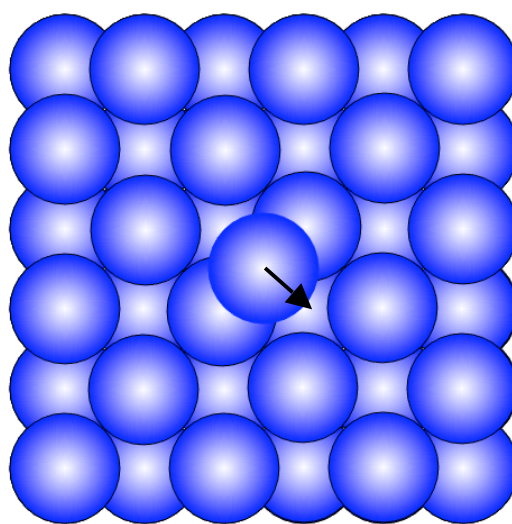
This behavior characterizes solid-state diffusion, as well as many other processes.

Computing the rate for a known mechanism

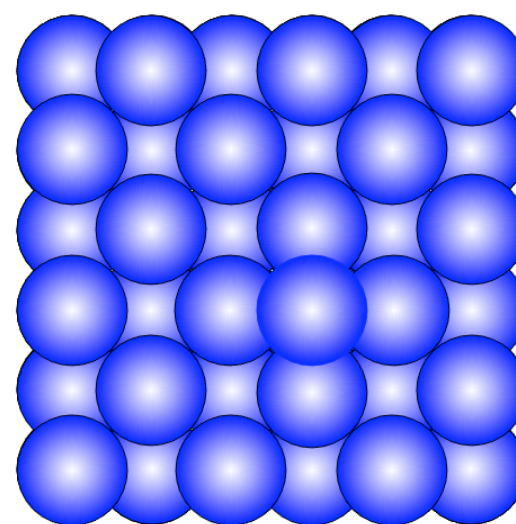
If initial and final states are known, as well as the reaction coordinate, we can use transition state theory (TST) to compute the rate.



initial state



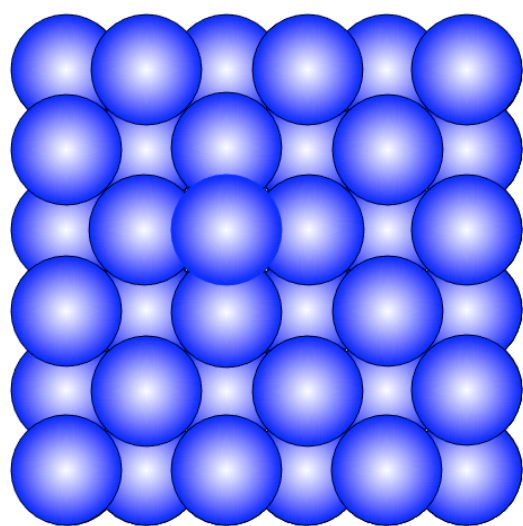
saddle point
(rxn coord shown)



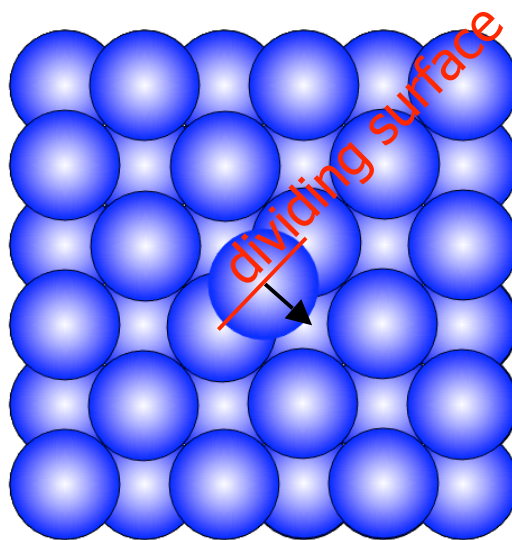
final state

Computing the rate for a known mechanism

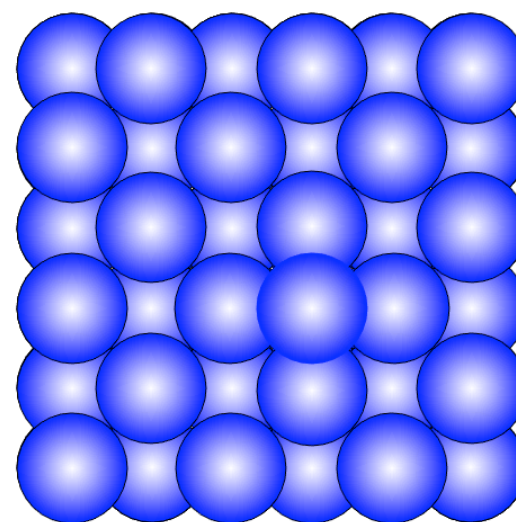
If initial and final states are known, as well as the reaction coordinate, we can use transition state theory (TST) to compute the rate.



initial state



saddle point
(rxn coord shown)



final state

Many-dimensional reaction coordinate

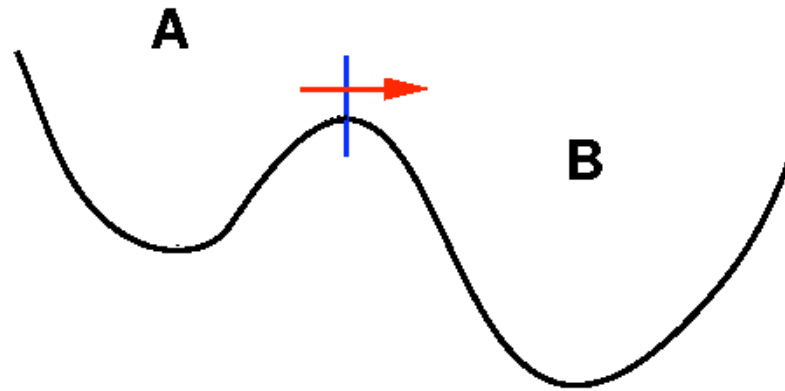
The potential energy basin is $3N$ -dimensional. The reaction coordinate (and hence the dividing surface) can involve multiple atoms.

Example - exchange event on Ag(100)

(barrier = 0.64 eV, rxn time = ~ 1 ms at $T=300\text{K}$)

(Feibelman, 1990)

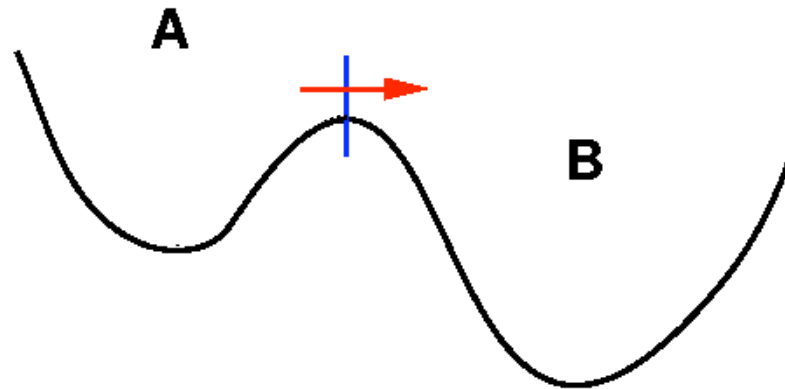
Transition State Theory (TST)



Marcelin (1915)
Wigner, Eyring,.....

TST escape rate = equilibrium flux through dividing surface

Transition State Theory (TST)

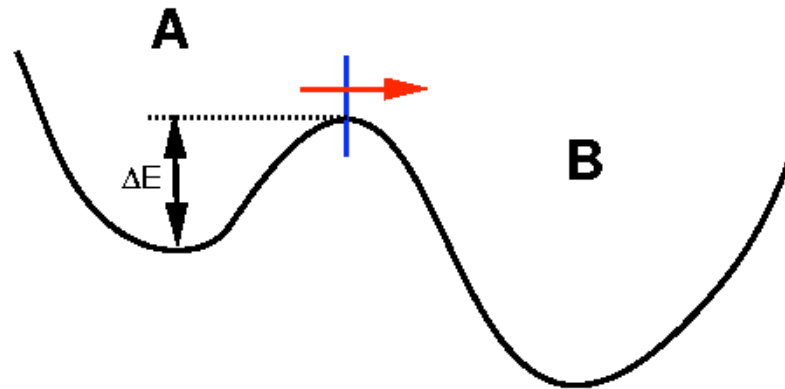


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TST escape rate = equilibrium flux through dividing surface at $x=q$

$$k_{A \rightarrow B}^{TST} = \langle \delta(x - q) | \dot{x} | \rangle_A$$

Transition State Theory (TST)



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Wigner, Eyring,.....

TST escape rate = equilibrium flux through dividing surface at $x=q$

$$k_{A \rightarrow B}^{TST} = \langle \delta(x - q) | \dot{x} | \rangle \quad (\text{exact flux})$$

$$k_{A \rightarrow B}^{HTST} = \nu_0 e^{-\Delta E / k_B T} \quad (\text{harmonic approx.})$$

- classically exact rate if no recrossings or correlated events
- no dynamics required
- very good approximation for materials diffusion

Canonical ensemble average

System in canonical ensemble has a fixed number of atoms (N), volume (V), and temperature (T)

Definition of ensemble average for some property P:

$$\langle P \rangle = \frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} P e^{-\beta H} dx dp}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\beta H} dx dp}$$

$$H = V(x) + p^2/2m$$

$$\beta = \frac{1}{k_B T}$$

Transition state theory - canonical ensemble

Because Hamiltonian is separable (H = p stuff + x stuff),
we can integrate out the momentum part

$$k_{A \rightarrow}^{\text{TST}} = \langle |dx/dt| \delta(x - q) \rangle_A$$
$$= \frac{\int_{-\infty}^{\infty} |dx/dt| e^{-\beta p^2/2m} dp}{\int_{-\infty}^{\infty} e^{-\beta p^2/2m} dp} \frac{\int_{-\infty}^q \delta(x - q) e^{-\beta H(x)} dx}{\int_{-\infty}^q e^{-\beta H(x)} dx}$$

average 1-D speed

Probability of being at
dividing surface relative to
anywhere in state

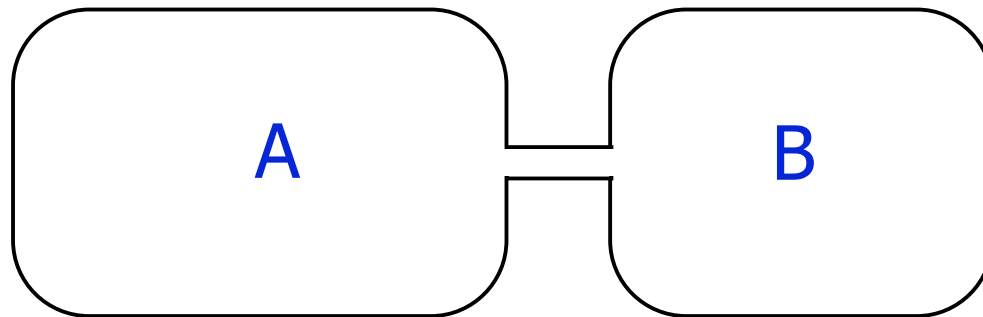
$$k_{A \rightarrow}^{\text{TST}} = \left[\frac{2k_B T}{\pi m} \right]^{1/2} \langle \delta(x - q) \rangle_A$$

Transition State Theory - generality

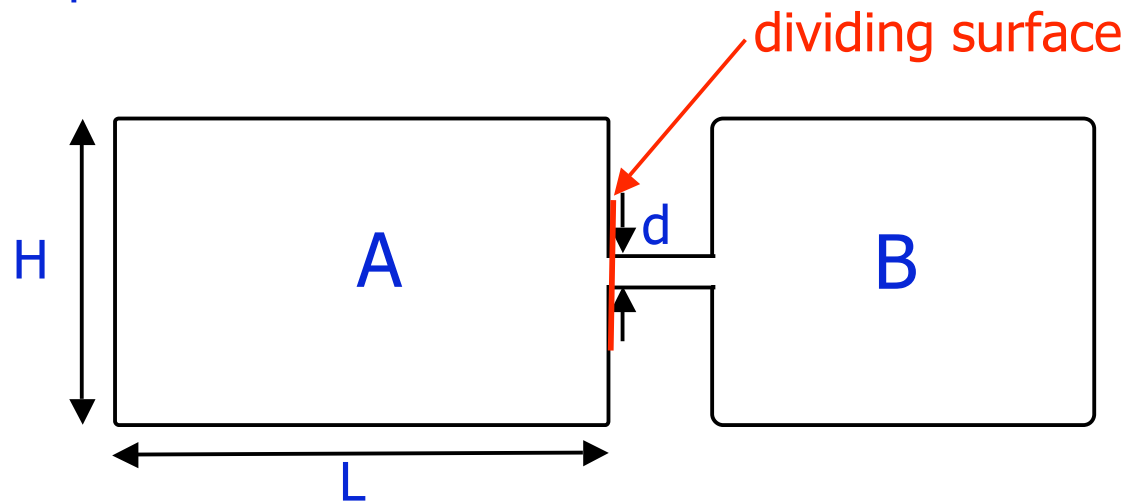
TST is very general -- simply based on flux through D.S.

No requirement that the bottleneck be an energy barrier.

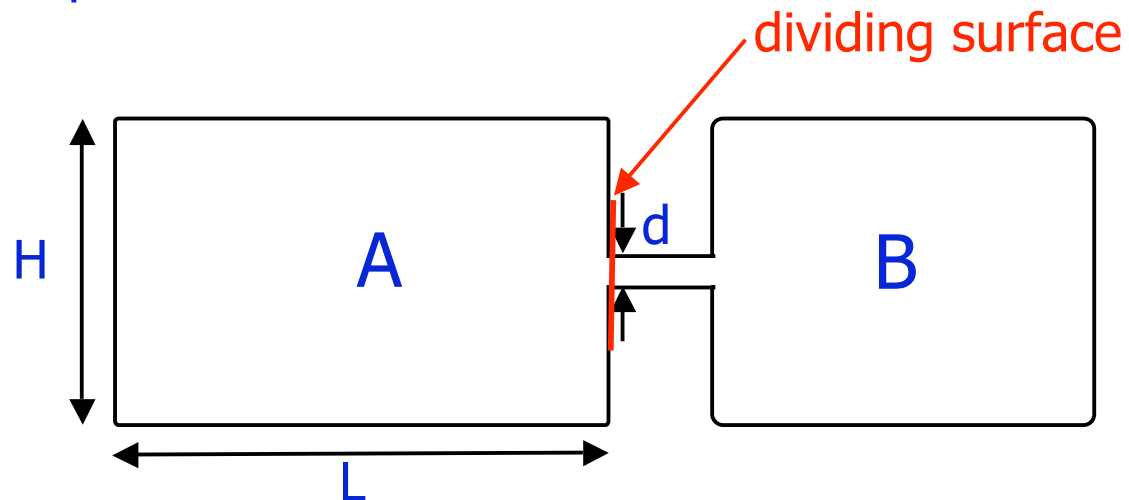
Entropic bottleneck:



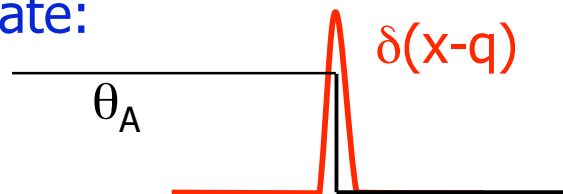
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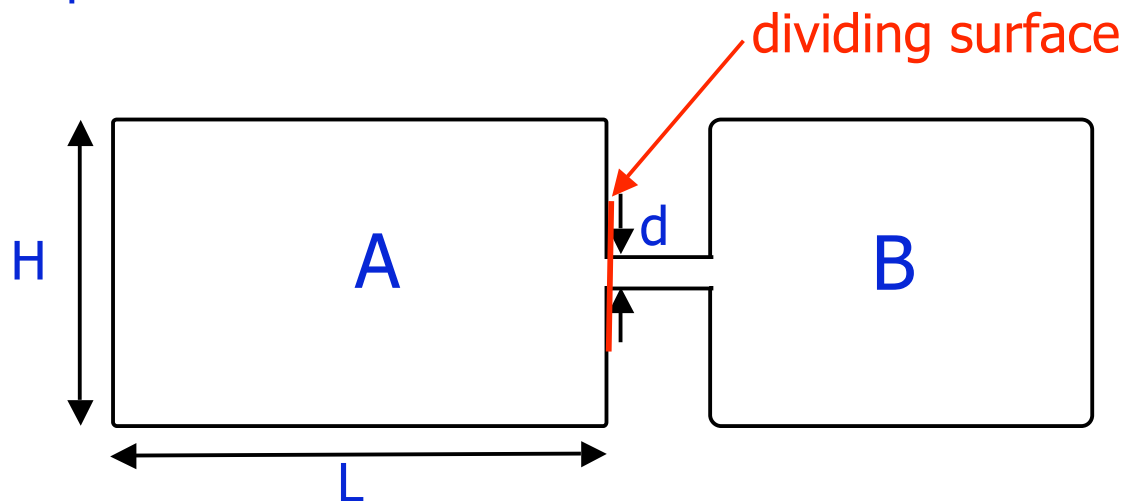
Entropic bottleneck:



Note that the delta function is cut in half by the boundary to the state:



Entropic bottleneck:



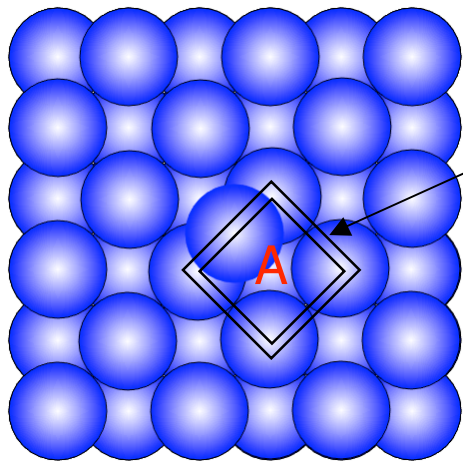
Rate of escape from state A

$$k^{\text{TST}} = [2k_B T / \pi m]^{1/2} \langle \delta(x-q) \rangle$$

$$= [2k_B T / \pi m]^{1/2} d / 2LH$$

Monte Carlo transition state theory

We can evaluate $\langle \delta(x-q) \rangle$ exactly using Metropolis Monte Carlo



TST box width = w

$$\langle \delta(x-q) \rangle = (1/2) (1/w) (N_{in}/N_{tot})$$

N_{in} = steps inside TST "box"

N_{tot} = steps anywhere in state A

Metropolis walk of adatom and top few layers of substrate

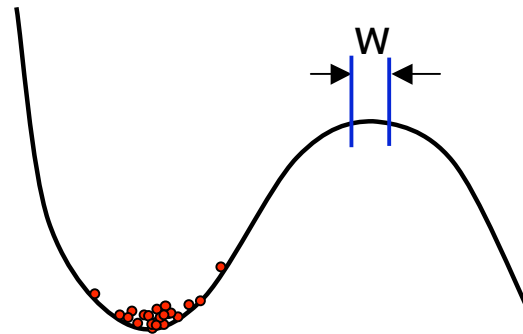
Steps attempting to leave state A are rejected

Extrapolate to $w=0$

$k^{TST} = [2k_B T / \pi m]^{1/2} \langle \delta(x-q) \rangle$ is exact TST escape rate at temperature T
(with statistical error bars)

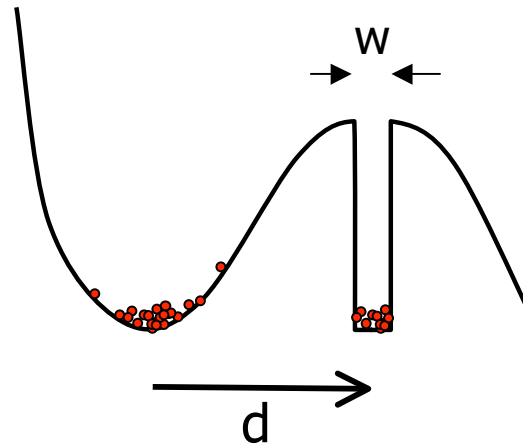
Importance Sampling

A simple Metropolis walk at low T will rarely reach the TST box



Importance Sampling

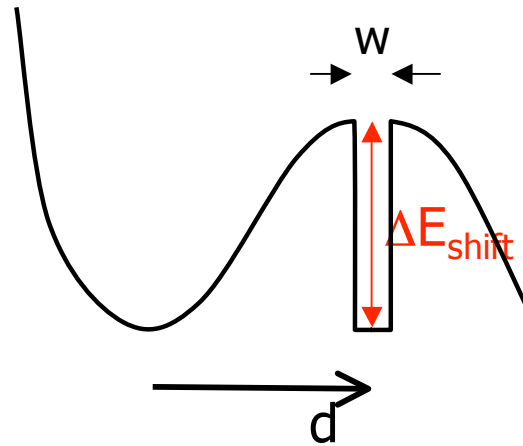
One way to improve statistics:



Include displacement vector, $+d$ and $-d$, in attempted Metropolis steps

Importance Sampling

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[AFV, J. Chem. Phys. 82, 1890 (1985)]

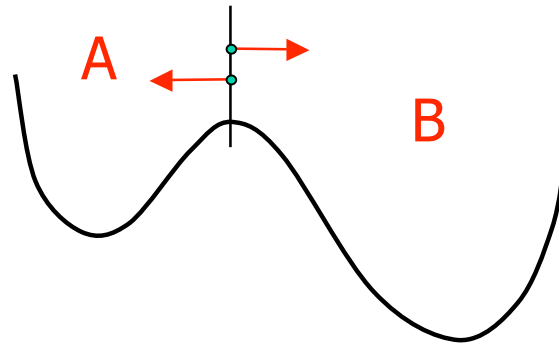
Still a valid Metropolis walk, but much more efficient

$$\langle \delta(x-q) \rangle = (1/2) (1/w) (N_{\text{in}}/N_{\text{tot}}) \exp(-\Delta E_{\text{shift}}/kT)$$

Dynamical corrections theory

(Keck, Anderson, Bennett, ... 1960's-1970's)

- Use saddle-point trajectories to correct TST

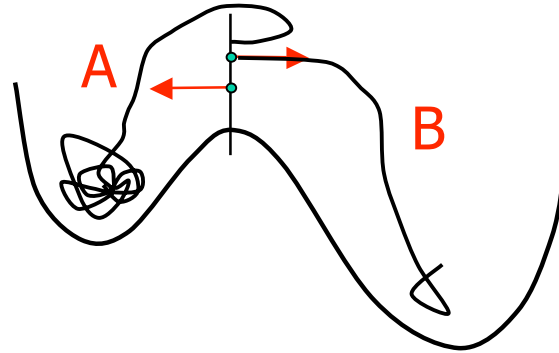


Follow for time τ_{corr}
see where they land

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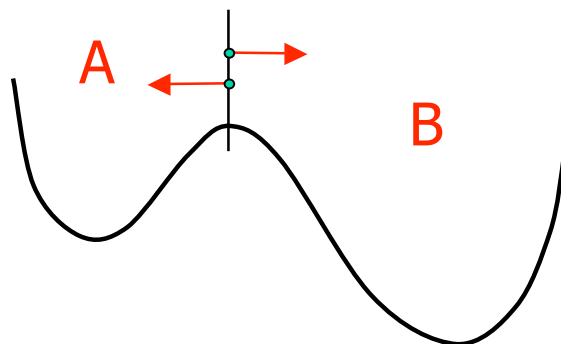


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D. Chandler, J. Chem. Phys 68, 2959 (1978):

$$k_{A \rightarrow B}^{\text{exact}} = \frac{\langle v_A(0) \delta_A(0) \theta_B(t) \rangle}{\langle |v_A(0)| \delta_A(0) \theta_B(0+) \rangle} k_{A \rightarrow B}^{\text{TST}}$$

$$= k_{A \rightarrow B}^{\text{TST}} \frac{2}{N} \sum_I^N \gamma(I) \theta_B(I, t)$$

$$= k_{A \rightarrow B}^{\text{TST}} f_d(t)$$

Key requirement:

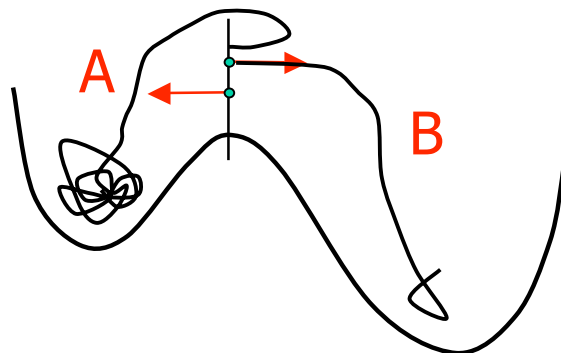
“separation of time scales”

$$\tau_{\text{rxn}} \gg t > \tau_{\text{corr}}$$

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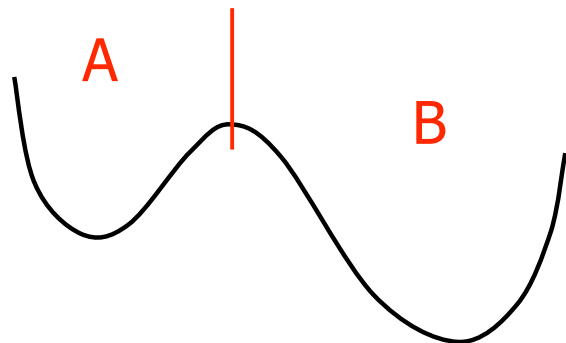
$f_d(t)$ reaches a plateau value

Dynamical corrections theory (cont.)

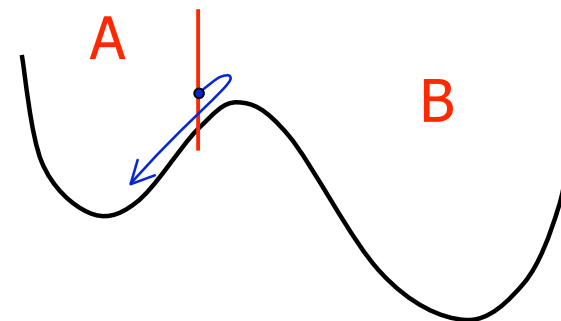
Neat property:

$$k_{\text{exact}} = k^{\text{TST}} f_d$$

regardless of position of TST dividing surface!



obvious choice



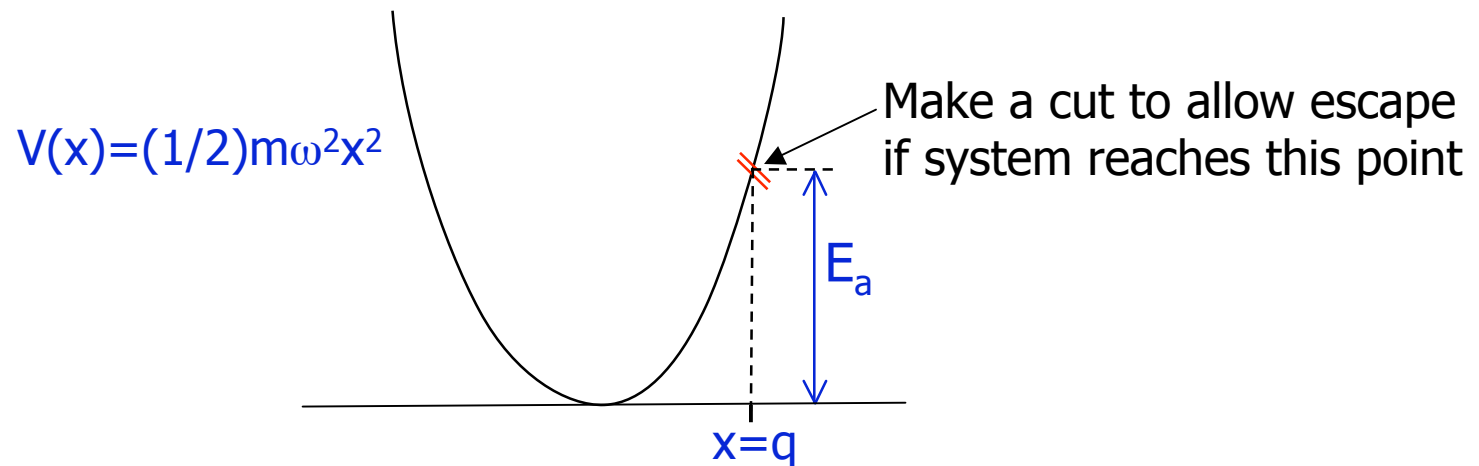
"bad" choice

k^{TST} increases (more flux)
 f_d decreases (more recrossings)

"Variational TST" (Garrett and Truhlar) - vary dividing surface position
to minimize k^{TST} (exploiting fact that $k^{\text{TST}} \geq k^{\text{exact}}$)

Harmonic TST

One-dimensional system; assume potential is perfectly harmonic



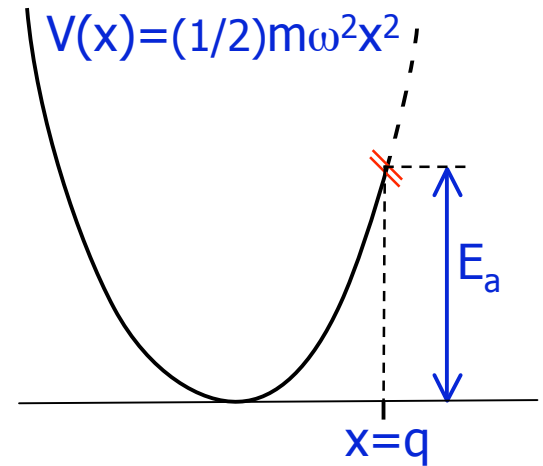
$$k^{\text{HTST}} = \nu_0 \exp[-E_a/k_B T]$$

$\omega/2\pi$

Harmonic TST - derivation

$$k_{A \rightarrow}^{\text{TST}} = \left[\frac{2k_B T}{\pi m} \right]^{1/2} \langle \delta(x - q) \rangle_A$$

$$= \left[\frac{2k_B T}{\pi m} \right]^{1/2} \frac{\int_{-\infty}^q \delta(x - q) e^{-\beta \frac{1}{2} m \omega^2 x^2} dx}{\int_{-\infty}^q e^{-\beta \frac{1}{2} m \omega^2 x^2} dx}$$



take this q to infinity so we can integrate analytically

$$= \left[\frac{2k_B T}{\pi m} \right]^{1/2} \frac{\frac{1}{2} e^{-\beta E_a}}{\left[\frac{2k_B T}{\pi m} \right]^{1/2} \frac{\pi}{\omega}}$$

$$k_{A \rightarrow}^{\text{HTST}} = \nu_0 e^{-\beta E_a}$$

Vineyard Expression

Vineyard, J. Phys. Chem. Solids, **3**, 121 (1957)

Harmonic TST in 3N dimensions



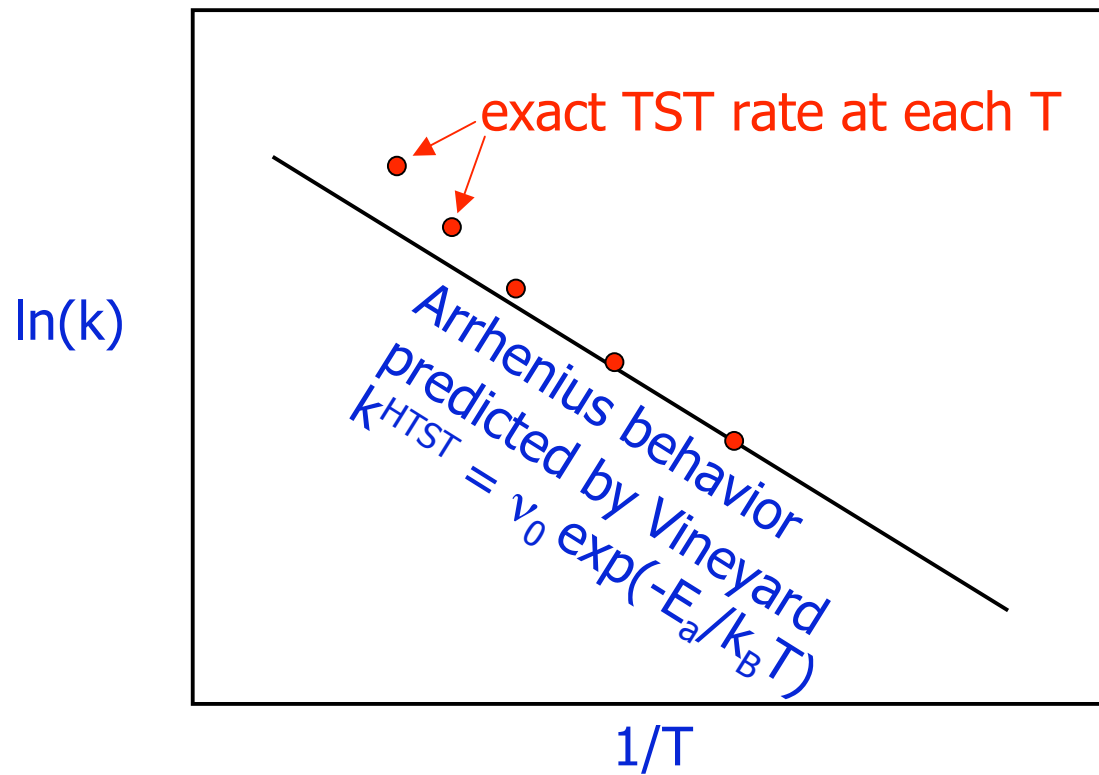
$$k_{A \rightarrow}^{\text{HTST}} = \frac{\prod_i^{3N} \nu_i^{\text{min}}}{\prod_i^{3N-1} \nu_i^{\text{sad}}} e^{-\beta E_a}$$

$\{\nu_i^{\text{min}}\}$ = 3N normal-mode frequencies at minimum

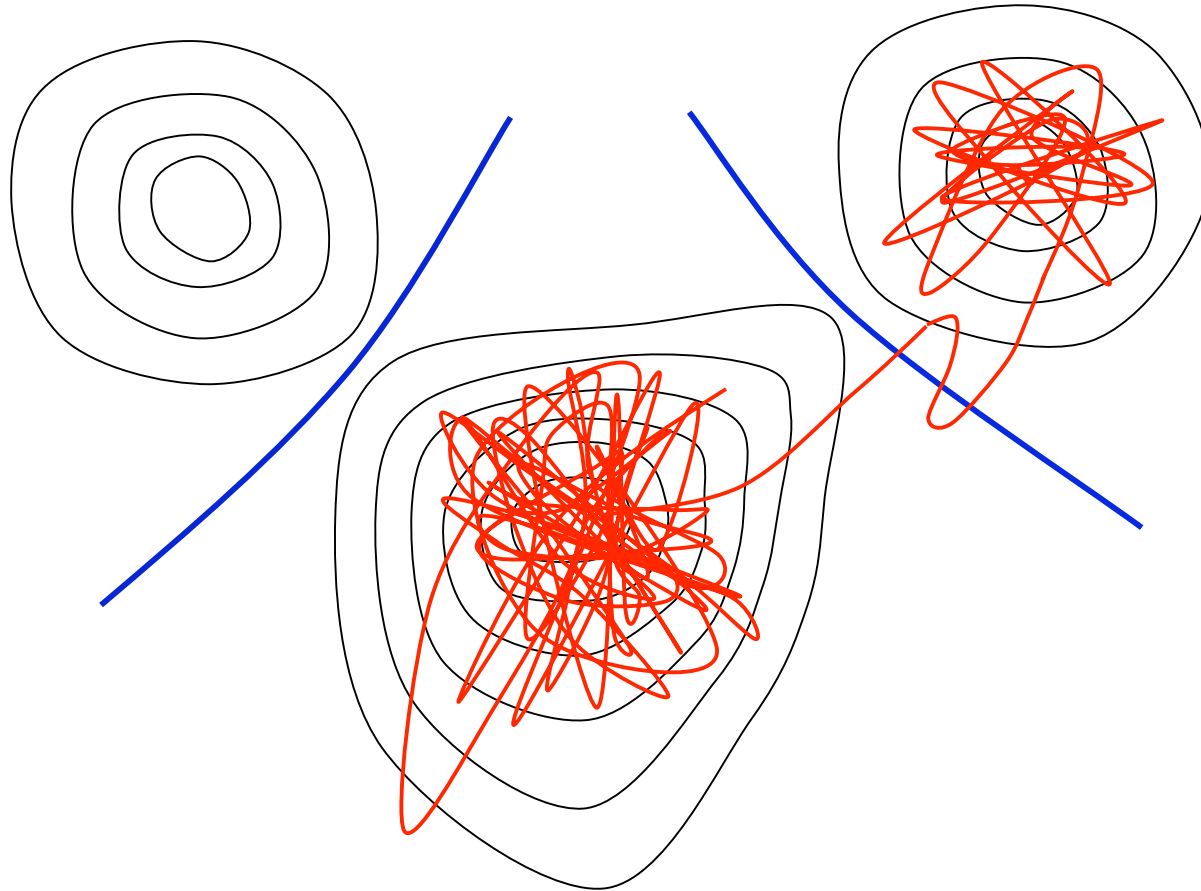
$\{\nu_i^{\text{sad}}\}$ = 3N-1 nonimaginary frequencies at saddle

- Predicts rate constant for any T, using only the information at the minimum and the saddle point.
- Typically a very good approximation below half of T_{melt}
- For metal systems, typical prefactor is $10^{12} - 10^{13}$

Effects of Anharmonicity



Infrequent Event System



The system vibrates in 3N dimensional basin many times before finding an escape path. The trajectory finds an appropriate way out (i.e., proportional to the rate constant) without knowing about any of the escape paths except the one it first sees. Can we exploit this?

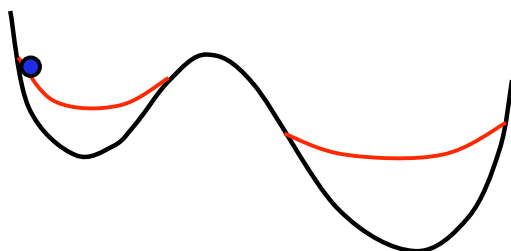
Accelerated dynamics concept

Let the trajectory, which is smarter than we are, find an appropriate way out of each state. The key is to coax it into doing so more quickly, using statistical mechanical concepts (primarily transition state theory).

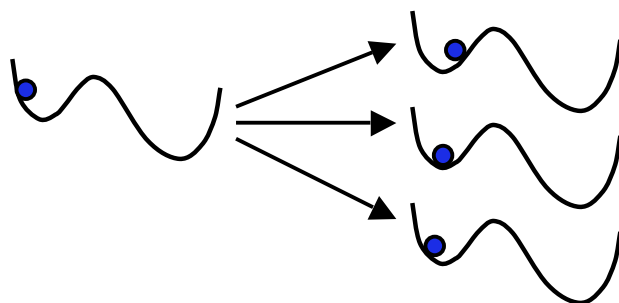
With these accelerated dynamics methods, we can follow a system from state to state, reaching time scales that we can't achieve with molecular dynamics.

Accelerated Molecular Dynamics Methods

Hyperdynamics (1997)



Parallel Replica Dynamics (1998)



Temperature Accelerated Dynamics (2000)

