a Certain Set of
v

An Introduction to Theoretical Methods for Describing Rare Events

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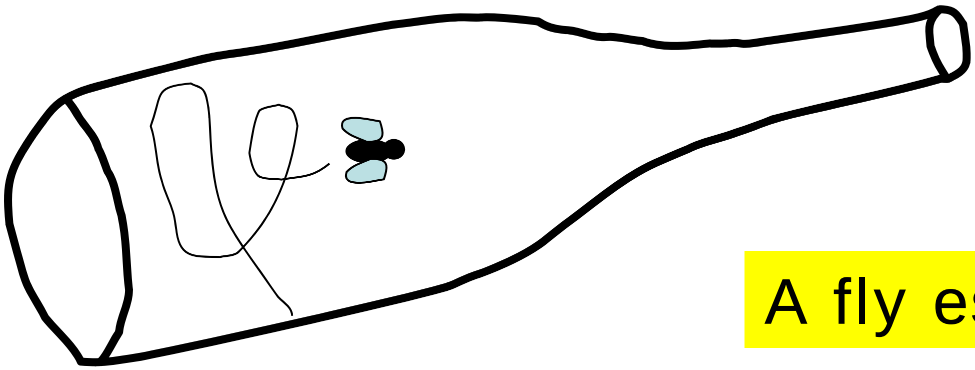
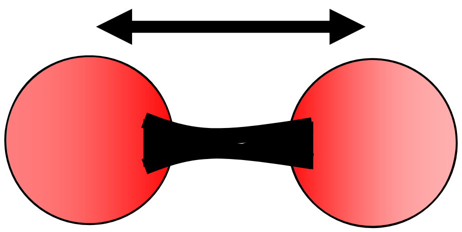
Rare Event: Motion of a System from One Free-Energy Minimum to Another

The time for motion between minima is long compared to translational/vibrational time scale in the minima

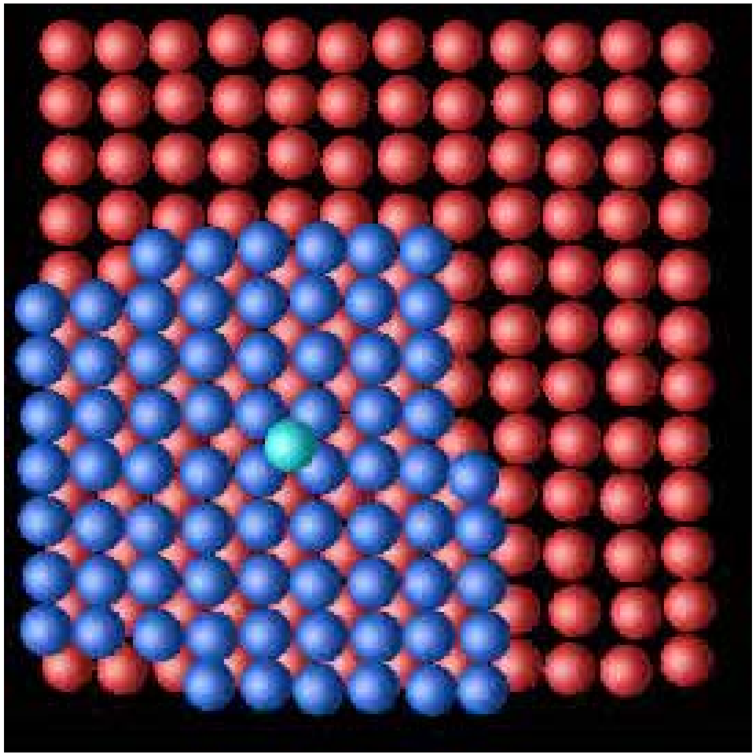


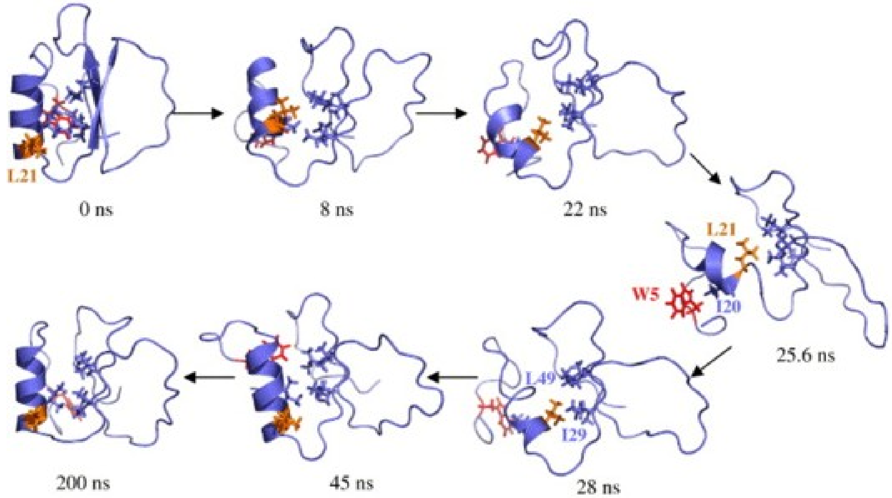
A fly escaping from a bottle



Chemical Bond Breaking

Rare Events: Examples





M. DeMarco, J. Silveira, B. Caughey, and V. Daggett, *Biochemistry* **45**, 15573 (2007).

Protein Folding, Catalysis at Solid Surfaces, Defect Motion in Solids, *etc.*

Diffusion of Atoms on Solid Surfaces – *e.g.*, Growth of Co on Cu

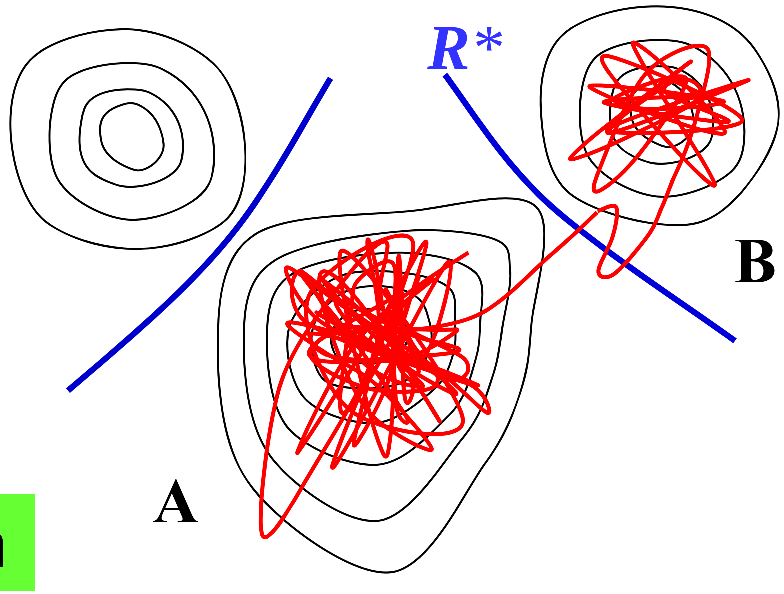
R. Miron and K. Fichthorn, *Phys. Rev. Lett.* **93**, 128301 (2004).

Rare Events Occur over an Uncomfortable Time Scale for Direct Molecular Dynamics

Transition-State Theory (TST)
How Fast Does It Happen?

$$k_{TST,A\rightarrow B} = \nu \frac{\int_A \delta(\mathbf{R}-\mathbf{R}^*)\exp(-E(\mathbf{R})/k_B T)}{\int_A \exp(-E(\mathbf{R})/k_B T)}$$

$$= \nu_0 \frac{Q^*}{Q_A} \exp(-E_0/k_B T)$$

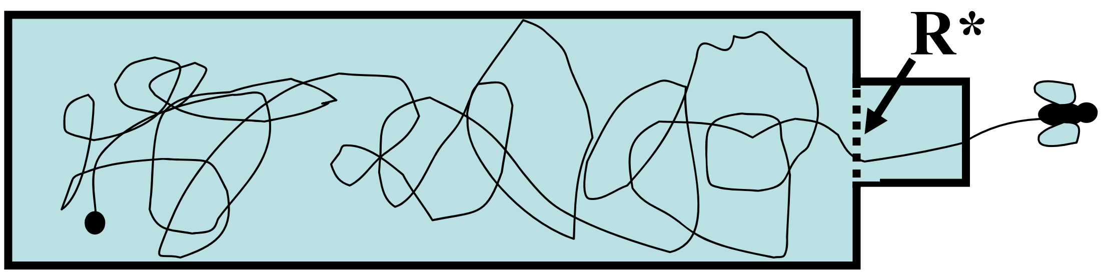


$$\nu_0 = \frac{kT}{h} [=] \text{ time}^{-1}$$ **A Loose Vibration**

$$= \frac{1}{2}\left(\frac{2kT}{\pi m}\right)^{1/2} [=] \frac{\text{length}}{\text{time}}$$ **1D Translation**

J. Steinfeld, J. Francisco, and W. Hase, Chemical Kinetics and Dynamics, 2nd Ed., Prentice-Hall (1999).

Fly in the Bottle: An Entropic Transition



"Hard" Walls: $E(\mathbf{R}) = \begin{cases} \infty, & \text{if } \mathbf{R} \text{ is at the wall} \\ 0, & \text{otherwise} \end{cases}$

$$k_{TST} = \nu \frac{\int_V \delta(\mathbf{R}-\mathbf{R}^*)\exp(-E(\mathbf{R})/k_B T)}{\int_V \exp(-E(\mathbf{R})/k_B T)}$$

ν_0 is the Fly's Velocity!!!

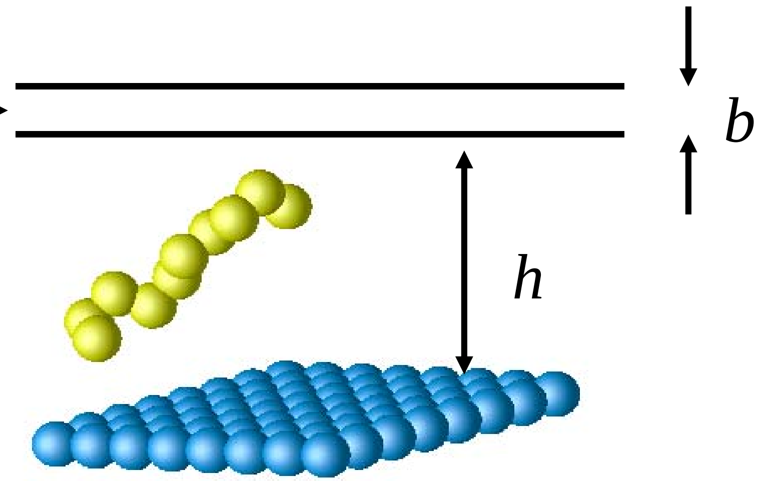
$$k_{TST} = \nu_0 \frac{A_{\text{neck}}}{V_{\text{bottle}}} [=] \frac{1}{\text{time}}$$

Average Escape Time

$$\tau = 1/k_{TST}$$

TST Rates for Thermal Desorption:

Transition State →



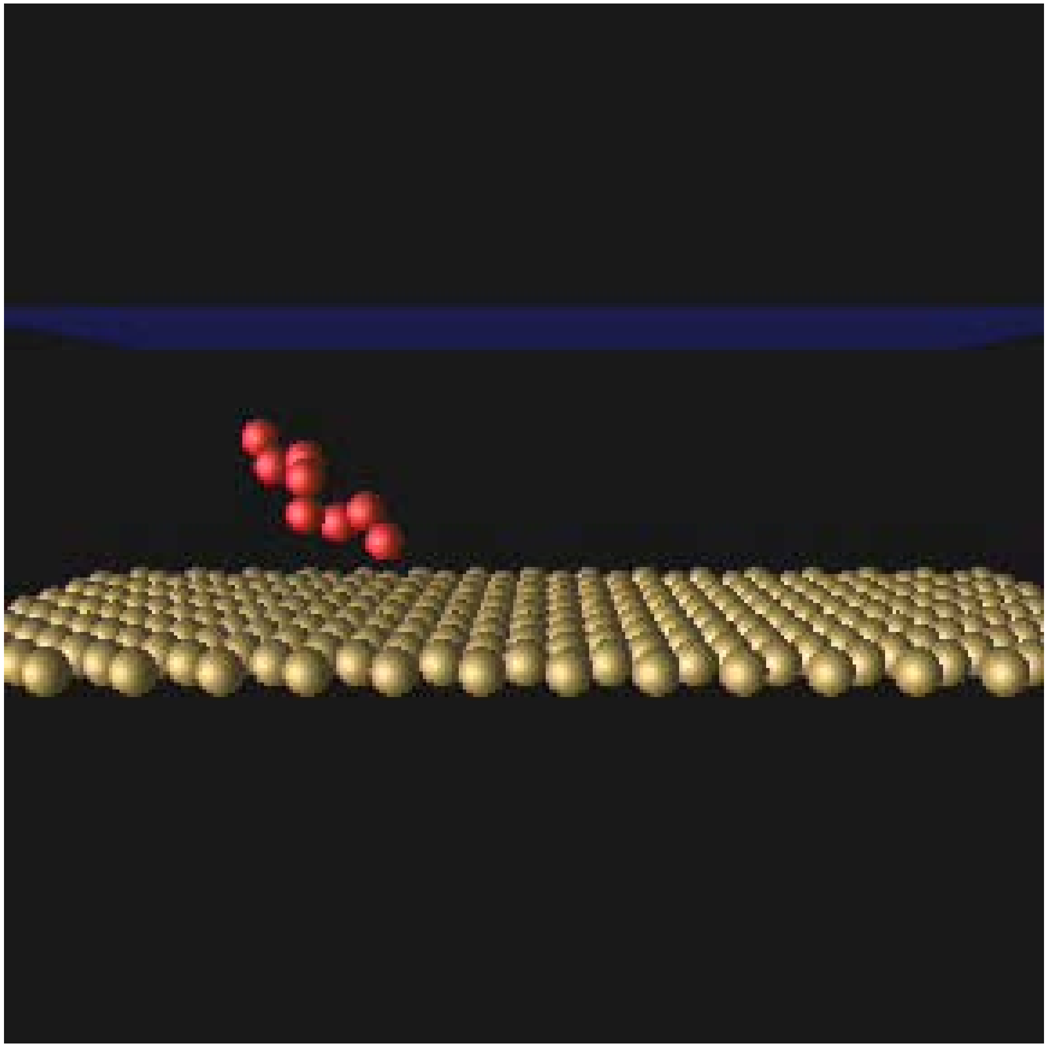
Track trajectories of molecules as they leave the surface for the gas

$$k_{TST} = \frac{1}{2}\left(\frac{2k_BT}{\pi m}\right)^{1/2} \frac{\int \delta(\mathbf{R}-\mathbf{R}^*)\exp(-E(\mathbf{R})/k_BT)}{\int \exp(-E(\mathbf{R})/k_BT)}$$

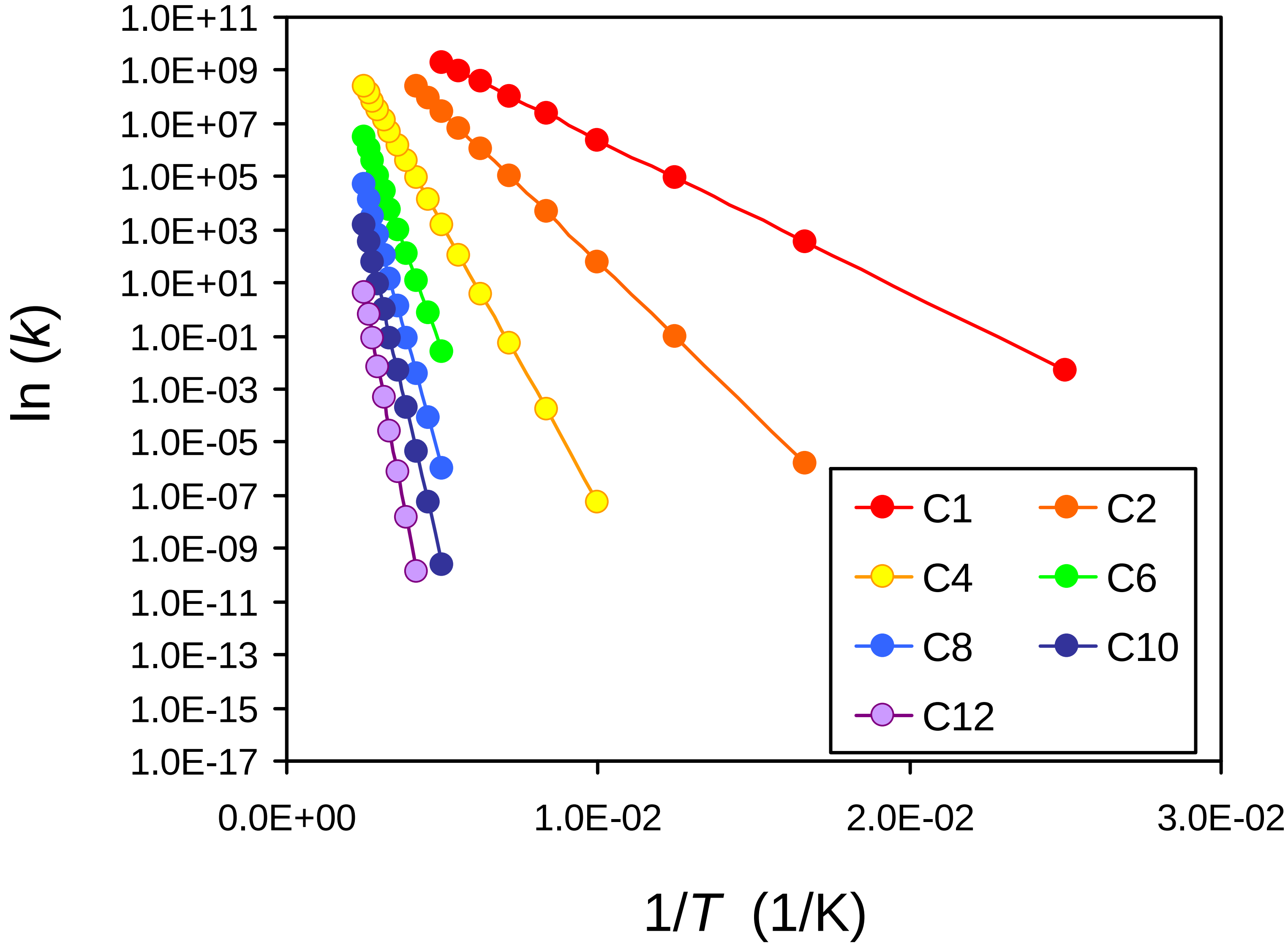
$$= \frac{1}{2}\left(\frac{2k_BT}{\pi m}\right)^{1/2} \frac{1}{b}\left(\frac{N_{box}}{N_{total}}\right)$$

K. Fichthorn and R. Miron,
Phys. Rev. Lett. **89**, 196103 (2002).

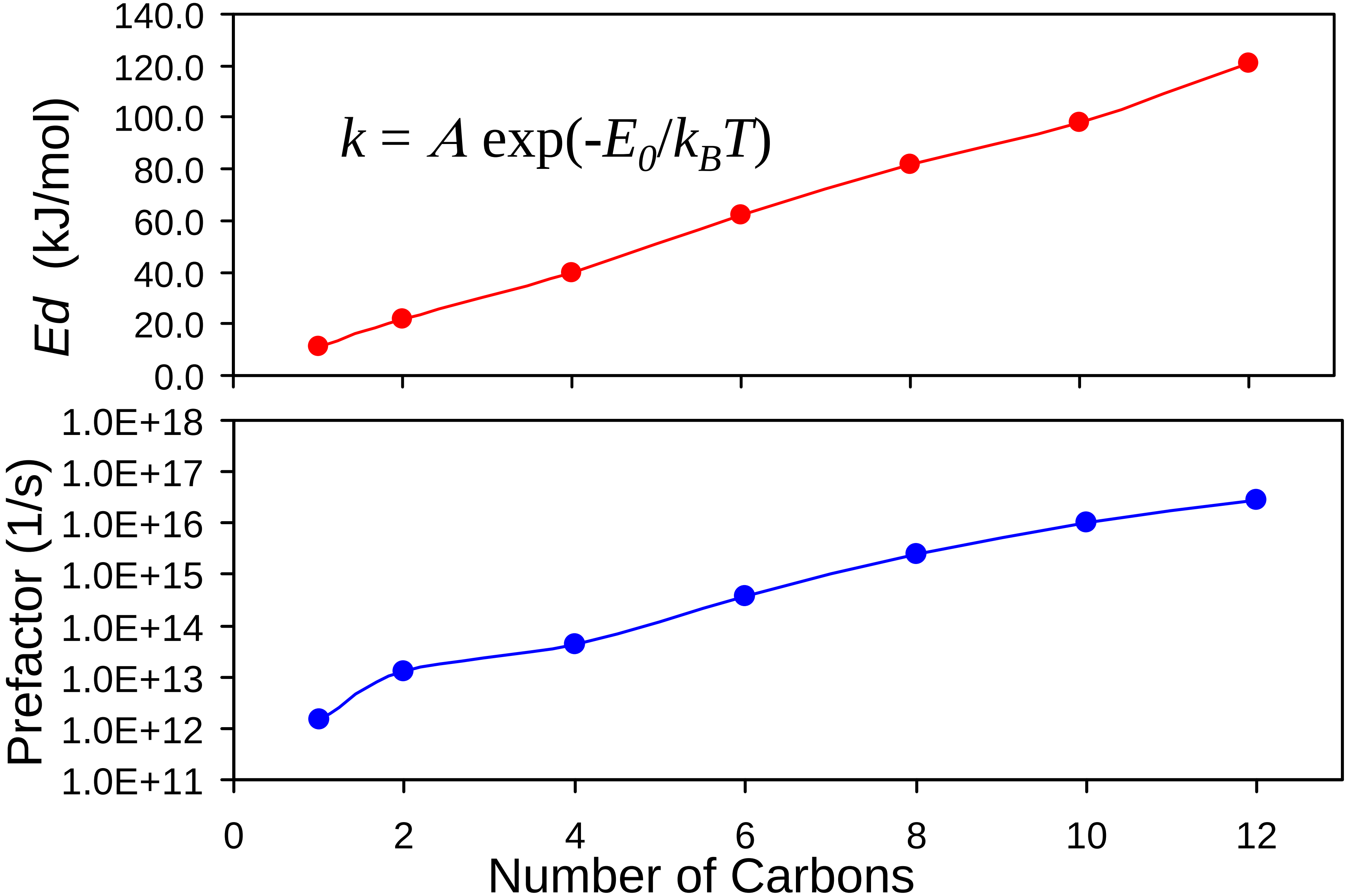
Thermal Desorption: A Sample Molecular Dynamics Trajectory



Desorption Rate Constants

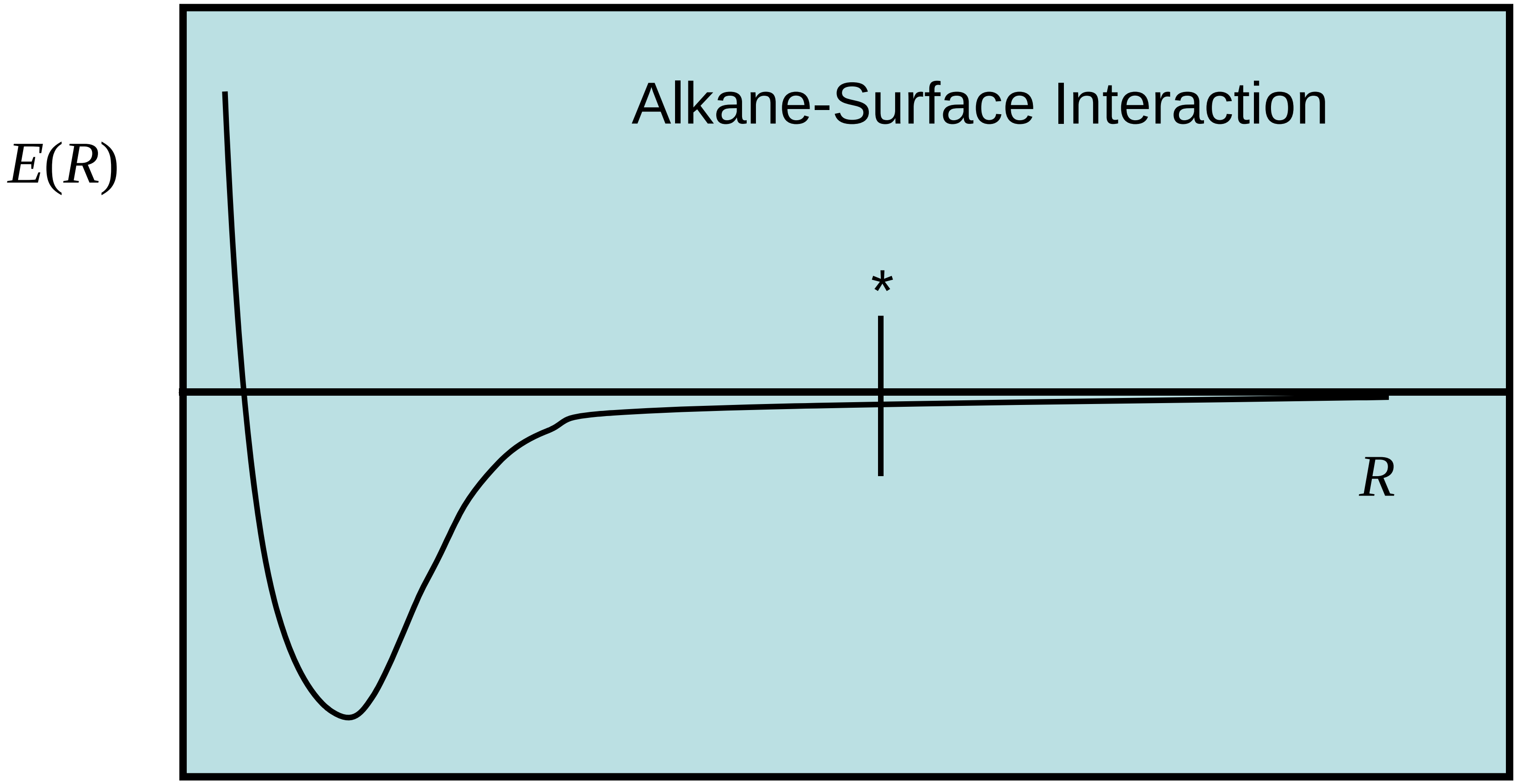


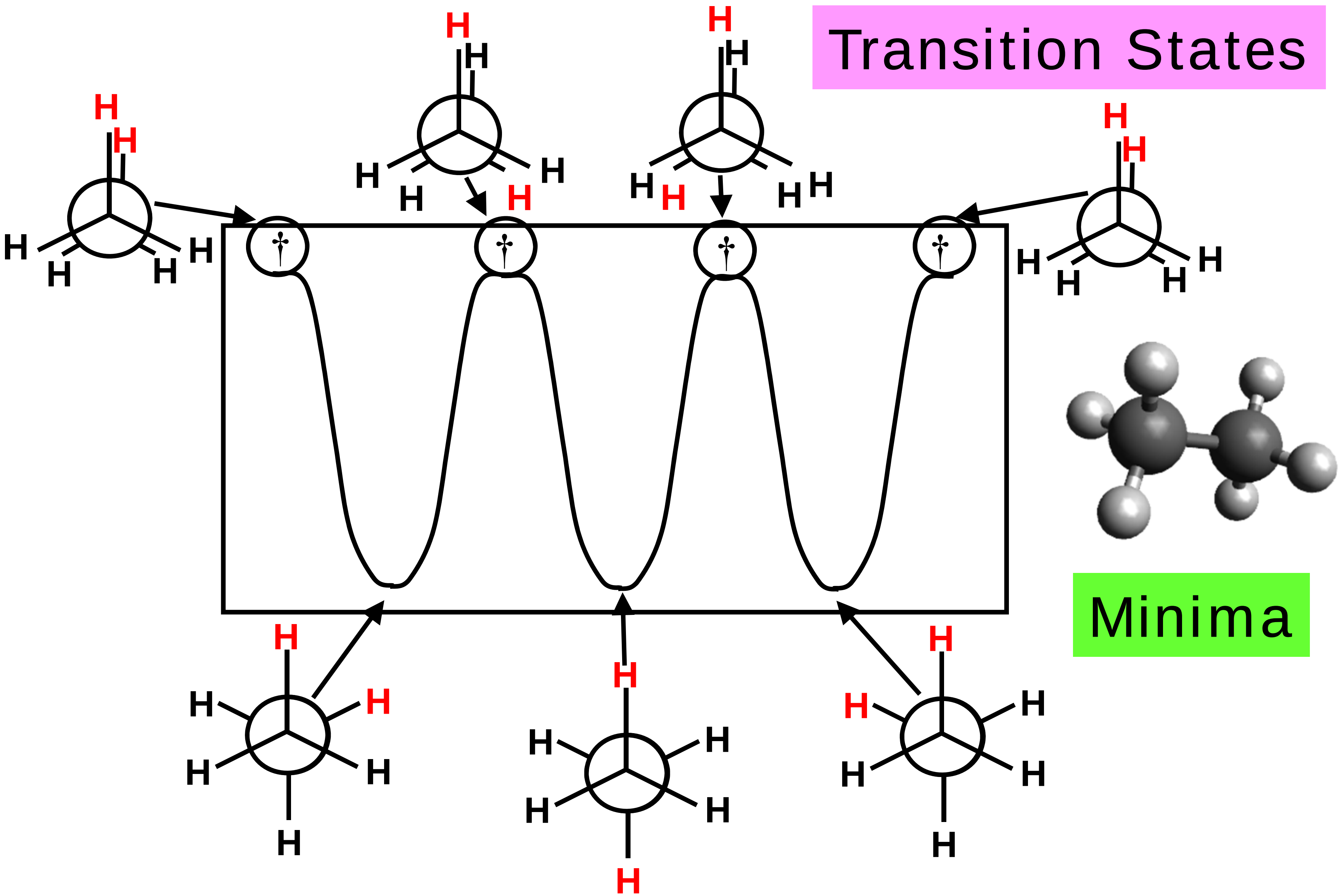
Activation Energies and Prefactors



What is the Transition State?

The Potential-Energy Surface





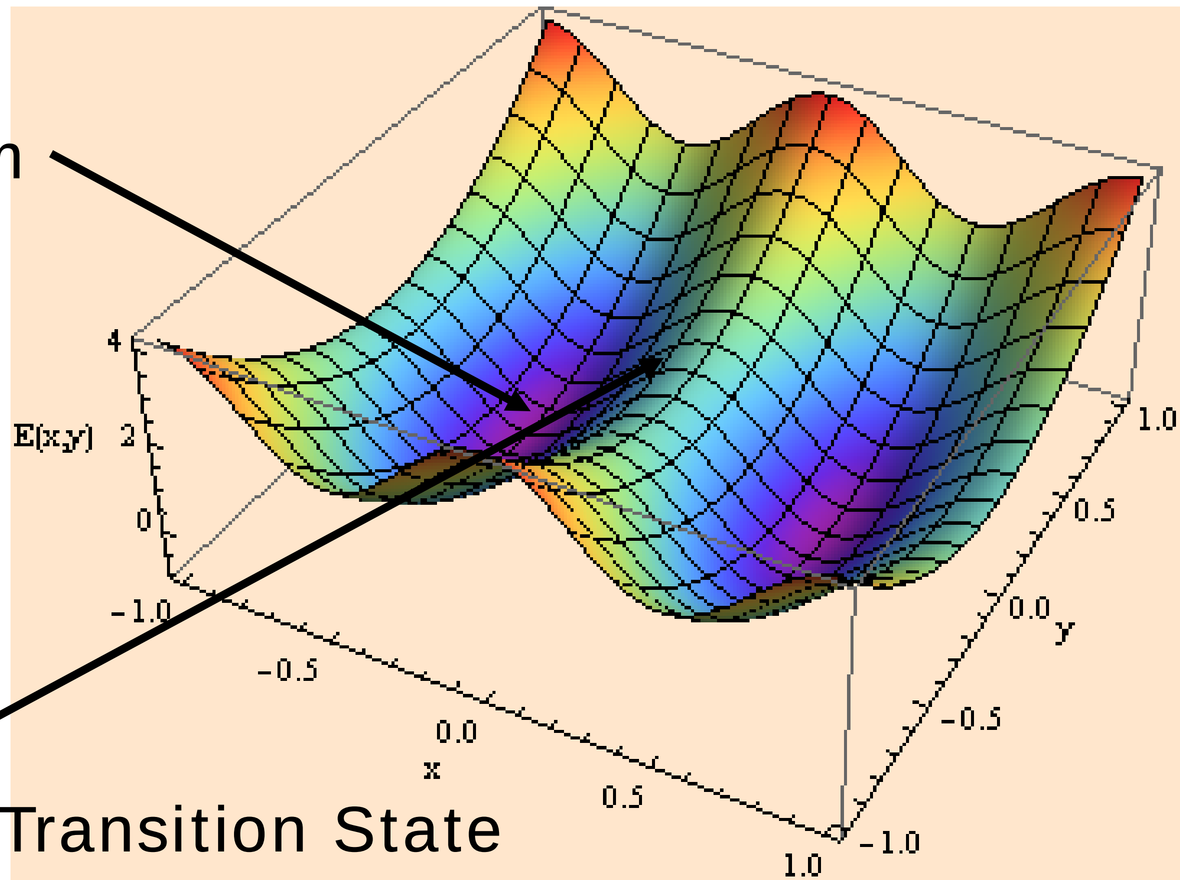
Rotational Transitions in Ethane

What is the Transition State?

A 2D Potential-Energy Surface

$$E(X,Y) = \cos(2\pi X) + \pi Y^2$$

Minimum



Saddle Point – the Transition State

What is the Transition State?
Critical Points on the Potential Surface

Minima, Maxima, Saddle Points:

$$\nabla E(\mathbf{R}) = 0$$

$$\mathbf{R} = \{x_1, x_2, x_3, ...\}$$

The Hessian Matrix:

- 3Nx3N for N atoms
- Positive Eigenvalues at Minima
- One Negative Eigenvalue at Transition States (1^{st}-Order Saddles)

$$\begin{pmatrix} \frac{\partial^2 E}{\partial x_1^2} & \frac{\partial^2 E}{\partial x_1 \partial x_2} & \cdots \\ \frac{\partial^2 E}{\partial x_2 \partial x_1} & \frac{\partial^2 E}{\partial x_2^2} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}$$

The Barrier:

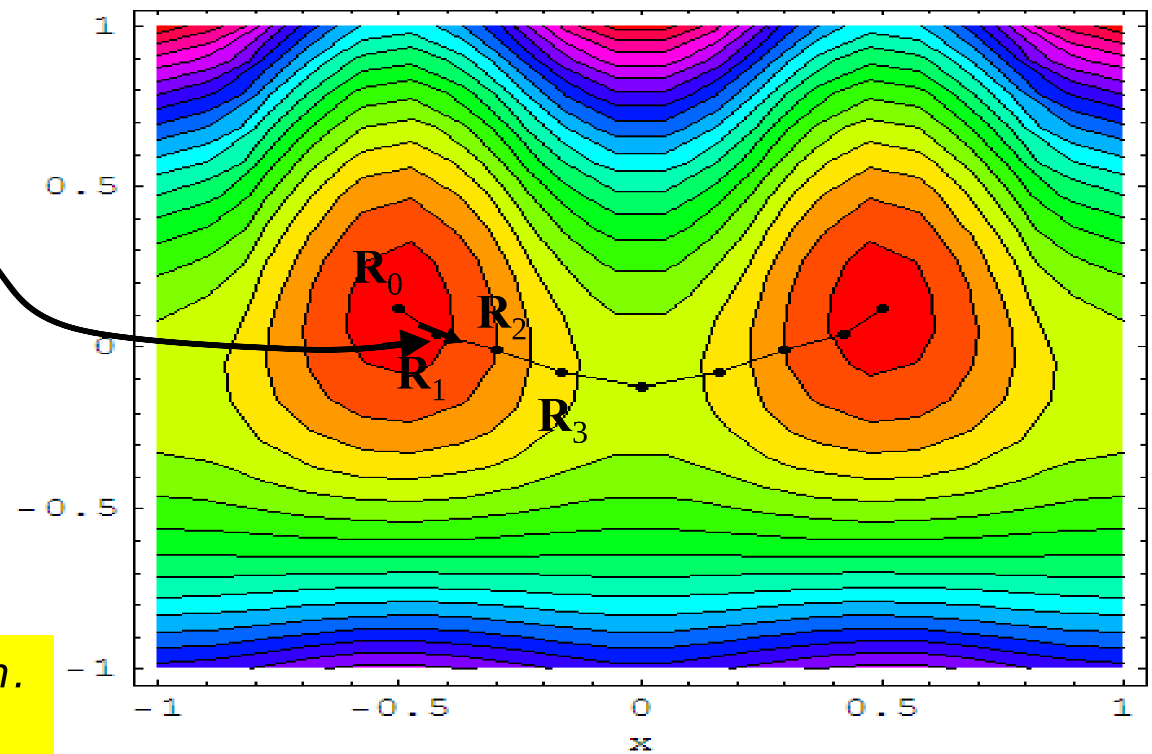
$$E_0 = E(\text{saddle}) - E(\text{minimum})$$

The Minimum-Energy Path
(AKA The Reaction Coordinate)

$$\underbrace{\nabla E(\mathbf{R}_i)}_{\text{Gradient}} - \underbrace{\left[\nabla E(\mathbf{R}_i)\cdot\hat{\boldsymbol{\tau}}_i\right]\hat{\boldsymbol{\tau}}_i}_{\text{Gradient Along MEP}} = 0; \qquad \frac{d\mathbf{R}_i}{dt} = -\nabla E(\mathbf{R}_i)\left[1-\hat{\boldsymbol{\tau}}_i\hat{\boldsymbol{\tau}}_i\right]$$

$$\hat{\boldsymbol{\tau}}_1 = \frac{\mathbf{R}_2-\mathbf{R}_0}{\left|\mathbf{R}_2-\mathbf{R}_0\right|}$$

$\hat{\boldsymbol{\tau}}_i$ = tangent to the path at *i*



A. Ulitsky and R. Elber, *J. Chem. Phys.* **92**, 1510 (1990).

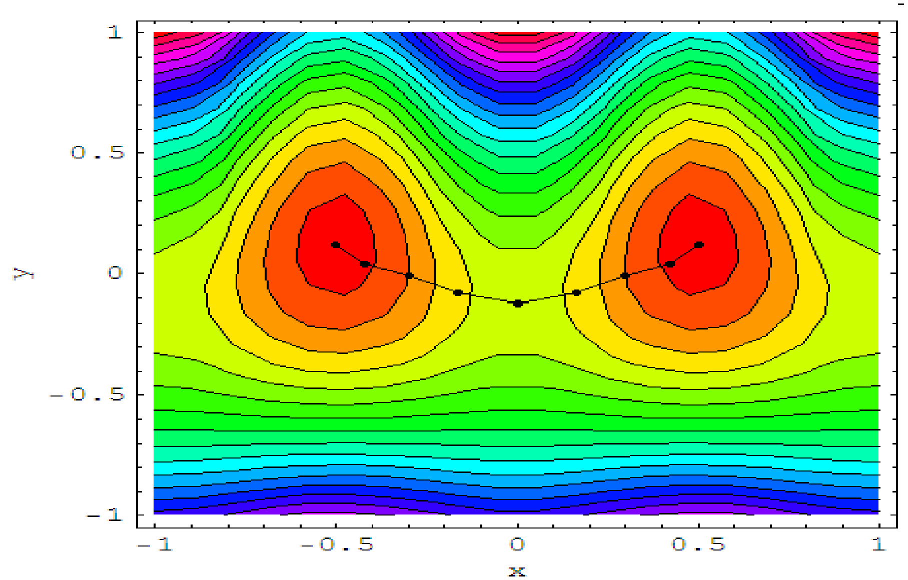
The Nudged Elastic Band Method

$$\underbrace{-\left\{\nabla E(\mathbf{R}_i) - \left[\nabla E(\mathbf{R}_i)\cdot\hat{\boldsymbol{\tau}}_i\right]\hat{\boldsymbol{\tau}}_i\right\}}_{\text{Force Orthogonal to Path }(=0)} + \underbrace{\mathbf{F}_i^s}_{\text{Spring Force Along Path (=0 for Equidistant Images)}} = 0$$

Springs Keep Images Distributed On the Path

$$\mathbf{F}_i^s = k\left(\left|\mathbf{R}_{i+1} - \mathbf{R}_i\right| - \left|\mathbf{R}_i - \mathbf{R}_{i-1}\right|\right)\cdot\hat{\boldsymbol{\tau}}_i$$

$$\frac{d\mathbf{R}_i}{dt} = -\nabla E_i\left(1 - \hat{\boldsymbol{\tau}}_i\hat{\boldsymbol{\tau}}_i\right) + \mathbf{F}_i^s$$



H. Jónsson, G. Mills, K. W. Jacobsen, in *"Classical and Quantum Dynamics in Condensed Phase Simulations"*, Ed. B. J. Berne, G. Ciccotti and D. F. Coker (World Scientific, 1998)

An Improved Tangent

$$\boldsymbol{\tau}_\mathbf{i} = \frac{\mathbf{R}_\mathbf{i} - \mathbf{R}_{\mathbf{i-1}}}{\left|\mathbf{R}_\mathbf{i} - \mathbf{R}_{\mathbf{i-1}}\right|} + \frac{\mathbf{R}_{\mathbf{i+1}} - \mathbf{R}_\mathbf{i}}{\left|\mathbf{R}_{\mathbf{i+1}} - \mathbf{R}_\mathbf{i}\right|}; \qquad \hat{\boldsymbol{\tau}}_\mathbf{i} = \boldsymbol{\tau}_\mathbf{i}/\left|\boldsymbol{\tau}_\mathbf{i}\right|$$

G. Henkelman and H. Jónsson, J. Chem. Phys. 113, 9978 (2000).

The Zero-Temperature String Method

W. E, W. Ren, and E. Vanden-Eijnden, *Phys. Rev. B* **66**, 052301 (2002).

The Climbing-Image NEB Method: Homing in on the Saddle Point

$$-\underbrace{\left\{\nabla E(\mathbf{R}_i) - \left[\nabla E(\mathbf{R}_i)\cdot\hat{\boldsymbol{\tau}}_i\right]\hat{\boldsymbol{\tau}}_i\right\}}_{\text{Force Orthogonal to Path }(=0)} + \underbrace{\mathbf{F}_i^s}_{\text{Spring Force Along Path (=0 for Equidistant Images)}} = 0$$

$$\mathbf{F}_i^s = k\left(\left|\mathbf{R}_{i+1} - \mathbf{R}_i\right| - \left|\mathbf{R}_i - \mathbf{R}_{i-1}\right|\right)\cdot\hat{\boldsymbol{\tau}}_i$$

Identify the Image with the Maximum Energy “max”
Walk that Image “Uphill” to the Saddle

$$F_{\text{max}} = -\nabla E(\mathbf{R}_{\text{max}}) + 2\nabla E(\mathbf{R}_{\text{max}})\cdot\hat{\boldsymbol{\tau}}_{\text{max}}\hat{\boldsymbol{\tau}}_{\text{max}}$$

G. Henkelman, B.Uberauga, and H. Jónsson,
J. Chem. Phys. 113, 9901 (2000).

The Significance of the Barrier

$$k_{TST} = \nu \frac{\int \delta(\mathbf{R}-\mathbf{R}^*) \exp(-E(\mathbf{R})/k_B T)}{\int \exp(-E(\mathbf{R})/k_B T)}$$

$$= \nu_0 \frac{Q^*}{Q} \exp(-E_0/k_B T)$$

$$= A \exp(-E_0/k_B T)$$

Q, Q^* - partition functions
E_0 - barrier

Equilibrium and Kinetics

$$A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B$$

$$K_{eq} = \exp(-\Delta G / k_B T)$$

$$= \exp(-(\Delta E - T\Delta S)/k_B T)$$

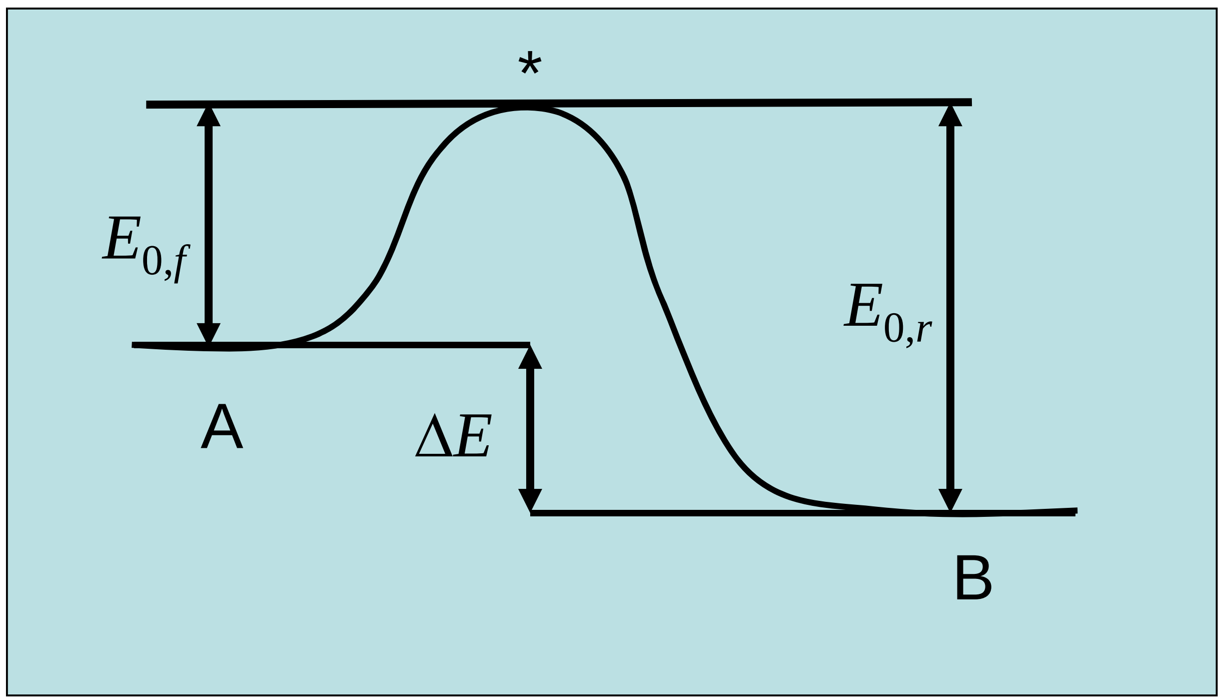
$$= \exp(\Delta S / k_B)\exp(-\Delta E / k_B T)$$

$$= \frac{k_f}{k_r} = \frac{A_f}{A_r}\exp(-(E_{0,r} - E_{0,f})/k_B T)$$

$$k_f = A\exp(-E_{0,f}/k_B T)$$

$$A = \nu_0 \exp(\Delta S^* / k_B)$$

$$E_{0,f} = \Delta E^*$$



Cooking with TST: The Partition Functions

D. A. McQuarrie, *Statistical Mechanics*, University Science Books, Sausalito, CA, 2000.

$$k_{TST} = A\exp(-E_0 / k_B T)$$

$$A = \nu_0 \frac{Q^*}{Q}$$

$$Q = q_t q_r q_v q_e$$

q_t - translational partition function
q_r - rotational partition function
q_v – vibrational partition function
q_e – electronic partition function

$$q_t = \frac{(2\pi m k_B T)^{3/2}}{h^3} [=] \, length^{-3}$$

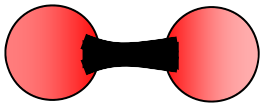
m = mass

$$q_v = \frac{1}{1 - \exp(-h\nu / k_B T)}$$

ν = frequency [=] time^{-1}

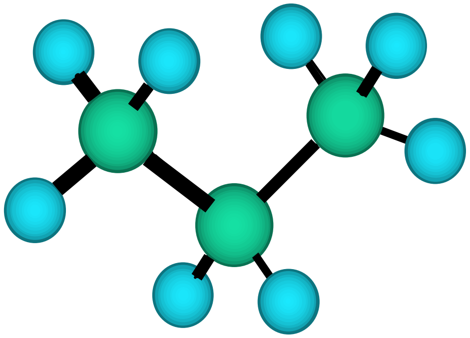
Cooking with TST: The Partition Functions

$$q_{2r} = \frac{\left(8\pi^2 I k_B T\right)}{\sigma h^2}$$



I = moment of inertia
σ = symmetry number

$$q_{3r} = \frac{8\pi^2\left(8\pi^3 I_A I_B I_C\right)^{1/2}\left(k_B T\right)^{3/2}}{\sigma h^3}$$



I_A, I_B, I_C = moments of inertia – 3 principal axes

$$q_{ir} = \frac{\left(8\pi^2 I' k_B T\right)^{1/2}}{h}$$

I' = moment of inertia for internal rotation

Cooking with TST: The Partition Functions

$$q_e = \sum_i g_i \exp(-\varepsilon_i / k_B T)$$

ε_i = energy of i^{th} excited state
g_i = degeneracy of state i

$$Q = \underbrace{q_e}_{\text{electronic}} \cdot \underbrace{q_t q_r q_v}_{\text{configurational}}$$

electronic → Has the form given above

configurational → Depends on the structure of the molecule or system

Constructing the Partition Function

A molecule/system with N atoms has 3N degrees of freedom

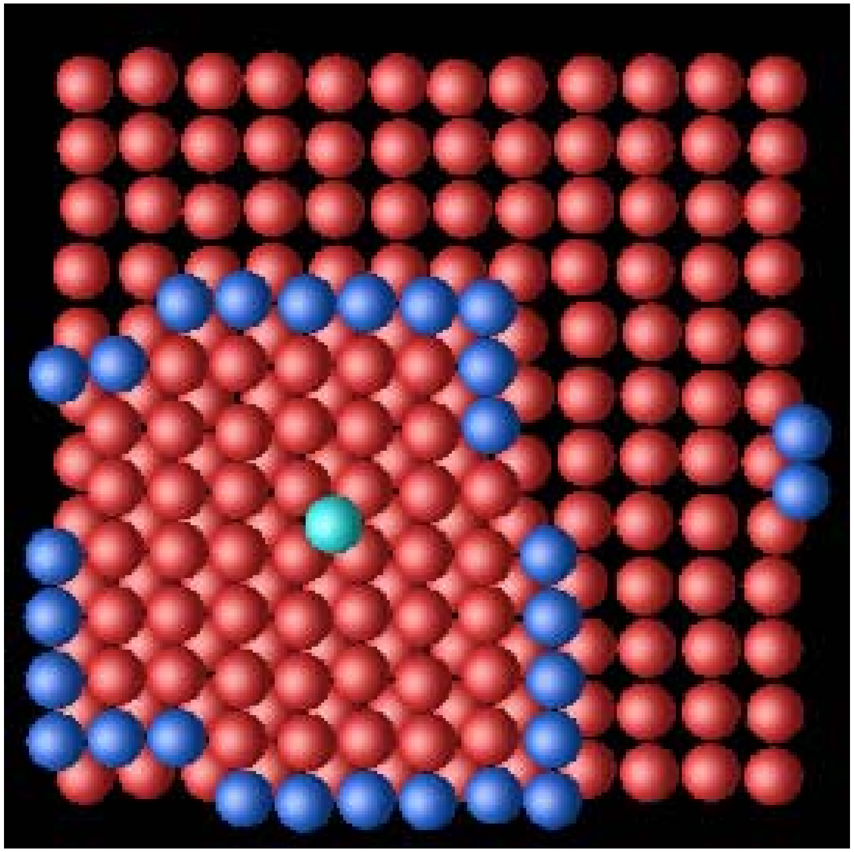
3 Translation – q_t

Rotation: 3 d.o.f. for nonlinear molecules – q_{3r}
2 d.o.f. for linear molecules – q_{2r}
1 d.o.f. for each internal rotation - q_{ir}
e.g., $q_r = q_{3r} q_{ir}$ – 4 d.o.f.

Vibration: 1 d.o.f. for each vibration - q_v

Subtract 1 d.o.f. for motion over the transition state

The Harmonic Approximation: Good for Motion in and on Solids



A Case of Special Interest for Solids: The Harmonic Approximation

$$k_{TST} = \nu_0 \frac{Q_{A^*}}{Q_A} \exp(-E_0 / k_B T) \quad ; \quad \nu_0 = \frac{k_B T}{h}$$

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

A – 3N d.o.f.
- 3 translation
- 3 rotation
- 3N-6 vibration

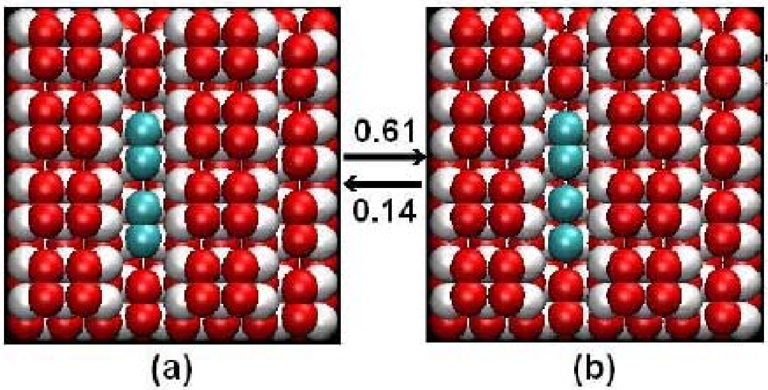
$$Q_A = q_t q_{3r} \prod_{j=1}^{3N-6} \left[1 - \exp\left(-h\nu_j / k_B T\right)\right]^{-1}$$

A* - 3N d.o.f. – 1 for motion over the saddle
- 3 translation
- 3 rotation
- 3N-7 vibration

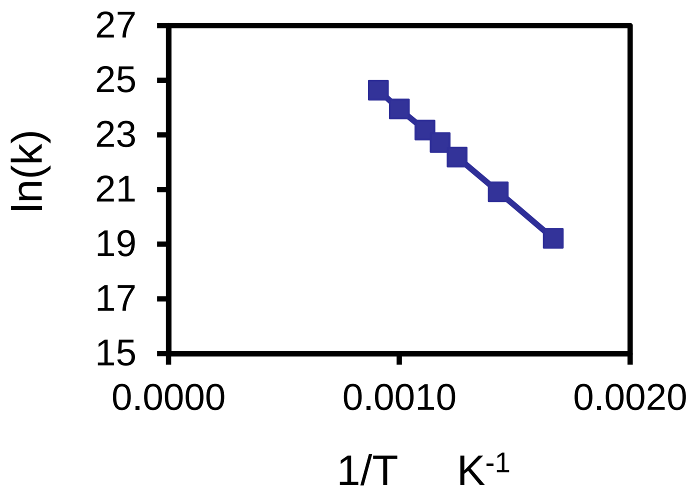
$$Q_{A^*} = q_t q_{3r} \prod_{j=1}^{3N-7} \left[1 - \exp\left(-h\nu_j / k_B T\right)\right]^{-1}$$

$$k_{TST} = \nu_0 \frac{\prod_{j=1}^{3N-7} q^*_{v,j}}{\prod_{j=1}^{3N-6} q_{v,j}} \exp(-E_0 / k_B T) \xrightarrow{\text{High } T \text{ Limit}} \frac{\prod_{j=1}^{3N-6} \nu_j}{\prod_{j=1}^{3N-7} \nu^*_j} \exp(-E_0 / k_B T)$$

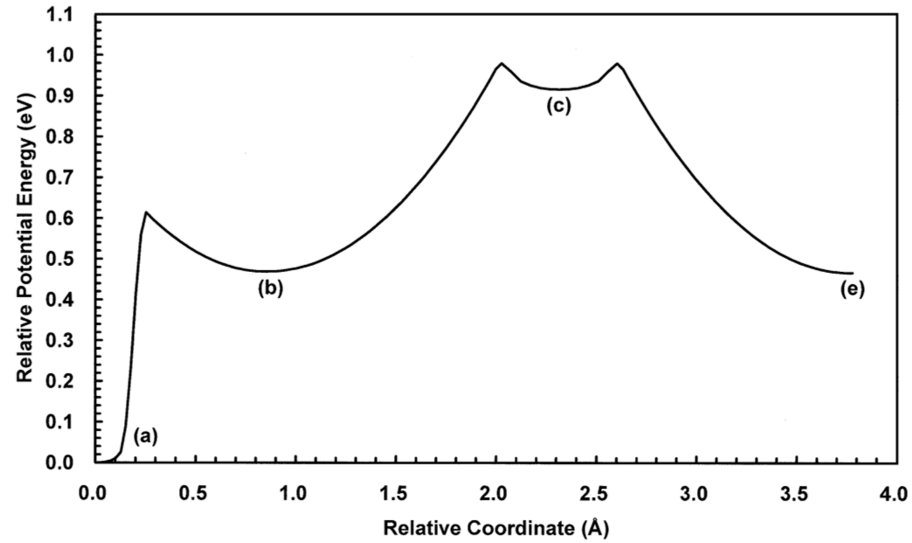
GaAs(001) $\beta 2(2\times4)$ Initiation of Trench Shifting: A Test of HTST



Molecular Dynamics Arrhenius Plot



Y. Lin and K. Fichthorn
(Submitted to Phys. Rev. B)



Minimum-Energy Pathway: CI-NEB

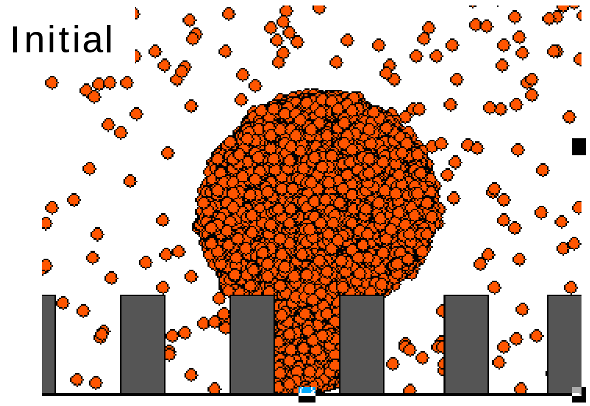
From HTST: $\nu_0 = 2.29\times10^{13}\ s^{-1}$
Normal-Mode Analysis

From MD: $\nu_0 = 3.33\times10^{13}\ s^{-1}$
$E_0 = 0.614$ eV

Forward Flux Sampling

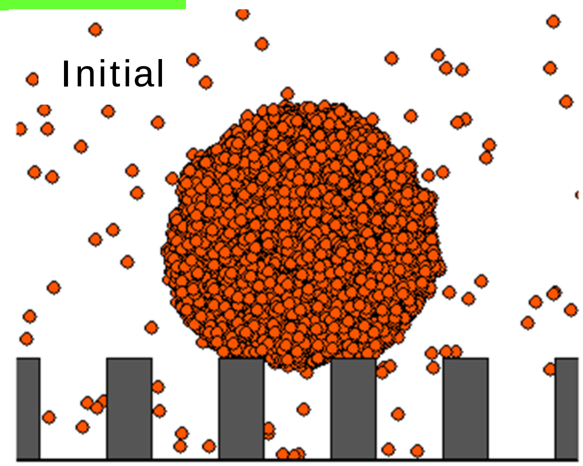
R. J. Allen, C. Valeriani, and P. R. ten Wolde, J. Phys.: Condens. Matter 21, 463102 (2009)

Rare Events with a Significant Entropic Component e.g., Liquid Droplet Wetting on Patterned Surfaces



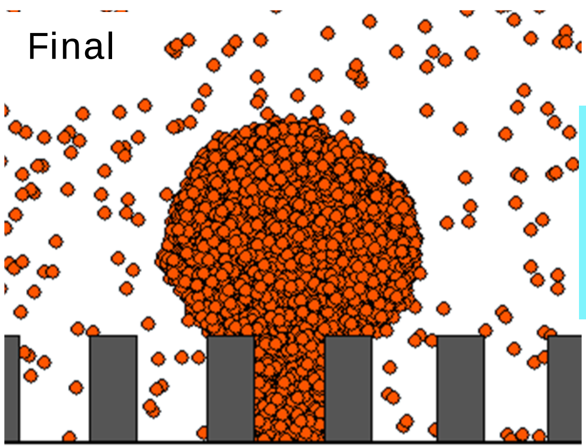
$\theta_0 = 147^\circ \pm 2^\circ$

$\theta_0 = 155^\circ \pm 2^\circ$



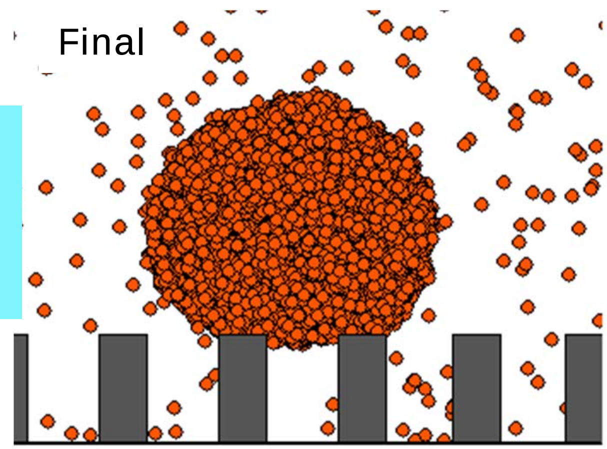
Wenzel State

Cassie State



$\theta = 145^\circ \pm 2^\circ$

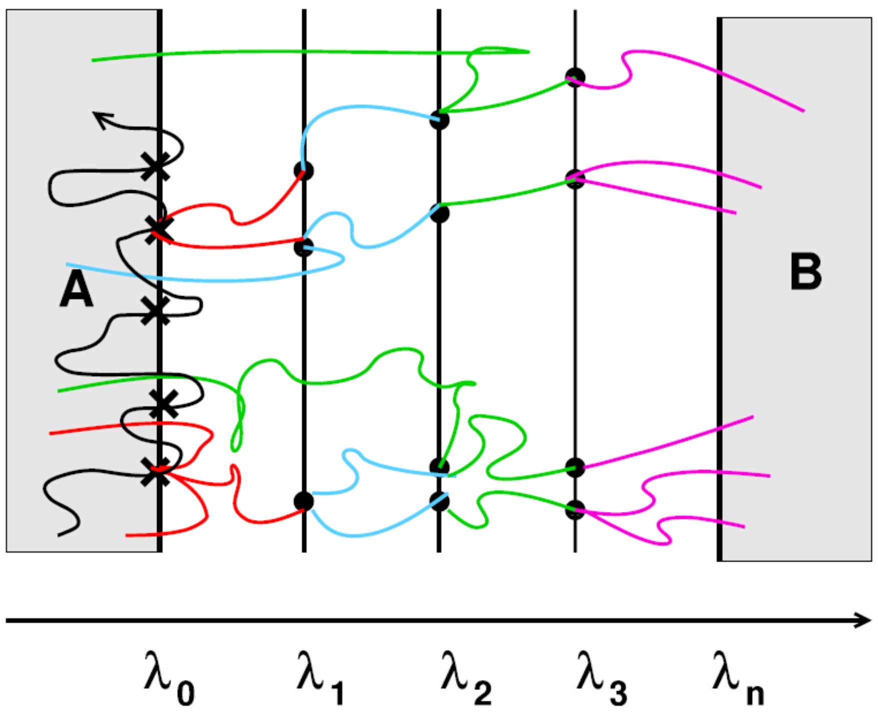
$\theta = 150^\circ \pm 2^\circ$



There is a Free-Energy Barrier Between Cassie and Wenzel States

Forward Flux Sampling

λ = Order Parameter for the Transition
A variable that monitors the transition.



Obtain transitions between successive values of λ to calculate k_{AB}

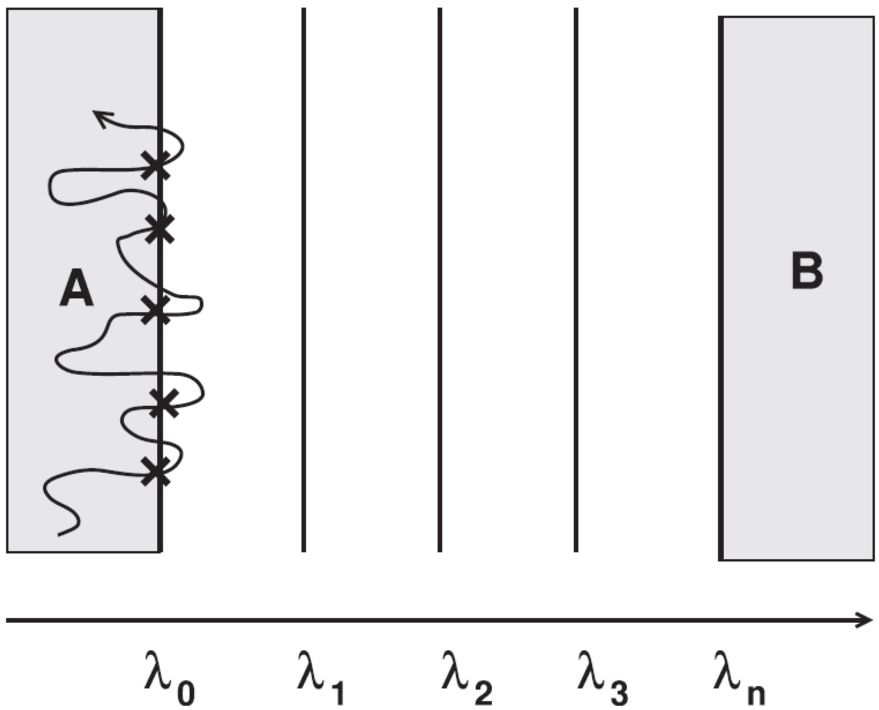
$$k_{AB} = \Phi_{A,0} P(\lambda_n \mid \lambda_0)$$

Computationally Intensive!!

Forward Flux Sampling

λ = Order Parameter for the Transition
A variable that monitors the transition.

$$k_{AB} = \Phi_{A,0} P(\lambda_n | \lambda_0) = \Phi_{A,0} \prod_{i=0}^{n-1} P(\lambda_{i+1} | \lambda_i)$$



Calculating $\Phi_{A,0}$

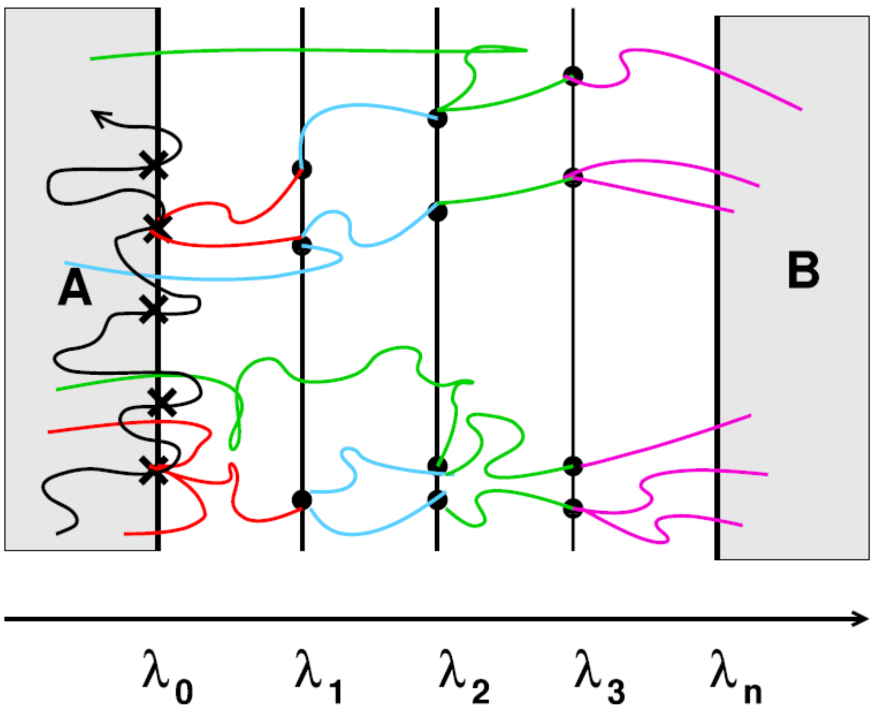
- Equilibrate System in A
- Monitor λ at each time step
- When λ crosses λ_0 coming from A, increment counter N

$$\Phi_{A,0} = N / t$$

Forward Flux Sampling

λ = Order Parameter for the Transition
A variable that monitors the transition.

$$k_{AB} = \Phi_{A,0} P(\lambda_n \mid \lambda_0) = \Phi_{A,0} \prod_{i=0}^{n-1} P(\lambda_{i+1} \mid \lambda_i)$$



Calculating $P(\lambda_{i+1}|\lambda_i)$

For a Trajectory from λ_i:

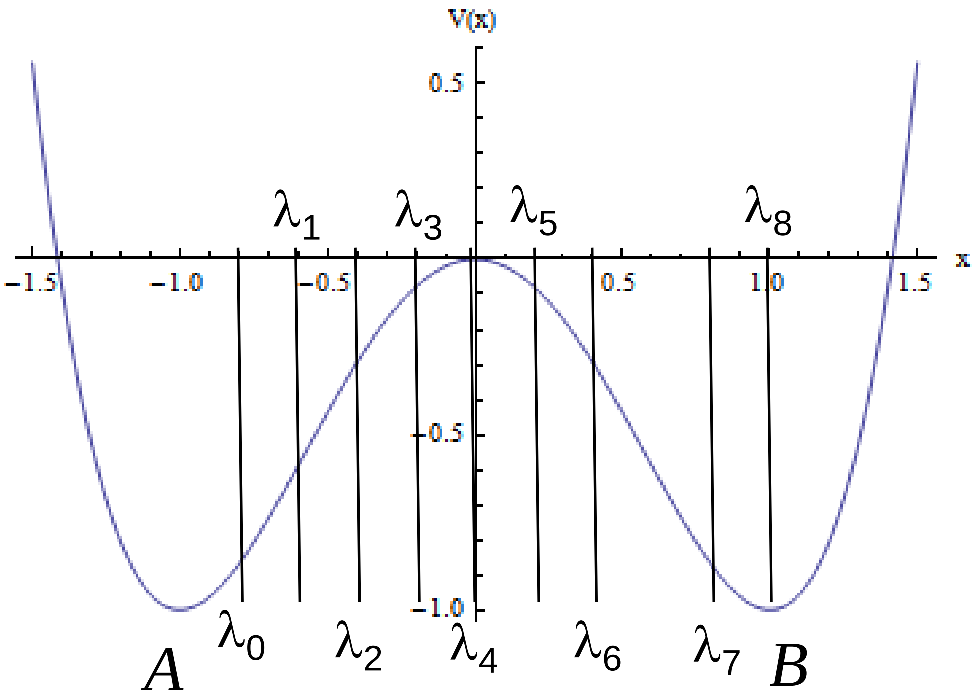
- Monitor λ at each time step
- If λ reaches λ_{i+1} coming from λ_i, increment counter N, increment total counter M
- If λ reaches λ_0, increment total counter M

$$P(\lambda_{i+1} \mid \lambda_i) = N / M$$

Forward Flux Sampling

λ = Order Parameter for the Transition

$P_B(x)$ = Committor: Probability that a trajectory initiated from x will reach B before it reaches A



$$V(x) = -bx^2 + cx^4$$

For Our Example:

$$P_B(x) = P_B(\lambda_i) = \prod_{j=i}^{n-1} P(\lambda_{j+1} \mid \lambda_j)$$

P_B=0.5 for the Transition State Ensemble