Physical Sampling II: Kinetics

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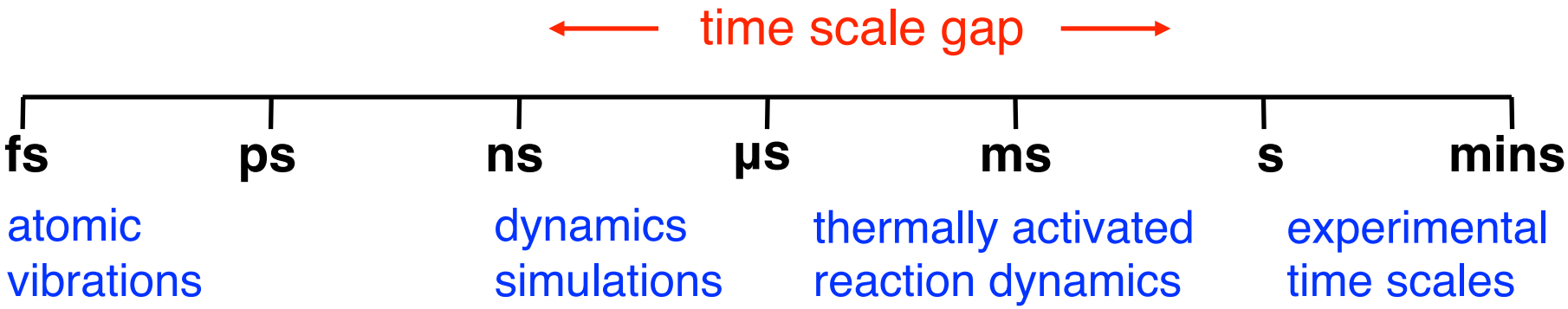
University of Texas at Austin

A problem of time scale

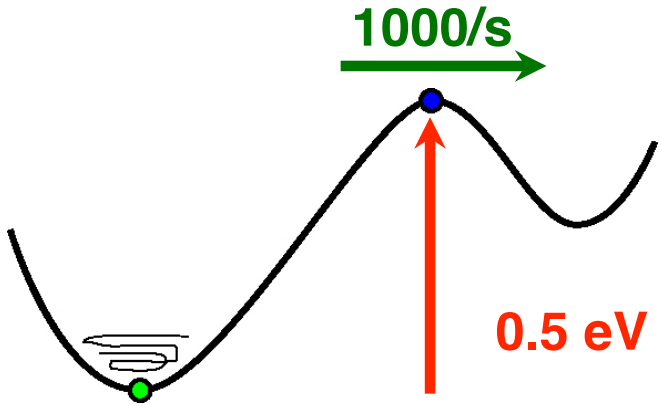
Atoms move on a femtosecond time scale, but many interesting processes occur on a human time scale of seconds or minutes.



We need computational methods which can reach time scales that are orders of magnitude longer than possible with classical dynamics

How can we use parallel computational resources to extend the time scale of atomistic simulations?

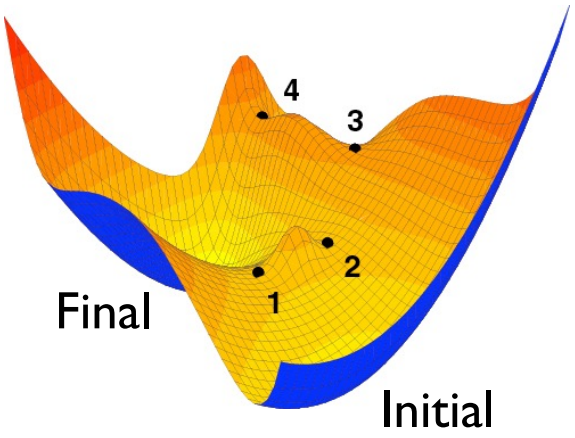
A classical dynamics simulation of a typical rare event requires ~10^{12} steps!

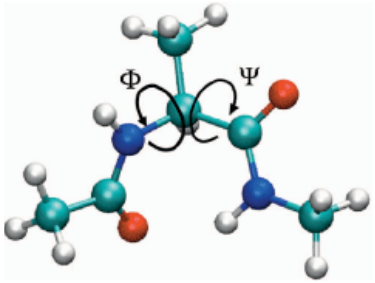


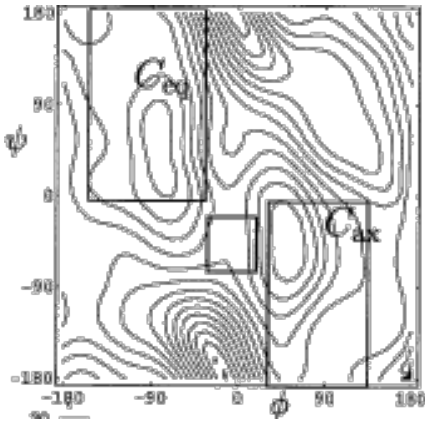
Classes of Dynamical Systems

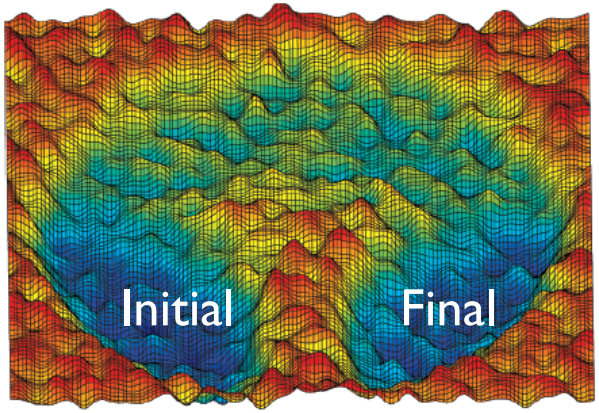
Energy Landscape: Smooth → Rough

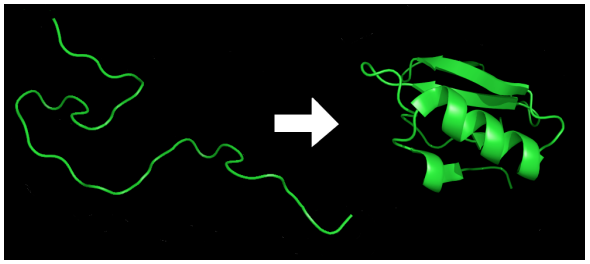
Final State: Known → Unknown

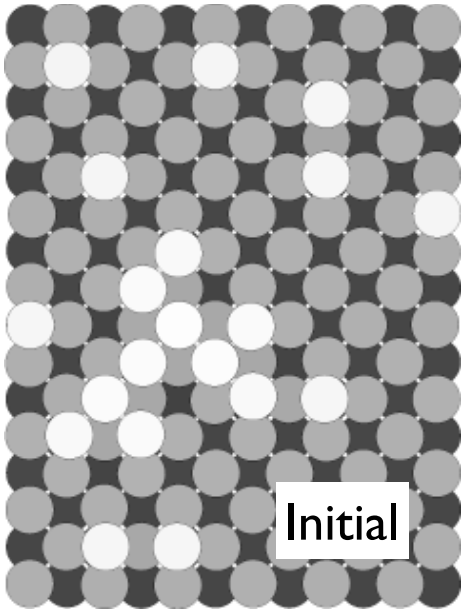


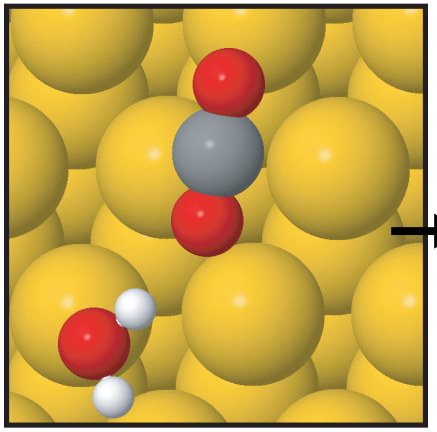












?

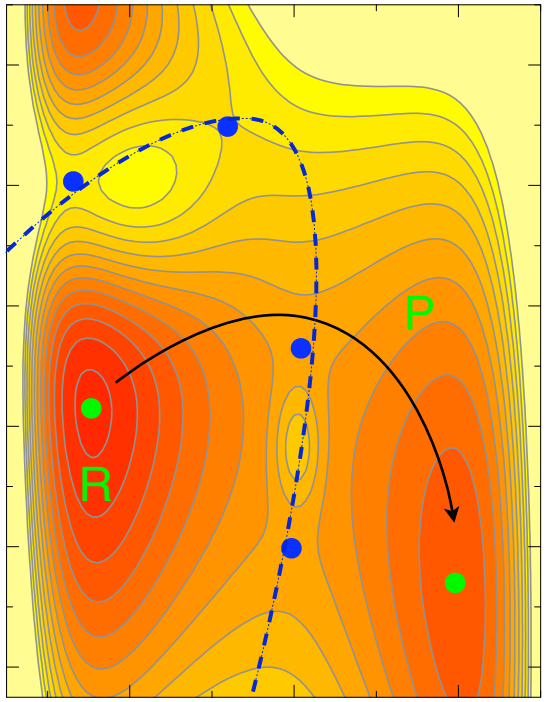
Transition state theory

A statistical theory for calculating the rate of slow thermal processes — rare event dynamics

Requires an N-1 dimensional dividing surface that is a bottleneck for the transition:

$$x = x^\dagger$$

$$k_{\mathrm{TST}} = \frac{1}{2} \left\langle \delta(x - x^\dagger) |v_\perp| \right\rangle_R$$



Minima
Saddle Points

Variational TST

TST assumes that all trajectories that cross the *TS* are reactive trajectories.

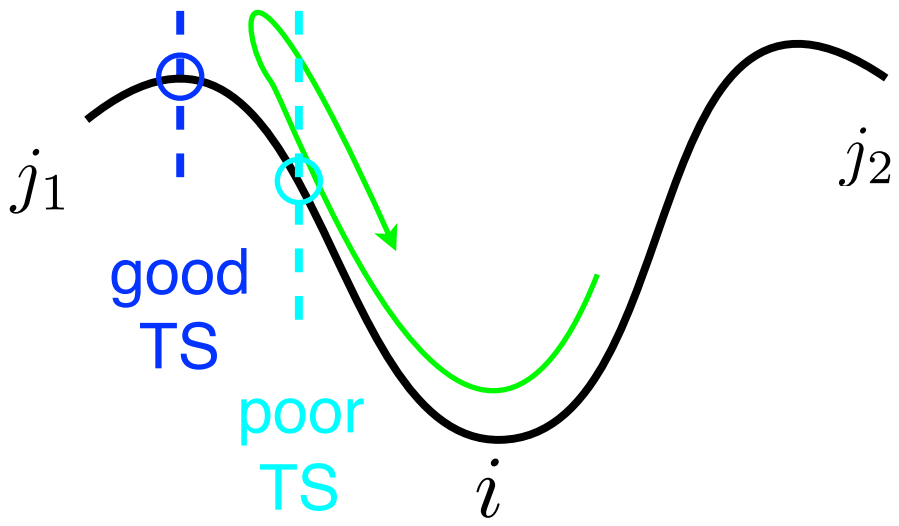
$$\mathrm{k}_{i\rightarrow}^{\mathrm{TST}} = \tfrac{1}{2}\langle \delta(x - x^{\dagger}) |v_{\perp}| \rangle_R$$

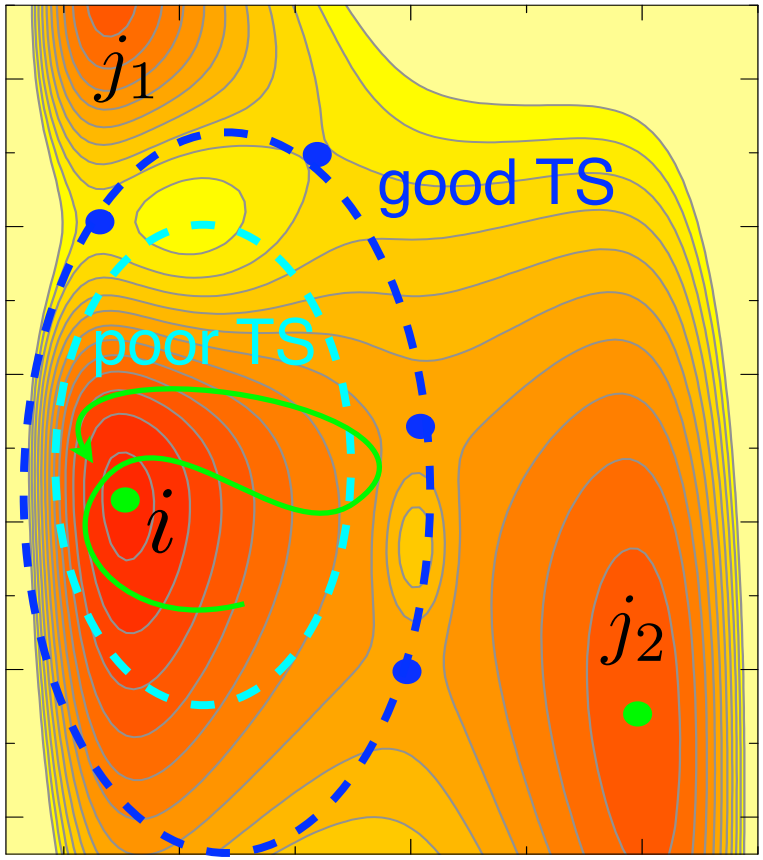
TST variationally overestimates the true rate:

$$\mathrm{k}_{i\rightarrow}^{\mathrm{TST}} \geq \mathrm{k}_{i\rightarrow}$$

Good TS surface:

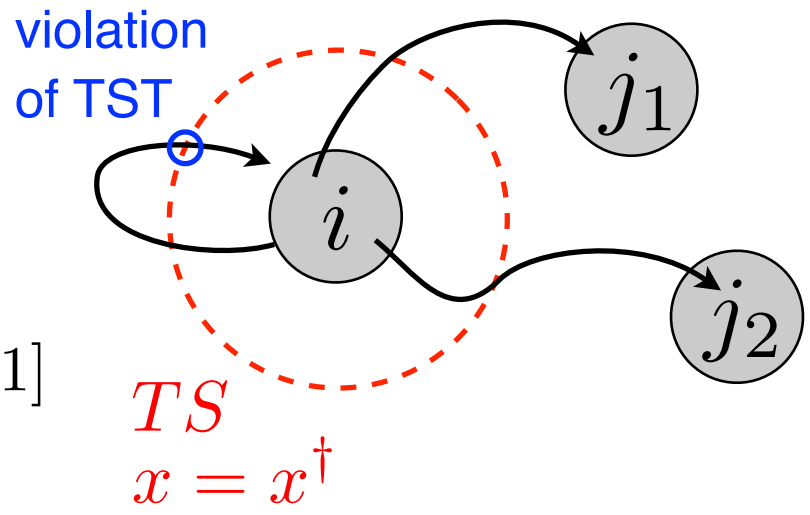
- separates reactants from products
- minimizes recrossings
- maximizes its free energy





Dynamical corrections to TST

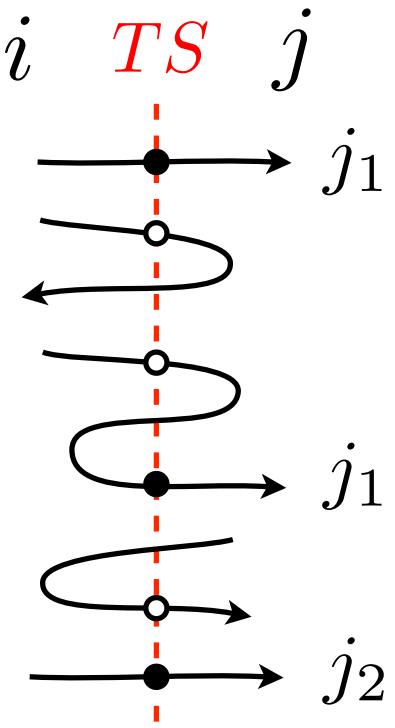
TST assumes that all trajectories that cross the *TS* are reactive trajectories.



Dynamical correction factor:

$$\kappa = \frac{\langle \theta(x(t) - x^\dagger) v_\perp \delta(x_0 - x^\dagger) \rangle}{\langle \theta(v_\perp) v_\perp \delta(x_0 - x^\dagger) \rangle} \in [0, 1]$$

- ratio of successful trajectories to number of TS crossing points
- ratio between the TST and true rate: $\mathrm{k}_{i\to} = \kappa_{i\to}\ \mathrm{k}_{i\to}^{\mathrm{TST}}$



A successful trajectory:

1) trajectory must go directly to products without recrossing the TS

2) trajectory must start in initial state

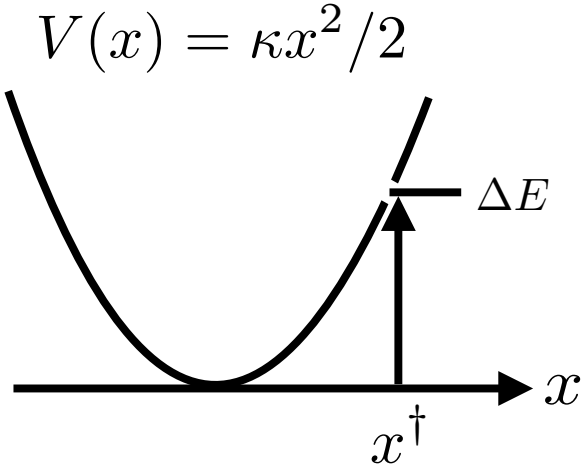
Example:

$$\kappa_{i\to} = 1/2$$
$$\kappa_{i\to j_1} = 1/3$$
$$\kappa_{i\to j_2} = 1/6$$

Harmonic transition state theory

Transition state theory

$$k_{\mathrm{TST}} = \frac{1}{2}\left\langle \delta(x - x^{\dagger})|v_{\perp}|\right\rangle_{R}$$



Momentum

here, independent of position and direction

$$\langle|p|\rangle = \frac{\int_p |p| e^{-p^2/2mkT} dp}{\int_p e^{-p^2/2mkT} dp} = \frac{mkT}{\sqrt{2\pi mkT}} = \sqrt{\frac{2mkT}{\pi}} \qquad \langle|v|\rangle = \sqrt{\frac{2kT}{\pi m}}$$

and configuration

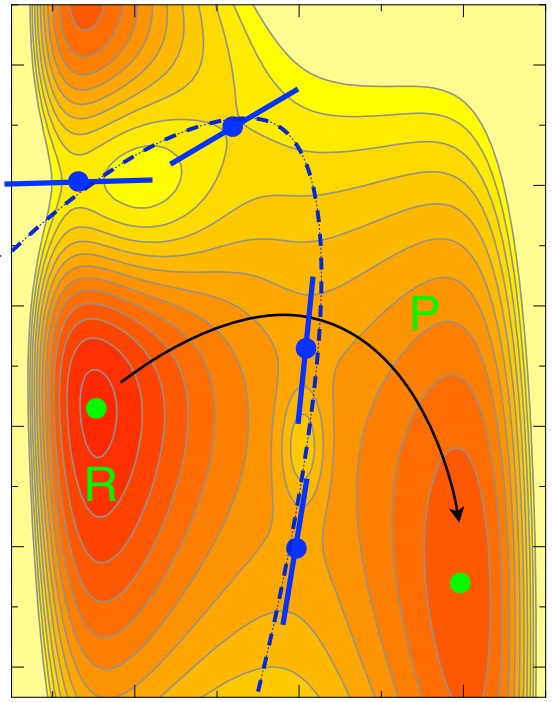
$$\begin{aligned} k_{\mathrm{TST}}^{\mathrm{HO}} &= \frac{1}{2}\sqrt{\frac{2kT}{\pi m}}\left\langle \delta(r - r^{\dagger})\right\rangle_{R} \\ &= \frac{1}{2}\sqrt{\frac{2kT}{\pi m}}\frac{\int_x e^{-\kappa x^2/2kT}\delta(x - x^{\dagger})dx}{\int_x e^{-\kappa x^2/2kT}dx} \\ &= \frac{1}{2}\sqrt{\frac{2kT}{\pi m}}\frac{e^{-\Delta E/kT}}{\sqrt{2\pi kT/\kappa}} \\ &= \frac{1}{2\pi}\sqrt{\frac{\kappa}{m}}\, e^{-\Delta E/kT} = \nu e^{-\Delta E/kT} \end{aligned}$$

Transition state theory

A statistical theory for calculating the rate of slow thermal processes — rare event dynamics

Requires an N-1 dimensional dividing surface that is a bottleneck for the transition:

$$x = x^\dagger$$



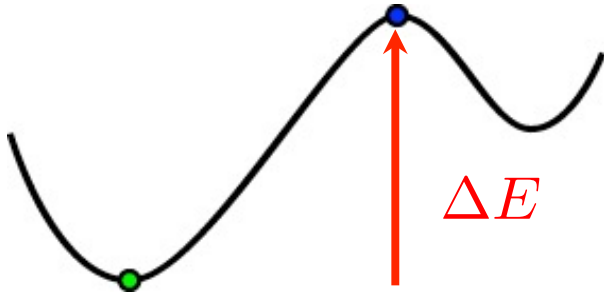
$$k_{\mathrm{TST}} = \frac{1}{2}\left\langle \delta(x - x^\dagger)|v_\perp|\right\rangle_R$$

Harmonic transition state theory

Find saddle points on the energy surface

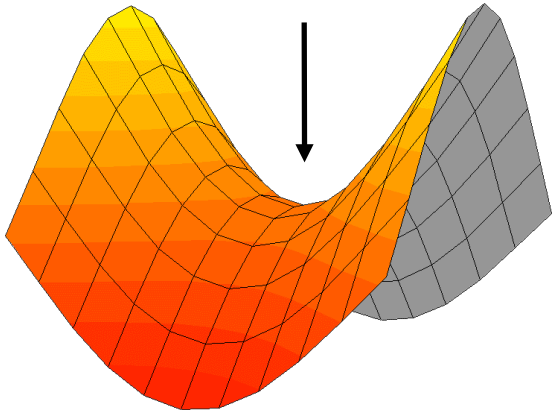
Rate of escape through each saddle point region:

$$k_{\mathrm{HTST}} = \frac{\prod_{i=1}^{N} \nu_i}{\prod_{j=1}^{N-1} \nu_j^\dagger} \exp\left(-\frac{\Delta E}{k_{\mathrm{B}} T}\right)$$



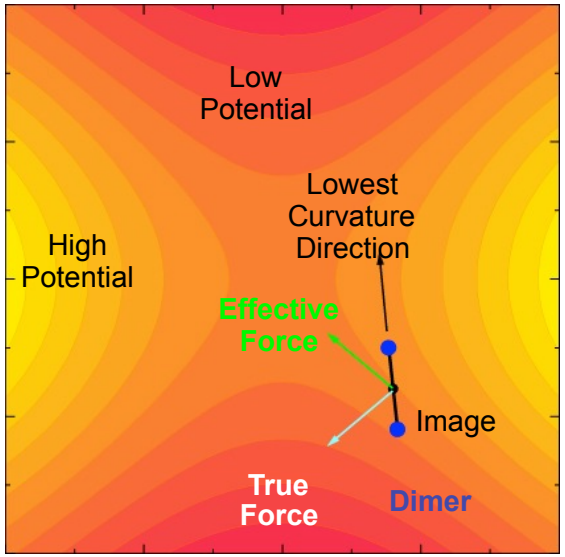
Methods for finding transition states

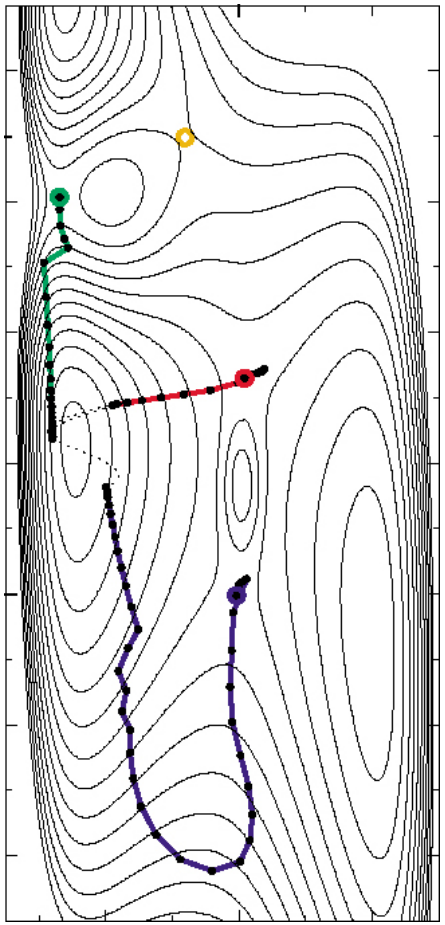
Find saddle points



Min-mode following:

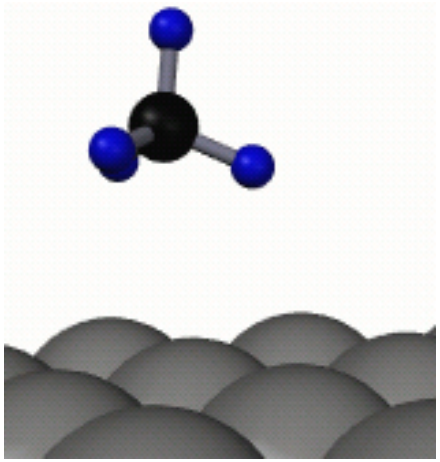
Unknown final state

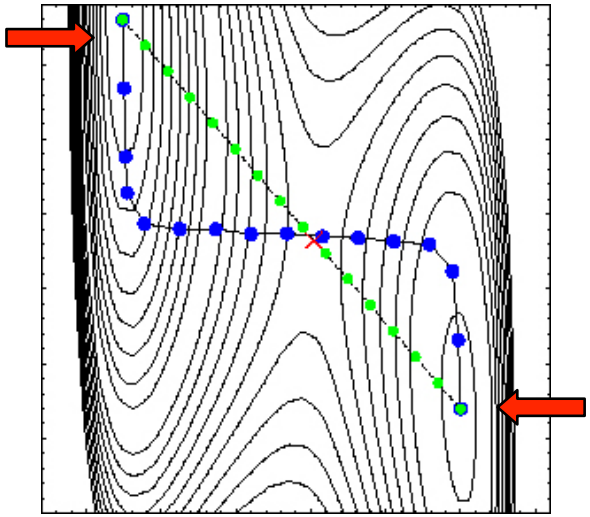


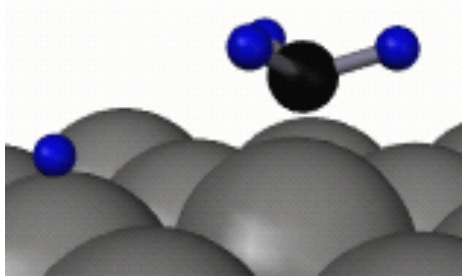


Nudged elastic band:

Known final state







Nudged elastic band method

Pioneering work

Pratt, Elber, Karplus, ... and others

Nudged elastic band

Images connect initial and final states

NEB force on each image:

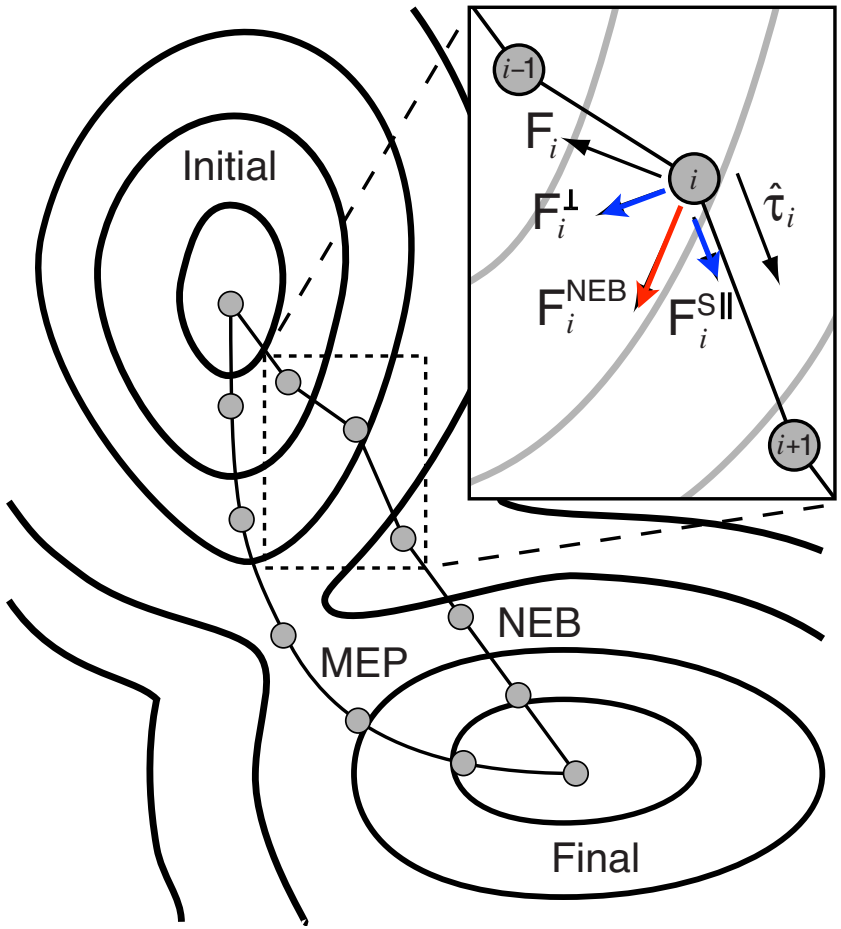
$$\mathbf{F}_i^{\mathrm{NEB}} = \mathbf{F}_i^{\perp} + \mathbf{F}_i^{\mathrm{S}\parallel}$$

Perpendicular component (potential):

$$\mathbf{F}_i^{\perp} = -\nabla(\mathbf{R}_i) + \nabla(\mathbf{R}_i) \cdot \hat{\boldsymbol{\tau}}_i \hat{\boldsymbol{\tau}}_i$$

Parallel component (springs):

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



[1] H. Jónsson, G. Mills, and K.W. Jacobsen, in *Classical and Quantum Dynamics in Condensed Phase Simulations*, 385 (1998).
[2] G. Henkelman and H. Jónsson, *J. Chem. Phys.* **113**, 9978 (2000).
[3] G. Henkelman, B. P. Uberuaga, and H. Jónsson, *J. Chem. Phys.* **113**, 9901 (2000).

Related methods

Adaptive nudged elastic band

P. Maragakis, S. A. Andreev, Y. Brumer, D. R. Reichman, E. Kaxiras *J. Chem. Phys.* **117**, 4651 (2002).

add images along the path to improve resolution where needed

Doubly nudged elastic band

S. A. Trygubenko D. J. Wales, *J. Chem. Phys.* **120**, 2082 (2004).

include projected spring forces to maintain a short path

String method replace springs with constraints

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

Growing string

P. Maragakis, S. A. Andreev, Y. Brumer, D. R. Reichman, E. Kaxiras *J. Chem. Phys.* **117**, 4651 (2002).

start from points in the initial and final states

Ridge method follow a ridge between minima down to a saddle

I. V. Ionova and E. A. Carter, *J. Chem. Phys.* **98**, 6377 (1993).

Step and slide follow potential contours up from minima to a saddle

R. A. Miron and K. A. Fichthorn, *J. Chem. Phys.* **115**, 8742 (2001)

Drag method drive the system along an assume reaction coordinate

No one should take credit for this method

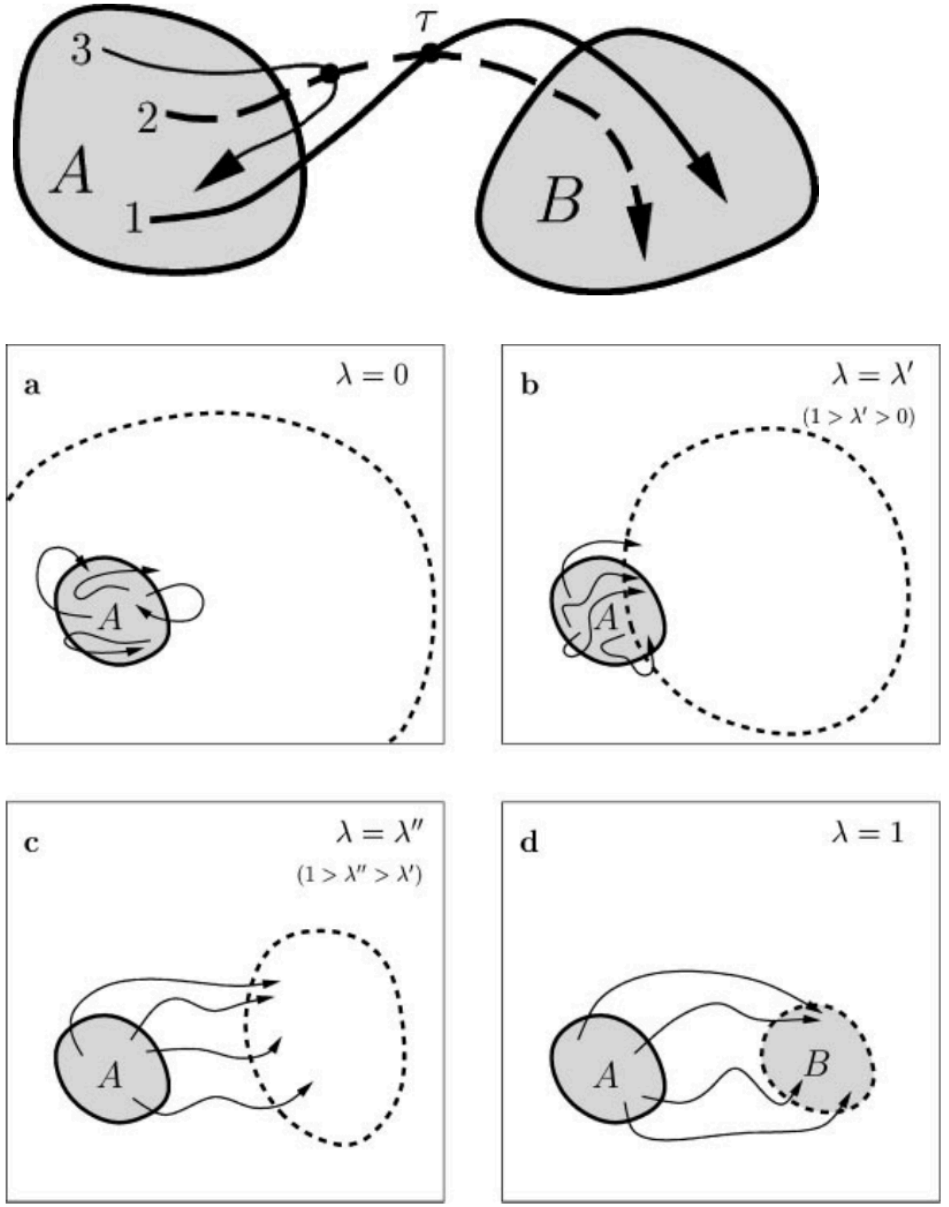
Transition path sampling

Sample paths

that go from A to B with shifting (moving forward or backward in time) or shooting (selecting new momenta at a point)

Calculate rates

need to define a reaction coordinate from A to B along which the probability of having successful trajectories can be calculated

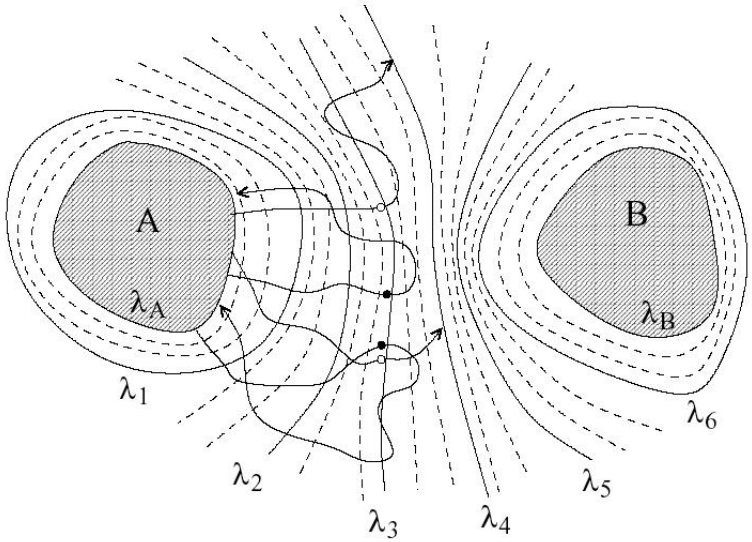


P. G. Bolhuis, D. Chandler, C. Dellago, and P. L. Geissler, *Annu. Rev. Phys. Chem.* **53,** 291 (2002)

Sampled reaction path methods

Transition interface sampling

for 2-state systems



$$k_{AB} = \frac{\langle \Phi_{A,\lambda_1} \rangle}{\langle h_A \rangle} \prod_{i=1}^{n-1} \langle \bar{h}^f_{\Omega_{\lambda_{i+1}},A} \rangle_{\Phi_{A,\lambda_i}} \langle \bar{h}^f_{B,A} \rangle_{\Phi_{A,\lambda_n}}$$

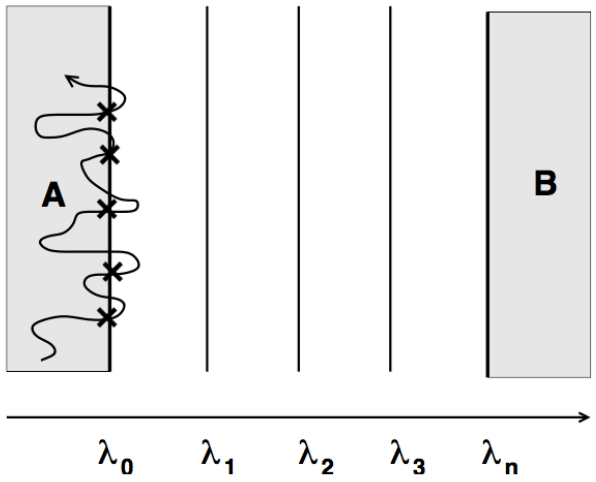
$$\equiv \frac{\langle \Phi_{A,\lambda_1} \rangle}{\langle h_A \rangle} \prod_{i=1}^{n-1} \mathcal{P}(\lambda_{i+1}|\lambda_i) \mathcal{P}(\lambda_B|\lambda_n)$$

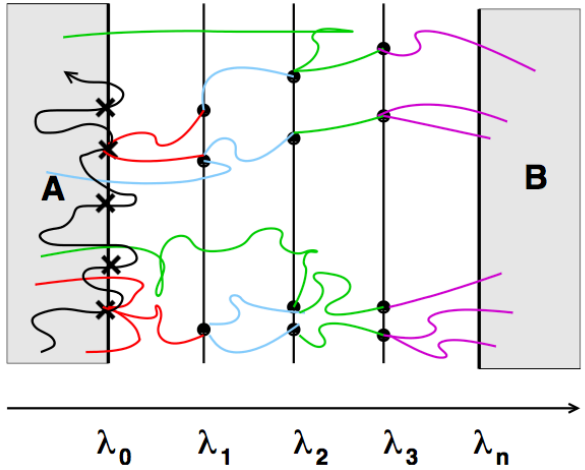
$$= \frac{\langle \Phi_{A,\lambda_1} \rangle}{\langle h_A \rangle} \langle \bar{h}^f_{B,A} \rangle_{\Phi_{A,\lambda_1}} \equiv \frac{\langle \Phi_{A,\lambda_1} \rangle}{\langle h_A \rangle} \mathcal{P}(\lambda_B|\lambda_1).$$

T. S. van Erp and P. G. Bolhuis.
J. Comp. Phys. **205**:157, (2005).

Forward flux

does not assume equilibrium





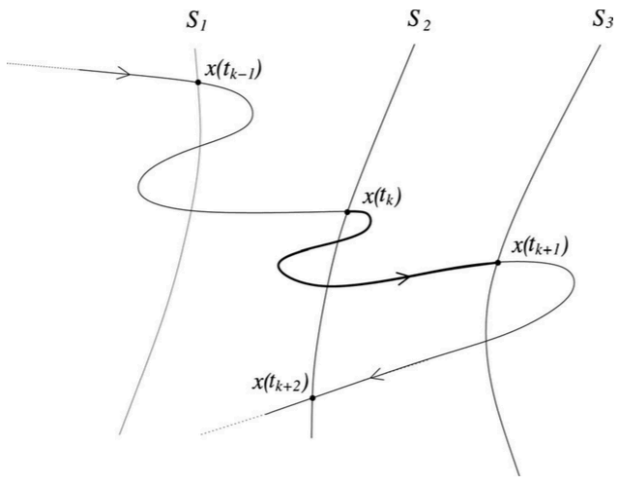
R. J. Allen, P. B. Warren, and P. R. ten Wolde, *Phys. Rev. Lett.* **94**, 018104, (2005).

Related reaction path methods

Milestoning

system must lose memory between milestones

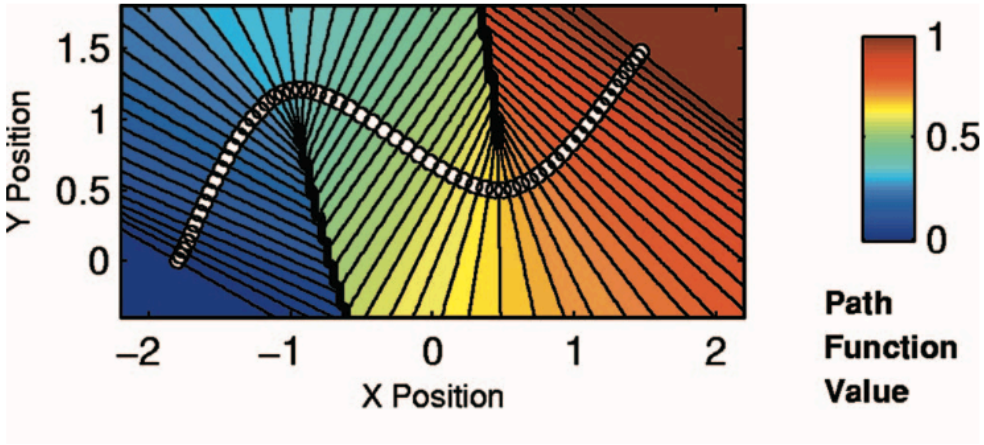
appropriate for diffusive and multistep reactions



A. K. Faradjian and R. Elber, *J. Chem. Phys.* **120,** 10880 (2004)

Multi-dimensions

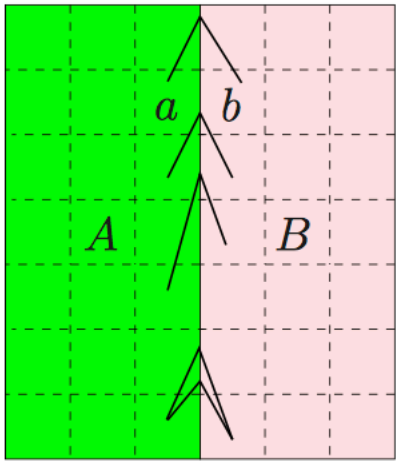
with Voronoi construction



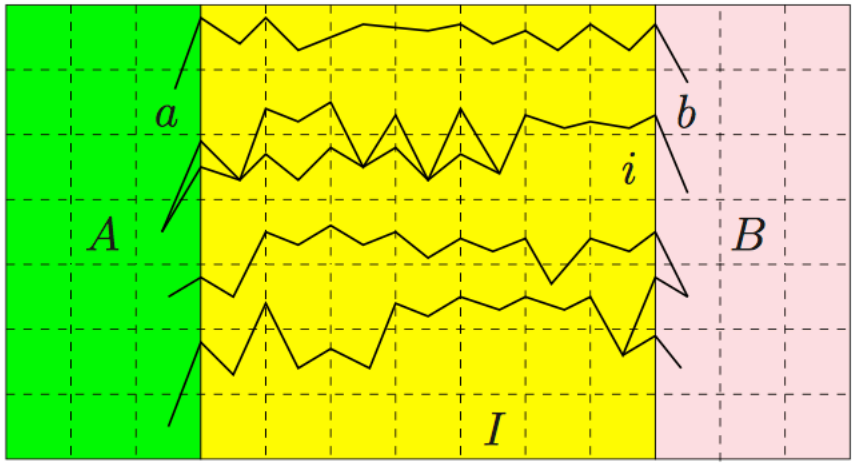
E. Vanden-Eijnden and M. Venturoli, *J. Chem. Phys.* **130**, 194101 (2009)

Discrete path sampling

Sample minimum energy paths for an entire network between A and B; solve the master equation for the steady state rate between them

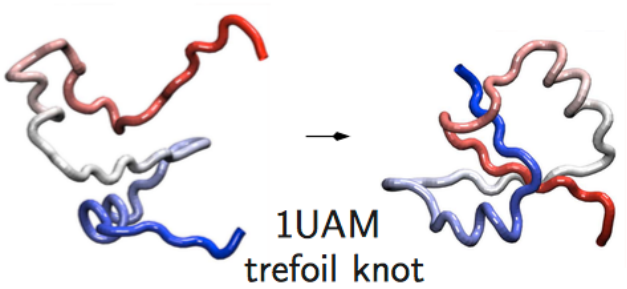


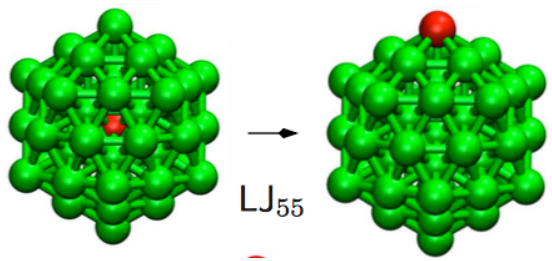
no intervening minima

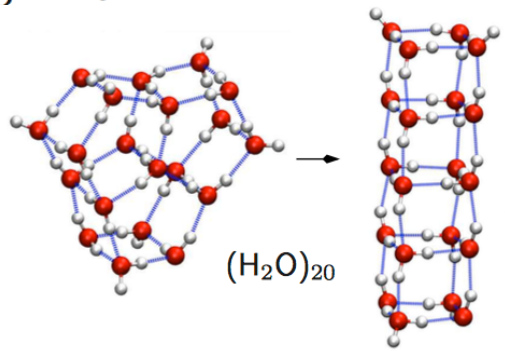


$$\frac{p_a(t)}{p_{a'}(t)} = \frac{p_a^{\rm eq}}{p_{a'}^{\rm eq}} \qquad \dot{p}_i(t) = 0 \qquad \frac{p_b(t)}{p_{b'}(t)} = \frac{p_b^{\rm eq}}{p_{b'}^{\rm eq}}$$

$$k_{AB}^{\rm SS} = \frac{1}{p_B^{\rm eq}} \sum_{a \leftarrow b} P_{ai_1} P_{i_1 i_2} \cdots P_{i_{n-1} i_n} P_{i_n b} \tau_b^{-1} p_b^{\rm eq} = \frac{1}{p_B^{\rm eq}} \sum_{b \in P} \frac{C_b^A p_b^{\rm eq}}{\tau_b}$$





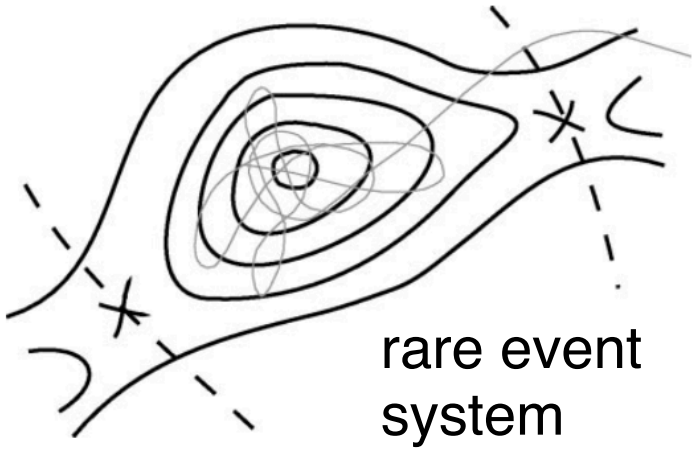


D. J. Wales, *Mol. Phys.* **100**, 3285 (2002).

Accelerated molecular dynamics

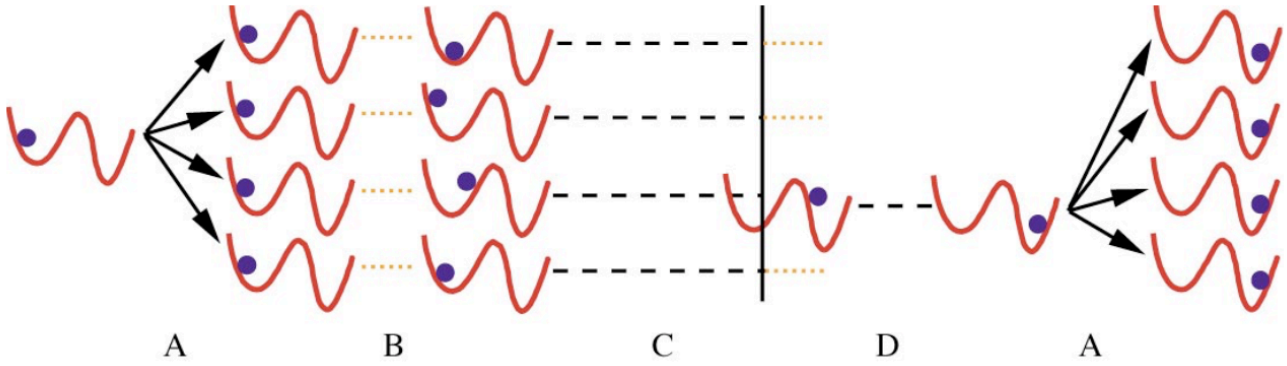
Philosophy

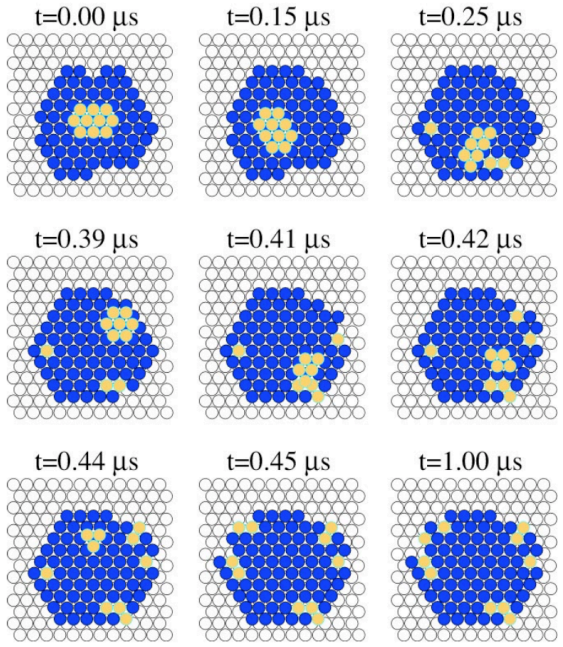
accelerate the evolution of a trajectory
while retaining the correct dynamics
over rare events



Parallel replica dynamics

~linear speedup with parallel resources





A. F. Voter, *Phys. Rev. B* **57**, R13985 (1998)

A. F. Voter, F. Montalenti and T. C. Germann,
Ann. Rev. Mater. Res. 32, 321 (2002).

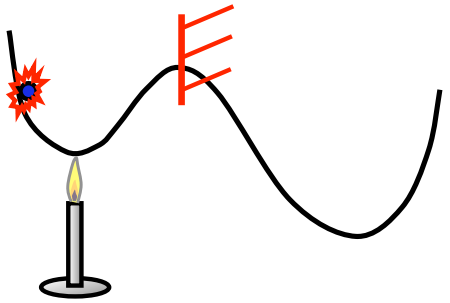
Temperature accelerated dynamics

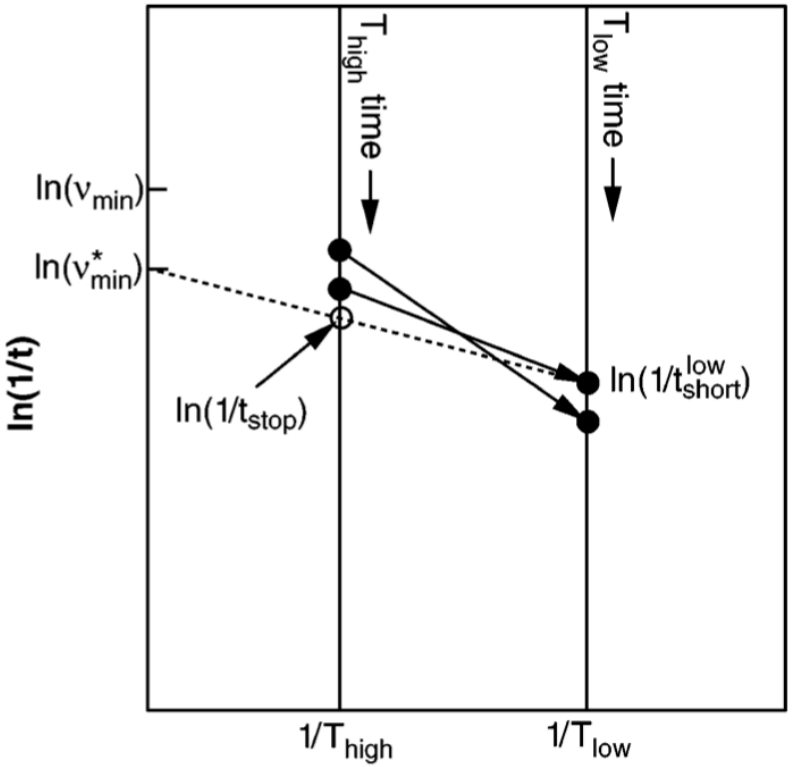
run basin constrained high-temperature trajectories

determine the mechanism and barrier of each escape attempt

use harmonic transition state theory to extrapolate the escape time to the low temperature of interest

upon reaching confidence, choose the first event that would have happened at the low temperature

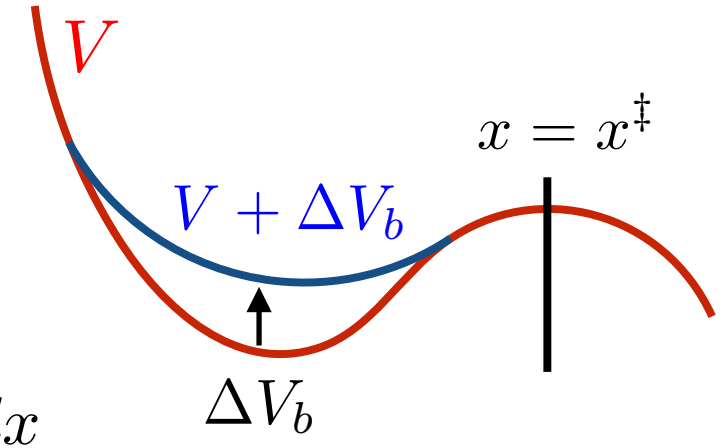




M. R. Sorensen and A. F. Voter, *J. Chem. Phys.* **112**, 9599 (2000)

Hyperdynamics

Transition state theory rate



$$k_{\mathrm{TST}} = \frac{1}{2}\langle \delta(x - x^{\dagger})|v_{\perp}|\rangle$$

$$= \frac{\frac{1}{2}\int e^{-V(x)/kT}\ \delta(x - x^{\dagger})|v_{\perp}|dx}{\int e^{-V(x)/kT}dx}$$

$$= \frac{\frac{1}{2}\int e^{-(V(x)+\Delta V_b(x))/kT}\delta(x - x^{\dagger})|v_{\perp}|\ e^{\Delta V_b(x)/kT}dx}{\int e^{-(V(x)+\Delta V_b(x))/kT}\ e^{\Delta V_b(x)/kT}dx}$$

$$= \frac{\frac{1}{2}\langle e^{\Delta V_b(x)/kT}\delta(x - x^{\dagger})|v_{\perp}|\rangle_b}{\langle e^{\Delta V_b(x)/kT}\rangle_b}$$ ← choose $\Delta V_b(x^{\dagger}) = 0$

$$= \frac{\frac{1}{2}\langle \delta(x - x^{\dagger})|v_{\perp}|\rangle_b}{\langle e^{\Delta V_b(x)/kT}\rangle_b}$$ ← TST rate on the biased potential ← boost factor

A. F. Voter, *J. Chem. Phys.* **78**, 3908 (1997).

Minimum mode following methods

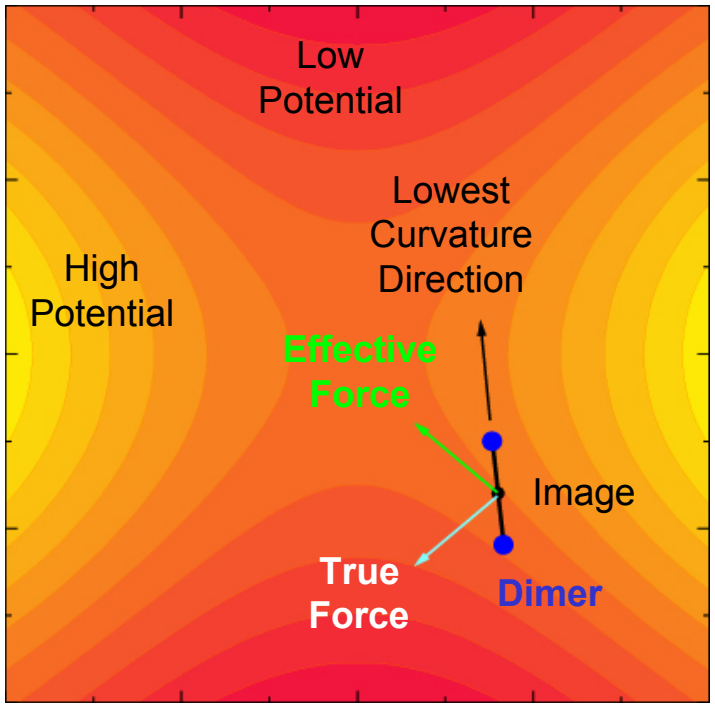
Find the lowest curvature mode using:

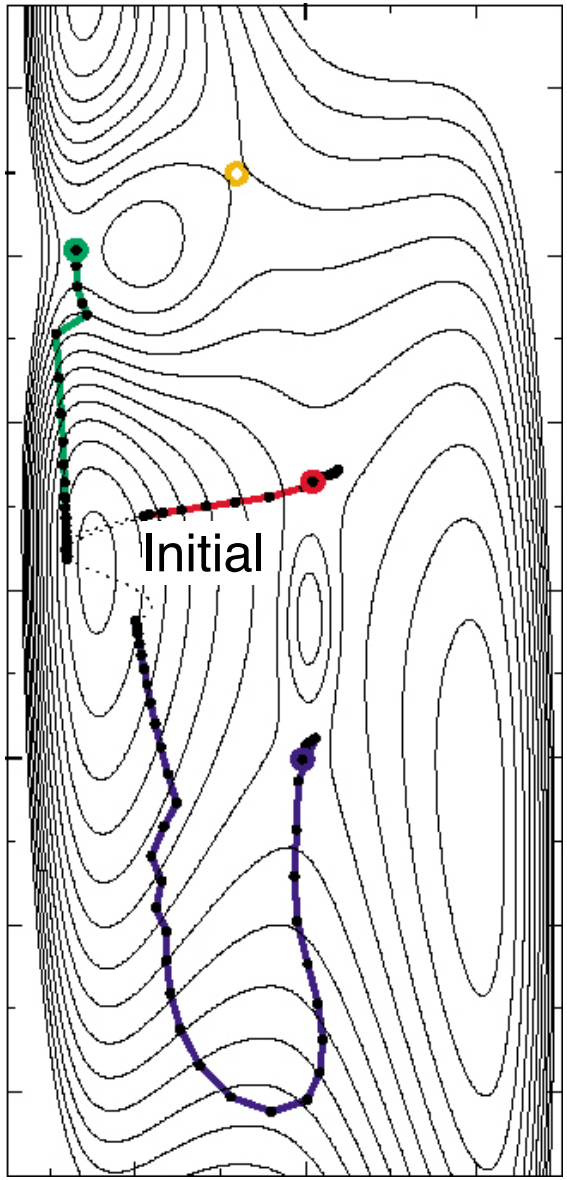
- Rayleigh-Ritz (Wales)
- Dimer method (Voter, Henkelman, Jónsson)
- Lanczos (Barkema, Mousseau)

Start from an initial state, near a minimum

Follow the minimum mode up to the saddle point

Independent searches are used to find unknown and complex reaction mechanisms





G. Henkelman and H. Jónsson *JCP* **111,** 7010 (1999)
R. Olsen et al. *JCP* **121,** 9776 (2004)

Adaptive kinetic Monte Carlo (AKMC)

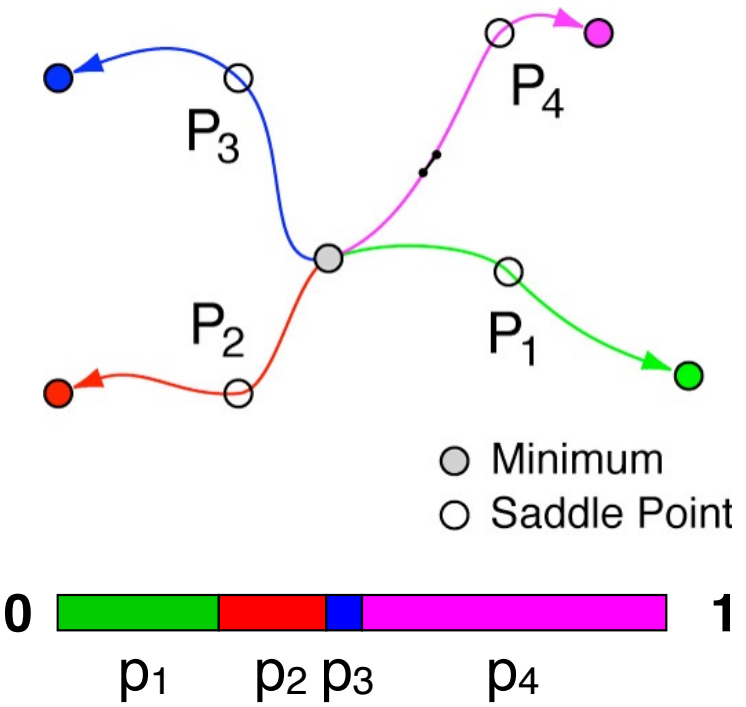
Combine saddle point searches with kinetic Monte Carlo

Adaptive Step

1. Find low energy saddle points using a min-mode following method

Standard KMC

2. Choose one processes from a Boltzmann distribution
3. Hop to the final state of the chosen process
4. Increment time by an average amount Δt
5. Repeat



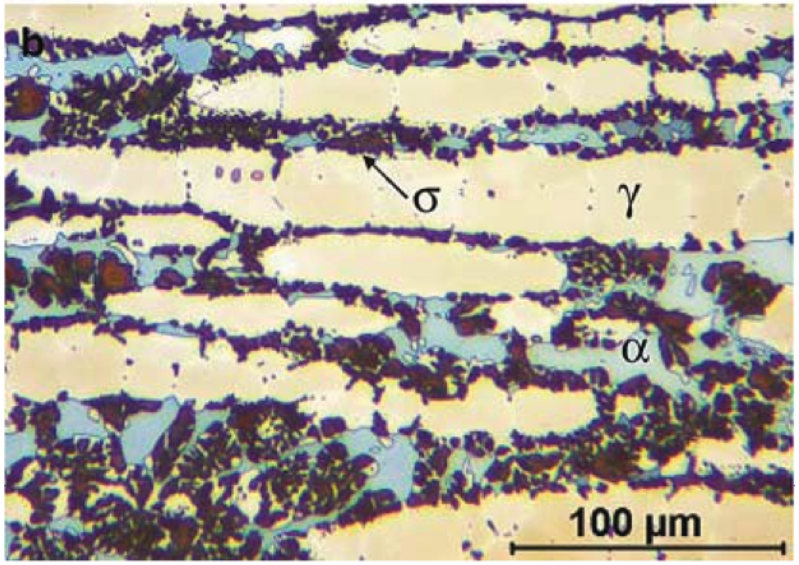
Probability: $p_i \propto r_i$

Rate: $r_i = \nu\, e^{-\Delta E_i / k_B T}$

Time: $\overline{\Delta t} = \dfrac{1}{\sum r_i}$

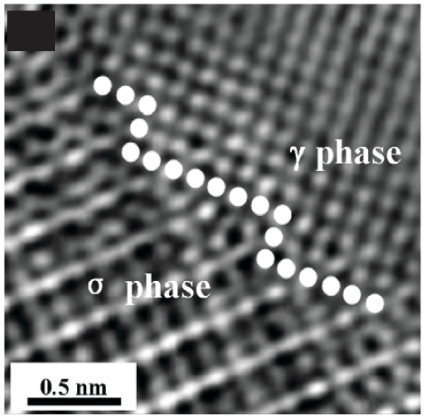
G. Henkelman and H. Jónsson *JCP* **115,** 9657 (2001)

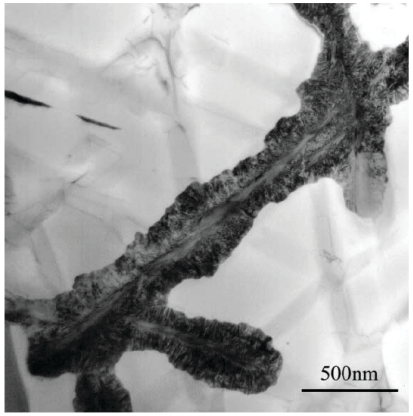
Example: Complex phases in metals



FeCr

Ni

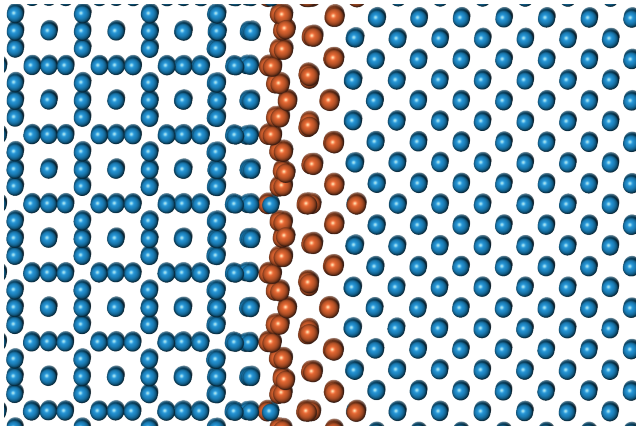




Model system:

Some pure metals (Mo and W) have TCP phases; try to understand the mechanism and rate of transition

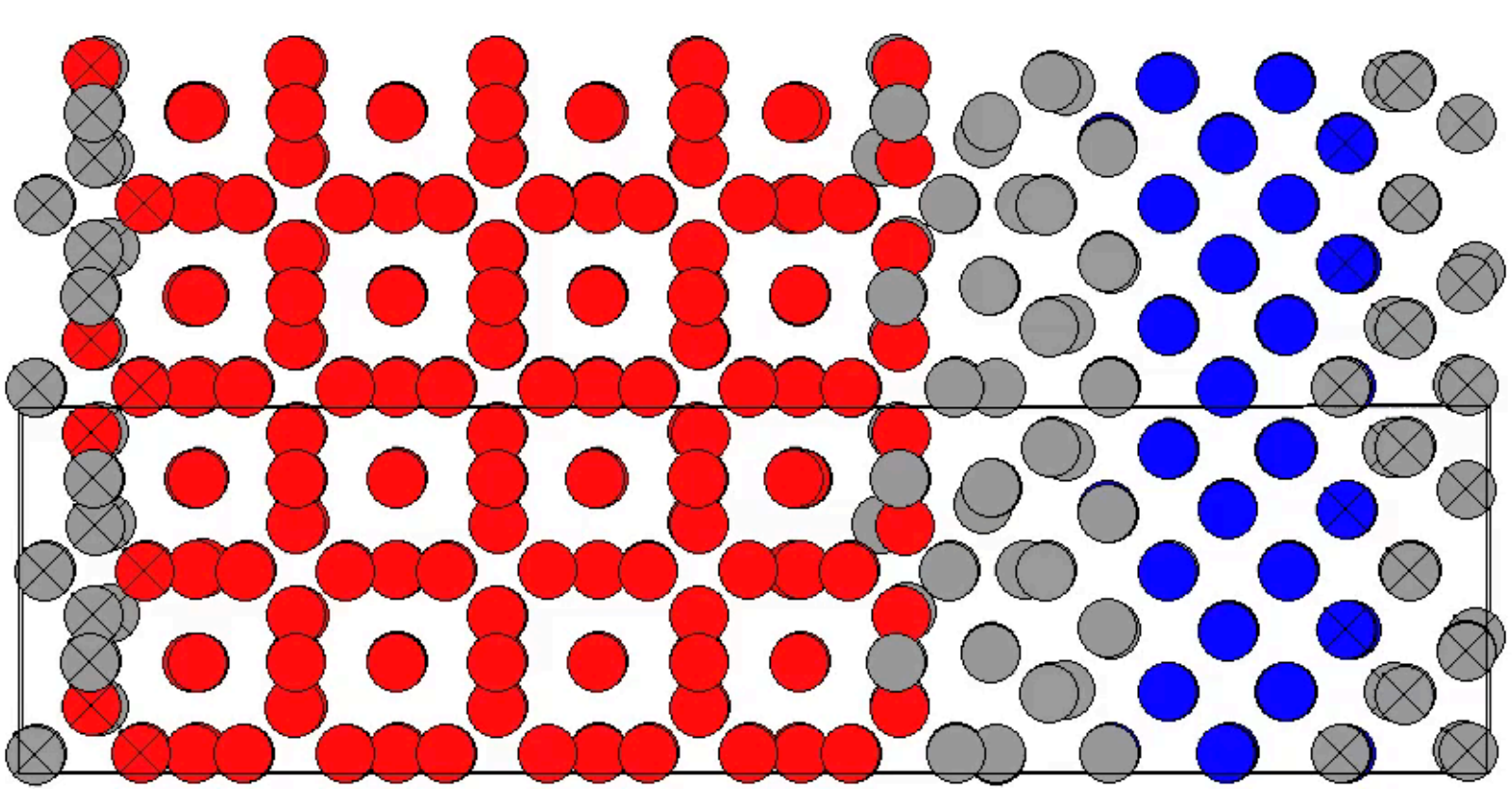
A15



BCC

C.M.F. Rae and R.C. Reed. Acta Mat., 49(19):4113, 2001.
F. Sun, J. Zhang, P. Liu, Q. Feng, X. Han, and S. Mao. *J. Alloy. Compd.*, 536:80, 2012.
J.W. Elmer, T.A. Palmer, and E.D. Specht. *Metall. Mater. Trans. A,* 38A(3):464–475, 2007.

Local mechanism of interface motion in 3D



frozen atoms

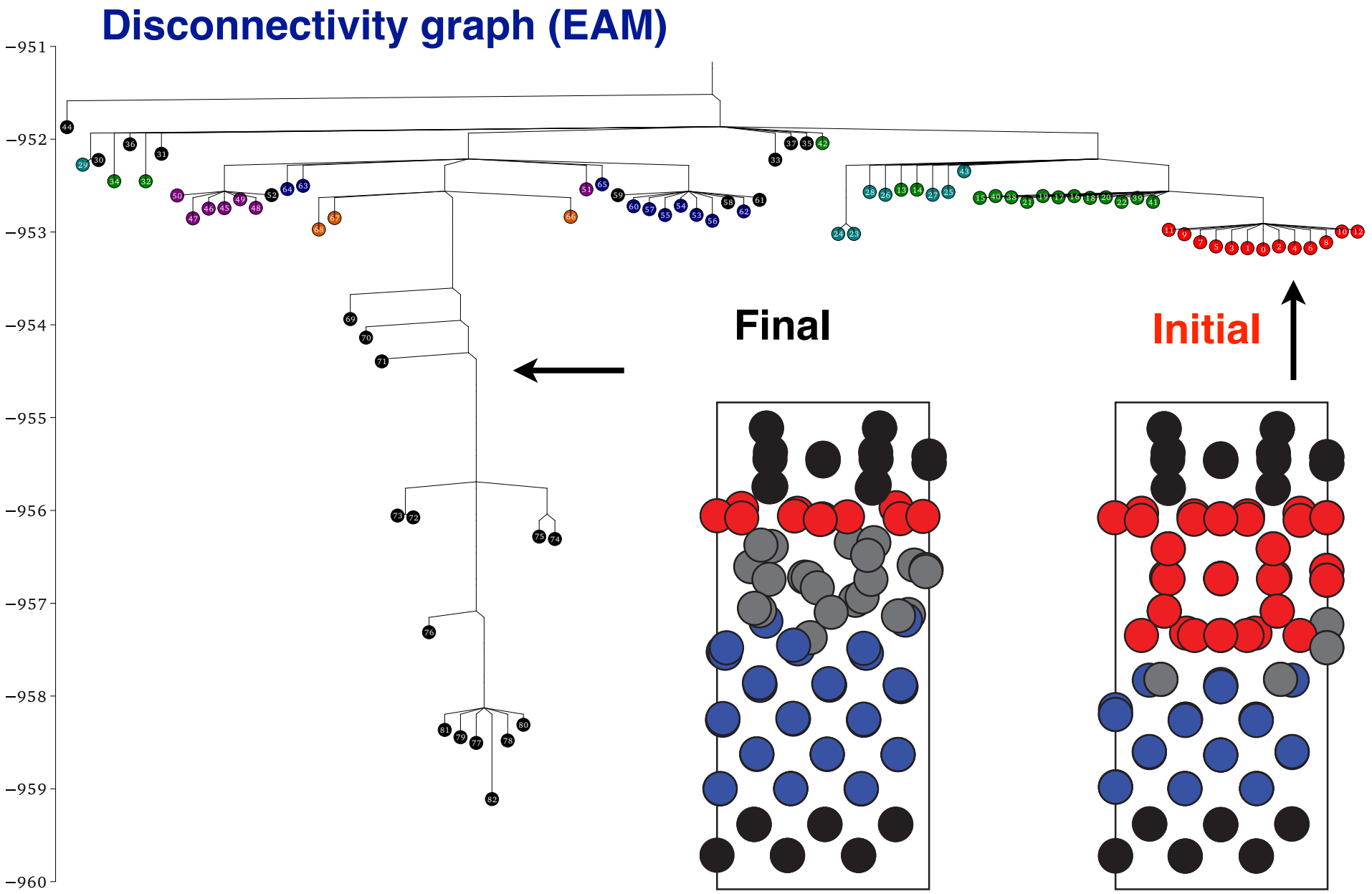
A15

interface atoms

BCC

frozen atoms

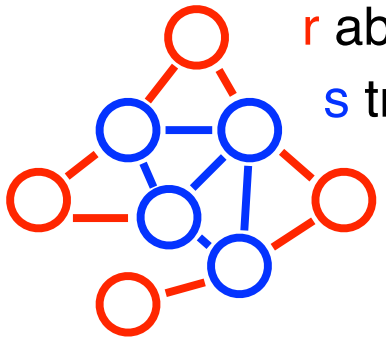
Interface disorder leads to superbasins



Monte Carlo with Absorbing Markov Chains

Probability transition matrix:

$$\mathbf{M}_{(r+s)\times(r+s)} = \begin{pmatrix} \mathbf{I}_{r\times r} & \mathbf{0}_{r\times s} \\ \mathbf{R}_{s\times r} & \mathbf{T}_{s\times s} \end{pmatrix}$$



r absorbing states

s transient states

Initial state vector: $(\vec{0}^{\mathrm{T}} \quad \vec{v}_{\mathrm{I}}^{\mathrm{T}})$

good, but not necessary:

Time evolution:

$$(\vec{0}^{\mathrm{T}} \quad \vec{v}_{\mathrm{I}}^{\mathrm{T}})\,\mathbf{M}^m = (\vec{v}_{\mathrm{I}}^{\mathrm{T}}\left(\mathbf{I}+\mathbf{T}+\cdots+\mathbf{T}^{m-1}\right)\mathbf{R} \quad \vec{v}_{\mathrm{I}}^{\mathrm{T}}\mathbf{T}^m)$$

Probabilities:

$$p_{\text{still in transient subspace}} = \vec{v}_{\mathrm{I}}^{\mathrm{T}}\mathbf{T}^m\vec{e}$$

$$\vec{p}^{\,\mathrm{T}}_{\text{absorption after } m \text{ time steps}} = \vec{v}_{\mathrm{I}}^{\mathrm{T}}\left(\mathbf{I}+\mathbf{T}+\cdots+\mathbf{T}^{m-1}\right)\mathbf{R}$$

$$p_{\text{absorbed at time } m} = \vec{v}_{\mathrm{I}}^{\mathrm{T}}\left(\mathbf{T}^{m-1}-\mathbf{T}^{m}\right)\vec{e}$$

$$\vec{p}^{\,\mathrm{T}}_{\text{absorption given exit at time } m} = \vec{q} = \frac{\vec{v}_{\mathrm{I}}^{\mathrm{T}}\mathbf{T}^{m-1}\mathbf{R}}{\vec{v}_{\mathrm{I}}^{\mathrm{T}}\mathbf{T}^{m-1}\mathbf{R}\vec{e}}$$

Absorbing time:

$$\vec{v}_{\mathrm{I}}^{\mathrm{T}}\mathbf{T}^m\vec{e} < \bar{r} \le \vec{v}_{\mathrm{I}}^{\mathrm{T}}\mathbf{T}^{m-1}\vec{e}$$

solve for m

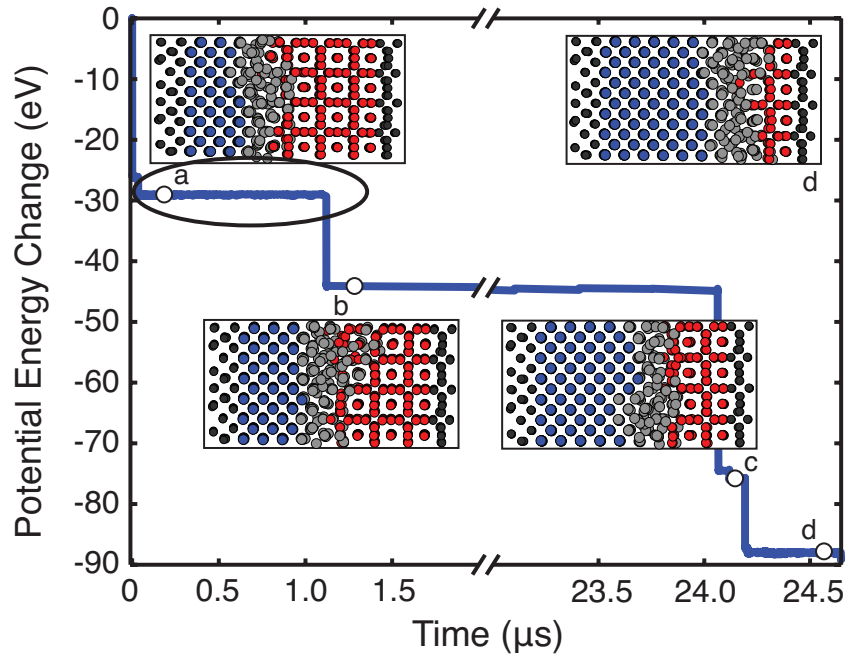
Absorbing state:

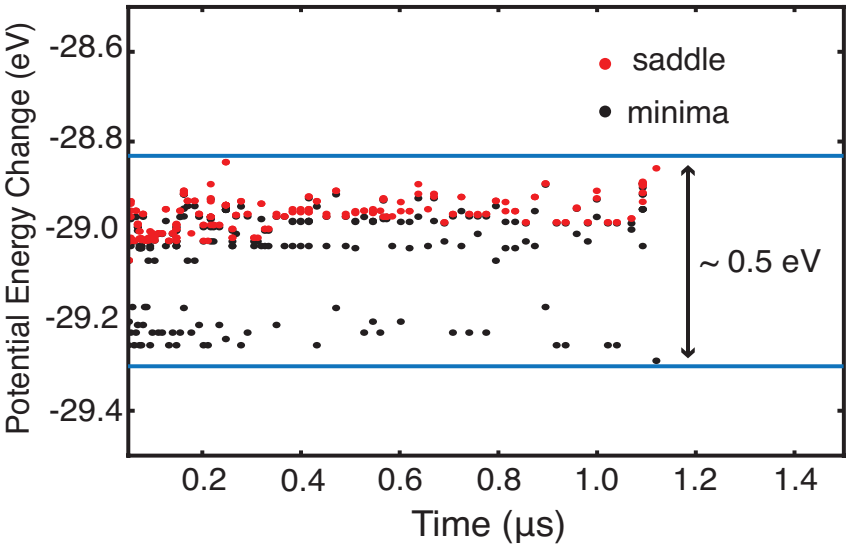
$$\sum_{i=1}^{j-1} q_i \le \tilde{r} < \sum_{i=1}^{j} q_i$$

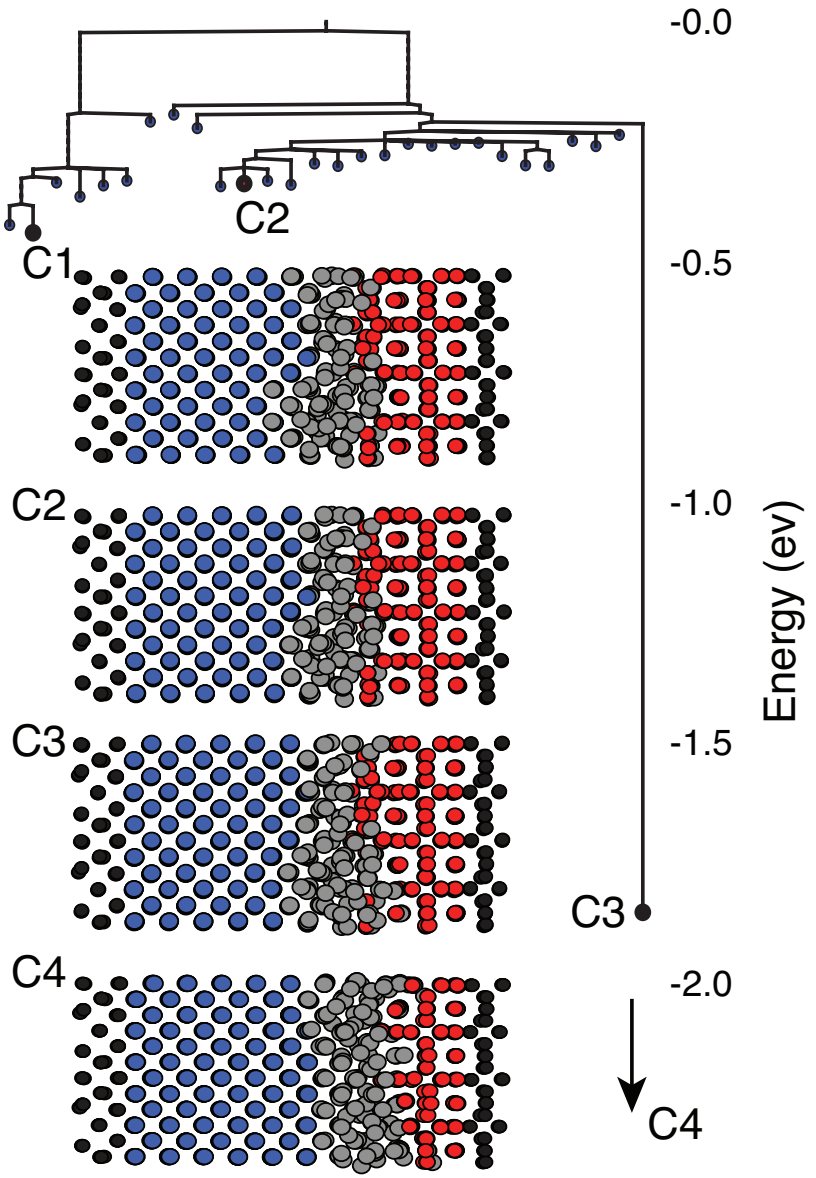
for random numbers $\bar{r}, \tilde{r} \in [0,1]$

Mark Novotny *PRL* **74**, 1 (1994).

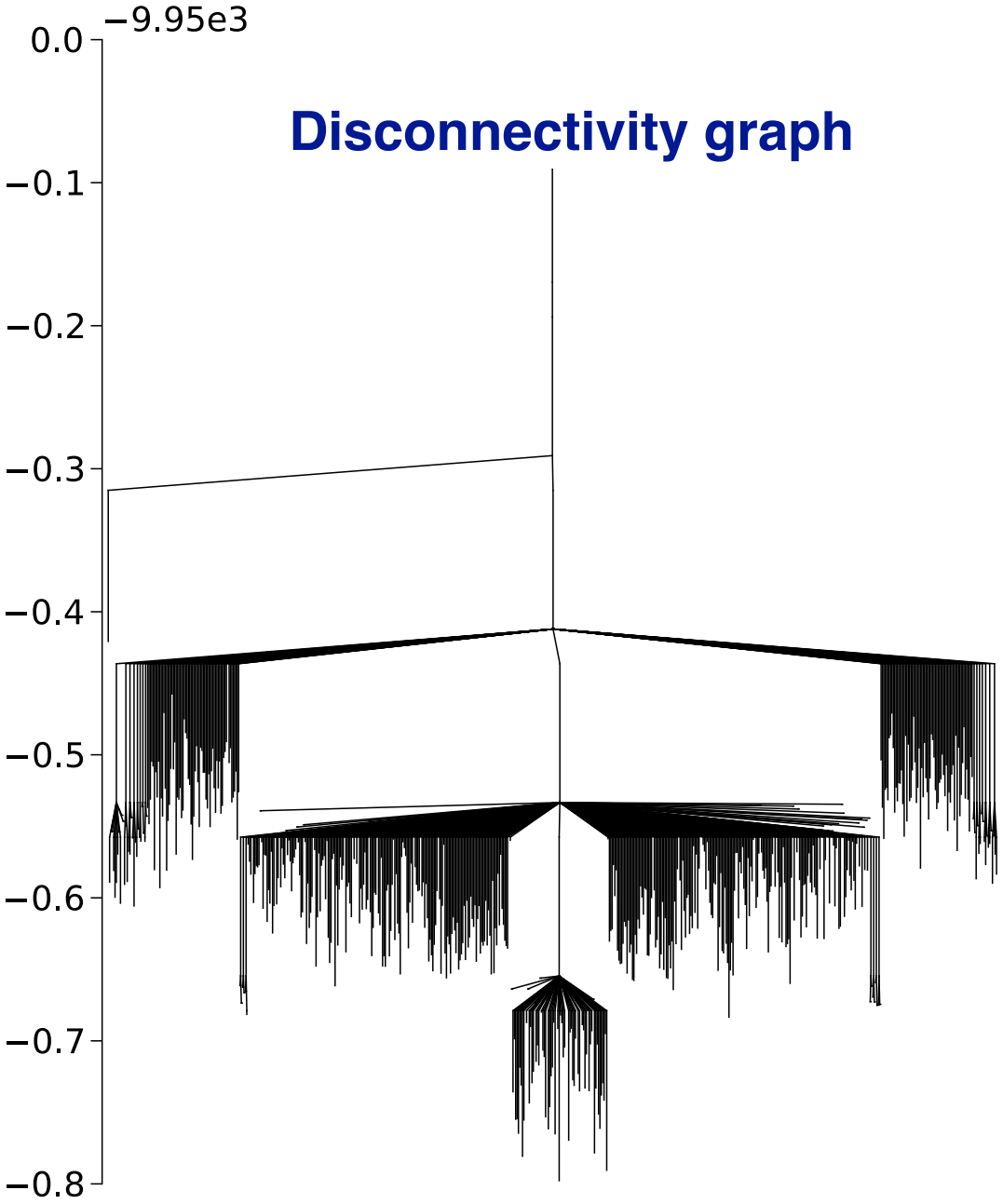
Slow interface motion





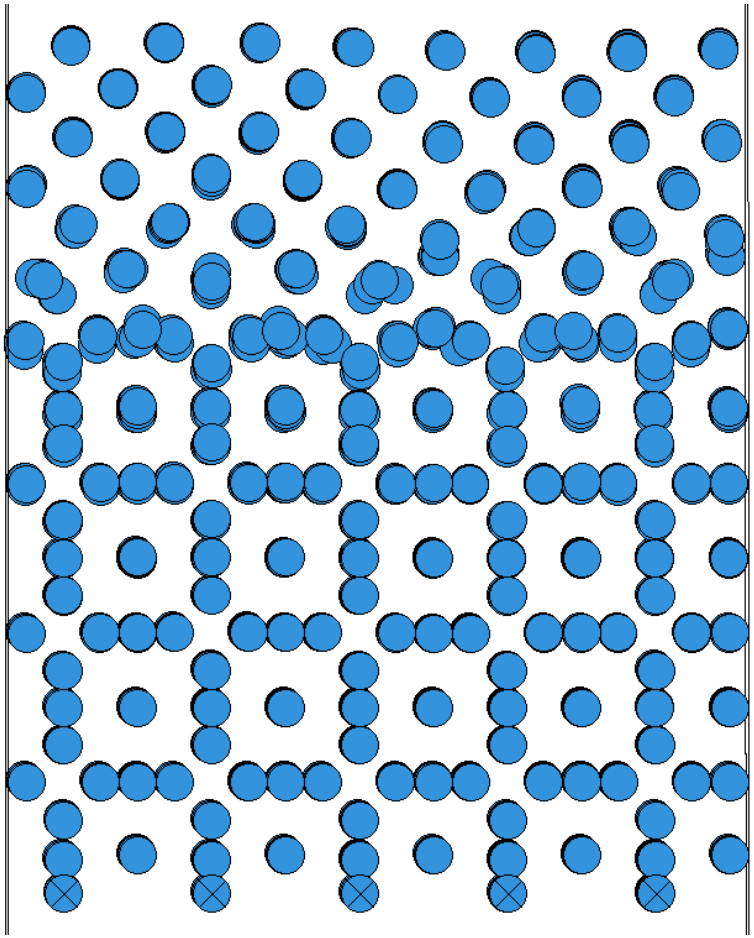


Ongoing challenges



Disconnectivity graph

A15-BCC interface
1183 atoms, EAM



Discussion / questions?