Methods for calculating rare event dynamics and pathways of solid-solid phase transitions

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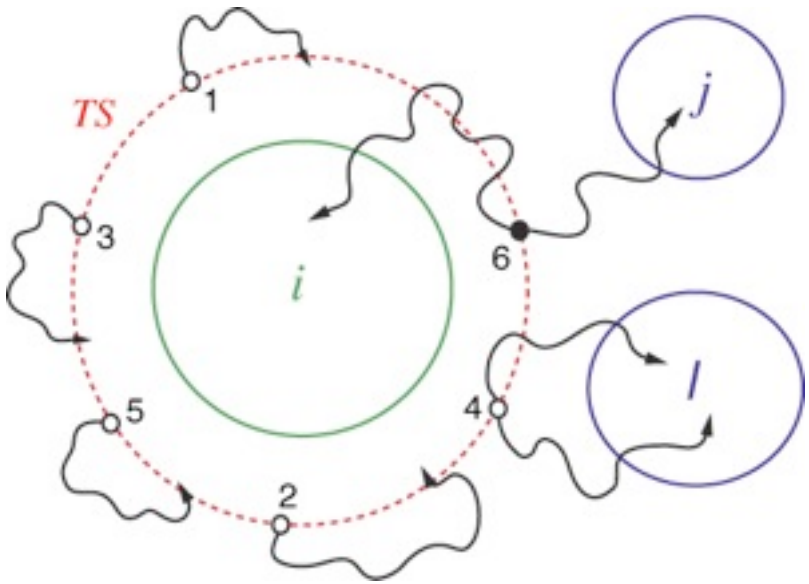
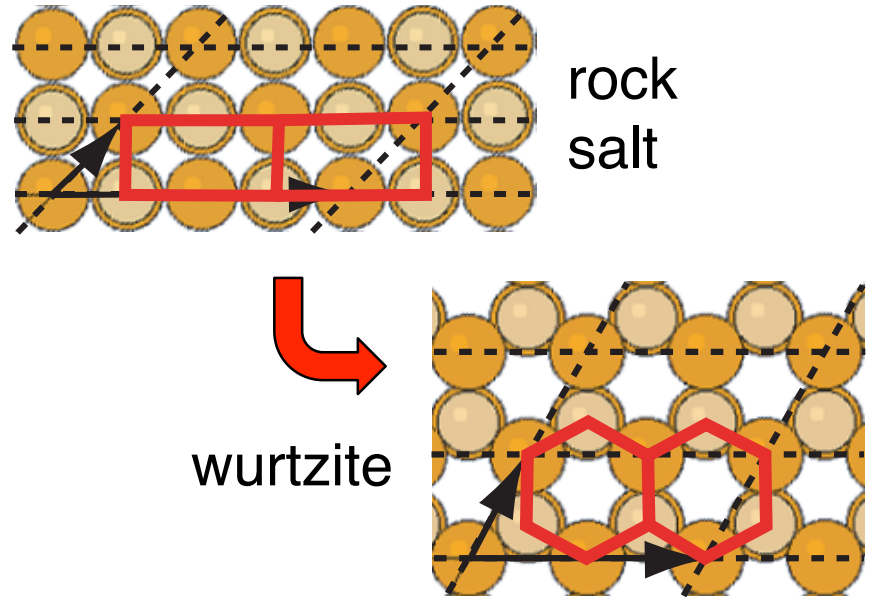
κ-dynamics



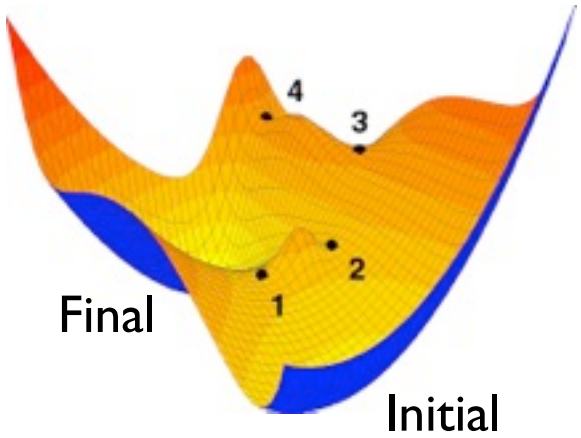
Solid-state nudged elastic band

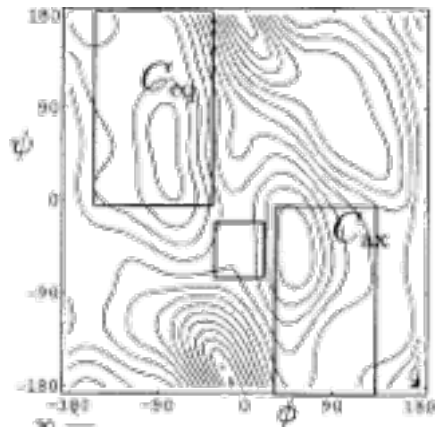


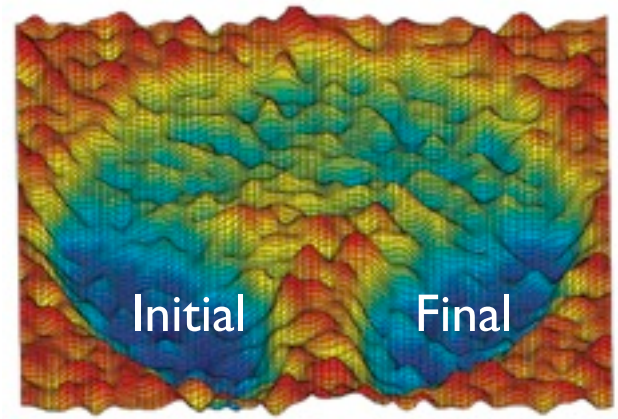
Classes of Dynamical Systems

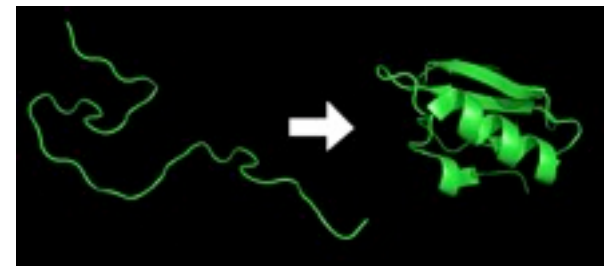
Energy Landscape: Smooth → Rough

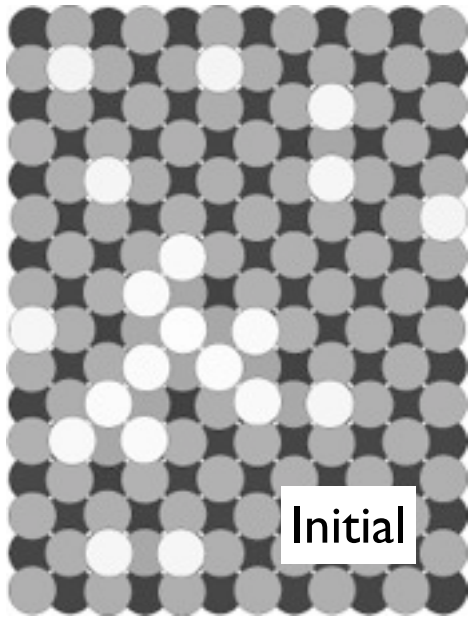
Final State: Known → Unknown

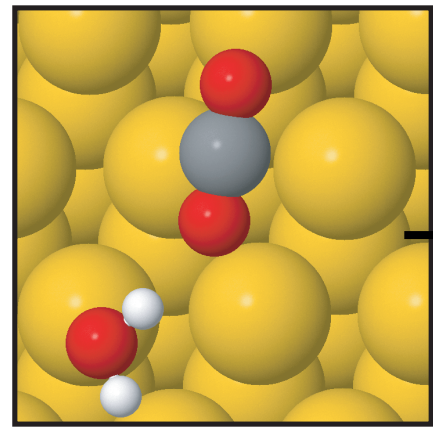








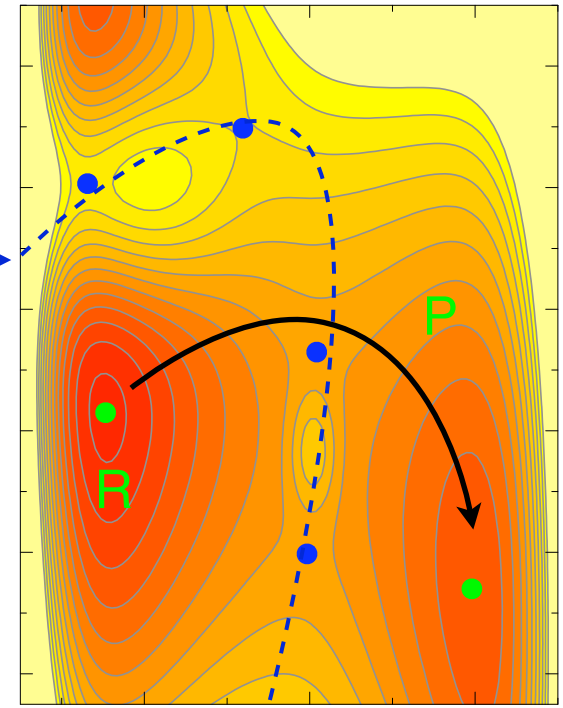




Transition state theory

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: $x = x^\dagger$



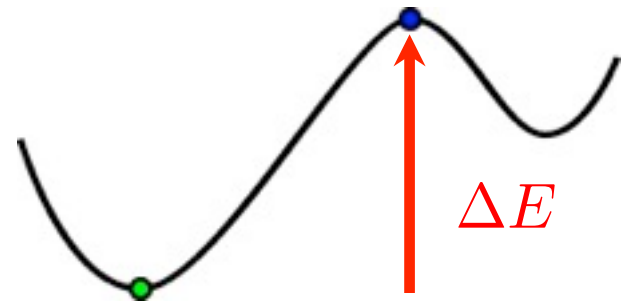
$$k_{\mathrm{TST}} = \frac{1}{2}\left\langle \delta(x - x^\dagger)|v_\perp|\right\rangle_R$$

Harmonic transition state theory

Find saddle points on the energy surface

Rate of escape through each saddle point region:

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



KMC: the Good, the Bad, and the Ugly

The Good

For rare event systems where transition rates are defined by first-order rate constants, KMC is an exact stochastic solution to the kinetic master equation.

$$\frac{dP_i}{dt} = \sum_j -\mathrm{k}_{i\to j}\, P_i + \mathrm{k}_{j\to i}\, P_j$$

$$P_{i\to j} = \frac{\mathrm{k}_{i\to j}}{\mathrm{k}_{i\to}} \quad \text{where} \quad \mathrm{k}_{i\to} = \sum_j \mathrm{k}_{i\to j}$$

$$t = \frac{\ln(1/\mu)}{\mathrm{k}_{i\to}} \quad \text{where } \mu \text{ is random on (0,1]}$$

The Bad

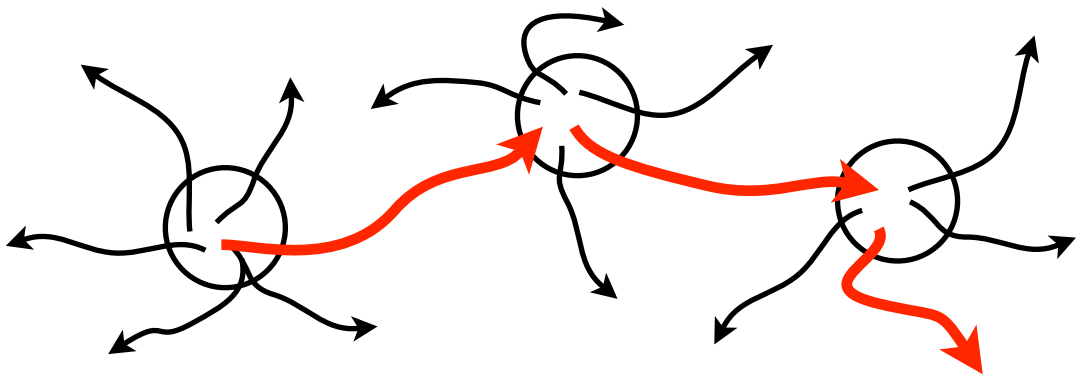
It is very hard to determine all possible kinetic events available to the simulation.

It is very hard to calculate an exact rate for a process, let alone all of them.

Typically limited to transition state theory (e.g. harmonic TST within aKMC).

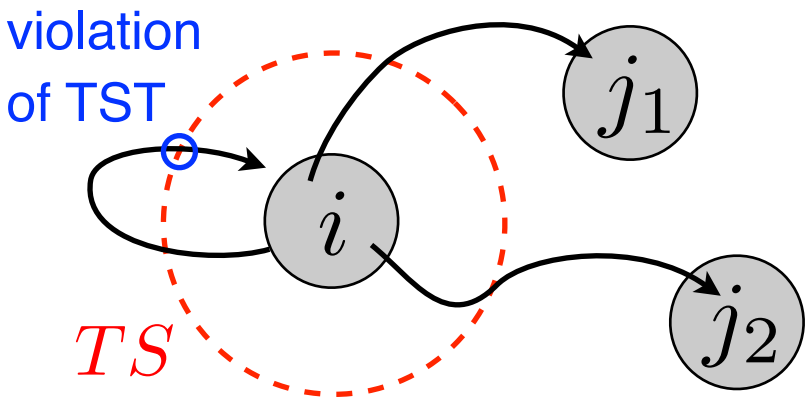
The Ugly

It's a lot of work calculating all possible events and rates to find one trajectory.



Dynamical corrections to TST

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



Dynamical correction factor

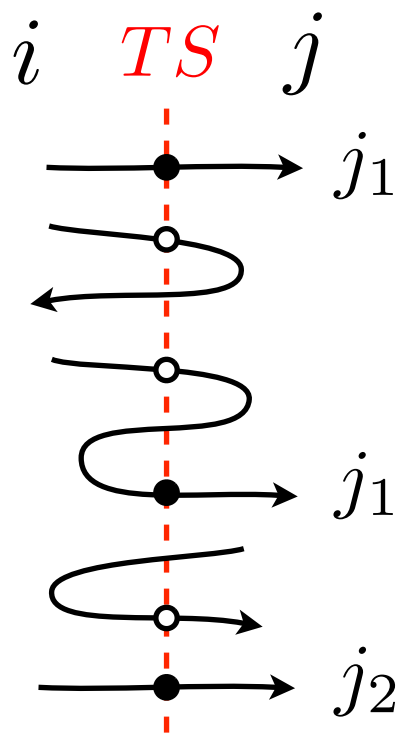
κ : the ratio of successful trajectories to number of crossing points

ratio between the TST and true rate:

$$\mathrm{k}_{i\to} = \kappa_{i\to}\ \mathrm{k}^{\mathrm{TST}}_{i\to}$$

both total escape rate and by product:

$$\mathrm{k}_{i\to j} = \kappa_{i\to j}\ \mathrm{k}^{\mathrm{TST}}_{i\to}$$



A successful trajectory:

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

2) trajectory must start in initial state

Example:

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

The κ-dynamics algorithm

1. Choose a reaction coordinate and sample a transition state (TS) surface

2. Launch short time trajectories until one goes directly to a product and starts in the initial state; record the number, *N*

3. If no successful trajectory within N_{max}, push TS up in free energy and go to 2

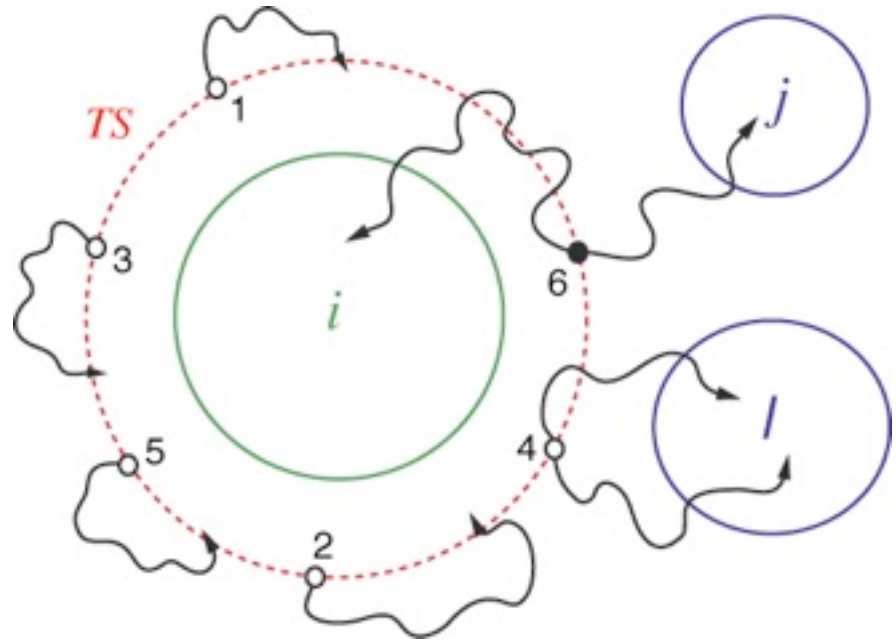
4. Calculate k_{TST} for successful TS surface (parallel tempering, WHAM)

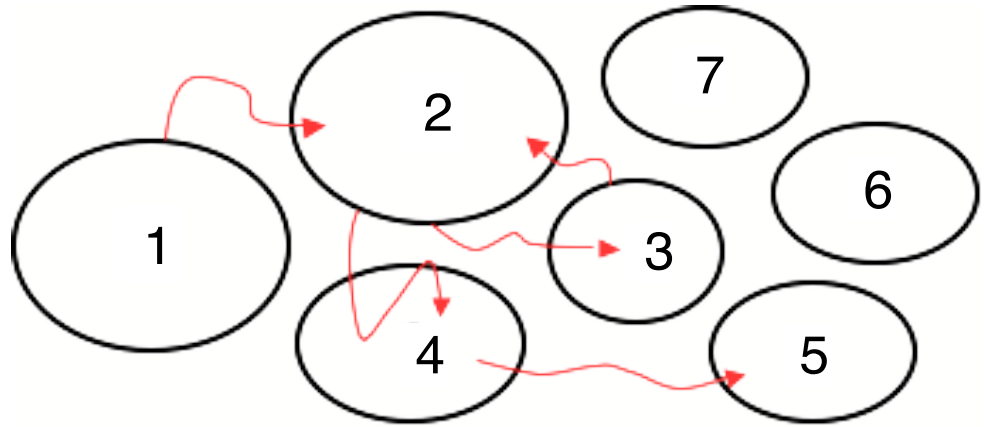
5. Update the simulation clock by

$$t = \sum_{n=1}^{N} \frac{\ln(1/\mu_n)}{\mathrm{k}_{i\rightarrow}^{\mathrm{TST}}}$$

where μ_n are random numbers on (0,1]

6. Repeat procedure in product state





C.-Y. Lu, D. E. Makarov, and G. Henkelman, *J. Chem. Phys.* **133**, 201101 (2010).

Sketch of proof that κ-dynamics is exact

(1) Branching ratio

The probability of reaching state j is:

$$P_{i\to j} = \boxed{\frac{\kappa_{i\to j}}{\kappa_{i\to}}} = \frac{\mathrm{k}_{i\to j}}{\mathrm{k}_{i\to}} \qquad \text{where} \quad \mathrm{k}_{i\to j} = \kappa_{i\to j}\mathrm{k}_{i\to}^{\mathrm{TST}}$$

sampled

A. Voter and J. D. Doll *JCP* **82,** 1 (1985)

(2) Reaction time

What we want: $P_{i\to}(t) = \mathrm{k}_{i\to}\exp(-\mathrm{k}_{i\to}t)$ where $\mathrm{k}_{i\to}$ is the true rate

What we have in κ-dynamics:

$$t = \sum_{n=1}^{N} \frac{\ln(1/\mu_n)}{\mathrm{k}_{i\to}^{\mathrm{TST}}} \qquad \text{where} \quad P(N) = (\kappa_{i\to})(1-\kappa_{i\to})^{N-1}$$

(1 success)(N-1 failures)

Connection with TST rate:

$$P_{i\to}^{\mathrm{TST}}(t) = \mathrm{k}_{i\to}^{\mathrm{TST}}\exp(-\mathrm{k}_{i\to}^{\mathrm{TST}}t)$$

$$P_{i\to}(t;N) = \frac{(\mathrm{k}_{i\to}^{\mathrm{TST}})^N t^{N-1}\exp(-\mathrm{k}_{i\to}^{\mathrm{TST}}t)}{(N-1)!}$$

Erlang N-distribution

Combining:

$$P_{i\to}(t) = \sum_{N=1}^{\infty} P(N)P_{i\to}(t;N)$$

$$= \kappa_{i\to}\mathrm{k}_{i\to}^{\mathrm{TST}}\exp(-\kappa_{i\to}\mathrm{k}_{i\to}^{\mathrm{TST}}t)$$

$$= \boxed{k_{i\to}\exp(-\mathrm{k}_{i\to}t)}$$

the correct distribution based upon the true rate

Reaction coordinate test

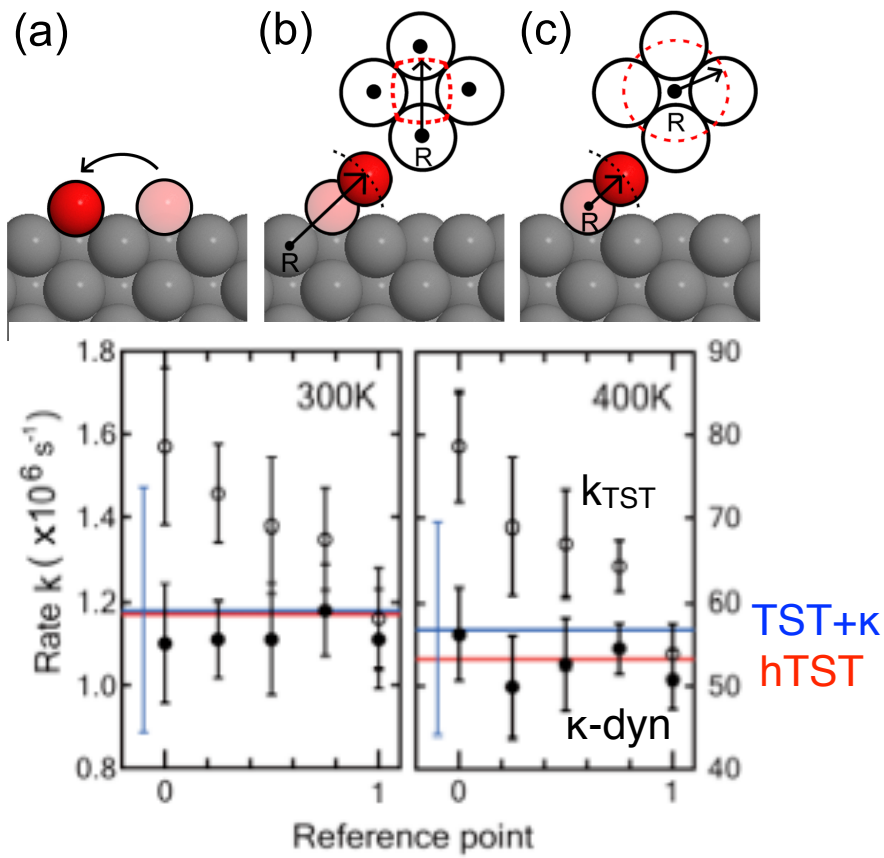
Bond-boost: specifies the stretch in the most-stretched bond:

Bond stretching parameter

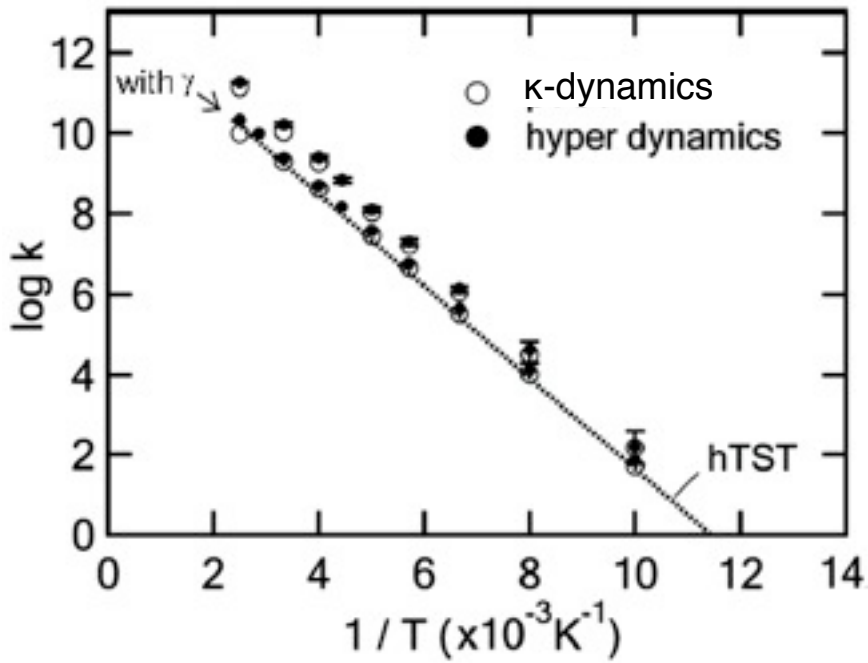
$$Z_k = \left\{ \{r\} \left| MAX\left(\frac{d_{i,j} - d^0_{i,j}}{d^0_{i,j}} \right) - C_k = 0,\ d_{i,j} = |r_i - r_j| \right. \right\}$$

R. A. Miron and K. A. Fichthorn, *JCP* **119,** 6210 (2003)

Al/Al(100), hop on frozen surface



Exchange on relaxed surface

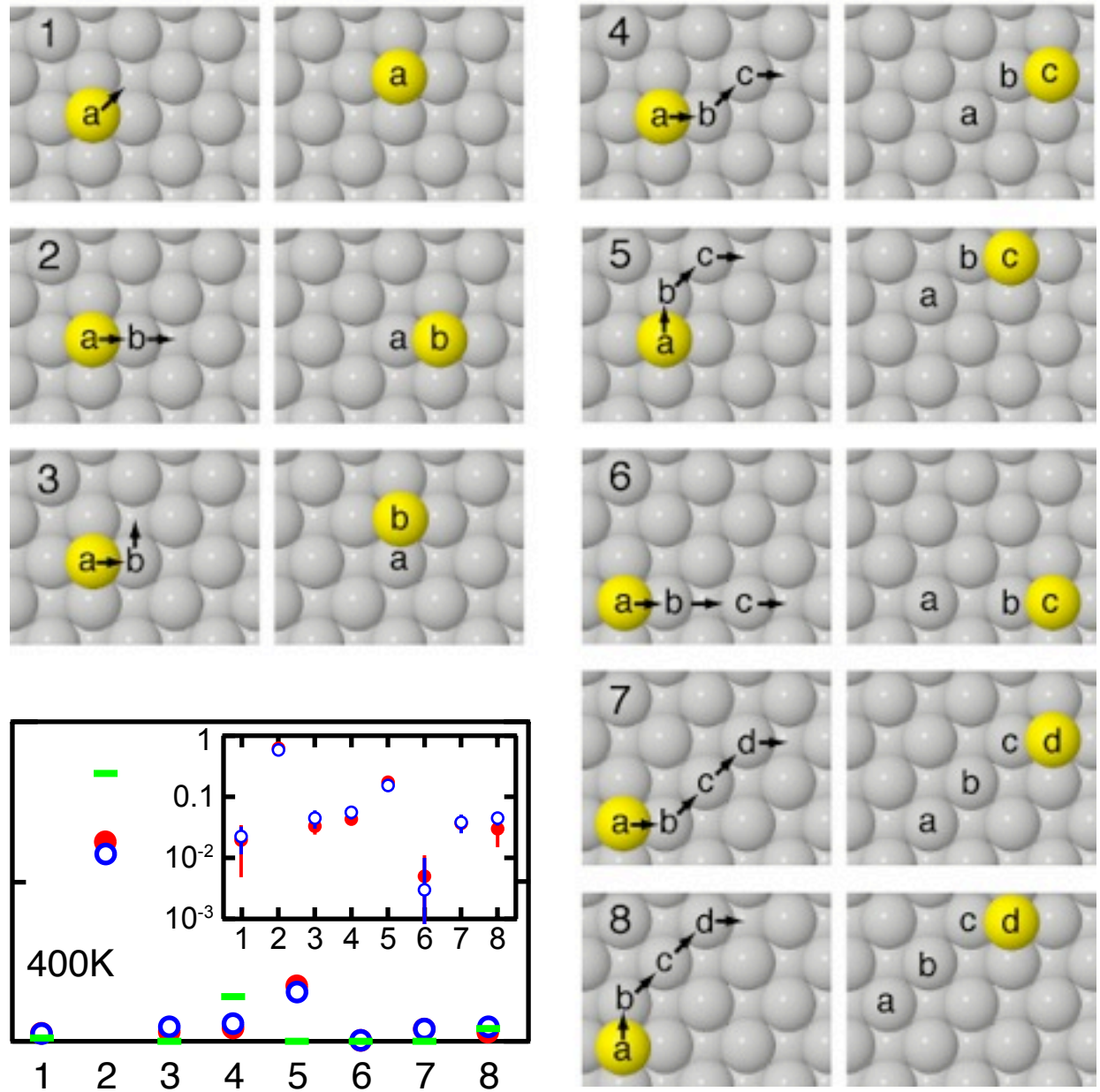


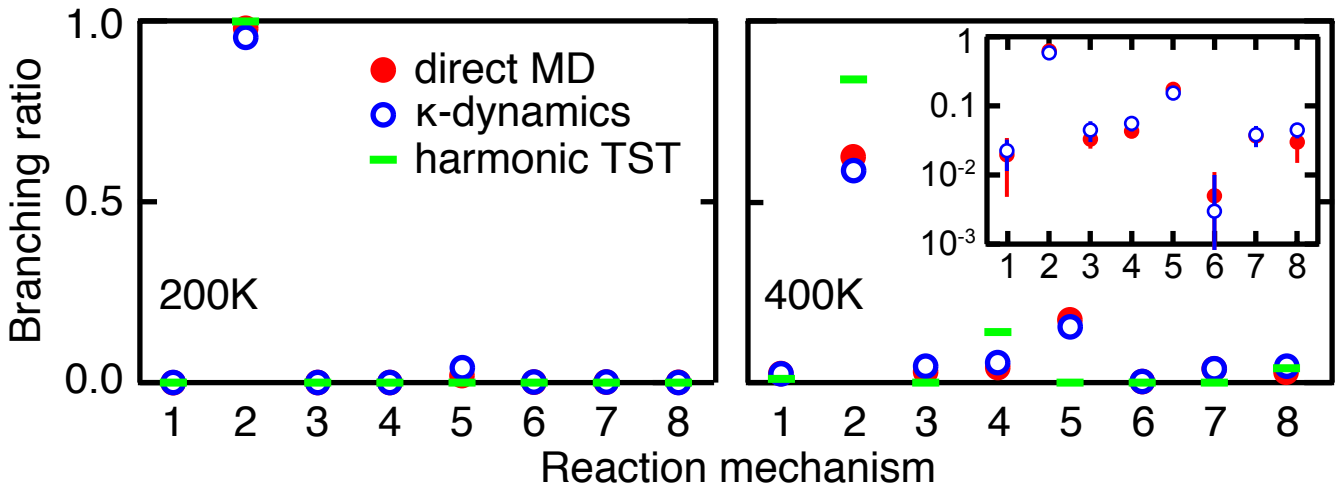
κ-dynamics rates are correct and independent of reaction coordinate

Branching ratio test

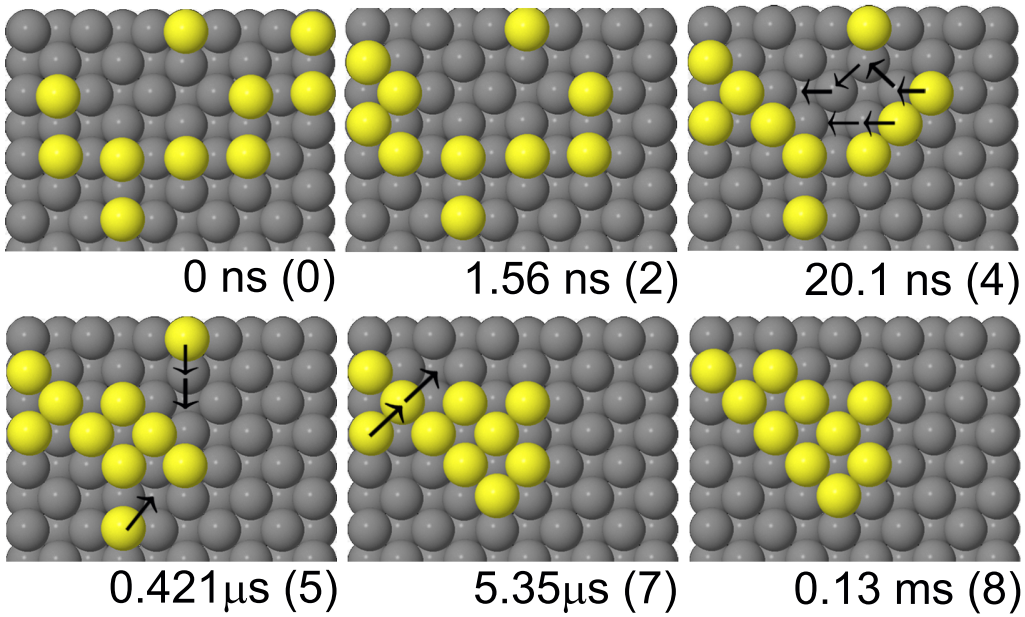
Comparison of reaction products for classical dynamics and κ-dynamics

Al/Al(100), relaxed surface



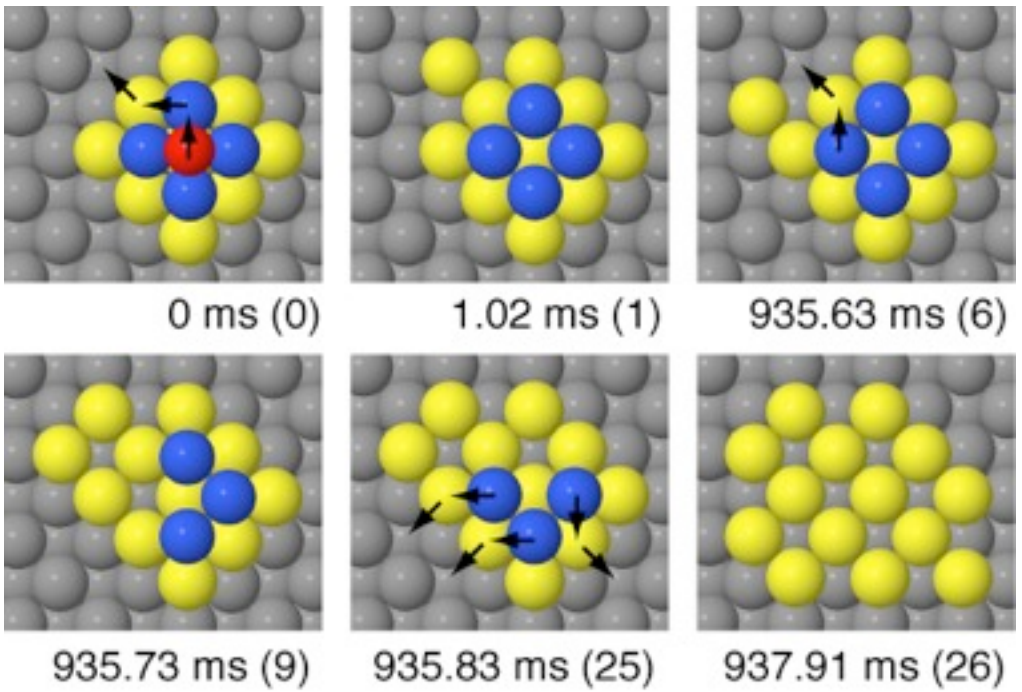


κ-dynamics trajectories



Al/Al(100) island ripening

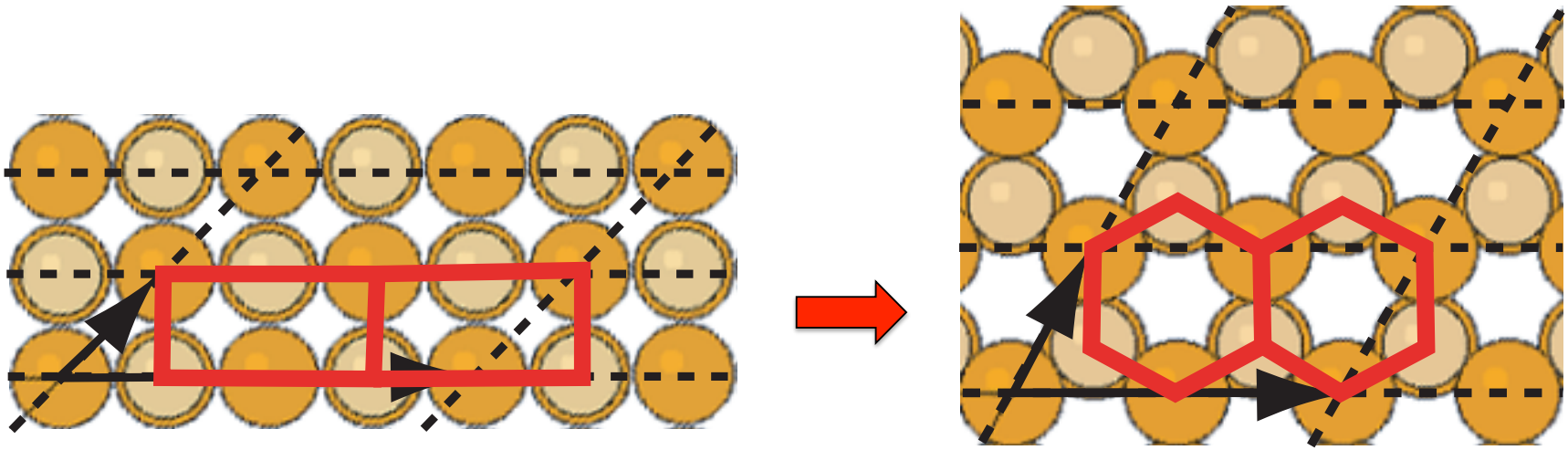
Al/Al(100) pyramid collapse



Solid-solid phase transitions

Some transitions involve both change in atomic and cell degrees of freedom

E.g. CdSe:



rock salt wurtzite

Potential parameters: E. Rabani, *J. Chem. Phys.* **116**, 258 (2002).

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:

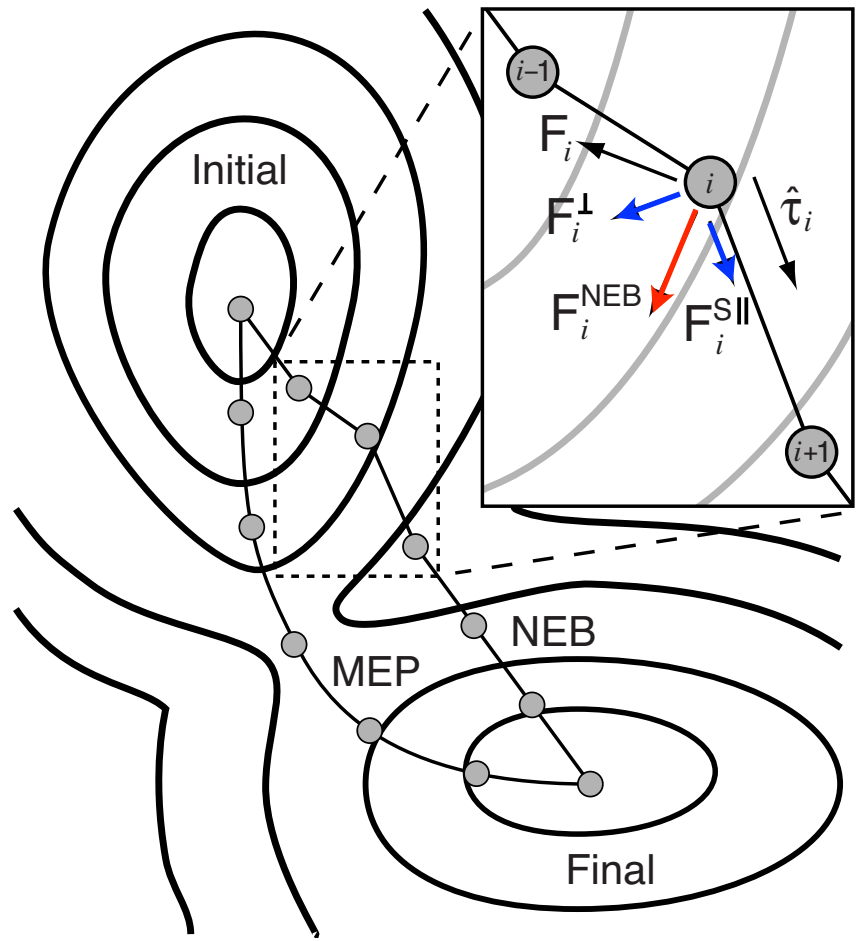
$$\mathbf{F}_i^{\mathrm{NEB}} = \mathbf{F}_i^{\perp} + \mathbf{F}_i^{\mathrm{S}\parallel}$$

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):

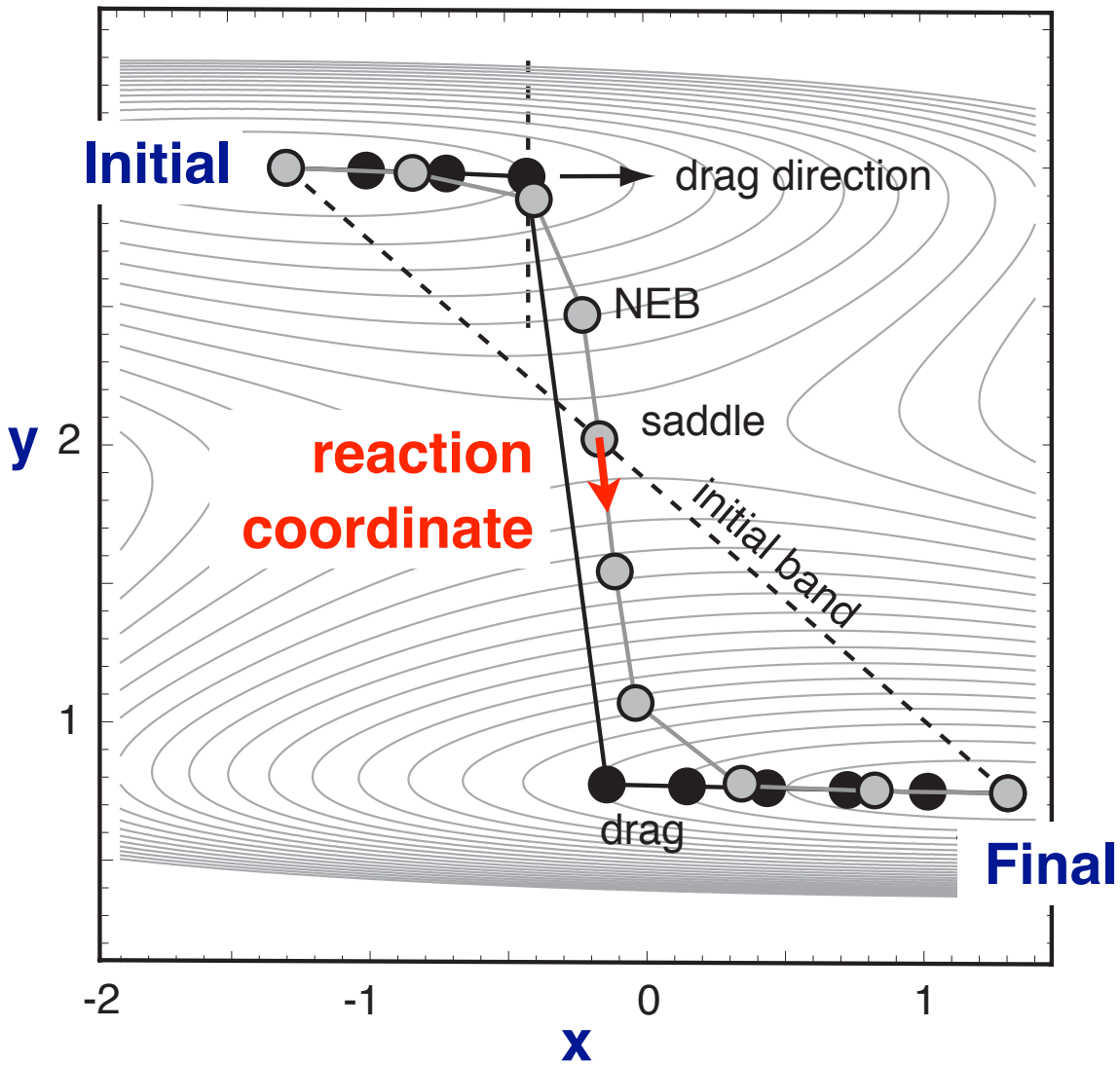
$$\mathbf{F}_i^{\mathrm{S}\parallel} = k\left(|\mathbf{R}_{i+1} - \mathbf{R}_i| - |\mathbf{R}_i - \mathbf{R}_{i-1}|\right)\hat{\boldsymbol{\tau}}_i$$



[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).

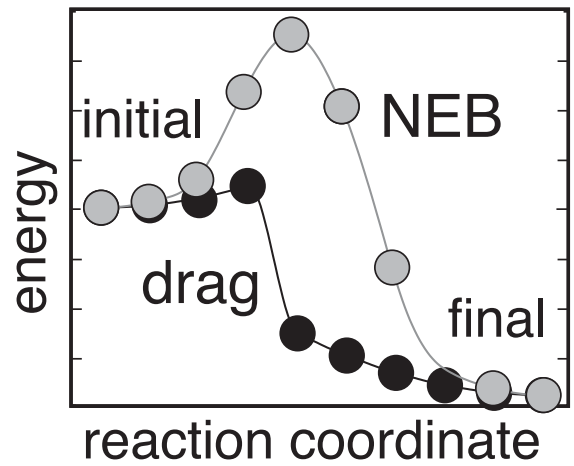
Danger of assuming a reaction coordinate

The x-coordinate separates initial from final state, but is not a suitable reaction coordinate:



A drag calculation along **x** (black points) misses the saddle point where the reaction coordinate follows the **y**-direction

The resulting barrier is under-estimated:

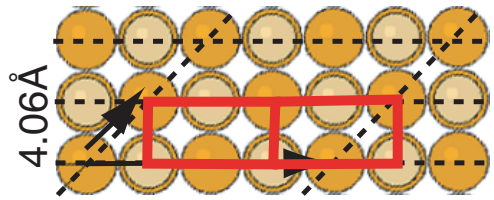


Cell variables vs atomic coordinates

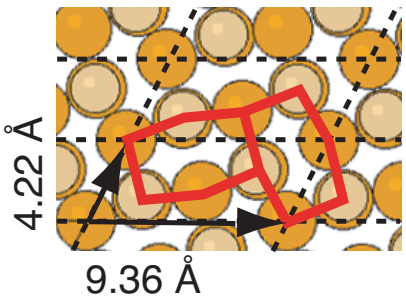
Two pathways for the same solid-solid phase transition in CdSe

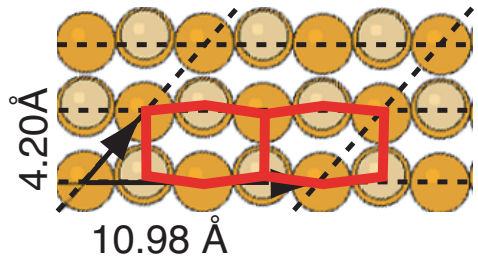
atom dominated **cell dominated**

initial (rock salt)

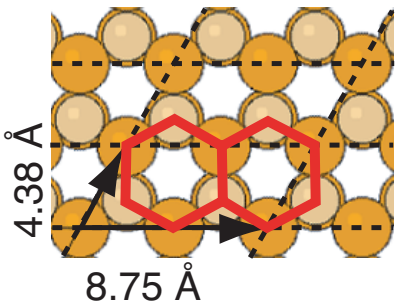


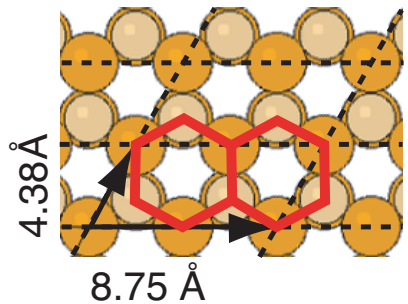
transition state



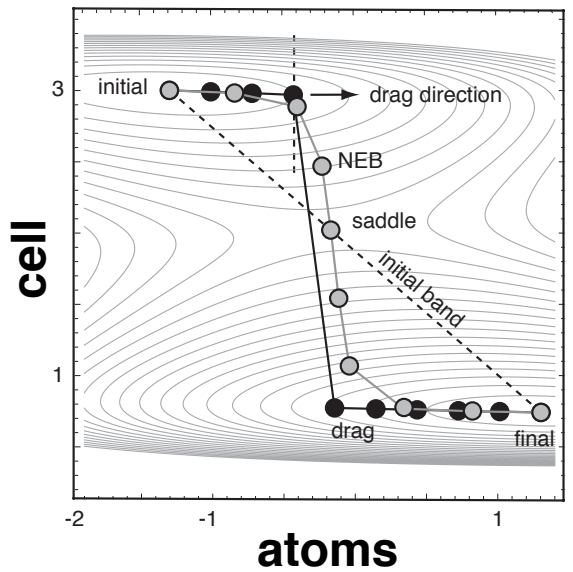


final (wurtzite)





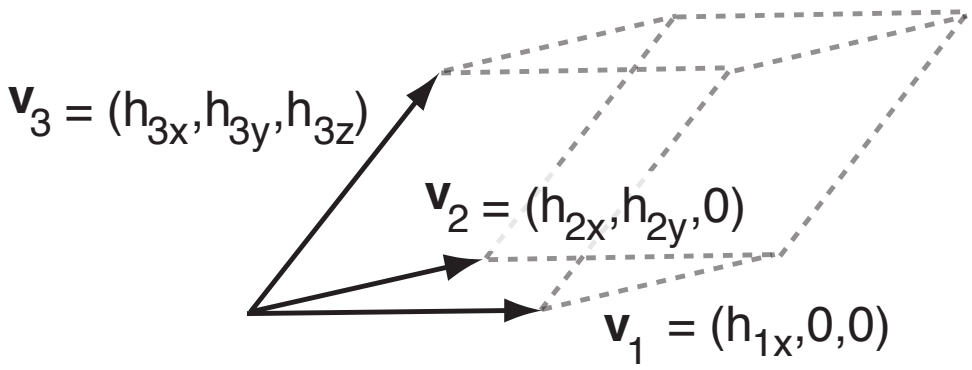
NEB calculations in only atomic [1] or cell (RNM) [2] coordinates have the errors found in drag methods. **Requires a unified approach**



[1] D. R. Trinkle, R. G. Hennig, S. G. Srinivasan, et al., *PRL* **91**, 025701 (2003).
[2] K. J. Caspersen and E. A. Carter, *PNAS* **102**, 6738 (2005).

Choice of cell representation

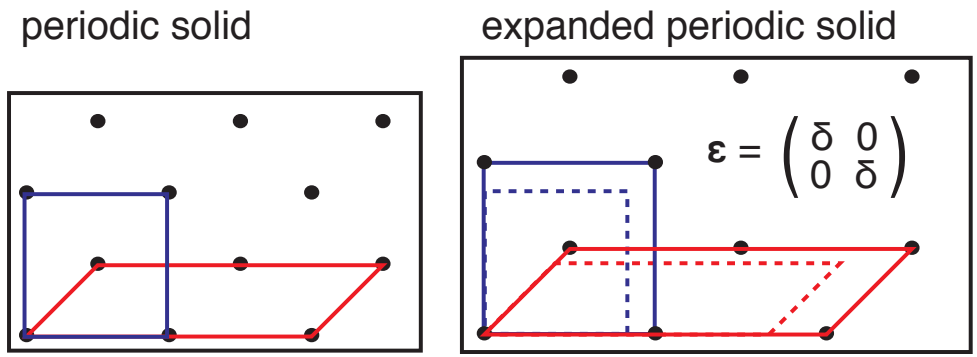
Cell coordinates



Choose a representation which does not allow for net rotation of the lattice

$$\mathbf{h} = \begin{pmatrix} \mathbf{v}_1 \\ \mathbf{v}_2 \\ \mathbf{v}_3 \end{pmatrix} = \begin{pmatrix} \mathrm{h}_{1x} & 0 & 0 \\ \mathrm{h}_{2x} & \mathrm{h}_{2y} & 0 \\ \mathrm{h}_{3x} & \mathrm{h}_{3y} & \mathrm{h}_{3z} \end{pmatrix}$$

Changes in the cell are represented as strain



Strain describes changes in the lattice which is invariant to the unit cell

$$\varepsilon = \mathbf{h}^{-1} \cdot (\mathbf{h}^{\mathrm{def}} - \mathbf{h})$$

Combining atomic and cell variables (G-SSNEB)

Single displacement vector: $\Delta\mathbb{R} = \{J\boldsymbol{\varepsilon}, \Delta\mathbf{R}\}$

change in cell shape — change in atom positions

Jacobian to combine different units

Requirement: reaction pathways should be independent of unit cell size and shape -- the path should be a property of the infinite solid

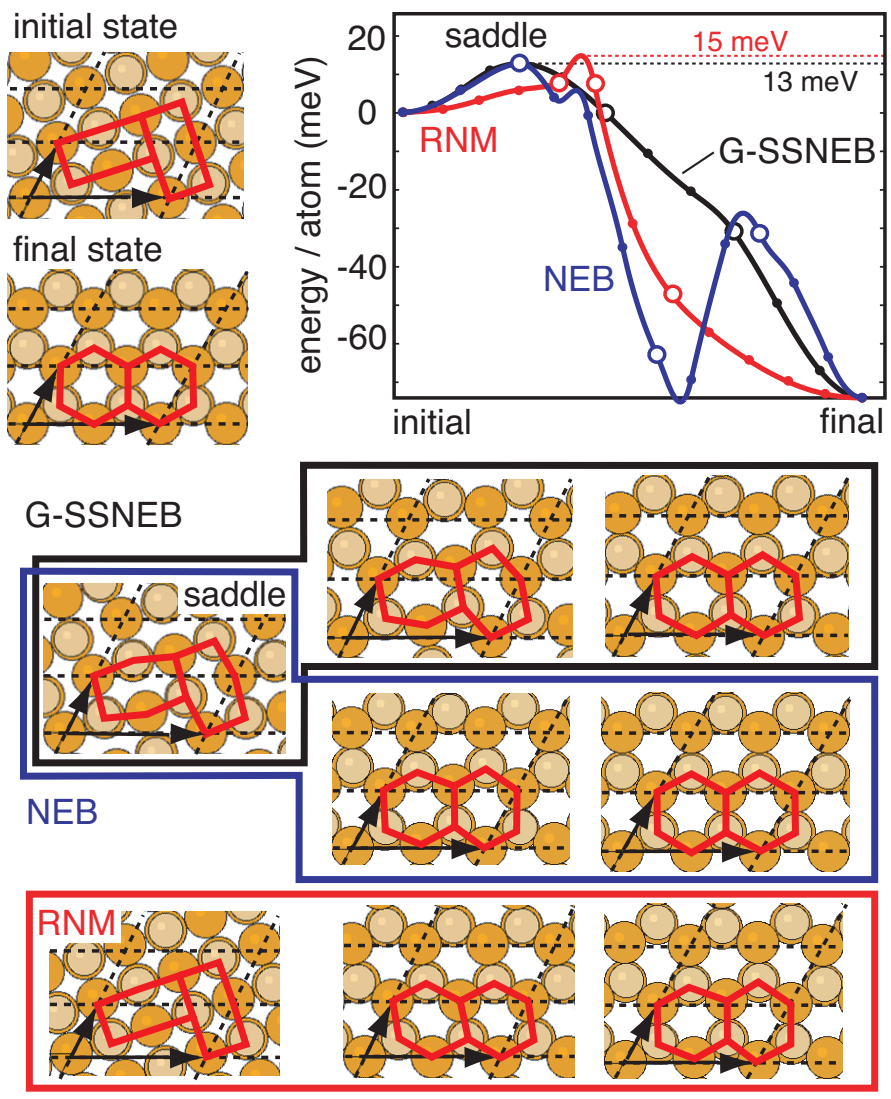
Unit of length, average distance between atoms: $L = \left(\frac{\Omega}{N}\right)^{1/3}$ (Ω: volume)

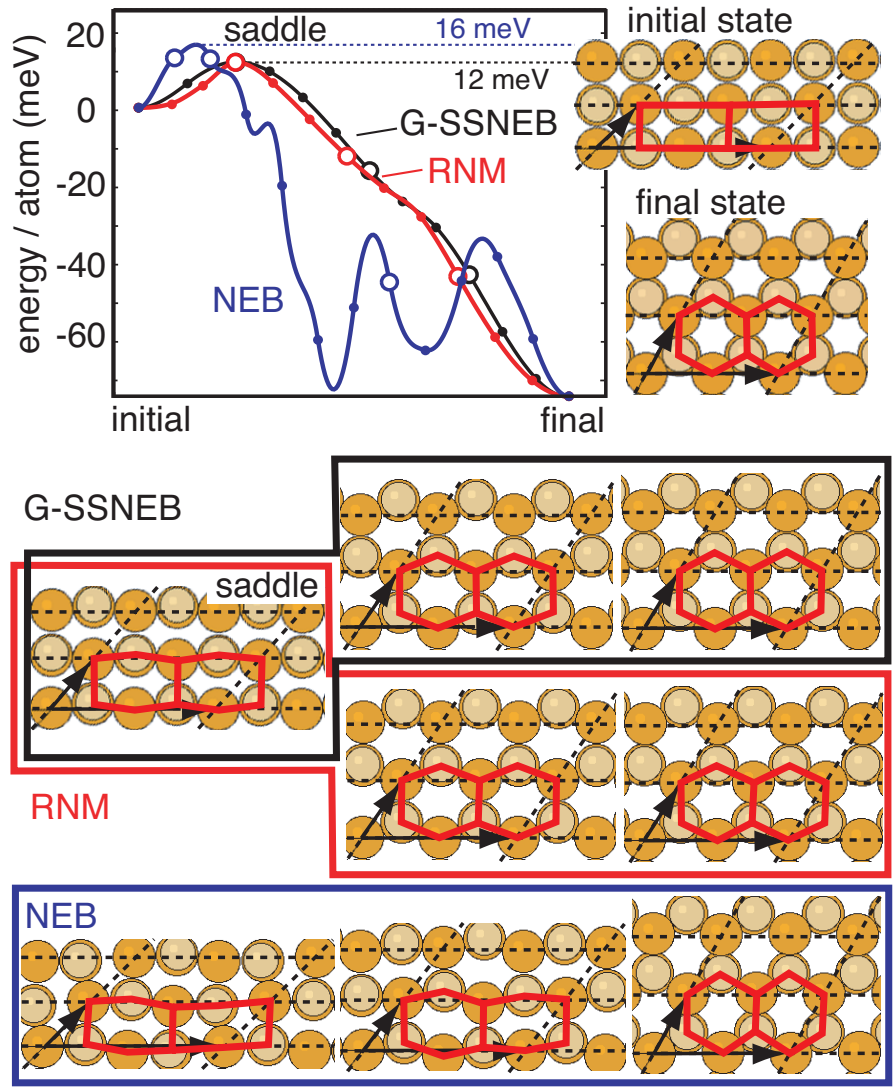
Scaling of atomic displacements with size: $\Delta\mathbf{R}_N = \left(\sum_{i=1}^{N} \Delta\mathbf{R}_i^2\right)^{1/2} = \sqrt{N}\Delta\mathbf{R}_0$

Choose *J* so that *Jε* has same units and scaling as **ΔR**: $J = L\sqrt{N}$

Similar logic applies to the stress / force vector: $\mathbb{F} = (-\Omega\boldsymbol{\sigma}/\mathrm{J}, \mathbf{F})$

Results





Atom-dominated process:

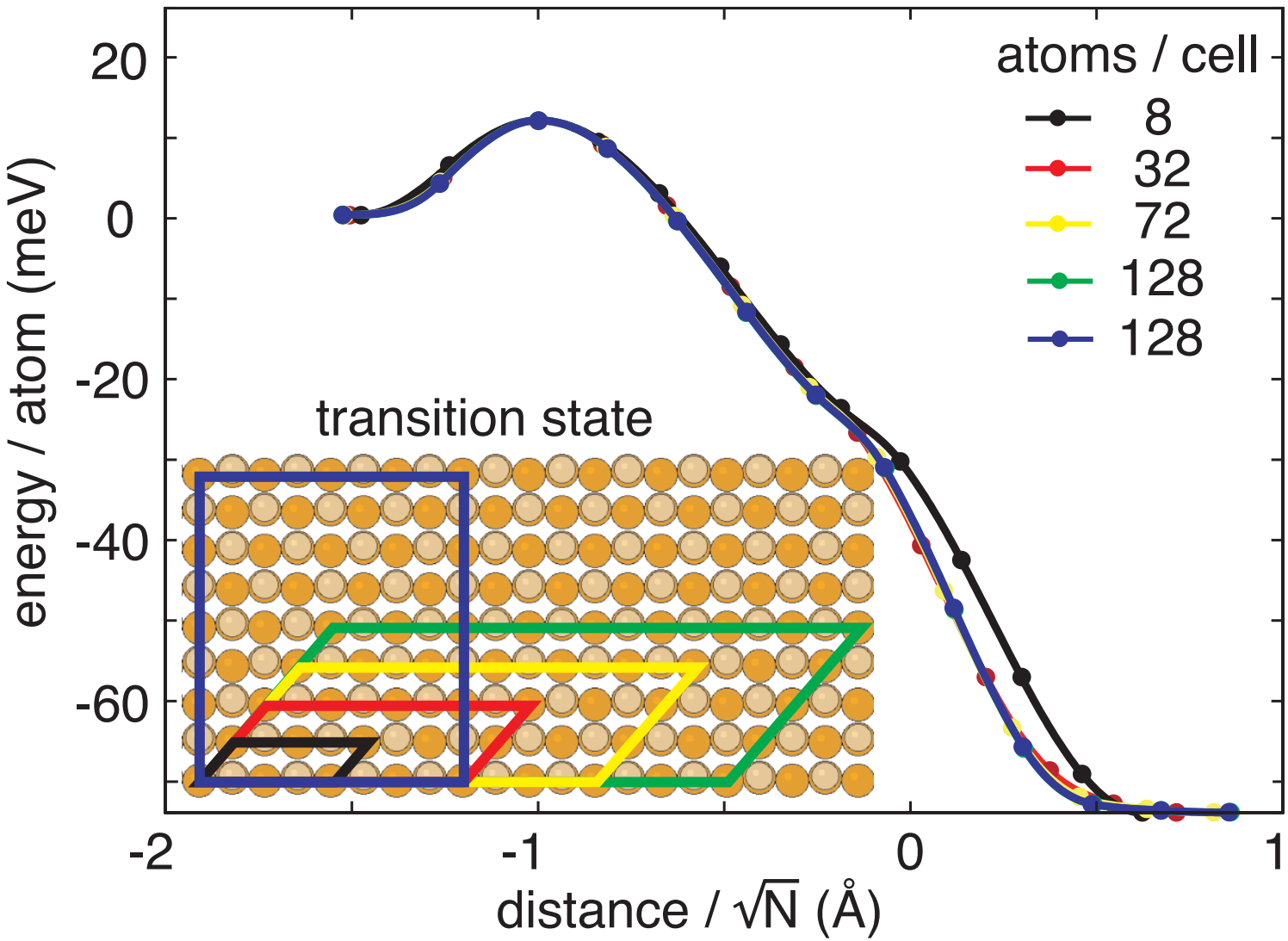
RNM fails; NEB / G-SSNEB work

Cell-dominated process:

NEB fails; RNM / G-SSNEB work

Scaling with system size

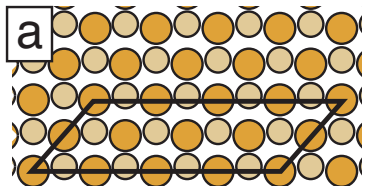
Minimum energy path is insensitive to unit cell size and shape:



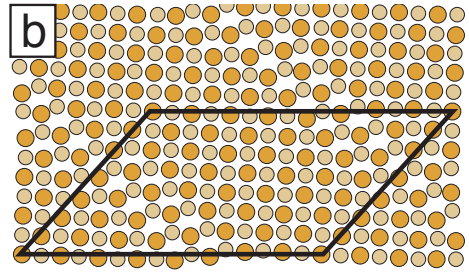
Change of mechanism

With increasing system size:

The mechanism changes from a concerted bulk process (cell dominated) to a local (atom dominated)

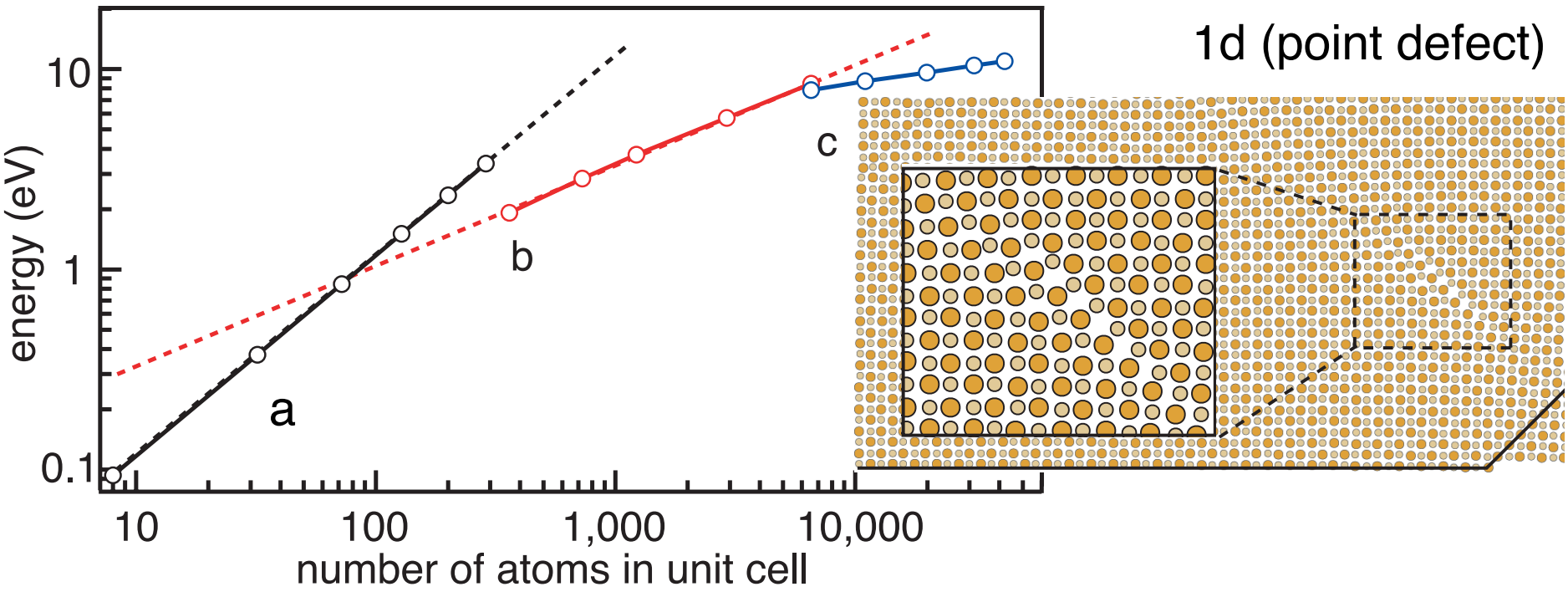


3d (bulk concerted)



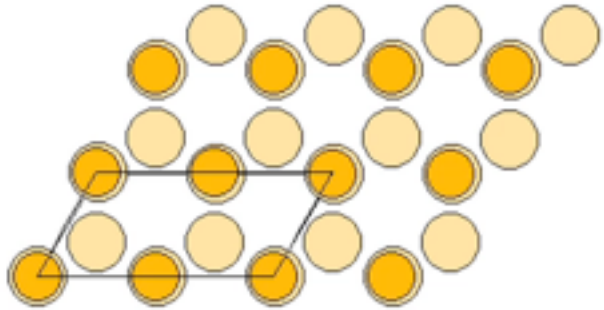
2d (line defect)

1d (point defect)

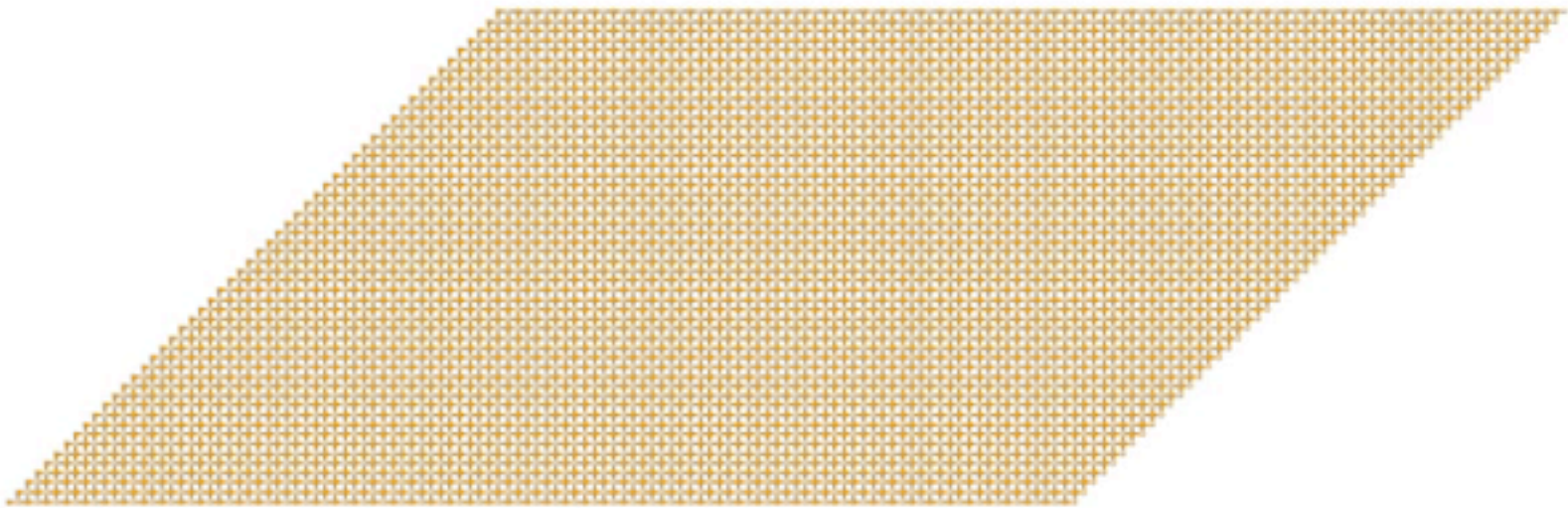


Movies

Concerted mechanism

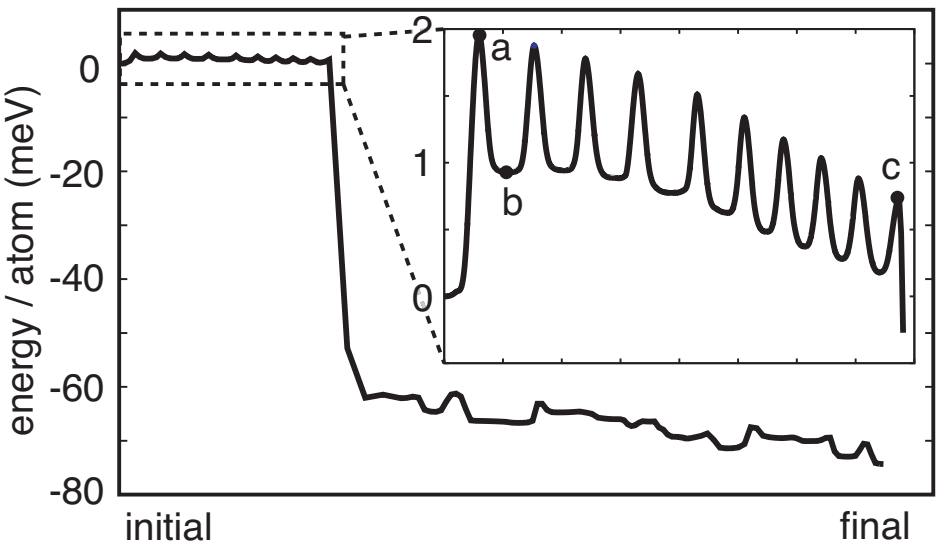


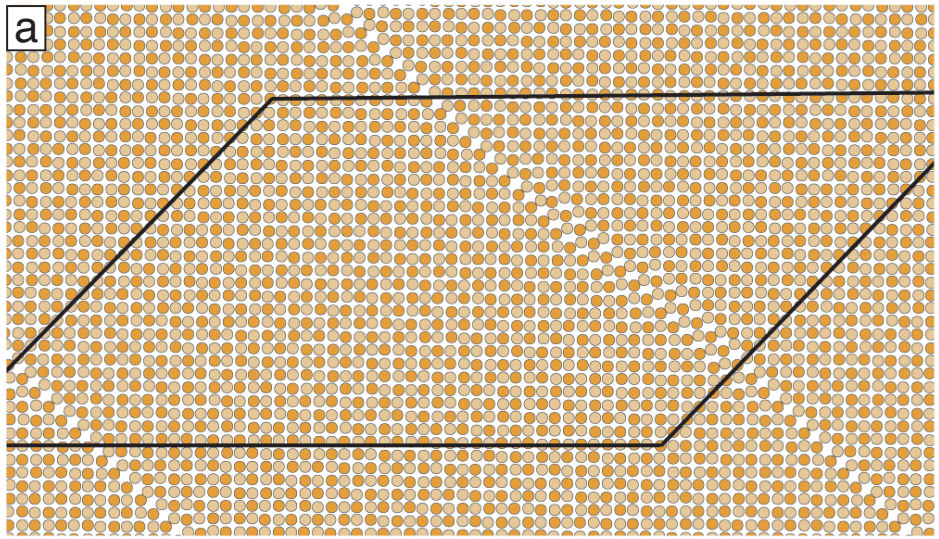
Local mechanism

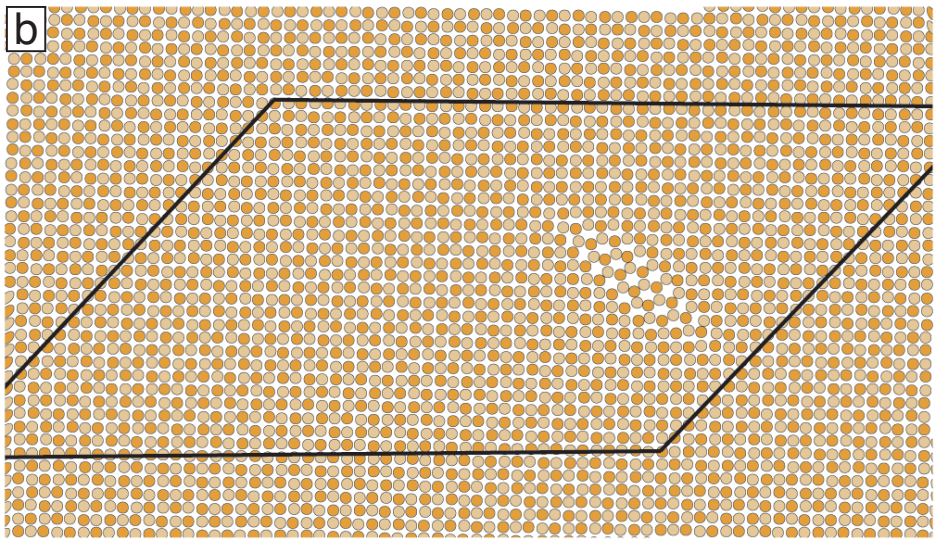


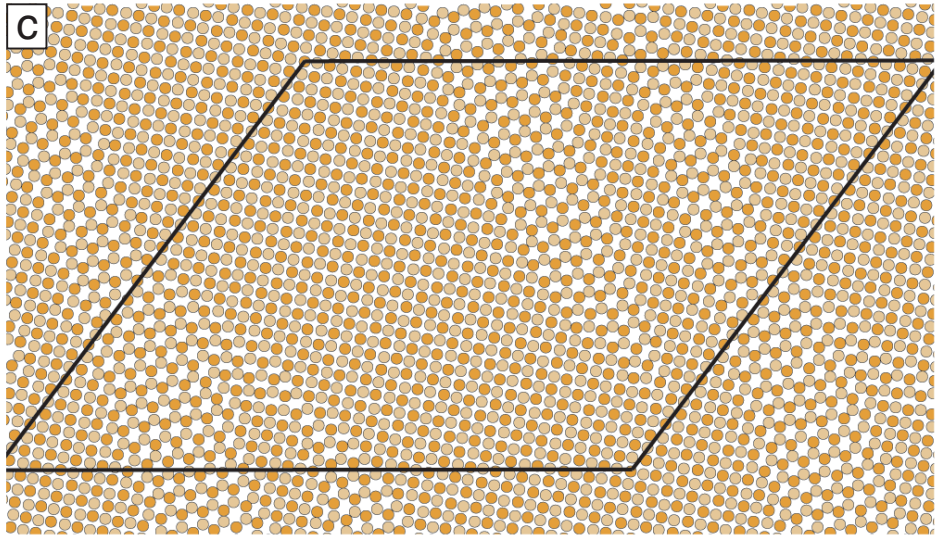
Local process in detail

Complex mechanism:









Research Group

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Sam Chill (graduate student)
Will Chemelewski (graduate student)

Dmitrii Makarov (U. Texas, Austin)
Hannes Jónsson (U. Iceland)
Andreas Pederson (U. Iceland)
Duane Johnson (Iowa State/Ames Lab)

Software tools

http://theory.cm.utexas.edu/vtsttools/	**AKMC**, Dimer, **(SS)NEB**, and dynamical matrix methods implemented in the VASP code
http://theory.cm.utexas.edu/bader/	Bader charge density analysis
http://theochem.org/EON/	The EON project for long time scale simulations
http://theory.cm.utexas.edu/code/tsase/	Transition state simulation environment (for ASE)