Lecture 3: MMF & Adaptive kinetic Monte Carlo method

Hannes Jónsson *University of Iceland* www.hi.is/~hj

Lecture 1. The rare event problem and transition state theory (TST)
- Transition state theory, dividing surfaces and reaction coordinates
- Recrossing corrections and the variational principle
- The WKE two step procedure for finding the mechanism and 'exact' rate
- Optimal hyperplanar TST

Lecture 2. Harmonic TST and adaptive kinetic Monte Carlo (AKMC)
- The harmonic approximation to TST (HTST)
- Methods for finding minimum energy paths, NEB and CI-NEB
- Variants and improvements on NEB method
- Example applications

Lecture 3. MMF method and adaptive kinetic Monte Carlo (AKMC)
- Methods for finding saddle points when only initial state is known, MMF
- Long time scale simulations using AKMC
- Coarse graining, recycling, distributed computing
- Example applications

Second step in Born-Oppenheimer procedure:

Displacements of the atoms

Theoretical methods:

a. Transition state theory (TST) for thermally activated transitions
and WKE two step procedure

b. Harmonic approximation to TST (HTST) – easy to use with DFT

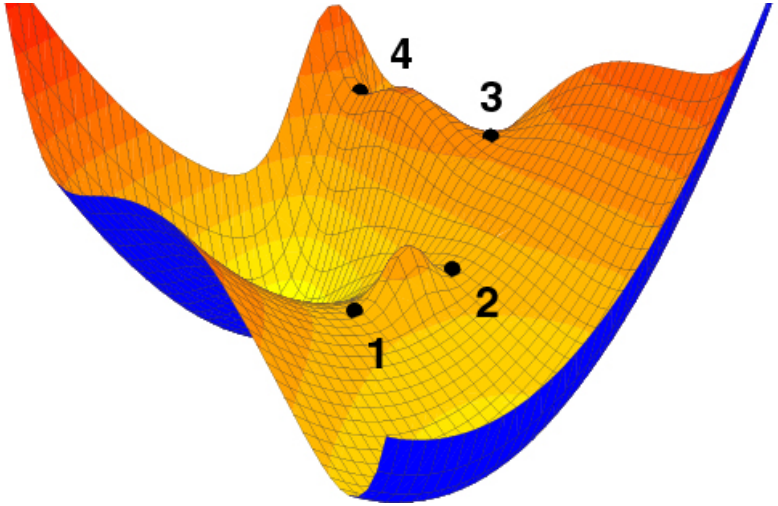
c. Minimum energy paths – the NEB and CI-NEB methods

d. Saddle point searches without specifying a final state

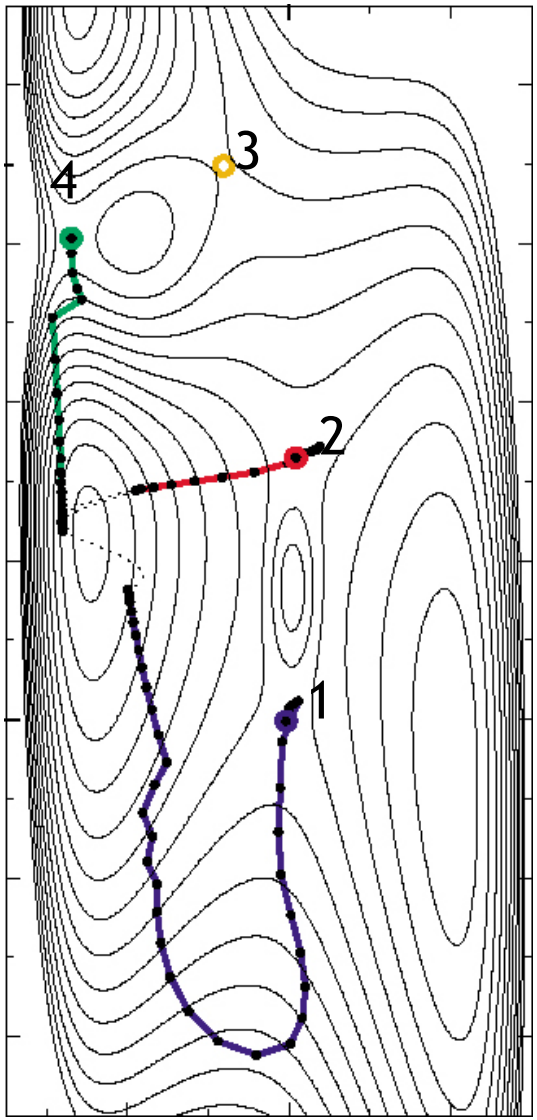
e. Adaptive kinetic Monte Carlo for simulating time evolution

Minimum mode following method *(G. Henkelman and HJ, 1999)*

Within HTST, need to find all the relevant saddle points on the energy rim surrounding the current state minimum.



Make a displacement from the minimum, then follow effective gradient



Transform the force by inverting the component along the minimum mode, $\hat{\mathbf{v}}_{i,min}$, of the Hessian (the matrix of second derivatives)

$$\mathbf{F}_{i,eff} = \mathbf{F}_i - 2\left(\mathbf{F}_i \cdot \hat{\mathbf{v}}_{i,min}\right)\hat{\mathbf{v}}_{i,min}$$

The direction along the minimum mode is found by minimizing the energy of a **dimer** (two replicas of the system,) or by using the **Davidson** algorithm.
No need to construct the Hessian matrix.

Use some minimization algorithm that only requires derivative of the objective function (not the objective function itself) and it will converge on a first order saddle point.
The force projection locally transforms a first order saddle point to a minimum.

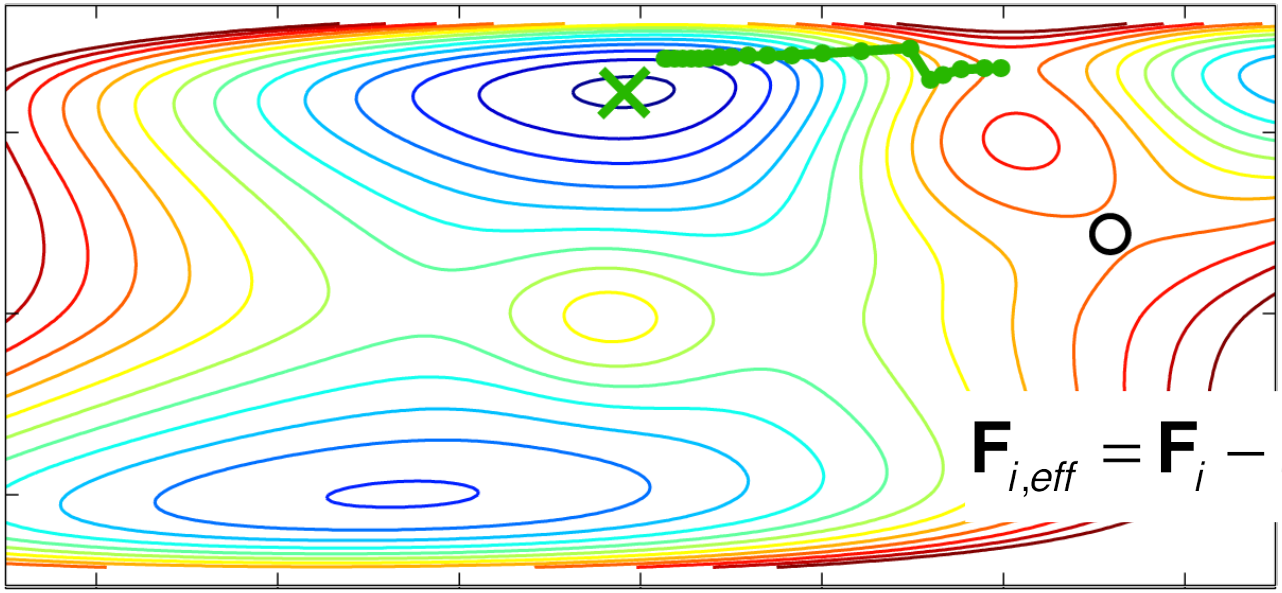
Use random initial displacement and then climb up the PES

Two phases:

1. When lowest eigenvalue of H is positive,
   move along minimum mode.
2. After lowest eigenvalue of H becomes negative, include also
   force perpendicular to the minimum mode.

Little or no bias from preconceived notion of the mechanism, perhaps displace under-coordinated atoms and their neighbors.

– Can discover unexpected mechanism and final state(s).



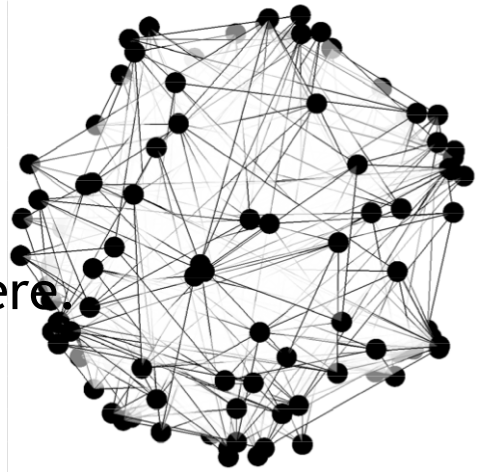
$$\mathbf{F}_{i,eff} = \mathbf{F}_i - 2\left(\mathbf{F}_i \cdot \hat{\mathbf{v}}_{i,min}\right)\hat{\mathbf{v}}_{i,min}$$

Use hypersphere to distribute initial points

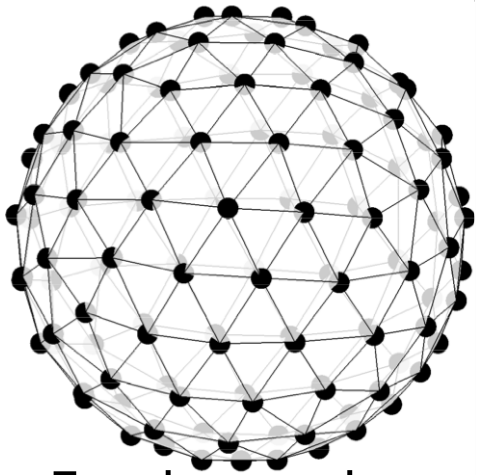
Reduce number of function evaluations by distributing initial points on a hypersphere.

Push radius out after a few saddle points have been found. Use information about distance to saddle points and to points where lowest eigenvalue is zero.

(M.P. Gutierres *et al.* JCTC 13, 125 (2017))

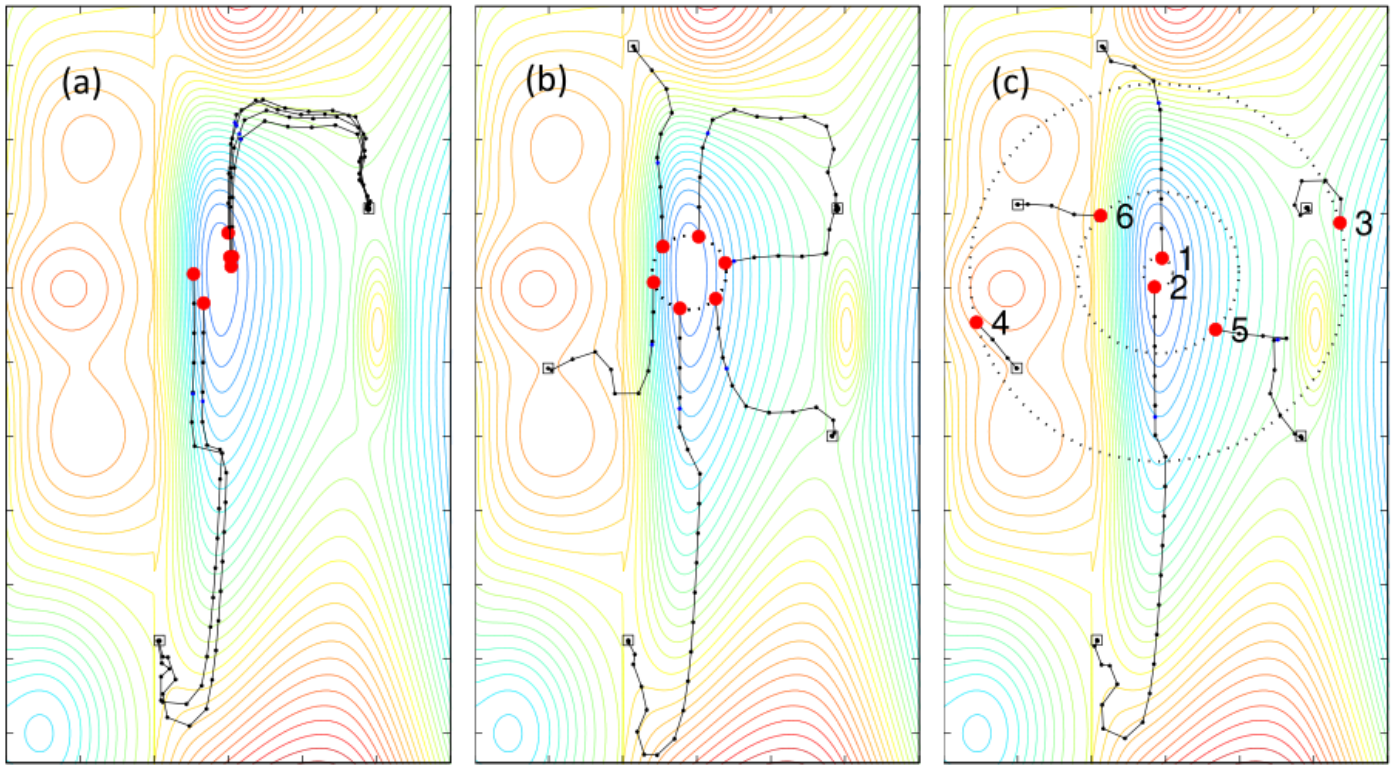


Randomly on sphere

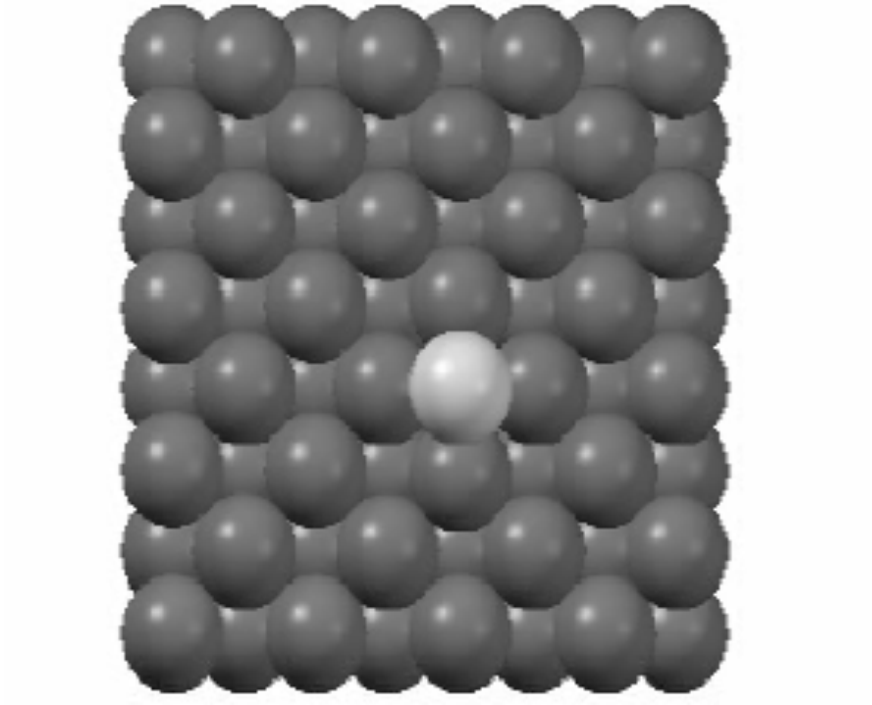


Evenly on sphere

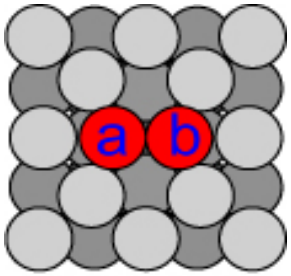
first small radius then larger radi



Example: Adatom diffusion on Al(100)



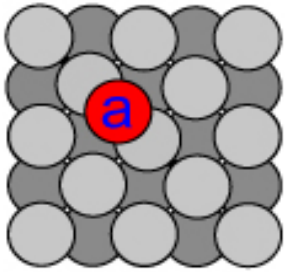
Saddle point



EAM (DFT)

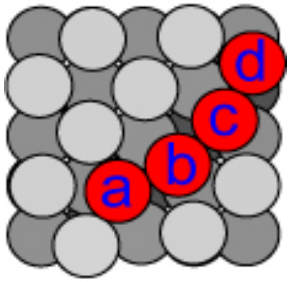
ΔE = **0.23 eV (0.24 eV)**

ν = **$7 \cdot 10^{13}$ s^{-1} ($1 \cdot 10^{14}$ s^{-1})**



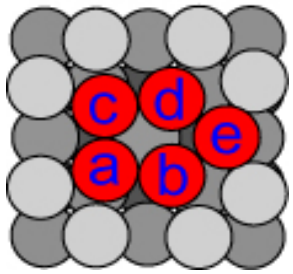
ΔE = **0.37 eV (0.52 eV)**

ν = **$5 \cdot 10^{13}$ s^{-1} ($7 \cdot 10^{13}$ s^{-1})**



ΔE = **0.41 eV (0.50 eV)**

ν = **$2 \cdot 10^{15}$ s^{-1} ($8 \cdot 10^{14}$ s^{-1})**

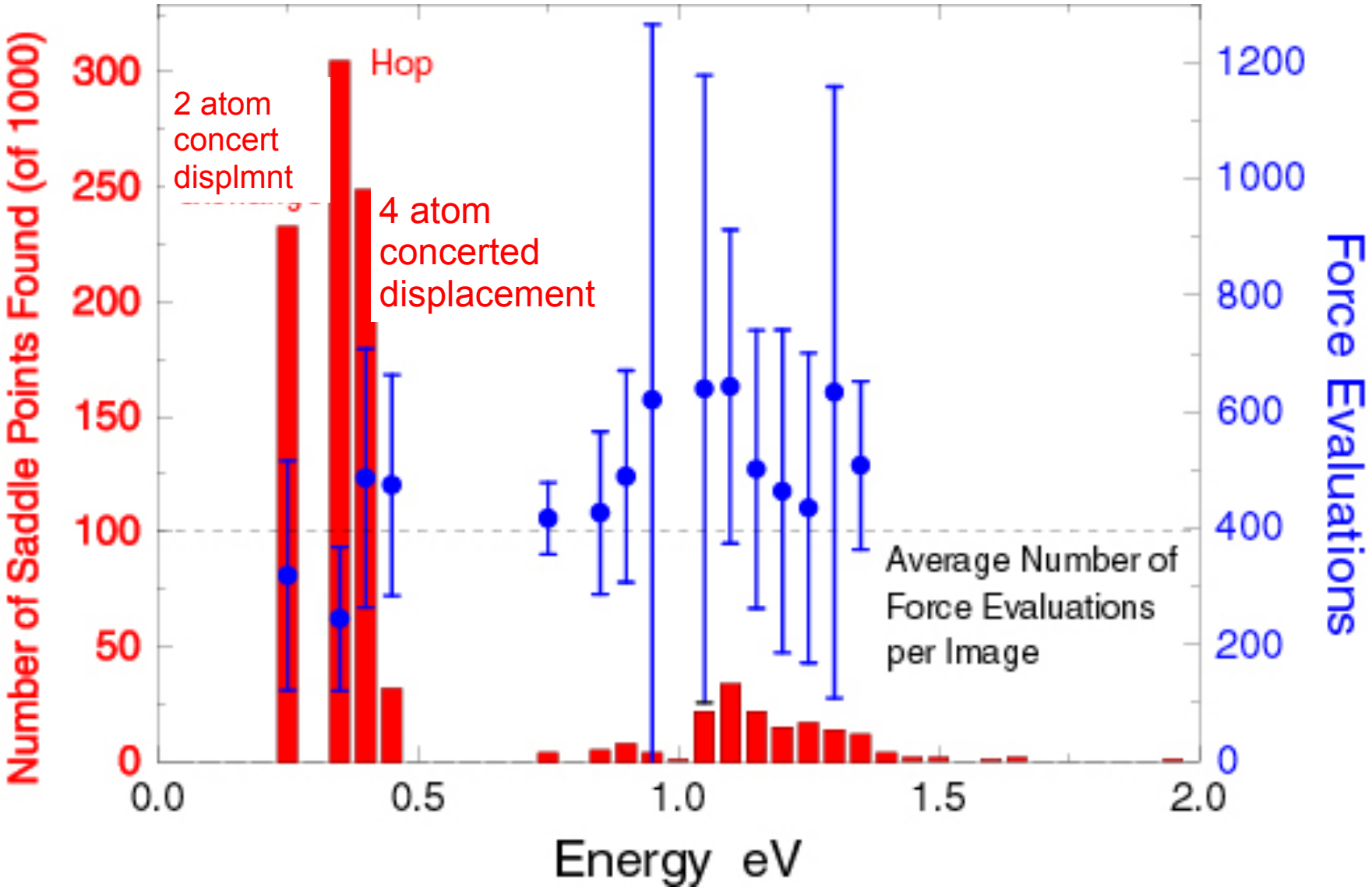


ΔE = **0.44 eV**

ν = **$3 \cdot 10^{14}$ s^{-1}**

Satistics on saddle point searches

1000 searches for Al/Al(100) were carried out,
over 60 saddle points with energy less than 2 eV were found



Second step in the Born-Oppenheimer procedure:

Displacements of the atoms

Theoretical methods:

a. Transition state theory (TST) for thermally activated transitions and WKE two step procedure

b. Harmonic approximation to TST (HTST) – easy to use with DFT

c. Minimum energy paths – the NEB and CI-NEB methods

d. Saddle point searches without specifying a final state

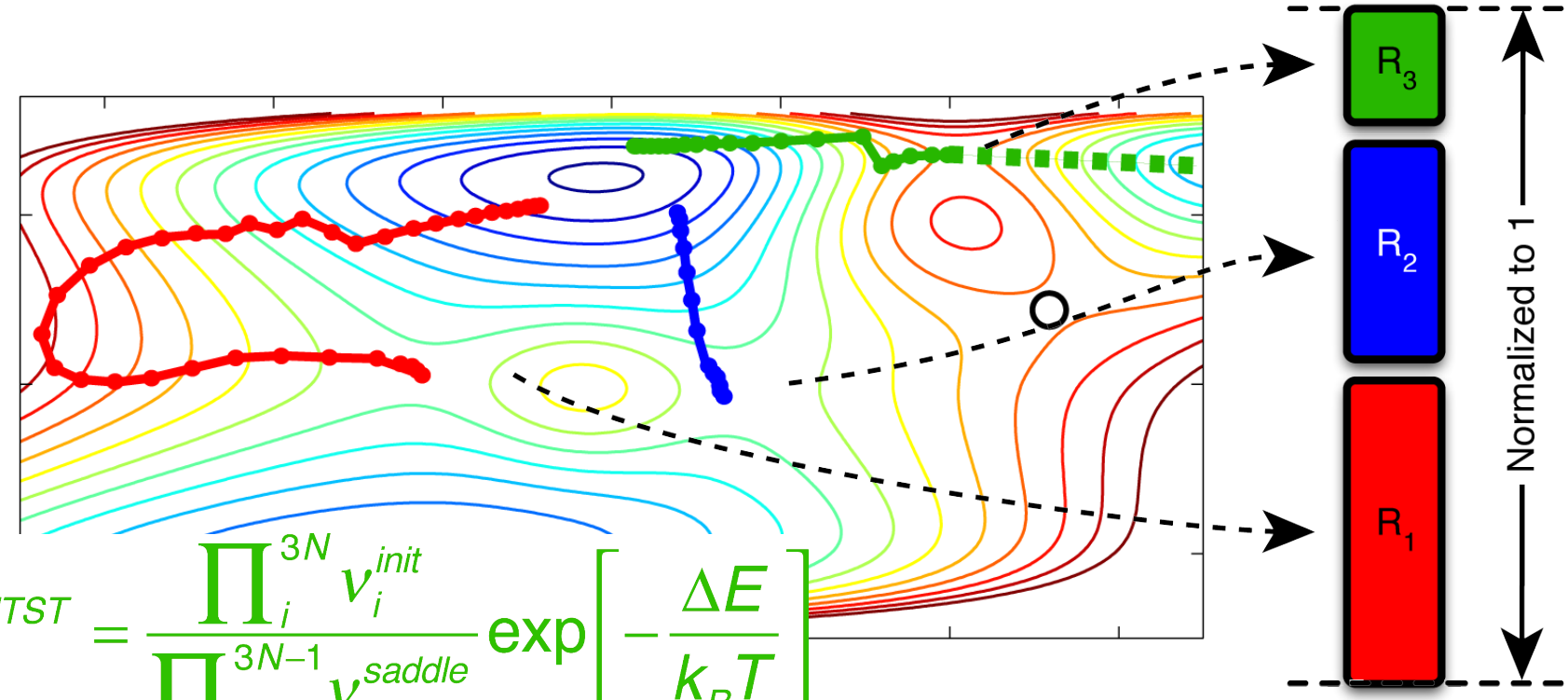
e. Adaptive kinetic Monte Carlo for simulating time evolution

e. Adaptive Kinetic Monte Carlo

Obtain a table of possible transitions from a given minimum:

- Locate saddle points on the energy ridge surrounding the minimum.
- Slide down PES, to determine product state (and check initial state).
- Estimate rate through each hyperplane using HTST.

Then, use a random number to pick the next transition



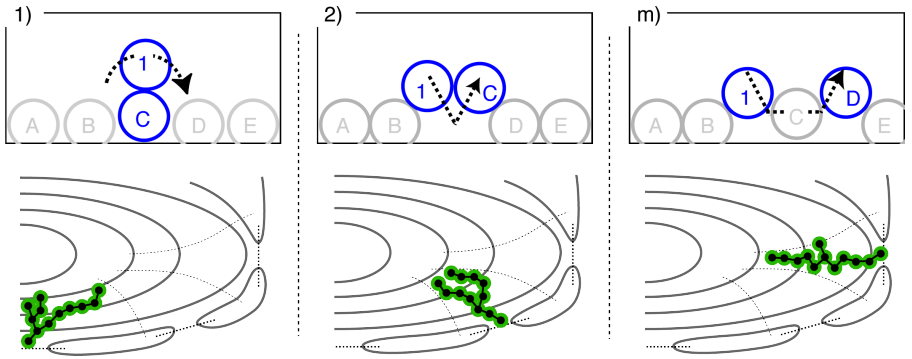
$$k^{HTST} = \frac{\prod_i^{3N} \nu_i^{init}}{\prod_i^{3N-1} \nu_i^{saddle}} \exp\left[-\frac{\Delta E}{k_B T}\right]$$

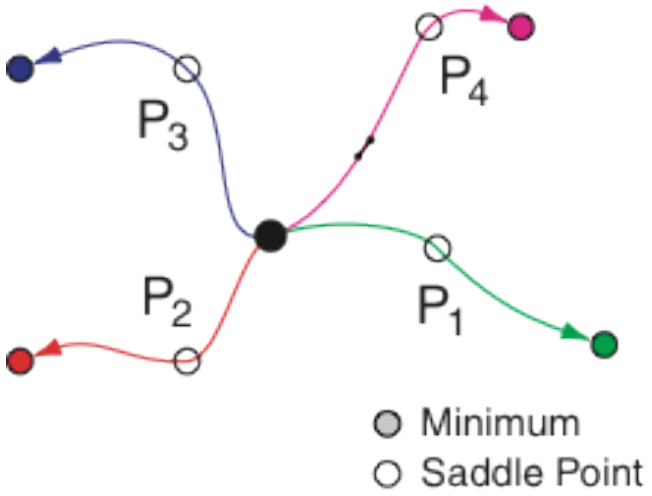
Adaptive Kinetic Monte Carlo

G. Henkelman and HJ, *JCP.* (2001)

1. Find low energy saddle points near the current minimum using multiple SP searches started at random (Gaussian distributed)
2. Find the prefactor, ν, from normal mode analysis and calculate the rate of each process $r_i = \nu e^{-\Delta E_i / k_B T}$
3. Use a random number to pick one of the transitions according to the relative transition rates
4. Advance system to the final state of the chosen process (trajectory or slide down)
5. Increment time by an amount $\Delta t = 1/\Sigma\, r_i$

Repeat 1 - 5 until the desired time interval has been reached



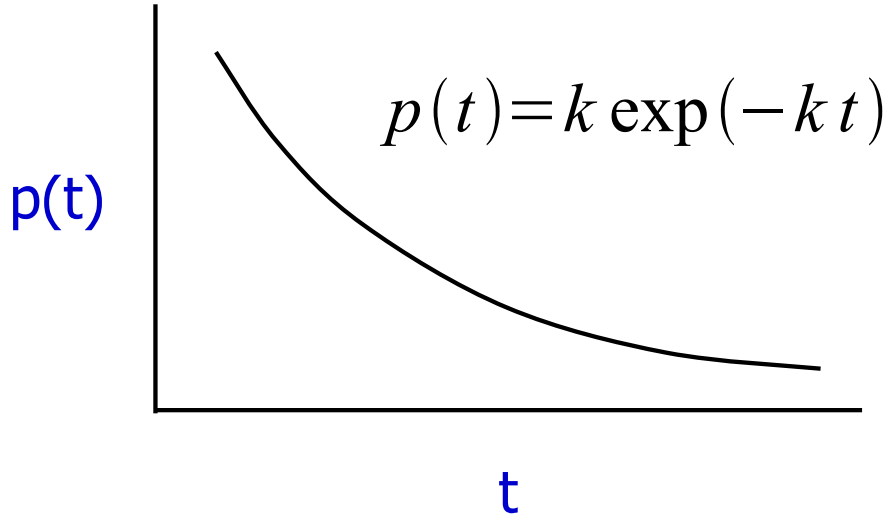


- No need to create a table of transitions and their rates *before* the simulation as in regular KMC

- Also, no need to assign atoms to lattice sites (defects, glass, …)

Can take into account fluctuations in life time

exponential distribution of first-escape times



Rather than using just the estimate of the mean life time of the current state

$$\tau_{ave} = 1/\Sigma_m k_m$$

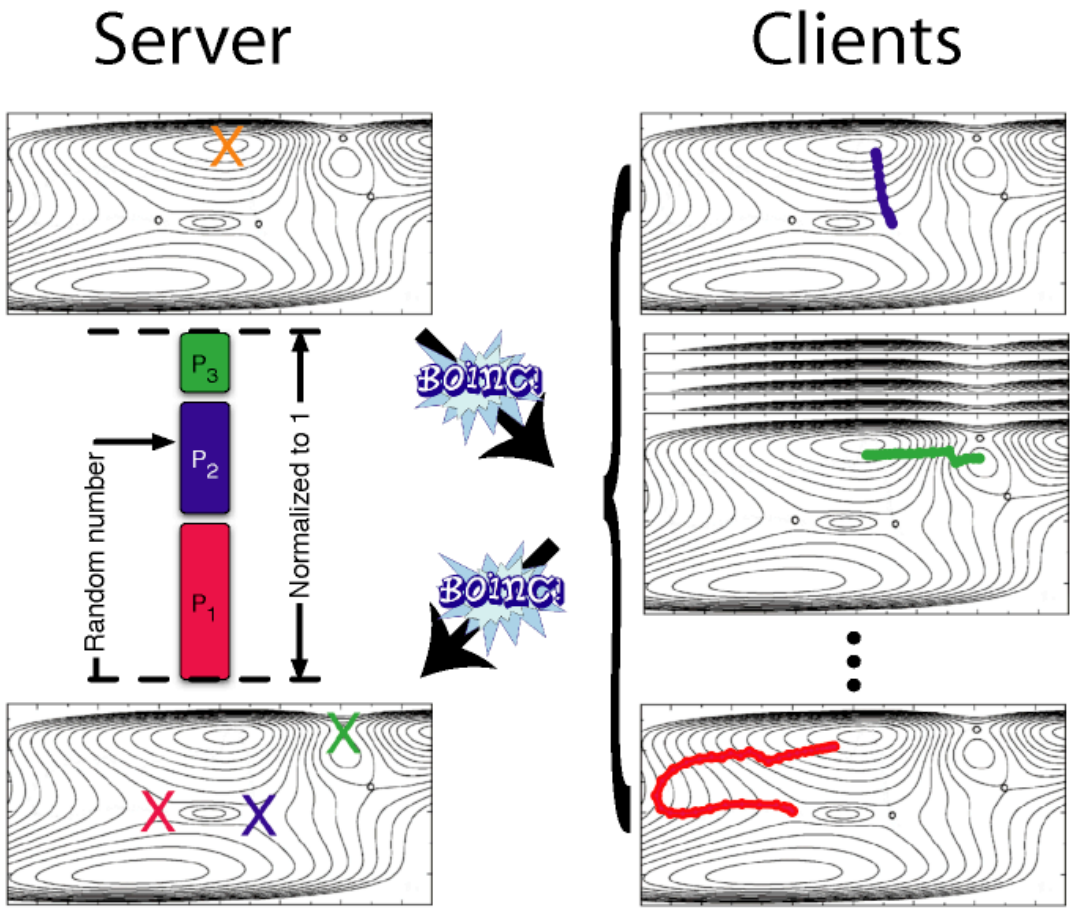
draw a point from the exponential distribution using a random number

$$\tau_i = -\ln \zeta / \Sigma_m k_m$$

where ζ is a random number between 0 and 1.

EON Distributed software for rate calculations

- Distribute saddle point searches over internet
  - Communication builds on BOINC
  - Communication and computation are not entangled
  - Client runs as stand-alone
- Atomic Forces
  - Can use DFT or potential functions for atomic forces
- Implementation
  - Client side C++
  - Server side Python

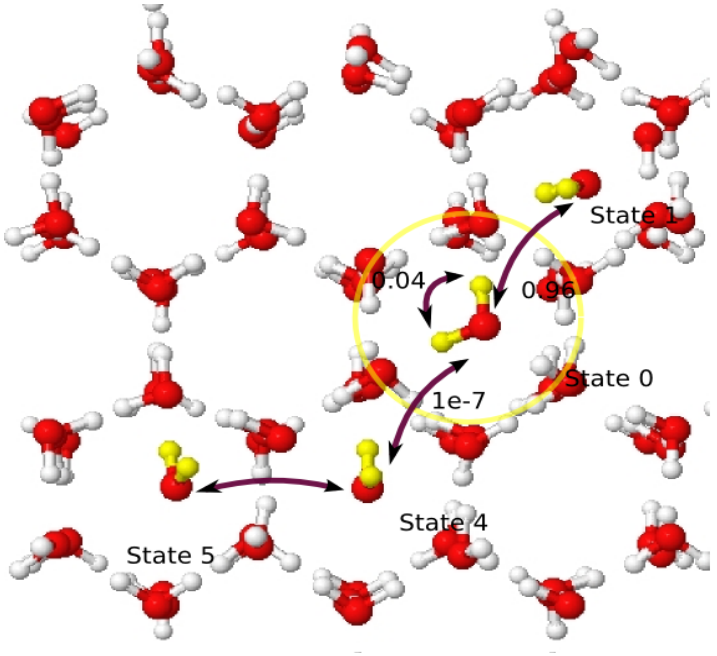


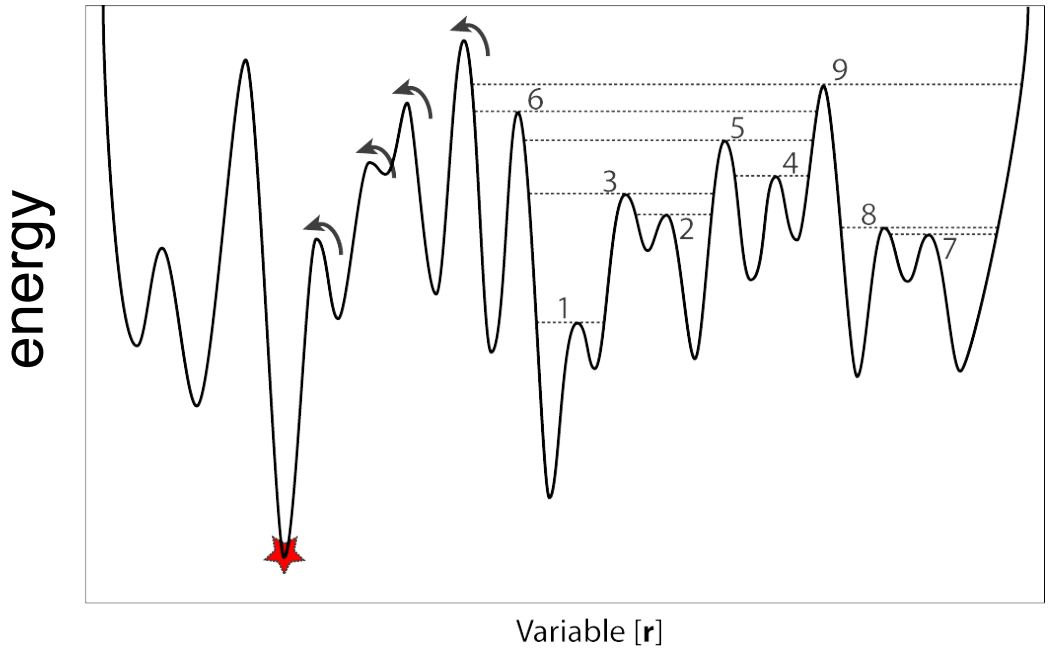
Several tricks to improve efficiency:
Skipping path, systematic coarse graining, recycling, …

(Andreas Pedersen and H.J., *Mathematics and Computers in Simulation*, 2009;
Sam Chill et al., *Modelling and Simulation in Mat. Sci. & Eng.*, 22, 055002 (2014))

Coarse Graining

Problems arise when two or more states are connected by low energy barriers while barriers leading out of this group of states are several k_BT higher (as in regular KMC simulations)





Coarse graining

- Visited minima are assigned a reference energy value
- At each visit the reference value is increased
- A composite state is created when reference value exceeds the saddle point energy
- Composite states can merge

Accurate estimate of time spent in coarse grained state and selection of exit state by using *absorbing Markov chain* theory (Novotny: http://arxiv.org/abs/cond-mat/0109182)

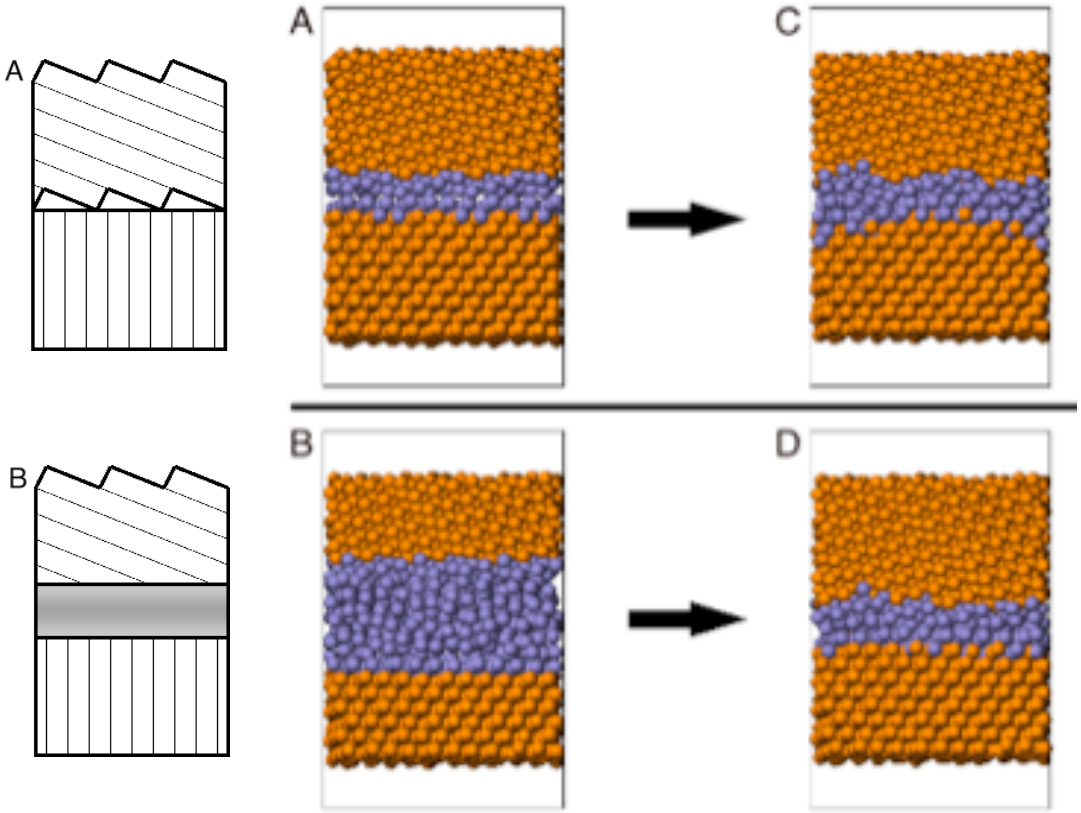
Example application:

Annealing of a tilt-and-twist grain boundary in Cu

- Start with both thin (the two grains brought in contact) and thick (add layer of amorphous Cu in between) configurations for the grain boundary.
- Use EMT potential function.

After annealing the final result is similar, only about 3 atomic layers are not FCC according to Common Neighbor analysis (icosahedral order increases upon annealing)

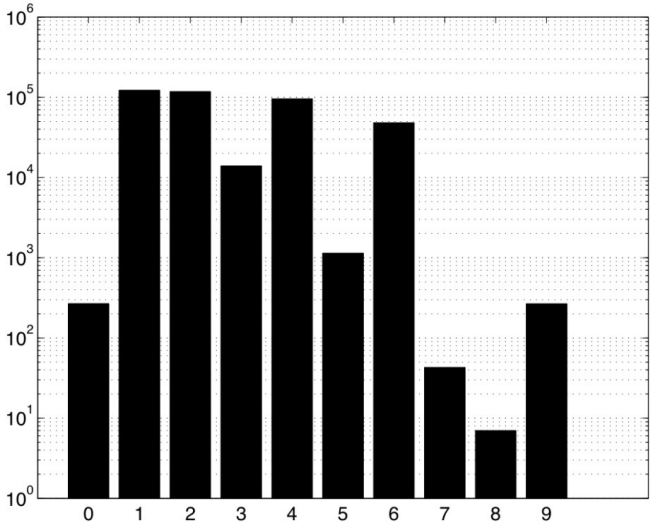
Each system simulated for about 0.1 ms



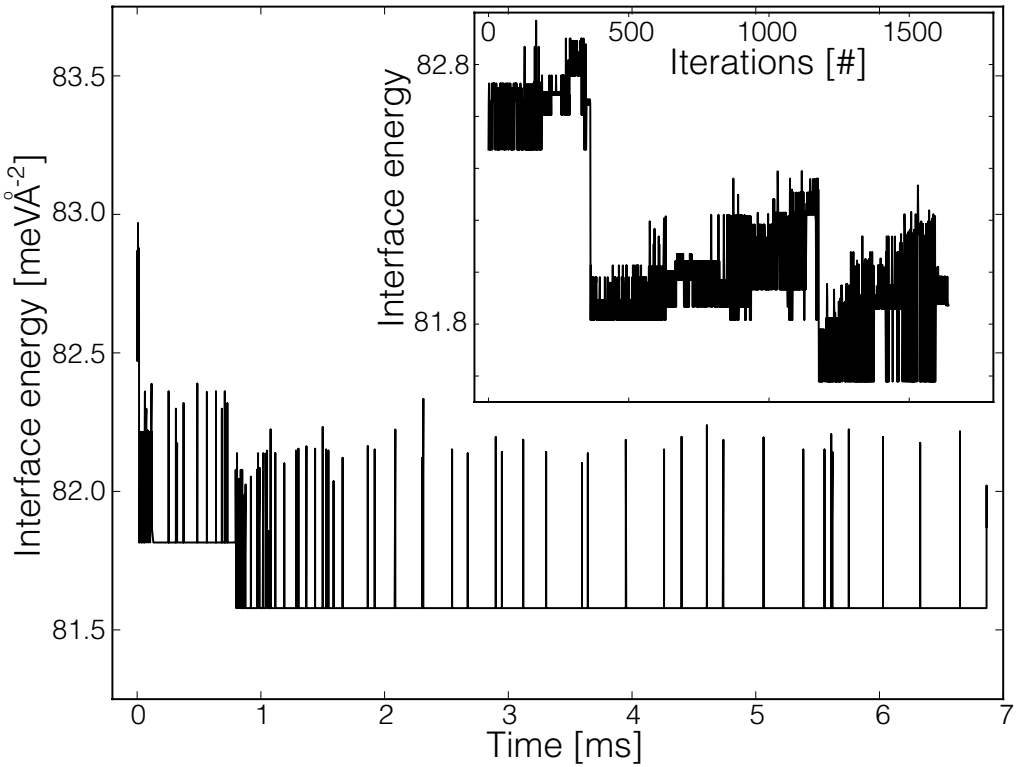
Annealing events found during the AKMC simulation

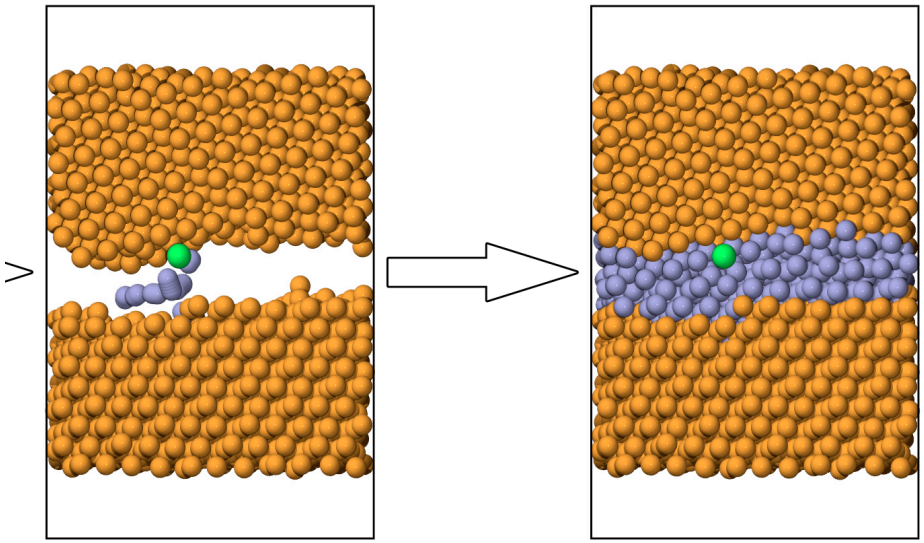
Annealing events often involve concerted displacement of up to 9 atoms.

An atom which is locally coordinated as in an HCP crystal (according to CN-analysis) is formed at the grain boundary in both samples.



# of atoms displaced by > 0.5 A





(A. Pedersen et al., New J. of Physics. 2009)

Example: H-atom diffusion at grain boundaries in Al

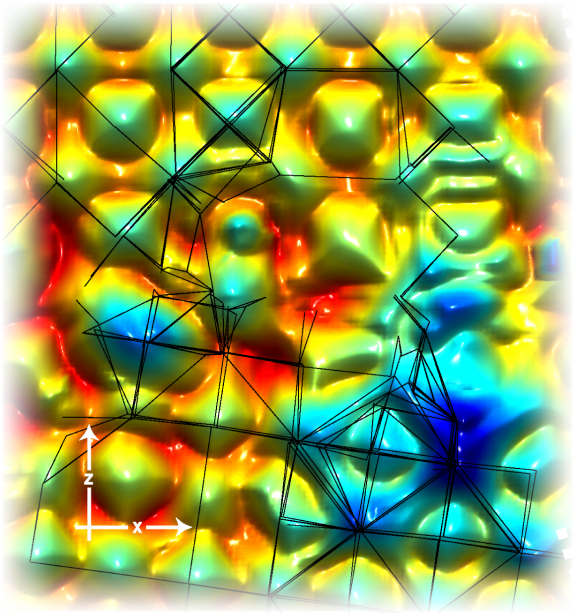
AKMC simulation using EMT potential

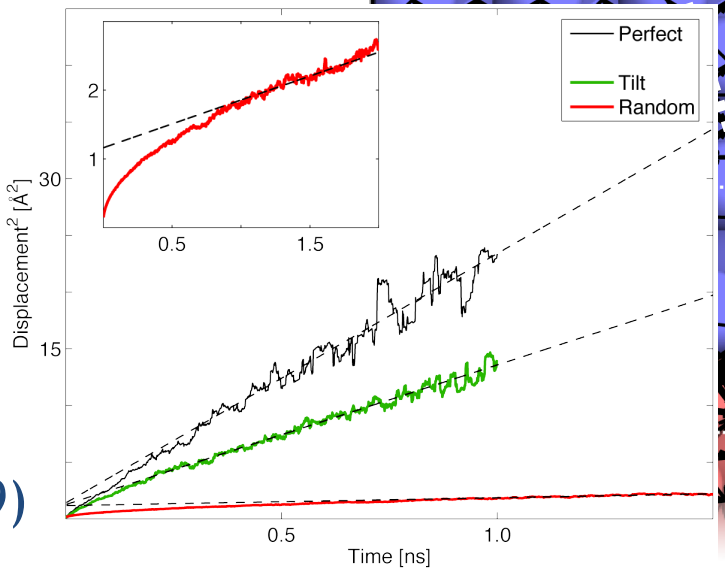
Long time simulation:
- Observe long time diffusion paths of H-atom.

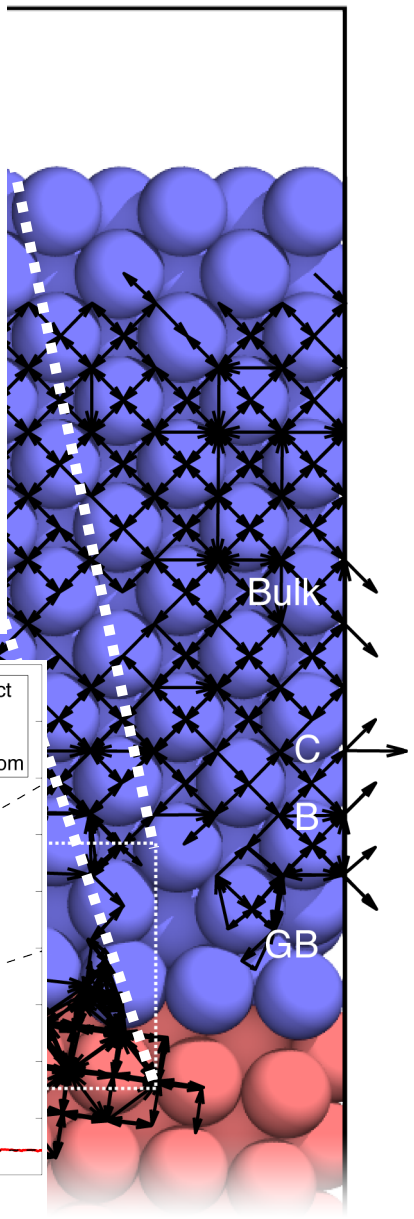
No trapping in Σ5 twist grain boundary.
But, long time trapping in tilt and twist+tilt grain boundary.

Effective potential energy surface:
- Projected onto xz-plane
  - Red high energy
  - Blue low energy
- Two low-energy basins within GB-region

Parallel-diffusivity decreases to one-half of the bulk value for twist+tilt GB







A. Pedersen & HJ, Acta Materialia (2009)

H_2O diffusion on Ice I_h(0001) surface

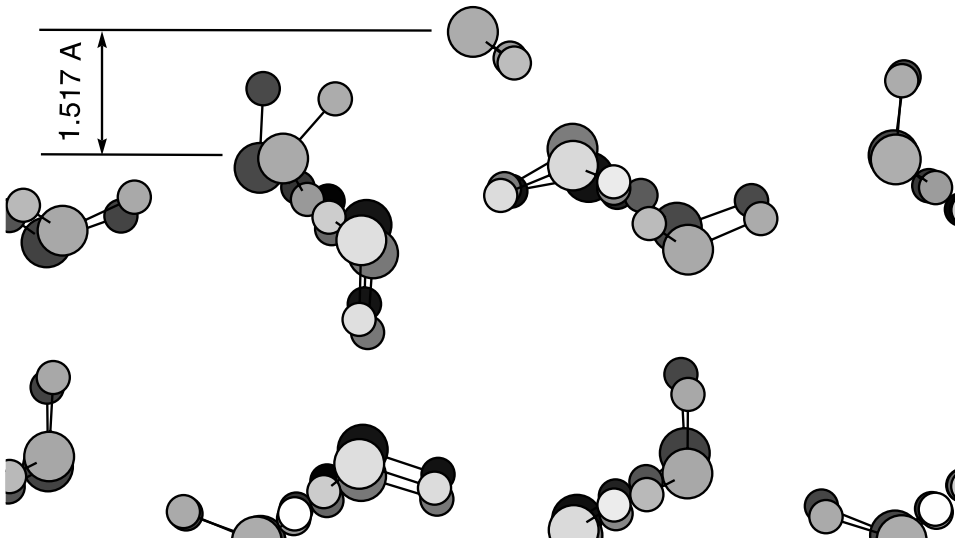
Use TIP4P potential.

Simulate admolecule diffusion, find meachanism and rate of hops from one surface site to another.

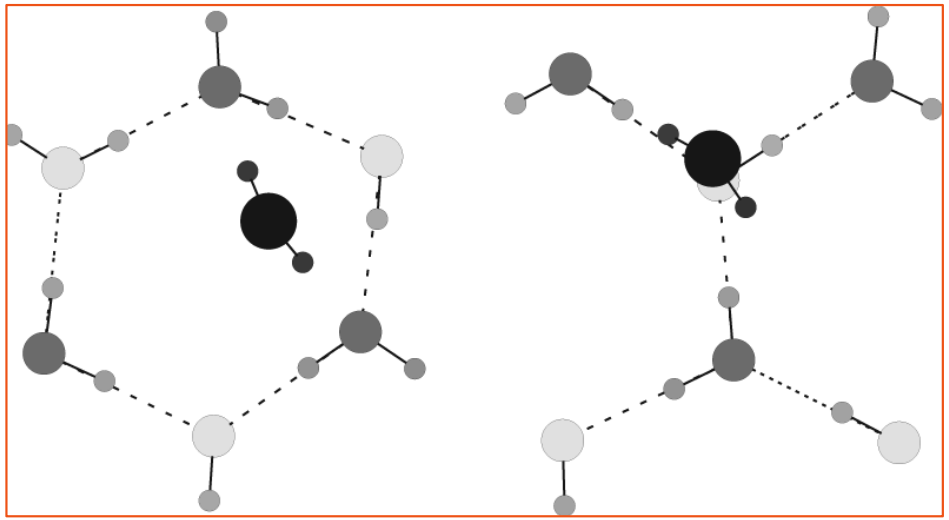
H_2O admolecule sees a disordered surface because of the proton disorder in ice Ih.

It sits in sites that do not fit in with the crystal structure.

side view

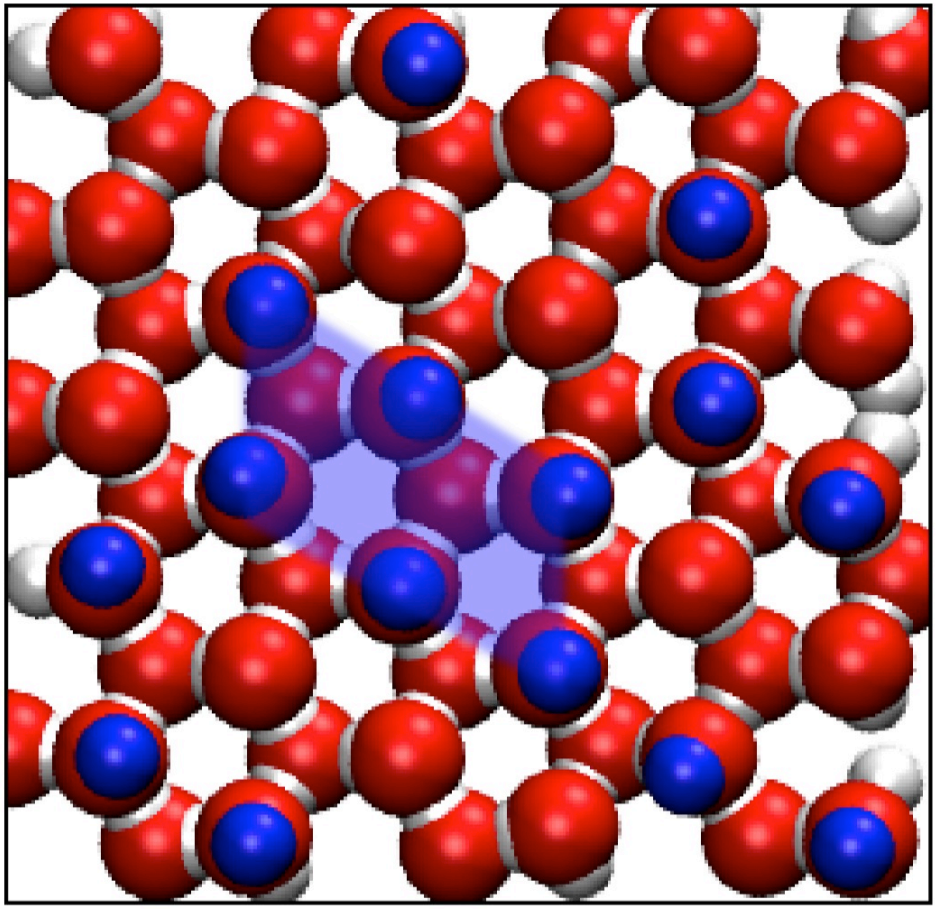


on top view

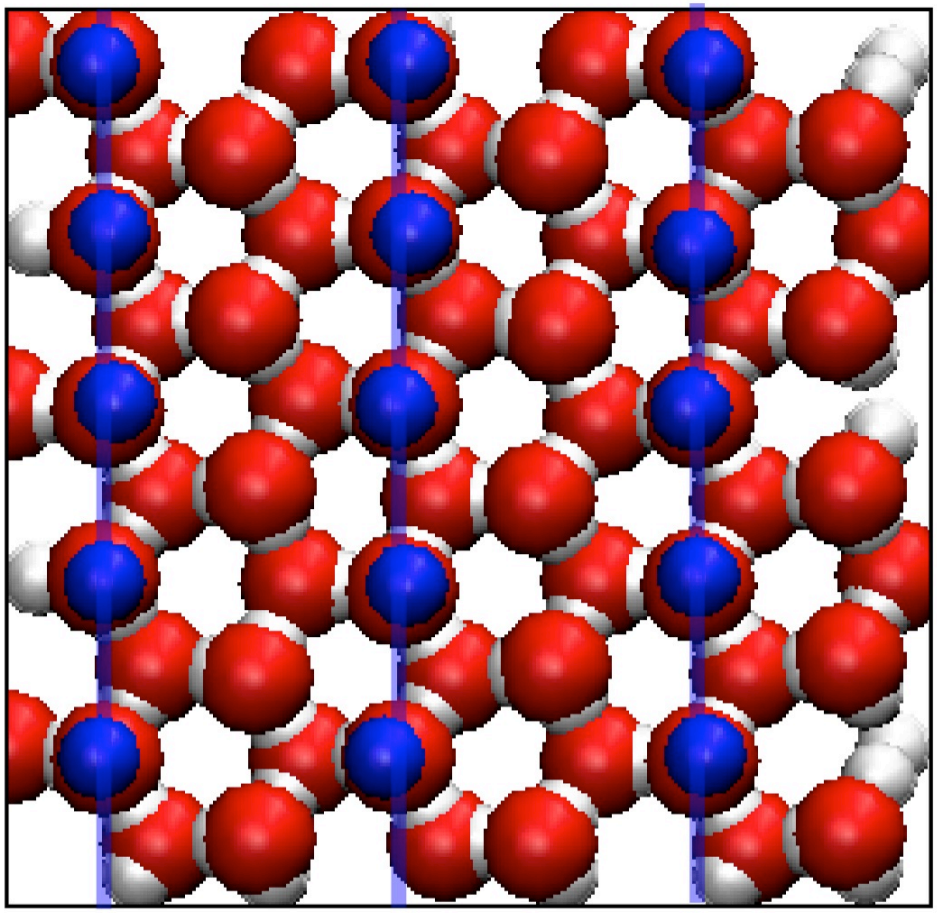


Ordering of dangling H-bonds on the surface

Disordered

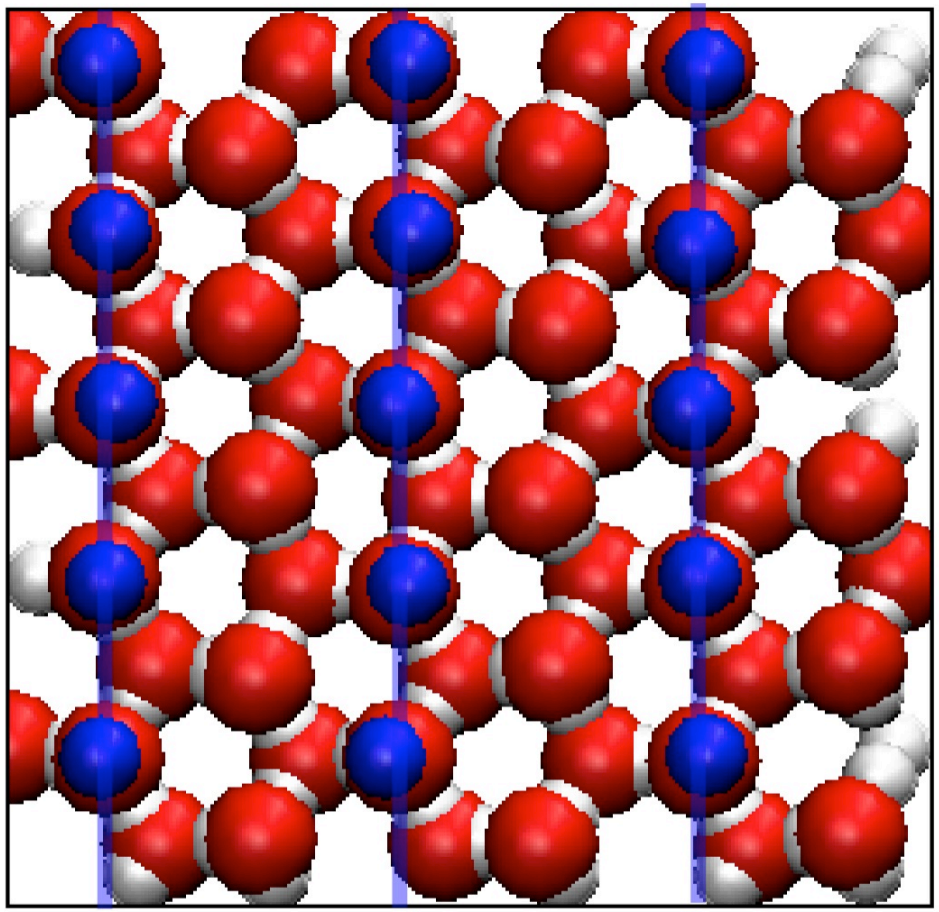


Fletcher

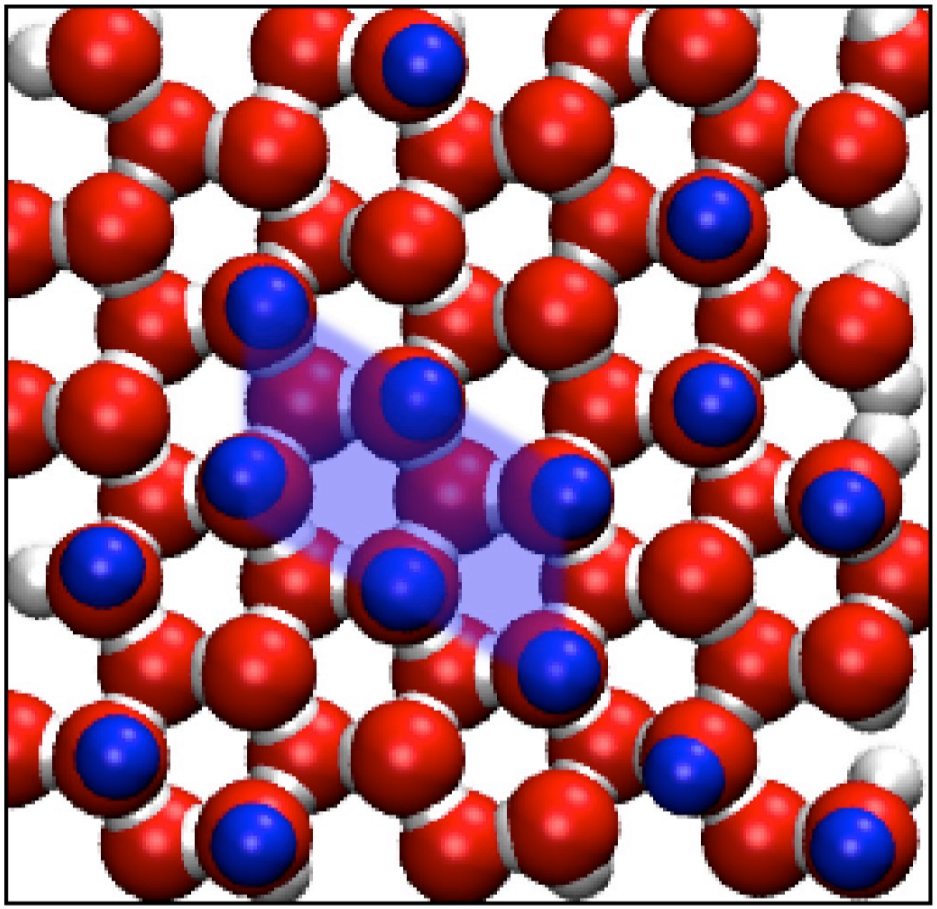


Evolves towards Fletcher surface ordering

Fletcher



Disordered

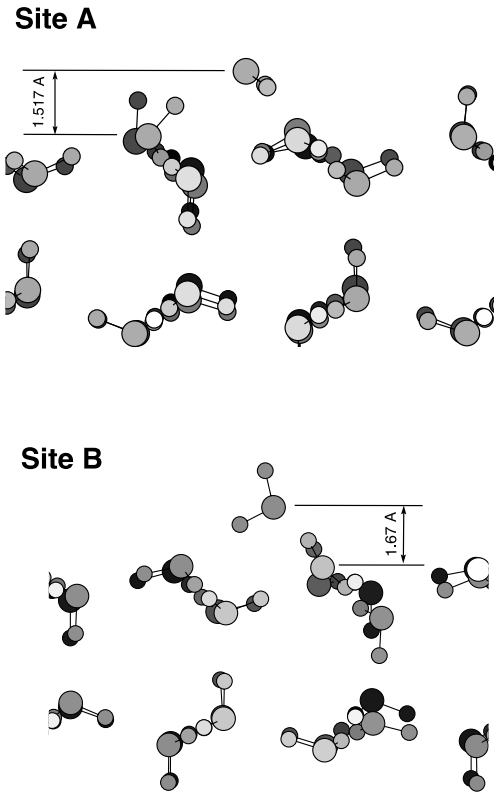


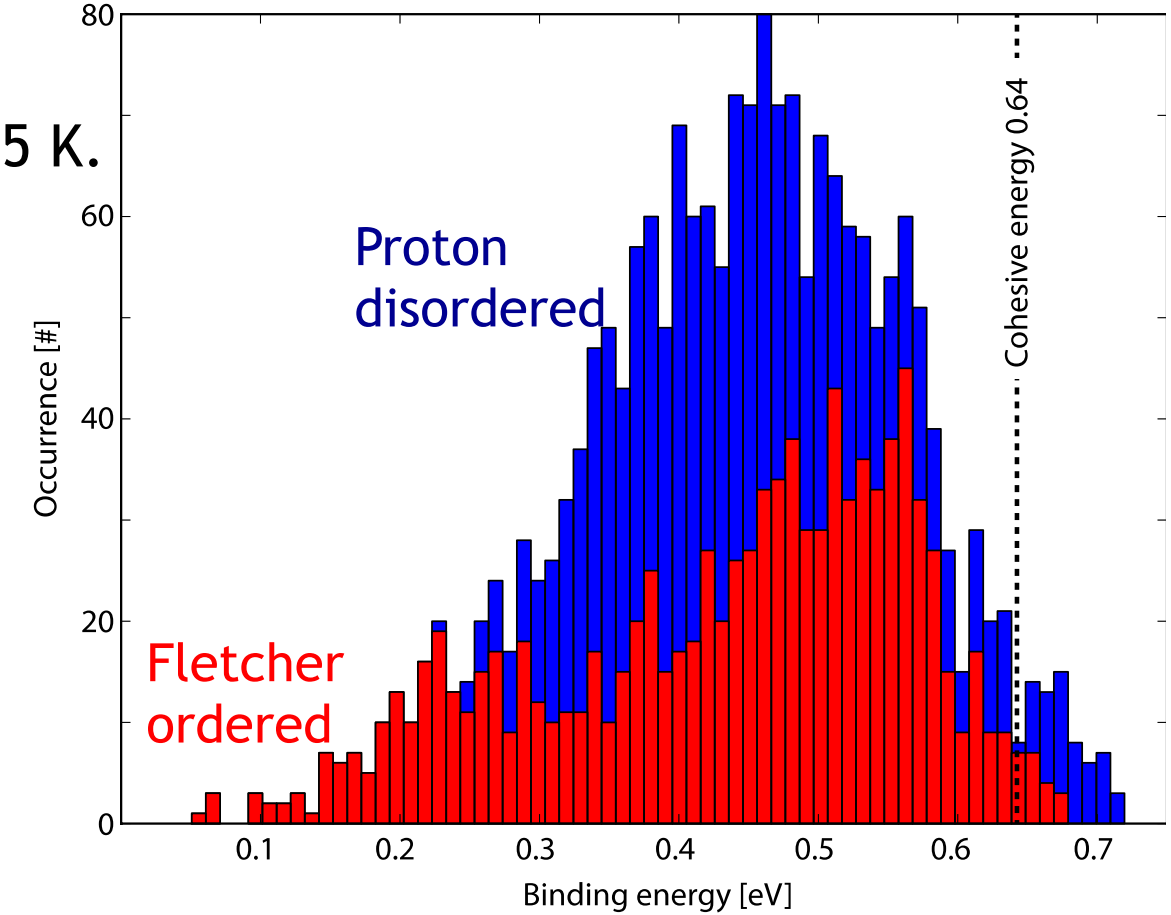
Binding sites for H_2O admolecule

Simulate admolecule diffusion:

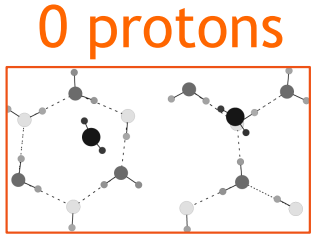
276 minima visited,

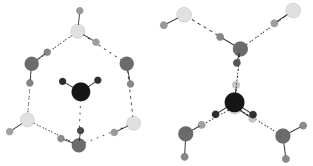
0.25 milliseconds simulated at 175 K.

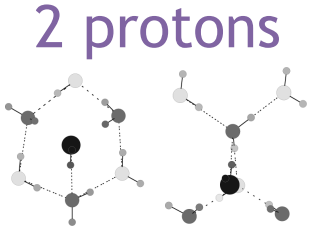




Binding energy of admolecule can be larger than the cohesive energy (when using TIP4P and TIP4P/2005f)!







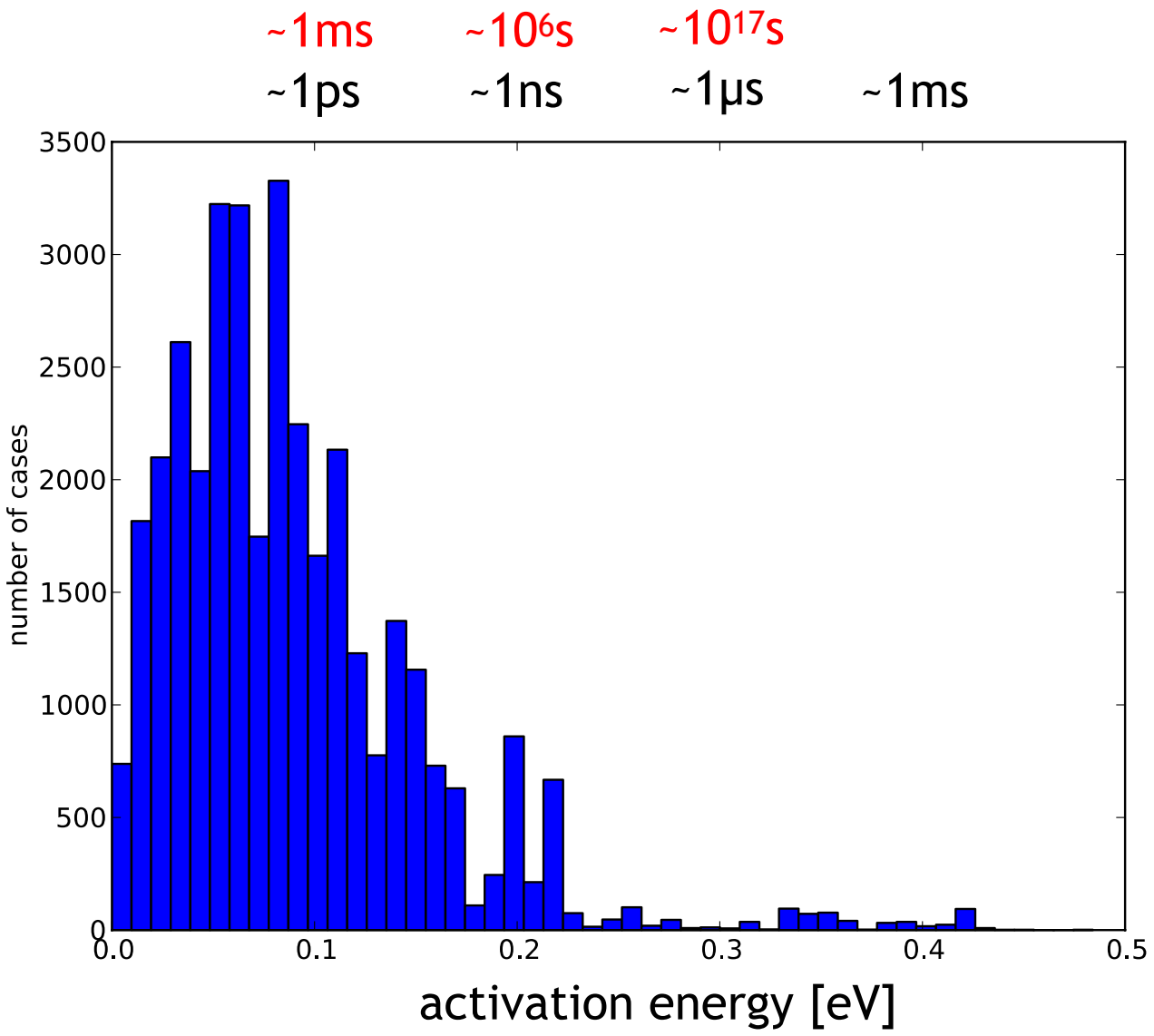
Energy Barriers for H_2O Admolecule Diffusion Hops

291 unique states
0.27 ms simulated
36.000 iterations

High energy barriers can be overcome because coarse graining is used.

The difference in time scale is more than a factor of 1000!

(time given assuming a prefactor of 10^{13} s^{-1} and T=175K, T=50K)



Diffusivity of H_2O admolecule

Long time scale simulation gives displacement as a function of time.

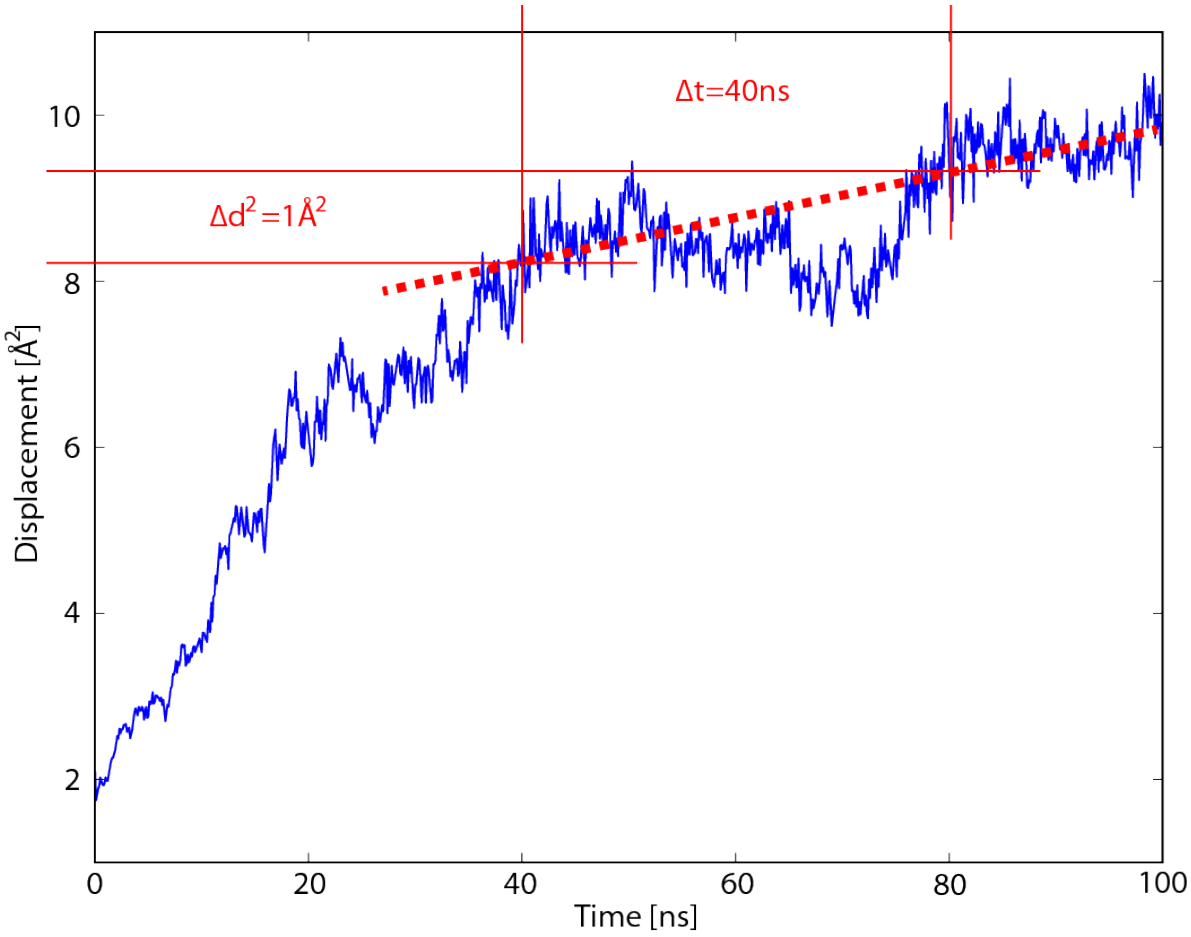
Einstein–Smoluchowski equation used to estimate diffusion constant:

$$D = \frac{\left\langle \left| \mathbf{r}(t+\tau) - \mathbf{r}(t) \right|^2 \right\rangle}{2d\tau}$$

Giving

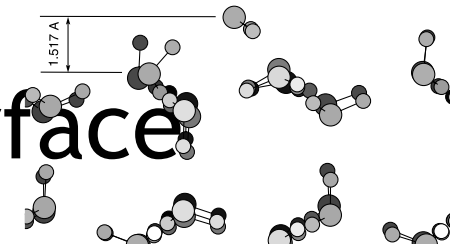
$D = 6.3\ 10^{-10}\ cm^2/s$

(consistent with upper bound determined experimentally by Brown and George in ’96).



A. Pedresen, L.J. Karssemeijer, H. M. Cuppen and H. Jónsson, J. Phys. Chem. C 119, 165

Ex 2: H_2O diffusion on Ice $I_h(0001)$ surface



Use TIP4P potential.

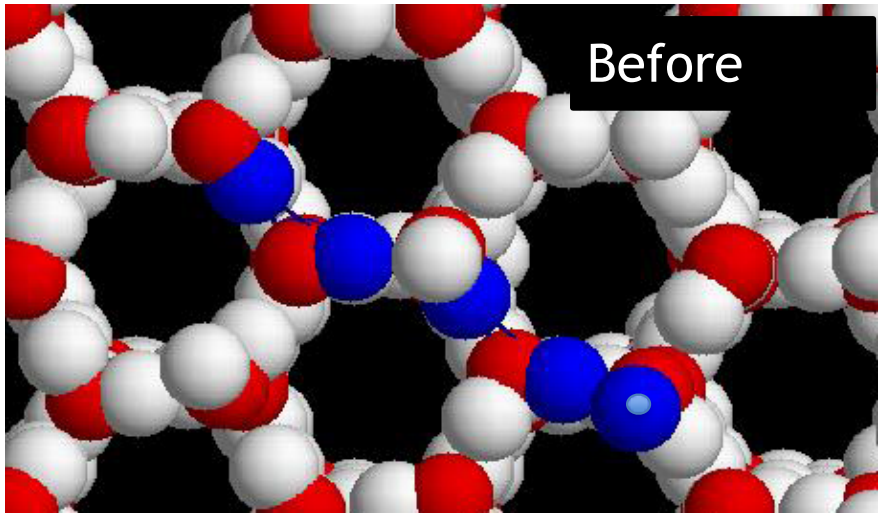
Simulate admolecule diffusion, but observe also change in the location of the 'dangling' H-bond (marked with a dot).

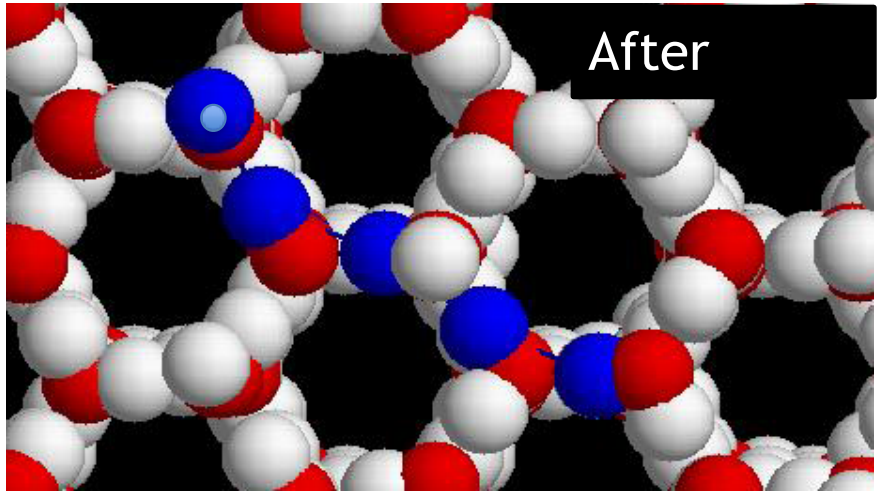
Blue protons displaced by more than 1 Å.

Energy lowered by 0.24 eV

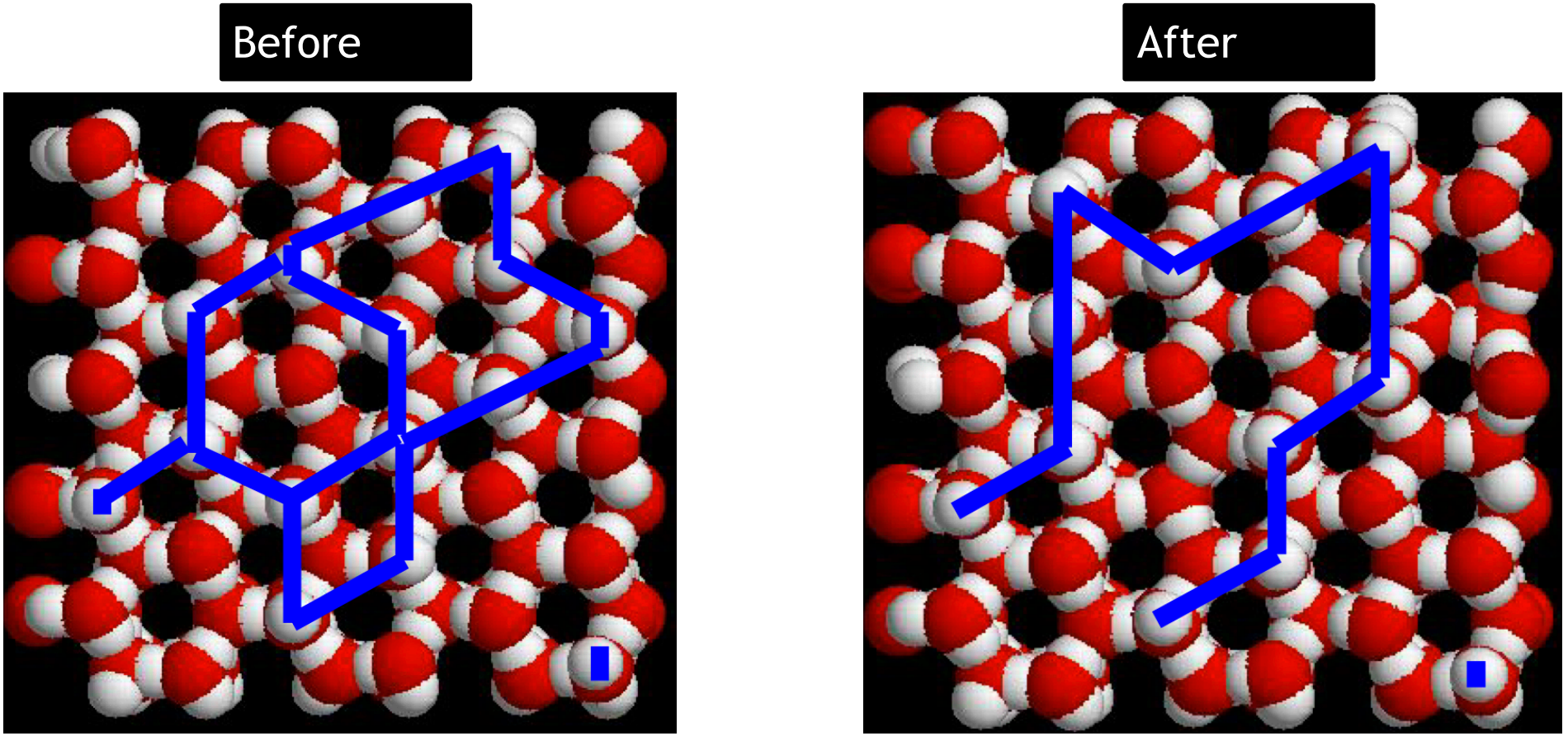
(~1 hydrogen-bond).

Induced by the presence of a H_2O admolecule.





After several surface annealing events



Smaller repulsion between dangling bonds in linear ordering.

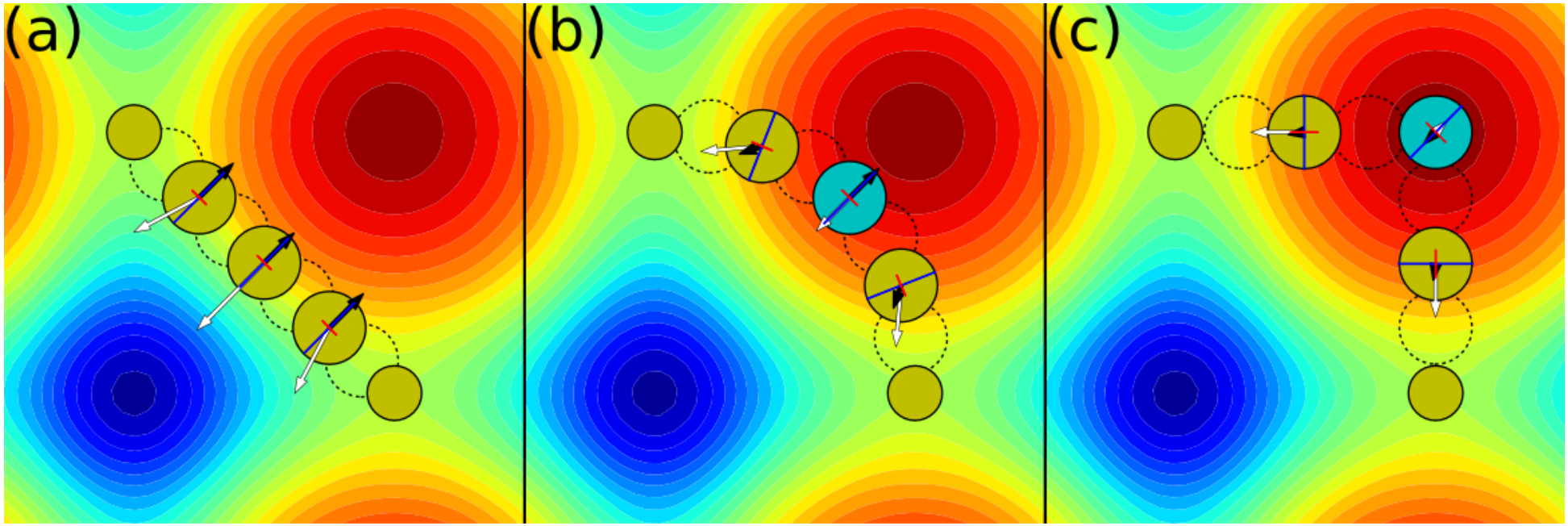
Consistent with structural analysis of D. Pan et al. (PRL, 2008).

Check how good HTST is: Find the energy ridge

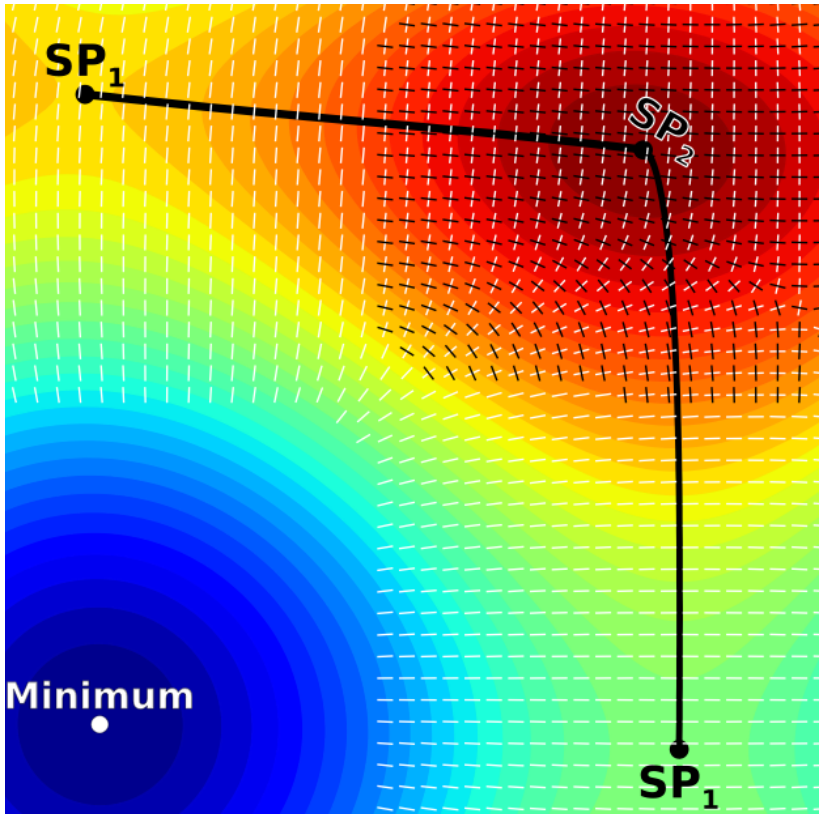
For HTST to be valid, second order saddle points need to be significantly higher than first order saddle points compared with $k_B T$.

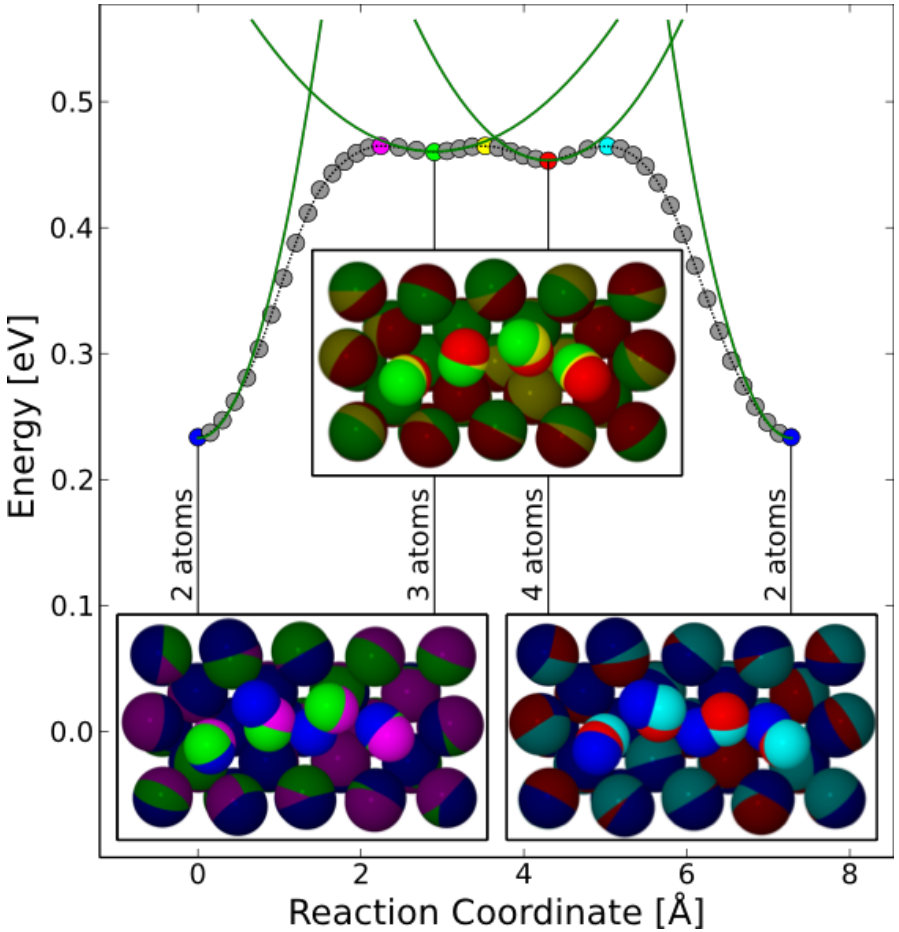
Goal: Given two first order saddle points, find the energy ridge between them, including second order saddle pt(s) and possibly unknown intermediate first order saddle points.

Method: Form an elastic band (NEB method) where the force along the minimum mode at each image is inverted, analogous to the minimum mode following method. This transforms an energy ridge to a MEP.



Method: Not quite so simple, sometimes two unstable modes and neither of them perpendicular to the ridge.
Instead, find the minimum mode in the subspace orthogonal to the current estimate of the ridge.
About a factor of three larger computational effort than calculation of a minimum energy path.





Application to Al adatom diffusion on Al(100). Find ridge between two-, three- and four- atom concerted displacement processes.
(the two first order SP and the intermediate second order SP shown).

(J. B. Maronsson et al. , PCCP 2012))

AKMC based on full TST (not harmonic approximation)

Use full WKE approach:

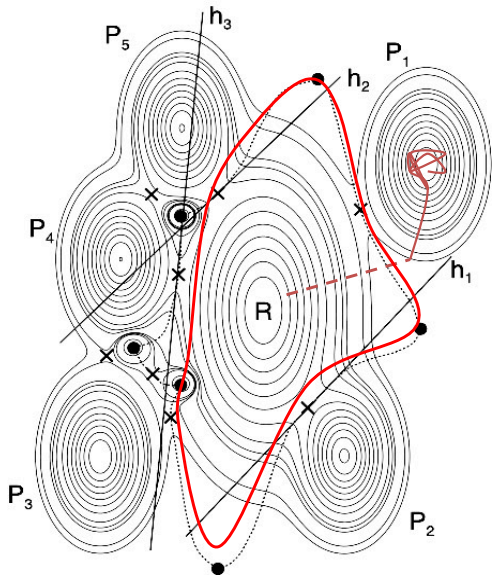
1. Find optimal transition state dividing surface and obtain $\Delta t^{TST}=1/\ k^{TST}$
2. Run (short time) dynamics trajectory from a point chosen from Boltzmann distribution over the transition state.

If the trajectory goes to a product without recrossing TS, and if the trajectory run backwards in time ends up in the current state,
then accept the product state as the new state and advance the clock by $\Delta t^{TST}=1/\ k^{TST}$

If not, then pick a new point in TS and calculate another trajectory, ...
If it takes M trajectories to find a reactive trajectory, advance the clock by

$$M\ \Delta t^{TST}= M\ /\ k^{TST}$$

Has not been implemented yet.
Needs work!!!!



WKE trajectory

stat.mech. classical dyn.

Extensions of TST and HTST as well as NEB and MMF methods

Quantum mechanical tunneling:

Quantum transition state theory (QTST) based on statistical Feynman path integrals.
Cannot define the transition state in the space of classical coordinates, need to extend to shape as well as average location of the Feynman paths.

Harmonic QTST (instanton theory), expand around first order saddle points on a higher dimensional effective potential that takes quantum delocalization into account.

Magnetic systems:

Rate theory for transitions between magnetic states. For example, find lifetime of localized non-collinear states such as skyrmions.

Quantum mechanical tunneling of magnetic moments, for example in molecular magnets.

Magnetic atoms should be described by {x, y, z, theta, phi}
and all needs to be extended to transitions involving both changes in location of atoms and orientation of magnetic moments in the system.