Long Time Scale Simulations of Atomic and Spin Systems

Andreas Pedersen, Jean-Claude Berthet, Pavel F. Bessarab, Jón B. Maronsson
Andri Arnaldssson and **Hannes Jónsson** *University of Iceland*

Overview:

Theoretical approach - WKE dynamics, harmonic TST, min-mode following, AKMC
Implementation - EON software, distributed computing, coarse graining, recycling
Testing - finding the energy ridge, including second order saddle points
Applications - a. grain boundary structure
b. diffusion of atoms at grain boundaries
c. Au clusters
d. structure and diffusion on ice
e. crystal growth
f. kinks on dislocations in Si
g. amorphous CuZr alloy
Extension to quantum tunneling
Extension to spin systems

publications at www.hi.is/~hj

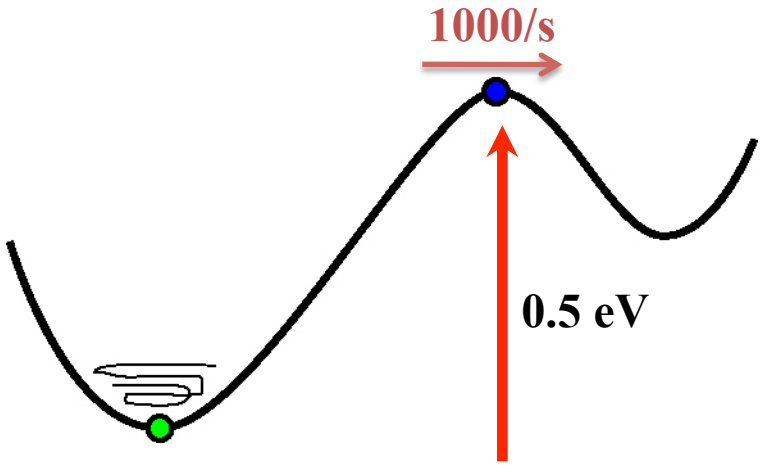
Eyjafjallajökull, 2010

Challenge: To simulate the time evolution of complex systems undergoing thermally induced rearrangements (reactions, diffusion, growth, pattern formation, spin flips etc.) starting ***only*** with an **initial configuration** and a method to evaluate **interactions** (potential functions, DFT, …)

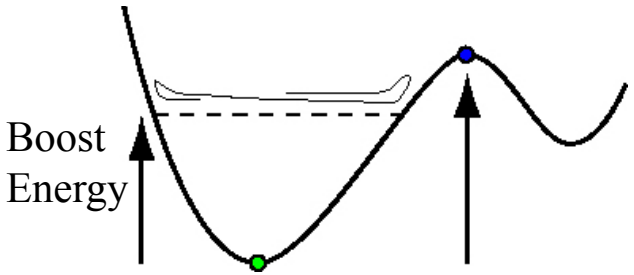
Focus here: Solids where atoms are tightly packed, many degrees of freedom (10^2-10^3), no preconceived notion of the mechanism of the transitions.

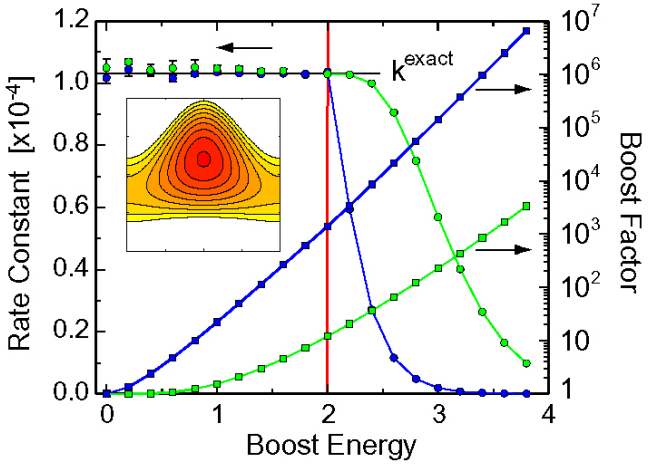
Rare event problem: Direct dynamical simulation using equations of motion takes way too long:

A transition with an energy barrier of 0.5 eV and a typical prefactor occurs 1000 times per second at room temperature – *fast!*. A video of a direct classical dynamics simulation where each vibration spans a second in the video would would go on for more than 100 years in between such reactive events - *no time for that!*



Cannot:
- Simply heat the system, there can be cross over to different mechanism (melting …)
- Fill up the well to flatten potential





G. Henkelman & HJ, JCP (2001)

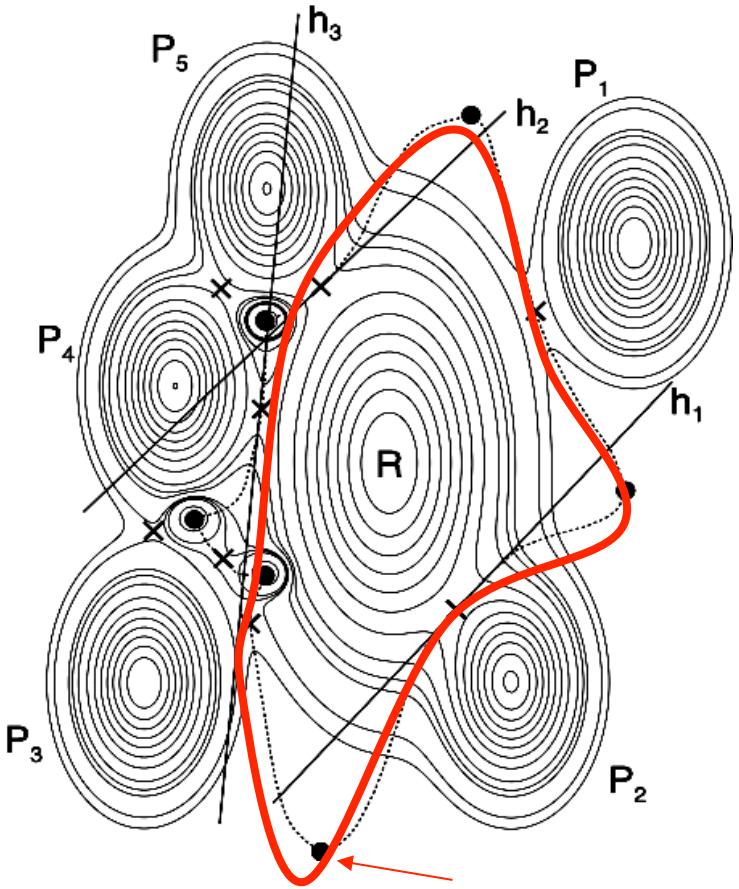
Transition State Theory (Wigner, Keck, Eyring)

1. Born-Oppenheimer
2. Classical dynamics of nuclei (*can extend to quantum systems …*)
3. Boltzmann distribution in initial state (*OK if slow enough*, $k_B T < E_a/5$)
4. No recrossings of TS, (*often most serious, but can be fixed using trajectories)*

Note:

- TST gives the lifetime, $\tau=1/k$, of a given initial state - no knowledge of final state(s).
- Can run short time scale dynamics starting from TS to find the final state(s).
- Such trajectories can be used to take recrossings into account - *dynamical corrections*

$$k^{exact} = \kappa\, k^{TST}$$



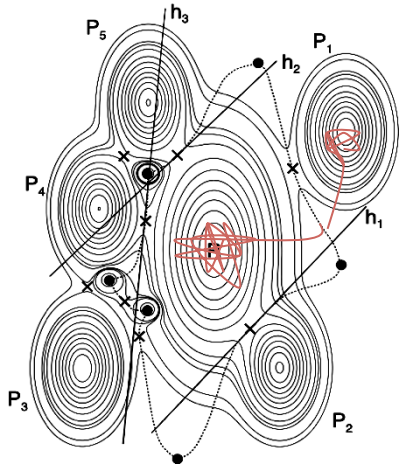
Need to create a TS dividing surface that encloses the initial state, R

Use **Wigner-Keck-Eyring (WKE)** to generate reactive trajectories with much smaller computational effort

1. Find optimized transition state dividing surface (maximize free energy)
2. Run (short time) dynamics trajectories from the transition state to find product states and dynamical correction, $k^{exact} = \kappa\, k^{TST}$

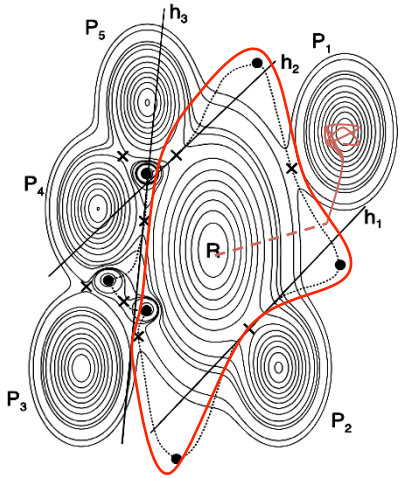
Note: Step 2 is hard unless a good job has been done in 1, need to optimize the dividing surface!

WKE procedure generates (pseudo) trajectories over long time scale



dynamical trajectory

time



WKE trajectory

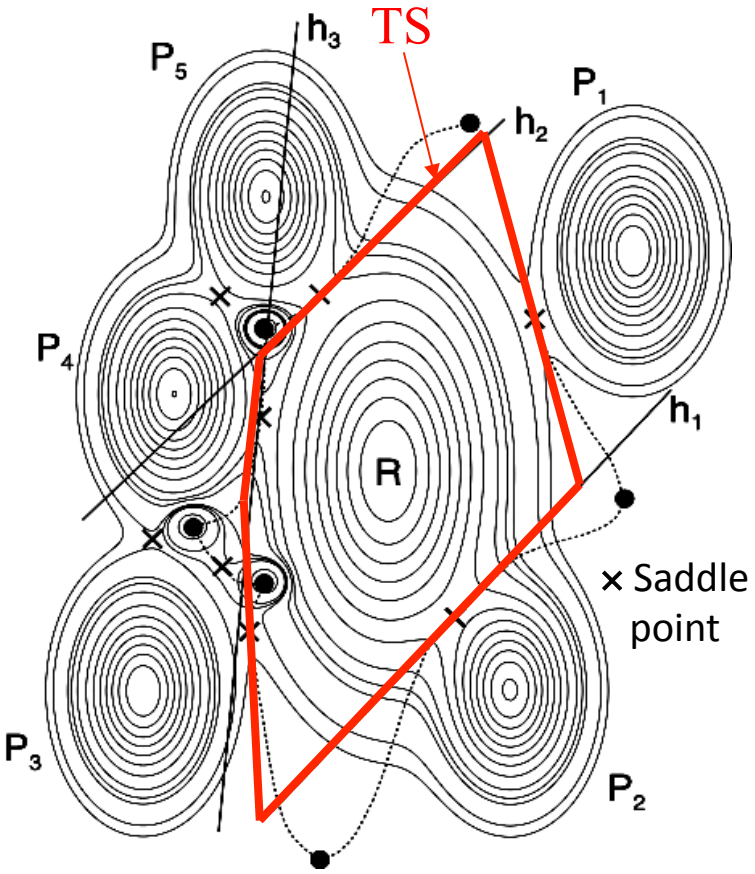
stat.mech.

For solids, a harmonic approximation is often valid, HTST:

- Need to find **all relevant** saddle points on the potential energy rim surrounding the energy basin corresponding to the initial state.
- The transition state is approximated as a set of hyperplanes going through the saddle points with the unstable mode normal to the hyperplane, and a second order Taylor approximation to the PES at minimum and saddle points is used.
- For each hyperplanar segment:

$$k^{\mathrm{HTST}} = \frac{\prod_{i=1}^{D} \nu_{R,i}}{\prod_{i=1}^{D-1} \nu_{\ddagger,i}} e^{-(V_{SP} - V_{\min})/k_B T}$$

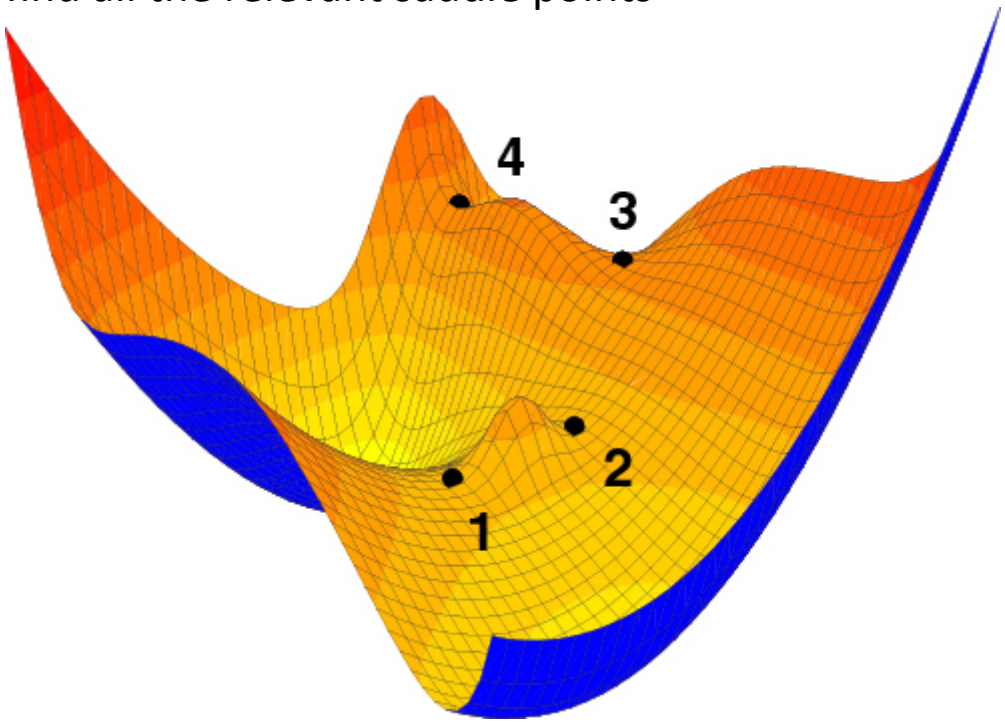
Temperature and entropy are taken into account within the normal mode approximation

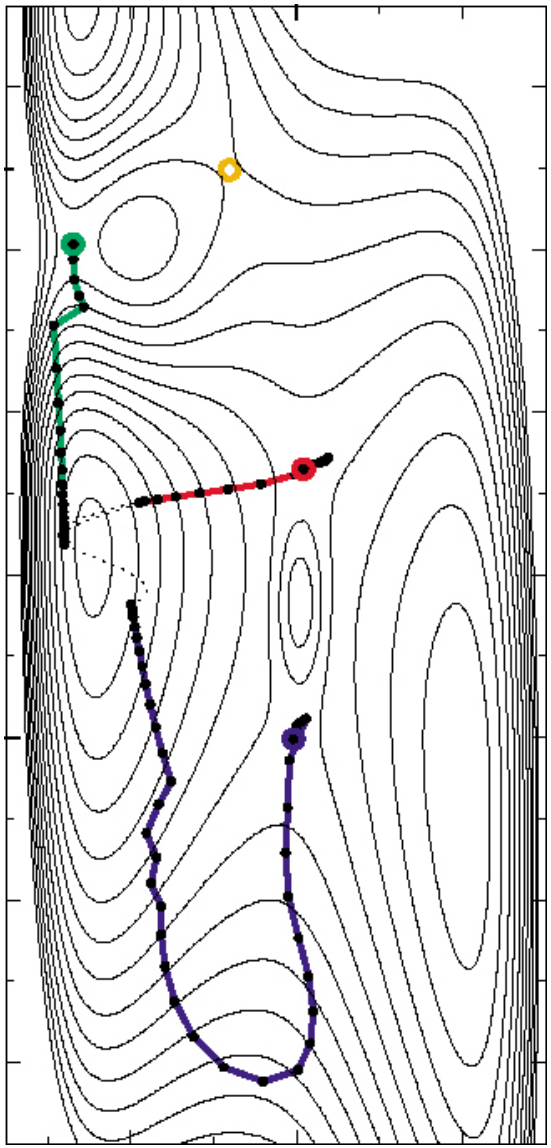


HTST is typically ca. 10^3 faster than full TST!

Use inverted force to climb up energy surface from the initial state configuration

Within HTST, need to
find all the relevant saddle points





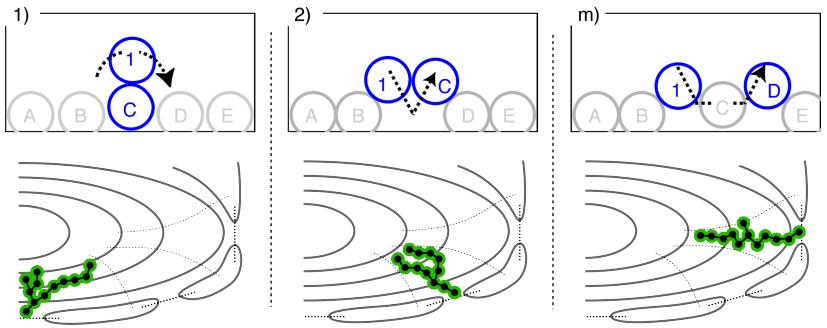
Use minimum mode following method to search for saddle points: transform first order saddle point to a minimum by inverting the force along the minimum mode of the Hessian

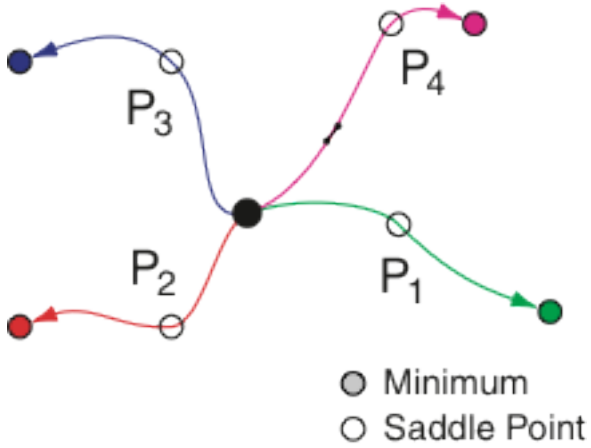
$$\mathbf{F}_{i,eff} = \mathbf{F}_i - 2\left(\mathbf{F}_i \cdot \hat{\mathbf{v}}_{i,min}\right)\hat{\mathbf{v}}_{i,min}$$

Adaptive Kinetic Monte Carlo (AKMC) 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





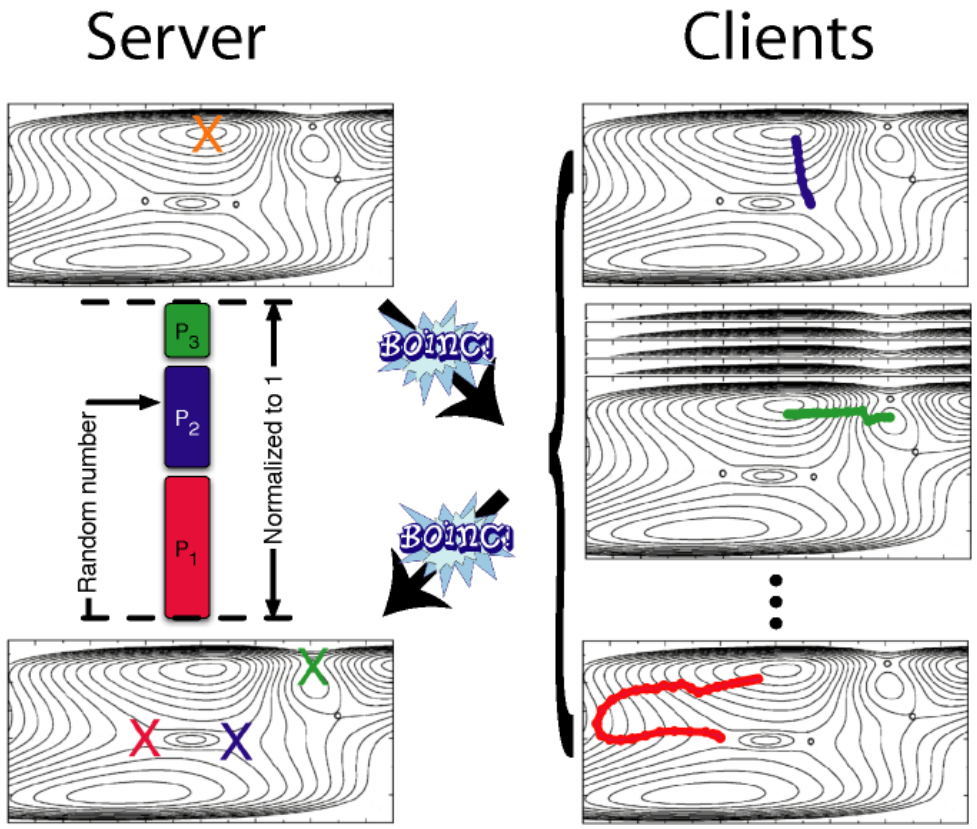
- No need to create a table of transitions and their rates *before* the simulation as in regular KMC

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

EON Software for distributed computing of long time scale evolution, in particular AKMC method

- 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

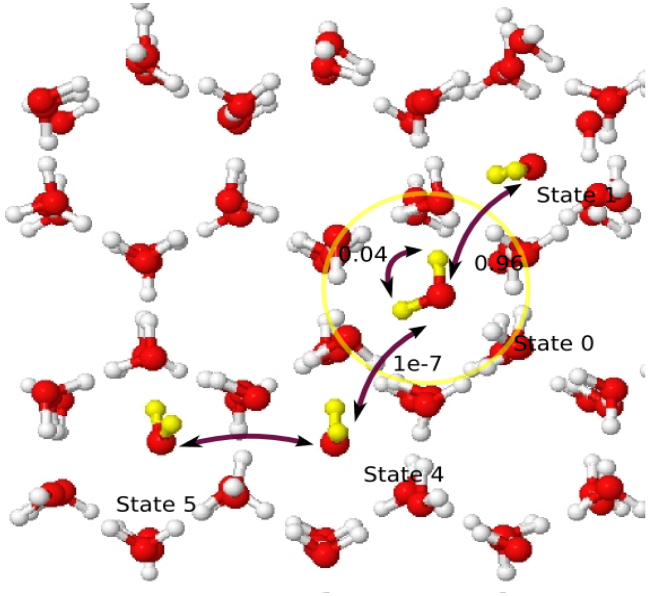
Collaborative effort between the Henkelman group at UT and the group in Iceland.

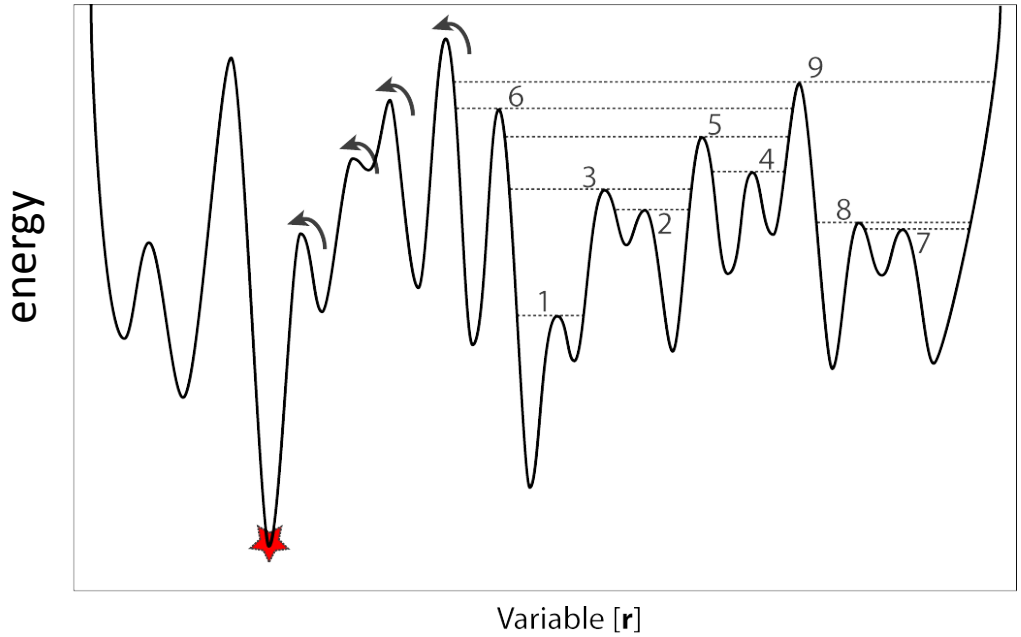


Available for download at http://theochem.org/EON/

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

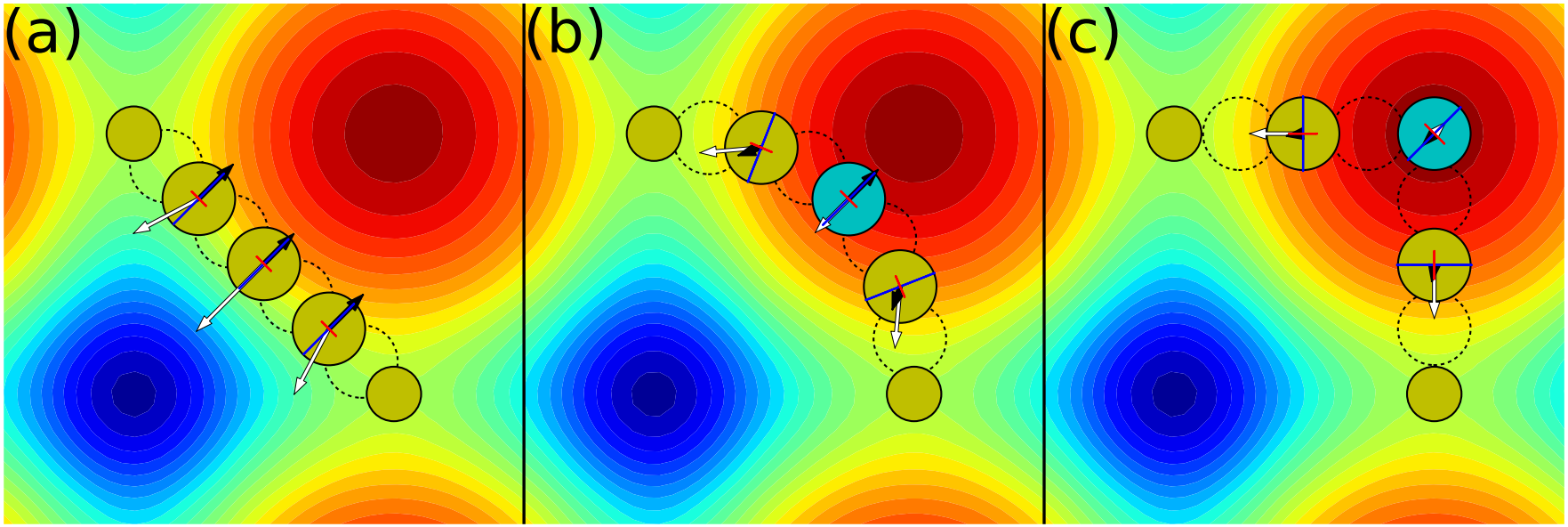
(A. Pedersen et al. Lecture Notes in Computer Science, 2012)

Checking: Find the energy ridge

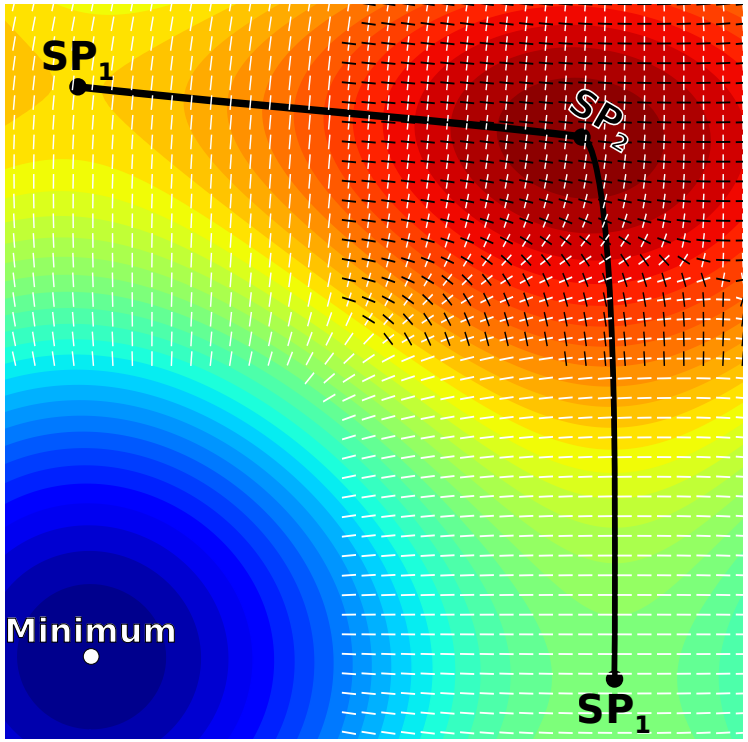
For HTST to be valid, second order saddle points need to be significantly higher than first order saddle points compared with $k_B T$.

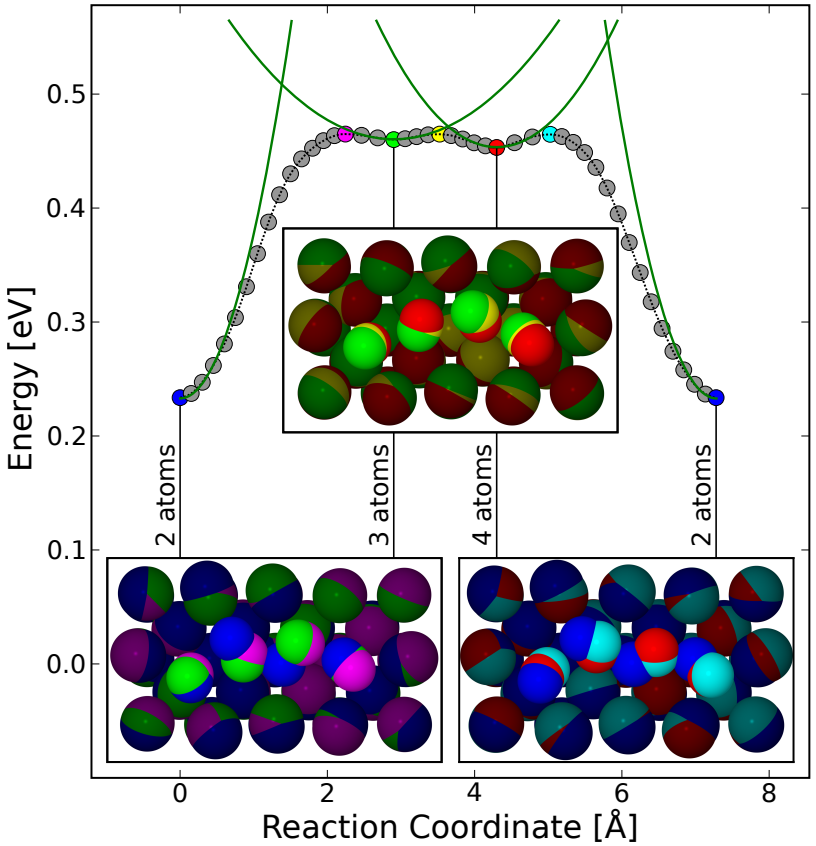
Goal: Given two first order saddle points, find the energy ridge between them, including second order saddle pt(s) and possibly unknown intermediate first order saddle points.

Method: Form an elastic band (NEB method) where the force along the minimum mode at each discretization point (system image) is inverted, analogous to the minimum mode following method. Transforms ridge to 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 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*
Collaboration with Tejs Vegge at DTU).

Examples of long time scale simulations:

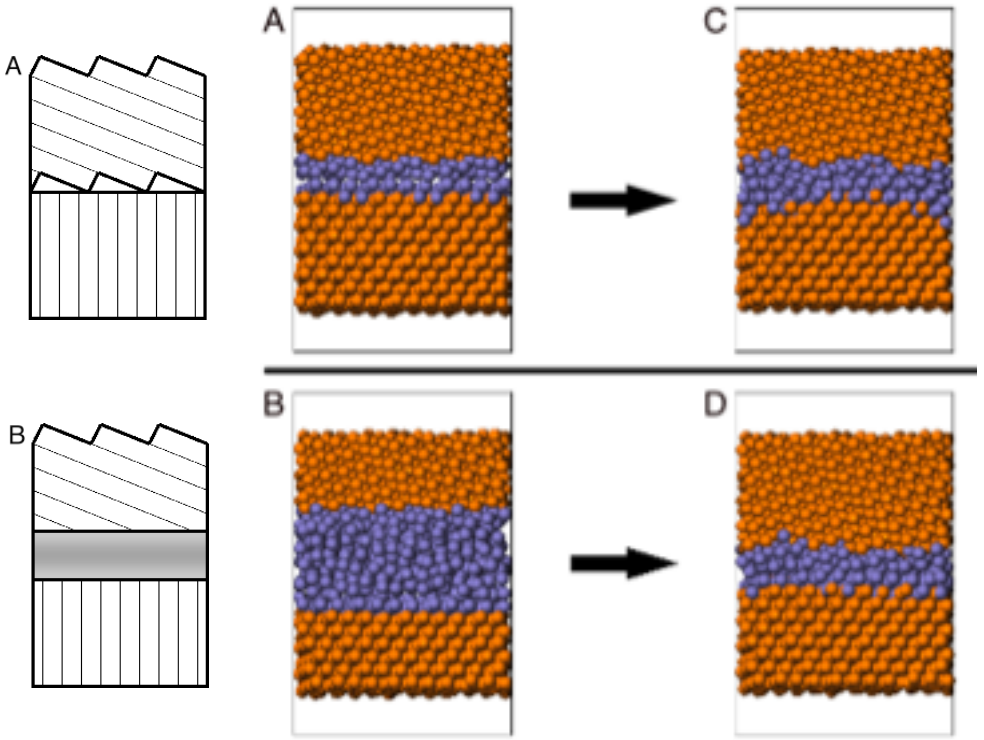
Application a:

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)

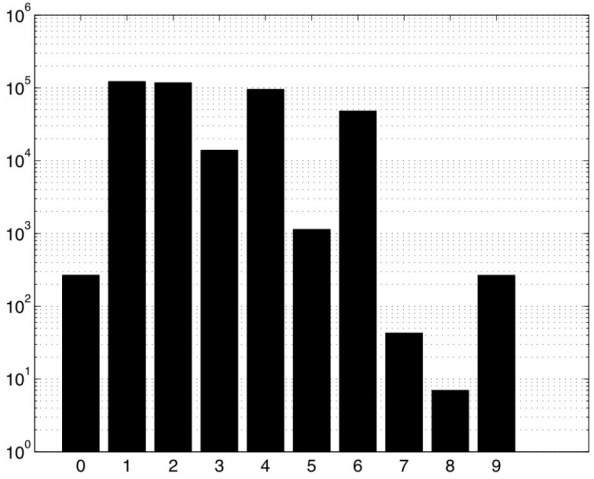
Each system simulated for about 0.1 ms



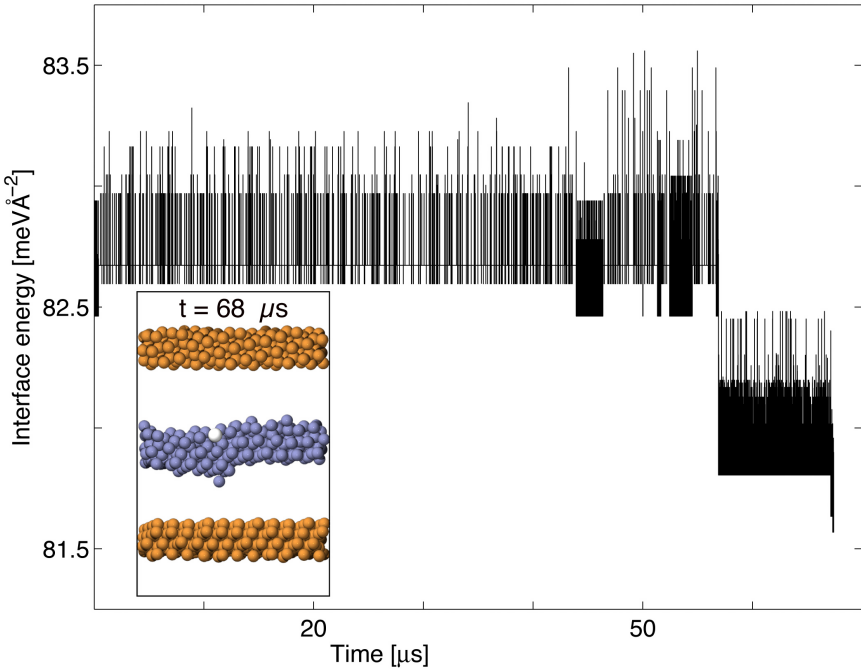
Annealing events found during the AKMC simulation

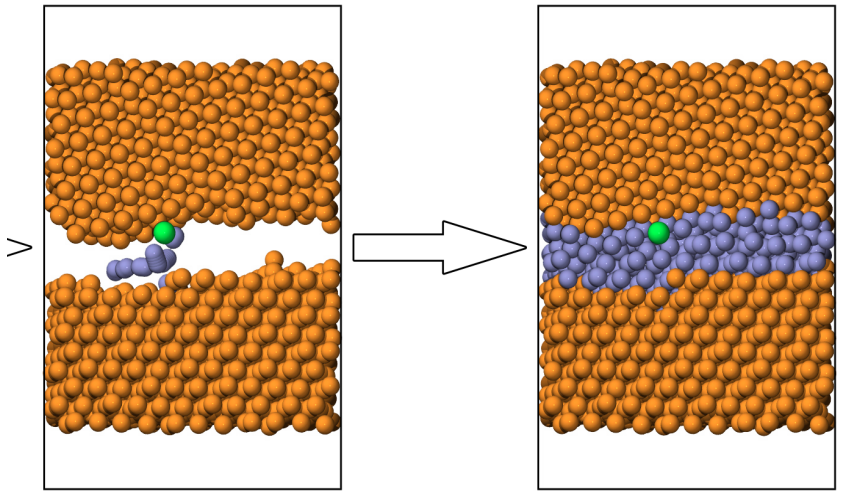
Annealing events often involve concerted displacement of up to 9 atoms.

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)

Application b:

H-atom diffusion at grain boundaries in aluminum

b1. Twist+Tilt grain boundary:

Arrows show trajectory of H-atom

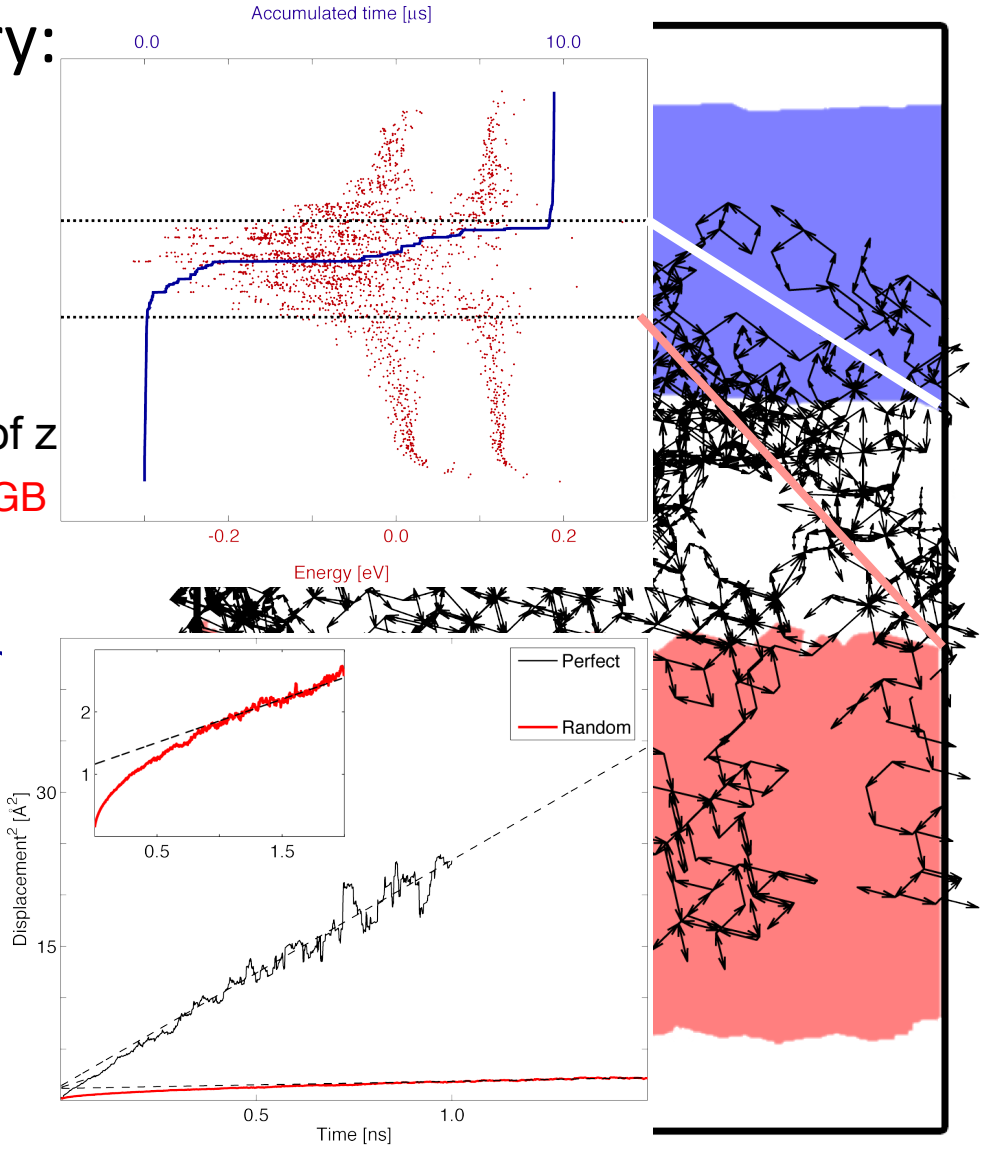
- White, not locally in FCC coordination
- Mainly trapped in the GB-region

Site-energies and time as functions of z

- Strong binding of H-atom within GB
- H-atom, most time spend in GB

Parallel-diffusivity is 10 times smaller as compared to perfect crystal

A twist+tilt GB acts as a trap rather than a fast track for diffusion!



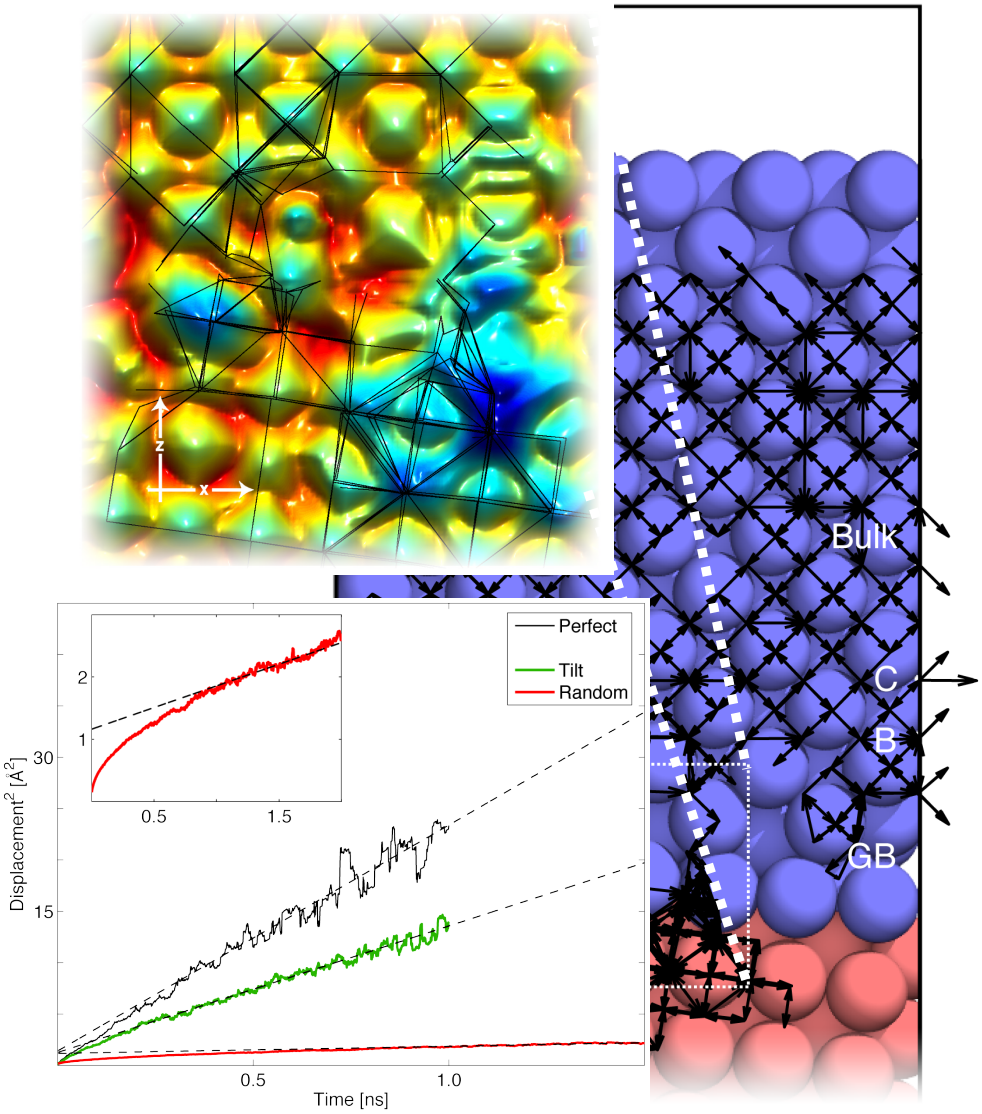
b2. H-atom at Σ5 tilt grain boundary in Al

Trajectory
- Few paths go through the GB

Potential Energy Surface
- Projected onto xz-plane
  - Red means high energy
  - Blue means low energy
- Two low energy basins within the GB region

Parallel diffusivity decreases to ½ of diffusivity in perfect crystal

Some trapping in the GB!



b3. H-atom at Σ5 twist grain boundary in Al

Trajectory

- NO crossing of GB
- H-atom stays within the grain

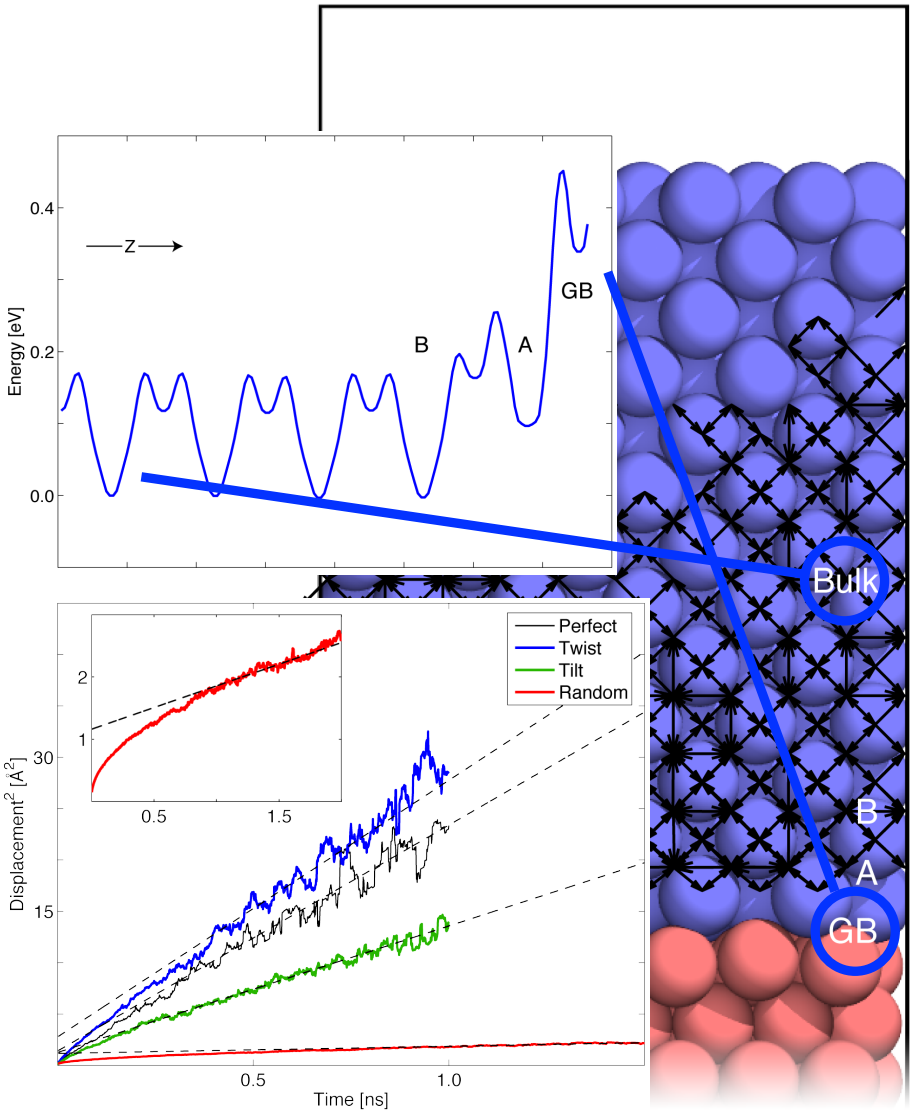
Energy landscape

- At GB, H-atom energy is high

Twist GB hinders diffusion!

Parallel diffusivity is slightly enhanced, because of reflection from GB

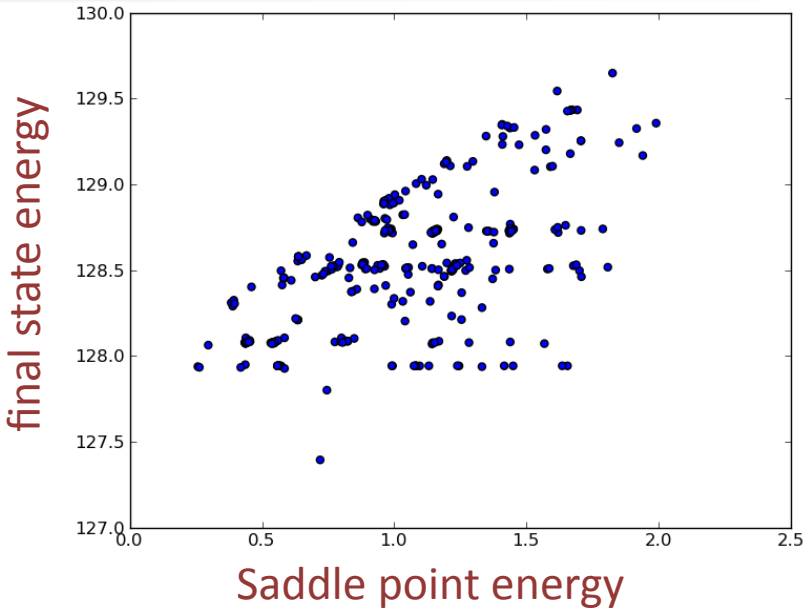
(A. Pedersen & HJ, Acta Mat. 2009)

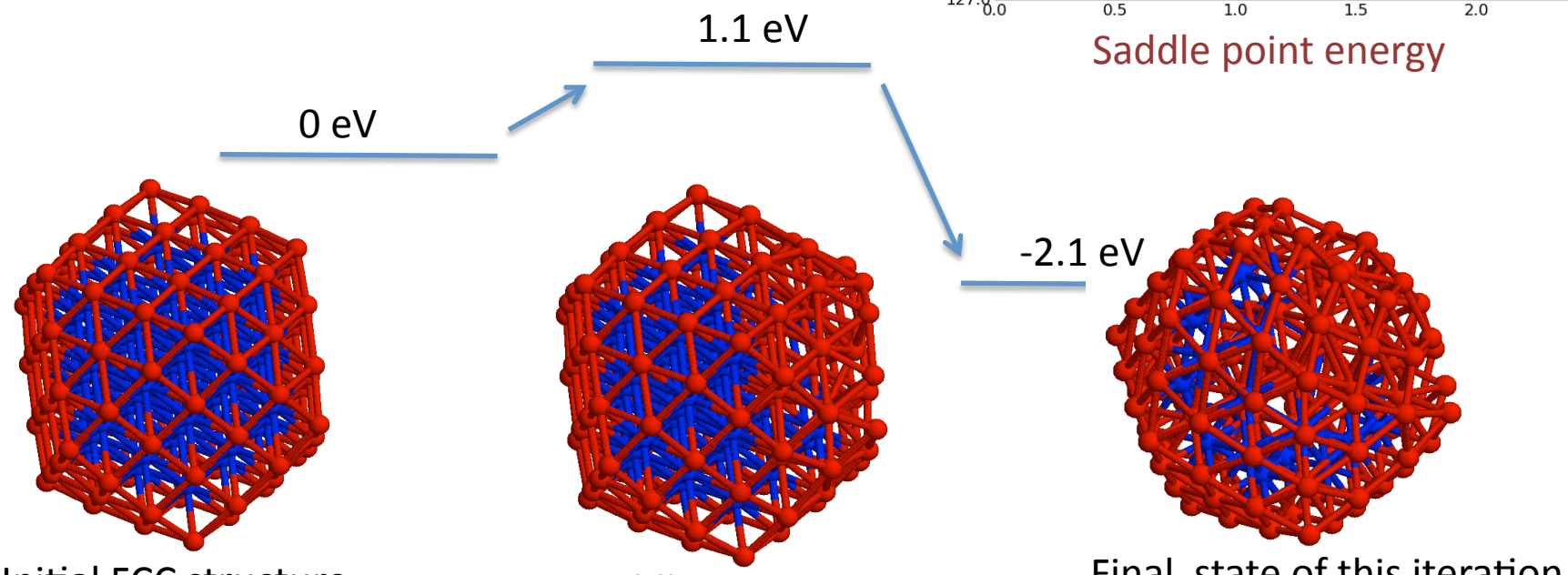


Application c: Au_{147} cluster

Start with the FCC structure for the cluster.
Use EMT potential function.

Saddle point nr. 89 found in a search starting from perfect FCC cluster brings the cluster into a distorted icosahedron





Initial FCC structure

Saddle point #89

Final state of this iteration

(A. Pedersen et al., in prep.)

Application d: Ice I_h(0001) surface

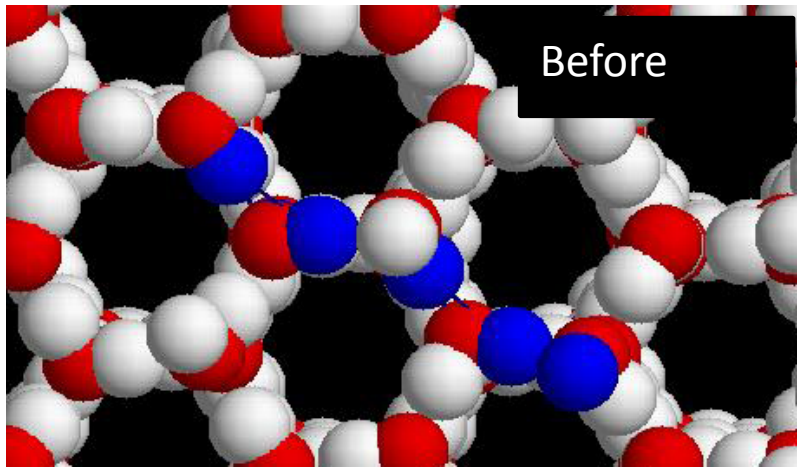
Use TIP4P potential.

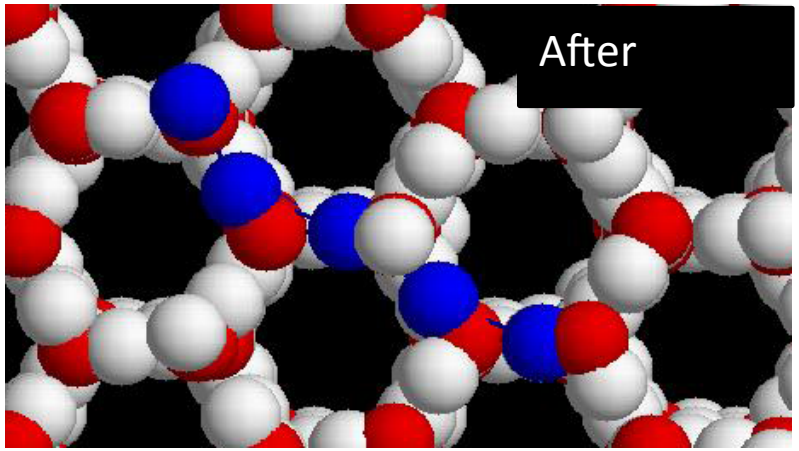
Simulate admolecule diffusion, but observe also rearrangements of the 'dangling' protons.

Blue protons displaced by more than 1 Å.

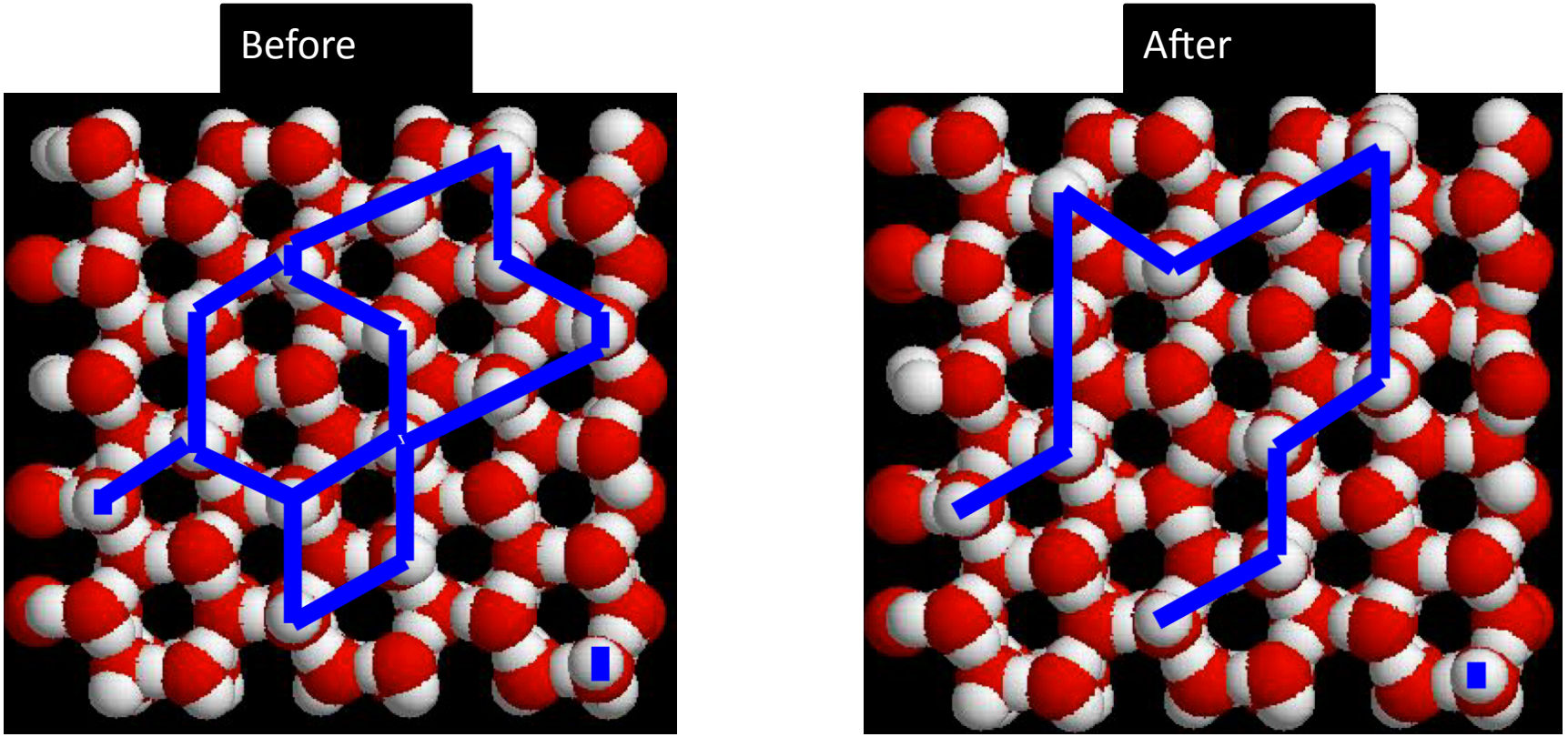
Energy lowered by 0.24 eV (~1 hydrogen-bond).

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).

Energy Barriers for H_2O Admolecule Diffusion Hops

291 unique states

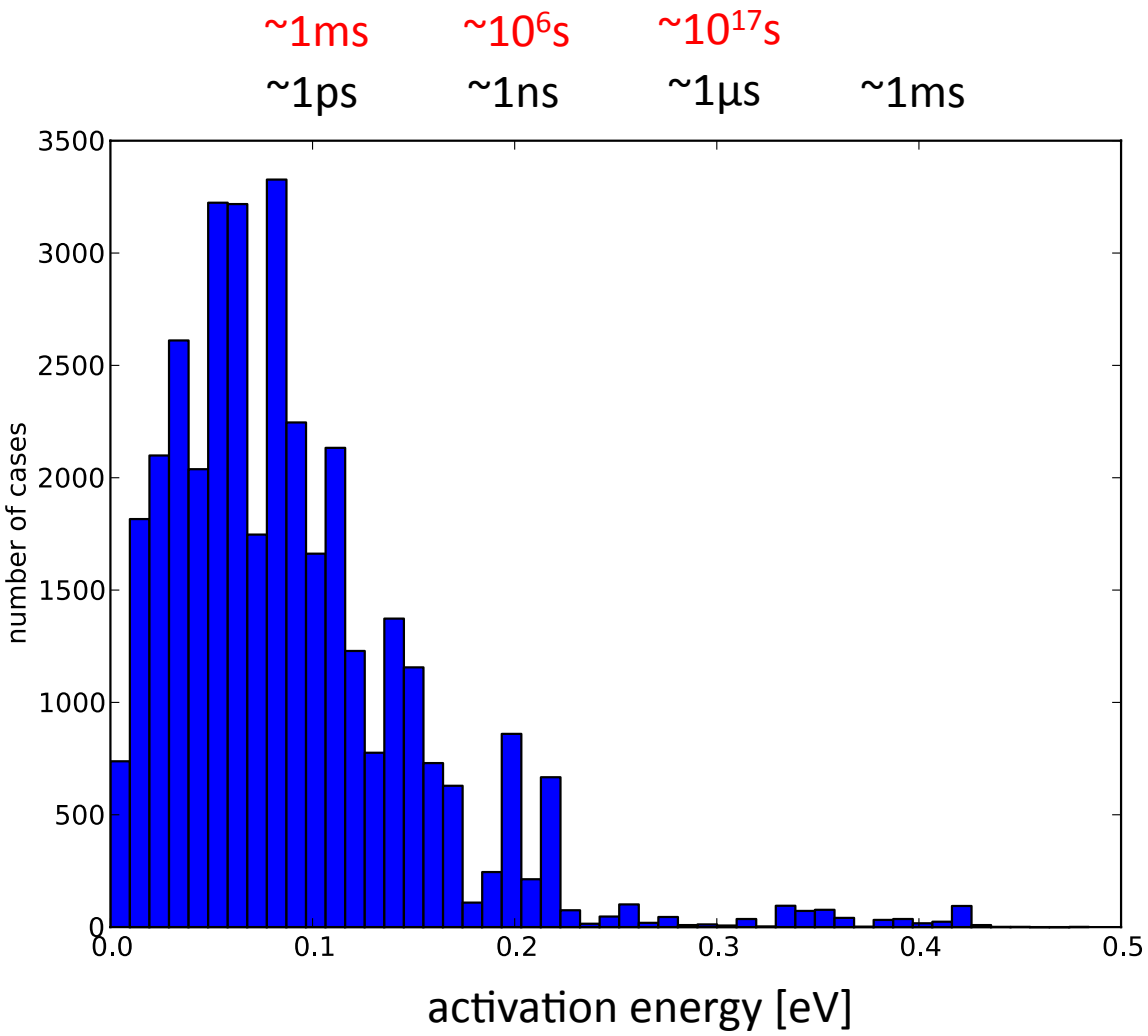
0.27 ms simulated

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.

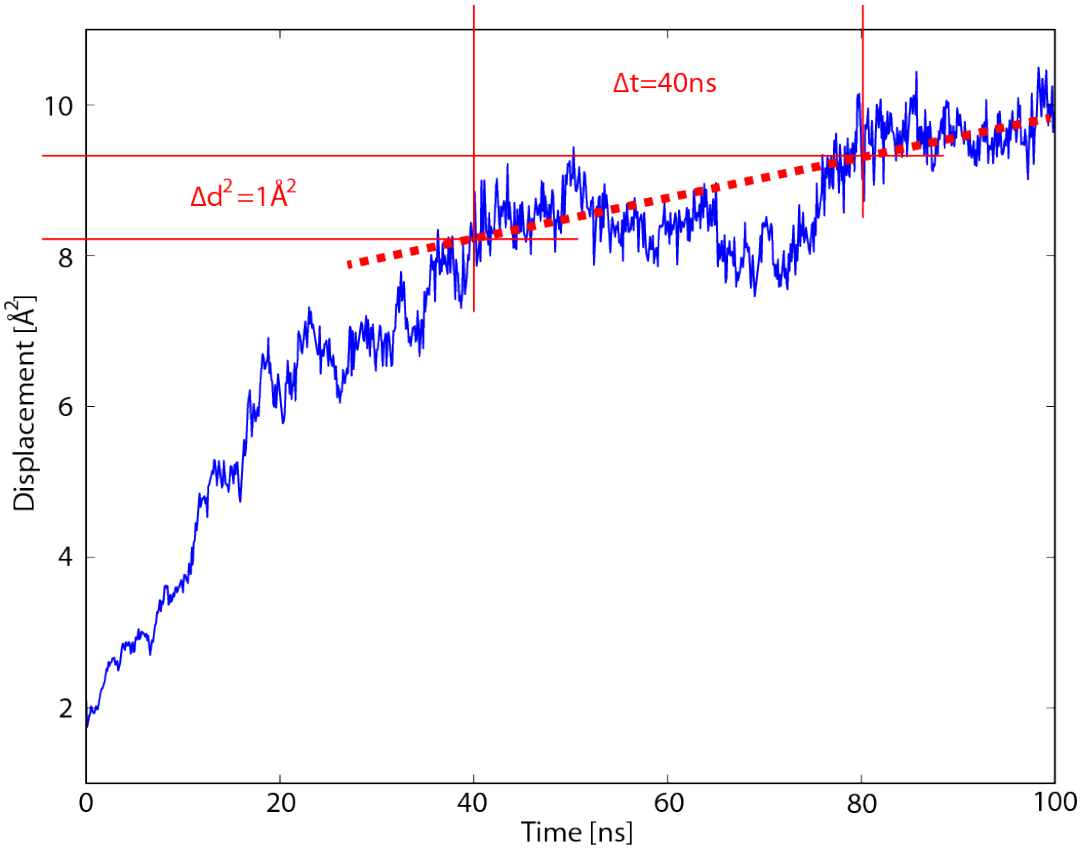
Einstein–Smoluchowski equation used to estimate diffusion constant:

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

Giving

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

(Consistent with upper bound determined experimentally by Brown and George in '96).



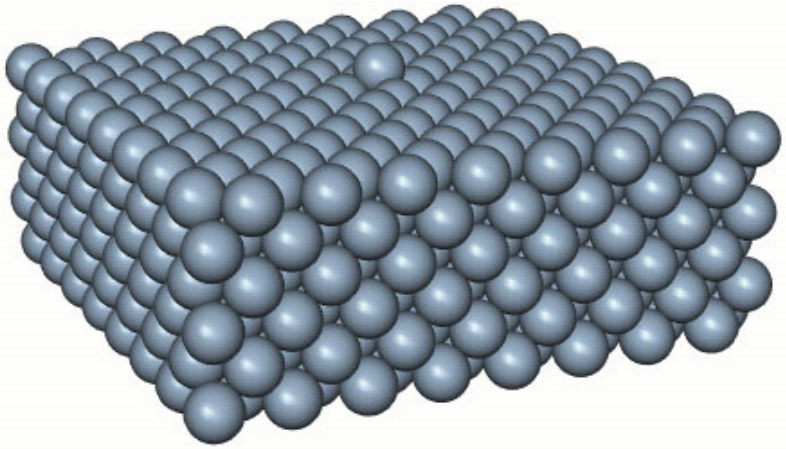
see talk by Andreas Pedersen, Tue. 16:20

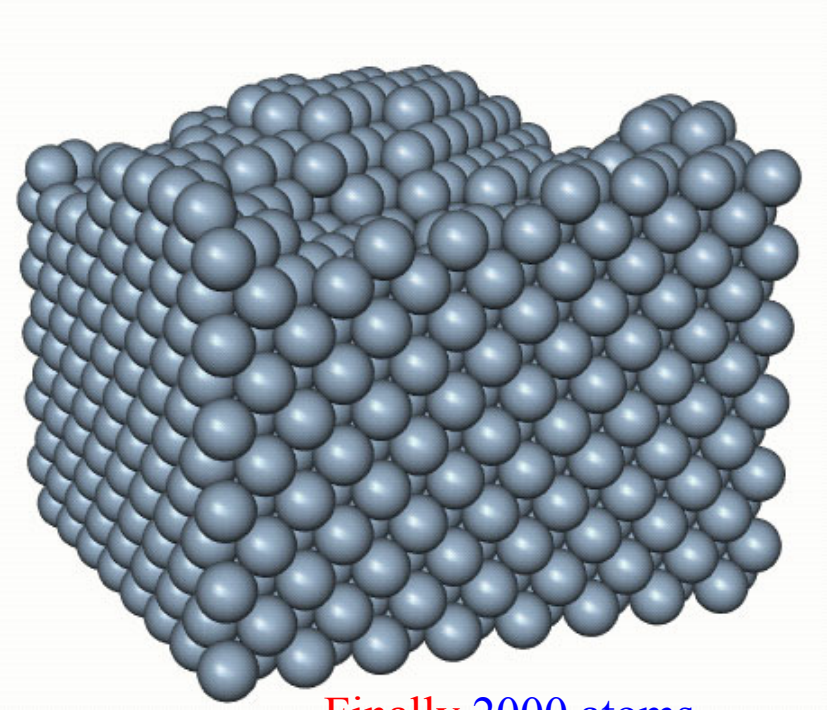
e. Multiple time-scale simulation of metal crystal growth

-Is the surface of a growing crystal smooth or rough?
-What are the atomic scale processes that determine the morphology?

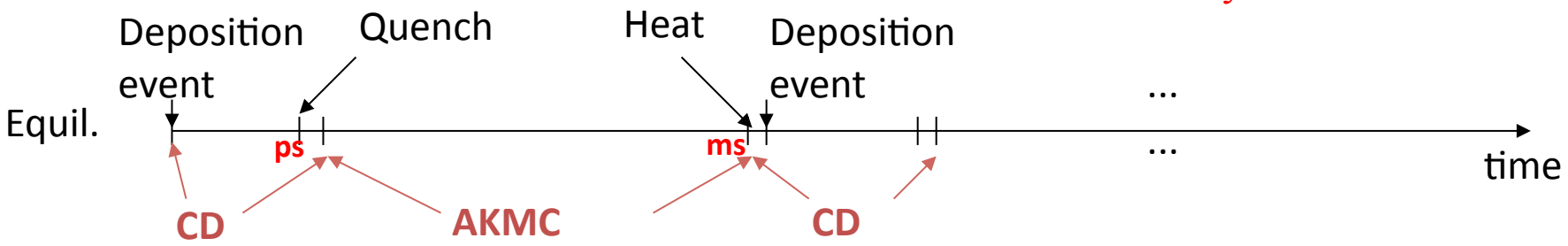
Ex: simulation where 10 monolayers were deposited in 1 second, T=30 K

Initially 768 atoms





Finally 2000 atoms



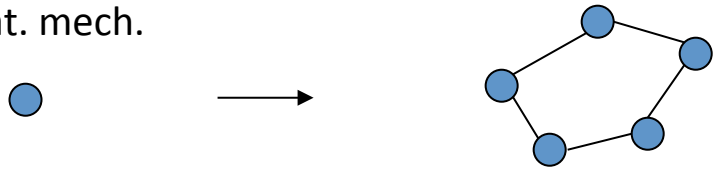
(G. Henkelman & HJ, PRL 2003)

Extension to include quantum tunneling

Assume thermalization and decoherence after each transition.

Use Feynman path integrals:

qantum stat. mech. → classical stat. mech.



$$k_{sp} = mP\,(2\pi k_B T/h)^2$$

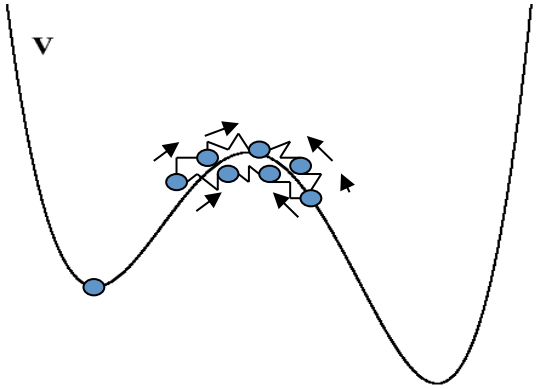
$$V(r) \longrightarrow V^{eff}(r_1,\ldots r_P) = \Sigma^P\,[k_{sp}(r_i - r_{i-1})^2 + V(r_i)]/P$$

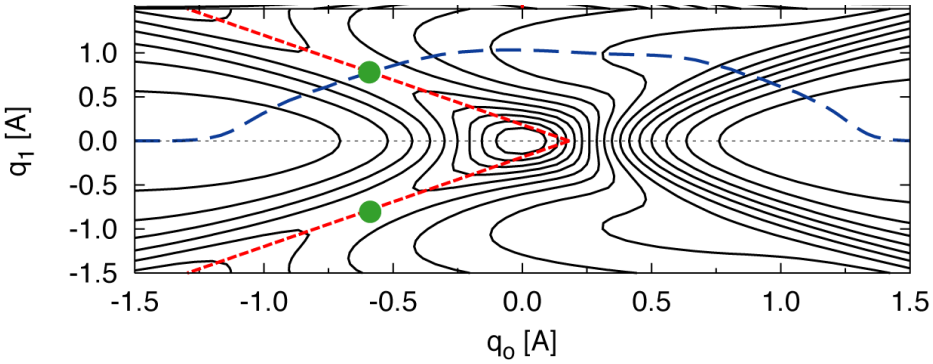
Again, use harmonic approximation to the effective potential, harmonic quantum TST.

Often referred to as '**instanton theory**' (Miller, 1975, Callan and Coleman, 1977)

or '**Im F**' theory (Langer, 1969) .

$$Q^R\ k_{inst} = \sqrt{\frac{S_0}{2\pi\hbar}}\ \frac{1}{\Delta\tau\,|\prod_j' \lambda_j|}\ e^{-V_{\mathrm{eff}}(T,P)/k_B T}$$





Cross over temperature for tunneling

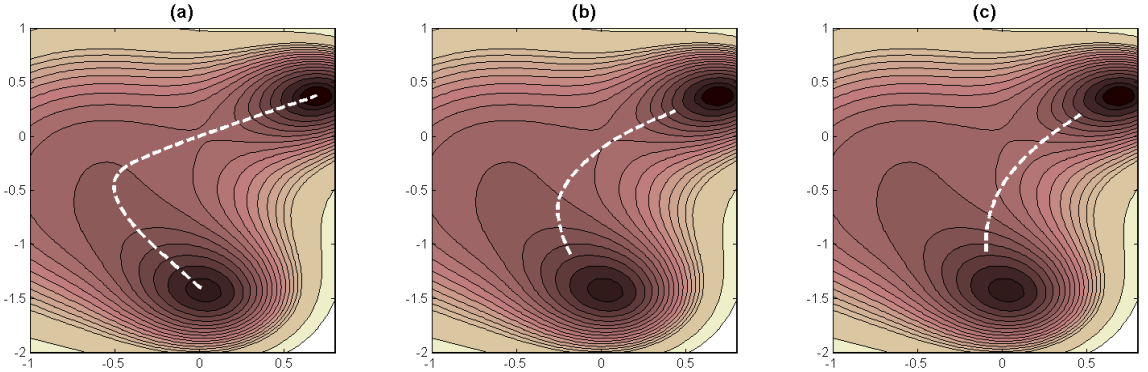
$$T_c = \frac{\hbar \cdot \Omega}{2\pi \cdot k_B}$$

Find optimal tunneling path by minimizing the action

$$\theta(\mathbf{R}) = \frac{1}{\hbar}\int_{s_1}^{s_2}\sqrt{2\mu(V(\mathbf{R})-E_c)}d\mathbf{R}$$

$$\theta(\mathbf{R}) \approx \frac{1}{2}\sum_{i=1}^{n}(\xi_i+\xi_{i-1})\,|\mathbf{R}_i-\mathbf{R}_{i-1}|$$

$$\xi_i \equiv \frac{1}{\hbar}\sqrt{2\mu(V(\mathbf{R}_i)-E_c)}$$



Inital guess **Intermediate step** **Converged path**

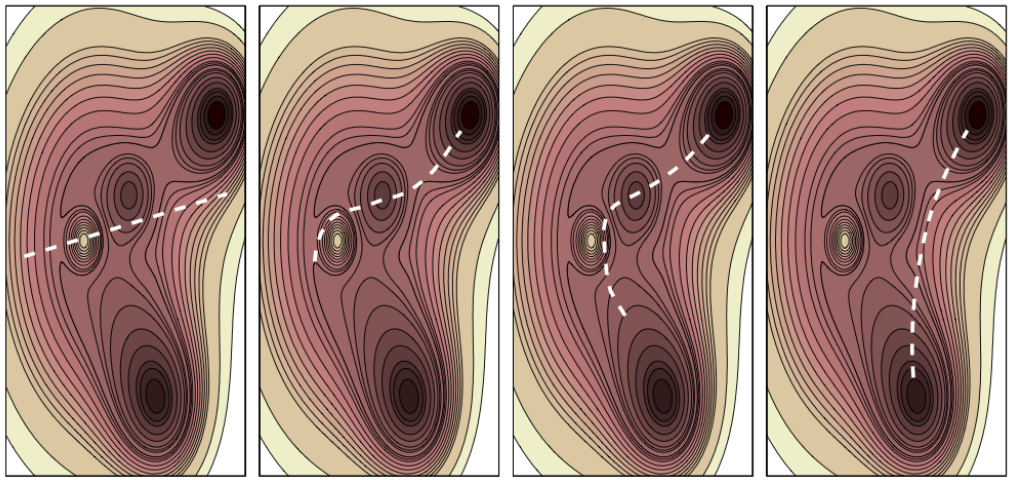
$$\boldsymbol{\phi}_j = -\frac{\partial\theta}{\partial\mathbf{R}_j} \qquad j=2,3,...,n-1$$

force in image j

$$\boldsymbol{\phi}_j^{\text{eff}} = \boldsymbol{\phi}_j^{\perp} + k\left(|\mathbf{R}_{j+1}-\mathbf{R}_j| - |\mathbf{R}_j-\mathbf{R}_{j-1}|\right)\widehat{\tau}_j$$

$$\boldsymbol{\phi}_{0,n}^{\text{eff}} = \boldsymbol{\phi}_{0,n}^{sp} - (\boldsymbol{\phi}_{0,n}^{sp}\cdot\widehat{\mathbf{F}}_{0,n})\widehat{\mathbf{F}}_{0,n} + (V(\mathbf{R}_{0,n})-V_{1,2})\widehat{\mathbf{F}}_{0,n}$$

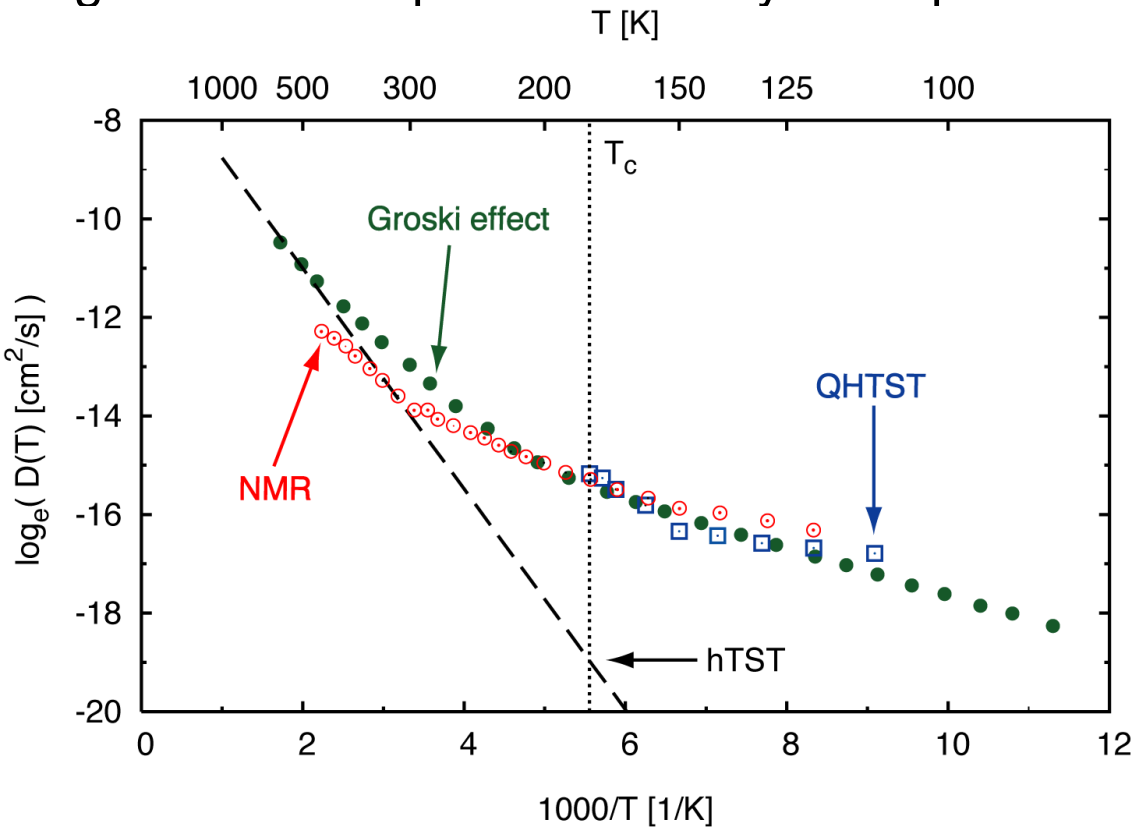
End points made to converge to given energy (not fixed as in NEB)



(Einarsdóttir et al., Lecture Notes in Comp. Sci., 2012)

Hydrogen diffusion in the BCC metal Ta

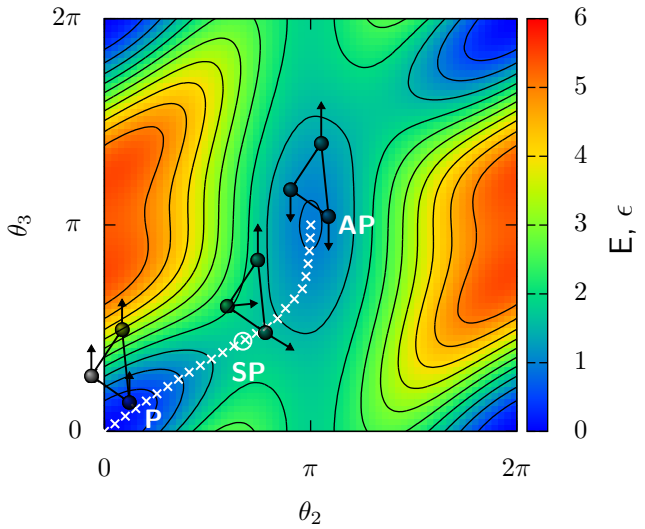
DFT calculations using PAW, PW91 (VASP)
16 Ta atoms, 1 H atom
Hops between adjacent tetrahedral holes
Up to 58 images used to represent the Feynman paths



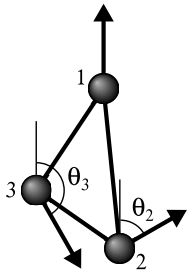
Excellent agreement with experiments at low temperature *(no fitting!).*
Tunneling dominates at below room temperature.

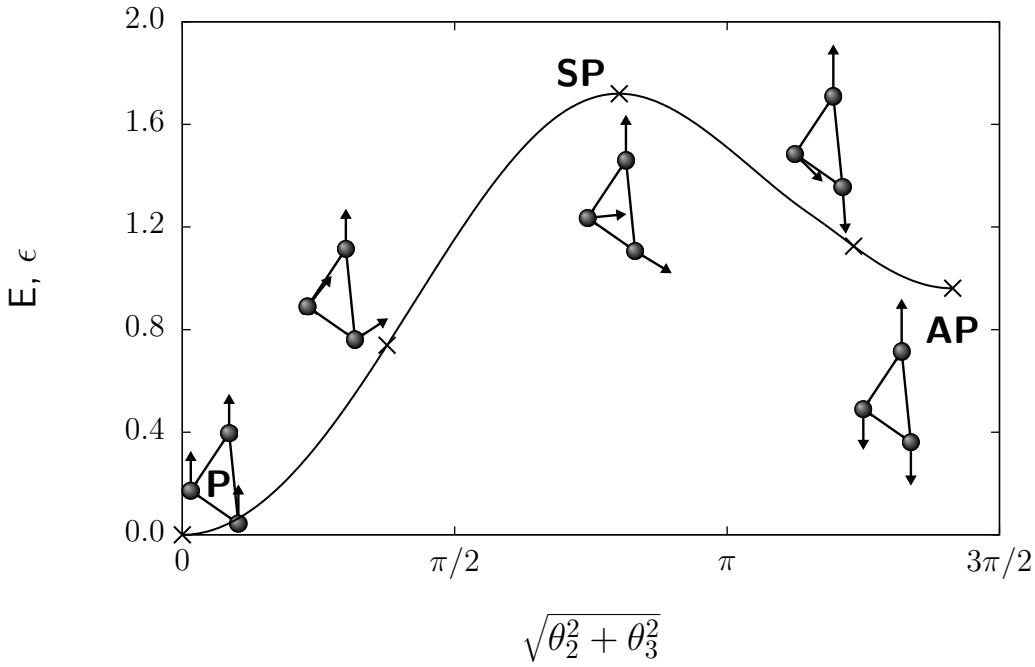
Extension to spin systems

Want to estimate thermal stability of spin states of, for example, nano-clusters
Interesting for magnetic recording.



Non-colinear spins,
use Heisenberg or Anderson models.
Find saddle points and minimum energy paths.
But, what is the prefactor?





Derive harmonic transition state theory for thermal spin transitions

Landau-Lifshitz equation of motion:

$$\frac{dM_i}{dt} = \gamma\ M_i \times \frac{\partial E}{\partial M_i}$$

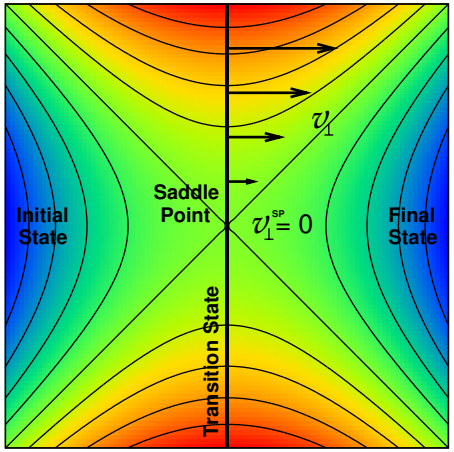
$$\dot{\phi}_i = \frac{\gamma}{M_i \sin\theta_i}\frac{\partial E}{\partial \theta_i} \qquad \text{and} \qquad \dot{\theta}_i = -\frac{\gamma}{M_i \sin\theta_i}\frac{\partial E}{\partial \phi_i}$$

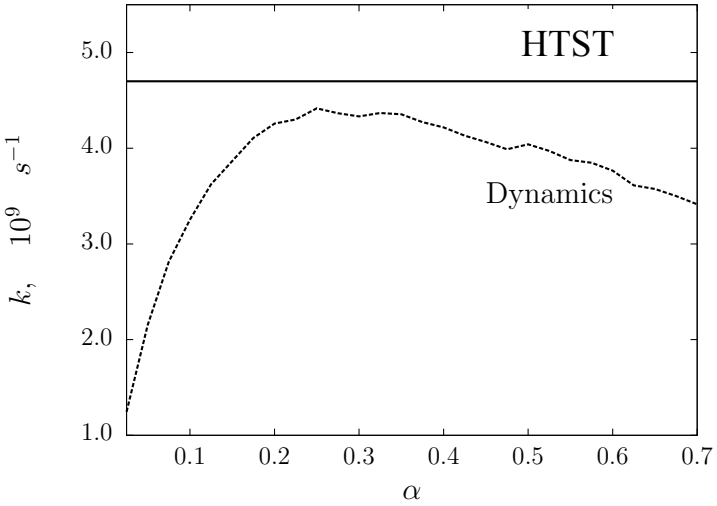
Zero velocity at the saddle point! Need to integrate over half of the hyperplanar transition state surface, get:

$$k^{HTST} = \frac{1}{2\pi}\frac{J_s}{J_m}\sqrt{\sum_{j=2}^{D}\frac{a_j^2}{\epsilon_{s,j}}}\ \frac{\prod_{i=1}^{D}\sqrt{\epsilon_{m,i}}}{\prod_{i=2}^{D}\sqrt{\epsilon_{s,i}}}\ e^{-(E^s-E^m)/k_BT}$$

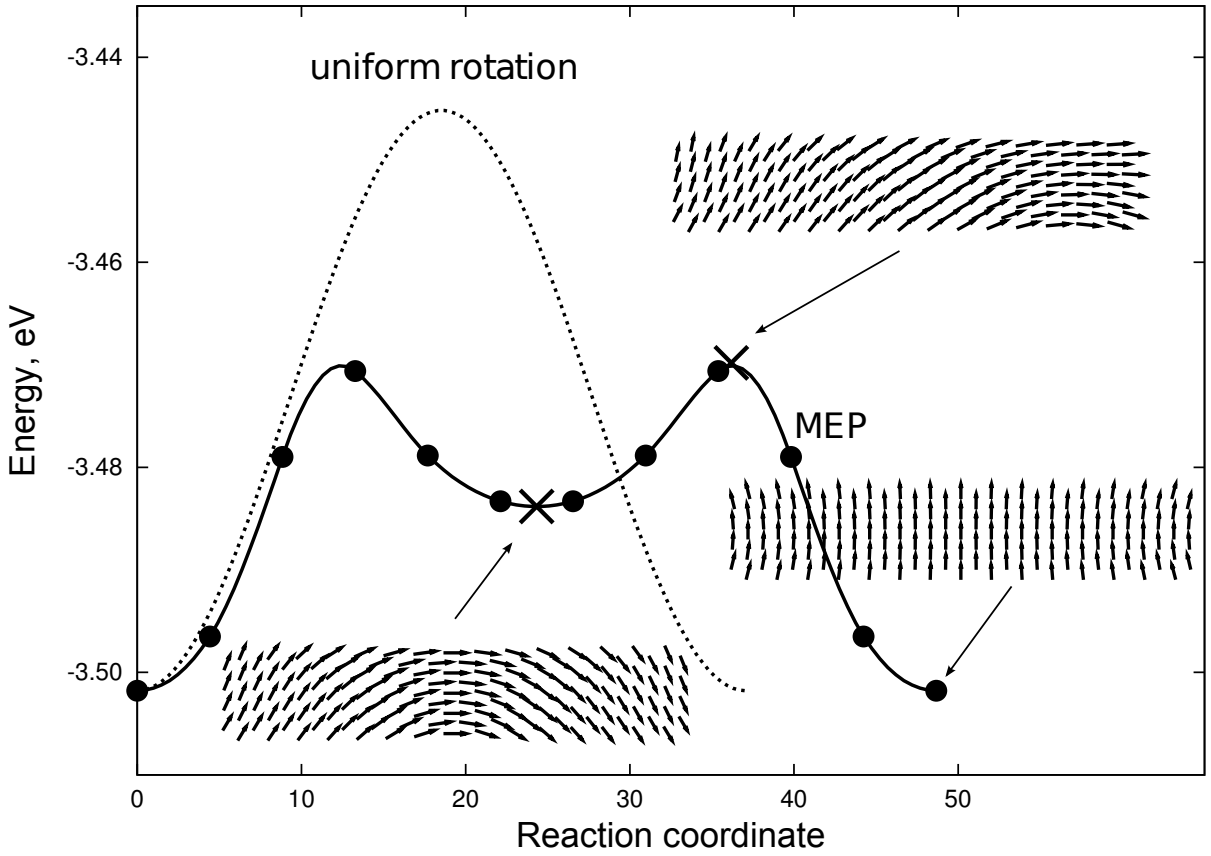
where

$$v_\perp = \sum_{i=2}^{D} a_i q_{s,i} \qquad J(\theta,\phi) \equiv \prod_i M_i^2(\theta,\phi)\sin\theta_i$$





Apply to clusters of Fe atoms on W(110) surface



Intermediate state identified.

Prefactor estimated to be $7.4 \cdot 10^{12}$ s^{-1}

(*P. F. Bessarab, V. M. Uzdin and HJ, PRB (in press)*)

Long Time Scale Simulations of Atomic and Spin Systems

Andreas Pedersen, Jean-Claude Berthet, Pavel F. Bessarab, Jón B. Maronsson
Andri Arnaldssson and **Hannes Jónsson** *University of Iceland*

Overview:

Theoretical approach - WKE dynamics, harmonic TST, min-mode following, AKMC
Implementation - EON software, distributed computing, coarse graining, recycling
Testing - finding the energy ridge, including second order saddle points
Applications - a. grain boundary structure
b. diffusion of atoms at grain boundaries
c. Au clusters
d. structure and diffusion on ice
e. crystal growth
f. kinks on dislocations in Si
g. amorphous CuZr alloy
Extension to quantum tunneling
Extension to spin systems

publications at www.hi.is/~hj

Eyjafjallajökull, 2010