Computer Simulations and Nanotechnology

Intro:

- Making use of high speed modern computers, and therefore nanotechnology
- Contributing to the development of nanotechnology

Tools:

A. Starting from basic equations of physics, predict the properties of chemicals such as structure, stability and transitions

B. Gain intuition and insight, useful when designing experiments

Applications:

1. Metal overlayer growth, formation of nanostructures
2. Clustering of boron dopant atoms in semiconductors
3. New methods for ammonia synthesis, nanopatterned catalysts

Computer Simulations

A new approach to scientific research

Simulations based on basic equations of phyiscs are capable of predicting the properties of new materials

Necessarily approximate and needs to be tested against experiments on similar systems

Can be used to screen ideas, prioritize more expensive experimental research

in vitro ---- in vivo ----- in silico

First principles (ab initio) calculations

Paul Dirac, 1929:

The fundamental laws necessary for the mathematical treatment of large parts of physics and the whole of chemistry are thus fully known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved'.

Nobel price in Chemistry in 1998 went to Kohn and Pople for the development of methods to solve these equations in an approximate way. Can use to find energy and atomic forces $E(R_1,R_2, ...,R_N)$ and $F_i = -\partial E/\partial x_i$

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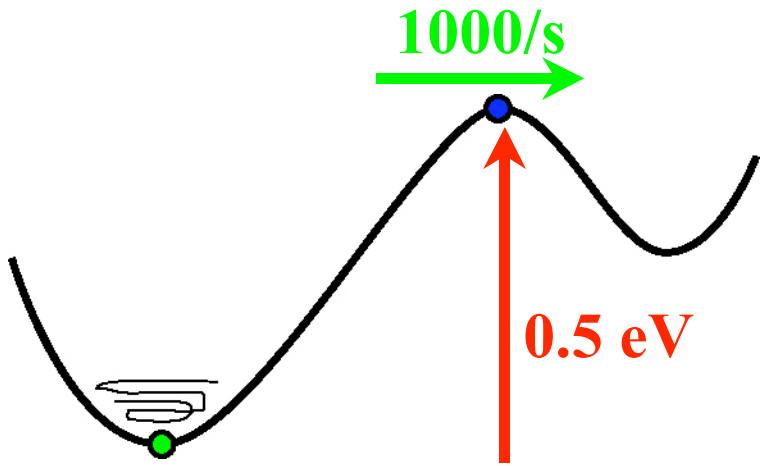
Motion of the atoms: Want to know the mechanism as well as the rate of atomic rearrangements: Simulate the evolution of a system undergoing atomic rearrangements and bond breaking (diffusion, catalysis, growth, pattern formation, etc).

Time scale problem:

- Most interesting transitions are rare events (ie, much slower than vibrations).
- A transition with an energy barrier of 0.5 eV and a typical prefactor occurs 1000 times per second at room temperature. A direct classical dynamics simulation would require 10^{12} force evaluations and thousands of years of CPU time to cover the average time period between such events.



Cannot simply heat the system, the mechanism can change!

A walk on the potential energy surface $E(R1,R_2,...,R_N)$

Use Transition State Theory wich assumes

1. Born-Oppenheimer
2. Classical dynamics for nuclei
3. Boltzmann distribution in R
4. No recrossings of TS

Result:

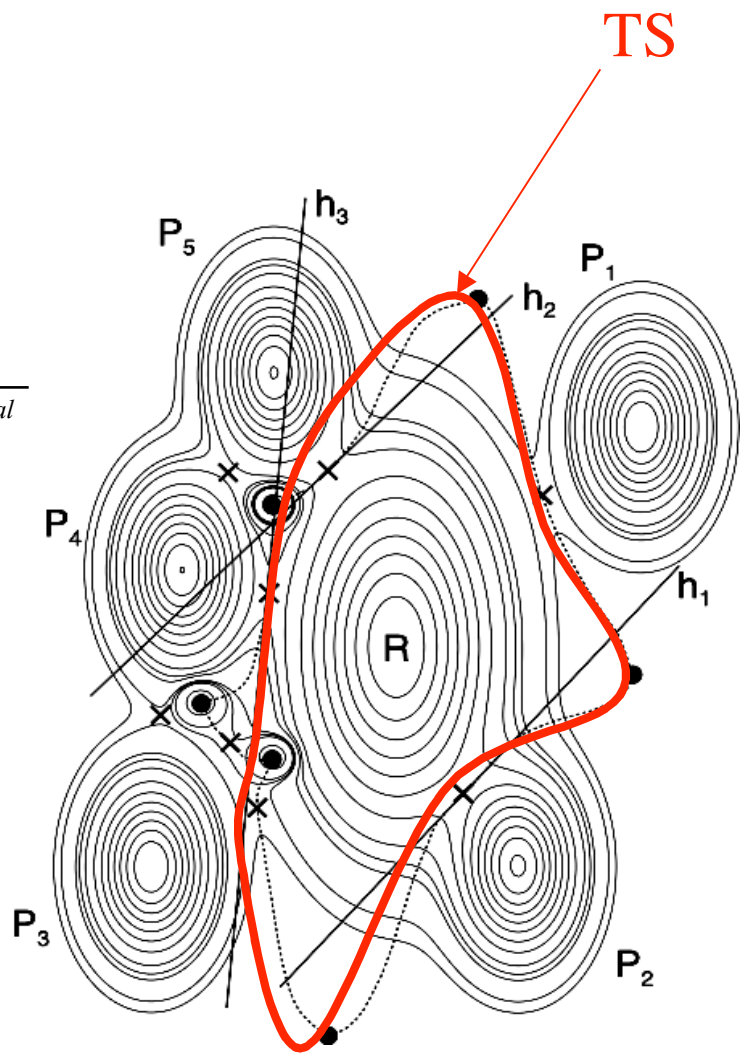
$$k^{TST} = \frac{<|v_\perp|>}{2} \frac{Q^{TS}}{Q^{Initial}}$$

- TST gives the lifetime, $\tau=1/k$, of a given initial state, no knowledge of final state(s)

  Need to run (short time) dynamics starting from TS to find the final state(s)

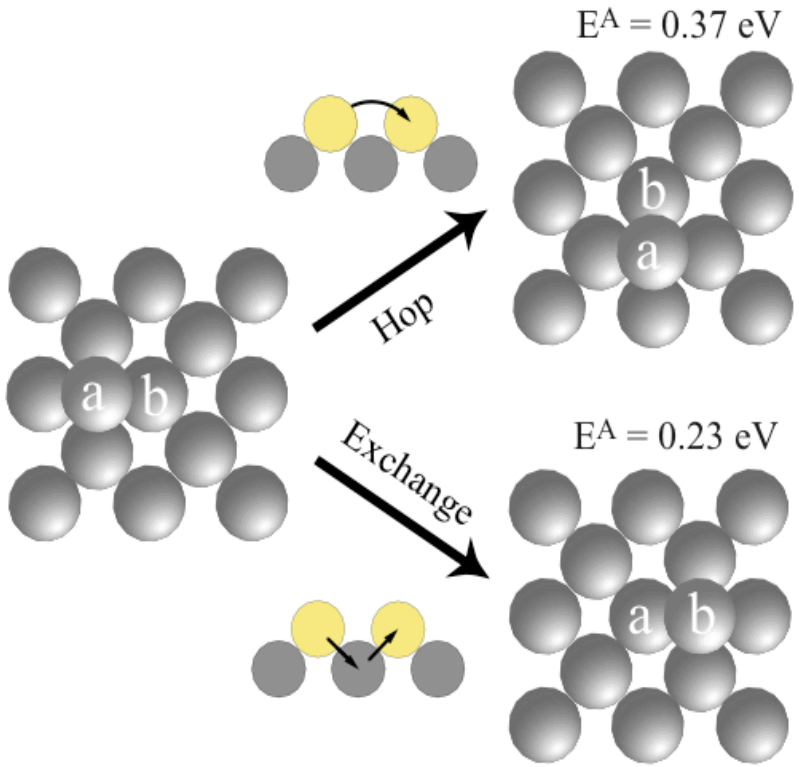
- Such trajectories can be used to take recrossings into account - dynamical corrections

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



An example of unexpected mechanism (P. Feibelman 1990)

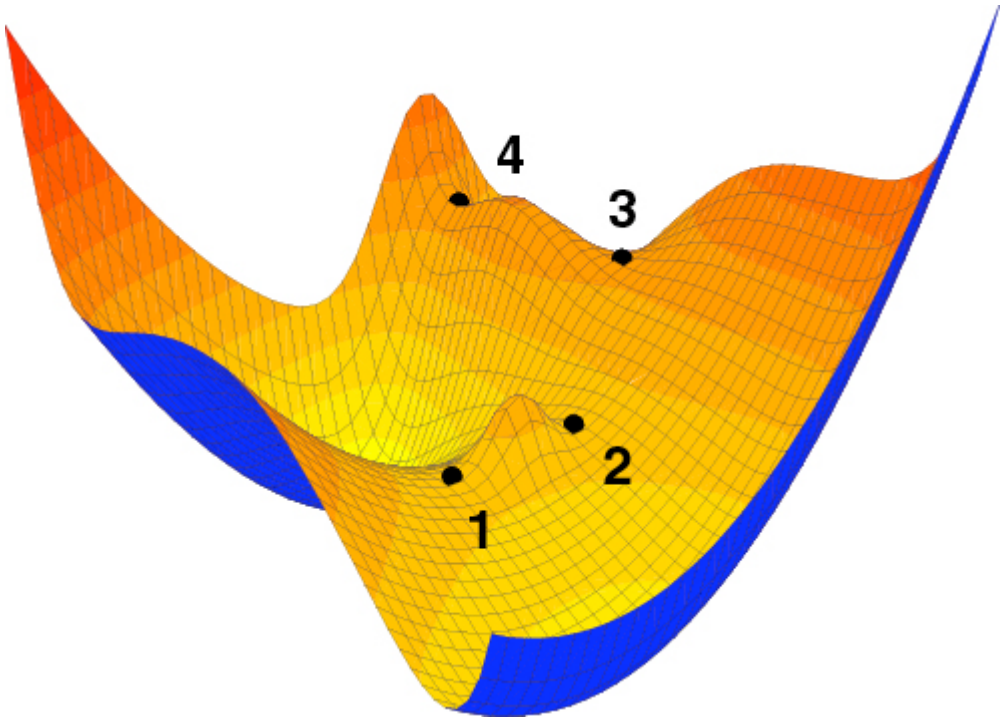
diffusion of an Al adatom on an Al(100) surface



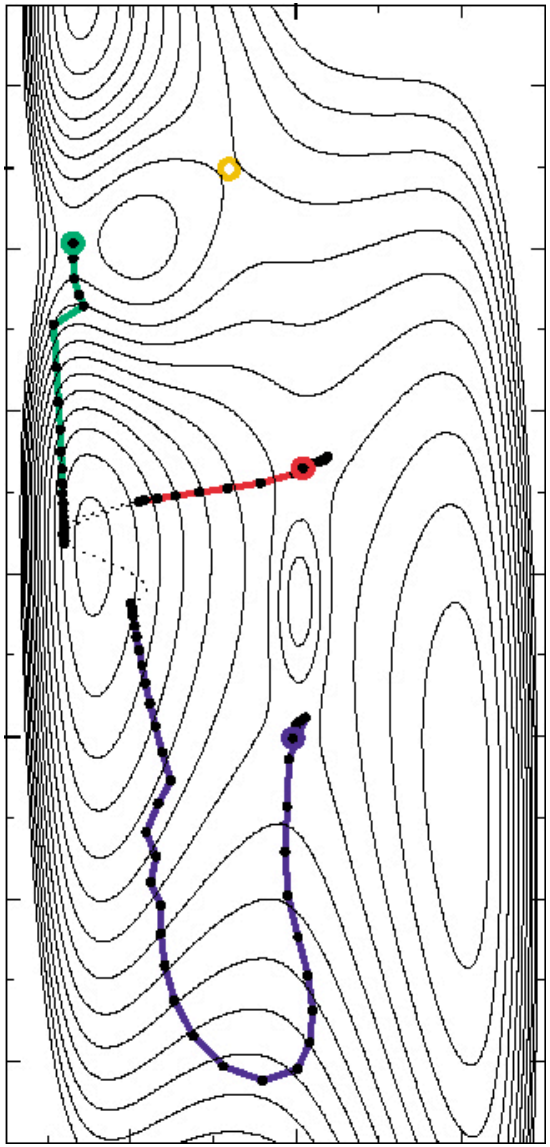
Note: The final state is different in the two cases!

Instead of guessing, FIND relevant processes from atomic forces:

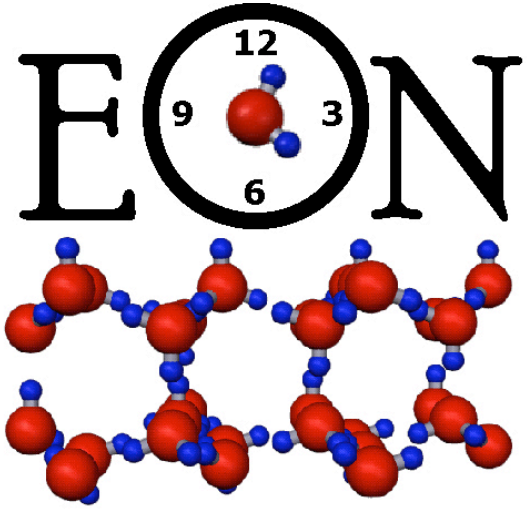
Within HTST, need to
find all the relevant saddle points



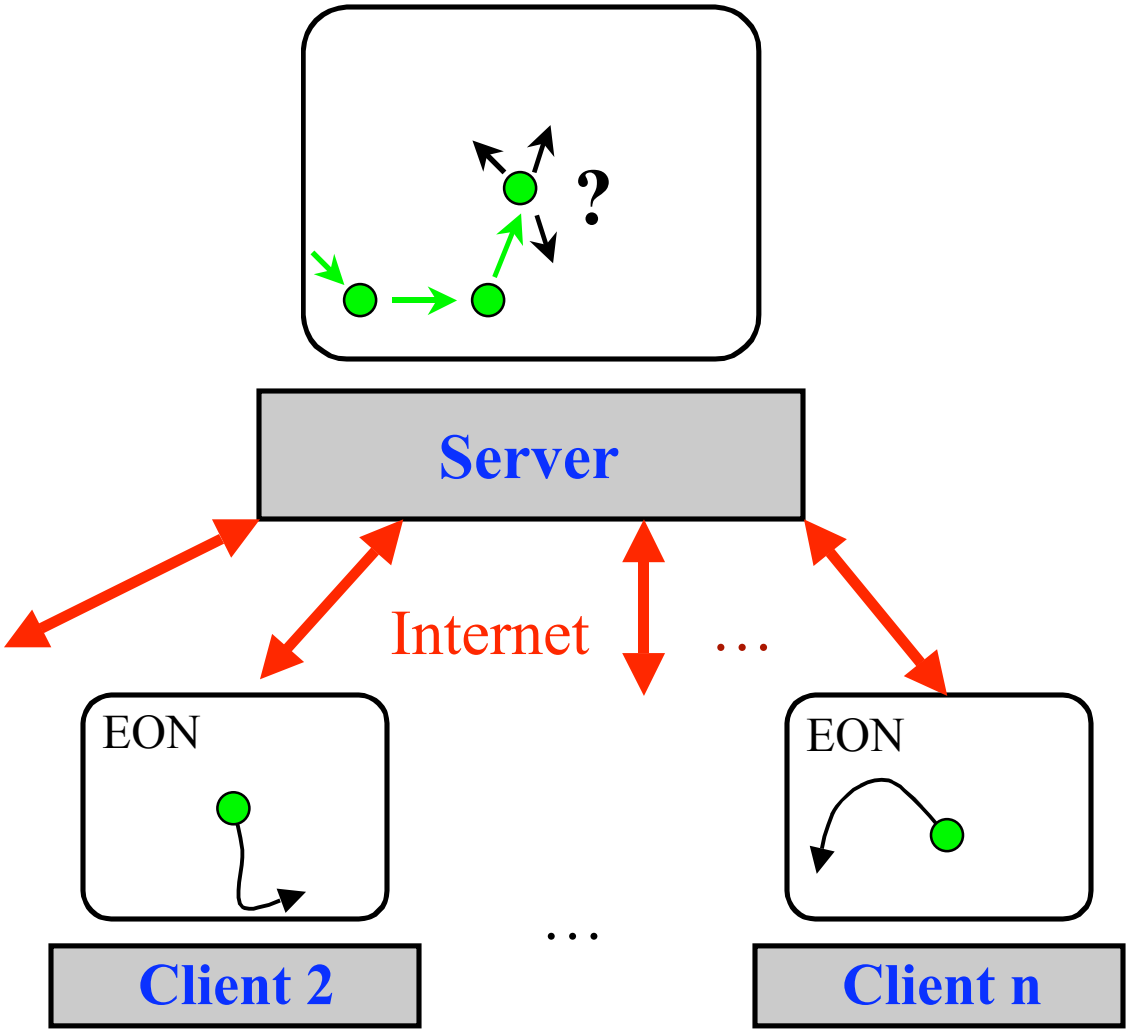
Min mode method searches for saddle points



Distributed long time scale simulations of solids

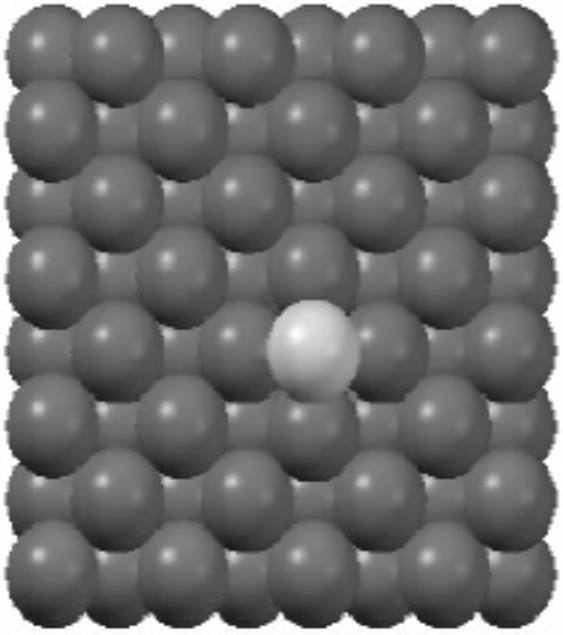


- Simulations of crystal and amorphous thin film growth, diffusion/ripening



Distributed screen saver clients:

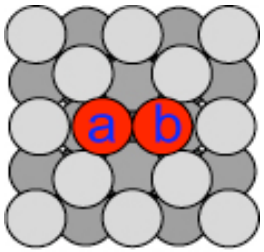
Adatom diffusion on Al(100)



Statistics

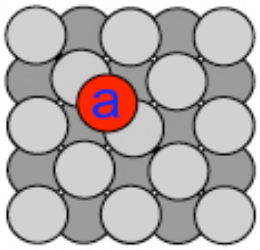
temperature: 300 K
total transitions: 1000
distinct transitions: 112
total time: 55 ns
dimer searches per step: 50
distinct processes per step: 15

Compare EAM with DFT



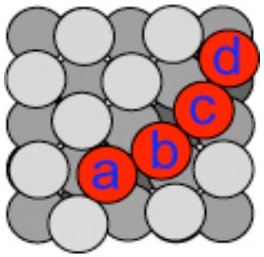
ΔE = **0.23 eV (0.24 eV)**

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



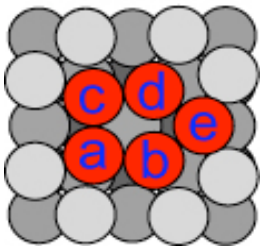
ΔE = **0.37 eV (0.52 eV)**

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



ΔE = **0.41 eV (0.50 eV)**

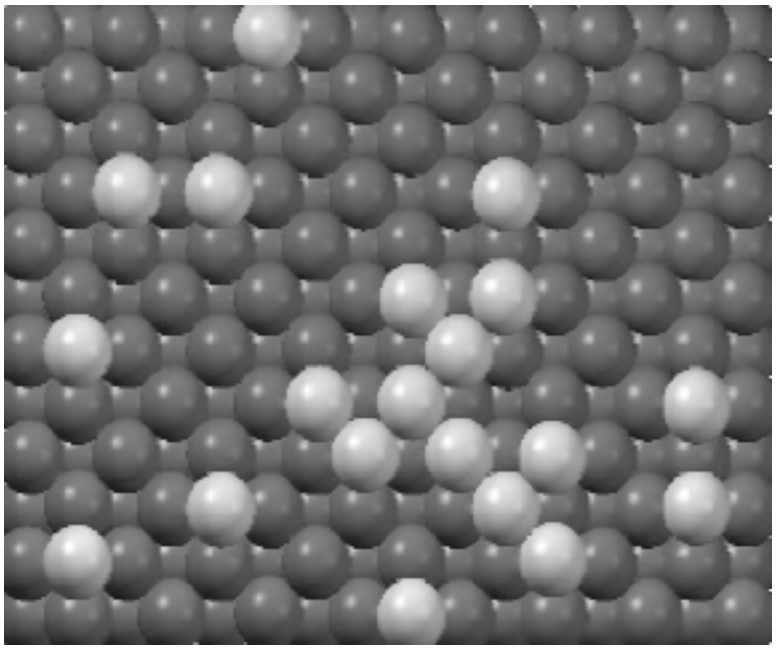
ν = **$2 \cdot 10^{15}\ s^{-1}$ ($8 \cdot 10^{14}\ s^{-1}$)**

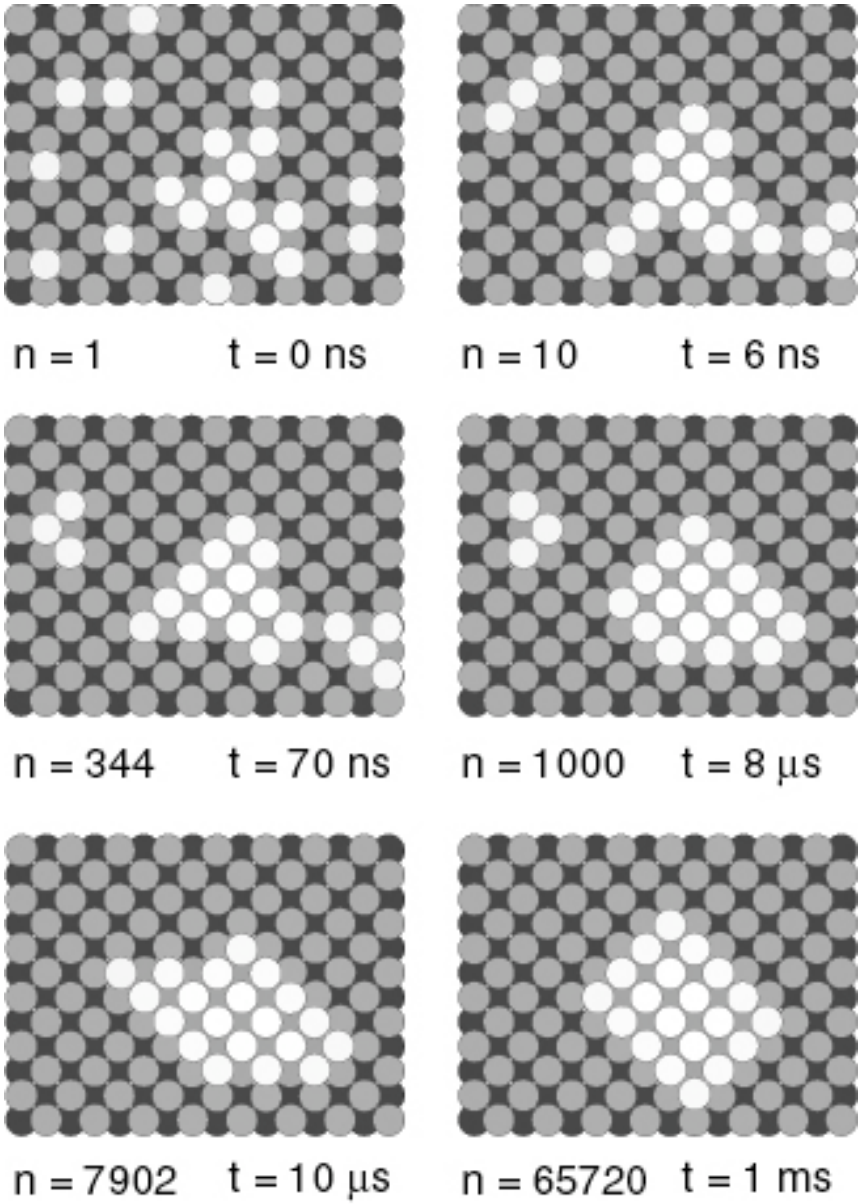


ΔE = **0.44 eV**

ν = **$3 \cdot 10^{14}\ s^{-1}$**

Long time dynamics: Ripening on Al(100)



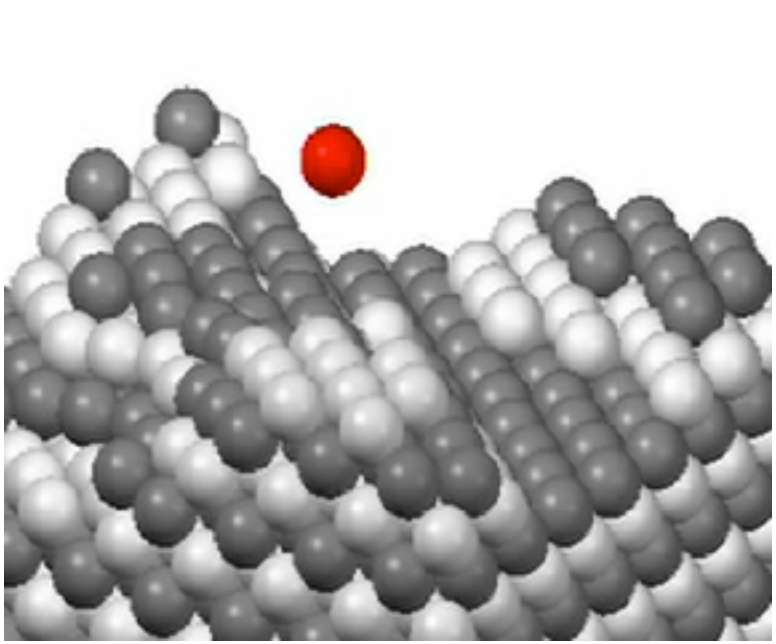


Statistics

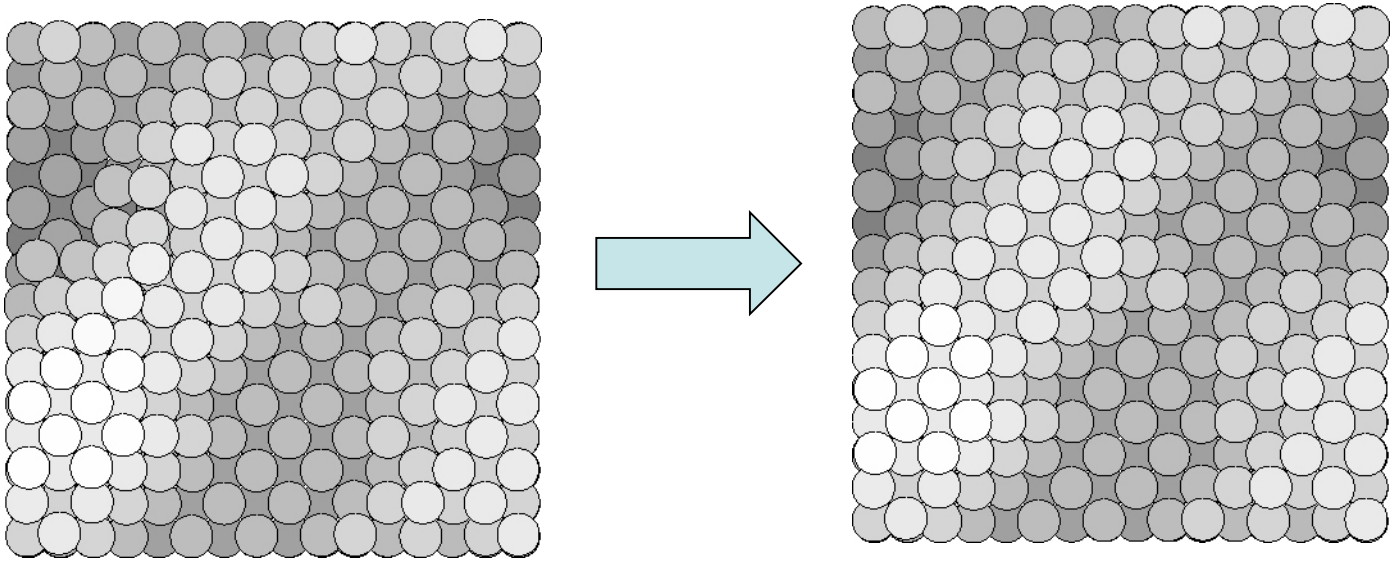
temperature: 300K
total transitions: 129,000
distinct transitions: 341
total time: 1 ms
dimer searches per step: 50
distinct processes per step: 26

Simulate deposition of atoms on a surface

Deposition event creates a local hot spot that cools down in ca. 1 ps

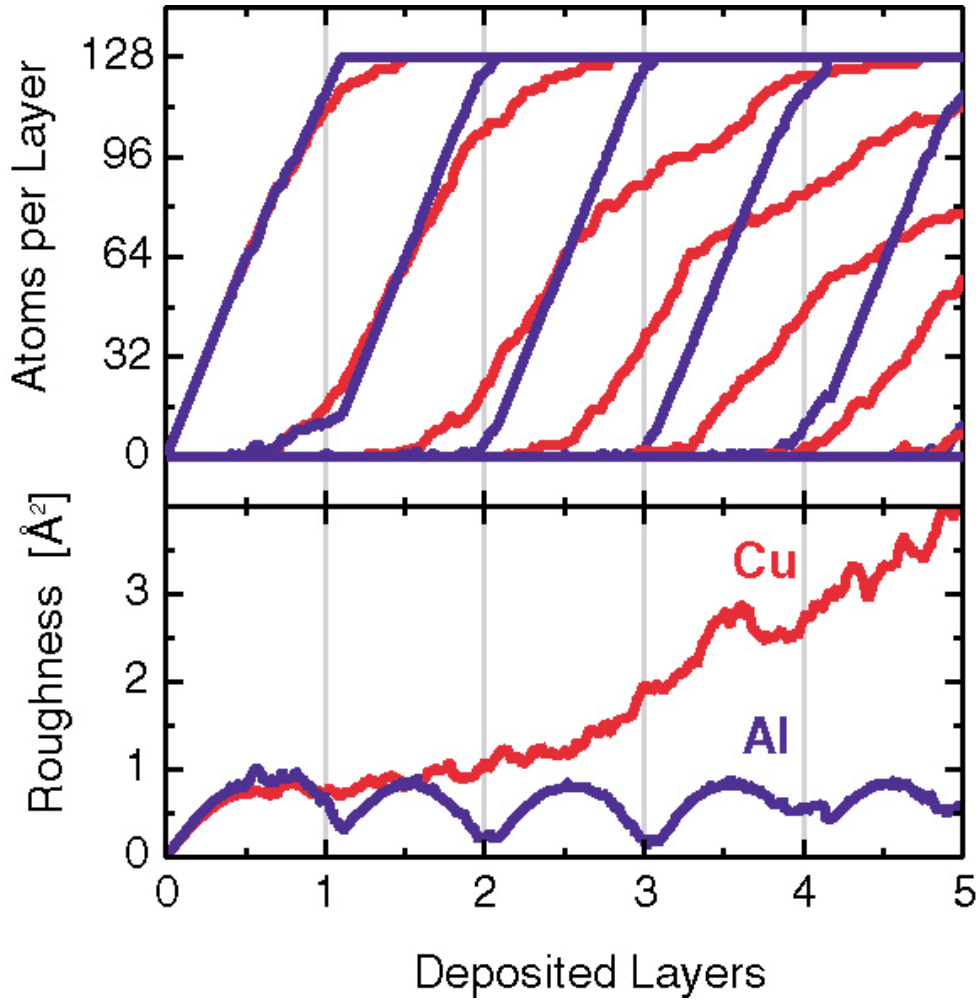


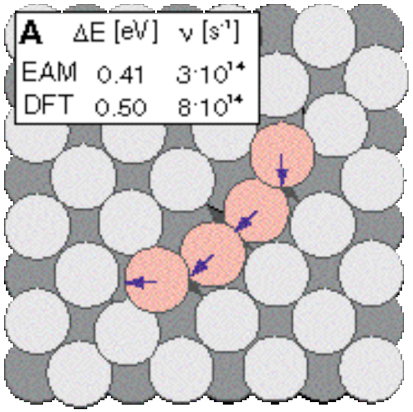
'Landslide'occurs in this case

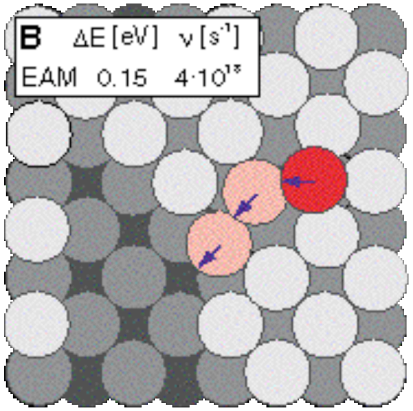


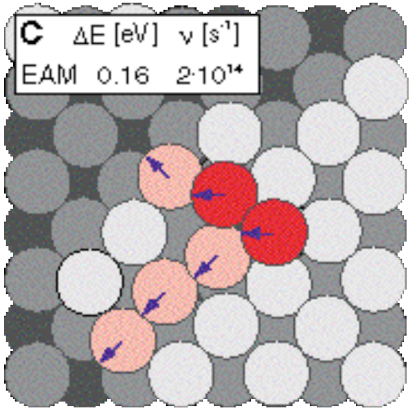
Compare Al(100) and Cu(100) crystal growth

Aluminum grows much smoother than copper at 80K, largely because of multi-atom smoothening events





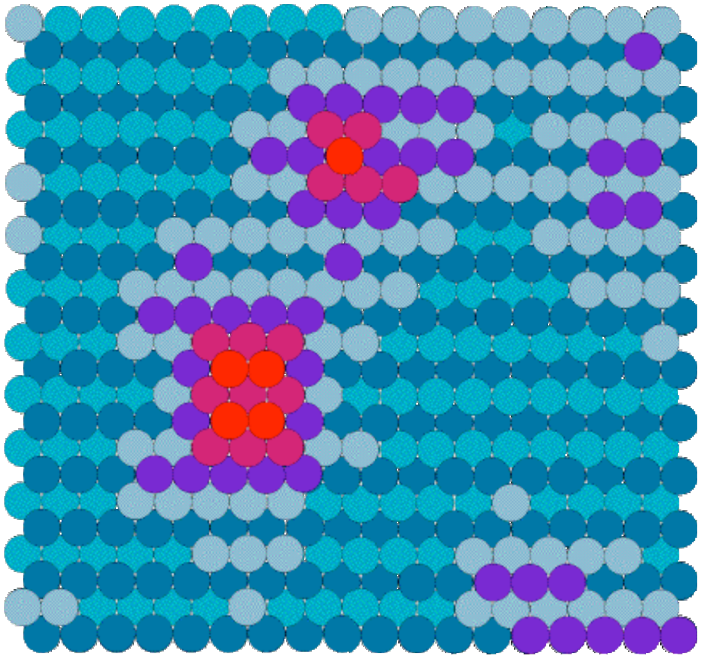




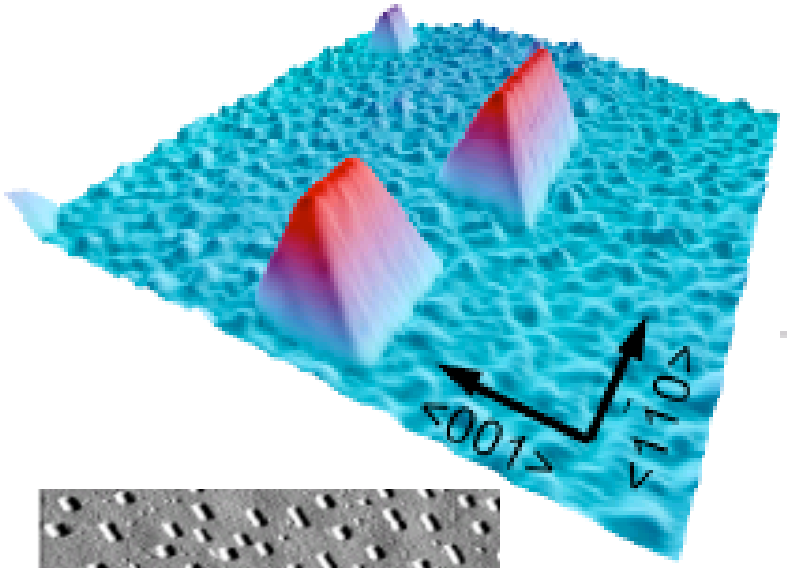
Pyramids on Al(110)

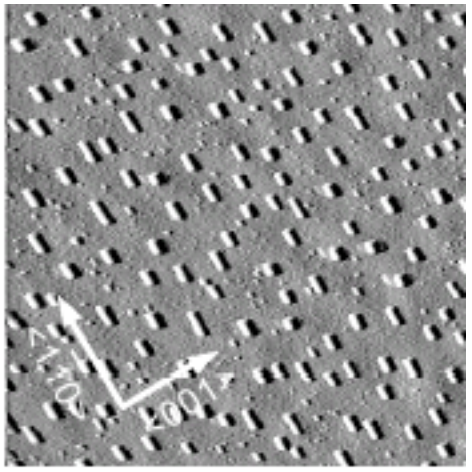
Simulations: EON screen saver

10 layers of atoms have been deposited in ten milliseconds at a temperature of 80K

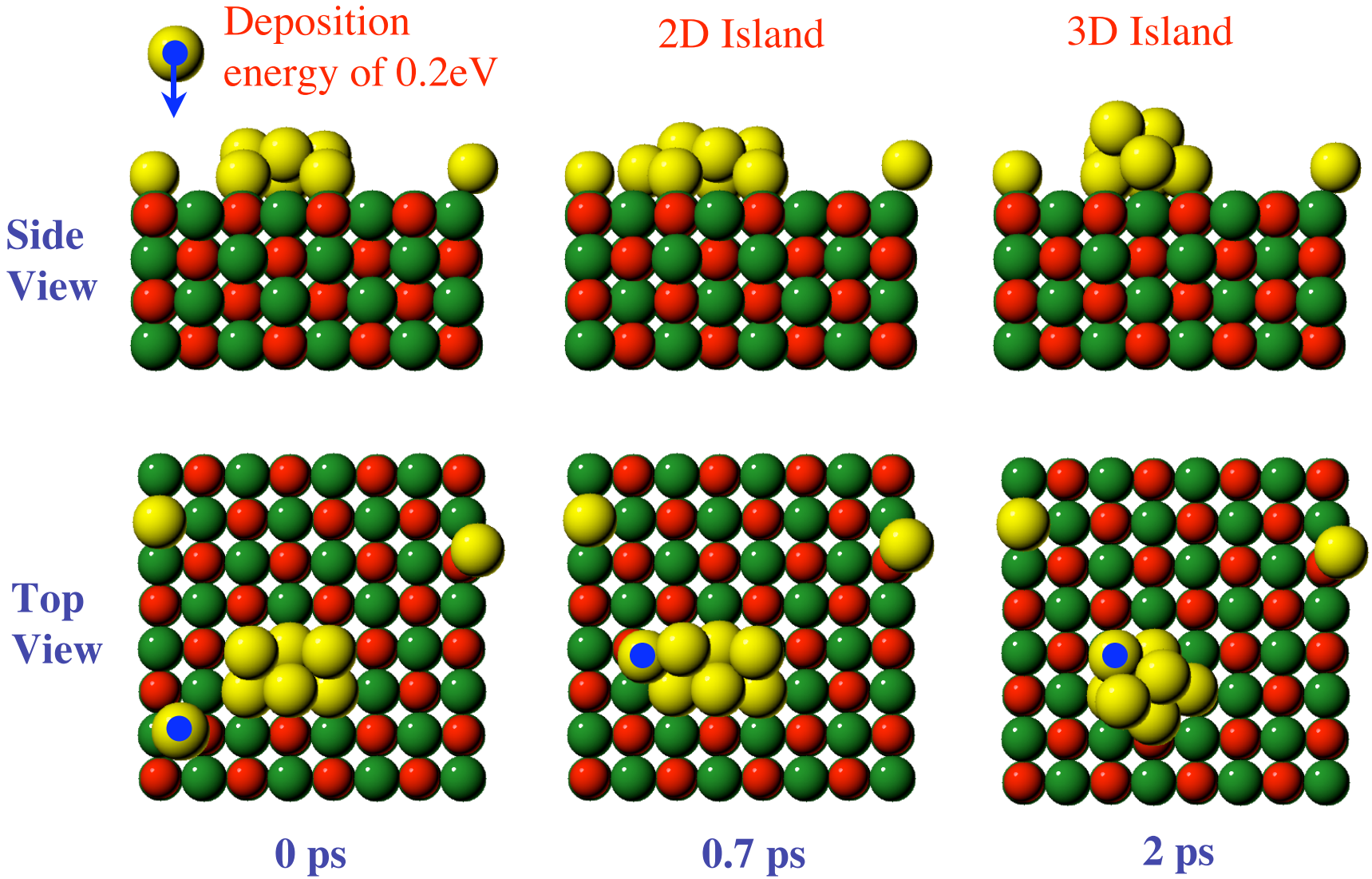


Experiments: Valbusa *et. al. (Genoa)*





Growth of metal islands on MgO (model catalyst)
Catlytic properties depend strongly on size and shape of islands



Another application of AKMC: Boron clustering in silicon

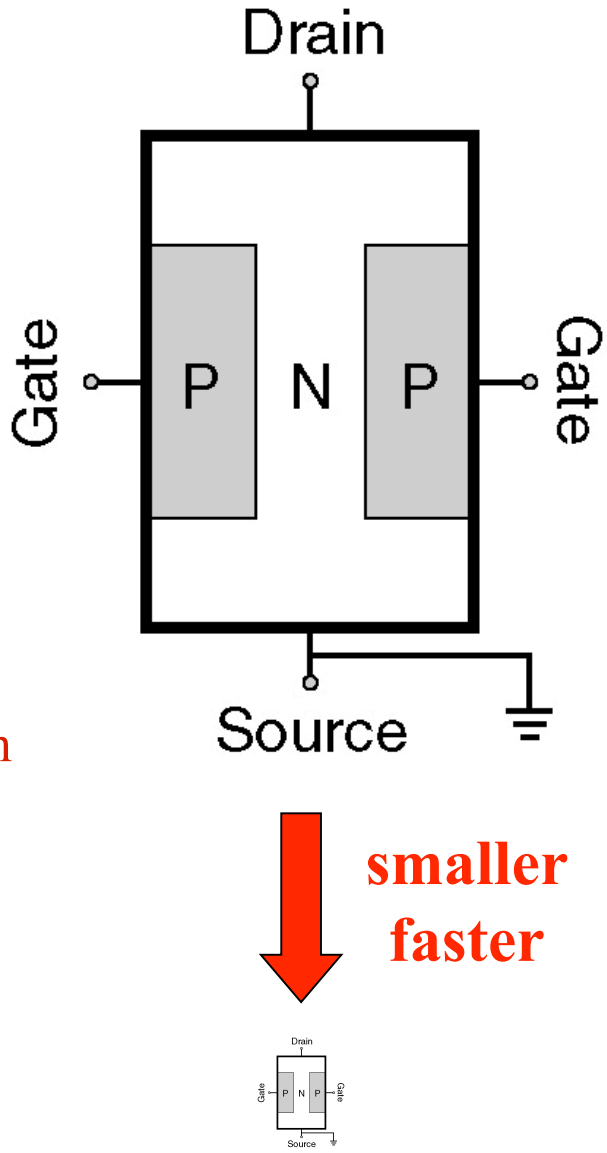
As semiconductor devices become smaller, dopant concentration needs to be increased to give the same electric current throughput

Boron concentration has become high enough that clusters form after implantation and low T annealing. The boron clusters are not active

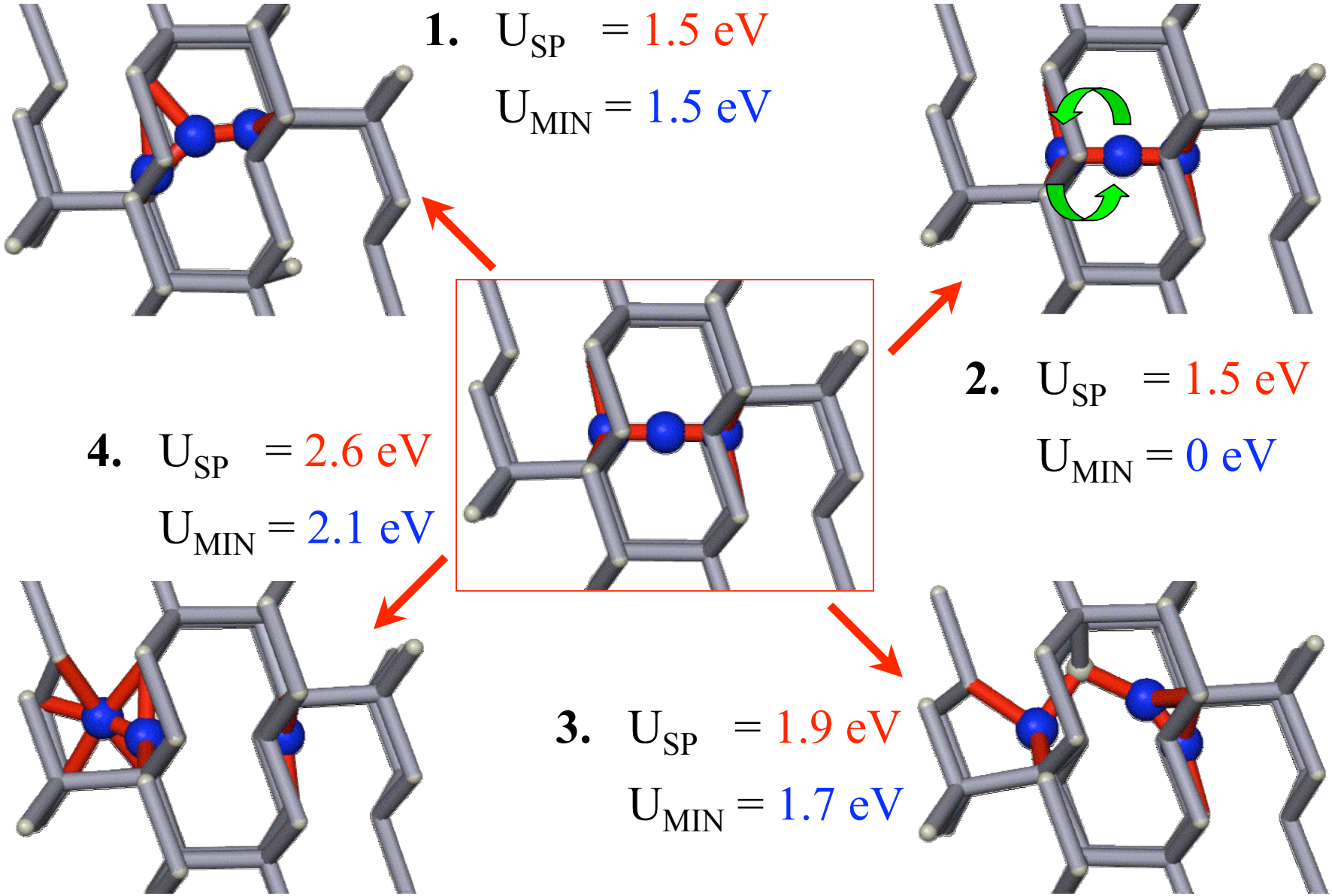
High temperature, short time annealing is used to dissociate boron clusters and re-activate the dopant

It is important to understand how dopant clusters form and dissociate, and what their properties are

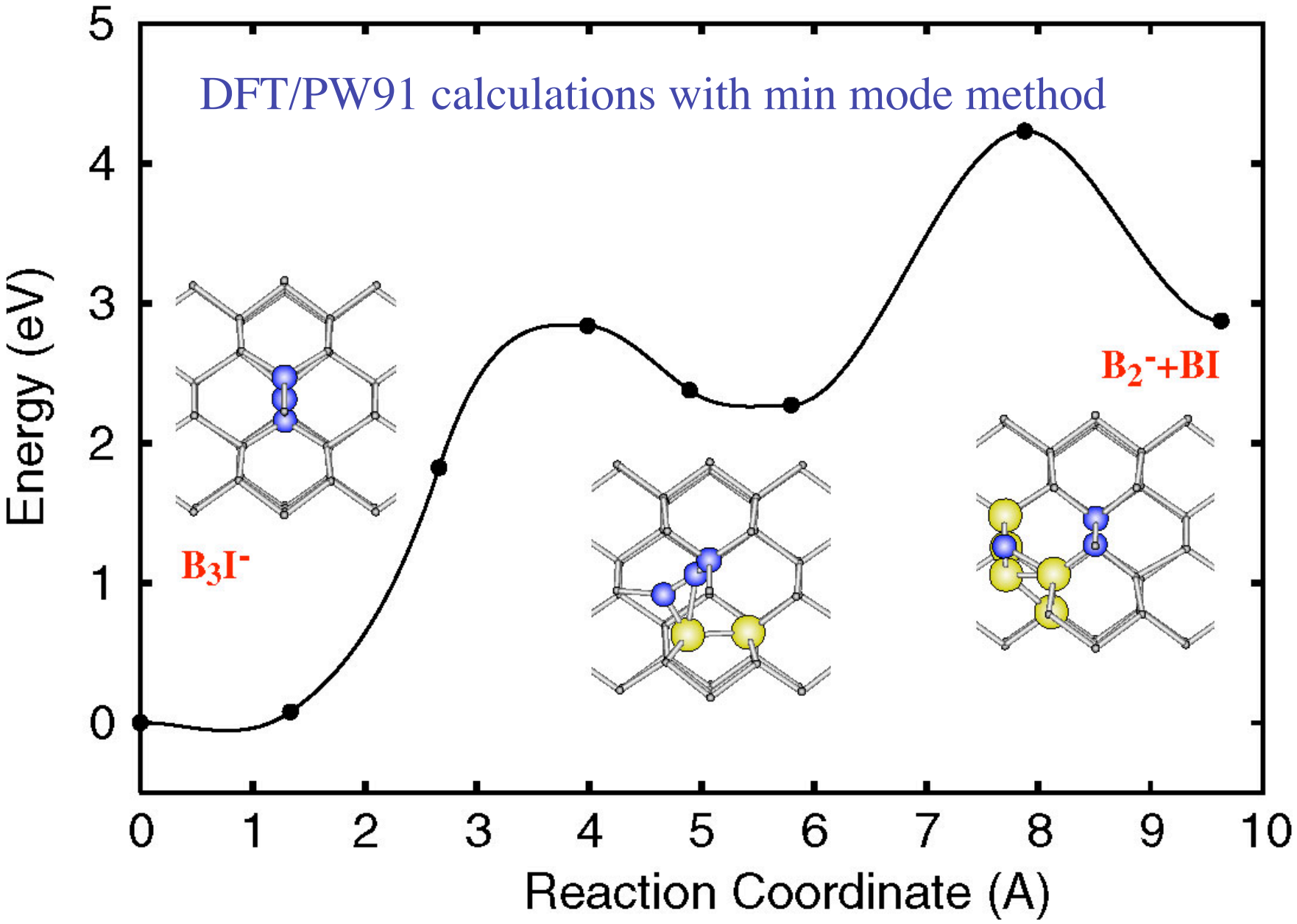
Rates of dopant clustering/dissolution are needed as input parameters for modeling device manufacturing.



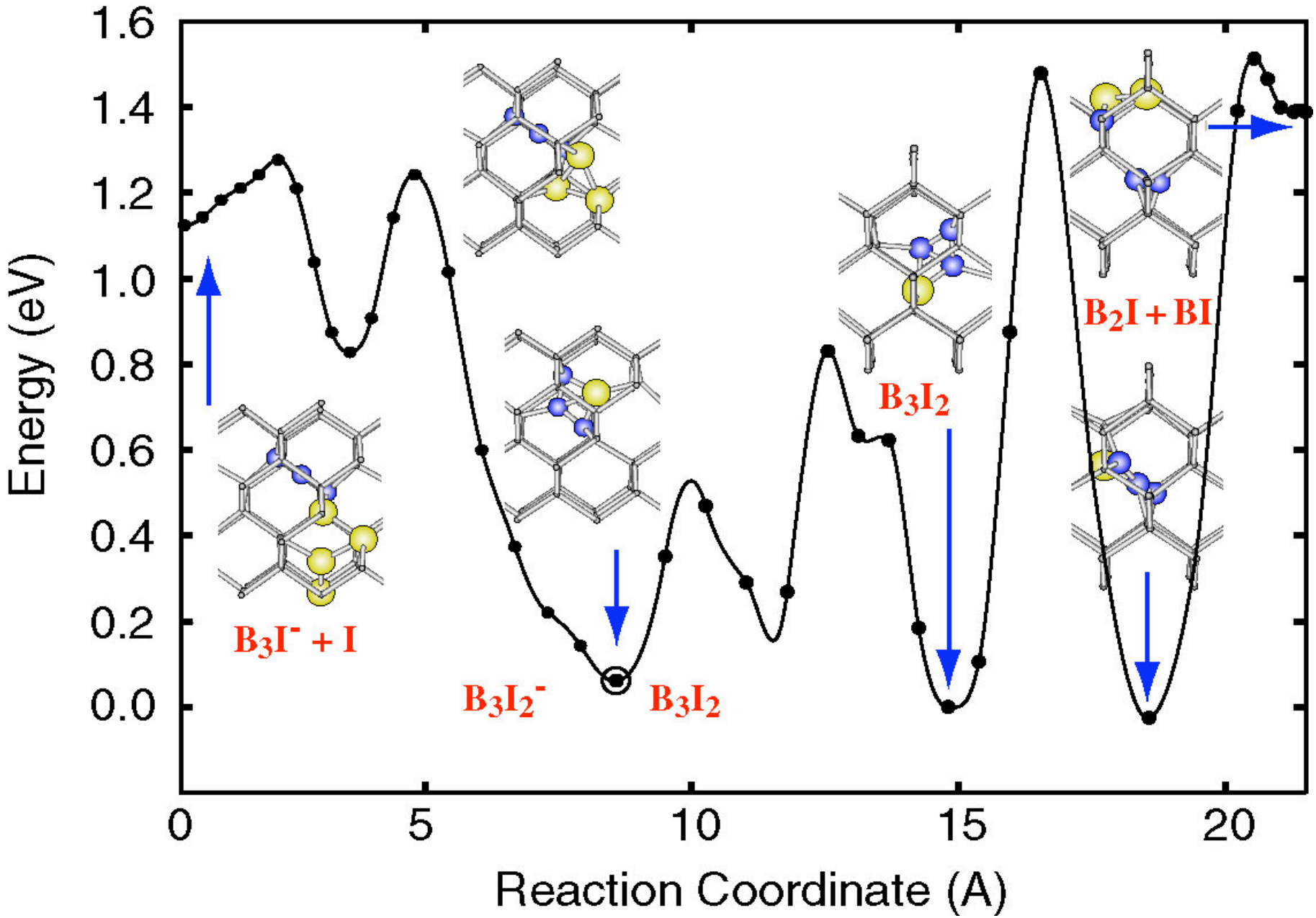
Calculations: Possible B_3I^- cluster breakup processes, Step 1



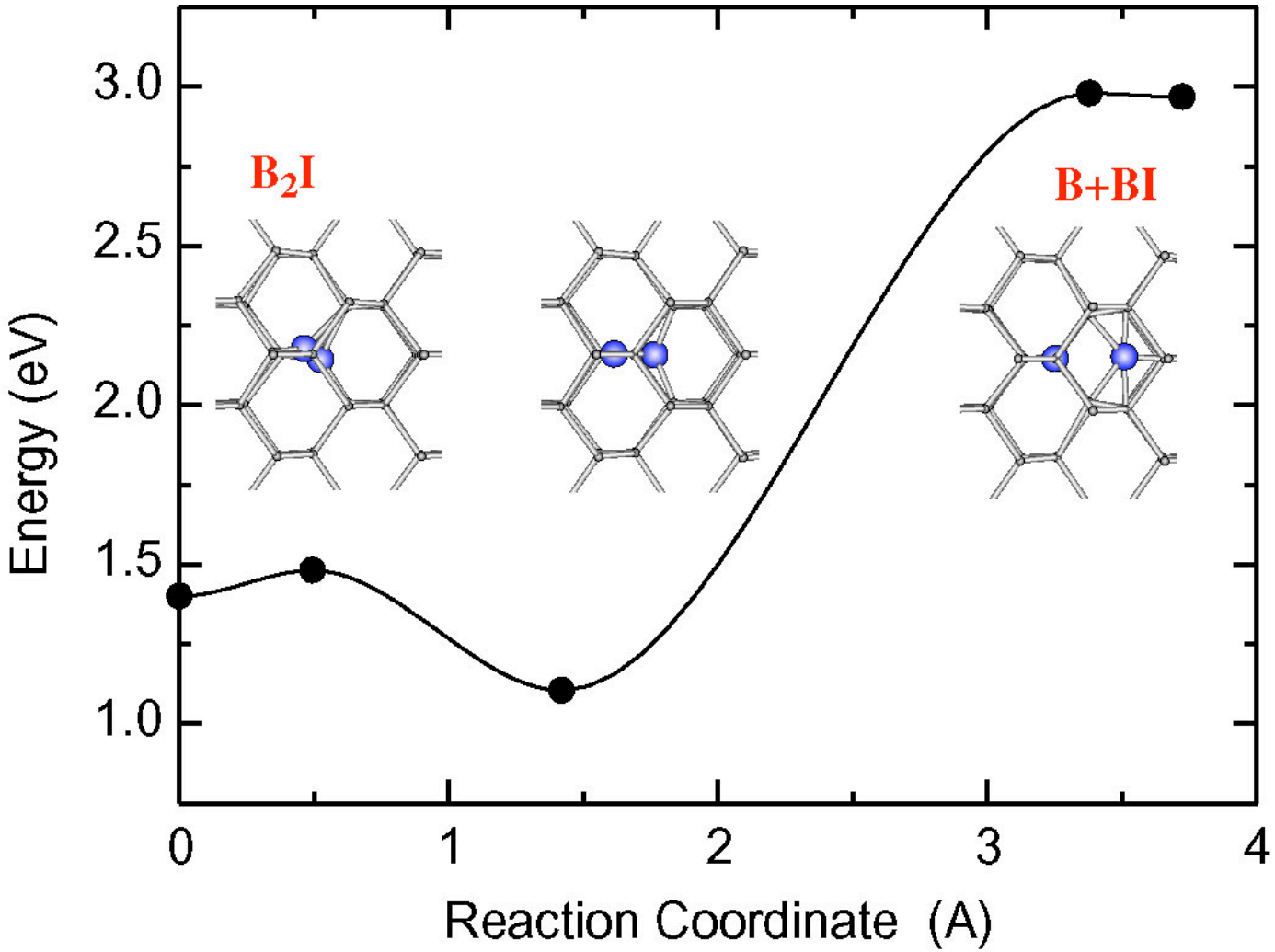
Direct breakup of the highly stable B_3I^- cluster: High activation barrier



Si interstitial mediated breakup of B_3I^- : Lower activation energy



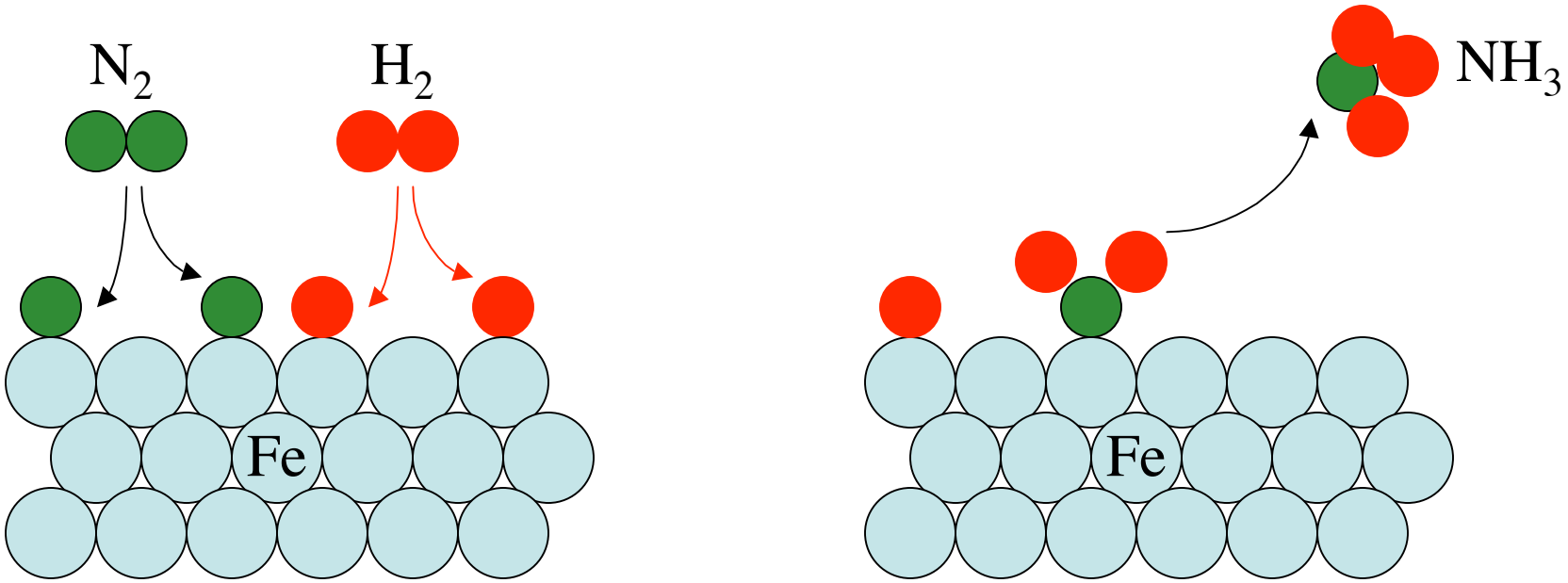
Further breakup of B_2I: Overall activation energy 3.0 eV



New catalyst for ammonia synthesis

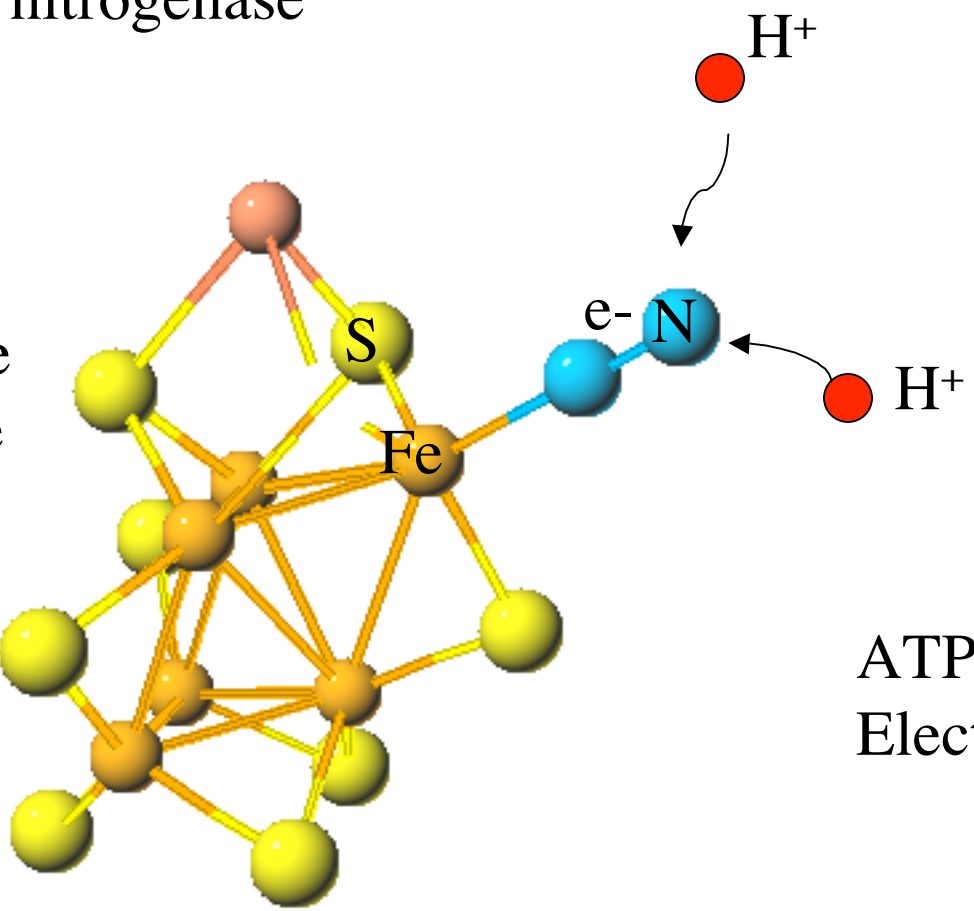
The essential step of fertilizer production

Industrial plants today use a method that is more than 100 years old



The N-N triple bond is broken in the beginning,
a rate limiting step

Nitrogen fixing bacteria (on the roots of lupine, for example)
Enzyme nitrogenase

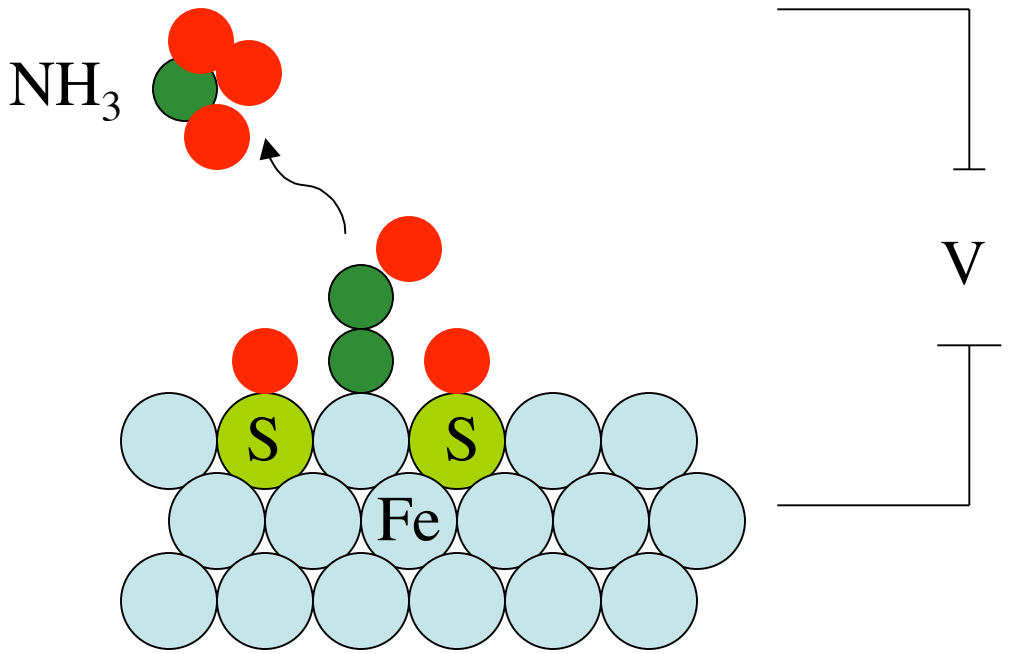


Active site
of enzyme

ATP used to pump
Electrons on the N_2

The N-N bond is the last to be broken,
addition of first proton is the rate limiting step

Can nanotechnology be used to pattern a Fe surface to catalyze ammonia production along the same route as nitrogenase?
Use applied voltage to pump electrons onto N_2 molecule



Future vision: Create small rods that can produce fertilizer using sunlight, water and air. Stick one down with each plant!

EU funded collaboration with Jens Norskov at DTU, Denmark

Summary

- The Adaptive KMC method can be used to simulate long time scale dynamics. Within harmonic transition state theory, saddle point searches using Min Mode method typically require 400 force evaluations and a few tens to hundreds of saddle point searches started in random directions can suffice to simulate long time scale dynamics with reasonable accuracy.
- When full TST is needed, an optimal TS dividing surface can be found by using the variational principle. This can reveal the mechanism of transitions as well as giving an estimate of the rate. OH-TST is a step in that direction, limited to hyperplane representation of TS. In the case of Al adatom diffusion, the optimization of the orientation of the hyperplane converged to the lower energy exchange mechanism, while initially the hyperplane was set up for the hop mechanism.

Acknowledgements

VASP code

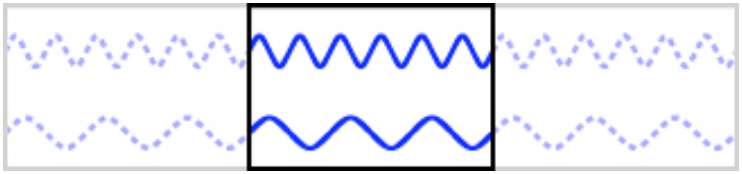
Funding from NSF-KDI and Semiconductor Research Corporation

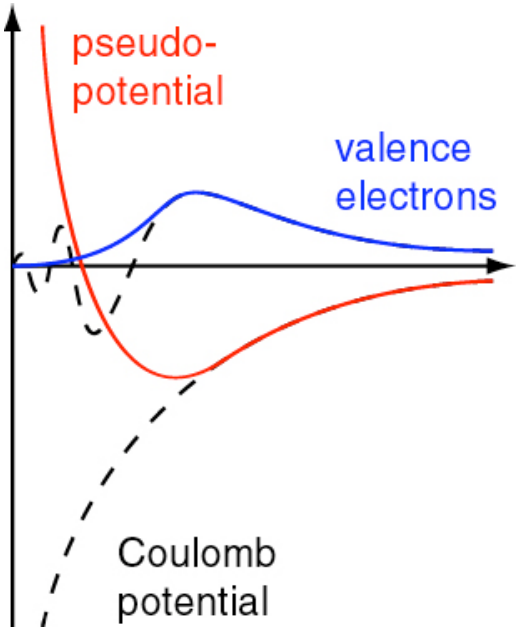
Available software

- Screensaver for long time dynamics:
  http://eon.chem.washington.edu
- Template for distributed computing:
  http://fida.chem.washington.edu
- The software (code plug-ins and additions) for doing dimer, CI-NEB and prefactor calculations with VASP is available from:
  http://ikazki01.chem.washington.edu/vasp/

DFT Calculations of B cluster breakup

- PW91 GGA functional
- Ultrasoft Pseudo-potentials, 64+ atoms
- Plane waves basis, 2x2x2 k-points





Search for saddle points of boron cluster breakup processes using the dimer method

- 350 force evaluations per image to find a saddle
- 10 min per force evaluation (IBM Power 2 workst.)
- Of 20 saddle point searches, typically
  18 converge to good saddle points
  11 yield distinct processes of which 5 might be low in energy