Long-Time Scale Dynamics Simulations of Surface Segregation in Pd-Au Nanoparticles

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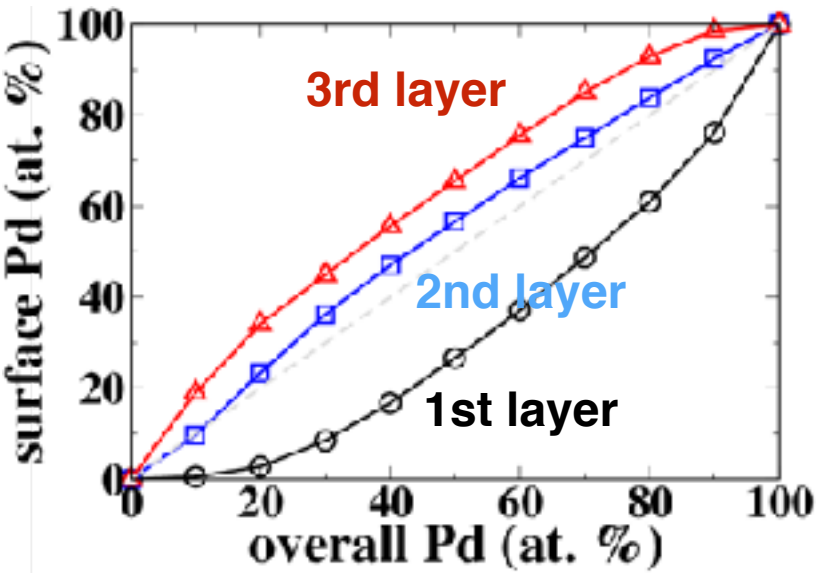
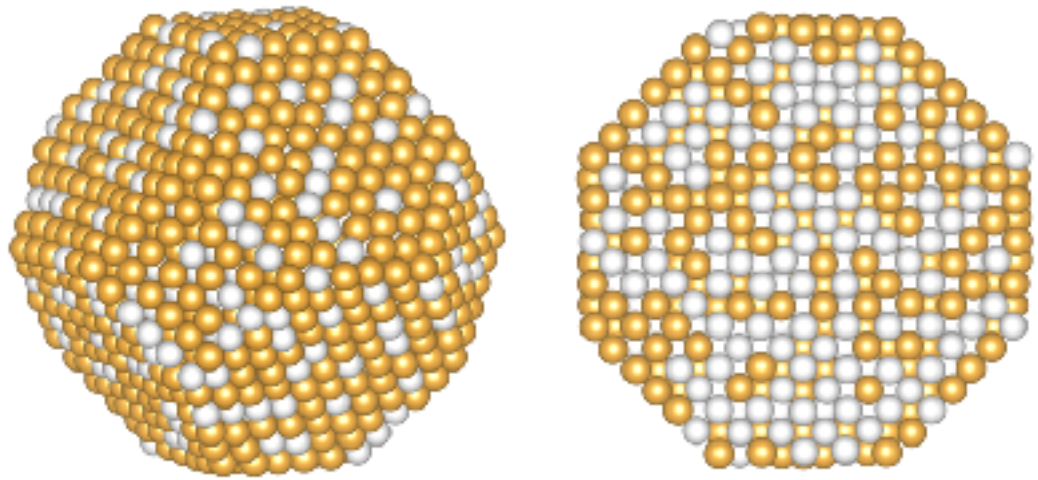
Surface segregation phenomenon

Surface segregation in metal alloys: preferential enrichment of the surface by one of the constituents.

Equilibrium structures of PdAu nanoparticles



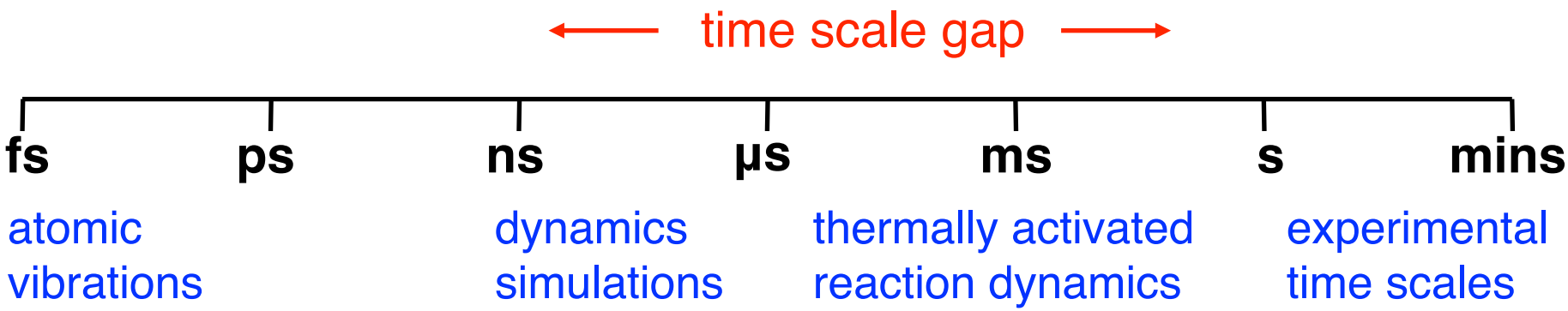


50 at.% Pd

- **Mechanism of surface segregation?**
- **Kinetic Trapping?**

A problem of time scale

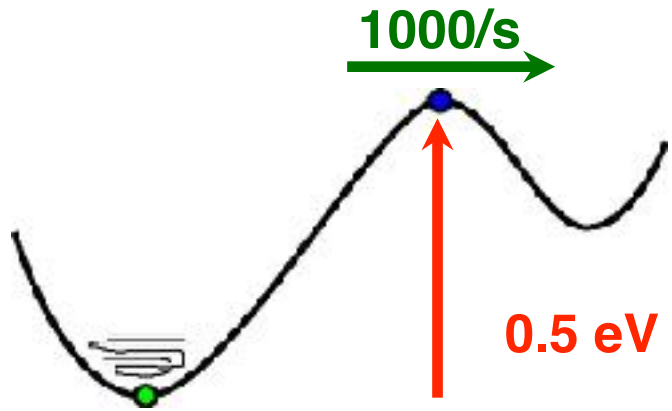
Atoms move on a femtosecond time scale, but many interesting processes occur on a human time scale of seconds or minutes.



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!



Adaptive kinetic Monte Carlo (AKMC)

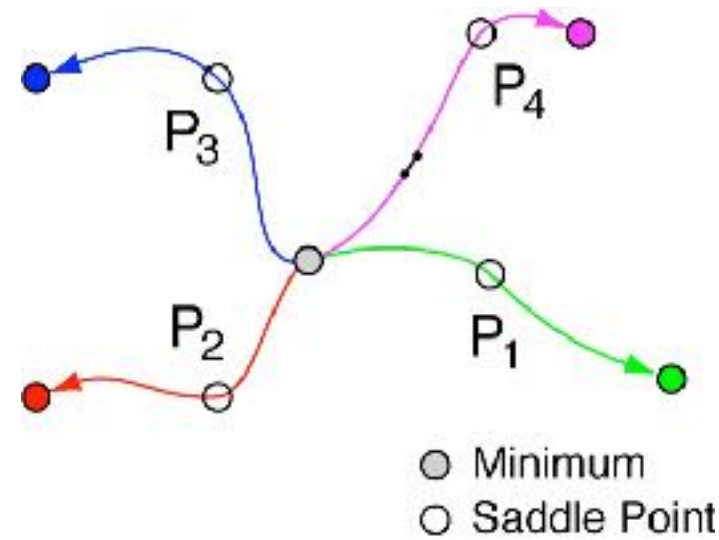
Combine saddle point searches with kinetic Monte Carlo

Adaptive Step

1. Find low energy saddle points on-the-fly

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

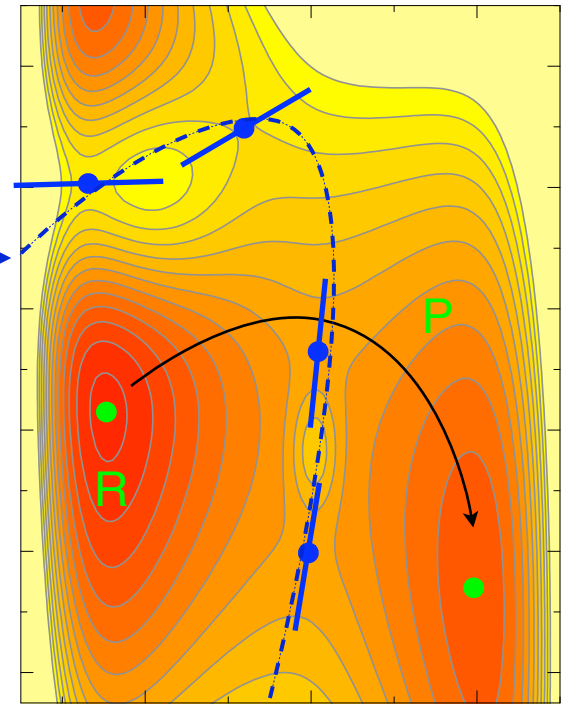
G. Henkelman and H. Jónsson *JCP* **115,** 9657 (2001)

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:

$$x = x^\dagger$$



- Minima
- Saddle Points

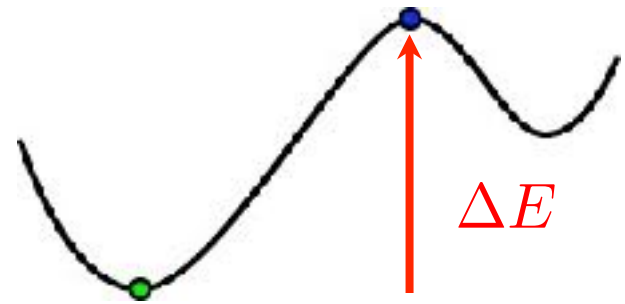
$$k_{\mathrm{TST}} = \frac{1}{2}\left\langle \delta(x - x^\dagger)|v_\perp|\right\rangle_R$$

Harmonic transition state theory

Find saddle points on the energy surface

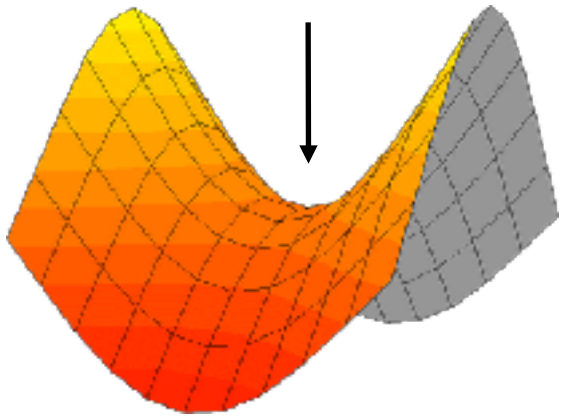
Rate of escape through each saddle point region:

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



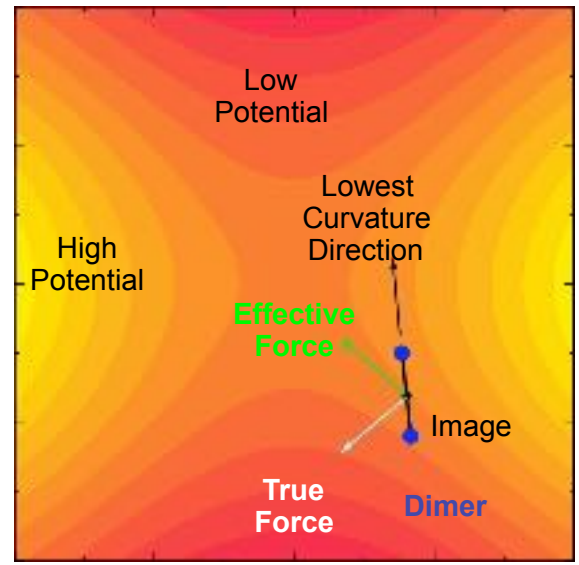
Methods for finding transition states

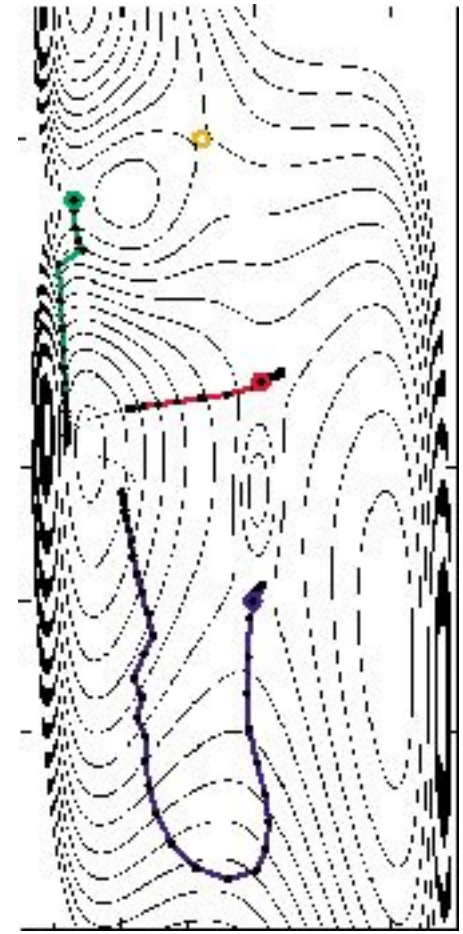
Find saddle points



Min-mode following:

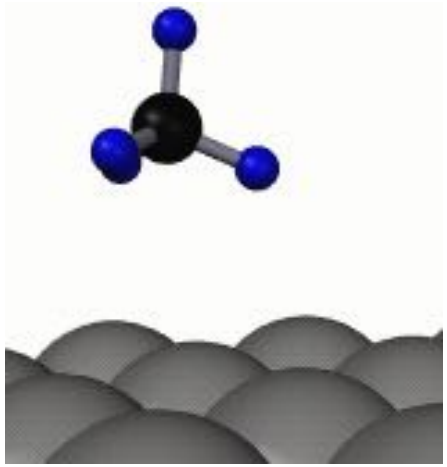
Unknown final state

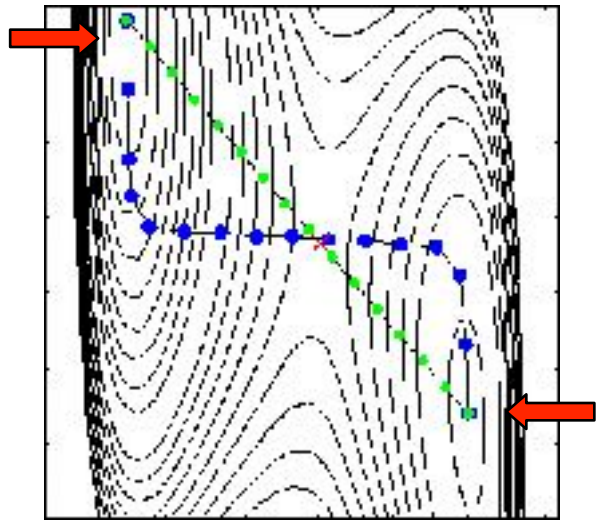


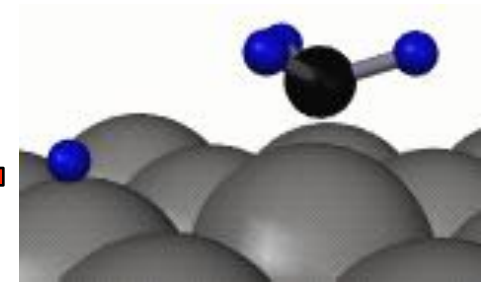


Nudged elastic band:

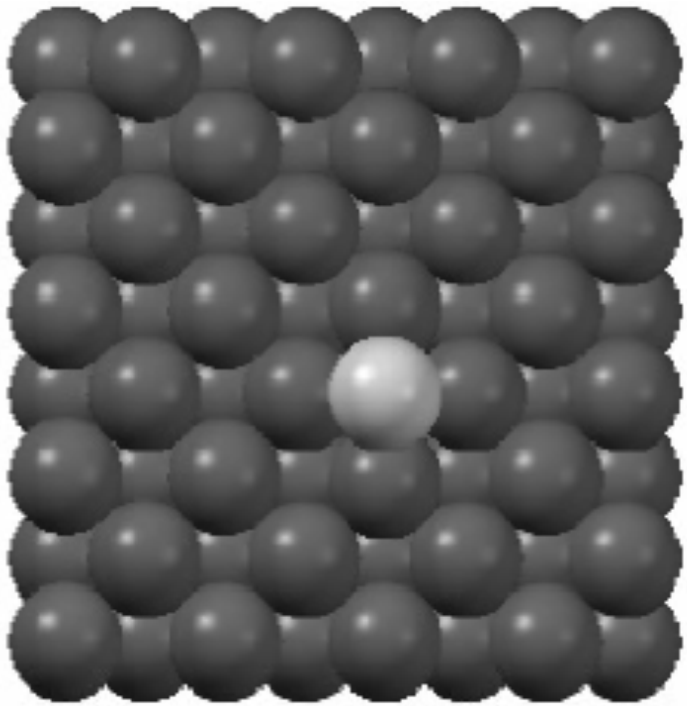
Known final state





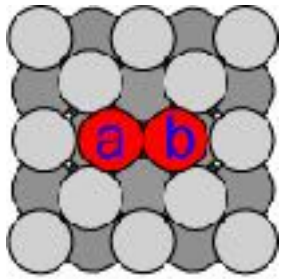


Adatom diffusion on Al(100)



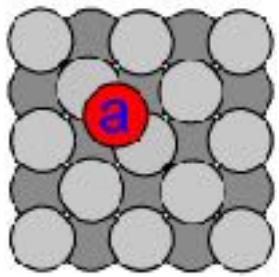
Statistics

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



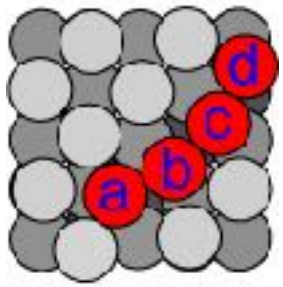
ΔE: **0.23** eV

ν: **7 ·10^{13}** s^{-1}



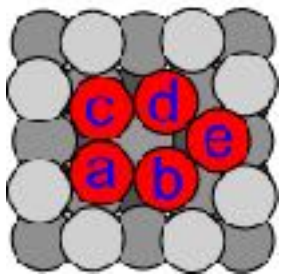
ΔE: **0.37** eV

ν: **5 ·10^{13}** s^{-1}



ΔE: **0.41** eV

ν: **2 ·10^{15}** s^{-1}

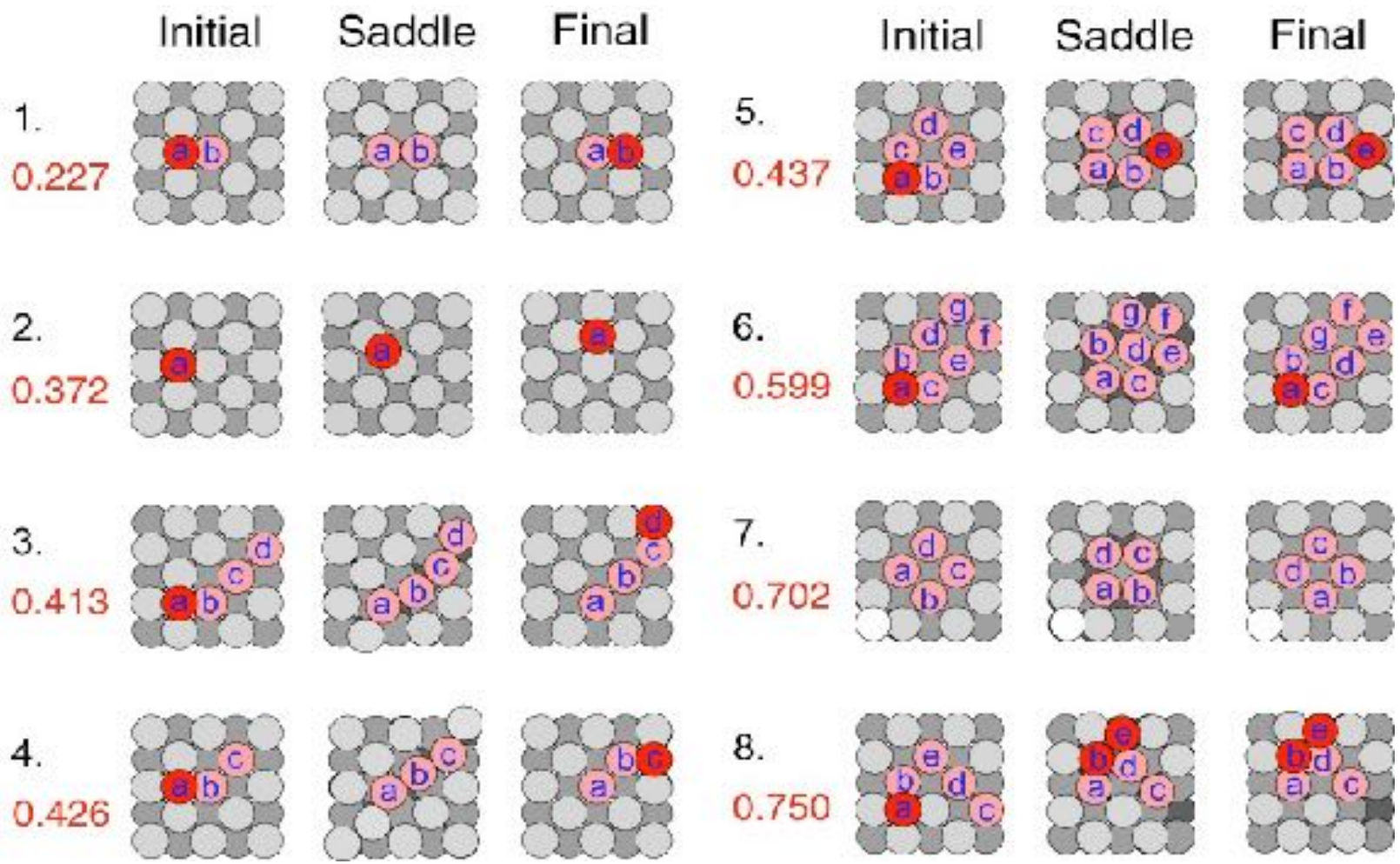


ΔE: **0.44** eV

ν: **3 ·10^{14}** s^{-1}

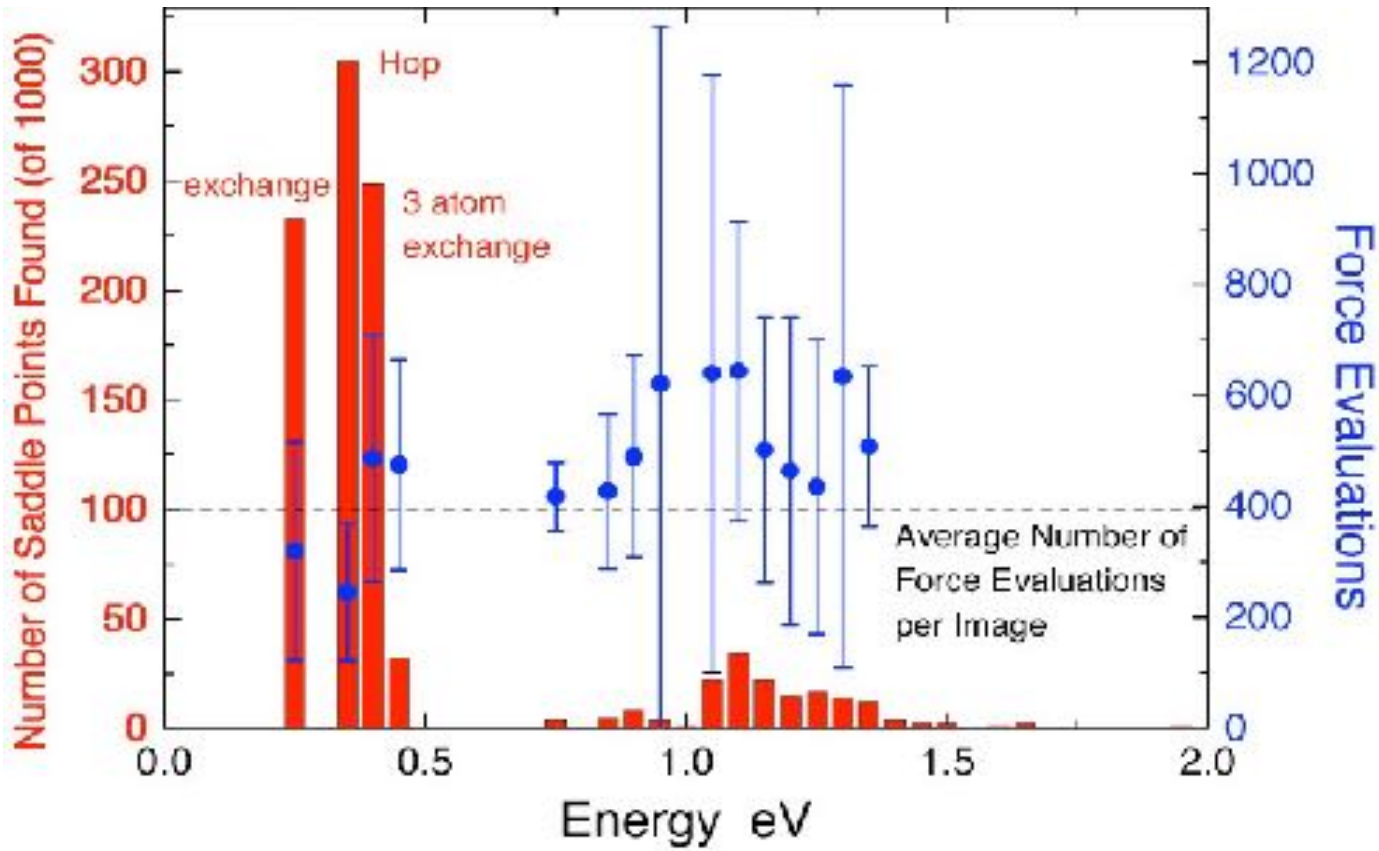
Adatom diffusion on Al(100)

Lowest energy mechanisms found in 1000 searches, using an EAM potential.



Dimer method: efficiency

The Good: 60 processes with energy less than 2 eV were found with 1000 searches with a relatively low computational cost.

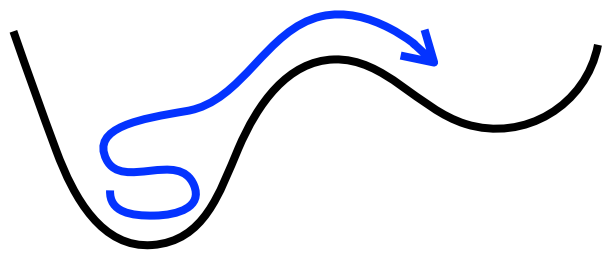


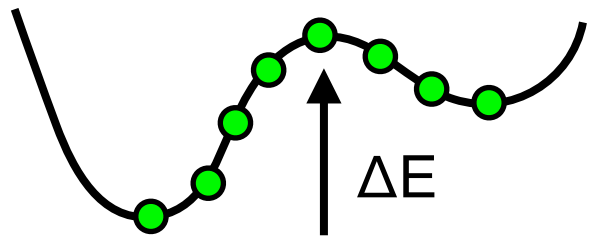
The Bad: some saddles are hard to find; it is hard to estimate how complete the event table is; some are not connected.

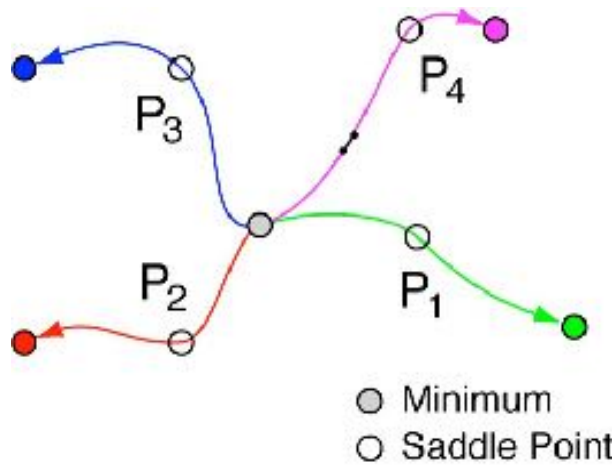
Molecular dynamics saddle search AKMC

Method:

1. Determine the initial state minimum.
2. Run high temperature MD until a minimization converges to a new minimum.
3. Use (for example) a nudged elastic band to find a saddle corresponding to the escape.
4. Calculate the TST escape rate and update the confidence in the rate table.
5. When an error estimator in the total escape rate drops below a desired value, use KMC to advance the simulation to a new state.
6. Repeat.







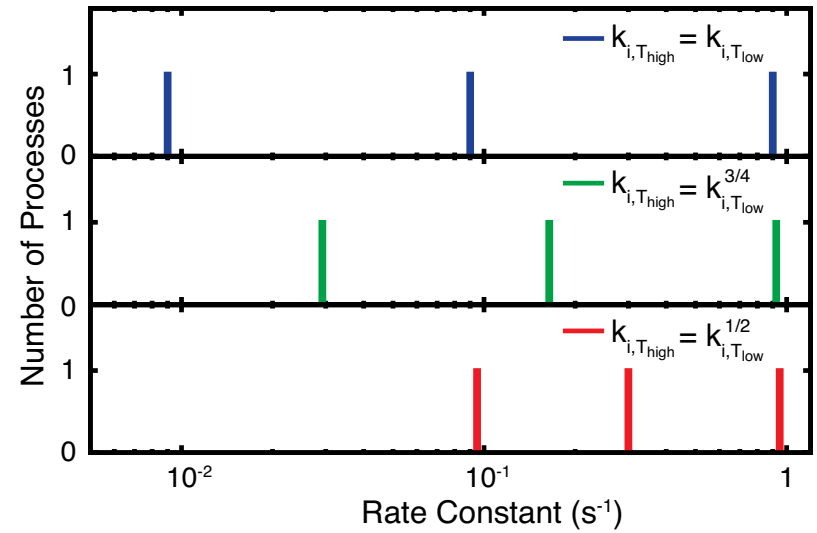
S. Chill and G. Henkelman *JCP* **140,** 214110 (2014)

MDSS rate table error estimator

Error in the rate table

$$E(\mathbf{F}) = 1 - \frac{1}{K} \sum_{k_i \in \mathbf{F}} k_{i,T_{\text{low}}}$$

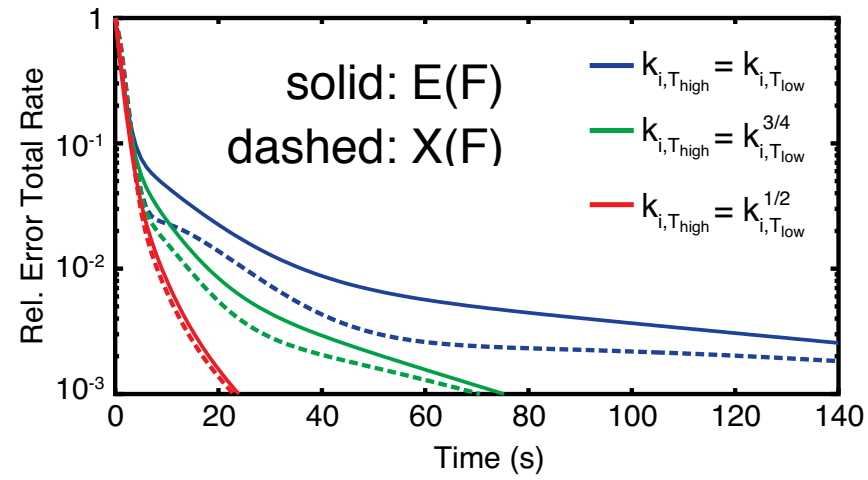
where **F** is the set of events found and *K* is the total rate



Probability of finding a saddle

$$p(t; k_i) = 1 - \exp(-k_i t)$$

for a process with rate k_i in MD time *t*



Approximate estimator for E(F)

$$X(\mathbf{F}) = 1 - \sum_{k_i \in \mathbf{F}} p(t; k_{i,T_{\text{high}}}) k_{i,T_{\text{low}}} \Big/ \sum_{k_i \in \mathbf{F}} k_{i,T_{\text{low}}}$$

assume the k_i found in **F** are characteristic of the full set in *K*

MDSS: Efficiency

1. Pt heptamer

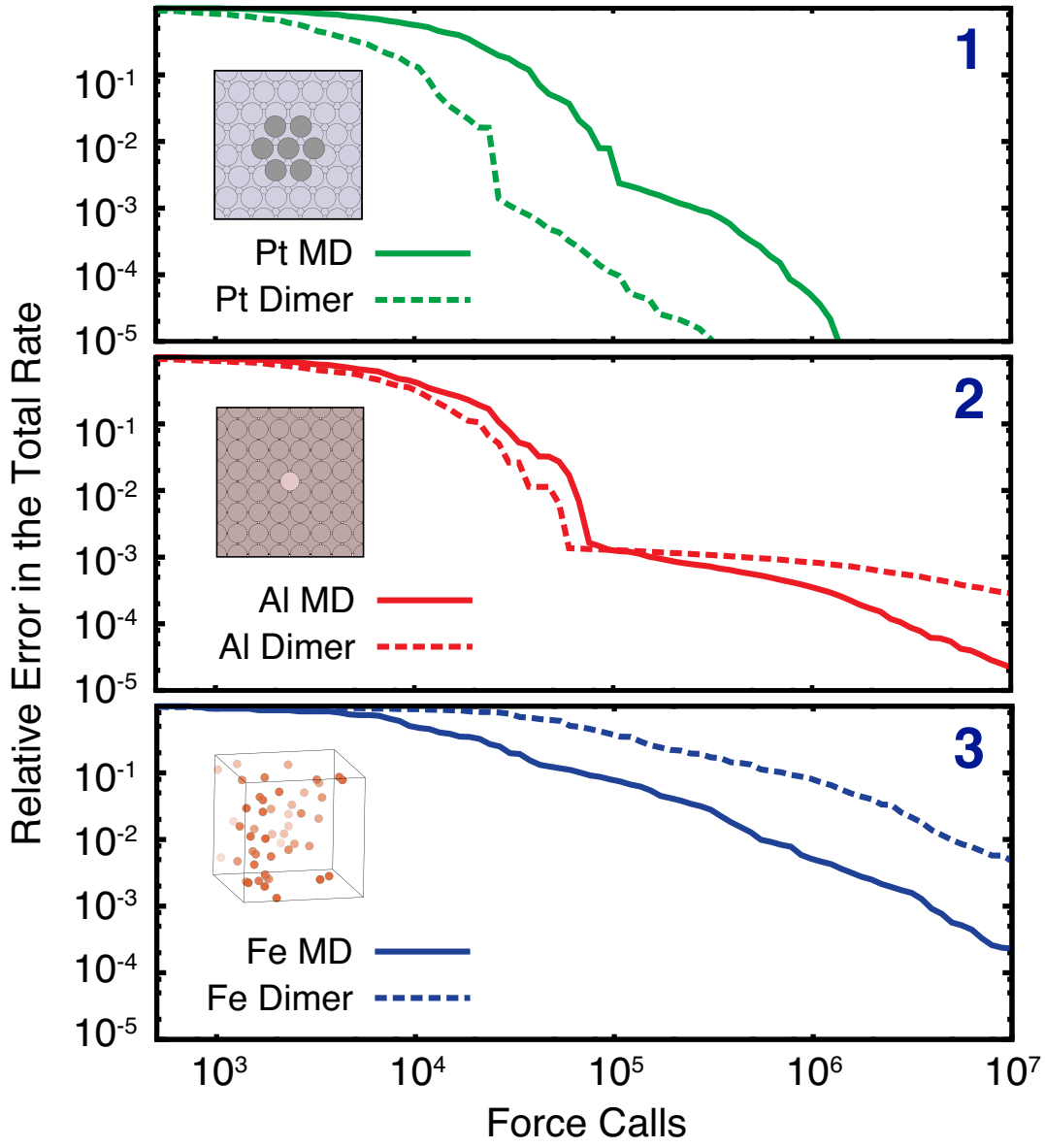
dimer quickly finds the few important saddles

2. Al adatom

more complicated processes are found by both methods

3. Fe vacancies

many processes available with only a few contributing significantly to the rate; dimer must find all of them



More importantly

MDSS has an accurate error estimator; min-mode searches do not

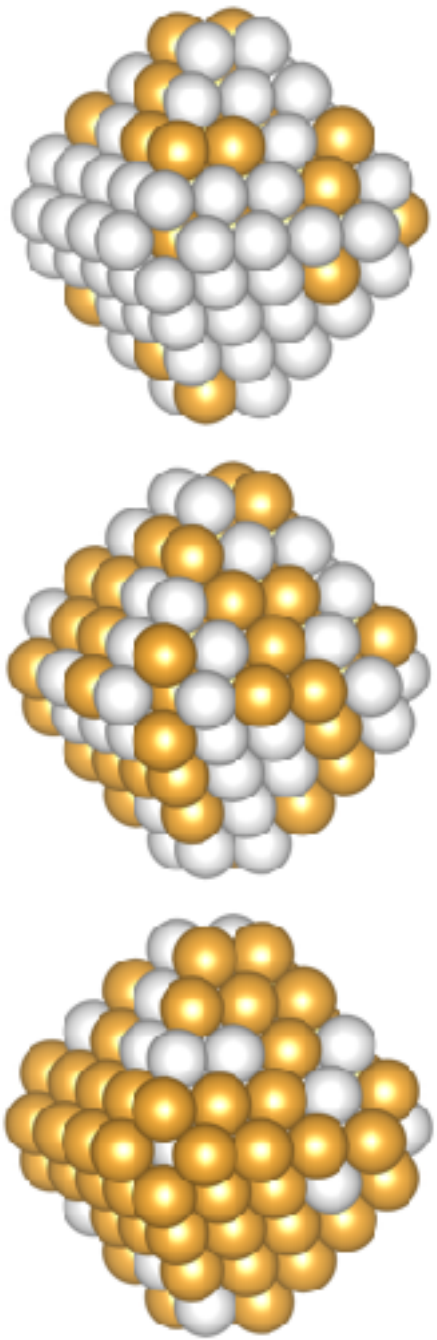
EON code

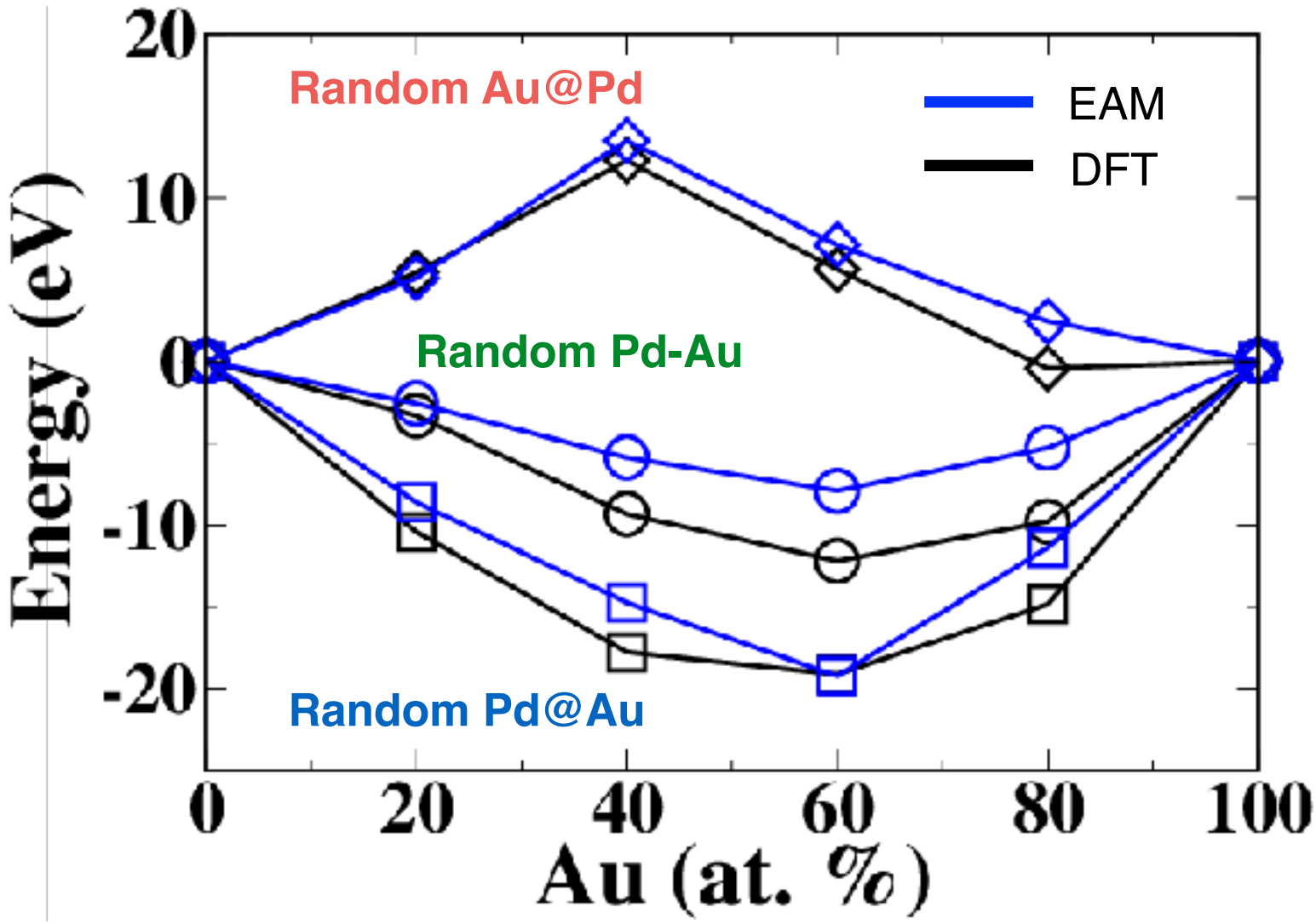
http://theory.cm.utexas.edu/eon/

- Adaptive KMC
- Parallel replica method
- Hyperdynamics using bond boost method
- Molecular dynamics
- Saddle search: NEB, Dimer, Lanczos
- Minimization: LBFGS, FIRE, CG
- Use vasp, lammps for energy and force

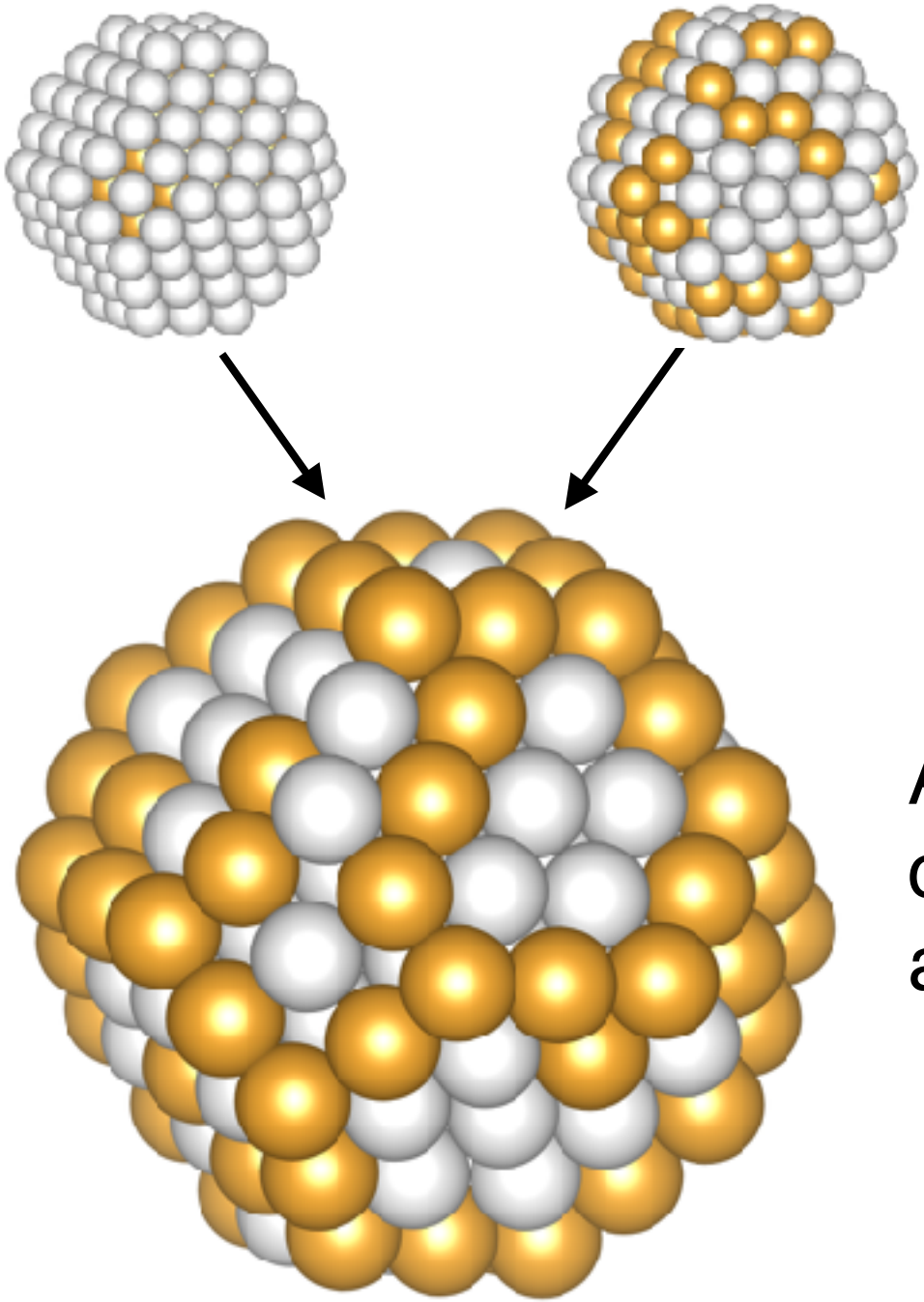
S. T. Chill et al., Model. Simul. Mater. Sci. Eng. **22**, 055002 (2014)

Surface Segregation Tendency in Pd-Au





Pd-Au Monte Carlo simulations

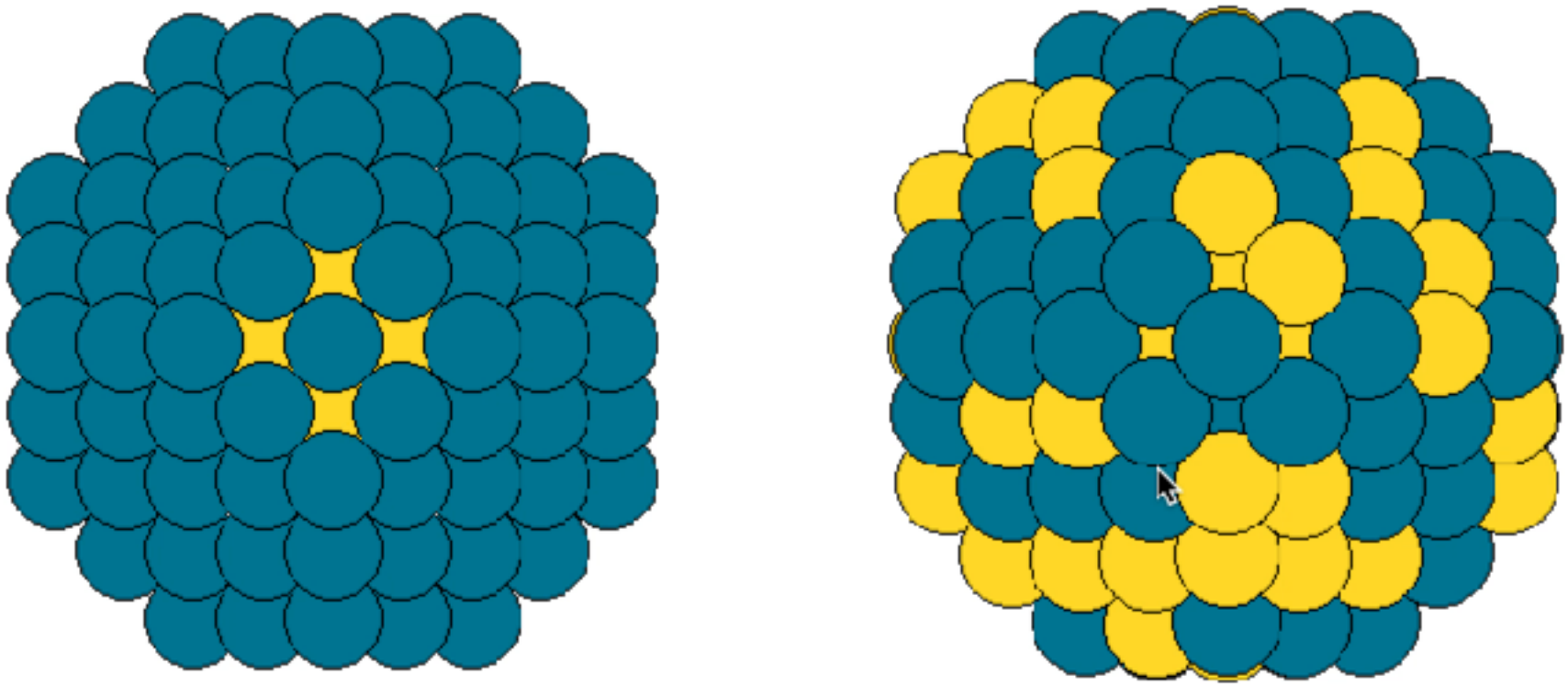


201 atoms in total
122 Pd l 79 Au

MC at 600K

Au surface segregation occur preferentially at corner and edges

Results of AKMC



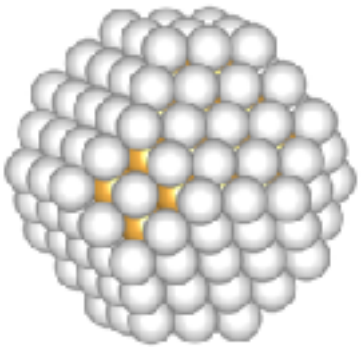
Fastest path: eliminate processes jumping back and forth between states.

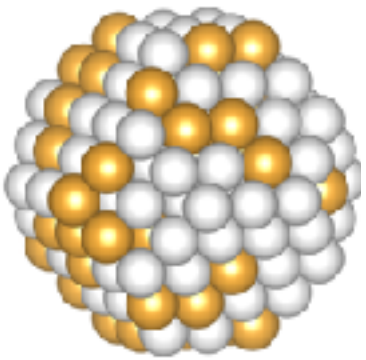
AKMC temperature: 600K

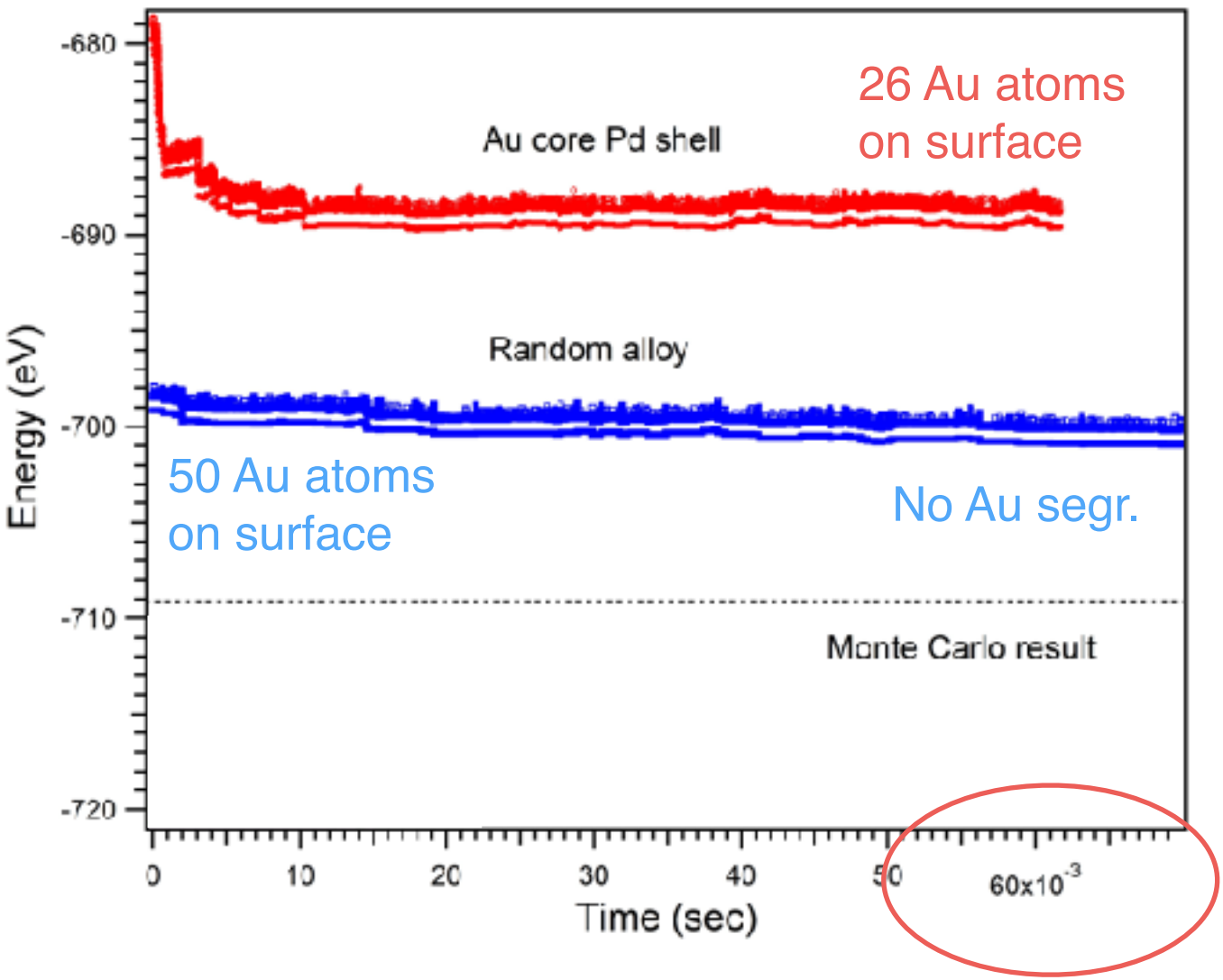
MDSS: 2000K

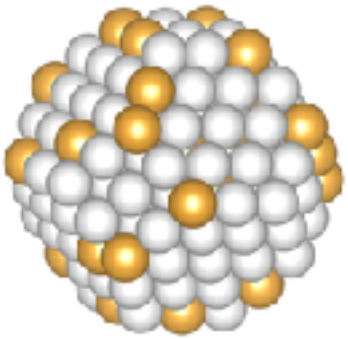
Results of AKMC

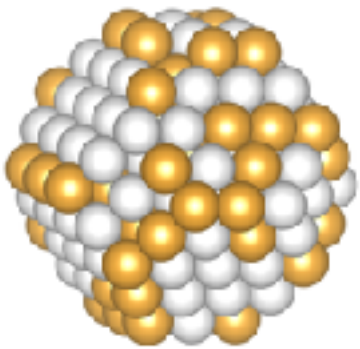
Simulated time ~60 ms, ~15000 unique states, ~85000 transitions



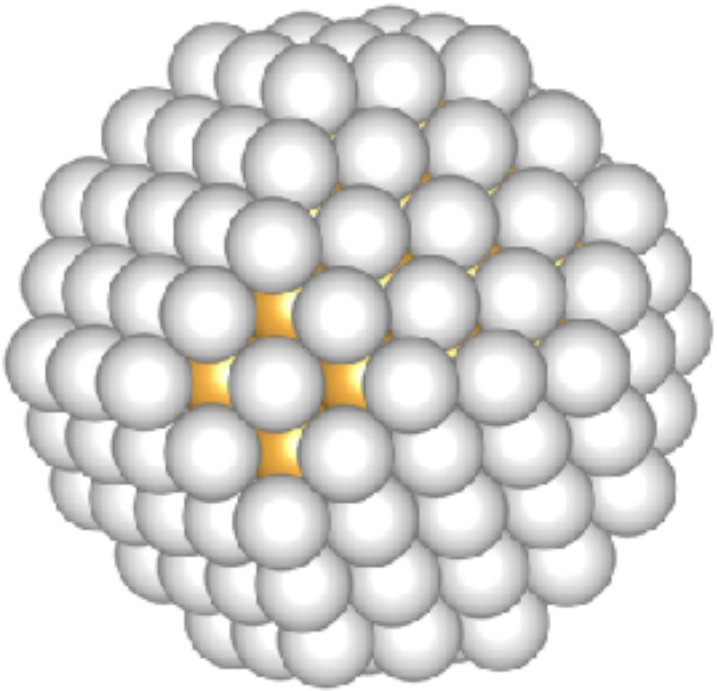


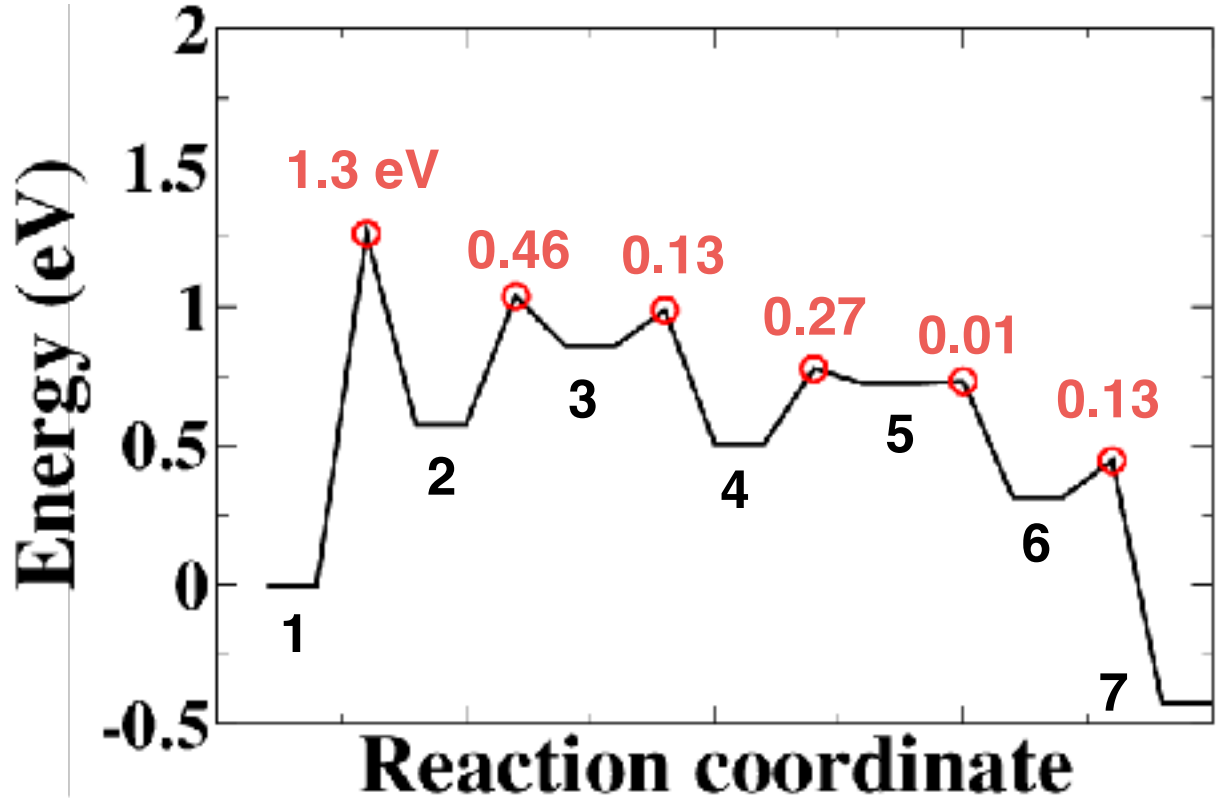


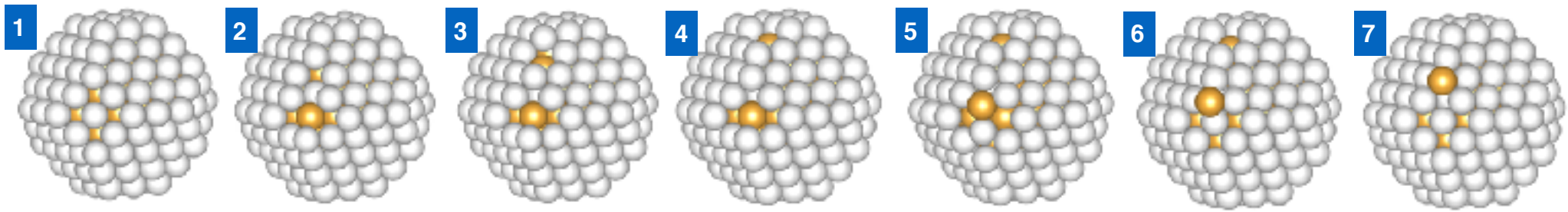




Au surface segregation process 1

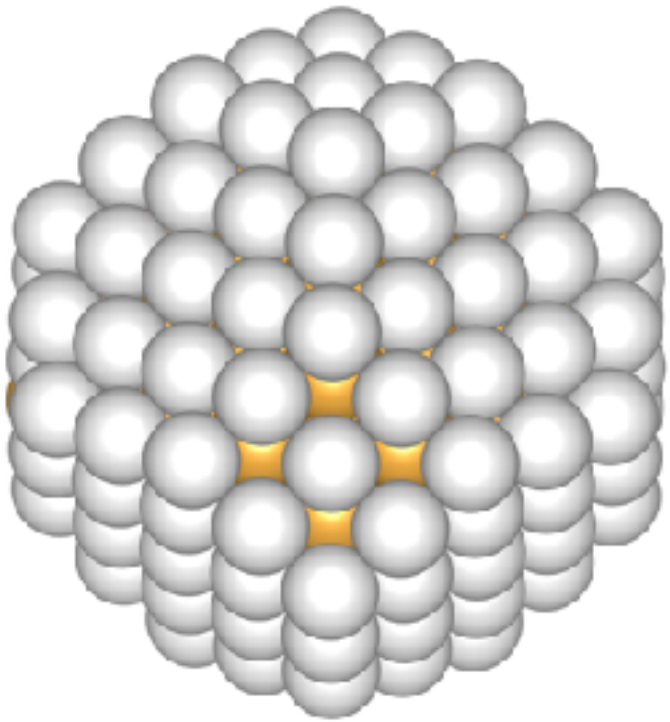


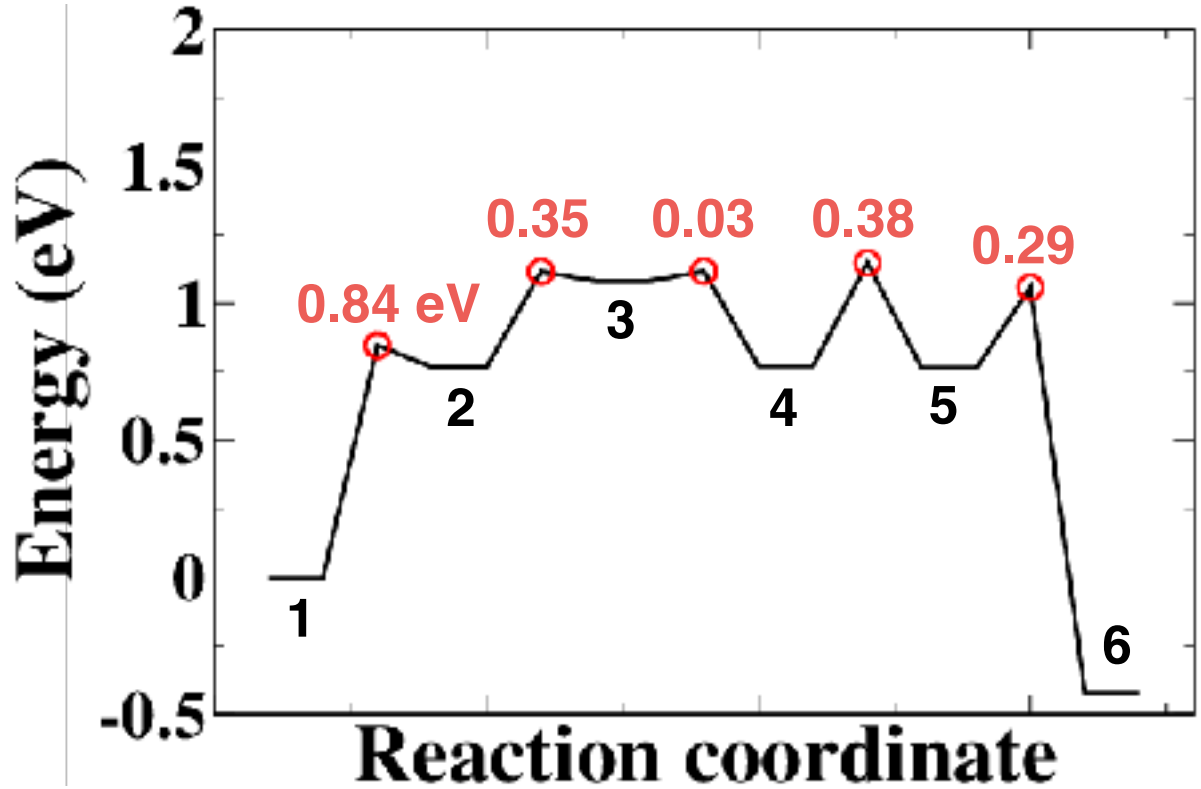


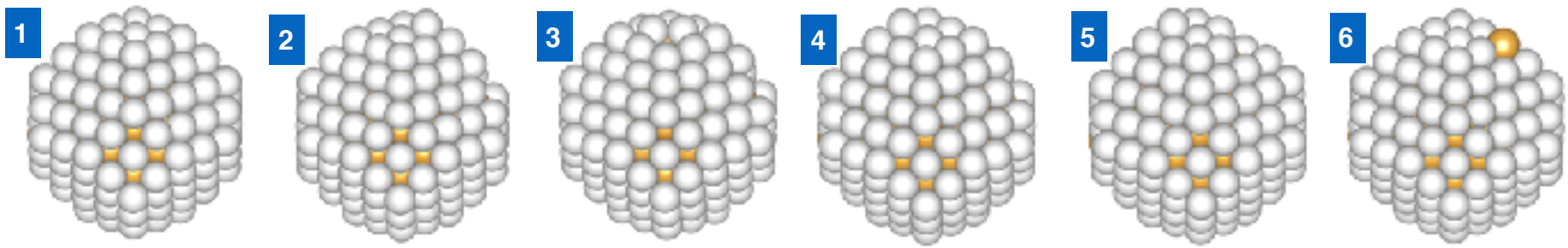


1-2: edge Pd push downward leading to Au surface segregation and generation of Pd adaatom and surface vacancy.
2-3 and 3-4: Pd diffusion along edge
4-5 and 5-6: exchange process on 100 surface;Au adatom generation
6-7: 3-atom linear chain diffuse along the edge to fill the vacancy

Au surface segregation process 2

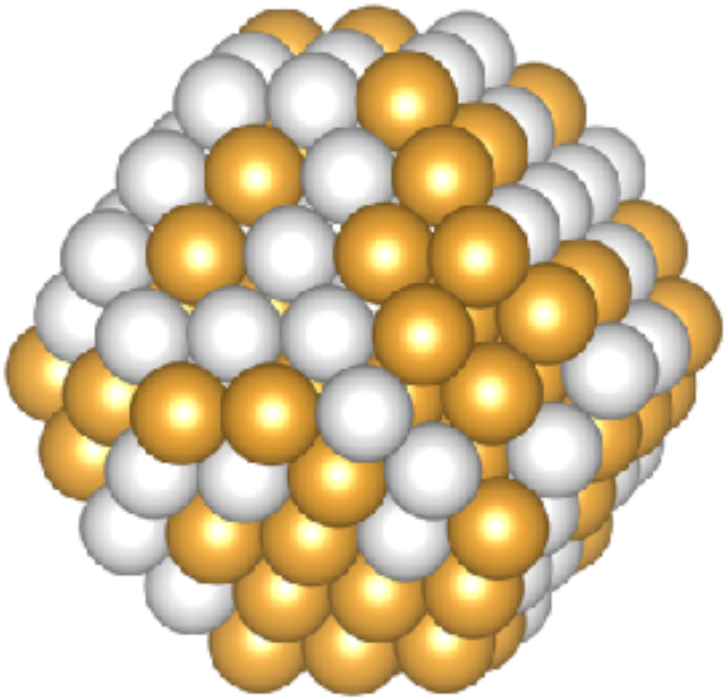


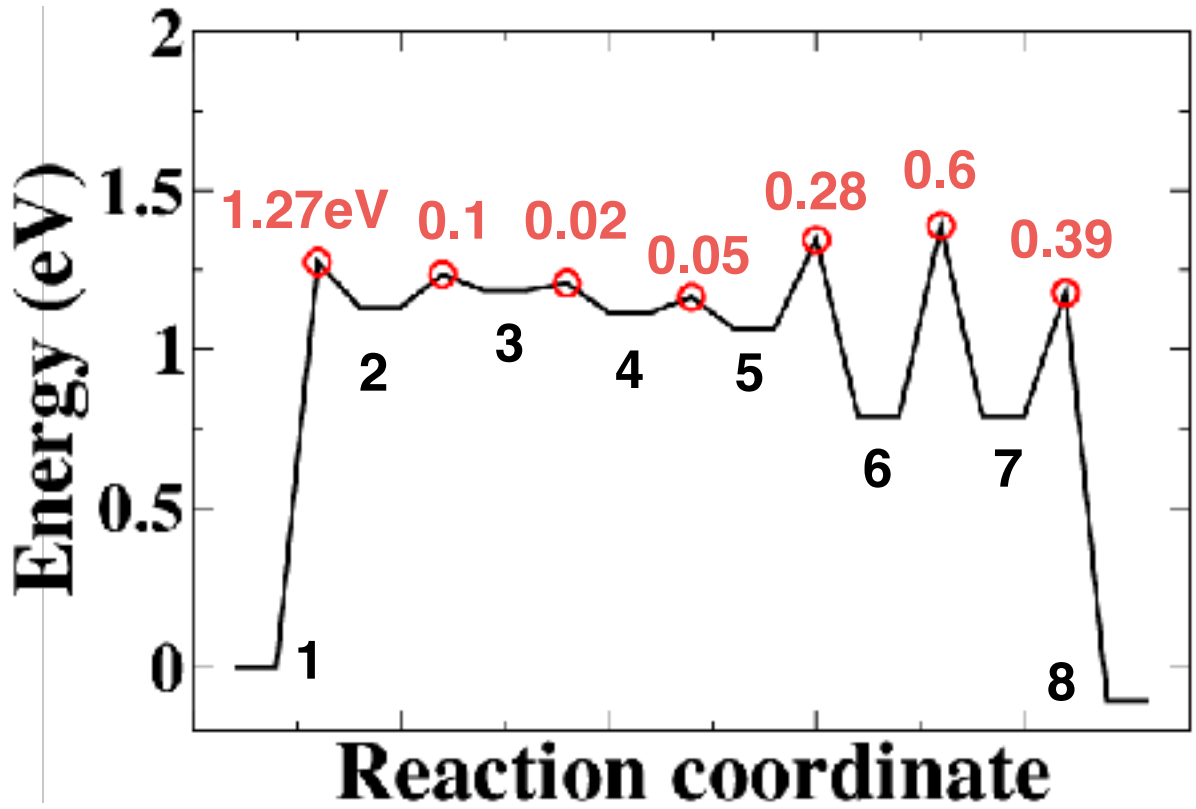


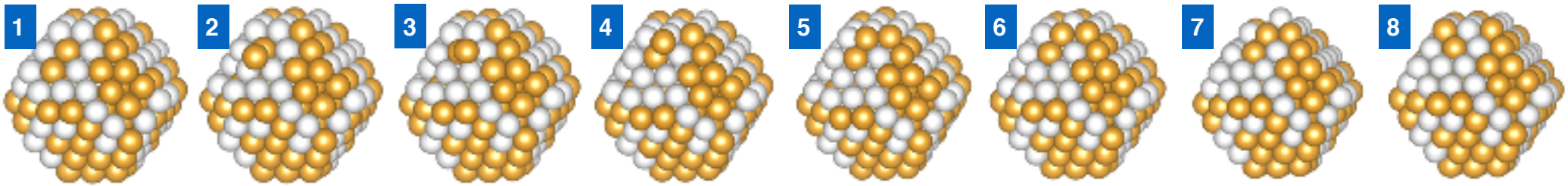


1-2: 3-atom linear chain diffusion along the edge; generation of Pd adaatom and surface vacancy.
2-3 and 3-4: Pd adatom diffusion via exchange
4-5: vacancy diffusion along edge via a Pd dimer hop
5-6: Pd adatom push downward leading to Au segregation

Rearrangement of surface atoms

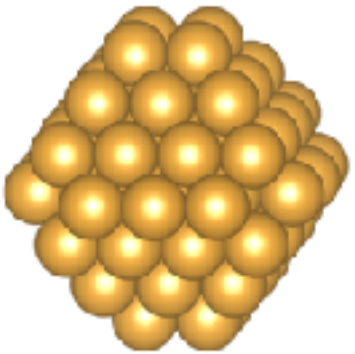


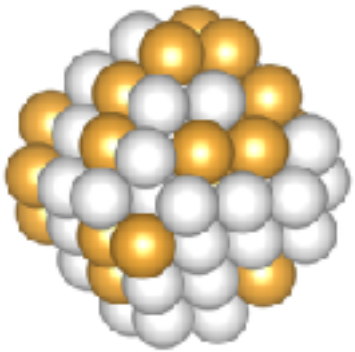


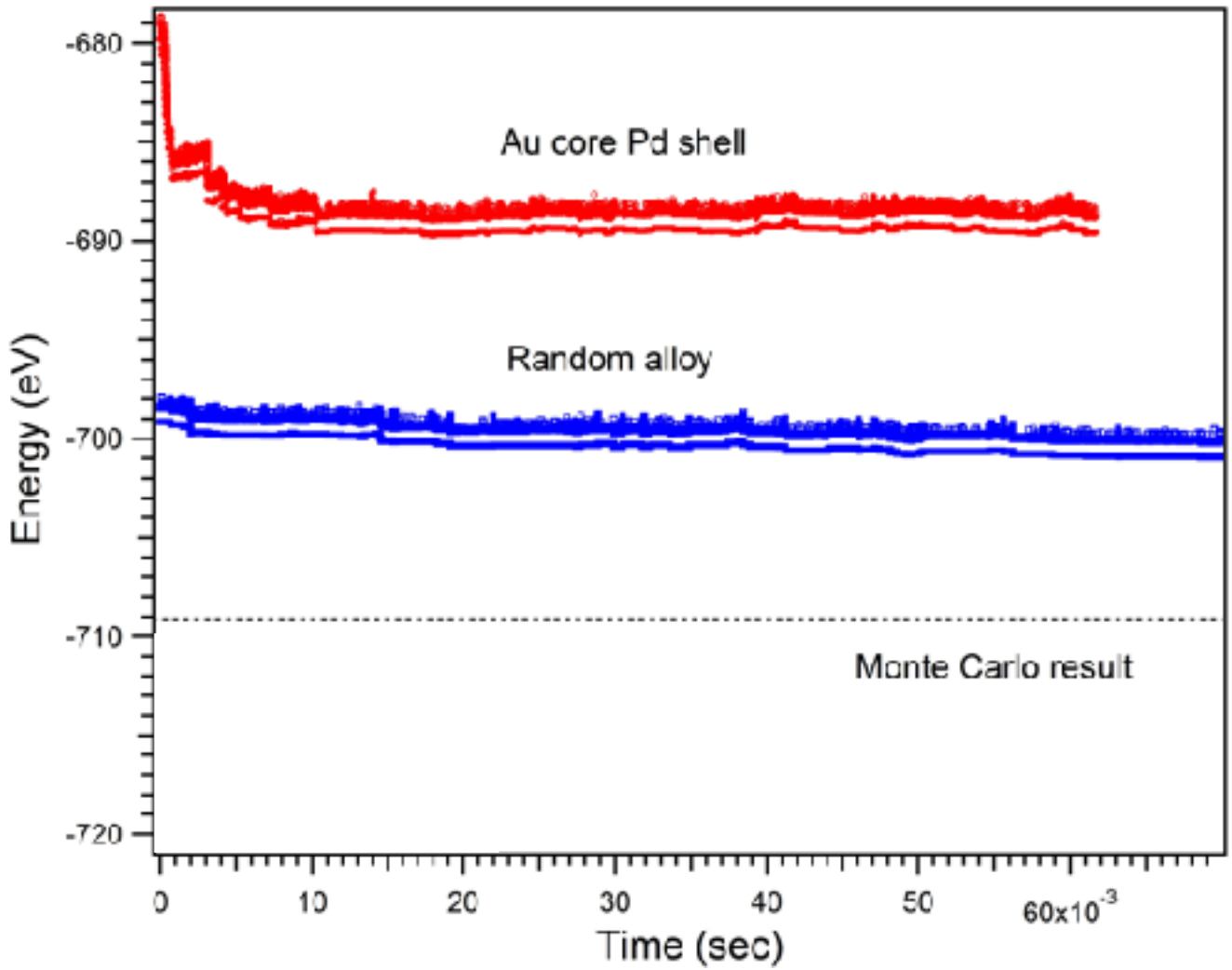


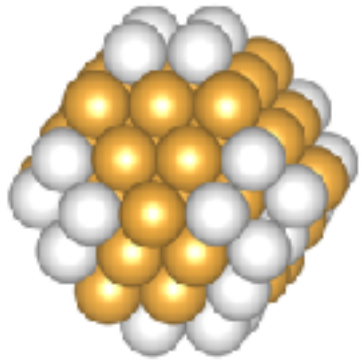
1-2: Pd atom push into facet; generation of Au adatom and surface vacancy
2-3 and 3-4: Au adatom hopping
4-5: formation of a 4-atom chain at 100 facet.
5-6: 4-atom chain decay to form a Pd adatom
6-7: vacancy diffusion
7-8: Pd adatom push Au atom to fill the vacancy

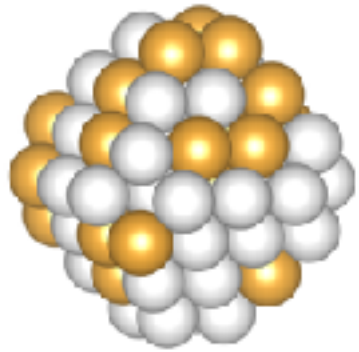
Kinetic trapping



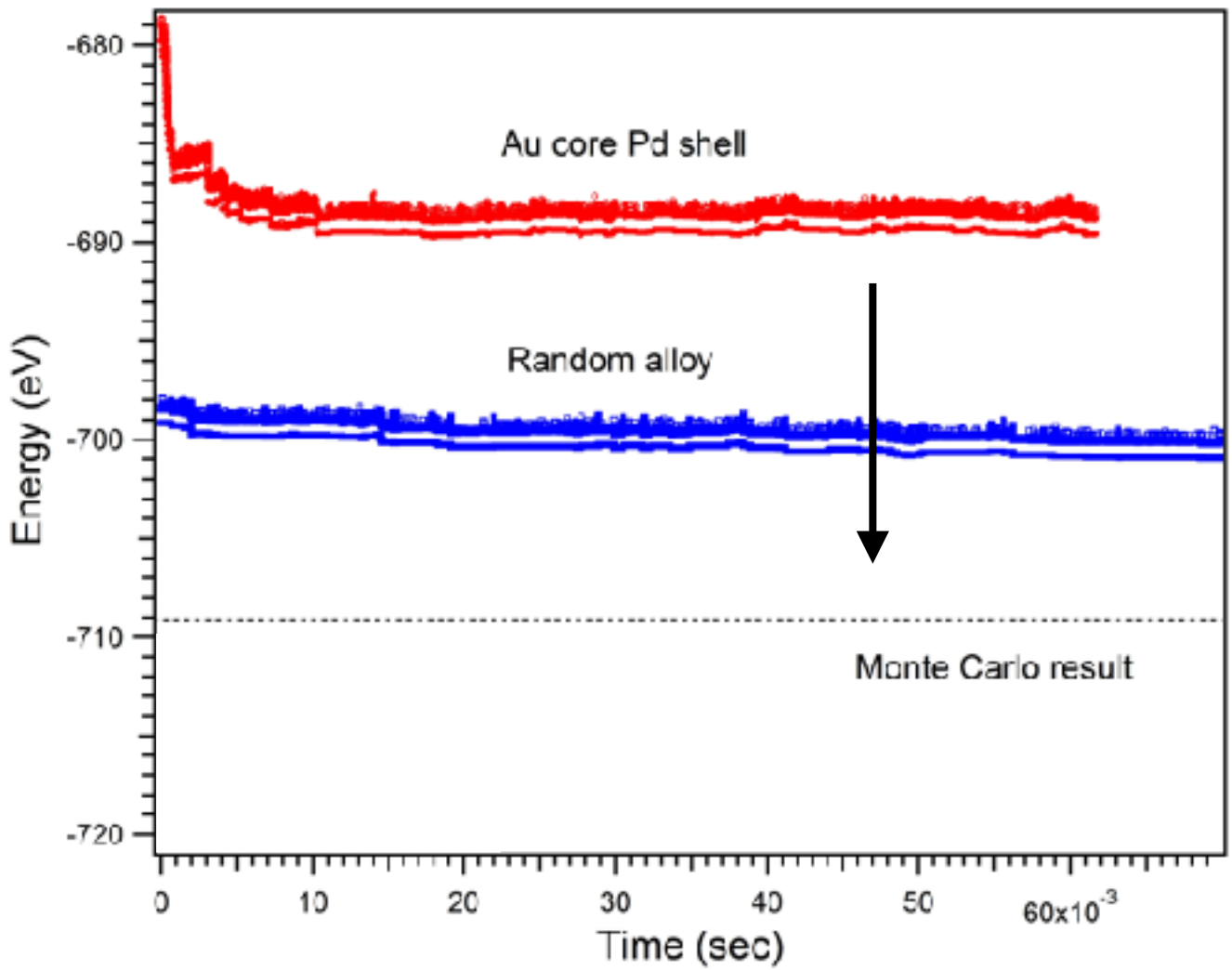








Challenges


-680
-690
-700
-710
-720
Energy (eV)
Au core Pd shell
Random alloy
Monte Carlo result
0
10
20
30
40
50
60x10^-3
Time (sec)

Thank you !