## Long Timescale Simulations Using the KMC Method Without Having to Generate a Predefined Rate Table

Hannes Jónsson, Univ. of Iceland, hj@hi.is

See lecture notes at www.hi.is/~hj

Motivation: Unexpected transition mechanisms

Use a method for finding mechanism and estimate rate of atomic rearrangements without specifying final states.

Long time scale simulations using kinetic Monte Carlo with event tables created from saddle point searches.



Applications:

- 1. crystal growth simulations
- 2. grain boundary annealing and diffusion
- 3. diffusion and islanding of water molecule(s) on ice surfaces

#### CECAM workshop

#### Simulations of long time scale dynamics, molecular and continuum descriptions

June 26-30. 2000

Held at the University of Iceland, Reykjavík

Organizers: Hannes Jónsson and Giovanni Ciccotti



### **Kinetic Monte Carlo**

- Assign atoms to a lattice.
   Create a table of possible transitions and assign a rate to each transition.
   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.
- 5. Increment time by an amount  $\Delta t = \ln z / \Sigma r_i$

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



- Need to assign atoms to a lattice
- Need to create a table of transitions and their rates, typically based on nearest neighbors, most often rates fitted to exp. data.

#### **Rates estimated using a potential energy function and HTST**

PHYSICAL REVIEW B

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**15 NOVEMBER 1986** 

#### Classically exact overlayer dynamics: Diffusion of rhodium clusters on Rh(100)

Arthur F. Voter

Theoretical Division (Mail Stop J569), Los Alamos National Laboratory, University of California, P.O. Box 1663, Los Alamos, New Mexico 87545 (Received 30 June 1986)

A new method is presented for describing the classical dynamics (e.g., diffusion, desorption) of adsorbed overlayers of atoms or molecules, starting from arbitrary interatomic potentials. Provided that a certain dynamical criterion is met, the method yields classically exact results, but with many orders of magnitude less computation than direct molecular dynamics. The approach provides, for what we believe to be the first time, a connection between stochastic lattice-gas dynamical methods and the interatomic potential function. As a sample application, the diffusion constants are computed for two-dimensional rhodium clusters of up to 75 atoms on the Rh(100) surface at T=2000K. For clusters larger than n=15 atoms, the diffusion constant scales as  $n^{-1.76\pm0.06}$ , and the dominant mechanism for the diffusion is found to be atoms running along the edges of the cluster blocks.



FIG. 6. Diffusion constants for  $Rh_n$  clusters on Rh(100). Units for  $D_n$  are cm<sup>2</sup> sec<sup>-1</sup>.



FIG. 8. Diffusion pathway for n=5 cluster, effecting repli-

#### Rates in KMC table estimated using DFT calculations

#### Example 1:

Diffusion of Si adatom on Si(100) surface and formation of dimers Activation energy calculated using PW91 functional (a GGA functional)

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PHYSICAL REVIEW LETTERS

12 AUGUST 1996

#### **Dimer and String Formation during Low Temperature Silicon Deposition on Si(100)**

A.P. Smith<sup>1</sup> and H. Jónsson<sup>1,2</sup>

<sup>1</sup>Department of Chemistry, University of Washington, Box 351700, Seattle, Washington 98195-1700 <sup>2</sup>Center for Atomic-Scale Materials Physics, Department of Physics, Technical University of Denmark, DK-2800 Lyngby, Denmark (Received 13 March 1996)

We present theoretical results based on density functional theory and kinetic Monte Carlo simulations of silicon deposition and address observations made in recently reported low temperature scanning tunneling microscopy studies. A mechanism is presented which explains dimer formation on top of the substrate's dimer rows at 160 K and up to room temperature, while between-row dimers and longer strings of adatoms ("diluted dimer rows") form at higher temperature. A crossover occurs at around room temperature between two different mechanisms for adatom diffusion in our model. [S0031-9007(96)00849-6]

#### Controversy:

STM images show dimers form preferably *on top* of dimer rows, while DFT gives lowest energy for dimers *in between* rows, and SW empirical potential gives lowest energy in between rows ...

## **Unexpected transition mechanisms** Example 1: Al adatom diffusion on Al(100)





### **Example 2:** Key processes in crystal growth

Lowest energy barrier for down-stepping of a Pt adatom on top of a Pt(111) island is *near* but not *at a* kink!

Energy barriers do NOT scale with energy difference between initial and final states



Explains unexpected temperature dependence observed in crystal growth (Poelsema *et al.*).

- High temperature, T = 620 K: layer-by-layer growth
- Intermediate temperature T = 425 K: multilayer growth
- Low temperature, T = 275 K: re-entrant layer-by-layer growth

Leads to formation of more kinks. (HJ, *Annals of Physical Chemistry* 2000, Fractal islands at low temperature, T = 275 K . A. Ali and HJ, Surfaces&Interfaces 2022)

## **Example 2,** continued: Diffusion of a Pt adatom on an island on Pt(111)



Ehrlich-Schwöbel barrier for descent of an adatom at a step



Long range interaction due to strain! Not enough to tabulate rates based on nearest neighbors.

AKMC simulations using a turbo-GAP potential for Pt (Kloppenburg, L. B. Pártay, H. Jónsson and M. A. Caro, J. Chem. Phys. 2023) Agrees well with FIM measured visitation map (Ehrlich and co. 1996)

### **Example 3:** Au adatom diffusion on Si(100) surface



(A. Pena-Torres, A. Ali, M. Stamatakis, HJ, Phys. Rev. B 2022)

# Rumsfeld processes

"Unknown unknowns are risks that come from situations that are so unexpected that they would not be considered"

(Donald Rumsfeld, US Secretary of Defense, February 12, 2002).



Important NOT to simply assume the mechanisms and final states of processes, rather obtain these as output from the simulations!

#### Need to find low energy saddle points

The given initial state of the system corresponds to a local minimum on the energy surface.

Within harmonic approximation to transition state theory (HTST), need to find all the relevant saddle points on the energy rim surrounding the current state minimum (here labeled 1, 2, 3 and 4).



1. The transition state is a first order saddle point (what does TS mean?).

2. Transition state theory estimate of the rate constant is most accurate if there is a dip in the energy surface near the top of the potential energy curve (*see picture in Atkins' P-Chem book*).



Reaction coordinate

3. Transition state theory assumes strong coupling to the heat bath so that a Boltzmann distribution of energy is maintained as the system climbs up the potential energy surface. Minimum mode:

Found using dimer method, or Lanczos, or Davidson algorithms.

Use only first derivatives of the energy.

No need to even construct the Hessian matrix!

Then, transform the force by inverting the component along the minimum mode,  $\hat{\mathbf{V}}_{i min}$ 

 $\mathbf{F}_{i,eff} = \mathbf{F}_{i} - 2(\mathbf{F}_{i} \cdot \hat{\mathbf{v}}_{i,min}) \hat{\mathbf{v}}_{i,min} \quad \text{if min eigenvalue} < 0$  $= - (\mathbf{F}_{i} \cdot \hat{\mathbf{v}}_{i,min}) \hat{\mathbf{v}}_{i,min}$  else



J. Chem. Phys. (1999)

Then can use any force based minimisation to converge on the saddle point.







basins of attraction

#### Only the initial state minimum needs to be given (not final state)

- No (or little) bias from preconceived notion of the mechanism, typically displace under-coordinated atoms and their neighbors (e.g. spherical region).
- Can discover unexpected mechanisms and final states.

Include force perpendicular to the minimum mode only when the lowest eigenvalue is negative.



# Adaptive Kinetic Monte Carlo (AKMC) (off-lattice, self-learning, on-the-fly, k-ART, ...)

#### Obtain a table of possible transitions from a given minimum:

- Locate first order saddle points that are adjacent to the current state minimum on the PES.
- Slide down PES, to determine possible product states (and check connectivity to the initial state).
- Estimate rate using harmonic approximation to transition state theory.



G. Henkelman and HJ, `Long time scale KMC simulations without lattice approximation and predefined event table', *J. Chem. Phys.* **115**, 9657 (2001).

### Adaptive Kinetic Monte Carlo

- 1. Find low energy saddle points near the current minimum using multiple SP searches started at random (Gaussian distributed)
- 2. Find the prefactor, v, from normal mode analysis and calculate the rate of each process  $r_i = V e^{-\Delta E_i / k_B T}$
- 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  $\Delta t = \ln z / \Sigma r_i$

Repeat 1 - 5 until the desired time interval has been reached (Henkelman and Jónsson, J. Chem. Phys. 2001)



- 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 AKMC simulations

Multiple length scales:

from atomic scale (Ångström) to macroscopic length (meter)

Multiple time scales:

from atomic vibrations periods to time scale of thermally activated transitions



Multiple length scales:

from atomic scale (Ångström) to macroscopic length (meter)

Multiple time scales:

from atomic vibrations periods to time scale of thermally activated transitions



#### **ReaxPro:** Multiscale simulation software for heterocatalysis

Horizon2020 network of 10 research groups



Software suite for simulations, ranging from atomic scale calculations using DFT on small systems, using MMF calculations to identify mechanism and estimate rates of elementary reactions, to reactor scale simulations including mass transport.



# EGIN software, originally for distributed AKMC calcs.

- Can 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 VASP to obtain atomic forces, or LAMMPS, or ...
- Implementation
  - Client side C++
  - Server side Python



Several additional tricks to improve efficiency:

Systematic coarse-graining (see below), recycling, skipping path ...

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

## **OptBench**

#### **Saddle Search Benchmark**





Entries for these benchmarks must record the average number number of force calls as *force\_calls* in benchmark.dat, the standard error as *force\_calls\_mean\_error*, the average fraction of saddles that are connected to the initial minimum as *fraction\_connected*, the average to searches *total\_searches*, and the average number of unique saddles found *unique\_saddles*.

#### **Pt Heptamer Island**

This benchmark measure the effiency of finding saddles for a Pt heptamer island. The initial geometry is provided in con and POSCAR form is given by a Morse potential:

$$V(r) = D(e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)})$$

with D = 0.7102,  $\alpha = 1.6047$ , and  $r_0 = 2.897$ .

The goal of the benchmark is to deterimine how many force calls it takes to find the 27 connected saddles with a barrier below 1.5 eV. A inconsidered complete when the norm of the force is reduced to below 10<sup>-3</sup> eV/Angstrom.

In the table below  $\rho$  is the fraction of saddles found that were connected to the initial minimum, N<sub>u</sub> is the number of unique connected sade number of saddle searches, and N<sub>f</sub> is the total number of force calls.

| Entry  | N <sub>f</sub>    | ρ    | Ns    | Nu  |
|--|-------------------|------|-------|-----|
| <pre>adaptive_HSphere-lbfgs-davidson-sm50</pre>            | 4.2e+05 ± 1.8e+05 | 0.80 | 1738  | 115 |
| <pre>adaptive_HSphere-lbfgs-lanczos-sm50</pre>             | 8.1e+05 ± 3.1e+05 | 0.90 | 3072  | 143 |
| <pre>adaptive_HSphere-lbfgs-lanczos-sm0</pre>              | 1.0e+06 ± 4.2e+05 | 0.90 | 2752  | 130 |
| eon-dimer-lbfgs-5-rotations-20-bowl_breakout <sup>1</sup>  | 1.3e+06 ± 4.1e+05 | 0.85 | 6560  | 126 |
| eon-md   | 1.5e+06 ± 1.2e+05 | 0.89 | 800   | 52  |
| eon-dimer-lbfgs-5-rotations <sup>1</sup>                   | 1.7e+06 ± 5.5e+05 | 0.75 | 4665  | 113 |
| eon-dimer-lbfgs-20-rotations-20-bowl_breakout <sup>1</sup> | 2.7e+06 ± 1.2e+06 | 0.80 | 7772  | 101 |
| eon-dimer-lbfgs-20-rotations <sup>1</sup>                  | 3.3e+06 ± 1.6e+06 | 0.75 | 9666  | 108 |
| eon-dimer-cg-5-rotations-20-bowl_breakout <sup>1</sup>     | 3.5e+06 ± 2.2e+06 | 0.70 | 5312  | 125 |
| eon-dimer  | 3.8e+06 ± 5.3e+05 | 0.75 | 11367 | 109 |
| eon-dimer-cg-20-rotations-20-bowl_breakout <sup>1</sup>    | 7.2e+06 ± 2.9e+06 | 0.75 | 11850 | 123 |
| eon-dimer-cg-20-rotations <sup>1</sup>                     | 7.9e+06 ± 2.7e+06 | 0.63 | 12618 | 122 |

(a)

(c)

(g)





Initial state

saddle points



#### final states











(f)

Figure 5. Initial state and three of the transitions in the benchmark system. (a and b) initial state, on-top and side view; (c) saddle point with E = 0.986 eV and (d) corresponding final state; (e) saddle point with E = 1.197 eV and (f) corresponding final state. (g) saddle point with E = 1.494 eV and (h) corresponding final state.

## 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.

Also, use Davidson with preconditioner derived from approximate Hessian, starting from numerical evaluation at initial state.

(M.P. Gutiérrez, C. Argáez and HJ, *JCTC* 13, 125 (2017))









Place 504 points on a 21 dimensional hypersphere and optimize in such a way as to maximize the distance between the points.

Figure 6. Efficiency of saddle point searches started from a regular arrangement of points on a hypersphere (see Figure 4, left) as a function of the hypersphere radius. (Top) The number of saddle points found increases as the radius is increased and the number of function evaluations needed in each saddle point search also increases. (Bottom) The number of saddle points found that are connected to the initial state minimum (black filled circles) has a maximum at around 2.3 Å. The number of connected saddle points with energy  $\leq 4.0 \text{ eV}$  (red filled circles) has a maximum for a similar radius, and the number of low energy saddle points with  $\leq 1.5 \text{ eV}$  (blue filled circles) drops when the radius is larger than 2.1 Å. Each data point represents the mean value obtained from 500 saddle point searches.

## Systematic 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<sub>B</sub>T higher (as in regular KMC simulations)





Coarse graining

- A composite state is created when minima are separated by a low barrier that gets traversed repeatedly.
- 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)

A. Pedersen, J-C. Berthet and H. Jónsson, Lecture Notes in Computer Science 7134, 34 (2012)

#### Apply to admolecule diffusion on an ice $I_h(0001)$ surface

Use TIP4P potential function

During AKMC simulation, the admolecule rattles between just a few of the minima.

End up forming a composite state consisting of 10 local minima, then finally make it to state H



(1) From which one of the states will the system escape the composite state?(2) How long time will the system spend in the composite state before escaping?

Use absorbing Markov chain theory (Novotny Int.J.of Mod.Physics C10,1483, 1999)

Illustrate with two states, 1 and 2, that have been joined in a composite state. From 1 it is possible to escape to state 3, from 2 it is possible to escape to state 4

$$\begin{pmatrix} \dot{p}_1 \\ \dot{p}_2 \end{pmatrix} = \begin{pmatrix} -v_{1\to 2} - v_{1\to 3} & v_{2\to 1} \\ v_{1\to 2} & -v_{2\to 1} - v_{2\to 4} \end{pmatrix} \begin{pmatrix} p_1 \\ p_2 \end{pmatrix}$$
$$\mathbf{\dot{P}} = \mathbf{v}_T \mathbf{P}$$

Finite difference approximation  $\mathbf{P}(\Delta t) = \mathbf{P}(0) + \Delta t \mathbf{v}_T \mathbf{P}(0)$ 

Define T matrix  $\mathbf{T} = \mathbf{I} + \mathbf{v_T} \Delta t$ 

So  $\mathbf{P}(\Delta t) = \mathbf{T} \mathbf{P}(0)$  and  $\mathbf{P}(n\Delta t) = \mathbf{T}^n \mathbf{P}(0)$ 

#### Estimate escape from a composite state

Introduce explicitly the probability of the escape (absorbing) states:

$$\begin{pmatrix} \dot{p}_{1} \\ \dot{p}_{2} \\ \dot{p}_{3} \\ \dot{p}_{4} \end{pmatrix} = \begin{pmatrix} -v_{1\rightarrow2} - v_{1\rightarrow3} & v_{2\rightarrow1} & 0 & 0 \\ v_{1\rightarrow2} & -v_{2\rightarrow1} - v_{2\rightarrow4} & 0 & 0 \\ v_{1\rightarrow3} & 0 & 0 & 0 \\ 0 & v_{2\rightarrow4} & 0 & 0 \end{pmatrix} \begin{pmatrix} p_{1} \\ p_{2} \\ p_{3} \\ p_{4} \end{pmatrix}$$
Define M
$$\mathbf{M} = \mathbf{I} + v_{\mathbf{M}} \Delta t$$
and R
$$\mathbf{R} = \begin{pmatrix} +v_{1\rightarrow3} & 0 \\ 0 & +v_{2\rightarrow4} \end{pmatrix} \Delta t$$

$$\mathbf{SO} \qquad \mathbf{M} = \begin{pmatrix} \mathbf{T} & 0 \\ \mathbf{R} & \mathbf{I} \end{pmatrix}$$
Then
$$(\mathbf{M} = \mathbf{I} + \mathbf{M} \mathbf{M} = \mathbf{I} + \mathbf{$$

$$\mathbf{P}(t) = \begin{pmatrix} \mathbf{T}^{\mathbf{n}} & 0\\ \mathbf{R}(\mathbf{T}^{\mathbf{n}-1} + \ldots + \mathbf{T} + \mathbf{I}) & \mathbf{I} \end{pmatrix} \mathbf{P}(0) = \begin{pmatrix} \mathbf{T}^{\mathbf{n}} & 0\\ \mathbf{R}\frac{\mathbf{I}+\mathbf{T}^{\mathbf{n}}}{\mathbf{I}-\mathbf{T}} & \mathbf{I} \end{pmatrix} \mathbf{P}(0)$$

#### Estimate escape from a composite state

After long time,  $\mathbf{T}^n \to 0$  since this is an open system.

$$\mathbf{P}(\infty) = \begin{pmatrix} 0 & 0 \\ \mathbf{R}(\mathbf{I} - \mathbf{T})^{-1} & \mathbf{I} \end{pmatrix} \mathbf{P}(0)$$

So,

Since  $p_3(0) = 0$  and  $p_4(0) = 0$  the escape probabilities are

$$\left(\begin{array}{c}p_3(\infty)\\p_4(\infty)\end{array}\right) = \mathbf{R} \mathbf{N} \left(\begin{array}{c}p_1(0)\\p_2(0)\end{array}\right)$$

where 
$$\mathbf{N} = (\mathbf{T} - \mathbf{I})^{-1}$$

The average time spent in the composite state can be obtained from

$$\langle t \rangle = \sum_{i=1,2} \sum_{j=1,2} \Delta t (1 + T_{ij} + T_{ij}^2 + \dots) p_j(0)$$
  
=  $\sum_{i=1,2} \sum_{j=1,2} \Delta t N_{ij} p_j(0)$   
=  $\sum_{j=1,2} v_{\mathbf{T},ij}^{-1} p_j(0)$ 

#### **Application 1. Simulation of metal crystal growth**

#### (G. Henkelman & HJ, PRL 2003)

-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



#### Simulate crystal growth from vapor (cont.)

**Deposition** events (short time scale) and **annealing** events (long time scale)

Many unexpected events were observed

Most transitions involved concerted displacement of multiple atoms





#### Example applications:

#### 2 (cont.) Annealing of a tilt-and-twist grain boundary in Cu

- Start with either thin (the two grains brought in contact) or thick (add layer of amorphous Cu in between) configurations for the grain boundary.
- Use EMT potential function.
- After annealing with AKMC the final result is similar, only *ca*. 3 atomic layers are not FCC according to Common Neighbor analysis (icosahedral order increases upon annealing) Each system simulated for *ca*. 0.1 ms



A. Pedersen, G Henkelman, J Schiøtz and H Jónsson, New Journal of Physics 11, 073034 (2009)

## 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 CNanalysis) is formed at the grain boundary in both samples.





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

## Example 2: H-atom diffusion at grain boundaries in Al

#### Are grain boundaries highways for diffusion or do they slow down diffusion?

AKMC simulation using EMT potential

Long time simulation:

 Only a few paths go through the grain boundary

Effective potential energy surface:

- Projected onto xz-plane
  - Red high energy
  - Blue low energy
- Two low-energy basins within the grain boundary

# Parallel-diffusivity decreases to one-half of the bulk value

Trapping in the grain boundaries

A. Pedersen & HJ, Acta Materialia (2009)



## Application 3: Simulation of H<sub>2</sub>O adsorption and diffusion on ice I<sub>h</sub> (0001) surface

Interaction potential

- TIP4P/2005f

360 substrate molecules

- Surface area 23 Å x 22 Å
- Bottom bi-layer frozen
- 3 surface bi-layers free

Temperature 100-200 K



Initial random displacement of admolecule and neighbors within a spherical region

# Example 3: $H_2O$ diffusion on Ice $I_h(0001)$ surface

# Use TIP4P/2005f potential (flexible).

Simulate admolecule diffusion, find meachanism and rate of hops between surface sites.

H<sub>2</sub>O admolecule sees a disordered surface because of the proton disorder in ice Ih.

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



A. Pedersen, L.J. Karssemeijer, H. M. Cuppen and H. Jónsson, JPC-C 119, 16528 (2015)

## Ordering of dangling H-bonds on the surface



Proton disordered

#### Fletcher (dangling H-bonds line up)



Has lower energy because repulsive dipole-dipole interaction is reduced

# Binding sites for H<sub>2</sub>O admolecule



# Energy Barriers for H<sub>2</sub>O Admolecule Diffusion Hops

0.27 ms simulated at 175 K 36.000 iterations

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

The difference in rates is huge



## Binding sites and diffusion paths on ice I<sub>h</sub>(0001)



At A-type site, two protons point up.



At B-type site, one proton points up.



E. Batista and H. Jónsson, Comp. Mat. Sci. 20, 325 (2001)

# Diffusivity of an H<sub>2</sub>O admolecule

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

Einstein-Smoluchowski equation used to estimate diffusion constant:

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

Giving

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

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



A. Pedersen, L.J. Karssemeijer, H. M. Cuppen and H. Jónsson, J. Phys. Chem. C 119, 16528 (2015)

# The surface rearranges during the simulation

Observe also change in the location of the 'dangling' proton (marked with a dot).

Transition involving a single energy barrier (saddle point): 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 occurred during the diffusion simulation





#### Smaller repulsion between dangling bonds in linear ordering.

# **Clustering of admolecules on the surface**



Non-crystallographic sites until the hexamer is formed

## non-crystallographic — crystallographic



#### Side remark: This can be extended to rougher energy landscapes: **Find optimal location and orientation of hyperplanar dividing surfaces**

Need to enclose the initial state. One possibility: Use a mosaic of hyperplanar segments, and variationally using  $k^{TST} > k$ 

to optimize orientation and placement of each one (as well as the number of segments).





T. Bligaard and HJ, Comp. Phys. Comun. 2005

Ongoing quest ...

#### Coworkers from the group in Iceland:





Andreas Pedersen

Jean-Claude Berthet



Manuel Plasencia



Alejandro Pena-Torres



Rohit Goswami

Other co-workers: Graeme Henkelman, U. Texas Enrique Batista, Los Alamos Jacob Schiøtz, DTU, Denmark Herma Cuppen, Radboud U. & U. of Amsterdam Leendertjan Karssemeijer, Radboud U. Michail Stamatakis, Oxford

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### Summary

- Simulations of long time scale evolution in small systems can be carried out with the AKMC method and the EON software without preconceived notion of transition mechanisms and possible states of the system, no need for lattice.
- Transition mechanisms and rates obtained from the energy landscape given by a potential energy function or DFT, now accelerated by machine learning.
- Information on mechanism and rate of transitions obtained with AKMC can be transferred to regular KMC (for example Zacros) for carrying out simulations of larger systems and covering longer timescale.
- Can be extended to include tunneling (instantons), full TST (free energy), spin, excited electronic states, applied electric field, ...



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