Accelerated Molecular Dynamics with the Bond Boost Method

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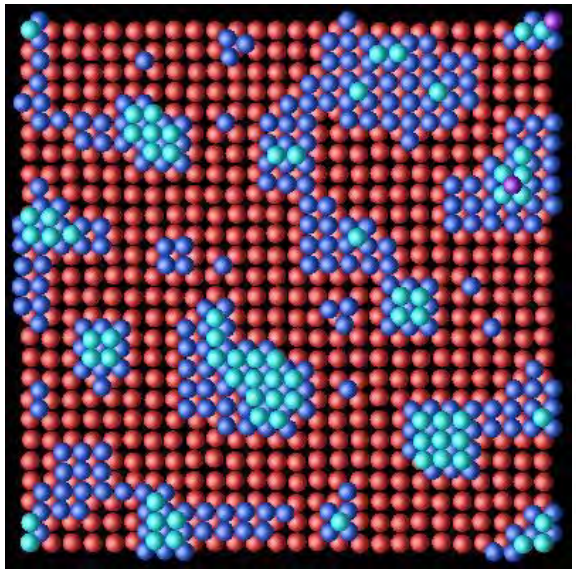

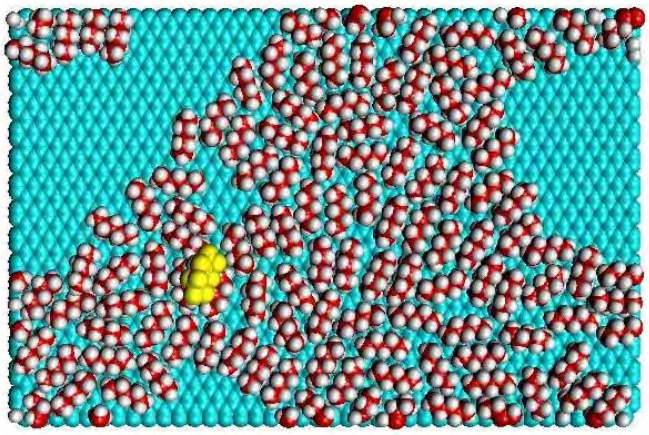

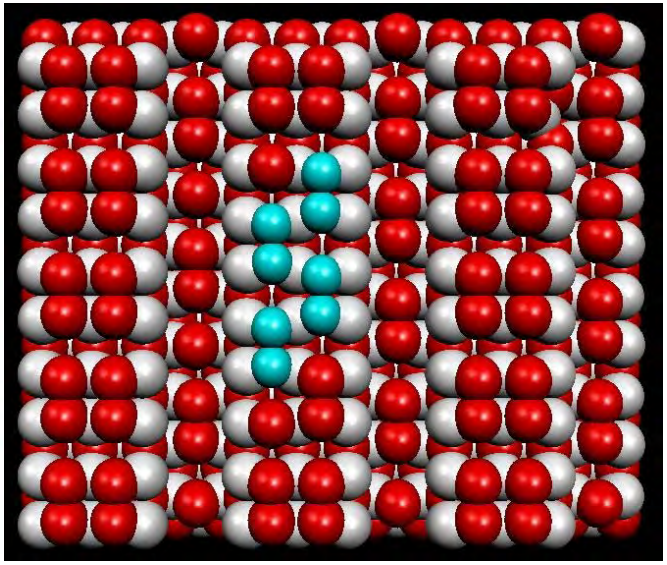

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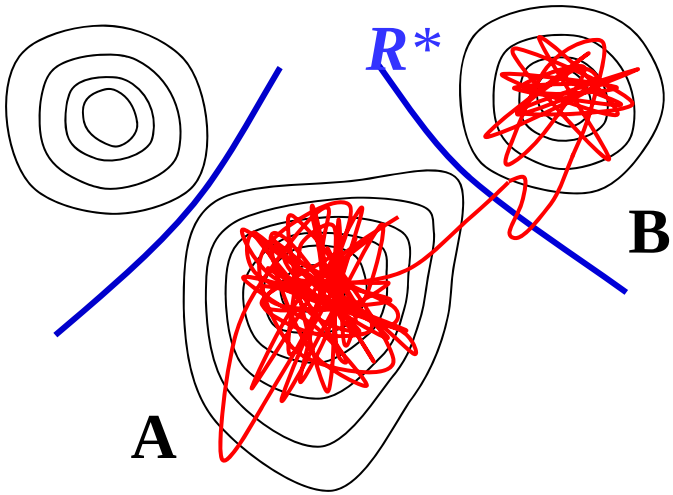
DMR-1006452

U.S. DEPARTMENT OF ENERGY
DE-FG0207ER46414

Rare-Event Methods



Rare-Event Simulation

Kinetic Monte Carlo:

K. Fichthorn and W. Weinberg,
J. Chem. Phys. **95**, 1090 (1991).

Kinetic ART:

El-Mallouhi, N. Mousseau, Phys. Rev. B **78**,1532002 (2008).

Master Equation

Search and Characterization

Nudged Elastic Band:

G. Henkelman, B.Uberuaga, and H. Jonsson,
J. Chem. Phys. **113,** 9901 (2000).

Dimer Method:

G. Henkelman and H. Jonsson, J. Chem. Phys. **111**, 7010 (1999).

Transition Path Sampling:

P. Bolhuis, D. Chandler, et al.
Ann. Rev. Phys. Chem. **53**, 291 (2002).

Forward-Flux Sampling:

R. J. Allen, D. Frenkel, P. R. ten Wolde,
J. Chem. Phys. **124**, 194111 (2006).

String Method:

W. E., W. Ren , E. Vanden-Eijnden,
Phys. Rev. B **66**, 052301 (2002).

AND.....

Molecular Dynamics Simulations Naturally Find Rare Events and Can Simulate Rare-Event Systems...

Accelerated Molecular Dynamics
(Hyperdynamics)

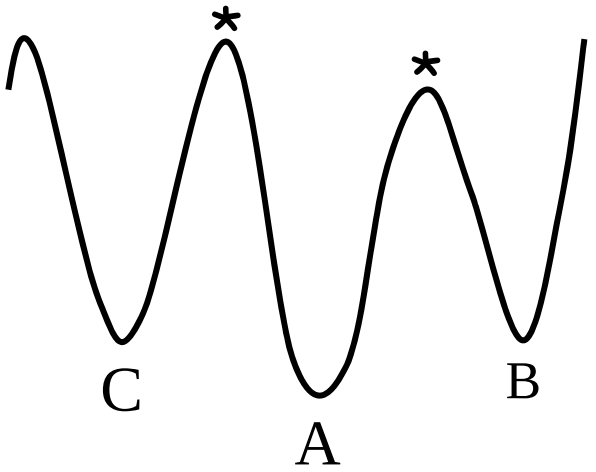
A. Voter, *J. Chem. Phys.* **106**, 11 (1997).

$$k_{A\to B}^{TST} = \frac{1}{2}\frac{\int_A \delta_{AB}^* |v_{\perp,AB}| e^{-V(\mathbf{R})/k_B T}}{\int_A e^{-V(\mathbf{R})/k_B T}}$$

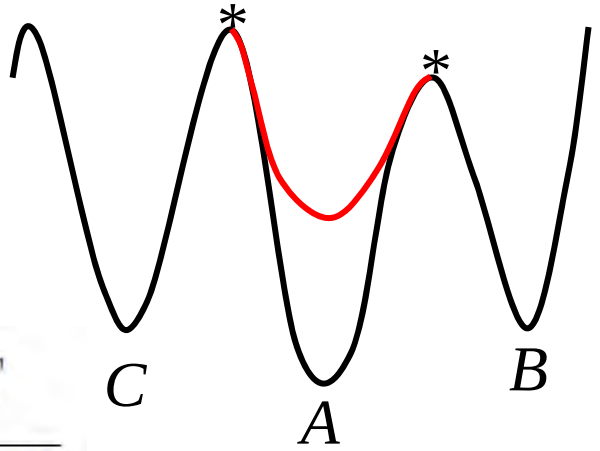
$$k_{A\to B}^{TST} = \nu \frac{\int \delta_{AB}^* W(\mathbf{R}) e^{-V(\mathbf{R})/k_B T} / W(\mathbf{R})}{\int W(\mathbf{R}) e^{-V(\mathbf{R})/k_B T} / W(\mathbf{R})}$$

$$W(\mathbf{R}) = \exp\left(\frac{V(\mathbf{R}) - V(\mathbf{R})}{k_B T}\right)$$

$$k_{A\to B}^{TST} = \nu \frac{\int \delta_{AB}^* e^{-V(\mathbf{R})/k_B T} / \int e^{-V(\mathbf{R})/k_B T}}{\int e^{-V(\mathbf{R})/k_B T} / W(\mathbf{R}) / \int e^{-V(\mathbf{R})/k_B T}}$$



Relative Rates



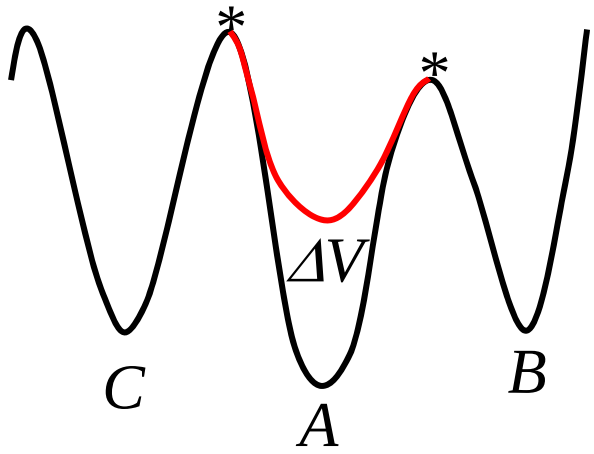
Accelerated Molecular Dynamics
(Hyperdynamics)

A. Voter, *J. Chem. Phys.* **106**, 11 (1997).

$$k_{A\to B}^{TST} = \frac{k_{A\to B}^{TST}}{\langle W(\mathbf{R})\rangle_A}$$

$$k_{A\to C}^{TST} = \frac{k_{A\to C}^{TST}}{\langle W(\mathbf{R})\rangle_A}$$

$$\frac{k_{A\to B}^{TST}}{k_{A\to C}^{TST}} = \frac{k_{A\to B}^{TST}}{k_{A\to C}^{TST}}$$



MD Time:

$$t_{MD} = N\Delta t$$

Real Time:

$$t = \sum_{i=1}^{N} \frac{\Delta t}{W(R_i)} = \Delta t \sum_{i=1}^{N} \exp\left(\Delta V_i / kT\right)$$

$$\text{Boost} = \left\langle \exp\left(\frac{\Delta V}{kT}\right)\right\rangle$$

The Trick is How to Construct *ΔV(R)*...

Accelerated Molecular Dynamics

The Bond-Boost Method

R. Miron & K. Fichthorn, *J. Chem. Phys.* **119**, 6210 (2003)

Define Local Minima by Bond Lengths

$$\{r_i^o\}_{i=1,N}$$

Transitions Occur via Bond Breaking

$$\max_i \left| \frac{\delta r_i}{r_i^o} \right| > q$$

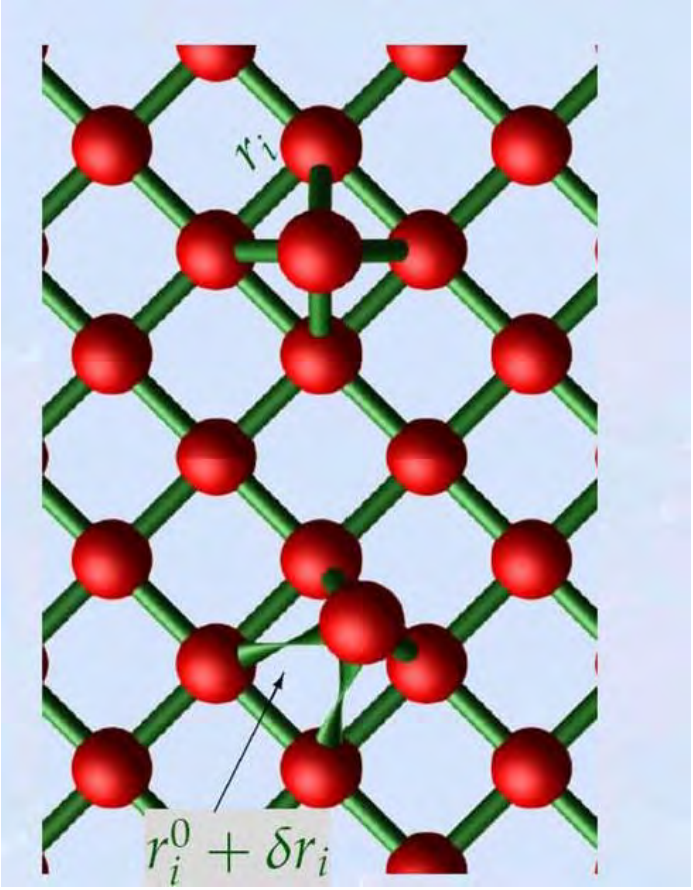
Empirical Threshold

Boost the Bonds: Purely Geometric

$$\Delta V\{x\} \sim A\{r_i\} \sum_{i=1}^{N} \delta V(r_i)$$

Envelope Function

Boost per Bond



Details of the Bond Boost Method

Boost Potential

$$\Delta V(\mathbf{r}) = \frac{\Delta V_{\max}}{N} A(\varepsilon_{\max}) \sum_{i=1}^{N} \delta V(\varepsilon_i)$$

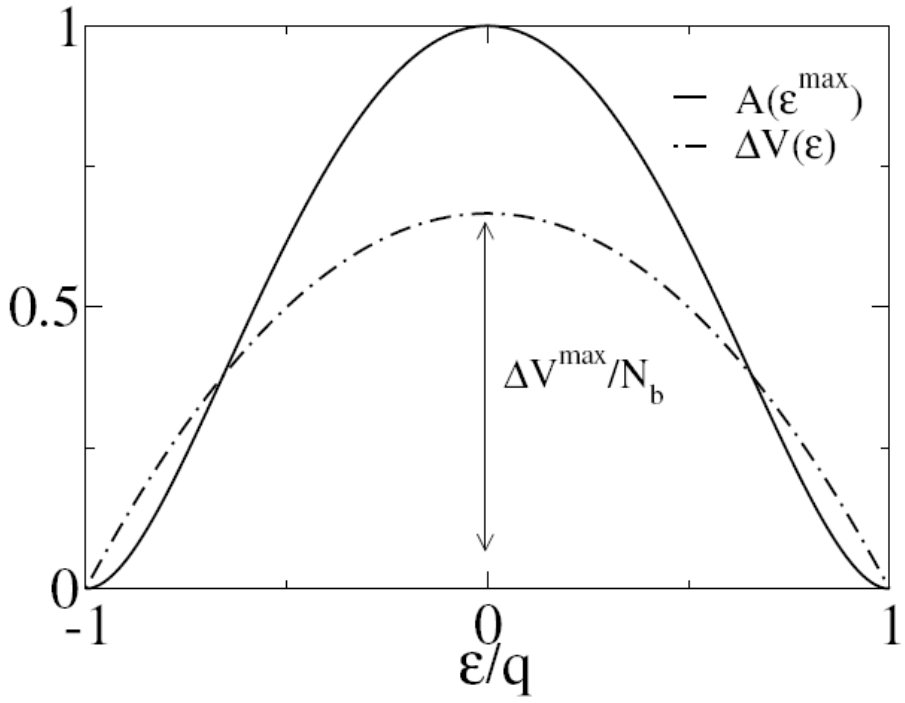
$$\varepsilon_i = \frac{\delta r_i}{r_i^0}$$

Nominal Boost per Bond

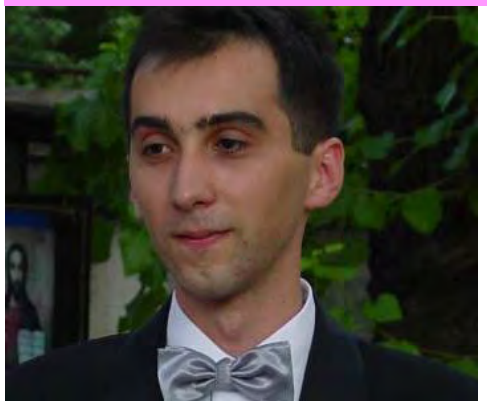
$$\delta V(\varepsilon_i) = 1 - \left(\frac{\varepsilon_i}{q}\right)^2$$

Envelope: Channels Boost into the Bond Most Ready to Break

$$A(\varepsilon_{\max}) = f \times \left[1 - \left(\frac{\varepsilon_{\max}}{q}\right)^2\right]$$



Overview of the Bond Boost Method



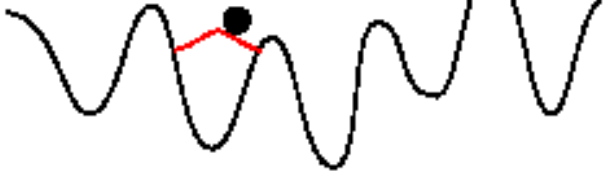
R. Miron & K. Fichthorn, *J. Chem. Phys.* **119**, 6210 (2003)

find local minimum
(conjugate-gradient minimization)

MD on boosted PES

$$\delta t = \delta t_{simulation} e^{\beta \Delta V}$$

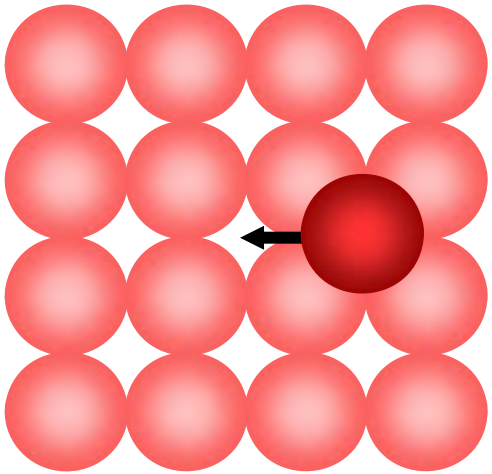
detect transition , find new state



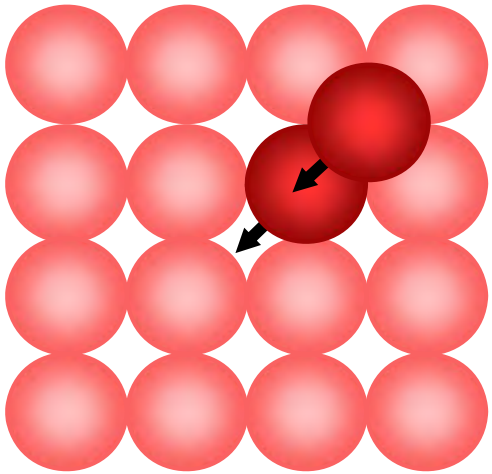
MD on boosted PES

detect transition ...

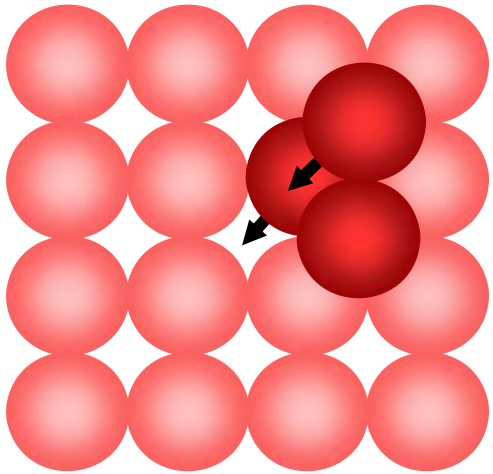
Diffusion on Cu(100): Elementary Processes



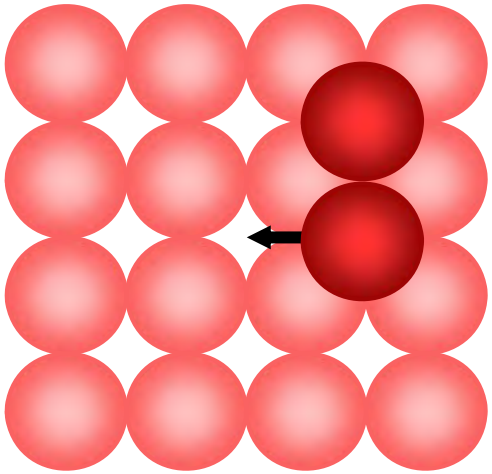
Adatom Hop



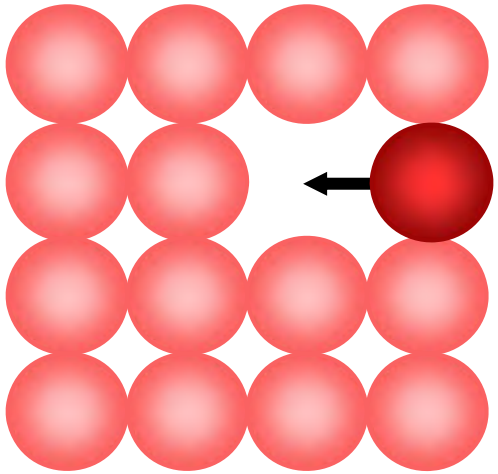
Adatom Exchange



Dimer Exchange



Dimer Hop



Vacancy Hop

R. Miron & K. Fichthorn, *J. Chem. Phys.* **119**, 6210 (2003)

The Bond-Boost Method: Diffusion on Cu(100)

Rates :

$$k = \frac{N_{events}}{time} = \Gamma_0 e^{-\beta E_A}$$

R. Miron & K. Fichthorn, *J. Chem. Phys.* **119**, 6210 (2003)

Prefactors Γ_0(THz) and activation energies E_A(eV) :

Process	Γ_0^{boost} $(\times e^{\pm 0.7})$	Γ_0^{MD} $(\times e^{\pm 0.6})$	E_A^{boost} (± 0.05)	E_A^{MD} (± 0.04)	E_A^{static}
Adatom hop	40	20	0.52	0.49	0.51
Adatom exchange	270	437	0.73	0.70	0.71
Vacancy hop	54	27	0.44	0.47	0.44
Dimer hop	30	13	0.47	0.48	0.49
Dimer exchange	190	320	0.71	0.73	0.69

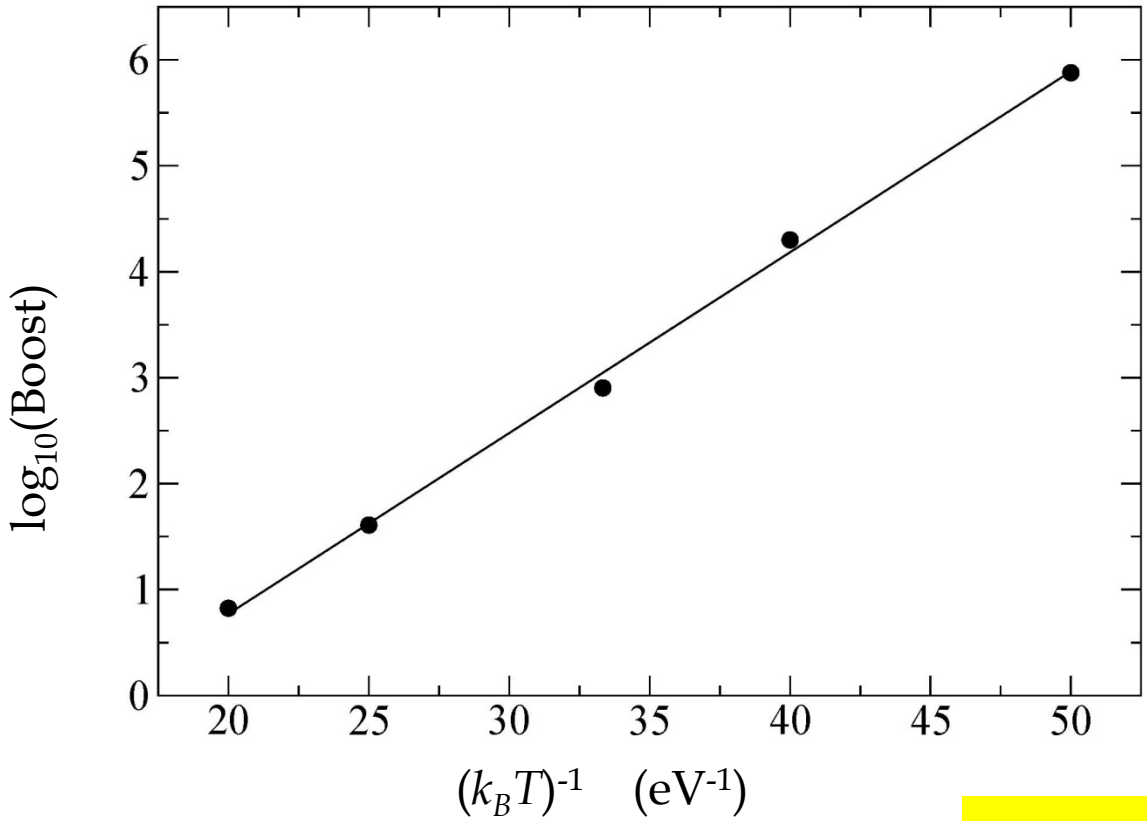
^{boost} accelerated MD at T = 230 - 600 K

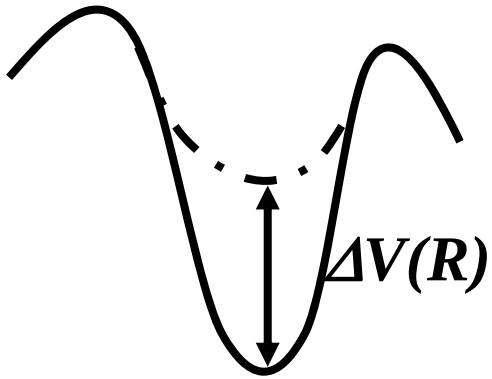
^{MD} regular MD at T = 650 - 900 K $\rightarrow$ Boisvert, Lewis *Phys.Rev.* B **65** (1997)

^{static} using Step-and-Slide method $\rightarrow$ Miron, Fichthorn *J.Chem.Phys.* **115** (2001)

The Bond-Boost Method: Diffusion on Cu(100)

Boost = Physical Time / Simulation Time

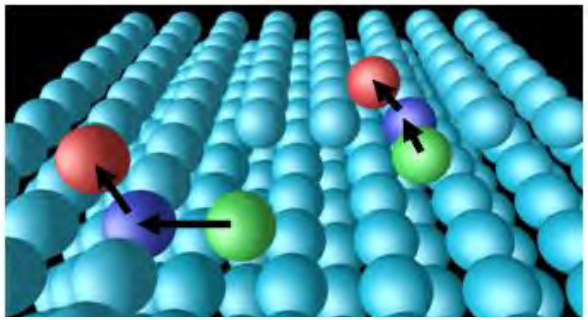




R. Miron & K. Fichthorn,
J. Chem. Phys. **119**, 6210 (2003)

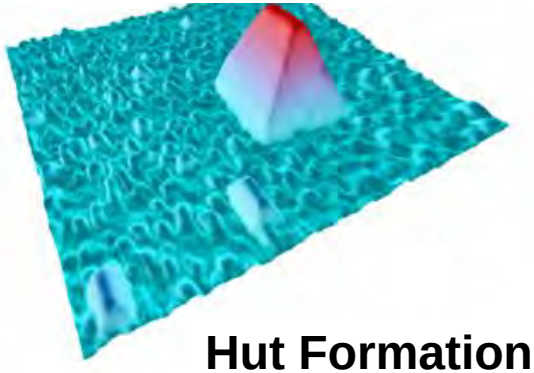
$$Boost = \left\langle \exp\left(\frac{\Delta V}{k_B T} \right) \right\rangle$$

Hut Formation in Al(110) Homoepitaxy

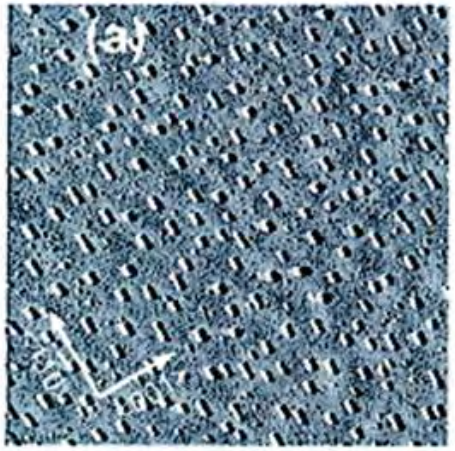


Bautier de Mongeot *et al.*, *Phys. Rev. Lett.* **91**, 016102 (2003).

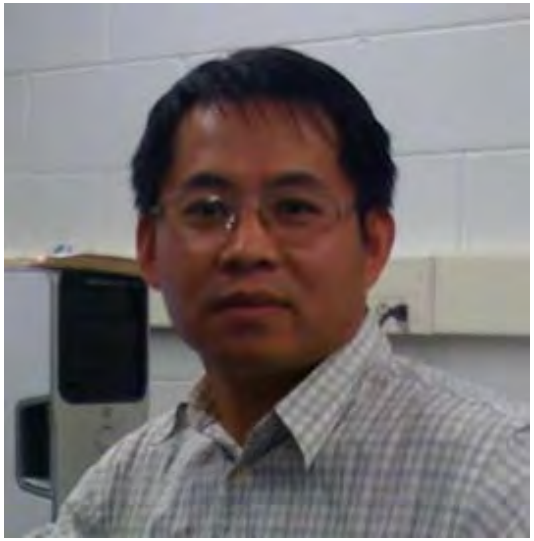
Atoms Hopping (Å, ps)



Hut Formation (nm, min)

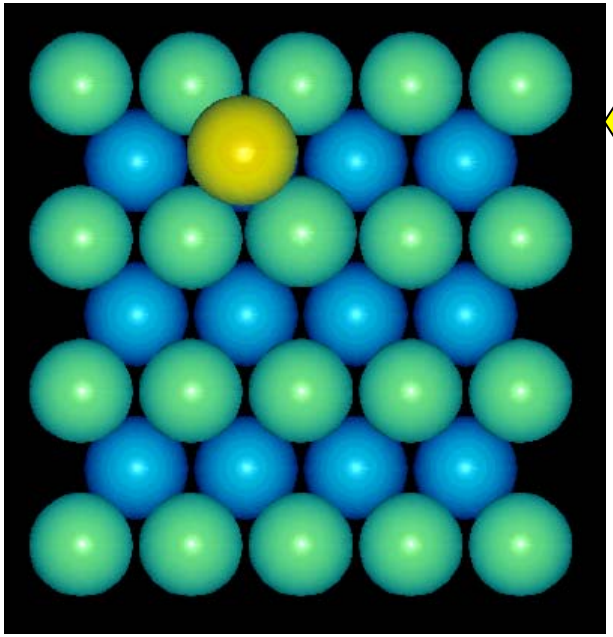


Hut Organization (μm, min)



K. Fichthorn and M. Scheffler, *Nature* **429**, 617 (2004).

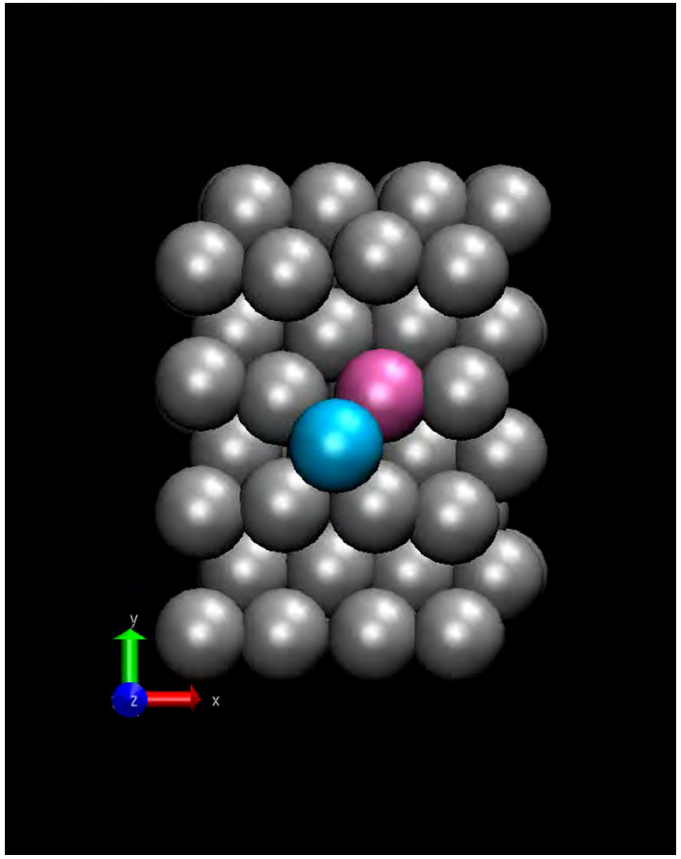
Accelerated AIMD (VASP): Diffusion on Al/Al(110)

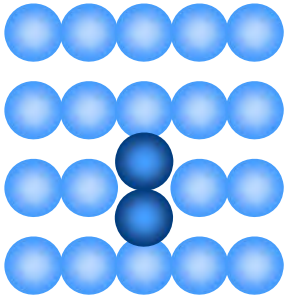


Climbing-Image Nudged Elastic Band Method

vs.

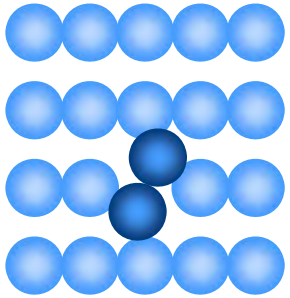
Accelerated AIMD





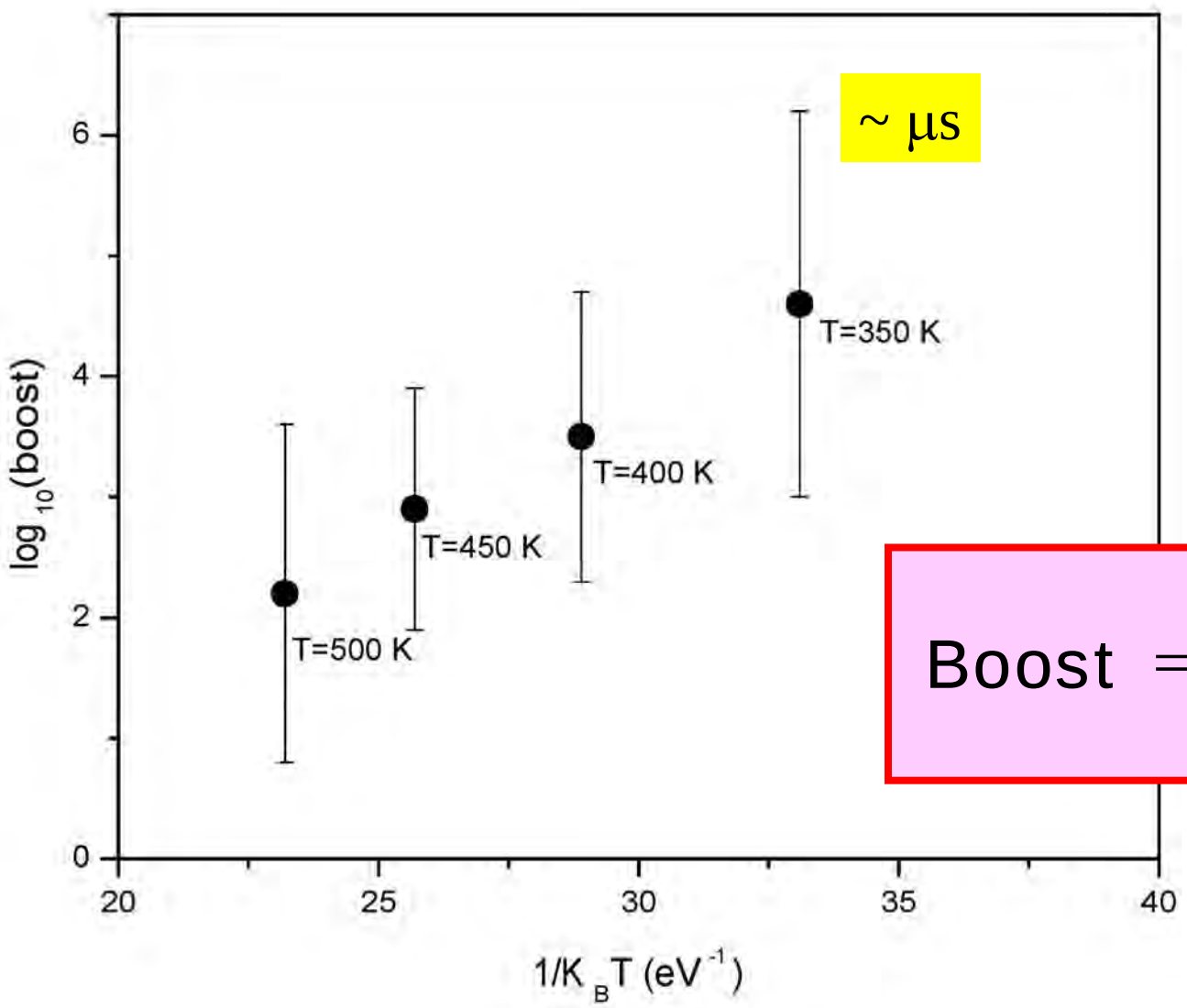
$E_B = 0.38$ eV

Fichthorn *et al., J. Phys. Cond. Matt.* **21**, 084212 (2009).



$E_B = 0.33$ eV

The Boost in *ab initio* MD



$$\text{Boost} = \left\langle \exp\left(\frac{\Delta V}{kT} \right) \right\rangle$$

Rare Events and the Small Barrier Problem

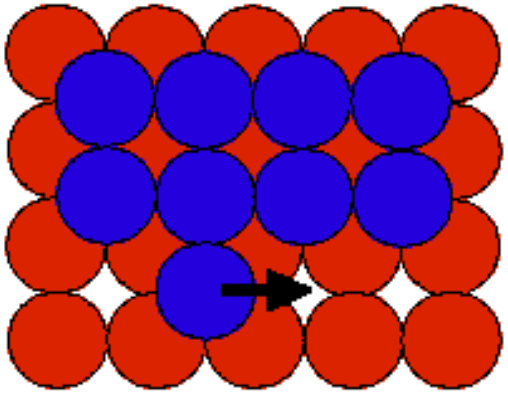
Co on Cu(100) surface with tight-binding (TBSMA) potential

(Levanov *et al.*, *Phys. Rev.* **B 61**, 2000)

TST barriers: $\Delta E^{\dagger} = 0.66\,eV$ for isolated adatom hop

$\Delta E^{\dagger} = 0.86\,eV$ for isolated adatom exchange

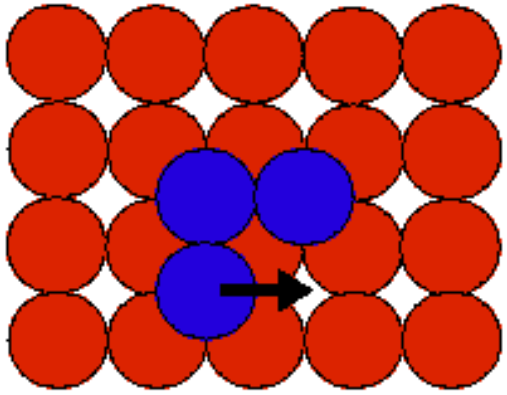
Annoyingly Small Barriers



step diffusion $\Delta E^{\dagger} = 0.2\,eV$

10^6 faster $(T = 350K)$

than isolated hop



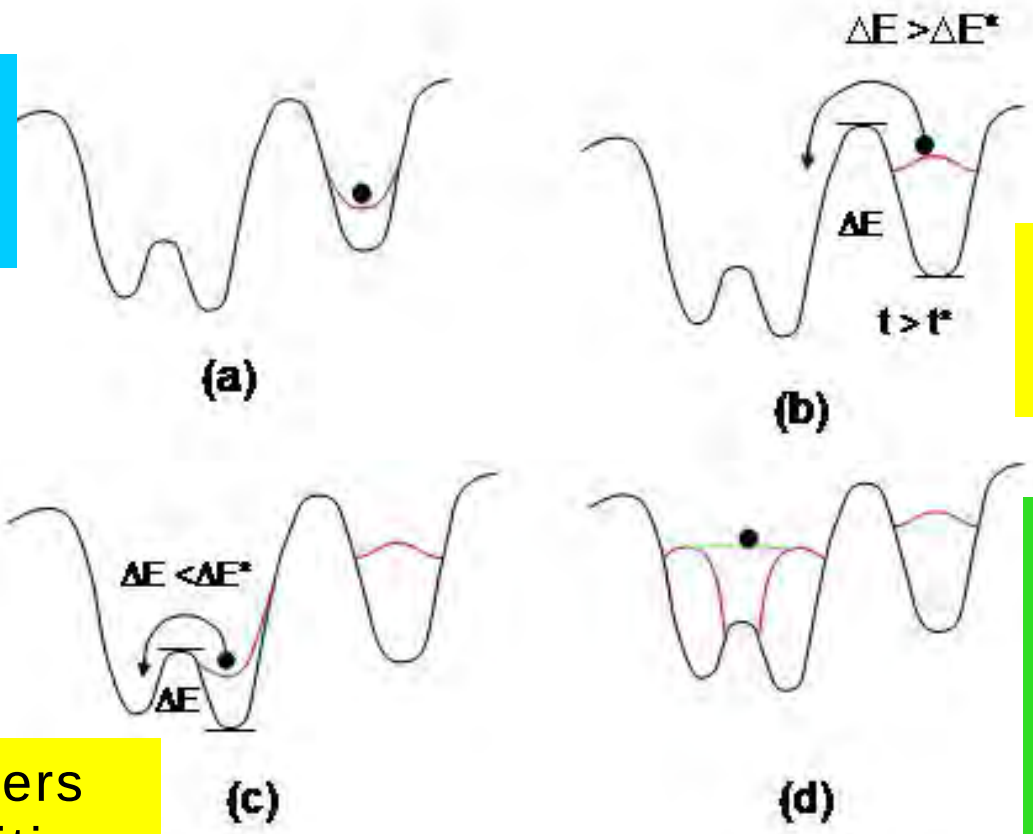
trimer rotation $\Delta E^{\dagger} = 0.1\,eV$

10^8 faster $(T = 350K)$

than isolated hop

State-Bridging Accelerated MD to Solve the Small-Barrier Problem

Commence With a Low Boost



Raise the Boost After A Waiting Time

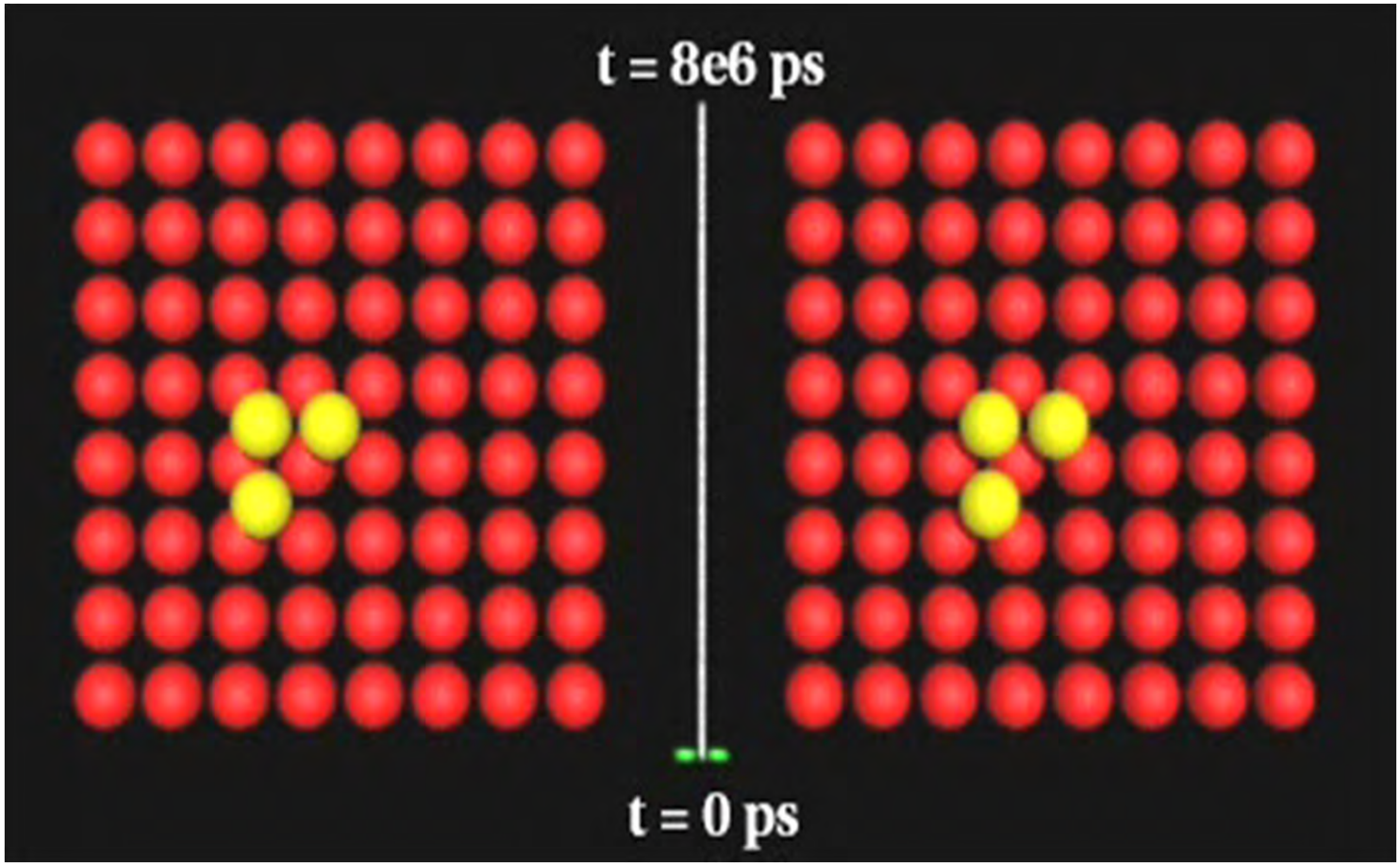
Miron, Fichthorn, J. Chem. Phys. 115, 2001.

Memorize and Consolidate Pairs of States Connected by Low Barriers

Detect Barriers When Transitions Occur, Compare To Threshold

R. Miron, K. Fichthorn, Phys. Rev. Lett. 93, 2004.

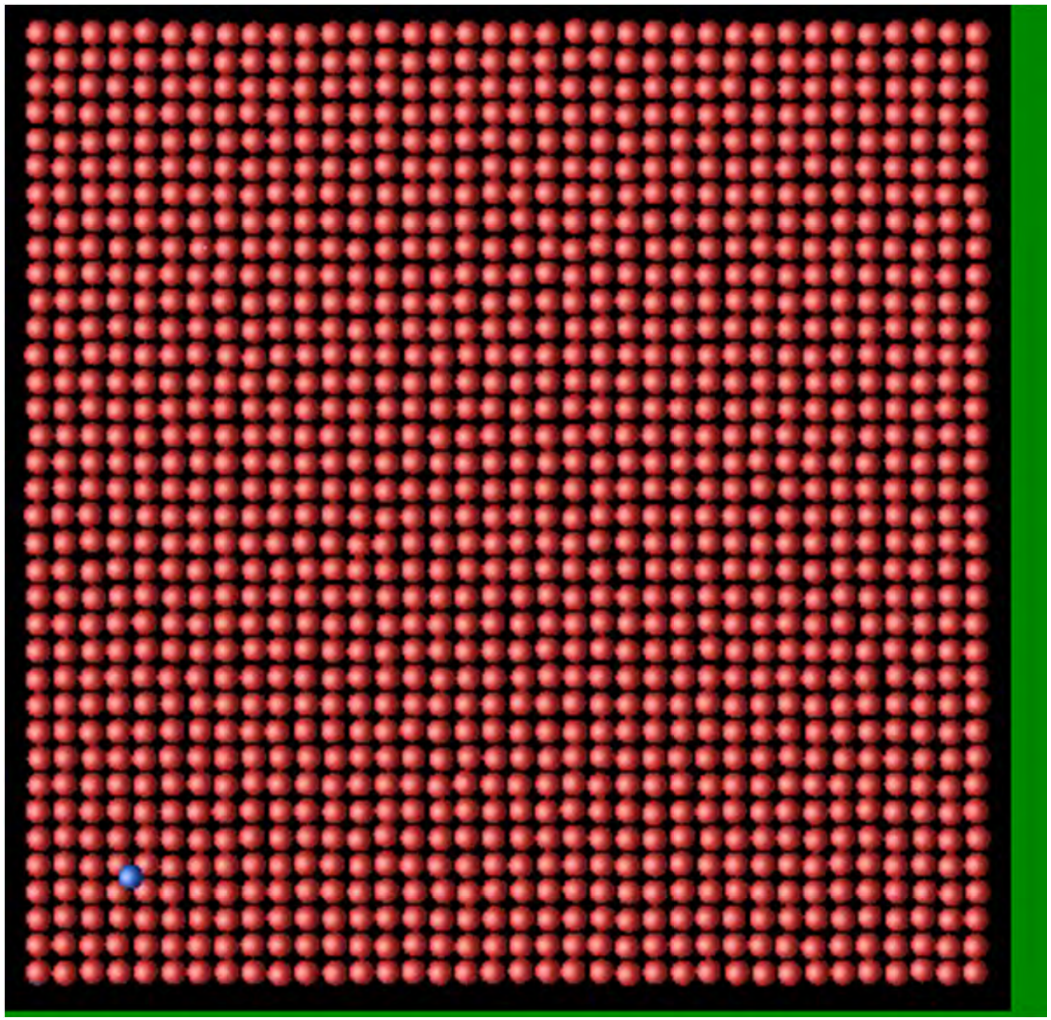
Co on Cu(001): Benefits of State Bridging



State-Bridging Accelerated MD

Regular Accelerated MD

Thin Film Growth at 250 K, F = 0.1 ML/s

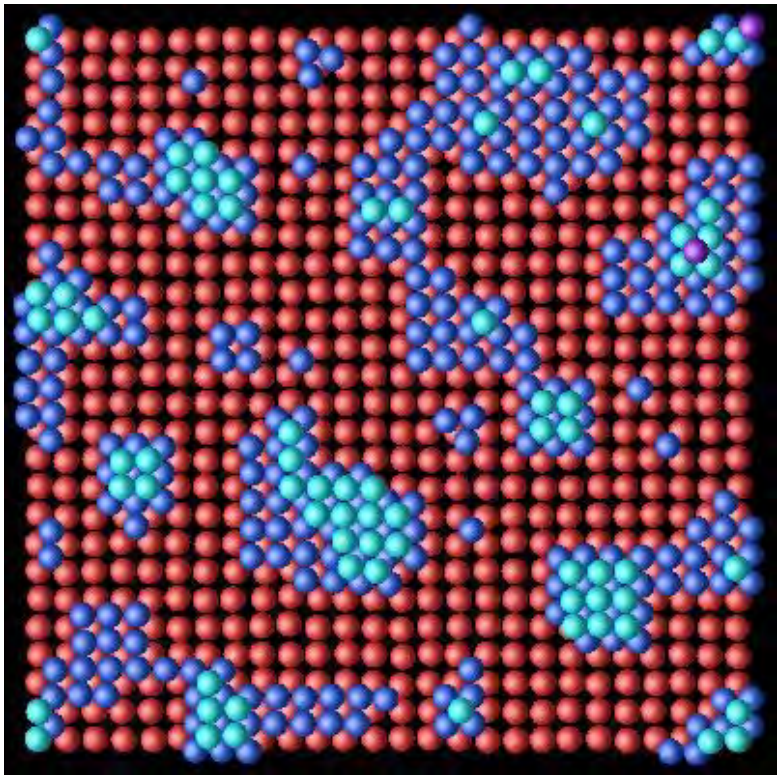


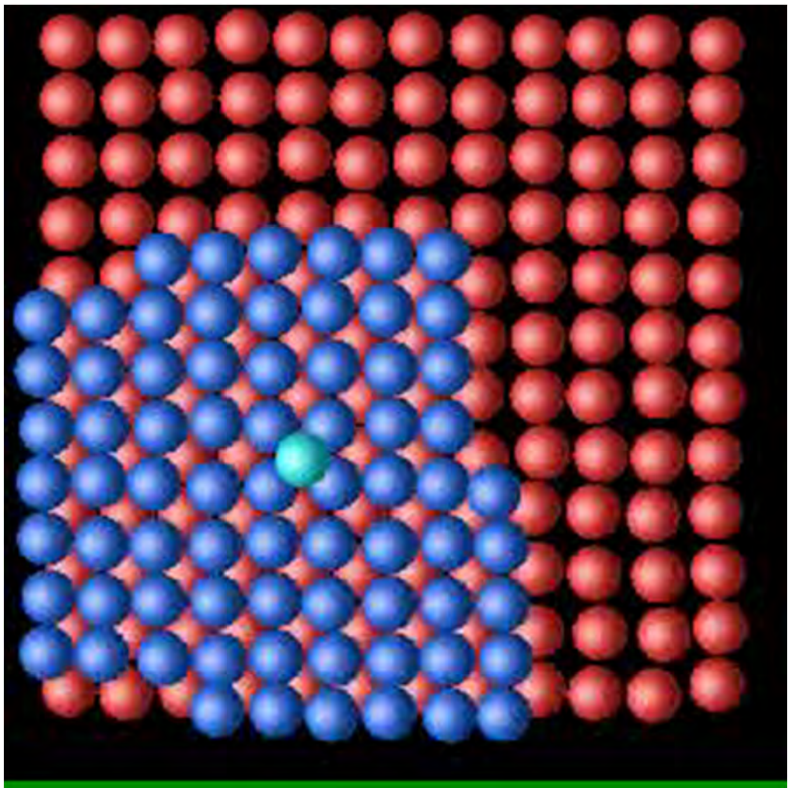
R. Miron, K. Fichthorn,
Phys. Rev. Lett. 93, 2004.

Note Cluster Mobility

State-Bridging Accelerated MD of Co/Cu(001) Heteroepitaxy: T = 250 K, F = 0.1 ML/s, Θ = 0.54 ML

MD Simulations were run for 5.4 s





R. Miron and K. Fichthorn, *Phys. Rev. B* **72**, 115433 (2005).

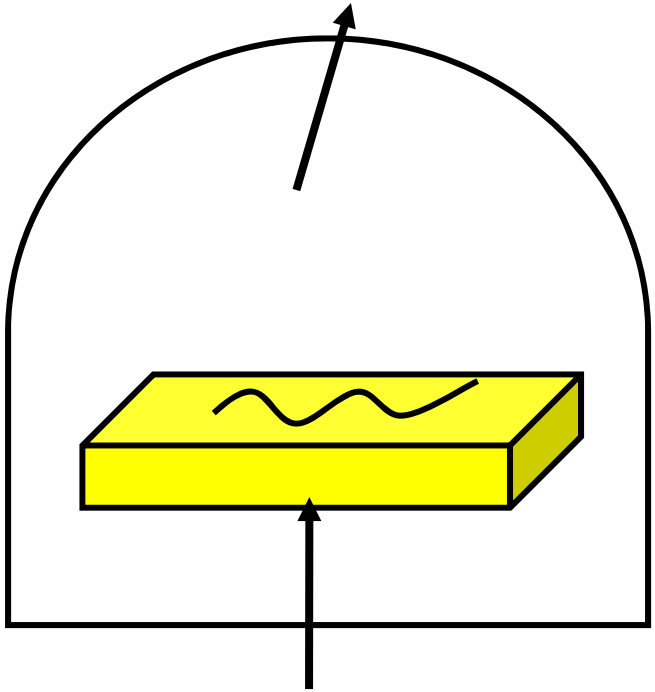
Mechanism of Bilayer Island Formation

Temperature-Programmed Desorption

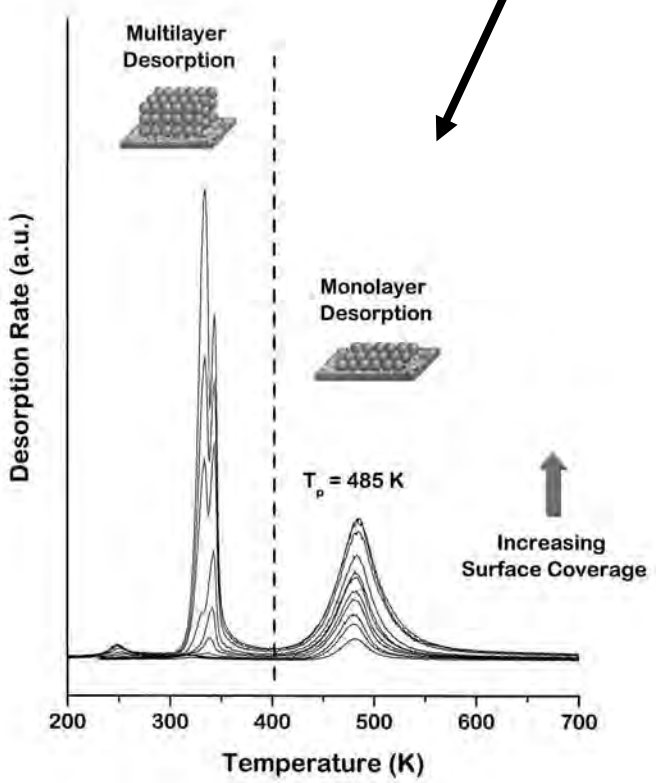
K. Becker, M. Mignogna, K. Fichthorn, *PRL* **102**, 046101 (2009).

$$-\frac{d\theta}{dt} = \nu_0 \exp\left(-\frac{E_d}{k_B T}\right)\theta$$

$$\ln\left(\frac{\beta}{T_p^2}\right) = -\ln\left(\frac{E_d}{k_B \nu_0}\right) - \frac{E_d}{k_B T_p}$$

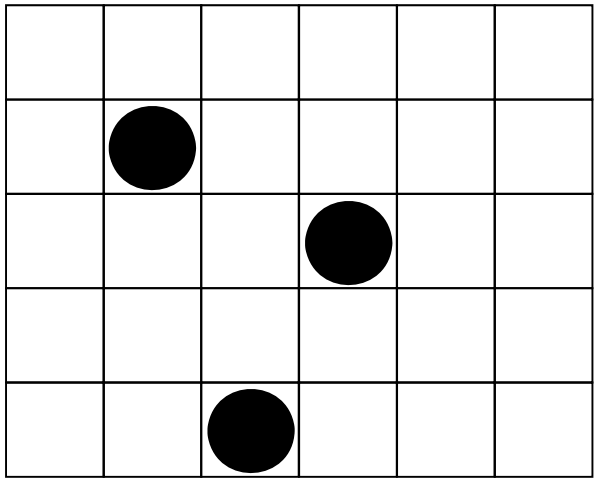


$$T = T_0 + \beta t$$

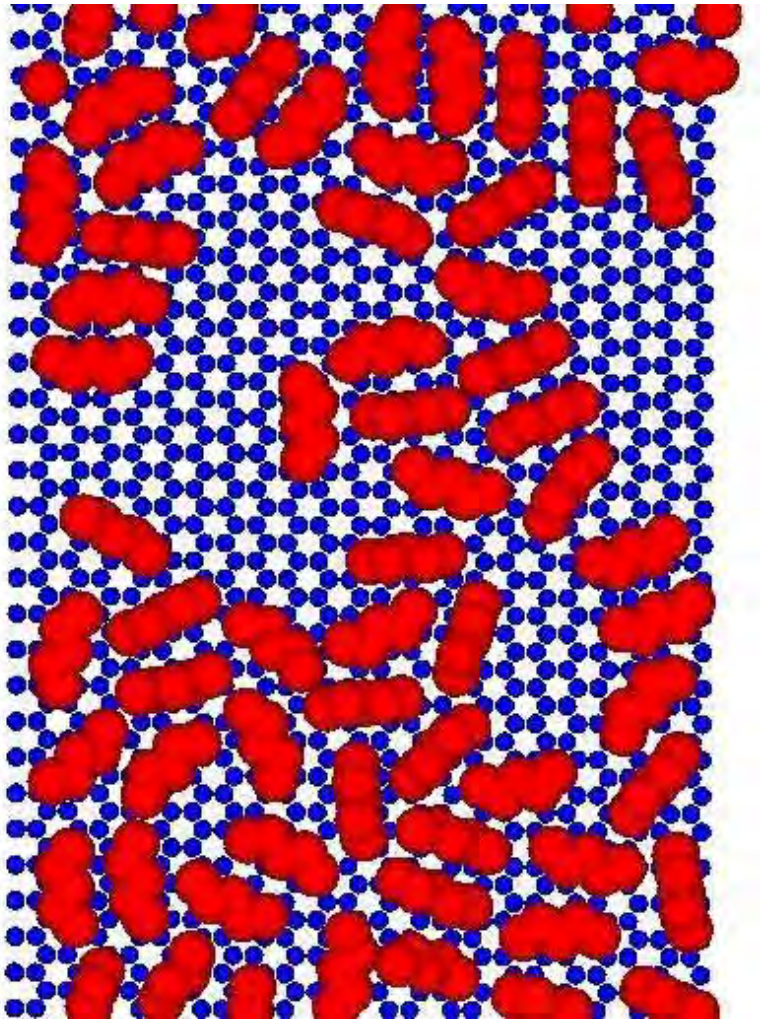


P. A. Redhead, *Vacuum* **12**, 203 (1962).

Simulation of TPD



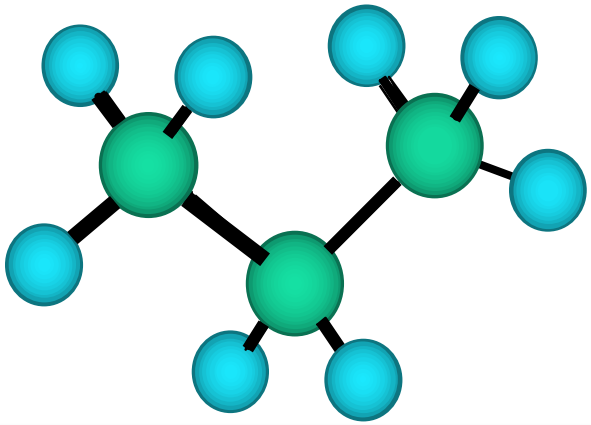
vs.

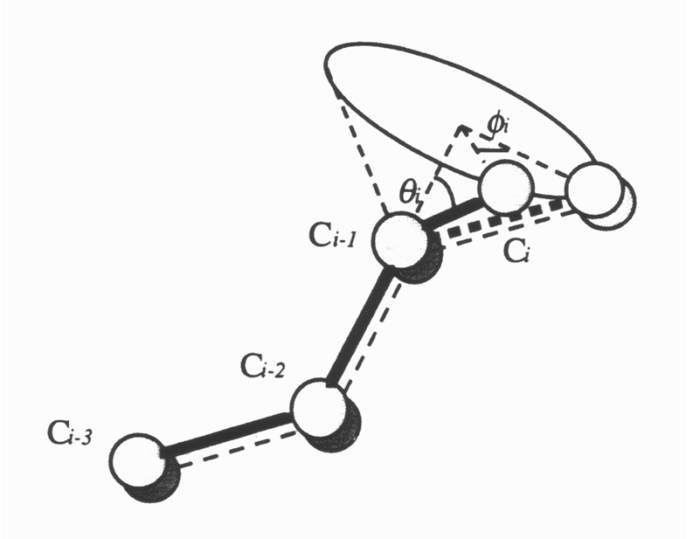


Large Molecules Don't Work in Lattice Models....

Goal: To Simulate TPD with Accelerated MD!!

Accelerated MD of Adsorbed Alkanes





OPLS All-Atom Force Field [1]

$$V_{intra} = V_b + V_t + V_{LJ}$$

$$V_b(\theta_i) = K_\theta(\theta_i - \theta_{eq})^2$$

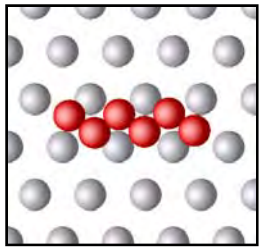
$$V_t(\varphi_i) = \frac{1}{2}\sum_{j=1}^{3} V_j\left[1 + \cos\left(j\varphi_i\right)\right]$$

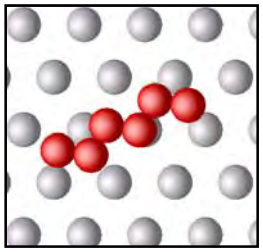
Constrained Bond Stretching: RATTLE [2]

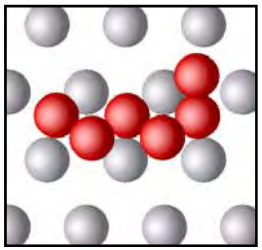
Steele's Potential for Molecule-Surface Interaction [3]

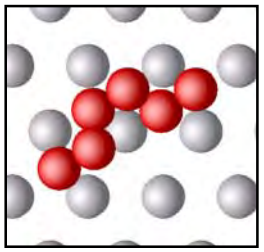
[1] Jorgensen et al., *J. Am. Chem. Soc.* **118**, 11225 (1996)
[2] H.C. Andersen, *J. Comput. Phys.* **52**, 24 (1983)
[3] W. A. Steele, *Surf. Sci.* **36**, 317 (1973)

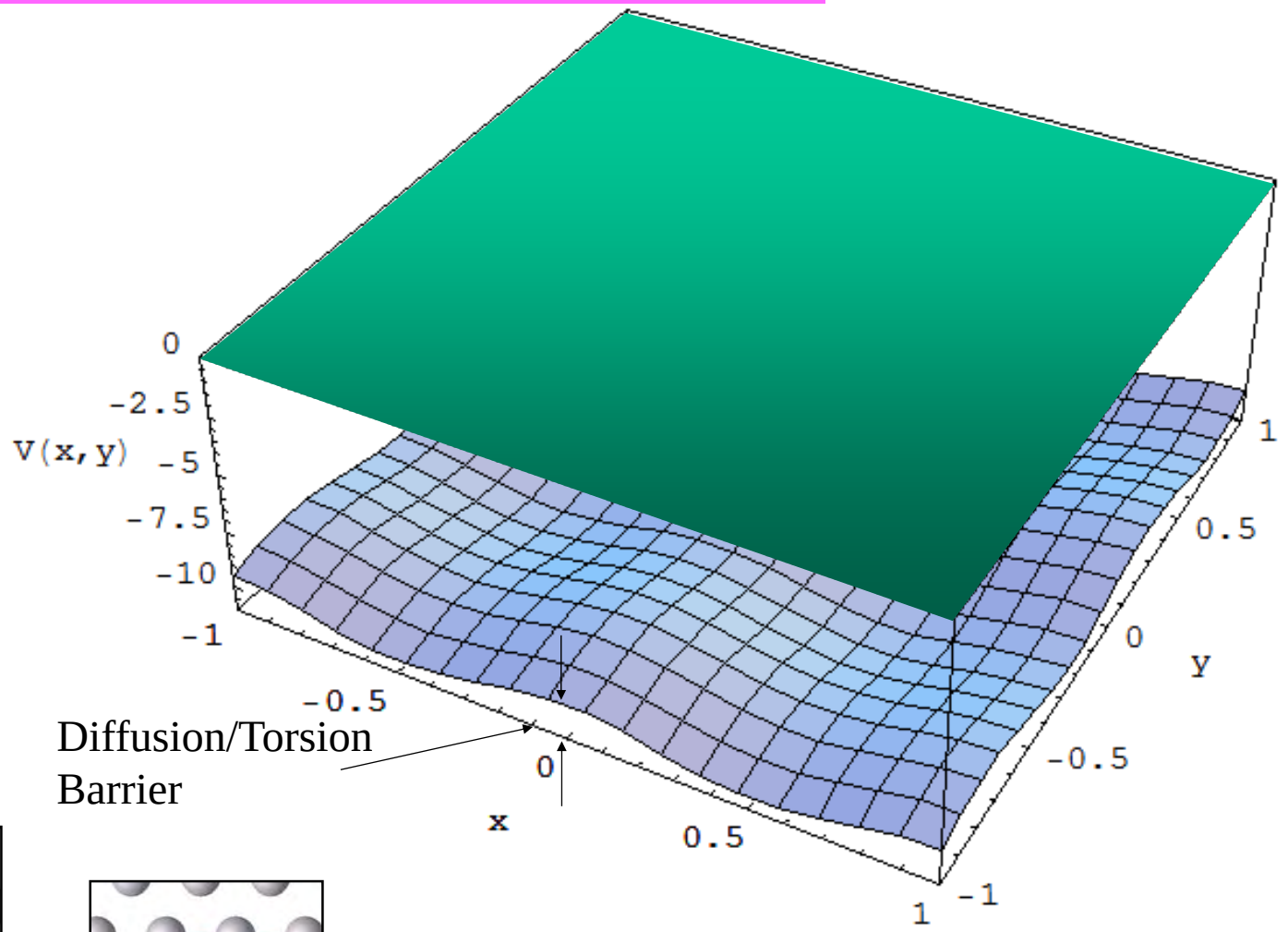
Many Local Minima, Fast Transitions But Desorption is the Slow Step











Diffusion/Torsion Barrier

• • •

Accelerated MD of TPD with the Bond-Boost Method

$$\Delta V(\mathrm{R}) = \frac{A(\varepsilon_{\max})}{N}\sum_{i=1}^{N}\delta V_i(\mathrm{R})\ ; \quad \delta V_i = (\alpha_1 - 1)\,V_{s,i} + (\alpha_2 - 1)\,V_{inter,i}; \quad \alpha_i < 1$$

Weaken Molecule-Molecule + Molecule-Surface Attraction

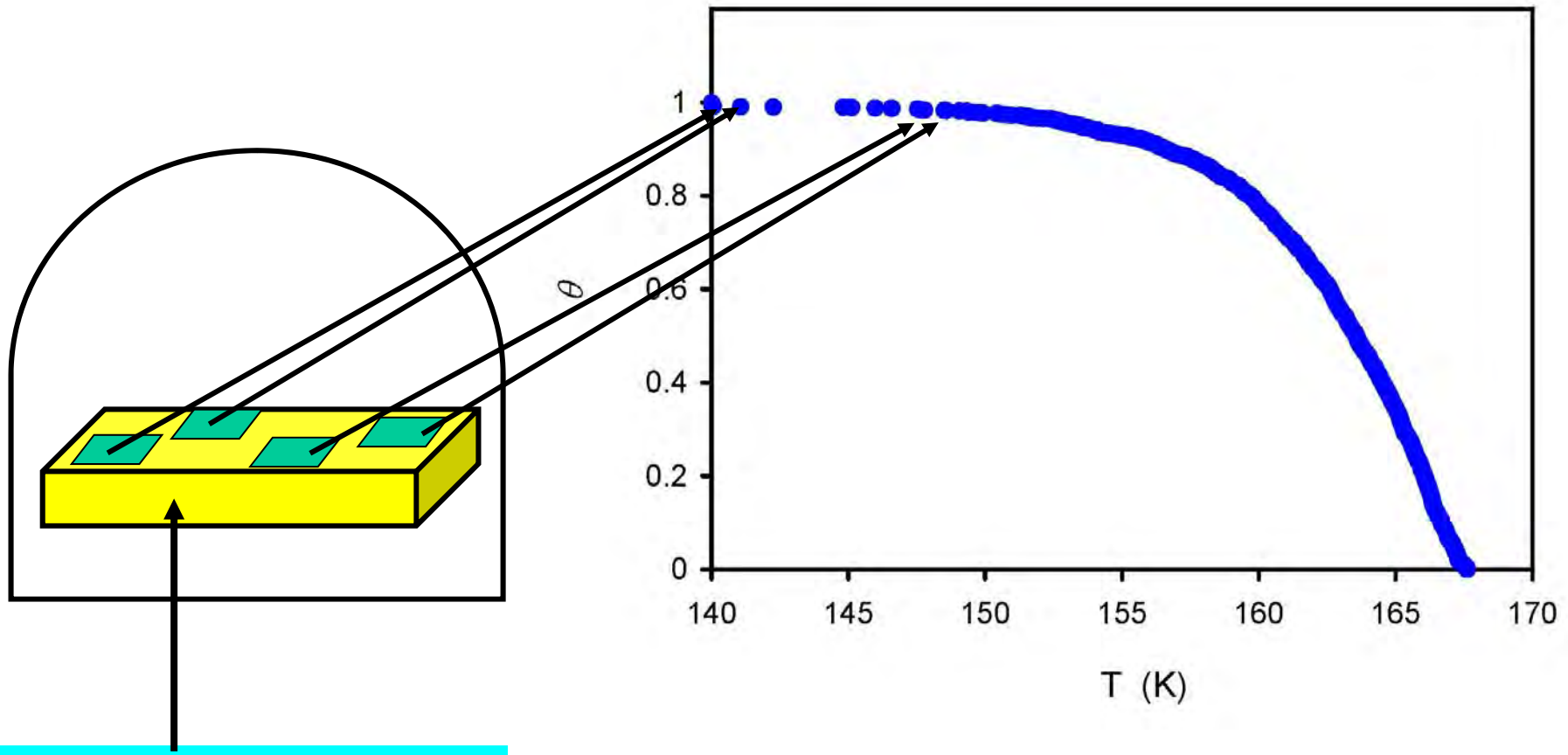
$$A = \left[1 - \left(\frac{\varepsilon_{\max}}{q}\right)^2\right]; \qquad \varepsilon_i = \frac{z_{com,i} - z_{eq}}{z_{eq}}$$

Funnels Boost into Molecule Farthest from the Surface

$$t = \sum_i \exp\left(\frac{\Delta V(\mathbf{R}_i)}{k_B T}\right)\Delta \mathrm{t}$$

K. Becker, M. Mignogna, K. Fichthorn
PRL **102**,046101 (2009).

Accelerated MD of TPD



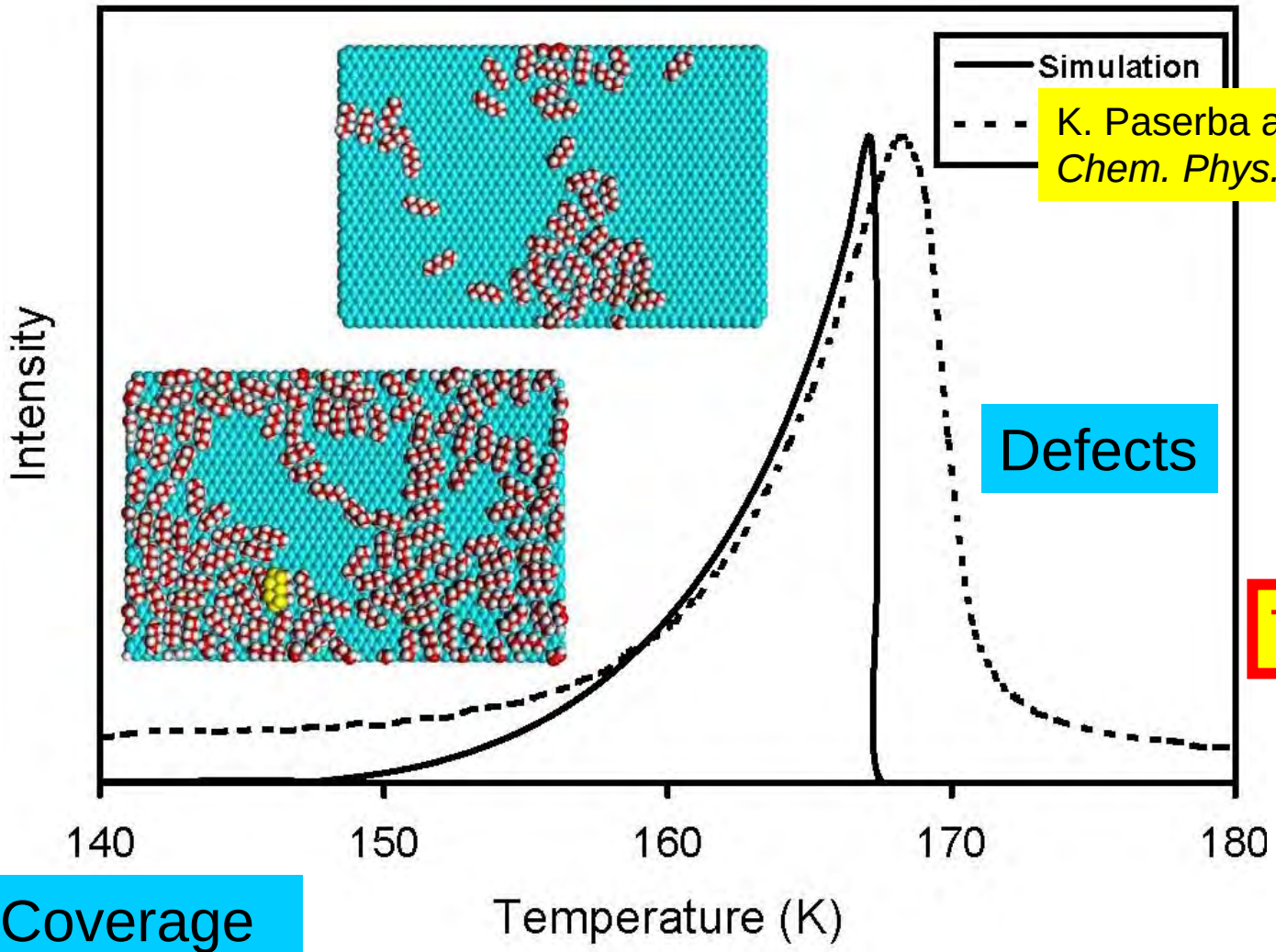
$T = T_0 + \beta t;$
β = Heating Rate

$$t = \Delta t \sum_i \left(\sum_j \exp\left(\Delta V_j / kT\right) + n_e \right)$$

desorptions

K. Becker, M. Mignogna, K. Fichthorn, *PRL* **102**, 046101 (2009).

TPD: Simulation vs. Experiment



K. Paserba and A. Gellman, *J. Chem. Phys.* **115**, 6737 (2001)

Defects

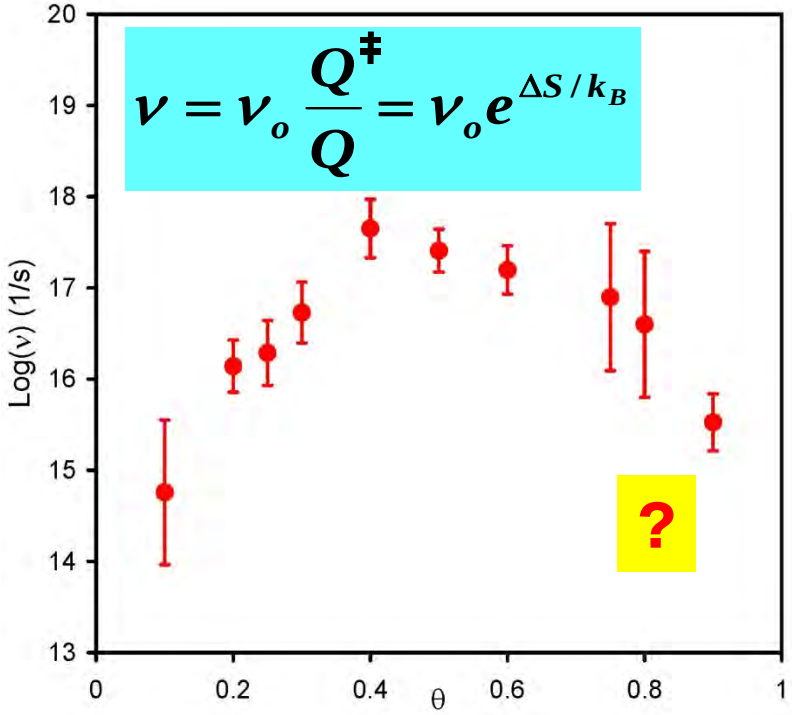
T_0 = 120 K
1 ML Initially
β = 2 K/s

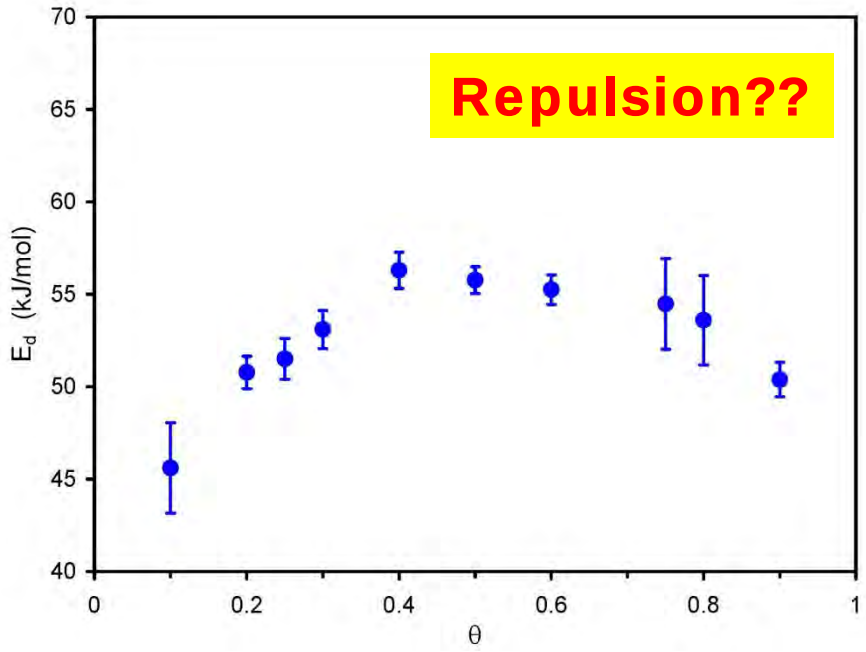
Total Time: 15 s

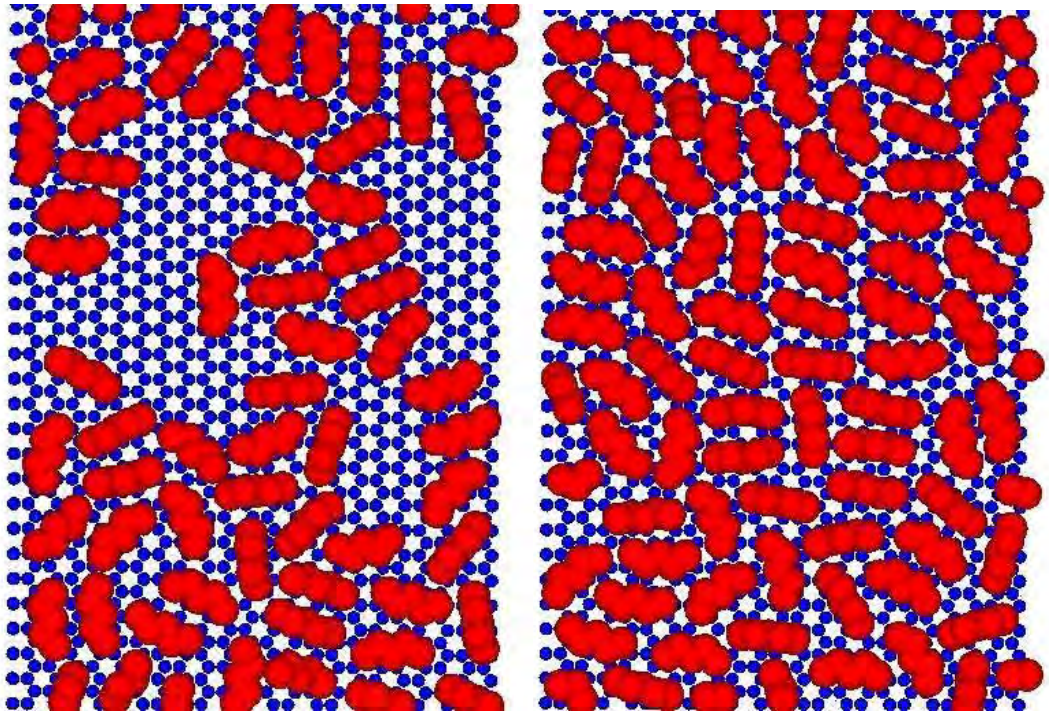
Coverage Calibration

K. Becker, M. Mignogna, K. Fichthorn, *PRL* **102**, 046101 (2009).

Desorption Energy And Prefactor



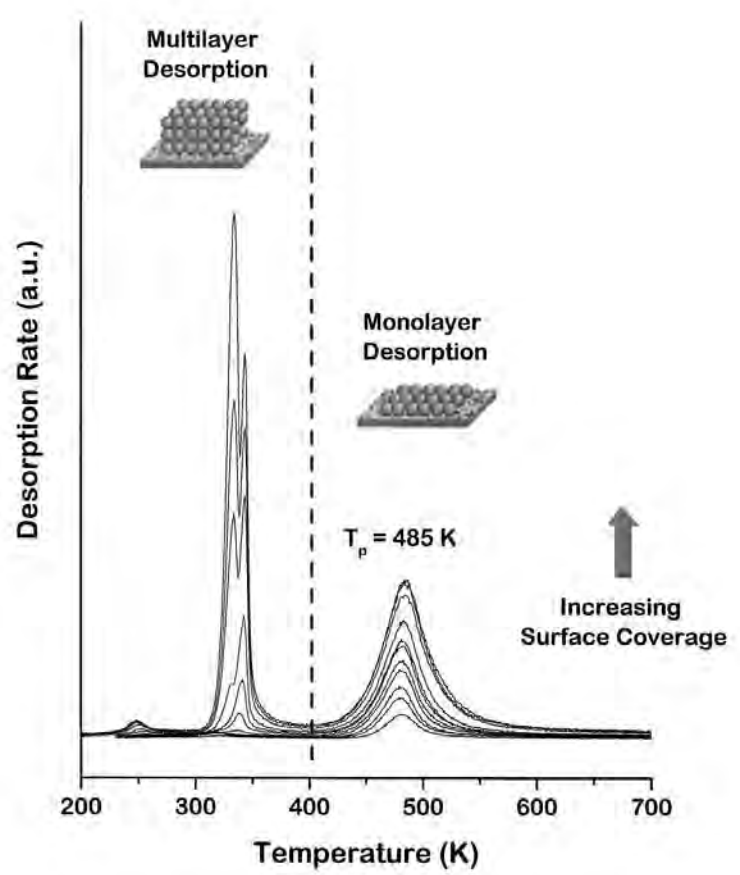


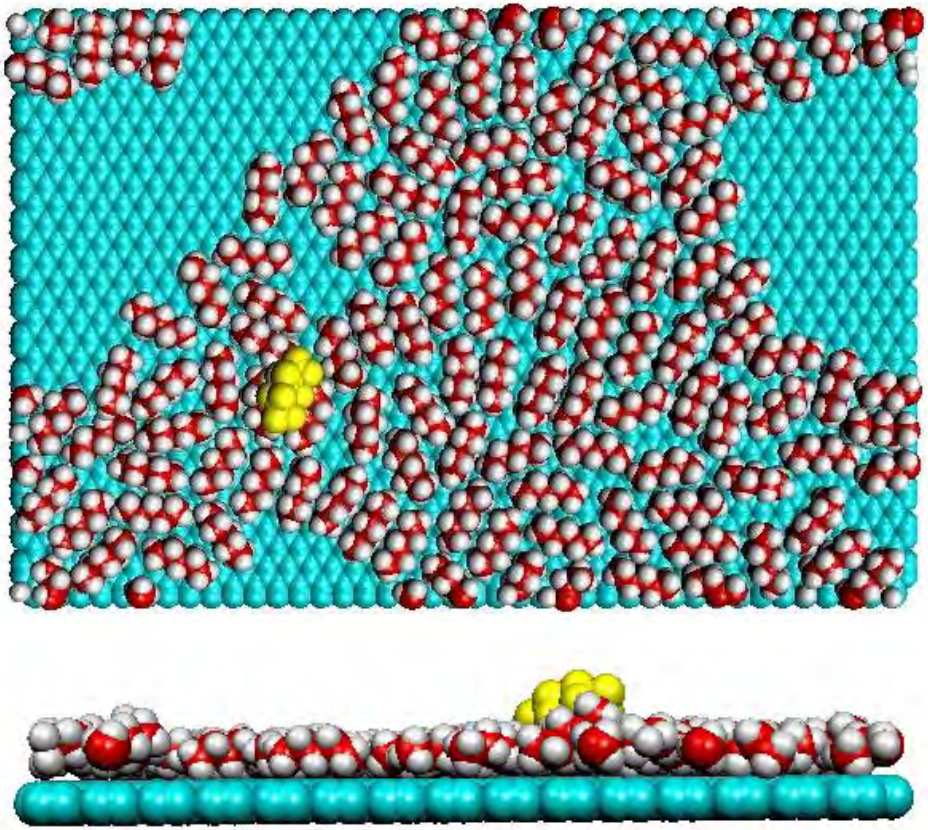


Large prefactors because of loss in rotational entropy on adsorption.

K. Fichthorn and R. Miron, *Phys. Rev. Lett.* **89**, 196103 (2002).
K. Becker and K. Fichthorn, *JCP* **125**, 184706 (2006).

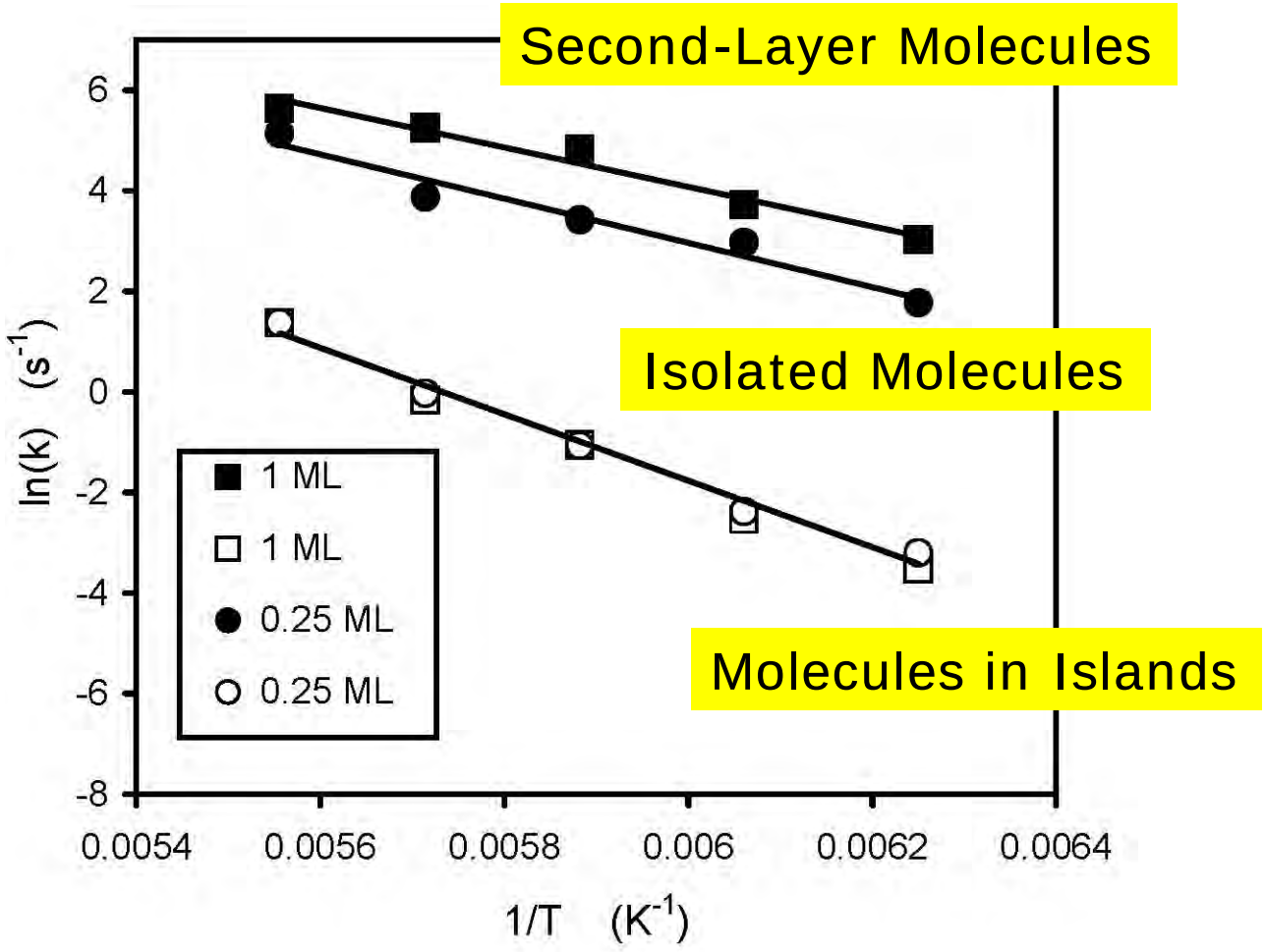
Second-Layer Desorption Can Occur At (Sub) Monolayer Coverage





Second-Layer Desorption at $\theta = 0.75$

Rate Processes in Pentane Desorption



E_d = 32.5 kJ/mol

ν_0 = 9.2E+11

E_d = 36.5 kJ/mol

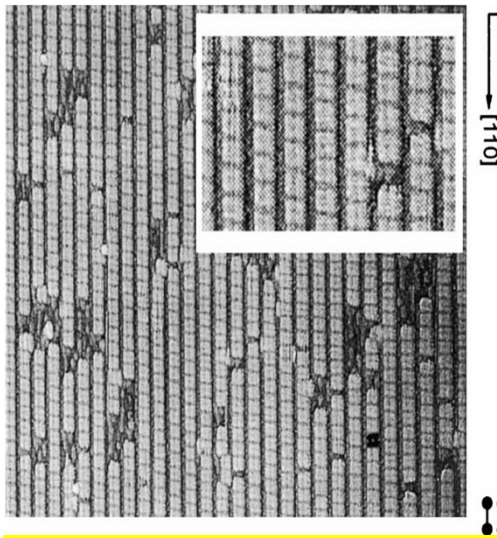
ν_0 = 5.5E+12

E_d = 58.1 kJ/mol

ν_0 = 2.4E+17

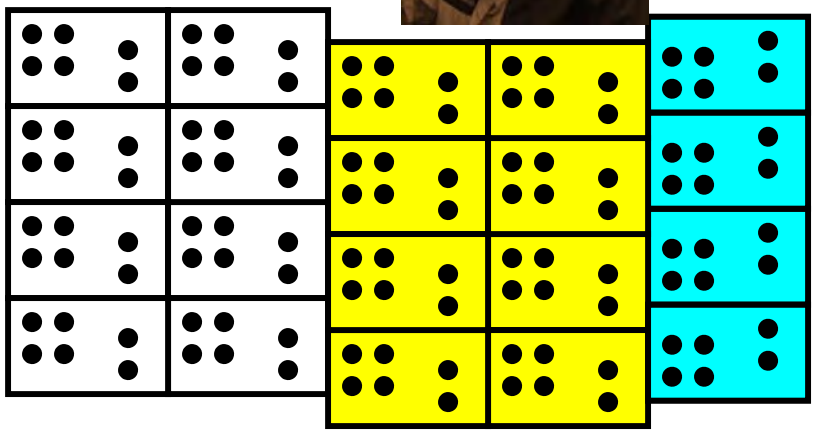
K. Becker, M. Mignogna, K. Fichthorn, *PRL* **102**, 046101 (2009).

What is the Structure of a Real GaAs(001)β2(2x4) Surface?



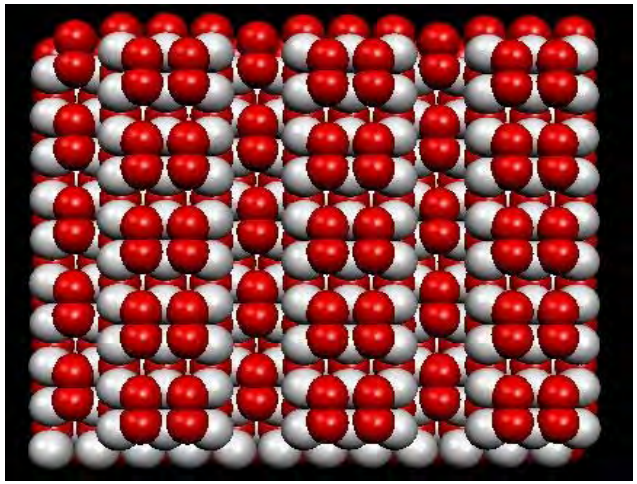
STM

(2x4) Unit Cell



D.W. Pashley, J.H. Neave, B.A. Joyce, Surf. Sci. **582,** 189 (2005)

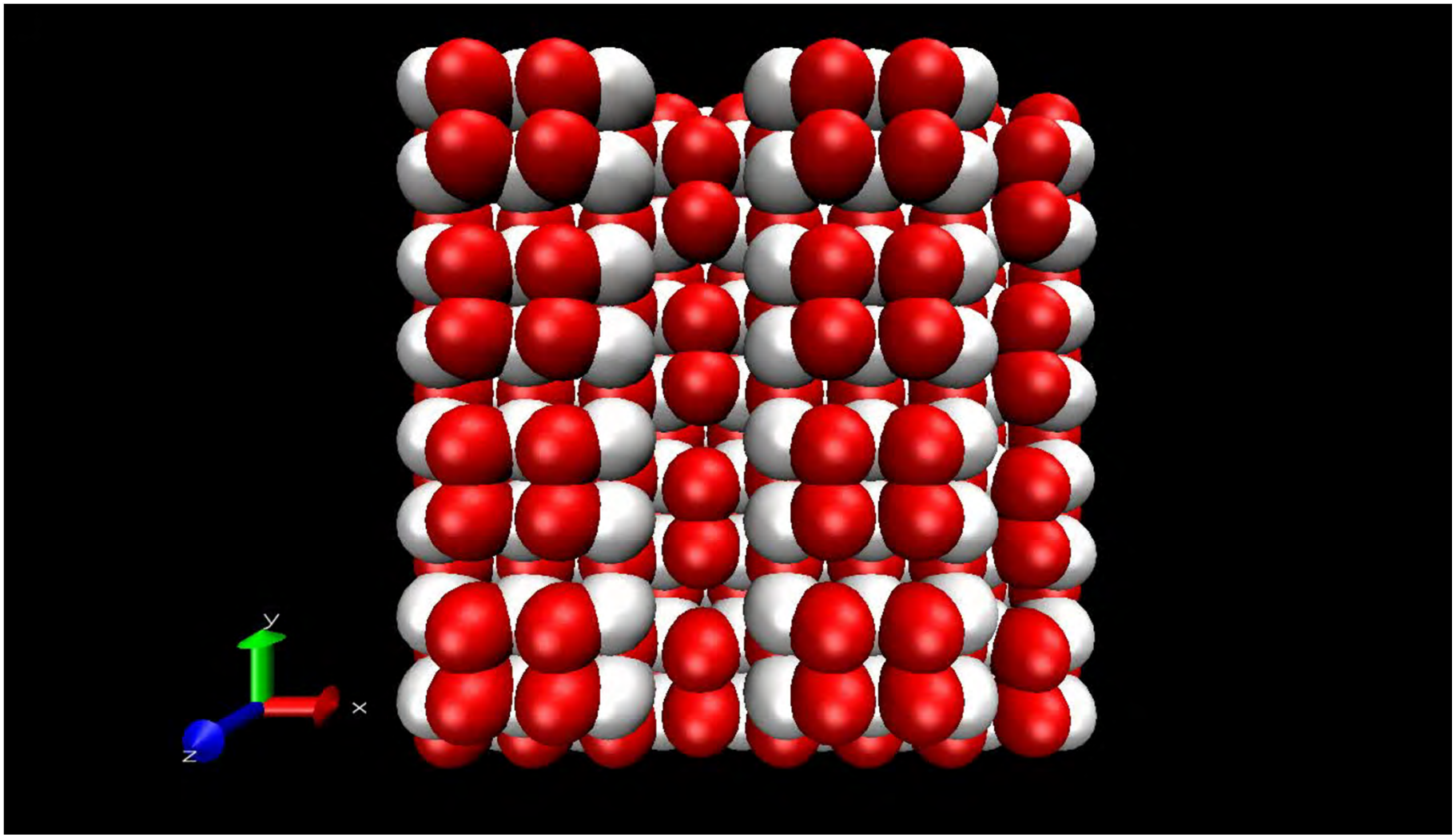
Hypothesis: Disordering Involves Shifting of Dimer Rows and Trenches



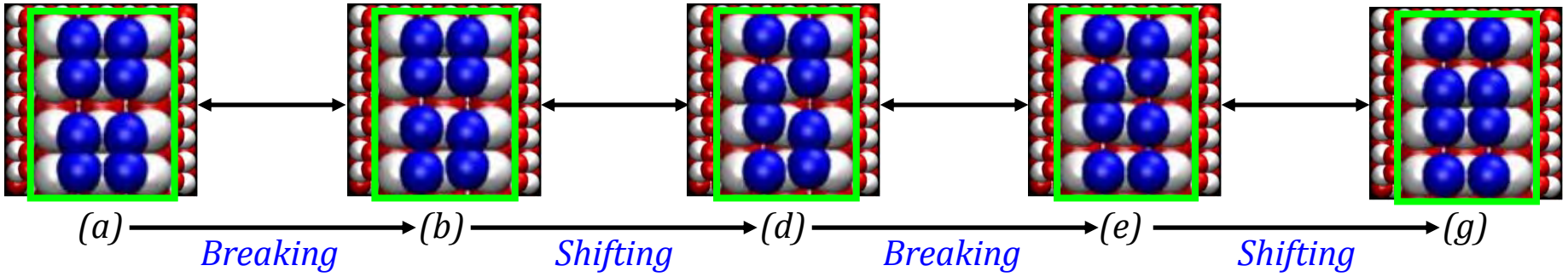
How Does this Surface Disorder? What Does This Mean for Diffusion and Growth??

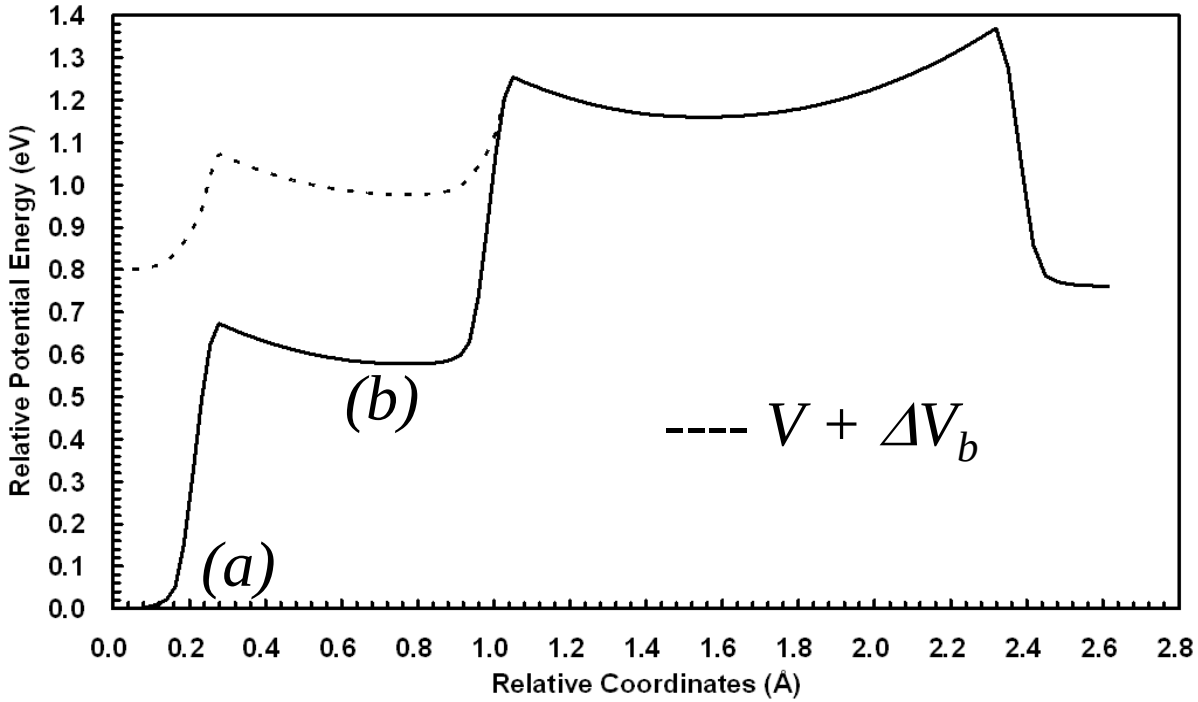
K. A. Fichthorn, *et al*., Phys. Rev. B, **83**, 195328 (2011)

Regular MD of GaAs (001): T = 600 K



Minimum-Energy Path for Row Shift: Another Form of the Small-Barrier Problem

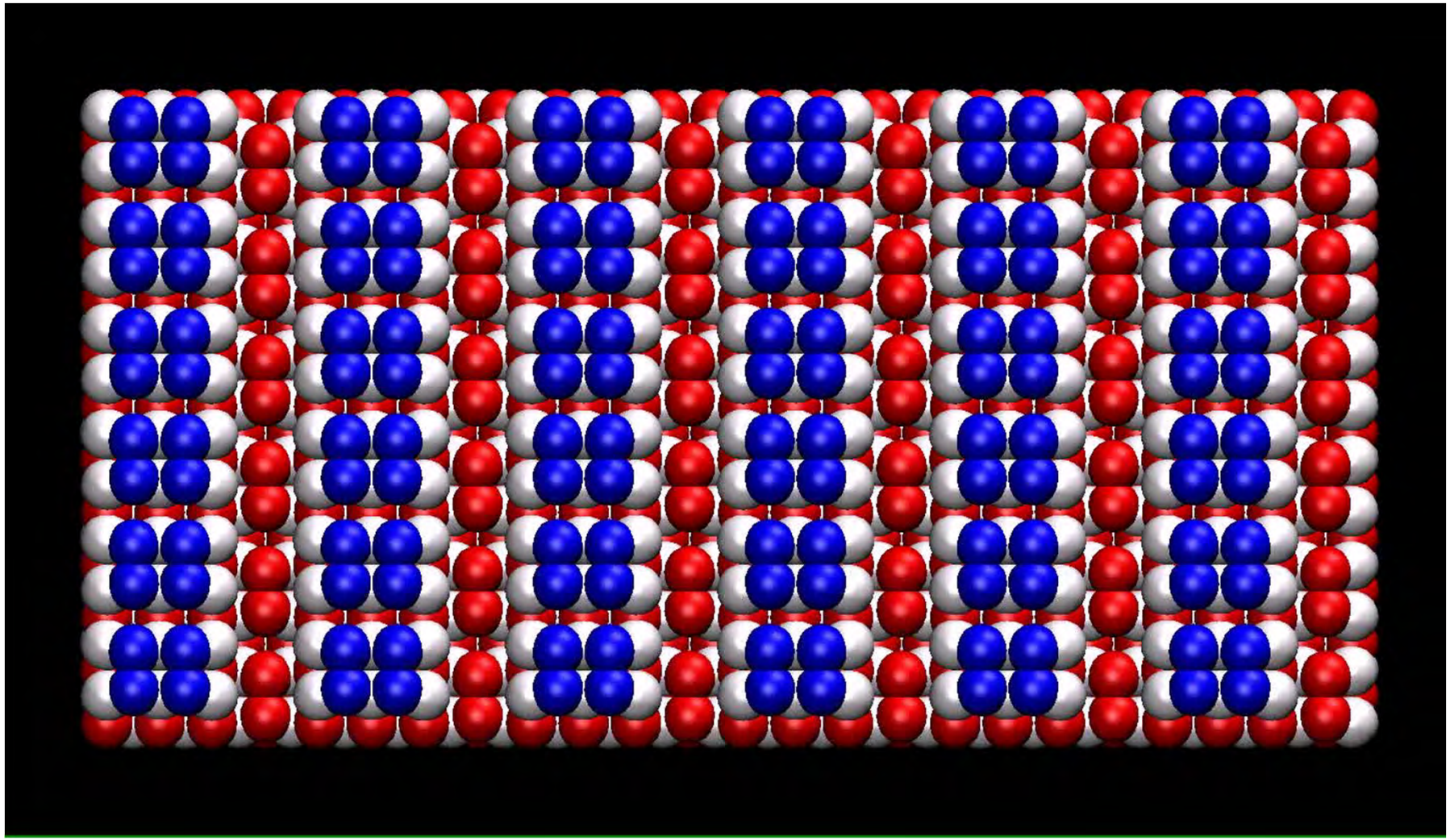




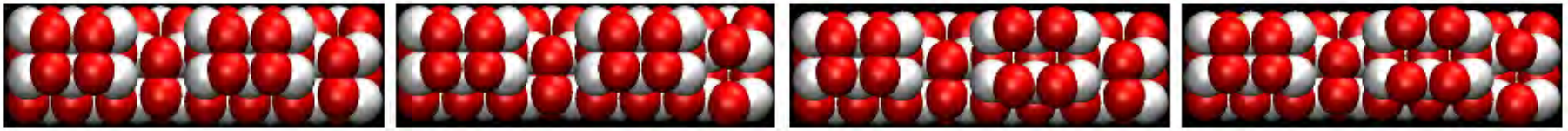
CI-NEB Method

G. Henkelman, B.Uberuaga, and H. Jonsson, J. Chem. Phys. **113,** 9901 (2000).

Accelerated MD Simulation at 800 K



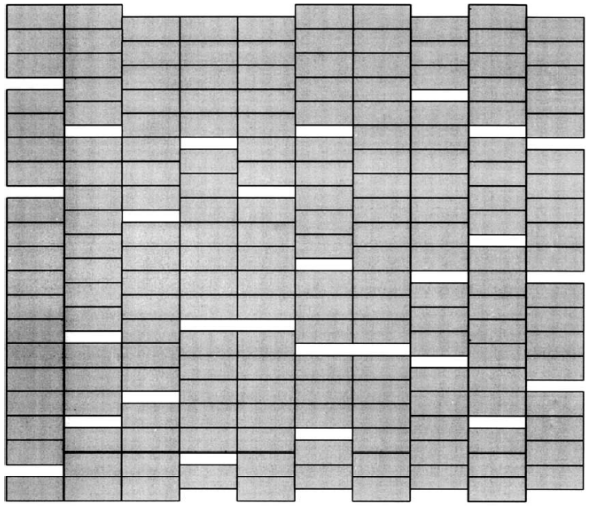
Equilibrium Fraction of β2(2x4) and c(2×8) from 1 μs - 4 s Accelerated MD



(a) $\gamma = 68.73$ meV/Å^2 (b) $\gamma = 68.71$ meV/Å^2 (c) $\gamma = 68.68$ meV/Å^2 (d) $\gamma = 68.67$ meV/Å^2

(a) and (b) β2(2×4) (c) and (d) c(2×8)

	900K	850K	800K	700K	600K
β2(2×4)	0.43±0.03	0.45±0.03	0.44±0.03	0.42±0.15	0.46±0.13
c(2×8)	0.52±0.03	0.52±0.03	0.54±0.03	0.58±0.15	0.53±0.13
Others	0.053±0.003	0.031±0.005	0.019±0.002	0.007±0.003	0.008±0.008



Arrangement based on STM image

Comparison with Experiment

STM (300K, UHV)

β2(2×4) **0.41**; c(2×8) **0.52**; Other **0.07**

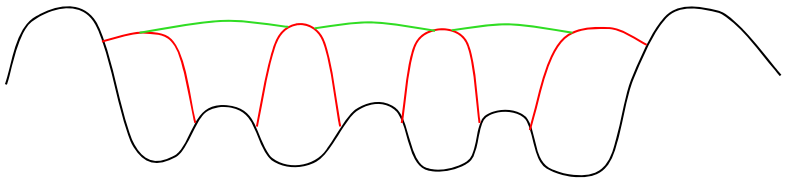
RHEED (850 K As Over Pressure, 300 K Vacuum)
No Difference

D. W. Pashley, J. H. Neave, and B. A. Joyce, Surf. Sci. **582**, 189 (2005)

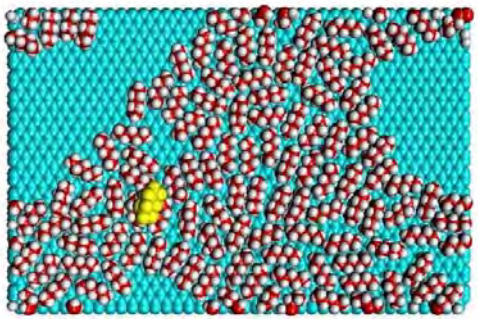
Conclusions: Progress in Accelerated MD

- The Bond-Boost Method is Useful for Modeling and/or Discovering Rare Events
- The Challenge is Dealing with the Small-Barrier Problem in a General Way
  - Consolidating Pools of Shallow States

    R. Miron & K. Fichthorn, Phys. Rev. Lett. 93, 2004;
    Phys. Rev. B**72**, 035415, 2005.

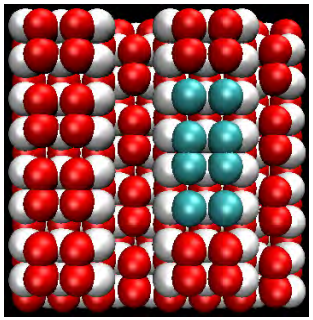


Conclusions: Progress in Accelerated MD



- Bond = Order Parameter
  K. Becker, M. Mignogna, K. Fichthorn, *PRL* **102**, 046101 (2009)

- Pathway Boost for GaAs(001)
  Y. Lin and K. Fichthorn, in preparation.



The key to future progress is a general solution to the small barrier problem

Look for our **NEW SOLUTION** to the Small-Barrier Problem Using KMC+Master Equation!!!!

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