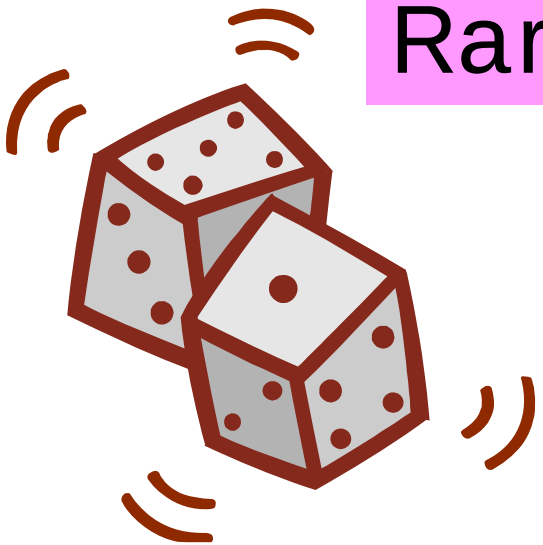
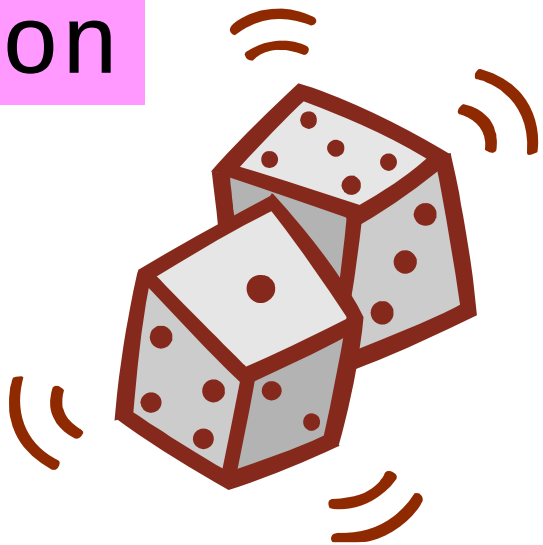
An Introduction to Rare-Event Simulation





Kristen A. Fichthorn
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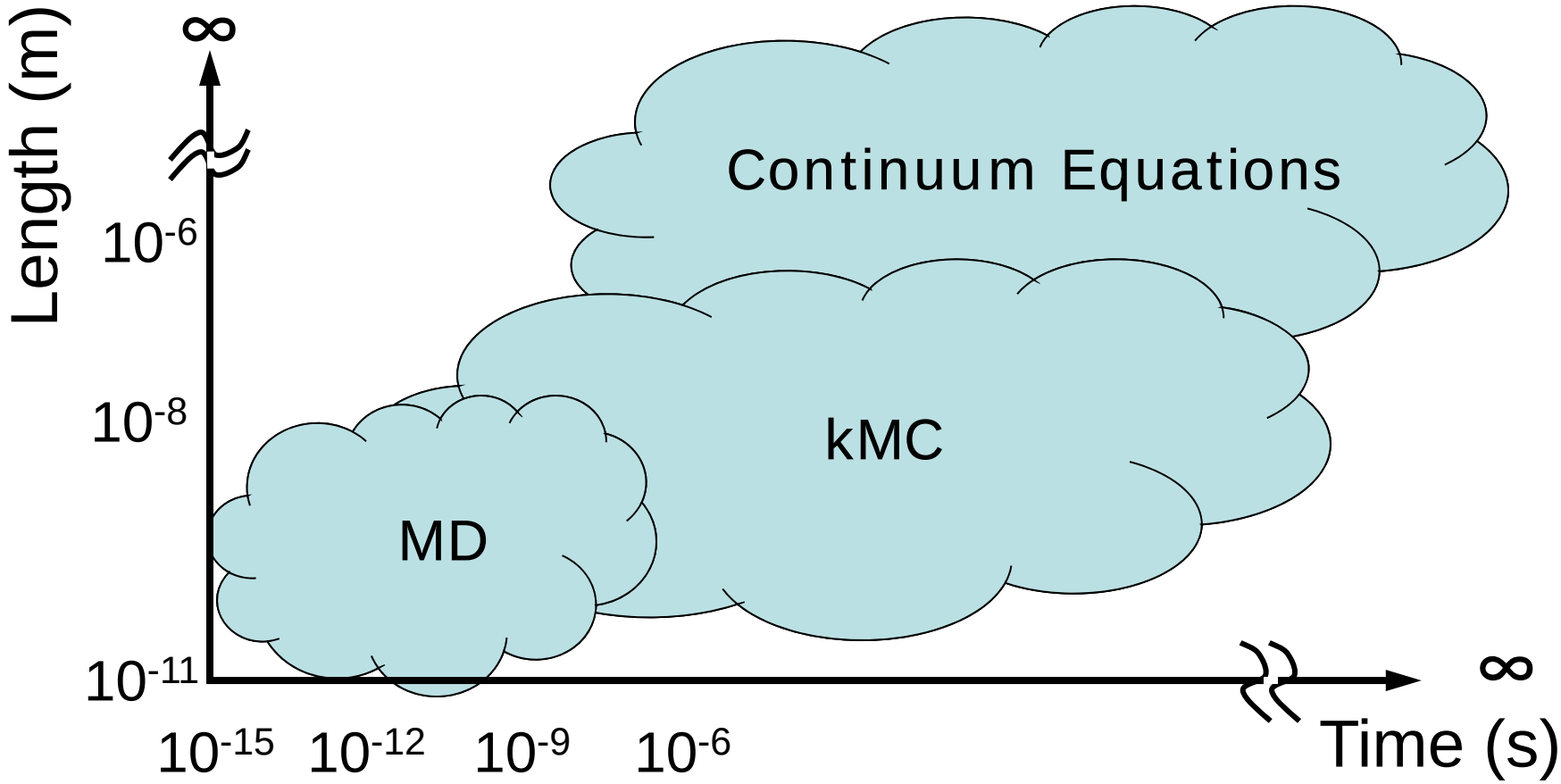
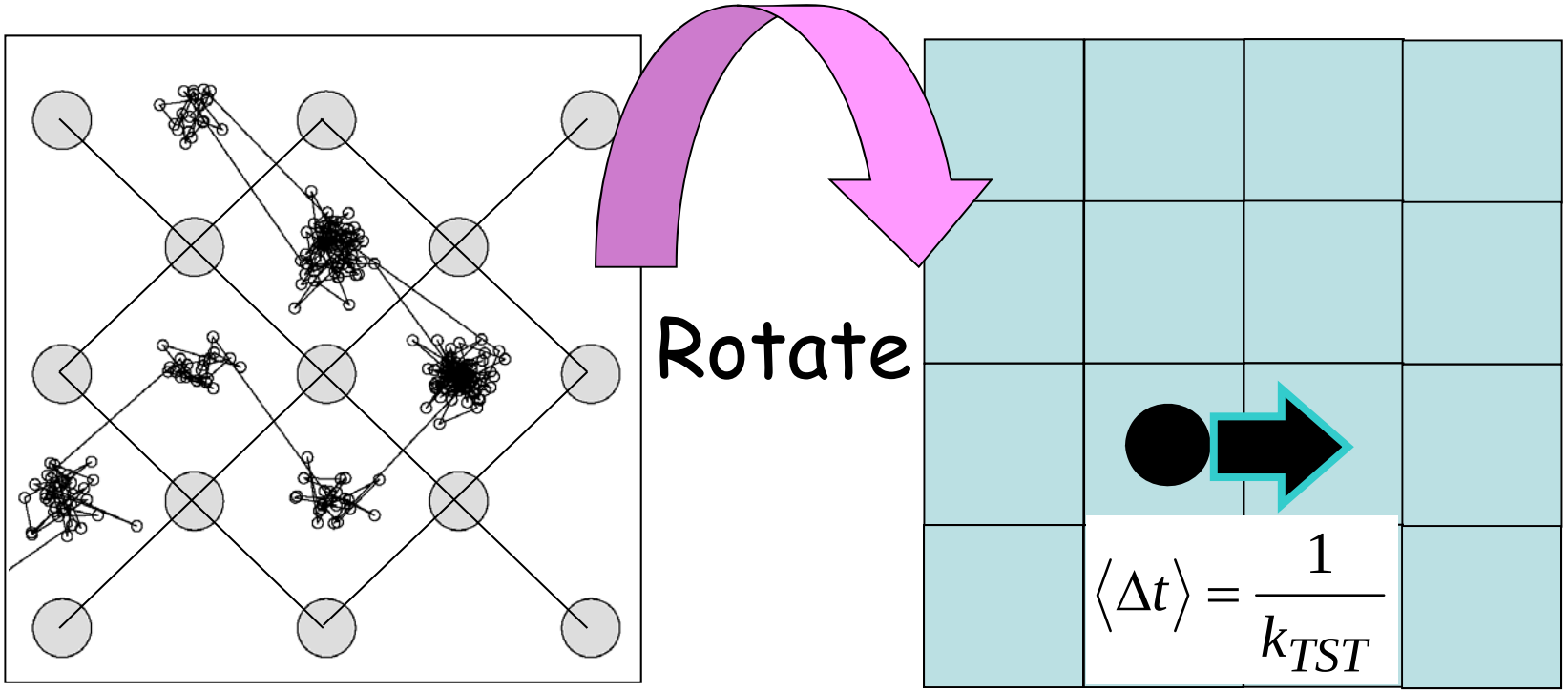
Kinetic Monte Carlo: A Coarse-Grained, Atomistic, Lattice-Based Technique for Time Evolution of Condensed Matter



Kinetic Monte Carlo: Coarse-Graining MD



MD of Co on Cu(001): The Whole Trajectory

kMC: Coarse-Grained Hops

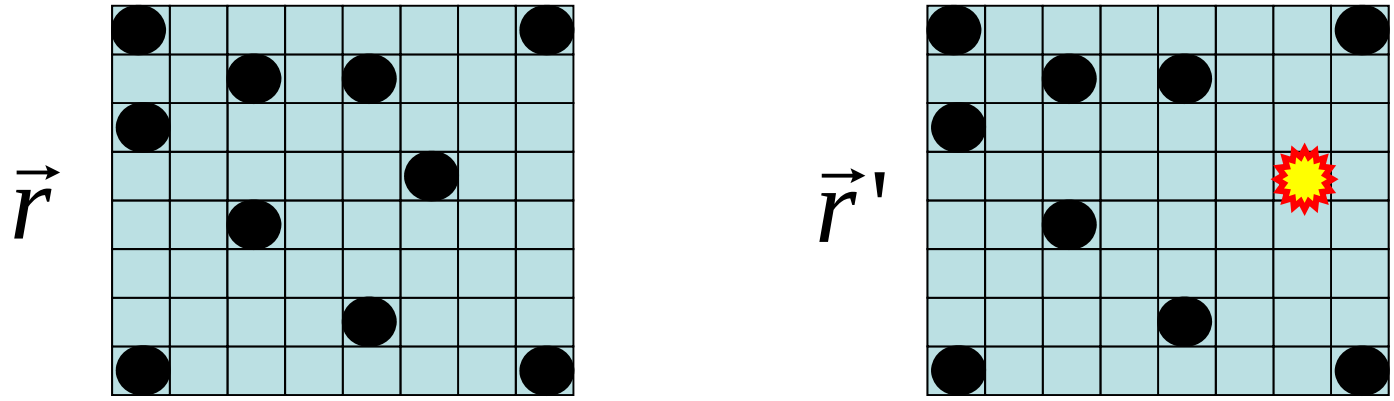
Rare Events: $k_{TST} = \left\langle \frac{\nu}{2} \right\rangle \frac{\int \delta(\mathbf{R}-\mathbf{R}^{\dagger}) \exp(-V(\mathbf{R})/k_B T)}{\int \exp(-V(\mathbf{R})/k_B T)}$

Kinetic Monte Carlo as an Accurate Solution to the Master Equation

$$\frac{dP(\vec{r},t)}{dt} = -\sum_{\vec{r}'} W(\vec{r} \rightarrow \vec{r}')P(\vec{r},t) + \sum_{\vec{r}'} W(\vec{r}' \rightarrow \vec{r})P(\vec{r}',t)$$

$P(\vec{r},t)$: Probability to be at State $\vec{r}$ at Time t

$W(\vec{r} \rightarrow \vec{r}')$: Transition Probability per Unit Time from $\vec{r}$ to $\vec{r}'$



Kinetic Monte Carlo as a More Accurate Solution to the Master Equation

$$\frac{dP(\vec{r},t)}{dt} = -\sum_{\vec{r}'} W(\vec{r} \to \vec{r}')P(\vec{r},t) + \sum_{\vec{r}'} W(\vec{r}' \to \vec{r})P(\vec{r}',t)$$

$$= 0 \quad \text{at equilibrium}$$

Detailed-Balance Criterion

$$W(\vec{r}' \to \vec{r})P_{eq}(\vec{r}',t) = W(\vec{r} \to \vec{r}')P_{eq}(\vec{r},t)$$

$$\frac{W(\vec{r} \to \vec{r}')}{W(\vec{r}' \to \vec{r})} = \exp\left[-\Delta A / k_B T\right]$$

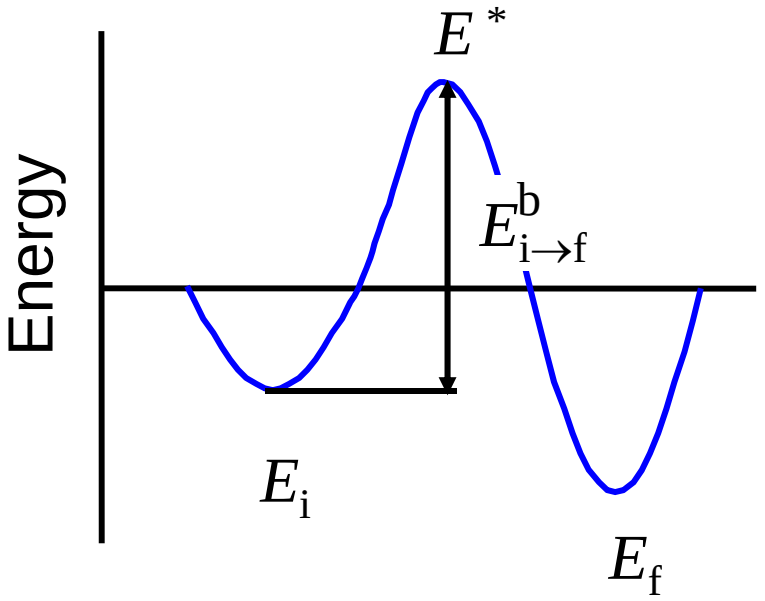
kMC Transition Probabilities Satisfy Detailed Balance and are also Based on a Kinetic Model

KMC Transition Probabilities and the Detailed-Balance Criterion

$$\frac{W(\vec{r} \to \vec{r}')}{W(\vec{r}' \to \vec{r})} = \exp\left[-\Delta A / k_B T\right]$$

Metropolis MC Satisfies Detailed Balance, but not Kinetics

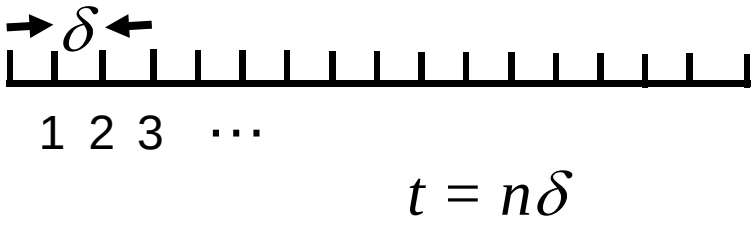
$$W(i \to f) = \begin{cases} 1 & if \quad E_f \le E_i \\ e^{-\Delta E / k_B T} & if \quad E_f > E_i \end{cases}$$



$$W(i \to f) = \nu_0 \exp(-E^b_{i \to f} / k_B T)$$

TST Satisfies Detailed Balance and Kinetics

KMC Simulates a Poisson Process



Events Can Happen Any Time with an Equal Probability per Unit Time *r*

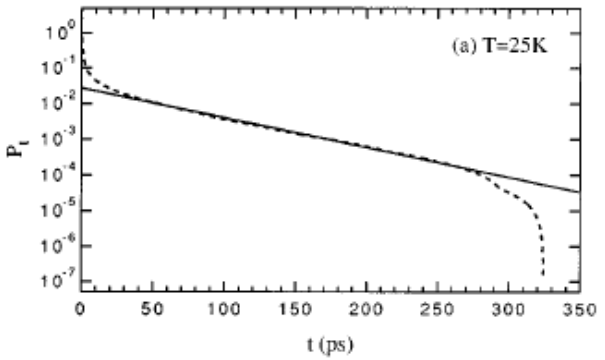
How Long Must We Wait?

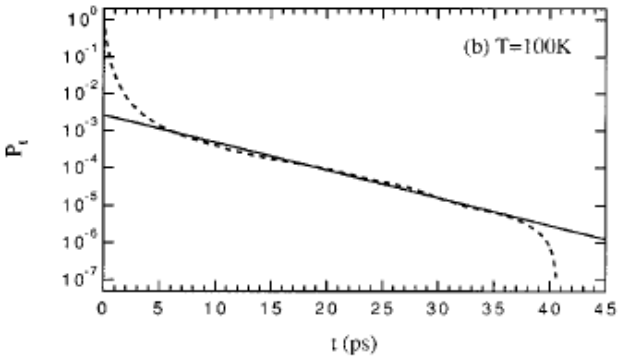
$$P(n) = (1-\delta r)^n \delta r$$

$$\frac{P(n)}{\delta} \xrightarrow{\delta \to 0} p(t) = re^{-rt}$$

$$\langle t \rangle = 1/r$$

Adsorbate Hopping is A Poisson Process





J. Raut and K. Fichthorn, *J. Chem. Phys.* **103**, 8694 (1995).

Multiple Independent Poisson Processes: One Big Poisson Process

$$p(t) = \mathrm{R}e^{-Rt}; \qquad R = \sum_i r_i$$

A 

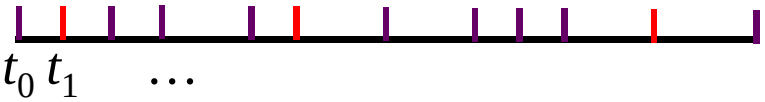
$$\langle t_A \rangle = \frac{1}{r_A}$$

+

B 

$$\langle t_B \rangle = \frac{1}{r_B}$$

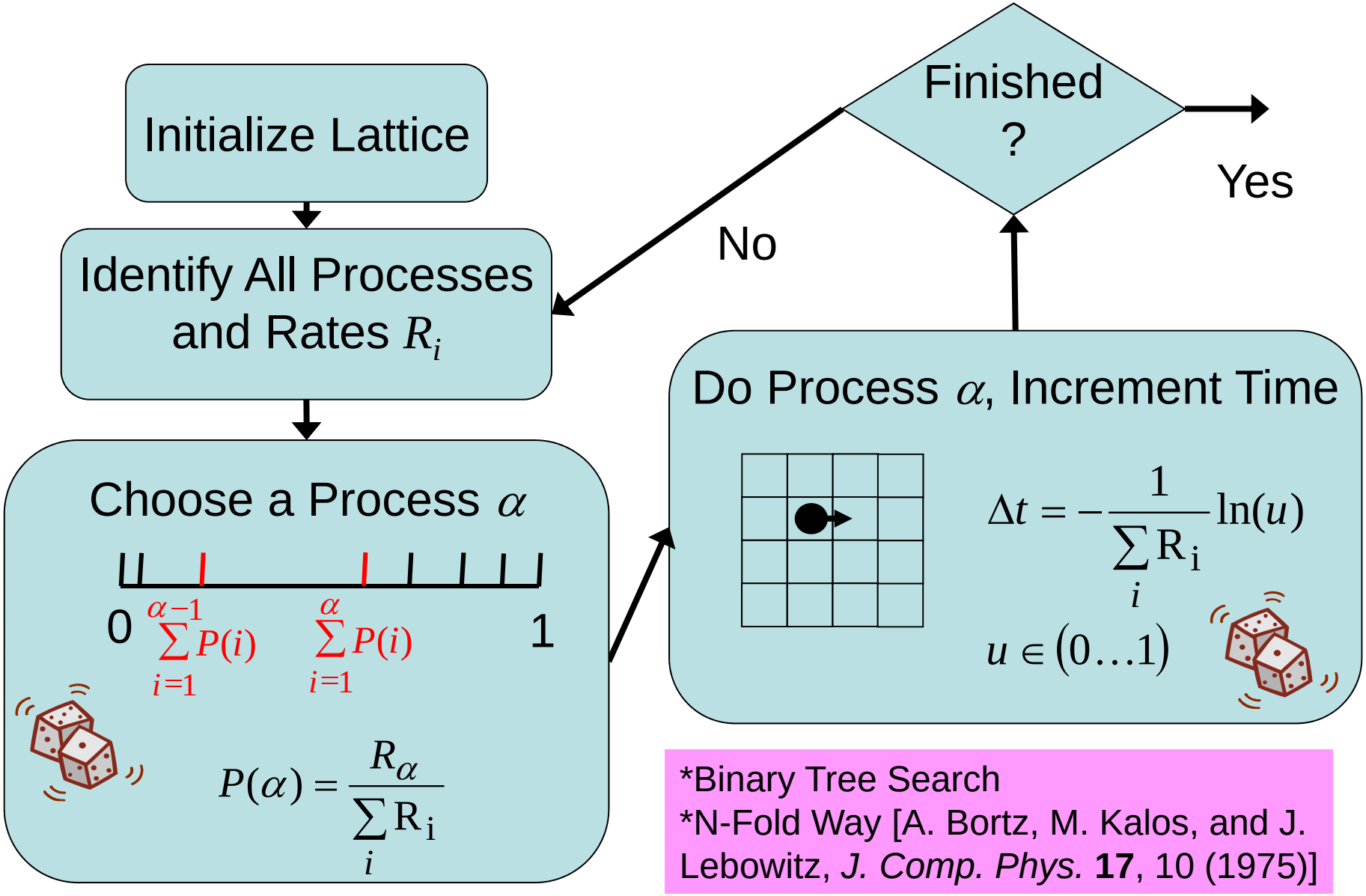
=



$$\langle t_{A+B} \rangle = \frac{1}{r_A + r_B}$$

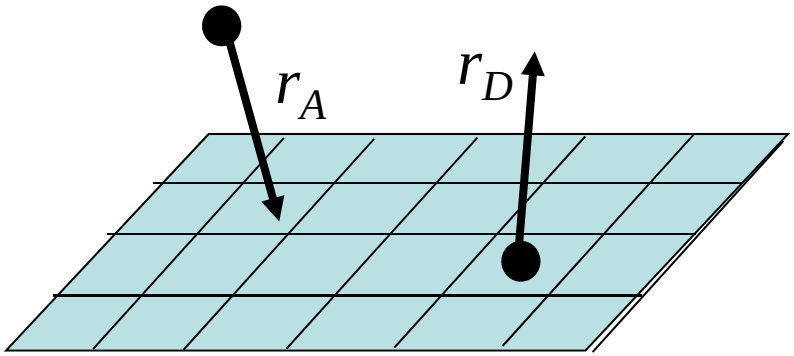
$$P(A) = \frac{r_A}{r_A + r_B}; \quad P(B) = \frac{r_B}{r_A + r_B}$$

A Generic kMC Algorithm



*Binary Tree Search
*N-Fold Way [A. Bortz, M. Kalos, and J. Lebowitz, *J. Comp. Phys.* **17**, 10 (1975)]

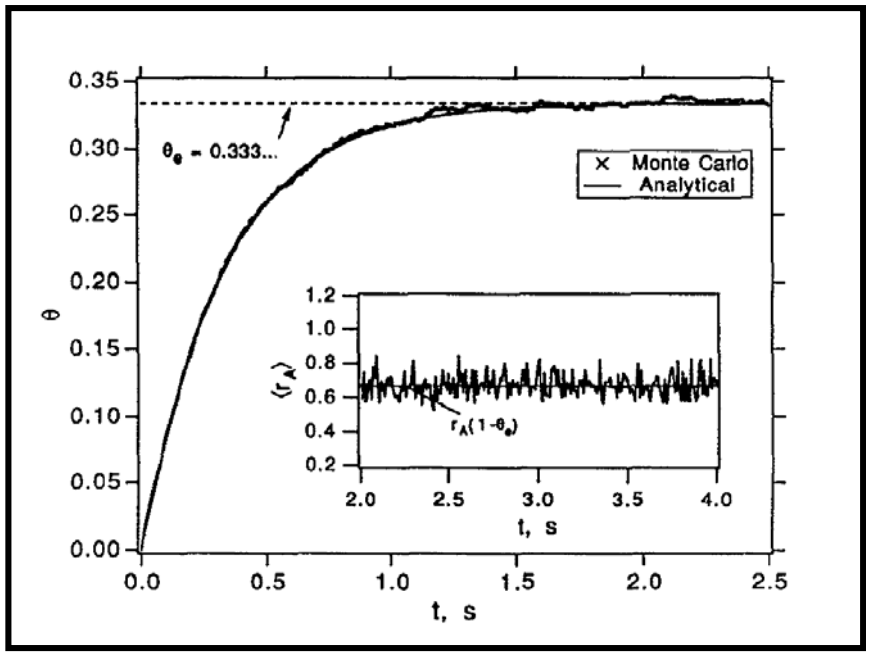
Application of kMC to Langmuir Adsorption / Desorption



$$\frac{d\theta}{dt} = r_A(1-\theta) - r_D\theta; \quad \theta(0) = 0$$

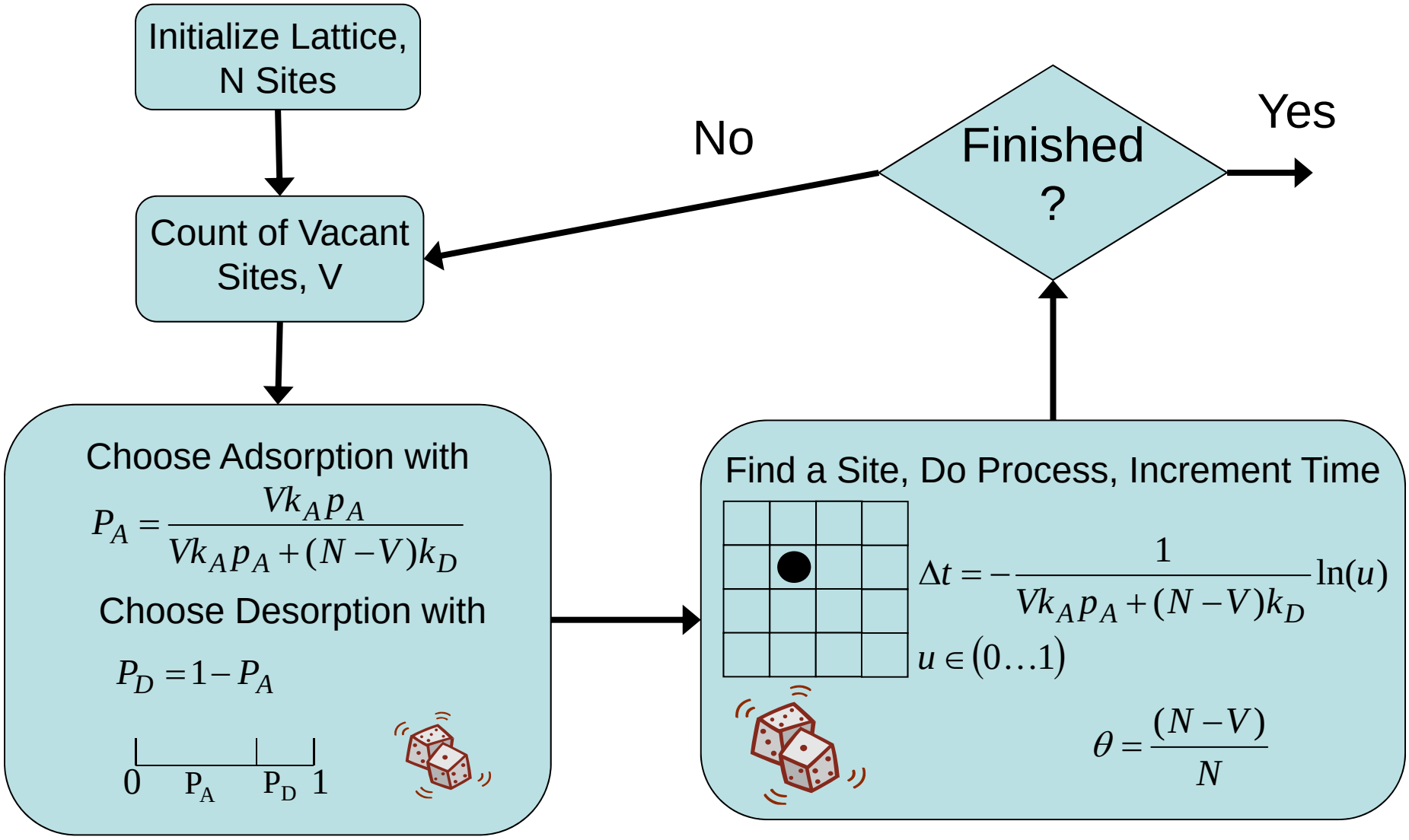
$$\theta(t) = \frac{r_A}{r_A + r_D}\left[1 - \exp\left(-\left(r_A + r_D\right)t\right)\right]$$

$$r_A = 1\,\mathrm{s}^{-1}; \qquad r_D = 2\,\mathrm{s}^{-1}$$



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

kMC of Langmuir Adsorption / Desorption



kMC Model of Langmuir-Hinshelwood Reaction

$$A_g + B_g \xrightarrow{catalyst} C_g$$

$$A_g + S \rightarrow A \bullet S$$

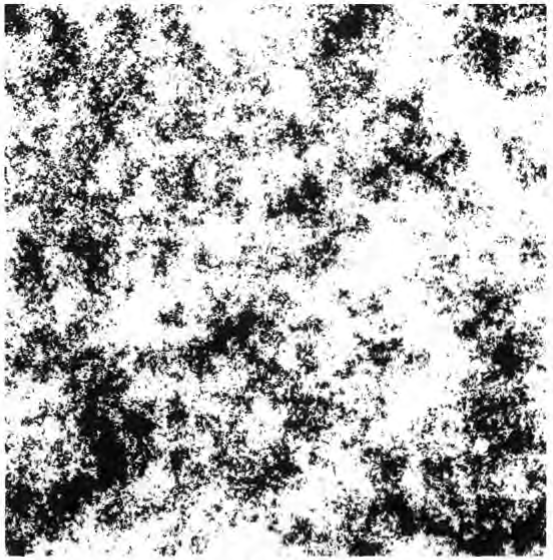
$$B_g + S \rightarrow B \bullet S$$

$$A \bullet S + B \bullet S \rightarrow C_g + 2S$$

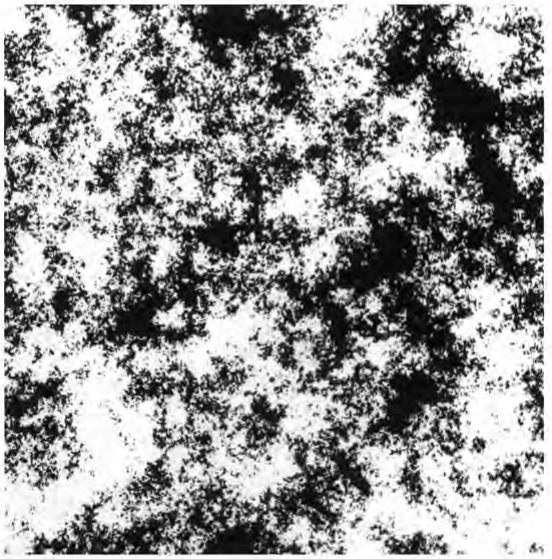
$$-r_A = k\theta_A\theta_B$$

The Mean-Field Approximation Isn't Always Accurate.....

R. Ziff and K. Fichthorn, *PRB* **34**, 2038 (1986).



(a)

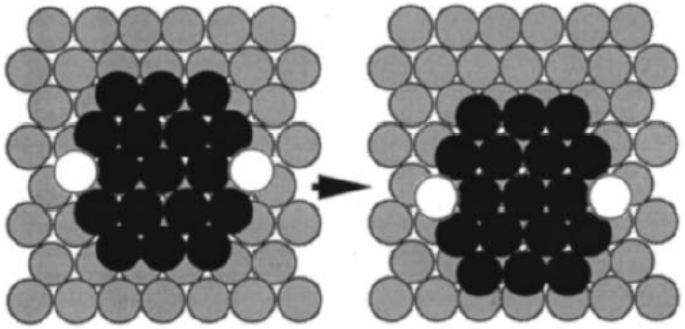


(b)

FIG. 1. A representation of the adsorbed A (a) and B (b) molecules on a 1024×1024 catalyst surface after 6.8×10^9 trials or 6500 time steps at $P_A = \frac{1}{2}$.

Pitfalls of kMC Coarse-Graining

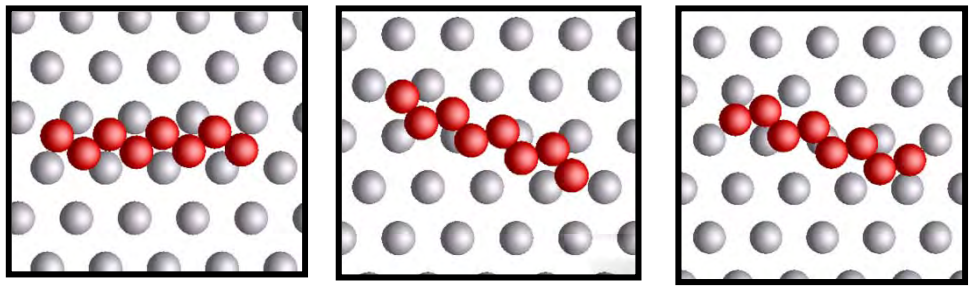
Identifying All Events



J. Hamilton, M. Sorenson, and A. Voter, *PRB* **61**, 5125 (2000).

Also see:
R. A. Miron and K. A. Fichthorn, *J. Chem. Phys*. **115**, 8742 (2001).

Assumption of a Lattice, TST



K. Fichthorn and R. Miron, *PRL* **89**, 196103 (2002).

Accelerated Molecular Dynamics
(Hyperdynamics)

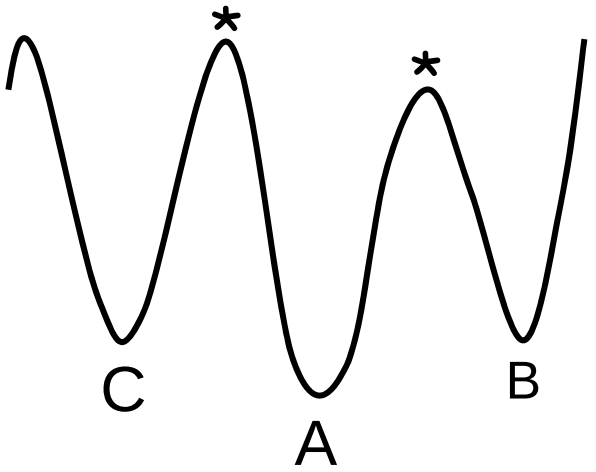
A. Voter, J. Chem. Phys. **106**, 11 (1997).

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

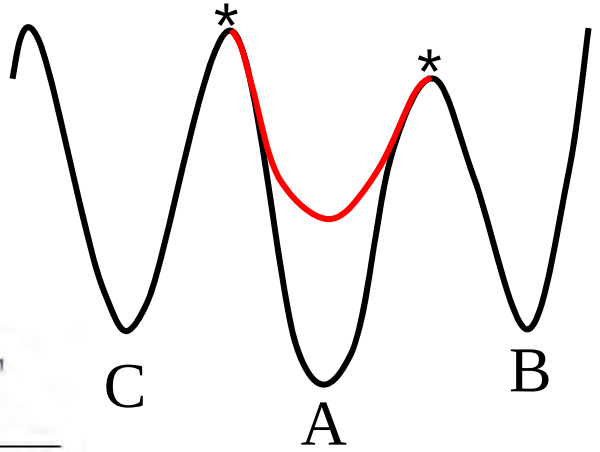
$$k_{A\to B}^{TST} = \nu \frac{\int \delta_{AB}^* W(\mathbf{R}) e^{-V(\mathbf{R})/k_B T} / W(\mathbf{R})}{\int W(\mathbf{R}) e^{-V(\mathbf{R})/k_B T} / W(\mathbf{R})}$$

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

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



Relative Rates



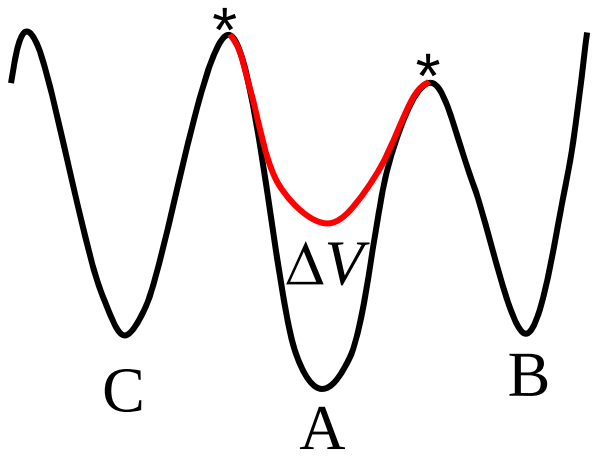
Accelerated Molecular Dynamics
(Hyperdynamics)

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 $\Delta V(R)$...

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

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

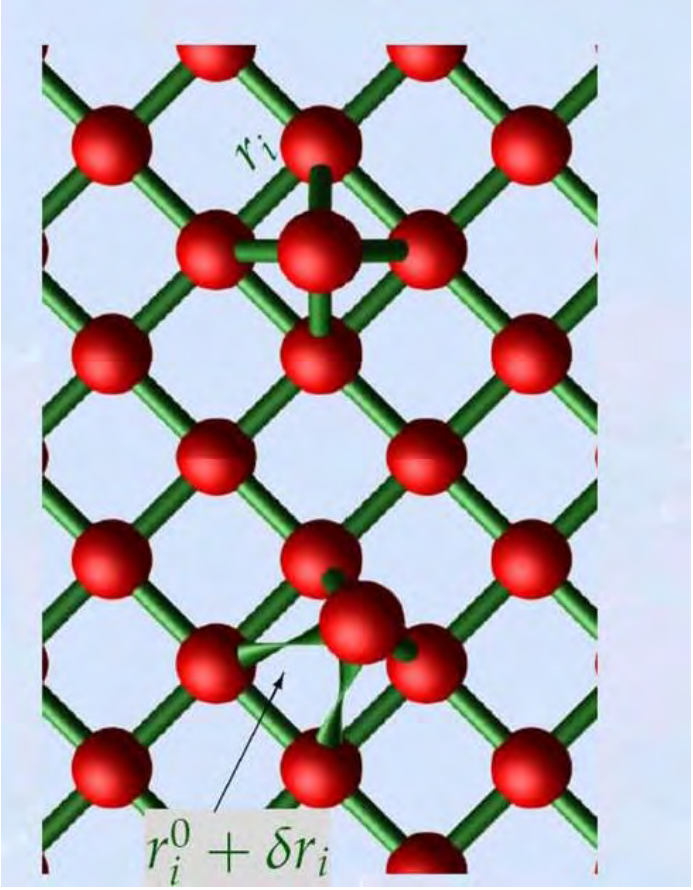
Empirical Threshold

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

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

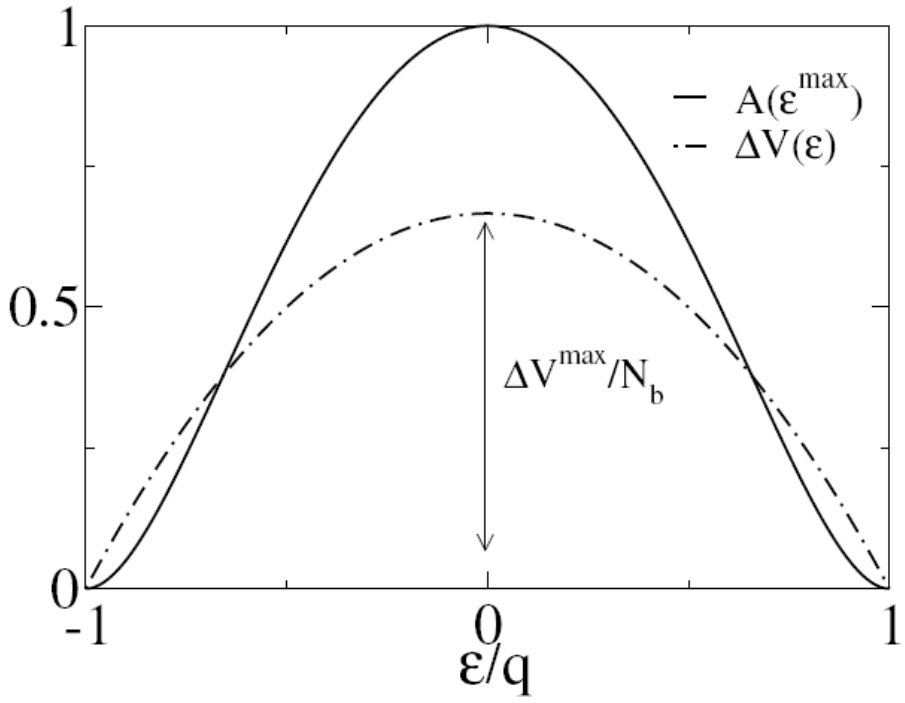
$$\varepsilon_i = \frac{\delta r_i}{r_i^0}$$

Nominal Boost per Bond

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

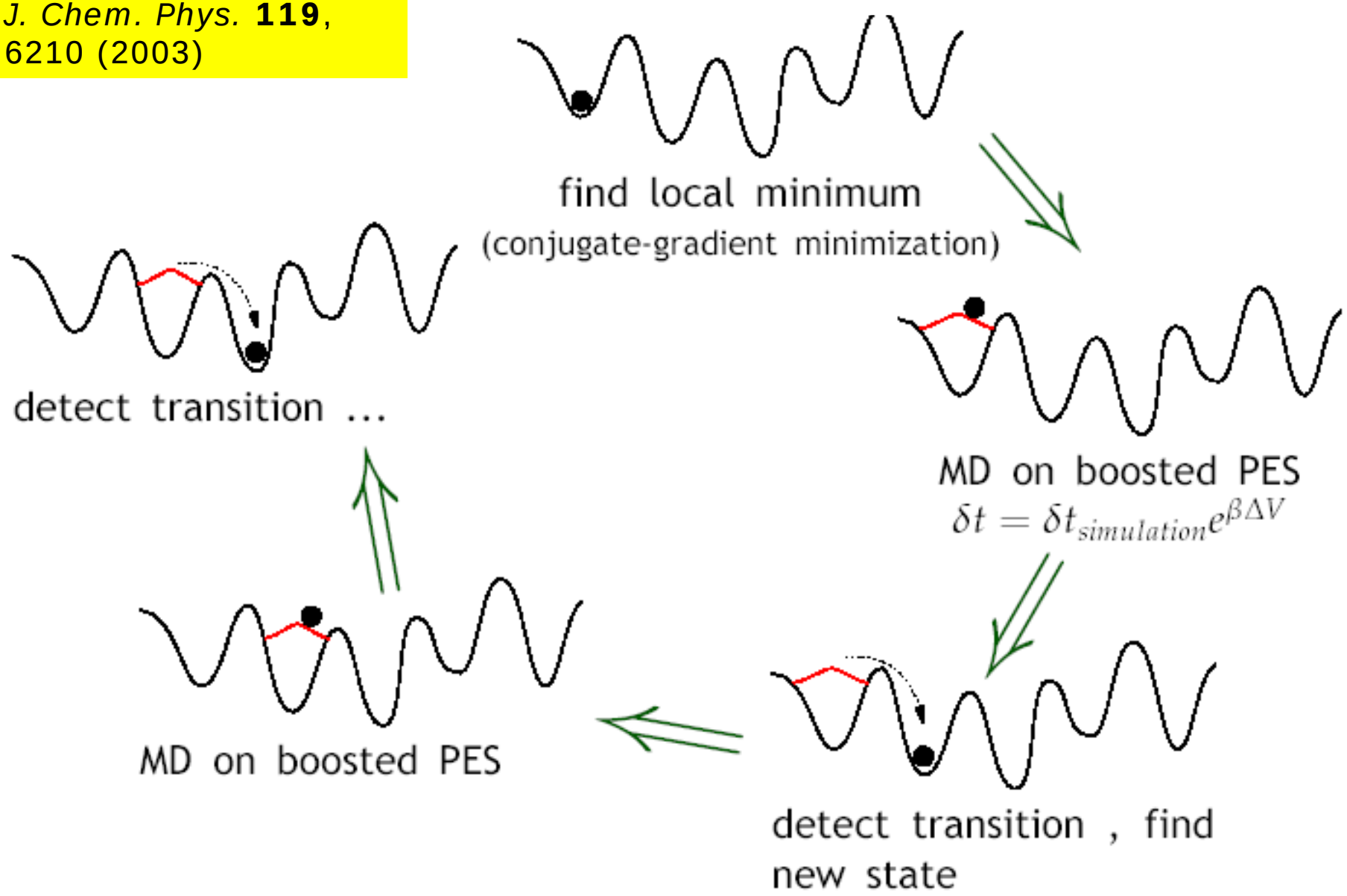
Envelope: Channels Boost into the Bond Most Ready to Break

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

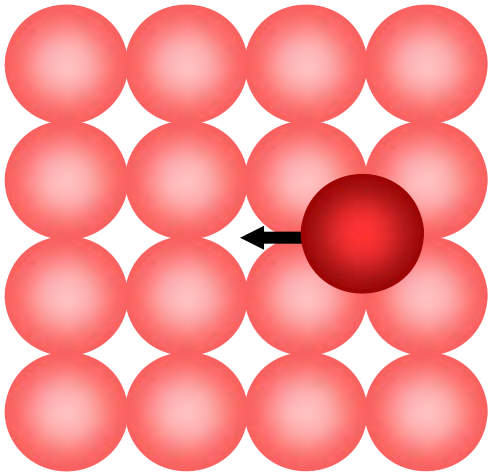


Overview of the Bond Boost Method

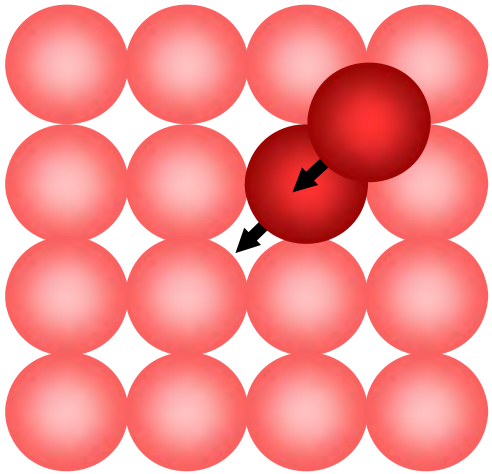
R. Miron & K. Fichthorn,
J. Chem. Phys. **119**,
6210 (2003)



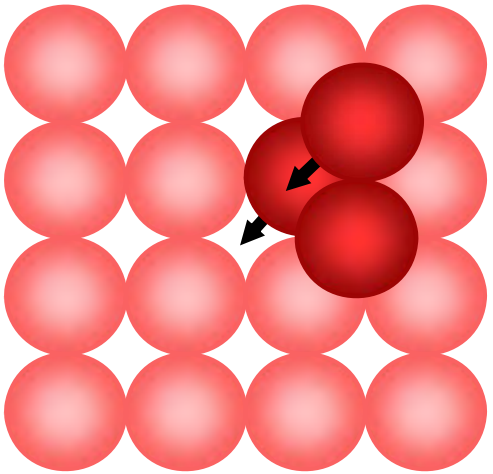
Diffusion on Cu(100): Elementary Processes



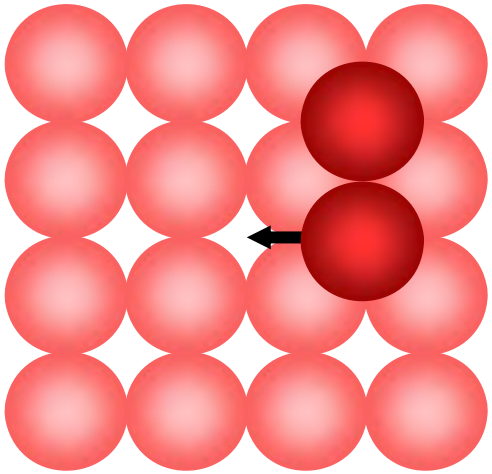
Adatom Hop



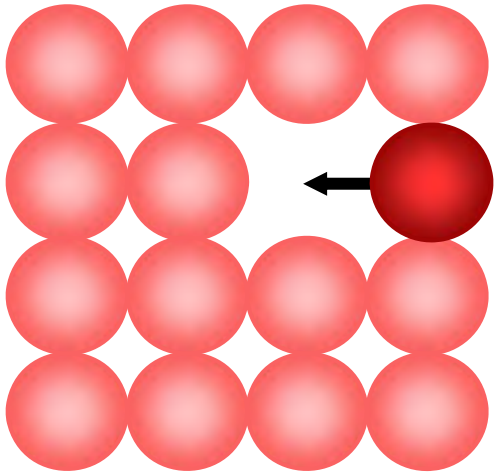
Adatom Exchange



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

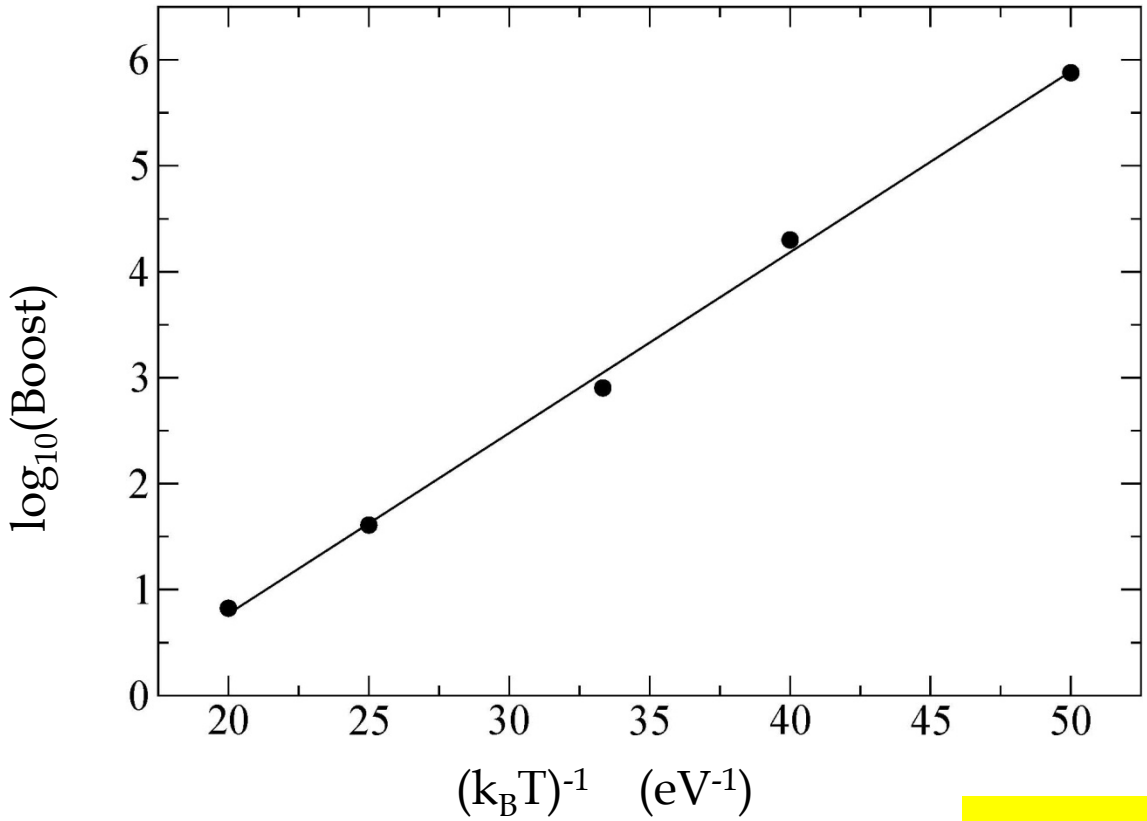
^{boost} accelerated MD at T = 230 - 600 K

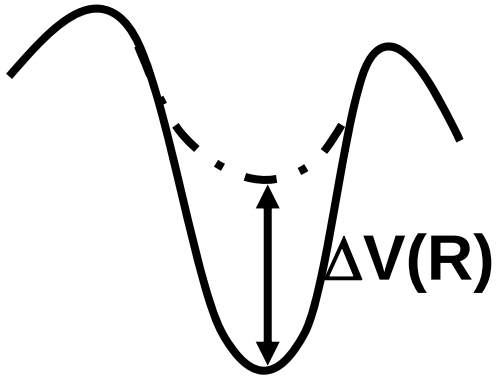
^{MD} regular MD at T = 650 - 900 K $\rightarrow$ Boisvert, Lewis *Phys.Rev.* B **65** (1997)

^{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

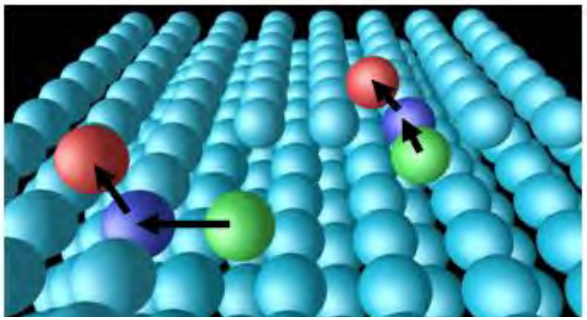




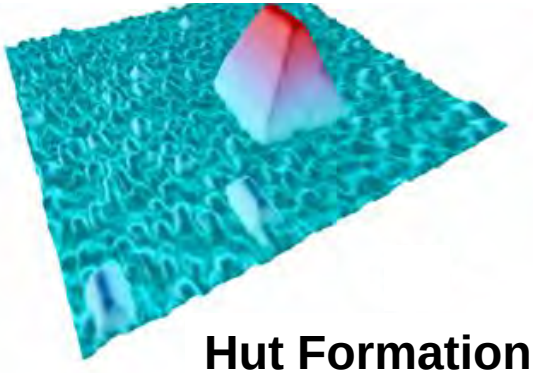
R. Miron & K. Fichthorn,
J. Chem. Phys. **119**, 6210 (2003)

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

Hut Formation in Al(110) Homoepitaxy

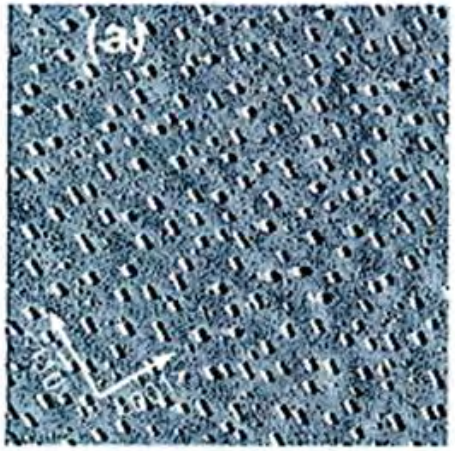


Atoms Hopping (Å, ps)



Hut Formation (nm, min)

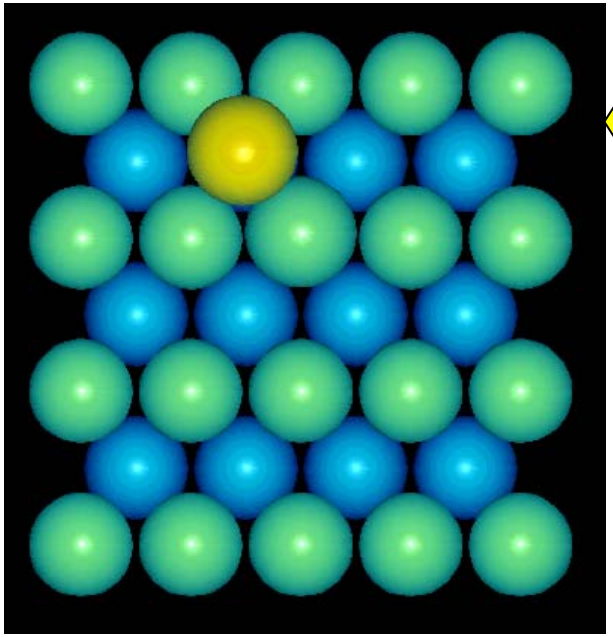
Bautier de Mongeot et al., Phys. Rev. Lett. **91**, 016102 (2003).



Hut Organization (μm, min)

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

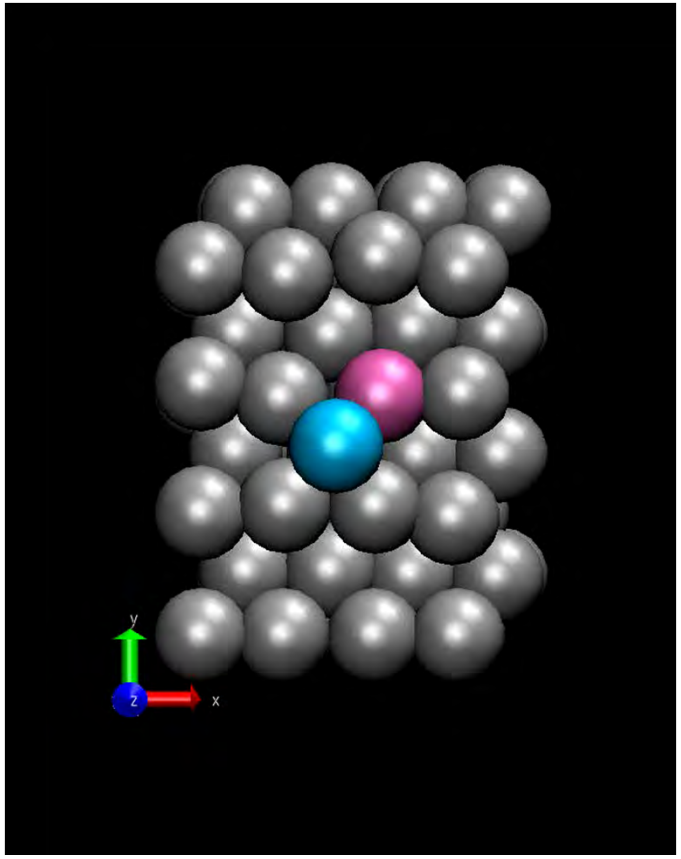
Accelerated AIMD (VASP): Diffusion on Al/Al(110)

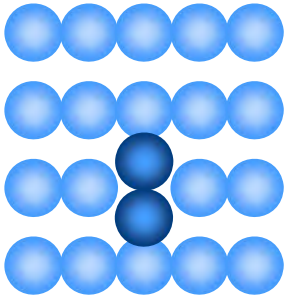


Climbing-Image Nudged Elastic Band Method

vs.

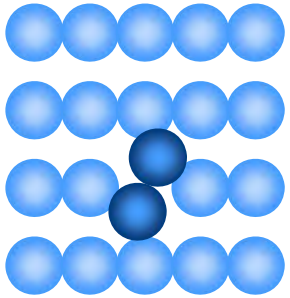
Accelerated AIMD





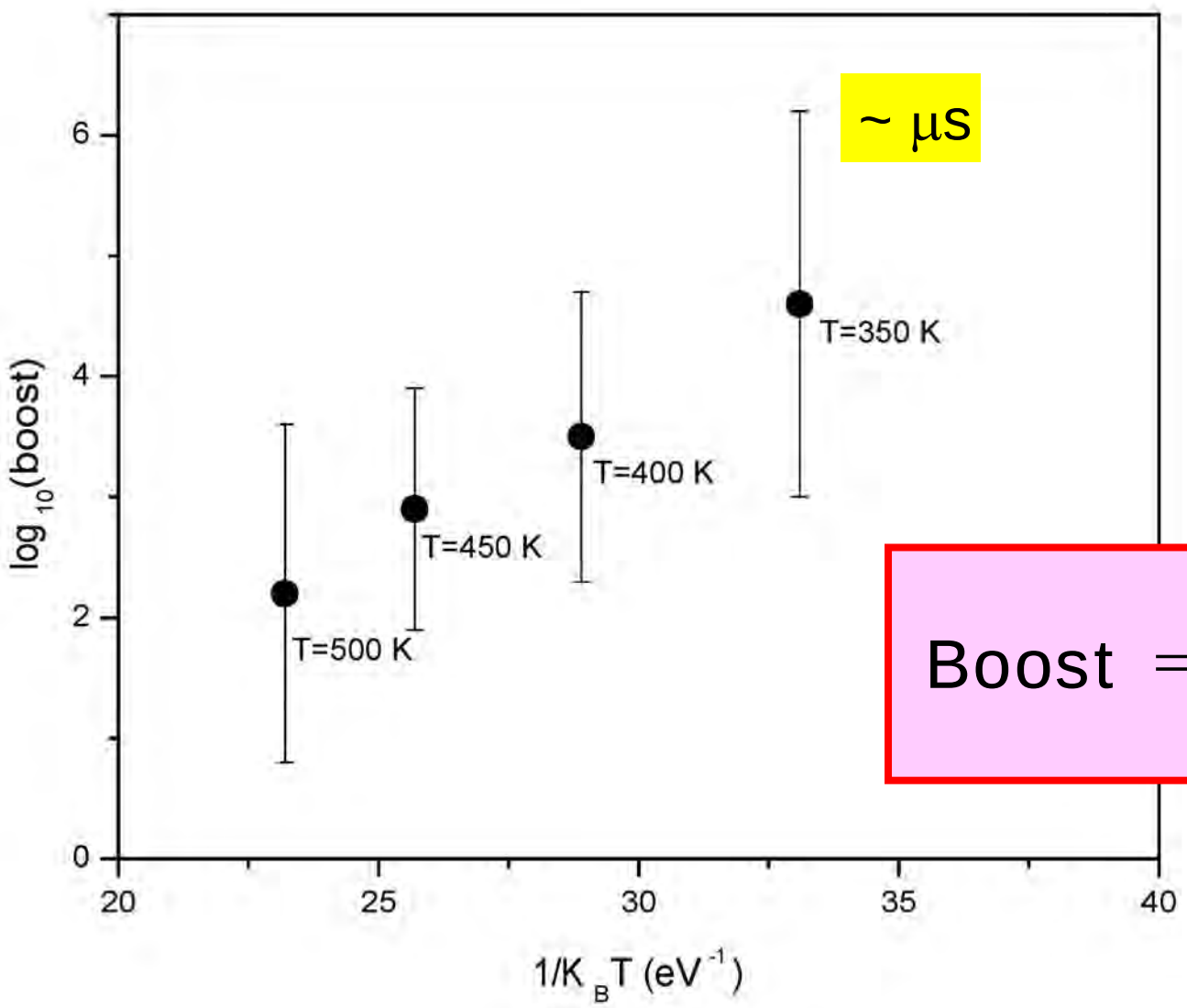
$E_B = 0.38$ eV

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

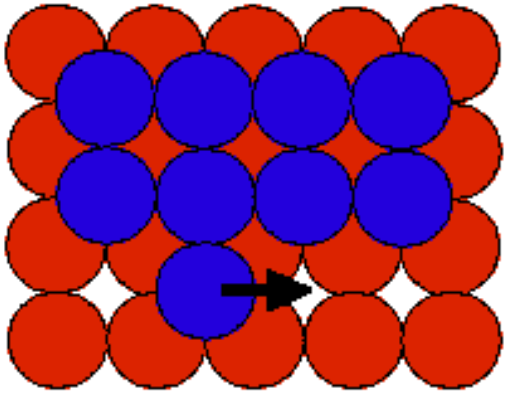
Co on Cu(100) surface with tight-binding (TBSMA) potential

(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

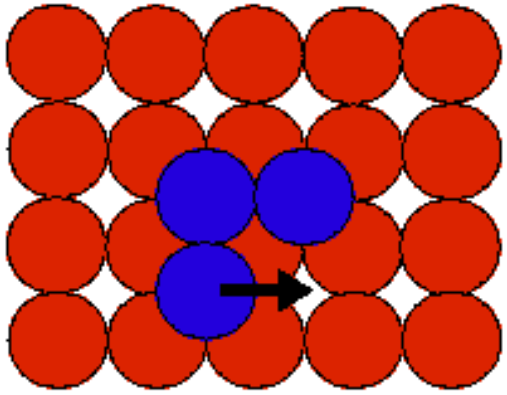
Annoyingly Small Barriers



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

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

than isolated hop



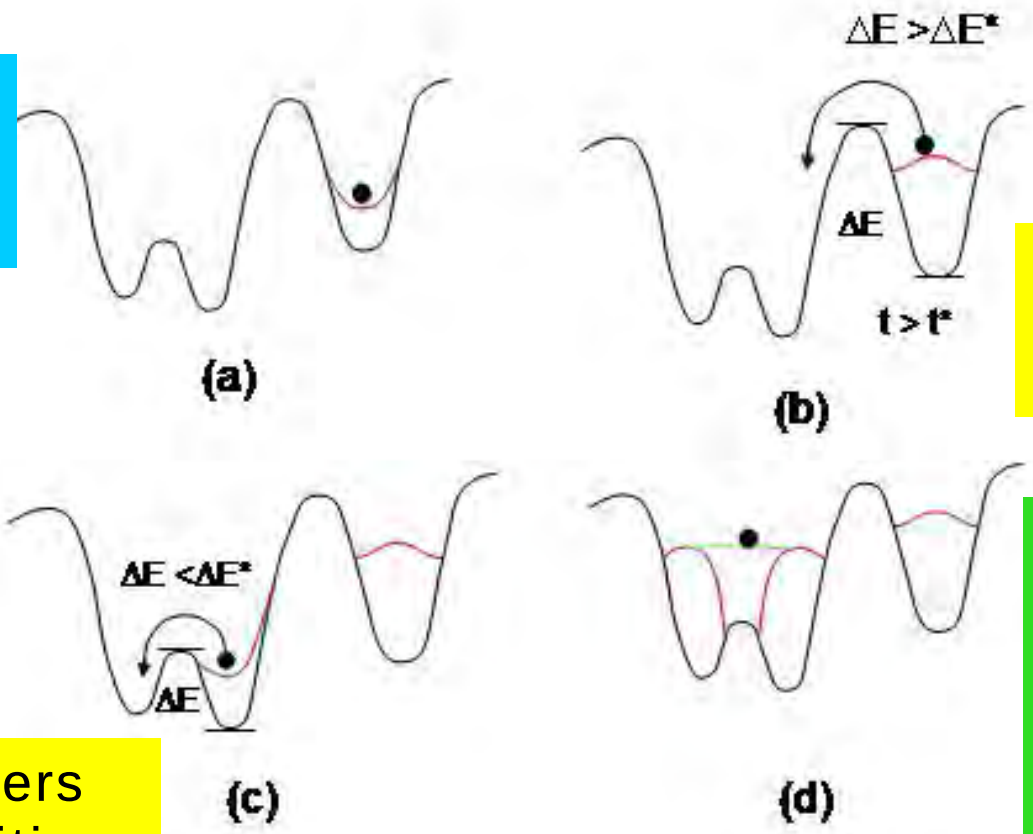
trimer rotation $\Delta E^{\dagger} = 0.1\,eV$

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

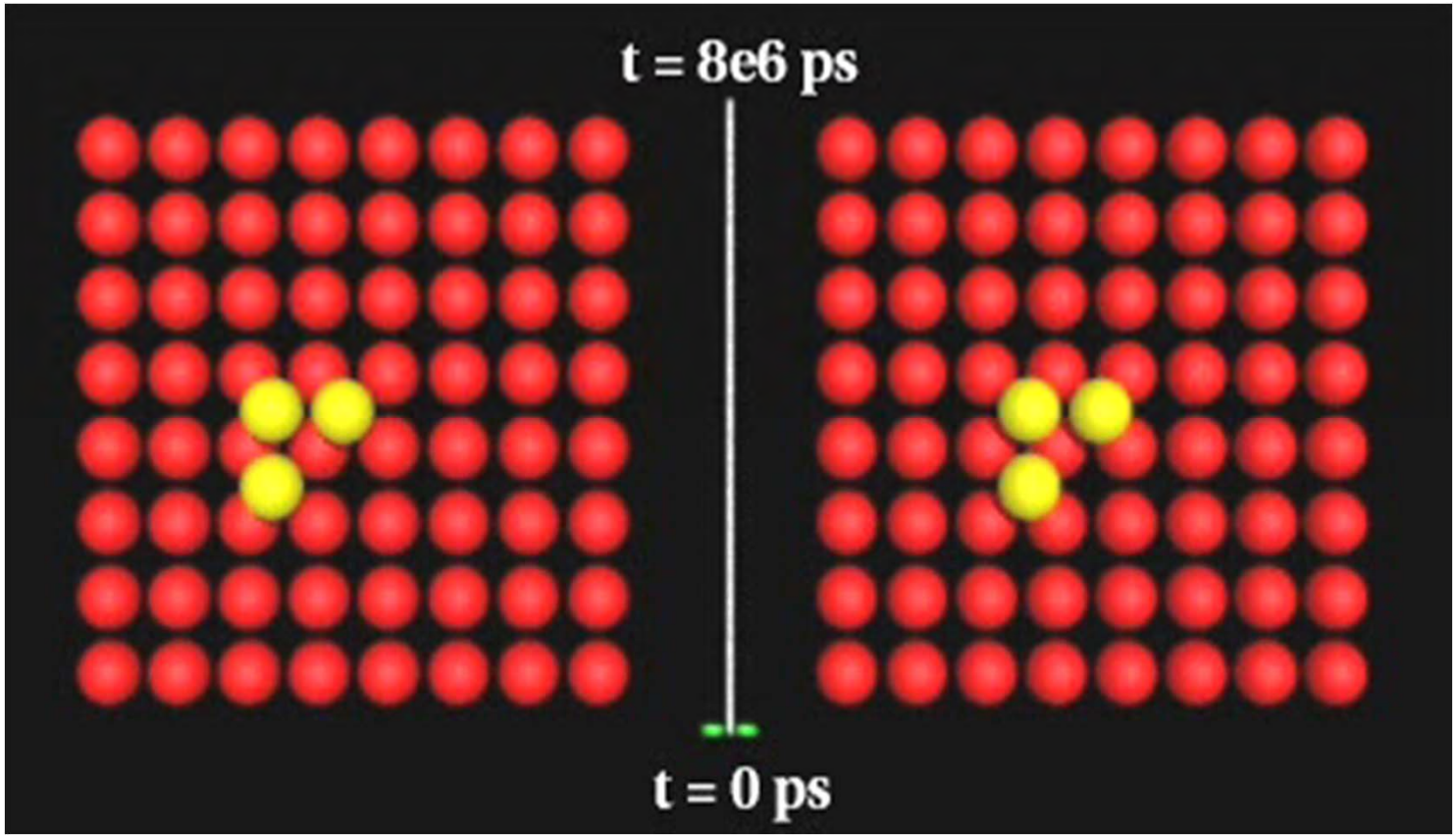
Miron, Fichthorn, J. Chem. Phys. 115, 2001.

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

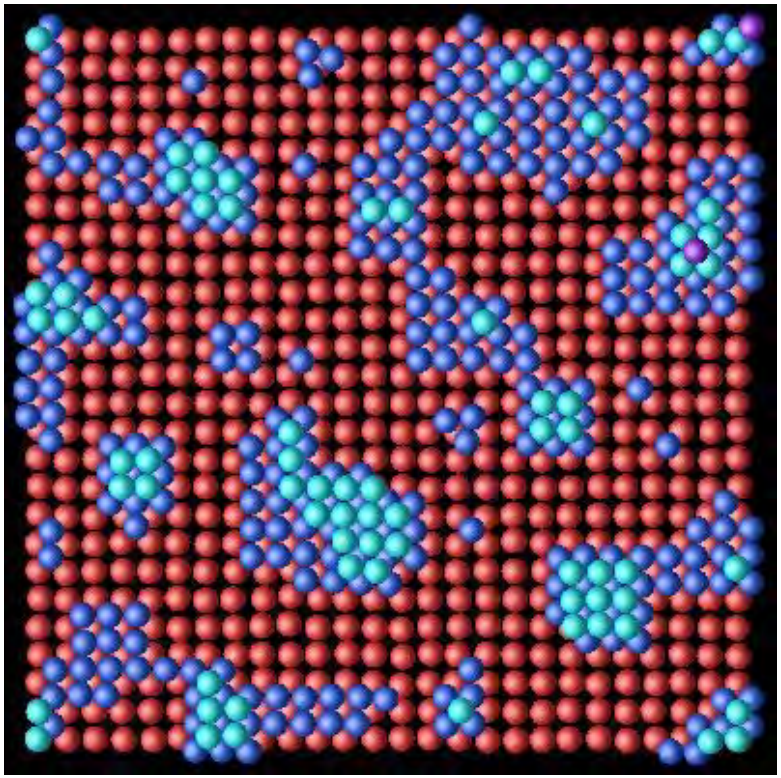


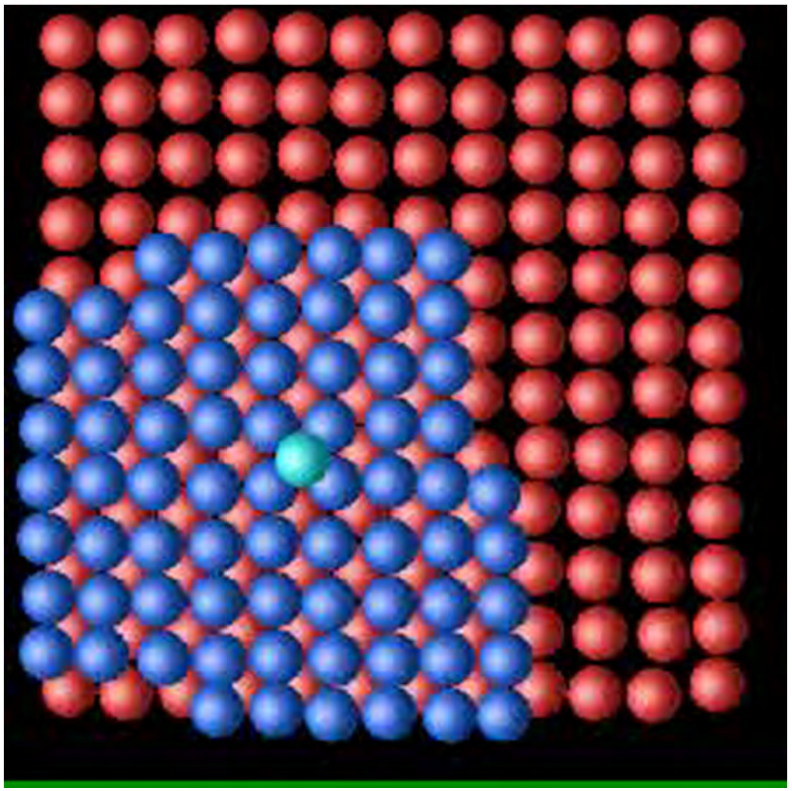
State-Bridging Accelerated MD

Regular Accelerated MD

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

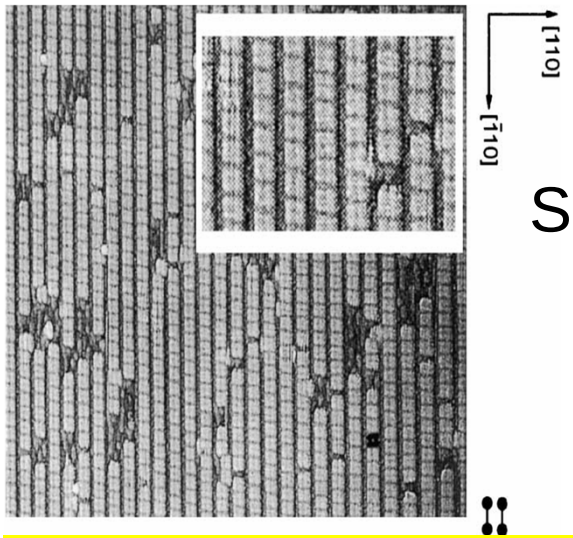




R. Miron and K. Fichthorn, Phys. Rev. B **72**, 115433 (2005).

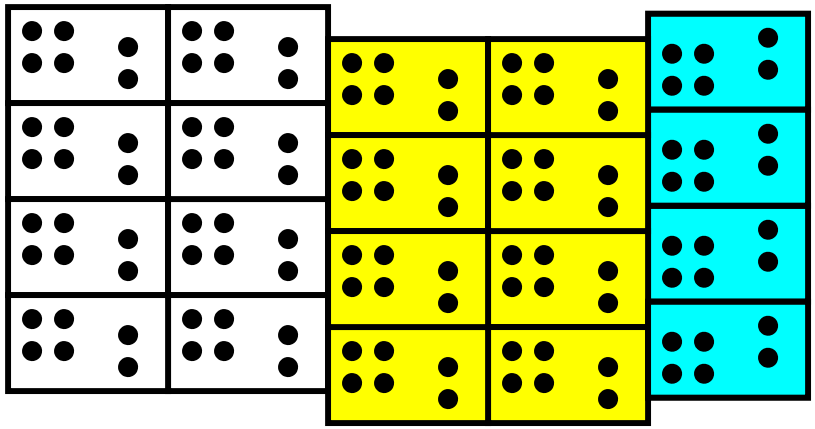
Mechanism of Bilayer Island Formation

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



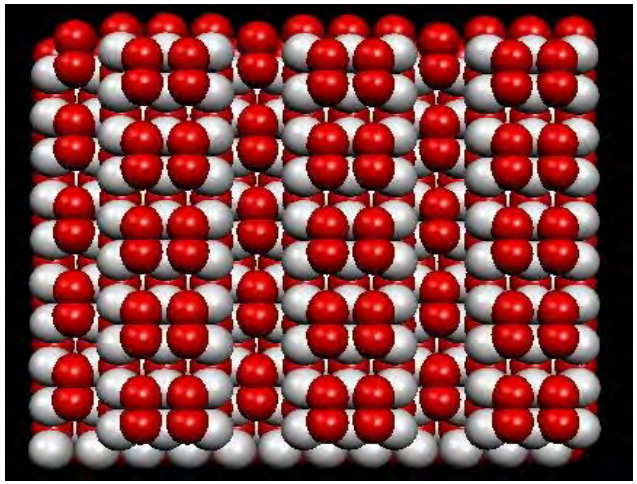
STM

(2x4) Unit Cell



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

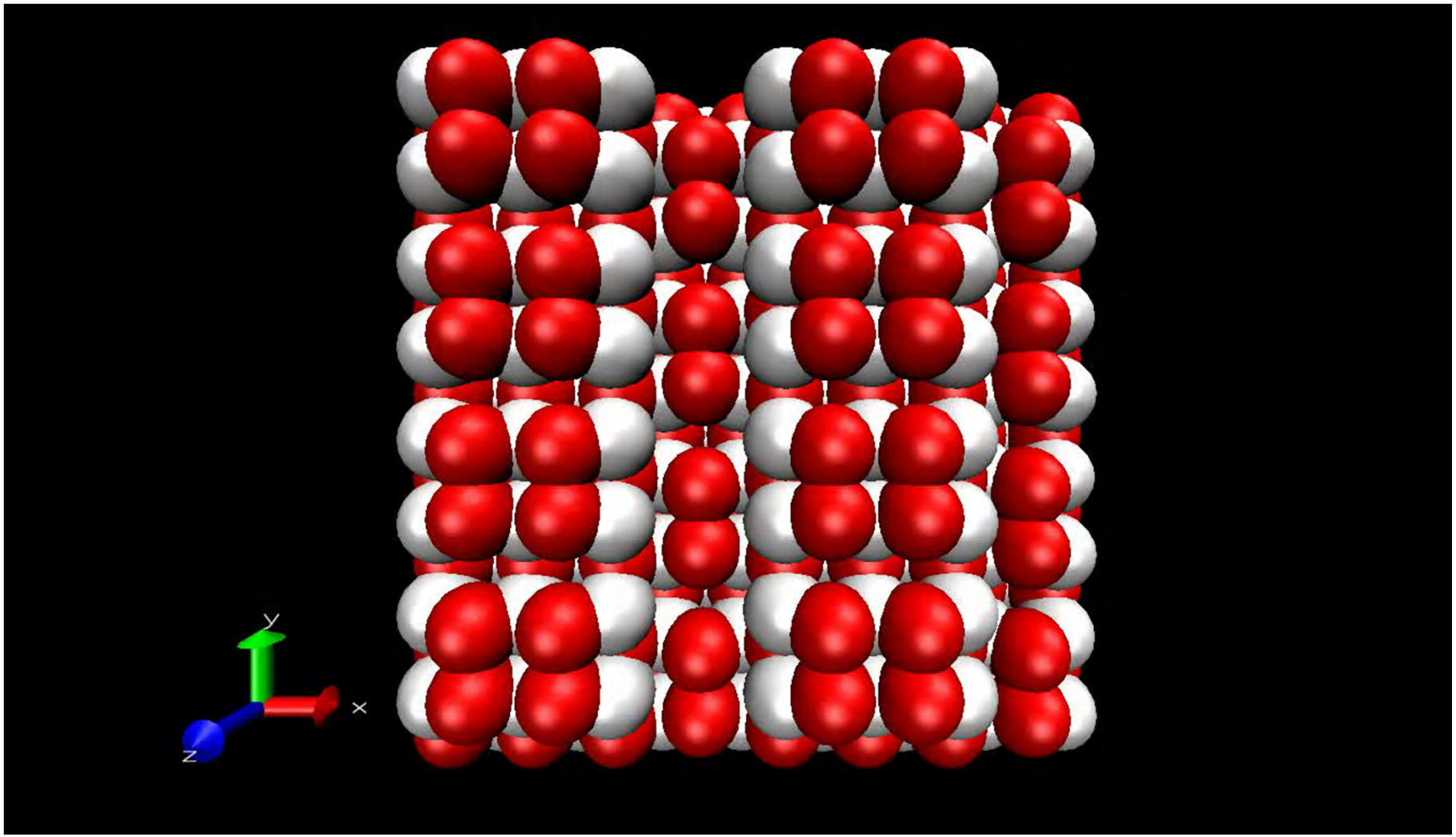
Hypothesis: Disordering Involves Shifting of Dimer Rows and Trenches



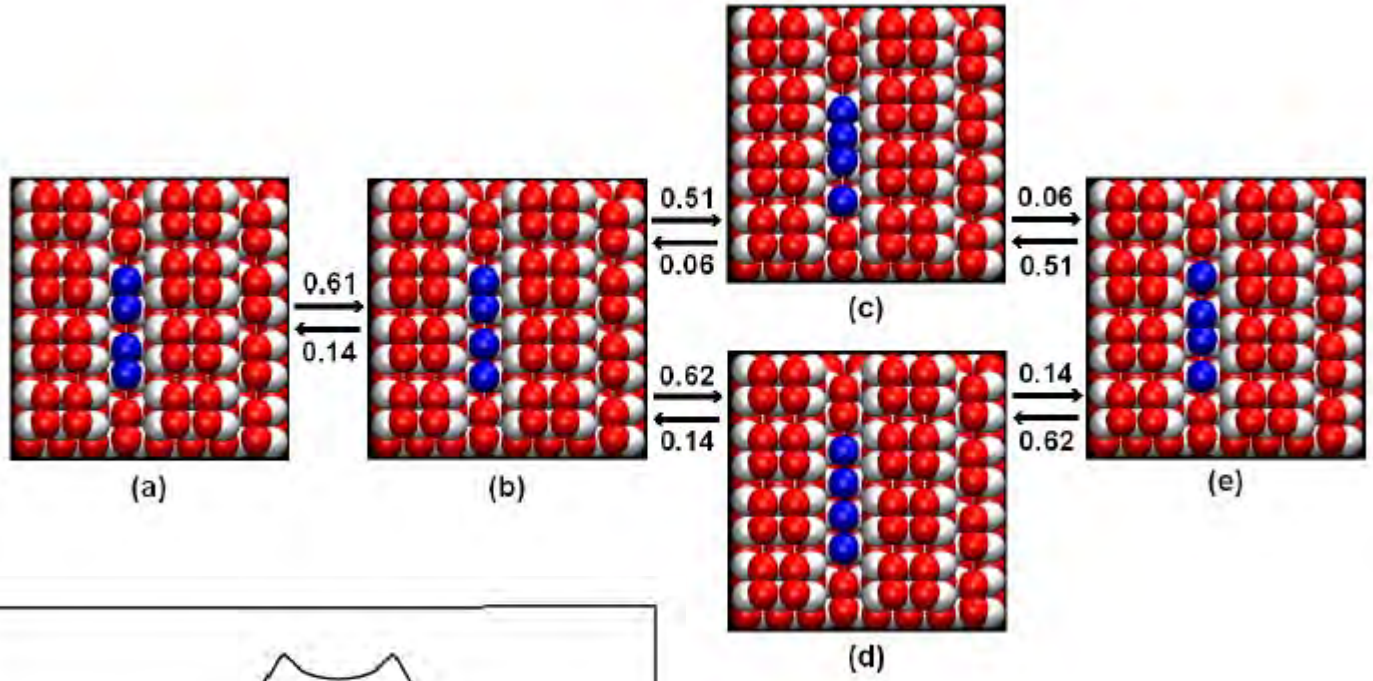
How Does this Surface Disorder? What Does This Mean for Diffusion and Growth??

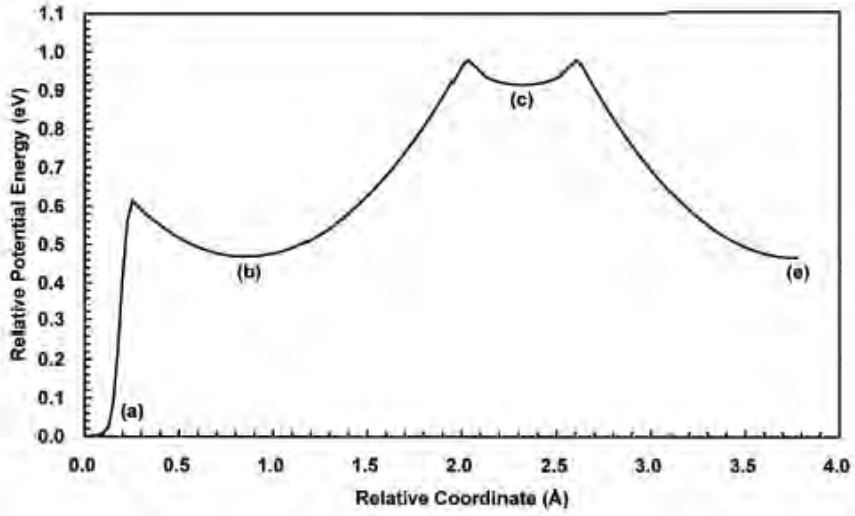
K. A. Fichthorn et al., Phys. Rev. B **83**, 195328 (2011)

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



Minimum-Energy Path for Trench Initiation: A Small-Barrier Problem





CI-NEB Method

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

Boost Details

$$\Delta V_i = \Delta V_{i1} + \Delta V_{i2}$$

$$\Delta V_{ik} = \begin{cases} \Delta V_{ik}^{max} \left[1 - \left(\frac{\varepsilon_{ik}}{q_{ik}^-}\right)^2\right]^2 \Big/ \left[1 - P_{ik}^2 \left(\frac{\varepsilon_{ik}}{q_{ik}^-}\right)^2\right] & q_{ik}^- \le \varepsilon_{ik} \le 0 \\ \Delta V_{ik}^{max} \left[1 - \left(\frac{\varepsilon_{ik}}{q_{ik}^+}\right)^2\right]^2 \Big/ \left[1 - P_{ik}^2 \left(\frac{\varepsilon_{ik}}{q_{ik}^+}\right)^2\right] & 0 < \varepsilon_{ik} \le q_{ik}^+ \end{cases}, k = 1, 2 \quad .$$

$$\Delta V_b(\mathbf{R}) = \frac{A_{min}(\mathbf{R})\,\Delta V_{min}}{N_b} \sum^{N_b} A_i(\mathbf{R})$$

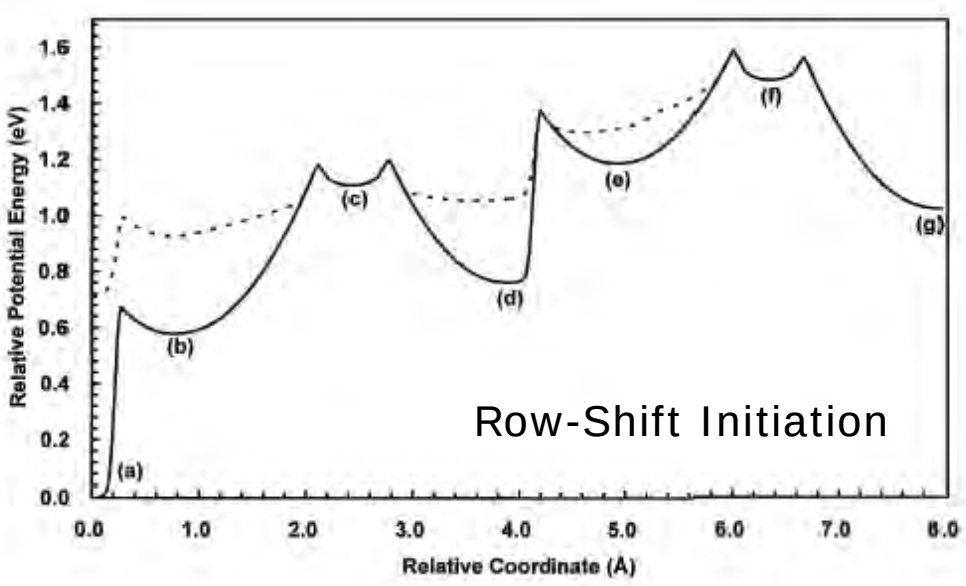
$$A_i(\mathbf{R}) = \Delta V_i(\mathbf{R}) / \Delta V_i^{max} \quad ,$$

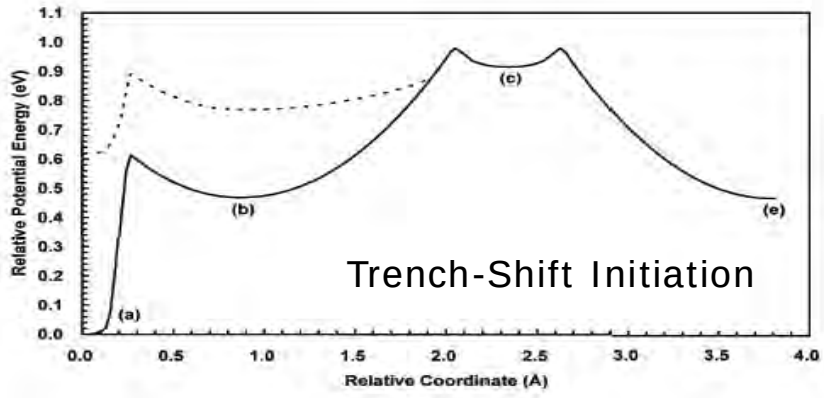
$$\Delta V_i(\mathbf{R}) = \sum_{k=1}^{M_i} \Delta V_{ik}(\mathbf{R}) \quad ,$$

$$\Delta V_i^{max} = \sum_{k=1}^{M_i} \Delta V_{ik}^{max} \quad ,$$

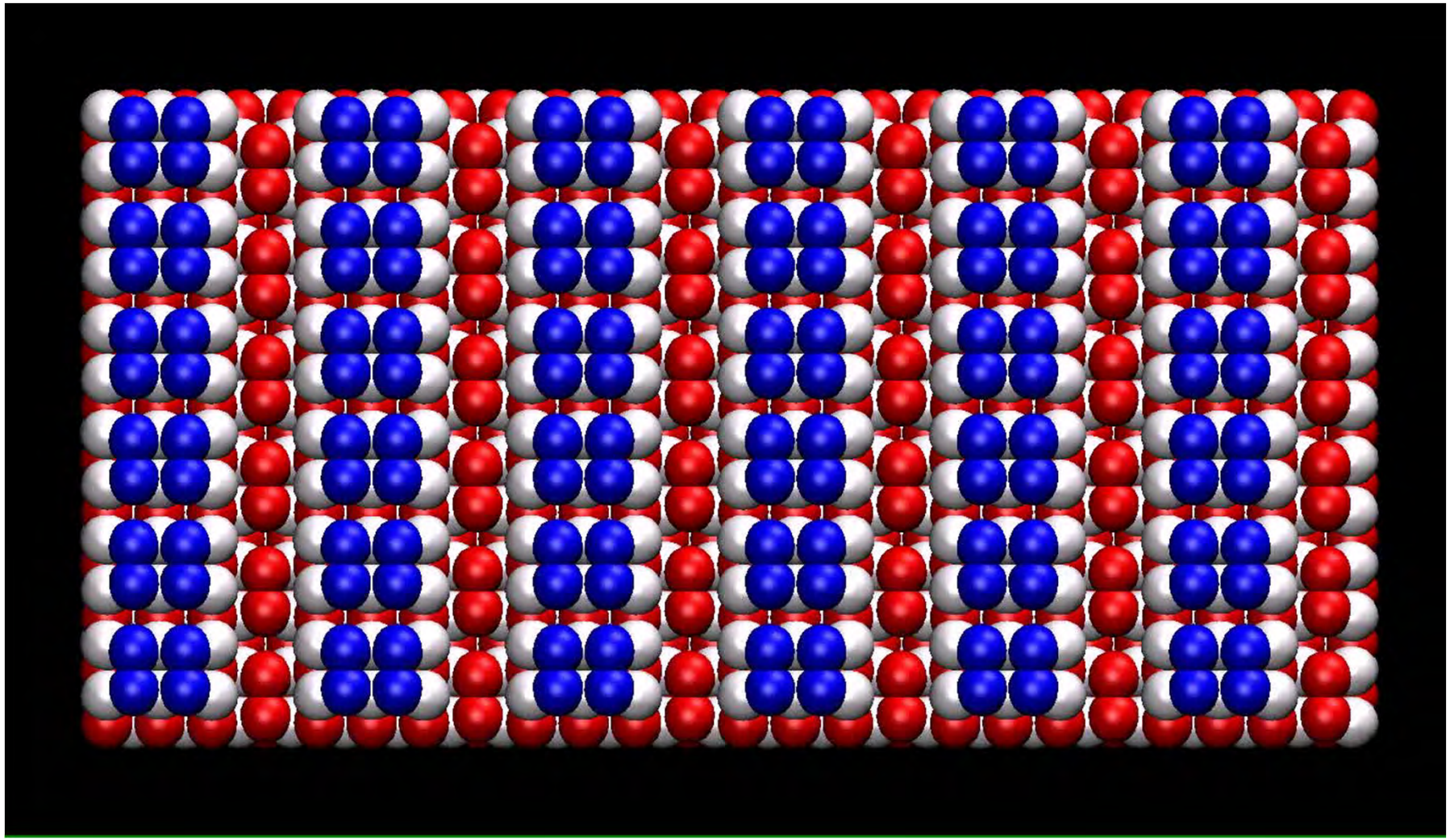
$$A_{min}(\mathbf{R}) = \min\{A_1(\mathbf{R}), A_2(\mathbf{R}), ..., A_{N_b}(\mathbf{R})\} \quad ,$$

$$\Delta V_{min} = \min\{\Delta V_1^{max}, \Delta V_2^{max}, ..., \Delta V_{N_b}^{max}\} \quad .$$





Accelerated MD Simulation at 800 K



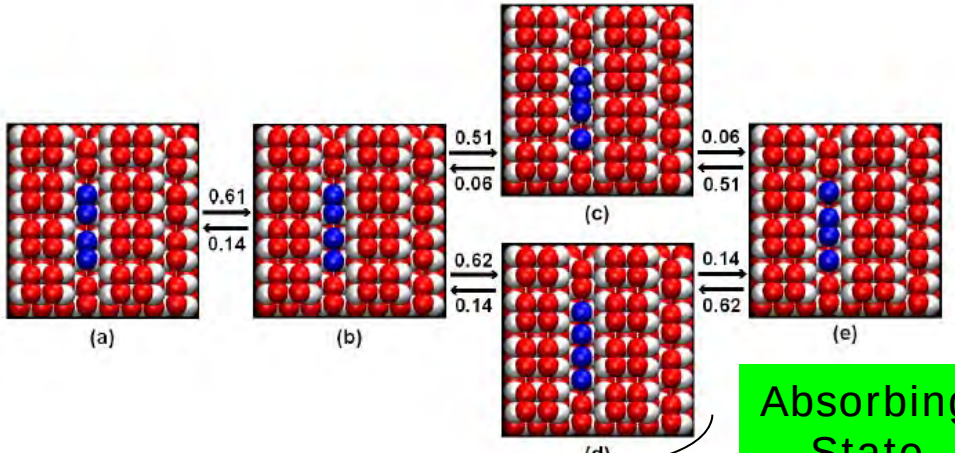
Trench Initiation: Comparison of MD, Accelerated MD, Markov Chain Based on HTST

$$\mathbf{T} = \begin{pmatrix} 0 & r_{ab}\tau_a & 0 & 0 \\ r_{ba}\tau_b & 0 & r_{bc}\tau_b & r_{bd}\tau_b \\ 0 & r_{cb}\tau_c & 0 & 0 \\ 0 & r_{db}\tau_d & 0 & 0 \end{pmatrix}$$

$$\tau_i = \left(\sum_{k \text{ in } a+t} r_{ik} \right)^{-1}$$

$$\langle t_{exit} \rangle = \vec{p}_0 \cdot (\mathbf{I} - \mathbf{T})^{-1} \cdot \vec{\tau} \;\; ; \;\; \vec{p}_0 = \{1,0,0,0\}$$

$$r_{exit} = 1 / \langle t_{exit} \rangle$$



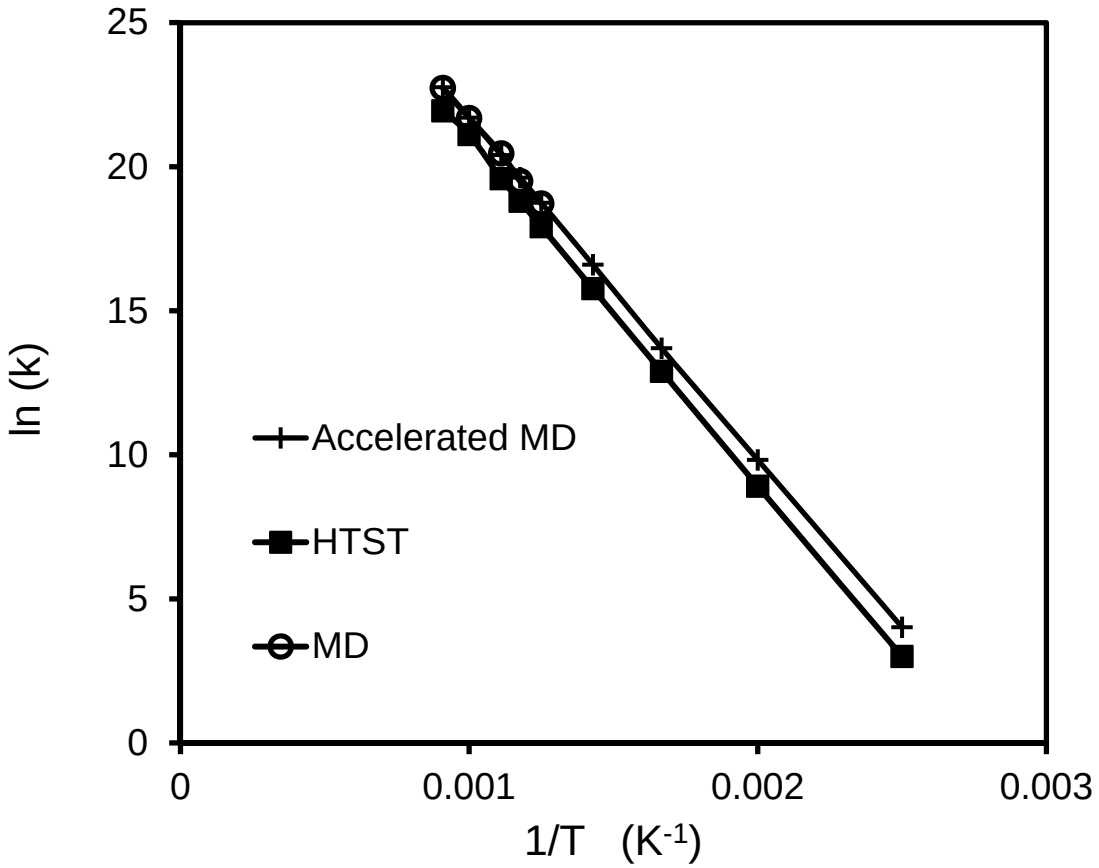
Absorbing State

Transient States

Rates from HTST:
ν_i ranges from 2.4×10^{12} – 2.5×10^{13}

E. Cinlar, *An Introduction to Stochastic Processes* (Prentice-Hall, Englewood Cliffs, 1975).

Comparison of MD, Accelerated MD, HTST for As Trench-Dimer Shifting

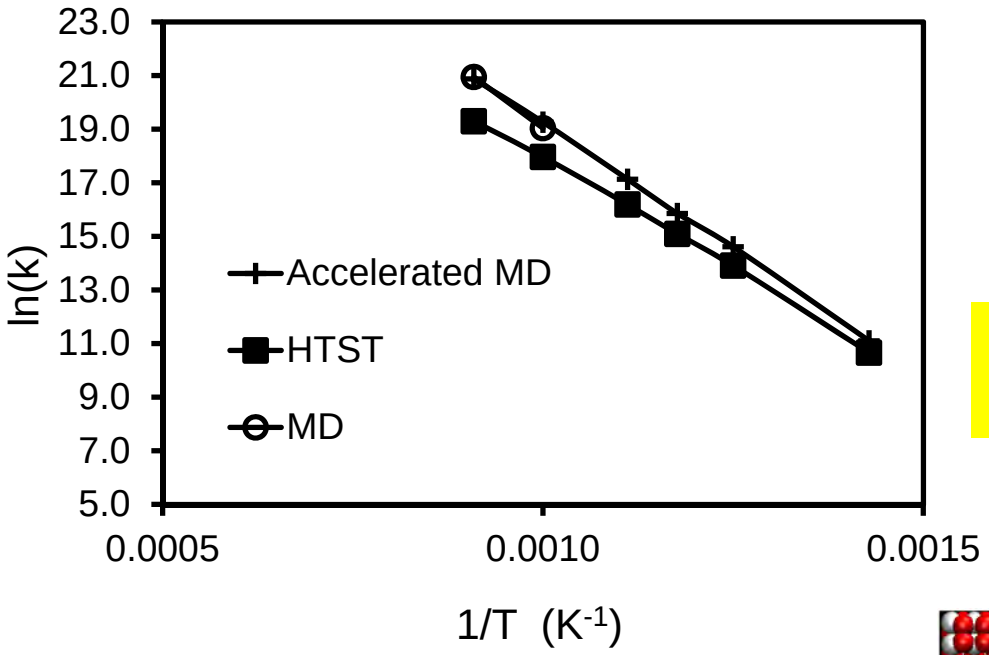


Fit of Accelerated MD

$A = 3.5 \times 10^{14}\ s^{-1}$

$E = 1.02$ eV

Comparison of MD, Accelerated MD, HTST for As Row-Dimer Shifting



Fit of Accelerated MD

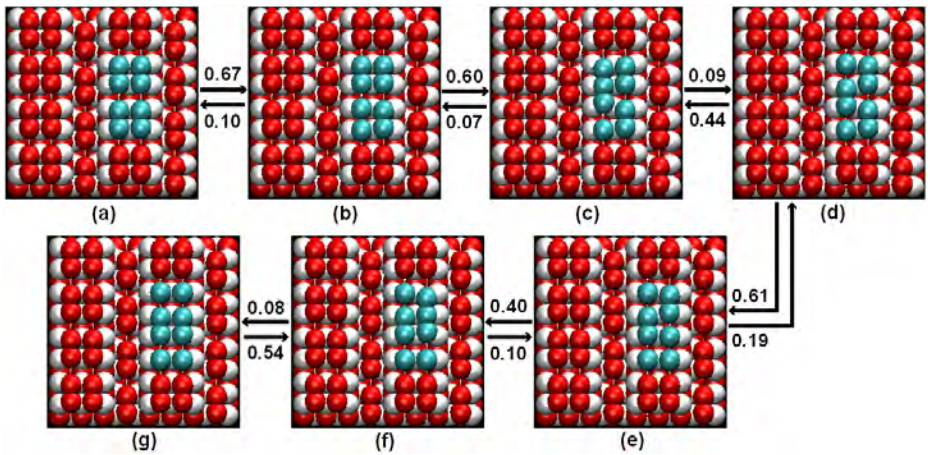
$A = 3.3 \times 10^{16}\ s^{-1}$

$E = 1.62$ eV

Rates from HTST:

ν_i ranges from 1.4×10^{12} – 4.8×10^{13}

Deviations Because Rate Eqn. (or kMC) Approach Does Not Include All Processes



kMC and the Small-Barrier Problem

kMC Solution = Master Equation Solution
(although full Master Eqn. solution isn't practical)

$$\frac{dP(\vec{r},t)}{dt} = -\sum_{\vec{r}'} \pi(\vec{r} \to \vec{r}')P(\vec{r},t) + \sum_{\vec{r}'} \pi(\vec{r}' \to \vec{r})P(\vec{r}',t)$$

Combine kMC and Master Equation to Solve the Small-Barrier Problem!!!

M. A. Novotny, Phys. Rev. Lett. **74**, 1 (1995).
B. Puchala, M. L. Falk, and K. Garikipati, J. Chem. Phys. **132**, 134104 (2010).
K. Fichthorn and Y. Lin (In preparation).