Accelerated Molecular Dynamics with the Bond Boost Method
(mostly of thin-film growth)

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Multi-Scale Simulation of Interfaces from First Principles

“Well Understood”

Solid-State Systems
- Thin-Film Growth
- Assembly at Surfaces
 **ENERGY DOMINATES**
 **DFT IS GREAT!**

Molecules on Surfaces
- Diffusion
- Thermal Desorption
- Adsorption
 **ENTROPY PLAYS A ROLE**
 **DFT IS LIMITED**

Nanoparticles in Solution
- Interparticle Forces
- Assembly in Solution
 **ENTROPY PLAYS A BIG ROLE**
 **DFT IS LIMITED**

HELP!

W. Al-Saidi, ..., and KF
Submitted to *J. Phys. Chem. C*

R. Sathiyannarayanan, ..., and KF
In preparation.
Surface Phenomena Involve Multiple Length and Time Scales... 

Thin-Film Growth e.g. fcc(110) homoepitaxy

Also Catalysis at Surfaces, CVD, and More...


Challenge: Reactor Design
From First Principles

Example: Growth of GaAs Thin Films

Charge-Density Contours for GaAs(001) from Density-Functional Theory (Å)

Kinetic Monte Carlo Simulation of Growth of GaAs(001) (nm, s)

Continuum Equations for Fluid Flow, Heat Transfer, Mass Transfer, Kinetics in a Rotating Disk Reactor (m,h)

Rare-Event Methods
This Link Needs Work!

This Link Really Needs Work!!!!!
Rare-Event Methods
[e.g., Transition-State Theory (TST)]

\[ k_{TST, A \rightarrow B} = \nu \frac{\int_A \delta(R - R^*) \exp(-V(R)/k_BT)}{\int_A \exp(-V(R)/k_BT)} \]

\[ = \nu_0 \frac{q^*}{q_A} \exp(-E_0 / k_BT) \]

TST Search, Sampling Methods

Nudged Elastic Band Method: Henkelman and Jonsson
Dimer Method: Henkelman and Jonsson
Step and Slide Method: Miron and Fichthorn
Transition Path Sampling: Dellago, Bolhuis, Geissler, Chandler
String Method: E, Ren, Vanden-Eijnden

Molecular Dynamics Simulations
Naturally Find Rate Processes...
Accelerated Molecular Dynamics (Hyperdynamics)


\[ k_{A \rightarrow B}^{TS} = \frac{1}{2} \int_A \delta^*_{AB} |v_{\perp, AB}| e^{-V(R)/k_BT} \int_A e^{-V(R)/k_BT} \]

\[ k_{A \rightarrow B}^{TS} = \nu \frac{\int \delta^*_{AB} W(R) e^{-V(R)/k_BT}}{\int W(R) e^{-V(R)/k_BT}} / W(R) \]

\[ W(R) = \exp \left( \frac{V(R) - V(R)}{k_BT} \right) \]

\[ k_{A \rightarrow B}^{TS} = \nu \frac{\int \delta^*_{AB} e^{-V(R)/k_BT}}{\int e^{-V(R)/k_BT} / W(R)} / \int e^{-V(R)/k_BT} \]
Accelerated Molecular Dynamics (Hyperdynamics)

\[ k_{TST}^{A \rightarrow B} = \frac{k_{TST}^{A \rightarrow B}}{\langle W(R) \rangle_A} \]

\[ k_{TST}^{A \rightarrow C} = \frac{k_{TST}^{A \rightarrow C}}{\langle W(R) \rangle_A} \]

\[ \frac{k_{TST}^{A \rightarrow B}}{k_{TST}^{A \rightarrow C}} = \frac{k_{TST}^{A \rightarrow B}}{k_{TST}^{A \rightarrow C}} \]

**MD Time:**

\[ t_{MD} = N \Delta t \]

**Real Time:**

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

The Trick is How to Construct \( \Delta V(R) \) and Where to Apply it

Define Local Minima by Bond Lengths

\[ \{r_i^0\} \quad i=1,N \]

Transitions Occur via Bond Breaking

\[ \max_i \left| \frac{\delta r_i}{r_i^0} \right| > q \]  
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

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

\[ \varepsilon_i = \frac{\delta r_i}{r_i^0} \]

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

\[ A(\varepsilon_{\text{max}}) = f \times \left[ 1 - \left( \frac{\varepsilon_{\text{max}}}{q} \right)^2 \right] \]
Overview of the Bond Boost Method


1. detect transition ...
2. find local minimum (conjugate-gradient minimization)
3. MD on boosted PES
   \[ \delta t = \delta t_{\text{simulation}} e^{\beta \Delta V} \]
4. MD on boosted PES
5. detect transition, find new state
Diffusion on Cu(100): Elementary Processes

- **Adatom Hop**
- **Adatom Exchange**
- **Dimer Exchange**
- **Dimer Hop**
- **Vacancy Hop**

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

Rates:

\[ k = \frac{N_{\text{events}}}{\text{time}} = \Gamma_0 e^{-\beta E_A} \]

Prefactors \( \Gamma_0 \) (THz) and activation energies \( E_A \) (eV):

<table>
<thead>
<tr>
<th>Process</th>
<th>( \Gamma_0^{\text{boost}} \times e^{\pm 0.7} )</th>
<th>( \Gamma_0^{MD} \times e^{\pm 0.6} )</th>
<th>( E_A^{\text{boost}} \pm 0.05 )</th>
<th>( E_A^{MD} \pm 0.04 )</th>
<th>( E_A^{\text{static}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adatom hop</td>
<td>40</td>
<td>20</td>
<td>0.52</td>
<td>0.49</td>
<td>0.51</td>
</tr>
<tr>
<td>Adatom exchange</td>
<td>270</td>
<td>437</td>
<td>0.73</td>
<td>0.70</td>
<td>0.71</td>
</tr>
<tr>
<td>Vacancy hop</td>
<td>54</td>
<td>27</td>
<td>0.44</td>
<td>0.47</td>
<td>0.44</td>
</tr>
<tr>
<td>Dimer hop</td>
<td>30</td>
<td>13</td>
<td>0.47</td>
<td>0.48</td>
<td>0.49</td>
</tr>
<tr>
<td>Dimer exchange</td>
<td>190</td>
<td>320</td>
<td>0.71</td>
<td>0.73</td>
<td>0.69</td>
</tr>
</tbody>
</table>

\( \text{boost} \) accelerated MD at \( T = 230 - 600 \) K

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

\( \text{static} \) 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

\[ \log_{10}(\text{Boost}) = \frac{\Delta V(R)}{k_B T} \]

R. Miron & K. Fichthorn, 

\[ \text{Boost} = \exp\left(\frac{\Delta V}{k_B T}\right) \]
Co on Cu(100) surface with tight-binding (TBSMA) potential


TST barriers: $\Delta E^\dagger = 0.66 \text{eV}$ for isolated adatom hop
$\Delta E^\dagger = 0.86 \text{eV}$ for isolated adatom exchange

Annoyingly Small Barriers

- Step diffusion $\Delta E^\dagger = 0.2 \text{eV}$
  10^6 faster ($T = 350K$) than isolated hop

- Trimer rotation $\Delta E^\dagger = 0.1 \text{eV}$
  10^8 faster ($T = 350K$) than isolated hop
State-Bridging Accelerated MD to Solve the Small-Barrier Problem

Commence With a Low Boost

Detect Barriers When Transitions Occur, Compare To Threshold

Raise the Boost After A Waiting Time


Memorize and Consolidate Pairs of States Connected by Low Barriers

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


Note Cluster Mobility
State-Bridging Accelerated MD of Co/Cu(001) Heteroepitaxy: $T = 250 \text{ K}, F = 0.1 \text{ ML/s}, \Theta = 0.54 \text{ ML}$

MD Simulations were run for 5.4 s


Mechanism of Bilayer Island Formation
Hut Formation in Al(110) Homoepitaxy

Bautier de Mongeot et al.,

K. Fichthorn and M. Scheffler,
Exchange of Al on Al(110): The CI-NEB Method in First-Principles DFT (VASP)

In-Channel

Cross-Channel

$\Delta E = 0.39$

$\Delta E = 0.38$

$\Delta E = 0.33$

$\Delta E = 0.49$

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

Climbing-Image Nudged Elastic Band Method

vs.

Accelerated AIMD

$E_B = 0.38 \text{ eV}$

$E_B = 0.33 \text{ eV}$

The Boost in \textit{ab initio} MD

\[
\text{Boost} = \exp\left(\frac{\Delta V}{kT}\right)
\]

\(\sim \mu\text{s}\)
Temperature-Programmed Desorption


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

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

\[ T = T_0 + \beta t \]

Simulation of TPD vs. Large Molecules Don’t Work in Lattice Models. . . .

Goal: To Simulate TPD with MD!!
Accelerated MD of Adsorbed Alkanes

OPLS All-Atom Force Field [1]

\[ V_{\text{intra}} = V_b + V_t + V_{LJ} \]
\[ V_b(\theta_i) = K_\theta(\theta_i - \theta_{eq})^2 \]
\[ V_t(\varphi_i) = \frac{1}{2} \sum_{j=1}^{3} V_j [1 + \cos(j \varphi_i)] \]

Constrained Bond Stretching: RATTLE [2]

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

Many Local Minima, Fast Transitions
But Desorption is the Slow Step
Accelerated MD of TPD with the Bond-Boost Method

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

Weaken Molecule-Molecule + Molecule-Surface Attraction

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

Funnels Boost into Molecule Farthest from the Surface

\[
t = \sum_i \exp \left( \frac{\Delta V(R_i)}{k_B T} \right) \Delta t
\]

K. Becker, M. Mignogna, K. Fichthorn

*PRL* 102, 046101 (2009).
$T = T_0 + \beta t$;
$\beta =$ Heating Rate

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

desorptions

TPD: Simulation vs. Experiment

Defects

Coverage
Calibration

$T_0 = 120$ K
1 ML Initially
$\beta = 2$ K/s

Total Time: 15 s


A Total Differential Analysis

\[ -\frac{1}{\theta} \frac{d\theta}{dt} = v_0 \exp \left( -\frac{E_d}{k_B T} \right) = k(\theta, T) \]


This is Difficult Experimentally...
Desorption Energy And Prefactor

\[ \nu = \nu_o \frac{Q_+}{Q} = \nu_o e^{\Delta S / k_B} \]

Large prefactors because of loss in rotational entropy.

Multi-Exponential Time Distribution

\[ P(t) = \sum_{i} a_i e^{-k_i t} \]

Fast, Second-Layer Desorption

Slow, First-Layer Desorption

\[ \Theta = 1 \text{ ML} \]

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

Second-Layer Desorption at $\theta = 0.75$
Multiple Time Scales at All Coverages

Fast Desorption of Isolated Molecules

Slow Desorption of Molecules in Islands

\( t \) (s)

\( \ln[P(t)] \)

\( \Theta = 0.25 \)

\( T = 160 \text{ K} \)
Rate Processes in Pentane Desorption

Second-Layer Molecules

\[ E_d = 32.5 \text{ kJ/mol} \]
\[ \nu_0 = 9.2 \times 10^{11} \]

Isolated Molecules

\[ E_d = 36.5 \text{ kJ/mol} \]
\[ \nu_0 = 5.5 \times 10^{12} \]

Molecules in Islands

\[ E_d = 58.1 \text{ kJ/mol} \]
\[ \nu_0 = 2.4 \times 10^{17} \]

Coverage Dependence of Kinetics

Island Desorption

Increasing Second-Layer

Fewer Entropy Loss

Isolated Molecule

Entropy Gain

Isolated Molecule

Second-Layer

$E_d$ (kJ/mol)
What is the Structure of a Real GaAs(001)β2(2x4) Surface?

(2x4) Unit Cell

Hypothesis: Disordering Involves Shifting of Dimer Rows and Trenches


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

Gallium Arsenic
Modified Tersoff Potential for GaAs

\[ E_{pot}(r_1, \ldots, r_N) = \frac{1}{2} \sum_{i,j \neq i} f_{ij}^{c}(r_{ij}) \left[ V_{ij}^{R}(r_{ij}) - B_{ij}(r_{ij}) - V_{ij}^{A}(r_{ij}) \right] \]

Cutoff

Pair: Repulsive

Three Body: Bond Order

Pair: Attractive

\[ B_{ij}(r_{ij}) = \left[ 1 + (\gamma_{ij} \cdot \chi_{ij}(r_{ij})) \right]^{-\frac{1}{2}} \]

\[ \chi_{ij}(r_{ij}) = \sum f_{ik}^{c}(r_{ik}) \cdot g_{ik}(\theta_{ijk}) \cdot \exp \left[ (\alpha_{ik}(r_{ij} - r_{ik})) \right] \]

\[ g_{ik}(\theta_{ijk}) = \delta_{ik} \left( 1 + \frac{c_{ik}^2}{d_{ik}^2} - \frac{c_{ik}^2}{d_{ik}^2 + (h_{ik} - \cos \theta_{ijk})^2} \right) \]

Regular MD of GaAs (001): $T = 600 \text{ K}$
Barrier Energy for As Dimer Breaking

![Graph showing the energy barrier for As dimer breaking.

The graph plots the energy difference ($\Delta E$) in eV against the As-As distance ($r_{As-As}$) in Å.

The line with black dots represents the energy barrier for a row dimer, and the line with red dots represents the energy barrier for a trench dimer.

The graph indicates a significant energy barrier for both types of dimers, with the energetic barriers for the trench dimer being higher than those for the row dimer.

Additionally, there are images of molecular structures showing the arrangement of As atoms before and after dimer breaking.
Regular MD of GaAs (001)

$T = 600K$

0.0 ns

24.084 ns

24.089 ns

24.090 ns

24.216 ns

24.217 ns

24.224 ns
n-Bond-Boost Method

Achieve Systematic Temporal Coarse-Graining by Increasing n

n = 3 – lose information about kinetics of two transitions

n = 2 – lose information about kinetics of single transitions

n = 1 – lose information about vibration in minima

\[ \Delta V(r) = \frac{L - N + n}{L} \sum_{i=1}^{n} A_i \delta V_i(r_i) + \frac{A_1 + \cdots + A_n}{L} \sum_{j=n+1}^{N} \delta V_j(r_j) \]

\[ \{A_1, \cdots, A_n\} = \min_n(A_1, \cdots, A_N) \]

n \leq N, \ L > 0 \ (e.g., \ L = nN)
n-Bond-Boost Method in a Model 3-Bond System

\[
V_{123}(x_1, x_2, x_3) = \begin{cases} 
-0.15 + \frac{(x_1-1)^2}{x_1} & 0 < x_1 \leq 1 \\
-0.15\cos[4\pi(x_1 - 1)] & 1 < x_1 \leq 1.25 \\
0.125 + 0.025\cos[\pi(x_1 - 1.25)] & 1.25 < x_1 \leq 2.25 \\
0.1 + (x_1 - 2.25)^2 & x_1 > 2.25 \\
\end{cases}
\]

+ \begin{cases} 
-0.1 + \frac{(x_2-1)^2}{x_2} & 0 < x_2 \leq 1 \\
-0.1\cos[2\pi(x_2 - 1)] & 1 < x_2 \leq 1.5 \\
0.1\cos[2\pi(x_2 - 1.5)] & 1.5 < x_2 \leq 2 \\
-0.1 + (x_2 - 2)^2 & x_2 > 2 \\
\end{cases}

+ \begin{cases} 
-0.05 + \frac{(x_3-1)^2}{x_3} & 0 < x_3 \leq 1 \\
-0.05\cos[\pi(x_3 - 1)] & 1 < x_3 \leq 2 \\
-0.05 + 0.1\cos[4\pi(x_3 - 2)] & 2 < x_3 < 2.25 \\
-0.15 + 2(x_3 - 2.25)^2 & x_3 > 2.25 \\
\end{cases}
n-Bond-Boost Method: 3-Bond System

<table>
<thead>
<tr>
<th>Method</th>
<th>$k_3^{2(1,2)}$</th>
<th>$k_3^{2(1,3)}$</th>
<th>$k_3^{2(2,3)}$</th>
<th>$k_3^{3(1,2,3)}$</th>
<th>boost</th>
</tr>
</thead>
<tbody>
<tr>
<td>TST</td>
<td>$8.39 \times 10^{-4}$</td>
<td>$2.83 \times 10^{-3}$</td>
<td>$4.86 \times 10^{-2}$</td>
<td>$1.925 \times 10^{-3}$</td>
<td>-</td>
</tr>
<tr>
<td>Regular MD</td>
<td>$8.34 \times 10^{-4}$</td>
<td>$2.89 \times 10^{-3}$</td>
<td>$4.92 \times 10^{-2}$</td>
<td>$1.930 \times 10^{-3}$</td>
<td>-</td>
</tr>
<tr>
<td>2-bond-boost MD</td>
<td>$8.07 \times 10^{-4}$</td>
<td>$3.00 \times 10^{-3}$</td>
<td>$4.87 \times 10^{-2}$</td>
<td>-</td>
<td>16.0</td>
</tr>
<tr>
<td>3-bond-boost MD</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$1.921 \times 10^{-3}$</td>
<td>179.6</td>
</tr>
</tbody>
</table>
n-Bond-Boost Method: 2 As Trench Dimers Breaking

The blue atoms were boosted

<table>
<thead>
<tr>
<th>$\Delta V_{\text{max}}$ (eV)</th>
<th>0.0</th>
<th>0.4</th>
<th>0.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\langle t_{\text{esc}} \rangle$ (ps) (at 900K)</td>
<td>82.87</td>
<td>85.07</td>
<td>80.42</td>
</tr>
<tr>
<td>boost</td>
<td>1.0</td>
<td>$2.323 \times 10^2$</td>
<td>$7.382 \times 10^2$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature</th>
<th>900K</th>
<th>800K</th>
<th>700K</th>
<th>600K</th>
<th>500K</th>
<th>400K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\langle t_{\text{esc}} \rangle$ (ps) (at $\Delta V_{\text{max}} = 0.5$eV)</td>
<td>92.75</td>
<td>$4.107 \times 10^2$</td>
<td>$5.036 \times 10^3$</td>
<td>$8.861 \times 10^4$</td>
<td>$5.782 \times 10^6$</td>
<td>$4.249 \times 10^9$</td>
</tr>
<tr>
<td>boost</td>
<td>$5.018 \times 10^2$</td>
<td>$2.029 \times 10^3$</td>
<td>$1.990 \times 10^4$</td>
<td>$2.819 \times 10^5$</td>
<td>$1.119 \times 10^7$</td>
<td>$4.363 \times 10^9$</td>
</tr>
</tbody>
</table>
2-Bond Boost, $T = 600$ K
Total Time = 26 $\mu$s
4-Bond Boost, $T = 600$ K
Total Time = 14 ms
Conclusions: Progress in Accelerated MD

The Big Problem is Multiple Time-Scale Phenomena

- Consolidating Pools of Shallow States

- Focusing on Only One Transition Type
  K. Becker, M. Mignogna, K. Fichthorn, PRL 102, 046101 (2009)

- n-Bond Boost
  Lin and Fichthorn, In Progress.
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