Atomic-Scale Simulations in the Nanoscience of Interfaces

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We Care About Including Relevant Atomic-Scale Details into Macroscopic Models (that might be) Relevant for Engineering Design
The Challenge: Predicting Assembly from First Principles

Solid-State Systems
- Energy Dominates
- DFT Enables Detailed Understanding
- Rare-Event Dynamics
- Theory Developed

Molecules on Surfaces
- Entropy Plays a Role
- DFT Not As Good, Sampling!
- Rare-Event Dynamics, Hydrodynamics
- Some Theory

Nanoparticles in Solution
- Entropy Plays a Big Role
- DFT is Limited, van der Waals, Sampling!
- Some Rare-Event Dynamics, Hydrodynamics
- Macroscopic Theories

Most Problem We Work on Have a Fluid Near a Solid Surface….

Two Examples:

Forces and Assembly of Colloidal Nanoparticles

Nanostructured Interfaces from First Principles
Nanostructured Surfaces from First Principles

Non-Equilibrium Kinetics + Interactions =

Ag/ 2 ML Ag / Pt(111)

InAs/GaAs(001)

Al / Al(110)
F. Bautier de Mongeot et al., PRL 91, 016102 (2003).

....And More!!!
Surface Phenomena Involve Multiple Length and Time Scales...

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

Also Crystal Growth,
Catalysis at Surfaces
and More...


Atoms Hopping (Å, ps)

Hut Formation (nm, min)

Hut Organization (µm, min)

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)

Transition-State Theory

Kinetic Monte Carlo Simulations

- Deposition, $F$
- Aggregation
- Nucleation
- Terrace Diffusion, $D$
- Edge Diffusion


Concerted Cluster Diffusion Mechanisms
Difficult to Characterize and Include in kMC...

R. Miron & K. Fichthorn,
“Electronic” Pair Interaction on Ag/Pt(111): Still New Frontiers...


\[ E_0^b = 52 \text{ meV} \]
Challenges in Multi-Scale Modeling

• Accurate Semi-Empirical Potentials
• Efficient Algorithms for Finding ALL TST Rate Processes
• “Stiff” Systems
• Length and Time Scale of KMC
• Atomic – Continuum Link
Challenges in Multi-Scale Modeling

- Accurate Semi-Empirical Potentials
- Efficient Algorithms for Finding ALL TST Rate Processes
- Incorporating TST Rates into KMC
- “Stiff” Systems
- Appropriate Atomic Detail in Continuum Reactor Design
Co/Cu Heteroepitaxy

Promising for “spintronic” recording media


Interesting heteroepitaxial growth modes
**ab initio kMC of Submonolayer Co/Cu(001) Heteroepitaxy**

Spin-Polarized, FP-LAPW DFT For Energy Barriers.....

- Hopping / Exchange of Co & Cu Adatoms
- Cu Hopping Away from Exchanged Co
- Co Hopping Away from Exchanged Co

Experiment

- Co Grows on Top of Cu
- Co Trapped at Exchanged Co
- Co, Cu Escape from Exchanged Co

### Tight Binding Potential Fit to DFT

Based on potential by Levanov et al.,


<table>
<thead>
<tr>
<th>Structure</th>
<th>TBSMA</th>
<th>TBSMA</th>
<th>DFT</th>
<th>Image</th>
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<tbody>
<tr>
<td>Cu(001)</td>
<td>0.55</td>
<td>0.58</td>
<td>0.61</td>
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<tr>
<td>Co(001)</td>
<td>0.79</td>
<td>0.82</td>
<td>0.86</td>
<td></td>
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<tr>
<td>Co/Cu</td>
<td>0.99</td>
<td>1.12</td>
<td>1.22</td>
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<td>1.09</td>
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<td>Cu/Co/Cu</td>
<td>0.73</td>
<td>0.87</td>
<td>0.99</td>
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<tr>
<td>Co/Co/Cu</td>
<td>0.73</td>
<td>0.78</td>
<td>0.86</td>
<td></td>
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<tr>
<td>Cu/2Co/Cu</td>
<td>0.66</td>
<td>0.72</td>
<td>0.73</td>
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<table>
<thead>
<tr>
<th>Process</th>
<th>TBSMA</th>
<th>TBSMA modified</th>
<th>DFT</th>
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<tr>
<td>Cu/Cu hop</td>
<td>0.44</td>
<td>0.48</td>
<td>0.51</td>
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<tr>
<td>Cu/Cu exchange</td>
<td>0.87</td>
<td>0.92</td>
<td>1.02</td>
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<tr>
<td>Co/Co hop</td>
<td>0.58</td>
<td>0.58</td>
<td>0.54</td>
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<tr>
<td>Co/Co exchange</td>
<td>1.32</td>
<td>1.48</td>
<td>1.54</td>
</tr>
<tr>
<td>Co/Cu hop</td>
<td>0.67</td>
<td>0.63</td>
<td>0.61</td>
</tr>
<tr>
<td>Co/Cu exchange</td>
<td>0.89</td>
<td>0.93</td>
<td>1.00</td>
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<tr>
<td>Co/Cu step</td>
<td>0.42</td>
<td>0.39</td>
<td>0.35</td>
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Accelerated Molecular Dynamics (Hyperdynamics)  

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

\[ k_{TST} = \nu \frac{\int \delta(R - R_B^*) W(R) \exp(-V(R)/k_BT)}{\int W(R) \exp(-V(R)/k_BT)} \]

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

\[ k_{TST} = \nu \frac{\int \delta(R - R_B^*) \exp(V(R)/k_BT)}{\int \exp(V(R)/k_BT)} \]

Accelerated Molecular Dynamics
(Hyperdynamics)


\[
\begin{align*}
    k_{TST,A \rightarrow B} &= \frac{k_{TST,A \rightarrow B}}{\langle 1/W(R) \rangle_A} \\
    k_{TST,A \rightarrow C} &= \frac{k_{TST,A \rightarrow C}}{\langle 1/W(R) \rangle_A} \\
    \frac{k_{TST,A \rightarrow B}}{k_{TST,A \rightarrow C}} &= \frac{k_{TST,A \rightarrow B}}{k_{TST,A \rightarrow C}}
\end{align*}
\]

Detailed Balance!
Accelerated Molecular Dynamics Challenge: How to Build $V(R)$ On The Fly?

Monitor Smallest Eigenvalue of Hessian Matrix - Expensive!

Monitor Changes in Single-Particle Or Total Potential Energy

*Can’t Easily Define for Many-Body Interactions!*

*Fluctuations in Total Energy!*

Monitor Changes in Single-Particle Energy
Accelerated Molecular Dynamics
The Bond Boost Method

- Local minima defined by bond lengths: $\{r_i^0\}_{i=1...N}$

- Transitions occur via bond breaking: $\max_i \left| \frac{\delta r_i}{r_i^0} \right| > q$

- Define bias potential

\[ \Delta V\{x\} \sim A\{r_i\} \sum_{i=1}^{N} \delta V(r_i) \]
Overview of the Bond Boost Method


find local minimum
(conjugate-gradient minimization)

detect transition ...

MD on boosted PES
\[ \delta t = \delta t_{\text{simulation}} e^{\beta \Delta V} \]

MD on boosted PES

detect transition, find new state
Diffusion on Cu(100): Elementary Processes

- Adatom hop
- Vacancy hop
- Dimer hop
- Adatom exchange
- Dimer exchange
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>
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<tbody>
<tr>
<td>Adatom hop</td>
<td>40</td>
<td>20</td>
<td>0.52</td>
<td>0.49</td>
<td>0.51</td>
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<tr>
<td>Adatom exchange</td>
<td>270</td>
<td>437</td>
<td>0.73</td>
<td>0.70</td>
<td>0.71</td>
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<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

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

Rare Events and the Small Barrier Problem

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


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

Annoyingly Small Barriers

\[ \Delta E^\dagger = 0.2 \text{ eV} \]
10^6 faster (\(T = 350K\)) than isolated hop

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

Fast Motion in a Group of Recurrent States Connected by Small Barriers
State-Bridging Accelerated MD to Solve the Small-Barrier Problem

Fast Motion in a Group of Recurrent States Connected by Small Barriers: The Maximum Boost is Limited
State-Bridging Accelerated MD to Solve the Small-Barrier Problem

Consolidate Groups of Recurrent States Connected by Small Barriers into One Big State

Ignore the Dynamics and Achieve a High Boost

Overview of State-Bridging Accelerated MD

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


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
Island Density vs. Coverage from Accelerated MD
Cluster Mobility Reduces Island Density

At $T = 250K$ : $N_x^{MD} \approx 0.7 N_x^{KMC}$

Mean-field theory: $N_x^{\text{adatom+dimer}} \approx 0.74 N_x^{\text{adatom}}$

† Pentcheva et al., PRL 90 (2003).

Growth Approaching Multi-Layers: Monolayer or Bilayer?

F = 0.03 ML/s
Bilayer for T = 80-300 K

T = 330 K
Monolayer for F = 0.003 ML/s
Bilayer for F = 0.3 ML/s

Monolayer: Low F / Medium T
Bilayer: High F / Low T
State-Bridging Accelerated MD of Co/Cu(001) Heteroepitaxy: $T = 250$ K, $F = 0.1$ ML/s, $\Theta = 0.54$ ML

MD Simulations were run for 5.4 s


Mechanism of Bilayer Island Formation
When an atom is pulled up, it stays there!

Interlayer transport barriers:

**downward:**

\( \Delta E^\dagger = 1.1eV \)
\( \Delta E^\dagger = 0.62eV \)
\( \Delta E^\dagger = 0.92eV \)

**upward:**

\( \Delta E^\dagger = 0.68eV \)
\( \Delta E^\dagger = 0.63eV \)
Flux Dependence of Bilayer Formation

Fractional filling at $T = 310K$, $\theta = \theta_1 + \theta_2 = 0.42 \text{ ML}$

- Small, Irregular Islands Grow Bilayer
- Large, Smooth Islands Grow Monolayer

\[ \frac{\theta_2^{1\rightarrow 2}}{\theta_2} = 0.35 \]

\[ \frac{\theta_2^{1\rightarrow 2}}{\theta_2} = 0.37 \]

\[ \frac{\theta_2^{1\rightarrow 2}}{\theta_2} = 0.4 \]
Conclusions

• Simple and Efficient Accelerated MD With the Bond-Boost Method

• Accelerated MD Lets Us Find Complex Kinetic Mechanisms AND Simulate Experiments

• Cluster Diffusion Influences Island Density

• Origins of Monolayer vs. Bilayer Island Growth in Co/Cu(001) Epitaxy
Nanoparticles: Potential Building Blocks For New and Existing Materials...

• Catalysts
• Optical Materials
• Structural Materials
• Electronic Materials

... but Difficult to Assemble or Disperse Nanoparticles.

C. Keating, Penn State Chemistry

Nano-Electronics: Replace Lithography by Self-Assembly?

Nanoparticle Forces are POORLY UNDERSTOOD!
Colloidal Forces from Molecular Dynamics Simulations

- van der Waals and Electrostatic Forces: DLVO theory
- Solvation Forces: Solvent Ordering
- Depletion Forces: Entropic

How Do These Work for Colloidal Nanoparticles?
Parallel Molecular Dynamics Simulation

- Solid Nanoparticles in Liquid Solvent (~ 10^5 Atoms):
  
  Lennard-Jones: \( \rho^* = 0.7, \ T^* = 1.0 \)
  
  \( n \)-Decane: \( \rho = 0.7729 \text{g/ml}, \ T = 293.15 \text{K} \)

\[
U_{\text{intra}}(r) = \sum_{i=3}^{n} U_b(\theta_i) + \sum_{i=4}^{n} U_t(\phi_i) + \sum_{i=1}^{n-4} \sum_{j=i+4}^{n} U_{LJ}(r_{ij})
\]

\[
U_b(\theta_i) = \frac{1}{2} k_b (\theta_i - \theta_0)^2
\]

\[
U_t(\phi_i) = \sum_{l=0}^{5} a_l (\cos \phi_i)^l
\]

- Solvophilic Nanoparticles: (\( \varepsilon_{fs} = 3.0, 5.0 \varepsilon_{ff} \))
- Solvophobic Nanoparticles: (\( \varepsilon_{fs} = 0.2 \varepsilon_{ff} \))
Model Nanoparticles

Probing the Size and Shape Dependence of Forces

Small Sphere
d = 4.9 \sigma
64 atoms
~1.7 nm

Large Sphere
d = 17.6 \sigma
2048 atoms
~6 nm

Icosahedron
d = 4.0 \sigma
55 atoms
~1.4 nm

Cube
d = 13.2 \sigma
2744 atoms
~4.5 nm
Solvation and van der Waals Forces

**Solvation Force**

\[ F^{\text{solv}}(\delta) = \left( \hat{r}_{AB} \cdot \left( \sum_{i} F_{A,S_i} - \sum_{i} F_{B,S_i} \right) \right) \]

**Free-Energy Change**

\[ \Delta A_{ij} = \int_{\delta_i}^{\delta_j} F_{\text{solv}}(\delta) d\delta \]

**van der Waals Force**

\[ F^{\text{vdw}}(\delta) = \sum_{i \in A} \sum_{j \in B} -\frac{dU_{ij}}{dr_{ij}} \cdot \hat{r}_{AB} \]

Fluid Ordering: Origin of Solvation Forces

Solvent Density Profile

Solvent ordering around solvophilic nanoparticles
Forces Depend on Particle Size and Shape......
Derjaguin Approximation for Shape Dependence: Influenced by Surface Roughness

\[
\frac{\Delta A(\delta)}{2A_C \rho_C^2} = \frac{F_{Solv}^{Solv}(\delta)}{\pi D \rho_S^2}
\]

Derjaguin Approximation Describes the Envelope

Derjaguin Approximation Works

Solvophilic

Solvophobic

\[\frac{\Delta A}{2A_C \rho_C^2} \text{ or } \frac{F_{Solv}}{\pi D \rho_S^2} \]

\[\delta/\sigma\]

\[0.5 \quad 1.5 \quad 2.5 \quad 3.5 \quad 4.5 \quad 5.5 \quad 6.5\]

Small Sphere

Large Sphere

Cube

\[\delta/\sigma\]

\[0.5 \quad 1.5 \quad 2.5 \quad 3.5 \quad 4.5 \quad 5.5 \quad 6.5\]

Small Sphere

Large Sphere

Cube

Derjaguin Approximation Works
Influence of Surface Roughness on Solvation Forces: LJ Liquid

Particles will Rotate in Solution for a Minimum Free-Energy Approach

Interestingly, Roughness Destroys Solvation Forces For Macroscopic Surfaces...
Influence of Rotation on Solvation Forces

Nanoparticles Rotate About Fixed Center of Mass

Solvophilic
Without Rotation

Solvophobic
With Rotation

F·σ/kT

δ/σ
Minimum-Energy Path for Approach of Nanocrystals

Solvation Forces can Control Alignment in Assembly

Nanoparticle Rotation Driven by Solvent Ordering

Nanoparticles Rotate to Reduce Solvent Density in the Gap

$\rho / \rho_{bulk}$
Applications: Aligned Nanoparticle Assemblies

Cubic Pt Nanoparticles

Nanocrystalline Au Arrays

T. Ahmadi et al., Chem. Mater. 8, 1161 (1996).

Solvation Forces Could Cause Oriented Attachment in Crystal Growth

See Also:

HRTEM Image Showing Oriented Attachment of 5 TiO$_2$ Nanoparticles
Solvation Forces can be Important!

Solvation Forces Depend on:
- particle/solvent size
- particle shape
- particle-solvent interactions

Solvation Forces Can Cause Nanoparticle Alignment in Assembly/Crystal Growth

Nanoparticle Suspensions can be Engineered......
Collaborators

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Yogesh Tiwary
Dr. Vishal Kopardé
Josh Howe
Ryan Muthard
David Condon
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Dr. Weiwei Luo

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Dr. Darrell Velegol

Funding

NSF ECC-0085604, DMR-9617122, IGERT DGE-9987598, DMR-0514336, NIRT CCR-0303976
ACS PRF, EPA, Alexander von Humboldt Foundation