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Title: METHOD FOR LONG TIME SCALE SIMULATIONS OF SOLIDS: APPLICATION TO CRYSTAL GROWTH AND DOPANT CLUSTERING

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Method for Long Time Scale Simulations of Solids: Application to Crystal Growth and Dopant Clustering

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An important challenge in theoretical chemistry is the time scale problem. Atomic motion can be simulated directly by integrating Newton's equations over a time scale of nanoseconds, but most interesting chemical reactions take place on a time scale of seconds. We have developed a methodology to bridge this time scale gap using harmonic transition state theory suitable for solid systems. Possible reactive events and their rates are found with a saddle point finding method called the dimer method. When enough events are found, a kinetic Monte Carlo algorithm is used to choose which event occurs so that the system's position can be advanced in time. This technique has two major advantages over traditional kinetic Monte Carlo -- atoms do not have to map onto lattice sites for classification and kinetic events can be arbitrarily complicated. We have studied the homoepitaxial growth of aluminum and copper using an EAM potential at 80K with experimentally relevant deposition rates of monolayers per minute using a multiple time scale approach. Atomic deposition events are simulated directly with classical dynamics for several picoseconds until the incident energy has dissipated, and the long time between deposition events is simulated with the adaptive kinetic Monte Carlo method. Our simulations indicate that the Al(100) surface grows much smoother then Cu(100) at temperature between 0 and 80K due in part to long range multi atom processes which enable aluminum atoms to easily descend from atop islands. The high rate of such processes is due to their low activation energy, which is supported by density functional theory calculations, and the trend that processes involving more atoms tend to have larger prefactors and be favored by entropy. The scheme is efficient enough to model the evolution of systems with ab-initio forces as well, for which I will show an example of the breakup of dopant clusters in silicon.

Slide 1

Method for long time scale simulations of solids: Application to crystal growth and dopant clustering

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Surface of Al(100) after
10 layers deposited in
1 second at 30K

Slide 2

Goals:

- To calculate the evolution of a system over time scales which are much longer than can be calculated with direct classical dynamics.

Problem

- Most interesting transitions are rare events (ie, much slower than vibrations).

- A transition with an energy barrier of 0.5 eV and a typical prefactor occurs 1000 times per second at room temperature. A direct classical dynamics simulation would require 10^{12} force evaluations, and many thousands of years of CPU time to see a single transition.

1000/s

0.5 eV

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Transition state theory

A statistical theory for calculating the rate of slow thermal processes

The primary task is to find an N-1 dimensional dividing surface that represents a bottle neck for the transition

Harmonic transition state theory

Need to find saddle points on the energy surface

Rate of escape through each saddle point region:

$$Rate = \frac{\prod\limits_{i=1..N} v_i}{\prod\limits_{j=1..N-1} v^\dagger_j} \cdot e^{-\frac{\Delta E}{k_B T}}$$

- Minima
- Saddle Points

ΔE

Slide 4

The dimer method: Model potential

A two-dimensional potential

4
3
1
2

Dimer method calculation

Slide 5

The dimer method

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

Low Potential

Lowest Curvature Direction

High Potential

Effective Force

Image

True Force

Dimer

1. Form a 'dimer' around an image of the system.

2. Minimize the energy of the dimer while keeping the center (image) fixed. This finds the lowest curvature mode. (Voter '97)

3. Invert the force component along the dimer to define an effective force.

4. Minimize effective force to find a saddle point.

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The dimer method: Adatom diffusion on Al(100)

The 10 lowest energy mechanisms found in 1000 searches.

	Initial	Saddle	Final		Initial	Saddle	Final
1. 0.227				5. 0.437			
2. 0.372				6. 0.599			
3. 0.413				7. 0.702			
4. 0.426				8. 0.750			

Slide 1

Long time dynamics: Al(100) ripening processes

ΔE: **0.16** eV

v: **1.9 · 10¹⁴ s⁻¹**

ΔE: **0.05** eV

v: **8.1 · 10¹³ s⁻¹**

ΔE: **0.24** eV

v: **3.8 · 10¹⁴ s⁻¹**

Slide 2

Distributed long time scale simulations

eon.chem.washington.edu

- Simulations of crystal and amorphous thin film growth, diffusion/ripening

Server

Internet

Distributed screen saver on hundreds of clients:

EON — Client 1   EON — Client 2   ...   EON — Client n

Slide 3

Long time dynamics: Growth of Cu(100) and Al(100)

10 monolayers are deposited at 0-80K in 1 second.

Multiple time scale simulation in which atoms are deposited with classical dynamics and activated processes are simulated with dynamic event table kinetic Monte Carlo

0.1 eV

Initial: 768 atoms t = 0   **Final:** 2000 atoms t = 1.1s

Slide 4

Long time dynamics: Growth on Al(100)

Statistics

temperature: 100K	temperature: 30K
total transitions: 276	total transitions: 163
distinct transitions : 272	distinct transitions: 162
total time: 6.1 ms	total time: 3.2 ms
dimer searches per step: 50	dimer searches per step: 50
distinct processes per step: 20	distinct processes per step: 22

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Long time dynamics: 30K Al(100) growth processes

ΔE: **0.004** eV

v: **3.6 · 10¹³ s⁻¹**

ΔE: **0.048** eV

v: **1.7 · 10¹⁴ s⁻¹**

ΔE: **0.045** eV

v: **4.5 · 10¹³ s⁻¹**

Slide 6

Long time dynamics: EON growth simulation

Aluminum grows much smoother than copper at 80K, in part because of multiatom smoothening events

B₃I cluster formation via a B₃I₂ intermediate

Conclusions

• The dimer method can be used to simulate long time dynamics within harmonic transition state theory.

• A distributed computing environment can make use of the parallel nature of the long time algorithm making it possible to simulate the deposition of 1000 atoms over a second at 80K in several weeks of wall clock time.

• Simulations indicate that Al will grow much smoother than Cu on the <100> surface at a deposition rate of 10 ml/s at 80K. This is due in part to the fact that aluminum atoms can easily down-step from islands with long range, multi-atom processes.

• The dimer method has been implemented with plane wave DFT calculations and used to simulate the breakup of triatomic boron clusters in silicon.