Using KMC Techniques to Model the Growth of TiO_2

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BACKGROUND

During the recent few decades, atomistic simulation has been used as an outstanding partner with experiment in addressing problems in materials science. Molecular dynamics (MD) method would be the most direct simulation techniques, since it follows the actual dynamical evolution of the system. However, due to the huge amount of calculation, simulation of classical dynamics is not feasible. Simulating individual atomic vibrations requires a time step of several femtoseconds (10^{-15}s), so reaching even one microsecond (10^{-6}s) on today's fastest computer is very difficult.

In the past decade, some new methods have been developed to solve this time scale problem. These methods can simulate the system which is characterized by a sequence of activated event, i.e. diffusion event, within an accessible time scale while retaining full atomistic details. So far these methods have been used in modelling surface growth and surface diffusion.

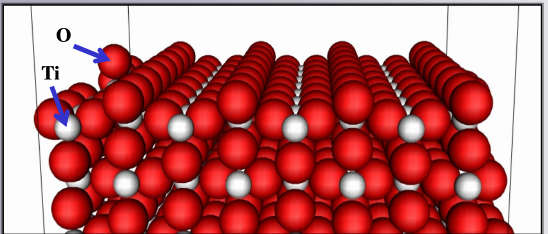

Fig1. Titanium dioxide (TiO_2) model. Red balls are oxygen atoms and white ones are titanium atoms.

PURPOSE

- Learning and analyzing several new numerical techniques.
- Modeling the deposition process of specific materials (TiO_2).See Fig1.
- Finding transition energy barriers with different numerical techniques and comparing the results.
- Modeling the diffusion process of specific materials.
- Analyzing collected data and producing visualized results.

MATERIALS AND METHODS

Finding Saddle Point

The **minimum energy path (MEP)** is the path connecting the initial and final states that typically has the greatest statistical weight. The maxima on the MEP are saddle points on the potential energy surface. In this project, we use the following methods to find saddle points and initial states:

- **The Dimer Method:** G. Henkelman and H. Jónsson (1999)
- **The Activation-Relaxation Technique (ART):** N.Mousseau and G.T. Barkema (1998)
- **The Translation and Relaxation Method (RAT):** L.Vernon

Fig2 shows a saddle point in 3 dimensional case. But since each atom has 3 degrees of freedom, we consider saddle points in 3N (N is the number of atoms) dimensional surfaces.

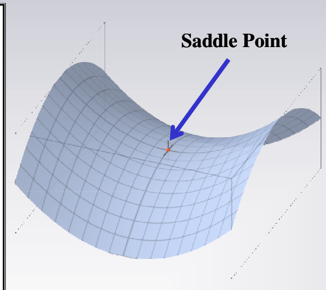

Fig2. A saddle point in 3D surface
(http://en.wikipedia.org/wiki/Saddle_point)

Barrier Calculating

After finding final states with one of above techniques, we use **Nudged Elastic Band (NEB)** method to calculate the energy barriers of transitions. In this method, a series of linearly interpolated images are created and conceptual springs are added between adjacent images. The springs ensure the continuity of the path and mimic an elastic band which convergences to the MEP.

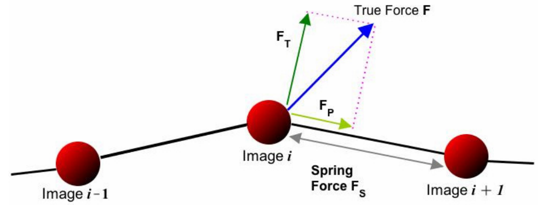

Fig3. Force decomposition and spring force of one image in NEB method

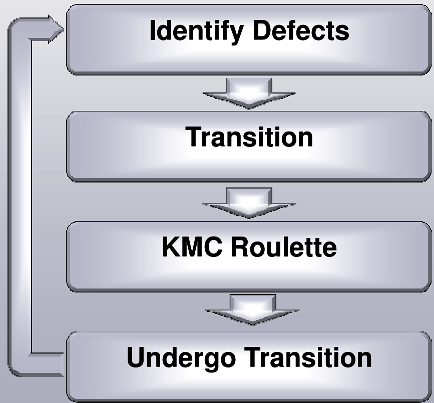

Fig4. Flow chart of KMC

On –the-fly Kinetic Monte Carlo (OFKMC)

Kinetic Monte Carlo (KMC) method is an promising computer simulation intended to simulate the time evolution of processes. It has been widely used in simulating physical systems like surface diffusion and surface growth. G. Henkelman and H. Jónsson (2001) proposed a variation on the KMC method, the OFKMC, in which one builds a state-specific catalog on the fly. It is used in this project to simulate the deposition process. Fig4 shows the flow chart for each KMC step.

RESULTS

Computer Simulation

Several deposition process were simulated with the software LBOMD, which is produced by mathematical modelling group in School of Mathematics, LU. Fig5 & Fig6 show the visualized results of initial and final states of 1st step in a TiO_2 deposition process under 40eV charge. They illustrate one oxygen atom jumped from initial energy basin to the final one. (Red arrow shows the jumping direction). Then Fig.7 shows how energy barriers change against distance in this process. In this deposition, RAT and NEB methods were used.

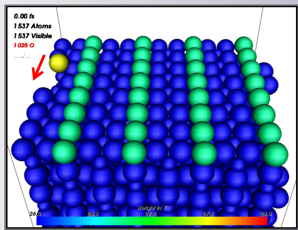

Fig5. 1st step of TiO_2 deposition under 40eV charge. INITIAL STATE

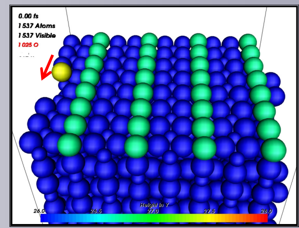

Fig6. 1st step of TiO_2 deposition under 40eV charge. FINAL STATE

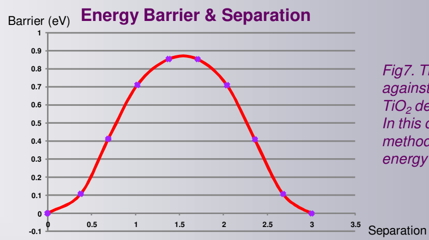

Fig7. The energy barrier changes against separation in the 1st step of TiO_2 deposition under 40eV charge. In this deposition process, NEB method was used to calculate energy barriers and MEP.

TO-DO WORK

- Simulating deposition & diffusion process in more situations, including different charges and different ratios of oxygen and titanium atoms.
- Simulating deposition & diffusion process with different methods, comparing the data and analyzing results.

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