Atomistix ToolKit

Modeling Kinetics in Nanoelectronics using ATK

Virtual NanoLab

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Motivation

Reactions in the solid state are too slow to efficiently study with molecular dynamics (MD) simulations. This because the MD timestep must be on the timescale of atomic vibrations (1-5 fs), while the timescale of solid-state reactions range from nanoseconds (vacancy diffusion), to milliseconds (surface catalysis), to years (material aging). A typical solid-state system will spend many vibrational periods oscillating around the minimum before recievingenough kinetic energy along the correct degree of freedom to cause a reaction to occur.

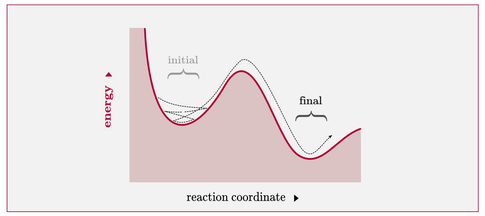


Figure 1. Time trace of a MD trajectory projected along a reaction coordinate. The barrier is larger than the average kinetic energy (k_BT), which means there will be a large timescale seperation between vibrations in the initial state and the reaction.

Harmonic Transition State Theory

Harmonic trajectory state theory (HTST)[1] uses saddle points to identify bottleneck regions of the potential energy surface that separate reactants from products.

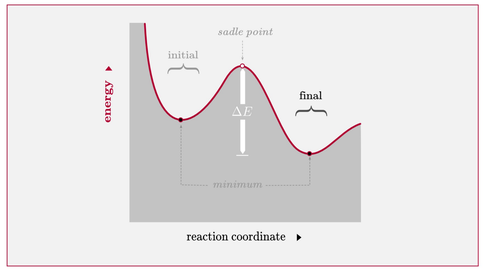


Figure 2. Location of stationary points along a reaction coordinate. The saddle point (first order) is the lowest energy point that divides the initial and final states.

The rates are then calculated using a rate equation that is similar to the Arrhenius rate law, however it uses properties that can be computed directly from the potential energy surface:

$$\Gamma_{HTST} = \frac{\prod_{i=1}^{3N} \nu_i^R}{\prod_{i=1}^{3N} \nu_i^S} \exp\left[\left(E^S - E^R\right)/k_BT\right] \quad (1)$$

N : number of atoms
ν_i^R, ν_i^S : stable vibrational frequencies at the reactant and saddle point
E^R, E^S : energies at the minimum and saddle point
k_B : Boltzmann's constant
T : temperature

Locating Saddle Points

HTST casts the problem of calculating reaction rates into one of locating the relevant saddle points. Once a saddle point has been located Eqn. 1 can be used to compute the reaction rate at any temperature (although HTST is typically valid from about 200 - 800 K).

1. Run high temperature MD simulations
2. Run high temperature MD simulations
3. Find the saddle point that connects them using a nudged elastic band (NEB) calculation[2]

More details about using high temperature MD to locate saddle points is given in Ref. [3].

Kinetic Monte Carlo

Kinetic Monte Carlo (KMC)[4] models state-to-state dynamics as a Markov chain.

- Reactions are chosen in proportion to their rate (Γ_i)
- Escape time drawn from exponential distribution

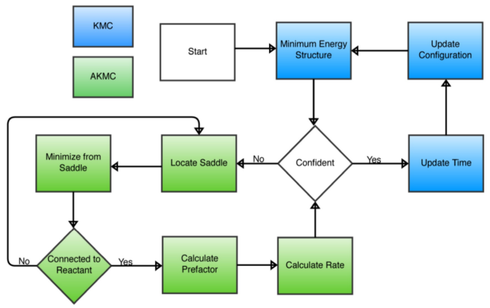
$$P[\Delta t] = \exp\left(-\Delta t \sum_i \Gamma_i\right) \quad (2)$$

- Computationally efficient (two random numbers)

KMC requires knowledge of the reaction rates, which can be obtained from HTST.

Adaptive Kinetic Monte Carlo

Combining a method for locating saddle points, HTST, and KMC gives rise to adaptive kinetic Monte Carlo (AKMC)[5], which is an efficient ab-initio method for calculating the long timescale dyanamics of solid-state systems.



Breakup of a Boron Cluster

The break-up of a boron cluster in a bulk silicon lattice was modeled at 500 K using energies and forces from GGA DFT.[6] Boron is commonly used as a dopant for p-type silicon. The high B concentration required for nanoscale devices can lead to dopant clustering and deactivation. Thus, the kinetics of dopant cluster formation and break-up is of interest to the semiconductor industry.

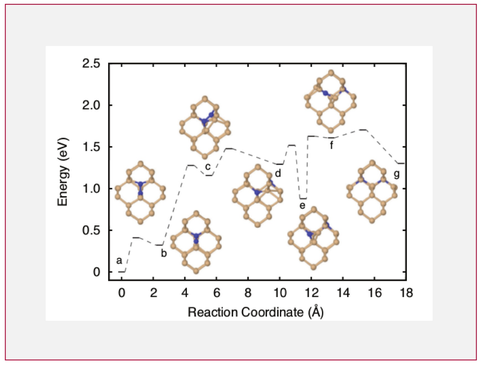


Figure 4. A reaction coordinate diagram that shows the full pathway for the breakup of a SiB_2I cluster.

Vacancy Cluster Formation in Iron

High energy particles produced in nuclear chain reactions can cause significant damage to nearby materials. It is often energetically favorable for these vacancies to cluster together and the formation of large clusters can lead to a sudden structural failure.

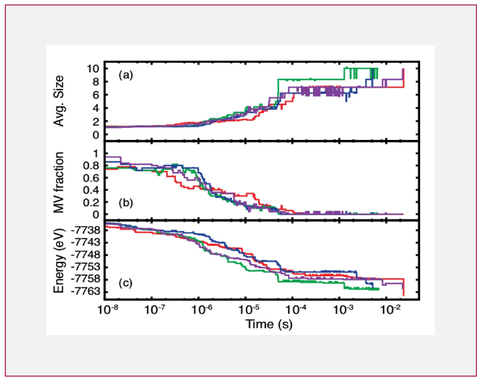


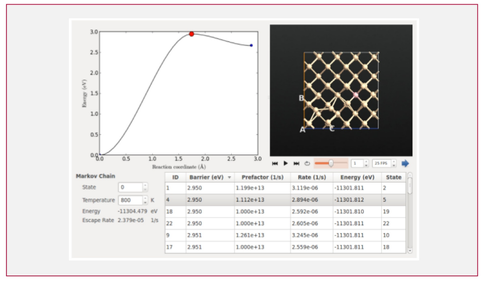
Figure 5. Four AKMC trajectories of 50 randomly distributed vacancies in a 10×10×10 supercell of bcc Fe. (a) Average vacancy cluster size; (b) fraction of monovacancies (MV); and (c) potential energy of the minima along the trajectories.

In this simulation we examined the timescale of vacancy cluster formation at 150°C using an EAM interatomic potential.[3] The initial configuration had 50 randomly placed vacancies in a 10×10 ×10 supercell of bcc Fe.

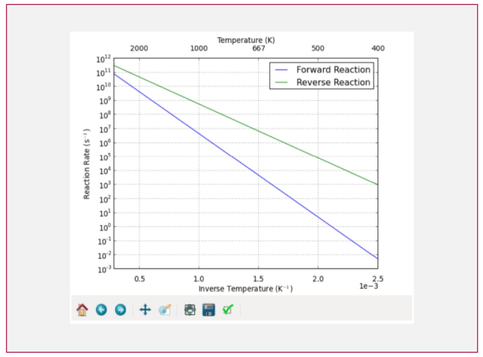
Long Timescale Dynamics in VNL/ATK

The Atomistix ToolKit developed by QuantumWise supports a number of methods for calculating long timescale dyanmics. All of these methods can be used with DFT, semi-empirical methods, and classical force fields.

- Adaptive Kinetic Monte Carlo Simulations



- HTST reaction rates from NEB calculations



- Kinetic Monte Carlo simulations
- Saddle point optimization

References

[1] George H. Vineyard. Frequency factors and isotope effects in solid state rate processes. *Journal of Physics and Chemistry of Solids*, 3(1):121 – 127, 1957.

[2] Graeme Henkelman, Blas P. Uberuaga, and Hannes Jonsson. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. *The Journal of Chemical Physics*, 113(22):9901–9904, 2000.

[3] Samuel T. Chill and Graeme Henkelman. Molecular dynamics saddle search adaptive kinetic monte carlo. *The Journal of Chemical Physics*, 140(21):–, 2014.

[4] Arthur F. Voter. Introduction to the kinetic monte carlo method. In Kurt E. Sickafus, Eugene A. Kotomin, and Blas P. Uberuaga, editors, *Radiation Effects in Solids*, volume 235 of *NATO Science Series*, pages 1-23. Springer Netherlands, 2007.

[5] Lijun Xu and Graeme Henkelman. Adaptive kinetic monte carlo for first-principles accelerated dynamics. *The Journal of Chemical Physics*, 129(11), 2008.

[6] Samuel T. Chill, Matthew Welborn, Rye Terrell, Liang Zhang, Jean-Claude Berthet, Andreas Pedersen, Hannes Jonsson, and Graeme Henkelman. Eon: Software for long time simulations of atomic scale systems. *Modelling and Simulation in Materials Science and Engineering*, 22(5):055002, 2014.

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