Kinetic Monte Carlo Simulation

1 Introduction

In this practical we investigate the kinetic Monte Carlo simulation method and its application to diffusion problems of varying complexity. We first summarize the method and then apply it to the following problems: 1) Atomistic modelling of diffusion in a time-dependent temperature field; 2) Coarse grained description of the same problem; 3) Diffusion of Au atoms in Si via the kick-out mechanism.

1.1 KMC method

We consider a system with a set of possible states i with transitions $i \to j$. The rate for transition $i \to j$ is ν_{ij}. Then a kinetic Monte Carlo simulation consists of the following:

- Start with an initial state i at time t.
- Evaluate the total jump rate.
$$\Gamma = \sum_j \nu_{ij}. \tag{1}$$
- Evaluate the jump probabilities
$$p_j = \frac{\nu_{ij}}{\Gamma} \tag{2}$$
and cumulative jump probabilities
$$P_j = \sum_{j'<j} p_{ij}. \tag{3}$$
- Choose a random number $R1$ which is uniformly distributed between 0 and 1. Determine the current jump $i \to j$ from the condition that $P_{ij} = min\{P_{il}, P_{il} > R1\}$.
- Choose a second random number $R2$ and evaluate the jump time as $t_{ij} = -ln(R2)/\Gamma$.
- Set the system into the new state j, re-evaluate the rates if necessary, increase time by setting $t \to t + t_{ij}$, and repeat.

Remarks: (i) The first step in a KMC simulation consists in specifying the possible states of the system and the transition rates. This process is crucial but outside the realm of KMC - it must be based on physical insight, lower-scale simulation, or intuition. (ii) It is not necessary that the states are actual microstates of the system (configurations of atoms). Coarse grained state variables may be more convenient. (iii) Usually the time limiting factor in KMC is the search for the current jump. Hence, if the system can be split into non-interacting subsystems, it is always advisable to do so.

2 Some Diffusion Problems to be solved with KMC

2.1 Diffusion in a Cu thin film with time dependent diffusion rate.

Aluminum is at low concentrations located on substitutional sites in Cu. Consider a sandwich structure consisting of a Cu film with a thickness of 100 nanometers and a Cu-10% Al film of the same thickness. At time 0 the sample is at room temperature. The

temperature is then over 10 seconds linearly increased to 600K. Evaluate the evolution of the Al concentration profile over this time. Parameters: Diffusion coefficient of single Al atoms in Cu:

$$D = 1.49 \times 10^{-7} \exp\left(-\frac{137,1kJ}{RT}\right) \frac{\mathrm{m}^2}{\mathrm{s}}$$

The nearest-neighbor spacing in Cu is $b = 2.54$ Angstroms.

Hints:

- Think how to best represent your system - what is the geometry, how do you treat the directions parallel to the film?
- How does the macroscopic diffusion coefficient given above relate to the frequency of atomic jumps? Look up the BEng lecture "Festkörperkinetik" if needed.
- Al moves between substitutional sites - keep in mind that an atom cannot move on a site already occupied by another Al atom.

2.2 Diffusion with time-dependent temperature - coarse grained description.

If you want to simulate larger systems, a description with atomic resolution may not be feasible. Consider the same problem as above, but now with a layer thickness of 2 x 0.01 millimetres and a heating time of 10^6 seconds (about 12 days). To speed up things, no longer consider jump rates between atomic sites but transition rates between cells comprising many atoms. Using basic knowledge of diffusion processes, formulate rates for the transition of diffusors between cells of size L, using the requirement that the overall diffusion coefficient must be identical in the atomistic and the coarse-grained description. How can you deal with the fact that the diffusion coefficient depends (due to the 'blocked site' problem) on concentration?

Implement a simulation of the same diffusion problem as in Problem 1 but using coarse grained cells and projecting the diffusion process on a single coordinate. Compare the results with those obtained for the same number of diffusors in Problem 1.

2.3 Diffusion of Gold in Silicon via the Kick-Out Mechanism.

This problem is here as a challenge - it is quite a bit more complicated than the two other ones. If you do not succeed, don't worry.

The diffusion of Gold in Silicon is of tremendous technological importance. The diffusion process is characterized by the fact that intersitial Gold atoms (Au[i]) are fast diffusors while substitutional Gold atoms (Au[s]) are virtually immobile. Gold atoms can, however, switch between interstitial and substitutional configurations by the so-called kick-out mechanism:

$$Au[i] + Si \rightarrow Au[s] + I \quad , \quad Au[s] + I \rightarrow Au[i] + Si$$

where I denotes a Si interstitial.

Simulate the diffusion of Gold into a Si wafer of 1 millimetre thickness at a temperature of 1050 °C. The concentration of substitutional Au at the left surface of the wafer is kept at the equilibrium solubility of 5.38×10^{-7}/atom. The equilibrium concentration of interstitials can be neglected, i.e., the surfaces can be treated as ideal sinks for interstitials. The diffusivities of interstitial Gold and intersitial Silicon are $D_{Au} \approx D_I = 10^{-9}$ m^2/s. The lattice constant of Si is 5.4 Å. The rates of the kick-out reaction are:

- For a Au interstitial kicking out an adjacent Si atom: 600 s^{-1}
- For a Si intersitial kicking out an adjacent Au atom: 10 s^{-1}

In view of the scales involved you will again need a coarse grained description. Choose a cell size for your coarse graining and set up all the relevant rates. For the kick out reactions you will need to write these rates as functions of the numbers of Si and Au interstitials and of substitutional Si atoms contained within a cell.

Set up your simulation and evaluate the diffusion profiles that emerge over an annealing time of 1000 seconds. If everything has been done correctly, they will look very weird. Try to explain how these profiles come about.