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Efficient energy basin finding method for atomistic kinetic Monte Carlo models

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ABSTRACT

Presence of energy basins significantly slows down simulations with the kinetic Monte Carlo (kMC) method. Various methods of the kMC acceleration are available nowadays, but all of them require efficient energy basin finding algorithm. We present the algorithm providing significant acceleration of the kMC calculations. Use of the acceleration speeds up calculations and allows to reach experimental timescales in simulations. During the simulation of the Pt/Cu(1 1 1) surface alloy formation the acceleration is greater than 5000 times. Results of our simulation qualitatively agree with experiment.

1. Introduction

Kinetic Monte Carlo (kMC) [1,2] is a widely used method for studying the formation and evolution of nanostructures. It allows to reach experimental times in simulations, compare their results with experiment and verify theoretical assumptions. For the relatively simple systems combined Molecular Dynamics and kMC (MD-kMC) method is usually applied. This approach uses prepared in-advance database with all possible barriers. Despite its simplicity, this method often gives good qualitative agreement of experiments and simulations. For example, MD-kMC was used to simulate self-diffusion on Al(1 1 1) surface [3] and growth of the Co islands on the Cu(1 1 1) substrate [4]. Both simulations resulted in a good qualitative agreement with the experimental data. MD-kMC method can also explain growth of nanocontacts [5,6], electromigration [7,8] and influence of the STM tip [9,10].

However, MD-kMC algorithm can be used only if it is possible to predict and calculate diffusion barriers for all possible events. This requirement severely limits the possibility of obtaining results that quantitatively coincide with experiments. To solve this problem the Self-learning kMC (SLkMC) method was proposed, which calculates barriers on-the-fly. For the first time, this method was successfully used for studying the formation of Cu clusters on the Cu(1 1 1) [11] surface. Use of the SLkMC method allowed to describe in details such processes as diffusion of islands, voids and their coalescence. This method was recently used to describe self-diffusion of Ni islands on the Ni(1 1 1) surface [12]. Similar method was used to simulate growth of Al clusters on the Al(1 0 0) surface [13]. The SLkMC method is widely used for modeling of multicomponent alloys. It was used to simulate vacancy diffusion in the Al/Mg [14] alloy, self-organization of the Co/Cu(1 0 0) and Fe/Cu(1 0 0) surface alloys [15].

Sometimes there are groups of states with low diffusion barriers between them in the energy landscape. If all of the diffusion barriers to exit this group are high, then such group is called an energy basin. If the system falls to an energy basin, the kMC algorithm has to spend much time to compute numerous repeated events. At the same time, there is almost no increase in the simulated time, due to the presence of low diffusion barriers on each simulation step. Therefore, the kMC algorithm requires acceleration in such situations.

There are several methods to accelerate simulations with the kMC algorithm. The simplest solution is to use the Memory only method [16]. In this method a database with states of the system and transition rates between them is stored in memory, in order to not recalculate them in the future. This method is quite simple, but is not very effective [17]. Another method, called kinetic path sampling (KPS), was presented in work [18]. The KPS method is based on the path factorization of the evolution operator. It was successfully applied to simulate the kinetics of copper precipitation. First passage time analysis [19] (FPTA) was initially used to study Ising model nucleation events at very low temperatures. In FPTA the direct solution of the master equation is used to calculate next kMC event. Mean Rate method (MRM) [20] is also an effective way of accelerating the kMC method. In this method mean rates of escape from transient states to absorbing states are calculated. MRM is faster than FPTA and gives the same results in most of practically important cases [17]. Also it is worth to mention equilibrating basin approach, which was used to study dynamics of vacancies in Si [21]. In this method probabilities of being in particular transient states

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are determined by the Boltzman equation. Equilibrating basin method is quite fast. Unfortunately, it can be used only for deep energy basins when system is fully equilibrated. This restriction severely limits number of situations when the equilibrating basin method can be applied. For instance, it is impossible to use this method to accelerate the SLkMC algorithm because in this situation we cannot predict in advance depth of energy basins.

Regardless of what method is used, there is still a serious problem of finding energy basins. Two methods were proposed by Puchala et al. [17]: the jump-first method and the look-first method. However, it is difficult to apply these schemes in a situation when system has a lot of degrees of freedom, due to the complex definition of the energy basin. The problem can be significantly simplified by using a threshold diffusion barrier [22,23]. Based on this idea, we developed new method of the energy basin finding, including the simple rules of handling transient states and transient atoms. In this article we present our implementation of this method for the 2D alloy, containing thousands of Cu and Pt atoms. The dimension of this system in the configurational space is so high, that its full consideration without simplifications is almost impossible. Therefore, we distinguish small parts of this multidimensional system and operate with them.

Our article has the following structure. In Section 2the kMC and the MRM methods are described. In Section 3.1we discuss in details our method of the energy basins finding. In Section 3.2application of our method to the Pt/Cu(1 1 1) alloy formation is considered. Section 4summarizes our results.

2. Methods

We apply our basin finding method to the simulation of the Pt/Cu (1 1 1) surface alloy formation using the rigid-lattice atomistic kMC method. In this section details of the kMC algorithm together with a brief outlook of the MRM are presented.

2.1. Rigid-lattice atomistic kinetic Monte Carlo method

Temperature of substrate in our kMC simulations is 315 K. This value was taken similar to the one from the experimental article [24]. All frequency prefactors are equal to 10^{12} s^{-1}. This value is typical for the atomic diffusion on the fcc (1 1 1) metal surfaces [4,25,26]. Maximum amount of the Pt atoms in our calculations is 0.05 ML. The deposition flux in this simulation is 0.0025 ML/s which is close to the value of the deposition flux in the experiment [24]. To improve accuracy of our calculations we use random number generator (ran2) from the book [27].

Platinum adatoms are highly mobile on the Cu(1 1 1) surface. The diffusion barrier for the short jump from the fcc to the hcp site of Pt adatom is $E_d^{short} = 0.04$ eV. In the simulation the average length of the terrace is ~ 10 nm. Therefore, Pt adatom reaches the step edges in less than 10^{-8} s after its deposition at 315 K. And, thus, all the interactions between the Pt adatoms far from the step edges can be completely ignored. During the diffusion of Cu and Pt atoms along the step edges they jump between sites of the same type. In the initial configuration all Cu atoms stand in the fcc sites. Let us suppose that Cu atom stands near step. If this atom is moved to the nearest hcp site, then it returns to the fcc site during the relaxation process. Probability that this atom jumps away from the step to the fcc site is low, because the diffusion barrier for the jump along the step (0.22 eV) is much lower than to jump away from the step (0.58 eV). Nevertheless, even if Cu atom jumps away from the step edge to the fcc site, then on the next kMC step this Cu atom returns to the fcc site near the step edge. This happens because the diffusion barrier to return to the step (<0.01 eV) is much lower than the diffusion barrier for the long jump of the Cu atom (0.09 eV) on the Cu (1 1 1) surface. Therefore, only the long jumps of the Pt and Cu atoms are considered in our model.

To simulate the formation of the Pt/Cu(1 1 1) surface alloy the kMC method very similar to [11] is applied. It retains all of the following advantages: (i) calculating diffusion barriers on the fly; (ii) storing them in a database; and (iii) recognizing and retrieving diffusion barriers using labeling. In this work, we offer two improvements of this kMC method. Firstly, the method is generalized to the case of heterogeneous system. Secondly, the simplest “drag” method for the calculation of diffusion barriers is replaced by more accurate nudged elastic band (NEB) method [28,29]. Similar kMC model was applied to the simulation of Co nanostructures embedded in a Cu(1 0 0) surface self-organization [30].

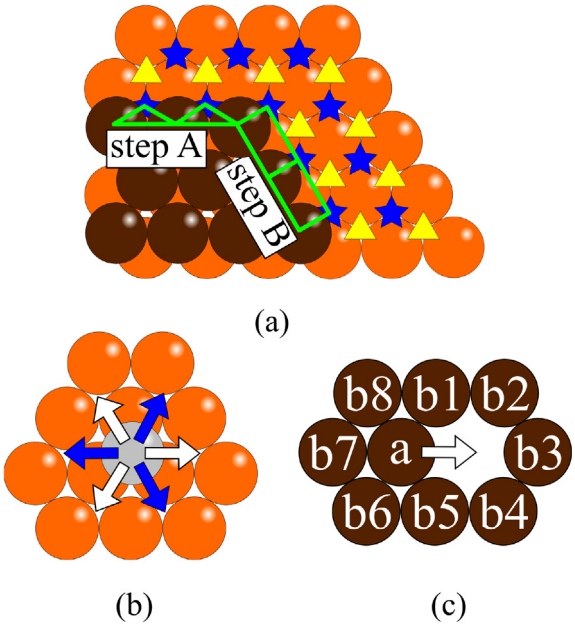

Fig. 1. (a) Schematic view of the fcc and the hcp sites and two types of steps on the (1 1 1) surface. Yellow triangles symbolize fcc sites and blue stars symbolize hcp sites. Green lines connect centers of boundary atoms from the step edge and the nearest hcp sites. (b) Long jumps of type 1 and type 2 on the Cu(1 1 1) surface are denoted by white and blue arrows, respectively. (c) Atomic transition to the right on the (1 1 1) surface and its local environment. Initial position of the atom is denoted by *a*; *b*1–*b*8 are the nearest-neighbor positions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

In our kMC simulations we use rigid lattice single-layer model, where only single-atomic transitions are considered for simplicity. Computational cell consists of 100 × 100 atomic positions with periodic boundary conditions applied to the surface plane. The stripe consisting of 50 atomic rows mimic Cu steps in our simulations. Such choice of the calculation cell allows to consider the evolution of the step A and step B (their difference is shown in Fig. 1a) simultaneously. Initial configuration of the calculation cell is shown in Fig. 7a.

Defects play an important role in some systems. Movement of dumbbell interstitial defects in Fe is guided by diffusion barriers ~0.3 eV [31] and occur at low temperatures. Pt/Cu(1 1 1) surface alloy was investigated using both spectroscopic [32] methods and STM scanning [24]. Presence of defects was not detected in their results.

For the calculation of the diffusion barriers the nudged elastic band (NEB) [28,29] method is used. Barriers are calculated in the calculation cell, consisting of eight layers with 1080 atoms in each layer. Two bottom layers are fixed and periodic boundary conditions are applied in the surface plane. To compute the interatomic interactions we use the TB-SMA potentials [33–35]. Parameters of the potentials and the cut-off function can be found in [36]. In the kMC simulation we consider stepped Cu(1 1 1) surface as a substrate. Elastic effects [37,38] have a significant impact on the results of the simulations. To take them into account we calculate all the diffusion barriers near the step edges.