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Migration barriers for surface diffusion on a rigid lattice: Challenges and solutions

Ekaterina Baibuz [a,*], Simon Vigonski [b,a], Jyri Lahtinen [a], Junlei Zhao [a], Ville Jansson [a], Vahur Zadin [b,a], Flyura Djurabekova [a,c]

[a] Helsinki Institute of Physics and Department of Physics, P.O. Box 43 (Pietari Kalmin Katu 2), FI-00014 University of Helsinki, Finland
[b] Institute of Technology, University of Tartu, Nooruse 1, 50411 Tartu, Estonia
[c] National Research Nuclear University MEPhI, Kashirskoye sh. 31, 115409 Moscow, Russia

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ABSTRACT

Atomistic rigid lattice Kinetic Monte Carlo is an efficient method for simulating nano-objects and surfaces at timescales much longer than those accessible by molecular dynamics. A laborious part of constructing any Kinetic Monte Carlo model is, however, to calculate all migration barriers that are needed to give the probabilities for any atom jump event to occur in the simulations. One of the common methods of barrier calculations is Nudged Elastic Band. The number of barriers needed to fully describe simulated systems is typically between hundreds of thousands and millions. Calculations of such a large number of barriers of various processes is far from trivial. In this paper, we will discuss the challenges arising during barriers calculations on a surface and present a systematic and reliable tethering force approach to construct a rigid lattice barrier parameterization of face-centred and body-centred cubic metal lattices. We have produced several different barrier sets for Cu and for Fe that can be used for KMC simulations of processes on arbitrarily rough surfaces. The sets are published as Data in Brief articles and available for the use.

1. Introduction

Atomic diffusion on metal surfaces is a long term process that may induce undesirable topological modifications down to nanoscale, making these changes practically unnoticeable on large experimental surface areas which easily range from square micrometers to square centimetres. Understanding diffusion processes, including surface diffusion, becomes particularly important when dealing with applications that demand high technological precision ($\leqslant 1$ μm), such as the components of accelerating structures of the future Compact Linear Collider (CLIC) [1]. In CLIC, the accelerating structures are designed to operate for extensive times under high gradient electromagnetic fields, which present additional challenges for keeping the metal surfaces unmodified. For instance, surface diffusion enhanced by an electric field is believed to induce nanoscale surface roughening on copper parts of the accelerating structures. The roughening leads to uncontrollable appearance of local vacuum discharges, damaging the surface and increasing the power consumption, thus decreasing the efficiency of the accelerator [2,3].

It is important to note that surface diffusion may play a crucial role also on a nanoscale, in the process of shaping of growing nanoparticles. For example, in [4], we showed that in a magnetron sputtering inert gas condensation chamber, iron nanoclusters grow cubic or spherical depending on sputtering intensity through the competition between surface diffusion and atom deposition.

The evolution of surfaces is even on a nanoscale a long-term process, not easily accessible by many existing simulation models. The kinetic Monte Carlo (KMC) method was specifically developed to simulate slow diffusional processes, which take place while the system evolves towards the potential energy minimum. Unlike other Monte Carlo methods, KMC is not only able to capture the ground state of thermodynamic equilibrium, but also able to estimate sufficiently well the kinetic path and the required time of a system to move towards the ground state [5]. The latter is enabled through the residence time algorithm [6], which estimates the time needed to complete a single transition.

The physics behind the KMC model is described by the probabilities of diffusion transitions. These probabilities can be estimated via transition energy barriers. Thus, a successful KMC model relies on appropriate estimation of the energy barriers of all possible transitions in the system. The most accurate methods, thus far, involve calculations of the barriers on the fly using the dimer

* Corresponding author.
E-mail address: ekaterina.baibuz@gmail.com (E. Baibuz).

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method of finding potential transition paths on the potential energy surface [7] or applying self-learning procedures during the simulation [8–10]. Such methods usually operate off-lattice, allowing the inclusion of a large variety of possible transitions in the system, and require heavy computational resources. It is also common to use more simplified approaches for estimating the barriers, such as the approach of counting broken and newly forming bonds (the bonds before and after the transition) [11–13]. Such methods are less time consuming and easy to implement but they inevitably increase the uncertainty of the simulation results. Sophisticated mathematical techniques have been recently applied to calculate the energy barriers. Among them are cluster expansion [14,15], genetic programming [16], and artificial neural network [17–19] approaches. These methods are used to predict the energy barriers based on the local atomic environment. In [3], we presented the atomistic KMC (AKMC) model Kimocs for metal surfaces, in which we predefine the allowed transitions in the system and calculate the sets of energy barriers in advance.

Kimocs was designed to simulate evolution of nanofeatures on metal surfaces. It is clear that e.g. molecular dynamics (MD) methods are able to describe similar processes more accurately, since all the atomic configurations, which the system may have while evolving towards the energy minimum, occur naturally in MD. However, the limited time scale of MD methods does not allow to obtain any appreciable changes of a surface morphology with significant features and at temperatures well below the melting point. KMC, on the other hand, offers the possibility to reach rather long time scales with reasonable computational costs, provided that all the atomic jumps are described within the rigid lattice framework.

Since Kimocs was developed with the aim of simulating the temporal evolution of large nanofeatures, it was crucial to employ a parameterization scheme, which is both efficient and sufficiently accurate. We adopted the rigid lattice approximation, which describes an atomic system with all atoms occupying well defined positions in a given crystal structure. Within the rigid lattice approximation, a local atomic environment can be described by a finite number. Although, the rigid lattice approximation has inevitable intrinsic limitations (for example, if surface reconstruction is expected to occur during the process simulated by KMC on a rigid lattice, such process will not be taken into account), it is an efficient approximation to develop fast algorithms that are minimizing computational costs.

In Kimocs, we constrain the transitions in a system to atomic jumps into vacant lattice sites, which we will henceforth call vacancies. The jumps may happen on the surface as well as in the bulk.

The use of a rigid lattice and the limitation on the variety of transitions make it possible to precalculate the sets of barriers for each material (Cu and Fe in this work). Precalculation of the barriers allows us to reach the desired efficiency of the simulation algorithm that only needs to assign tabulated barrier values to atomic jumps in this case. To assure the accuracy of calculated barriers we use the Nudged Elastic Band method. Although such a parameterization scheme seems to be straightforward and easy to implemented, we faced a number of challenges, which are difficult to circumvent.

In this article, we will focus on the calculations of energy barriers for AKMC models with a rigid lattice. We will discuss the challenges of the rigid lattice parameterization and how these challenges can be overcome in order to precalculate the migration energy barrier sets. We will present the tethering force approach, which allows to create nearly complete sets of barriers for all possible transitions on a rigid lattice. We are using this approach together with the parameterization scheme of the Kimocs model, but it is applicable for any other parameterization scheme in a rigid lattice, where possible transitions are restricted to a certain type, e.g. first nearest neighbour jumps in face-centred cubic (FCC) lattices (as is the case in Kimocs).

The structure of this paper is as follows. In Section 2, we provide some details of our KMC model Kimocs and parameterizations that have been used with it earlier. In Section 2.3 we describe the challenges that arise when migration barriers are calculated on a rigid lattice of FCC and BCC structures. In Section 2.4 we present the possible solutions to circumvent the problems described in Section 2.3 and introduce the tethering force approach (Section 2.4.2), which allows for calculations of the barriers on semi-rigid lattice, restricting the freedom of surface atoms to relax far away from they positions on a rigid lattice. In Section 3, we present different sets of migration barriers and discuss the limitations of each set along with the limitations of the Kimocs parameterization approach in general. In Section 3.2 we concentrate specifically on the sets where tethering is used and how this approach affects the KMC simulation results. Finally, we summarize our conclusions in Section 4.

2. Methodology

2.1. Atomistic Kinetic Monte Carlo on a rigid lattice

Before describing the challenges, which we encountered during the parameterization of our AKMC code Kimocs [3] for simulations of surface diffusion processes, we will briefly outline the basic principles of a rigid lattice AKMC model in general and describe in detail special features of our Kimocs code. In an AKMC algorithm within the rigid lattice approximation, a diffusion process proceeds via atomic jumps to a neighbouring vacancy. The event, which includes the choice of an atom to jump and the jump itself, is selected randomly, but with respect to the magnitude of the corresponding transition rates, which are compared for all events. This way, more probable events occur more frequently. The transition rates for all events in the system are calculated according to the Arrhenius formula for thermally activated processes:

$$\Gamma = \nu \exp\left(\frac{-E_m}{k_B T}\right), \tag{1}$$

where ν is the attempt frequency for the transition to occur, k_B is the Boltzmann constant, T is the temperature of the system, E_m is the migration energy barrier, which the atom needs to overcome in order to move from one lattice site to another. For simplicity, ν is considered to be the same for all the transitions.

In Kimocs, the possible jumps in the system are restricted to primarily 1nn jumps in FCC and BCC materials, but 2nn jumps may also be allowed if necessary.

We precalculate the full set of the migration energy barriers, E_m, for all possible 1nn (and 2nn for BCC) jumps in the system to reduce the computation costs of simulations. The parameterization of the E_m barriers is done within the 1nn and 2nn shell. Taking into account only the atoms in the nearest neighbourhood would result in insufficient accuracy, since the interaction with the atoms in the 2nn position is also quite strong in both FCC and BCC lattices.

Using both 1nn and 2nn shells in the parameterization scheme allows us to reach higher accuracy but leads to the full 26 (20 in BCC) neighbouring atoms description, which we will further refer to as the 26D parameterization scheme. In this scheme, if all barriers are to be calculated, then even in a mono-elemental metal $\sim 2^{26}$ barriers are needed.

The original more approximative parameterization scheme of Kimocs uses only four parameters to describe events and we will therefore refer to it as the 4D parameterization scheme. Within this scheme, each jump event is represented by four numbers,