Simulating complex atomistic processes: On-the-fly kinetic Monte Carlo scheme with selective active volumes

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An accelerated atomistic Monte Carlo (KMC) approach for evolving complex atomistic structures has been developed. The method incorporates on-the-fly calculations of transition states (TSs) with a scheme for defining active volumes (AVs) in an off-lattice (relaxed) system. In contrast to conventional KMC models that require all reactions to be predetermined, this approach is self-evolving and any physically relevant motion or reaction may occur. Application of this self-evolving atomistic Monte Carlo (SEAK-MC) approach is illustrated by predicting the evolution of a complex defect configuration obtained in a molecular dynamics (MD) simulation of a displacement cascade in Fe. Over much longer times, it was shown that interstitial clusters interacting with other defects may change their structure, e.g., from glissile to sessile configuration. The direct comparison with MD modeling confirms the atomistic fidelity of the approach, while the longer time simulation demonstrates the unique capability of the model.

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comparing it to an MD simulation for a particular system. Finally we extend it to a case that cannot be modeled using current KMC and MD methods.

The present framework, which we refer to as self-evolving atomistic kinetic Monte Carlo (SEAK-MC), combines multiple techniques. We first introduce the concept of active volumes (AVs) in which the dynamic processes of interest may occur, and then we search for TSs in the AVs. This determines saddle-point configurations and activation energies for potential atomic movements or reactions. As in the case of adaptive KMC, the saddle points in the subsequent time step are found on-the-fly, i.e., based on the state of the evolving system. A schematic diagram of the approach is shown in Fig. 1. Initially, we start from the fully relaxed system that includes all the microstructures of interest. The AVs in the system are identified based on the presence of defects (solutes, precipitates, interstitials, vacancies, clusters, or other extended defects). The location and nature of these defects in the crystal, will lead to the selection of a large AV, particularly for defects with a long-range strain field. The optimum criterion is chosen as a compromise between accuracy and computational expense. An example of how the chosen AV size determines the accuracy is shown in Fig. 2 for the case of the activation barrier for self-interstitial atom (SIA) rotation from (111) into the (111) configuration using a body-centered cubic (bcc) Fe-interatomic potential. This example employed a spherical AV since the SIA can rotate in different directions. However, in general, the AV shape can be determined by the specific lattice and defect properties, and its optimization provides additional enhancements in calculations.

A number of techniques can be employed for the TS search, such as Lanczos, dimer or ABC, and each has its own advantages. Here, we choose the dimer method to illustrate the concept. Since the dimer method is based on the harmonic approximation of TS theory, the corresponding limitations of this theory also exist here. For each defect in an AV, several dimer searches are performed, and the corresponding positions and forces are stored. To move the system over the chosen saddle point, information on the atom positions and gradient are used, and relaxation is applied only in the current AV. This is significantly more efficient than the adaptive KMC because the equilibrium states after all possible saddles do not need to be calculated before the current KMC step. It is also more efficient than ABC application in which the NEB calculations are required to determine the height of saddle point after the final state has been found.

FIG. 1. Schematic diagram of SEAK-MC method.
FIG. 2. (Color online) Illustration of the effect of AV size: interstitial rotation energy from [110] to [111] determined during the saddle point search for different AV radii. The target value is the rotation energy from [110] to [111] in the bulk system.

The accuracy of the SEAK-MC was validated by direct comparison with MD simulations. The case we present here for demonstration was selected from many others we made because of its complexity. Interstitial-type defects are characteristic of irradiated materials, and a fundamental understanding of the evolution of interstitial clusters is of vital importance and yet not complete. The accuracy of the SEAK-MC was validated by direct comparison with MD simulations. Both sessile and glissile interstitial clusters have been observed in MD simulations. The glissile configurations consist of ⟨111⟩ crowdions, while the sessile typically appear as a combination of ⟨110⟩ dumbbells and ⟨111⟩ crowdions. The ability of small SIA clusters to exist in configurations with completely different properties was studied quite extensively by ab initio, KMC, MD, and statics techniques because of the expected important consequences in microstructure evolution under irradiation. With SEAK-MC, we demonstrate that an advanced KMC approach can reproduce a sequence of reactions between fast (SIA and glissile SIA cluster) and slow (vacancy) objects observed in MD and determine the fate of a sessile SIA cluster at a timescale not amenable by MD. We simulated the evolution of defect configurations obtained from an MD cascade simulation in bcc iron, which is the base material for many structural applications. In the current example the system size was a 16 × 16 × 16 supercell and included ~8200 atoms. The bcc Fe-interatomic potential from Ref. was used in order to compare results with the existing MD simulations. Within the dimer component the vector length between dimer endpoint and midpoint is 0.001 Å, and the maximum move is 0.1 Å. The relaxation is converged when the change in force is less than 10⁻⁴ eV/Å. The activation energy difference between AV and total volume is 0.005 eV. The attempt frequency used in the KMC step is 10¹² s⁻¹.

The initial defect configuration taken from the MD simulation is shown in Fig. 3(a). It consists of a glissile cluster containing nine parallel ⟨111⟩ crowdions, a single vacancy, and a SIA in a ⟨110⟩ dumbbell configuration. The dashed circles in Fig. 3 indicate the extent of the corresponding AVs. Figure 3(b) shows the system after the cluster has interacted with the vacancy, reducing it to an eight-SIA cluster still in glissile configuration. The cluster moved toward the single dumbbell, interacted with it, and created a complex sessile cluster, forming a complex sessile cluster; (d) Transformation of the sessile cluster into a glissile set of parallel crowdions.

Circles in dashed line represent active volumes (AVs)

FIG. 3. (Color online) Defect interactions and subsequent change in configuration. Only the defects are shown and their size is adjusted to be easily seen. The figure on the right is a magnified view from a different angle of the object shown in the left. (a) Initial configuration, including cluster of 9 parallel crowdions, a single vacancy, and a single SIA; (b) Interaction between the 9 SIA glissile cluster and vacancy; (c) Interaction between the 8 SIA glissile cluster and single interstitial, forming a complex sessile cluster; (d) Transformation of the sessile cluster into a glissile set of parallel crowdions.
precise configurations are observed. Furthermore, the average time predicted by SEAK-MC for this entire process is in good agreement with the time observed in MD, a few picoseconds, which indicates that SEAK-MC found the corresponding saddle points with accurate activation energies. Previously, formation of complex sessile SIA clusters was observed only in MD cascade simulations. 19,21 The process described previously proves that small complex sessile SIA clusters can be also created in reactions between mobile defects.

For a second test we use SEAK-MC to extend the previous MD simulations to a time scale beyond the MD limit. In MD modeling at 100 K, the SIA cluster shown in Fig. 3(c) remains sessile over the whole simulated time, \(~1.5\) ns, whereas SEAK-MC modeling showed that it eventually transforms into a glissile cluster of parallel crowdions [Fig. 3(d)] in \(\sim 8\) \(\mu s\), based on multiple simulations. Although the mobility of a glissile SIA cluster after transformation is quite high, the effective diffusivity is strongly reduced by the sessile metastable state, resulting in a change in the microstructure evolution process, as was pointed out in Ref. 14. SEAK-MC takes this into account naturally in a simulation of atomistic defect dynamics that can be easily extended over mesoscale times.

From the previous discussion it can be seen that SEAK-MC is able to accurately describe the complex diffusion process of an interstitial cluster as well as its interactions with other defects within the same framework with no input of any details of the defects or processes. Similar to MD, the only input SEAK-MC requires is the atom positions and the interatomic potential. This is a capability not possessed by current KMC methods because it is impossible to predetermine any details of the defects or processes. Similar to MD, the SEAK-MC method may thus have been observed.

In summary we have developed a general framework that combines multiple methods to simulate the long-term evolution of a material with atomistic fidelity. Similar to the previous uses of on-the-fly KMC, we calculated accurate TS energies and obtained corresponding stable and/or metastable defect structures. The concept of selective AV is introduced to accelerate the method, which can accurately describe both the dynamics and the interactions between complex defects. This is a significant improvement over all current KMC models. It allows complicated and realistic situations to be simulated to much longer times than MD. Modeling the behavior of interstitial clusters formed in bcc iron with SEAK-MC revealed that glissile interstitial defects can interact with each other, creating metastable sessile clusters, which may then transform back into a glissile state. Although some aspects of this scenario can be simulated individually by MD or existing KMC-based techniques, the SEAK-MC reproduces all the phenomena in a single model. Other potential applications of SEAK-MC are also discussed.

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