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

Haixuan Xu (徐海謜), Yury N. Osetsky, and Roger E. Stoller*
Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6138, USA
(Received 5 April 2011; revised manuscript received 14 September 2011; published 12 October 2011)

An accelerated atomistic kinetic 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 kinetic 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.

DOI: 10.1103/PhysRevB.84.132103 PACS number(s): 61.72.Bb, 07.05.Tp, 81.05.Bx

Prediction of the long-term evolution of defect structures is essential for understanding the properties and performance of materials for practical applications. The majority of the relevant mechanisms operate at the atomic scale, and modeling the corresponding processes is challenging due to the range of time and length scales involved. For example, structural materials employed in nuclear energy systems are exposed to fast neutrons,[1] and this irradiation leads to the creation of atomic displacement cascades consisting of many point defects (vacancies and interstitials) and small point-defect clusters. The subsequent evolution of these defect structures results in phenomena such as void swelling, hardening, and embrittlement, which can lead to property degradation and possibly component failure.[2,3] This evolution spans many orders of magnitude in time, from picoseconds to years. In order to simulate the required evolution, different techniques are used to cover processes from the atomic to continuum levels. In the picoseconds regime molecular dynamics (MD) simulations are widely employed to elucidate the underlying atomistic mechanisms.[4] However, the time scale of MD is greatly limited because the time step needs to be small enough to accurately account for atomic vibrations.

To extend the time scale, mesoscale techniques based on kinetic Monte Carlo (KMC), including object KMC (OKMC)[5] and atomistic KMC (AKMC),[6,7] are commonly employed. However, current KMC methods suffer severe limitations. OKMC simulations are based on a predefined list of activation energies for each event; no event can occur that is not anticipated in this list. Accounting for the migration and interaction of defects with complicated configurations is almost impossible due to the difficulty in finding corresponding activation energy barriers for all the possible transitions. AKMC applies an on-lattice approximation to all defects. No explicit relaxation of the lattice is included, losing the required accuracy to accurately describe the properties of complex defects. Furthermore, neither method is able to accurately describe the atomistic interactions between defects, which are critical in predicting the evolution process. The fundamental difficulty is the lack of an integrated theoretical method able to account for long-term evolution of complex atomic systems with defect motion, interaction, and transformation simultaneously.

Recently the concept of so-called "on-the-fly" search of transition states (TSs) has been introduced in an attempt to overcome the shortcomings of KMC. For example, in adaptive KMC,[8,9] the dimer technique[10,11] is applied to search the TS involving all atoms in the system to identify the saddle points for potential atom movements. After an event is chosen, a KMC step is used to move the system into a new state. To accelerate the process, a method called TS recycling is employed. In this case previously identified TSs are used if the atoms involved do not move more than a threshold displacement Δr ($\Delta r = 0.2a$ in Ref. 9). This scheme seems to be most efficient for small systems where all the TSs and the corresponding relaxed configurations can be kept and reoptimized. Another technique suggested in Ref. 12 uses autonomous basin climbing (ABC) to find the closest new configuration for all the defects and applies the nudged elastic band (NEB) technique to reproduce the corresponding TSs. KMC is then used to advance time by choosing among all the available TSs and utilize the corresponding configuration relaxed previously. In this method only the minimum energy saddle is used in KMC for each defect. The transitions are therefore limited; the system evolution is biased toward a ground state, and high energy fluctuations in states are prohibited.

It is apparent that neither adaptive KMC nor the ABC method is sufficiently general and robust enough to treat complex and high energy defect configurations. Such environments frequently arise in deformed or irradiated structural materials and involve long-range interactions between internal microstructural components. In this Brief Report we describe the development and application of an integrated theoretical framework for evolving complex physical systems, which includes the on-the-fly approach, while bringing a unique quality to mesoscale KMC modeling of large systems with atomistic accuracy. First we describe the main details of the method. Then we demonstrate the fidelity of the method by

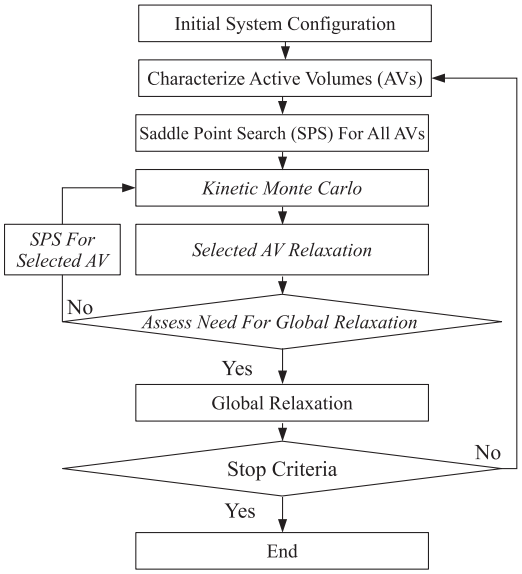

FIG. 1. Schematic diagram of SEAK-MC method.

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,[9] 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 simulation do not need to be identified *a priori*. The boundary of each AV is determined by a criterion which limits the allowed deviation in energy, strain, or stress for the boundary atoms relative to the bulk value. We require that the effect of the internal defect(s) is negligible at the AV boundary. The primary source of acceleration in the method is provided by focusing on evolution within these AVs. These are the only parts of the system where dynamic processes can occur, and the TS search, which is the most time-consuming part of the on-the-fly modeling, is applied within these relatively small volumes.

Once the TSs and the corresponding activation energies within each AV are found, a KMC step is taken by choosing a random event among all possible reactions in all AVs based on the probability and the time advances using the residence time algorithm. The corresponding configuration is then pushed over the selected saddle point and relaxed to another local minimum state in its own AV. Any possible reaction may occur during the relaxation step. After the system relaxes into a new state, normally only the AV in which the event occurred requires a new search of TSs. This allows frequent events to progress with the highest efficiency in their local AVs. Based on the criteria used to establish the original AV boundaries, defect evolution may lead to sufficient energy or strain changes at the boundary of one or more AVs to require that their boundaries be redetermined. In this case the whole system is re-equilibrated by relaxing to the minimum potential energy. This step serves to update interactions between evolving objects and leads to the definition of new AVs. This may also lead AV to interact or even merge. In small systems with few atoms and/or closely spaced objects, SEAK-MC works similarly to other on-the-fly KMC methods, such as in Refs. 9 and 12. However, its efficiency increases with increasing system size, and it is particularly efficient when evolving objects that are well separated. The vast majority of calculations in SEAK-MC involve a search of TSs in the single AV where the event occurred at the previous step. That means that only a few hundred/thousand atoms are computationally active in a large multimillion atom system. After a new set of AVs is identified, the process is repeated, as shown in Fig. 1. A unique aspect of the SEAK-MC method is that reactions between defects can occur either *locally* within the same AV as a result of the saddle point search or *globally* when AVs are merged during the relaxation of the whole system.

Different localization techniques can be applied to determine the AVs within a given system. For example, a very simple and fast criterion is the increase of local atomic energy over the perfect crystal. This criterion for AV identification is the primary parameter influencing the performance of the SEAK-MC model. Choosing a strong criterion, e.g., a weak deviation of potential energy/stress relative to the perfect 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 ⟨110⟩ into the ⟨111⟩ configuration using a body-centered cubic (bcc) Fe-interatomic potential.[13] 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,[4,14] and its optimization provides additional enhancements in calculations.

A number of techniques can be employed for the TS search, such as Lanczos,[15] dimer,[10,11] or ABC,[16,17] 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[9] 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[12] in which the NEB calculations are required to determine the height of saddle point after the final state has been found.

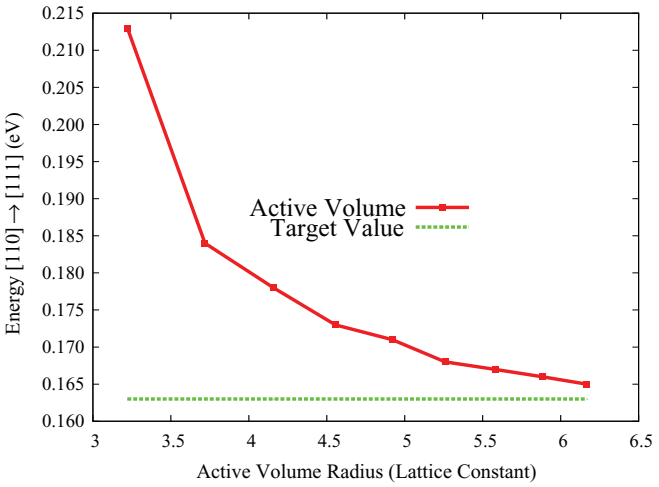

FIG. 2. (Color online) Illustration of the effect of AV size: interstitial rotation energy from [110] to [111] determined during the saddle point search for different AV radii. The target value is the rotation energy from [110] to [111] in the bulk system.

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.[4,14,18] Both sessile and glissile interstitial clusters have been observed in MD simulations.[14] 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*,[18] KMC,[6] MD, and statics techniques[4,19] 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[4] 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. 20 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 10^{12} 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

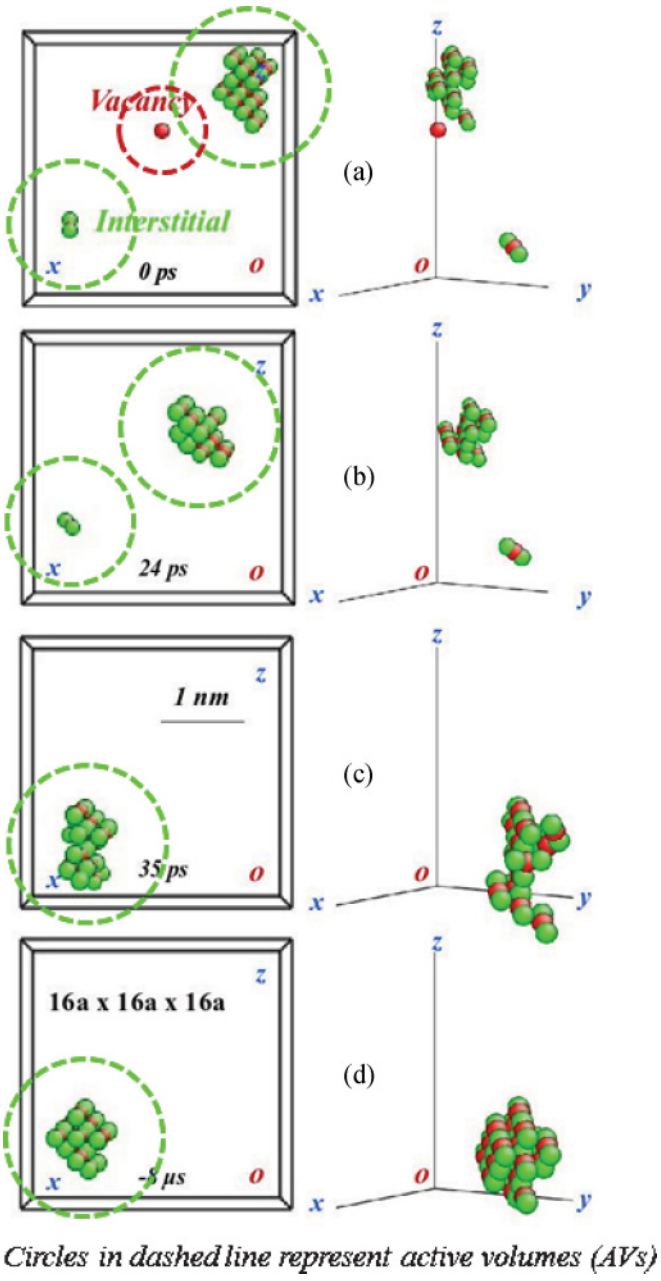

FIG. 3. (Color online) Defect interactions and subsequent change in configuration. Only the defects are shown and their size is adjusted to be easily seen. The figure on the right is a magnified view from a different angle of the object shown in the left. (a) Initial configuration, including cluster 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 to into a glissile set of parallel crowdions.

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 configuration, shown in Fig. 3(c). Note that the number of AVs reduces from three to two to one due to interactions between defects. The sequence of the processes shown in Fig. 3 is exactly the same as found in the MD simulation, while statistical variations in the

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 ∼8 μs, 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 the activation energy of all the necessary events. In addition the SEAK-MC method is inherently compatible with both *ab initio* and semi-empirical calculations. For example, the force calculations for the saddle-point search in the previous analysis were carried out using a classic many-body interatomic potential. In general, forces can also be evaluated using first principles calculations or the reactive force field (ReaxFF) approach.[22] The SEAK-MC method may thus have broad applications to any process in which atomistic accuracy and long simulation time are needed. For example, we will use SEAK-MC to simulate cascade annealing with consideration of impurities, dislocations, grain boundaries, or interfaces with no assumptions, rather than the interatomic potentials used. In addition SEAK-MC will also be employed to investigate processes under deformation, such as the formation, growth, interactions, and motion of dislocations on a significantly larger time scale than can be obtained by MD. This means that more physically realistic load rates can be applied, such as those obtained in creep and nano-indentation simulations.

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.

Research at the Oak Ridge National Laboratory supported as part of the Center for Defect Physics, an Energy Frontier Research Center funded by the US Department of Energy, Office of Science, Office of Basic Energy Sciences under Award No. ERKCS99.

*rkn@ornl.gov

[1] B. D. Wirth, Science **318**, 923 (2007).
[2] G. Ackland, Science **327**, 1587 (2010).
[3] X. M. Bai, A. F. Voter, R. G. Hoagland, M. Nastasi, and B. P. Uberuaga, Science **327**, 1631 (2010).
[4] R. E. Stoller, G. R. Odette, and B. D. Wirth, J. Nucl. Mater. **251**, 49 (1997).
[5] C. S. Becquart, A. Barbu, J. L. Bocquet, M. J. Caturla, C. Domain, C. C. Fu, S. I. Golubov, M. Hou, L. Malerba, C. J. Ortiz, A. Souidi, and R. E. Stoller, J. Nucl. Mater. **406**, 39 (2010).
[6] F. Soisson, C. S. Becquart, N. Castin, C. Domain, L. Malerba, and E. Vincent, J. Nucl. Mater. **406**, 55 (2010).
[7] W. D. Guo, T. P. Schulze, and E. Weinan, Commun. Comput. Phys. **2**, 164 (2007).
[8] G. Henkelman and P. Johnsson, J. Chem. Phys. **115**, 9657 (2001).
[9] L. J. Xu and G. Henkelman, J. Chem. Phys. **129**, 114104 (2008).
[10] G. Henkelman and H. Jonsson, J. Chem. Phys. **111**, 7010 (1999).
[11] A. Heyden, A. T. Bell, and F. J. Keil, J. Chem. Phys. **123**, 224101 (2005).
[12] Y. Fan, A. Kushima, S. Yip, and B. Yildiz, Phys. Rev. Lett. **106**, 125501 (2011).
[13] G. J. Ackland, D. J. Bacon, A. F. Calder, and T. Harry, Philos. Mag. A **75**, 713 (1997).
[14] N. Anento, A. Serra, and Y. N. Osetsky, Modell. Simul. Mater. Sci. **18**, 025008 (2010).
[15] R. Malek and N. Mousseau, Phys. Rev. E **62**, 7723 (2000).
[16] T. T. Lau, A. Kushima, and S. Yip, Phys. Rev. Lett. **104**, 175501 (2010).
[17] M. Kabir, T. T. Lau, D. Rodney, S. Yip, and K. J. Van Vliet, Phys. Rev. Lett. **105**, 095501 (2010).
[18] C. C. Fu, J. Dalla Torre, F. Willaime, J. L. Bocquet, and A. Barbu, Nat. Mater. **4**, 68 (2005).
[19] R. E. Stoller, J. Nucl. Mater. **237**, 999 (1996).
[20] M. W. Finnis and J. E. Sinclair, Philos. Mag. A **50**, 45 (1984).
[21] F. Gao, D. J. Bacon, Y. N. Osetsky, P. E. J. Flewitt, and T. A. Lewis, J. Nucl. Mater. **276**, 213 (2000).
[22] A. C. T. van Duin, S. Dasgupta, F. Lorant, and W. A. Goddard, J. Phys. Chem. A **105**, 9396 (2001).