Self-Evolving Atomistic Kinetic Monte Carlo simulations of defects in materials

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ABSTRACT

The recent development of on-the-fly atomistic kinetic Monte Carlo methods has led to an increased amount attention on the methods and their corresponding capabilities and applications. In this review, the framework and current status of Self-Evolving Atomistic Kinetic Monte Carlo (SEAKMC) are discussed. SEAKMC particularly focuses on defect interaction and evolution with atomistic details without assuming potential defect migration/interaction mechanisms and energies. The strength and limitation of using an active volume, the key concept introduced in SEAKMC, are discussed. Potential criteria for characterizing an active volume are discussed and the influence of active volume size on saddle point energies is illustrated. A procedure starting with a small active volume followed by larger active volumes was found to possess higher efficiency. Applications of SEAKMC, ranging from point defect diffusion, to complex interstitial cluster evolution, to helium interaction with tungsten surfaces, are summarized. A comparison of SEAKMC with molecular dynamics and conventional object kinetic Monte Carlo is demonstrated. Overall, SEAKMC is found to be complimentary to conventional molecular dynamics, especially when the harmonic approximation of transition state theory is accurate. However it is capable of reaching longer time scales than molecular dynamics and it can be used to systematically increase the accuracy of other methods such as object kinetic Monte Carlo. The challenges and potential development directions are also outlined.

1. Introduction

Simulating materials processes from femtoseconds to millennia is a grand challenge [1]. This challenge is extremely daunting, partially because many long-term material properties and phenomena are driven by a unit event occurring at a split second, and partially because no experimental or theoretical tool has the capability to cover such huge span in time so far. For instance, the defect production event in structural materials for nuclear energy systems is on the order of picoseconds, while subsequent defect evolution and interaction that lead to property changes last for many decades [2–4]. However, the need to bridge the time scale is imperative, not only for fundamental understanding of how unit events and final outcomes are correlated, but also for practical applications, such as predicting the lifetime of nuclear structural materials or a modern battery.

A framework of multiscale simulation methods has been established to address the gap in time and length scale [5,6]. The methods include electronic structure calculations, primarily density functional theory [7–9], atomistic simulations using molecular dynamics (MD), mesoscale models, such as kinetic Monte Carlo (KMC) [10–19], and continuum-level models based on elasticity theory. However, the connection between different methods to enable information passing is still a major difficulty. For instance, the parameters for a new empirical potential may be fitted using the data generated by first principles calculations in order to improve the accuracy and fidelity. However, there is no guarantee the new potential will maintain this accuracy and fidelity for properties beyond those used to fit the potential. Another example is the passing of kinetic defect parameters from MD simulations to object KMC (OKMC) [10–12]. Because only the migration energy barrier and prefactor that are extracted from MD and used as input in OKMC, the details of defect configurations and how they interact with each other are severely simplified and lost because all the defects are treated as abstract objects. Therefore, the predictive capability and fidelity of the overall model is greatly limited. Therefore, the potential to improve the current multiscale simulation framework is tremendous and recent developments in accelerated molecular dynamics [20–23] and atomistic kinetic Monte
Carlo (AKMC) [13–17] have greatly extended the limit in accessible time and therefore allow more systematic improvement of the framework.

Accelerated molecular dynamics [23], including Hyperdynamics [20], Parallel Replica Dynamics (PRD) [21], and Temperature Accelerated Dynamics (TAD) [22], remains in the framework as MD, the time scale of which is generally limited to nanoseconds due to the need to sample atomic vibrations. Through the introduction of a bias potential, such as those in Hyperdynamics [20], or increasing the temperature, such as in TAD, the transition from state to state is accelerated and some long-term behavior or phenomenon may be revealed. The details of these techniques are reviewed in another article in this issue. In this review, we primarily focus on an alternative approach, which is KMC.

System evolution in KMC simulations is based on the saddle point energies or barriers that separate distinct states of the system. In contrast, evolution in MD requires sampling many local atomic configurations on the time scale of atomic vibrations; therefore KMC offers great potential for accelerating events when barriers are high. Generally speaking, KMC can be separated into OKMC and AKMC. OKMC or event-based KMC considers every defect as an abstract object and the potential system change as an event. Most AKMC have been lattice based, which generally works for point defects, such as vacancies or substitutional impurities, but fails for more complex defect configurations, such as interstitial clusters.

Recently there has been an increased amount of attention and effort in developing on-the-fly atomistic KMC, in which the saddle point configurations and energetics are determined as system evolves. The recent developments include adaptive KMC [13,14], self-learning KMC [24,25], local environment KMC [26], kinetic Activation Relaxation Technique (k-ART) [15,18,27], and Self-Evolving Atomistic Kinetic Monte Carlo (SEAKMC) [16,17]. This type of simulation has several obvious advantages. First, the requirement of pre-determining the potential saddle points has been eliminated, which by itself is a very challenging and time-consuming process. Second, the catalog of potential processes evolves as simulation progresses. More importantly, the atomistic interactions provide significant improvement over assumed simplified or artificial interactions in previous models.

2. Self-Evolving Atomistic Kinetic Monte Carlo (SEAKMC)

The development of SEAKMC is motivated by several facts. First, defects in crystalline materials govern material properties and phenomena. Second, many defects, such as vacancies and interstitials, are localized; their influence is rather short-ranged. Therefore, it is imperative to focus on defects, which are the key to revealing the structure–property relationship in materials. Third, it is found that the successful rate of finding useful saddle points decreases rapidly as system size gets larger. This is because the system energy increases during the initial phase of saddle point searches. As the system size expands, the total system energy correspondingly increases, sometimes to a very high-energy state compared with the initial configuration. This result in saddle points being found with too high energy or not connected to the initial configuration. Taking vacancy diffusion in bcc iron as a simple example, the successful rate of finding a saddle point associated with first nearest neighbor jump is close to 100% when a small volume (2.5 lattice-parameters) is employed during the saddle point search. When this volume is expanded to 5.5 lattice-parameters, the success rate decreases significantly. Almost all the saddle point searches did not lead to the correct configurations. The energy changes during the search for these two different volumes are given in Fig. 1. The implication from this simple case is that without some type of localization technique, even vacancy diffusion in large systems is very inefficient. The situation is worse for complex defects or defect clusters, which require an even larger system size. Without proper handling of this issue, the system size in these on-the-fly techniques is very limited, which can prohibit certain processes or phenomena from being studied. We note that modifications to the activation scheme that limit the number of atoms deformed in the first step of the dimer saddle-search leads to more favorable outcomes, but it still performs badly at large lat-

![Fig. 1. The effect of active volume on saddle point searches: (a) the percentage of failed saddle searches and configuration with unrealistic high energy barriers using global deformations; (b) the system energy increase for active volume size with 2.5 and 5.5 nm, respectively; (c) the potential energy increase as a functional of active volume sizes; (d) the percentage of successful saddle searches with realistic energy barriers using different activation schemes.](image-url)
tice-parameters. The choice of a Gaussian function to limit the displacements also produces a special feature; with a 5.1 lattice-parameter-radius active volume, the dimer method converges preferably (with a higher success rate than a simple step function) towards the second-highest energy-barrier available for vacancy diffusion.

We note that this problematic behavior of saddle-point searches in large volumes is not present in all min-mode following methods. For instance, the Activation–Relaxation Technique nouveau (ARTn) converges with a high success rate in systems with tens of thousands of atoms [28]. This suggests that the choice of scheme to escape the harmonic basin is a defining factor of the saddle-search. In the case of the dimer method, using an active volume corrects this problem. As can be seen in Fig. 1(d), converging to the scheme to escape the harmonic basin is a defining factor of the saddle with a small active volume and then increasing the volume to allow long-range effects leads to good performance.

The algorithm of SEAKMC is illustrated in Fig. 2 [16]. An interatomic potential is used in the same manner as molecular dynamics to describe the atomistic interactions. From a local minimum configuration, we first characterize active volumes (AVs). For instance, the AVs can be determined based on the location of defects, for example, interstitials, vacancies, solutes, precipitates, point defect or solute clusters, and dislocations. These defects can be automatically determined in the simulations by using a Wigner–Seitz cell analysis or the local energy deviation from the bulk value [17]. The unique feature of SEAKMC is that transition state searchers are then carried out only within the identified AVs since they are the only regions where processes of interest may occur [17]. Since the saddle point search is only carried out in the identified AVs, the number of atoms in the force calculations is reduced, which increases the simulation efficiency. The effect of the internal defect(s) should be negligible at the AV boundaries, which can be easily examined by a convergence test of saddle point energies as a function of the AV size.

After enough sampling of the saddle points and corresponding barriers in each AV, a KMC step is taken to advance the time using the residence time algorithm [29] and a random event is chosen from possible reactions sampled during the saddle point search. A small perturbation is then introduced in the chosen saddle point configuration to allow relaxation in its own AV. This relaxation will not only move the system to another local minimum state and but may also lead to possible atomistic defect reactions. After the system relaxes into another local minimum configuration, the process repeats itself. It should be noted that when defects are apart from each other and AVs are separated, searches for new saddle points are only required in the AV, which was chosen in the last KMC step. This reduces the number of saddle point searches and allows frequent events, such as point defect diffusion, to progress with the higher efficiency [17]. If defect evolution leads to sufficient energy changes at the AV boundary, the AVs will be re-characterized and their boundaries will be redetermined. This may lead to interactions between AVs or even the merger of AVs.

The key concept that SEAKMC introduced is active volumes, which is a local region within the whole system to allow efficient saddle point sampling while maintaining desired accuracy and fidelity. This is based on the fact that atoms that are distant from the identified defects are insignificant and hardly affect the internal defect. In essence, the interaction between defects and atoms far away is significantly weakened as the distance increases. In the context of SEAKMC, the AVs are required to be sufficiently large so as to allow saddle points to be accurately determined. In contrast with a previous method [13], the positions of the atoms outside the AVs are kept fixed during saddle point searches. Active volumes significantly speed up the simulations, sometimes by several orders of magnitude, due to two main reasons: (i) the force calculations are only performed in the AV with a specific buffer region, and (ii) the degree of freedom during the saddle point search is greatly limited, which results in very efficient sampling. However, employing AV also means bearing the risk of neglecting certain very long-range processes. If the process involves atom movement or diffusion at a distance beyond the radius of AV, it will not be included in the searches. However this is extremely rare, since the radius of AV employed is at least a few lattice constants. It should be noted that this is different from the interactions between atoms, e.g. in the center of the AV, and atoms outside the AV. This interaction is implicitly included already and is generally accurate enough when the AV is sufficiently large, as demonstrated in Ref. [17].

Depending on the nature of defect or the investigated process, the AV can be characterized in different ways. For instance, the AV can be characterized based on the position of the defects, which is determined by their distance to a corresponding site in the perfect lattice. In this case, a geometrical representation of AVs is very convenient and allows systematic improvement of accuracy through convergence tests. Other criteria can be employed as well, such as the energy or stress deviation from the bulk value. The dimer method [30–32] or the activation relation technique nouveau [27,33–35], both of which assume the harmonic approximation of transition state theory (HTST), have been implemented in SEAKMC [36].

To demonstrate the process of determining active volume size, the deviation of a given atom’s energy from the bulk value is shown in Fig. 3. Here we considered a vacancy and a dumbbell self-interstitial atom in bcc iron. In Fig. 3, the difference in energy reduces as the distance between the defect and an atom increases. The energy difference approaches zero at ~4 lattice constants for a vacancy, which is shorter than for the interstitial (~6 lattice constants), indicating vacancy is more localized than the interstitial. This shows that same criterion may lead to different active volume sizes for different defects. In addition, this shows that required size of the AV can potentially be a small, nanometer-sized sphere (radius of a few lattice parameters). To illustrate this point, the saddle point energies were determined as a function of active vol-

![Fig. 2. Schematic illustration of SEAKMC algorithm [16].](image-url)
The active volume size and are shown in Fig. 4. As expected, when the AV size is small, the migration energies are significantly different from the bulk value. However, the saddle point energies converge to the bulk value as the AV size gets larger. If the energy deviation is used as the criterion for defining AVs, examining the saddle point energies vs. AV size can enable the proper AV size to be determined, providing feedback on what energy deviation criterion should be used. Therefore, these two steps are complementary.

It was found that the initial displacement of atoms for the saddle point searches has a significant effect on the saddle point found and the performance of the SEAKMC. For instance, randomly displacing all the atoms in the AV by the same magnitude or with the magnitude following a Gaussian distribution could lead to different performance of the code. Generally speaking, using a Gaussian distribution was found to be more efficient, especially when AVs are relatively large, which is consistent with previous studies [13].

In addition, the active volume size or the criterion for selecting active volumes can also evolve. We developed a multi-step procedure to provide further acceleration. This procedure initially uses a relatively small AV to find an approximate saddle point configuration. Then, this initial estimate is used as input for larger AVs to allow systematic convergence to the desired accuracy [17]. Employing a reasonable initial estimate significantly speeds up the convergence to the actual saddle points in the larger AVs. To achieve similar accuracy, this multistep procedure has been found much faster than directly employing a large AV. The active volume size can be increased until the variation in saddle point energy is less than a threshold, e.g. 0.01 eV. Furthermore, the computational speedup is larger as the number of atoms increases because the active volume becomes a smaller fraction of the whole system volume. Similar to the inherent limitation of using an AV, initially using a relatively small AV may prevent certain saddle points from being found. Therefore, this procedure should be only used when the potential movement due to dynamic processes is localized.

3. Applications

In this section, several examples of SEAKMC applications are provided, ranging from simple point defect diffusion to complex interstitial loop interactions and to even more complicated simulations of the atomic displacement cascade annealing. From these examples, not only the strength of SEAKMC but also the weakness can be clearly seen, which will provide critical information on how to improve SEAKMC and other on-the-fly KMC methods.

3.1. Single point defect diffusion

To demonstrate atomistic fidelity of SEAKMC, the self-diffusivity of vacancy and dumbbell interstitial in bcc iron were determined; direct comparison with conventional MD simulations were made (Fig. 5). To achieve statistically meaningful results, a large number of defect jumps (5000–10,000 successive jumps) was sampled, particularly in SEAKMC [17]. For MD simulation, especially at the low temperatures, sampling statistically meaningful results are quite challenging, due to the computational cost of covering very long simulation times. For both vacancy and interstitial diffusion, a ~2000 atom system was used. One defect was introduced, resulting in 0.05% defect concentration.

At low and intermediate temperatures, excellent agreement was found between SEAKMC and MD results [17]. Unlike the case of OKMC simulations, SEAKMC does not need the diffusion path or migration energy barrier to be initially specified as input information; saddle points and prefactors were found using the same interatomic potential as employed in the MD simulations. Therefore, SEAKMC and MD demonstrate a similar capability to determine point defect diffusion. The agreement shown in Fig. 5 illustrates the accuracy of the migration energies determined using the Dimer method and attempted frequencies calculated through Vinyard’s formulation [37] in the SEAKMC calculations. Nevertheless, SEAKMC deviates from the MD results at higher temperatures. This is because the saddle point search methods employed in SEAKMC are based on HTST while MD can capture anharmonicity [17]. It is known that the harmonic approximation describes the system well when the system is close to ground state, e.g. at low temperatures. However, the anharmonicity of the atomic vibrations is significant at high temperatures, leading to the observed difference in diffusivity between SEAKMC and MD. It should be noted that the temperature at which dynamics department from HTST depends on the defect type and empirical potentials employed. For example, the SEAKMC results of interstitial diffusivity using the Ackland-04 potential [38] deviates from MD around 600 K. In comparison, vacancy diffusion agrees well up to ~1000 K. In addition, the discrepancy between SEAKMC and MD is relatively small compared with the statistical error obtained in low-temperature MD simulations (e.g. vacancy results at 700 K in Fig. 5).
interstitial, the potential well for a vacancy is more harmonic and the difference in vacancy diffusion is smaller for all the temperatures calculated. Consistent with a previous study [38], the migration energy determined from the Arrhenius relationship for vacancy and interstitial diffusion are 0.630 and 0.309 eV, respectively.

The tracer correlation factors for point defect diffusion were calculated as well. The value obtained for vacancy diffusion is 0.73, which matches the theoretical value (0.727) [39] very well. For interstitial diffusion via the dumbbell mechanism, obtaining the tracer correlation factor through MD simulations is very time consuming and has not been reported previously. If only the first nearest neighbor (FNN) jump is involved [17], the tracer correlation factor was predicted to be 0.44. Including dumbbell rotation leads to a higher value of the tracer correlation factor. It should be noted that the relative probability for each process, depending on the corresponding saddle point energies and empirical potential being used, can be different and lead to slightly different tracer correlation factors. Interestingly, while rotation only involves mass transport, the FNN jump involves both mass transport and defect diffusion [17]. Determining the tracer correlation factor not only requires correct defect dynamics but also determining how the defects interact with surrounding atoms. Therefore, the accuracy of the point defect tracer correlation factor illustrates the power and unique performance of the SEAKMC for atomistic processes.

The above comparison clearly reveals how SEAKMC and MD complement each other. MD is accurate at all temperature but obtaining sufficient statistical sampling of diffusion using MD at low temperature is very challenging and time-consuming. When HTST is valid and accurate, such as at lower temperatures, SEAKMC provides better statistics with much higher efficiency. It is also easier to decouple different mechanisms or atomistic processes using SEAKMC, such as the above mentioned defect transport vs. mass transport, which provides fundamental insights that are otherwise not possible.

3.2. Defect clusters

In this section, SEAKMC is demonstrated to enable investigation of defect cluster evolution beyond the time scale accessible by MD. The defect clusters investigated are a specific type of interstitial cluster in bcc iron, which have a structure similar to the Laves phase or C15 structure. Such clusters have been observed directly from MD cascade simulations [40,41]. Within the MD-accessible time scale, these defects remain stable and sessile. Recently, a study by Marinica et al. [42] claimed that these C15 clusters can affect microstructural evolution and grow by capturing additional interstitials in iron and iron-based alloys.

Two examples of the C15 clusters were investigated using SEAKMC [43]. The first of these small clusters was a di-interstitial (IC2), involving twelve atoms occupying ten lattice sites; the second was a tetra-interstitial (IC4), with 18 atoms occupying 14 sites. We used the Ackland-04 [38] for the study here, while the previous study employed the M07 potential [42].

Consistent with the previous study [42], IC2 and IC4 are highly stable in SEAKMC simulations. However, it was found that they could transform into the glissile (1 1 1) configuration at longer times. The details of the transformation process have been published in [43] and involve some complicated intermediate configurations, as shown in Fig. 6. The energy barriers determined from SEAKMC are ~0.69 eV and ~0.89 eV for IC2 and IC4, respectively. These correspond to $2.66 \times 10^{-2}$ and $3.88 \times 10^{-3}$ s at 300 K. Obviously, as temperature increases, the required time for such transformations is shorter. For example, milli-seconds are adequate for the IC4 transformation at 600 K. Using this information, the transformation process observed in SEAKMC was subsequently confirmed using high-temperature MD simulations [43].

As mentioned in Ref. [43], the SEAKMC simulations do not support the growth of C15 defect clusters. First, the structure of a C15 cluster essentially involves multiple atoms occupying fewer lattice sites. In comparison with (1 1 1)-glissile interstitial cluster, the C15 defect clusters have lower configurational entropy. It is has been observed in the SEAKMC simulations that the IC4 breaks into an IC2 surrounded by two separate interstitials (Fig. 6f). However, the reverse process has not been observed [43]. Second, the defect clusters are formed under irradiation conditions. This means both self-interstitial atoms and vacancies can interact with C15 clusters, since both defects have lower migration energies than the C15. SEAKMC simulations reveal that the vacancy capture can easily turn IC2 and IC4 into (1 1 1) configurations. Therefore, although these defect clusters are immobile and highly stable, these simulations show they can transform into glissile (1 1 1) configurations by multiple processes at longer-time scales [43]. We note that these conclusions are highly dependent upon the choice of classical potential. Further investigation concerning this problem should clarify the issue.
3.3. Interstitial loop interaction

The conventional way to accelerate processes in MD simulations is to increase the temperature. However, this also introduces the risk of altering defect dynamics since the relative ordering of different processes may change as temperature increases, which is a well-known issue [23]. Here, we present a case where increasing temperature did lead to incorrect physics but because of a more subtle reason. This is the case of the interactions between two $\frac{1}{2}[111]$ interstitial loops in bcc iron. The detailed results have been published in Ref. [44]. Three empirical potentials were employed in this study. Here, we briefly summarize the main findings.

From SEAKMC simulations, it was found that the sessile configuration produced by two interacting $\frac{1}{2}[111]$ interstitial loops can turn into a $[100]$ interstitial loop without Burgers vector conservation, which provided answers to a long standing question in the field of radiation damage [45–50]. For example, when a $\frac{1}{2}[111]$ and $\frac{1}{2}[1–11]$ cluster react, the Burgers vector of the product was $[100]$ instead of the $[001]$ Burgers vector predicted by dislocation theory. Moreover, the $[110]$ loop that was proposed previously as an intermediate configuration [48] has not been observed in SEAKMC simulations. These observations indicate that the dislocation loop interaction mechanism is different from the classic picture of dislocation interaction, which is based on the assumption of infinite long dislocation lines. The observed dislocation loop interaction process involves rearrangement of and coordinated motion of individual interstitials in the clusters and is a rather complex atomistic process [44].

Fig. 7 shows the intermediate configurations for the observed interaction of two $\frac{1}{2}[111]$ loops. Fig. 7a is the initial configuration of two interstitial loops with each containing 37 interstitials (IC-37). The loops’ Burgers vectors are intentionally set to be $\frac{1}{2}[111]$ and $\frac{1}{2}[1–11]$. These loops are in a glissile configuration and are highly mobile [51]. Due to a high binding energy, these two loops encounter one another, forming a sessile junction (Fig. 7b), which have been reported previously but no significant further evolution has been observed [16]. Using SEAKMC, the sessile junction was observed to change substantially within $\sim$0.2 μs at 600 K as shown in Fig. 7c [44]. However, accurately determining the migration energy barrier is very challenging since it is a multi-step process and essentially all observed individual processes are different from one another, resulting in a relatively large statistical variation of the transformation time (approximately one order of magnitude). Two factors were considered as the primary cause of the large statistical variation. First, the saddle points may be under sampled in this case; second, the complex nature of the defect cluster and the corresponding transformation process may lead to multiple transformation paths. As the configuration continues to evolve, a critical configuration has been found. This configuration contains both $[100]$ and $[111]$ orientation (Fig. 7d), with approximately equal fractions. The $[100]$ half may continue to grow (Fig. 7e), resulting in a complete $[100]$ loop (Fig. 7f). The shape of the final loop is rectangular and the habit plane can be either (100) or (110) [44].

In addition, the evolution process is found to be stochastic; the same starting configuration may generate completely distinct outcomes [44]. For instance, four different outcomes are observed from the Fig. 7d configuration. The result can be the $[100]$ loops described previously with a Burgers vector of either $[100]$ or $[010]$, or the (111)$^-$type loop with either a $\frac{1}{2}[111]$ or $\frac{1}{2}[111]$ Burgers vector. The reaction pathways for various outcomes are very different as well. The $[100]$ loop formation generally involves an intermediate configuration with part of it in a $[100]$ orientation. However, the formation process of $\frac{1}{2}[111]$ loops does not necessarily involve the $[100]$ orientation. The stochastic outcomes obtained here also confirm that these atomistic processes are fundamentally different from the dislocation reactions that have been commonly assumed (see Fig. 7).

It appears that the reasons why previous attempts to use MD simulations to observe the $[100]$ formation process were unsuccessful are: (i) a limitation of the empirical potential being used [48], and (ii) very high temperatures to speed up the transformation processes [52]. However, increasing the temperatures in MD simulations not only accelerates processes but also changes the relative stability of $[100]$ and $\frac{1}{2}[111]$ interstitial loops. The vibrational entropy of $\frac{1}{2}[111]$ is considered much larger than the value of $[100]$ loops [53]. Therefore, increasing to very high temperature strongly favors the outcome of $\frac{1}{2}[111]$ loops, neglecting other possible outcomes. The stability of $\frac{1}{2}[111]$ and $[100]$ was found to be similar using Ackland-04 [38] and Marinica-07 potentials [42,54] in SEAKMC and the possibility of different loop reactions is clearly observed. This clearly demonstrates the unique performance of SEAKMC.

It should be noted that saddle points are undersampled in this case. Based on our previous study of small interstitial clusters with four or five SIAs, the number of unique saddle points did not fully converge even with several thousands of distinct saddle points. Therefore, obtaining a complete catalog of saddle points for these IC-74 interstitial loops is not computationally feasible. This will directly affect the simulated time. However, we do not think this error in the time will affect any of the conclusions since the same
process has been confirmed using MD simulations. This also illustrates that undersampling to certain extent does not necessary lead to the wrong conclusion although ideally a complete catalog is preferred.

3.4. Cascade simulations and comparison

The SEAKMC is compared with traditional OKMC in this section (Fig. 8). The problem chosen for this comparison is long-term annealing of point defects and defect clusters from MD cascade simulations. The atomic system configuration from MD cascade simulations was used as the initial condition in the SEAKMC simulations [55]. Two cases with cascade energies of 10 keV and 25 keV with 128,000 atoms and 250,000 atoms, respectively, were annealed at 650 K [56]. To determine how many defects escape the cascade region an absorbing boundary condition was used [56]. The OKMC simulations predict about seventy percent of the interstitial-type defects survive and move away from the cascade region [56], while significantly fewer surviving interstitial defects were predicted using SEAKMC. For both 10 keV and 25 keV, SEAKMC results show approximately one half of the interstitial-type defects survive. The probability of vacancy-interstitial recombina-

Fig. 7. Configuration observed during the interaction of \( \frac{1}{2}[111] \) loops. Defects are analyzed using Wigner-Seitz cell method with boxes for lattice sites and spheres representing atoms. The orientation of individual interstitial range from blue (1 11) to red (1 00) [44]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 8. Comparison between SEAKMC and OKMC in long-term annealing simulations [43].
tion is therefore higher in SEAKMC. In addition, the SEAKMC results are also different from OKMC in the fraction of surviving interstitial clusters, with a smaller surviving cluster fraction obtained using SEAKMC. In OKMC models, the defect interaction mechanism and radii are essentially artificial. Therefore, this observed difference is likely to be caused by the absence of atomistic details in OKMC simulations [56]. The surviving defect fraction, especially the cluster fraction, are critical information in order to accurately determine the subsequent evolution and interactions with other defects. Therefore, the observed difference between OKMC and SEAKMC might lead to significant differences in high-level models that are used to predict microstructural evolution at a much longer time scale.

Since defect interactions and evolution in SEAKMC are rather complicated and depend on the specific atomistic configurations, it is not feasible to determine which particular OKMC parameters would need to be adjusted to improve the accuracy. As mentioned previously, the defect reaction radii are essentially artificial in OKMC and one approach to improving the OKMC results could be to adjust these radii. It was found that applying the same fractional adjustment to all the defect interaction radii did not improve the results [56]. However, modifying the interaction radii differently for defect reactions based on SEAKMC results can lead to improved fidelity of OKMC models.

3.5. Helium interaction with tungsten surface

In addition to the evolution of radiation-induced point defects and defect clusters, the interaction of small helium clusters with bcc tungsten surfaces has also been investigated using SEAKMC using the empirical potential developed by Juslin and Wirth [57]. First, the saddle point energies and system energetics of a small helium cluster with three He atoms in the interstitial position were sampled as a function of the distances to the tungsten (100) surface (Fig. 9). No significant dependence on the cluster location has been observed except when the He cluster is very close to the surface [58]. Detailed analysis of saddle point configurations reveals that three major types of events are associated with the configuration changes of these He clusters:

1. Rotation events with an activation energy on the order of ~0.01 eV, which do not change the center of mass of the cluster.
2. Migration of the cluster with an activation energy in the range of 0.13–0.35 eV, and
3. Creation of an immobile He3-vacancy complex and a tungsten adatom on the surface, releasing an energy of ~3 eV.

Individual He atoms and their small clusters are highly mobile in bulk tungsten [57]. It has been reported that when the number of He atoms in the cluster exceeds a certain number, depending on temperature, a Frenkel pair of tungsten can be created, resulting in an immobile He-vacancy complex [59]. In comparison to the bulk system, the study here revealed that when helium clusters are close to surface, similar processes happen at a much smaller helium cluster size, leading to a significant increase in He atom retention. The interstitial helium atoms created during this process move easily to the surface as adatoms and alter surface morphology. The resulting vacancy is incorporated into a helium-vacancy cluster, resulting in an immobile configuration over the accessible time scales for the temperatures of interest here. This lack of mobility makes it more likely to interact and trap addition helium atoms, which could lead to growth of the helium-vacancy cluster and increase the pressure of the helium-vacancy cluster. Eventually, when the pressure reaches a critical point, additional Frenkel pair will be created to release the pressure and this process further modifies the surface morphology and properties.

In addition, multiple simulation trajectories of clusters at different initial positions were analyzed. Unfortunately, the observed behavior is dominated by the rotation events, due to their lower saddle point energies. This is a common challenge of the KMC simulations [23]; small barrier significantly limit the time scale that these KMC method could provide. Furthermore, in contrast to the high-temperature MD simulations [60], we have not observed any dissociation events. This is likely due to the lack of thermal vibrations in SEAKMC. It should be noted that although this lack of vibration effects is main reason dissociation events were missed here; it helped enable the observation of the new mechanism in the case of the interstitial loop interactions. In addition, physical gas pressure is not accounted for in the SEAKMC simulations, which may lead to an underestimate of the elastic interactions in the system. Otherwise, the two simulation approaches lead to quite similar predictions.

4. Summary

Overall, the SEAKMC method provides a powerful means for simulating atomistic processes beyond the MD time scale, especially when defects are the key in determining microstructural evolution and material properties. SEAKMC particularly focuses on defect interaction and evolution with atomistic fidelity and only requires an interatomic potential as input without assuming potential defect migration mechanisms and energies. The unique component of SEAKMC is the introduction of active volumes, which not only speed up the simulations but also allow investigation of processes and phenomena requiring large system size that are
otherwise not possible. The criteria for determining an appropriate AV size, and the dependence of saddle point energies on AV size were discussed. The proposed multi-step procedure for dynamically adjusting the AV size has been found to show higher computational efficiency.

Several applications of SEAKMC have been demonstrated, including simple point defect diffusion in bcc iron to test the accuracy and fidelity, long-term evolution of highly stable interstitial clusters clearly beyond MD time scale, interstitial loop interactions that lead to new observations about the loop transformation mechanism, complicated cascade annealing in comparison with conventional OKMC, and the interaction between a free surface and small helium clusters in tungsten. It was found SEAKMC and MD agree with each other well at low to intermediate temperatures, when HTST is valid and accurate. When the temperature is high enough, the lack of anharmonicity in SEAKMC make the results deviate from MD simulations.

5. Challenges and outlook

Although on-the-fly KMC methods have recently demonstrated many successes, outstanding challenges remain. One example is the need to extend the current methods to model long-term influence of dislocations or grain boundaries on defect dynamics and damage accumulation. These extended defects have much more complex geometries and the resulting degrees of freedom are significantly larger than what has been explored so far. Although the concept of the AV remains valid, e.g. the AV for a dislocation could be a cylindrical region dislocation core, how to efficiently sample saddle points for these systems is still unclear and needs further investigation to clarify. Furthermore, due to the complexity of these defects, the overall efficiency of the simulation may be greatly affected by the small barrier issue. These issues are currently be investigated by the authors and we hope to provide some fundamental insights on how to simulate these extended defects at longer scales, which has not been demonstrated by other on-the-fly KMC techniques or accelerated dynamics.

In spite of the challenges, it is the opinion of authors that on-the-fly KMC methods such as SEAKMC hold great potential for studying defect evolution with atomistic fidelity into the meso-timescale and therefore bridging experiments and atomistic simulations. Moreover, they achieve this without any artificial assumptions. Therefore, these new KMC methods might be the key to revealing rate dependent mechanisms in various materials processes and phenomena, e.g. strain rate dependence in deformation mechanisms. These on-the-fly KMC methods can be also used to systematically improve the accuracy and fidelity of higher-level models, such as the demonstrated comparison between SEAKMC and OKMC.

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