Comment on "Mechanism of Void Nucleation and Growth in bcc Fe: Atomistic Simulations at Experimental Time Scales"

The validity of kinetic Monte Carlo (KMC) methods is based on the quality of the event cataloging process. In a recent Letter [1], Fan *et al.* present a KMC simulation of void nucleation and growth in bcc iron. Their simulations of 50 vacancies implanted at random into a $10a_0 \times 10a_0 \times 10a_0$ cubic supercell of bcc iron show that a long time scale of 20 000 seconds at a temperature exceeding 150 °C is necessary for the average vacancy cluster size to increase beyond 6.5 vacancies, due to the existence of a critical 1.6 eV barrier. While this result is impressive, off-lattice KMC simulations with an extensive event catalog constructed on the fly show that there exist trajectories crossing much lower barriers and leading to times of milliseconds at 50 °C.

This problem is a perfect example of a complex structural system that cannot be studied with a preconstructed catalog, as the number of possible conformations grows rapidly with that of initial vacancies. For the event-catalog assembly, Fan *et al.* use the autonomous basin climbing (ABC) method that attempts to identify the dominant barriers at each step of their simulation. The ABC method [2] constructs the potential energy surface by filling minima with Gaussians to identify the barriers. The trajectory and barrier heights are then reconstructed with the nudged elastic band method. This yields a 1D trajectory through the complex $3N$-dimensional configuration space onto which the KMC method is applied, providing a time scale as vacancies assemble into voids. The simulation is stopped when these voids contain an average of ten vacancies.

We repeated this study using the kinetic activation-relaxation technique (k-ART) [3] at constant temperature (50 °C) with the same forcefield [4] in order to obtain an upper bound for the time needed for the vacancies to aggregate. Contrary to ABC, k-ART's kinetics is controlled by an extensive catalog that is expanded on the fly, takes full account of elastic deformations for barrier height, and includes detailed balance. At every step, all new environments, as defined by their topology, are identified and a minimum of 50 event searches are launched for each previously unseen environment. All low-energy barrier configurations, i.e., those with a 99.9% probability of being executed, are then reconstructed and fully reconverged to account for long-range elastic deformations. The clock is then updated based on the sum of the transition rates of between 3000 and 30 000 barriers at any step and one event is selected randomly according to its weight. Four sample trajectories over 4733 to 5997 KMC steps are shown in Fig. 1.

Contrary to the results of Fan *et al.*, we find that the effective barrier to overcome in order to increase the average cluster size above 6.5 vacancies is under 0.9 eV. At 50 °C, the potential energy drops under −7761 eV (beginning of Regime III in Ref. [1]) within 0.5 ms. This is supported by positron annihilation spectroscopy experiments [5], which show a significant fraction of nanovoids present in as-irradiated Fe at 50 °C. Moreover, monovacancies remain present until an energy of −7760 eV, while for Fan *et al.*, they effectively disappear at −7757 eV, the onset of Regime II, which suggests that the trajectories we find are fundamentally different. This shows that in KMC simulations, an extensive catalog is necessary to get a complete description of the accessible configuration space and visit the right nonequilibrium states.

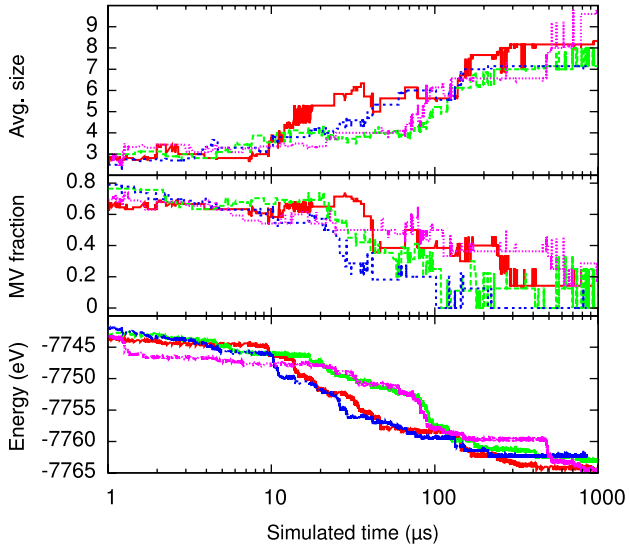

FIG. 1 (color online). Four k-ART trajectories of 50 randomly distributed vacancies in a $10a_0 \times 10a_0 \times 10a_0$ cubic supercell. Top: Average vacancy cluster size. Center: Fraction of monovacancies (MV) among all defects. Bottom: Potential energy trajectory passing through local minima and saddle points.

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