EPJ Web of Conferences **302**, 06005 (2024) https://doi.org/10.1051/epjconf/202430206005
SNA + MC 2024

Overview of kinetic Monte Carlo methods used to simulate microstructural evolution of materials under irradiation

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Abstract. Kinetic Monte Carlo (KMC) methods are commonly used to simulate the microstructure evolution of metals under irradiation due to their ability to generate the random walks underlying defect-mediated diffusion processes at the atomic scale. However, the range of applicability of KMC methods is severely limited by the kinetic trapping of the simulated trajectories within low energy basins presenting small intra-basin barriers. This results in dramatically reducing the efficiency of the classical KMC algorithm. Kinetic trapping can be alleviated by implementing non-local jumps relying on the theory of absorbing Markov chains. A factorisation of an auxiliary absorbing transition matrix then allows to generate escaping paths and first-passage times out of trapping basins. Although, the speed-up can be of several orders of magnitudes, this is sometimes not enough for very long-term prediction. We must then turn to homogenised rate-equation formulation of the problem. Usually solved deterministically, the corresponding large ordinary differential equation system often suffers from the curse of dimensionality. Dedicated Monte Carlo schemes can simulate the coarse-grained rate equations based on a chemical master equation. Finally, we show the relevance of relaxing the rigid-lattice assumption in the calculation of the free energy barriers and attempt frequencies to capture elastic effects that are important for certain systems, such as high entropy alloys. The activation-relaxation technique can be used for this purpose in kinetic Monte Carlo studies of slow diffusion processes.

1 Introduction

1.1 Context

In a nuclear power plant, the reactor pressure vessel is a critical component as it considered as the only component that cannot be changed. Other components, like those forming the internal structures, are potentially replaceable but they are exposed to much larger doses. In all cases, the evolution of their properties originates from neutron irradiation which results in a production of large amounts of crystalline point defects such as vacancies

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and self-interstitial atoms after the cascade process. Over time, these defects migrate, recombine or agglomerate to form vacancy clusters and loops of interstitials. This can modify mechanical properties by radiation hardening or embrittlement, among other phenomena like radiation induced segregation.

1.2 Assumptions and limits of kinetic Monte Carlo methods

An important goal of research studies in this area is to simulate the microstructural evolution occurring in irradiated materials [1]. In this context, rigid-lattice Monte Carlo techniques are used to calculate thermodynamic and kinetic properties at the atomic scale. Predicting the formation and evolution kinetics of nanometric clusters of crystalline defects which form in irradiated metallic components requires covering considerable time scales: from the picosecond typical of the Brownian motion of these defects on the crystal lattice, up to the decades of evolution of the mechanical properties that they influence. The usual so-called "kinetic" Monte Carlo methods, which directly simulate these complex random walks (which can be one-dimensional, three-dimensional randoms walk in the 3D crystal lattice, or more complex combinations [2]), offer a great capacity for modelling elementary atomic mechanisms, but are limited to short cumulated times (being single event-based methods). Nevertheless, they enable us to straightforwardly implement the energy models underlying the interactions between clusters of defects and solutes (with either density functional theory methods or classical molecular dynamics calculations [3]) and potentially take into account the vast and complex combinatorics associated with them. A typical application of this method is the simulation of the formation of solute atoms atmospheres in reactor pressure vessel (RPV) steels, leading to radiation embrittlement. Being a low alloy steel (the major solutes involved in ageing being Mn, Ni, Si and Cu), this kind of dilute system considerably relieves the computational burden for the built-up of the atomic jumps parameterization. This leaves us with the challenges of the very long-term simulations. Typically, the very long times to be simulated can be above 1.3×10^{9} s (corresponding to about 40 years of reactor operation), while elementary events like interstitial's jumps only increment the physical clock by steps of 10^{-12} s. In fact, the computational efficiency is plagued by the fact that non-reactive diffusion events (i.e., which leave the microstructure intact) are, by far, the most numerous events. These transitions correspond to very low energy barriers (also called "flickers") which monopolise the computational power, in contrast with rare-events where solute clusters actually evolve. Accelerated Monte Carlo methods based on the factorization of absorbing Markov matrices make it possible to rigorously construct the distributions of first passage times towards sites of recombination between clusters of defects so, large sequences of non-reactive events are directly drawn. The latter methods are exact and allow for accelerations of many orders of magnitude, but they are currently limited to one type of solute atoms, and modest densities of defects.

Beyond that, very long-term kinetics is within the sole reach of mean field methods such as "cluster dynamics", but at the cost of drastic simplifications on the treatment of complex clusters: homogenization, neglecting of correlations, coarse-graining and use of steady state solutions of diffusion equations. The systems of ordinary differential equations associated with these methods are integrated using deterministic time-steppers [4] or using stochastic methods (Langevin dynamics or random walks in the space of cluster sizes). More recently, a hybrid approach combining deterministic and stochastic integration has also been proposed [5]. The latter should make it possible to limit the computational burden linked to the combinatorial complexity of the clusters while maintaining the capacity to simulate long times by the rate-equation approach.

For some prospective applications such as high entropy alloys, variants such as Monte Carlo on a relaxed lattice with on-the-fly prefactor calculations account for the vibrational degrees of freedom and the stabilizing distortion of the lattice, with a moderate computational overhead thanks to indexing on defect's neighbourhood graphs.

2 Advanced Monte-Carlo methods

2.1 First passage kinetic Monte-Carlo algorithm

More formally, the efficiency of the kinetic Monte Carlo method is drastically reduced whenever the transition rate matrix describing the evolution of the system exhibits a wide spectrum. In this situation, the system transitions a huge number of times between configurations separated by small energy barriers. These connected configurations form trapping basins from which the average escape time is much larger than the characteristic time for crossing the small barriers inside the basins. This issue is recurrent in KMC simulations [6]. Cavities may form under irradiation and remain stable over a long period of time due to the low vacancy emission rate resulting from the strong attraction between cavities and neighbouring vacancies. Kinetic trapping may also be caused by the formation of dynamically stable clusters of manganese or copper substitutional atoms and vacancies in α-Fe. These solute clusters migrate slowly without dissociating owing to numerous atomic rearrangements. A second situation causing a drastic loss of efficiency of the KMC method is when the distances a mobile defect must travel before interacting with another mobile defect (e.g. a dislocation, a solute cluster or precipitate) is large. It takes a huge number of KMC hops to observe a small change of the microstructure.

The so-called "first-passage" algorithms allow accelerating the KMC simulations in both aforementioned situations. To achieve this goal, nonlocal events involving mobile defects may be randomly selected using exact probability rules [7-9]. Avoiding conflicts between defects evolving in parallel requires spatial protection of defects and exact time synchronization. Spatial protection serves to prevent distant walkers from colliding or conversely to enable two neighbouring defects to recombine. To satisfy the time synchronization requirement, the theory of absorbing Markov chains [10] is used to draw first-passage times, and paths to distant states located on the periphery of the protection, which acts as an absorbing sink. Drawing a first-passage time and escape from the exact probability distributions may be achieved through the direct factorization of the absorbing transition rate matrix [9] or through its eigenvalue decomposition [7,8,11]. The former randomization technique is based on the probabilistic interpretation of the factorization in term of paths [12] and is referred to as kinetic path sampling. Note that the factorization relates to matrix inversion and that the Green's functions used in atomic transport theory, which appear as pseudoinverses of transition rate matrices, may also be interpreted as geometric sums of path probabilities. This connection makes it possible to compute atomic diffusion coefficients very efficiently using kinetic path sampling (KPS) with the help of mass transport theory [13]. The KPS algorithm was used to estimate the diffusion coefficients

of vacancy-trapping Mn clusters in BCC iron [11] and to simulate the early stage of anomalous nucleation of copper precipitates [9].

2.2 Stochastic resolution of rate-equations for cluster dynamics

The family of kinetic Monte Carlo methods for diffusion-based phenomena also encompasses resolution methods of stochastic integration of many dynamical systems that are governed by master equations, chemical master equations (formed from chemical rate equation) or partial differential equations. This method consists of propagating one or more stochastic trajectories [14,15]. The great advantage of this stochastic approach is that it is almost immune to the dimension curse: one can simulate dynamical systems with very large numbers of degrees of freedom, which is impossible to do using purely deterministic methods. The kinetic Monte Carlo method can be implemented using the so-called "next-reaction algorithm" [16]. Its algorithmic complexity is linear with respect to the number of new reactions to evaluate after each reaction and logarithmic with respect to the total number of potential reactions [17] if a binary stack is used to prioritize the times of all possible reactions. We show how to adapt this algorithm to effectively simulate a huge system of rate-equations cluster dynamics. A chemical master equation is constructed from monomolecular and bimolecular reactions rates. These rates correspond to propensities and depend on the number of clusters of each reacting species in the associated reaction. The propensities associated with bimolecular reactions (controlling the agglomeration of two clusters for example), therefore depend on the product of the number of clusters of the two species reacting by a process controlled by the diffusion of a mobile cluster. Consequently, after a bimolecular reaction, the propensities associated with each of the two defect clusters are recalculated and associated reaction times removed from the priority list. These tasks represent a substantial part of overall computational cost. We show how to avoid these tasks by combining an internal time scale and a binary stack to each mobile cluster. The internal time relative to a binary stack re-normalises the physical time by the considered number of mobile species. Owing to its logarithmic complexity with respect to immobile clusters, and linear complexity with respect to the number of mobile species, this algorithm happens to be very efficient when the number of mobile species is small, which corresponds to the typical cases of cluster dynamics. One typical application of the method is the microstructure evolution in an FeHe system.

2.3 Kinetic Activation Relaxation Technique with on-the fly prefactor calculations

Diffusion rates of simple point defects, such as vacancies and interstitials, are generally assumed to depend on energy barriers only, as evidenced by the large number of kinetic Monte Carlo studies that rely on constant jump rate prefactors (as known as attempt frequencies). While this is mostly correct when energy barriers are well separated from each other (i.e. typically in simple crystals), entropic variations between the local minima and associated activated states become increasingly important as energy barriers of diffusion-mediating mechanisms get closer, typically in disordered environments. The unexpected slowdown in defect diffusion observed in high entropy alloys, characterized by the presence of many different elements in roughly equal proportions, led us to revisit the role of prefactors.

We use the Activation-Relaxation Technique (ART nouveau) [18,19] to sample the energy landscape and compute the transition rate for each specific event using the harmonic Transition State Theory (hTST) [20]. At variance with rigid lattice KMC, this relaxed-lattice

kinetic Monte Carlo technique, naturally accounts for elastic effects and lattice distortion effects, which are crucial in disordered systems. Monte Carlo Metropolis type trial displacements centred on all first, second and third-neighbour atoms surrounding a vacancy are randomly generated to build an extensive catalogue of events containing the initial, saddle and final configurations. For each event, the prefactor is either computed within the harmonic approximation as described in Eq. (2) or given a constant value of 10^{13} s^{-1}. Combining the prefactor with the energy barriers, we obtain the total rate associated with moving out of the current configuration. To facilitate the operations on the event-based catalogue and ensure that specific events are only counted once, we use, more specifically, the kinetic Activation-Relaxation Technique (k-ART) package [21,22] and launch 10 event searches per unique topology for each atoms surrounding the vacancy. This value ensures a rich sampling of the energy landscape surrounding the vacancy. The harmonic Transition State Theory (hTST) [20] defines the transition rate as a function of temperature T as

$$\Gamma(T) = \nu_{hTST}\, e^{-\frac{E_s - E_m}{k_B T}} \tag{1}$$

where and E_s and E_m are the configurational energies at the saddle point and the minimum, and ν_{HTST} , the hTST attempt frequency, is given by

$$\nu_{hTST} = \frac{\prod_{i=1}^{N} \nu_i^m}{\prod_{i=1}^{N-1} \nu_i^s} \tag{2}$$

where $\nu_i^s$and ν_i^m are real vibrational frequencies at the saddle point and the minimum, respectively, and are obtained by computing the dynamical matrix

$$D_{i\alpha j\beta} = \frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 V}{\partial x_{i,\alpha}\, \partial x_{j,\beta}} \tag{3}$$

where i, j run over all atoms, α, β are the cartesian coordinates (x, y, 0), V is the interaction potential, and m_i the atomic mass. The matrix can be obtained through a centred-finite difference formulate with small finite displacements of 0.01 Å, for the selected potential. Frequencies correspond to the square root of the dynamical matrix eigenvalues. Combining the Activation-Relaxation Technique nouveau (ART nouveau) and the harmonic approximation for computing diffusion prefactors, we find that vacancy diffusion prefactors in a 55Fe-28Ni-17Cr concentrated solution alloy modelled with EAM empirical potentials can vary by up to six orders of magnitude, at almost constant energy barrier [23]. This variation, mostly associated with changes in local pressure, suggests that prefactor could play a much more important role than previously thought in the defect kinetics of high entropy alloys [24] and of disordered systems in general.

3 Conclusion

Monte Carlo methods are central in irradiated microstructures modelling. In the case of rigid lattice KMC, the ability of the algorithm to reach long evolution times is often limited by kinetic trapping of the simulated trajectories within low energy basins presenting small intra-basin barriers. This can be alleviated by implementing non-local jumps relying on the theory of absorbing Markov chains. To reach even larger time scales, many models rely on huge systems of rate-equation cluster dynamics equations which are usually solved deterministically. Dedicated Monte Carlo schemes can solve them using dedicated algorithms relying on binary heaps to make them more efficient. To study the origin phenomena like slow diffusion processes in HEA with KMC techniques, one must address

first other types of limitations of KMC such as, the rigid lattice approximation, the absence of elastic fields and of vibrational entropy contributions. An improved version of the activation-relaxation technique can be used for such purpose and reveals substantial effects of the jump rate prefactors diversity.

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