Atomistic Kinetic Monte Carlo and Solute Effects

Charlotte S. Becquart, Normand Mousseau,
and Christophe Domain

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Abstract

The atomistic approach of the kinetic Monte Carlo methods allows one to explicitly take into account solute atoms. In this chapter, we present and discuss the different pathways available at this point to go behind nearest neighbor pair interaction for binary alloys on rigid lattices as well as their perspectives. Different strategies to treat complex alloys with several solutes with improved cohesive models are exposed and illustrated as well as the modeling of self-

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C. S. Becquart (✉)
Univ.Lille, CNRS, INRA, ENSCL, UMR 8207, UMET, Unité Matériaux et Transformations, Lille, France
e-mail: charlotte.becquart@univ-lille.fr

N. Mousseau
Département de physique and Regroupement québécois sur les matériaux de pointe, Université de Montréal, Montréal, QC, Canada

C. Domain
Département MMC, Les Renardières, Moret sur Loing, France

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interstitial diffusion under irradiation and its complexity compared to vacancy diffusion.

Abbreviations

AKMC	Atomic kinetic Monte Carlo
BKL	Bortz, Kalos, and Lebowitz
CE	Cluster expansion
DFT	Density functional theory
FIA	Foreign interstitial atom
FISE	Final initial system energy
GAP	Gaussian approximation potential
KMC	Kinetic Monte Carlo
KRA	Kinetically resolved activation
LAE	Local atomic environment
NEB	Nudged elastic band
PD	Point defect
RPV	Reactor pressure vessel
RTA	Residence time algorithm
SFT	Stacking fault tetrahedra
SIA	Self interstitial atom
SNAP	Spectral neighbor analysis potential

1 Introduction

The kinetics of alloy microstructures under nonequilibrium conditions such as irradiation is driven by the evolution of the population of point defects introduced by the energetic particles impinging the materials. Being capable of predicting such evolution is an important academic as well as industrial issue that needs to be tackled starting at the atomistic level. For this purpose, Atomistic kinetic Monte Carlo (AKMC) is a very versatile method that can be used to simulate the evolution of complex microstructures at the atomic scale, dealing with elementary atomic mechanisms. It was developed more than 40 years ago to investigate diffusion events triggered by the motion of a single vacancy (Young and Elcock 1966) in a binary alloy. Since then, hetero-interstitials (Clouet et al. 2006; Hin et al. 2008) and self interstitials (Ngayam-Happy et al. 2010) have been introduced in the models and alloys of more complex nature have been investigated (Cerezo et al. 2003; Liu et al. 1997). The purpose of this chapter is to discuss how the effect of solutes can be taken into account in this approach. We will first start by describing briefly the basis of the AKMC method and its key ingredients. In the following sections, we present and discuss the different strategies available to build Hamiltonians that take into account solute atoms as well as the techniques used to estimate the activation barriers. We conclude by discussing the outlooks and perspectives of the different approaches described in the previous sections.

2 AKMC Method

Kinetic Monte Carlo (KMC) methods are techniques intended to simulate the time evolution of processes that occur with a given known rate, used as inputs to the algorithm (Voter 2007). It is usually applied at two scales: the atomistic scale, where processes that can take place are the ones atoms undergo during the evolution of a microstructure, and the mesoscopic scale, where the microstructure is coarse grained into objects that can evolve on a lattice or not. The first papers presenting a kinetic Monte Carlo approach were published by Young and Elcock (1966) and by Bortz et al. (1975), the first dealing with the kinetic of the vacancy diffusion in ordered alloys, the latter dealing with the kinetic evolution of an Ising spin system. A full theoretical description and formalization of the AKMC algorithm was proposed by Fichtorn (Fichthorn and Weinberg 1991). The most important feature of the AKMC technique – as compared to atomistic Metropolis Monte Carlo (MMC) simulations (Metropolis 1953) – is the fact that a time step can be related to each simulation step, i.e., for instance, the jump of a point defect. In AKMC simulations, configurations are not generated as a Markov chain and sampled respecting a given probability distribution (usually a thermodynamic equilibrium distribution) – as it is done in the MMC approach; rather, the configuration at step *i* is obtained from configuration at step *i-1* by realizing a point defect or an atom move, i.e., the Markov chain is constructed taking into account the kinetics of the system.

We will not give an extensive description of the KMC algorithm which can be found for instance in (Voter 2007) but rather focus on its applications to model alloys and solute effects. We will remain in the context of diffusion controlled phase transformation under classical conditions (for instance under thermal ageing) or in the presence of external forcing: here irradiation. A review of AKMC applied to precipitation can be found in Becquart and Soisson (2018). Atomistic kinetic Monte Carlo models are based on the residence time algorithm (Young and Elcock 1966) sometimes referred to as the BKL approach (Bortz et al. 1975). The elementary mechanisms are the point defect jumps or the interstitial jumps in the case of C or other hetero-interstitials. In the rigid lattice approach, which is the approach most used so far, vacancies and interstitials (dumbbells or mixed dumbbells) can jump from one lattice site to another lattice site (typically first nearest neighbor sites). If hetero-interstitial atoms are included in the model, they lie on an interstitial sublattice and jump on this sublattice. Typically one atom is assumed to move and the rates of possible transitions are determined from the local environment around the moving atom. According to harmonic standard transition state theory (Vineyard 1957), the frequency of a thermally activated event such as a vacancy jump in an alloy can be expressed as:

$$\Gamma = \nu e^{-\frac{E_a}{k_B T}} \tag{1}$$

where ν denotes the attempt frequency and E_a corresponds to the activation energy of the jump or the migration energy obtained as the difference between the energies of the system at the saddle-point and in its initial configuration. Such a description is derived from the theory of thermally activated processes and is justified when the thermal fluctuations are smaller than the activation energies: $k_B T \ll E_a$. The attempt frequency can be expressed as:

$$\nu = \frac{\prod_{j=1}^{3N-3} \nu_j}{\prod_{j=1}^{3N-4} \nu_j^*} \tag{2}$$

where $\mathrm{\nu_j}$ and $\mathrm{\nu_j}^*$ are the normal frequencies for vibrations at the local minimum and saddle states, respectively, and N is the number of atoms. Note that, at constant pressure, one should consider the enthalpies and free enthalpies of migration, but the difference is often negligible in solids. The jump frequencies obtained using this theory appear to be a very good approximation for the real jump frequencies up to at least half the melting point in most solid materials (Voter 2007).

For sake of simplicity, constant prefactors of the order of Debye's frequency are used most of the time (typical values for transition metals are 10^{12}–10^{13} s^{-1}). This commonly chosen assumption is based on the fact that small variations of the activation energy are more likely to have a greater impact on the transition probability than variations of the attempt frequency which are second-order effects (because of the exponential dependency of the former). This assumption is supposed to be valid especially for systems where all species have similar sizes such as 3d transition metal typical alloying elements in steels (Fe, Ni, Cr, Mn). However, it has been shown recently (Lazauskas et al. 2014) using Vineyard approach (Vineyard 1957) that the prefactor has an impact on the primary damage evolution and that the use of a constant prefactor, as is done in many lattice KMC simulations, may change the self interstitial atom (SIA) migration mechanisms, the amount of vacancy SIA recombinations, and enhance the difference between the diffusion rates of vacancies and interstitials. This work also concluded that the vibrational internal energy contributes little to the attempt frequencies of small point defect cluster migration mechanisms in Fe and that Vineyard approach was thus accurate enough to obtain them for each of the defects simulated.

At each KMC step, the algorithm determines the jump frequencies of all possible jumps in the system, chooses one of them according to its probability, and evaluates the time that the system would have taken to do the jump. The associated time-step length δt and average time-step length Δt is given by:

$$\delta t = \frac{-\ln r}{\sum\limits_{n} \Gamma_X} \Delta t = \frac{1}{\sum\limits_{n} \Gamma_X} \tag{3}$$

where r is a random number between 0 and 1.

The key issue of this method is the estimation of the jump frequency and the activation barrier, E_a, which, when the local chemical environment is complex, i.e., when the system is composed of several atomic elements, is not straightforward to calculate.

Three kinds of methods have been used, so far, to obtain E_a:

(i) **Direct calculation of E_a**: This approach is possible for simple cases, for example, in the study of solute transport mechanisms where only one solute and one point defect (vacancy or interstitial) are considered, i.e., when the number of different barriers to determine is small. Such a study was performed by Costa (2012), using an empirical potential and assuming a limited range of interaction, e.g., first and second nearest neighbor interactions, to study thermal ageing and spinodal decomposition in the FeCr system, or, more recently, Messina et al. (2015) using ab initio-computed binding energies and migration barriers in the FeMnNi system. Usually, the activation energies are tabulated, to speed up the calculations; however, it is also possible to obtain them on-the-fly, using approaches such as k-ART (El-Mellouhi et al. 2008) or SEAKMC (Xu et al. 2015) discussed elsewhere in this volume (chapters "▶ Off Lattice Kinetic Monte Carlo Methods" and "▶ Computational Methods for Long-Timescale Atomistic Simulations").

Another possibility to obtain E_a is to perform a cluster expansion (CE) at the saddle point, as proposed in Rehman et al. (2013) again when the system is not too complex or to use machine learning method based methods, such as artificial neural network, that can be trained to estimate the activation energy as a function of the local environment as proposed 10 years ago by Djurabekova (Djurabekova et al. 2007), see Behler (2016) for a review.

(ii) **Broken bond or cut bond models** (Soisson et al. 1996): In these models, the activation energy is given by the difference between the energy at the saddle point position and the energy due to the interactions of the bonds broken during the jump. The activation/migration energy is obtained as:

$$E_a = e_k^{sp} - \sum_j \varepsilon_{k-j} - \sum_{j \neq k} \varepsilon_{PD-j} \tag{4}$$

where e_k^{sp} is the binding energy of atom k at the saddle point position and where the summations over j extend over all the broken bonds of the migrating atom k and of the moving point defect (PD). This scheme is illustrated in Fig. 1. Another form of cut bond model has been developed in Vincent et al. (2008a). In this method, it is considered that the migrating atom jump does not lead to the destruction of the bonds with the point defect but that the bonds between the migrating atom and its neighbors are replaced by bonds with the PD and the same neighbors. The activation energy is then given by:

$$E_a = \sum_j \varepsilon_{k-j}^{sp} + \sum_j \varepsilon_{PD-j} - \sum_j \varepsilon_{k-j} \tag{5}$$

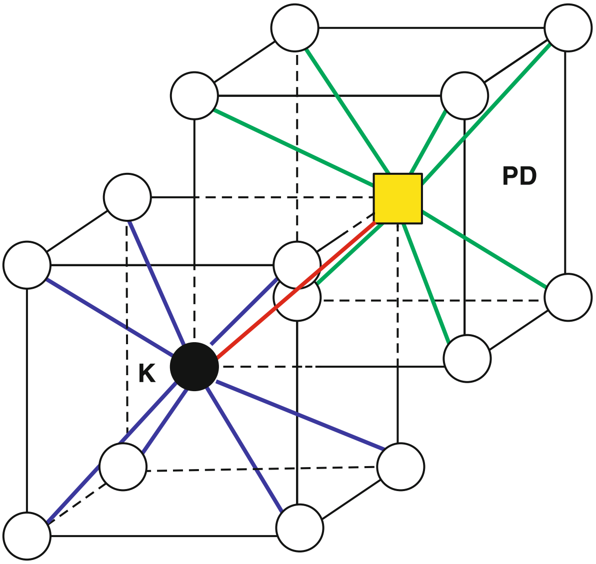


Fig. 1 Illustration of the broken bond model. The green lines represent the bonds around the jumping point defect and the blue lines the bonds around its final position

(iii) **Methods based on the energy of the final and initial states:** They require that a Hamiltonian is available to obtain the energy of any equilibrium configurations and can be used with any Hamiltonian (simple ones like pair interactions or more complex ones). The kinetically resolved activation (KRA) according to van der Ven (Van der Ven et al. 2001), or final initial state energy (FISE) approximation, according to the terminology adopted by Vincent et al.(2008a) in the context of Fe-cu alloys, is based on the Kang and Weinberg decomposition of migration energy barriers (Kang and Weinberg 1989), which consists in computing the migration energy as follows:

$$E_a = E_a^0 + \frac{\Delta E}{2} \tag{6}$$

where E_a^0 depends usually on the migrating atom type but not on the chemical environment. The method, originally applied to vacancies, can be easily extrapolated to the migration of SIAs or foreign interstitial atoms (FIAs).

Whatever the method chosen to determine E_a, it must fulfill the detailed balance. Broken bond and FISE/KRA approaches have been compared in a study of FeCu alloys thermal ageing (Vincent et al. 2008a), and it was found, not very surprisingly, that it is the parameterization rather than the method which impacts the most on the results, i.e., the density and mean precipitate radii.

The next section describes the different approaches used to determine the activation energies as well as build the energetic model of the system. The energetic model has to be built on a compromise between the complexity of the system (e.g., the number of solutes to treat) and the combinatorial increase of parameters to determine and adjust, as well as a computational simplicity in order to be able to perform a very large number of KMC steps to simulate the target microstructure evolution.

3 Hamiltonians for AKMC Simulations

3.1 Exact Hamiltonians Based on DFT and Empirical Potentials

The evolution of the microstructure is driven by the point defects and the hetero-interstitials motions in the lattice. The key issue in these models is, as already mentioned in the previous section, the calculation of the jump probabilities. In the case of perfect and pure elements with simple defects, jump probabilities are not difficult to determine as it is easy to calculate the migration barrier and the attempt frequency using density functional theory (DFT) (i.e. *ab initio* or first principles approaches) calculations. However, in reals systems, solute atoms and strains will impact the activation barriers as described for instance in Tchitchekova et al. (2014) which can lead to incorrect predictions for the barriers even with a highly accurate energy calculation. The ideal way to compute jump frequencies would be to use a first principles approach on a box sufficiently large to limit size effects. Even though first principles calculations are not strictly exact, since they are based on a certain number of approximations which are more or less well controlled according to the different cases, its use represents, at the moment, the most reliable approach to obtain the potential energy for a given atomic distribution. Many methods for finding barriers exist and are implemented in DFT-based codes to determine activation barriers or migration energies. They include the nudged elastic band (NEB) (Henkelman et al. 2000), the growing spring method (Peters et al. 2004), the dimer (Henkelman and Jónsson 1999), autonomous basin climbing (ABC) (Fan et al. 2010) or eigen-vector following methods such as ART-nouveau (Barkema and Mousseau 1996; El-Mellouhi et al. 2008). However, these methods are computationally very demanding when applied to DFT calculations, and they have been used so far only in simple cases such as the estimation of tracer diffusion coefficients that require the calculations of only a few jump frequencies (Mantina et al. 2008; Messina et al. 2014). This is why it is often necessary to turn to empirical potential or force field approach to assess energy barriers. While these potentials are cheap enough to avoid strain artefacts due to small boxes, one of their recurring problems is their transferability, and more precisely their ability to correctly model the desired material under conditions far from the conditions used when adjusting the parameters. Even with empirical potentials, methods such as "on-the-fly" AKMC simulations that can require billions of point defects, jumps remain time consuming without additional tricks (Athènes and Bulatov 2014).

Furthermore, the empirical potentials available at the moment are mostly limited to binaries, a few ternaries and even less quaternaries. Often, therefore, simpler models based on strong approximations typically associated with rigid lattices that are described in the following subsections, and illustrated with a few applications, must be used.

3.2 Effective Hamiltonians Based on Cluster Expansions

Cluster expansion methods provide a formalism to derive Hamiltonian, based on a decomposition of the interaction into pairs (that can be between different nearest neighbor distances), triplets (ε_{ijk}), quadruplets (ε_{ijkl}), quintuplet, and so on (Sanchez et al. 1984). The total energy of the system is obtained as:

$$E_{tot} = \sum_{i} \varepsilon_i + \sum_{i} \sum_{j<i} \varepsilon_{ij} + \sum_{i} \sum_{j<i} \sum_{k<j} \varepsilon_{ijk} + \sum_{i} \sum_{j<i} \sum_{k<j} \sum_{l<k} \varepsilon_{ijkl} + \cdots \tag{7}$$

3.2.1 Pair Models

The simplest approach is to use pair interaction models (Fig. 2). These models, based simply on the presence or absence of a given atom, require a rigid lattice and are often parameterized on experimental or DFT thermodynamical data.

In the case of an Fe alloy containing vacancies, the total energy of the system can be obtained as:

$$\begin{aligned} E = & \sum_{j} \varepsilon^{(i)}_{(Fe-Fe)} + \sum_{k} \varepsilon^{(i)}_{(V-V)} + \sum_{l} \varepsilon^{(i)}_{(Fe-V)} + \sum_{m} \varepsilon^{(i)}_{(Fe-X)} \\ & + \sum_{n} \varepsilon^{(i)}_{(V-X)} + \sum_{p} \varepsilon^{(i)}_{(X-Y)} \end{aligned} \tag{8}$$

where V stands for the vacancy, X and Y are solute atoms.

When interactions are limited to first nearest pairs, the thermodynamical properties of the system are easily determined using the Bragg Williams approximation. This approach has been applied for instance to study the precipitation of Cu in Fe,

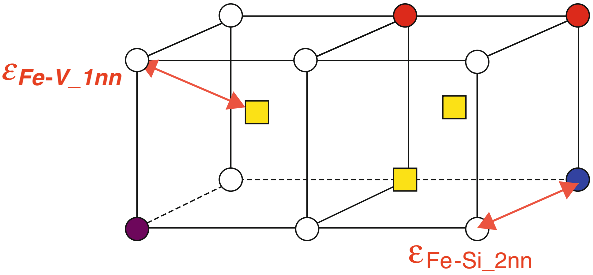


Fig. 2 Illustration of a pair interaction model

either using a broken bond model (Soisson et al. 1996) or FISE model (Vincent et al. 2008a) to determine E_a. This is the approach also chosen by Liu et al. to investigate complex Fe-CuNiMnSi alloys (Liu et al. 1997) using only first nearest neighbor parameters adjusted on binary mixing enthalpies. It has since then been shown that in bcc metals, one needs to go beyond the first nearest neighbor interaction to correctly reproduce the interaction of solutes with vacancies or to describe properly solute transport mechanism predicted by DFT calculations (Olsson et al. 2010) (Vincent et al. 2006; Messina et al. 2014).

Hamiltonian-based pair models have also been derived for SIAs. These defects are more complex than vacancies: different dumbbells form in fcc or bcc metals, with off-lattice positions. The models have to be simplified as in Soisson (2006) or Soisson and Jourdan (2016) for which only the elements of the dumbbell X–Y are stored without considering the detailed migration mechanism and the dumbbell orientation or adapted on the main diffusion mechanisms as in Vincent et al. (2008b). In bcc Fe, most of the time, only the ⟨110⟩ dumbbell is considered, with eight possible jumps (Fig. 3a). It migrates in general according to the Johnson mechanism (Johnson 1964; Vincent et al. 2008b; Ngayam-Happy et al. 2010). In fcc alloys such as Ni, Ni alloys or FeNiCr model fcc alloys used to simulate austenitic materials, the ⟨100⟩ dumbbell is considered with eight possible translation rotation jumps (Fig. 3b).

One possible approach decomposes the SIA interaction into pairs that take into account the different nearest neighbor sites and the sign of the strains of these sites as illustrated on Fig. 4. Using this approach, the dumbbell contribution to the total energy of the system can be obtained as (Vincent et al. 2008b):

$$E_{\text{dumb}} = \sum_i \left(E_f + \sum_j E_l^{1nn\text{Comp}} \left(\text{dumb}_i - X_j\right) + \sum_j E_l^{1nn\text{Tens}} \left(X_j\right) \right. \\ \left. + \sum_{i,j} E_l^{\text{mixte}} \left(X_j - X_k\right) + \sum E_l \left(\text{dumb} - \text{dumb}\right) \right)$$

where three kinds of interactions are considered: dumbbell-dumbbell, dumbbell-compression, and dumbbell-tension sites.

FIAs can also be introduced on a sublattice as shown in Hin et al. (2008), where the precipitation of carbides in Fe and FeNb alloys has been modeled under thermal ageing using a broken bond model.

Pair interactions and a broken bond model have been used, for instance, to study radiation induced segregation by electrons and neutrons in Fe-15 at %Cr alloys (Soisson and Jourdan 2016) taking into account replacement collision sequences and ballistic mixing as well as the migration of both vacancies and ⟨110⟩ dumbbells. Hocker et al. (Hocker et al. 2014) used a similar approach to study precipitation in FeCuNiMn alloys whereas Vincent and coworkers (Vincent et al. 2008b) chose the FISE/KRA approach and pair interactions to model FeCuNiMnSi alloys under irradiation.

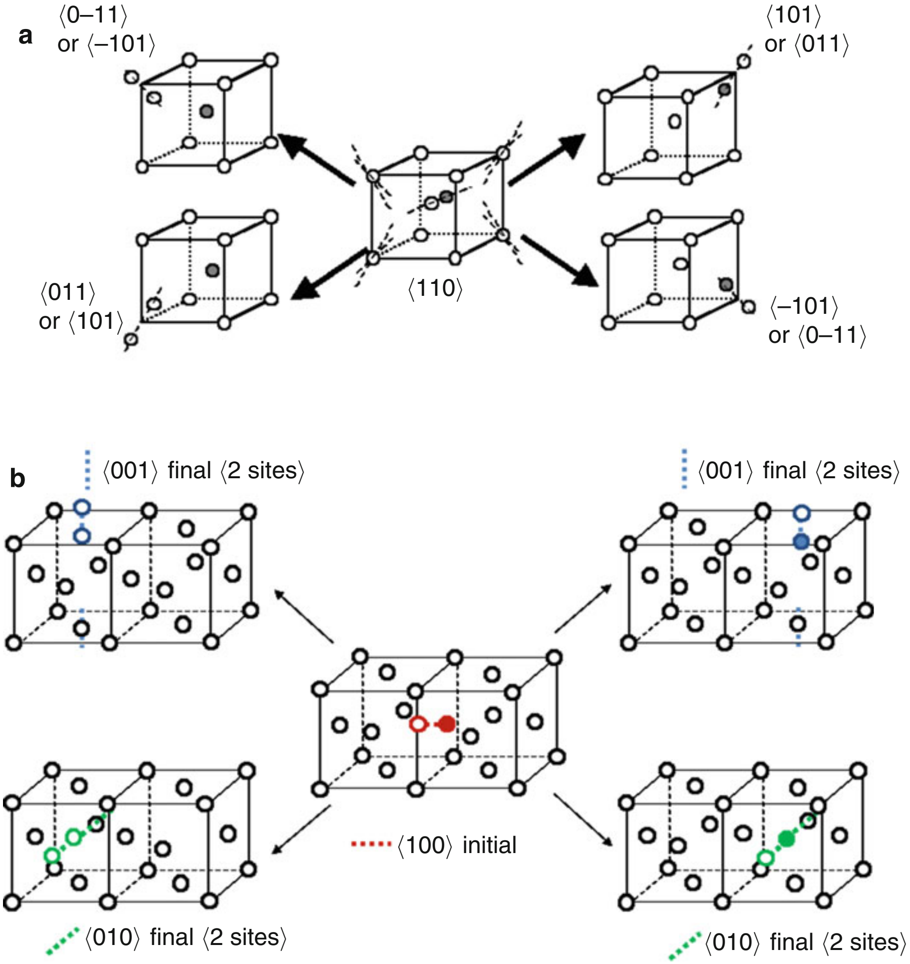


Fig. 3 SIA migration mechanisms considered (a) in bcc Fe, (b) in fcc Ni, Ni alloys, FeNiCr model fcc alloys

3.2.2 Higher Order Cluster Expansion Models

When expanding the model beyond pair interactions, complexity increases rapidly as different geometries must be defined for all n-uplets. The most compact ones, as illustrated for bcc in Fig. 5, can be privileged in order to limit the possible choices to the most significant interactions – with the selection, in general of solute atoms close to each other.

Since each triplet has a different energy contribution, function of the three species considered, the number of energy parameters (i.e., n-uplets containing combinations of all the solutes) that need to be defined increases exponentionally as the number of solute species increases (Fig. 6). As in the case of pair interaction models,

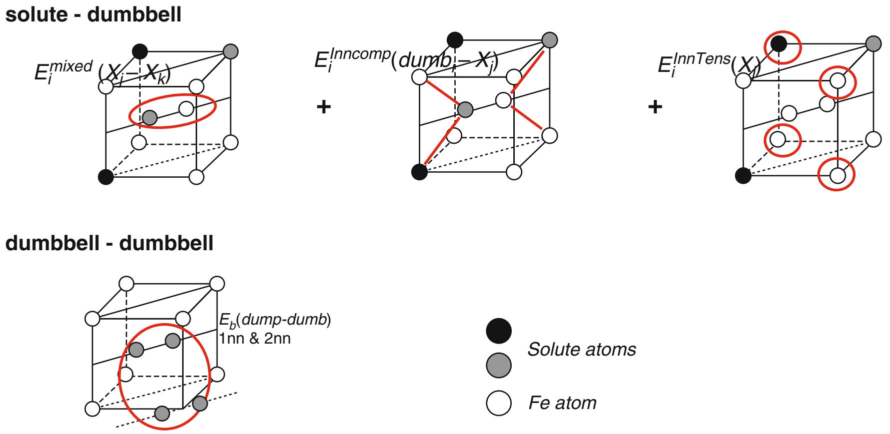
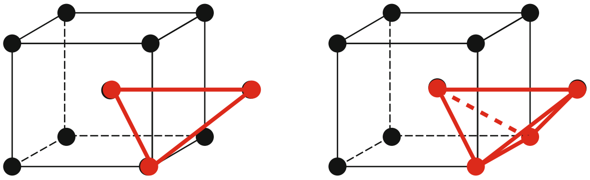


Fig. 4 SIA-solute pair interaction model proposed by Vincent et al. (Vincent et al. 2008b). Three kinds of interactions are considered: dumbbell-dumbbell, dumbbell-compression, and dumbbell-tension sites interactions

Fig. 5 Most compact structure for a triplet and a quadruplet in a bcc lattice



parameters can be adjusted on experimental thermodynamical data and/or DFT calculations. This method can be easily used in conjunction with the FISE/KRA method as done in (Nguyen-Manh et al. 2008) to model thermal ageing in FeCr alloys or more recently to simulate thermal annealing in Fe–20Cr–xW alloys at 773 K (Bonny et al. 2017). The same approach was used to study ordering in NiCr fcc alloys by Barnard et al. (2014) who used the CASM package (CASMcode 2017; CASM Developers 2016) to build their cluster expansion Hamiltonian which was then used with the FISE/KRA approach to follow the formation of the Ni_2Cr ordered phase under thermal ageing. Van de Walle has developed the Alloy Theoretic Automated Toolkit (ATAT) (2017) that builds cluster expansion Hamiltonian interfaced with DFT. ATAT includes tools for thermodynamical analysis and Monte Carlo simulation but cannot perform kinetic Monte Carlo.

Note that even with simple pair models, the number of parameters required increases very quickly with the amount of species that needs to be modeled as can be seen from Fig. 6. Modelling realistic steels for instance remains a not straightforward task, especially if the adjustment of the parameters is done "by hand."

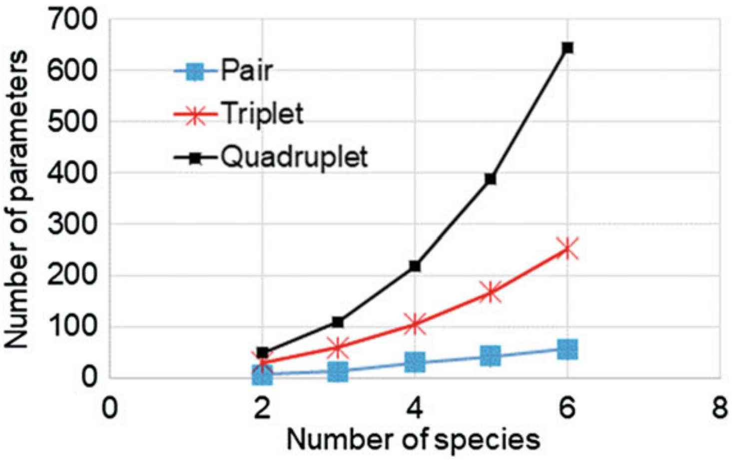


Fig. 6 Evolution of the number of parameters versus the number of species for different approaches

3.3 Neural Network and Machine Learning Methods

One promising approach by taking into account the local environment influence on the migration energies is the use of artificial neural network (ANN) as proposed by Djurabekova et al. 10 years ago (Djurabekova et al. 2007). The more accurate the training sets, the better the predictions, thus building training sets from DFT calculations appears to be the direction to take, as long as elastic effects are correctly accounted for. For accuracy the training set should cover a large set of configurations. This starts now to be possible with DFT, despite requiring large computing resources. Castin et al. (2017) and Messina et al. (2017) combining DFT and ANN proved this approach to be manageable to accurately model the thermal ageing of two very well-known systems: FeCr and FeCu. The training sets have been limited to 2,000–10,000 configurations, with extra care taken to choose different environments in order to reproduce both the solid solution and the vacancy environment close to a precipitate. Another possible approach is genetic algorithm implemented for instance in the open source code *potfit* that constructs force matching empirical potentials (Brommer et al. 2015).

4 Taking into Account Solute Effects in the Activation Barriers

The effect on the local atomic environment on the migration barrier can be introduced using different approaches that are discussed in that section.

A first approach is to have E_{sp} or E_a^0 depend on the local environment, and in a first-order approximation on the number of solute atoms in the vicinity of the jumping atom. In a typical FISE/KRA approach, such as the one employed in (Vincent et al. 2008b), all the effects of the environment on the migration barrier are carried by the ΔE term. This simple model can be improved by introducing a dependence of the E_a^0 term on the local atomic environment. In particular, an explicit dependence of E_a^0 on the migrating atom's saddle point local atomic environment – whose effect on the vacancy migration energy is particularly strong (Nguyen-Manh et al. 2008; Costa et al. 2014; Bouar and Soisson 2002), can be easily introduced. This has been done, with the FISE/KRA model, to study Cu precipitation in FeCu (Bouar and Soisson 2002) with a broken-bond model, thermal ageing in FeCr (Nguyen-Manh et al. 2008) or the spinodal decomposition in the same system (Costa 2012). All studies show, however, that saddle point energies are very sensitive to both the nature of the jumping atom and that of the first neighbours of the saddle point. As a result, the kinetics pathways are changed and, for instance, in the FeCu study, Le Bouar et al. observed that the dependence of the saddle-point binding energies on the local atomic configurations modifies the relative mobility of small Cu clusters and Cu monomers.

A more sophisticated model to take into account the LAE in a pair interaction model has been proposed by Martinez et al. (Martínez et al. 2012) to study FeCr alloys. In this approach, the pair interactions are fitted on DFT data and depend on the local concentration as well as temperature. This allows a much better description of the FeCr phase diagram and its miscibility gap.

Recently, this method has been adapted for multi-component dilute alloys and, more precisely, to model the Fe-CuNiMnSi system representative of Reactor Pressure Vessel (RPV) steels (Pannier 2017). In a first and second nearest neighbor pair interaction model, the pair interaction values depend on whether the vacancy is in a solid solution or in a precipitate. This method introduces some additional degrees of freedom as compared to the original method proposed in Vincent et al. (2008b) with a limited increase of the number of parameters that need to be adjusted (2× more compared to the original pair model).

The cluster expansion method can also be applied to determine the activation barrier. In their study of Li diffusion in $\mathrm{Li_xCoO_2}$ oxides, Van der Ven et al. (Van der Ven et al. 2001) added a cluster expansion contribution to the first term (i.e., E_a^0 in Eq. 6) of the FISE /KRA equation, introducing a dependence of E_a^0 on the local environment, independently of the jump direction. Rehman et al. (Rehman et al. 2013) proposed a procedure based on cluster expansion to obtain directly the migration barriers encountered during diffusion of Ag on Ag(100) surfaces. They trained the cluster expansion on activation barriers obtained using the NEB method and found that they were able to generate an accurate process rate catalogue using this approach.

A mean field approach to include the influence of the local environment in the migration barrier has been proposed recently to study the diffusion of H in zircaloy (Zhang et al. 2017). At each KMC step, the migration barrier of each jump, E_a, is modified as:

$$E_a = E_a^0 + E_t^i \text{ if } R < c_t^i$$

where E_a^0 is the barrier without trapping, i.e., the activation energy in pure Zr. E_t^i is the binding energy of H at a trapping site t with a concentration c_t^i induced by solute i, the concentration of which is c_i. R is a random number drawn each time the jump rate is evaluated.

A last approach uses many body potentials or DFT calculations, recognizing that they take into account naturally the effects of mean local solute concentrations. Potentials based on the embedded atom method (EAM) (Daw and Baskes 1984) are usually a good compromise to describe metals and their alloys. Such potentials, with additional refinements, have been used to describe the evolution of FeCr systems during short range ordering (Pareige et al. 2009) and spinodal decomposition (Pareige et al. 2011). In Kushima and Yildiz (2010), a database of migration barrier energies as a function of lattice strain for a set of representative defect distributions in the vicinity of the migration path in yttria stabilized zirconia was constructed using DFT and the NEB.

5 Specific Issues Linked to Irradiated Microstructures

Real microstructures contain interfaces such as grain boundaries, phase boundaries, and so on. They are important to take into account as segregation or depletion of solutes can take place in their vicinity because they can act as sinks or traps.

In the AKMC approach, grain boundaries can be modeled using different methods. They can simply be introduced as an atomic plane in the simulation boxes that has perfect sink properties for vacancies and SIAs (Soisson and Jourdan 2016) or with specific trapping properties in the energetic model (Soisson and Jourdan 2016; Piochaud 2013).

Another issue is the impact of energetic particles impacting alloys as in the case of irradiation. Depending on the energy of the incident particle, isolated Frenkel pairs (e.g., with electron irradiation) or displacement cascades with the formation of vacancies and self interstitials isolated and in clusters in a localized zone, few nanometers large (e.g., for high energy ions and neutrons) are created in a few pisoseconds. The associated time scale being much smaller than the atomic migration time scale, the point defects associated to one energetic particle interaction can be introduced between two atomic migration kinetic Monte Carlo steps.

Different approaches are possible to model such events which, in the case of a pure metal, can lead to similar microstructures; however, in alloys, they are not equivalent. In the case of Frenkel pairs, one can either introduce a vacancy and a SIA, at with or without a correlation distance between them, randomly in the simulation box as in Ngayam-Happy et al. (2010) or introduce a series of replacements ending by one vacancy and one SIA at the other end as in Soisson and Jourdan (2016). In the case of displacement cascades, they can be simulated by introducing, in the simulation box, the positions of vacancies and SIAs from a cascade database debris obtained by MD (Vincent et al. 2008b) or they can be obtained as a superposition of channeling sequences (along the <111> direction in bcc crystals for instance), replacement collision sequences (with a specific length), and replacement cascades, i.e., the introduction of vacancies and SIAs within the volume of a sphere (Soisson and Jourdan 2016). When replacements are made in alloys, solute mixing can occur, which may be important in concentrated alloys as they can lead to precipitation or ordering (Lear et al. 2017).

6 Future Directions and Perspectives

Modeling the microstructure evolution of alloys, during thermal ageing, irradiation, or under any external constrain, is a difficult task as one has to deal with multiple solutes and/or several point defects. A balance between the computational cost, the cohesive model accuracy and the number of input parameters to build it, the chemical complexity (e.g., multi solute treatment) has to be found. This is why, even as off-lattice AKMC methods are introduced, the need will remain for lattice-based approaches as these are much faster and can achieve the billions of time steps required to understand the physics of defects and alloys in complex environments.

There is still considerable place for improvements, and we consider, in this section, a few directions that must be considered.

For dilute alloys, methods that estimate the activation energies in a specific local environment as a correction of the activation energy in a perfect unary matrix as in Zhang et al. (2017) can be used as long as the local environment remains dilute. These methods are thus appropriate to determine for instance the diffusion coefficients in dilute alloys but not precipitation or solute segregation.

Without a doubt, the most urgent advance must come from force field developers particularly when it comes to complex alloys and solutes. Since, *ab initio* approaches will remain confined to relatively small systems for the foreseeable future, we must turn to approximation. As far as the cohesive model is concerned, machine learning methods that are under development to build improved empirical potentials or cohesive models are currently the most promising path to provide a satisfactory solution both in terms of computational costs and precision. “Quantum accurate interatomic potentials” such as the Gaussian approximation potentials (GAP) (Bartók and Csányi 2015) or the Spectral Neighbor Analysis Potential (SNAP) (Thompson et al. 2015) can now be built, by constituting a very large DFT database and the use of machine learning tools. Fitting empirical potentials to functional forms based on the knowledge of the chemical interactions responsible for the material cohesion has limitations and the development of methods that uses very generic functional forms, not based on physical considerations, is well under way (Handley and Behler 2014). This is where machine learning algorithms become even more necessary. A recent review of these methods that discusses the central ideas behind machine learning potentials as well as their current applicability and limitations can be found in Behler (2016). Among the latter, the size of the database required to fit multicompound systems remains, nevertheless, a major hurdle that has not yet been solved. It is, however, only a matter of time before more complex systems become treatable, especially in the context of AKMC, where only local minima and transition require accuracy.

An accurate description of the energetics is not always sufficient, however. In many cases, variations in the entropy associated with diffusion mechanisms can completely change the kinetics. Yet, evaluating the contribution of entropy on the migration barriers is very computational demanding and will depend significantly, again, on the cohesive model used. Theoretical methods exist to do so, see a review in Van der Ven et al. (2010); however, there require a considerable amount of additional calculations as one should calculate the configurational, vibrational, electronic, and magnetic entropic contributions as it has been done for defect and defect clusters formation energies (Marinica and Willaime 2007; Murali et al. 2015; Tucker et al. 2010; Posselt et al. 2017). This becomes especially important for inhomogeneous conditions such as grain boundaries, high entropy alloys, and surfaces. For example, the tetrahedral vacancy cluster, formed by a three-vacancy cluster with a displaced atom in the center (Aidhy et al. 2016) is very unstable at low temperature in Ni, with an energy 0.4 eV above ground state, separated by a barrier of only 0.08 eV, but is found to be stable above 400 K, due to entropic effects (Mahmoud et al. 2018).

Incorporating these effects in lattice-based AKMC will require a better approach to evaluate barriers, including energy and entropy, without exploding the event catalog and the number of local environments increases with solutes. This could be done by expending on cluster expansion methods. One promising improvement in this approach towards modeling more realistic microstructures is the methods derived by Yuge and co-worker (Yuge and Okawa 2014) to take into account strain effects which can be non negligible during alloys phase transitions, and handle multiple lattices (Yuge 2012). The performance of three CE fitting algorithms have been investigated in Herder et al. (2015) who find that performance depends on system details and complexity and becomes a trade-off between accuracy and computational cost. They find that quality of a CE depends on the data that it is fit to and the algorithm used to identify terms to introduce in the CE.

Clearly, CE methods will have to consider more complex and larger objects containing 10 or 20 atoms. To do that requires a better description and classification of local environments. Topological analysis tools such as NAUTY (McKay and Piperno 2014) or the graph approach proposed in Yuge (2017), for example, while first used with off-lattice KMC approaches, provide a very efficient way to differentiate between local environments, even with a large number of solutes, while automatically taking symmetry operations into account.

Even if this is not the purpose of this chapter, one important issue is the speeding up of the simulations as the calculation speed has to be taken into account in the choice of the cohesive models. In particular, when both low and high migration barriers can be encountered during the point defect motion, the defect can be trapped and many KMC steps are necessary to change configuration which can drastically slow down the evolution of the microstructure. Different methods are being developed to boost the simulation, see for instance Athènes and Bulatov (2014) or Danielson et al. (2017).

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