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Diffusion and coupled fluxes in concentrated alloys under irradiation: a self-consistent mean-field approach

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Abstract

When an alloy is irradiated, atomic transport can occur through the two types of defects which are created: vacancies and interstitials. Recent developments of the self-consistent mean field (SCMF) kinetic theory could treat within the same formalism diffusion due to vacancies and interstitials in a multi-component alloy. It starts from a microscopic model of the atomic transport via vacancies and interstitials and yields the fluxes with a complete Onsager matrix of the phenomenological coefficients. The jump frequencies depend on the local environment through a 'broken bond model' such that the large range of frequencies involved in concentrated alloys is produced by a small number of thermodynamic and kinetic parameters. Kinetic correlations are accounted for through a set of time-dependent effective interactions within a non-equilibrium distribution function of the system. The different approximations of the SCMF theory recover most of the previous diffusion models. Recent improvements of the theory were to extend the multi-frequency approach usually restricted to dilute alloys to diffusion in concentrated alloys with jump frequencies depending on local concentrations and to generalize the formalism first developed for the vacancy diffusion mechanism to the more complex diffusion mechanism of the interstitial in the dumbbell configuration. ***To cite this article: M. Nastar, C. R. Physique 9 (2008).***
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Résumé

Diffusion et couplage de flux dans les alliages concentrés sous irradiation : une approche de champ moyen auto-cohérente.
Dans un alliage sous irradiation, le transport des atomes est contrôlé par deux types de défauts créés, les lacunes et les interstitiels. Les récents développements de la théorie de champ moyen auto-cohérente (SCMF) permettent de traiter dans le même formalisme la diffusion des lacunes et des interstitiels dans un alliage multi-composant. A partir d'un modèle de fréquence de saut atomique, la théorie (SCMF) en déduit les coefficients phénoménologiques de la matrice d'Onsager et les flux de matière associés. Les fréquences de saut dépendent de l'environnement local par un modèle dit « de liaisons coupées », ce qui permet de prédire la grande variété de fréquences impliquées dans un alliage concentré à partir d'un petit nombre de paramètres thermodynamiques et cinétiques. Les corrélations cinétiques sont prises en compte par un ensemble d'interactions effectives dépendant du temps et introduites dans une fonction de distribution du système hors d'équilibre. Les différentes approximations de la théorie SCMF incluent la plupart des autres modèles de diffusion. Les derniers progrès furent d'étendre l'approche multi-fréquence habituellement réservée aux alliages dilués aux alliages concentrés avec des fréquences de saut qui dépendent de l'environnement local et de généraliser le formalisme initialement développé pour le mécanisme de diffusion lacunaire à celui plus complexe de l'interstitiel dans la configuration dissociée (dumbbell). ***Pour citer cet article : M. Nastar, C. R. Physique 9 (2008).***
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1. Introduction

When a metallic alloy is irradiated with particles, the atomic transport is not only supported by vacancies but also by interstitials, both concentrations being fixed by the irradiation conditions. Those point defects in supersaturation tend to eliminate at point defect sinks like grain-boundaries, surfaces, dislocations and cavities, producing atomic fluxes. The coupling between point defect and atomic fluxes sustained by irradiation determines the variations of composition (also called segregations) we may observe close to point defect sinks. It can be formulated and quantified by means of the Onsager matrix (L_{ij}) within the framework of thermodynamics of irreversible processes [1]. A characteristic of open systems like the irradiated ones is that not only the kinetic path but also the final steady state depends on the details of the Onsager matrix. The terms of the matrix are written as the product of an uncorrelated transport coefficient, $L_{ii}^{(0)}$, multiplied by a correlation function that is the problematic term to calculate: $L_{ij} = L_{ii}^{(0)} f_{ij}^{(i)}$. The latter measures the deviation of the atomic migration paths from a random path due to the correlations between the successive jumps inherent to the diffusion mechanism. These correlations usually slow down a kinetics and in some cases block the reaction [2] or lead to an inversion of atomic fluxes with respect to the vacancy flux [3]. Although there is an experimental procedure to determine the L_{ij}, experiments are usually performed at high temperature, for a few compositions, and only some terms of the Onsager matrix are measured. The previous models relating the diffusion coefficients of isotopes with the L_{ij} turn out to be less and less valid as the Monte Carlo simulations become a more reliable test [4]. An irradiation induced grain boundary segregation implies knowing the variation of the L_{ij} with local composition within a large range of composition and at low temperature. For the interstitial diffusion, except for a few values of effective migration energies deduced from resistivity measurements at low temperature, there is almost no experimental data. This is perhaps the reason why phenomenological approaches like the DICTRA software widely used to predict phase transformation kinetics never tried to simulate kinetics of irradiated systems. On the other hand, first principle methods are now able to provide us with accurate values of jump frequencies in alloys not only for the vacancy diffusion mechanism [5] but also for the interstitials in the split configuration (dumbbell) [6–8]. Therefore an appropriate solution to estimate the L_{ij} is to start from an atomic diffusion model for which the parameters are fitted on first principle calculations. The time evolution of the system is then described by a master equation.

Several methods have adopted this point of view but only two of them are general enough to account for the different diffusion mechanisms and short range order effects over a wide range of compositions explored by the alloys under irradiation: the Path Probability Method (PPM) [9,10] and the self-consistent mean field (SCMF) theory [3]. However, the PPM has been mainly applied to diffusion of vacancy in body centered cubic alloys (BCC). Numerical approaches like Monte Carlo simulations have proved their efficiency, however, the achievement of a predictive model by these methods is limited to short ranges of composition and temperature and they become rapidly unworkable when for example binding energies between interstitials and neighbouring atoms are significant [8,11]. We present the self-consistent mean field theory (SCMF) which was proved to be general enough to recover the results of the previous theories [12,13,2] and to provide diffusion models including short range effects when they were lacking as for example the diffusion of interstitials in a multi-component body centered alloy [14,11,15,16] and the diffusion of vacancies in a face centered cubic alloy (FCC) [13,3].

The principles and results of the SCMF theory are detailed in the previous articles cited above. Section 2 will begin with a presentation of the diffusion atomic models, followed by an introduction of the SCMF theory. The third section is a short presentation of selected results both for vacancies and interstitials, and the last section is a description of the main alternative diffusion models in the objective of comparing them with the present SCMF theory.

2. The SCMF theory

2.1. Atomic diffusion models

The large set of jump frequencies associated to species α in a concentrated alloy is assumed to follow a classical thermally activated form:

$$w_\alpha = \gamma_\alpha \exp\left(-\beta E_\alpha^{\text{mig}}\right) \tag{1}$$

where β is the inverse of the Boltzmann's constant multiplied by temperature T. γ_α is the attempt frequency which is assumed to depend only on the jumping atom, and the term in the exponential is the 'migration enthalpy', that is the difference between the total energy of the system in the initial configuration and when the jumping atom is at the saddle point. w_α depends on local concentration. We assume a bond breaking model for both energies limited to nearest neighbour (nn) pair interactions of the migration energy. Such a model satisfies the detailed balance and insures a consistency between kinetics and thermodynamics [9,17]. Therefore, the migration energy depends on the chemical species of the jumping and surrounding atoms:

$$E_\alpha^{\text{mig}} = \beta \left(\sum_{k,\beta} \gamma_{i'k}^s V_{\alpha\beta}^s n_k^\beta - \sum_{k,\beta} \gamma_{ik}^s V_{\alpha\beta} n_k^\beta \right) \tag{2}$$

where the first term in the exponential corresponds to the new binding energies created by the atom at the saddle point and the second term to the binding energies to be cut by the exchanging species at the initial state. $\gamma_{i'k}^s$ is equal to 1 if site k is an nn site of atom α at the saddle point and zero otherwise; and γ_{ik}^s is equal to 1 if lattice sites i and k are nn. Occupation of a site i is specified by a set of occupation numbers (n_i^α): n_i^α is equal to 1 if site i is occupied by α and 0 otherwise. Note that the mean occupancy of site i by species α is the ensemble average $\langle n_i^\alpha \rangle$. The interactions are fitted on first principle calculations and on existing experimental data (mainly phase diagrams and diffusion coefficients). This type of model was applied to real systems with vacancy like the ferritic steels [18] and the aluminium alloys [19,20]. It should be noted that first principle methods are now able to compute the whole atomic jump frequency [6–8,18].

An adaptation of this breaking bond model for the complex interstitial jump mechanism was recently introduced in a body centered cubic (BCC) alloy [15,16]. A first part was devoted to an extension of the Cluster Variation Method (CVM) [21] to take into account the dumbbell configuration of interstitial defects followed by a calculation of the relative amount of dumbbell compositions and the averaged local surrounding of a given species as a function of nominal composition and temperature [15]. Single jumps of the defect involve the displacement of one atom of the dumbbell toward a target atom to form a new defect while the remaining atom is left in substitutional position:

$$AB_\alpha + C \rightarrow A + BC_\beta \tag{3}$$

where we can see that the defect can change composition and orientation within one jump. We take the example of Fe-rich or Fe–Cr BCC alloys, where the stable configuration of the dumbbell has a $\langle 110 \rangle$ orientation (cf. Fig. 1). Two types of jump are allowed, i.e. a simple translation T with $\alpha = \beta$ and a rotation–translation RT which combines a translation and a rotation of 60 degrees.

To determine the jump frequency corresponding to Eq. (3), we consider every bond involved in the initial configuration $AB_\parallel C$ and that is broken during the jump. For convenience, we will denote $k = 1, 7$ the neighbours of the
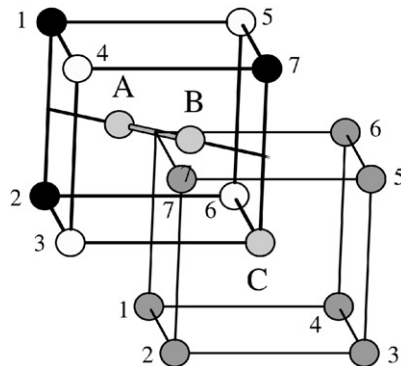

Fig. 1. Nearest neighbours of an $AB_\parallel C$ configuration. In the text, neighbours of the dumbbell are denoted k and neighbours of C are denoted k'; black atoms $k = 1, 2$ are on target sites for A, $k = 7$ is a target for B, and white atoms are on nn non-target sites.

Fig. 1. Plus proches voisins d'une configuration $AB_\parallel C$. Dans le texte, les voisins du dumbbell sont notés k et ceux de C k'; les atomes noirs $k = 1, 2$ sont sur les sites cibles de A, $k = 7$ est un site cible de B, et les atomes blancs sont les sites plus proches voisins et non-cibles du dumbbell.

dumbbell and $k' = 1, 7$ the neighbours of the target atom, and use the numeration of Fig. 1. The migration energy associated to a given configuration is:

$$E_{AB/C}^{\mathrm{mig}} = E^{(s)} - \sum_{D, k'=1,7} V_{CD} n_{k'}^D - \epsilon_{AB} - V_{AB_\parallel C} - \sum_{D, k=1,2} V_{BA_\parallel D} n_k^D - \sum_{D, k=3,6} V_{AB_\perp D} n_k^D$$
$$- \sum_{D, k=7} V_{AB_\parallel D} n_k^D \tag{4}$$

where $E^{(s)}$ is a contribution of the saddle point position. Note that the binding energy of the dumbbell itself ϵ_{AB} must not be forgotten. The attempt frequency introduced in Eq. (1) is assumed to depend only on the moving atom B.

2.2. The phenomenological coefficients L_{ij}

In the SCMF theory, the phenomenological coefficients are calculated using a non-equilibrium function of a system submitted to an homogeneous, constant in time, and vanishingly low gradient of chemical potential. Following Vaks [22], we express the non-equilibrium distribution function in terms of the equilibrium distribution function plus a time dependent *effective* Hamiltonian $\hat{h}(t)$:

$$\widehat{P}(\mathbf{n}, t) = \widehat{P}_0(\mathbf{n}) \widehat{P}_1(\mathbf{n}, t) \tag{5}$$

where $\widehat{P}_0(\mathbf{n}) = \exp[\beta(\Omega + \sum_{i, A} N_i^A \mu_A - H)]$ is the equilibrium distribution function with Ω a normalization constant and μ_A the chemical potential of chemical species A. The interactions of the Hamiltonian H are the binding energies introduced in Eqs. (2) and (4). Also, $\widehat{P}_1(\mathbf{n}, t) = \exp\{\beta[\delta\Omega(t) + \sum_{\alpha, i} \delta\mu_i^\alpha(t) n_i^\alpha - \hat{h}(t)]\}$ is the non-equilibrium contribution which is equal to one at equilibrium.

By analogy with the physical Hamiltonian, the time-dependent effective Hamiltonian may be written as a polynomial function of the occupation numbers[1]

$$\hat{h}(t) = \frac{1}{2!} \sum_{\alpha\beta, i \neq j} v^{(2)}{}_{ij}^{\alpha\beta}(t) n_i^\alpha n_j^\beta + \frac{1}{3!} \sum_{\alpha\beta\gamma, i \neq j \neq k} v^{(3)}{}_{ijk}^{\alpha\beta\gamma}(t) n_i^\alpha n_j^\beta n_k^\gamma + \cdots \tag{6}$$

where $v^{(N)}{}_{ij\ldots}^{\alpha\beta\cdots}(t)$ are time dependent N-body effective interactions, which are unknown and must be obtained by solving the master equation:

$$\frac{\mathrm{d}\widehat{P}(\mathbf{n}, t)}{\mathrm{d}t} = \sum_{\tilde{\mathbf{n}}} \left[\widehat{W}(\tilde{\mathbf{n}} \to \mathbf{n}) \widehat{P}(\tilde{\mathbf{n}}, t) - \widehat{W}(\mathbf{n} \to \tilde{\mathbf{n}}) \widehat{P}(\mathbf{n}, t) \right] \tag{7}$$

where $\widehat{W}(\mathbf{n} \to \tilde{\mathbf{n}})$ is the transition probability from a configuration $\mathbf{n}$ to a configuration $\tilde{\mathbf{n}}$ per time unit: it is defined in terms of the microscopic frequencies controlling the diffusion of atoms (see Eq. (1)).

To solve the master equation it is convenient to multiply Eq. (7) by the occupation numbers n_i^α, $n_i^\alpha n_j^\beta$, $n_i^\alpha n_j^\beta n_k^\gamma$, etc. and average the products over all the configurations. That yields the kinetic equations for the mean occupations $\langle n_i^\alpha \rangle$, $\langle n_i^\alpha n_j^\beta \rangle$, $\langle n_i^\alpha n_j^\beta n_k^\gamma \rangle$, etc. Under steady state conditions those kinetic equations should be equal to zero. A pair effective interaction $v_{ij}^{\alpha\beta}$ is introduced and calculated to satisfy the stationarity of the mean two-site occupations $\langle n_i^\alpha n_j^\beta \rangle$. The obtained values give then an estimation of the correlation contribution to the L_{ij}. Indeed a careful treatment of the mean two-site occupations by means of these pair effective interactions allows to take into account a possible jump back of a point defect after a first jump which corresponds to a correlated event in the jump sequence. Note that, if stationarity is also required for the mean three-site occupations, in addition to the pair effective interactions the triplet effective interactions are to be considered. Those triplets become non negligible in alloys with high disparities of jump frequencies between two atomic species (frequency ratios greater than 10^3) [2].

A level of approximation of the SCMF theory will be fixed by two hierarchies. The first one is determined by the number of effective interactions used to describe the kinetic correlations. It determines the number of kinetic equations to solve. Whereas for the vacancy mechanism the first effective interaction to be considered is between

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[1] Referred to the 'cluster expansion theorem' [23], any quantity which is a function of configuration only can be written in the form of Eq. (6).

two nearest neighbours, for the interstitial it is between the two atoms forming a dumbbell. In a binary alloy, the first shell approximation which considers the first pair effective interaction leads to analytical expressions of the transport coefficients. The second level of approximation concerns the statistical approximation used to calculate the average over all the configurations of the jump probabilities multiplied by the occupation numbers. In opposition to a point approximation, a pair approximation keeps the variation of jump frequencies with local concentrations including short range order effects. As a result, a pair approximation of the SCMF theory recovers the exact L_{ij} of the multi-frequency diffusion models of dilute binary alloys [24] and predicts their variation as a function of the solute concentration. Both approximations, point and pair approximations were first developed for the vacancy diffusion mechanism [13,3] and generalized to the more complex diffusion mechanism of the interstitial dumbbell configuration [15,16].

3. Some examples of results

Successive approximations of the SCMF theory were used to study the convergence of the results with different values of interactions and attempt frequencies. As explained above, for a good description of short range order effects it is necessary to use a better statistical approximation than the point approximation. These short range effects were recognized to be essential for the calculation of the uncorrelated part of the phenomenological coefficients. Indeed, errors of several orders of magnitude could be avoided by using a statistical pair approximation instead of the point approximation in particular to calculate the probability of forming atom-point defect pairs on nn sites [3,16]. Fig. 2 is an illustration of this point for the interstitial diffusion mechanism in BCC alloys (the details of the simulations and calculations are given in [16]). One observes that a statistical pair approximation of the uncorrelated part of the phenomenological coefficients is required to converge to the exact results of the Monte Carlo simulations, whereas a point approximation is sufficient to predict collective correlation coefficients in good agreement with the Monte Carlo simulations.

The variation of a vacancy–atom exchange frequency with local composition may produce strong correlation effects as for example a negative sign of the off-diagonal correlation coefficients with the extreme case of an atomic flux inversion. A statistical pair approximation of the SCMF theory did predict this effect in specific FCC alloys with nn interactions (cf. Fig. 3 and [3] for the details of the calculation). Anthony [25] was the first one to deduce the
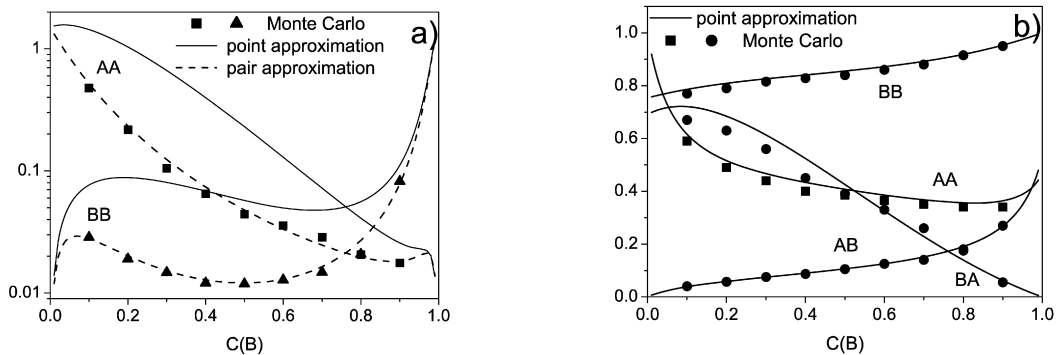

Fig. 2. Transport coefficients as a function of the concentration $C(B)$ in a BCC solid solution AB with an interstitial concentration $c_I = 0.002$: (a) uncorrelated transport coefficients $L_{AA}^{(0)}$ and $L_{BB}^{(0)}$ in the reduced unit of the attempt frequency multiplied by the square of the lattice parameter, divided by the atomic volume and temperature; and (b) the correlation coefficients. Interaction energies are all equal to zero except the one between an AA dumbbell and a B substitutional target atom ($\beta V_{AA_\parallel B} = -2$). The attempt frequencies are equal and the temperature is equal to 1200 K. The symbols stand for Monte Carlo simulations, the solid lines for the point approximation and dashed lines for the pair approximation. In (b) only curves associated to the point approximation are plotted since the pair approximation curves are almost the same.

Fig. 2. Coefficients de transport dans une solution solide cubique centré AB en fonction de la concentration $C(B)$ avec une concentration d'interstitiel égale à $c_I = 0{,}002$: (a) coefficients non-corrélés $L_{AA}^{(0)}$ et $L_{BB}^{(0)}$ avec pour unité réduite la fréquence d'attaque associée à l'atome A multipliée par le carré du paramètre de maille divisé par le volume atomique ; (b) coefficients de corrélation. Les énergies d'interaction sont toutes égales à zéro sauf celle entre le dumbbell AA et l'atome cible substitutionel B ($\beta V_{AA_\parallel B} = -2$). Les fréquences d'attaque de A et B sont égales. La température est égale à 1200 K. Les simulations Monte Carlo sont représentées par les symboles, l'approximation de point par les lignes continues et l'approximation de paire par les lignes pointillées. Dans (b) seules les courbes associées à l'approximation de point sont représentées puisque celles associées à l'approximation de paire sont pratiquement confondues.
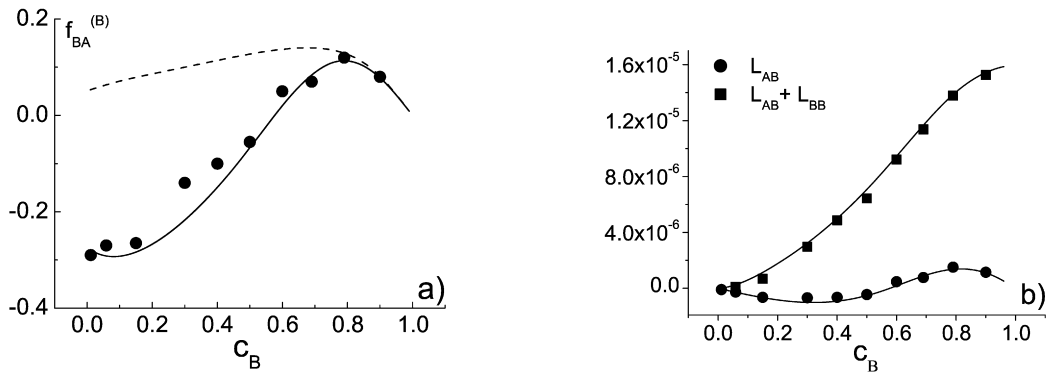
Fig. 3. Transport coefficients as a function of the concentration c_B in a FCC solid solution AB with a vacancy concentration $c_V = 10^{-8}$: (a) collective correlation coefficients $f_{BA}^{(B)}$; and (b) phenomenological coefficient L_{AB} and the sum $(L_{AB} + L_{BB})$ in the reduced unit of the attempt frequency of atom A multiplied by the square of the lattice parameter, divided by the atomic volume and temperature. Interaction energies are all equal to zero except the interaction of a migrating A atom at the saddle point with a nearest neighbour B atom: $\beta V_{AB}^{(s)} = -1.55$. The attempt frequency ratio ν_B/ν_A is equal to 16. The temperature is equal to 3000 K. The symbols stand for Monte Carlo simulations, the solid lines for the pair approximation and dashed line for the point approximation.

Fig. 3. Coefficients de transport en fonction de la concentration c_B dans une solution solide cubique à faces centrées avec une concentration de lacunes $c_V = 10^{-8}$: (a) coefficient de corrélation $f_{BA}^{(B)}$; (b) coefficient phénoménologique L_{AB} et la somme $(L_{AB} + L_{BB})$ avec pour unité réduite la fréquence d'attaque associée à l'atome A multipliée par le carré du paramètre de maille divisé par le volume atomique. Les énergies d'interaction sont toutes égales à zéro sauf celle entre l'atome qui saute en position de col avec un atome B en position de plus proche voisin : $\beta V_{AB}^{(s)} = -1,55$. Le rapport des fréquences d'attaque ν_B/ν_A est égal à 16. La température est égale à 3000 K. Les simulations Monte Carlo sont représentées par les symboles, l'approximation champ moyen de point par la ligne pointillée et l'approximation de paire par les lignes continues.

complete Onsager matrix of FCC dilute aluminum alloys from an ensemble of diffusion and solute segregation experiments. He related the amount of solute segregation observed at the proximity of cavities formed at the interface between the alloy and the aluminum oxide to the flux of solutes. For a binary alloy AB, he formulated the solute flux J_B in terms of the gradient of vacancy chemical potential $\nabla \mu^v$ and the phenomenological transport coefficients L_{ij}:

$$J_B = (L_{AB} + L_{BB})\nabla\mu^v = L_{BB}^{(0)}(f_{BA}^{(B)} + f_{BB})\nabla\mu^v \tag{8}$$

whereas the vacancy flux is equal to the opposite sum of the atomic fluxes. In Anthony's experiments, the gradient of vacancy chemical potential, $\nabla\mu^v$, was formed during a quench from high temperature but could also be produced by irradiation. Usually we observe an inverse Kirkendall effect which means that atomic fluxes are in the opposite direction to the vacancy flux. But it can be that an atomic species follows the vacancy flux. It happens when $f_{BA}^{(B)}$ and the sum of the correlation coefficients appearing in Eq. (8) are negative. Anthony observed both negative and positive sign of the off-diagonal coefficient $f_{BA}^{(B)}$ depending on the chemical nature of solute B in aluminum A. Such a type of measurement does not exist in concentrated alloys. Recent first principle calculations of atomic jump frequencies in dilute alloys Fe(Cu) [26] and Fe(P) [27,7] lead to a negative sign of the sum entering Eq. (8). Although the calculation for P is partly based on empirical potentials and would require a new calculation with the recent first principle data of Ref. [7]. Thus under irradiation, P and Cu are expected to be dragged by vacancies and segregated at point defect sinks as long as P and Cu concentrations remain low. Indeed, Fig. 3 shows an example where $f_{BA}^{(B)}$ and related L_{AB} are negative over a large range of solute concentration but the sum of the phenomenological coefficients $(L_{AB} + L_{BB})$ determining the sign of the solute flux becomes positive as soon as c_B is greater than 0.01.

4. The diffusion models

A phenomenological approach like DICTRA was developed to simulate diffusion-controlled phase transformations using thermodynamic and kinetic data of CALPHAD [28]. The starting point for the model is an atomic mobility for element B defined as the tracer diffusion coefficient D_{B*} divided by temperature and fitted on the experimental data of D_{B*}. The diagonal term of the Onsager matrix L_{BB} is assumed to be proportional to D_{B*}. In other words the corresponding correlation terms, f_B and f_{BB}, are considered to be equal and the off-diagonal terms of the Onsager

matrix are neglected. Although this method is claimed to be assessed kinetically it may produce wrong predictions when extrapolated to other alloy compositions and temperatures especially in concentrated alloys for which f_B differs from f_{BB}. But, in concentrated alloys, there is no experimental work for which every term of the Onsager matrix is measured. It is then difficult to validate or invalidate a diffusion model. In the limited case of dilute alloys, the experimental work of Anthony is an example which invalidates the CALPHAD technique since non-zero negative or positive off-diagonal terms are observed [25]. The previous section emphasized the importance of the amplitude and the sign of those off-diagonal terms for the prediction of grain-boundary segregation induced by irradiation. Note that the phase field method widely used to describe microstructure evolutions uses the same diffusion formalism than DICTRA, although recently some authors succeeded in constructing phase field equations from a microscopic model of direct exchange between atomic species [29]. In principle, this approach should lead to the definition of a complete Onsager matrix for a point defect diffusion mechanism.

The first models starting from vacancy jump frequencies were restricted to dilute binary solutions in which a limited number of frequencies were involved and only the mixing enthalpy between vacancy and atomic species was accounted for [30,24]. In concentrated alloys, the number of distinct jump frequencies becomes very large. To overcome such a difficulty Manning [31] (and earlier references cited therein) based his theory on a random lattice gas model where atoms do not interact and where vacancies jump at a frequency which only depends on the species they exchange with (two frequencies in a binary alloy). Using complex arguments Manning could express the correlation factors as a function of the few jump frequencies [31]. His expressions were reformulated and improved using a self-consistent formalism and extended to finite vacancy concentrations [32,2]. Such diffusion models which consider a limited number of jump frequencies already make appear spectacular correlation effects like a percolation limit when the host atoms are immobile. But they provide with a very simplified view of thermodynamics and are not appropriate to study kinetics of phase transformation controlled by both the transport properties and the thermodynamic driving force. Some attempts were made to incorporate short range order in a Manning type formulation of the phenomenological coefficients L_{ij} but coherency with thermodynamics was not guaranteed [33,34].

In the case of a vacancy diffusion in a BCC alloy, the first shell and pair approximations of the SCMF theory lead to the same kinetic equations than the PPM ones [9]. Although, those two mean-field like approximations use different approaches. The SCMF theory introduces pair effective interactions to ensure the steady state conditions for the mean occupation of a pair of nn sites. The PPM considers the ensemble of one jump transition variables of a pair of species on two nn sites and associates to it a so-called free energy. The transport coefficients are deduced from the most probable path by minimizing this so-called free energy with respect to the transition variables of the pair of sites under the constraint that the sum of transition variables is normalized to one. The concepts introduced by both approaches remind us the two methods to establish the CVM for thermodynamics [21]. First one consists in decomposing the total distribution function in local distribution variables associated to pairs of nn sites. This pair distribution is defined in terms of the interaction between the two atoms forming the pair and effective pair interactions accounting for the interactions between the atoms of the pair and the atoms outside. Those effective interactions are calculated in such a way that an appropriate product of these pair distributions is equal to the total distribution function. The second derivation of the CVM is a variational approach where the free energy of the system is an approximate function of pair macro-variables (mean occupations of a pair of nn sites). The equilibrium free energy is assumed to be the minimum of the approximate free energy with respect to the pair macro-variables under the constraint that the sum of macro-variables related to a pair of sites is normalized to one.

The particularity of the SCMF formalism is to separate the statistical approximation used to calculate the thermodynamic quantities from the kinetic approximation used to calculate the correlation effects. While the PPM considers a statistical pair approximation both for the equilibrium averages and for the calculation of the most probable path between two successive times, the SCMF theory uses a statistical point approximation for the equilibrium averages and a pair approximation like for the kinetic correlations to calculate the exact value of the self-diffusion correlation factor [12] or a 'multiplet approximation like' with N-body effective interactions to study percolation effects in alloys with high jump frequency ratios [2]. That flexibility allows one to tackle complex diffusion mechanisms and to be the first theory to propose a calculation of the transport coefficients for the dumbbell mechanism in BCC concentrated alloys [14–16]. We justify this two-level treatment by the fact that correlations between kinetic paths and correlations between thermodynamic variables are fundamentally different. For example, at high temperature the thermodynamic correlations are negligible although the kinetic correlations can be high.

5. Conclusion

The SCMF theory based on a microscopic model of vacancy and interstitial jumps yields general expressions of the L_{ij}. It allows a sound description of diffusion and coupled fluxes of atoms and point defects in multi-component alloys. The limitations and future improvements of the SCMF approach are easily related to the statistical approximation of the thermodynamic correlations and to the time-dependent effective interactions used to describe the kinetic correlations. A first example of application emphasizes the importance of using a better statistical approximation than the point approximation to estimate the probability of an atom-point defect pair and the resulting transport coefficients. As a second example of application, the SCMF theory tackles the variation of sign of an off-diagonal L_{ij} and predicts a possible inversion of solute flux with respect to the vacancy flux in concentrated alloys. Finally, the SCMF theory is compared to the main existing models and is shown to be essential to describe diffusion in alloys under irradiation.

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