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Split interstitials in an interacting bcc alloy. II. Transport coefficients

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The transport coefficients are derived in a concentrated interacting body centered cubic alloy for diffusion with the dumbbell mechanism. We use the self-consistent mean field theory in both point and pair approximations on the basis of the first paper of the series, and present two independent approximations (first and second shell approximations) for the calculation of the corresponding correlation coefficients. Correlation coefficients and uncorrelated transport coefficients obtained by those approximations are compared with Monte Carlo simulations for different sets of interactions. In the specific case of a strong clustering tendency and/or strong dumbbell-atom interactions, good agreement with Monte Carlo simulations requires a statistical pair approximation for the uncorrelated transport coefficients and a second shell approximation for the correlation coefficients.

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I. INTRODUCTION

After having treated the thermodynamics of dumbbells in an interacting concentrated body centered cubic (bcc) alloy,[1] we use those results to investigate the kinetics of the alloy and calculate the associated transport coefficients. All notations will be conserved.

Dumbbell diffusion in such an interacting concentrated alloy has actually never been investigated, mainly due to the geometrical complexity of the dumbbell mechanism. A first simplification was to consider a noninteracting concentrated alloy.[2,3] Interactions have been introduced up to now only in the case of dilute bcc[4] and face centered cubic[5] (fcc) alloys. In contrast, for the vacancy mechanism, atomic interactions were introduced via a "bond-breaking" model both in bcc[6] and, more recently, in fcc alloys using the self-consistent mean field (SCMF) theory.[7] We take advantage of those previous treatments of concentrated interacting alloys for this simple mechanism to extend it to the dumbbell mechanism. The fcc structure has not been selected for this study, despite its more simple jump mechanism, because it may require a better statistical approximation than the pair approximation.[8] As a matter of fact, most applications of the pair approximation were performed in bcc structures, at least for the kinetic aspect.[9–12] Recently, a reasonably simple expression of the transport coefficients for the dumbbell mechanism has been derived in a noninteracting concentrated bcc alloy.[3] This result was achieved by using the SCMF theory, initially developed for the vacancy mechanism.[7,13–16] Following the procedure adopted for the vacancy mechanism, we propose a bond-breaking model for the dumbbell jump frequency, which will depend on local composition through thermodynamic interactions. Interactions are restricted to the nearest-neighbor distance, consistent with the statistical description.[1]

We recall in Sec. II the main notations, introduced elsewhere,[3,4] for the description of a system containing dumbbell-type defects and include a generalization of the classical bond-breaking model for the calculation of single jump frequencies w. Section III is then devoted to the expression of the corresponding jump probabilities W, defined as the product of the jump frequency and the probability of the initial configuration, in both point and pair approximations. With the help of those values, we use the SCMF theory in Sec. IV to derive the transport coefficients in various kinetic approximations. Section V gives a brief description of the Monte Carlo simulations performed to validate the theoretical results, which are discussed in the last section: focus is set on the importance of each approximation.

II. ATOMIC MODEL

A. Equilibrium description of the system

The following notations are the same as presented in previous papers,[3,4] extended when necessary to include the atomic interactions.

We consider a number N_s of lattice sites on which N_I defects and N_s+N_I atoms are distributed and describe any configuration of the system by the occupation numbers n_i^a of site i by the species a. Hence, n_i^A is equal to 1 if site i is occupied by an atom A in substitutional position and 0 otherwise. Concerning the defects, $n_i^{AB\alpha}$ is equal to 1 if site i is occupied by a dumbbell of composition AB with the B atom pointing in the α direction and 0 otherwise. It will be convenient to use the generalized site occupation numbers N_i^A and N_i^I referring respectively to the number of A atoms or dumbbells present on site i:

$$N_i^A = n_i^A + 2\sum_{\alpha} n_i^{AA\alpha} + \sum_{\alpha,b\neq A} n_i^{Ab\alpha}, \tag{1a}$$

$$N_i^I = \sum_{\alpha,a,b} n_i^{ab\alpha}, \tag{1b}$$

with the relation

$$\sum_a N_i^a - N_i^I = 1. \tag{2}$$

In each sum, as in the preceding paper, symbols a, b, and c refer to the chemical species and α to the six independent $\langle 110\rangle$ directions.

The internal energy corresponding to any configuration $\mathbf{n}$ of the system is expressed by the Hamiltonian H as

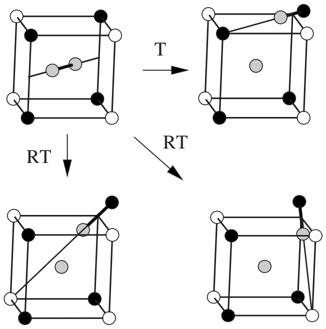

FIG. 1. Jump mechanisms of one dumbbell toward the same target atom.

$$H=\sum_{i,a,b,\alpha}\epsilon_{ab}n_i^{ab_\alpha}+\sum_{i,j,a,b}\gamma_{ij}V_{ab}n_i^a n_j^b+\sum_{i,j,a,b,c,\alpha}\gamma_{ij}V_{ij}^{ab/c}n_i^{ab_\alpha}n_j^c, \tag{3}$$

where $\gamma_{ij}=1$ if i and j are in nearest-neighbor (NN) position and 0 otherwise. The interactions are defined as in Ref. [1] except for the dumbbell-substitutional notation $V_{ij}^{ab/c}$, which refers to $V_{ab_\parallel c}$, $V_{ba_\parallel c}$, or $V_{ab_\perp c}$ as a function of the relative positions of i and j. This energy partly controls the equilibrium probability of any configuration in the grand canonical ensemble:

$$P_0(\mathbf{n})=\exp\left[\beta\left(\Omega+\sum_{i,a}N_i^a\mu_a-H\right)\right], \tag{4}$$

where $\beta=1/k_BT$ is the inverse temperature, Ω is a normalization constant, and μ_a is the chemical potential of the chemical species a. It should be noted that instead of a grand canonical ensemble, we use the semigrand canonical ensemble with a fixed number of sites. A way to include this constraint is to introduce a pseudointerstitial chemical potential μ_I systematically added to the chemical potentials. In other words, μ_A is replaced by $\mu_A+\mu_I$, meaning that an introduction of an atom into the system implies a creation of a dumbbell in order to keep the number of sites constant.

B. Jump frequency model

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:

$$AB_\alpha+C\rightarrow A+BC_\beta, \tag{5}$$

where we can see that the defect can change composition and orientation within one jump. Actually, as the stable configuration of the dumbbell is a $\langle 110\rangle$ orientation, 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°. Those jumps are sketched on Fig. 1, including the twofold degeneracy of the RT mechanism.

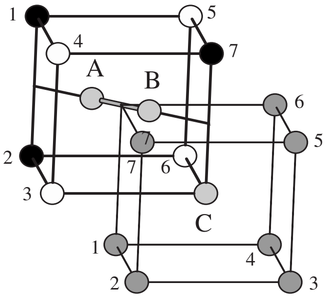

FIG. 2. Nearest neighbors of an $AB_\parallel C$ configuration. In the text, neighbors of the dumbbell are denoted k and neighbors of C are denoted k'; black atoms $k=1,2$ are on target sites for A, $k=7$ is a target for B, and white atoms are on NN nontarget sites. Note that in Eq. (8), $k=8$ will be used for the site of C.

To ensure the consistency with the statistical description, we introduce a bond-breaking model for the jump frequency associated with Eq. (5): the principle is to break all binding energies involved in the initial configuration $AB_\parallel C$. For convenience, we will denote $k=1,7$ the neighbors of the dumbbell and $k'=1,7$ the neighbors of the target atom, and use the numeration of Fig. 2. The migration energy associated to a given configuration is

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

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.

Eventually, the associated jump frequency is written as

$$w_{AB/C}=\gamma_B\exp(-\beta E^{\mathrm{mig}}_{AB/C}). \tag{7}$$

Here, γ_B is an attempt frequency which depends, for simplicity, only on the moving atom B. As in Refs. [3,4], the notation $w_{AB/C}$ denotes the RT mechanism, the simple translation frequency being noted $\tau w_{AB/C}$: $\tau=0$ discards the translation mechanism and $\tau=1$ sets a degeneracy between the three possible jumps.

The last mechanism to take into account is the on-site 60° rotation of the defect. With the same notations, one can write a rotation barrier

$$E^{\mathrm{rot}}_{AB}=E^{(s)}_{AB}-\epsilon_{AB}-\sum_{d,k=1,2}V_{BA_\parallel d}n_k^d-\sum_{d,k=3,6}V_{AB_\perp d}n_k^d-\sum_{d,k=7,8}V_{AB_\parallel d}n_k^d, \tag{8}$$

which leads to the rotation frequency

$$w^R_{AB}=\gamma_R\exp(-\beta E^{\mathrm{rot}}_{AB}). \tag{9}$$

III. AVERAGE JUMP PROBABILITY

In the preceding section, energy barriers as well as jump or rotation frequencies were all implicitly dependent on the local surroundings of the dumbbell-target pair. However, previous works on the SCMF formalism[3,4] have highlighted the importance of the mean probability of a jump of type $AB\rightarrow C$, defined as

$$W_{AB/C} = \langle n_i^{AB_\alpha} n_j^C w_{AB/C} \rangle, \tag{10}$$

where $\langle \cdot \rangle$ denotes an equilibrium average over all possible configurations. As the frequency itself involves all neighboring atoms, the configuration to consider within the brackets is the one sketched in Fig. 2 and contains 16 atoms. We call $N_{AB/C}$ any realization of this configuration, i.e., any configuration $\{D_k, D_{k'}\}$ for the sites $k=1,7$ and $k'=1,7$:

$$N_{AB/C} = n_i^{AB_\alpha} n_j^C \prod_{k=1,7} n_k^{D_k} \prod_{k'=1,7} n_{k'}^{D_{k'}}. \tag{11}$$

$N_{AB/C}$ is nothing but a 16-site occupation number, which is equal to 1 if the $\{D_k D_{k'}\}$ set is the configuration around the AB/C pair and 0 otherwise. The calculation of $W_{AB/C}$ is derived in the following paragraphs in the statistical point and pair approximations.

A. Point approximation

The use of the point approximation to calculate the jump probability is not trivial because of the presence of the exponential terms. Hence, it is not sufficient to merely count the configurations and use the property of the occupation numbers:

$$n_k^a n_k^b = \delta_{ab} n_k^a, \tag{12}$$

where δ_{ab} is the Kronecker symbol. We hereby adopt the averaging process already used for the vacancy mechanism, which consists in decoupling all occupancies, including those in the exponential term.[13,14] The resulting expression of the average jump frequency is

$$W_{AB/C}^{(1)} = x_{AB} c_C \bar{w}_{AB/C}^{\text{point}}. \tag{13}$$

Here, c_C is the concentration of C, x_{AB} corresponds to the equilibrium value calculated in the point approximation [Eqs. (12) and (13) of Ref. 1], and $\bar{w}_{AB/C}^{\text{point}}$ is a mean jump frequency expressed as

$$\bar{w}_{AB/C}^{\text{point}} = \gamma_B \frac{\exp(-\beta E^{(s)})}{\tilde{E}_{AB} \tilde{E}_C}, \tag{14}$$

where the $\tilde{E}$'s are the point approximation embedding factors given by Eqs. (14) and (15) in Ref. 1.

In the same manner, the rotation probability W_{AB}^R is expressed as

$$W_{AB}^R = x_{AB} \gamma_R \frac{\exp(-\beta E_{AB}^{(s)})}{\tilde{E}_{AB}}. \tag{15}$$

Note that the saddle point contributions have been assumed independent of the local surroundings, so that they remain unchanged through the averaging process.

B. Pair approximation

A jump probability $w_{AB/C}$ of Eq. (7) depends on the local surroundings of the pair AB-C. The variable $N_{AB/C}$ defined in Eq. (11) represents the realizations of these local surroundings. Thus, the calculation of a mean jump probability requires to know the probability of the $N_{AB/C}$ realizations.

On the one hand, a lattice of NN bonds put on a bcc lattice is a Bethe lattice since it does not contain closed circuits of NN bonds. It is then possible to deduce the probability of one realization of $N_{AB/C}$ as a function of pair correlations.[8] Following the procedure of Kikuchi[6] applied to the transport via vacancy and extended to the study of composition fluctuations,[17] we write

$$\langle N_{AB/C} \rangle = x_{AB} c_C \prod_{k=1}^{7} c_{D_k} \prod_{k'=1}^{7} c_{D_{k'}} \prod_{k'=1}^{7} \frac{y_{CD_{k'}}}{c_C c_{D_{k'}}} \frac{y_{AB_\parallel C}}{x_{AB} c_C} \times \prod_{k=1}^{2} \frac{y_{BA_\parallel D_k}}{x_{AB} c_{D_k}} \prod_{k=3}^{6} \frac{y_{AB_\perp D_k}}{x_{AB} c_{D_k}} \frac{y_{AB_\parallel D_7}}{x_{AB} c_{D_7}}. \tag{16}$$

Here, capital letters are used for the D's because those values are conserved during this stage of the averaging process. We may re-express Eq. (16) with the help of the pair approximation variables q determined in Ref. 1:

$$\langle N_{AB/C} \rangle = \frac{(q_{AB} q_C)^8}{(c_{AB} c_C)^7} \prod_{k'=1}^{7} \exp(-\beta V_{CD_{k'}}) q_{D_{k'}} \times \prod_{k=1}^{2} \exp(-\beta V_{BA_\parallel D_k}) q_{D_k} \prod_{k=3}^{6} \exp(-\beta V_{AB_\perp D_k}) q_{D_k} \times \exp(-\beta V_{AB_\parallel D_7}) q_{D_7} \exp(-\beta V_{AB_\parallel C}). \tag{17}$$

One can see that the binding energies appearing in Eq. (17) are exactly the same as in the frequency $w_{AB/C}$ [see Eq. (6), though with an opposite sign]. Thus, to calculate the mean probability $W_{AB/C}$, we can simply multiply each realization of $\langle N_{AB/C} \rangle$ by the corresponding value of $w_{AB/C}$ and sum this product over all possible $\{d_k, d_{k'}\}$ configurations, which leads to

$$W_{AB/C}^{(2)} = \frac{(q_{AB} q_C)^8}{(c_{AB} c_C)^7} \gamma_B \exp[-\beta(E^{(s)} - \epsilon_{AB})] \times \sum_{d_1 \cdots d_7, d'_1 \cdots d'_7} q_{d_1} \cdots q_{d_7} q_{d'_1} \cdots q_{d'_7}, \tag{18a}$$

which is easily transformed into

$$W_{AB/C}^{(2)} = \frac{(q_{AB} q_C)^8}{(c_{AB} c_C)^7} \gamma_B \exp[-\beta(E^{(s)} - \epsilon_{AB})] \left(\sum_d q_d \right)^{14}. \tag{18b}$$

As in the preceding paragraph, an equivalent notation is found for the average rotation probability in the pair approximation:

$$W_{AB}^R = \frac{q_{AB}^8}{c_{AB}^7} \gamma_R \exp[-\beta(E_{AB}^{(s)} - \epsilon_{AB})] \left(\sum_d q_d \right)^8. \tag{19}$$

C. Detailed balance

By construction, interstitial jump frequencies satisfy the detailed balance and the statistical equilibrium function is a steady state solution of the master equation. We demonstrate that the detailed balance is also satisfied by the following averaged jump frequencies:

$$W_{AB/C} = W_{CB/A}. \tag{20}$$

In the point approximation, this result is straightforward by examining the expression of x_{AB}, Eq. (3) in Ref. 1: the term $\widetilde{E}_{AB}$ eliminates in the jump probability $W_{AB/C}$ and the detailed balance is trivially fulfilled.

In the pair approximation, we eliminate again the q_{AB} and x_{AB} values by use of Eq. (28) in Ref. 1 and obtain an expression of $W_{AB/C}$ as a function of the Lagrange multipliers:

$$W^{(2)}_{AB/C} = \gamma_B \exp[-\beta(\lambda_A + \lambda_B + \lambda_C + \lambda_I + E^{(s)})]\left(\sum_d q_d\right)^{14} \tag{21a}$$

$$= W^{(2)}_{CB/A}. \tag{21b}$$

This property is extended to the case when one of the k or k' sites is occupied by a given E atom, the average being performed on every other site. The corresponding jump probability is $W^{(1)}_{AB/C}c_E$ in the point approximation and becomes $W^{(2)}_{AB/C}Q_E$ in the pair approximation, where Q_E is a weighted local surrounding variable:

$$Q_E = \frac{q_E}{\sum_i q_i}, \tag{22}$$

which does not depend on whether the E atom is a nearest neighbor of the dumbbell or of the target.

IV. TRANSPORT COEFFICIENTS

The transport coefficients L of an alloy relate the macroscopic fluxes to the thermodynamic forces applied to the system, here the gradients of chemical potentials:

$$J_A = -\sum_B L_{AB} \nabla \mu_B. \tag{23}$$

Within those coefficients, the correlation effects contain the "nonrandom" character of the atom and defect paths. They can be expressed by the correlation coefficients f by

$$J_A = -L^{(0)}_{AA}\left(f_{AA} \nabla \mu_A + \sum_{B\neq A} f^{(A)}_{AB} \nabla \mu_B\right), \tag{24}$$

where $L^{(0)}_{AA}$ is named "uncorrelated transport coefficient."

The SCMF theory has proven to be an efficient tool for calculating the transport coefficient in an interacting alloy for the vacancy mechanism,[7,13,14,16] and it was recently extended to noninteracting alloys[3] and to dilute alloys[4] for the dumbbell mechanism. We first recall the key features of the model, then derive the results for an interacting alloy. All necessary equations for the present calculations are to be found in Ref. 3: as the derivation can be lengthy for the dumbbell mechanism, we will only give the modifications induced by the presence of thermodynamic interactions.

A. Self-consistent mean field theory

The model we consider is a system close to a homogeneous equilibrium state, submitted to a homogeneous set of gradients of chemical potentials. The SCMF theory assumes that a nonequilibrium state is characterized by a modified partition function containing the given nonequilibrium chemical gradients and a set of unknown "effective interactions," which stand for the dynamic correlations between atomic sites.

The time evolution of the system is described by the master equation:

$$\frac{dP(\mathbf{n},t)}{dt} = \sum_{\tilde{\mathbf{n}}} [w(\tilde{\mathbf{n}} \to \mathbf{n})P(\tilde{\mathbf{n}},t) - w(\mathbf{n} \to \tilde{\mathbf{n}})P(\mathbf{n},t)], \tag{25}$$

where $P(\mathbf{n},t)$ is the nonequilibrium probability of the configuration $\mathbf{n}$, and $w(\mathbf{n}\to\tilde{\mathbf{n}})$ is the transition frequency from configuration $\mathbf{n}$ to configuration $\tilde{\mathbf{n}}$.

We use then the first assumption of the model, which states that the system must be in steady state: under this condition, one determines the value of the effective interactions by solving kinetic equations of the type

$$\frac{d\langle n_i^{AB_\alpha}\rangle}{dt} = 0, \tag{26a}$$

$$\frac{d\langle n_i^{AB_\alpha} n_j^C\rangle}{dt} = 0. \tag{26b}$$

Eventually, transport coefficients are identified by recognizing the fluxes between two neighboring sites in the one-site kinetic equation:

$$\frac{d\langle N_i^A\rangle}{dt} = -\sum_j \gamma_{ij} J_A^{i\to j}, \tag{27}$$

where γ_{ij} is equal to 1 if i and j are nearest-neighbor sites and 0 otherwise. The accuracy of the model is partly controlled by the truncation of the set of effective interactions, also called "effective Hamiltonian." The first shell approximation reduces the effective Hamiltonian to effective interactions between both atoms of a dumbbell, for which it is sufficient to solve Eq. (26a). In the more accurate second shell approximation, effective interactions between a dumbbell and a neighboring atom are also included, and one has to solve Eq. (26b) in addition to Eq. (26a).

B. Uncorrelated transport coefficients

As the effective interactions stand for the dynamic correlation effects in the alloy, they do not affect the value of the uncorrelated transport coefficient $L^{(0)}_{AA}$, so that it depends on the statistical approximation only. Actually, in a noninteracting alloy, it is simply expressed as the mean probability of the displacement of an A atom between two given neighboring sites (see Ref. 3):

$$L_{AA}^{(0)} = 3(2+\tau)\sum_{B,C} W_{BA/C}. \tag{28}$$

The factor 3 comes from the fact that three orientations of BA_α allow a jump of A toward the same given target site; the factor $(2+\tau)$ stands for the two RT jumps and the one T jump which are possible from any initial configuration. Note that the rotation frequencies do not appear in the uncorrelated motion of the dumbbell, as it causes no atomic displacement.

Formally, the result is absolutely equivalent in an interacting alloy, except that the jump probability $W_{BA/C}$ is replaced by $W_{BA/C}^{(1)}$ or $W_{BA/C}^{(2)}$ as a function of the chosen statistical approximation.

It should be noticed that the present expression of $L_{AA}^{(0)}$ relates a flux between two neighboring lattice sites to the difference of chemical gradients between both sites: it differs from the classical definition of Eq. (23) by a constant factor $4k_BT/na^2$ ($2a$ is the lattice parameter and n the number of atoms by unit volume), which will be omitted in the rest of the paper.

C. Correlation coefficients

The correlation part of the transport coefficient implies the solving of Eqs. (26), and the results strongly depend on the kinetic approximation.

In the first shell approximation, Eq. (26a) contains only terms of the type $\langle n_i^{AB_\alpha} n_j^C w_{AB/C}\rangle$, so that the results obtained for an interacting alloy are still formally equivalent to the noninteracting case and it is sufficient to replace $W_{AB/C}$ by its new value $W_{AB/C}^{(i)}$ $(i=1,2)$. In particular, one can maintain the analytical expression of the correlation coefficients in the first shell approximation:

$$f_{AA} = 1 - \frac{(2+\tau)W_{AB/X}^2/W_A}{W_{AB}+2W'}, \tag{29a}$$

$$f_{AB}^{(A)} = \frac{(2+\tau)W_{AB/X}W_{BA/X}/W_A}{W_{AB}+2W'}, \tag{29b}$$

and the coefficients f_{BB} and $f_{BA}^{(B)}$ are obtained by inverting A and B in the above expressions. To shorten these formulations, we have used the following compact notations:

$$W_{AB/X} = \sum_C W_{AB/C}, \tag{30a}$$

$$W_A = \sum_{B,C} W_{BA/C}, \tag{30b}$$

$$W_{AB} = (2+\tau)(W_{AB/X}+W_{BA/X}) + W_{AB}^R, \tag{30c}$$

$$2W' = (1+\tau)(W_{AB/A}+W_{BA/B}). \tag{30d}$$

In the second shell approximation, on the contrary, terms of the form $\langle n_i^{AB_\alpha} n_j^C n_k^D w_{AB/C}\rangle$ appear in the two-site kinetic equations (see Ref. 3). As was shown in Sec. III C, such expressions are equal to $c_D W_{AB/C}^{(1)}$ in the point approximation and to $Q_D W_{AB/C}^{(2)}$ in the pair approximation. Thus, the calculation of the transport coefficients in an interacting alloy involves only the replacement of the quantities cW by $cW^{(1)}$ or $QW^{(2)}$ within the very same kinetic equations as in Ref. 3.

As a final remark, note that the kinetic approximation (first and second shells, based on the number of kinetic equations) and the statistical approximation (point or pair approximation) are treated independently in the SCMF formalism. In contrast, in the path probability method approach,[6] there is only one hierarchy of approximation, the statistical and kinetic approximations being set at the same level.

V. MONTE CARLO SIMULATIONS

As was done for the repartition of the dumbbells, we tested the results of our kinetic model against reference values given by the same kinetic Monte Carlo simulations. The transport coefficients were calculated following the generalized Einstein relations:[18]

$$Vk_BTL_{AB} = \frac{\langle R_A R_B\rangle}{6t}, \tag{31a}$$

$$f_{AB}^{(A)} = \frac{\langle R_A R_B\rangle}{\langle M_A\rangle a^2}, \tag{31b}$$

where V is the atomic volume, R_A the total displacement of all atoms of species A during the simulation time t, and M_A the number of jumps performed by all atoms of species A. The brackets stand for an average over many observations, where each observation consists in a trajectory of the defect. We performed our simulations with 10^5 observations, such that each one contains at least an average of five jumps by atom of the slowest species. These conditions ensured a relative error of 2% in the transport and correlation coefficients. The uncorrelated transport coefficients were deduced from those values as

$$L_{AA}^{(0)} = \frac{L_{AA}}{f_{AA}}. \tag{32}$$

The energetic description of the explored alloy systems is the same as in the preceding study, but the kinetic description is hereby fundamental, while it had no effect on the equilibrium properties. For the sake of simplicity, the RT and T mechanisms were allowed with $\tau=1$. Alloys without interactions (hereafter referred to as system I) were already treated elsewhere[3] and are not studied here. In the systems exhibiting only substitutional interactions (hereafter referred to as system II), we assumed $E^{(s)}$ of Eq. (6) equal to zero. Finally, the system with a dumbbell-target interaction only (hereafter referred to as system III) was attributed a zero saddle point contribution except for the $AA\rightarrow B$ jump (and the reverse jump $BA\rightarrow A$): this more physical description makes the system face different jump frequencies from the same configuration, which enhances the correlation effects. We chose the value $E_{AA\rightarrow B}^{(s)} = E_{BA\rightarrow A}^{(s)} = -2k_BT$.

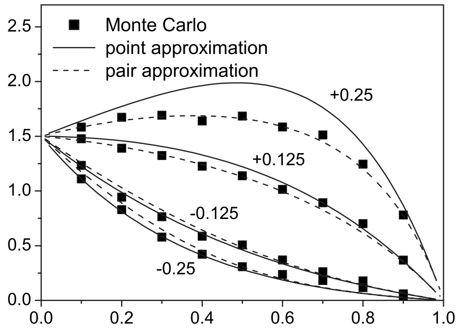

FIG. 3. Uncorrelated transport coefficient $L_{AA}^{(0)}$ in a concentrated bcc alloy with interactions between A and B substitutional atoms as a function of the concentration $C(B)$. The symbols stand for Monte Carlo simulations, the solid lines for the point approximation, and dashed lines for the pair approximation. From top to bottom: $\beta V_{AB}=1/4$, $\beta V_{AB}=1/8$ (clustering tendency), $\beta V_{AB}=-1/8$, and $\beta V_{AB}=-1/4$ (ordering tendency). The temperature is equal to 1200 K, corresponding to a ratio of $T/T_c \simeq 1.3$ for $\beta|V_{AB}|=1/4$ and $T/T_c \simeq 2.6$ for $\beta|V_{AB}|=1/8$, when normalized with the critical temperature T_c.

VI. DISCUSSION

The main part of the discussion is devoted to the comparison of the present SCMF results with Monte Carlo calculations. We will try to separate the importance of both approximations of this theory to show the advantage of treating them separately in the formalism itself. Finally, we shortly explore some perspectives to broaden the possible application of the present upgrade of the SCMF.

A. Comparison with the Monte Carlo simulations

1. Uncorrelated transport coefficients

We observe in Fig. 3 that point approximation is sufficient for system II for reasonable values of the interactions. The agreement is even better for ordering tendency, while the pair approximation makes a visible improvement for a strong clustering tendency.

On the contrary, the pair approximation is necessary for system III, or one risks an error of 1 order of magnitude (see Fig. 4). This aspect is easy to understand because the jump probabilities $W_{AB/C}$ are directly proportional to the probability of pair clusters of type $AB_{\parallel}C$, which naturally depends on the dumbbell-target interaction $V_{AA_{\parallel}B}$. In the case of strong dumbbell-target interactions, those pair clusters and jump probabilities will be affected, and a good description can only be expected in the pair approximation.

We notice that those results are in complete consistency with the relative accuracy of the point and pair approximations regarding the equilibrium properties of the alloy.[1]

2. Correlation coefficients

Surprisingly, the effect of the statistical approximation on the correlation coefficients was found marginal. On the contrary, the kinetic approximation appeared to play a major role in the accuracy of the SCMF in this particular aspect.

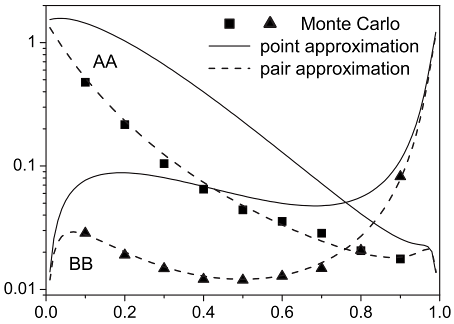

FIG. 4. Uncorrelated transport coefficients $L_{AA}^{(0)}$ and $L_{BB}^{(0)}$ in a concentrated bcc alloy with interactions between an AA dumbbell and a B substitutional target atom ($\beta V_{AA_{\parallel}B}=-2$), as a function of the concentration $C(B)$. The temperature is equal to 1200 K. The symbols stand for Monte Carlo simulations, the solid lines for the point approximation, and dashed lines for the pair approximation.

Figures 5 and 6 show the correlation coefficients calculated by the SCMF theory within the point approximation in systems II and III. The importance of the kinetic approximation (first or second shell) is in agreement with a previous

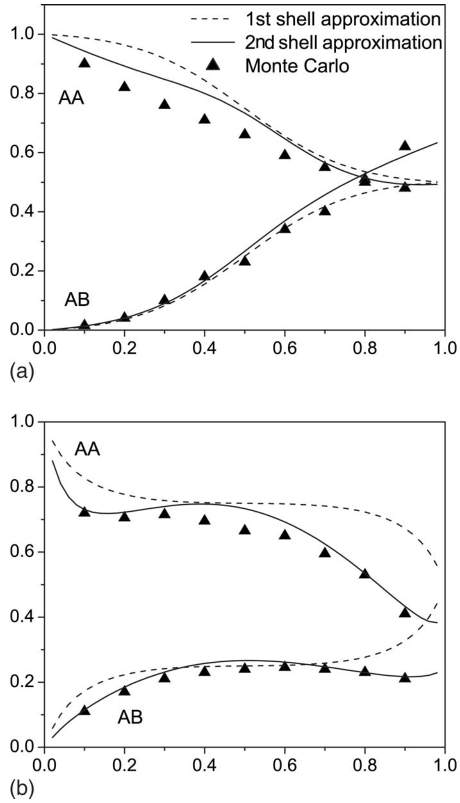

FIG. 5. Correlation coefficients f_{AA} and $f_{AB}^{(A)}$ in a concentrated bcc alloy with interactions between A and B substitutional atoms as a function of the concentration $C(B)$. The temperature is equal to 1200 K. The symbols stand for Monte Carlo simulations, the dashed lines for the first shell approximation, and solid lines for the second shell approximation, all in the statistical point approximation. Top: $\beta V_{AB}=-1/4$ (ordering tendency); bottom: $\beta V_{AB}=1/4$ (clustering tendency).

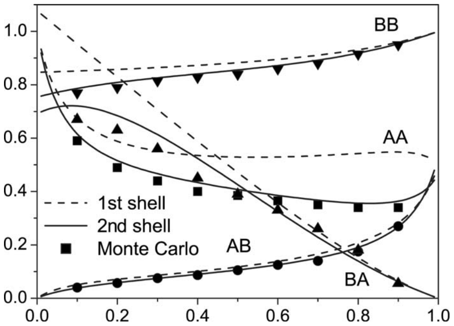

FIG. 6. Correlation coefficients in a concentrated bcc alloy with interactions between an *AA* dumbbell and a *B* substitutional target atom ($\beta V_{AA_{\|}B}=-2$), as a function of the concentration $C(B)$. The temperature is equal to 1200 K. The symbols stand for Monte Carlo simulations, the dashed lines for the first shell approximation, and solid lines for the second shell approximation, all in the statistical point approximation.

analysis of the SCMF theory:[1] most generally, the second shell is to be used when the difference between return and escape frequencies is strong, which is, in general, the case when the same configuration can face different possible jump frequencies. A simple criteria to identify cases where the first shell approximation can be sufficient is not available yet.

On the other hand, the lack of importance of the statistical approximation may be partially understood by an analysis of Fig. 4. A representation of the ratio between the two average jump frequencies, $L_{AA}^{(0)}$ and $L_{BB}^{(0)}$, using both the point and pair approximations would lead to similar curves (except in the dilute limit). In the first shell approximation, it just happens that the correlation coefficients are expressed as a quotient of the same kind of average jump probabilities. Hence, one expects that the correlation coefficients are not strongly affected by a change of statistical approximation. One interesting conclusion is that correlation effects in a bcc concentrated alloy can be calculated without the lengthy formalism of the pair approximation; however, this formalism may be necessary to calculate the complementary uncorrelated transport coefficients.

3. Beyond the bcc binary alloy

Although the derivation of the calculation was performed for simplicity in a binary alloy, the point and pair approximations are easily derivable for a multicomponent alloy, both for the equilibrium and kinetic approaches. Within the pair statistical approximation, however, the analytical approach presented to calculate the cluster variation method (CVM) variable q_i, solution of Eq. (32) in Ref. 1, will no longer apply.

Furthermore, it is straightforward to derive the point approximation in the fcc structure. The only notable difference concerns the orientation of the dumbbell, ⟨100⟩ instead of ⟨110⟩, and consequently, the number of target and nontarget neighbors. We could then easily obtain an analytical expression of the repartition of the defects. From the kinetic point of view, a mean jump probability $W_{AB/C}^{(1)}$ would not present any additional difficulty, taking advantage of the solution for a noninteracting fcc alloy, which is available elsewhere.[3] Using a statistical pair approximation to treat the thermodynamics of a fcc alloy is less justified because it does not account for the possible frustrations present in NN triangles and tetrahedra.[8] However, transport coefficients involve average jump frequencies where almost all the probabilities of triangle and tetrahedra are summed up over several configurations associated with the same jump frequency. Hence this specific averaging procedure diminishes the importance of frustration and leads to satisfactory results for the vacancy mechanism.[7]

4. Saddle point energy

In this paper, the contribution to the saddle point energy was set constant except in system III, where a simple form $E_{ABC}^{(s)}$ common to the jumps $AB\rightarrow C$ and $CB\rightarrow A$ was used. This saddle point contribution is then independent of the local surroundings and fully compatible with the whole formalism derived in this paper, though it already allows for a very wide choice of kinetic behaviors of the alloy. In a binary alloy without interactions between neighboring lattice sites, this model reduces to Bocquet's five two-frequency sets.[19] A preliminary study of this type of saddle point energies in a concentrated alloy has proven the primary importance of each factor in the resulting transport coefficients, including the temperature and concentration dependences. As was already done for the vacancy jump mechanism, one could fit a saddle point energy model on *ab initio* and/or experimental data.[20,21] Furthermore, the saddle point energy may no longer be independent of the local surroundings, and a broken bond model for the energy contribution of the saddle point has been developed in some specific systems.[22–24] Such a model for the interstitial would require a new derivation of the SCMF kinetic equations.

VII. CONCLUSION

We presented a self-consistent mean field (SCMF) theory to calculate the transport coefficients in interacting bcc alloys with interstitial mechanism. The resulting kinetic equations are equivalent to the ones obtained in the limit of a noninteracting alloy[3] except that the average jump frequencies are replaced by new expressions based on the CVM calculation of Ref. 1 within the point and pair approximations. A comparison with Monte Carlo simulations shows that uncorrelated transport coefficients do not require a pair approximation as long as there is no strong clustering tendency or strong dumbbell-atom interactions. In addition to the statistical approximation, the SCMF theory applied to the calculation of the correlation functions introduces another hierarchy of approximations that sets the number of kinetic equations to solve. The first shell approximation in a binary alloy reduces to one kinetic equation and leads to analytical expressions of the transport coefficients. The effect of the statistical approximation on the correlation functions was found marginal. On the contrary, in the case of a strong clustering tendency and/or strong dumbbell-atom interactions, good agreement with Monte Carlo simulations is achieved with a second shell approximation only. This theory is consistent with the previous results obtained in the limiting cases of noninteracting[3] and dilute alloys.[4] As was done for the vacancy mechanism, it is possible to extend the approach to more sophisticated diffusion models including interactions at the saddle point and to other crystallographic structures.[7]

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