PHYSICAL REVIEW B **76**, 054205 (2007)

Split interstitials in an interacting bcc alloy. I. Extension of the cluster variation method

V. Barbe and M. Nastar*
Service de Recherche en Métallurgie Physique, CEA, 91191 Gif-sur-Yvette, France

(Received 20 February 2007; revised manuscript received 14 June 2007; published 14 August 2007)

We present an extension of the cluster variation method to take into account the dumbbell configuration of interstitial defects in a body centered cubic alloy. In addition to the interaction between both atoms of a dumbbell, we consider nearest-neighbor interactions between substitutional atoms and dumbbells. A point approximation leads to simple expressions of the relative amount of dumbbell compositions and the averaged local surrounding of a given species as a function of nominal composition and temperature. In contrast, a pair approximation requires a more complex local surrounding variable q first introduced by Kikuchi [J. Phys. Chem. Solids **20**, 17 (1961)]. The predicted mean compositions of the dumbbell using both approximations are compared with Monte Carlo simulations. The point approximation leads to good agreement with Monte Carlo simulations as long as the dumbbell-atom interactions are not too strong.

DOI: 10.1103/PhysRevB.76.054205 PACS number(s): 61.72.Ji, 81.30.Bx

I. INTRODUCTION

This paper is the first part of a two-paper series devoted to the diffusion by dumbbell mechanism in an interacting body centered cubic (bcc) alloy. We hereby treat equilibrium spatial correlations before turning to kinetics in the following paper. This two-step approach has been used by earlier diffusion theories for the vacancy mechanism.[2–5]

Dumbbell-type interstitial defects occur in metals mainly under irradiation and often exhibit low migration energies (a few 0.1 eV) when compared to the vacancies (around 1 eV), so that they must contribute to the diffusion in irradiated materials. As a consequence, kinetic models including dumbbells for the calculation of the transport coefficients have been built in the past decades, mainly in dilute[6–8] and concentrated face centered cubic (fcc) alloys[9–13] and in dilute[14–16] and concentrated bcc alloys.[13,17,18] In concentrated alloys, up to now, calculations of the transport coefficients including correlation effects are restricted to noninteracting systems because of the complex geometry already present in those "simple" systems. By "noninteracting" system we mean a system without interactions between species on different *lattice sites*, the binding energies between both atoms of a dumbbell being considered.[10] The advantage of such a model is that the occupancy probability of a given cluster of sites is always the product of the corresponding point occupancy probabilities.

However, recent *ab initio* calculations[19,20] showed that strong interactions, both attractive or repulsive, can occur between a dumbbell and nearest-neighbor (NN) substitutional atoms. These observations supported the nearest-neighbor interaction model introduced by Barbu[6] and Allnatt *et al.*[7] in the fcc dilute alloy, which was recently extended to the bcc dilute alloy.[16] Considering the value of the observed interactions (1 eV), clusters involving several solute atoms are expected to play a major role in diffusion: as a consequence, the present work further extends the treatment of an interacting alloy to the concentrated bcc alloy.

The first difficulty to be considered when introducing NN interactions is their effect on the local environment of atoms and defects, as was already studied for the vacancy-type defects.[2] In the dumbbell case, these interactions can also affect the relative amount of the different dumbbell compositions. Both results are of primary importance in treating the kinetics of the alloy.

In the previous models, all results could be achieved by simply solving a limited set of detailed balance equations for the different configurations of dumbbell,[13,15,16] though this procedure is not compatible with a concentrated interacting alloy. We use the cluster variation method (CVM) formalism introduced by Kikuchi,[1] which we find particularly suitable for our problem. We restrict the study to NN interactions and to the point and pair statistical approximations. The latter approximation is known to lead to a correct phase diagram of a bcc alloy.[21] Furthermore, the CVM can be extended to longer-range interactions or many-body approximations.[22]

In Sec. II, we introduce the specific notations that will be used along the two-paper series. As often as possible, the symbols used for the interactions or the description of a particular configuration are the same ones previously used in the dilute case.[16] Sections III and IV will be devoted to the application of the CVM in the point and pair approximations, respectively. A comparison between the predicted repartition of the dumbbell compositions in a binary alloy and Monte Carlo simulations is presented and discussed in Sec. V.

II. SPECIFIC NOTATIONS

As in the previous papers devoted to the dumbbell mechanism,[5,13,16] we consider only the ⟨110⟩ orientation of the defect in a bcc crystal. The dumbbell composed of atoms A and B, with B pointing in the α direction (out of 12 possible ⟨110⟩ directions), is noted AB_α. As we are interested in this study in the equilibrium properties of the system, all 12 directions are equivalent and we can write x_{AB} as the probability to find on any site an AB dumbbell in an arbitrary direction.[27] The corresponding conservation equation in a binary alloy writes

$$6x_{AA} + 6x_{BB} + 12x_{AB} = c_I, \tag{1}$$

where c_I is the total dumbbell concentration. We can define the relative occurrence (or proportion) of each composition of the defect as

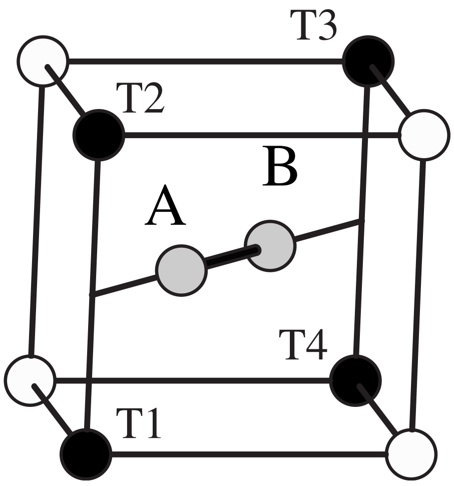

FIG. 1. Nearest neighbors of a ⟨110⟩ dumbbell: white atoms are on nontarget sites, black atoms $T1$ and $T2$ are target atoms for A, and black atoms $T3$ and $T4$ are target atoms for B.

$$p_{AA} = \frac{6x_{AA}}{c_I}, \tag{2a}$$

$$p_{AB} = \frac{12x_{AB}}{c_I}, \tag{2b}$$

with the obvious relation in a binary alloy

$$p_{AA} + p_{AB} + p_{BB} = 1. \tag{3}$$

While those proportions are easily calculated in a noninteracting alloy,[10,13] one of the goals of this paper is to generalize those results to more realistic interacting systems.

Due to the orientation of the defect, all nearest neighbors are not equivalent. It is worth differentiating them on the basis of their relative position to the defect: we call "target sites" the four sites that the defect can reach within one jump, and "nontarget sites" the four other sites (see Fig. 1). One distinguishes the two target sites for atom A from the two target sites for atom B, and the substitutional atom situated on a target site is called "target atom."

As this geometry implies different distances between atoms, it is logical to introduce different sets of interactions. We hereby follow the definitions of Ref. 13:

(1) ϵ_{AB} is the interaction between both atoms of the dumbbell, also called binding energy of the defect;

(2) V_{AB} is the binding energy between two NN substitutionnal atoms;

(3) $V_{AB_\parallel C}$ between an AB dumbbell and a substitutional C atom on a target site for atom B;

(4) $V_{BA_\parallel C}$ between an AB dumbbell and a substitutional C atom on a target site for atom A;

(5) $V_{AB_\perp C}$ between an AB dumbbell and a NN nontarget C atom.

All those values are taken negative for attractive interactions; positive for repulsive interactions.

In the following application of the CVM, we need to define the conditions of the equilibrium that we intend to describe: the observed system is the canonical ensemble, where the number of atoms of each chemical species, the total number of dumbbells, the volume, and the temperature T are fixed. For each species i (chemical species or dumbbell), the number of items N_i defines the concentration

$$c_i = \frac{N_i}{N_s}, \tag{4}$$

where N_s is the number of sites of the system. Throughout this study, we will consider only concentrated alloys with a vanishingly low concentration of dumbbells, which implies the assumption

$$c_I \ll c_A, c_B \ldots\ . \tag{5}$$

III. CLUSTER VARIATION METHOD IN THE POINT APPROXIMATION

In the point approximation, the only unknown variables are the x's, which correspond to one-site occupations. In a binary alloy for which the concentration of atomic species and interstitials is specified, there are two independent variables to be calculated such as x_{AA} and x_{AB}. Following the CVM formalism,[1] they are obtained by minimizing the free energy F of the system, which is usually divided into three parts.

The internal energy represents the contribution of all binding energies involved in the system. A careful counting leads to the simple expression

$$\frac{E}{N_s} = \frac{1}{2}\sum_{a,b} 8x_a x_b V_{ab} + \sum_{a,b,\alpha} \epsilon_{ab_\alpha} x_{ab_\alpha} + \sum_{a,b,\alpha,c} 4x_{ab_\alpha} x_c (V_{ab_\parallel c} + V_{ab_\perp c}), \tag{6}$$

where the indices a, b, and c refer to chemical species and α to the orientation of the dumbbell.

The second part is the entropy contribution, expressed as

$$\frac{S}{N_s} = -k_B\left[\sum_a L(x_a) + \sum_{a,b,\alpha} L(x_{ab_\alpha})\right], \tag{7}$$

where k_B is the Boltzmann constant and the function L is defined as

$$L(x) = x\ln(x) - x. \tag{8}$$

The CVM equations are obtained by equating the variation of the free energy to zero for any variation of one-site occupation of each species c_i. In practice, we treat the atomic and dumbbell occupations, x_a, as independent variables and add Lagrange multipliers to the free energy to satisfy the constraints of conservation of each species (chemical species and dumbbell). They are denoted as λ_i for species i, including one multiplier λ_I for the dumbbells:

$$\Lambda = -\sum_a \lambda_a\left[c_a - x_a - \sum_{b,\alpha}(x_{ab_\alpha} + x_{ba_\alpha})\right] - \lambda_I\left(c_I - \sum_{a,b,\alpha} x_{ab_\alpha}\right). \tag{9}$$

The free energy is

$$F = \frac{E}{N_s} - \frac{TS}{N_s} + \Lambda, \tag{10}$$

and the variables x_a are obtained by solving the system

$$\forall a, \quad \frac{\partial F}{\partial x_a} = 0,$$

$$\forall a,b,\alpha, \quad \frac{\partial F}{\partial x_{ab_\alpha}} = 0, \tag{11}$$

taking care that the factors of each Lagrange multiplier remain equal to zero.

Under the assumption of Eq. (5), solving this system is straightforward, with the resulting equality $x_A = c_A$ for chemical species and the following expressions for the dumbbells:

$$x_{AA} = \frac{c_A^2 \tilde{E}_{AA} \tilde{E}_A^{-2}}{\sum_{a,b} c_a c_b \tilde{E}_{ab} \tilde{E}_a^{-1} \tilde{E}_b^{-1}} \frac{c_I}{6}, \tag{12}$$

$$x_{AB} = \frac{c_A c_B \tilde{E}_{AB} \tilde{E}_A^{-1} \tilde{E}_B^{-1}}{\sum_{a,b} c_a c_b \tilde{E}_{ab} \tilde{E}_a^{-1} \tilde{E}_b^{-1}} \frac{c_I}{6}. \tag{13}$$

Here, the $\tilde{E}$'s are the contribution of the average energy of one species embedded in a mean medium. $\tilde{E}_A$ expresses the mean binding energy experienced by a substitutional atom A in a mean medium and $\tilde{E}_{AB}$ is the equivalent for an AB dumbbell:

$$\tilde{E}_A = \exp\left[-8\beta \sum_b V_{Ab} c_b \right], \tag{14}$$

$$\tilde{E}_{AB} = \exp\left\{ -\beta \left[\epsilon_{AB} + \sum_c (4V_{AB_\perp c} + 2V_{AB_\parallel c} + 2V_{BA_\parallel c}) c_c \right] \right\}, \tag{15}$$

where β is the inverse temperature $1/k_B T$. It should be noted that the dumbbell's orientation is not specified in Eqs. (12) and (13) because the result does not depend on the orientation.

IV. CLUSTER VARIATION METHOD IN THE PAIR APPROXIMATION

A. Two-point clusters

The pair approximation consists in taking the pair occupation variables y as the new independent unknowns, the one-site occupation variables x being expressed as sums of the pair occupations. When compared to the preceding applications of the CVM,[22,23] the main difficulty arises from the necessary classification of the different NN pairs. We use the following notation:

(1) y_{AB} for two NN substitutional atoms,

(2) $y^{\parallel}_{AB_\alpha C}$ if C is on a target site for the B atom of the dumbbell AB_α,

(3) $y^{\perp}_{AB_\alpha C}$ if C is on a NN nontarget site of the dumbbell AB_α.

Entropy contributions of pairs beyond the NN distance are not considered; i.e., the occupancies of two distant sites are considered as independent. This assumption is consistent with our energetic model limited to NN interactions. Furthermore, the corresponding phase diagram when the interstitial concentration is set to zero is known to be correct.[22] The two maximal clusters to be considered are the two pairs corresponding to $y^{\perp}_{AB_\alpha C}$ and $y^{\parallel}_{AB_\alpha C}$. These two clusters are equivalent when they are occupied by substitutional atoms. In a canonical ensemble with two atomic species, A and B, there are three variables of type y_{AB}, eight of type $y^{\perp}_{AB_\alpha C}$, and eight of type $y^{\parallel}_{AB_\alpha C}$. Due to symmetry relations and conservation laws, only 11 variables are independent, e.g., y_{AA}, y_{AB}, $y^{\perp}_{AB_\alpha A}$, $y^{\perp}_{AB_\alpha B}$, $y^{\perp}_{BA_\alpha A}$, $y^{\perp}_{AA_\alpha A}$, $y^{\perp}_{AA_\alpha B}$, $y^{\perp}_{BB_\alpha A}$, $y^{\parallel}_{AB_\alpha A}$, $y^{\parallel}_{AA_\alpha A}$, and $y^{\parallel}_{BB_\alpha A}$. Yet, formally, all 19 variables are assumed to be independent for the symmetry of the calculation.

The point variables are deduced from the pair variables:

$$x_A = \sum_b y_{Ab} + \frac{1}{2} \sum_{a,b,\alpha} (y^{\parallel}_{ab_\alpha A} + y^{\perp}_{ab_\alpha A}), \tag{16}$$

where the sum $\Sigma_b y_{Ab}$ can be replaced by its symmetric form: $\Sigma_b y_{bA}$. On the other hand, the one-site occupancy of a dumbbell can be obtained by several combinations:

$$x_{AB_\alpha} = \sum_c y^{\parallel}_{AB_\alpha c} = \sum_c y^{\parallel}_{BA_\alpha c} = \sum_c y^{\perp}_{AB_\alpha c}, \tag{17}$$

where the pairs involving two dumbbells are neglected following Eq. (5). For the minimization of the free energy, it is convenient to use the symmetrical expressions

$$x_{AB_\alpha} = \frac{1}{4} \sum_c (y^{\parallel}_{AB_\alpha c} + y^{\parallel}_{BA_\alpha c} + y^{\perp}_{AB_\alpha c} + y^{\perp}_{BA_\alpha c}), \tag{18}$$

$$x_A = \frac{1}{2} \sum_b (y_{Ab} + y_{bA}) + \frac{1}{2} \sum_{a,b,\alpha} (y^{\parallel}_{ab_\alpha A} + y^{\perp}_{ab_\alpha A}), \tag{19}$$

although any other combination would be mathematically equivalent.

B. Free energy

The internal energy contribution now involves pair probabilities:

$$\frac{E}{N_s} = \frac{1}{2} \sum_{a,b} 8 y_{ab} V_{ab} + \sum_{a,b,\alpha} \epsilon_{ab} x_{ab_\alpha} + \sum_{a,b,\alpha,c} (4 y^{\parallel}_{ab_\alpha c} V_{ab_\parallel c} + 4 y^{\perp}_{ab_\alpha c} V_{ab_\perp c}), \tag{20}$$

where the indices a, b, c, and α still refer to chemical species and direction.

The entropy contribution is more deeply affected by the pair approximation, and one must now calculate the CVM coefficients,[22] a_1, $a_2^{\parallel}$, and $a_2^{\perp}$, which control the contribution of each cluster:

$$-\frac{S}{k_{\mathrm{B}N_s}} = (2a_2^{\parallel}+2a_2^{\perp})\sum_{a,b} L(y_{ab}) + 4a_2^{\parallel}\sum_{a,b,\alpha} L(y^{\parallel}_{ab_\alpha c}) + 4a_2^{\perp}\sum_{a,b,\alpha} L(y^{\perp}_{ab_\alpha c}) + a_1\left[\sum_a L(x_a) + \sum_{a,b,\alpha} L(x_{ab_\alpha})\right]. \tag{21}$$

These coefficients are fixed to 1 for every maximal cluster, i.e., every kind of pair in our case:

$$a_2^{\parallel} = a_2^{\perp} = 1. \tag{22}$$

The point coefficient is then calculated by counting the number of pairs in which one point can be involved. For a dumbbell or a substitutional atom, this number is 8, and the following relation must be obeyed:

$$4a_2^{\parallel} + 4a_2^{\perp} + a_1 = 1, \tag{23}$$

so that the one-point coefficient is $a_1 = -7$.

The last change with respect to the point approximation consists in introducing additional Lagrange multipliers in Eq. (9), which take into account the triple equality of Eq. (17):

$$\Lambda = -\sum_a \lambda_a\left[c_a - x_a - \sum_{b,\alpha}(x_{ab_\alpha}+x_{ba_\alpha})\right] - \lambda_I\left(c_I - \sum_{a,b,\alpha} x_{ab_\alpha}\right) - \sum_{a,b,c,\alpha}\lambda^{\parallel}_{ab}(y^{\parallel}_{ba_\alpha c} - y^{\parallel}_{ab_\alpha c}) - \sum_{a,b,c,\alpha}\lambda^{\perp}_{ab}(y^{\perp}_{ab_\alpha c} - y^{\parallel}_{ab_\alpha c}). \tag{24}$$

The free energy still being expressed as the sum of the three variables of Eq. (10). The system to solve is now formed of the following equations:

$$\frac{\partial F}{\partial y} = 0, \tag{25}$$

for any pair. Particular attention must be paid to the terms of the form $\partial x/\partial y$, which require that only one form be formally chosen among the expressions (17)–(19). Equations (18) and (19) will be used in the present paper.

C. Results

In the general case, the results of the pair approximation could not be expressed analytically. We hereby present two sets of formulas which can be useful in different situations. The calculations leading to those formulations are lengthy but straightforward, although special attention must be paid to the counting of the pairs and to the symmetry properties.

We begin by expressing the pair variables as a function of reduced variables q_i:

$$y_{AB} = q_A q_B \exp(-\beta V_{AB}), \tag{26a}$$

$$y^{\parallel}_{AB_\alpha C} = q_{AB} q_C \exp[-\beta(V_{AB_\parallel C} + \lambda^{\parallel}_{AB} - \lambda^{\parallel}_{BA} - \lambda^{\perp}_{AB})], \tag{26b}$$

$$y^{\perp}_{AB_\alpha C} = q_{AB} q_C \exp[-\beta(V_{AB_\perp C} + \lambda^{\perp}_{AB})]. \tag{26c}$$

The variables q_i contain the independent contribution of each point occupancy of the pair cluster and are defined as

$$q_A = x_A^{(7/8)} \exp\left(-\frac{\beta}{8}\lambda_A\right), \tag{27}$$

$$q_{AB} = x_{AB}^{(7/8)} \exp\left[-\frac{\beta}{8}(\lambda_A + \lambda_B + \lambda_I + \epsilon_{AB})\right]. \tag{28}$$

The relative simplicity of these equations will make them useful in the kinetic treatment of the diffusion by the dumbbell mechanism. Nevertheless, the q_i's as well as the "geometrical" Lagrange multipliers of the type $\lambda^{\parallel}_{AB}$ or $\lambda^{\perp}_{AB}$ are still to be solved at this stage of the calculation. As their expression is very complex in the general case, we will focus in this study on the point occupancy variables x. It will be shown that they can be obtained without the help of the geometrical Lagrange multipliers.

For convenience, we define $E_{AB} \equiv \exp(-\beta V_{AB})$ and $E_{AB_\parallel C} \equiv \exp(-\beta V_{AB_\parallel C})$. We point out that they correspond to one given pair only and are not to be confused with the $\tilde{E}$'s previously introduced in Eq. (14). By using Eq. (17), the site occupancy x_{AB} can be calculated in three different ways:

$$\begin{aligned} x_{AB} &= q_{AB}\exp[\beta(\lambda^{\parallel}_{AB} - \lambda^{\parallel}_{BA} - \lambda^{\perp}_{AB})](q_A E_{AB_\parallel A} + q_B E_{AB_\parallel B}) \\ &= q_{AB}\exp[\beta(\lambda^{\parallel}_{BA} - \lambda^{\parallel}_{AB} - \lambda^{\perp}_{AB})](q_A E_{BA_\parallel A} + q_B E_{BA_\parallel B}) \\ &= q_{AB}\exp(\beta\lambda^{\perp}_{AB})(q_A E_{AB_\perp A} + q_B E_{AB_\perp B}). \end{aligned} \tag{29}$$

Hence, the Lagrange multipliers can be eliminated to obtain the expression

$$x_{AB} = q_{AB}(q_A E_{AB_\perp A} + q_B E_{AB_\perp B})^{1/2}(q_A E_{AB_\parallel A} + q_B E_{AB_\parallel B})^{1/4}(q_A E_{BA_\parallel A} + q_B E_{BA_\parallel B})^{1/4} \tag{30a}$$

$$\equiv q_{AB}\tilde{V}_{AB}, \tag{30b}$$

where the term $\tilde{V}_{AB}$ corresponds to the interaction of the dumbbell AB with only one averaged neighbor atom.

The last step of the calculation is then to determine the reduced variables q_i. We take advantage of Eq. (19) to treat the case of the substitutional atoms, the pairs involving dumbbells being neglected following Eq. (5). It becomes

$$y_{AA} + y_{AB} = c_A = q_A^2 E_{AA} + q_A q_B E_{AB}, \tag{31a}$$

$$y_{BA} + y_{BB} = c_B = q_A q_B E_{AB} + q_B^2 E_{BB}. \tag{31b}$$

This system can be decoupled into two independent quadratic equations of the type

$$q_A^4 E_{AA}(E_{AA}E_{BB} - E_{AB}^2) - q_A^2[2c_A E_{AA}E_{BB} - (c_A - c_B)E_{AB}^2] + E_{BB}c_A^2 = 0, \tag{32}$$

the calculation of the one-point reduced variables now being straightforward. Eventually, determining the value of the q_{ij}'s requires the use of Eq. (28) together with Eq. (30b). One obtains

$$q_{AB} = \frac{(q_A q_B)^8}{(c_A c_B)^7} \tilde{V}_{AB}^7 \exp(-\beta\epsilon_{AB}) \exp(-\beta\lambda_I)$$

$$= \frac{(q_A q_B)^8}{(c_A c_B)^7} \frac{\tilde{E}_{AB}}{\tilde{V}_{AB}} \exp(-\beta\lambda_I), \qquad (33)$$

where the average "embedding factor" $\tilde{E}_{AB}$ has been introduced by analogy with Eq. (15) of the point approximation

$$\tilde{E}_{AB} = \tilde{V}_{AB}^8 \exp[-\beta\epsilon_{AB}]. \qquad (34)$$

The last unknown is the Lagrange multiplier λ_I, which helps satisfy the conservation condition of Eq. (1):

$$\exp(-\beta\lambda_I) = \left[\frac{q_A^{16}}{c_A^{14}} \tilde{E}_{AA} + 2\frac{(q_A q_B)^8}{(c_A c_B)^7} \tilde{E}_{AB} + \frac{q_B^{16}}{c_B^{14}} \tilde{E}_{BB} \right]^{-1} \frac{c_I}{6}. \qquad (35)$$

The calculation of the q_{AB}'s and x_{AB}'s is now a simple combination of Eqs. (30)–(35). Note that all values but q_A and q_B are expressed analytically as a function of the binding energies V or ϵ and of the concentrations c_i. An analytical expression of q_A and q_B can be obtained from Eq. (32), but we found its complexity unnecessary for the interest of this paper.

We also notice that the given results are sufficient to calculate the one-point occupancies x_{AB} but not the two-point occupancies $y^{\parallel}_{AB_\alpha C}$; the latter requires the expression of the geometrical Lagrange multipliers $\lambda^{\parallel}_{AB}$ and $\lambda^{\perp}_{AB}$. However, as will be shown in Ref. 25 the two-point occupancies are not required to treat the kinetic aspect of the system, so we will omit this lengthy though straightforward calculation.

V. COMPARISON WITH MONTE CARLO SIMULATIONS

A. Principle of the simulations

To test the accuracy of point and pair approximations, we performed a series of Monte Carlo simulations to measure the proportions p_{AB} [see Eq. (2)] of each dumbbell composition in a bcc alloy for different sets of interactions. We used a simulation box of 512 atomic sites containing 513 atoms and one dumbbell, and employed a classical kinetic residence time algorithm[24] to perform kinetic Monte Carlo (KMC) simulations. The dumbbell jump frequencies w_i are calculated at each jump following a bond-breaking model with a constant saddle point energy,[13,25] consistent with the above energetic description. At each KMC step, one of the possible jumps is chosen with a probability proportional to its jump frequency, and one adds a time increment given by

$$\tau_{MC} = \frac{1}{\sum_i w_i}. \qquad (36)$$

Eventually, we calculate the proportion of each composition by observing the time proportion that the defect spent with a given composition within a long enough sequence of jumps. Considering a simulation box containing N_A atoms A and N_B atoms B, the length of the sequence was set so that at least $100N_A$ jumps of atoms A and $100N_B$ jumps of atoms B were performed during the sequence. For such a simulation, the time proportions are observed to reach stationary values, which are then compared with Eq. (2), the x values being calculated within the point or pair approximations.

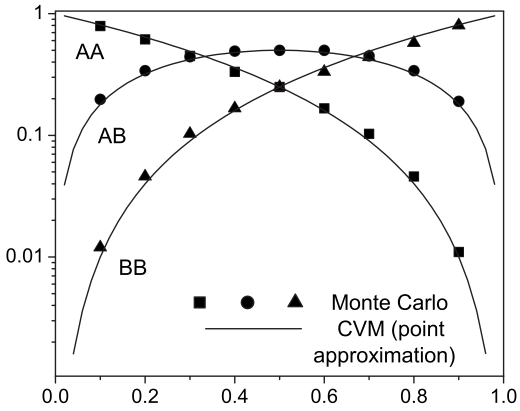

FIG. 2. Proportion of the different dumbbell compositions in a concentrated bcc alloy without interactions as a function of the concentration $C(B)$. The temperature is equal to 1200 K. The symbols stand for Monte Carlo simulations and the solid lines for the CVM prediction (point and pair approximations are equal).

If binding energies between substitutional atoms are present, we performed a 10^5-step Metropolis algorithm[26] before the kinetic simulation so that the short-range order is established between substitutional atoms before the first jump of the dumbbell interstitials.

B. Comparison with the cluster variation method predictions

Three types of systems were explored. The first one is used as a reference, where all interactions are set to zero (Fig. 2): in this case, the point and pair approximations of the CVM are equivalent and give exact values. This will also be the case in any system without two-site interactions, i.e., when the energetic description is limited to the dumbbell stabilities ϵ_{ij}. The corresponding results are the same as those already calculated[10,13] by simply solving the detailed balance equations.

In the second type of systems, we explored the effect of binding energies between substitutional atoms and set to zero all energies involving the interstitials. In this case, the main effect is the appearance of a short-range order in the alloy, but the equilibrium of the defect compositions is also affected. Figure 3 shows the different proportions for an ordering tendency (top; $\beta V_{AB}=-1/4$, all other interactions are equal to zero) and a clustering tendency (bottom; $\beta V_{AB}=1/4$). The temperature is set to 1200 K, corresponding to a ratio of $T/T_c \simeq 1.3$ when normalized with the critical temperature T_c.[22] Although those interactions are relatively strong, we can see that the point approximation is sufficient to describe the weight of the different compositions of the defect. The improvement obtained by the pair approximation is marginal.

Eventually, we consider in Fig. 4 a system where all interactions are set to zero, except for an attractive binding

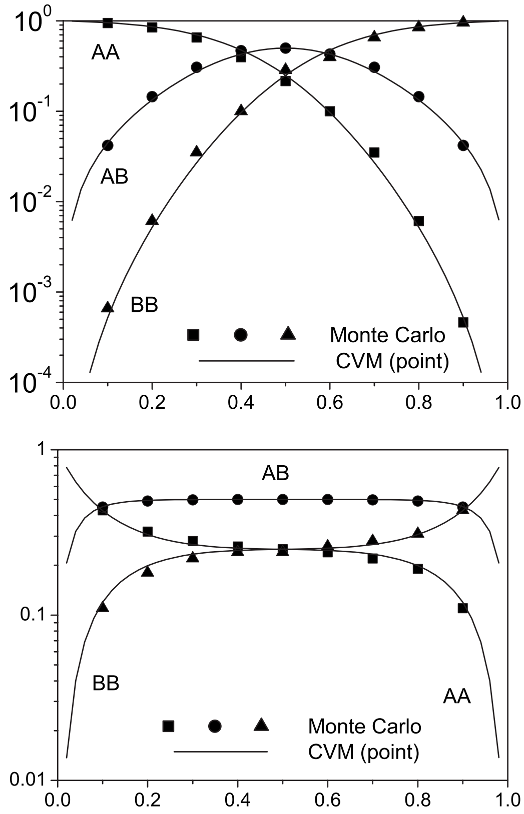

FIG. 3. Proportion of the different dumbbell compositions in a concentrated bcc alloy with interactions between *A* and *B* substitutional atoms as a function of the concentration $C(B)$. The temperature is equal to 1200 K. The symbols stand for Monte Carlo simulations and the solid lines for the CVM prediction in the point approximation. Top: $\beta V_{AB}=-1/4$; bottom: $\beta V_{AB}=1/4$. The point and pair approximations are indistinguishable.

energy between an *AA* dumbbell and a *B* atom in target position: the value $\beta V_{AA_{\parallel}B}=-2$ is used, a much higher value than typical interactions between substitutional atoms; this difference being supported by *ab initio* calculations in dilute alloys.[19,20] We can see that the point approximation fails to describe the repartition of the dumbbell compositions in the concentrated range, while the pair approximation is sufficient even for such strong interactions. Note that, in the dilute limit, the CVM results within the pair approximation are

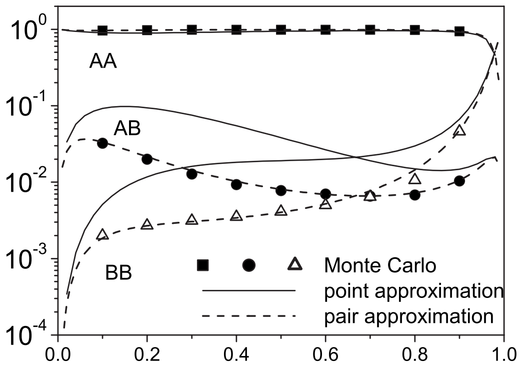

FIG. 4. Proportion of the different dumbbell compositions in a concentrated bcc alloy with interactions between an *AA* dumbbell and a *B* substitutional target atom, as a function of the concentration $C(B)$. The temperature is equal to 1200 K. The symbols stand for Monte Carlo simulations, solid lines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

identical to the direct resolution of the detailed balance equations performed in Ref. 16.

VI. CONCLUSION

We have extended the CVM formalism to systems containing dumbbell-like defects: in the point approximation, the main difficulty was accounting for the different compositions of a defect, while in the pair approximation, an additional difficulty arose from the different types of pairs involving the same dumbbell. Analytical or quasianalytical results were obtained for the proportion of different dumbbells in a concentrated alloy dilute in defects, which are consistent with earlier results in noninteracting alloys[13] or dilute interacting alloys.[16]

The CVM results were compared to Monte Carlo simulations: for realistic values of the interactions, the point approximation is found sufficient to describe the repartition of the dumbbell interstitials in the presence of binding energies between substitutional atoms only, but the pair approximation is needed when strong dumbbell-substitutional atom interactions are added.

This formalism will now be applied to a study of the diffusion by dumbbell mechanism in an interacting concentrated bcc alloy.

---

*maylise.nastar@cea.fr

[1] R. Kikuchi, Phys. Rev. **81**, 988 (1951).
[2] R. Kikuchi, J. Phys. Chem. Solids **20**, 17 (1961).
[3] N. A. Stolwijk, Phys. Status Solidi B **105**, 223 (1981).
[4] Z. Qin, A. R. Allnatt, and E. L. Allnatt, Philos. Mag. A **71**, 296 (1995).
[5] M. Nastar and V. Barbe, Faraday Discuss. **134**, 331 (2007).
[6] A. Barbu, Acta Metall. **28**, 499 (1980).
[7] A. R. Allnatt, A. Barbu, A. D. Franklin, and A. B. Lidiard, Acta Metall. **31**, 1307 (1983).
[8] Y. Okamura and A. R. Allnatt, Philos. Mag. A **54**, 773 (1986).
[9] J.-L. Bocquet, Philos. Mag. A **47**, 547 (1983).
[10] J.-L. Bocquet, Res. Mech. **22**, 1 (1987).
[11] D. K. Chaturvedi and A. R. Allnatt, Philos. Mag. A **69**, 821 (1994).
[12] D. K. Chaturvedi and A. R. Allnatt, Philos. Mag. A **70**, 657 (1994).
[13] V. Barbe and M. Nastar, Philos. Mag. **86**, 3503 (2006).
[14] A. Barbu and A. B. Lidiard, Philos. Mag. A **74**, 709 (1996).
[15] S. Sharma, D. K. Chaturvedi, I. V. Belova, and G. E. Murch,

Philos. Mag. A **81**, 431 (2001).

[16] V. Barbe and M. Nastar, Philos. Mag. **87**, 1649 (2007).

[17] J.-L. Bocquet, Philos. Mag. A **63**, 157 (1991).

[18] S. Sharma, D. K. Chaturvedi, I. V. Belova, and G. E. Murch, Philos. Mag. A **80**, 65 (2000).

[19] C. Domain and C. S. Becquart, Phys. Rev. B **71**, 214109 (2005).

[20] E. Meslin, C.-C. Fu, A. Barbu, F. Gao, and F. Willaime, Phys. Rev. B **75**, 094303 (2007).

[21] D. D. Fontaine, Solid State Phys. **34**, 73 (1979).

[22] F. Ducastelle, *Phase Stability in Alloys* (North Holland, Amsterdam, 1991).

[23] T. Mohri, J. M. Sanchez, and D. D. Fontaine, Acta Metall. **33**, 1463 (1985).

[24] G. E. Murch, Philos. Mag. A **45**, 941 (1982).

[25] V. Barbe and M. Nastar, following paper, Phys. Rev. B **76**, 054206 (2007).

[26] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, and A. H. Teller, J. Chem. Phys. **21**, 1087 (1953).

[27] Although every direction is equivalent at equilibrium, at some stages of the derivation it is necessary to specify the direction α of a given dumbbell AB and to introduce the notation x_{AB_α}.