

Kinetic approach for matter transport by the dumbbell mechanism in a dilute random fcc alloy

Rajinder Singh and D. K. Chaturvedi

Department of Physics, Kurukshetra University, Kurukshetra 132119, India

(Received 9 December 1992; revised manuscript received 29 June 1993)

This paper describes a theory for matter transport by the dumbbell mechanism in a random fcc alloy. By means of kinetic equations we have evaluated the phenomenological coefficients, L_{ij} , from the linear-response expressions. It is shown that all the exact expressions for L_{ij} ($i, j = A, B$) can be obtained from this method in a random binary alloy dilute in component B when rotation and translation-plus-rotation jumps are allowed for all the dumbbells. The method can be extended to the more complex system of concentrated AB alloys.

I. INTRODUCTION

When an alloy is irradiated with high-energy particles both vacancy and interstitial defects are produced. The matter transport in such materials is described by the phenomenological transport coefficients L_{ij} , which relate the flux of atoms of species i to the thermodynamic force acting on species j in the equations of linear nonequilibrium thermodynamics (see Refs. 1–3). In a solid solution of a dilute solute B in a solvent A it is shown that there are only four independent phenomenological coefficients, namely L_{AA} , $L_{AB} = L_{BA}$, L_{BB} and $L_{A^*A^*}$ where A^* is the tracer of solvent A . The last two of these are trivially related to the diffusion coefficients. The calculations of the tracer diffusion coefficients are mainly based on the Einstein relation for the diffusion coefficients. For the nontracer coefficients L_{AA} , L_{AB} the kinetic approach⁴ and the exact time correlation formulas for the L_{ij} have been employed.⁵

In this paper we are concerned with the calculation of the transport coefficients for a particular model of matter transport, i.e., the dumbbell model due to Bocquet⁶ in a random fcc alloy. The dumbbell comprises a pair of atoms associated with one substitutional site with the axis of the pair in the $\langle 100 \rangle$ direction. In an elementary jump the dumbbell is translated to a nearest-neighbor (NN) site with the axis of the pair rotated through $\pi/2$. Recently Chaturvedi and Allnatt⁷ obtained accurate expressions for L_{AA} , L_{AB} , and L_{BB} in a binary alloy dilute in component B when the rotation about a lattice site is allowed for all dumbbells in addition to the usual translation-plus-rotation jumps. Their method is based on the well-known matrix method of random walks^{8–11} and proceeds by a classification of jumps into “types” followed by matrix inversion to evaluate the generating functions of random walks of the point defect between successive tracer atom jumps. The method is, however, specific for dilute alloys. There is considerable practical interest in alloys where the solute concentration is sufficiently large. So far there are no generally agreed upon approximation schemes in these concentrated systems, even for vacancy mechanism; earlier studies have been made only by rather *ad hoc* analogies with dilute systems and the vacancy mechanism. The aim of this pa-

per is, therefore, to develop a method that reproduces all the exact expressions obtained earlier⁷ for L_{ij} in dilute alloys and can be extendable to the much more complex system of concentrated alloys.

We start with the exact linear-response formulas for L_{ij} and obtain expressions for the fcc alloy in which matter transport is accomplished through the interstitial migration. The correlation functions appearing in L_{ij} for dilute alloy are obtained through the use of kinetic equations in line with Okamura and Allnatt¹² for the vacancy mechanism. We, however, work entirely in Fourier space, which is much more convenient as compared to Okamura and Allnatt who solved the kinetic equations in Fourier space but go back to real space to obtain the correlation functions.

II. ATOMIC MODEL

We consider a solid solution dilute in solute B in host A in which the transport of matter is given by the motion of the dumbbell interstitial. We denote by $W_{ij/k}$ the jump frequency for an ij dumbbell to be displaced to a nearest-neighbor site occupied by a k atom, thus leaving i at the original site of the dumbbell and forming a jk dumbbell at the new site. The transport of matter thus takes place by the atom of species j alone; the atoms of species i and k merely relax around their lattice sites. The model also allows the dumbbell ij to rotate through $\pi/2$ with frequency W_{ij}^R , while remaining at the same lattice site.

We further assume that the solution is dilute enough that close pairs of solute atoms and the pairs of solute defect and solute atom are neglected. The condition of detailed balance is then given by

$$C_{AB} C'_A W_{BA/A} = 2C_{AA} C'_B W_{AA/B}, \quad (2.1)$$

where C_{AA} and C_{AB} are concentrations of solvent and mixed dumbbells, respectively, and C'_A and C'_B denote the respective concentrations of A and B atoms which are not members of dumbbells. The total concentrations of A and B atoms, C_A and C_B , are given by

$$C_A = C'_A + 2C_{AA} + C_{AB}, \quad (2.2)$$

$$C_B = C'_B + C_{AB}. \quad (2.3)$$

All the concentrations (C and C') are defined as substitutional site fractions. For very low defect concentration ($C_I = C_{AA} + C_{AB}$) the distinction between C and C' can be ignored.

III. LINEAR-RESPONSE EXPRESSION FOR L_{ij}

The theory of nonequilibrium thermodynamics introduces a set of phenomenological coefficients L_{ij} , which relates the flux of atoms of species i to the thermodynamic force acting on species j . Exact expressions for these coefficients have been obtained by Allnatt and Okamura⁵ from linear-response theory, which expresses L_{ij} as a sum of two contributions:

$$L_{ij} = L_{ij}^{(0)} + L_{ij}^{(1)} \quad (3.1)$$

in which $L_{ij}^{(0)}$ is the uncorrelated part and $L_{ij}^{(1)}$ contains correlations between successive states of the system. For a crystal of volume V and temperature T we have

$$L_{ij}^{(0)} = \frac{1}{6VKT} \sum_{b,a} \mathbf{r}_{ba}(i) \cdot \mathbf{r}_{ba}(j) W_{ba} p_a \quad (3.2)$$

Here p_a is the probability of finding the system in state a and W_{ba} is the jump frequency of the jump that changes the state from a to b . $\mathbf{r}_{ba}(i)$ is the sum of the displacements of all atoms of species i in the transition from state a to b . The dynamical part $L_{ij}^{(1)}$ can be expressed as

$$L_{ij}^{(1)} = -\frac{1}{3VKT} \sum_{c,b} \left[\sum_d \mathbf{r}_{dc}(i) W_{dc} \right] \cdot G_{cb} \left[\sum_a \mathbf{r}_{ab}(j) W_{ab} \right] p_b \quad (3.3)$$

$$L_{ij}^{(0)} = \frac{4}{3} \left[\frac{Na^2}{KT} \right] \delta_{i,j} \sum_{m,n} C_{im} (1 + \delta_{i,m}) C_n W_{mi/n} \quad (3.5)$$

$$L_{ij}^{(1)} = -2 \left[\frac{Na^2}{KT} \right] \sum_{\mathbf{s}, \mathbf{s}_0} \left[\frac{\mathbf{S} \cdot \mathbf{S}_0}{S^2} \right] \sum_{m,n,p,q} W_{mi/n} W_{pj/q} \sum_l \sum_\beta \{ [\Theta_{\beta^-}(\mathbf{s}) \bar{\Psi}_{(mi)\beta^n:(pj)_{xq}}^{(l,l-s;I_0,I_0-s_0)} + \Theta_{\beta^+}(\mathbf{s}) \bar{\Psi}_{(im)\beta^n:(pj)_{xq}}^{(l,l-s;I_0,I_0-s_0)}] \Theta_{x^-}(\mathbf{s}_0) + [\Theta_{\beta^-}(\mathbf{s}) \bar{\Psi}_{(mi)\beta^n:(jp)_{xq}}^{(l,l-s;I_0,I_0-s_0)} + \Theta_{\beta^+}(\mathbf{s}) \bar{\Psi}_{(im)\beta^n:(jp)_{xq}}^{(l,l-s;I_0,I_0-s_0)}] \Theta_{x^+}(\mathbf{s}_0) \} \quad (3.6)$$

in which translation and orientation symmetry has been used for the defect at site I_0 . Here N is the number of lattice sites per unit volume, a is the distance between fcc lattice planes and δ is the Kronecker delta function. The notation $(mi)_\beta$ denotes that the dumbbell (mi) is in β orientation at site l and the atom of species i is in the positive β direction. The summations over m , n , p , and q are over atomic species and \mathbf{s}_0, \mathbf{s} are the initial and final NN jump vectors, respectively; the jump length $s = \sqrt{2}a$. The Θ functions are defined as

$$\Theta_{\beta^\pm}(\mathbf{r}) = \begin{cases} 1 & \text{if } r_\beta = \pm a \\ 0 & \text{otherwise,} \end{cases} \quad (3.7)$$

where r_β is the β component of the vector \mathbf{r} . $\Theta_{\beta^\pm}(\mathbf{r})$

in which

$$G_{cb} = \int_0^\infty dt G_{cb}(t) \quad (3.4)$$

Here $G_{cb}(t)$ is the conditional probability that if the system is initially in state b it will be in state c after time t . P_b is the equilibrium probability of finding the system in state b after a jump of atoms of species j from state a . In our analysis we shall refer to the transition from state a to state b as the initial jump and the transition from state c to state d as the final jump.

Applying the above results to a dumbbell model in an earlier paper, Chaturvedi and Allnatt⁷ considered a finite dissociation distance of the dumbbell defect which appeared only transiently in the expressions of the direct and correlated parts of the L_{ij} 's, but finally canceled out in the total expression. It seems that it comes from the separation between direct and correlated terms: It interrupts the description of the trajectory of an atom at the point where the latter has just been pushed into an interstitial location by the defect. We know however that this separation is somewhat arbitrary and has been introduced for mathematical convenience. From a physical point of view, a defect coming from a source, approaches the atom, lets it perform a finite number of jumps (at least in three dimensions), and goes back to infinity or to a sink. The traveling distance for the atom cannot be anything else than a lattice vector. Therefore, in this paper we assume a dumbbell as a point defect whose direction determines those sites towards which the defect will be able to jump at the next step. In a transition, denoted by jump frequency $W_{ij/k}$, only the atom of species j gets displaced by a nearest-neighbor vector. Thus in a random fcc alloy, Eqs. (3.2) and (3.3), respectively, yield

selects contributions from only those sites which are NN to the origin and lie on the \pm side of it with respect to the β axis. The correlation function

$$\bar{\Psi}_{(mi)\beta^n:(pj)_{xq}}^{(l,l-s;I_0,I_0-s_0)} = \int_0^\infty dt \Psi_{(mi)\beta^n:(pj)_{xq}}^{(l,l-s;t;I_0,I_0-s_0;t=0)} \quad (3.8)$$

in which

$$\Psi_{(mi)\beta^n:(pj)_{xq}}^{(l,l-s;t;I_0,I_0-s_0;t=0)} = \sum_{c,b} \rho_c^{(mi)\beta} (l) \rho_c^n (l-s) G_{cb}(t) \rho_b^{(pj)_{xq}} (l_0) \rho_b^q (l_0 - \mathbf{s}_0) p_b \quad (3.9)$$

Here $\rho_b^{(y)}(l)$, where y denotes an atom species or a

dumbbell species, is defined to be unity when site l is occupied by a "particle" of species y and the molecular state is b and zero otherwise. The function $\Psi_{(mi)\beta^n:(pj)_xq}^{(l,l-s;t:I_0,I_0-s_0)}$ is then defined as the joint probability of finding $(mi)_\beta$ dumbbell at site l and an atom of species n at its NN site $(l-s)$ at time t when initially $(pj)_x$ dumbbell was at any site I_0 and an atom of species q at its NN site (I_0-s_0) .

Equations (3.5) and (3.6) give a general expression for the phenomenological coefficients in a random fcc alloy in which matter transport is accomplished through dumbbell interstitials. We now obtain explicit expressions in an AB alloy dilute in component B . Equation (3.5) readily yields

$$L_{BB}^{(0)} = \left[\frac{4Na^2}{3KT} \right] C_{AB} W_{AB/A}, \quad (3.10a)$$

$$L_{AB}^{(0)} = 0, \quad (3.10b)$$

$$L_{AA}^{(0)} = \left[\frac{4Na^2}{3KT} \right] (2C_{AA} W_{AA/A} + C_{AB} W_{BA/A}). \quad (3.10c)$$

To obtain correlated part we introduce the function

$$\phi_{(mi)\beta^n:(pj)_xq}^{(s;s_0)} = \sum_l \bar{\Psi}_{(mi)\beta^n:(pj)_xq}^{(l,l-s;I_0,I_0-s_0)}, \quad (3.11)$$

which depends on the distance between the defect and the atom in the initial and final states. In order to keep $L_{ij}^{(1)}$

$$\phi(\mathbf{s};\mathbf{s}_0) = \left[\frac{a}{2\pi} \right]^6 \int \int d^3K d^3K_0 \exp(i\mathbf{k}\cdot\mathbf{s} + i\mathbf{k}_0\cdot\mathbf{s}_0) \phi(\mathbf{k};\mathbf{k}_0), \quad (3.17)$$

$$\phi(\mathbf{s};) = \left[\frac{a}{2\pi} \right]^3 \int d^3k \exp(i\mathbf{k}\cdot\mathbf{s}) \phi(\mathbf{k};), \quad (3.18)$$

$$\phi(;\mathbf{s}_0) = \left[\frac{a}{2\pi} \right]^3 \int d^3k_0 \exp(i\mathbf{k}_0\cdot\mathbf{s}_0) \phi(;\mathbf{k}_0), \quad (3.19)$$

in which limits for each k integral are from $-\pi/a$ to π/a . The final expressions for $L_{BB}^{(1)}$, $L_{AB}^{(1)}$, and $L_{AA}^{(1)}$ respectively yield

$$L_{BB}^{(1)} = -16 \left[\frac{Na^2}{KT} \right] (W_{AB/A})^2 [\chi_{(AB)_x:(AB)_x} - \chi_{(AB)_x:(BA)_x}], \quad (3.20a)$$

$$L_{AB}^{(1)} = 16 \left[\frac{Na^2}{KT} \right] W_{AB/A} (F_{x:(AB)_x} - F_{x:(BA)_x}), \quad (3.20b)$$

$$L_{AA}^{(1)} = -16 \left[\frac{Na^2}{KT} \right] \left\{ W_{AB/A} (F_{x:(AB)_x} - F_{x:(BA)_x}) + i\Delta W \sum_{\alpha,\beta} [\delta_{\alpha,x}(1-\delta_{\beta,x}) + \delta_{\beta,x}(1-\delta_{\alpha,x})] \right. \\ \left. \times \left[\frac{a}{2\pi} \right]^3 \int d^3K_0 \cos(K_{0\beta}a) \sin(k_{0\alpha}a) \cdot F_{\alpha:(AA)_xB}^{(;\mathbf{k}_0)} \right\}. \quad (3.20c)$$

In the above we have introduced for any initial state the following final state functions:

$$\chi_{(AB)_\alpha} = \phi_{(AB)_\alpha} - \phi_{(BA)_\alpha}, \quad (3.21)$$

exact to the lowest order in B concentration, we substitute

$$\rho_b^A(I) = 1 - \rho_b^B(I) \quad (3.12)$$

in each ϕ function in Eqs. (3.6)–(3.11), in which $n = A$ or $q = A$. This introduces four kinds of ϕ functions, the functions that are independent of \mathbf{s} and \mathbf{s}_0 and the functions that depend on either \mathbf{s} or \mathbf{s}_0 , or both. for example,

$$\phi_{(mi)\beta^A:(pj)_x}^{(s;s_0)} = \phi_{(mi)\beta:(pj)_x} - \phi_{(mi)\beta:(pj)_xB}^{(s_0)} - \phi_{(mi)\beta^B:(pj)_x}^{(s)} \\ + \phi_{(mi)\beta^B:(pj)_xB}^{(s;s_0)}, \quad (3.13)$$

where

$$\phi_{(mi)\beta:(pj)_x} = \sum_l \bar{\Psi}_{(mi)\beta:(pj)_x}^{(l;I_0)}, \quad (3.14)$$

$$\phi_{(mi)\beta:(pj)_xB}^{(s_0)} = \sum_l \bar{\Psi}_{(mi)\beta:(pj)_xB}^{(l;I_0,I_0-s_0)}, \quad (3.15)$$

$$\phi_{(mi)\beta^B:(pj)_x}^{(s)} = \sum_l \bar{\Psi}_{(mi)\beta^B:(pj)_x}^{(l,l-s;I_0)}. \quad (3.16)$$

We refer to the functions ψ and ϕ defined in Eqs. (3.14) and (3.15) as one-site functions and those defined by (3.16) as two-site functions, according to the number of lattice sites whose occupancy specified at time t . The sum over \mathbf{s} and \mathbf{s}_0 in Eq. (3.6) can then be carried out if we introduce the Fourier transforms

$$I_{(AA)_\alpha B}^{(1)} = \left[\frac{a}{2\pi} \right]^3 \int d^3k \sin(k_\alpha a) \\ \times \sum_{\beta \neq \alpha} \cos(k_\beta a) \phi_{(AA)_\beta B}^{(\mathbf{k})}, \quad (3.22)$$

$$I_{(AA)\alpha B}^{(2)} = \left[\frac{a}{2\pi} \right]^3 \int d^3k \sin(k_\alpha a) \times \left[\sum_{\beta \neq \alpha} \cos(k_\beta a) \right] \phi_{(AA)\alpha B}^{(\mathbf{k})}, \quad (3.23)$$

and for brevity used the notations

$$F_\alpha = W_{BA/A} \chi_{(AB)\alpha} + i\Delta W (I_{(AA)\alpha B}^{(1)} + I_{(AA)\alpha B}^{(2)}), \quad (3.24)$$

$$\Delta W = W_{AA/B} - W_{AA/A}. \quad (3.25)$$

IV. KINETIC EQUATIONS

In order to evaluate $L_{ij}^{(1)}$ ($i, j = A, B$) from Eqs. (3.20a)–(3.20c) it is evident that the same one- and two-site-correlation functions are to be evaluated for different initial states. Therefore we first obtain a general expression, i.e., for any given initial state, for these correlation functions through the use of kinetic equations which relate an n -site function to the $(n+1)$ -site functions. For example, the kinetic equation for the one-site function $\psi_{(AB)\alpha}(l)$, the probability of finding a $(AB)_\alpha$ dumbbell at site l , can be written as

$$\begin{aligned} \frac{d\Psi_{(AB)\alpha}(l)}{dt} = & \sum_{\mathbf{r}} \left\{ W_{AB/A} \Theta_{\alpha-}(\mathbf{r}) \left[\sum_{\beta \neq \alpha} \Theta_{\beta-}(\mathbf{r}) \Psi_{(BA)\beta A}^{(l-\mathbf{r}, l)} + \Theta_{\beta+}(\mathbf{r}) \Psi_{(AB)\beta A}^{(l-\mathbf{r}, l)} \right] \right. \\ & + W_{AA/B} \Theta_{\alpha+}(\mathbf{r}) \left[\sum_{\beta \neq \alpha} [\Theta_{\beta-}(\mathbf{r}) + \Theta_{\beta+}(\mathbf{r})] \Psi_{(AA)\beta B}^{(l-\mathbf{r}, l)} \right] \\ & \left. - [W_{AB/A} \Theta_{\alpha-}(\mathbf{r}) + W_{BA/A} \Theta_{\alpha+}(\mathbf{r})] \left[\sum_{\beta \neq \alpha} [\Theta_{\beta-}(\mathbf{r}) + \Theta_{\beta+}(\mathbf{r})] \Psi_{(AB)\alpha A}^{(l, l-\mathbf{r})} \right] \right\} \\ & + W_{AB}^R \left[\sum_{\beta \neq \alpha} [\Psi_{(AB)\beta}(l) + \Psi_{(BA)\beta}(l)] - 4\Psi_{(AB)\alpha}(l) \right]. \end{aligned} \quad (4.1)$$

The labels referring to the initial state of the system have been omitted, since they are the same for every probability function in this and subsequent kinetic equations. Equation (4.1) gets simplified when we make use of (3.12) and neglect terms that contain more than one B atom for an alloy dilute in B . Then integrating with time and sum over l we get

$$-\sum_l \Psi_{(AB)\alpha}(l, t=0) = (W_{AB/A} + W_{AB}^R) \sum_{\beta \neq \alpha} [\phi_{(BA)\beta} + \phi_{(AB)\beta}] - 4W \phi_{(AB)\alpha} + W_{AA/B} \sum_{\mathbf{r}} \Theta_{\alpha+}(\mathbf{r}) \sum_{\beta \neq \alpha} [\theta_{\beta-}(\mathbf{r}) + \theta_{\beta+}(\mathbf{r})] \phi_{(AA)\beta B}^{(-\mathbf{r})}, \quad (4.2)$$

in which

$$W = W_{AB/A} + W_{BA/A} + W_{AB}^R. \quad (4.3)$$

Similarly one can write the kinetic equation for the probability function $\psi_{(BA)\alpha}(l)$. Then subtracting (4.2) from the latter equation we get

$$\chi_{(AB)\alpha}^{(0)} = 4W \chi_{(AB)\alpha} + i4W_{AA/B} I_{(AA)\alpha B}^{(1)}, \quad (4.4)$$

in which

$$\chi_{(AB)\alpha}^{(0)} = \sum_l [\psi_{(AB)\alpha}(l, t=0) - \psi_{(BA)\alpha}(l, t=0)]. \quad (4.5)$$

Equation (4.4) relates the one-site function $\chi_{(AB)\alpha}$ to the two-site function $\phi_{(AA)\alpha B}^{(\mathbf{k})}$ [see Eq. (3.22)]. We now write the kinetic equation for two-site function by using the arguments of gain and loss in the probability as

$$\begin{aligned} \frac{d\Psi_{(AA)\alpha B}^{(l, l-\mathbf{r})}}{dt} = & [\Theta_{\alpha-}(\mathbf{r}) + \Theta_{\alpha+}(\mathbf{r})] \\ & \times \left\{ W_{BA/A} \sum_{\beta \neq \alpha} [\Theta_{\beta-}(\mathbf{r}) \Psi_{(AB)\beta A}^{(l-\mathbf{r}, l)} + \Theta_{\beta+}(\mathbf{r}) \Psi_{(BA)\beta A}^{(l-\mathbf{r}, l)}] - W_{AA/B} \left[\sum_{\beta \neq \alpha} [\Theta_{\beta-}(\mathbf{r}) + \Theta_{\beta+}(\mathbf{r})] \Psi_{(AA)\alpha B}^{(l, l-\mathbf{r})} \right] \right\} \\ & + 2W_{AA}^R \left[\sum_{\beta \neq \alpha} [\Psi_{(AA)\beta B}^{(l, l-\mathbf{r})} - 2\Psi_{(AA)\alpha B}^{(l, l-\mathbf{r})}] \right] \\ & + W_{AA/A} \sum_{\mathbf{r}' \neq \mathbf{r}} \left[\Theta_{\alpha-}(\mathbf{r}') + \Theta_{\alpha+}(\mathbf{r}') \right] \sum_{\beta \neq \alpha} [\Theta_{\beta-}(\mathbf{r}') + \Theta_{\beta+}(\mathbf{r}')] \\ & \times \left[\Psi_{(AA)\beta B A}^{(l-\mathbf{r}', l-\mathbf{r}, l)} - \Psi_{(AA)\alpha B A}^{(l, l-\mathbf{r}, l-\mathbf{r}')} \right]. \end{aligned} \quad (4.6)$$

Now making use of (3.12) in (4.6) and neglecting the terms that are higher order in B we see that the three-site functions reduce to the two-site functions only. We now sum over l and integrate with time and follow the procedure used by Okamura and Allnatt¹² in the vacancy mechanism. That is, after adding and subtracting the terms $\mathbf{r}' = \mathbf{r}$ in (4.6) we keep the terms with sum over \mathbf{r}' on the left and take rest of the terms on the right-hand side. The Fourier transform then yields,

$$\begin{aligned} \phi_{(AA)\alpha B}^{(k)} = & \frac{1}{8W_{AA/A}} \sum_{\mathbf{r}} G_{\alpha\beta}^{-1}(k) \left\{ -\phi_{(AA)\beta B}^{(0)(k)} - 2W_{BA/A} \cos(k_{\alpha}a) \sum_{\gamma \neq \beta} [\Theta_{\gamma} - (\mathbf{k})\phi_{(AB)\gamma} + \Theta_{\gamma} + (\mathbf{k})\phi_{(BA)\gamma}] \right. \\ & + 4\Delta W \left[\frac{a}{2\pi} \right]^3 \int d^3k' \cos(k_{\beta} - k'_{\beta})a \\ & \left. \times \left[\sum_{\gamma \neq \beta} \cos[(k_{\gamma} - k'_{\gamma})a] \right] \phi_{(AA)\beta B}^{(k')} \right\}, \end{aligned} \quad (4.7)$$

in which

$$\phi_{(AA)\beta}^{(0)(k)} = \sum_{\mathbf{r}} \exp(-i\mathbf{k} \cdot \mathbf{r}) \sum_l \Psi_{(AA)\beta B}^{(l, l - \mathbf{r}; t=0)}, \quad (4.8)$$

and G^{-1} is the inverse of the matrix whose elements are given by

$$G_{\alpha\beta}(k) = -\delta_{\alpha\beta} \left[1 + \frac{W_{AA}^R}{2W_{AA/A}} \right] + \frac{1}{2}(1 - \delta_{\alpha\beta}) \left[\cos(\mathbf{k}_{\alpha}a) \cos(\mathbf{k}_{\beta}a) + \frac{W_{AA}^R}{2W_{AA/A}} \right]. \quad (4.9)$$

We may mention that $G_{\alpha\beta}^{-1}(\mathbf{k})$ is the Fourier transform of the generating function of the dumbbell for the random walk in the host matrix from a β orientation to an α orientation at the vector distance \mathbf{r} . Equation (4.7) is an integral equation for $\phi_{(AA)\alpha B}^{(k)}$ but in the evaluation of $L_{(ij)}^{(1)}$ we need its integral forms, given by (3.22) and (3.23), which can be evaluated by the following sequence of simple steps.

We first note the two symmetry properties of the Brillouin-zone integral in cubic lattices. A Brillouin-zone integral vanishes whenever (1) the integrand is an odd function of one of the wave-vector components k_{α} or (2) the integrand is simply a function of odd powers of $\cos(k_{\alpha}a)$, where $\alpha = x, y$ or z . In order to use these properties it is necessary to note from (4.9) that $G_{\alpha\beta}(\mathbf{k})$ is an even function of the wave vector and for $W_{AA}^R = 0$ is also a function of the even powers of $\cos(k_{\alpha}a)$ and $\cos(k_{\beta}a)$ when it is multiplied by these cosines.

When Eq. (4.7) is substituted into Eqs. (3.22) and (3.23) the contribution to I can be factored into a product of independent integrals over \mathbf{k} and \mathbf{k}' if we expand $\cos(\mathbf{k}_{\alpha} - \mathbf{k}'_{\alpha})a$, appearing in the \mathbf{k}' integral of Eq. (4.7) as a sum of products of cosines and sines. The contributions from the summation over γ in Eq. (4.7) arising from $\gamma = \alpha$ and $\gamma \neq \alpha$ are next considered separately. A straightforward application of the above-mentioned symmetry properties then yields

$$\begin{aligned} W_{AA/A} I_{(AA)\alpha B}^{(1)} = & -iW_{BA/A} Q_0 \chi_{(AB)\alpha} + \Delta W [Q_0 I_{(AA)\alpha B}^{(1)} + Q_0' I_{(AA)\alpha B}^{(2)}] \\ & - \frac{1}{8} \left[\frac{a}{2\pi} \right]^3 \int d^3k \sin(k_{\alpha}a) \sum_{\beta \neq \alpha} \cos(k_{\beta}a) \sum_{\gamma} G_{\beta\gamma}^{-1}(k) \phi_{(AA)\gamma B}^{(0)(k)}, \end{aligned} \quad (4.10)$$

$$\begin{aligned} W_{AA/A} I_{(AA)\alpha B}^{(2)} = & -iW_{BA/A} Q_0' \chi_{(AB)\alpha} + \Delta W [Q_0' I_{(AA)\alpha B}^{(1)} + Q_0'' I_{(AA)\alpha B}^{(2)}] - \frac{1}{8} \left[\frac{a}{2\pi} \right]^3 \int d^3k \sin(k_{\alpha}a) \\ & \times \sum_{\beta \neq \alpha} \cos(k_{\beta}a) \sum_{\gamma} G_{\alpha\gamma}^{-1}(k) \phi_{(AA)\gamma B}^{(0)(k)}, \end{aligned} \quad (4.11)$$

where

$$Q_0 = \frac{1}{4} \left[\frac{a}{2\pi} \right]^3 \int d^3k \sin^2(k_{\alpha}a) \sum_{\beta \neq \alpha} \sum_{\gamma \neq \alpha} G_{\beta\gamma}^{-1}(k) \cos(k_{\beta}a) \cos(k_{\gamma}a), \quad (4.12)$$

$$Q_0' = \frac{1}{4} \left[\frac{a}{2\pi} \right]^3 \int d^3k \sin^2(k_{\alpha}a) \sum_{\beta \neq \alpha} \sum_{\gamma \neq \alpha} G_{\beta\alpha}^{-1}(k) \cos(k_{\beta}a) \cos(k_{\gamma}a), \quad (4.13)$$

$$Q_0'' = \frac{1}{4} \left[\frac{a}{2\pi} \right]^3 \int d^3k \sin^2(k_{\alpha}a) G_{\alpha\alpha}^{-1}(k) \sum_{\beta \neq \alpha} \sum_{\gamma \neq \alpha} \cos(k_{\beta}a) \cos(k_{\gamma}a). \quad (4.14)$$

Equations (4.4), (4.10), and (4.11) provide coupled sets of equations from which $\chi_{(AB)\alpha}^{(1)}$, $I_{(AA)\alpha B}^{(1)}$ and $I_{(AA)\alpha B}^{(2)}$ can be obtained in terms of the integrals with initial time correlation functions, which can be evaluated explicitly for a given initial condition. In the next section we shall evaluate these functions for the initial conditions required in Eqs. (3.20a)–(3.20c).

V. FINAL EXPRESSIONS FOR $L_{ij}^{(1)}$

Let us consider that initially there is a mixed dumbbell $(AB)_x$ at any site I_0 . Then, we have

$$\chi_{(AB)\alpha:(AB)_x}^{(0)} = \frac{1}{6} C_{AB} \delta_{\alpha,x} = -\chi_{(AB)\alpha:(BA)_x}^{(0)}, \quad (5.1)$$

$$\phi_{(AA)\alpha B:(AB)_x}^{(0)(\mathbf{k})} = \phi_{(AA)\alpha B:(BA)_x}^{(0)(\mathbf{k})} = 0. \quad (5.2)$$

Using the above results in (4.4), (4.10), and (4.11) we finally obtain

$$L_{BB}^{(1)} = -\frac{4}{3} \left[\frac{Na^2}{KT} \right] C_{AB} \frac{W_{AB/A}^2}{(W + W_{BA/A}Q)}, \quad (5.3)$$

$$L_{AB}^{(1)} = -L_{BB}^{(1)} \frac{W_{BA/A}}{W_{AB/A}} \left[1 + \frac{\Delta W}{W_{AA/B}} (Q + Q') \right], \quad (5.4)$$

$$L_{AA}^{(1)} = - \left[\frac{4Na^2 C_{AB}}{3KT} \right] \left\{ \left[\frac{W_{BA/A}^2}{W + W_{BA/A}Q} \right] * \left[-2(Q + Q') \frac{\Delta W}{W_{AA/B}} - (Q + Q')^2 \left[\frac{\Delta W}{W_{AA/B}} \right]^2 - 1 \right] + W_{BA/A} (Q + 2Q' + Q'') \left[\frac{\Delta W}{W_{AA/B}} \right]^2 \right\}. \quad (5.10)$$

The expression for $L_{AA}^{(1)}$ agrees with that obtained by Chaturvedi and Allnatt;⁷ Q'' given by their Eq. (50) should be read as $-Q''$. Here Q'' can be obtained from (5.5) if Q and Q_0 are interchanged by Q'' and Q_0'' , respectively.

VI. CONCLUSION

In this paper linear-response formulas are used to obtain the nonlinear phenomenological coefficients in a dilute random fcc alloy where matter transport is accomplished through the migration of dumbbell interstitials. With the help of kinetic equations accurate expressions for all the phenomenological coefficients L_{AA} , $L_{AB} = L_{BA}$ and L_{BB} are obtained when the rotation about a lattice site is allowed for all dumbbells in addition to the usual translation-plus-rotation jumps. Similar expressions were obtained by Chaturvedi and Allnatt⁷ using the well-known matrix method of random-walk theory as originally described by Mullen⁸ and Howard.⁹ This method proceeds by a classification of jumps into nonequivalent types which are not known *a priori*; physical arguments are required to know them for a particular model. Also, a perturbative approach is used to obtain the generating functions. In this sense, the present results can be treated

in which

$$Q = W_{AA/B} [W_{AA/A} Q_0 + \Delta W \{-Q_0 Q_0'' + (Q_0')^2\}] / D, \quad (5.5)$$

$$Q' = [W_{AA/A} W_{AA/B} Q_0'] / D, \quad (5.6)$$

$$D = (W_{AA/A} - \Delta W Q_0)(W_{AA/A} - \Delta W Q_0'') - (\Delta W Q_0')^2. \quad (5.7)$$

Equations (5.3) and (5.4) are the same as obtained earlier by different approaches.^{6,7} To obtain $L_{AA}^{(1)}$ from (3.20c) we also need to know the function F_α , defined by (3.24), when initially an $(AA)_x$ dumbbell is at site I_0 and a solute atom at site $(I_0 - \mathbf{s}_0)$. For this we have

$$\chi_{(AB)\alpha:(AA)_x B}^{(0)(\mathbf{k}_0)} = 0 \quad (5.8)$$

and

$$\phi_{(AA)\alpha B:(AA)\alpha B}^{(0)(\mathbf{k};\mathbf{k}_0)} = \frac{1}{6} \delta_{\alpha,x} C_{AB} \frac{W_{BA/A}}{W_{AA/B}} \delta(\mathbf{k} + \mathbf{k}_0). \quad (5.9)$$

Using the above results we finally obtain

as first-principles calculations, since the correlation functions appearing in $L_{ij}^{(1)}$ are obtained through the kinetic equations. The present method can be further extended to the concentrated alloy, where to the best of our knowledge, there is no reasonable theory for the interstitial's motion. Bocquet¹³ has investigated models of interstitial behavior in binary alloys using both Monte Carlo simulations and analytical techniques based on the random-alloy model developed by Manning¹⁰ for diffusion via the vacancy mechanism. Recently Murphy¹⁴ has used kinetic equations to study the migration of dumbbell interstitials along the principle x direction but for simplicity neglected the influence of correlation between successive jumps of the interstitials. The present method is quite general and can be extended to the calculations of tracer and nontracer transport coefficients in a concentrated random alloy. These works are currently under progress and will be reported in future publications.

ACKNOWLEDGMENT

One of us (D.K.C.) wishes to thank Professor A. R. Allnatt for several stimulating discussions during the course of this work.

- ¹Y. Adda and J. Philibert, *Le Diffusion Dans les Solids* (Presses Universitaires de France, Paris, 1966).
- ²R. E. Howard, *Phys. Rev.* **144**, 650 (1966).
- ³A. R. Allnatt and A. B. Lidiard, *Rep. Prog. Phys.* **50**, 373 (1987).
- ⁴A. B. Lidiard, *Philos. Mag.* **46**, 1218 (1955).
- ⁵A. R. Allnatt and Y. Okamura, in *Nontraditional Methods in Diffusion*, edited by G. E. Murch, H. K. Birnbaum, and J. R. Cost (Met. Soc. A.I.M.E., Warrendale, PA, 1984), p. 237.
- ⁶J. L. Bocquet, *Philos. Mag.* **47**, 547 (1983).
- ⁷D. K. Chaturvedi and A. R. Allnatt, *Philos. Mag. A* **65**, 1169 (1992).
- ⁸J. G. Mullen, *Phys. Rev.* **121**, 1649 (1961).
- ⁹R. E. Howard, *Phys. Rev.* **144**, 650 (1966).
- ¹⁰J. R. Manning, *Diffusion Kinetics for Atoms in Crystals* (Van Nostrand, Princeton, NJ, 1968).
- ¹¹A. R. Leclaire, in *Physical Chemistry—An Advanced Treatise*, edited by H. Eyring, D. Henderson, and W. Jost (Academic, New York, 1970), Vol. 10, p. 261.
- ¹²Y. Okamura and A. R. Allnatt, *Philos. Mag. A* **54**, 773 (1986).
- ¹³J. L. Bocquet, *Acta Metall.* **34**, 571 (1986); *Res. Mechanica* **22**, 1 (1987).
- ¹⁴S. M. Murphy, *J. Nucl. Matter.* **182**, 73 (1991).