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Theory of many-body diffusion by the path-probability method: Conversion from ensemble averaging to time averaging

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The formalism of the path-probability method (PPM) of irreversible statistical mechanics as applied to transport processes is examined in connection with the calculation of the "correlation factor" in many-body diffusion problems. Tracer diffusion in disordered binary alloys is taken as an example for this treatment. The essential characteristic of the PPM is to evaluate the evolution of state with time under nonequilibrium conditions with the use of ensemble averaging at an instant in time. It is pointed out that time averaging rather than ensemble averaging is to be taken in order to evaluate the time correlation of the motion of a small number of particles necessary for the calculation of properties such as the correlation factor in tracer diffusion and the flow of particles in general. The conversion from ensemble averaging to time averaging is made in the "linear range," in which the Onsager equations are valid, without changing the nature of approximation of the treatment. Comparisons of results in these two different averaging methods are thus given. In particular, the percolation sensitivity of tracer diffusion in the time average is discussed.

I. INTRODUCTION

The role of irreversible statistical mechanics such as the path-probability method[1] (PPM) in transport phenomena is to derive analytically the Onsager equations (for diffusion) based on atomistic models. From the knowledge of the kinetic matrix, one can draw conclusions with respect to observable quantities such as the correlation factor for tracer diffusion and ionic conductivity under appropriate boundary conditions in many-body diffusion problems. We call any general diffusion problem, except those such as self-diffusion in nearly perfect crystals, a many-body diffusion problem because diffusing atoms or ions cannot be considered independent of surroundings due to mutual interactions with surroundings. So far, systematic treatments of many-body diffusion problems other than the PPM are lacking.

In the pair approximation of the PPM, the tracer diffusion coefficient D_T (in the limit of negligible concentration of tracer ions) and the ionic conductivity σ for many-body diffusion problems[2-6] in fast ionic conductors with a single diffusing constituent,[5,6] for example, were found to be represented by

$$D_T = a^2 \vartheta \exp(-\beta u) V W f \tag{1a}$$

and

$$\sigma = \frac{ne^2}{kT} a^2 \vartheta \exp(-\beta u) V W f_I \ . \tag{1b}$$

Here, a is a numerical factor related to the jump distance and the dimensionality of the crystal lattice, $\beta = (kT)^{-1}$, and $\vartheta \exp(-\beta u)$ gives the basic jump frequency of an atom of an ion to be observed. Also, in Eq. (1b), n is the number of ions per unit volume and e is the charge on the ion. The factors V, W, and f or f_I represent the many-body effect; V is related to the vacancy (vacant available site) distribution with respect to a diffusing atom and is called the vacancy availability factor, and W is related to the effect of interaction with neighboring atoms on the jump frequency and is called the effective jump-frequency factor. These two factors are determined by the distribution of atoms and $\vartheta \exp(-\beta u) V W$ represents the jump frequency in the statistically averaged system. The factors f and f_I then are interpreted to represent the efficiency of motion of tracer atoms and the total assembly of atoms, respectively, toward long-range diffusion relative to the random-walk motion in the statistically averaged system represented by its jump frequency $\hat{w} = \vartheta \exp(-\beta u) V W$. The factors f and f_I are thus defined as the generalized correlation factor by Eq. (1). In the limit of self-diffusion of nearly perfect crystals, the definition of f becomes identical to the correlation factor customarily defined. The difference between f and f_I is due to the fact that the number of tracer atoms is far smaller than the number of the total assembly of atoms and f/f_I has been referred to by the present authors as the geometrical correlation factor f_G while f_I is referred to as the physical correlation factor.[7] The ratio $f/f_I = f_B$ represents the Haven ratio.[5]

Although the PPM is very versatile in dealing with many-body diffusion problems, unsatisfactory features in connection with the calculation of the correlation factor have been noticed. In the first place, the numerical values for the correlation factor calculated by the PPM have been found to be rather unsatisfactory for the degree of approximation utilized[3] if judged relative to the random-walk theory of diffusion,[8,9] which is capable of giving exact values of f for simple cases such as self-diffusion. Further, the pair approximation of the PPM predicts the value of f in self-diffusion for the vacancy mechanism (in nearly perfect crystals) to be $(2\omega - 1)/(2\omega + 1)$, where 2ω is the coordination number of the lattice. However, an appropriate value of f by the pair approximation of the

PPM should rather be $(2\omega-2)/2\omega$ based on the prediction of the percolation limit at $2\omega=2$ by the pair approximation of the cluster-variation method[10] (CVM), which is the static version of the PPM (diffusion is essentially a dynamical percolation problem and diffusion has to stop at the percolation limit predicted by static statistical mechanics). The work has since been examined by the Monte Carlo method under a similar condition.[11,12] These results clearly showed that, although the values for V and W agreed very well with those of the simulation, a marked but systematic discrepancy in the values of f was found between the results of these two methods. We also showed that, in the "ideally disordered" binary alloys (in which no interactions among atoms are assumed, so that the alloys are always in the completely disordered state), f predicted by the PPM shows a systematic deviation from that obtained by the extension of the random-walk theory[13] in its composition dependence if the relative jump frequencies of constituent atoms deviate strongly from unity,[3] and the pair approximation of the PPM is even found to be incapable of predicting the percolation limit suggested by the pair approximation of the CVM.[3] Among V, W, and f, which indicate many-body effects in diffusion, V and W are essentially determined by the equilibrium distribution of atoms and vacancies on the crystal lattice sites and they (and hence the averaged jump frequency) can be calculated by the application of the CVM only,[14–16] while f is calculated through the nonequilibrium process of the PPM. Therefore, the problem should be connected to the process of extending the CVM to include the time dependence. On the other hand, the application of the pair approximation of the PPM to other kinetic processes such as the kinetics of the order-disorder transformation in alloys has been shown to give results compatible with the pair approximation of the CVM.[17] This discrepancy in behavior of the PPM in predicting kinetic processes has prompted us to reexamine the formalism of the PPM as applied to the transport processes.

The result of the analysis of the PPM clearly indicates that the difficulty in the calculation of f by the PPM is due to its formalism in evaluating the flow. The PPM works out how the system changes with time and is based on the contention that the most probable change of state is the one observed macroscopically.[1] The PPM thus starts with the path-probability function, which represents the probability that a specified path, i.e., a change of state, occurs. This probability is calculated using the combinatorial counting in an ensemble which is made of a large number of replicas of the paths. Because of mathematical restrictions, the path-probability function is formulated for a short-time interval Δt only. Therefore, a path treated by the PPM has the meaning of a change of state of a single system only for the short-time span Δt. Further, in evaluating the time sequence, the state at each time instant is represented by an ensemble of systems in the same fashion as the CVM. Hence, the time correlation calculated by the PPM is that of the average of the system. In other words, the flow of individual particles is not followed by the PPM. Because of this situation, the result of the PPM becomes especially unsatisfactory when the time correlation of the motion of a small number of particles has to be followed for a long time: for example, in the case of calculating the correlation factor in tracer diffusion. In order to calculate properties such as the correlation factor, one has to follow the time evolution of a single system rather than following the time evolution of an ensemble of states.

The recognition of the difficulty of the PPM in predicting the long-time behavior has led us to convert the results of the PPM in the ensemble average at each time instant into those of the time average by following the time evolution of a single system without changing the degree of approximation. This has added a further versatility to the treatment by the PPM. At the same time, a clear recognition of the two different statistical averages with respect to the derivation of the correlation factor enables us to judge the validity of predictions based on these two types of averaging methods relative to individual experimental techniques. The conversion process will be explained for diffusion in disordered binary alloys as an example. A brief but systematic derivation of the correlation factor in disordered binary alloys in the pair approximation of the original PPM is presented in the Appendix as a basis for explaining the conversion process.

II. EXAMINATION OF RESULTS BY THE ORIGINAL PPM

In this section, pertinent results concerning flows of particles obtained by the original PPM are explained as the basis for the conversion into the time average. In order to predict the properties at time $t+\Delta t$ based on the properties at time t (Δt is a short-time interval during which, at most, one unit process can occur as defined by the PPM), the PPM considers an ensemble of paths in a single system during Δt.[1] Because the state at each time instant is represented in terms of an ensemble of systems similar to the CVM, the paths are eventually those which connect the states in the ensemble at time t to those in the ensemble at time $t+\Delta t$, which are accessible, at most, by a unit process. Such paths are expressed by the path variables such as $Y_{iv,ij}(t,t+\Delta t)$ (Appendix, Sec. 3). The procedure of selecting the most probable path, which makes the "path-probability function" maximum (Appendix, Sec. 3), corresponds to the process of selecting the most probable values of state variables, which make the free energy a minimum in the CVM. Based on this relation, the prediction of the time evolution of the state by the ensemble averaging method at an instant in time is called the ensemble averaging method.

The Onsager equations for diffusion are linear equations which relate the flows of particles of individual species and the respective chemical-potential gradients as conjugate driving forces. The Onsager equations are defined across a reference plane and at a time instant t by the PPM. Flows of particles are evaluated in terms of the path variables which represent the exchange of particles across the reference plane (Appendix, Sec. 3). For the tracer diffusion by the vacancy mechanism in disordered binary alloys composed of A, B, and B^* with the compositions x_A, x_B, and x_{B^*} (species 1, 2, and 3 where B^* is an isotope atom of B used as a tracer), the Onsager equations are expressed in terms of three chemical potentials μ_1, μ_2, and μ_3 (or in α_i's) defined by $\beta\mu_i=\alpha_i$:

$$\Phi_i=\sum_j L_{ij}\dot{\alpha}_j \;, \tag{2a}$$

$$L_{ij}=L_{ji} \;, \tag{2b}$$

where $\dot{\alpha}_j$ signifies the gradient of α_j, and Φ_i is the flow of the ith species across the reference plane and is defined by Eq. (A7) as $\Phi_i=Y_{+i}-Y_{-i}$, where $Y_{\pm i}$ are path variables and represent the flow of the ith particles across the reference plane to the $+x$ direction and to the $-x$ direction, respectively [Eq. (A4)].

The elements of the kinetic matrix, L_{ij}'s derived by the PPM are thus expressed in terms of the probable paths of path variables given in the ensemble average at time t. Furthermore, in the linear range in which the Onsager equations are valid, L_{ij}'s are expressed in terms of the equilibrium values which represent those of the reference plane. Therefore, the derivation of the correlation factor by the PPM is essentially the evaluation of the self-correlation function of the motion of a particle in equilibrium but at a time interval Δt.

In order to derive the correlation factor, the Onsager equations, Eqs. (2), are transformed, under an appropriate boundary condition, to a one-variable equation of the form (see Appendix, Sec. 5)

$$\Psi_3=-M_3\dot{\alpha}_3=-\frac{(2\omega-1)Z}{2+(2\omega-3)Z}\dot{\alpha}_3 \;, \tag{3a}$$

utilizing the normalized flow Ψ_3 defined as $\Psi_3=\Phi_3/Y_3$ [Eq. (A11)], where Y_3 is the value of Y_{+3} or Y_{-3} under the equilibrium condition. The diffusion coefficient of tracer atoms $D_T(=D_3)$ is defined in (A23) as

$$\omega a^2\Phi_3=-D_3\dot{x}_3\Delta t \;, \tag{3b}$$

where 2ω is the coordination number and $\omega a^2\Phi_3$ represents the flow of B^* atoms per unit area. $\dot{x}_3$ is the concentration gradient of B^* atoms (Table I). In terms of Ψ_3 and rewriting $\dot{x}_3$ in terms of $\dot{\alpha}_3$ [Eq. (A28)], Eq. (3b) can be rewritten as

$$D_3\Delta t=-(\omega a^2/x_3)Y_3\Psi_3/\dot{\alpha}_3 \;. \tag{3c}$$

The quantity Y_3 represents the jump probability of a B^* atom under equilibrium in the statistically averaged solid and can be related to the jump frequency of a B^* atom w_3 (or $\hat{w}_3$ if the effect of surroundings is included) [see Eq. (A14)]. Therefore, if the diffusion coefficient represented by the random walk of the jump probability Y_3 is denoted by D_{3R}, then

$$D_{3R}\Delta t=(\omega a^2/x_3)Y_3 \;. \tag{3d}$$

The correlation factor f_B is defined as the ratio of D_3/D_{3R} (Appendix, Sec. 4) or as the efficiency of the motion of B^* atoms with respect to the random walk as

$$D_3/D_{3R}=-\Psi_3/\dot{\alpha}_3=f_B \;. \tag{3e}$$

It is clear that this definition agrees with the one commonly given in the self-diffusion (f_B for $x_A=0$).

The correlation factor f_B is then obtained from (3a) as

$$f_B=\frac{(2\omega-1)Z}{2+(2\omega-3)Z} \;, \tag{4a}$$

where

$$Z=\frac{x_Aw_A}{w_A+w_{B^*}}+\frac{x_Bw_B}{w_B+w_{B^*}}+\frac{x_{B^*}w_{B^*}}{w_{B^*}+w_{B^*}} \tag{4b}$$

for the ideally disordered alloys [Eq. (A31)] and, more generally, for disordered alloys with short-range order in terms of effective jump-frequency parameters $\hat{w}_i$ [Eq. (A14)] as

$$Z=\sum_j\frac{Q_j\hat{w}_j}{\hat{w}_3+\hat{w}_j} \;, \quad j=1,2, \text{ and } 3 \;. \tag{4c}$$

TABLE I. Glossary.

x_i	Probability of having constituent i on a lattice site. In disordered alloys, x_i indicates the density of ith species.
y_{ij}	Probability of having a constituent i on a lattice site and a constituent j on a nearest-neighbor lattice site.
ν	Index for a plane through lattice points perpendicular to the concentration gradient in the [100] direction of the bcc lattice (atomic plane) (see Fig. 8).
n	Index for a plane through the center of two atomic planes ν and $\nu+1$ (bond plane) (see Fig. 8).
ϵ_{ij}	Interaction energy between a nearest-neighbor pair of constituents i and j.
ϵ	$\epsilon_{AA}+\epsilon_{BB}-2\epsilon_{AB}$.
U	$\frac{1}{4}(\epsilon_{AA}-\epsilon_{BB})$; we assume $\epsilon_{iv}=0$ and $U=0$.
β	$(kT)^{-1}$; k is the Boltzmann constant, T the absolute temperature.
ρ_i	Density of species i; in dealing with alloys, we assume that $\rho_v\approx 0$. $\rho_B+\rho_{B^*}$ or ρ_A then specifies the composition of the system.
$\dot{x}_i$	Concentration gradient of constituent i due to the existence of the concentration gradient B^*.
$K_{ij}=K_{ji}=\exp(-\beta\epsilon_{ij})$.	
q_l	$y_{ij}=q_iq_jK_{ij}^{-1}$.
$Q_l\equiv q_l\left[\sum_{m=1}^{4}q_m\right]^{-1}$.	
$\alpha_i\equiv\beta\mu_i$.	μ_i represents the chemical potential of the ith species. α_i is given by Eq. (A16a); it is also used to specify state variables in Sec. II.
2ω	Coordination number of the lattice. For bcc, $2\omega=8$.

Equation (4) gives for self-diffusion ($x_A=0$)

$$f_B=\frac{2\omega-1}{2\omega+1}=\frac{7}{9} \quad \text{for } 2\omega=8 \ . \tag{4d}$$

Q_j is a quantity which specifies the probability of finding a species j neighboring to a vacancy as calculated by the CVM (Appendix, Sec. 2 and Table I). It also can be utilized to specify the same quantity next to a specific lattice point.

It is to be noted that, although the formulation of $D_T=D_3$ was made for any concentration of B^*, f_B obtained in Eqs. (3) and (4),

$$[(2\omega-1)Z]/[2+(2\omega-3)Z] \ ,$$

is independent of the composition (Appendix, Sec. 5). This is due to the specific boundary conditions adopted for calculating D_T (Appendix, Sec. 6).

For the purpose of future use, let us examine the physical meaning of Z derived in (A27) and given in Eq. (4). As is explained in Sec. 4 of the Appendix and as is seen in Fig. 1, which illustrates the physical situation expressed in Eq. (4c), Z can be interpreted as the probability that an atom which may be represented by A, B, or B^* across a vacancy at the nearest neighbor of a tagged B^* atom jumps into the vacancy in competition with the tagged B^* atom under the equilibrium condition. As Eq. (A21) indicates, in calculating the flow of Ψ_i, i atoms (B^*) are to be hereafter interpreted as individually tagged. The situation is also explained in Sec. 4 of the Appendix. The recognition of the tagging process in the calculation of Ψ_i is quite important and this procedure plays an important role in the conversion process as will be shown later. Moreover, if Z is to be interpreted as a competition between a tagged atom and an atom across a vacancy, the situation indicated in Fig. 1 [and hence Eq. (4c)] is to be interpreted to represent an instant immediately after the tagged atom has replaced the vacancy (Appendix, Sec. 5). Therefore, here the probability of its jumping back of the tagged atom into the vacancy it has just replaced is being calculated. The quantity $1-Z$ thus represents the jump-back probability of the tagged atom (which corresponds to the return probability P_r in the random-walk theory), while Z is the probability that any other atom which forms a pair with the tagged atom B^* across the vacancy jumps into the vacancy [which corresponds to the escape probability $P_e=(2\omega-1)Z$ in the random-walk theory].

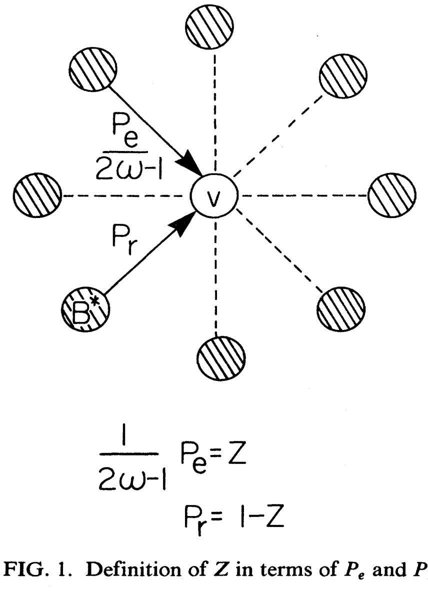

FIG. 1. Definition of Z in terms of P_e and P_r.

There are $2\omega-1$ pairs of atoms with respect to the tagged atom across the vacancy. Therefore, the normalized probability τ of jumping back of the tagged atom in competing with $2\omega-1$ atoms is defined as

$$\tau=\frac{P_r}{P_r+P_e}=\frac{1-Z}{(1-Z)+(2\omega-1)Z}=\frac{1-Z}{1+(2\omega-2)Z} \ . \tag{5}$$

In other words, in terms of Z it is possible to specify the probability among possible jumps which contribute to the drift as $1-\tau$. Utilizing τ, the efficiency f of the drift of the tagged atom is then

$$f=\frac{1-\tau}{2\tau+(1-\tau)}=\frac{1-\tau}{1+\tau}=\frac{(2\omega-1)Z}{2+(2\omega-3)Z}=f_B \ . \tag{6}$$

Equation (6) coincides with the definition of f_B given by Eq. (4). In the random-walk theory, the definition of the correlation factor is given in terms of similarly defined τ as in Eq. (6) and the relation between the PPM and the random-walk theory in calculating the correlation factor is now clear. However, in the random-walk theory, τ is calculated for an infinite span of time, while in the PPM, τ is an efficiency of a jump at a time instant t.

In Z defined in (4c), a B^* atom is interpreted as tagged even if a large number of B^* atoms can exist (Appendix, Sec. 4). Let us denote Z, therefore, as Z_{B^*} in this case. In general, however, any species i can be taken as a tagged species. Therefore, it is possible to define Z_A and Z_B, likewise, and hence the jump-back probabilities τ_A, τ_B, or τ_{B^*} of an A, B, or a B^* atom, in disordered binary alloys, can be defined in terms of Z_i as

$$\tau_i=\frac{1-Z_i}{1+(2\omega-2)Z_i} \ , \tag{7}$$

where Z_i is defined in terms of Y_i's [Eq. (A31b)],

$$Z_i=1-\sum_{j=1}^{3} Q_j\frac{Y_i/Q_i}{Y_i/Q_i+Y_j/Q_j}=\sum_{j=1}^{3}\frac{Y_j}{Y_i/Q_i+Y_j/Q_j} \ . \tag{8}$$

In terms of Z_{B^*} it is easy to show how the ensemble average is responsible for the lack of the percolation limit, the presence of which is expected when only one (B) of the constituent species can move. As is shown in Fig. 1, Z_{B^*} represents the probability of jump of the nearest-neighboring atoms in competition with the tagged B^* atom. Because the ensemble average is utilized, Z derived by the PPM indicates that the atom to which the vacancy escapes (away from the tagged B^* atom) can simultaneously be an A atom or a B atom with probabilities x_A and x_B, respectively, as shown in Fig. 2. Therefore, as long as

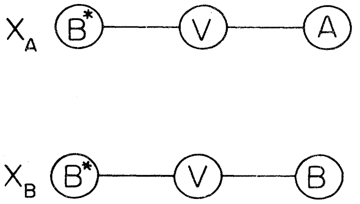

FIG. 2. Graphical representation of Z in the ensemble averaging at a time instant t.

the concentration of B (B and/or B^*) is finite, Z indicates that there is a finite probability of having a B atom (or B^*) competing with the (tagged) B^* atom opposite the vacancy, and an escape path for the vacancy is always provided however small the concentration of B atoms may be.

III. TIME AVERAGING IN DIFFUSION PROCESS

As explained earlier, the PPM is designed to follow the motion only during Δt and not to follow the motion of particles for a long time. In the pair approximation, this situation leads to a result which can be described as the "superposition relation"[1,2] and the change (or the most probable path) is determined solely by the condition at time t (the initial condition). In other words, in the PPM, the calculated tracer diffusion coefficient D_T corresponds to $D_T(\infty)$ or the diffusion coefficient measured in the limit of infinite frequency. On the other hand, the so-called correlation factor is a time correlation of the motion of a single (tagged) particle for a long time. Under such a condition, rather than the ensemble averaging process at a time instant, the averaging of jumps over a long-time period or the time averaging process should be taken. In contrast to $D_T(\infty)$, it is therefore necessary to calculate $D_T(0)$ to obtain the correlation factor.

The flow Ψ_i, from which the diffusion coefficient is derived [Eq. (A21)], is obtained directly from the most-probable-path expressions derived in the PPM in the ensemble average. If these expressions can be converted in the time average, the flow Ψ_i is also converted to that in the time average. Therefore, the aim of the present section is to convert the expressions of the most probable path into the time averaging.

Under the equilibrium condition, the time averaging is generally replaced by the ensemble averaging. In such a case, the ensemble averaging is taken independent of time and there is no distinction between the two averaging processes. In the derivation of the time correlation by the PPM, the ensemble is defined at each time instant t and the averaging process based on this definition of ensemble is called the ensemble averaging. If measurements are made over a long period of time, on the other hand, the system observed changes with time. The assembly of the states created by the evolution of a single system with time is thus called the time ensemble in the present paper (Fig. 3). The average taken with respect to the time ensemble is then called the time average. Under the nonequilibrium condition, the ensemble average and the time average thus defined are not the same and the conversion from the one to the other is generally not possible.

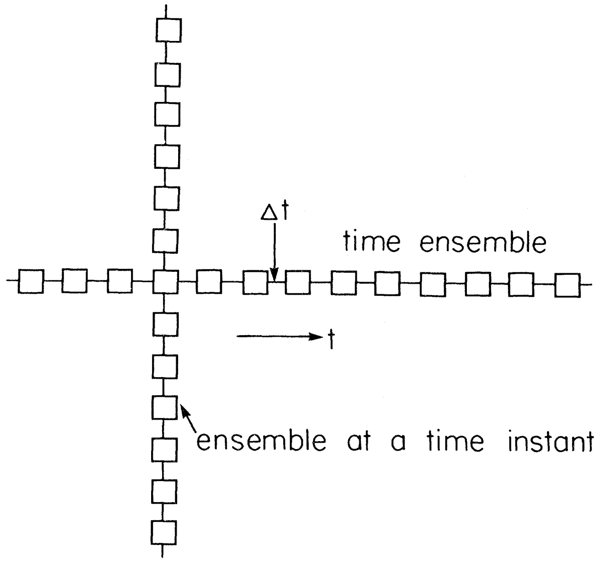

FIG. 3. Relation between the ensemble taken by the PPM and the time ensemble. Each square represents a single system.

In the linear range in which the Onsager equations are valid, on the other hand, the most-probable-path expressions of the PPM are eventually expanded linearly with respect to the chemical-potential gradients, and the elements of the kinetic matrix are expressed in terms of equilibrium values (Appendix). In other words, the evaluation of flows are eventually made based on the motions of particles under the equilibrium condition. If this is so, the ensemble of states defined at each time instant t is equivalent to the content of the equilibrium ensemble. The situation is the same for the time ensemble. In other words, except for the fact that the one refers to a time instant while the other refers to an infinite span of time, the content in these two types of ensembles are equivalent. This equivalence allows us to convert the results in the ensemble average at a time instant into those in the time average uniquely.

The ensemble of paths represented by a path variable $Y_{ij,iv}(t,t+\Delta t)$ in the PPM, in its original form, refers to a single system. However, since a state at each time instant is represented by an ensemble of systems in evaluating the time correlation, in the most probable path found by maximizing the path-probability function, the i-j pair at time t and the i-v pair at time $t+\Delta t$ do not necessarily belong to the same single system. This is the trouble with the PPM in finding the time correlation in a single system as explained earlier.

Let us define the corresponding expression of the path variable $\widetilde{Y}_{ij,iv}(t',t'+\Delta t)$ at a time instant t' in the time ensemble. If we adopt the same definition of Δt during which only one jump can occur, $\widetilde{Y}_{ij,iv}(t',t'+\Delta t)$ represents a single path in the time ensemble and, moreover, the i-j pair at time t' and the pair i-v at $t'+\Delta t$ belong to the same system. The assembly of $\widetilde{Y}_{ij,iv}(t',t'+\Delta t)$ for an infinite period of time, $[\widetilde{Y}_{ij,iv}(t',t'+\Delta t)]$, thus corresponds to $Y_{ij,iv}(t,t+\Delta t)$ of the PPM. Since the equivalent ensembles are utilized, the $Y_{ij,iv}(t,t+\Delta t)$ and

$[\tilde{Y}_{ij,iv}(t',t'+\Delta t)]$ are equivalent as long as the ensemble of paths is considered. Therefore, it is meaningful to calculate the most probable path in $[\tilde{Y}_{ij,iv}(t',t'+\Delta t)]$ in exactly the same fashion as that in $Y_{ij,iv}(t,t+\Delta t)$. The difference between the most probable paths in the PPM and those referring to the time ensemble is that, in the former, they are represented by the ensemble average in the choice of *i-j* pairs at a time instant *t*, but there is no guarantee that the pairs *i-j* and *i-v* belong to the same system, while in the latter, they are represented by the average in the choice of pairs for an infinite period of time, but the *i-j* pair and the *i-v* pair should belong to the same system. The task is to find the correspondence of the two kinds of the most probable paths knowing that they both are found by the same mathematical procedure because $Y_{ij,iv}(t,t+\Delta t)$ and $[\tilde{Y}_{ij,iv}(t',t'+\Delta t)]$ are equivalent as far as the ensemble of paths is concerned.

In evaluating the flow of *i*, the most probable path $Y_{ij,iv}(t,t+\Delta t)$, etc., are eventually calculated by fixing *i* as emphasized earlier. In other words, *i* atoms are tagged individually at a time instant. The corresponding situation in $[\tilde{Y}_{ij,iv}(t',t'+\Delta t)]$ is that an individual *i* atom is tagged for a long-time span. From here, it directly follows that the motion of a single particle is followed for a long-time span in the time averaging process. For a particular tagged *i* atom, possibilities exist that a different species *j* ($j=1$, 2, or 3) comes to its neighbor in the course of time. The selection of the most probable path in $Y_{ij,iv}(t,t+\Delta t)$ or in $[\tilde{Y}_{ij,iv}(t',t'+\Delta t)]$ means that, with respect to the choice of *i-j*, the probability of the choice of a particular *j* among all other possibilities is to be found. In the ensemble average, all the possibilities are found at a time instant. In the time ensemble, these possibilities appear as time evolves. In $[\tilde{Y}_{ij,iv}(t',t'+\Delta t)]$, therefore, the species of *j*

TABLE II. Path variables and most-probable-path expressions. Path variable column can be continued with *i* and *j* indices interchangeable.

Path variables	Relations with $Y_{\pm i}$'s	First-order expression of the most probable path
$Y^{(n)}_{ij,vj;+i}$	$\dfrac{y^{(n)}_{ij}K_{ij}}{\sum_{j=1}^{4} y^{(n)}_{ij}K_{ij}}Y^{(n)}_{+i}$	$Q_j Y_i \left[1+\delta\ln\dfrac{y_{ij}K_{ij}}{\sum_{j=1}^{4} y_{ij}K_{ij}}+\tfrac{1}{2}\Psi_i\right]$
$Y^{(n)}_{ij,vj;-i}$	$\dfrac{y^{(n)}_{ij}K_{ij}}{\sum_{j=1}^{4} y^{(n)}_{ij}K_{ij}}Y^{(n-1)}_{-1}$	$Q_j Y_i \left[1+\delta\ln\dfrac{y_{ij}K_{ij}}{\sum_{j=1}^{4} y_{ij}K_{ij}}-\tfrac{1}{2}\Psi_i-\dfrac{d}{n}\ln Y_i\right]$
$Y^{(n)}_{vj,ij;+i}$	$\dfrac{y^{(n)}_{vj}}{x^{(\nu)}_{v}}Y^{(n-1)}_{+i}$	$Q_j Y_i \left[1+\delta\ln\dfrac{y_{vj}}{\sum_{j=1}^{4} y_{vj}}+\tfrac{1}{2}\Psi_i-\dfrac{d}{dn}\ln Y_i\right]$
$Y^{(n)}_{vj,ij;-i}$	$\dfrac{y^{(n)}_{vj}}{x^{(\nu)}_{v}}Y^{(n)}_{-i}$	$Q_j Y_i \left[1+\delta\ln\dfrac{y_{vj}}{\sum_{j=1}^{4} y_{vj}}-\tfrac{1}{2}\Psi_i\right]$
$Y^{(n)}_{ij,iv;+j}$	$\dfrac{y^{(n)}_{ij}K_{ij}}{\sum_{i=1}^{4} y^{(n)}_{ij}K_{ij}}Y^{(n+1)}_{+j}$	$Q_i Y_j \left[1+\delta\ln\dfrac{y_{ij}K_{ij}}{\sum_{i=1}^{4} y_{ij}K_{ij}}+\tfrac{1}{2}\Psi_j+\dfrac{d}{dn}\ln Y_j\right]$
$Y^{(n)}_{ij,iv;-j}$	$\dfrac{y^{(n)}_{ij}K_{ij}}{\sum_{j=1}^{4} y^{(n)}_{ij}K_{ij}}Y^{(n)}_{-j}$	$Q_i Y_j \left[1+\delta\ln\dfrac{y_{ij}K_{ij}}{\sum_{i=1}^{4} y_{ij}K_{ij}}-\tfrac{1}{2}\Psi_j\right]$
$Y^{(n)}_{iv,ij;+j}$	$\dfrac{y^{(n)}_{iv}}{x^{(\nu+1)}_{v}}Y^{(n)}_{+j}$	$Q_i Y_j \left[1+\delta\ln\dfrac{y_{iv}}{\sum_{j=1}^{4} y_{jv}}+\tfrac{1}{2}\Psi_j\right]$
$Y^{(n)}_{iv,ij;-j}$	$\dfrac{y^{(n)}_{iv}}{x^{(\nu+1)}_{v}}Y^{(n+1)}_{-j}$	$Q_i Y_j \left[1+\delta\ln\dfrac{y_{iv}}{\sum_{j=1}^{4} y_{jv}}-\tfrac{1}{2}\Psi_j+\dfrac{d}{dn}\ln Y_j\right]$

which pairs with the tagged i atom can be different at each time instant t, but, after a long-time span, the probability of the appearance of a particular j should be specified by its (time) average and is the same as the ensemble average. In the most-probable-path expression, the specification of j in $Y_{ij,iv}(t,t+\Delta t)$ appears in the form of Q_iY_j or $Q_iQ_j(Y_j/Q_j)$ (Table II). In other words, when an i atom is tagged, the contribution of j atoms at a time instant is $Q_j(Y_j/Q_j)$, where Y_j/Q_j is proportional to the jump frequency of a j atom. If the species of j is to be averaged over a long-time span, the time average of the jump frequency is then the weighted average of Y_j/Q_j or

$$\frac{\sum_k Q_k(Y_k/Q_k)}{\sum_k Q_k}=\sum_k Y_k\,.$$

In other words, in the most-probable-path expressions, Y_j is to be replaced by $Q_j\sum_k Y_k$ in the time average. Because the time average is exactly the same as the ensemble average under the equilibrium condition for the state variables, it is not necessary to change expressions for the state variables which appear in the linearly expanded part of the most-probable-path expressions. Rather, the requirement that the average values (with respect to space) are the same in both averaging methods thus introduces the proper time correlation consistent with the approximation in the time averaging through the relation above.

Let us look into the second type of correspondence between the ensemble averaging and the time averaging by using $Y_{iv,ij}(t,t+\Delta t)$, for example. That an i atom is tagged for a long-time span while j should represent the average of species over a long-time span in $[\tilde{Y}_{iv,ij}(t',t'+\Delta t)]$ is explained above. Now, $Y_{iv,ij}(t,t+\Delta t)$ indicates the probability that a j atom jumps into a vacancy which happens to be neighboring with a tagged ith atom at a time instant t. The vacancy indicated in $Y_{iv,ij}(t,t+\Delta t)$ is the vacancy which has just exchanged places with the tagged atom, and t indicates the time the tagged atom is about to jump back into the vacancy as explained earlier. Therefore, here the jump of the jth atom into the vacancy is a forward jump which contributes to the drift motion. In the preceding section, we have defined the forward jump probability for a j atom at the time instant as $1-\tau_j$ in the ensemble average in Eq. (7). In the time average, as in the species of atoms, the time average over a long time of the jump of the jth atom should be utilized rather than the jump at a time instant t'. In other words, the time average of the forward jump probability of the jth atom $Y_j(1-\langle\tau_j\rangle)$ should be thus used rather than the instantaneous value Y_j as in the ensemble average. The quantity $\langle\tau_j\rangle$ indicates the time average of τ_j.

Combining the two processes described above with respect to the correspondence concerning the most probable path in the two kinds of averages, the conversion process is summarized as follows. First, the most-probable-path expressions are given in the PPM and these are then expanded linearly with respect to chemical-potential gradients. The coefficients of the gradients thus indicate the most probable path evaluated based on the equilibrium ensemble and are given in the ensemble average. In the linearly expanded part of the most-probable-path expressions (Table II), Y_j in the ensemble average is to be replaced by

$$Y_j\to\frac{Q_j\sum_{k=1}^{3}Y_k(1-\langle\tau_k\rangle)}{\sum_{k=1}^{3}Q_k}=Q_j\sum_{k=1}^{3}Y_k(1-\langle\tau_k\rangle)\,. \tag{9a}$$

The species i is tagged in this case. Therefore, Y_i is not averaged and hence is not involved in the conversion. State variables are the same in the ensemble average and in the time average under the equilibrium condition and are to be kept the same in the conversion process. The quantity $\langle\tau_k\rangle$ in Eq. (9a) is the time average of τ_k defined in Eq. (5) in terms of Z_k [refer also to Eq. (7)] and is given by

$$\langle\tau_k\rangle=\frac{Y_k/Q_k}{Y_k/Q_k+(2\omega-1)\sum_{m=1}^{3}Y_m(1-\langle\tau_m\rangle)}\,. \tag{9b}$$

Equation (9b) is directly obtained by introducing Eq. (9a) into Eqs. (7) and (8). This procedure converts τ_k and Z_k into their time averages, $\langle\tau_k\rangle$ and $\langle Z_k\rangle$. In $\langle\tau_k\rangle$ and $\langle Z_k\rangle$, the species k is tagged. More specifically

$$\langle\tau_k\rangle=\frac{1-\langle Z_k\rangle}{1+(2\omega-2)\langle Z_k\rangle}\,, \tag{10a}$$

$$\langle Z_k\rangle=\frac{\sum_{m=1}^{3}Y_m(1-\langle\tau_m\rangle)}{Y_k/Q_k+\sum_{m=1}^{3}Y_m(1-\langle\tau_m\rangle)}\,. \tag{10b}$$

Equations (9a) and (9b) combined thus constitute the conversion relations. On the other hand, $\langle\tau_k\rangle$ has to be obtained from Eqs. (10a) and (10b) self-consistently. Because of this self-consistency, the conversion relations, Eqs. (9), have been called the space and the time consistency relations and $\langle\tau_k\rangle$ are the time consistency parameters for short.[18] The conversion is to be used in Eq. (A21) (and in the steady-state relations to be used there) in summing over j where the meaning of tagging of the ith species becomes apparent.

The quantity $1-Z_i$ indicates the probability that the single (tagged) i atom jumps back into the neighboring vacancy under the equilibrium condition as explained earlier through Fig. 2 and, in the time averaging, $1-\langle Z_i\rangle$ indicates the probability that a tagged atom jumps back into the original vacancy in a long-time span. In Fig. 4, the physical situation represented by Eqs. (10) in ideally disordered binary alloys with composition x_A and x_B is shown. Here, a central site and its nearest-neighboring sites are depicted in which the centrally located (tagged) B^* has exchanged position with a vacancy at its nearest-neighboring site and is about to jump back into the central site. As indicated by Eq. (10a), this situation physically shows how the jump-back probability τ_{B^*} in competition with other atoms on the neighboring sites is calculated. This situation is to be compared with Fig. 2 which shows the same relation by the ensemble averaging. The species of atoms on the nearest-neighboring sites is represented by the same

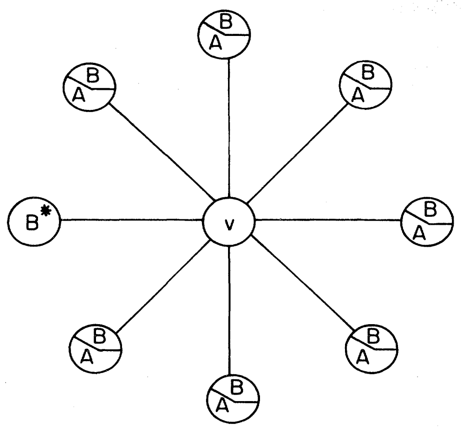

FIG. 4. Schematic representation of the situation in which the time consistency parameters based on the pair approximation are calculated. This figure indicates that for $\langle \tau_{B^*} \rangle$.

average values and represents the situation that the long-time average is taken, while the tagged atom keeps its identity. The jump frequencies of the neighboring atoms are also represented by the long-time average as $w_A(1-\langle \tau_A \rangle)$ and $w_B(1-\langle \tau_B \rangle)$ instead of w_A and w_B. This exactly corresponds to the concept of the Bethe approximation,[19] to determine the molecular field $1-\langle \tau_{B^*} \rangle$ in a self-consistent fashion. The Bethe approximation corresponds to the pair approximation of the CVM in the case of the bcc structure. This relation also shows how the requirement that the average values (with respect to the space) are the same introduces the proper time correlation in the time averaging as pointed out earlier. By the conversion, the time correlation is calculated in terms of the pair approximation, while in the original PPM, it corresponds to the point (molecular-field) approximation.

The application of the conversion relation to Z_{B^*} converts this to its counterpart in the time average $\langle Z_{B^*} \rangle$ (this is hereafter specified as Z'_{B^*}) and for the ideally disordered binary alloys

$$Z'_B = \frac{x_A w_A(1-\tau'_A)+x_B w_B(1-\tau'_B)}{w_B + x_A w_A(1-\tau'_A)+x_B w_B(1-\tau'_B)} \, , \tag{11a}$$

where $\tau'(=\langle \tau \rangle)$'s are specified as

$$\tau'_A = \frac{w_A}{w_A+(2\omega-1)[x_A w_A(1-\tau'_A)+x_B w_B(1-\tau'_B)]} \, , \tag{11b}$$

$$\tau'_B = \frac{w_B}{w_B+(2\omega-1)[x_A w_A(1-\tau'_A)+x_B w_B(1-\tau'_B)]} \, . \tag{11c}$$

Further in this expression, the difference between B and B^* is disregarded, and $x_B + x_{B^*}$ is rewritten as x_B as in our earlier publication.[3] The correlation factor in the time average f'_B, can then be defined as

$$f'_B = \frac{(2\omega-1)Z'}{2+(2\omega-3)Z'} \, . \tag{12}$$

By utilizing the relation Eqs. (10), f'_B can be rewritten in the form

$$f'_B = \frac{1-\tau'_B}{1+\tau'_B} \, . \tag{13}$$

The symmetry for τ'_A and τ'_B given in Eq. (9b) rationalizes that the correlation factor of tracer diffusion of the A atom in the time average f'_A is also given by a similar equation as

$$f'_A = \frac{1-\tau'_A}{1+\tau'_A} \, . \tag{14}$$

In the ensemble average, f_A and f_B are given by the same equation in terms of τ_A and τ_B, respectively.

The dependence of f'_B on the composition x_B as a function of w_B/w_A in ideally disordered alloys ($\epsilon_{ij}=0$, hence the alloys are completely disordered at any temperature) is then calculated based on Eqs. (11) and is shown in Fig. 5(b). This should be compared with the results in the ensemble averaging shown in Fig. 5(a). A major difference of the results in the time average from those in the ensem-

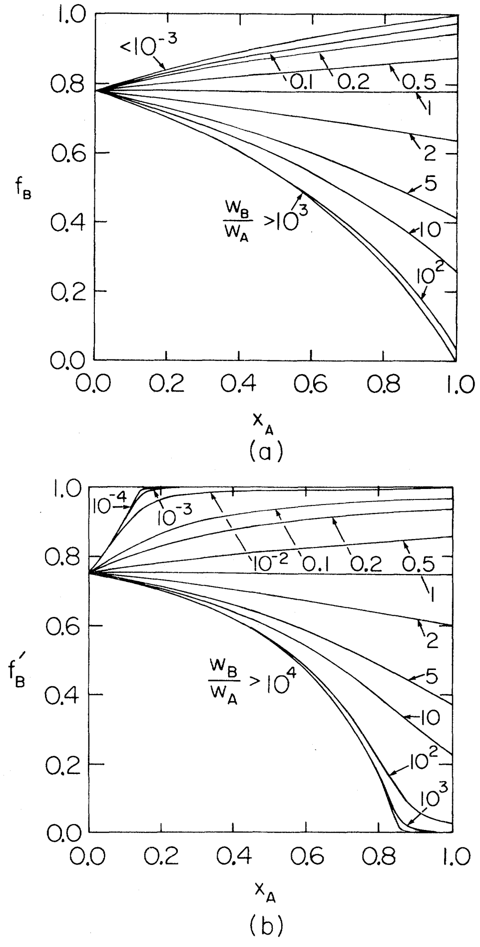

FIG. 5. Dependence of the correlation factor on composition for ideally disordered alloys as a function of w_B/w_A. (a) Calculation based on the ensemble averaging process: f_B. (b) Calculation based on the time averaging process: f'_B.

ble average is that the correlation factor for self-diffusion is $(2\omega-2)/2\omega$ rather than $(2\omega-1)/(2\omega+1)$. Also, the difference between the value for the time averaging and that for the ensemble averaging becomes more conspicuous as the ratio w_B/w_A deviates more from 1. Especially, as $w_B/w_A \rightarrow \infty$, the percolation of B^* atoms is found to stop ($f'_B \rightarrow 0$) at a finite concentration of B atoms as expected. The percolation limit (the concentration where f'_B becomes zero as $w_B/w_A \rightarrow \infty$) is calculated to be $1/(2\omega-1)$, which agrees with the value calculated by the pair approximation of the CVM.[10] The effect of the percolation limit for A atoms (the concentration where f'_A becomes zero as $w_B/w_A \rightarrow 0$) on f'_B is also well demonstrated at $x_A = 1/(2\omega-1)$.

In Fig. 6 a comparison of f_B and f'_B for binary alloys with short-range order is shown. The time average f'_B is obtained by applying Eqs. (9) to Eq. (A31). Here, the dependence of f_B and f'_B on the composition is given as a function of w_B/w_A. The short-range order, or the values of Q_i's are calculated as a function of composition and temperature with the knowledge of the interaction parameter ϵ. Temperature is specified by a normalized scale T/T_c in which T_c is the critical temperature ($kT_c/\epsilon \approx 13.9$) of order disorder at $x_A = x_B = \frac{1}{2}$. Here, we limit ourselves to the comparison of the converted results with the previous treatment.[3]

The change of f_B in the ensemble average to f'_B in the time average is physically due to a redefinition of the diffusion coefficient D_T with respect to the flow of isotope atoms, Ψ_3 given in Eqs. (3):

$$D_T \Delta t = -cY_3\Psi_3/\dot{\alpha}_3 \; , \qquad \Psi_3 = -\frac{(2\omega-1)Z}{2+(2\omega-3)Z}\dot{\alpha}_3 \; . \tag{15}$$

By the conversion from the ensemble averaging to the time averaging, Z_3 is converted to Z'_3 while Ψ_3 is converted to Ψ'_3. Therefore, in the time average

$$D'_T \Delta T = -cY_3\Psi'_3\dot{\alpha}_3 \; , \quad c = \omega a^2/x_3 \tag{16}$$

$$\Psi'_3 = -\frac{(2\omega-1)Z'}{2+(2\omega-3)Z'}\dot{\alpha}_3 \; , \tag{17}$$

and

$$f'_B = D'_T/(cY_3) \; . \tag{18}$$

The comparison of Z_3 and Z'_3 shows that Ψ'_3 is a part of Ψ_3 and represents a part of flow which continues for an infinite time period or which percolates through the whole crystal. This indicates that the value of the correlation factor depends on the type of measurement of the diffusion coefficient. D_T corresponds to the measurement of flow across a reference plane at a time instant or $D_T(\infty)$, while D'_T corresponds to the measurement for counting only those isotope atoms which percolate through the whole crystal or $D_T(0)$. f'_B corresponds to the correlation factor calculated by the random-walk theory.

As pointed out earlier, the factors such as τ_i and Z_i derived by the PPM have essentially the same meaning as those introduced in the random-walk theory. As converted to the time average, therefore, f'_B calculated by the PPM essentially coincides with that calculated by the random-walk theory (ideally disordered alloys[13]) and the discrepancies between the PPM and the random-walk theory[13] and computer simulations[11,12] with respect to numerical values of the correlation factor and the percolation limit are removed.

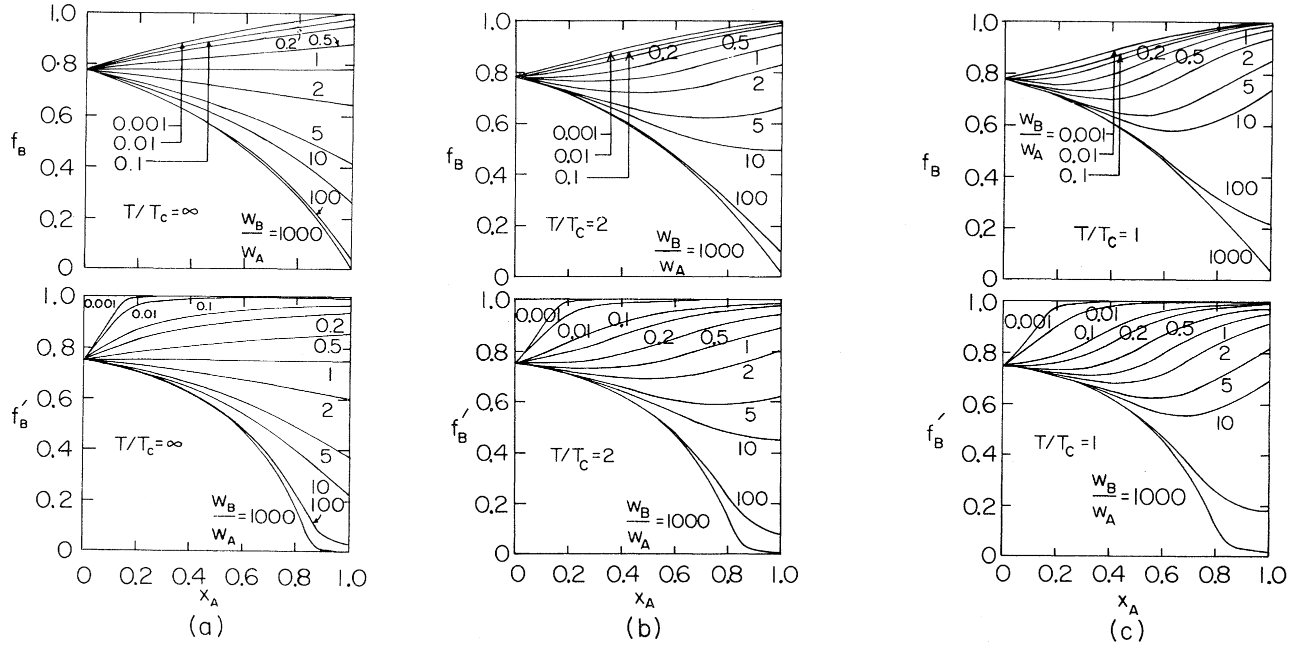

FIG. 6. Dependence of the correlation factor f_B and f'_B for disordered binary alloys with short-range order on composition as a function of w_B/w_A. The degree of short-range order is indicated indirectly by temperature T/T_c. (a) $T/T_c=\infty$, (b) $T/T_c=2$, (c) $T/T_c=1$.

IV. SUMMARY AND DISCUSSION

A general method of the conversion from the ensemble average characteristic of the PPM into the time average in evaluating a flow of particles is discussed. The importance of the time average in evaluating flow of particles is emphasized. The calculation is specifically applied to the calculation of the correlation factor of one of the constituent species in disordered binary alloys. It has been shown that, by the conversion, the results of the PPM with respect to flow agree with those derived by the random-walk theory[13,20,21] and by computer simulations[11,12] for corresponding cases.

As mentioned in the Introduction, the character of the PPM will eventually evaluate the statistical expectation value at a time instant t by the technique of the CVM and, then, will calculate the time correlation of this expectation value. Therefore, if the problem requires obtaining the time correlation of expectation values, such as that found in the treatment of the relaxation of order,[17] the PPM works very satisfactorily. This is why the specific disadvantage of the PPM or similar statistical methods in its application to transport problems has not been detected. This procedure of the PPM also results in calculating the instantaneous response of the system. From this point of view too, the procedure of the PPM is not very suitable to calculate the time correlation of the motion of particles involved in flow, especially that of a small number of particles for a long period of time, such as that required for the calculation of the correlation factor. This is the reason why the calculation has been converted into the time average. It is shown that, in the linear range in which the Onsager equations for diffusion are applicable, the results calculated in the ensemble average can be converted uniquely into the time average without changing the nature of approximation adopted. We have already treated a variety of many-body diffusion problems by the PPM.[2-7] Conversion of these results into the time average is now in order.

It is important to point out here that, in the calculation of the flow of i atoms, i atoms are individually tagged. In the ensemble average of the PPM, however, i and j appear symmetric and this tagging process is not obvious until the final result of the correlation factor [Eq. (4)] is obtained. On the other hand, in evaluating the most probable path in the time average, the species whose flow is observed is tagged clearly, and hence i and j become asymmetric. This is a direct consequence of following the flow of a specific species of atoms for a long time.

The conversion to the time averaging is far more important in the tracer diffusion than in the mass diffusion where the motion of a large number of equivalent particles is followed. Indeed, the original PPM describes well the behavior of mass diffusion except in the neighborhood of the percolation limit. The involvement of the time averaging in tracer diffusion physically means that, for tracer atoms to be detected, the tracer atoms should percolate through the whole crystal because the number of tracer atoms is small. This means that tracer diffusion or the correlation factor is far more sensitive to the percolation problem than the mass diffusion. The Haven ratio in ionic conductors is the ratio of the tracer diffusion coefficient and the charge diffusion coefficient (or the ionic conductivity). Here, for the latter, the "ensemble" averaging is allowable except at the percolation limit and beyond, while for the former, the time averaging has to be adopted.[18] Because the tracer diffusion coefficient in the time averaging is far more sensitive to the percolation problem than the charge diffusion coefficient, the Haven ratio is expected to show an anomalous dip near the percolation limit. An anomalous dip in the temperature dependence observed in the Haven ratio in β-alumina[22] is suggested by the present author to be connected to the percolation problem.[18,23]

Comparison of treatments of diffusion by the PPM and their statistical counterparts (treatments of the percolation problem by the CVM) presents some interesting correspondences. Specifically, the pair interaction among nearest neighbors in the CVM, for example, corresponds to the atomic exchange between nearest-neighboring sites in the PPM. On the other hand, the percolation (a long-range connection of jumps) of an atom in the PPM corresponds to the long-range order in the CVM. The correlation factor in the PPM is then related to the long-range order in the CVM. Therefore, the onset of the percolation and the onset of the phase transition is related and the techniques utilized in (statical) percolation problems are closely related to those in the theory of phase transitions.

The advantage of the PPM is that complicated many-body diffusion problems can be treated generally and relatively easily with a reasonable degree of approximation. Therefore, the results allow straightforward interpretations. Furthermore, results obtained by the PPM in the past can be readily converted into the corresponding results in the time average. Some of these are correlation factors for high concentrations of tracer atoms, those for cases in which a large number of vacancies are included and for ordered alloys. Some simpler cases of such many-body diffusion problems have been treated by the extension of the customary random-walk approach and similar results to the present treatment have been obtained.[13,18,20] However, these theories have to rely on some *ad hoc* assumptions in the process of derivation whose validity is not always clear. Furthermore, computer-simulation techniques compatible with the PPM are now being developed.[24] In complicated cases, computer-simulation techniques sometimes provide numerical results more easily than analytical derivations by the PPM. Therefore, the combination of an analytical technique based on the PPM and numerical results based on computer-simulation techniques would be very useful in understanding many-body diffusion problems such as those in highly defective solids.

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APPENDIX: CORRELATION FACTOR IN SUBSTITUTIONAL DIFFUSION IN DISORDERED BINARY ALLOYS: CALCULATED BY THE PAIR APPROXIMATION OF THE PPM

In order to explain the basis of the conversion process from the ensemble average (PPM) to the time average, key steps of deriving the correlation factor in substitutional diffusion (vacancy mechanism) in disordered binary alloys in the pair approximation of the PPM are explained briefly. Although the problem has been worked out in the past,[3] the treatment has been reorganized to make the conversion process clearer and with enough details so that future applications to more complicated cases can readily be made.

1. Model

In Fig. 7, a homogeneous binary alloy of the bcc structure, composed of A and B atoms with concentration x_A and x_B $(x_A+x_B=1)$, is shown. The use of the bcc structure is to apply the pair approximation of the CVM and the PPM, since the validity of the pair approximation of the CVM for problems in the bcc lattice is well established.[17] On the left-hand side of the crystal (in the $-x$ direction) a source of isotope atoms of B (B^* atoms) is placed, while on the right-hand side (in the $+x$ direction) an infinite sink of B^* atoms is assumed. Because of the concentration gradient of B^*, B^* atoms would flow toward the $+x$ direction, but after some time, the steady state would be reached, a certain concentration gradient of B^* would be set up in the crystal, and B^* atoms would flow without changing the distribution of atoms. The flow of B atoms in the reverse direction is allowed to keep the concentration profile fixed. We will deal with such a steady state in which the total concentration of B and B^* atoms is kept constant at x_B (but with a small concentration gradient of B^*) over the entire solid. Under the condition of the steady state, the tracer diffusion coefficient characteristic of the equilibrium binary alloy of a fixed composition is calculated. In the steady state, the flow rate of B^* along the x direction is independent of both time and location, and the flow can be calculated across any plane inside the crystal perpendicular to the concentration gradient of B^* at any instant of time. The diffusion coefficient of each constituent and hence the correlation factor is calculated by deriving the Onsager equation with respect to flow.

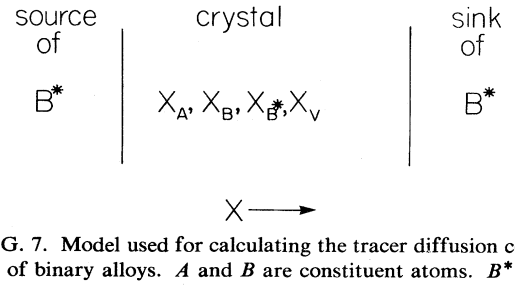

FIG. 7. Model used for calculating the tracer diffusion coefficient of binary alloys. A and B are constituent atoms. B^* indicates the tracer atom of B and v indicates the vacancy. x_A, etc., indicate the concentrations of constituent species.

In order to calculate flow, a plane midway between two atomic planes (a bond plane) perpendicular to the x direction is taken as the reference plane. In the bcc lattice, the [100] direction is taken conveniently as the $+x$ direction for the reason of symmetry. For the purpose of dealing with problems with the concentration gradient, subsequent equivalent (100) planes are numbered along the x direction and the reference plane is taken as the nth plane. Parallel (100) atomic planes are also numbered in a way that the closest atomic plane to the left of the nth plane is the νth atomic plane and that to the right is then the $(\nu+1)$th plane. The local atomic configuration is thus shown in Fig. 8. The flow is defined as the deviation from the equilibrium condition at the reference plane.

2. Equilibrium distribution of atoms

In this section, pertinent results of the CVM (Refs. 14—16) are shown because the equilibrium treatment essentially forms the basis for the calculation of the elements of the kinetic matrix of the Onsager equations as shown in Sec. 3. The bcc lattice (with the coordination number $2\omega=8$) can be divided into two simple cubic (sc) sublattices and the nearest neighbors of an atom on a given sublattice are all on the other sublattice. The atoms on one (100) plane all belong to one sublattice and, hence all the nearest-neighbor pairs bridge the gap between the two (100) atomic planes. This is an important feature of

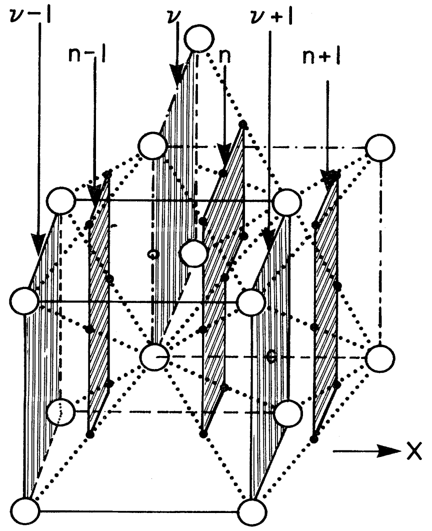

FIG. 8. Nomenclature of atomic planes (ν's) and bond planes (n's).

the bcc lattice which makes the application of the pair approximation valid. The species of atoms A, B, B^*, and v (vacant site) are denoted by i ($i=1,2,3,4$). (For the convenience of the treatment, we often use v instead of specifying it as the fourth species in order to distinguish vacancies from atoms.) In disordered alloys, the two sublattices are equivalent. Therefore, if the nearest-neighbor-pair interaction model is adopted and the pair approximation is used, the state variables required are x_i's, which indicate the probability of finding the ith species on one lattice point, and y_{ij}'s ($y_{ij}=y_{ji}$, $j=1,2,3,4$), which indicate the probability of finding a pair of the ith species and the jth species at the nearest-neighbor distance.

Pairwise interactions among atoms at the nearest-neighbor distance are assumed. The interaction energy parameters are represented by ϵ_{ij}. Further, the interaction with v is assumed to be zero ($\epsilon_{iv}=\epsilon_{vi}=0$). Also, the interaction energy parameters ϵ and U are introduced as

$$4\epsilon=\epsilon_{AA}+\epsilon_{BB}-2\epsilon_{AB}\ , \tag{A1a}$$

$$U=\tfrac{1}{4}(\epsilon_{AA}-\epsilon_{BB})\ . \tag{A1b}$$

Although U does not affect the equilibrium distribution of constituent atoms over the lattice sites, it can be important for kinetic properties such as diffusion processes.[2] In the present derivation, however, $U=0$ is assumed for the sake of simplicity. Then, 14 state variables can be defined. Among them, there are the following geometrical relations:

$$1=\sum_{i=1}^{4} x_i\ , \tag{A2a}$$

$$x_i=\sum_{j=1}^{4} y_{ij},\quad i=1,2,3,4\ . \tag{A2b}$$

The treatments of homogeneous alloys, both ordered and disordered, including the present problem, by the CVM are already described in many places,[2] so it is not necessary to describe them in detail here. The role of the CVM is to determine y_{ij} as a function of temperature in terms of energy parameters at a fixed composition under the equilibrium condition. The equilibrium state is given by those state variables x_i's and y_{ij}'s, which make the free-energy function minimum. In order to give the relation between equilibrium values of state variables and temperature, some parameters are introduced for convenience. Some important ones used in the treatment of diffusion in disordered alloys are given. These are

$$y_{ij}=q_i q_j K_{ij}^{-1}\ , \tag{A3a}$$

$$K_{ij}=\exp(\beta\epsilon_{ij})^{-1}\ , \tag{A3b}$$

$$q_i=x_i^{[(2\omega-1)/2\omega]}\exp(\beta\lambda_i)\ , \tag{A3c}$$

$$Q_j=q_i\left[\sum_{j=1}^{4} q_i\right]^{-1}\ . \tag{A3d}$$

Here, q_i and q_j are introduced to represent y_{ij} in the form of multiplication of these quantities. For example, in ideally disordered alloys ($\epsilon_{ij}=0$), we know $y_{ij}=x_i x_j$, and thus in this limiting case, q_i tends to x_i. We especially use Q_i as normalized q_i through Eq. (A3d) because in general $\sum q_i\neq 1$. The quantity λ_i introduced in Eq. (A3c) is the parameter to control the density constant to be determined by Eqs. (A2). The quantities Q_i's thus represent effective concentrations. Specifically, Q_i indicates the probability of finding an ith species next to a vacancy. At the same time, it also indicates the same quantity next to any specified lattice site. The state variables and useful parameters used are summarized in Table I.

3. The path variables and the most probable paths

The major step of the treatment is to calculate the flow based on the PPM which deals with the change of state described by the CVM. As described in Sec. 2 the first step is to define path variables suitable for the problem. The state variables are now given at time t by $x_i(t)$'s and $y_{ij}(t)$'s based on the treatment of the CVM. When the unit process of the change of state is due to the jump of an atom into a vacancy at the nearest-neighbor distance, the necessary path variables should be of the form of $X_{iv}(t,t+\Delta t)$ and $Y_{ij,iv}(t,t+\Delta t)$. Specifically, $X_{iv}(t,t+\Delta t)$ indicates the probability of finding a lattice site which is occupied by an ith atom at t and a vacancy at $t+\Delta t$, and $Y_{ij,iv}(t,t+\Delta t)$ indicates the probability of finding a lattice pair which is i-j at t and i-v at $t+\Delta t$. These variables depend on the position ν or n, and thus we write them as $x_i^{(\nu)}(t)$ and $Y_{ij,iv}^{(n)}(t,t+\Delta t)$. In treating the flow of the ith species across the nth plane, the basic quantities are $Y_{iv,vi}^{(n)}$ and $Y_{vi,iv}^{(n)}$. The former indicates the probability of the exchange of i and v across the nth plane with the flow of an ith atom in the $+x$ direction while the latter is that in the $-x$ direction, and hence these are specified as $Y_{+i}^{(n)}$ and $Y_{-1}^{(n)}$ (Fig. 9). Then, by geometry, these are related to $X^{(\nu)}$, $X^{(\nu+1)}$, $Y^{(n)}$, $Y^{(n+1)}$, and $Y^{(n-1)}$ as shown in Eqs. (A4). In order to avoid confusion, we add the species of atoms and its direction of flow such as $+i$ to the notation of path variables so that these appear as $X_{i,v;+i}$, $Y_{iv,vi;+i}$, etc.:

$$\begin{aligned} X_{i,v;+i}^{(\nu)} &= \sum_{j=1}^{4} Y_{ji,jv;+i}^{(n-1)} \\ &= \sum_{j=1}^{4} Y_{ij,vj;+i}^{(n)} = Y_{iv,vi}^{(n)} \equiv Y_{+i}^{(n)}\ , \end{aligned} \tag{A4a}$$

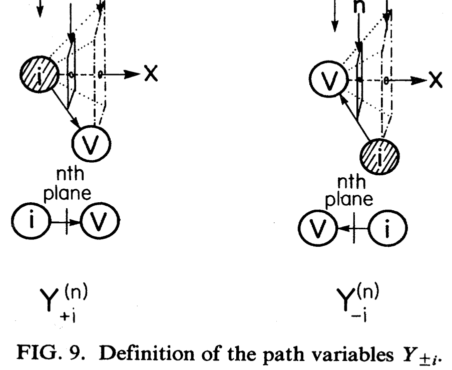

FIG. 9. Definition of the path variables $Y_{\pm i}$.

$$X^{(\nu)}_{i,v;-i}=\sum_{j=1}^{4} Y^{(n-1)}_{ji,jv;-i}$$

$$=\sum_{j=1}^{4} Y^{(n)}_{ij,vj;-i}=Y^{(n-1)}_{vi,iv}\equiv Y^{(n-1)}_{-i}\ , \qquad \text{(A4b)}$$

$$X^{(\nu)}_{v,i,+i}=\sum_{j=1}^{4} Y^{(n)}_{vj,ij;+i}$$

$$=\sum_{j=1}^{4} Y^{(n-1)}_{jv,ji;+i}=Y^{(n-1)}_{iv,vi}\equiv Y^{(n-1)}_{+i}\ , \qquad \text{(A4c)}$$

$$X^{(\nu)}_{v,i;-i}=\sum_{j=1}^{4} Y^{(n)}_{vj,ij;-i}$$

$$=\sum_{j=1}^{4} Y^{(n-1)}_{jv,ji;-i}=Y^{(n)}_{vi,iv}\equiv Y^{(n)}_{-i}\ . \qquad \text{(A4d)}$$

The path variables with respect to the nth planes are listed in Table II.

In connection with a jump of a specific atom i, we assume a specific jump frequency, $w_i=\vartheta_i\exp(-\beta u_i)$, where ϑ_i corresponds to the attempt frequency and u_i is the activation energy characteristic of the ith constituent atom. The effect of surrounding due to the interaction with nearest-neighboring atoms (which we call the bond breaking factor) is to be accounted for in addition to this factor (see below).

The most probable path is defined by those values of the path variables which make the path-probability function maximum. This procedure is the counterpart of finding the most probable state (the equilibrium state) as a minimum of the free-energy function in the CVM. The construction of the path-probability function in terms of the path variables is the essence of the PPM and is the counterpart of constructing the free-energy function in terms of the state variables in the CVM.[1] For the details of the construction of the path-probability function and of its maximization process for this particular problem one should refer to Refs. 1 and 25.

A major consequence of maximizing the path-probability function with respect to independent path variables in the pair approximation of the PPM is that superposition relations hold in writing down the most probable path.[1,2] Therefore, the most-probable-path expression can be obtained by inspection. In the case of an atomic jump into a vacancy, this eventually means that a jump of an atom solely depends on the initial condition or on the direct surroundings of the particular jumping atom at time t. In Fig. 10, the relation in which an ith atom is about to jump across the reference plane into an adjacent vacancy is schematically shown. By definition, the jump represents $Y^{(n)}_{+i}$. This is written down in the case of the bcc lattice,[4]

$$Y^{(n)}_{+i}=\vartheta_i e^{-\beta u_i}\Delta t y^{(n)}_{iv}\times\left[\frac{\sum_{j=1}^{4} y^{(n)}_{ij}K_{ij}}{x^{(\nu)}_i}\right]^{\omega-1}\left[\frac{\sum_{j=1}^{4} y^{(n-1)}_{ji}K_{ji}}{x^{(\nu)}_i}\right]^{\omega}. \qquad \text{(A5a)}$$

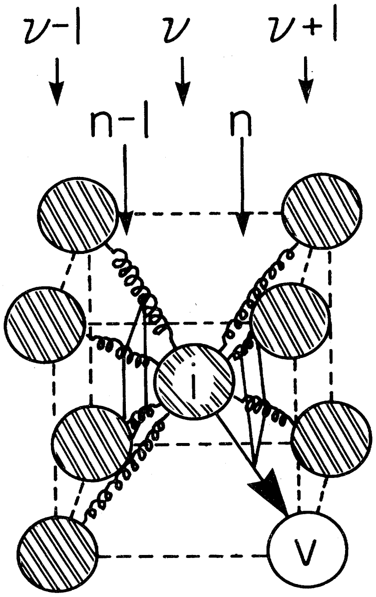

FIG. 10. Effect of bond breaking as the ith atom on the νth atomic plane jumps into a vacancy on the $(\nu+1)$th plane. "Springs" indicate the bonds.

This is called the superposition relation[3] as indicated above in a sense that $Y^{(n)}_{+i}(t,t+\Delta t)$, a jump of an ith atom across the nth reference plane, is proportional to Δt, to the jump frequency of the ith atom $w_i=\vartheta_i\exp(-\beta u_i)$, to the probability of having a vacancy at its nearest-neighbor distance across the reference plane at time t, $y^{(n)}_{iv}/x^{(\nu)}_i$ and to the effect of breaking the bonds with the neighboring atoms at time t [indicated by "springs" in Fig. 10 and the last two terms in Eqs. (A4)]. Similarly, we also obtain

$$Y^{(n)}_{-i}=\vartheta_i e^{-\beta u_i}\Delta t y^{(n)}_{vi}\times\left[\frac{\sum_{j=1}^{4} y^{(n)}_{ji}K_{ji}}{x^{(\nu+1)}_i}\right]^{\omega-1}\left[\frac{\sum_{j=1}^{4} y^{(n+1)}_{ij}K_{ij}}{x^{(\nu+1)}_i}\right]^{\omega}, \qquad \text{(A5b)}$$

Utilizing the geometrical relations (A4), the other path variables are shown to be related to $Y_{\pm i}$'s:

$$Y^{(n)}_{ij,vj;+i}=\frac{y^{(n)}_{ij}K_{ij}}{\sum_{j=1}^{4} y^{(n)}_{ij}K_{ij}}Y^{(n)}_{+i}\ , \qquad \text{(A5c)}$$

$$Y^{(n)}_{ij,vj;-i}=\frac{y^{(n)}_{ij}K_{ij}}{\sum_{j=1}^{4} y^{(n)}_{ij}K_{ij}}Y^{(n-1)}_{-i}\ , \qquad \text{(A5d)}$$

$$Y^{(n)}_{vj,ij;+i}=\frac{y^{(n)}_{vj}}{x^{(\nu)}_v}Y^{(n-1)}_{+i}\ , \qquad \text{(A5e)}$$

$$Y^{(n)}_{vj,ij;-i}=\frac{y^{(n)}_{vj}}{x^{(\nu)}_v}Y^{(n)}_{-i}\ , \qquad \text{(A5f)}$$

etc., and the most probable values of these path variables are known through $Y^{(n)}_{\pm i}$'s. These values determine the path on the free-energy surface. These relations are also listed in Table II. These expressions for the most probable path of individual path variables are given in terms of ensemble averaging at a time instant t.

4. The definition of flow and the Onsager equations

Once the expectation values of the necessary path variables which indicate the change of state in the time interval Δt can be expressed in terms of the state variables at time t, the time dependence of the state can be obtained. The flow of the ith species of atoms across the nth plane, $\Phi_i^{(n)}$, can be defined as

$$\Phi_i^{(n)} = Y_{+i}^{(n)} - Y_{-i}^{(n)} \ . \tag{A6}$$

Because in the steady state the flow is independent of the location of the reference plane, the superscripts on Φ_i can be dropped as

$$\Phi_i = Y_{+i}^{(n)} - Y_{-i}^{(n)} \ . \tag{A7}$$

The derivation of the Onsager equations is then reduced to the evaluation of Φ_i, or the evaluation of $Y_{\pm i}$, in the linear range when the concentration gradient is small [see Eq. (10)]. The deviation of the system from the equilibrium is the existence of the concentration gradients of the constituent species. Because the flow is evaluated across the nth plane, the reference state should be the equilibrium state of the alloy having the concentration corresponding to that at the nth plane.

The next step is to express values of the state and the path variables which appear in the most probable path [Eqs. (A5)] in terms of the equilibrium values (at the nth plane which is taken as the reference plane) under the condition that the concentration gradient is small. For variables such as $x_j^{(\nu+m)}$ (m is an integer), the deviation from the equilibrium value $x_{je}^{(n)}$ is determined by its location only. Therefore, $x_j^{(\nu+m)}$ is expanded around n as

$$x_j^{(\nu+m)} = x_{je}^{(n)} \left[1 + (m - \tfrac{1}{2}) \frac{d}{dn} \ln x_{je}^{(n)} \right] , \tag{A8}$$

where d/dn indicates the derivative with respect to the distance measured in units of the distance between lattice planes. Although the nth plane is not an atomic plane, $x_j^{(n)}$ is to be understood as the probability of finding the jth species of atom on a lattice point of the homogeneous, equilibrium alloy taken as the reference.

On the other hand, for the variables such as $y_{ij}^{(n+m)}$ and $Y_{+j}^{(n+m)}$, the values not only depend on the distance from the nth plane, but the values of $y_{ij}^{(n)}$, and $Y_{+j}^{(n)}$ also depend on the concentration gradient. In such a case

$$\begin{aligned} Y_{+j}^{(n+m)} &= Y_{+j}^{(n)} \left[1 + m \frac{d}{dn} \ln Y_{+j}^{(n)} \right] \\ &\approx Y_{je}^{(n)} \left[1 + m \frac{d}{dn} \ln Y_{je}^{(n)} + \delta \ln Y_{+j}^{(n)} \right] . \end{aligned} \tag{A9}$$

Here the symbol δ refers to the deviation from the equilibrium value (indicated by the subscript e) due to the concentration gradient, written specifically

$$\delta \ln Y_{+j}^{(n)} = \frac{Y_{+j}^{(n)} - Y_{je}^{(n)}}{Y_{je}^{(n)}} \ . \tag{A10}$$

Using this quantity, we can write the normalized flow $\Psi_j^{(n)}$ across the nth plane as

$$\Psi_j^{(n)} = \frac{\Phi_j^{(n)}}{Y_{je}^{(n)}} = \frac{Y_{+j}^{(n)} - Y_{-j}^{(n)}}{Y_{je}^{(n)}} = \delta \ln \frac{Y_{+j}^{(n)}}{Y_{-j}^{(n)}} \ . \tag{A11}$$

Then the most probable values of the path variables connected to the flow of i referring to the nth plane can now be expanded to first order based on Eqs. (A5), (A8), and (A9):

$$Y_{\pm i}^{(n)} = Y_i^{(n)} (1 + \delta \ln Y_{\pm i}^{(n)}) \ , \tag{A12a}$$

$$Y_{ij,\upsilon j;+i}^{(n)} = Q_j^{(n)} Y_i^{(n)} \left[1 + \delta \ln \frac{y_{ij}^{(n)} K_{ij}}{\sum_{j=1}^{4} y_{ij}^{(n)} K_{ij}} + \delta \ln Y_{+i}^{(n)} \right] , \tag{A12b}$$

$$Y_{ij,\upsilon j;-i}^{(n)} = Q_j^{(n)} Y_i^{(n)} \left[1 + \delta \ln \frac{y_{ij}^{(n)} K_{ij}}{\sum_{j=1}^{4} y_{ij}^{(n)} K_{ij}} + \delta \ln Y_{-1}^{(n)} - \frac{d}{dn} \ln Y_{-i}^{(n)} \right] , \tag{A12c}$$

$$Y_{\upsilon j,ij;+i}^{(n)} = Q_j^{(n)} Y_i^{(n)} \left[1 + \delta \ln \frac{y_{\upsilon j}^{(n)}}{\sum_{i=1}^{4} y_{\upsilon j}^{(n)}} + \delta \ln Y_{+i}^{(n)} - \frac{d}{dn} \ln Y_{+i}^{(n)} \right] , \tag{A12d}$$

$$Y_{\upsilon j,ij;-i}^{(n)} = Q_j^{(n)} Y_i^{(n)} \left[1 + \delta \ln \frac{y_{\upsilon j}^{(n)}}{\sum_{j=1}^{4} y_{\upsilon j}^{(n)}} + \delta \ln Y_{-i}^{(n)} \right] , \tag{A12e}$$

etc., where

$$Y_i^{(n)} \equiv Y_{+ie}^{(n)} = Y_{-ie}^{(n)} \ . \tag{A13}$$

The $Y_i^{(n)}$'s are the flow of the ith atom, etc., across the nth plane in either direction in the equilibrium state and we shall not use the suffix e to indicate equilibrium in this case. Also, because all variables are now expressed in reference to the nth plane and because any plane can be taken as the reference plane in the steady state, the superscript (n) will be dropped hereafter unless confusion is expected. In deriving Eqs. (A12), similar expansions for $y_{ij}^{(n+m)}$'s are required. The results are summarized in Table II.

In view of the fact that Y_i is a characteristic quantity of the equilibrium state as indicated in Eq. (A13), it is physically meaningful to define the effective jump-frequency parameter $\hat{\omega}_i$, which includes the effect of the surroundings, as

$$\hat{\omega}_i = \vartheta_i e^{-\beta u_i} \left[\frac{\sum_{j=1}^{4} y_{jie} K_{ji}}{x_{ie}} \right]^{2\omega-1} = \frac{Y_i}{q_i q_v \Delta t} \tag{A14a}$$

$$w_i = \vartheta_i e^{-\beta u_i} \tag{A14b}$$

The quantity w_i is the jump frequency of an atom of the species i ordinarily defined.

The next step is to reorganize expanded terms. After lengthy transformations we arrive at[4,5]

$$\Psi_i = -\dot{\alpha}_i + \sum_{j=1}^{3} Q_j \psi_{ji} , \tag{A15}$$

where

$$\alpha_i = (2\omega - 1) \ln \frac{q_i}{x_{ie}} , \tag{A16a}$$

$$\dot{\alpha}_i = \frac{d}{dn} \alpha_i , \tag{A16b}$$

and

$$\psi_{ji} = \delta \ln \frac{y_{ji} y_{iv} y_{vj}}{y_{ij} y_{jv} y_{vi}} . \tag{A16c}$$

Here $\dot{\alpha}_i$ is the chemical-potential gradient of the ith constituent atoms ($\alpha_i = \beta\mu_i$) in the system, and ψ_{ji}, which is introduced for the convenience of the calculation, is a measure of the deviation of state variables from equilibrium due to the existence of the concentration gradient [see Eq. (A9)]. The latter has the properties

$$\psi_{ji} = -\psi_{ij} , \tag{A17a}$$

$$\psi_{iv} = 0 = \psi_{vj} . \tag{A17b}$$

That Eq. (A16) gives the chemical-potential gradient $\dot{\alpha}_i$ of the ith constituent can be seen in Ref. 2. Q_j in Eq. (A15) refers to the equilibrium state [Eq. (A3d)]. Equation (A15) indicates that the flow Ψ_i can be expressed in terms of the chemical-potential gradient of the ith constituent atoms and quantities represented by the first-order derivatives.

Another essential step to derive the Onsager equations is the steady-state condition. Here, the steady-state condition means specifically that the state variables which specify the state of the system do not change with time. In order to take advantage of the symmetry, we write

$$\frac{d}{dt}(y_{ij} - y_{ji}) = 0 . \tag{A18}$$

Time derivatives of configuration variables such as $(d/dt)y_{ij}$ can be readily written in terms of the path variables, making use of the geometrical relation, as

$$\begin{aligned} \frac{d}{dt} y_{ij} = {} & (\omega - 1) Y_{iv,ij;+j} + \omega Y_{iv,ij;-j} \\ & - (\omega - 1) Y_{ij,iv;-j} - \omega Y_{ij,iv;+j} \\ & + (\omega - 1) Y_{vj,ij;-i} + \omega Y_{vj,ij;+i} \\ & - (\omega - 1) Y_{ij,vj;+i} - \omega Y_{ij,vj;-i} . \end{aligned} \tag{A19}$$

The expression $(d/dt)y_{ji}$ can be obtained from Eq. (A19) by exchanging i and j.

By introducing Eqs. (A12) into the steady-state condition Eq. (A18), together with Eq. (A19), we obtain to the first order in small deviations

$$\begin{aligned} & Q_i Y_j \left[\psi_{ji} + \sum_{i=1}^{3} Q_i \psi_{ij} - \frac{2}{2\omega - 1} \Psi_j \right] \\ & \quad = Q_j Y_i \left[\psi_{ij} + \sum_{j=1}^{3} Q_j \psi_{ji} - \frac{2}{2\omega - 1} \Psi_i \right] . \end{aligned} \tag{A20}$$

This equation yields, by summing over j and utilizing Eq. (A15),

$$\sum_{j=1}^{3} Q_j \psi_{ji} = \frac{\sum_{j=1}^{3} (Q_j W_j)}{1 - \sum_{j=1}^{3} (Q_j W_j)} \left[\frac{-2}{2\omega - 1} \Psi_i - \frac{\sum_{j=1}^{3} (Q_j (1 - W_j) \{ \dot{\alpha}_j + [(2\omega - 3)/(2\omega - 1)] \Psi_j \})}{\sum_{j=1}^{3} Q_j (1 - W_j)} \right] , \tag{A21}$$

where

$$W_j = \frac{\hat{\omega}_i}{\hat{\omega}_i + \hat{\omega}_j} .$$

By introducing Eq. (A21) in Eq. (A15), we then obtain equations which correspond to Eqs. (2),

$$\Psi_i = - \sum_{j=1}^{3} L'_{ij} \dot{\alpha}_j , \tag{A22}$$

where [(A11)]

$$\Psi_i = \Phi_i / Y_i .$$

As is seen from Eq. (A22), L'_{ij} only includes equilibrium properties with respect to spatial distribution of atoms and to atomic jumps such as $\hat{\omega}_i$. In other words, as long as the concentration gradient is small enough, it is possible to derive the Onsager equations, and the kinetic matrix L'_{ij} from equilibrium properties, although the application of the PPM is not limited to the near equilibrium state.[17]

5. Correlation factor

For the calculation of the correlation factor as defined in Eq. (1a), it is necessary to derive the tracer diffusion coefficient D_{B^*} (D_i for $i = 3$) from Eq. (A22) in the form

$$\omega a^2 \Phi_i = -D_i \dot{x}_i \Delta t , \tag{A23}$$

where $\dot{x}_i$ is the concentration gradient of B^*, while a is the jump distance and 2ω is the coordination number under appropriate boundary conditions. For this purpose we first introduce the Gibbs-Duhem relation as such a boundary condition, which is supposed to hold under the steady-state condition

$$\sum_{j=1}^{3} x_j \dot{\alpha}_j = 0 \; . \tag{A24}$$

Further, since we deal only with the steady state, the condition

$$\dot{\alpha}_i = 0 \tag{A25}$$

readily follows. This is due to the fact that B and B^* are chemically identical so that the distribution of A atoms is not affected when the isotopes B^* are diffusing and changing places with B. Equation (A22), combined with Eqs. (A24) and (A25), thus reduces to a relation between Φ_3 and $\dot{\alpha}_3$ [Eq. (12)]. Further, from the condition (A24) and the condition that the profile of the atomic distribution does not change,

$$x_2 \Psi_2 = -x_3 \Psi_3 \tag{A26}$$

follows. Therefore, we obtain from Eq. (A21)

$$\sum_{j=1}^{3} Q_j \psi_{j3} = \frac{1-Z}{Z} \frac{-2}{2\omega - 1} \Psi_3 \; , \tag{A27a}$$

where

$$Z = 1 - \sum_{j=1}^{3} Q_j \frac{\hat{\omega}_3}{\hat{\omega}_3 + \hat{\omega}_j} = \sum_{j=1}^{3} \frac{Q_j \hat{\omega}_j}{\hat{\omega}_3 + \hat{\omega}_j} \; . \tag{A27b}$$

B and B^* should be regarded as chemically the same and, hence $\hat{\omega}_1 = \hat{\omega}_A$, $\hat{\omega}_2 = \hat{\omega}_3 = \hat{\omega}_B$, and $Q_2 + Q_3 = Q_B$. Q_B is given by the CVM for homogeneous binary alloys and is substituting x_B for the case of ideally disordered alloys.

Also, the relation

$$\dot{x}_3 = x_{3e} \dot{\alpha}_3 \tag{A28}$$

can be derived readily.[4] Then, the relation Φ_3 and $\dot{x}_3$, and thus the correlation factor f_B defined in Eq. (12), is obtained. f_B is equivalent to define with respect to Eq. (A22a),

$$f_B = -\frac{\Psi_3}{\dot{\alpha}_3} \; . \tag{A29}$$

From Eqs. (A27a), (A15), and (A29), we can obtain

$$f_B = \frac{(2\omega - 1)Z}{2 + (2\omega - 3)Z} \; , \tag{A30}$$

where

$$Z = \frac{Q_A \hat{\omega}_A}{\hat{\omega}_A + \hat{\omega}_B} + \frac{Q_B \hat{\omega}_B}{\hat{\omega}_B + \hat{\omega}_B} \; . \tag{A31a}$$

In terms of Y_i's,

$$\begin{aligned} Z &= 1 - \sum_{j=1}^{3} Q_j \frac{Y_3/Q_3}{Y_j/Q_j + Y_3/Q_3} \\ &= \sum_{j=1}^{3} Q_j \frac{Y_j/Q_j}{Y_j/Q_j + Y_3/Q_3} \; . \end{aligned} \tag{A31b}$$

For ideally disordered alloys, where $\epsilon = 0$,

$$Z = \frac{x_A w_A}{w_A + w_B} + \frac{x_B w_B}{w_B + w_B} \; . \tag{A31c}$$

Q_i and $\hat{\omega}_i$ for any disordered homogeneous alloy (with short-range order) can be obtained readily at a given temperature T from the knowledge of ϵ, and f_B for any disordered alloy can be readily calculated. Based on Eq. (A27b), $1 - Z$ gives the probability that a single B^* atom jumps back into the vacancy it has just replaced under the equilibrium condition.

6. Examination of the definition of the correlation factor

In the present treatment, the correlation factor f_B is defined as the ratio of the tracer diffusion coefficient D_T [Eq. (A23)] and the diffusion coefficient expected from the random walk of tracer atoms, Y_3, in the statistically averaged solid. In multicomponent systems, D_T naturally depends on the boundary conditions imposed on the system to measure Ψ_3. In other words, f_B is not uniquely defined. Therefore, the meaning of f_B obtained by the PPM in the past is examined here.

The boundary conditions given here are the Gibbs-Duhem relation, [Eq. (A24)] and $\dot{\alpha}_1 = 0$ [Eq. (A25)], which follows from the condition that the profile of the atomic distribution with respect to the second and the third species is kept the same [Eq. (A26)]. Under the above boundary conditions, Z_3 in Eq. (A27b) has a more general form Z_3^0:

$$Z_3^0 = Z_3 + Q_3 \Delta \; , \tag{A32a}$$

where

$$\Delta = \frac{\hat{\omega}_3}{\hat{\omega}_3 + \hat{\omega}_3} - \frac{\hat{\omega}_2}{\hat{\omega}_3 + \hat{\omega}_2} \; . \tag{A32b}$$

Because $\hat{\omega}_2 = \hat{\omega}_3$,

$$Z_3^0 \equiv Z_3 \tag{A33}$$

follows. This means, under the boundary condition that the profile of atomic distribution with respect to the second and the third species is kept the same, the (normalized) flow of a third species, Ψ_3, is equivalent to the drift motion of a single (tagged) atom of the third species under the equilibrium condition Z_3, irrespective of its composition. The possible effect of the additional contribution due to a high concentration of the third species, $Q_3 \Delta$, vanishes because of the equality $\hat{\omega}_2 = \hat{\omega}_3$. This means that Z_3 is an expression for a negligible amount of atoms of the third species ($Q_3 = 0$). Although the expression f_B [Eq. (A30) with Eq. (A31)] has been derived for any amount of B^*, f_B does not depend on the composition x_{B^*} for the reason explained above, and Z_3 represents the relative efficiency of the drift motion of a single atom (a tagged atom) with respect to that of the random walk as commonly defined in the random-walk theory of the correlation factor. This does not mean that D_T should always be independent of the amount of tracer atoms under general conditions of diffusion measurement.

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