Ionic conductivity in binary systems

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The ionic conductivity of a binary system consisting of two kinds of monovalent ions in the two-dimensional honeycomb lattice is calculated by the path probability method of irreversible statistical mechanics. The main purpose is to gain insight into the probable cause of the mixed-alkali effect observed in β-alumina-type systems and glass systems in general. It is shown that if the interaction between the two components is attractive, the existence of a sharp minimum which is caused by ordering can be expected at a certain composition. The minimum is shown to be mainly due to a *percolation difficulty* created by mutual arrangements of two kinds of ions. Based on these findings, it is suggested that the major cause of the mixed-alkali effect is the drop in the percolation efficiency due to the blocking of the diffusion (percolation) path created by mutual interaction of different kinds of ions.

I. INTRODUCTION

The problem we deal with here is a general theoretical treatment of ionic conductivity of two-component systems in which conduction ions are mutually interacting strongly. We deal with this problem utilizing the pair approximation of the path probability method (PPM) of irreversible statistical mechanics.[1-4] Our major interest in dealing with this problem is to get an insight into physical causes of so-called mixed-alkali effect. The mixed-alkali effect (MAE) has been known for some time in glass systems.[5,6] In binary glass systems in which one kind of alkali ion is progressively substituted by another kind of alkali ions, it is observed that the conductivity does not vary linearly with the fraction substituted. Instead, one often finds a substantial decrease in the conductivity at intermediate compositions without any apparent physical causes. Irrespective of the effort of many researchers, the cause of the effect has not been satisfactorily explained.[5,6] However, recently the existence of a similar effect in crystalline systems such as in β-alumina-type systems has also been observed.[7-10] The existence of the effect in β-alumina systems indicates that MAE is a common phenomenon whether the system is crystalline or not. If this is so, there is possibility that the origin of MAE, at least its qualitative features, can be understood by the treatment in crystalline lattice systems which is theoretically far more easily tractable than in glass systems.

The theoretical basis of ionic conduction in solids so far has been essentially the random-walk theory. In other words, if there are n conduction ions with the charge e and the mobility μ, the conductivity σ is considered to be given by

$$\sigma = ne\mu . \qquad (1.1)$$

Based on this expression, past efforts in explaining MAE have been to give reasonable causes to reduce n and/or μ by the addition of other ions as exemplified by theories such as the theory of Hendrickson et al.[11] and the weak

electrolyte theory.[12,13] However, in the ion conduction in solids, there is another factor f_I which may be called the percolation efficiency which was introduced by Sato and Kikuchi with the name of the physical correlation factor.[2,3] If explanations of MAE based on n and μ only are not satisfactory, the explanation of the effect should then be based on the percolation efficiency.[14] Indeed we will show that there are some experimental evidences which indicate that the percolation efficiency is really playing the essential role in MAE.

Our interest in the present theory is to show in binary systems in general that how the percolation efficiency can be defined and that under what condition the decrease in the percolation efficiency becomes conspicuous. By knowing this condition, our next task is to relate this condition and the probable cause of MAE which may be occurring in glass systems and β-aluminas. Indeed, for extracting the percolation efficiency in the conductivity of solids, any simple lattice system will suffice. However, because we will be dealing with MAE of β-alumina-type systems, the adoption of the two-dimensional honeycomb lattice which was already utilized by Sato and Kikuchi for the idealized model of β''-alumina[2,3] explained in Sec. II would be convenient. The model is essentially a lattice-gas model and many-body effects in transport are contained because mutual interactions among constituent conduction ions are included. As a theory of diffusion, the model represents a generalized vacancy mechanism. However, as was pointed out in the original treatment,[2,3] the model is sufficiently general to include other mechanisms such as the interstitial mechanism and interstitialcy mechanism which has been claimed to be operative in β-aluminas[15,16] and in glasses.[17]

The treatment of mass transport by PPM has been made extensively. However, the treatment for binary systems has been limited to the derivation of the correlation factor of isotope diffusion of one of the constituents and the treatment of ionic conductivity of binary systems has never been shown. Therefore, in the following we show the outline of the derivation of required quantities by the

pair approximation of PPM although the basic concepts utilized are the same. In Sec. II, we describe the specific model for which the ionic conductivity is calculated. In Sec. III, an outline of the mathematical procedure of the PPM is given in order to make the presentation of the model system unambiguous. There, all the variables needed to define the model system are given. In Sec. IV, the flux expression is given, and the Onsager equation for mass transport is derived under the steady-state condition. Expression of conductivity and its analysis are given in Sec. V. We calculate the composition dependence of the total conductivity as well as that of individual components. The correlation factor of the isotope diffusion of one of the constituents are also calculated because the isotope diffusion is often helpful in understanding the mechanism of diffusion. In the last section, we try to organize these results so that MAE in β-alumina and glasses can be properly understood.

II. MODEL

The specific theoretical model proposed in this work is that when an electric field (and/or a generalized chemical potential gradient) is imposed, two kinds of monovalent ions move on the two-dimensional honeycomb lattice (Fig. 1). The major task of the theory is then to derive the Onsager equation for mass transport,

$$\Phi_A = -L_{AA}\dot{\alpha}_A - L_{AB}\dot{\alpha}_B ,$$
$$\Phi_B = -L_{BA}\dot{\alpha}_A - L_{BB}\dot{\alpha}_B ,$$

(2.1)

in an analytical fashion.[4] The letters A and B indicate the two components. Symbols Φ_A and Φ_B represent the flows of A and B, respectively, and $\dot{\alpha}_A$ and $\dot{\alpha}_B$ are the chemical potential gradients for A and B ions, respectively, which serve as the driving forces. Knowing the expression of L_{ij}'s, we can obtain detailed information of the kinetic properties of the system. The kinetic coenfficients L_{ij}'s thus determine properties such as conductivities, the mobilities of ions, the percolation efficiency, and the correlation factors for isotope diffusion.
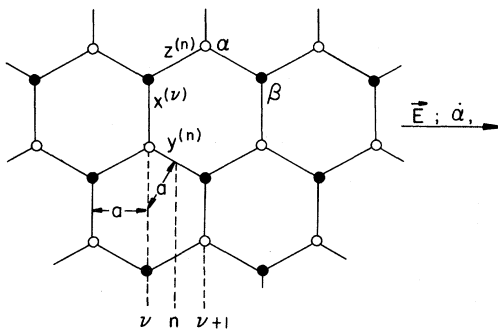

FIG. 1. Honeycomb lattice. Two sublattices are marked by open (α) and solid (β) circles. These lattice sites are occupied by two kinds of ions (A or B) or vacancy (V). Some sites, called α sites, are favored sites for an A ion and some called β sites are favored sites for a B ion. Conduction and/or diffusion take(s) place on this plane via a vacancy migration mechanism. ν and $\nu + 1$ indicate the position of lattice sites while n indicates a bond between the νth and the ($\nu + 1$)th lattice sites.

The two-dimensional honeycomb lattice consists of two kinds of ions and vacant sites. We assume that the conduction (and/or diffusion) takes place via vacant sites as was done earlier.[2-4] That is, the motion of ions is assumed to be a hopping into the nearest-neighboring vacant site. We further assume mutual interactions among conduction (or diffusing) ions. Introduction of mutual interactions among diffusing species of ions is a necessary feature to discuss the many-body nature of ionic transport. Here we assume that the interactions among mobile ions are taken into account in the form of nearest-neighbor pair interactions. The new feature in the present model is that two interpenetrating sublattices are conveniently introduced to define the ordered states of the system which may be set in at low temperatures in dealing with ion transport.

III. GENERAL OUTLINE OF THE METHOD

We work on a system consisting of two kinds of ions A and B in the two-dimensional honeycomb lattice. Each lattice site is occupied by ions (A or B) or vacancy (V). Hereafter, i stands for the ions (A or B) or vacancy, and we shall refer to A, B, and V as 1, 2, and 3, respectively, when convenient. Ions A and B have charges $Z_1 e$ and $Z_2 e$, respectively, where Z_i is the valence and e the electronic charge. We eventually assume $Z_1 = Z_2 = 1$ in order to avoid complications due to charge-compensation problems arising from possible change in distribution of charge particles. Figure 1 shows one of the lattice planes which forms the two-dimensional honeycomb lattice. We introduce a coordination axis as shown in Fig. 1 in order to define the variables needed in specifying the state of the system. Lattice lines parallel to the x direction are numbered by an integer written as ν. A lattice point on the νth line may be called a νth lattice point (or a ν site). The center of a bond connecting a νth lattice point and a ($\nu + 1$)th point is designated by n which is equal to $\nu + \frac{1}{2}$.

We assume the ions move from lattice sites to adjacent vacancies due to the driving force such as an applied electric field $\vec{E}$ and/or a concentration gradient of these ions. Although the direction of the force can be taken arbitrarily, here we take it in a symmetric direction along the plane as shown in Fig. 1 for the sake of simplifying the mathematical treatments.

A. The state and the path variables
(relations among variables)

In PPM we first define a certain number of variables called the *state* and the *path* variables. The state variables are introduced to describe the state of the system at time t. To describe the kinetics of the system, that is, how the state of the system changes with time, we need the path variables which connect the state of the system at t and $t + \Delta t$.

In our model, two sublattices called the α and the β sites in the honeycomb-lattice net (see Fig. 1) are introduced to define the possible ordering of the two components which may appear at low temperatures due to the mutual interactions among ions. We assume that the interactions among ions are taken into account in the form

of nearest-neighbor pair interactions.

Let us define the state variables. The fraction that an α site is occupied by the ith species is defined as p_i. Hence, p_1 expresses the fraction that an α site is occupied by an A ion. The corresponding fraction on a β site is defined as q_i. A configuration of a nearest-neighbor bond is of the form i-j, where the first member i is for the α site and the second member j is for the β site, where i and j take 1, 2, and 3, depending on whether the sites are occupied by an A ion, a B ion, or a vacancy. Then it is convenient to define the fractions of bonds in three directions which are in the i-j configuration as x_{ij}, y_{ij}, and z_{ij}, respectively. These state variables are summarized in Table I. So far we have defined the state variables of the system which specify the state of the system at time t. In kinetics the system is generally observed as it changes toward the eventual equilibrium state. This state changes to a different state in a short time interval Δt. Hence it is convenient to define its conjugate path variable, which gives the fraction (or probability) for a certain unit jump in a certain cluster configuration between t and $t + \Delta t$. Here we assume Δt much larger than the time required to complete a unit jump but sufficiently small so that for any cluster (any pair) there is a negligible probability that more than one ion jumps. Under these conditions, the number of types of possible changes during Δt is greatly reduced when we consider the migration mechanism, and the possible types of changes are then found based on simple geometrical arguments. Let us define the path variables which depend on time t and $t + \Delta t$. The conjugate path variables of p_i and q_i are, respectively, defined as $P_{ij}(t, t + \Delta t)$ and $Q_{ij}(t, t + \Delta t)$. Here $P_{ij}(t, t + \Delta t)$ describes the fraction (or probability) of the path which connects the state of an α site occupied by the ith species at t and by the jth species at $t + \Delta t$ due to a unit jump of ions through the vacancy-migration mechanism. The same interpretation is applied to Q_{ij} for a β site. It should be noted that we also include the case where i and j can be the same species, otherwise one of

TABLE I. Definition of state fractionals. $i = 1$, 2, and 3 corresponds to A, B, and V, respectively.

Configuration on a νth site	State fractional of i's on a νth state
i on $\alpha^{(\nu)}$	$p_i^{(\nu)}(t)$
i on $\beta^{(\nu)}$	$q_i^{(\nu)}(t)$

Configuration	State fractional of an i-j pair
νth bond $\alpha^{(\nu)}$ $\beta^{(\nu)}$ (i)—(j)	$x_{ij}^{(\nu)}(t)$
nth bond $\alpha^{(\nu)}$ $\beta^{(\nu+1)}$ (i)—(j)	$y_{ij}^{(n)}(t)$
nth bond $\beta^{(\nu)}$ $\alpha^{(\nu+1)}$ (i)—(j)	$z_{ji}^{(n)}(t)$

them must be 3 (i.e., a vacancy). When i and j are different, we need a third subscript on which of the three bonds the vacancy migration occurs; as is seen in Fig. 1, each point has three bonds associated with it: the right, the center, and the left. A subscript R, C, or L is used to indicate the location of the migration activity. For example, $P_{1,3,R}^{(\nu)}$ is the fraction of the path which connects the state of the occupant at an α site in a νth lattice line due to the configurational change. That is, an A ion at an α site on a νth lattice plane at t moves to the right, leaving the site vacant at $t + \Delta t$. The possible cases for the P's and Q's are listed in Table II.

Similarly we can define the conjugate path fractionals of the configurational state of the pair, x_{ij}, y_{ij}, and z_{ji}, as $X_{ij,kl}(t, t + \Delta t)$, $Y_{ij,kl}(t, t + \Delta)$, and $Z_{ji,lk}(t, t + \Delta t)$, respectively. Here X's, Y's, and Z's connect the fraction (or probability) of the path associated, respectively, with the configurational change of the state fractionals x_{ij}, y_{ij}, and z_{ji} at time t and $t + \Delta t$ on the same sites. When the configuration does not change, $i = k$ and $j = l$ hold. When it does change, the change is in either i or j so that either $j = l$ or $i = k$ holds. When it changes, say $i \neq k$ and $j = l$, either i or k must be 3 (i.e., a vacancy). For this sort of configurational change, we introduce a subscript R, C, or L to indicate the bond direction on which the migration occurs. For instance, $X_{12,32,L}^{(\nu)}$ is for an A-B pair at t and a V-B pair at $t + \Delta t$, the A ion having moved toward the left in Δt, by breaking an interaction energy ϵ_{AB} between ions A and B. Hereafter, ϵ_{ij} stands for the nearest-neighbor interaction energy between the i and the j species, where we assume $\epsilon_{iV} = \epsilon_{Vi} = \epsilon_{VV} = 0$ ($i = A$ and B). The similar interpretation holds for Y's and Z's. It should be noted that these configurational changes of a pair cluster in time interval Δt is assumed due to a unit jump of an ion through the vacancy-migration mechanism. Possible path fractions of the configurational changes of the pair state at an α and a β site are listed in Table III. It should be noted that our formulation will be made in the lattice-fixed frame of reference.

Now that we define the appropriate variables to describe the system, it is easy to write the relations between these variables. The normalization conditions for p's and q's are

$$\sum_{i=1}^{3} p_i^{(\nu)} = \sum_{i=1}^{3} q_i^{(\nu)} = 1 . \tag{3.1}$$

Geometrical consideration leads us to the following relations between the point-state variables and the pair-state variables:

$$p_i^{(\nu)} = \sum_{j=1}^{3} x_{ij}^{(\nu)} = \sum_{j=1}^{3} y_{ij}^{(n)} = \sum_{j=1}^{3} z_{ij}^{(n-1)} ,$$

$$q_i^{(\nu)} = \sum_{j=1}^{3} x_{ji}^{(\nu)} = \sum_{j=1}^{3} y_{ji}^{(n-1)} = \sum_{j=1}^{3} z_{ji}^{(n)} , \tag{3.2}$$

where i takes 1, 2, and 3. The path variables are for the configurational changes during the time interval Δt. Therefore the state fractionals (p's and q's) and their conjugate path fractionals (P's and Q's) at time t and $t + \Delta t$ are related as

TABLE II. Definition of the path fractions: $P_{ij}^{(v)}$ and $Q_{ij}^{(v)}$. $i=1$ and 2.

Configuration change on $\alpha^{(v)}$ site	Path fractional	Configuration change on $\beta^{(v)}$ site	Path fractional
	$P_{i,i}^{(v)}(t,t+\Delta t)$		$Q_{i,i}^{(v)}(t,t+\Delta t)$
	$P_{i,3,L}^{(v)}$		$Q_{i,3,L}^{(v)}$
	$P_{i,3,C}^{(v)}$		$Q_{i,3,C}^{(v)}$
	$P_{i,3,R}^{(v)}$		$Q_{i,3,R}^{(v)}$
	$P_{3,3}^{(v)}$		$Q_{3,3}^{(v)}$
	$P_{3,i,L}^{(v)}$		$Q_{3,i,L}^{(v)}$
	$P_{3,i,C}^{(v)}$		$Q_{3,i,C}^{(v)}$
	$P_{3,i,R}^{(v)}$		$Q_{3,i,R}^{(v)}$

$$p_i^{(v)}(t)=P_{ii}^{(v)}+P_{i3L}^{(v)}+P_{i3C}^{(v)}+P_{i3R}^{(v)}+P_{33}^{(v)} ,$$
$$p_i^{(v)}(t+\Delta t)=P_{ii}^{(v)}+P_{3iL}^{(v)}+P_{3iC}^{(v)}+P_{3iR}^{(v)}+P_{33}^{(v)}$$

(3.3)

for an α site. Here i takes 1 and 2. The same expressions are obtained for a β site by replacing p's by q's and P's by Q's. Similarly we can relate the state fractionals of bonds (x's, y's, and z's) and their conjugate path fractionals (X's, Y's, and Z's) by looking at the occupant at an α and a β site at time t and $t+\Delta t$, respectively. These relations are given in Appendix B.

From geometrical considerations, we see the following relations among the path fractionals:

$$P_{i,3,C}^{(v)}=Q_{3,i,C}^{(v)}=X_{i3,3i}^{(v)}\equiv X_{\alpha i}^{(v)} ,$$
$$P_{3,i,C}^{(v)}=Q_{i,3,C}^{(v)}=X_{3i,i3}^{(v)}\equiv X_{\beta i}^{(v)} ,$$
$$P_{i,3,R}^{(v)}=Q_{3,i,L}^{(v+1)}=Y_{i3,3i}^{(n)}\equiv Y_{\alpha i}^{(n)} ,$$
$$P_{3,i,R}^{(v)}=Q_{i,3,L}^{(v+1)}=Y_{3i,i3}^{(n)}\equiv Y_{\beta i}^{(n)} ,$$ (3.4)
$$P_{i,3,L}^{(v)}=Q_{3,i,R}^{(v-1)}=Z_{i3,3i}^{(n-1)}\equiv Z_{\alpha i}^{(n-1)} ,$$
$$P_{3,i,L}^{(v)}=Q_{i,3,R}^{(v-1)}=Z_{3i,i3}^{(n-1)}\equiv Z_{\beta i}^{(n-1)} ,$$

for $i=1$ and 2. In the above expressions abbreviated notations are introduced, indicating an α or a β site is occupied by the ith species either at time t or $t+\Delta t$.

B. Change of state

When we define the change of a quantity f in Δt as

$$\Delta f =f(t+\Delta t)-f(t)$$ (3.5)

then the change of states at the α and the β sites on a vth lattice plane perpendicular to a conduction (or diffusion) plane is given by making use of p_i's in Eq. (3.3) and the similar expressions for q_i's and the relations (3.4):

$$\Delta p_i^{(v)}=(P_{3,i,C}^{(v)}-P_{i,3,C}^{(v)})+(P_{3,i,R}^{(v)}-P_{i,3,R}^{(v)})+(P_{3,i,L}^{(v)}-P_{i,3,L}^{(v)})$$
$$=(X_{\beta i}^{(v)}-X_{\alpha i}^{(v)})+(Y_{\beta i}^{(n)}-Y_{\alpha i}^{(n)})+(Z_{\beta i}^{(n-1)}-Z_{\alpha i}^{(n-1)}) ,$$

(3.6a)

$$\Delta q_i^{(v)}=(Q_{3,i,C}^{(v)}-Q_{i,3,C}^{(v)})+(Q_{3,i,L}^{(v)}-Q_{i,3,L}^{(v)})+(Q_{3,i,R}^{(v)}-Q_{i,3,R}^{(v)})$$
$$=(X_{\alpha i}^{(v)}-X_{\beta i}^{(v)})+(Y_{\alpha i}^{(n-1)}-Y_{\beta i}^{(n-1)})+(Z_{\alpha i}^{(n)}-Z_{\beta i}^{(n)}) ,$$

(3.6b)

for $i=1$ and 2. It is clear that the expressions (3.6a) and (3.6b) show the configurational change of a site occupancy in an α and a β site in the vth lattice line of the conduc-

TABLE III. Definition of the path fractionals of bond pair. There are, in total, 60 possible configurational changes on the $x^{(v)}$, $y^{(n)}$, and $z^{(n)}$ bonds during time interval Δt. i and j take 1 and 2.

Bond pair	Configuration change on a bond	Path fractional	Configuration change on a bond	Path fractional
	$\alpha^{(v)}\,\beta^{(v)}$		$\alpha^{(v)}\,\beta^{(v)}$	
		$X^{(v)}_{\alpha i} \equiv X^{(v)}_{i3,3i}$		$X^{(v)}_{\beta i} \equiv X^{(v)}_{3i,i3}$
$x^{(v)}_{i,j}$		$X^{(v)}_{3i,ji}$ (L or R)		$X^{(v)}_{i3,ij}$ (R or L)
		$X^{(v)}_{ji,3i}$ (L or R)		$X^{(v)}_{ij,i3}$ (R or L)
	$\alpha^{(v)}\,\beta^{(v+1)}$		$\alpha^{(v)}\,\beta^{(v+1)}$	
		$Y^{(n)}_{\alpha i} \equiv Y^{(n)}_{i3,3i}$		$Y^{(n)}_{\beta i} \equiv Y^{(n)}_{3i,i3}$
$y^{(n)}_{i,j}$		$Y^{(n)}_{3i,ji}$ (L or C)		$Y^{(n)}_{i3,ij}$ (C or R)
		$Y^{(n)}_{ji,3i}$ (L or C)		$Y^{(n)}_{ij,i3}$ (C or R)
	$\beta^{(v)}\,\alpha^{(v+1)}$		$\beta^{(v)}\,\alpha^{(v+1)}$	
		$Z^{(n)}_{\alpha i} \equiv Z^{(n)}_{i3,3i}$		$Z^{(n)}_{\beta i} \equiv Z^{(n)}_{3i,i3}$
$z^{(n)}_{j,i}$		$Z^{(n)}_{i3,ij}$ (L or C)		$Z^{(n)}_{3i,ji}$ (C or R)
		$Z^{(n)}_{ij,i3}$ (L or C)		$Z^{(n)}_{ji,3i}$ (C or R)

tion (or diffusion) plane, respectively, during the time interval Δt via the vacancy-migration mechanism.

Similarly we can write the configurational change of pair-state variables Δx_{ij}, Δy_{ij}, and Δz_{ji} by making use of Eqs. (B1) and (B2) and the corresponding equations for the pair-state variables for z's. These relations are given in Appendix B. In fact as will be shown later (see Sec. IV), the difference $\Delta y_{ij}^{(n)} - \Delta z_{ji}^{(n)}$ will be used as the condition for the steady state. In terms of path variables, $\Delta y_{ij}^{(n)} - \Delta z_{ji}^{(n)}$ is given by

$$\Delta y_{ij}^{(n)} - \Delta z_{ji}^{(n)} = (Y^{(n)}_{i3,ij,C} - Y^{(n)}_{ij,i3,C}) + (Y^{(n)}_{3j,ij,C} - Y^{(n)}_{ij,3j,C}) + (Y^{(n)}_{i3,ij,R} - Y^{(n)}_{ij,i3,R}) + (Y^{(n)}_{3j,ij,L} - Y^{(n)}_{ij,3j,L})$$
$$- (Z^{(n)}_{i3,ij,C} - Z^{(n)}_{ij,i3,C}) - (Z^{(n)}_{3j,ij,C} - Z^{(n)}_{ij,3j,L}) - (Z^{(n)}_{3j,ij,R} - Z^{(n)}_{ij,3j,R}) - (Z^{(n)}_{i3,ij,L} - Z^{(n)}_{ij,i3,L}) , \qquad (3.7)$$

where i and j take 1 and 2.

C. Definition of flow

In order to derive the Onsager equation for mass transport, it is necessary to define the flow of the two components. The net flow of the ith species may be defined as

the average change of the fractionals at an α and a β site in an arbitrarily taken reference lattice line, say, a vth lattice line, and is given by

$$\Phi_i^{(n-1)} - \Phi_i^{(n)} \equiv \tfrac{1}{2}(\Delta p_i^{(v)} + \Delta q_i^{(v)}) . \qquad (3.8)$$

Then the average flow of the ith species across the nth lat-

tice line can be given by

$$\Phi_i^{(n)} = \tfrac{1}{2}[(Y_{\alpha i}^{(n)} - Y_{\beta i}^{(n)}) + (Z_{\beta i}^{(n)} - Z_{\alpha i}^{(n)})] \qquad (3.9)$$

for $i=1$ and 2. It is noted that the flow is expressed in terms of the path variables which indicate the fractionals of the exchange of an ith atom and a vacancy across the nth line.

In the PPM formalism, those path variables, X's, Y's, and Z's, are given in terms of the most probable path which determines the path on the free-energy surface and they are expressed in terms of the state variables at a time instant t and the physical parameters such as interaction energies ϵ_{ij}'s between ions. Expressions for the most probable path of individual path variables are given in Appendix C and Table IV.

IV. DERIVATION OF THE ONSAGER EQUATIONS

The Onsager equations for mass transport are linear equations which relate the flows of particles of individual species and the respective potential gradients such as chemical potential gradients as driving forces. The flows of ions induced by an electric field as a driving force are evaluated from Eq. (3.9) in terms of those expressions for

the most probable path of individual path variables defined for the jump of the ith species (Appendix C). Let us consider the case where a small chemical potential,

$$\dot{\alpha}_i^{(n)} \equiv d\alpha_i^{(n)}/dn , \qquad (4.1)$$

is further imposed on the system. Note that the chemical potential μ_i for an ith ion is defined by $\mu_i = \alpha_i \beta^{-1}$ $[\beta \equiv (k_B T)^{-1}$ is the reciprocal temperature] and that a dot notation is used for the spatial derivative rather than the conventional time derivative. In the PPM, the Onsager equations are defined across a reference plane at a time instant t. In the following our aim is therefore to obtain the relationship between the flows and the driving force, which arise from these potential gradients.

A. Expression of the flow

When $\dot{\alpha}_i$ and/or $\vec{E}$ exist(s), naturally we can expect the concentration gradients $\dot{p}_i$ and $\dot{q}_i$. Another quantity which is of a similar nature as $\dot{p}_i$ and $\dot{q}_i$ is the deviation from equilibrium, that is, the deviation from symmetry of the pair-fraction variables, $y_{ij}^{(n)} - y_{ije}^{(n)}$ and $z_{ij}^{(n)} - z_{ije}^{(n)}$, induced by $\dot{\alpha}_i$ and/or $\vec{E}$. It is noted that the latter appears in the following combination:

$$\psi_{ij}^{(n)} = \left[\frac{y_{ij}^{(n)} - y_{ije}^{(n)}}{y_{ije}^{(n)}} - \frac{y_{i3}^{(n)} - y_{i3e}^{(n)}}{y_{i3e}^{(n)}} - \frac{y_{3j}^{(n)} - y_{3je}^{(n)}}{y_{3je}^{(n)}} + \frac{y_{33}^{(n)} - y_{33e}^{(n)}}{y_{33e}^{(n)}} \right] - \left[\frac{z_{ij}^{(n)} - z_{ije}^{(n)}}{z_{ije}^{(n)}} - \frac{z_{i3}^{(n)} - z_{i3e}^{(n)}}{z_{i3e}^{(n)}} - \frac{z_{3j}^{(n)} - z_{3je}^{(n)}}{z_{3je}^{(n)}} + \frac{z_{33}^{(n)} - z_{33e}^{(n)}}{z_{33e}^{(n)}} \right]$$

$$= \delta \ln \left[\frac{y_{ij}^{(n)} z_{i3}^{(n)} z_{3j}^{(n)} y_{33}^{(n)}}{z_{ij}^{(n)} y_{i3}^{(n)} y_{3j}^{(n)} z_{33}^{(n)}} \right] \qquad (4.2)$$

for $i,j=1$ and 2. The subscript e indicates the equilibrium value when $\dot{\alpha}_i$ and $\vec{E}$ vanish and the δ notation is defined by

$$\delta y_{ij}^{(n)} \equiv y_{ij}^{(n)} - y_{ije}^{(n)} . \qquad (4.3)$$

As can be easily proved from Eq. (4.2), $\psi_{ij}^{(n)}$ satisfies the relations

$$\psi_{i3}^{(n)} = \psi_{3i}^{(n)} = 0 \qquad (4.4a)$$

for $i=1$ and 2; however, the symmetry relation

$$\psi_{ij}^{(n)} = -\psi_{ji}^{(n)} \qquad (4.4b)$$

does not hold. Therefore, $\psi_{ii}^{(n)}$ does not vanish. This is because of the fact that our system consists of two sublattices (α and β). Of course, for the disordered phase, there is no distinction between the lattice sites, and hence the relation (4.4b) does hold and $\psi_{ii}^{(n)} = 0$ is satisfied.[3]

When the potential gradient, i.e., the force $(\dot{\alpha}_i/\beta$ and/or $Z_i eE)$, is imposed on the system, we expect the net flux of ions, Φ_i in Eq. (3.9), is to be induced. Our aim is now to derive the dependence of Φ_i on the force and ψ_{ij}. To do this it is convenient to define the normalized flow

$$\Psi_i^{(n)} \equiv \frac{\Phi_i^{(n)}}{X_{ie}^{(n)}} = \left[\frac{Y_{\alpha i}^{(n)} - Y_{\beta i}^{(n)}}{Y_{ie}^{(n)}} - \frac{Z_{\alpha i}^{(n)} - Z_{\beta i}^{(n)}}{Z_{ie}^{(n)}} \right] \Big/ 2 , \qquad (4.5)$$

TABLE IV. Path variables and most probable path expressions. i and j take 1 and 2. Λ's and K_{ij} are defined by Eqs. (C3) and (C4), respectively.

Path variables	Most probable path	Path variables	Most probable path
$Y_{i3,ij,C}^{(n)}$	$X_{\alpha j}^{(v+1)} y_{i3}^{(n)}/q_3^{(v+1)}$	$Z_{i3,ij,C}^{(n)}$	$X_{\alpha j}^{(v)} z_{i3}^{(n)}/q_3^{(v)}$
$Y_{3j,ij,C}^{(n)}$	$X_{\beta i}^{(v)} y_{3j}^{(n)}/p_3^{(v)}$	$Z_{3j,ij,C}^{(n)}$	$X_{\beta i}^{(v+1)} z_{3j}^{(n)}/p_3^{(v+1)}$
$Y_{ij,3j,C}^{(n)}$	$X_{\alpha i}^{(v)} K_{ij} y_{ij}^{(n)}/\Lambda_{y,\alpha i}^{(n)}$	$Z_{ij,3j,C}^{(n)}$	$X_{\alpha i}^{(v+1)} K_{ij} z_{ij}^{(n)}/\Lambda_{z,\alpha i}^{(n)}$
$Y_{ij,i3,C}^{(n)}$	$X_{\beta j}^{(v+1)} K_{ij} y_{ij}^{(n)}/\Lambda_{y,\beta j}^{(n)}$	$Z_{ij,i3,C}^{(n)}$	$X_{\beta j}^{(v)} K_{ij} z_{ij}^{(n)}/\Lambda_{z,\beta j}^{(n)}$
$Y_{i3,ij,R}^{(n)}$	$Z_{\alpha j}^{(n+1)} y_{i3}^{(n)}/q_3^{(v+1)}$	$Z_{ij,3j,R}^{(n)}$	$Y_{\alpha i}^{(n+1)} K_{ij} z_{ij}^{(n)}/\Lambda_{z,\alpha i}^{(n)}$
$Y_{ij,i3,R}^{(n)}$	$Z_{\beta j}^{(n+1)} K_{ij} y_{ij}^{(n)}/\Lambda_{y,\beta j}^{(n)}$	$Z_{3j,ij,R}^{(n)}$	$Y_{\beta i}^{(n+1)} z_{3j}^{(n)}/p_3^{(v+1)}$
$Y_{ij,3j,L}^{(n)}$	$Z_{\alpha j}^{(n-1)} K_{ij} y_{ij}^{(n)}/\Lambda_{y,\alpha i}^{(n)}$	$Z_{ij,i3,L}^{(n)}$	$Y_{\beta j}^{(n-1)} K_{ij} z_{ij}^{(n)}/\Lambda_{z,\beta j}^{(n)}$
$Y_{3j,ij,L}^{(n)}$	$Z_{\beta i}^{(n-1)} y_{3j}^{(n)}/p_3^{(v)}$	$Z_{i3,ij,L}^{(n)}$	$Y_{\alpha j}^{(n-1)} z_{i3}^{(n)}/q_3^{(v)}$

where i takes 1 and 2. It is noted that in equilibrium

$$X_{ie}^{(n)} = Y_{ie}^{(n)} = Z_{ie}^{(n)} \qquad (4.6a)$$

holds, and that X_{ie}, Y_{ie}, and Z_{ie} are, respectively, the values of X_i, Y_i, and Z_i when the forces vanish. We can show the relations

$$2\Psi_i^{(n)} = \delta \ln \left[\frac{e^{\beta Z_i eEa} y_{i3}^{(n)} \Lambda_{z,ai}^{(n-1)} \Lambda_{x,ai}^{(v)} (q_i^{(v+1)})^2 z_{3i}^{(n)} \Lambda_{y,\beta i}^{(n-1)} \Lambda_{x,\beta i}^{(v)} (p_i^{(v+1)})^2}{e^{-\beta Z_i eEa} y_{3i}^{(n)} \Lambda_{z,\beta i}^{(n+1)} \Lambda_{x,\beta i}^{(v+1)} (p_i^{(v)})^2 z_{i3}^{(n)} \Lambda_{y,ai}^{(n+1)} \Lambda_{x,ai}^{(v+1)} (q_i^{(v)})^2} \right] \qquad (4.7)$$

for $i = 1$ and 2. Here Λ's are defined in Eq. (C3). We assume the change of properties along the forces (i.e., the potential gradient) is small and expand the right-hand side of Eq. (4.7) around the point n applying the following general formula:

$$\delta g^{(n+m)} = \delta g^{(n)} + m \dot{g}_e^{(n)} . \qquad (4.8)$$

Here $\delta g^{(n)}$ is the deviation caused by the potential gradient of $g^{(n)}$ from the equilibrium value $g_e^{(n)}$, and $\dot{g}$ is the spatial derivative with respect to n. Applying this to Eq. (4.7) (note that v and n are related by $n = v + \frac{1}{2}$), we can express Eq. (4.7) as

$$2\Psi_i^{(n)} = 2Z_i e\beta Ea + \delta \ln \left[\frac{y_{i3}^{(n)} z_{3i}^{(n)} \Lambda_{zai}^{(n)} \Lambda_{y\beta i}^{(n)}}{y_{3i}^{(n)} z_{i3}^{(n)} \Lambda_{z\beta i}^{(n)} \Lambda_{yai}^{(n)}} \right]$$

$$-(d/dn)[3\ln(\Lambda_{aie}^{(n)} \Lambda_{\beta ie}^{(n)}) - 2\ln(p_{ie}^{(n)} q_{ie}^{(n)})] , \qquad (4.9)$$

where $\Lambda_{aie}^{(n)}$ and $\Lambda_{\beta ie}^{(n)}$ are given by

$$\Lambda_{aie}^{(n)} = \frac{p_{3e}^{(n)} x_{i3e}^{(n)}}{x_{33e}^{(n)}} ,$$

$$\Lambda_{\beta ie}^{(n)} = \frac{q_{3e}^{(n)} x_{3ie}^{(n)}}{x_{33e}^{(n)}} . \qquad (4.10)$$

Λ's represent the effect of energy bonds being broken as an A or a B ion jumps. When Eqs. (4.10) and (A12) are used, the d/dn term is written as

$$(d/dn)[3\ln(\Lambda_{aie}^{(n)} \Lambda_{\beta ie}^{(n)}) - 2\ln(p_{ie}^{(n)} q_{ie}^{(n)})]$$

$$= 2\dot{\alpha}_i + (d/dn)\ln(p_{3e}^{(n)} q_{3e}^{(n)}) . \qquad (4.11)$$

Substituting Eq. (4.11) into Eq. (4.9), we obtain

$$2(\Psi_i^{(n)} + \dot{\alpha}_i - Z_i e\beta Ea) = \delta \ln \left[\frac{y_{i3}^{(n)} z_{3i}^{(n)} \Lambda_{zai}^{(n)} \Lambda_{y\beta i}^{(n)} p_3^{(v)} q_3^{(v)}}{y_{3i}^{(n)} z_{i3}^{(n)} \Lambda_{z\beta i}^{(n)} \Lambda_{yai}^{(n)} p_3^{(v+1)} q_3^{(v+1)}} \right]$$

$$\qquad (4.12)$$

for $i = 1$ and 2. To obtain the expression (4.12), we used the relation

$$\frac{d}{dn}\ln(p_{3e}^{(n)} q_{3e}^{(n)}) = \delta \ln \left[\frac{p_3^{(v+1)} q_3^{(v+1)}}{p_3^{(v)} q_3^{(v)}} \right] .$$

Differentiating Λ's in Eq. (4.12) and using Eq. (A11) for the equilibrium values, we obtain

$$X_{aie} = X_{\beta ie} \equiv X_{ie} = \vartheta_i e^{-\beta U_i} \Delta t \, x_{i3e} (\Lambda_{x,aie}/p_{ie})^2 ,$$

$$\qquad (4.6b)$$

and the same for Y's and Z's in equilbrium.

By making use of Eqs. (C2), (C3), and the δ notation defined in Eq. (4.3), we can write $\Psi_i^{(n)}$ as

$$\delta \ln \Lambda_{yai}^{(n)} = \sum_{j=1}^{3} \frac{y_{3je}^{(n)}}{p_{3e}^{(n)}} \delta \ln y_{ij}^{(n)} ,$$

$$\delta \ln \Lambda_{y\beta i}^{(n)} = \sum_{j=1}^{3} \frac{y_{j3e}^{(n)}}{q_{3e}^{(n)}} \delta \ln y_{ji}^{(n)} . \qquad (4.13)$$

Similar expressions are obtained for $\delta \ln \Lambda_{z,ai}^{(n)}$ and $\delta \ln \Lambda_{z,\beta i}^{(n)}$ by replacing y by z. Doing the same for p's and q's in Eq. (4.13), we obtain

$$\delta \ln p_i^{(v)} = \sum_{j=1}^{3} \frac{z_{ije}^{(n-1)}}{p_{ie}^{(v)}} \delta \ln z_{ij}^{(n-1)} ,$$

$$\delta \ln q_i^{(v)} = \sum_{j=1}^{3} \frac{z_{jie}^{(n)}}{q_{ie}^{(v)}} \delta \ln z_{ji}^{(n)} . \qquad (4.14)$$

Noting that at equilibrium

$$p_{ie} = p_{ie}^{(n)} = p_{ie}^{(n+1)} = p_{ie}^{(v)} = p_{ie}^{(v+1)} ,$$

$$q_{ie} = q_{ie}^{(n)} = q_{ie}^{(n+1)} = q_{ie}^{(v)} = q_{ie}^{(v+1)} , \qquad (4.15)$$

and

$$x_{ije} = y_{ije} = z_{jie}$$

hold, use of Eqs. (4.13), (4.14) and the related expressions in (4.12) transforms the latter to

$$2(\Psi_i^{(n)} + \dot{\alpha}_i^{(n)} - Z_i e\beta Ea)$$

$$= -\sum_{k=1}^{2} \frac{x_{3ke}^{(n)}}{p_{3e}^{(n)}} \psi_{ik}^{(n)} + \sum_{k=1}^{2} \frac{x_{k3e}^{(n)}}{q_{3e}^{(n)}} \psi_{ki}^{(n)} , \qquad (4.16)$$

where $\psi_{ij}^{(n)}$ is given by Eq. (4.2). It is noted that although ψ_{ij} is written in a general form, the significant elements among ψ_{ij} are ψ_{12} and ψ_{21} for the order phase whereas because of the symmetry relation (4.4b), either ψ_{12} or ψ_{21} is significant for the disordered phase.

B. The steady-state condition

In order to derive a relation between the flux $\Phi_i^{(n)}$ (or $\Psi_i^{(n)}$) and the force $(\dot{\alpha} - Z_i eEa)$, we must eliminate ψ_{ij} in Eq. (4.16). The necessary equation is supplemented by the steady-state condition. When the system reaches a steady state, there is no change of fractionals with time for a site occupant. This means that Δp_i and Δq_i must vanish at the steady state. As seen in Eqs. (3.6), Δp_i and Δq_i are the functions of X's, Y's, and Z's. It is convenient to introduce the relations as was done before:[3]

$$X^{(v)}_{\alpha i(\beta i)} = [X^{(v)}_{ie} + O(\Phi_i)] \pm \tfrac{1}{2}\Phi^{(v)}_{Xi} ,$$

$$Y^{(n)}_{\alpha i(\beta i)} = [X^{(n)}_{ie} + O(\Phi_i)] \pm \tfrac{1}{2}\Phi^{(n)}_{Yi} ,$$ (4.17)

$$Z^{(n)}_{\alpha i(\beta i)} = [X^{(n)}_{ie} + O(\Phi_i)] \pm \tfrac{1}{2}\Phi^{(n)}_{Zi} ,$$

where the plus sign applies to the subscript αi and the minus sign to βi. When Δp_i and Δq_i in Eqs. (3.6) vanish, we can derive the following relations among Φ's:

$$\Phi^{(v)}_{Xi} + \Phi^{(n)}_{Yi} + \Phi^{(n-1)}_{Zi} = 0 ,$$
$$\Phi^{(v)}_{Xi} + \Phi^{(n-1)}_{Yi} + \Phi^{(n)}_{Zi} = 0 .$$ (4.18)

Because of Eq. (3.9), Φ's in Eqs. (4.18) are related to $\Phi_i^{(n)}$ by

$$\Phi_i^{(n)} = \tfrac{1}{2}(\Phi^{(n)}_{Yi} - \Phi^{(n)}_{Zi}) = \tfrac{1}{2}(\Phi^{(n-1)}_{Yi} - \Phi^{(n-1)}_{Zi}) \equiv \Phi_i .$$ (4.19)

It should be noted that Eq. (4.19) is independent of n, as is expected in the steady state, since the net flow defined in Eq. (3.8) vanishes. In the steady state,

$$\Delta y^{(n)}_{ij} - \Delta z^{(n)}_{ji} = 0$$ (4.20)

should also be satisfied for the pair-state variables. By making use of Eqs. (C3), (4.5), (4.17), and (4.18) and the related expressions for the most probable path, the steady-state condition (4.20) can be expressed in terms of the ψ_{ij}'s and the equilibrium quantities

$$\frac{x^{(n)}_{i3e}}{q^{(n)}_{3e}X^{(n)}_{ie}}\left[-\psi^{(n)}_{ij} + \sum_{k=1}^{2}\frac{x^{(n)}_{k3e}}{q^{(n)}_{3e}}\psi^{(n)}_{kj} - \Psi^{(n)}_{j} \right] + \frac{x^{(n)}_{3je}}{p^{(n)}_{3e}X^{(n)}_{je}}\left[-\psi^{(n)}_{ij} + \sum_{k=1}^{2}\frac{x^{(n)}_{3ke}}{p^{(n)}_{3e}}\psi^{(n)}_{ik} + \Psi^{(n)}_{i} \right] = 0$$ (4.21)

for $i,j = 1$ and 2, where $\psi^{(n)}_{ij}$ is given by Eq. (4.2). Relations (4.16) and (4.21) form the basic equations to obtain the force-flux relation, and hence the kinetic coefficient for the system.

C. The Onsager equation

The relations between the fluxes and the potential gradients (forces) are derived by eliminating four ψ_{ij}'s ($i,j=1$ and 2) from Eqs. (4.16) and (4.21). The resultant expressions are of the form

$$\vec{\Psi}^{(n)} = -\overset{\leftrightarrow}{\mathbf{l}}\cdot\vec{A} \quad \text{viz} \quad \Psi^{(n)}_{i} = -\sum_{j=1}^{2} l_{ij}A_j ,$$ (4.22a)

$$A_i \equiv \dot{\alpha}_i - Z_i e\beta Ea ,$$ (4.22b)

for $i=1$ and 2. The current Φ_{UAi} is defined as the flux per unit area in a unit time. From Eq. (4.22) the Onsager equation is given by

$$\vec{\Phi}^{(n)}_{UA} = -\overset{\leftrightarrow}{\mathbf{L}}\cdot\vec{A} \quad \text{viz} \quad \Phi^{(n)}_{UAi} = -\sum_{j=1}^{2} L_{ij}A_j ,$$ (4.23a)

$$L_{ij} \equiv X^{(n)}_{ie}l_{ij}/(\sqrt{3}ac\,\Delta t)$$ (4.23b)

for $i=1$ and 2. Here a is the distance defined in Fig. 1, and c is the interplanar distance perpendicular to the plane where diffusion and/or ionic conduction take(s) place. The explicit expressions of l_{ij}'s are complicated and only the derivation of l_{ij}'s is given in Appendix D. Equation (4.23) shows the linear relation between the currents and the driving forces. The currents, $\Phi^{(n)}_{UAi}$ ($i=1$ and 2), and hence its linear coefficients L_{ij}'s, are evaluated across an arbitrarily taken reference plane (indicated as n in Fig. 1) which is perpendicular to the direction of the driving forces. $\Phi^{(n)}_{UA1}$ and $\Phi^{(n)}_{UA2}$ then represent the difference of the jumps of A and B ions, respectively, across the reference plane in the two directions. The interactions among ions create a certain distribution of two components and vacant sites. This distribution is eventually determined by the pair approximation of the cluster variation method

(CVM) of equilibrium statistical mechanics (see Appendix A).[18] Equation (4.23) was obtained under the steady-state condition where the current should occur without disturbing the overall distribution of ions. Hence the jumps of ions across the reference plane are calculated by knowing the local environment of jumping ions. It should be noted that the kinetic coefficients L_{ij}'s consist of four terms, namely, the diagonal terms (L_{11} and L_{22}) and the cross terms (L_{12} and L_{21}); the former elements are due to the independent flows of A and B ions and the latter elements are due to the interacting flows of A and B ions, respectively. In the PPM, each element of the kinetic coefficients is given in an analytical fashion. We can therefore obtain the detailed information about the conduction and/or the diffusion mechanism(s) of the system by examining these elements. It should be noted that the kinetic coefficients L_{ij}'s satisfy Onsager's reciprocity theorem, i.e., $L_{ij} = L_{ji}$ ($i \neq j$).

V. EXPRESSION OF CONDUCTIVITY AND ITS ANALYSIS

Ionic conductivity is calculated under the steady-state condition. Different from the diffusion treatment which will be reported elsewhere, we do not have a concentration gradient [i.e., $\dot{\alpha}_i = 0$ in A_i defined in Eq. (4.22b)] so that it is not necessary to specify the local ion of the reference plane and we may drop the superscripts n and v. From Eq. (4.23), the particle flux, Φ_{UAi} ($i=1$ and 2), are given by

$$\Phi_{UAi} = \beta ae\sum_{j=1}^{2}Z_jL_{ij}E ,$$ (5.1)

where L_{ij} is given by Eq. (4.23b). Hence the electric current J_i due to the conduction ion i is given by

$$J_i = Z_ie\Phi_{UAi} = \beta ae^2\sum_{j=1}^{2}Z_iZ_jL_{ij}E ,$$ (5.2)

where i takes 1 and 2. The total electric current J is then given by the current due to ions A and B;

$$J = \sum_{i=1}^{2} J_i \equiv \sigma_I E \ . \tag{5.3}$$

The last equation defines the conductivity σ_I of the system as a whole, which includes the contribution from the two kinds of ions A and B:

$$\sigma_I = \sigma_1 + \sigma_2 \ , \tag{5.4}$$

where σ_1 and σ_2 are the conductivity of the ions A and B, respectively, given by

$$\sigma_1 = \frac{Z_1^2 e^2}{\sqrt{3}c} \frac{\vartheta_1 e^{-\beta U_1}}{k_B T} \left[\frac{\Lambda_{x,\alpha 1e}}{p_{1e}} \right]^2 x_{13e} l_{11} \left[1 + \frac{Z_2}{Z_1} \frac{l_{12}}{l_{11}} \right] \ , \tag{5.5a}$$

$$\sigma_2 = \frac{Z_2^2 e^2}{\sqrt{3}c} \frac{\vartheta_2 e^{-\beta U_2}}{k_B T} \left[\frac{\Lambda_{x,\alpha 2e}}{p_{2e}} \right]^2 x_{23e} l_{22} \left[1 + \frac{Z_1}{Z_2} \frac{l_{21}}{l_{22}} \right] \ , \tag{5.5b}$$

where Λ's are given by Eq. (4.10) and the derivation of l_{ij}'s are illustrated in Appendix D. These quantities indicate the average distribution of ions in the steady state and hence can be evaluated by making use of the equilibrium distributions of species, which are determined by the CVM. They also include kinetic parameters U's and ϑ's which indicate the basic jump frequencies of ions.

In defining the percolation efficiency, it is necessary to refer to a random-walk system consisting of ions with appropriately defined average jump frequencies. In our treatments, these jump frequencies include the effect of bond breaking of immediate surroundings due to the pair interactions (effective jump frequency factor) and the distribution of accessible vacancies (the vacancy availability factor). The basic jump frequencies of A and B ions, w_1 and w_2, are defined as

$$w_1 \equiv \vartheta_1 e^{-U_1/k_B T}, \quad w_2 \equiv \vartheta_2 e^{-U_2/k_B T} \ , \tag{5.6}$$

respectively. Therefore, the average jump frequencies at a fixed distribution are given in the form

$$\hat{w}_1^{\alpha} = \vartheta_1 e^{-U_1/k_B T} V_1^{\alpha} W_1^{\alpha}, \quad \hat{w}_2^{\alpha} = \vartheta_2 e^{-U_2/k_B T} V_2^{\alpha} W_2^{\alpha} \ . \tag{5.7}$$

Here, $\hat{w}_i^{\alpha}$ ($i = 1$ and 2) indicates the average jump frequencies of an ith species at an α site. V_i^{α} and W_i^{α} are the corresponding vacancy availability factor[2] and the bond breaking factor (defined earlier as the effective jump frequency factor[2]) and are, respectively, given by

$$V_i^{\alpha} = x_{i3e} \ , \tag{5.8}$$

$$W_i^{\alpha} = \left[\frac{\Lambda_{x,\alpha ie}}{p_{ie}} \right]^2 \ ,$$

for $i = 1$ and 2. It is noted that in equilibrium, Eq. (4.6b) holds so that the following relation is expected to hold:

$$x_{i3e} \left[\frac{\Lambda_{x,\alpha ie}}{p_{ie}} \right]^2 = x_{3ie} \left[\frac{\Lambda_{x,\beta ie}}{q_{ie}} \right]^2 \tag{5.9}$$

viz.

$$V_i^{\alpha} W_i^{\alpha} = V_i^{\beta} W_i^{\beta}$$

for $i = 1$ and 2. Therefore, the average jump frequencies of ions so defined are the same for both from the α site and from the β site. The percolation efficiency is defined to that of the random walk. Therefore, the first factor of each equation in Eq. (5.5) is the contribution from the random walk of particles to the conductivity, but the second factor f_{Ii}'s ($i = 1$ and 2) defined as

$$f_{I1} = l_{11} \left[1 + \frac{Z_2}{Z_1} \frac{l_{12}}{l_{11}} \right] \ , \tag{5.10a}$$

$$f_{I2} = l_{22} \left[1 + \frac{Z_1}{Z_2} \frac{l_{21}}{l_{22}} \right] \tag{5.10b}$$

indicates the effect of the deviation from the random walk of particles and is defined as the percolation efficiency factors of individual species of ions.

There are contributions to the conductivity from the "cross terms" l_{12} and l_{21}. The importance of the cross terms are often discussed in terms of irreversible thermodynamics.[19,20] The cross terms indicate the effect of a finite flow of one species to those of others. These terms are often referred to as "wind" effects.[21] The advantage of the PPM is that these terms can be derived analytically and their meaning can be unambiguously understood. Referring to Eq. (5.2), the cross terms $\sigma_{12} = \sigma_{21}$ can be defined. These terms are mostly due to the correlation factor of different species of conduction ions. However, it is also noticed that these terms do not necessarily vanish in the limit of random walk (no interactions among ions). This is due to the requirement of the reference system that the total system be in the equilibrium state even if a mass motion Φ_i is measured with respect to the reference system. Therefore, in deriving the Onsager equations, the reference system should be clearly stated.

The isotope diffusion and hence the "correlation factor" is often utilized in identifying the diffusion mechanism and hence its meaning must be clarified. In a general case of diffusion, the correlation has been defined as the percolation efficiency of a single atom of the observing species with respect to the random walk.[4] It is to be noted that this definition of the correlation factor is not always the same as that defined as the ratio of the diffusion coefficients of isotope and of the self-diffusion or the Haven ratio. The derivation of the correlation factor for a corresponding case to the present one has been made by the PPM (Ref. 2) and it is not repeated here. Because we deal with two sublattice cases, we utilize the concept of partial correlation factors f_{B*}^{α} and f_{B*}^{β} for each sublattice in order to derive the correlation factor f_{B*} of the system. In other words, the correlation factor for the tracer diffusion of one of the components, f_{B*}, are calculated by[22]

$$\frac{1}{f_{B*}} = \frac{1}{2} \left[\frac{1}{f_{B*}^{\alpha}} + \frac{1}{f_{B*}^{\beta}} \right] \tag{5.11}$$

from the partial correlation factors f_{B*}^{α} and f_{B*}^{β} (these are related to the jump of a B^* atom from an α and a β site, respectively) and these are given by

$$f_{B*}^{\alpha} = \frac{Q_1^{\beta}\Omega_1^{\beta}}{\Omega_2^{\alpha}+\Omega_1^{\beta}} + \frac{Q_2^{\beta}\Omega_2^{\beta}}{\Omega_2^{\alpha}+\Omega_2^{\beta}} + Q_3^{\beta} ,$$

$$f_{B*}^{\beta} = \frac{Q_1^{\alpha}\Omega_1^{\alpha}}{\Omega_1^{\alpha}+\Omega_2^{\beta}} + \frac{Q_2^{\alpha}\Omega_2^{\alpha}}{\Omega_2^{\alpha}+\Omega_2^{\beta}} + Q_3^{\alpha} ,$$

(5.12)

where Q's and Ω's are defined in Eqs. (D1).

The actual calculations require the following parameters. First, we need interaction parameters. These parameters express the nearest-neighbor pair interaction energies among conduction ions and are denoted by ϵ_{AA}, ϵ_{BB}, and ϵ_{AB}, where ϵ_{AA}, etc., stand for an A-A pair interaction energy, etc., respectively. Here ϵ_{ij} is an effective interaction energy expressed in the form of a pair interaction energy but it includes both direct and indirect interactions. It has been found that the interactions among conduction ions are to be repulsive in order to expect superionic conduction.[2] We define that the positive sign of ϵ_{ij}'s indicate the attractive force so that the energy E is defined as $E = -\epsilon_{AA}$ and so on. We further assume that no apparent interaction exists with respect to vacancy; $\epsilon_{AV}=\epsilon_{BV}=\epsilon_{VV}=0$. The difference in the magnitudes of interactions between the same kind of ions and different kinds of ions creates either attractive or repulsive interactions between the two components. If no other interactions exist, the former tends to create ordering while the latter tends to produce phase separations. In view of several physical evidences, let us tentatively assume that the former is the case. Interaction between different kinds of ions are determined by the combination[23]

$$\epsilon = \epsilon_{AB} - \tfrac{1}{2}(\epsilon_{AA}+\epsilon_{BB}) .$$

(5.13)

Here $\epsilon > 0$ means an attractive interaction while $\epsilon < 0$ means a repulsive interaction based on the present sign convention. These parameters, along with the concentration of A and B ions and vacancies, are enough to determine the distribution of ions at a specified temperature by the pair approximation of the CVM (see Appendix A). In addition to this, ϑ's and U's appearing in Eqs. (5.5) determine the conductivity at a specified temperature and compositions. The actual calculations were made with the following values of parameters:

$$\epsilon_{AA} = \epsilon_{BB} = -1.0, \quad \epsilon_{AB} = -0.8 .$$

(5.14)

In other words, the interactions among ions are repulsive, but the combination is such that it tends to create an ordered distribution among different kinds of ions at low temperatures [Eq. (5.13)]. The phase diagram then takes the shape represented schematically in Fig. 2. In the absence of vacancies, the critical point of order-disorder at the stoichiometric composition $(\rho_A=\rho_B=0.5)$ is given by the pair approximation of the CVM:[23]

$$\frac{\epsilon}{k_B T_C} = \log_{10}\frac{\omega}{\omega-1} ,$$

(5.15)

where 2ω is the coordination number of the lattice ($2\omega=3$ for the two-dimensional honeycomb lattice). As the concentration of the vacancies ρ_V increases, the critical temperature lowers. All these properties can be calculated analytically by the pair approximation of the CVM.
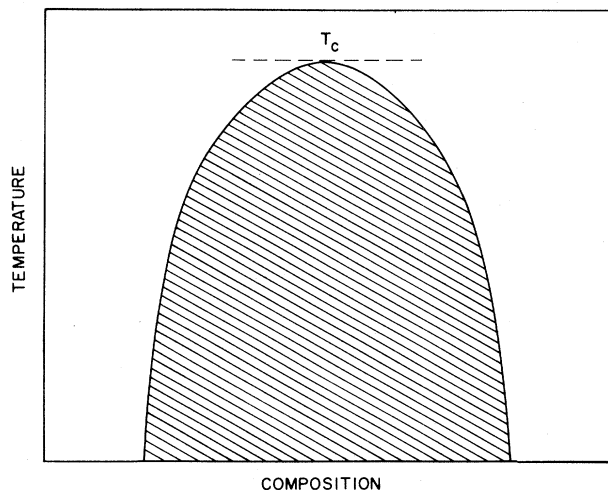

FIG. 2. Schematic phase diagram which separates the ordered (shaded) region from the disordered (unshaded) region.

However, we normalize the temperature utilizing T_C given in Eq. (5.15). We calculated necessary quantities for cases where ρ_V is 1×10^{-4} and 2×10^{-1} based on the formulas (5.5a) and (5.5b). For the sake of simplicity, we further assume that $\epsilon_{AA}=\epsilon_{BB}$, that the jump frequencies of ions A and B are the same, i.e., $w_1=w_2$ (or $\vartheta_1=\vartheta_2$ and $U_1=U_2$) and that these ions A and B are singly ionized $(Z_1=Z_2=1)$. The difference in the jump frequencies of the two species in the solid would then be due to the bond-breaking factor.

The results of calculation for $\rho_V=1\times10^{-4}$ and 2×10^{-1} at $T/T_C\approx0.5$ are shown in Fig. 3 as a function of concentration of A and B ions ρ_A and ρ_B ($\rho_A+\rho_B=1$), respectively. The calculated quantities are

$$\sigma_I=\sigma_A+\sigma_B, \quad \sigma_A=\sigma_{AA}+\sigma_{AB}, \quad \sigma_B=\sigma_{BB}+\sigma_{BA} \quad (5.16)$$

by making use of the formulas (5.5a) and (5.5b). It is to be noted that the cross term σ_{AB} ($=\sigma_{BA}$) is not negligible compared to the diagonal term σ_{AA} (or σ_{BB}). In addition, the percolation efficiency factor f_{Ii} ($i=1$ and 2) defined in Eqs. (5.10) (see Fig. 4) and the correlation factor for the tracer diffusion of one of the components f_{B*} (see Fig. 6) are also calculated. At $T/T_C\approx0.5$, for both $\rho_V=1\times10^{-4}$ and 2×10^{-1}, the system becomes ordered for concentrations near $\rho_A=\rho_B=\frac{1}{2}$. Further the distribution p_{Ae}, p_{Be}, etc. of ions and vacancies p_{Ve} and q_{Ve} on the two sublattices are shown in Fig. 5 in order to make interpretations easier. The calculated conductivity of the system, σ_I, σ_A, σ_B, and $\sigma_{AB}=\sigma_{BA}$, shows a very sharp minimum, especially for $\rho_V=1\times10^{-4}$, at the composition $\rho_A=\rho_B=\frac{1}{2}$. The change of the mobility or the change of the effective (average) jump frequency indicated in the figures by dotted-dashed lines also shows a minimum. This decrease in the mobility is due to the increase in the bond-breaking factor because of the increase of different ions at the nearest neighbor as the composition approaches to $\rho_A=\rho_B=\frac{1}{2}$ and as a result of ordering. At the same time, a very pronounced decrease in the percolation efficiency is noticed. This decrease in the percolation efficiency is due to the percolation difficulty[24] created by the ordering
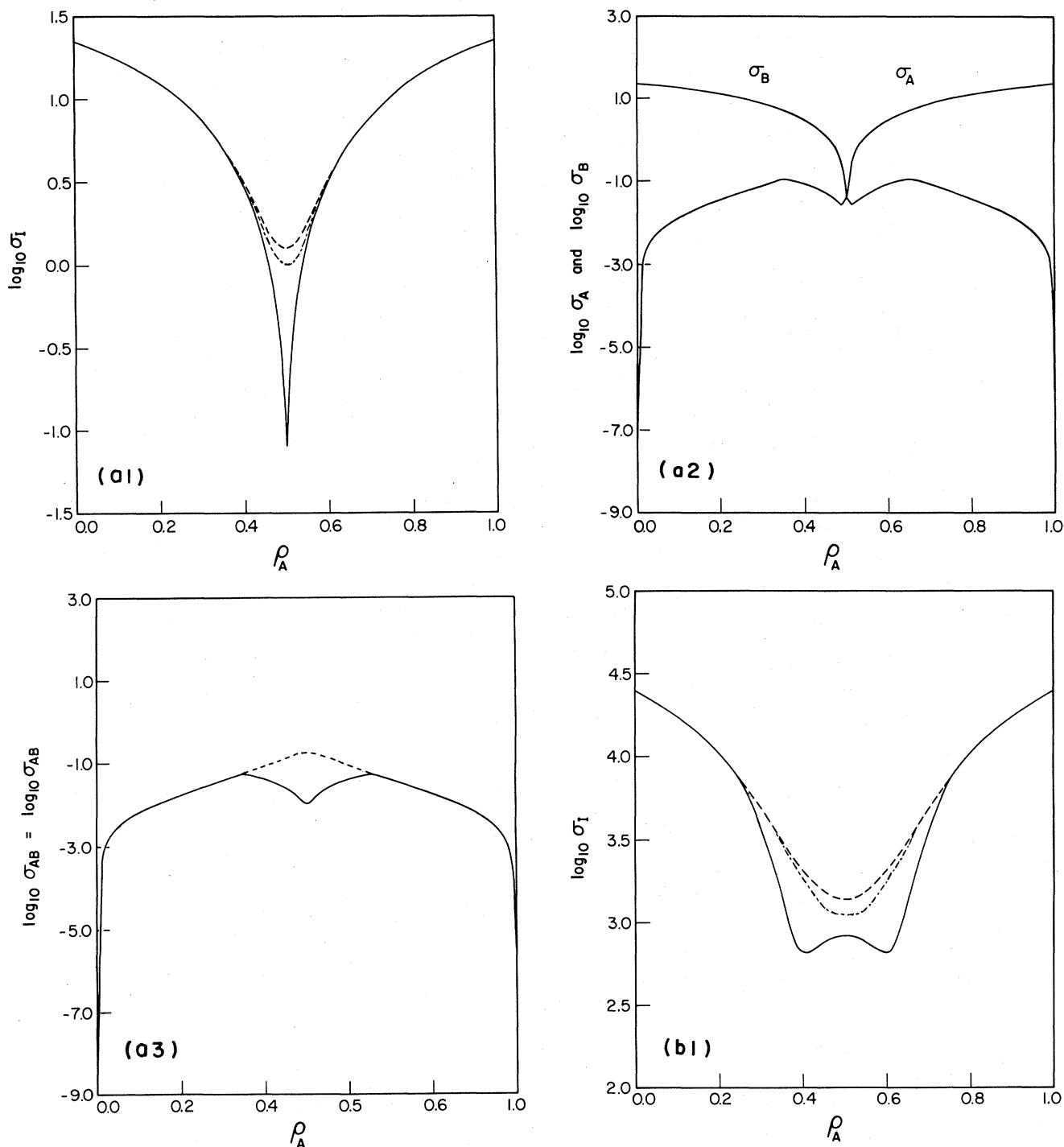
FIG. 3. Dependence of σ_I, σ_A, σ_B, and σ_{AB} (relative scale) on composition ρ_A at $T/T_C \approx 0.5$. The dot-dashed line shows the case where the percolation efficiency factors f_{IA} and f_{IB} in σ_I are artificially set equal to 1 to show the percolation efficiency whereas the dashed line shows the case where the development of the long-range order is artificially suppressed in order to show the effect of ordering. (a) $\rho_V = 1 \times 10^{-4}$; (b) $\rho_V = 0.2$.

among conduction ions.

The correlation factor (see Fig. 6) for the species B, f_{B^*}, also shows a sharp minimum at the same composition range. As was discussed earlier,[2,24] that decrease is due to the "physical correlation factor f_I" or the percolation efficiency. The correlation factor f_{B^*} is defined as the percolation efficiency of the motion of a single ion (of the species B) with respect to that of the random walk. The

ratio which differs from the value 1 of the percolation efficiency of a single ion and that of the assembly of ions (the Haven ratio[24]) is due to the difference in the statistical weight of the jump into a vacancy of the two cases.[2]

The correlation factor, f_{B^*}, is equal to 0.5 for the limit $\rho_B \to 1$, but is close to 1 for $\rho_A \to 1$. For $\rho_B \to 1$, f_{B^*} should take the accepted value of the correlation factor for self-diffusion[26] [the exact value is, however, $\frac{1}{3}$ rather
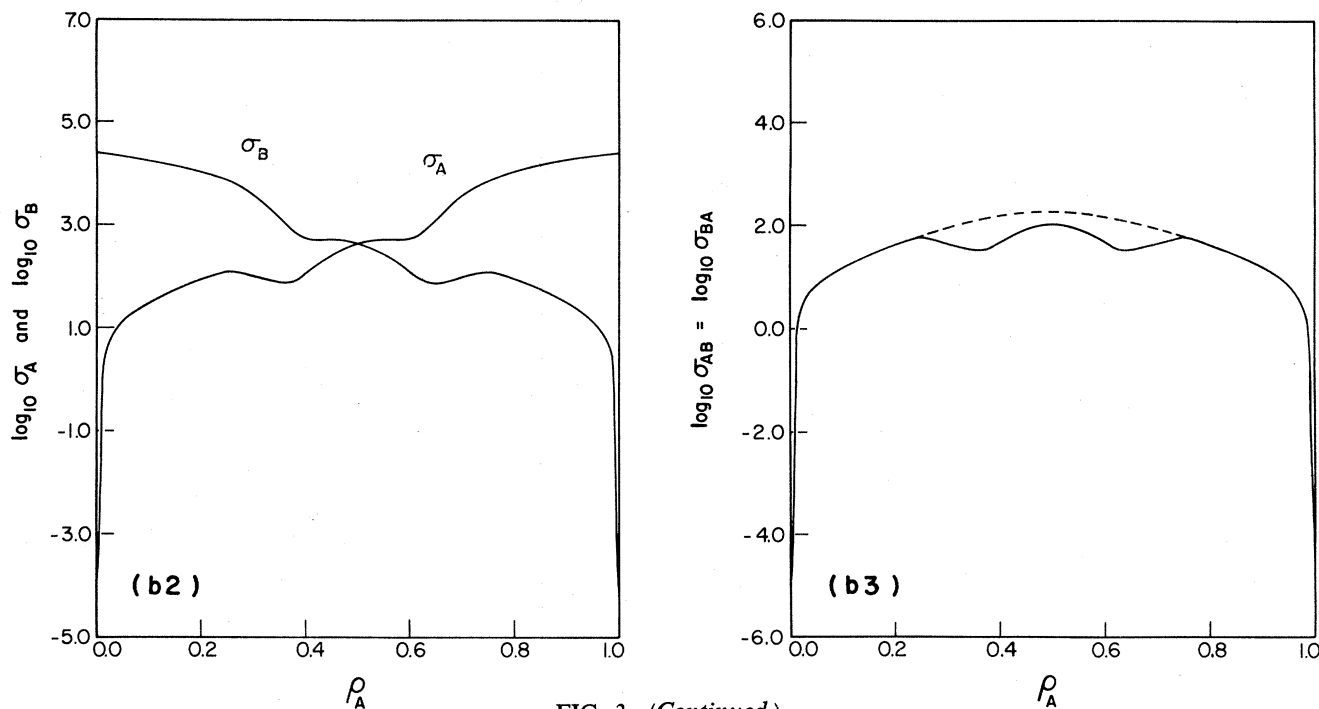
FIG. 3. (Continued.)

than $\frac{1}{2}$ (Refs. 4 and 28)], but for $\rho_A \to 1$, the value corresponds to that for the impurity diffusion for the case $\hat{w}_A \gg \hat{w}_B$.[26] The condition $\hat{w}_A \gg \hat{w}_B$ is created by the large bond-breaking factor for the B^* atom.

If ρ_V increases, the vacancies provide the percolation path and the percolation efficiency increases and the minimum in the conductivity broadens. Nevertheless, a considerable part of the decrease in the conductivity is yet ascribed to the decrease in the percolation efficiency in the ordered range. A conspicuous result for the case with a large number of vacancies $(\rho_V = 2 \times 10^{-1})$ is the appearance of two minima in the conductivity. This situation is an artifact and reflects the nonequal distribution of vacancies for the two sublattices as shown in Fig. 5. The unequal distribution for the case $\epsilon_{AA} = \epsilon_{BB}$ is created in order to make the pair interaction energy the minimum,[27] and hence the bond-breaking factor becomes maximum at this condition. However, Fig. 3 shows the the percolation efficiency yet plays a significant role to make the minima in the conductivity more distinctive. As the number of vacancies decreases, these two minima eventually coincide into one to make a broad minimum before it becomes a sharp cusp as $\rho_V \to 0$.

It is to be noted that, in the present approximation of the PPM, the percolation efficiency does not deviate from 1 unless the long-range order is created or the distinctive sublattices are created.[2] The effect of the short-range order plotted by broken lines in Fig. 3 is therefore solely due to the change in the mobility. However, it is to be pointed out that a substantial decrease in the percolation efficiency is expected in a system with a developed short-range order.[28] The expressions of the PPM with respect to this point has been corrected[29] and will be published shortly.

VI. DISCUSSION AND CONCLUDING REMARKS

We have developed a general theory of mass transport for a two-component system based on the two-dimensional honeycomb lattice-gas model by applying the PPM of irreversible statistical mechanics and obtained the Onsager equations. As far as we know, this is the first attempt to calculate the many-body features of ion transport in binary systems in a systematic fashion. Expressions of the conductivity [Eqs. (5)] consist of two factors: the *mobility* of ions and the *percolation efficiency*. The former is equivalent to the expression of the random walk of particles with the average jump frequencies of A and B ions including the bond-breaking factor which takes care of the effect of immediate surroundings due to the mutual interactions among ions, and the vacancy availability factor which ensures the motion of ions via a vacancy of averaged solid. The second factor expresses the efficiency of the motion of ions towards the long-range diffusion relative to that of the random walk.

The theory shows quite generally that a substantial decrease in the percolation efficiency occurs if the long-range order is developed in the system. A minor correction of the present approximation of the PPM further shows that the development of the short-range order is enough to expect a substantially equivalent result.[29] The decrease in the percolation efficiency is traced to the development of the percolation difficulty due to the development of ordered arrangements.[24]

The percolation efficiency is an efficiency of ionic motion toward the long-range diffusion and, hence, is expected to vanish if the measurement is carried out at high frequencies. We have shown, within a limited degree of
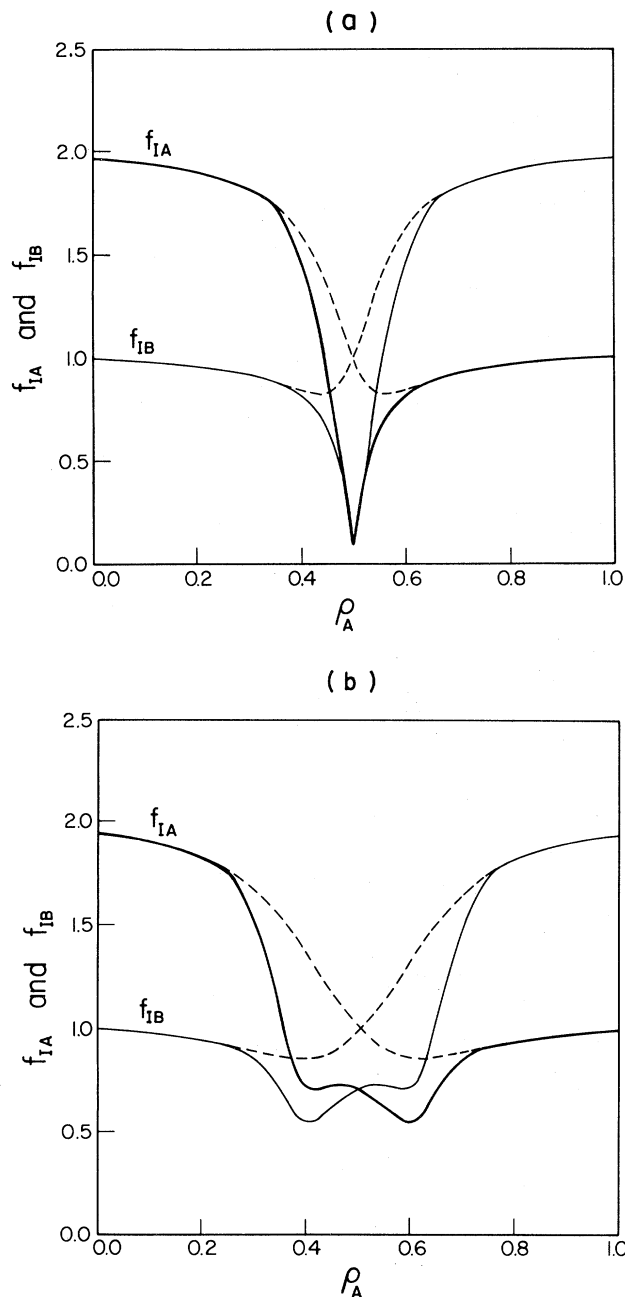
FIG. 4. Dependence of percolation efficiency factors f_{IA} and f_{IB} on composition ρ_A at $T/T_C \approx 0.5$. The dashed line shows the case where the development of the long-range order is artificially suppressed in order to show the effect of ordering. (a) $\rho_V = 1 \times 10^{-4}$; (b) $\rho_V = 0.2$.
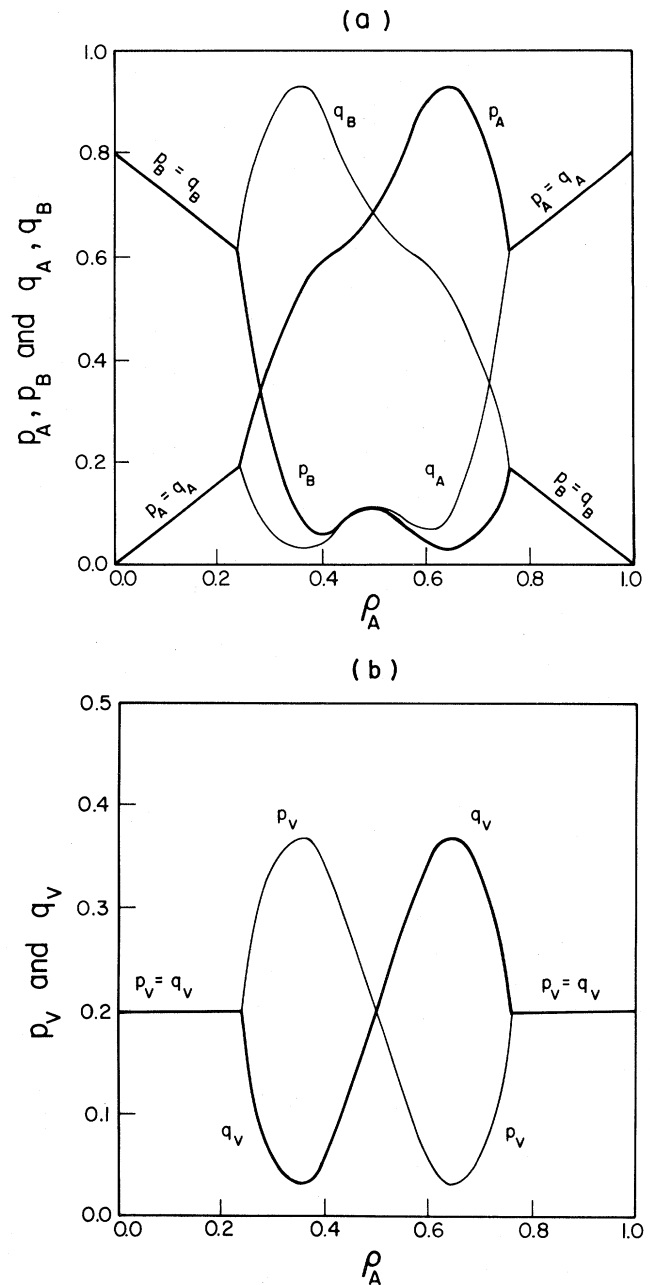
FIG. 5. Equilibrium distributions of (a) A and B ions and (b) vacancies (V) at an α and a β site, respectively, as a function of ρ_A.

approximation and under a certain condition of the stationary state, that the value of the correlation factor decreases by conversion from the ensemble averaging at an instant time to the time averaging [corresponding to the conversion from $\sigma(\infty)$ to $\sigma(0)$].[4] If the major cause of MAE is due to the percolation efficiency effect as expected, a substantial frequency dependence of MAE is expected. Indeed, the measurements by Hunter *et al.* on β-alumina systems[30] and Tomozawa *et al.* on glass systems[31] indicate that this is the case. In other words, our

expectation that MAE is mostly due to the percolation efficiency is quite likely.[14]

The second importance of the theory is that the decrease of the percolation efficiency is due to the (local) ordering of ions by mutual interactions of different kinds of ions. If this is true, we do not expect the existence of MAE in a binary system consisting of isotopes. Such an isotope effect has been investigated, and so far no MAE has been found in isotope mixtures.[32] This also indirectly supports our contention. On the other hand, this effect cannot distinguish our model from those models dealing with the decrease in the mobility by mutual interactions.[11,12]
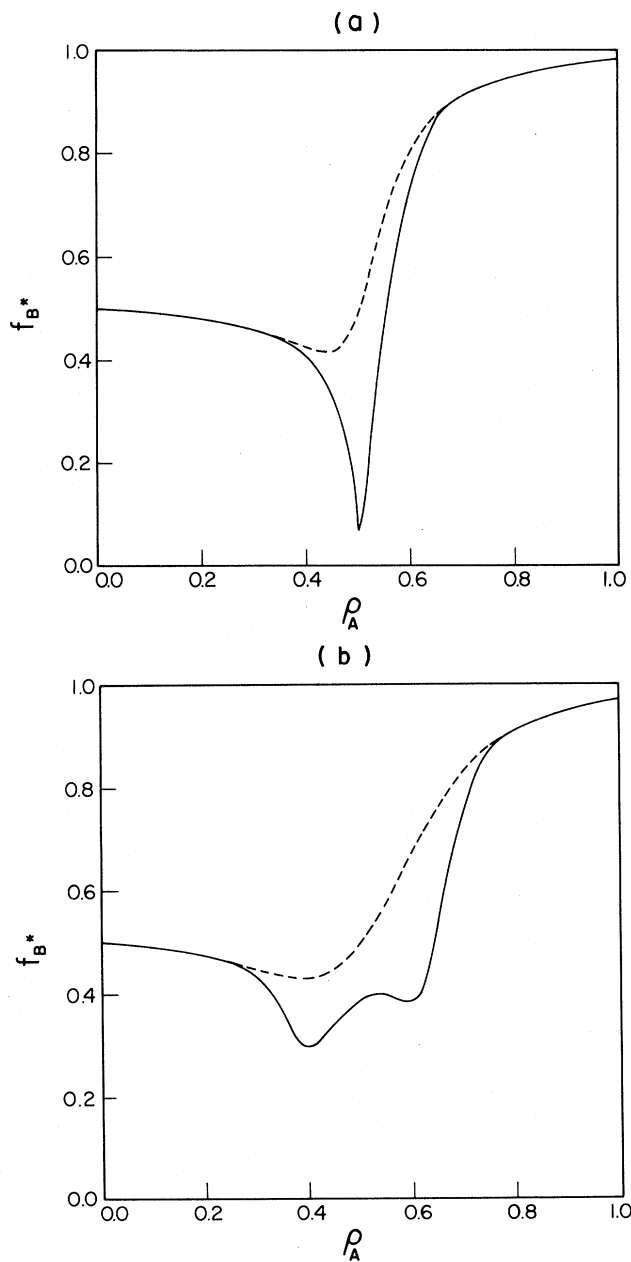
(a)

(b)

FIG. 6. Composition ρ_A dependence of correlation factors f_{B^*} at $T/T_C \approx 0.5$. The dashed line shows the case where the development of the long-range order is artificially suppressed in order to show the effect of ordering. (a) $\rho_V = 1 \times 10^{-4}$; (b) $\rho_V = 0.2$.

The present results of calculation can more or less be applied to β''-alumina systems and to β-alumina systems with some modifications. The decrease of the percolation efficiency by local ordering can also be interpreted as the effect due to decrease of the percolation efficiency by blocking of the diffusion path. It is, however, difficult to compare the present calculated results directly with effects found in glass systems. A major character of MAE in glass systems is that the ionic conductivity drops substantially by the substitution of a rather small amount of ions.[5,6] Although a quantitative calculation is difficult for

glass systems, we might add the following suggestions. The diffusion path of glass systems can be characterized by the mixture of low-dimensional parts (small coordination number and down to one dimension) in the three dimensional path. If the sites on these low dimensional parts are blocked, which is expected to occur at a relatively low value of substitution, a substantial drop in the conductivity is expected. However, a satisfactory explanation must await further study.

ACKNOWLEDGMENTS

APPENDIX A: DERIVATION OF α_i AND x_{ije}

We outline the equilibrium treatment of the system by the CVM.[18] The total configurational energy E of the system with N lattice points is written as

$$E = -\frac{N}{2} \sum_i \sum_j \epsilon_{ij}(x_{ije} + y_{ije} + z_{ije})$$

$$= -\tfrac{3}{2}N \sum_i \sum_j \epsilon_{ij} x_{ije} \tag{A1}$$

for $i,j = 1$, 2, and 3, where $-\epsilon_{ij}$ ($\epsilon_{ij} > 0$) is the interaction energy between the i-j species, and x_{ije}, y_{ije}, and z_{ije} are the state fractionals of the pair at equilibrium. According to the pair approximation of the CVM, the entropy is given by

$$S = k_B N \left[\sum_{i=1}^{3} L(p_{ie}) + \sum_{i=1}^{3} L(q_{ie}) - \tfrac{3}{2} \sum_{i=1}^{3} \sum_{j=1}^{3} L(x_{ije}) + \tfrac{1}{2} \right] \tag{A2}$$

where the function $L(x)$ is defined as

$$L(x) \equiv x \ln x - x . \tag{A3}$$

The L's in Eq. (A2) originate in the logarithm of the factorials in the number of ways of constructing the system, and are approximated as defined in (A3). The p_{ie} and the q_{ie} designate the fractionals of the ith species on the α and the β sites in equilibrium, respectively. These are related to the fractionals of the pair-state variables as

$$p_{ie} = \sum_{j=1}^{3} x_{ije}, \quad q_{ie} = \sum_{j=1}^{3} x_{jie} , \tag{A4}$$

and are normalized:

$$\sum_{i=1}^{3} p_{ie} = \sum_{i=1}^{3} q_{ie} = 1 .$$ (A5)

The fractional of the concentration of the ith species ρ_i is then expressed in terms of p's and q's as

$$2\rho_i = p_{ie} + q_{ie} ,$$ (A6)

and ρ_i satisfies

$$\sum_{i=1}^{3} \rho_i = 1 .$$ (A7)

In order to derive the equilibrium state, we minimize the Helmholtz free energy with the constraint given by (A6). The free energy per site is given from (A1) and (A2) as

$$F = -\tfrac{3}{2} \sum_i \sum_j \epsilon_{ij} x_{ije} - k_B T \left[\sum_i L(p_{ie}) + \sum_i L(q_{ie}) - \tfrac{3}{2} \sum_i \sum_j L(x_{ije}) + \tfrac{1}{2} \right] .$$ (A8)

Introducing a Lagrange multiplier λ_i, the minimization of F under the constraint (A6) is equivalent to that of

$$\beta F = -\tfrac{3}{2}\beta \sum_{i,j} \epsilon_{ij} x_{ije} - \left[\sum_i L(p_{ie}) + \sum_i L(q_{ie}) - \tfrac{3}{2} \sum_{i,j} L(x_{ij}) + \tfrac{1}{2} \right] + \tfrac{3}{2} \sum_i \lambda_i (p_{ie} + q_{ie} - 2\rho_i)$$ (A9)

with respect to x_{ije}:

$$\frac{\partial(\beta F)}{\partial x_{ije}} = 0 .$$ (A10)

Equation (A10) gives the equilibrium state x_{ije} as

$$x_{ije} = (p_{ie} q_{ie})^{2/3} e^{\beta \epsilon_{ij} - \lambda_i - \lambda_j}$$

$$= (x_{i3e} x_{3je} / x_{33e}) e^{\beta \epsilon_{ij}} ,$$ (A11)

where $\beta \equiv (k_B T)^{-1}$. The chemical potential μ_i is derived from (A9) as

$$\partial(\beta F)/\partial \rho_i \equiv \alpha_i = \beta \mu_i = 3(\lambda_3 - \lambda_i)$$

$$= \tfrac{3}{2}\ln(x_{i3e} x_{3ie} / x_{33e}^2) - \ln(p_{ie} q_{ie} / p_{3e} q_{3e})$$ (A12)

for $i = 1$ and 2.

Next our task is to determine the Lagrange multiplier λ_i. Let us introduce η_i and $\tilde{\eta}_i$ as

$$\exp(3\eta_i) \equiv p_{ie}/q_{ie} ,$$

$$\tilde{\eta}_i \equiv (p_{ie} q_{ie})^{1/3} \exp(-\lambda_i) .$$ (A13)

Then the expressions (A11) and (A12) are, respectively, written in terms of these quantities and K_{ij} defined by Eq. (C4):

$$x_{ije} = \tilde{\eta}_i \tilde{\eta}_j K_{ij}^{-1} \exp(\eta_i - \eta_j) \quad \text{for } i,j = 1, 2, \text{ and } 3 ,$$ (A14)

and

$$\alpha_i = 3 \ln(\tilde{\eta}_i / \tilde{\eta}_3) - 3(\eta_i - \eta_3) - 2 \ln \left[\frac{\tilde{\eta}_1 \tilde{\eta}_i K_{1i}^{-1} \exp(\eta_1 - \eta_i) + \tilde{\eta}_2 \tilde{\eta}_i K_{2i}^{-1} \exp(\eta_2 - \eta_i) + \tilde{\eta}_3 \tilde{\eta}_i \exp(\eta_3 - \eta_i)}{\tilde{\eta}_1 \tilde{\eta}_3 \exp(\eta_1 - \eta_3) + \tilde{\eta}_2 \tilde{\eta}_3 \exp(\eta_2 - \eta_3) + \tilde{\eta}_3 \tilde{\eta}_3} \right]$$ (A15)

for $i = 1$ and 2. Determination of λ_i and hence (A14) and (A15), is equivalent to expressing them in terms of the known parameters K_{ij}'s and ρ_i's. We can obtain the equations for unknown quantities η_i and $\tilde{\eta}_i$, where i takes 1, 2, and 3, when Eq. (A14) is substituted in Eq. (A4) and further in Eq. (A6), we have the equations

$$\rho_1 = \tilde{\eta}_1^2 K_{11}^{-1} + \tilde{\eta}_1 \tilde{\eta}_2 K_{12}^{-1} \cosh(\eta_1 - \eta_2) + \tilde{\eta}_1 \tilde{\eta}_3 \cosh(\eta_1 - \eta_3) ,$$

$$\rho_2 = \tilde{\eta}_1 \tilde{\eta}_2 K_{12}^{-1} \cosh(\eta_1 - \eta_2) + \tilde{\eta}_2^2 K_{22}^{-1} + \tilde{\eta}_2 \tilde{\eta}_3 \cosh(\eta_2 - \eta_3) ,$$ (A16)

$$\rho_3 = \tilde{\eta}_1 \tilde{\eta}_3 \cosh(\eta_1 - \eta_3) + \tilde{\eta}_2 \tilde{\eta}_3 \cosh(\eta_2 - \eta_3) + \tilde{\eta}_3^2 .$$

When Eq. (A14) is substituted in Eq. (A4) and the first equation in (A13) is used, we obtain the following equations:

$$\exp(3\eta_1) = \frac{\tilde{\eta}_1^2 K_{11}^{-1} + \tilde{\eta}_1 \tilde{\eta}_2 K_{12}^{-1} \exp(\eta_1 - \eta_2) + \tilde{\eta}_1 \tilde{\eta}_3 \exp(\eta_1 - \eta_3)}{\tilde{\eta}_1^2 K_{11}^{-1} + \tilde{\eta}_1 \tilde{\eta}_2 K_{12}^{-1} \exp(\eta_2 - \eta_1) + \tilde{\eta}_1 \tilde{\eta}_3 \exp(\eta_3 - \eta_1)} ,$$

$$\exp(3\eta_2) = \frac{\tilde{\eta}_1 \tilde{\eta}_2 K_{12}^{-1} \exp(\eta_2 - \eta_1) + \tilde{\eta}_2^2 K_{22}^{-1} + \tilde{\eta}_2 \tilde{\eta}_3 \exp(\eta_2 - \eta_3)}{\tilde{\eta}_1 \tilde{\eta}_2 K_{12}^{-1} \exp(\eta_1 - \eta_2) + \tilde{\eta}_2^2 K_{22}^{-1} + \tilde{\eta}_2 \tilde{\eta}_3 \exp(\eta_3 - \eta_2)} ,$$ (A17)

$$\exp(3\eta_3) = \frac{\tilde{\eta}_1 \tilde{\eta}_3 \exp(\eta_3 - \eta_1) + \tilde{\eta}_2 \tilde{\eta}_3 \exp(\eta_3 - \eta_2) + \tilde{\eta}_3^2}{\tilde{\eta}_1 \tilde{\eta}_3 \exp(\eta_1 - \eta_3) + \tilde{\eta}_2 \tilde{\eta}_3 \exp(\eta_2 - \eta_3) + \tilde{\eta}_3^2} .$$

Solving these simultaneous equations for η's and $\tilde{\eta}$'s for given values of ρ's and K's (i.e., ϵ's and T) we can, in principle, express x_{ije} and α_i in terms of these values and hence we can evaluate the kinetic coefficients derived in the text. For the disordered phase, $p_{ie}/q_{ie} = 1$ holds and hence from the first equation in (A13), $\eta_i = 0$ holds. Then Eqs. (A14) and (A15) are reduced to the function of $\tilde{\eta}$'s and Eqs. (A16) and (A17) to the three equations for $\tilde{\eta}_i$ ($i = 1$, 2, and 3).

APPENDIX B: RELATIONS BETWEEN THE PAIR-STATE FRACTIONALS AND THEIR CONJUGATE PATH FRACTIONALS

The state fractionals of bonds (x's, y's, and z's) and their conjugate path fractionals (X's, Y's, and Z's) are related as follows

$$x_{ij}^{(v)}(t) = \sum_{L,R} X_{ij,3j}^{(v)} + \sum_{L,R} X_{ij,i3}^{(v)} + X_{ij,ij}^{(v)} ,$$

$$x_{i3}^{(v)}(t) = X_{i3,3i}^{(v)} + \sum_{R,L,j} X_{i3,ij}^{(v)} + X_{i3,i3}^{(v)} , \qquad \text{(B1a)}$$

$$x_{3i}^{(v)}(t) = X_{3i,i3}^{(v)} + \sum_{R,L,j} X_{3i,ji}^{(v)} + X_{3i,3i}^{(v)} ,$$

$$x_{ij}^{(v)}(t+\Delta t) = \sum_{R,L} X_{i3,ij}^{(v)} + \sum_{R,L} X_{3j,ij}^{(v)} + X_{ij,ij}^{(v)} ,$$

$$x_{i3}^{(v)}(t+\Delta t) = X_{3i,i3}^{(v)} + \sum_{R,L,j} X_{ij,i3}^{(v)} + X_{i3,i3}^{(v)} , \qquad \text{(B1b)}$$

$$x_{3i}^{(v)}(t+\Delta t) = X_{i3,3i}^{(v)} + \sum_{R,L,j} X_{ji,3i}^{(v)} + X_{3i,3i}^{(v)} ,$$

$$y_{ij}^{(v)}(t) = \sum_{L,C} Y_{ij,3j}^{(n)} + \sum_{R,C} Y_{ij,i3}^{(n)} + Y_{ij,ij}^{(n)} ,$$

$$y_{i3}^{(n)}(t) = Y_{i3,3i}^{(n)} + \sum_{R,C,j} Y_{i3,ij}^{(n)} + Y_{i3,i3}^{(n)} , \qquad \text{(B2a)}$$

$$y_{3i}^{(n)}(t) = Y_{3i,i3}^{(n)} + \sum_{L,C,j} Y_{3i,ji}^{(n)} + Y_{3i,3i}^{(n)} ,$$

$$y_{ij}^{(n)}(t+\Delta t) = \sum_{L,C} Y_{3j,ij}^{(n)} + \sum_{R,C} Y_{i3,ij}^{(n)} + Y_{ij,ij}^{(n)} ,$$

$$y_{i3}^{(n)}(t+\Delta t) = Y_{3i,i3}^{(n)} + \sum_{R,C,j} Y_{ij,i3}^{(n)} + Y_{i3,i3}^{(n)} , \qquad \text{(B2b)}$$

$$y_{3i}^{(n)}(t+\Delta t) = Y_{i3,3i}^{(n)} + \sum_{L,C,j} Y_{ji,3i}^{(n)} + Y_{3i,3i}^{(n)} .$$

Similar expressions are obtained for the relations between z's and Z's by replacing y by z and Y by Z, and the subscripts (ij)'s by (ji)'s in Eqs. (B2). It is noted that in the above expressions i and j take 1 and 2, and the summation over L, R, and C means the sum over possible migration activities of a vacancy in a summand from the left, the right, and the center, respectively. These relations are used to obtain the condition for the steady state (see Secs. III B and IV B).

APPENDIX C: THE PATH VARIABLES AND THE MOST PROBABLE PATHS

The standard procedure of the PPM is to formulate the path probability function in terms of the path variables and then to maximize it with respect to the independent path variables keeping the state at t fixed.[1] This corresponds to the process of selecting the most probable values of state variables which make the free-energy minimum in the CVM.[18] It was shown in Ref. 1, that, when the pair approximation is employed, it is not necessary to go through the maximization procedure but the most probable path expression can be written down by inspection applying a superposition relation. This technique is explained in detail in Ref. 1, and we will present the results using this short-cut procedure.

When ϑ_i is the vibrational contribution to the jump fre-

quency for an ith species ($i=1$ and 2) and U_i is the activation energy for a jump of an ith species into a nearest-neighboring vacant site, the probability of a unit jump is given by

$$\vartheta_i e^{-\beta U_i} , \qquad \text{(C1a)}$$

where $\beta = (k_B T)^{-1}$ is the reciprocal temperature. This jump frequency is referred to the spatial jumping condition where the jumping ion is completely surrounded by the vacant sites. When the system is subject to the constant electric field $\vec{E}$ pointing to the right (see Fig. 1), the activation energy for the jumping ion i with charge $Z_i e$ along a y and a z bond is changed by $\pm Z_i e E a / 2$ depending on the sites where the ith ion is located. Then the probability of a unit jump is expressed by

$$\vartheta_i e^{-\beta(U_i \pm Z_i e E a / 2)} \qquad \text{(C1b)}$$

for $i=1$ and 2. The effect of surrounding [which is not taken into account in either (C1a) or (C1b)] is assumed to be entirely due to the interaction with nearest-neighboring ions. Introducing the nearest-neighboring ions's bonding energy ϵ_{ij} and applying the superposition relation, we easily write down the expressions for the most probable path of individual path variables defined for the jump of the ith species:

$$X_{\alpha i}^{(v)} = \vartheta_i e^{-\beta U_i} \Delta t \, x_{i3}^{(v)} \Lambda_{y,\alpha i}^{(n)} \Lambda_{z,\alpha i}^{(n-1)} / (p_i^{(v)})^2 ,$$

$$X_{\beta i}^{(v)} = \vartheta_i e^{-\beta U_i} \Delta t \, x_{3i}^{(v)} \Lambda_{y,\beta i}^{(n-1)} \Lambda_{z,\beta i}^{(n)} / (q_i^{(v)})^2 ,$$

$$Y_{\alpha i}^{(n)} = \vartheta_i e^{-\beta(U_i - Z_i e E a / 2)} \Delta t \, y_{i3}^{(n)} \Lambda_{z,\alpha i}^{(n-1)} \Lambda_{x,\alpha i}^{(v)} / (p_i^{(v)})^2 ,$$

$$\text{(C2)}$$

$$Y_{\beta i}^{(n)} = \vartheta_i e^{-\beta(U_i + Z_i e E a / 2)} \Delta t \, y_{3i}^{(n)} \Lambda_{z,\beta i}^{(n+1)} \Lambda_{x,\beta i}^{(v+1)} / (q_i^{(v+1)})^2 ,$$

$$Z_{\alpha i}^{(n)} = \vartheta_i e^{-\beta(U_i + Z_i e E a / 2)} \Delta t \, z_{i3}^{(n)} \Lambda_{x,\alpha i}^{(v+1)} \Lambda_{y,\alpha i}^{(n+1)} / (p_i^{(v+1)})^2 ,$$

$$Z_{\beta i}^{(n)} = \vartheta_i e^{-\beta(U_i - Z_i e E a / 2)} \Delta t \, z_{3i}^{(n)} \Lambda_{x,\beta i}^{(v)} \Lambda_{y,\beta i}^{(n-1)} / (q_i^{(v)})^2 ,$$

for $i=1$ and 2, where Λ's are defined by

$$\Lambda_{x,\alpha i}^{(v)} \equiv \sum_{j=1}^{3} K_{ij} x_{ij}^{(v)}$$

$$\text{(C3)}$$

$$\Lambda_{x,\beta i}^{(v)} \equiv \sum_{j=1}^{3} K_{ji} x_{ji}^{(v)} .$$

Similar expressions are obtained for Λ_y's and Λ_z's. Here i takes 1 and 2 and K_{ij} is defined by

$$K_{ij} \equiv \exp(-\beta \epsilon_{ij}) \qquad \text{(C4)}$$

and is assumed to satisfy

$$K_{ij} = K_{ji} . \qquad \text{(C5)}$$

It is noted that $\epsilon_{i3} = \epsilon_{33} = 0$ for $i=1$ and 2 is assumed. As seen from Eqs. (C2) a jump of an ith ion across the vth reference plane, is proportional to Δt, to the jump frequency of the ith ion, $\vartheta_i \exp(-\beta U_i)$, to the vacancy availability factor, i.e., the probability of having a vacancy at its nearest-neighbor distance across the reference plane at time $t, x_{i3}^{(v)}$, and to the bond-breaking factor, i.e., the effect of breaking bonds with the neighboring ions at time t.

The similar interpretation is applied for the jumps Y's and Z's. It is noted that the activation energy for a jump of an ion i along y and z bonds is lowered by $Z_i eEa/2$ for the $Y_{\alpha i}$ and $Z_{\beta i}$ jumps, and is raised by the same amount for the $Y_{\beta i}$ and the $Z_{\alpha i}$ jumps, respectively. The second group of the most probable path variables we need in formulating kinetic coefficients are those in Eq. (3.7). These are listed in Table IV.

APPENDIX D: DERIVATION OF l_{ij}'s

Let us define the quantities

$$\Omega_i^\alpha \equiv X_{ie}^{(n)}/Q_i^\alpha \equiv X_{ie}^{(n)} q_{3e}^{(n)}/x_{i3e}^{(n)} \; ,$$
$$\Omega_i^\beta \equiv X_{ie}^{(n)}/Q_i^\beta \equiv X_{ie}^{(n)} p_{3e}^{(n)}/x_{3ie}^{(n)} \; ,$$

(D1)

and further introduce the quantities

$$\widehat{\psi}_i(\alpha) \equiv \sum_{k=1}^{2} \psi_{ik}^{(n)} Q_k^\beta \; ,$$

$$\widehat{\psi}_i(\beta) \equiv \sum_{k=1}^{2} Q_k^\alpha \psi_{ki}^{(n)} \; .$$

(D2)

It is noted that q_{3e} and p_{3e} are related to the equilibrium distributions by Eq. (A4) and X_{ie} is given by Eq. (4.6b). The flux [Eq. (4.16)] can then be expressed in terms of Eq. (D2) as

$$\Psi_i^{(n)} = -A_i - \tfrac{1}{2}[\widehat{\psi}_i(\alpha) - \widehat{\psi}_i(\beta)] \; ,$$

(D3)

where A_i is defined by Eq. (4.22b) and i takes 1 and 2.

Substitution of $\Psi_i^{(n)}$ given by Eq. (D3) into Eq. (4.21) and use of Eqs. (D1) and (D2) lead to

$$\psi_{ij}^{(n)} = \frac{\Omega_i^\alpha \widehat{\psi}_i(\alpha) + \Omega_i^\alpha \widehat{\psi}_i(\beta) + \Omega_j^\beta \widehat{\psi}_j(\alpha) + \Omega_j^\beta \widehat{\psi}_j(\beta)}{2(\Omega_i^\alpha + \Omega_j^\beta)}$$
$$- \frac{A_i \Omega_i^\alpha - A_j \Omega_j^\beta}{\Omega_i^\alpha + \Omega_j^\beta} \; .$$

(D4)

Substituting Eq. (D4) into Eqs. (D2), we obtain the four simultaneous equations for $\widehat{\psi}_1(\alpha)$, $\widehat{\psi}_2(\alpha)$, $\widehat{\psi}_1(\beta)$, and $\widehat{\psi}_2(\beta)$. Solving these equations for $\widehat{\psi}_i(\alpha)$'s and $\widehat{\psi}_i(\beta)$'s and substituting these results into Eq. (D3), we obtain the flux expression in terms of the known quantities Ω_i^α's, Ω_i^β's, Q_i^α's, and Q_i^β's which are the function of the equilibrium distributions obtained in Appendix A and the given physical parameters ϑ_i and U_i ($i = 1$ and 2). After rearranging the flux expressions, we can write the fluxes in the form

$$\Psi_1^{(n)} = -l_{11}A_1 - l_{12}A_2 \; ,$$
$$\Psi_2^{(n)} = -l_{21}A_1 - l_{22}A_2 \; ,$$

(D5)

and hence we can obtain the explicit form of l_{ij}'s in terms of the known quantities by identifying the resultant expressions for the fluxes to Eqs. (D5). Explicit expressions of l_{ij}'s are given by the author (A.S.) upon request.

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