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Tracer Diffusion in an Ordered Alloy:  
Application of the Path Probability and Monte Carlo Methods

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## **Tracer Diffusion in an Ordered Alloy:**

### **Application of the Path Probability and Monte Carlo Methods**

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#### **1. Introduction**

Tracer diffusion technique has been extensively utilized to investigate diffusion phenomena and has contributed a great deal to the understanding of the phenomena. However, except for self diffusion and impurity diffusion, the meaning of tracer diffusion is not yet satisfactorily understood. Here we try to extend the understanding to concentrated alloys. The problem of tracer diffusion in concentrated alloys was recently reviewed in detail by Bakker.<sup>1</sup> Therefore, our major interest here is directed towards understanding physical factors which control diffusion through the comparison of results obtained by the Path Probability method (PPM) and those by the Monte Carlo simulation method (MCSM). A brief explanation of the background of the PPM as applied to transport problems is given in Ref. 2. The MCSM as applied to diffusion kinetics was also reviewed by one of the authors.<sup>3,4,5</sup>

Both the PPM<sup>6</sup> and the MCSM are basically in the same category of statistical mechanical approaches applicable to "random processes." In these methods, the change of state is evaluated based on appropriately defined probability. Therefore, the treatments are also basically the same as the "Master Equation Method."

The advantage of the Path Probability method in dealing with phenomena which occur in crystalline systems has been well established. The method uses a consistent and well-established (in equilibrium statistical mechanics) method of approximation. As applied to transport problems, the PPM can derive a set of linear equations corresponding to the Onsager equation for diffusion analytically from microscopic variables so that relations among measurable quantities, the meaning of cross terms, etc. can be clearly understood from an atomistic point of view.<sup>2</sup> This makes the method quite useful in understanding the overall situation of complicated phenomena of multicomponent diffusion. However, the approximations which are inevitably introduced to make the analytical treatment tractable, although their meaning may be well-established in equilibrium statistical mechanics, sometimes introduce unwarranted consequences the origin of which is often hard to trace. On the other hand, the MCSM which can be carried out in a parallel fashion to the PPM provides, with care, the numerically exact results. Thus a side-by-side comparison can give insight into the effect of approximations in the PPM. Therefore, with these two methods combined, it is expected to be able to obtain a far clearer picture of the mechanism of diffusion phenomena.

In the following, we first examine the concept of the correlation factor of diffusion in concentrated alloys in Section 2. In Section 3, a brief account of the characteristics of the ordered binary alloys treated by the pair approximation of the Cluster Variation method<sup>7,8</sup> (CVM; the equilibrium counterpart of the PPM) which are the basis of the treatment of diffusion in ordered alloys by the PPM is given.<sup>2</sup> In section 4, concepts of jump frequencies and local activation energy which are the basis of dealing with

diffusion in concentrated alloys are explained. Actual derivations of results by the PPM and by the MCSM are given in enough detail in Sections 5 and 6. Comparisons of these results are discussed in Section 7.

## 2. Concept of the Correlation Factor in Concentrated Alloys

In tracer diffusion study, the concept of the correlation factor is often used. It should be reminded that the concept was originated from the study of self diffusion. As such, if the concept is used in a more general case of diffusion, it is necessary to extend the concept accordingly. Because the extension to individual cases has not necessarily been unique, there exist some confusions with respect to its usage.

The correlation factor was originally defined empirically as the ratio of the tracer diffusion coefficient (using an isotope of the same species as tracer)  $D_T$  and the self diffusion coefficient,  $D_s$ , as<sup>9-12</sup>

$$D_T/D_s = f. \quad (1)$$

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The self diffusion coefficient  $D_s$  is defined as the hypothetical diffusion coefficient of the total assembly of particles of the same kind if the appropriate driving force were given. Therefore, this is equivalent to the charge diffusion coefficient,  $D_c$ , of the assembly of charged particles which is connected to the ionic conductivity  $\sigma$  by the Nernst-Einstein relation

$$\sigma = \frac{ne^2}{kT} D_c, \quad (2)$$

where  $n$  is the total number of charged particles per unit volume,  $e$  is the charge, and  $T$  is the temperature.

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Therefore, if the value of  $f$  is known, the self diffusion coefficient  $D_s$ , which cannot be evaluated directly from diffusion experiments, can be estimated through the measurement of  $D_T$ . In nearly perfect crystals, the number of defects through which atoms move is negligibly small, and the motion of the total assembly of atoms is represented by the random walk. Hence,  $D_s$  is supposed to be equal to the diffusion coefficient of the system  $D_R$  whose constituents are making the random walk. Therefore, Eq. (1) can be replaced by

$$D_T/D_R = f \quad (3)$$

The value of  $D_R$  can be calculated uniquely if the jump frequency  $w$  of the constituent particle is given. For three dimensional systems,  $D_R$  is given by

$$D_R = \frac{1}{6} l^2 n w, \quad (4)$$

where  $l$  is the jump distance and  $n$  is the density of moving particles (in the case of the vacancy mechanism,  $n$  represents the density of vacancies). In nearly perfect crystals, the correlation factor for self diffusion  $f$  is known to be uniquely related to the mechanism of diffusion and the geometry of the crystal lattice as long as the concentration of tracer atoms is negligibly small. Because of this relation, the measurement of  $f$  is used to investigate the mechanism of diffusion such as the vacancy mechanism, the interstitial mechanism and the interstitial mechanism.

In general diffusion problems, the situation is not as simple. There can be a large number of vacant available sites,<sup>13,14</sup> a coexistence of different types of available sites such as normal sites and interstitial sites,<sup>13,14</sup> or the environment of moving atoms is different from place to place such as in concentrated alloys. In such cases, the classification of diffusion mechanisms as mentioned above is almost meaningless. The self diffusion coefficient can also deviate from  $D_R$ . The definition of by Eq. (1) which is

exemplified by the measurement of such as the Haven ratio  $H_R = D_T/D_c$ , and that by Eq. (3) can be very much different.<sup>13,15</sup> Therefore, for generality, we prefer to use Eq. (3) as the definition of  $f$ . Based on this definition,  $f$  indicates the degree of deviation of the motion of tracer atoms from the random walk (for the random walk,  $f = 1$  by definition). Thus defined  $f$  is generally less than unity. However, in some cases,  $f$  can be larger than unity. In such a case, the motion of the particle can be called ~~the~~ channelling.

We deal with concentrated binary alloys composed of A and B atoms here. An isotope of B, or  $B^*$  is added as tracer. Then, according to Eq. (3), the correlation factor  $f_{B^*}$  is defined to be<sup>2,16-20</sup>

$$D_{B^*}/D_{B^*R} = f_{B^*} \quad . \quad (5)$$

Here,  $D_{B^*}$  is the diffusion coefficient for  $B^*$  whereas  $D_{B^*R}$  is the hypothetical (or calculated) diffusion coefficient of  $B^*$  which is making the random walk. In the case of ordinary binary alloys, we can generally assume that the number of vacancies is negligibly small and the jump distance  $l$  can be taken as constant. However, the jump frequency of tracer atoms can depend on the environment and the problem can arise with respect to how  $D_{B^*R}$  can be defined. In the linear range of diffusion, in which the Onsager equation for diffusion is valid, the flow is evaluated based on the equilibrium distribution of atoms, and, hence, the average of the jump frequencies based on the equilibrium distribution can be taken as the reference jump frequency. Theoretically, because the  $B^*$  atom has the same statistical characteristics as the rest of B atoms, the jump frequency automatically drops out when the ratio (Eq. (5)), is taken, and  $f_{B^*}$  is uniquely determined as shown later.

In the case of alloys, since the environment of moving atoms is different from place to place, the motion of B atoms inevitably deviates from the random walk. Therefore, the diffusion coefficient  $D_B$  of the total assembly of B atoms is related to  $D_{BR}$  ( $= D_{B^*R}$ )

by

$$D_B = D_{BR}f_I. \quad (6a)$$

The factor  $f_I$  is often called the physical correlation factor,<sup>13,21</sup> while the correlation factor  $f_G$  defined by

$$D_{B^*}/D_B = f_{B^*}/f_I = f_G \quad (6b)$$

is called the geometrical correlation factor and corresponds to the correlation factor defined in the self diffusion.

### 3. Ordered Binary Alloys

In Ref. 2, a brief account of the calculation of the correlation factor  $f_{B^*}$  in disordered binary alloys by the pair approximation of the PPM is given. The extension of this treatment to ordered alloys has been given in several publications by us,<sup>16-18</sup> and it would be relatively easy to follow them if one notes the following characters of ordered alloys as treated by the pair approximation of the CVM.<sup>6,7,14</sup>

In order to avoid unnecessary mathematical complications, we limit ourselves to the treatment of binary alloys of the bcc structure (or more generally structures with two sublattices). Except for differences derived from the difference in ordered structures, the results are qualitatively the same for alloys with the fcc structure and the differences can be reasonably well estimated.

We assume that interactions among atoms are limited to nearest neighbor pairs. In the ordered structure (the CsCl structure), the crystal lattice is divided into two sublattices, <sup>where</sup> ~~and the~~ one is predominantly occupied by A and the other by B. Further, a jump of an atom into its nearest neighboring vacant site is always from a site of one sublattice to that of the other.

In a static treatment of order-disorder transformations, only a combination  $\epsilon$  of pair interaction potentials among atoms

$$4\epsilon = 2\epsilon_{AB} - (\epsilon_{AA} + \epsilon_{BB}) \quad (7)$$

appears as the necessary parameter, where  $-\epsilon_{ij}$  is the pair interaction potential (attractive) between  $i$ - $j$  neighbors. For systems with ordered distribution of atoms, the relation  $\epsilon > 0$  should be satisfied. Because of this reason, in static treatments, it is often assumed that

$$\epsilon_{AA} = \epsilon_{BB} = 0 \quad (8)$$

On the other hand, in the treatments of diffusion (or of kinetics in general), in which jumps of atoms into nearest neighboring vacancies by breaking bonds with its nearest neighbors are to be considered, individual values of  $\epsilon_{AA}$  and  $\epsilon_{BB}$  are to be taken into account.<sup>16,20</sup> In other words, an extra parameter  $U$  defined as

$$4\epsilon U = \epsilon_{AA} - \epsilon_{BB} \quad (9)$$

is to be used. Further, in our treatment of diffusion by the vacancy mechanism, vacancies are taken into account explicitly. Here, interaction potentials involved with vacancies  $v$  are, however, generally assumed to be zero;

$$\epsilon_{Av} = \epsilon_{Bv} = \epsilon_{vv} = 0. \quad (10)$$

This means that interactions with vacancies are indirectly taken into account through  $U$ , because vacancies tend to distribute in the A-rich or in the B-rich neighborhood depending on whether  $U$  is positive or negative and the segregation of vacancies on different sublattices occurs in the ordered state. The energy parameter  $\epsilon_{ij}$  is always defined as positive.

The energy parameter  $\epsilon$  gives the measure of the critical point  $T_c$  of order-disorder. In the pair approximation of the CVM,  $T_c$  at the stoichiometric composition



( $x_A = x_B = \frac{1}{2}$ ) with a negligible amount of vacancies is given by<sup>20</sup>

$$2\epsilon/kT_c = \ln \frac{\omega}{\omega-1} \quad (11)$$

where  $2\omega$  specifies the coordination number of the crystal lattice ( $2\omega = 8$  for the bcc structure and  $2\omega = 3$  for the two dimensional honeycomb (2Dhc) lattice). Eq. (11) also serves to normalize the value of  $\epsilon$  with respect to  $kT_c$ . If the composition deviates from the stoichiometric composition, the critical point is lower and the phase diagram thus predicted which indicates the existence range of the ordered state is shown in Fig. 1. The phase boundary at  $T = 0$ , on the other hand, is given by the values of  $x_B$  as

$$x_B = 1/2 \pm \alpha \quad (12a)$$

where

$$\alpha = (\omega-1)/2\omega \quad (12b)$$

In the following treatment, the temperature is given by the reduced scale  $T/T_c$ . Therefore, if  $T/T_c < 1$ , a certain composition range of the alloy system is in the ordered state.

The pair approximation of the CVM determines the equilibrium values of  $y_{ij}$ , which indicates the probability of having a constituent  $i$  on a lattice site and a constituent  $j$  on a nearest neighbor lattice site, as a function of  $x_i$  and  $T$ . The long-range order  $S$  and the (Bethe) short-range order  $\sigma$  can then be derived from  $y_{ij}$  for the case of binary alloys as

$$S = y_{AB}^o - y_{BA}^o \quad (13)$$

where the superscript  $o$  indicates the values of  $y_{ij}$  in the ordered state, whereas in the subscript, such as  $AB$ , the left symbol indicates the species of atom on the one (A) sublattice and the right hand symbol indicates that on the other (B) sublattice. In specifying the short-range order, because the concept is used mostly in the disordered state, no

distinction between the sublattice is made. Then the relation such as

$$y_{AB} = \frac{y_{AB}^{\circ} + y_{BA}^{\circ}}{2} \quad (14)$$

holds, and  $\sigma$  is defined as

$$\sigma = \frac{y_{AB} - (y_{AB})_{\text{rand}}}{(y_{AB})_{\text{max}} - (y_{AB})_{\text{rand}}} \quad (15)$$

Here,  $(y_{AB})_{\text{max}}$  means the maximum possible value of  $y_{AB}$  and  $(y_{AB})_{\text{rand}}$  means the value in the completely random state for the given composition. In Fig. 2, the temperature dependence of  $y_{ij}$  for  $x_A = x_B = 1/2$  as well as the composition dependence of  $y_{ij}$  at temperature  $T/T_c = 0.5$  are shown. In Fig. 3, on the other hand, the temperature dependence of  $S$  and  $\sigma$  also for the composition  $x_A = x_B = 1/2$  is given. The value  $\sigma_d$  below  $T_c$  is calculated under the restriction of  $S = 0$ .

For the convenience of treatment,  $y_{ij}$  is also expressed in terms of two site variables (which indicate the value of a single site independent of the surroundings)  $q_i$  and  $q_j$  as

$$y_{ij} = q_i q_j K_{ij}^{-1} \quad (16)$$

where

$$K_{ij} = \exp(-\beta \epsilon_{ij}) \quad (\beta = 1/kT) \quad (17)$$

and  $Q_i$  and  $Q_j$ , as normalized value of  $q_i$  and  $q_j$  as

$$Q_i \equiv q_i \left[ \sum_m q_m \right]^{-1}. \quad (18)$$

In the completely random state,  $q_i$  tends to  $x_i$ . These variables indicate the probability of finding a species of atoms on the neighboring site of a lattice site being considered irrespective of the species of atoms on it when there is a finite degree of short-range order, but no succinct physical explanation can be given. In Fig. 4, the composition dependence of  $Q_A$  and  $Q_B$  at  $T/T_c = 0.5$  is given.

Diffusion is not a phenomenon in the equilibrium state. However, as is known in the Onsager equations for diffusion, linear deviations from the equilibrium state due to the existence of driving forces are treated as flows and hence the equilibrium distribution of atoms has to be known. This information is given by the (pair approximation of) CVM. Some useful variables utilized in the pair approximation of the CVM are summarized for reference in Table 1.

#### 4. Jump Frequencies of Atoms in Concentrated Alloys

In order to describe the phenomenon of self diffusion atomistically, the so-called jump frequency  $w$ 's defined as

$$w = \theta e^{-u/kT} \quad (18)$$

Here,  $\theta$  indicates the attempt frequency and  $u$  indicates the activation energy of motion. In a general case of diffusion such as that in alloys, however, it is necessary to introduce individual jump frequencies for A and B atoms which also depend on the environment of moving atoms. The activation energy is determined collectively by the total assembly of particles, and theoretical calculations of such jump frequencies and the activation energies are extremely complicated. However, in order to extend the treatment of self diffusion in terms of  $w$  in Eq. (18) to the case of alloys in the pair approximation of the PPM, it is convenient to split  $u$  to include the local contribution explicitly and define  $w$  as composing of two terms (in the case of self diffusion) such as

$$\hat{w}_A = \theta_A e^{-u_A/kT} \cdot \left[ \exp(-\beta \epsilon_{AA}) \right]^{2\omega-1} \quad (19)$$

$$= \theta_A e^{-\{u_A + (2\omega-1)\epsilon_{AA}\}/kT}$$

$$\beta = 1/kT$$

In other words, as is shown in Fig. 5, it is equivalent to take the activation energy as composed of a constant value plus a term contributed by interactions with nearest neighboring atoms. Because of this reason, the second term,  $[\exp(-\beta\epsilon_{AA})]^{2\omega-1}$ , is called the bond breaking factor. Then, in the case of (disordered) binary alloys, we can likewise define two jump frequencies

$$\hat{w}_i = \theta_i e^{-u_i/kT} \left[ \frac{\sum y_{ji} K_{ji}}{x_i} \right]^{2\omega-1} \quad (i, j = A, \text{ or } B) \quad (20)$$

$$K_{ji} = \exp(-\beta\epsilon_{ij})$$

Here,  $x_i$  is the probability of finding an atom of the  $i$ -th species on one lattice site and  $y_{ji} = y_{ij}$  is the probability of finding an  $i$ - $j$  pair on nearest neighboring sites as defined in the CVM. In ordered alloys, it is necessary to extend the definitions to include two sublattices.

The activation energy determined by experiment is thus represented by a certain average value of that given by Eq. (20) depending on the distribution of atoms. In the ordered case, the activation energy of diffusion generally increases. This can be explained as follows. Suppose we are dealing with the tracer diffusion of  $B^*$ . When the  $B^*$  atom is on a site of the B-sublattice, the surrounding atoms are predominantly A atoms. Therefore, the bond breaking factor increases due to the attractive interaction  $\epsilon_{AB}$ . In addition, under such condition, even if the  $B^*$  atom could jump out from the B-site by exchanging with a vacancy on the A-site, this  $B^*$  atom tends to go back to the original site, being pushed back by the surrounding B atoms on the B-site (resulting in a small correlation factor). These two factors contribute to a low diffusion coefficient in the ordered state as will be seen later.

## 5. Tracer Diffusion Coefficient and the Correlation Factor in Binary Alloys by the Path Probability Method

### i. Disordered Binary Alloys

Theoretical treatments of tracer diffusion in ordered binary alloys can be easily extended from those in disordered binary alloys. Therefore, succinct features of the treatment which are the basis for the extension to ordered systems are repeated here although these are explained in somewhat detail in Ref. 2 or in Ref. 21. The motion of atoms is assumed to occur via the vacancy mechanism and the number of vacancies is assumed to be negligible. In deriving the Onsager equations for diffusion by the PPM, a stationary state is treated. In other words, flows of atoms under the driving forces in one direction  $\dot{\alpha}_A$ ,  $\dot{\alpha}_B$  and  $\dot{\alpha}_B^*$  ( $\alpha_i = \mu_i/kT$  indicates the generalized chemical potential  $\mu_i$  divided by temperature) are treated which do not change the distribution of atoms with time. In deriving the Onsager equation by the PPM, the reference system is a laboratory frame fixed at a lattice plane. In other words, a reference plane fixed at a spatially fixed crystal lattice plane (actually a plane at a half distance between the two crystal lattice planes is treated) perpendicular to the direction of the driving forces is taken and flows across this plane is calculated based on the equilibrium distribution of atoms which is supposed to exist in the reference plane.

The flow of atoms of the  $i$ th species,  $\Phi_i$  across the reference plane in the direction of the driving force (taken as the  $+x$  direction) is defined as

$$\Phi_i = Y_{i+} - Y_{i-} \quad (21)$$

Here,  $Y_{i\pm}$  are path variables used in the PPM, which represent the probability of atom of the  $i$ th species jumping across the reference plane in the  $+x$  and in the  $-x$  direction, respectively, during a short time interval  $\Delta t$  at a time instant  $t$ . By calculating  $Y_{i+}$  and  $Y_{i-}$  explicitly under the driving force by the PPM and expanding the results

linearly with respect to the driving forces, we obtain an equation [Eq. (A15), Ref. 2]

$$\Psi_i = -\dot{\alpha}_i + \sum_j Q_j \psi_{ji} \quad (22)$$

Here,  $\Psi_i$  is the normalized flow defined as

$$\Psi_i = \Phi_i / Y_i \quad (23)$$

Here,  $Y_i$  is the probability of an atom of the  $i$ th species which jumps across the reference plane either in the  $+x$  or in the  $-x$  direction under the equilibrium condition (in the absence of the driving force,  $Y_i = Y_{i+} = Y_{i-}$ ). The term  $-\dot{\alpha}_i$  represents the driving force acting on the  $i$ th species expressed as the generalized chemical potential ( $\mu$ ) gradient ( $\dot{\alpha}_i = \beta \dot{\mu}_i$ ). The quantity  $Q_j$  indicates the probability of finding an atom of the  $j$ th species at a nearest neighboring site of a specific site (a site occupied by an atom of the  $i$ th species in consideration) as explained earlier. On the other hand,  $\psi_{ji}$  indicates the deviation of the distribution with respect to  $j$ - $i$  pairs from equilibrium in the direction of the driving force and is proportional to  $\dot{\alpha}_j$ , and eventually concerns the exchange of  $i$ - $j$  pairs. In the absence of the second term, Eq. (22) indicates the random walk of the particle of the  $i$ th species by the driving force  $\dot{\alpha}_i$ , and, hence, the second term indicates the effect of flows of other species on the flow of the  $i$ th species which deviate the motion of the  $i$ th species from the random walk. As indicated by the existence of  $Q_j$ , the second term is highly dependent on the nature of the diffusion path. The analysis of the nature of the second term is thus one of <sup>the</sup> central problems of dealing with transport phenomena by the PPM.

Because Eq. (22) represents a linear equation in terms of the driving forces,  $\dot{\alpha}_i$ 's, this expression eventually leads to the Onsager equations for diffusion. The correlation factor for the species  $i$ ,  $f_i$  (or the deviation of the motion of particles of the  $i$ th species from the random walk), is then calculated if one can transform Eq. (22) into the form

$$\Psi_i = -f_i \dot{\alpha}_i \quad (24)$$

The derivation can generally be made in the limit when the concentration of the  $i$ th species is negligible. However, in dealing with tracer diffusion in binary alloys, the derivation of Eq. (24) for the species  $B^*$  was achieved at any concentration of  $B^*$  by the assumption of a specific steady state condition. First, we assume that the concentration of the species A is kept constant in the specimen. Because the macroscopic flow of A does not exist and the distribution of A (with respect to  $B+B^*$ ) is the same as in the equilibrium state, the condition

$$\dot{\alpha}_A = 0 \quad (25)$$

holds. Secondly, the existence of the Gibbs-Duhem relation between B and  $B^*$  is assumed which leads to

$$x_B \dot{\alpha}_B = -x_{B^*} \dot{\alpha}_{B^*} \quad (26)$$

The application of the boundary conditions, Eqs. (25) and (26), to Eq. (22) then leads to

$$\Psi_{B^*} = -f_{B^*} \dot{\alpha}_{B^*} \quad (27)$$

The boundary condition, Eq. (26), gives the value of  $f_{B^*}$  which is independent of the concentration of  $B^*$  and constitutes a very strong restriction for the flow of B and  $B^*$  (see Ref. 2). Although the validity of this relation for high concentrations of  $B^*$  is debatable,<sup>2</sup> in the limit of negligible concentration of  $B^*$ , the relation is applicable, and the boundary condition, Eq. (26), will be retained for the convenience of handling of equations beyond Eq. (22).

The correlation factor  $f_{B^*}$  in Eq. (27) has the following form

$$f_{B^*} = \frac{(2\omega-1)Z_{B^*}}{2(1-Z_{B^*}) + (2\omega-1)Z_{B^*}} \quad (28)$$

where

$$Z_{B^*} = \frac{Q_A \hat{w}_A}{\hat{w}_A + \hat{w}_{B^*}} + \frac{Q_B \hat{w}_B}{\hat{w}_B + \hat{w}_{B^*}} + \frac{Q_{B^*} \hat{w}_{B^*}}{\hat{w}_{B^*} + \hat{w}_{B^*}} \quad (\hat{w}_B = \hat{w}_{B^*}) \quad (29)$$

The expression for  $Z_{B^*}$  follows from a more general expression

$$Z_i = \sum_j Q_j \frac{Y_j/Q_j}{Y_j/Q_j + Y_i/Q_i} \quad (30)$$

in terms of  $Y_i$ 's because of the relation

$$\hat{w}_i = \frac{Y_i}{q_i q_v \Delta t} \quad (31)$$

which connects the path variable  $Y_i$  and  $\hat{w}_i$ . The value  $Y_i$  or  $\hat{w}_i$  thus gives the average value of the jump frequency of the  $i$ th species.

The meaning of  $Z_{B^*}$  in Eq. (29) can be given as follows. In Fig. 6, a vacancy, its surrounding atoms and a (tagged)  $B^*$  atom are shown. This should be interpreted to be a time instant at which the tagged  $B^*$  atom has just jumped out from the central site, replacing a vacancy at its neighboring site. Therefore, the probability of jumping back of the tagged atom into the vacancy it has just replaced is being calculated here in competition with other atoms on the surrounding sites. The quantity  $Q_j$  specifies the species of atoms on the surrounding sites as defined earlier. As is clear from Eq. (29), the quantity  $1-Z_{B^*}$  represents the jump back probability of the tagged atom (which corresponds to the return probability  $P_r$ ) while  $Z_{B^*}$  is the probability that any other atom (specified as  $j$ ), which forms the pair with the tagged atom  $B^*$  across the vacancy, jumps into the vacancy and represents the escape probability of the vacancy  $P_e = (2\omega-1)Z_{B^*}$  or the probability of the forward jump of  $B^*$ . In the PPM formalism, however, the jumping back of  $B^*$  atom is treated as if the  $B^*$  atom jumps from the central site into a vacancy at a neighboring site as is seen from Eq. (29). The quantity  $f_{B^*}$  in Eq. (28) thus indicates the efficiency of the forward motion of the  $B^*$  atom as defined



in the random walk theory.<sup>10-12</sup>

That the calculation of  $f_{B^*}$  is reduced to the calculation of  $Z_{B^*}$ , Eqs. (27), (28) and (29), in a way represented by Fig. 6 is extremely useful in extending the treatment to

more complicated cases. The actual expressions for  $\hat{w}_i$  in Eq. (29) are given by

$$\begin{aligned} \hat{w}_A &= \theta_A e^{-u_A/kT} \left[ \frac{y_{AA} e^{-\beta\epsilon_{AA}} + y_{AB} e^{-\beta\epsilon_{AB}}}{x_A} \right]^{2\omega-1} \\ \hat{w}_B &= \hat{w}_{B^*} = \theta_B e^{-u_B/kT} \left[ \frac{y_{BA} e^{-\beta\epsilon_{BA}} + y_{BB} e^{-\beta\epsilon_{BB}}}{x_B} \right]^{2\omega-1} \end{aligned} \quad (32)$$

The expression such as  $Y_{AA}/x_A$  indicates the probability of finding an A atom at the neighboring site of an A atom. The expression for  $\hat{w}_{B^*}$  which appears in the denominators in Eq. (29) is for the tagged atom. It is to be noted at this point that the surroundings of the tagged atom are evaluated as if it jumped from the central site rather than from the surrounding site as shown in Fig. 6. In the disordered alloys such as above, because all sites are equivalent statistically, there is no distinction between the jump frequency from the central site and that from the surroundings. However, this distinction is important in dealing with ordered alloys which will be seen later.

Because, under the boundary condition, Eq. (26),  $f_{B^*}$  does not depend on the concentration of  $B^*$ ,  $Q_{B^*} = 0$  can be assumed or  $Q_B$  can be rewritten to indicate the sum of  $Q_B$  and  $Q_{B^*}$  to simplify the relation.

Eqs. (27) and (28) can be rewritten as

$$\Psi_{B^*} = \left[ 1 - \frac{2(1-Z_{B^*})}{2(1-Z_{B^*}) + (2\omega-1)Z_{B^*}} \right] \dot{\alpha}_{B^*} \quad (33)$$

The second term of the coefficient of  $\dot{\alpha}_{B^*}$  indicates the normalized return probability

$\pi = \frac{P_r}{P_r + P_e}$ ). By comparing this expression with Eq. (22), one obtains

$$\sum_j Q_j \psi_{ji} = \frac{2(1-Z_i)}{2(1-Z_i) + (2\omega-1)Z_i} \dot{\alpha}_i \quad (34)$$

under the boundary conditions of Eqs. (25) and (26). In the calculation of  $\sum_j Q_j \psi_{ji}$  by the PPM, this return probability is calculated from the comparison of the jump of the B\* atom from the central site and the jump of an atom whose species is specified by  $Q_j$ . Therefore, for the tagged atom to jump back, its surroundings are ~~yet~~<sup>still</sup> specified by  $Q_j$  in the calculation as mentioned earlier.

## ii. Ordered Binary Alloys

The extension of ~~the~~ tracer diffusion in disordered alloys to that in ordered alloys based on the treatment in the previous section is relatively easy. As pointed out in Section 3, in the ordered state, the bcc lattice is divided into two sublattices and the jump of atoms from a site in the one sublattice should always be into a site in the other sublattice. In this respect, the normalized flow  $\Psi_i$  can be divided into two contributions,  $\Psi_i^A$  and  $\Psi_i^B$ . It is easier to see this relation if one takes the reference plane which includes the A sites and the B sites in equal amount<sup>13,23</sup> such as the {110} plane rather than the {100} plane which includes either the A sites or the B sites alternately. In our earlier publication in which a {100} plane is taken as the reference plane, a concept of the transposed lattice is introduced to reach the above conclusion.<sup>18</sup> Here,  $\Psi_i^A$  indicates the flow of atoms of the  $i$ th species from the A sublattice (into the B sublattice) and  $\Psi_i^B$  is that from the B sublattice. Then the following relations follow:

$$\begin{aligned}
 \Psi_i &= \frac{1}{2}(\Psi_i^A + \Psi_i^B) \\
 \Psi_j^A &= -\dot{\alpha}_i^A + \sum_j Q_j^A \psi_{ji}^A \\
 \Psi_j^B &= -\dot{\alpha}_i^B + \sum_j Q_j^B \psi_{ji}^B \\
 \dot{\alpha}_i &= \frac{\dot{\alpha}_i^A + \dot{\alpha}_i^B}{2} = \dot{\alpha}_i^A = \dot{\alpha}_i^B = \dot{\alpha}_i
 \end{aligned} \tag{35}$$

Under the same boundary conditions, Eqs. (26) and (27), as before, we obtain similar expressions

$$\begin{aligned}
 \Psi_i^A / \dot{\alpha}_i^A &= -\frac{(2\omega-1)Z_{B^*}^A}{2(1-Z_{B^*}^A) + (2\omega-1)Z_{B^*}^A} \\
 \Psi_i^B / \dot{\alpha}_i^B &= -\frac{(2\omega-1)Z_{B^*}^B}{2(1-Z_{B^*}^B) + (2\omega-1)Z_{B^*}^B}
 \end{aligned} \tag{36}$$

$$\Psi_i / \dot{\alpha}_i = -\frac{(2\omega-1)Z_{B^*}}{2(1-Z_{B^*}) + (2\omega-1)Z_{B^*}} \tag{37}$$

and

$$\frac{1}{Z_{B^*}} = \frac{1}{2} \left( \frac{1}{Z_{B^*}^A} + \frac{1}{Z_{B^*}^B} \right). \tag{38}$$

The correlation factor  $f_{B^*}$  in the ordered state then follows from Eq. (28) using  $Z_{B^*}$  in Eq. (36). Here,  $Z_{B^*}^A$  means, in Fig. 7, the central site from which the tagged  $B^*$  atom has jumped out is the A site and  $Z_{B^*}^B$  is the corresponding quantity for the B site. On the other hand,  $Q_j^A$ , etc. in Eq. (35) indicate parameters related to the probability of finding an atom of the  $j$ th species at the nearest neighboring site of an A site (hence the site is in the B sublattice), etc. In order to avoid the confusion, therefore, the following rewriting is made:

$$Q_j^A = Q_j(B)$$

and (39)

$$Q_j^B = Q_j(A)$$

so that  $Q_j(A)$  and  $Q_j(B)$  indicates the probability of finding a  $j$  atom on the A and the B site, respectively at the surrounding of a vacancy (on the B and the A site, respectively). If so, based on Fig. 7,  $Z_B^A$ , etc. and  $\hat{w}_A(A)$ , etc. are obtained simply by inspection as

$$\begin{aligned} Z_B^A &= \frac{Q_A(B)\hat{w}_A(B)}{\hat{w}_A(B) + \hat{w}_{B^*}(A)} + \frac{Q_B(B)\hat{w}_B(B)}{\hat{w}_B(B) + \hat{w}_{B^*}(A)} + \frac{Q_{B^*}(B)\hat{w}_{B^*}(B)}{\hat{w}_{B^*}(B) + \hat{w}_{B^*}(A)} \\ Z_B^B &= \frac{Q_A(A)\hat{w}_A(A)}{\hat{w}_A(A) + \hat{w}_{B^*}(B)} + \frac{Q_B(A)\hat{w}_B(A)}{\hat{w}_B(A) + \hat{w}_{B^*}(B)} + \frac{Q_{B^*}(A)\hat{w}_{B^*}(A)}{\hat{w}_{B^*}(A) + \hat{w}_{B^*}(B)} \end{aligned} \quad (40)$$

where  $\hat{w}_A(B)$ , etc. indicate the jump frequency of an A atom from the B site, etc. and

$$\begin{aligned} \hat{w}_A(A) &= \theta_A e^{-u_A/kT} \left[ \frac{y_{AA} e^{-\beta\epsilon_{AA}} + y_{AB} e^{-\beta\epsilon_{AB}}}{x_A(A)} \right]^{2\omega-1} \\ \hat{w}_A(B) &= \theta_A e^{-u_A/kT} \left[ \frac{y_{AA} e^{-\beta\epsilon_{AA}} + y_{BA} e^{-\beta\epsilon_{AB}}}{x_A(B)} \right]^{2\omega-1} \\ \hat{w}_B(A) = \hat{w}_{B^*}(A) &= \theta_B e^{-u_B/kT} \left[ \frac{y_{BA} e^{-\beta\epsilon_{AB}} + y_{BB} e^{-\beta\epsilon_{BB}}}{x_B(A)} \right]^{2\omega-1} \\ \hat{w}_B(B) = \hat{w}_{B^*}(B) &= \theta_B e^{-u_B/kT} \left[ \frac{y_{BA} e^{-\beta\epsilon_{AB}} + y_{BB} e^{-\beta\epsilon_{BB}}}{x_B(B)} \right]^{2\omega-1} \end{aligned} \quad (41)$$

The existence of Eq. (38) means that, between the two processes, that having the

smaller  $Z_B$  is the rate determining process.

In terms of path variable  $Y_i$ , the expressions for  $Z_i^A$  and  $Z_i^B$  are

$$\begin{aligned} Z_i^A &= \sum_{j=1}^2 Q_j(B) \frac{Y_j/Q_j(B)}{Y_i/Q_i(A) + Y_j/Q_j(B)} \\ Z_i^B &= \sum_{j=1}^2 Q_j(A) \frac{Y_j/Q_j(A)}{Y_i/Q_i(B) + Y_j/Q_j(A)} \end{aligned} \quad (42)$$

Between  $Y_i$ 's and  $\hat{w}_i$ 's, the relation, Eq. (24), holds:

$$\begin{aligned} \hat{w}_i^A &= \frac{Y_i}{q_i(A)q_v(B)\Delta t} \\ \hat{w}_i^B &= \frac{Y_i}{q_i(B)q_v(A)\Delta t} \end{aligned} \quad (43)$$

$$\begin{aligned} Q_i(A) &= q_i(A) / \sum_m q_m(A) \\ Q_i(B) &= q_i(B) / \sum_m q_m(B) \end{aligned} \quad (44)$$

These quantities are derived from the definitions of pair variables  $y_{ij}$ 's in the ordered state. From the relations, Eqs. (43) and (44), the relation

$$\begin{aligned} \hat{w}_i^A &\propto \frac{Y_i}{Q_i(A)} \\ \hat{w}_i^B &\propto \frac{Y_i}{Q_i(B)} \end{aligned} \quad (45)$$

follows. The quantity  $Y_i$  is the probability of the jump of atoms of the species  $i$  across the reference plane (in one direction) in the equilibrium state and includes jumps from the A site and from the B site. Under the equilibrium condition, the number of jumps for the  $i$ th species from the A site to the B site and in the reverse direction is always balanced. Therefore, a relation  $Y_j^A = Y_j^B = Y_j$  holds.

---

In Fig. 8a, the composition dependence of the correlation factor  $f_B$  for a binary alloy in the bcc lattice and in Fig. 9a that in the 2Dhc lattice are shown as examples. The calculation is for  $U = 0$  for the sake of simplicity. The temperature is set at  $T/T_c = 0.5$ . Furthermore,  $\theta_A = \theta_B$  and  $u_A = u_B$  are assumed. Therefore, only the influence of the surroundings is calculated. A sharp decrease in the correlation factor in the ordered range is found. The upper curve in each figure in the ordered region shows the effect of the short-range order ( $\sigma_d$ ) only so that the effect of the existence of the long range order can be evaluated. The short-range order below  $T_c$  is calculated by artificially keeping the long range order zero as explained in section 3. The results agree qualitatively well with experiments. The decrease is mainly due to the blocking of the diffusion path by ordering (long-range order) and, hence, the decrease is mainly due to the decrease in the so-called percolation efficiency (the physical correlation factor  $f_l$  introduced in the calculation of the ionic conductivity in  $\beta$ -alumina). In the ordered case, when the isotope  $B^*$  atom is on the B site and exchanges places with a vacancy on the nearest neighboring A site, this  $B^*$  atom tends to go back immediately to the original B site, being pushed back by nearest neighboring B atoms on the B site. This effect is equivalent to a small correlation factor but is of physical origin (physical correlation factor). Some calculations for cases  $U \neq 0$  are found in our previous publications.<sup>16,18</sup>

### iii. Instantaneous Distribution Conversion

Although the PPM gives a reasonable and systematic treatment of diffusion problems in disordered and ordered alloys, some systematic deviations from the results of Monte Carlo simulation were reported.<sup>25,26</sup> These troubles have since been traced to some inadequacies with respect to the formalism of the PPM as applied to transport problems.

As is explained in Ref. 2 with respect to the formalism of the PPM, the original formalism of the PPM is designed to follow the time dependence of the state. A state is defined in terms of the state variables at a time instant in the PPM just as in the CVM. Hence, the state variables at a time instant  $t$  <sup>are</sup> first determined, and appropriate transition probabilities of these state variables to lead to state variables at  $t + \Delta t$  are evaluated by the PPM. In transport problems, the change of state variables with time is associated <sup>with</sup> to flows<sup>2</sup>. In other words, the PPM is designed to follow the time correlation of the assembly of particles. On the other hand, in transport problems, the time correlation of individual particles rather than that of the assembly of particles is at stake as is easily viewed from the calculation of the correlation factor which is derived from the drift motion of a single, tagged particle. This difference in <sup>the</sup> statistical nature of transport problems has prompted us to convert some of the averaging processes of the original PPM in calculating transport properties.<sup>22</sup> This situation was also briefly explained in Ref. 2. Here, we discuss these conversion processes in two different ways; the instantaneous conversion process and the time conversion process. The purpose of the following two sections is to handle these conversion processes specifically for tracer diffusion in binary alloys for the purpose of comparing results with those of the Monte Carlo simulation.

The situation is most clearly seen in the flow equation, Eq. (22)

$$\dot{\Psi}_i = -\dot{\alpha}_i + \sum_j Q_j \psi_{ji}$$

Based on the formalism of the PPM, the equation represents a flow at a time instant  $t$ . However, because the equation applies to the steady state, the equation is also valid at any time instant. In other words, the equation means that, as the tagged atom of the  $i$ -th species moves with time, its surrounding is always specified by the distribution  $Q_j$ . This occurs because the distribution is specified by the equilibrium values, or the average over a long time period. The consequence is that the tagged atom makes a random

walk in the homogeneous, averaged lattice although the surrounding of the tagged atom varies from place to place, and hence the physical correlation factor never deviates from unity unless the lattice is separated into sublattices. In order to avoid this trouble, therefore, it is necessary to use the instantaneous distribution of atoms for the surrounding of the tagged atom instead of using the time independent specification  $Q_j$ .

Without changing the formalism of the PPM, it is <sup>still</sup> yet possible to convert the situation within the pair approximation. The quantity  $Q_j$  specifies the surrounding of a site occupied by the tagged atom assuming that the probability of occupancy of any site is equal. However, the pair approximation of the CVM specifies two different kinds of surroundings; the surroundings of an A atom and that of a B atom, or the quantity called the short-range order  $\sigma$ . By doing this, the problem is converted to calculate the (ensemble) average of flows of a tagged atom of the  $i$ th species jumping out from the surrounding of an A atom,  $Q_j^\alpha$ , and that of a B atom,  $Q_j^\beta$ , just as the average of flows from the A sublattice and the B sublattice in the ordered alloys [Eqs. (35), (36), (37) and (38)]. The procedure is to convert the formalism of the PPM to utilize the averaged state variables at each time instant to that which includes the fluctuation.

The conversion relation in the present approximation is then represented by

$$Q_j \rightarrow x_A Q_j^\alpha + x_B Q_j^\beta \quad (46)$$

If the flows out of the surroundings of  $Q_j^\alpha$  and  $Q_j^\beta$ , respectively, are designated by  $\Psi_i^\alpha$  and  $\Psi_i^\beta$ , respectively.

$$\Psi_i = x_A \Psi_i^\alpha + x_B \Psi_i^\beta \quad (47)$$

holds just as in the treatment of ordered alloys in the previous section. In such a case, we can derive



$$\begin{aligned}
 \Psi_i^\alpha &= -\dot{\alpha}_i^\alpha + \sum_j Q_j^\alpha \psi_{ji}^\alpha \\
 \Psi_i^\beta &= -\dot{\alpha}_i^\beta + \sum_j Q_j^\beta \psi_{ji}^\beta \\
 \dot{\alpha}_i &= x_A \dot{\alpha}_i^\alpha + x_B \dot{\alpha}_i^\beta = \dot{\alpha}_i^\alpha = \dot{\alpha}_i^\beta = \dot{\alpha}_i
 \end{aligned} \tag{48}$$

where

$$\begin{aligned}
 Q_j^\alpha &= y_{Aj}/x_A \\
 Q_j^\beta &= y_{Bj}/x_B
 \end{aligned} \tag{49}$$

This rewriting, Eqs. (48) and (49), is justifiable because only the jump to the nearest neighbor is taken into account in the pair approximation of the PPM. Under the boundary conditions equivalent to Eqs. (26) and (27), we obtain

$$\begin{aligned}
 \Psi_i^\alpha / \dot{\alpha}_i^\alpha &= -\frac{(2\omega-1)Z_B^\alpha}{2(1-Z_B^\alpha) + (2\omega-1)Z_B^\alpha} \\
 \Psi_i^\beta / \dot{\alpha}_i^\beta &= -\frac{(2\omega-1)Z_B^\beta}{2(1-Z_B^\beta) + (2\omega-1)Z_B^\beta}
 \end{aligned} \tag{50}$$

$$\Psi_i / \dot{\alpha}_i = -\frac{(2\omega-1)Z_{B^*}}{2(1-Z_{B^*}) + (2\omega-1)Z_{B^*}} = -f_{B^*} \tag{51a}$$

where

$$\frac{1}{Z_{B^*}} = \frac{x_A}{Z_B^\alpha} + \frac{x_B}{Z_B^\beta} \tag{51b}$$

Here

$$Z_B^\alpha = \frac{y_{AA}}{x_A} \frac{\hat{w}_A}{\hat{w}_B(\alpha) + \hat{w}_A} + \frac{y_{AB}}{x_A} \frac{\hat{w}_B}{\hat{w}_B(\alpha) + \hat{w}_B} \quad (52a)$$

$$Z_B^\beta = \frac{y_{BA}}{x_B} \frac{\hat{w}_A}{\hat{w}_B(\beta) + \hat{w}_A} + \frac{y_{BB}}{x_B} \frac{\hat{w}_B}{\hat{w}_B(\beta) + \hat{w}_B}$$

and

$$\begin{aligned} \hat{w}_B(\alpha) &= \theta_B e^{-\beta u_B} \left[ \frac{y_{AA} e^{-\beta \epsilon_{AA}} + y_{AB} e^{-\beta \epsilon_{AB}}}{x_A} \right]^{2\omega-1} \\ \hat{w}_B(\beta) &= \theta_B e^{-\beta u_B} \left[ \frac{y_{BA} e^{-\beta \epsilon_{BA}} + y_{BB} e^{-\beta \epsilon_{BB}}}{x_B} \right]^{2\omega-1} = \hat{w}_B \\ \hat{w}_A &= \theta_A e^{-\beta u_A} \left[ \frac{y_{AA} e^{-\beta \epsilon_{AA}} + y_{AB} e^{-\beta \epsilon_{AB}}}{x_A} \right]^{2\omega-1} = \hat{w}_A(\alpha) \end{aligned} \quad (52b)$$

In Eqs. (52),  $Q_B = 0$  is assumed for the sake of simplicity.

Since this conversion is based on the nearest neighbor relations and not on the sublattices, it is not necessary to change the expression in the ordered state as long as we replace  $y_{ij}$ 's with the corresponding values in the ordered state such as  $y_{ij}^O$ . It is to be noted, in the ordered state, the following correspondences

$$\begin{aligned} y_{AA} &\rightarrow y_{AA}^O \\ y_{BB} &\rightarrow y_{BB}^O \\ y_{AB} &\rightarrow (y_{AB}^O + y_{BA}^O)/2 \end{aligned} \quad (53)$$

exist between the corresponding pair variables in the disordered state and the ordered state.

As mentioned earlier, in the ordered state,  $y_{ij}^O$  is defined in such a way that this specifies the probability of finding an i-j pair with an i atom on the A site and a j atom on the B site. For a pair with an i atom on the B site and a j atom on the A site, the symbol  $y_{ji}^O$  is used. Then  $y_{ij}^O = y_{ji}^O$  holds. In the disordered state,  $y_{ij} = y_{ji}$  holds, and no distinction need be made.

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In Figs. 8b and 9b, the results of the conversion are shown. The major difference between a (the original PPM) and b (after instantaneous distribution conversion) is a marked drop in  $f_B$  by the development of the short-range order. The tendency is especially conspicuous for the two dimensional honeycomb lattice where the fluctuation is important because of its low dimensional character. Also, in this case, the effect of the long-range order over that of the short-range order is extremely small. The difference between a and b is attributed to the decrease in the percolation efficiency (the physical correlation factor  $f_1$ ) by the development of ~~the~~ short-range order.

#### iv. Time Conversion

In connection with the time correlation of individual particles in transport problems, there is one more important problem to solve.

Diffusion problems are essentially percolation problems (kinetic percolation problem). This feature is clear if one thinks of tracer diffusion problems. Here, we ask how a single, tagged atom percolates through a solid with time. Therefore, if we view this situation in the four dimensional space including time, there exists an unbroken chain of the motion of tagged atoms through the solid. In other words, we are seeking for the "long-range order" of the motion of tagged atoms in the four-dimensional space. On the other hand, the PPM is a technique to seek the time correlation for a short period

of time  $\Delta t$ . In other words, we evaluate the "short-range order" of the motion of the tagged atom in the time axis here. Under the assumption of the steady state condition, we eventually assume, however, that the "short-range order" <sup>is</sup> was the same as the "long-range order." This has caused the lowering of the degree of approximation in evaluating the correlation factor by the PPM.<sup>22</sup> In actual measurements, the average of the flow of particles over a long period of time (compared to  $\Delta t$ ) is utilized. Therefore, the conversion from the "short-range order" to the "long-range order" in four-dimensional space with respect to the motion of tagged atoms corresponds to the conversion of the ensemble average at a time instant to the "time average."

In the linear range in which the Onsager equation for diffusion is valid, the flows are evaluated based on the equilibrium distribution of atoms. Therefore, the ensemble of states used in the PPM to determine the flow at a time instant is equivalent to the ensemble of states with the evolution of time (time ensemble). Because of this reason, by adding appropriate requirements in the selection process of states in the time ensemble, it is possible to convert directly the result of the PPM based on the ensemble averaging at a time instant to that of time averaging. If the diffusion trajectory in the four dimensional space is projected along the time axis to the cross section at a time instant, the projection represents the actual diffusion path in the three dimensional space. Because the PPM corresponds to <sup>choosing</sup> ~~choose~~ the diffusion path (selection of  $Y_j$ ) at a time instant, the task is to convert the result into the projected path.

The essential feature is to convert the expressions  $\tau_k$  and  $Z_k$  in the PPM to the time average  $\langle \tau_k \rangle$  and  $\langle Z_k \rangle$  utilizing the following simultaneous equations.

$$\langle \tau_k \rangle = \frac{1 - \langle Z_k \rangle}{1 + (2\omega - 1) \langle Z_k \rangle} \quad (54)$$

$$\langle Z_k \rangle = \frac{\sum_m Y_m (1 - \langle \tau_m \rangle)}{Y_k/Q_k + \sum_m Y_m (1 - \langle \tau_m \rangle)} \quad (55)$$

where k or m specifies the species of atoms summarily just as i or j. The quantity  $\tau_k$  is defined in the original PPM in terms of the escape probability  $P_e$  and the return (jump back) probability  $P_r$  of an atom of the kth species as

$$\tau_k = \frac{P_r}{P_r + P_e} \quad (56)$$

and indicates the normalized probability of jumping back of the tagged atom. Therefore, in terms of  $Z_k$  defined in Eq. (30),

$$\tau_k = \frac{1 - Z_k}{1 + (2\omega - 2)Z_k} \quad (57)$$

The time average of  $Z_k$ ,  $\langle Z_k \rangle$ , is obtained from  $Z_k$  by replacing the ensemble average of  $Y_j$  in it by its time average

$$Y_j \rightarrow \frac{Q_j \sum_k Y_k (1 - \langle \tau_k \rangle)}{\sum_k Q_k} = Q_j \sum_k Y_k (1 - \langle \tau_k \rangle) \quad (58)$$

The conversion relation, Eq. (58), represents what we called the projection of the jump probability,  $Y_j$ , along the time axis. Interested readers may refer to Ref. 22 for details. Important results achieved by this conversion process include the fact that the correlation factor for self diffusion evaluated by the pair approximation of the PPM changed from

$$f_B = \frac{2\omega - 1}{2\omega + 1} \quad (59)$$

in the ensemble average to a more reasonable value

$$f_B = \frac{2\omega-2}{2\omega} \quad (60)$$

in the time average.<sup>22</sup> In addition, the appearance of the percolation limit for the tracer diffusion of B (the composition where  $f_B \rightarrow 0$  for  $w_B/w_A = \infty$ ) in the completely random binary alloys at

$$x_B = 1/(2\omega-1) \quad (61)$$

is noticed.<sup>22</sup> This value is the same as that predicted by the pair approximation of the CVM. The original PPM failed to predict the appearance of the percolation limit.<sup>22</sup>

The extension of the conversion process to the ordered state is straightforward and the conversion equations are shown here without explanation. For the two sublattice treatment of the original PPM, the converted formulae are (the parenthesis indicating the time averaging is removed)

$$\begin{aligned} Z_i^{AT} &= \frac{\sum_j Y_j(1-\tau_j(B))}{Y_i/Q_i(A) + \sum_j Y_j(1-\tau_j(B))} \\ Z_i^{BT} &= \frac{\sum_j Y_j(1-\tau_j(A))}{Y_i/Q_i(B) + \sum_j Y_j(1-\tau_j(A))} \end{aligned} \quad (62)$$

where

$$\begin{aligned}\tau_i(A) &= \frac{1-Z_i^{AT}}{1-Z_i^{AT} + (2\omega-1)Z_i^{AT}} \\ \tau_i(B) &= \frac{1-Z_i^{BT}}{1-Z_i^{BT} + (2\omega-1)Z_i^{BT}}\end{aligned}\quad (63)$$

and for  $f_B$

$$\begin{aligned}\frac{1}{Z_B^T} &= 1/2 \left[ \frac{1}{Z_B^{AT}} + \frac{1}{Z_B^{BT}} \right] \\ f_B &= \frac{(2\omega-1)Z_B^T}{2(1-Z_B^T) + (2\omega-1)Z_B^T}\end{aligned}\quad (64)$$

On the other hand, for the treatment with the instantaneous distribution conversion, the converted formulae became

$$Z_A^{\alpha T} = \frac{\frac{y_{AA}}{x_A} \hat{w}_A(1-\tau_A) + \frac{y_{AB}}{x_A} \hat{w}_B(1-\tau_B)}{\hat{w}_A(\alpha) + \frac{y_{AA}}{x_A} \hat{w}_A(1-\tau_A) + \frac{y_{AB}}{x_B} \hat{w}_B(1-\tau_B)}$$

$$Z_A^{\beta T} = \frac{\frac{y_{BA}}{x_B} \hat{w}_A(1-\tau_A) + \frac{y_{BB}}{x_B} \hat{w}_B(1-\tau_B)}{\hat{w}_A(\beta) + \frac{y_{BA}}{x_B} \hat{w}_A(1-\tau_A) + \frac{y_{BB}}{x_B} \hat{w}_B(1-\tau_B)}\quad (65)$$

$$Z_B^{\alpha T} = \frac{\frac{y_{AA}}{x_A} \hat{w}_A(1-\tau_A) + \frac{y_{AB}}{x_A} \hat{w}_B(1-\tau_B)}{\hat{w}_B(\beta) + \frac{y_{AA}}{x_A} \hat{w}_A(1-\tau_A) + \frac{y_{AB}}{x_A} \hat{w}_B(1-\tau_B)}\quad (66)$$

$$Z_B^{\beta T} = \frac{\frac{y_{BA}}{x_B} \hat{w}_A(1-\tau_A) + \frac{y_{BB}}{x_B} \hat{w}_B(1-\tau_B)}{\hat{w}_B(\alpha) + \frac{y_{BA}}{x_B} \hat{w}_A(1-\tau_A) + \frac{y_{BB}}{x_B} \hat{w}_B(1-\tau_B)}$$

$$\tau_A = \frac{1-Z_A^{\alpha T}}{1-Z_A^{\alpha T} + (2\omega-1)Z_A^{\alpha T}} \quad (67)$$

$$\tau_B = \frac{1-Z_B^{\beta T}}{1-Z_B^{\beta T} + (2\omega-1)Z_B^{\beta T}}$$

In deriving  $f_B$ , first  $Z_B^T$  is obtained likewise by

$$\frac{1}{Z_B^T} = \frac{x_A}{Z_B^{\alpha T}} + \frac{x_B}{Z_B^{\beta T}} \quad (68)$$

and

$$f_B = \frac{(2\omega-1)Z_B^T}{2(1-Z_B^T) + (2\omega-1)Z_B^T}$$

The quantity  $f_A$  can also be obtained similarly as

$$f_A = \frac{(2\omega-1)Z_A^T}{2(1-Z_A^T) + (2\omega-1)Z_A^T} \quad (69a)$$

where

$$\frac{1}{Z_A^T} = \frac{x_A}{Z_A^{\alpha T}} + \frac{x_B}{Z_A^{\beta T}} \quad (69b)$$



The results with the time conversion for the body centered cubic lattice and for the 2Dhc lattice are shown in Figs. 8c and 9c, respectively, and those with both the instantaneous distribution and the time conversions are shown in Figs. 8d and 9d, respectively. In addition to the decrease in the correlation factor for the self diffusion, the addition of the time conversion further decreases the overall correlation factor. The decrease of  $f$  due to the time conversion is more conspicuous for cases with the instantaneous distribution conversion and also for low dimensional honeycomb lattice. The decrease is due to the decrease in the percolation efficiency along the diffusion path due to fluctuations.

## 6. The Monte Carlo Method

The application of the Monte Carlo method to diffusion has been reviewed in detail recently and we refer the reader to those treatises.<sup>4,5</sup> For the ordered alloy particular care must be taken that the starting configuration has been prepared correctly. Although long-range order extending over the entire lattice can be generated in principle by starting with a disordered distribution, this process is very slow because several ordered regions invariably occur which are separated by antiphase boundaries. These boundaries anneal out extremely slowly (this is in itself an interesting process)<sup>27</sup> but for our purposes their existence in nonequilibrium concentrations can provide short circuit paths for diffusion.

Accordingly, in these calculations we started with a fully ordered stoichiometric AB lattice of A and B atoms without a vacancy. Here, the relation  $\epsilon_{AA} = \epsilon_{BB} = 0$  [Eq. (8)] is assumed. For speed to equilibration, the grand canonical ensemble was chosen. In this, a site was chosen at random and a possible occupant, i.e., an A atom or B atom, was also selected. If the selected site happened to have the same occupant as was generated, the next state was, accordingly, identical with the old state. Otherwise, the

quantity

$$[(4\epsilon_{\text{new}} - (\mu_A - \mu_B)N_{A,\text{new}}] - [4\epsilon_{\text{old}} - (\mu_A - \mu_B)N_{A,\text{old}}] \quad (70)$$

was computed, where  $\mu_A$  and  $\mu_B$  are the chemical potentials and  $N_{A,\text{old}(\text{new})}$  is the number of A atoms in the old (new) state. The quantity  $4\epsilon$  here specifies the energy of the system and is equivalent to that given in Eq. (7) multiplied by the number of AB pairs. If this quantity was  $\leq 0$ , then the new state was accepted (this involved the change of a B atom to an A atom or vice versa). If this quantity was  $> 0$ , then the quantity

$$P = \exp[-4\epsilon_{\text{new}} - (\mu_A - \mu_B)N_{A,\text{new}}/kT] / \exp[-4\epsilon_{\text{old}} - (\mu_A - \mu_B)N_{A,\text{old}}/kT] \quad (71)$$

was calculated and compared with a random number,  $R$ , uniform on the interval  $[0,1]$ . The new state was accepted only if  $R < P$ .

Our alloy with periodic boundaries contained approximately 10,000 sites. The system was shuffled for 200,000 states. At this point, the system was frozen and this became the starting point of the diffusion simulation <sup>now in the petit canonical ensemble.</sup> For this part of the run, a single vacancy was introduced by removing, for convenience, a B atom. Diffusion was simulated by directing moves of the vacancy rather than the atoms. This is clearly more efficient. A random direction from the choice of (8 for b.c.c. and 3 for honeycomb) was chosen. The identity of the nearest neighbor atom  $i$  in that direction was ascertained. The normalized exchange frequency  $\hat{w}_i$  based on bond-breaking for that atom was determined by a scan of its environment. The calculated value of  $\hat{w}_i$  was compared to a random number,  $R$ , uniform on the interval  $[0,1]$ . If  $R < \hat{w}_i$ , the jump attempt was deemed successful and atom  $i$  and the vacancy were interchanged. If  $R \geq \hat{w}_i$ , the jump attempt was deemed unsuccessful and a direction was once again chosen at random.

The correlation factor for atoms of type  $i$  was calculated from the Einstein expression

$$f_i = \langle R_i^2 \rangle / n_i l^2 \quad i = A, B \quad (72)$$

where  $\langle R_i^2 \rangle$  is the mean square displacement of atoms of type  $i$  after an average of  $n_i$  jumps each with displacement  $l$ . The definition of  $f_i$  given in Eq. (72) is equivalent to that given in Eq. (5). We chose  $n_i$  to be  $\geq 5$ . This was sufficient for convergence.

The calculation of  $f_B$  was thus made for binary alloys with the bcc structure and the 2Dhc structure and the results are shown in Figs. 10 and 11, respectively. The data points show the scatter of calculated results. The temperature is given by  $T/T_c = 0.5$  where  $T_c$  is specified by Eq. (11). Here,  $T_c$  only serves to normalize the value of  $\epsilon$  in the simulation. Figs. 10 and 11 are to be compared with Figs. 8d and 9d, respectively. The agreement of results between these two methods are very good in view of the relatively simple approximation (the pair approximation) adopted in the PPM.

## 7. Discussion

The pair approximation of the PPM has been applied to the problem of tracer diffusion in binary alloys which undergo an order-disorder transition. The treatment here is limited to the composition dependence of the correlation factor at a fixed temperature. However, other properties such as the temperature dependence of the correlation factor at a fixed composition can also be obtained by the same kind of calculation. The major interest of this article is to clarify physical factors which contribute to tracer diffusion in concentrated alloys by comparing the analytical results by the PPM especially through its development of the approximation with those of the MCSM. The coupling of diffusion and atomic ordering is especially expected to make this comparison more instructive. Because of this reason, the development of the PPM as

applied to tracer diffusion in ordered alloys is treated rather in detail.

The calculations based on the pair approximation of the original PPM for the bcc and 2Dhc structures are shown in Figs. 8a and 9a, respectively. The results show a sharp drop of  $f_B$  in the region where the long-range order exists. This sharp drop is ascribed to the appearance of the physical correlation factor  $f_I$  (or the percolation efficiency) which deviates from unity.<sup>13,16,18</sup> The overall decrease in the composition range in the middle, however, is due to the decrease in the mobility (the jump frequency  $\hat{w}_j$ ) of the tracer atom due to interactions with surrounding atoms (the increase in the bond breaking factor, Eq. (20)). The appearance of the physical correlation factor or the percolation efficiency is due to the deviation of the motion of the assembly of atoms from the random walk. The deviation here is due to the existence of two sublattices. The contribution of  $f_I$  in the ionic conductivity in superionic conductors was first pointed out by one of the authors based on the treatment by the PPM.<sup>13</sup>

Results obtained by the pair approximation of the PPM for tracer diffusion in concentrated alloys,<sup>16-18</sup> and for tracer diffusion and ionic conductivity in superionic conductors<sup>13-15</sup> were found to explain experimental results at least qualitatively. However, the comparison of these results with corresponding results of MCSM later developed revealed a systematic difference between these supposedly equivalent two methods.<sup>25,26</sup> However, because the PPM had given a satisfactory description of phenomena such as the kinetics of order-disorder transformations, where the time evolution of averaged macrovariables such as the degree of order was involved,<sup>20</sup> it was not expected to find the origin of the trouble in the procedures of the PPM.

The feature of general tracer diffusion problems is clearly shown in the expression of the diffusion coefficient

$$D_{B^{\bullet}} = \underline{a} \hat{w}_{B^{\bullet}} V f_{B^{\bullet}} = \underline{a} w_{B^{\bullet}} V W f_{B^{\bullet}} \quad (73)$$

where  $\underline{a}$  is a numerical factor,  $V$  represents the probability of a vacancy available to the diffusing atom or the vacancy availability factor and  $W$  represents the bond breaking factor (effective jump frequency factor<sup>13</sup>). Among these three factors,  $V$ ,  $W$  and  $f_{B^{\bullet}}$ ,  $V$  and  $W$  are essentially determined by the equilibrium distribution of atoms, but the factor  $f_{B^{\bullet}}$  represents the time correlation of atomic motion and hence is determined through kinetic processes. Comparison of the PPM and the MCSM with respect to  $V$  and  $W$  showed an excellent agreement while  $f_{B^{\bullet}}$  predicted by both methods sometimes shows discrepancies.<sup>25</sup> The source of the discrepancy had thus been traced to the difference in evaluating the time correlation process in both methods. This finding eventually led to the instantaneous distribution<sup>2,24</sup> and time conversion<sup>22</sup> processes in applying the PPM to transport phenomena. These conversion processes are to change the averaging processes from that characteristic of the PPM to that required to evaluate the time correlation of the motion of a single particle characteristic to transport phenomena. In the MCSM, the averaging is not divided into steps as in the PPM. This division of averaging process into several steps in the PPM represents an approximation.

In Figs. 8 and 9, the changes due to the application of the conversion process are shown. The result of the application of the instantaneous distribution conversion (Figs. 8c and 9c) indicates that the existence of the short-range order is as effective as the existence of the long range order in lowering the value of  $f_{B^{\bullet}}$ . In other words, the diffusion process is very sensitive to the existence of fluctuation in distribution of atoms (the process having the smallest  $Z$  is the rate determining process). The application of the time conversion further enhances the effect (Figs. 8d and 9d). This conversion process emphasizes the fluctuation along the diffusion path as the tracer atom moves in a long time period. The effect of fluctuation is more important in low dimensional solids

(or solids with low dimensional diffusion paths), because, in such cases, diffusion paths are very easily blocked. Diffusion problems are essentially dynamical percolation problems, and hence the percolation efficiency, in addition to the effective number of diffusion particles and the mobility (jump frequency), is an important factor. The mixed alkali effect in glasses and in  $\beta$ -aluminas is believed to be closely connected to the problem of the percolation efficiency.<sup>23,28</sup>

After the time conversion, the expression for the correlation factor in terms of  $Z$  (the conversion from  $Z$  in Eq. (30) to  $\langle Z \rangle$  in Eq. (55)) becomes very close to the expression by the "random walk theory."<sup>10-12</sup> This is due to the fact that the random walk theory is set up to follow the motion of the tracer atom for a long period of time. Such similarity has been noted, especially by Bakker<sup>29</sup> and Stolwijk,<sup>30</sup> in developing the theory of diffusion in concentrated alloys.

Between the bcc structure and the 2Dhc structure, the change for the latter by the application of the conversion processes is especially remarkable. This is due to the fact that 2Dhc is low dimensional and the development of fluctuations by the formation of the short-range order is predominant. For both the bcc and the 2Dhc structures, the pair approximation of the PPM, with the two conversion processes, can provide a reasonable reproduction of the behavior of  $f_B$  as one can see from the comparison of Figs. 8d and 9d with Figs. 10 and 11. The degree of approximation for the pair approximation is yet rather poor and the statistical fluctuation is not well taken into account. Nevertheless, the agreement of the results of the PPM with those of MCSM is rather remarkable. This type of agreement with analytical calculations also indicates the reliability of the MCSM method adopted for this calculation.

The comparison on Figs. 8d and 9d with Figs. 10 and 11 shows yet a systematic deviation of  $f_B$  on the B rich side. The lowering of  $f_B$  in this region is far more pronounced in the MCSM. This is due to the fact that, in the pair approximation of the

CVM, the distribution in the completely random state is regarded as homogeneous (without fluctuations), and hence, the fluctuation in distribution is not well represented in the PPM. These examples thus show clearly how the comparison of analytical results with carefully carried out calculations by the MCSM guides the progress of theoretical treatments and gives insights into the mechanism of diffusion.

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## Table 1 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.
$\nu$	index for a plane through lattice points perpendicular to the concentration gradient in the [100] direction of the bcc lattice (atomic plane) (see Fig. 1).
$n$	index for a plane through the center of two atomic planes $\nu$ and $\nu+1$ (bond plane) (see Fig. 1).
$\epsilon_{ij}$	interaction energy between a nearest neighbor pair of constituents i and j.
$\beta$	$\equiv (kT)^{-1}$ ; k is the Boltzmann constant; T the absolute temperature.
$\dot{x}_i$	the concentration gradient of constituent i.
$K_{ij}$	$= K_{ji} = \exp(-\beta\epsilon_{ij})$ .
$q_i$	$y_{ij} = q_i q_j K_{ij}^{-1}$ .
$Q_i$	$\equiv q_i \left[ \sum_m q_m \right]^{-1}$ .
$\dot{w}_i$	$\equiv w_i \left[ \frac{\sum_j y_{ji} K_{ji}}{x_i} \right]^{2\omega-1}$
$w_i$	$= \theta_i e^{-\beta u_i}$
$\alpha_i$	$\equiv \beta \mu_i$ represents the chemical potential of the ith species.
$2\omega$	coordination number of the lattice. For bcc, $2\omega = 8$ .

### Figure Captions

- Fig. 1. Phase diagram of order-disorder in the bcc structure calculated by the pair approximation of the CVM.
- Fig. 2a. The temperature dependence of the pair variables  $y_{ij}$  for  $x_A = x_B = 1/2$  in the bcc structure.
- Fig. 2b. The composition dependence of  $y_{ij}$  in the bcc structure at temperature  $T/T_c = 0.5$ .
- Fig. 3. The temperature dependence of the long-range order  $S$  and the short-range-order  $\sigma$  for the composition  $x_A = x_B = 1/2$  in the bcc structure.
- Fig. 4. The composition dependence of  $Q_A$  and  $Q_B$  in the bcc structure at temperature  $T/T_c = 0.5$ .
- Fig. 5. Effect of bond breaking as the  $i$ th atom on the  $\nu$ th atomic plane jumps into a vacancy on the  $(\nu+1)$ th plane (Ref. 22). Springs indicate the bonds.
- Fig. 6. Definition of  $Z$  in terms of  $P_e$  and  $P_r$  in a concentrated, disordered alloy. The species of the neighboring atoms around the vacancy is specified by  $Q_j$  (Ref. 22).
- Fig. 7. Definition of  $Z_B^A$  and  $Z_B^B$  for a binary ordered alloy. The species of the neighboring atoms around the vacancy is specified by  $Q_j$  (B) and  $Q_j$  (A), respectively.
- Fig. 8a. The composition dependence of  $f_B$  in an ordered binary bcc alloy at  $T/T_c = 0.5$  calculated by the pair approximation of the PPM.
- Fig. 8b. The same quantity as shown in Fig. 8a after the time conversion process.
- Fig. 8c. The same quantity as shown in Fig. 8a after the instantaneous distribution conversion process.
- Fig. 8d. The same quantity as shown in Fig. 8a after the instantaneous distribution conversion and the time conversion processes.
- Fig. 9a. The composition dependence of  $f_B$  in an ordered binary 2Dhc alloy at  $T/T_c = 0.5$  calculated by the pair approximation of the PPM.
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- Fig. 10. The composition dependence of  $f_B$  in an ordered bcc alloy at  $T/T_c = 0.5$  calculated by the MCSM.
- Fig. 11. The composition dependence of  $f_B$  in an ordered 2Dhc alloy at  $T/T_c = 0.5$  calculated by the MCSM.

## Figure Captions

*at  $T/T_c = 0.5$ .*

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- 
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- Fig. 11. The composition dependence of  $f_B^*$  in an ordered 2Dhc alloy at  $T/T_c = 0.5$  calculated by the MCSM.

*The curve D corresponds to  $f_B^*$  of the system with  $\sigma_d$  (Fig. 3).*

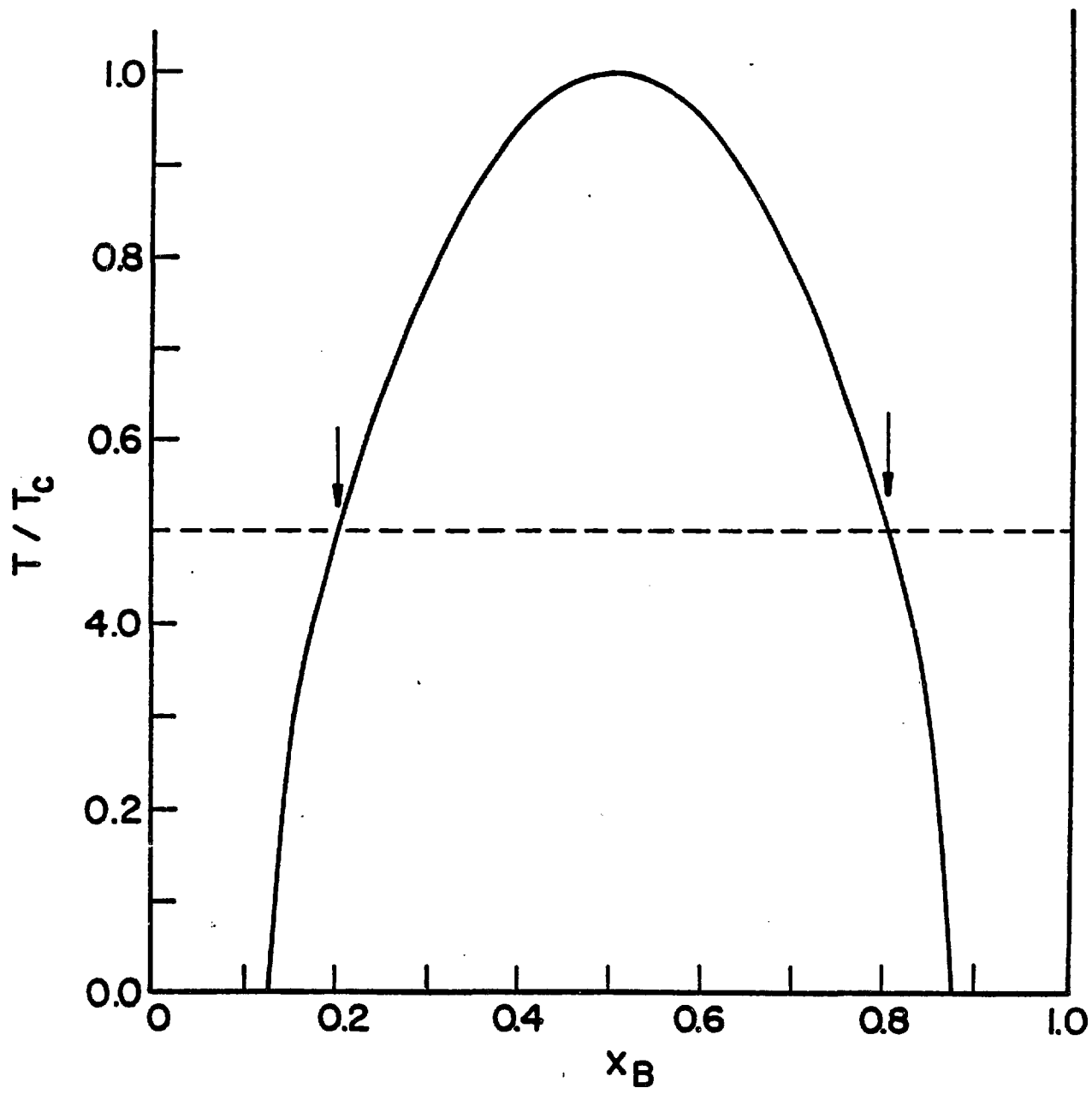


Fig. 1

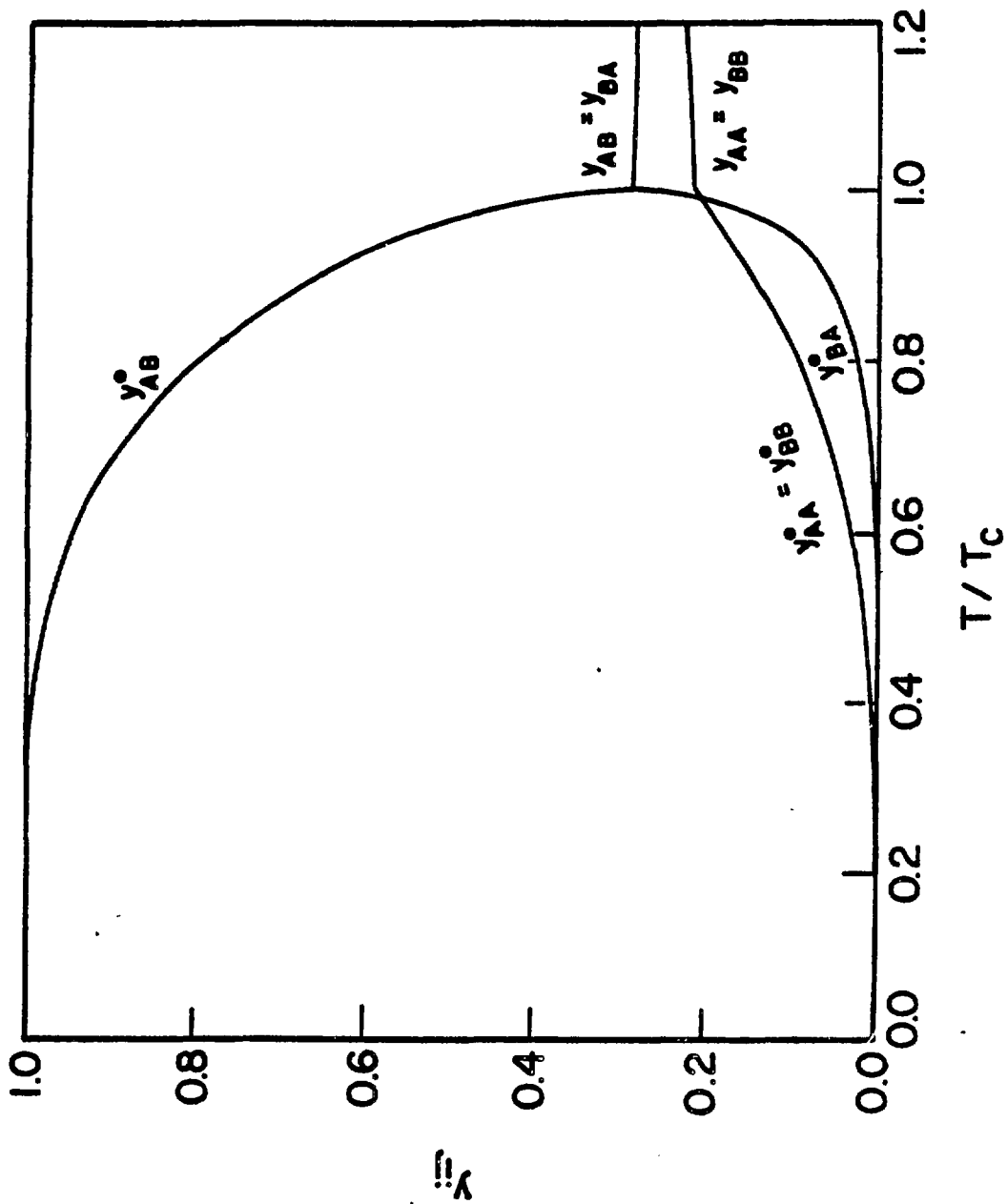


Fig. 29

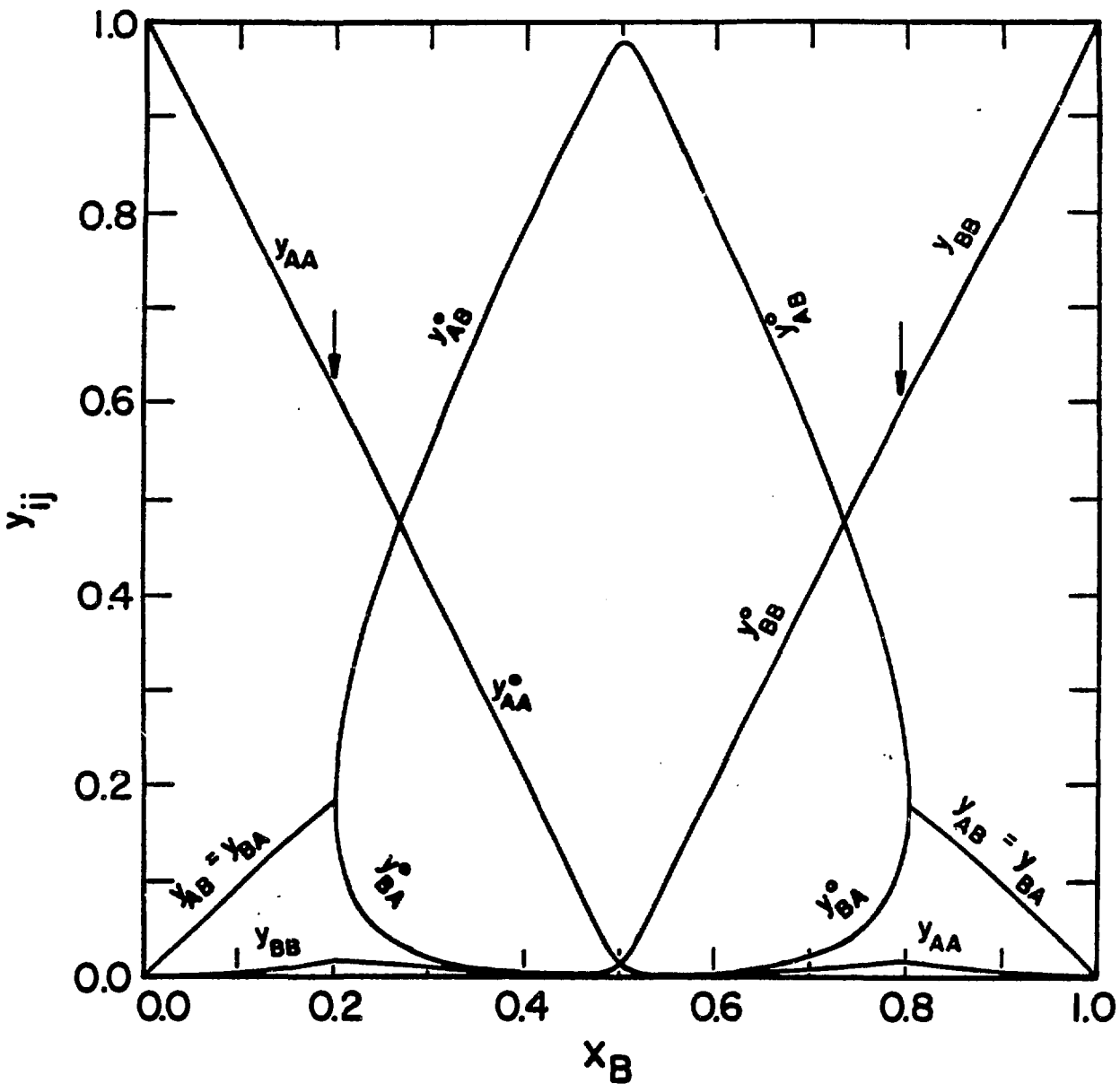


Fig. 2b



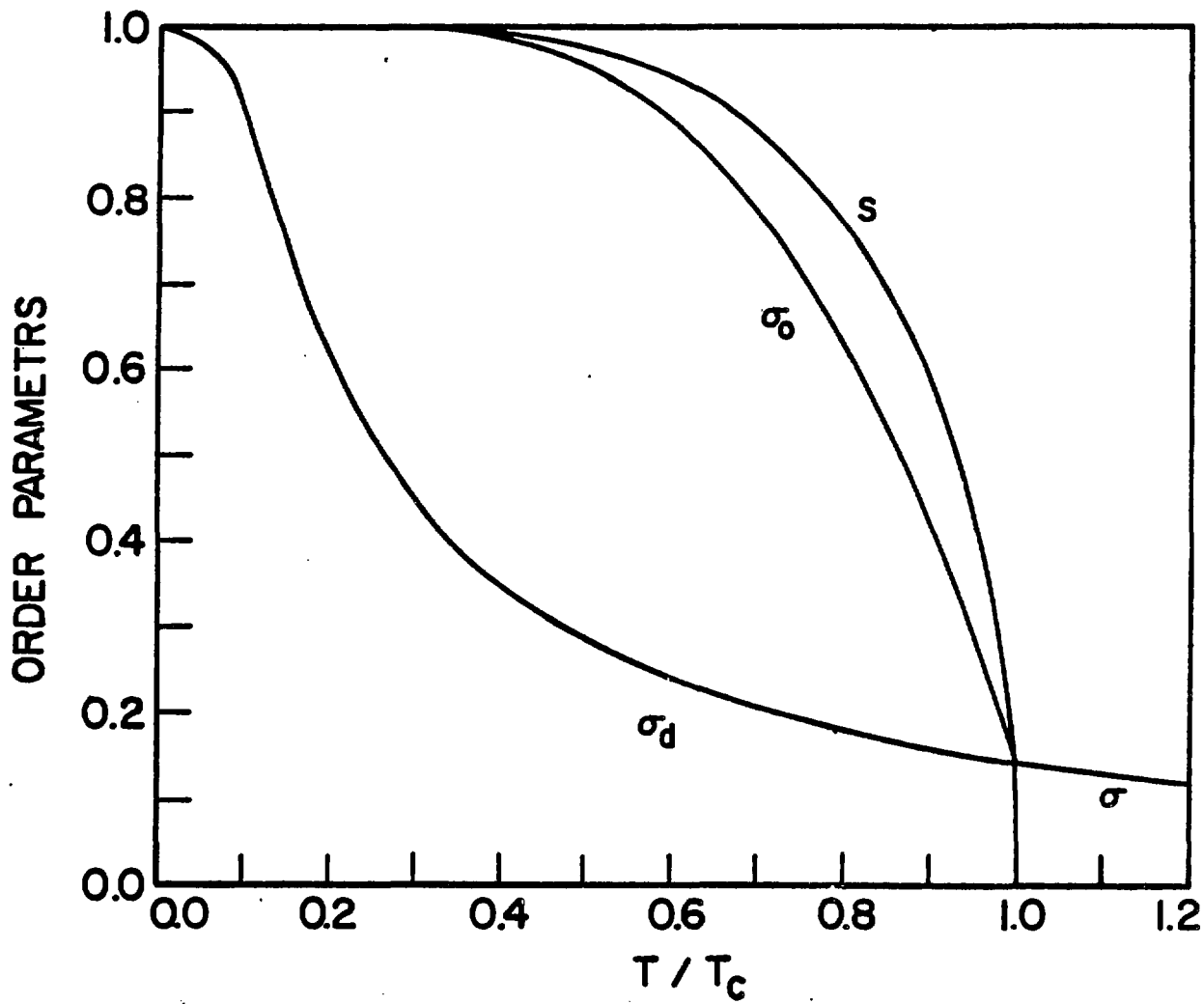


Fig. 3

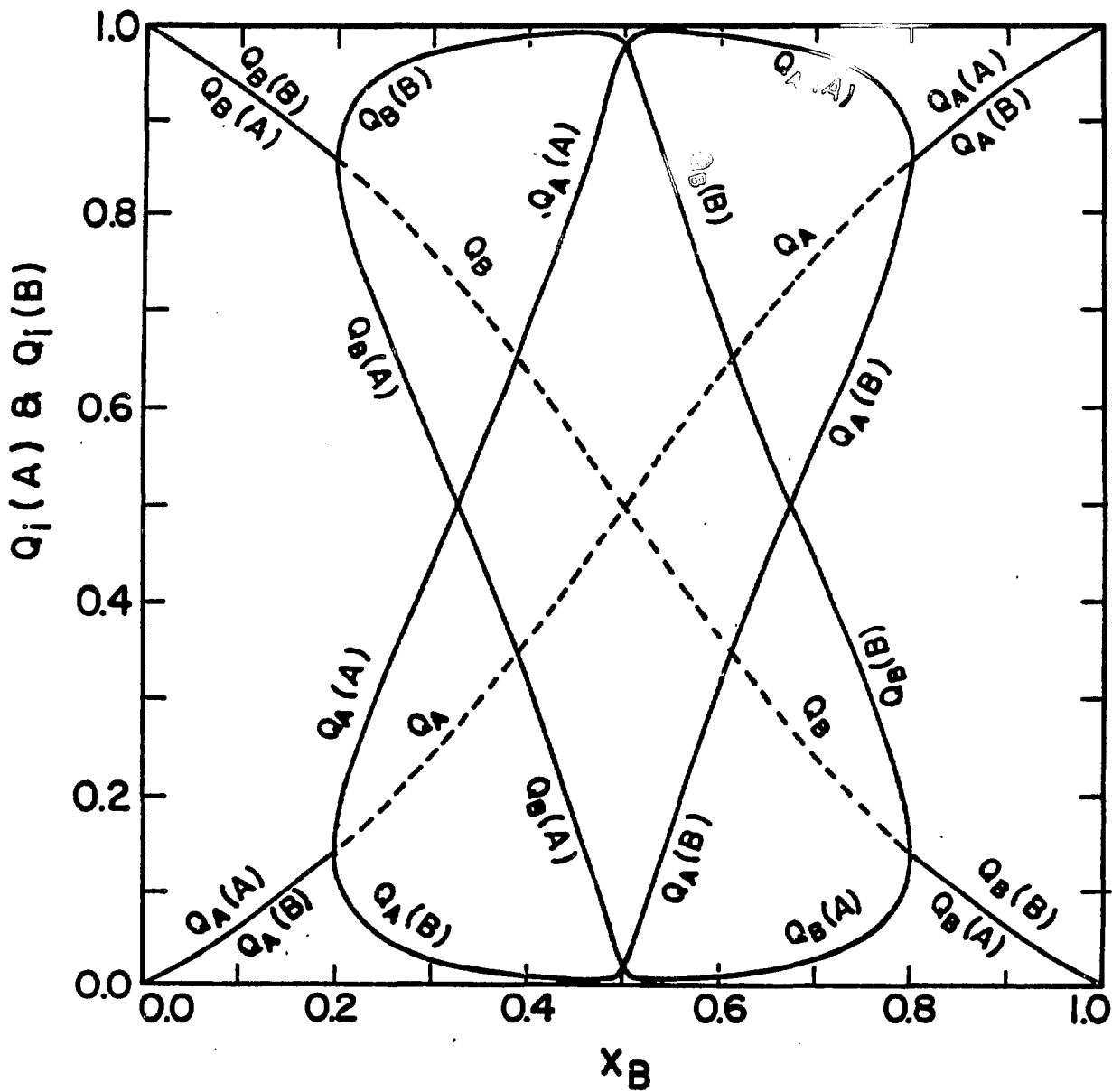


Fig. 4

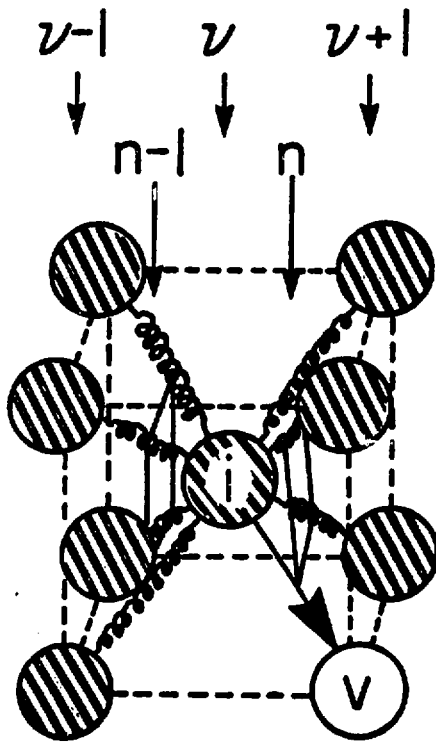
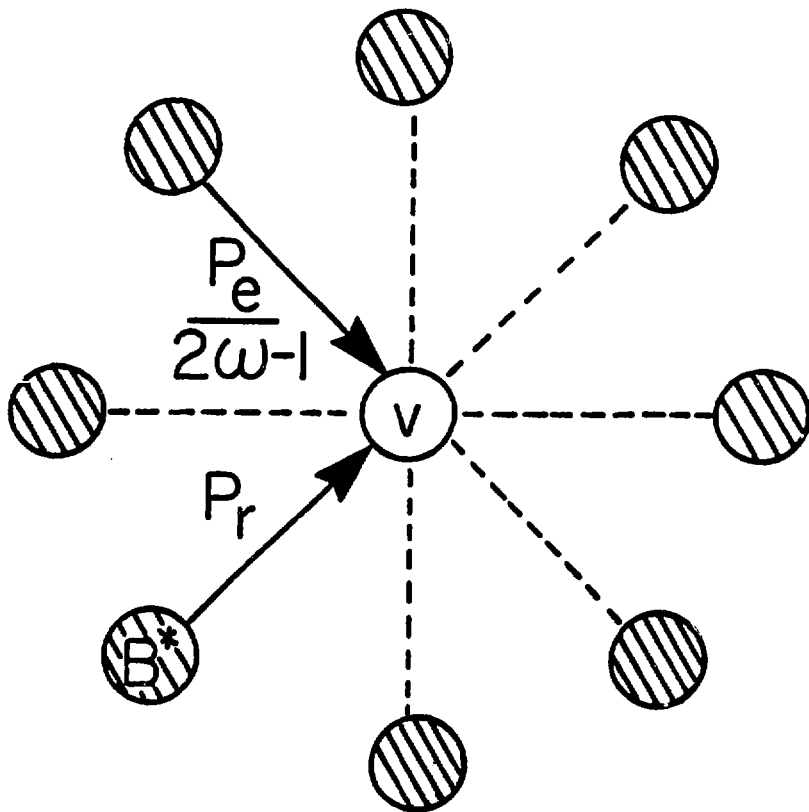


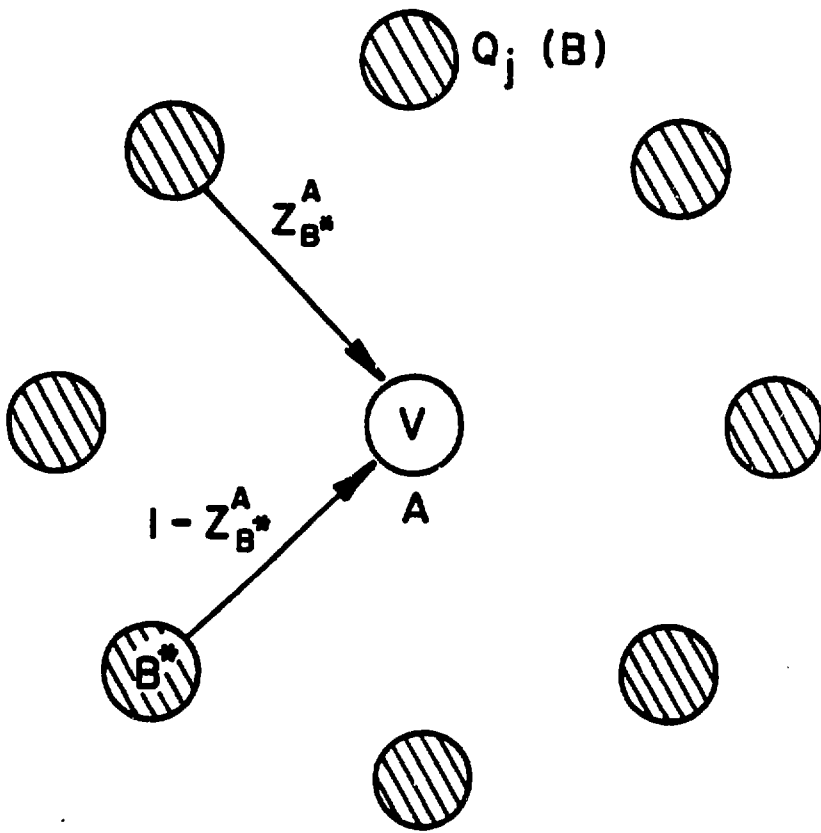
Fig. 5



$$\frac{1}{2\omega-1} P_e = Z_{B^*}$$

$$P_r = 1 - Z_{B^*}$$

Fig. 6



(a)

(b)  
for  $Z_{B^*}^B$

Fig. 7

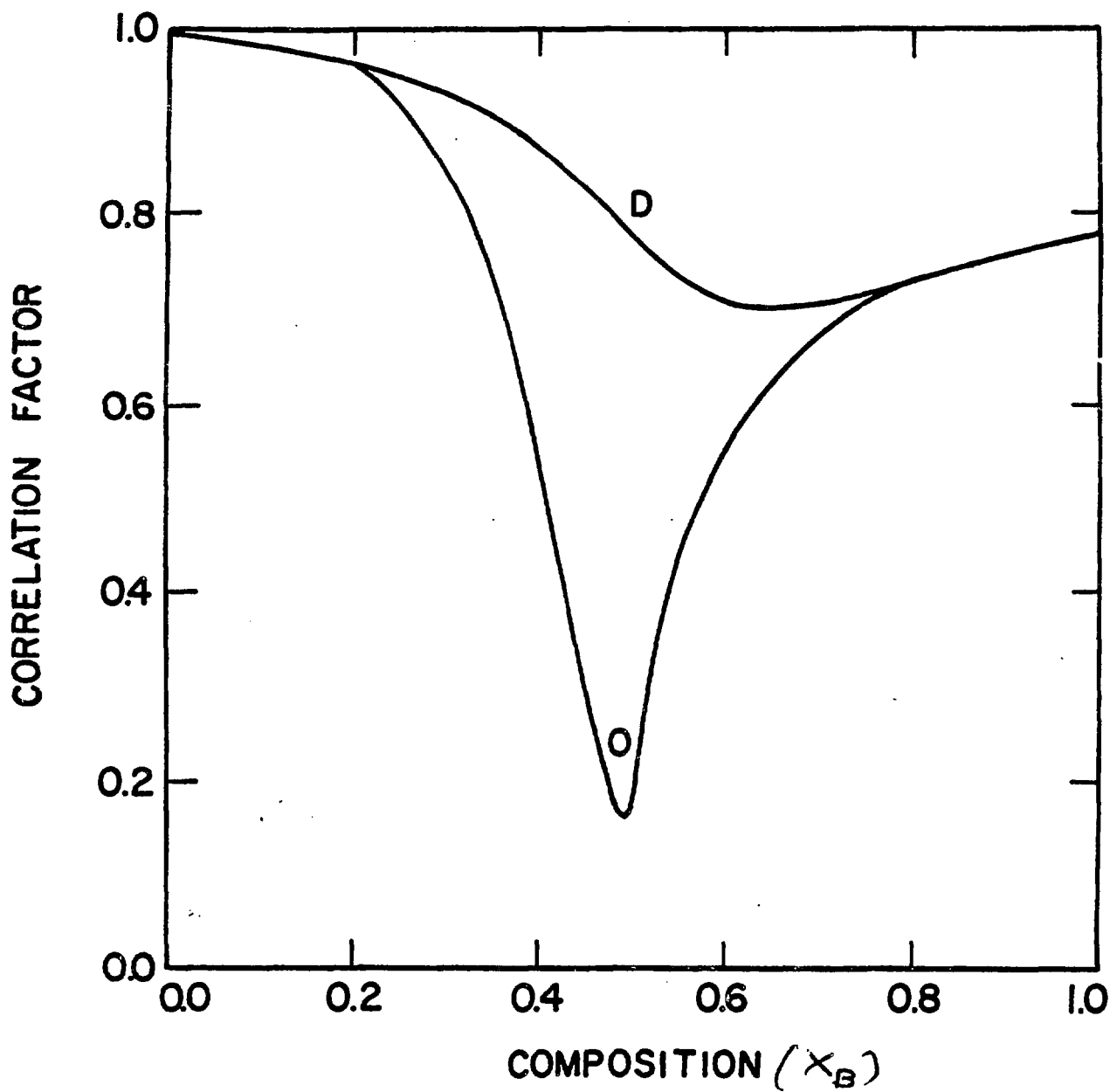


Fig. 8a

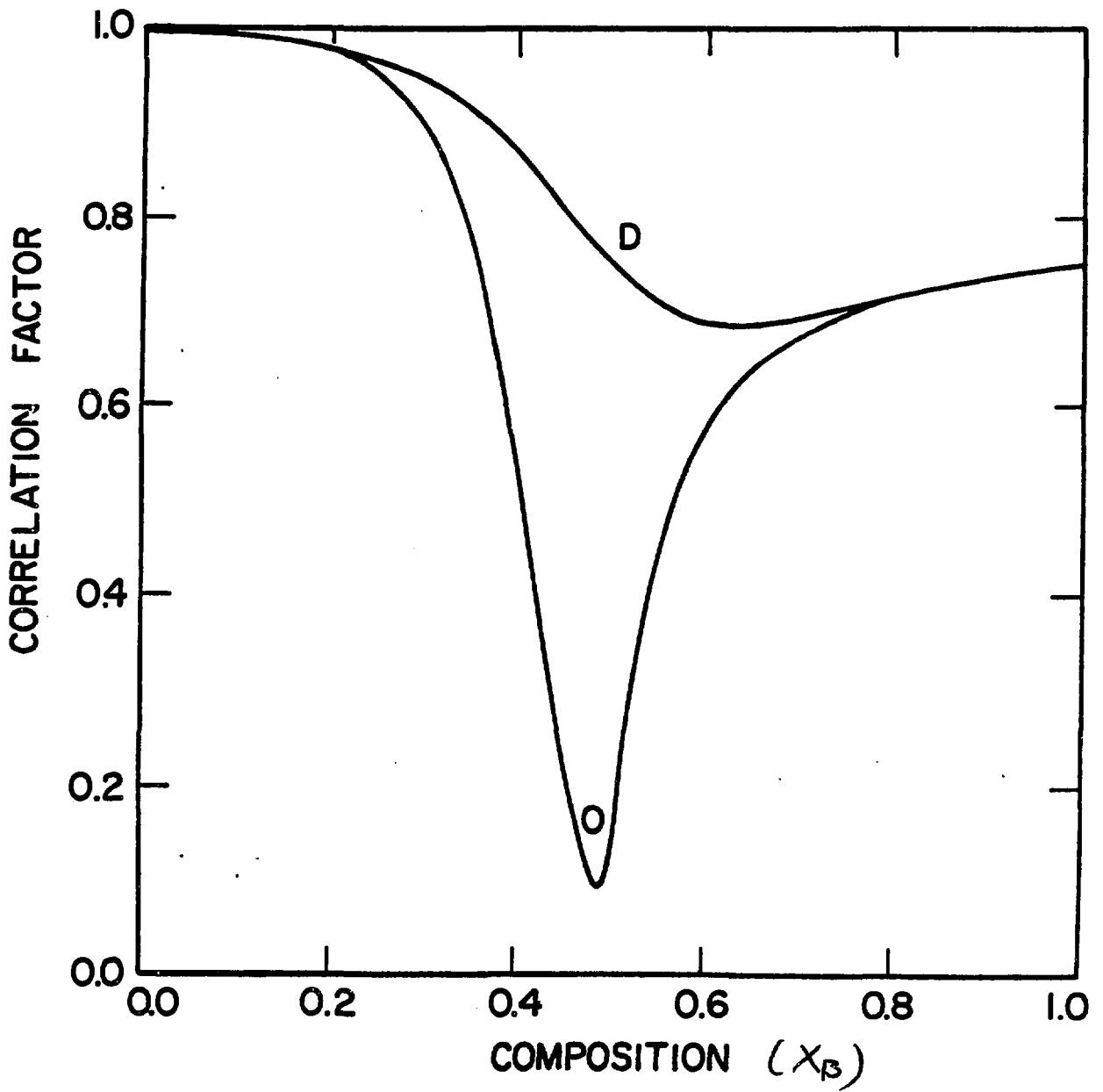


Fig. 8b

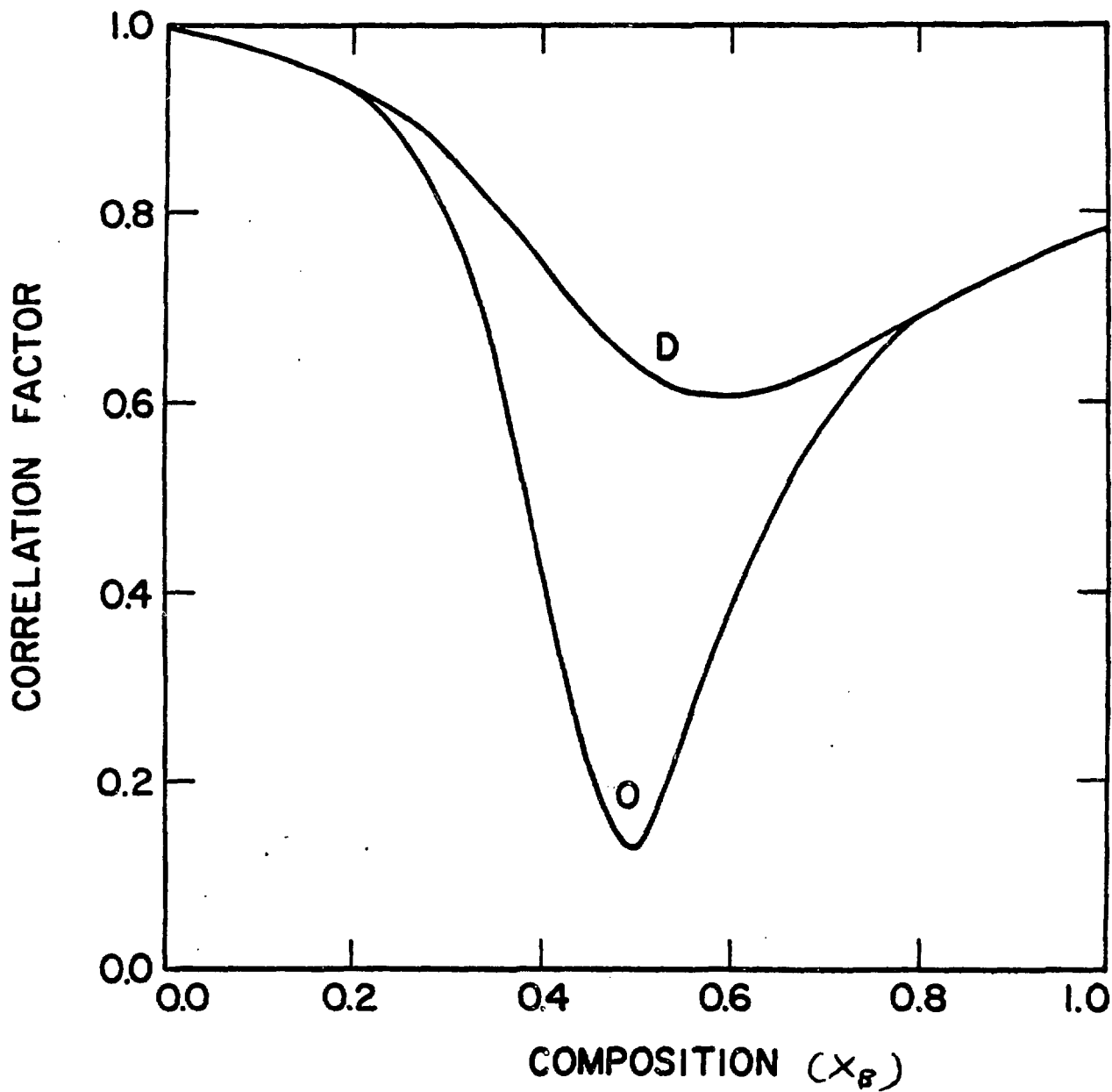


Fig. 8c



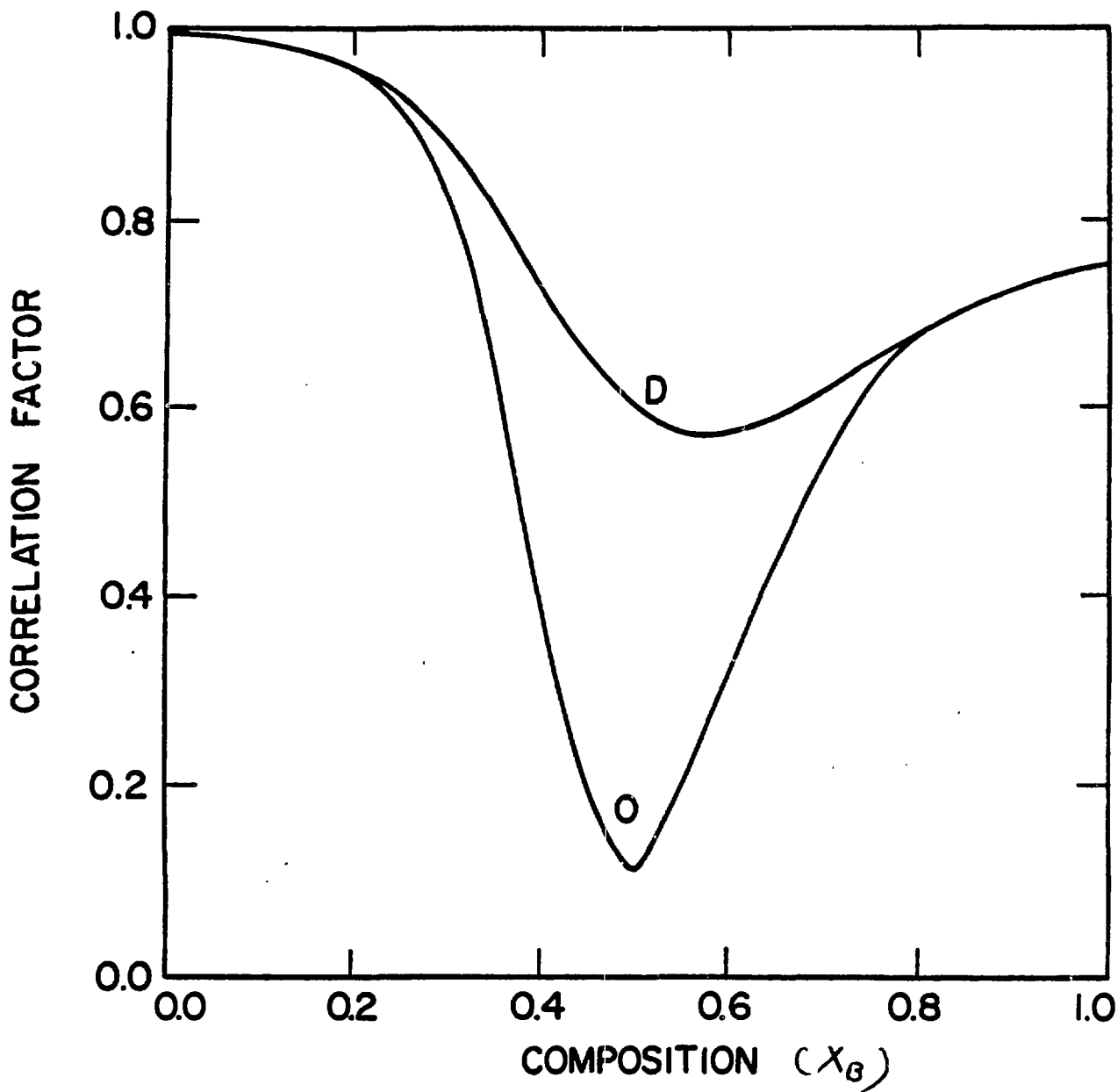


Fig. 8d

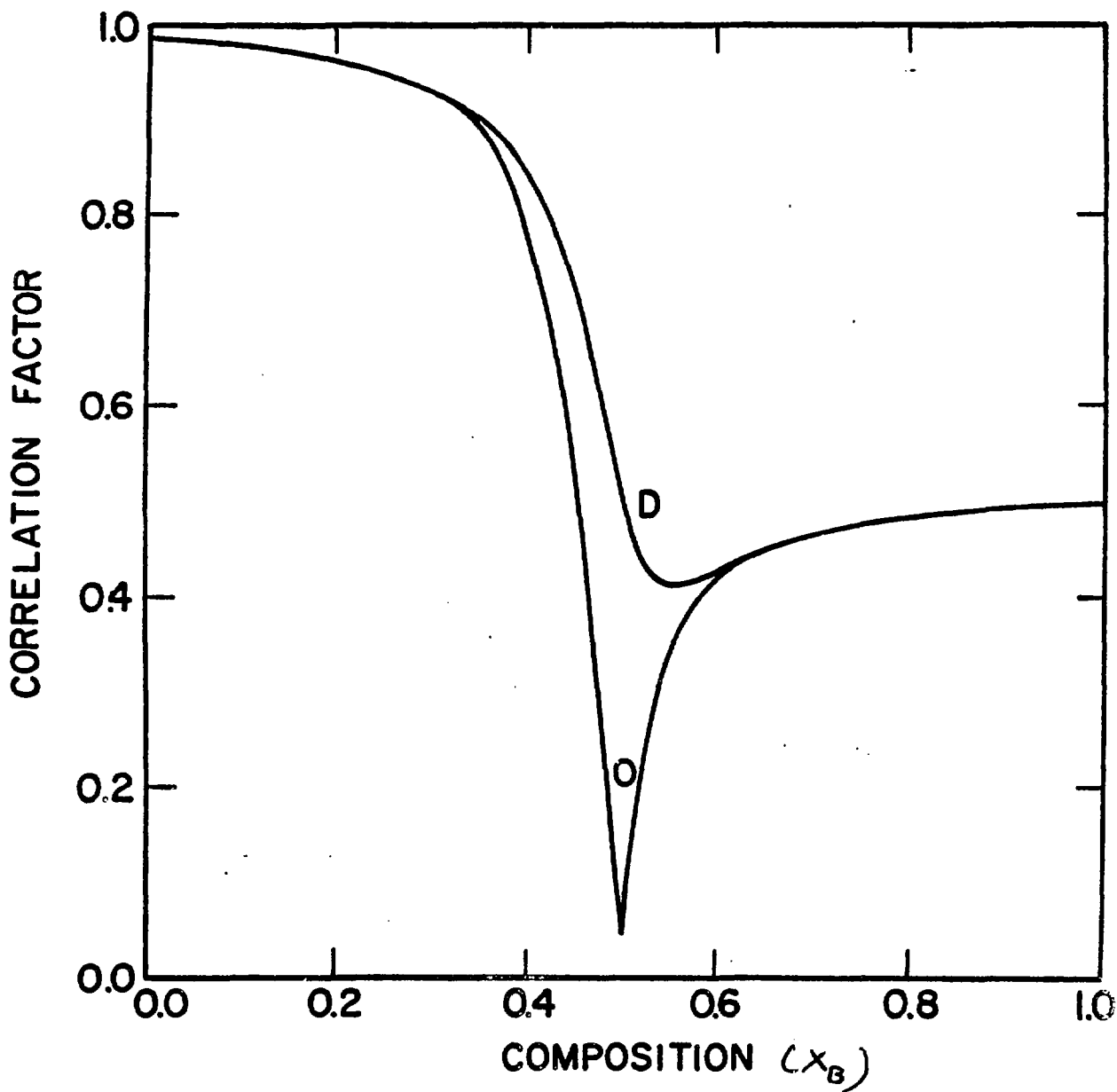


Fig. 9a

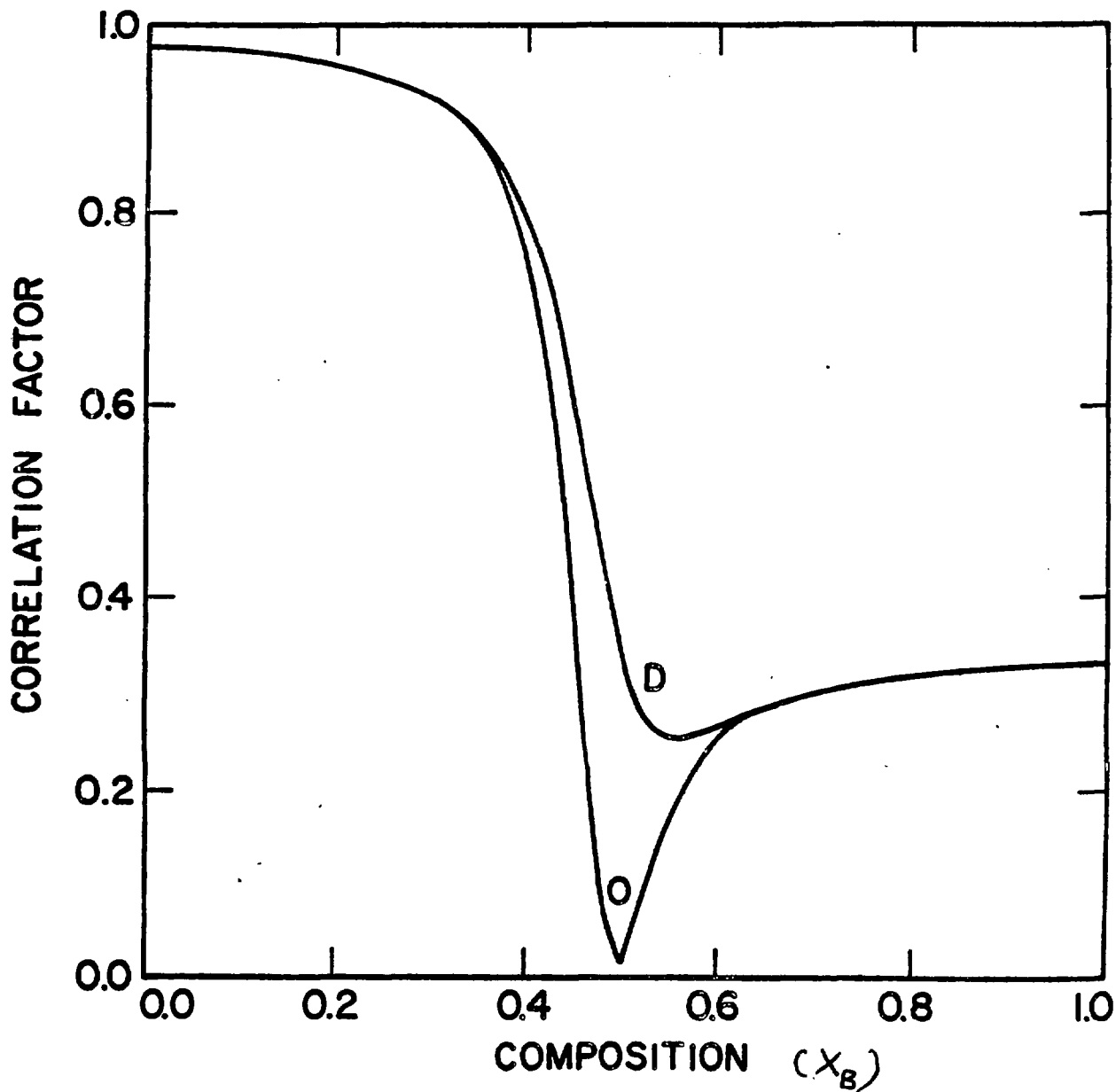


Fig. 9b

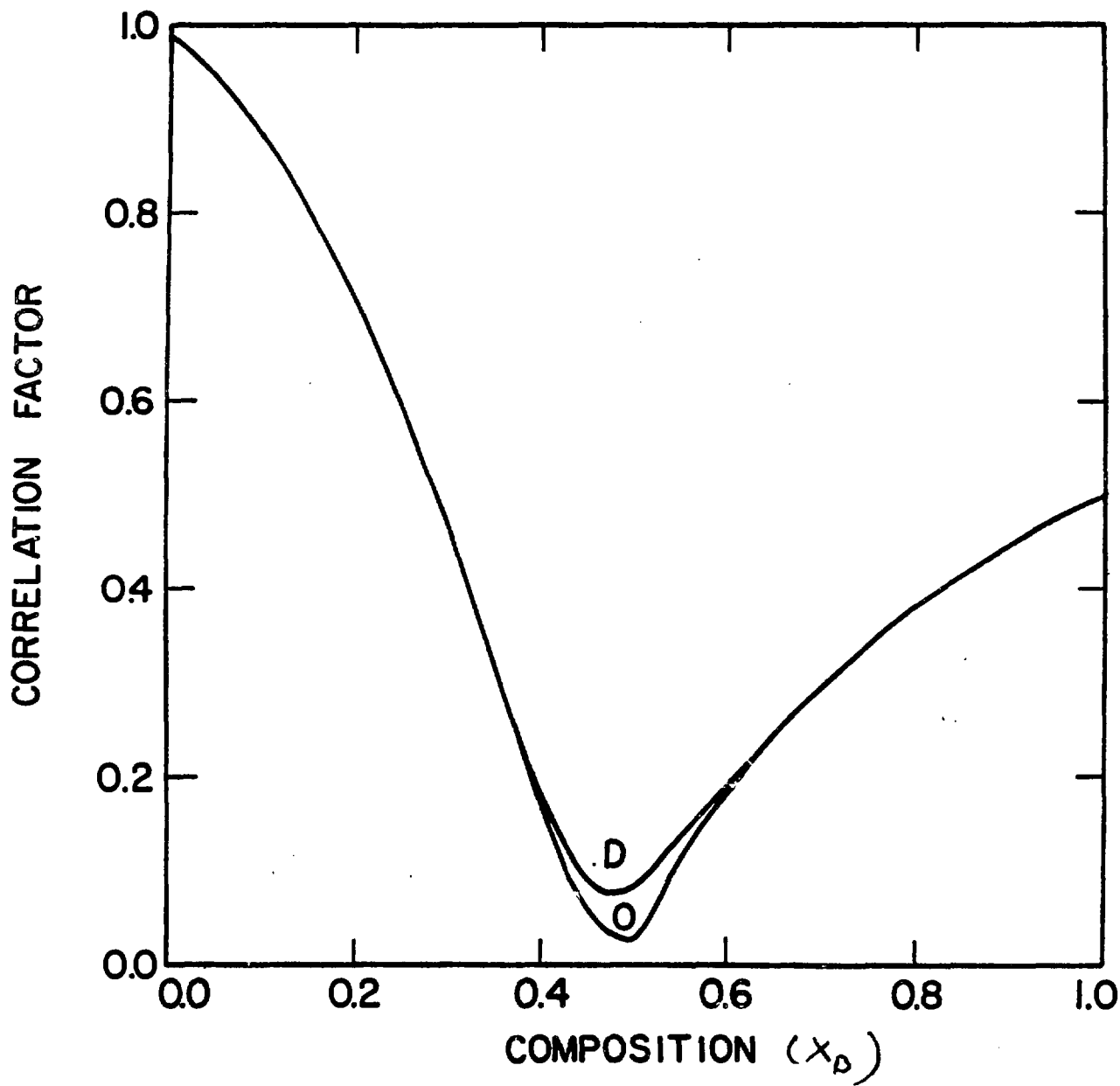


Fig. 9c

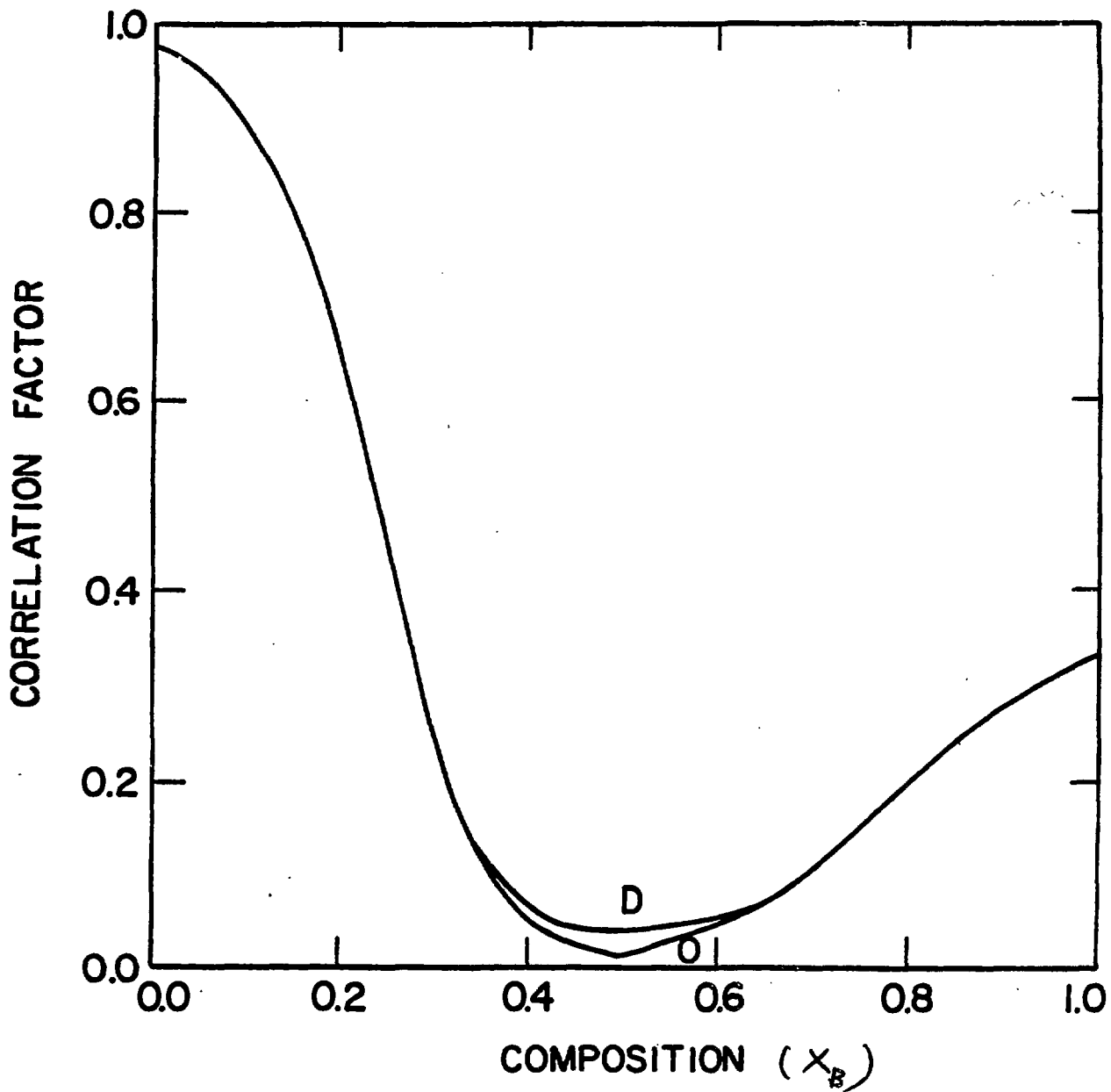


Fig. 9d

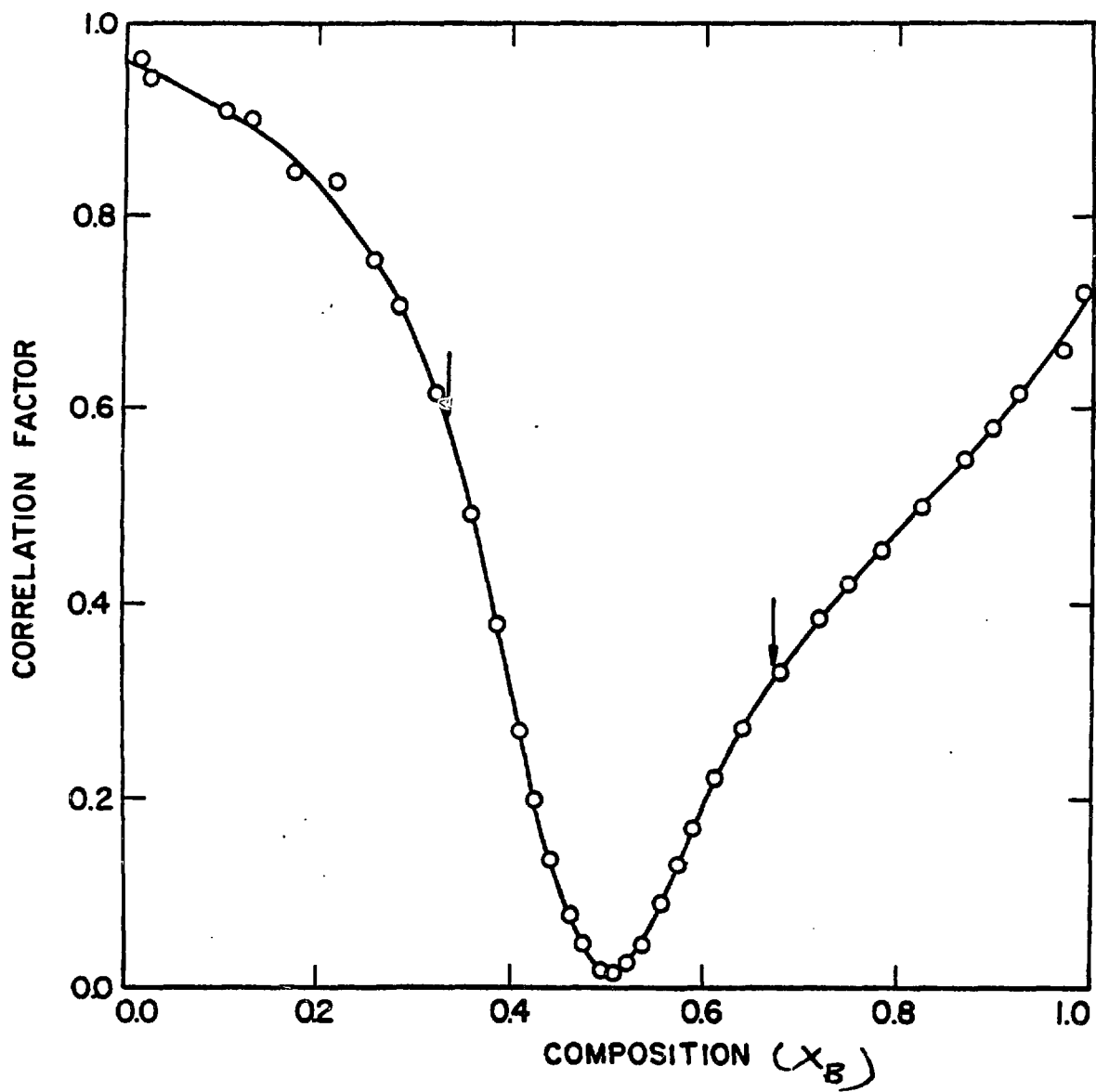


Fig. 10

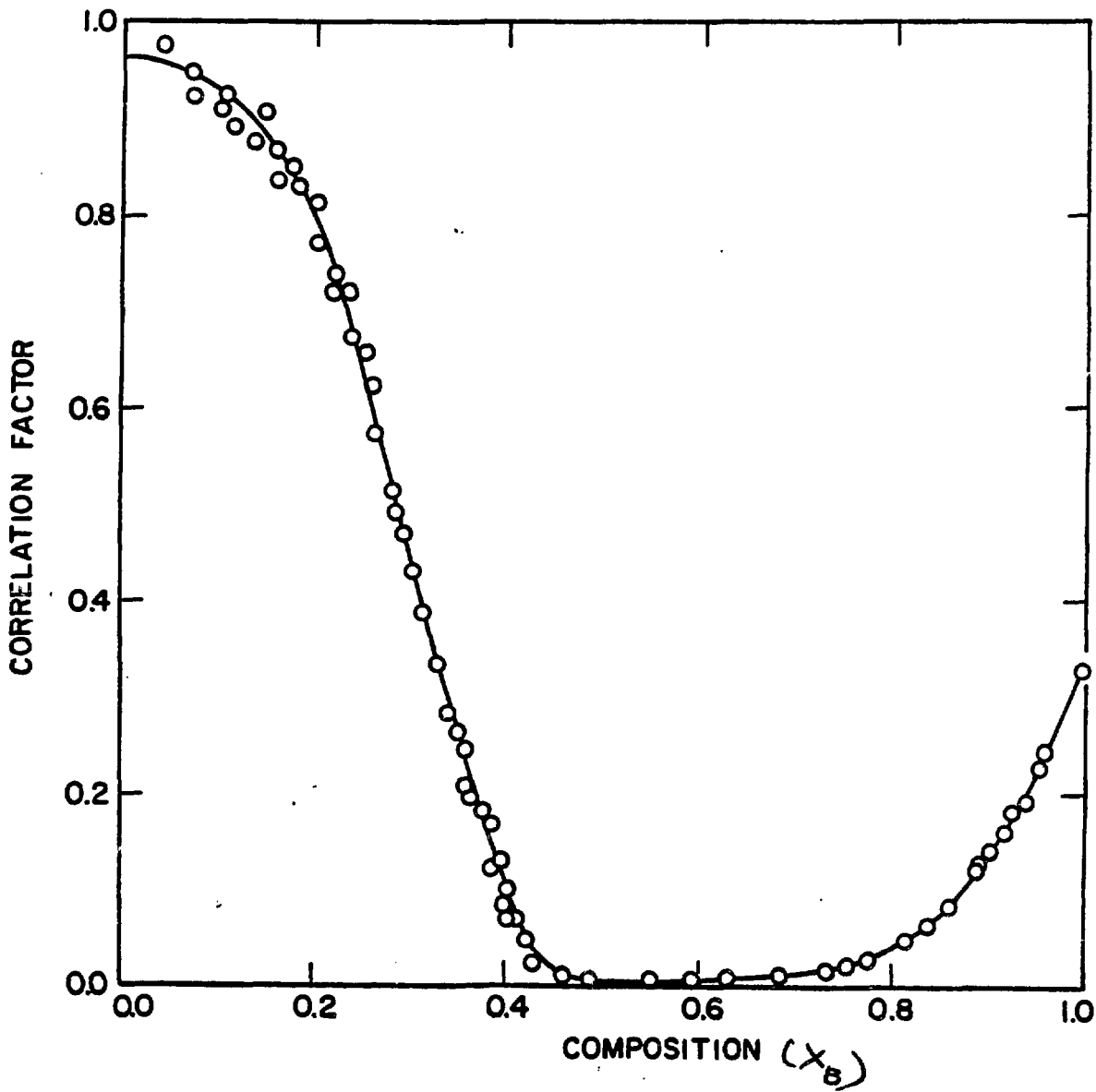


Fig. 11