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Self-consistent approach to the diffusion induced by a centrifugal field in condensed matter: Sedimentation

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A self-consistent approach to the Lamm sedimentation equation is proposed for describing the diffusion induced by a centrifugal (or gravitational) field in a two-component condensed system, particularly for a high solute concentration or a high centrifugal field. In this approach, the driving force inducing the diffusion is expressed by introduction of the effective mass of the surrounding mixture (solvent and solutes) which causes the buoyant force. It is self-consistently represented as a function of concentration in place of the constant value in the Lamm equation. The theory is constructed on the basis of nonequilibrium thermodynamics and the Nernst-Einstein relation considering the effect of concentration change. The resulting diffusion equation is presented in a nonlinear form instead of the linear one of the Lamm equation. The concentration profile in equilibrium state is found by solving the nonlinear diffusion equation. It is shown that the nonlinear effect is significant with increase either in the solute concentration or in the centrifugal field.

I. INTRODUCTION

The transport phenomenon of macroscopic solutes (macromolecules, small solid particles, etc.) induced by a gravitational or centrifugal field in a liquid solvent is widely known as sedimentation. This phenomenon has been used as a method for separating or concentrating matter and determining the molecular weight of macromolecules from the density gradient of a solution (the density-gradient method). This kind of transport phenomenon is expected to occur in another condensed system, where atoms or molecules play the same role as do macroscopic solutes in conventional sedimentation. So far, no extensive theoretical or experimental studies of these kinds of diffusion phenomena have been made. There have been only a few reports of such diffusion in the ultrafast diffusion system of Au atoms in very low concentration in some metals (potassium, sodium, lead, and indium).[1-4] Almost all of these sedimentation phenomena of both macroscopic solutes and atoms or molecules have been analyzed by using the Lamm sedimentation equation, which was first proposed by Lamm in 1929.[5] This classical equation was formulated for axially symmetric macroscopic particles on the basis of macroscopic mechanics and thermodynamics, and it is presented in a linear form.

The fundamental idea of Lamm is that the driving force induced by a centrifugal field acting on a macrosolute is given by the difference between the centrifugal force and the buoyant force caused by the surrounding liquid solvent. This is expressed in a form independent of the solute concentration. According to the theory, the flux of a solute crossing a unit area J is written in linear form as

$$J = D\left[-\nabla C + \frac{r\omega^2 M_{\mathrm{app}}(1-\bar{v}d)}{RT}C\right], \tag{1}$$

where C, D, M_{app}, $\bar{v}$, and d are, respectively, the concentration of solutes per unit volume, the diffusion coefficient, the apparent molecular weight, the specific volume of solute, and the density of solvent. R, T, r, and ω represent the gas constant, absolute temperature, the radius measured from the axis of rotation, and the angular velocity, respectively. In this equation, the first term is induced by the chemical-potential field and the second term represents the external force induced by the centrifugal field.

Several approaches to the Lamm's theory have since been made: for example, Brenner and Condiff extended it for particles of arbitrary shape considering the rotation effect.[6] However, in these theories, self-interaction effects among macroscopic solutes caused by the centrifugal field are not considered, and, therefore, the driving force is not expressed as a function of solute concentration.[7] On the other hand, in the density-gradient method which uses a liquid solvent consisting of two or more components (atoms or molecules), the density of the solvent is given without incorporating the centrifugal effect. In previous studies on liquid solvent,[8-10] the density was either assumed to be constant or else experimentally determined. In solids, the same kind of diffusion of atoms has been analyzed similarly by using the Lamm theory.[1-4] However, when the constituent particles are atoms or molecules, the density of the solvent mixture must change with concentration, especially at higher solute concentrations. Therefore, the Lamm theory is not strictly applicable to the sedimentation of atoms, molecules, or other Brownian particles, particularly for higher solute concentrations.

In this paper a self-consistent equation is proposed for describing the diffusion of atoms induced by a centrifugal field in a two-component condensed system, particularly for a high solute concentration or a high centrifugal field. Although the present theory is basically an extension of the Lamm theory, it is constructed taking account of self-interaction effects among the solutes, on the basis of nonequilibrium thermodynamics and the Nernst-Einstein relation considering the effect of concentration change. The resulting diffusion equation is presented in a nonlinear form, instead of the linear one of the Lamm sedimentation equation. Furthermore, an equilibrium-state solution for a special case is derived to demonstrate the effects of nonlinearity.

II. FORMULATION OF THE SELF-CONSISTENT SEDIMENTATION EQUATION

A. Effective thermodynamic force

In this section we discuss the interdiffusion of solute atoms A in solvent B, for a two-component A-B system. We start with the following assumptions: (1) no temperature gradient, (2) no gravitational field, (3) no electromagnetic field, (4) no effects of stress upon material flow or density change, (5) no appreciable effects of the Coriolis force, and (6) no effect of the shape of the solute particle. We further assume the vacancy mechanism which is usually assumed for diffusion of metals.[11] The theory based on this diffusion mechanism can immediately be applied to metals, and it may also be applicable to molecular or covalent matter. However, the assumptions do not strictly hold for ionic matter, in which diffusion is generally accompanied by electrical diffusion potentials.

In this theory the external force generated by a centrifugal field is formulated by using the buoyant force, as in the Lamm's theory. For a macroscopic particle in a liquid, the buoyant force is usually expressed as the change of potential energy of a solvent (excluding solutes) caused by the movement of solute; this is so that the buoyant force is not affected by the existence of the other solute atoms of the same species, and the term arising from the buoyant force does not contain the variable concentration. Now, we suppose that the external force F_a per atom A induced by the centrifugal field is given by the difference between the centrifugal force and the buoyant force caused by the effective mass of the surrounding solvent mixture including solutes acting on atom A, and expressed as

$$F_a = r\omega^2(m_a - m^*) , \tag{2}$$

where m_a is the mass of atom A, and m^* is the effective mass per atomic volume of A of the surrounding solvent mixture which includes atoms A. According to the present hypothesis, we can say that the buoyant force per atom is expressed as the average change of centrifugal potential energy, caused by statistically replacing a solute atom by one of neighboring atoms regardless of its species. This effective buoyant force defined in Eq. (2) is affected by the presence of the other solute atoms of the same species, and it is therefore self-consistently expressed as a function of concentration, as shown below.

The effective mass m^* per atomic volume of A can be expressed by using the masses and the concentrations of atoms as follows:

$$m^* = \frac{C_a m_a + C_b m_b'}{C_a + C_b} , \tag{3}$$

where C_a and C_b are the concentrations, i.e., numbers of A and B per unit volume, respectively, and m_b' is the mass of B per atomic volume of A which is represented by

$$m_b' = (v_a / v_b) m_b = \alpha m_b , \tag{4}$$

where v_a and v_b are the atomic volumes of A and B, respectively.

Next, we suppose that the density of the solvent mixture varies in proportion to the effective mass, ignoring vacancy increase or phase transition. Hence the density ρ is given by

$$\rho = \rho_0 \frac{m^*}{m_0^*} , \tag{5}$$

where the subscript 0 denotes an arbitrary reference state. The density can also be expressed alternatively as

$$\rho = C_a m_a + C_b m_b . \tag{6}$$

From Eqs. (3), (5), and (6), m^* is self-consistently given as a function of concentration C_a by the expression

$$\begin{aligned} m^*(C_a) = \{ & \rho_0(C_{a_0} + C_{b_0}) m_b' + (C_{a_0} m_a + C_{b_0} m_b')(m_a - m_b) C_a \\ & + [\rho_0^2 (C_{a_0} + C_{b_0})^2 m_b'^2 + \rho_0 (C_{a_0} + C_{b_0})(C_{a_0} m_a + C_{b_0} m_b')(4 m_a m_b - 2 m_a m_b' - 2 m_b m_b') C_a \\ & + (C_{a_0} m_a + C_{b_0} m_b')^2 (m_a - m_b)^2 C_a^2]^{1/2} \} / 2\rho_0 (C_{a_0} + C_{b_0}) . \end{aligned} \tag{7}$$

According to nonequilibrium thermodynamics, the thermodynamic force per atom A induced by the chemical-potential field is represented by

$$X_{a_1} = -T\nabla(\mu_a / T) = -kT \left[1 + \frac{\ln\gamma_a}{\ln c_a} \right] \frac{\nabla c_a}{c_a} , \tag{8}$$

where $c_a = C_a / n$. c_a, μ_a, γ_a, n, and k are, respectively, the fraction of A per unit volume, the chemical potential of A, the activity coefficient of A, the total number of atoms per unit volume, and the Boltzmann constant, and the subscript 1 denotes the chemical-potential field. As a result, the total thermodynamic force X_a relative to the local lattice per atom is expressed as

$$\begin{aligned} X_a &= X_{a_1} + F_a \\ &= -kT \left[1 + \frac{\ln\gamma_a}{\ln c_a} \right] \frac{\nabla c_a}{c_a} + r\omega^2 [m_a - m^*(C_a)] . \end{aligned} \tag{9}$$

B. Nonlinear diffusion equation

According to the phenomenological transport equations based on nonequilibrium thermodynamics,[11] the flux induced by the chemical-potential field and relative to the local lattice J_{a_1} is represented as follows (see Appendix):

$$J_{a_1} = -D_{a_1} \nabla C_a \ , \tag{10}$$

where D_{a_1} is the diffusion coefficient relative to the local lattice of A. On the other hand, if the Nernst-Einstein relation holds for the whole range of concentration, the absolute mobility λ_a of A for the diffusion induced by a centrifugal field is represented as

$$-\lambda_a = \frac{v_{a_2}}{F_a} = \frac{D_{a_2}}{kT} \ , \tag{11}$$

where v_{a_2} and D_{a_2} are, respectively, the velocity of A and the diffusion coefficient relative to the local lattice of A, and the subscript 2 denotes the centrifugal field. D_{a_1} and D_{a_2} are given by Eqs. (A6) and (A14), respectively. The flux induced by a centrifugal field and relative to the local lattice J_{a_2} is represented as follows:

$$J_{a_2} = V_{a_2} C_a = \frac{D_{a_2} F_a C_a}{kT} \ . \tag{12}$$

By transforming the coordinate from the local lattice to the fixed parts of the lattice (see Appendix), the total flux J'_a relative to the fixed parts of the lattice is given by using Eqs. (7), (10), and (12), as follows:

$$\begin{aligned} J'_a &= J'_{a_1} + J'_{a_2} \\ &= -\bar{D}_1 \nabla C_a + \frac{\bar{D}_2 r\omega^2 [m_a - m^*(C_a)]}{kT} C_a \\ &= -\bar{D}_1 \nabla C_a + \frac{\bar{D}_2 r\omega^2 [M_a - M^*(C_a)]}{RT} C_a \ , \end{aligned} \tag{13}$$

with $M_a = Nm_a$, $M^*(C_a) = Nm^*(C_a)$, and $R = Nk$, where M_a, $M^*(C_a)$, and N are the atomic weight of A, and the effective weight of the surrounding solvent mixture per molar volume of A, and Avogadro's number, respectively, and the prime denotes the fixed parts of the lattice. $\bar{D}_1$ and $\bar{D}_2$ are the chemical interdiffusion coefficients relative to the fixed parts of the lattice of A for the diffusion induced by the chemical-potential field and by the centrifugal field, respectively. These coefficients can be expressed in terms of the phenomenological coefficients L_{ij}, the concentrations $C_{i,j}$, etc., as follows (see Appendix):

$$\bar{D}_1 = \frac{kT}{n} \left[\frac{C_b}{C_a} L_{aa} + \frac{C_a}{C_b} L_{bb} - 2L_{ab} \right] \left[1 + \frac{n \ln\gamma}{\ln C} \right] , \tag{14}$$

$$\bar{D}_2 = \frac{kT}{n} \left[\frac{C_b}{C_a} L_{aa} + \frac{C_a}{C_b} L_{bb} - 2L_{ab} \right] . \tag{15}$$

It is noticed that the effect of concentration change on the expression of the fluxes was incorporated by using these chemical interdiffusion coefficients in this theory. The effective weight $M^*(C_a)$ is given from Eq. (7) as follows:

$$\begin{aligned} M^*(C_a) = \{ & \rho_0 N (C_{a_0} + C_{b_0}) M'_b + (C_{a_0} M_a + C_{b_0} M'_b)(M_a - M_b) C_a \\ & + [\rho_0^2 N^2 (C_{a_0} + C_{b_0})^2 M_b'^2 + \rho_0 N (C_{a_0} + C_{b_0})(C_{a_0} M_a + C_{b_0} M'_b)(4M_a M_b - 2M_a M'_b - 2M_b M'_b) C_a \\ & + (C_{a_0} M_a + C_{b_0} M'_b)^2 (M_a - M_b)^2 C_a^2]^{1/2} \} / 2\rho_0 N (C_{a_0} + C_{b_0}) \ , \end{aligned} \tag{16}$$

with $M'_b = Nm'_b$. From Fick's second law in a cylindrical-coordinate representation, the diffusion equation can be derived as follows:

$$\begin{aligned} \frac{\partial C_a}{\partial t} = {} & \bar{D}_1 \frac{\partial^2 C_a}{\partial r^2} + \left[\frac{\bar{D}_1}{r} + \frac{\partial \bar{D}_1}{\partial C_a} \frac{\partial C_a}{\partial r} - \frac{r\omega^2}{RT} \left[\bar{D}_2 [M_a - M^*(C_a)] + \frac{\partial \bar{D}_2}{\partial C_a} [M_a - M^*(C_a)] C_a - \bar{D}_2 \frac{\partial M^*(C_a)}{\partial C_a} C_a \right] \right] \frac{\partial C_a}{\partial r} \\ & - \frac{2\omega^2 \bar{D}_2}{RT} [M_a - M^*(C_a)] C_a \ . \end{aligned} \tag{17}$$

III. EQUILIBRIUM-STATE SOLUTIONS

The nonlinear equations derived in Sec. II are the fundamental equations for describing the diffusion of atoms induced by a centrifugal field in a two-component condensed system. They are clearly different from the equations of Lamm, in that the former are nonlinear while the latter are linear. As shown in the second term of Eq. (9), the nonlinearity comes from the dependency of the buoyant force upon the solute concentration.

In order to discuss the effect of this nonlinearity, we derive the equilibrium-state solution for a special case in which the ideal reference system ($\gamma = 1$, i.e., $\bar{D} = \bar{D}_1 = \bar{D}_2$) is assumed and the atomic volumes of the two components are equal [$\alpha = 1$ in Eq. (4)]. In this case the effective weight per molar volume of A of the surrounding solvent mixture is written as

$$M^*(C_a) = M_b + \frac{M_a - M_b}{C_{a_0} + C_{b_0}} C_a \ . \tag{18}$$

The flux crossing the unit area J'' is given by

$$J''=\bar{D}\left[-\nabla C_a+\frac{r\omega^2(M_a-M_b)}{RT}\left[C_a-\frac{1}{C_{a_0}+C_{b_0}}C_a^2\right]\right]. \tag{19}$$

The equilibrium-state equation can be obtained from Eq. (19) by setting $J''=0$. The solution of this differential equation is given by the concentration ratio C_a/C_{a_0} (or atomic fraction ratio c_a/c_{a_0}) per unit volume

$$C_a/C_{a_0}=c_a/c_{a_0}=\frac{(1+\beta)\exp Y}{1+\beta\exp Y}, \tag{20}$$

where

$$\beta=C_{a_0}/C_{b_0},\quad Y=(M_a-M_b)r^2\omega^2/2RT .$$

In this derivation we chose the reference state as $Y=0$ at the equilibrium state. Equation (20) describes the final concentration distribution as a function of Y for a given value of β. Here β represents the concentration (atomic fraction) ratio of A and B at the reference state. The calculated results of the C_a/C_{a_0} distribution for several values of β is shown in Fig. 1. The same solution for B can also be obtained in a similar way.

For a comparison, we show the equilibrium-state solution of the equation of Lamm [Eq. (1)], which is

$$C/C_0=\exp(Y'), \tag{21}$$

where

$$Y'=(1-\bar{v}d)M_{\text{app}}r^2\omega^2/2RT .$$

This solution corresponds to the solution of Eq. (19), where the limit of $\beta\rightarrow 0$ is taken. Figure 1 clearly shows that the distribution C_a/C_{a_0} (except that for $\beta\rightarrow 0$) deviates more from that of the Lamm solution with an increase either in the concentration or in the centrifugal field. Furthermore, when $M_a>M_b$ and $|Y|\rightarrow\infty$, unlike those of the Lamm solution, each C_a/C_{a_0} value (except that for $\beta\rightarrow 0$) approaches constant values of $1/\beta+1$ (at which conditions the lattice space is occupied by only one species of atom A). In other words, it is pointed out that the diffusion is not allowed any further at the point where only one species of solute occupies part of the lattice space. In contrast, at low concentration of one component, the diffusion can be well analyzed by using the Lamm sedimentation equation.

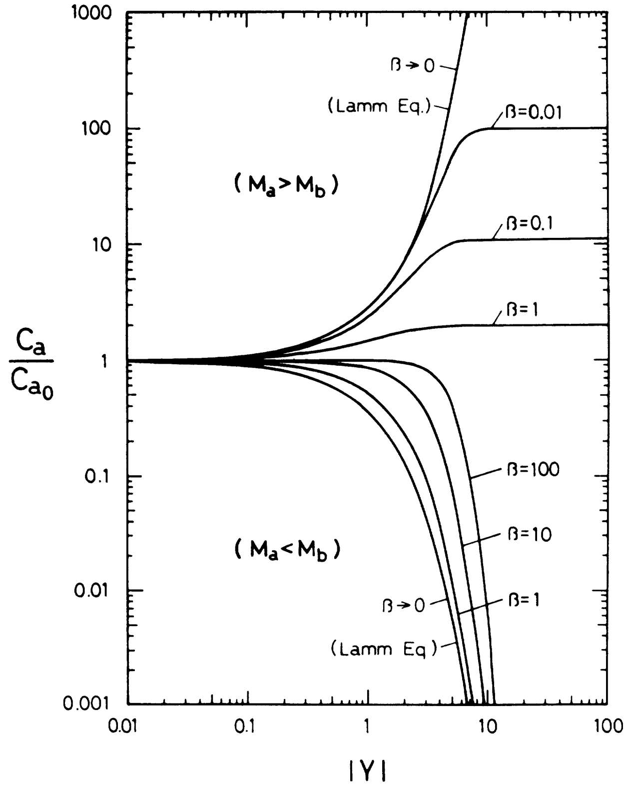

FIG. 1. The C_a/C_{a_0} distributions vs $|Y|$ at the equilibrium state, when the atomic volumes are equal ($\alpha=1$) in the ideal reference system ($\gamma=1$). Here $Y=(M_a-M_b)r^2\omega^2/2RT$ and $\beta=C_{a_0}/C_{b_0}$.

IV. CONCLUDING REMARKS

A self-consistent approach to the Lamm sedimentation equation is proposed for describing the diffusion of atoms induced by a centrifugal field in a two-component system of condensed matter. This theory is constructed on the basis of nonequilibrium thermodynamics, the vacancy mechanism, and the following main assumptions: (1) the external force is given by the difference between the centrifugal force and the buoyant force which is caused by the effective mass of the surrounding solvent mixture including solutes; (2) the phenomenological transport equations and the Nernst-Einstein relation hold for the whole range of concentrations; and (3) the density of the solvent mixture varies in proportion to the effective mass. The resulting nonlinear diffusion equations are different from the linear equations of Lamm. The effect of concentration change on the expression of the fluxes was considered by introducing the chemical interdiffusion coefficients in this theory. Furthermore, it is shown that the nonlinear effect becomes significant with an increase either in the concentration or in the centrifugal field.

In this paper we have limited our discussion to the cases of a two-component condensed system where the solute is atoms and the solvent is either of metallic, molecular, or covalent nature. However, this theory can also be applied to the diffusion of molecules and other Brownian particles, and can be extended to cases with three or more components, including ionic matter. In addition, if centrifugal field $r\omega^2$ is replaced by gravitational field g, this theory is also immediately applicable to gravitational-field-induced diffusion.

The diffusion phenomena of atoms induced by a centrifugal field in condensed matter may be used as a practical method of changing both the concentrations of impurities or solutes and the density distributions, of creating chemically nonequilibrium steady states, etc. The present theory is useful to analyze these diffusion phenomena of atoms, particularly for high solute concentrations or a high centrifugal (gravitational) field. In addition, the present theory may also be used in the field of conventional sedimentation, to describe the behavior of Brownian solid particles, to analyze precisely the density distributions of liquid solution solvent in the density-gradient method, and further to compute the sedimentation process in the planet, satellite, etc.

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APPENDIX: DERIVATION OF THE CHEMICAL INTERDIFFUSION COEFFICIENTS

Here the chemical interdiffusion coefficients relative to the fixed parts of the lattice for the diffusion of the components A and B induced by both a chemical-potential field and a centrifugal field are derived on the basis of the nonequilibrium thermodynamics and vacancy mechanism.[11]

If the vacancies exist everywhere in thermal equilibrium, fluxes induced by a chemical-potential field and relative to the local lattice of A and B crossing a unit area are represented as follows (phenomenological laws):

$$\begin{aligned} J_{a_1} &= L_{aa}X_{a_1} + L_{ab}X_{b_1} , \\ J_{b_1} &= L_{ab}X_{a_1} + L_{bb}X_{b_1} , \end{aligned} \tag{A1}$$

where L_{ij} are the phenomenological coefficients, X_i are the thermodynamic forces, and the subscript 1 denotes the chemical-potential field. Since temperature is uniform, the forces are related via the Gibbs-Duhem equation

$$c_a X_{a_1} + c_b X_{b_1} = 0 . \tag{A2}$$

From Eqs. (A1) and (A2), we have

$$J_{a_1} = \left[L_{aa} - \frac{c_a}{c_b} L_{ab} \right] X_{a_1} . \tag{A3}$$

The thermodynamic force induced by the chemical potential is

$$X_{a_1} = T\nabla(\mu_a / T) . \tag{A4}$$

The chemical potential of A can be written in the form

$$\mu_a = \mu_{0a}(T,P) + kT \ln(c_a \gamma_a) . \tag{A5}$$

Thus from Eqs. (A4) and (A5), Eq. (A3) becomes

$$J_{a_1} = -\left[L_{aa} - \frac{c_a}{c_b} L_{a,b} \right] kT \left[1 + \frac{\ln\gamma_a}{\ln c_a} \right] \frac{\nabla c_a}{c_a} ,$$

so that we may call

$$D_{a_1} = \frac{kT}{n} \left[\frac{L_{aa}}{c_a} - \frac{L_{ab}}{c_b} \right] \left[1 + \frac{\ln\gamma_a}{\ln c_a} \right] \tag{A6}$$

the diffusion coefficient relative to the local lattice of A for the diffusion induced by a chemical-potential field. There is a corresponding expression for the coefficient D_{b_1} relating J_{b_1} to $-\nabla c_b$, i.e.,

$$D_{b_1} = \frac{kT}{n} \left[\frac{L_{bb}}{c_b} - \frac{L_{ab}}{c_a} \right] \left[1 + \frac{\ln\gamma_b}{\ln c_b} \right] . \tag{A7}$$

The concentration distribution will therefore yield a diffusion coefficient linking the concentration gradient to the flux of atoms relative to the fixed part of the lattice. If the diffusion proceeds without the formation of pores within the specimens and without the occurrence of bumps or kinks on the surface, the fluxes relative to the fixed part of the lattice J'_{a_1} and J'_{b_1} are expressed by using J_{a_1}, J_{b_1}, c_a, and c_b as

$$J'_{a_1} = J_{a_1} - c_a(J_{a_1} + J_{b_1}) , \tag{A8}$$

$$J'_{b_1} = J_{b_1} - c_b(J_{a_1} + J_{b_1}) . \tag{A9}$$

In this ideal situation, the net flux of the atoms $J_{a_1} + J_{b_1}$ is counterbalanced by an opposite bulk movement of the lattice, and Eqs. (A8) and (A9) follow. From Eq. (A8)

$$J'_{a_1} = -(c_b D_{a_1} + c_a D_{b_1}) n \nabla c_a = -\bar{D}_1 n \nabla c_a . \tag{A10}$$

$\bar{D}_1$ is called the chemical interdiffusion coefficient relative to the fixed parts of the lattice of A. By Eqs. (A6) and (A7) it is

$$\bar{D}_1 = \frac{kT}{n} \left[\frac{c_b}{c_a} L_{aa} + \frac{c_a}{c_b} L_{bb} - 2L_{ab} \right] \left[1 + \frac{\ln\gamma}{\ln c} \right] . \tag{A11}$$

The similar chemical interdiffusion coefficient for the diffusion induced by a centrifugal field can be derived by using the Nernst-Einstein relation. If the Nernst-Einstein relation holds for the whole range of concentration, the absolute mobility λ_a of A for the diffusion induced by a centrifugal field is represented by

$$-\lambda_a = \frac{v_{a_2}}{F_a} = \frac{D_{a_2}}{kT} , \tag{A12}$$

where v_{a_2}, F_a, and D_{a_2} are, respectively, the velocity of A, the external force acting on an atom, and the diffusion coefficient relative to the local lattice of atom A for the diffusion induced by a centrifugal field; and the subscript 2 denotes the centrifugal field. Then, the flow J_{a_2} relative to the local lattice is written, like the Eq. (A3), as

$$J_{a_2} = \left[L_{aa} - \frac{c_a}{c_b} L_{ab} \right] F_a = v_{a_2} n c_a = \frac{D_{a_2} F_a n c_a}{kT} . \tag{A13}$$

Therefore the diffusion coefficient relative to the local lattice is written as

$$D_{a_2}=\frac{kT}{n}\left[\frac{L_{aa}}{c_a}-\frac{L_{ab}}{c_b}\right],\quad D_{b_2}=\frac{kT}{n}\left[\frac{L_{bb}}{c_b}-\frac{L_{ab}}{c_a}\right]. \tag{A14}$$

As a result, the chemical interdiffusion coefficient relative to the fixed parts of the lattice of A for the diffusion induced by a centrifugal field is written in the same way as in the derivation of Eq. (A11), as follows:

$$\bar{D}_2=\frac{kT}{n}\left[\frac{c_b}{c_a}L_{aa}+\frac{c_a}{c_b}L_{bb}-2L_{ab}\right]. \tag{A15}$$

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