

Application of refined theory of liquids to the diffusion in liquid Ag-Cu alloys

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Abstract

The diffusion phenomena in liquid mixtures have not well analyzed from the microscopic point of view. The theories required for their analysis are summarized on the basis of refined hard sphere model. The extended Rice-Alnatt theory for the friction coefficient of liquids mixtures is coupled with the Einstein relation whose friction coefficient can be evaluated with the aid of the molecular dynamics of binary hard sphere mixtures. The preliminary application of this approach is described for liquid Ag-Cu system.

1. Introduction

The diffusion in liquid alloys is complicated because of the existence of many kinds of diffusion coefficients. The mutual(inter) diffusion coefficient is the most popular diffusion coefficient in alloys and is practically important, for example, for the solidification processes and the crystal growth process of alloys, and semiconductors. The mutual diffusion coefficient is measured under the concentration gradient. Because of the existence of this concentration gradient, atoms in the mutual diffusion processes experience the different circumstances with the proceeding of diffusion. On the other hand, the impurity and the self- diffusion coefficients are measured under the lack of concentration gradient. Atoms in the self-diffusion and impurity diffusion processes experience the same circumstance with the proceeding of diffusion. Therefore, these diffusion coefficients must be strictly discriminated each other. Up to date, the theoretical study has been performed only for pure liquids. In this study, a simple prescription is given for the self-diffusion in liquid mixtures from a point of view of refined hard sphere model.

2. The self-diffusion in liquid mixtures from the hard sphere model

The self-diffusion coefficient in dense gas mixtures can be given in the form of Einstein relation.

$$D_i = \frac{k_B T}{\zeta_{HS,i}} \quad (1)$$

In this equation, $\zeta_{HS,i}$ represents the friction coefficient of component i ; k_B the Boltzmann's constant and T the absolute temperature. The explicit expression of friction coefficient is given as follows¹⁾:

$$\zeta_{HS,i} = \frac{8}{3} \sum n_j g_{HS,ij} (\sigma_{ij})^2 (2\pi M_{ij} k_B T)^{1/2} \quad (2)$$

In this equation, n_j is the number density of component j . The summation Σ is taken for $j=1$ and $j=2$. The symbol, M_{ij} , is the reduced mass per particle defined by the atomic mass per particle of respective

component, as in the following equation.

$$\frac{1}{M_{ij}} = \frac{1}{M_i} + \frac{1}{M_j}. \quad (3)$$

The symbol σ_{ij} is the distance of hard sphere contact between components i and j . The symbol $g_{HS,ij}(\sigma_{ij})$ is the radial distribution function at hard sphere contact, σ_{ij} of i - j pairs. In liquids, the effect of far higher density than the case of dense gas can be taken into account similarly to the case of pure liquids. That is, by using the back scattering factor, $C_{BS,i}$ of component i , the self-diffusion coefficient in liquid mixtures of species i is written in the following equation.

$$D_i = \frac{k_B T}{\zeta_{HS,i}} C_{BS,i}. \quad (4)$$

3. The determination of the back scattering factor

The back scattering factor in liquid mixtures is an extremely complicated and difficult many body problem. Therefore, as in the case of one component liquid, this is determined by comparing the results of computer simulations for the self-diffusion coefficient of component i with the so called Enskog formula of mixtures (Eqns.(1) and (2)). The program for the molecular dynamics of hard sphere mixtures has been already developed and is available for evaluation of $\zeta_{HS,i}$.

4. Determination of the hard sphere diameters and the packing fraction for liquid alloys based the refined theories of liquids.

4.1 The determination from Gibbs-Bogoliubov variational method

The Gibbs-Bogoliubov inequality can be used for the determination of hard sphere diameters for liquid mixtures. The Gibbs-Bogoliubov inequality can be written as the same form to that of pure liquids.

$$NF \leq NF^0 + \langle \Phi - \Phi^0 \rangle_0. \quad (5)$$

The symbols F and F^0 indicate the Helmholtz free energy of real system and that of reference system respectively. The symbols Φ and Φ^0 indicate respectively the potential energy of real system and that of reference system. The bracket, $\langle \rangle_0$, is the average of ensemble composed of reference system.

If the assembly of hard sphere mixtures is taken as the reference system, structure-dependent part of the excess free energy F_s is written as follows²⁾:

$$F_s \leq F_s^0 + 2\pi n \sum_{i,j=1}^2 c_i c_j \int_{\sigma_{ij}}^{\infty} r^2 g_{ij}^{HS}(r) \phi_{ij}(r) dr. \quad (6)$$

In this equation, $g_{ij}^{HS}(r)$ is the radial distribution function of hard sphere mixture between i - j pair and

$$F_s^0 = k_B T \left[-\frac{3}{2} (1 - y_1 + y_2 + y_3) + (3y_2 + 2y_3)/(1 - \eta) + \frac{3}{2} (1 - y_1 - y_2 - \frac{1}{3}y_3) + (y_3 - 1) \ln(1 - \eta) \right]. \quad (7)$$

Coefficients, y_1 , y_2 and y_3 are given as follows:

$$y_1 = x(1-x)(1-\alpha)^2(1+\alpha)/d, \quad (8)$$

$$y_2 = x(1-x)\alpha(1-\alpha)^2[(1-x)\alpha^2 + x]/d^2, \quad (8b)$$

$$y_3 = [(1-x)\alpha^2 + x]^3/d^2, \quad (8c)$$

$$d = (1-x)\alpha^3 + x. \quad (9)$$

In these equations, $x = n_2 / n(n = n_1 + n_2)$, where n_i is the number density of species i ; $\alpha = \sigma_1 / \sigma_2$ where σ_i is the hard sphere diameter of species i , and $\eta = \frac{\pi}{6}(n_1\sigma_1^3 + n_2\sigma_2^3)$. The hard sphere diameter is determined by the condition that the right hand side of Eqn.(6) may be as small as possible.

4.2 Determination of from the Weeks-Chandler-Andersen perturbation theory of liquids

In the WCA scheme³⁾, the interionic potentials of i - j pair can be divided into the repulsive part, ϕ_{ij}^0 and the attractive part ϕ_{ij}^1 , as follows:

$$\phi_{ij}(r) = \phi_{ij}^0(r) + \phi_{ij}^1(r). \quad (10)$$

$$\phi_{ij}^0(r) = \phi_{ij}(r) - \phi_{ij}^1(\lambda_{ij}), \quad r < \lambda_{ij} \quad (10a)$$

$$= 0, \quad r > \lambda_{ij} \quad (10b)$$

$$\phi_{ij}^1(r) = \phi_{ij}(\lambda_{ij}), \quad r < \lambda_{ij} \quad (10c)$$

$$= \phi_{ij}(r), \quad r > \lambda_{ij} \quad (10d)$$

In this equation, the symbol λ_{ij} is the distance at first minimum of potential.

The Blip function, $B_{ij}(r)$, for binary mixtures can be defined as follows:

$$B_{ij}(r) \equiv g_{ij}^0(r) - g_{ij}^{\text{HS}}(r). \quad (11)$$

In this equation, $g_{ij}^0(r) = y_{ij}^{\text{HS}}(r) \exp(-\phi_{ij}^0(r)/k_B T)$; $y_{ij}^{\text{HS}}(r) \equiv \exp(\phi_{ij}^{\text{HS}}(r)/k_B T) g_{ij}^{\text{HS}}(r)$.

Helmholtz free energy in the WCA method can be written as follows:

$$F_{\text{WCA}} = F_{\text{HS}} + \frac{n^2}{2} \sum_{i,j=1}^2 c_i c_j \int \mathbf{dr} B_{ij}(r) + \text{terms of higher order in } B_{ij}. \quad (12)$$

Hard sphere diameters are determined by following requirement.

$$\sum_{i,j=1}^2 c_i c_j \int \mathbf{dr} B_{ij}(r) = 0 \quad (13)$$

5. Preliminary application to liquid Ag-Cu systems

The application of these theories to liquid Ag-Cu alloys is only in the preliminary stage. In this study, only a self-diffusions in liquid Ag and liquid Cu are discussed as a starting point of the analysis described here. Interionic potential was calculated by using the empty core model potential⁴⁾ as a bare potential of ions and the Utsumi-Ichimar⁵⁾ form as the dielectric screening function. The core parameters adopted are respectively 0.099nm for liquid Ag and 0.093nm for liquid Cu. In Figure 1 the calculated results of the self-diffusion coefficient in liquid Ag and Cu is shown. The agreement between theory and experiment is rather good. Therefore the present study is a starting point of study of diffusion of liquid alloys. In future, this kind of calculation should be extended into liquid mixtures.

As described in Introduction, in liquid alloys there are many kinds of diffusion coefficients, such as impurity diffusion coefficient and mutual diffusion coefficient in addition to the self-diffusion coefficient discussed here. In principle, the impurity diffusion coefficient can be discussed similarly to the case of the self-diffusion coefficient described here. In the case of mutual diffusion coefficient in alloys, only the Darken's relation is known theoretically though its reliability has not been confirmed. Therefore, it is important to advance the Darken's relation from the experimental point of view and theoretical point of view.

References

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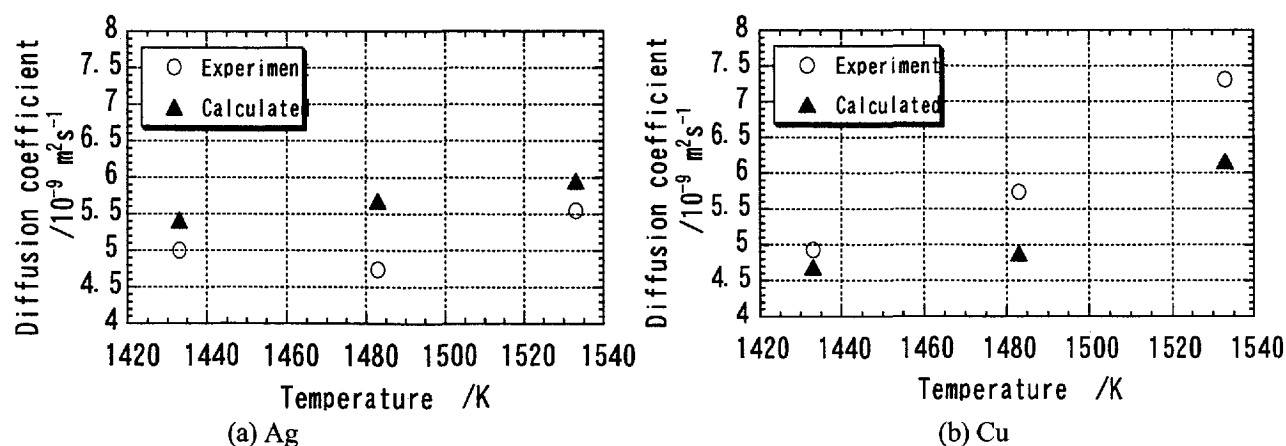


Fig.1 The prediction of self-diffusion coefficient in liquid Ag and liquid Cu based on the Gibbs-Bogoliubov variational method.