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SELF-DIFFUSION OF INDIUM AND BISMUTH IN MOLTEN $In_{0.5}Bi_{0.5}$ ALLOY AT DIFFERENT THERMODYNAMIC STATE

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ABSTRACT

This research work focuses on the theoretical study of atomic transport properties of molten $In_{0.5}Bi_{0.5}$ alloy at different thermodynamic states. Particularly, the self-diffusion coefficients (D_i) of indium (In) and bismuth (Bi) in $In_{0.5}Bi_{0.5}$ alloy are explored by utilizing Distribution Function Method, which is based on the statistical mechanical theory. Inter-ionic interactions and pair distribution function are two main components of this method. The inter-ionic interactions are modeled by using local pseudopotential known as Brettonet-Silbert model, while the pair distribution function is derived by the Ascroft –Langreth theory. The effective hard sphere diameter is the main ingredient to calculate the D_i, which is deduced from the thermodynamic perturbative theory called the Linearized Weeks-Chandler-Anderson method. The calculated results indicate that the value of D_i for In agrees well with the available experimental data in the low temperature region.

Keywords: *Self-diffusion coefficient, Liquid metal alloys, Distribution function method, Pseudopotential*

1. INTRODUCTION

Research on transport properties, particularly diffusion has garnered significant interest of scientists worldwide, including physicist, chemist, metallurgist, and biologist due to their multifaceted applications. For instance, the diffusion of reactant species is utilized for controlling rates of many important reactions involved in industrial production processes. In addition, the knowledge of diffusion is used to determine the cooling rates of glass formation. Moreover, metabolic activities in the human body are perceived by using the information of diffusion of various fluids [1-16].

In this study, a theoretical investigation is performed to examine the atomic transport properties (ATP) such as the self-diffusion coefficients (D_i) of less simple liquid metal alloy. Recently, the D_i of molten $In_{0.5}Bi_{0.5}$ alloy are measured experimentally by using capillary reservoir method and oscillating cup viscometer over a wide range of temperatures [17]. It is noticed that measurement of the D_i of liquid metals at different temperature is very challenging because of difficulty of controlling. This happens reasoning that metal undergoes interactions with the materials of the container and the ambient, as well as owing to their low viscosity. As far our best knowledge, there is not any theoretical model describing the D_i of molten $In_{0.5}Bi_{0.5}$ alloy. Therefore, it is essential to explore if any existing theory can be utilized to sufficiently elucidate the ATP, specifically the D_i of liquid metal alloys observed in experiments.

The ATP of metallic liquid and their binary alloys are advanced employing many theories [18]. The Mode Coupling Method (MCM) and the Distribution Function Method (DFM) are few of them, which are constructed following distinct principles, however, both methods have their own drawbacks. In the MCM approach, main ingredient is dynamic structure factor (S_{ij}), which can be complicated computing theoretically. On the contrary, the DFM, which is coined by Rice and Allnat (RA) [3] is very appropriate because of its convenient mathematical framework. Besides, this theory provides transparent realization of the criticality of each component and their specific contributions for various mechanism imbued. Furthermore, the RA theory has recently been modified capable of explaining the ATP of metallic binary alloys in the liquid state [4, 5].

In the RA theory, the effective pair potential (V_{ij}) is divided into two components: a long–range soft part and short–range hard core part. The reason for dividing the V_{ij} is that the statistical effects resulting from the short repulsive core of the V_{ij} at short interionic distances can be easily distinguished from the other statistical event. In the DFM, the D_i of an atom or ion varies inversely with the associated friction coefficient. The friction coefficient has hard part and soft part, and the D_i is determined from their combined effect. The hard part comes from momentum transfer during hard core collision, while the soft is associated with the region $r > \sigma$ (σ is the hard sphere diameter). The small step diffusion theory is exploited to derive the friction coefficient.

Since the RA theory directly depends on first and second derivatives of the V_{ij}, the ATP are very delicate to the nature of the potential. Thus, when studying ATP of liquid simple metal alloys, it is required to choose proper potential for the concerned system. Brettonet-Silbert (BS) suggested a local model [19] for describing the inter-ionic interactions of liquid simple metals. This model has already been succeeded in predicting the liquid structure for less simple [11] and transition metals [19-21]. Additionally, the BS model has successfully described the ATP of elemental [11] and binary alloys, as well as their electronic and thermodynamic properties [22, 23]. This model is used in this work because it has already been verified in the theory of ATP.

Partial correlation function (g_{ij}) is another essential ingredient needed to calculate the D_i, which is deduced from the static S_{ij} for hard spheres. The AL theory is employed to derive the static S_{ij}. In this process the effective σ is required, which are formulated using the Linearized Weeks-Chandler-Anderson (LWCA) theory [24].

In the present work, the DFM developed by RA [3] is used to investigate the D_i of In and Bi in molten $In_{0.5}Bi_{0.5}$ alloy that has previously been effectively implemented for liquid Ag_xSn_{1-x} alloys [23] and projected the values of D_i and viscosity with acceptable discrepancies. Therefore, the current work is a testament to examine the suitability of applying DFM for systems beyond Ag_xSn_{1-x}.

2. THEORY

Theories associated with the calculation of ATP using the distribution function method are as follows:

2.1 The effective pair potential

The local electron-ion interaction in the pseudopotential theory can be formulated considering the effects of *sp* and *d*-band contributions [19] for the metallic system as:

$$W(\mathrm{r}) = \begin{cases} \sum_{m=1}^{2} G_m exp\left(\frac{-\mathrm{r}}{\mathrm{ma}}\right), & \text{for } r < R_c \\ -\frac{Ze^2}{r}, & \text{for } r > R_c \end{cases} \qquad (1)$$

where a, R_c and Z are the softness parameter, core radius and the effective s-electron occupancy number, respectively. G_1 and G_2 can be expressed in terms of a, R_c and Z [20] as:

$$G_1 = \frac{Ze^2}{R_c}\left(1 - \frac{2a}{R_c}\right) exp\left(\frac{\mathrm{R_c}}{\mathrm{a}}\right) \qquad (2)$$

$$G_2 = \frac{2Ze^2}{R_c}\left(\frac{a}{R_c} - 1\right)\ exp\left(\frac{\mathrm{R_c}}{2\mathrm{a}}\right) . \qquad (3)$$

The effective partial pair interionic potentials are then described as [25]:

$$V_{ij} = \frac{Z_i Z_j e^2}{r}\left[1 - \frac{2}{\pi}\int \mathrm{F}_{\mathrm{ij}}^{\mathrm{N}} \frac{\sin(qr)}{q} \mathrm{dq}\right] \qquad (4)$$

where $F_{ij}^{N}(\mathrm{q})$ are the characteristics of normalized energy wave number and expressed as:

$$F_{ij}^{N}(\mathrm{q}) = \left[\frac{q^2}{4\pi e^2 \rho \sqrt{Z_i Z_j}}\right]^2 W_i(q) W_j(q)\left[1 - \frac{1}{\epsilon(q)}\right]\left[\frac{1}{1 - G(q)}\right] \qquad (5)$$

where $W(q)$, $\epsilon(q)$ and $G(q)$ are the form factor, dielectric function, and the local field correction, respectively. Here, $\epsilon\ (q)$ and $G\ (q)$ are obtained from the work of [26], as their form satisfies the compressibility sum rule and short-range correlation condition. Moreover, these functions are applicable over broad range of metallic densities.

2.2 The static structure factor

The partial structure factor (S_{ij}) are calculated according to original work of AL [27]:

$$S_{ij}(q) = \delta_{ij} + \left(C_i C_j\right)^2 \rho \int \left[g_{ij} - 1\right] exp[-\mathrm{i}\mathbf{q}.\mathbf{r}] d^3\mathrm{r} \qquad (6)$$

The concentrations of the two spheres in the mixture and the σ are two important parameters for enumerating S_{ij}, where σ are calculated by using LWCA theory [24]. The net packing fraction y of the mixture is taken as:

$$\mathrm{y} = y_1 + y_2 = \frac{\pi}{6}\left(C_1 \rho_1 {\sigma_1}^3 + C_2 \rho_2 {\sigma_2}^3\right) \qquad (7)$$

where C_j indicates the concentration of jth component. Now applying the inverse Fourier transformation of S_{ij} (q), we get the corresponding g_{ij}:

$$g_{ij} = 1 + \frac{1}{(2\pi)^3 \sqrt{C_i C_j}} \int \left(\mathrm{S_{ij}} - \delta_{\mathrm{ij}}\right) exp(\mathrm{i}\mathbf{q}.\mathbf{r}) d^3 r \qquad (8)$$

2.3 Diffusion coefficient for alloys

There are two types of diffusion coefficient: D_i and inter-diffusion coefficient. The theories for the calculation of D_i in pure metals are modified for the liquid alloys. The friction coefficient of atom i arises due to hard-core parts takes the form:

$$\xi_i^{(H)} = \frac{3}{8}\sum_{i=1}^{2}\rho_i g_{ij}\left(\sigma_{ij}\right)\sigma_{ij}{}^2\left(2\pi m_{ij}kT\right)^2 \tag{9}$$

where, reduced mass can be written as:

$$m_{ij} = \frac{m_i m_j}{m_i+m_j}\,.$$

According to small-step theory, the soft part of the friction coefficient is expressed as:

$$\xi_i^{(S)} = \rho_i\xi_{ii}^{(S)} + \rho_j\xi_{ij}^{(S)} \tag{10}$$

where
$$\xi_{ij}^{(S)} = \left(\frac{1}{\xi_i^{(S)}} + \frac{1}{\xi_j^{(S)}}\right)C_{ij} \tag{11}$$

with
$$C_{ij} = \frac{m_{ij}}{3}\int\left(v_{ij}'' + \frac{2}{r}v_{ij}'\right)r^2 g_{ij}(r)dr \tag{12}$$

here superscripts (H) and (S) indicate the contribution of hard and soft part, respectively. Single and double prime over v_{ij} denote the first and second derivatives with respect to r, respectively.

Finally, the diffusion coefficient for the liquid binary alloys can be written as:

$$D_i = \frac{kT}{\left(\xi_i^{(H)}+\xi_j^{(S)}\right)}\quad . \tag{13}$$

3. RESULTS AND DISCUSSION

The crucial ingredients for enumeration of the ATP, specifically the D_i are the V_{ij} and the g_{ij} for hard sphere. The V_{ij} involves the parameters such as core radius (R_c), softness parameter (a) and *s*–electron occupancy number (Z). Generally, the values of Rc are obtained by fitting to the physical properties of the system under study [27, 28], while the value of softness parameter a is established by fitting the S_{ij} at low q to available experimental data [20].

Table. 1: R_c (a. u), a (a. u) and Z for the calculations of D_i for molten $In_{0.5}Bi_{0.5}$ alloy.

Elements	R_c (a.u)	a (a.u)	Z
In	1.32	0.278	1.3
Bi	1.49	0.317	1.7

The values of R_c and a are given in the Table. 1, which are taken from the work of Bhuiyan *et al.* [21]. The authors in Ref. [21] have chosen the values of Z (Table. 1) for In and Bi in such a way that the best fit is ensured with the experimental data of g_{ij} from Ref. [28].

2.25

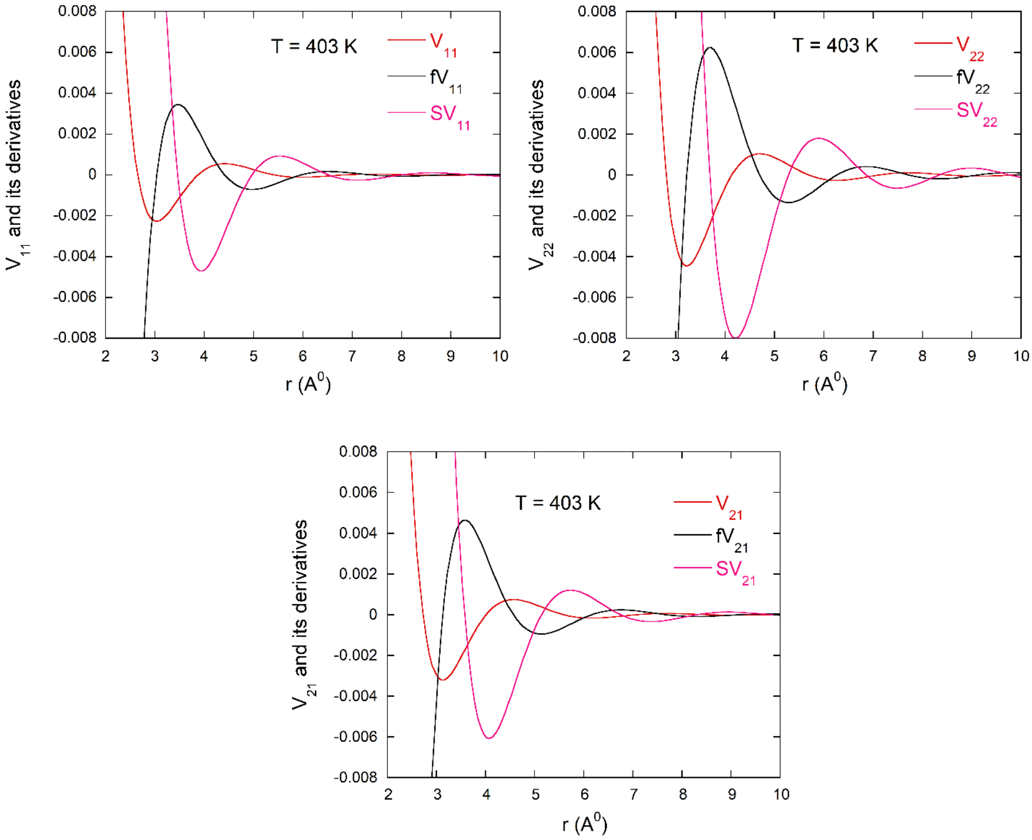

Fig. 1: The effective partial pair potentials (V_{ij}) and their derivatives for $In_{0.5}Bi_{0.5}$ for T= 403 K.

Figure 1 shows V_{ij} and their first and second derivatives, which are obtained inserting values of R_c, a and Z into the BS model for temperature at 403 K. The first derivative gives the slope, while the second derivative gives the curvature of the potential. Typically, when the slope is positive, the curvature is negative, and vice versa. This feature is excellently illustrated in the figures. This demonstration thus revealed accuracy of numerical calculations of this work.

Figure 2 illustrates g_{ij} for the molten $In_{0.5}Bi_{0.5}$ alloy at three (385 K, 403 K, and 573 K) representative temperature. At the same concentration, they are almost identical feature, and this consistent feature is clearly demonstrated.

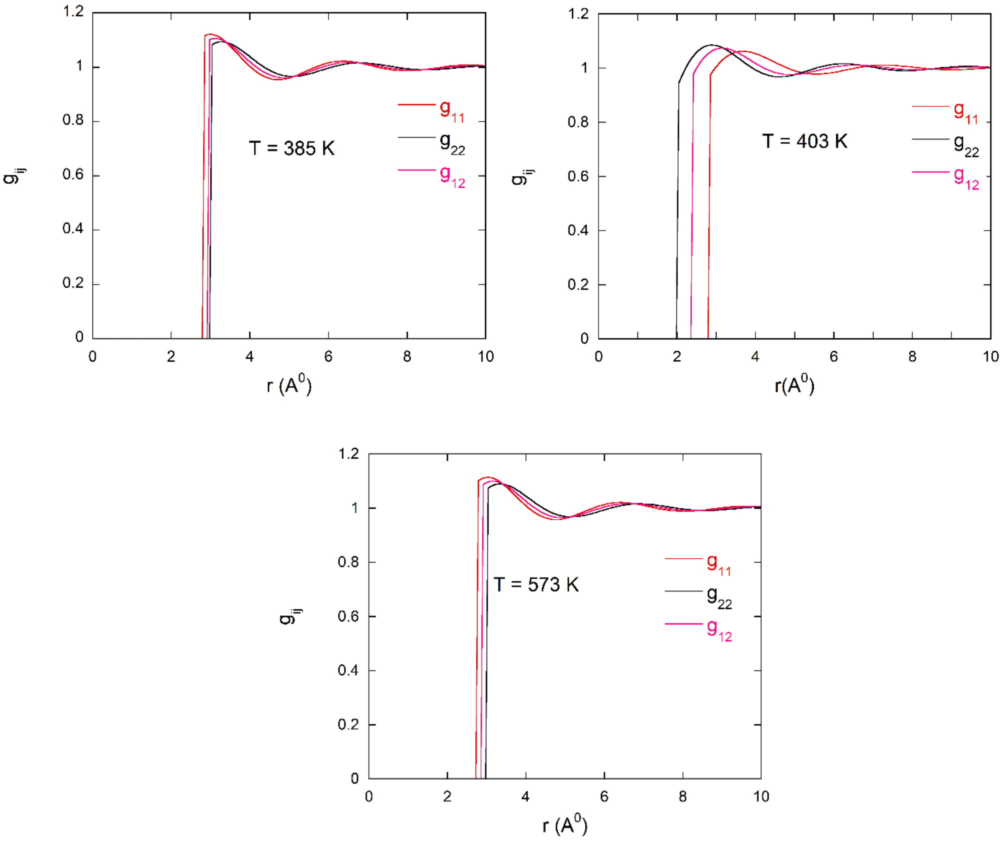

Fig. 2: The pair distribution function (g_{ij}) for the effective hard spheres (σ) representing $In_{0.5}$ $Bi_{0.5}$ binary alloys for T= 385 K, 403 K, and 573 K.

Table. 2 depicts the relationship between the friction coefficient and the Di. The hard-core part and the soft part of the friction coefficient increases with increasing temperature for In in $In_{0.5}Bi_{0.5}$ alloy. The increasing behavior of friction can be attributed to the fact that due to small σ of In more friction occurs among In atoms at higher temperature. This trend is concurrent with the findings in [29,30]. It is evident that if friction is higher, the diffusion would be lower. However, it is observed that this is true if concentration varies, while temperature remains constant [24]. In this work, since diffusion is measured as a function of temperature and T is appeared in the numerator of the D_i in equation (13), an increasing trend in D_i is observed as shown in Table. 3. The authors in Ref. [17] also found the same behavior of D_i for In at relatively low temperature region. The D_i for Bi is also calculated and presented in the table for different temperatures, however, due to the unavailability of experimental data, it is not possible to compare them. We strongly believe that since the values of D_i for In agree well with the available experimental results, our calculated values of D_i for Bi also would be a good agreement when the experiment is performed.

Table. 2: Temperature, T(K); average ionic number density, $\rho(A^0)$; the σ, soft and hard parts of the friction coefficients ξ (kgms$^{-1}\times 10^{-12}$); self-diffusion coefficient, D_i (m^{2}s$^{-1}\times 10^{-5}$) for components 1 and 2 of $In_{0.5}Bi_{0.5}$.

T	ρ_1	ρ_2	σ_{11}	σ_{22}	$\xi_1^{(H)}$	$\xi_1^{(S)}$	$\xi_2^{(H)}$	$\xi_2^{(S)}$	D_1 (In)	D_2 (Bi)
385	0.03699	0.02963	2.7989	3.0292	2.56	3.36	1.22	1.82	1.40	1.01
388	0.03698	0.02961	2.7981	3.0286	2.54	3.43	1.29	1.91	1.40	0.989
393	0.03697	0.02959	2.7966	3.0277	2.57	3.84	1.29	1.91	1.40	0.994
398	0.03695	0.02957	2.7951	3.0268	2.86	3.50	1.29	1.90	1.41	0.100
403	0.03693	0.02955	2.7937	3.0254	2.86	3.27	1.88	1.90	1.17	0.653
423	0.03690	0.02950	2.7852	3.0227	2.94	3.34	1.92	1.89	1.20	0.682
458	0.03670	0.02930	2.7818	3.0163	2.71	3.69	1.35	1.88	1.55	1.12
493	0.03660	0.02920	2.7751	3.0101	2.81	3.83	1.35	1.87	1.64	1.18
533	0.03650	0.02897	2.7674	3.0033	2.90	3.96	1.34	.86	1.73	1.25
573	0.03630	0.02889	2.7598	2.9964	3.03	4.13	1.34	1.86	1.81	1.30

Table. 3: Comparison of self-diffusion coefficient, D_i (m^{2}s$^{-1}\times 10^{-5}$) for In with experimental data.

T(K)	D_1 (Theoretical)	D_1 (Experimental) [17]
385	1.40	1.21±0.05
388	1.40	1.21±0.12
393	1.40	1.21±0.08
398	1.41	1.17±0.09
403	1.17	1.15
423	1.20	1.33±0.06
458	1.55	1.80±0.04
493	1.64	2.14±0.13
533	1.73	2.37±0.015
573	1.81	2.97

4. CONCLUSIONS

This research work conducts the computational study of atomic transport properties, specifically the self-diffusion coefficients (D_i) of In and Bi in molten $In_{0.5}Bi_{0.5}$ alloy using Distribution Function Method (DFM). Inter-ionic interactions (V_{ij}) and pair distribution function (g_{ij}) are key elements of the DFM framework. The V_{ij} are explained by the Brettonet-Silbert model, while g_{ij} is described by the Ascroft –Langreth theory. The effective hard sphere diameter (σ), essential for calculating g_{ij} is deduced from the LWCA theory. The results of this theoretical investigation are promising, particularly the values of D_i for In align well with the available experimental results at relatively in the low temperature region. In addition, we proposed the values of D_i for Bi which would be a good agreement when the experiment is performed. Consequently, the level of consistency of the results for the $In_{0.5}Bi_{0.5}$ alloy justifies the legitimacy and efficacy of the employed theory.

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