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# Study of size mismatches effect on transport properties in Cu-Sb and Cu-Sn liquid alloys

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### Abstract

We report a formalism that connects thermodynamics and transport properties such as viscosity and diffusion coefficient which has been used to calculate the concentration dependence of free energy of mixing, concentration-concentration fluctuations in the long wavelength limit and concentration dependence of diffusion and viscosity in Cu-Sb and Cu-Sn binary liquid alloys at 1190K and 1400K respectively with aid of size effect and no size effect. Our calculations show that a reasonable degree of chemical order exists in both alloys system. It can be concluded that size mismatch has more effects on the transport properties of Cu-Sb hetero-coordinated system with greater size ratio than Cu-Sn hetero-coordinated system.

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## 1. Introduction

Various empirical models have been used to study the structure and thermodynamics of the liquid binary alloys since midway of last century. However, it has been observed that establishing an empirical model that will link thermodynamics and transport properties of binary liquid alloys was a difficult task. To the best of our knowledge the empirical model of Singh and Sommer in ref. [1] was about the first pioneer work in providing the aforementioned essential link. In this model, they were able to link two transport quantities: viscosity ( $\eta$ ) and diffusion coefficient ( $D$ ) for binary liquid alloys with thermodynamic quantities like the Gibb's free energy of mixing ( $G_M$ ) and the concentration fluctuation in the long wavelength limit ( $S_{cc}(0)$ ). In essence, they related these four quantities by using enthalpic (i.e. energetics) and entropic (i.e. size) contributions to  $G_M$ . This model has been

applied at first by Akinlade et al [2] to two segregating alloys, Bi-Zn and Cu-Bi and later O. E. Awe applied it for four liquid alloys [3]. In the present paper, we employed the same empirical model of Singh and Sommer and Darken thermodynamic equation of diffusion to investigate the effect of size on the transport properties of two copper based alloys (i.e. Cu-Sb and Cu-Sn). Our choice of these two alloys was based on the fact that they are examples of alloys where size mismatch between atom-A and atom-B in each of the alloys is considered to be significant [4]. That is the volume or size difference between atom-A and atom-B does not lie within 50 percent and, hence, the difference is not negligible, i.e. at the melting points, in Cu-Sb, Sb atom is 2.56 times bigger than the Cu-atom and in Cu-Sn, Sn atom is 2.29 times bigger than Cu-atom [5]. In addition we are also aware that the two alloys represent the distinct classes of binary liquid alloys, namely, class of alloys that exhibit negative deviation from Raoult's law of linearity, known as hetero-coordinated or short-ranged ordered alloys. Another reason for choosing to work on these alloys is that each of the two alloys has either an interesting feature or is industrially relevant.

The next section focuses on formalism for each of the transport properties of interest. We present the results of our calculations and their discussion in section 3. In the last section, we round off with concluding remarks.

## 2. Formalism

### 2.1. Transport properties: diffusion and viscosity

Essentially, viscosity and diffusion measurements are employed by theoreticians as well as experimentalists to extract information about alloying or atomic association in liquids as they shed light on the understanding of the mixing behavior and can be used to ascertain the stoichiometric composition of associates that are formed [6, 5]. Also, from the point of view of ordering, diffusivity seems to be a more sufficient parameter than the Warren–Cowley short-range order,  $\alpha_1$  on the ground that its calculation does not require any need of  $Z$  as an input, and thus, the problems associated with its estimated value are overcome [6]. With a view to investigate the effect of size on the transport properties of the two alloys of present interest we have attempted to calculate their ratio of the mutual and self diffusion coefficients,  $D_M/D_S$  (or  $D_M/D_{id}$ ) as well as their viscosities using Darken's thermodynamic equation of diffusion as in Ref. [6] and the model of Singh and Sommer as in Ref. [1], respectively.

#### 2.1.1. Diffusion

The relationship between Darken's thermodynamic equation of diffusion and concentration-concentration fluctuation in long wavelength limits is given by Ref.[4] as

$$\frac{D_M}{D_{id}} = \frac{S_{cc}^{id}(0)}{S_{cc}(0)} \quad (1)$$

where  $D_M$  is the mutual or chemical diffusion coefficient and  $D_{id}$  is the self or intrinsic coefficients for ideal mixture while  $S_{cc}^{id}(0)$  is the ideal concentration-concentration fluctuations. The ratio  $D_M / D_{id}$  indicates the mixing nature of molten alloys;  $D_M / D_{id} < 1$  indicates the tendency of homo-coordination while  $D_M / D_{id} > 1$  indicates the tendency of hetero-coordination and  $D_M / D_{id}$  approaches 1 for ideal mixing. Consequently, the highest peak on the diffusivity curve (i.e. plot of  $D_M/D_{id}$  against

concentration of the species) suggest the presence of maximum chemical order in the liquid alloy system and the composition of the most probable associates to be formed in the liquid phase [6].

### 2.1.2. Viscosity

The relationship between the viscosity ( $\eta$ ) and chemical diffusion coefficient ( $D_M$ ) is given by Ref.[1,6,7] as

$$\eta = \frac{k_B T}{D_M} \left( \frac{c_A}{m_B} + \frac{c_B}{m_A} \right) \psi \quad (2)$$

where  $m_i$  ( $i=A$  or  $B$ ) is a parameter that depends on the size and shape of the particle i.e. ;  $k_B$  and  $T$  are the respectively Boltzmann's constant and absolute temperature;  $c_A$  and  $c_B$  are the concentrations for A and B atom respectively. Eq.(2) can be re-written as

$$\eta = \eta^0 \psi \quad (3)$$

$$\text{where } \eta^0 = \frac{k_B T}{D_M} \left( \frac{c_A}{m_B} + \frac{c_B}{m_A} \right) \quad (4)$$

The expression of  $\psi$  that incorporates both enthalpic and entropic effect is given by Ref.[1] as

$$\psi = 1 - c_A c_B f(\gamma, W) \quad (5)$$

$$\text{with } f(\gamma, W) = \frac{2\gamma^2 W - (\gamma - 1)^2 (c_A + \gamma c_B)}{(c_A + \gamma c_B)^3} \quad (6)$$

From Eq.(2) and (5),one obtains the expression for viscosity

$$\frac{\Delta\eta}{\eta} = -c_A c_B f(\gamma, W) \quad (7)$$

where  $\Delta\eta = \eta - \eta^0$ , deviation in  $\eta$ .

According to Ref.[1],when only enthalpic effect is considered, the expression for  $\psi$  is given as

$$\Psi = 1 - c_A c_B \left( \frac{2\omega}{k_B T} \right) \quad (8)$$

where  $\omega$  is the ordering energy.

When Eq.(2) and (8) are combined, we obtain an expression as

$$\frac{\Delta\eta}{\eta} = -c_A c_B \left( \frac{2\omega}{k_B T} \right) \quad (9)$$

In the light of Conformal solution it has been reported in Ref.[1] that Eq.(9) can be re-written in term of enthalpy of mixing,  $H_M$  as

$$\frac{\Delta\eta}{\eta} = -\frac{H_M}{RT} \quad (10)$$

where R is the molar gas constant.

We have used Eq.(9) to calculate the viscosity for each alloys when size mismatch is not taken into consideration and on the basis of eq.(10) considered the negative value of experimental enthalpy of mixing for each alloy as the corresponding experimental values of viscosity. Eq.(7) is used to obtained the calculated values of viscosity when size mismatch is taken into consideration for each alloy.

We shall employ the expressions for  $G_M$  and  $S_{cc}(0)$  which incorporate the two fitting parameters(  $W$  and  $\gamma$ ), are needed to calculate the transport properties. These expressions are based on Guggenheim's theory of mixture and quasi-lattice theory [9]. The equations which are used to compute  $G_M$  and  $S_{cc}(0)$  for each of two alloys when size mismatch is taken into consideration(i.e.WSE) are given as [9]

$$\frac{G_M}{RT}^{WSE} = c_A \ln(1-\beta) + c_B \ln\beta + c_A W\beta \quad (11)$$

where  $\beta = \frac{\gamma c_B}{c_A + \gamma c_B}$ ,  $W = \Omega_A \left( \frac{\omega}{k_B T} \right)$

$$S_{cc}(0)^{WSE} = \frac{c_A c_B}{1 - c_A c_B f(\gamma, W)} \quad (12)$$

Where  $\gamma = \Omega_B / \Omega_A$ , size ratio of the constituent atoms. However, for the purpose of completeness we have as well computed the  $G_M$  and  $S_{cc}(0)$  for each of the two alloys where size mismatch are immaterial (i.e.NSE) using the following equations in simple statistical model[10]

$$\frac{G_M}{RT}^{NSE} = c_A \ln c_A + c_B \ln c_B + c_A c_B \frac{\omega}{k_B T} \quad (13)$$

$$S_{cc}(0)^{NSE} = \frac{c_A c_B}{1 - c_A c_B \left( \frac{2\omega}{k_B T} \right)} \quad (14)$$

In order to investigate the effect of size mismatch on the diffusivity of each of the two alloys we put Eq.(12) and (14) in turns in Eq.(1) so as to obtain the following two equations which respectively represent the diffusivity when the size mismatch is taken into consideration (i.e.WSE) and the diffusivity when size mismatch is immaterial (i.e.NSE):

$$\frac{D_M}{D_{id}}^{WSE} = 1 - c_A c_B f(\gamma, W) \quad (15)$$

$$\frac{D_M}{D_{id}}^{NSE} = 1 - c_A c_B \left( \frac{2\omega}{k_B T} \right) \quad (16)$$

### 3. Result and discussions

Although, the emphasis in this paper is on transport properties, we nevertheless need to calculate two of the bulk properties ( $G_M$  and  $S_{cc}(0)$ ) so that we can obtain the two fitting parameters (i.e.  $W, \gamma$ ). We have no information on the experimental values of the transport properties while we have experimental data on  $G_M$  and  $S_{cc}(0)$ . In this light we shall employ the expressions for  $G_M$  and  $S_{cc}(0)$  which incorporate the two fitting parameters. Eqs.(11) and (12) have been used simultaneously to obtain the fitting parameters that give a good overall fit for  $G_M$  and  $S_{cc}(0)$ . The values obtained are shown in table 1. Experimental values of  $G_M$  for the two alloys obtained directly from Hultgren et al [11]. The values of  $S_{cc}(0)$  are obtained via the values of experimental activity [11] as given by

$$S_{cc}(0) = c_B a_A \left( \frac{\partial a_A}{\partial c_A} \right)^{-1} = c_A a_B \left( \frac{\partial a_B}{\partial c_B} \right)^{-1}$$

where  $a_A$  and  $a_B$  are the observed chemical activities of atom A and B respectively. The values of fitting parameters obtained as shown in Table 1 are quite reliable since Figs. 1 and 2 indicate that we have a good fits for  $G_M$  and  $S_{cc}(0)$  two alloys of current interest. A comparison of the plots of WSE and NSE in each of the figures show that the degree of asymmetry in Cu-Sb ( $\gamma=2.56$ ) is more than that of Cu-Sn ( $\gamma=2.29$ ). This implies that the effect of size mismatch on hetero-coordinated alloys is directly proportional to the size ratio. In addition, we observe that in these figures the plot of WSE shows that in the hetero-coordinated alloys there is crossover from a decrease in the degree of hetero-coordination to an increase in the degree of hetero-coordination.

Table 1

Essential parameters for the calculation of transport properties for Cu-Sb and Cu-Sn at 1190K and 1400K respectively.

Alloys	$(\omega / k_B T)^{WSE}$ or $(\omega / k_B T)^{NSE}$	$\gamma$
Cu-Sb	-0.211	2.56
Cu-Sn	-0.169	2.29

The plots of graph of ratio of diffusion coefficients against concentration for each of the two alloys are shown in Figs.3 and 4. In both alloys,  $D_M/D_{id}$  is greater than one, indicates that alloys are hetero-coordinated, as earlier confirmed in the bulk properties calculations. A comparison of the plots WSE and NSE reveals that the effect of size mismatch on Cu-Sb and Cu-Sn is to reduce the degree of hetero-coordination in the range of composition  $0 \leq c_{Cu} < 0.32$  and increase the degree of hetero-coordination in the rest of the composition. WE also observe that the effect of size mismatch on the diffusivity of Cu-Sb is more than that on Cu-Sn, since the asymmetry caused by size mismatch is more pronounced in Cu-Sb than in Cu-Sn. Also, in view of fact that size ratio of Cu-Sb is greater than Cu-Sn, we infer that there is direct relationship between size mismatch and diffusivity of hetero-coordinated alloys.

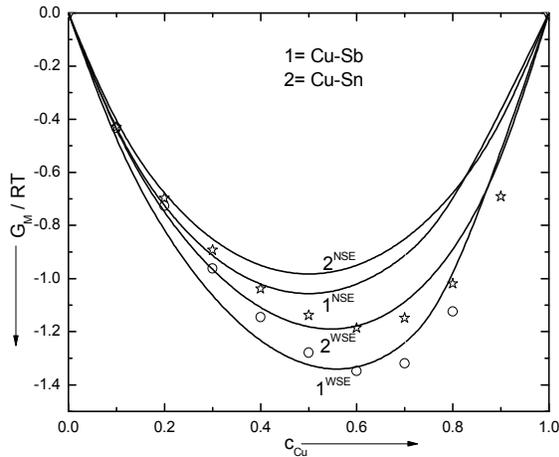


Fig.1

**Fig. 1:** Free energy of mixing ( $G_M/RT$ ) Vs concentration of copper( $c_{Cu}$ ) for Cu-Sb and Cu-Sn liquid alloys at 1190K and 1400K respectively; Circles and Stars represent experimental values[11] for Cu-Sb and Cu-Sn respectively;WSE means with size effect and NSE means no size effect.

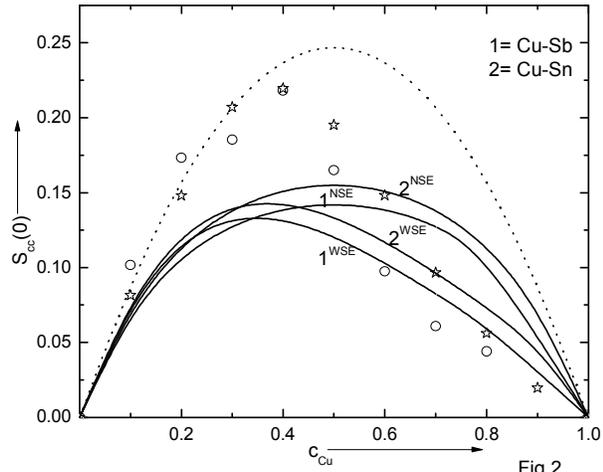


Fig.2

**Fig. 2:** Concentration-concentration fluctuation ( $S_{cc}(0)$ ) Vs concentration of copper( $c_{Cu}$ ) for Cu-Sb and Cu-Sn liquid alloys at 1190K and 1400K respectively; Circles and Stars represent experimental values[11] for Cu-Sb and Cu-Sn respectively;WSE means with size effect and NSE means no size effect.

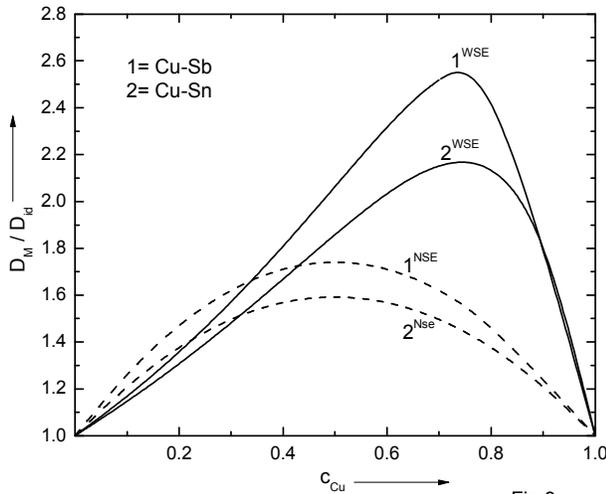


Fig.3

**Fig. 3:** Diffusion coefficient ratio ( $D_M/D_{id}$ ) Vs concentration of copper( $c_{Cu}$ ) for Cu-Sb and Cu-Sn liquid alloys at 1190K and 1400K respectively; WSE means with size effect and NSE means no size effect.

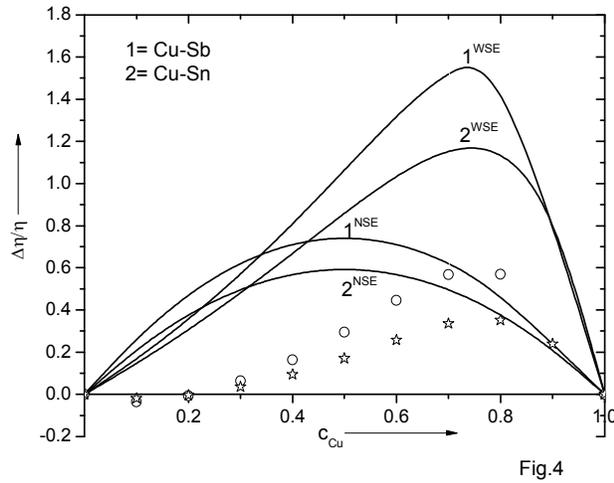


Fig.4

**Fig. 4:** Deviation of viscosity from ideal values ( $\Delta\eta/\eta^0$ ) Vs concentration of copper( $c_{Cu}$ ) for Cu-Sb and Cu-Sn liquid alloys at 1190K and 1400K respectively; Circles and Stars represent experimental values( $-H_M/RT$ ) taken from Ref.[11] for Cu-Sb and Cu-Sn respectively;WSE means with size effect and NSE means no size effect.

A perusal of the plots in Figs.3 and 4 for the two alloys shows that the plots NSE are symmetrical about equi-atomic composition while there is significant asymmetry in WSE plots due to size mismatch. In addition, we observe that asymmetry in Cu-Sb is more than in Cu-Sn. This is in agreement with the statement that asymmetry in  $\Delta\eta$  about equi-atomic composition is induced by size factors [1].

#### 4. Conclusions

Our studies of size mismatch effects on the transport properties of Cu-Sb at 1190K and Cu-Sn at 1400K have led to the following submissions:

The size mismatch is either solely or at least majorly responsible for the asymmetry and shaping of the asymmetry in each of the two alloys.

The degree of asymmetry of transport properties caused by size mismatch is directly proportional to the magnitude of size mismatch in the hetero-coordinated alloys.

Size mismatch has a crossover effect on the transport properties of the alloys studied: it reduces the degree of hetero-coordination in Cu-Sb and Cu-Sn in the range of composition  $0 \leq c_{Cu} < 0.32$  and increases the degree of hetero-coordination in the rest of composition.

This work has confirmed that the presented model and formulation can be used to study the size mismatch effects on the transport properties of binary liquid alloys on the basis thermodynamic data.

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