Science Vision 15(1), 2-7

Original Research

2015
January-March
ISSN (print) 0975-6175
ISSN (online) 2229-6026

The long-wavelength-limit of structure factor and chemical ordering in binary Ag-In melts

Raghvendu Pathak

Department of Chemistry, Pachhunga University College, Aizawl 796001, India

Received 7 September 2014 | Revised 25 January 2015 | Accepted 29 January 2015

ABSTRACT

The long-wavelength-limit partial structure factors, $S_{xy}(0)$, have been determined for liquid silver-indium (Ag-In) alloys using square well potential as perturbation over Percus-Yevick (PY) hard sphere reference system. Obtained $S_{xy}(0)$ at various compositions of In have been employed to calculate isothermal compressibility and chemical ordering in the alloys. Further, homo-coordination and hetero-coordination in Ag-In alloys have been studied at microscopic level in terms of mutual and intrinsic diffusion coefficients

Key words: Liquid alloys; structure factor; square well potential; diffusion coefficient.

INTRODUCTION

The microscopic structural, thermodynamic and dynamic properties of binary liquid alloys have been studied and of longstanding interest. These studies are also important from metallurgical point of view.[1] In recent years, many investigations regarding compound forming behavior and various thermodynamic properties as a function of concentration in binary liquid alloys from their long-wavelength-limit of structure factors have been reported, which are of importance from scientific and technological points of view.[2-10]

A good number of experimental, theoretical and simulation results on structure, dynamic and thermodynamic properties of Ag-In melts[11-15] are available in literature but knowledge about the chemical ordering in this alloy is desired. The complete structural characteristics in binary melts in momentum space can be described by three partial pair correlation functions (partial structure factors, PSFs) namely $S_{x\text{-}x}(k)$, $S_{y\text{-}y}(k)$ and $S_{x\text{-}y}(k)$. From these PSFs partial $g_{xy}(r)$ and total g(r) radial distribution functions can be obtained. Partial Y_{xy} and total Y coordination number can by integrating $g_{xy}(r)$ and g(r) functions in between first two minimum values of these functions.[16]

In present paper, the direct correlation functions (DCFs) of liquid Ag-In alloys were determined using Lebowitz solution[17] of Percus-

Corresponding author: Pathak
Phone: +91-9436370190
E-mail: rppuc41@yahoo.com

Yevick (PY) equation for hard sphere model with square well attractive tail in limit of zero wave vector. From the DCFs long-wavelength-limit of PSFs $S_{Ag\text{-}Ag}(0)$, $S_{In\text{-}In}(0)$ and $S_{Ag\text{-}In}(0)$ are evaluated. The total structure factor in long-wavelength limit S(0), isothermal compressibility K_T, Bhatia-Thornton (BT) concentration – concentration correlation function, in long-wavelength-limit $S_{CC}(0)$ were compute from long - wavelength-limit of PSFs. The ratio of mutual diffusion coefficients (D_M) and inter-diffusion coefficients (D_{id}) of components and chemical short range order parameter (CSRO), α are also presented in the later part of this paper.

THEORETICAL FORMALISM

Within the mean spherical model approximation (MSMA) the direct correlation functions (DCFs) in repulsive and attractive region of potential function can be given as [16]

$$C_{xy}(r) = C^0_{xy}(r) - \frac{\varepsilon_{xy}}{K_B T} \qquad (1)$$

where $C^0_{xy}(r)$ is the DCF in the hard sphere region, $0 < r < \sigma_{xy}$, obtained by Lebowitz [17] for Percus-Yevick equation, $-\frac{\varepsilon_{xy}}{K_B T}$ is the direct correlation function (DCF) in the square well attractive region, $\sigma_{xy} < r < \lambda_{xy}\sigma_{xy}$. The DCF beyond square well region is considered as 0 it means that there is no correlation between liquid atoms in the region $r > \lambda_{xy}\sigma_{xy}$.

Further r is the separation between pair of atoms whereas σ_{xx}, ε_{xx}, and σ_{xx} $(\lambda_{xx}\text{-}1)$ are the diameter, the potential energy depth and breadth respectively of the square well potential of the x^{th} species. The mixed parameters are determined through the use of Lorentz Berthelot rules [16]. Thus, the mixed parameters are given by

$$\left.\begin{aligned} \sigma_{12} &= (\sigma_1 + \sigma_2)/2 \\ \varepsilon_{12} &= (\varepsilon_{11}\ \varepsilon_{22})^{1/2} \\ \lambda_{12} &= \frac{\lambda_{11}\sigma_1 + \lambda_{22}\sigma_2}{2\sigma_{12}} \end{aligned}\right\} \qquad (2)$$

The Fourier transform of direct correlation functions (DCFs) have been well explained already [16] and will not be repeated here. However, in thermodynamic limit when k → 0, DCFs can be given as

$$\rho_1 C_{11}(0) = -24\,\eta_1 \left[\frac{a_1}{3} + \frac{b_1\sigma_1}{4} + \frac{d\sigma_1^3}{6}\right] + \frac{8\,\eta_1\,\varepsilon_{11}(\lambda_{11}^3 - 1)}{k_B T} \qquad (3)$$

$$\rho_2 C_{22}(0) = -24\,\eta_2 \left[\frac{a_2}{3} + \frac{b_2\sigma_2}{4} + \frac{d\sigma_2^3}{6}\right] + \frac{8\,\eta_2\,\varepsilon_{22}(\lambda_{22}^3 - 1)}{k_B T} \qquad (4)$$

$$C_{12}(0) = -\frac{4\pi\ \varepsilon_{12}\ \sigma_{12}^3\ (\lambda_{12}^3 - 1)}{3\,k_B T} - \frac{4\pi\ a_1\sigma_{12}^3}{3} - 4\pi\sigma_1^3\left\{\frac{b(\sigma_1 + 2\sigma_2)}{12} + \frac{\lambda\,d\,\sigma_1(3\sigma_1 + 5\sigma_2)}{10} + \frac{d\,\sigma_1^2(2\sigma_1 + 3\sigma_2)}{30}\right\} \qquad (5)$$

Here 1 stands for Ag (silver) and 2 for In (indium), rest of the symbols used in equations 3 to 5 have been already explained elsewhere [19].

Kirkwood and Buff [19] related the isothermal compressibility, K_T of the mixture to $\rho_x\ C_{xx}(0)$ and $\rho_{12}\ C_{12}(0)$ as follows

$$\rho\,k_B\,T\,\chi_T = [1 - c_1\,\rho_1\,C_{11}(0) - c_2\,\rho_2\,C_{22}(0) - 2\,c_1c_2\,\rho_{12}\,C_{12}(0)] \qquad (6)$$

Here ρ_x is the number density of pure component and $\rho_{12} = (\rho_1\ \rho_2)^{1/2}$.

Three partial structure factors (PSFs) in the long-wavelength-limits can be written in terms of direct correlation functions $C_{11}(0)$, $C_{22}(0)$ and $C_{12}(0)$

$$S_{Ag\text{-}Ag}(0) = [1 - \rho_{Ag}\, C_{Ag\text{-}Ag}(0) - \frac{\rho_{Ag}\, \rho_{In}\, C^2_{Ag\text{-}In}(0)}{1 - \rho_{In}\, C_{In\text{-}In}(0)}]^{-1} \tag{7}$$

$$S_{In\text{-}In}(0) = \frac{[1 - \rho_1\, C_{Ag\text{-}Ag}(0))]\, S_{Ag\text{-}Ag}(0)}{1 - \rho_{In}\, C_{In\text{-}In}(0)} \tag{8}$$

$$S_{Ag\text{-}In}(0) = \frac{(\rho_{Ag}\, \rho_{In})^{\frac{1}{2}}\, C_{Ag\text{-}In}(0)\, S_{Ag\text{-}Ag}(0)}{1 - \rho_{In}\, C_{In\text{-}In}(0)} \tag{9}$$

Thus for the binary alloy the total structure factor can be written as

$$\begin{aligned} S(0) = {} & [c_{Ag} f^2_{Ag}\, S_{Ag\text{-}Ag}(0) + 2\,(c_{Ag} c_{In})^{1/2} \\ & f_{Ag}\, f_{In}\, S_{Ag\text{-}In}(0) + c_{In}\, f^2_{In}\, S_{In\text{-}In}(0)] \\ & X\ [c_{Ag}\, f^2_{Ag} + c_{In}\, f^2_{In}]^{-1} \end{aligned} \tag{10}$$

Here f_{Ag} and f_{In} are atomic scattering factors and c_{Ag} and c_{In} are the atomic fractions of Ag and In respectively.

Important relations also exist between Bhatia-Thornton (BT) correlation functions in the long wave length limit and $S_{xy}(0)$ and also be [19]

$$\begin{aligned} S_{CC}(0) = {} & c_{Ag} c_{In}\, [c_{In}\, S_{Ag\text{-}Ag}(0) \\ & + c_{Ag} S_{In\text{-}In}(0) \\ & - 2\,(c_{Ag} c_{In})^{\frac{1}{2}}\, S_{Ag\text{-}In}(0)] \end{aligned} \tag{11}$$

The CSRO can be obtained from $S_{CC}(0)$ as [8]

$$\begin{aligned} \alpha & = \frac{S_{CC}(0) - S_{CC}(0),id}{\psi\, S_{CC}(0) - S_1} \\ & = \frac{S_1}{\psi\, S_{CC}(0) - S_1} \end{aligned} \tag{12}$$

Here

$$S_{CC}(0),id = c_1\, c_2 \tag{13}$$

and S_1 is the deviation of the concentration – concentration correlation function in the long wavelength limit from its ideal value, ψ is the coordination number can be computed from the total radial distribution function obtained from the Fourier transformation of the total structure factor S(k)

$$\Psi = 4\pi\rho \int_0^{r_{min}} g(r)\, r^2\, dr \tag{14}$$

Further, D_M and D_{id} can be given by Darken thermodynamic relation as [10]

$$\frac{D_M}{D_{id}} = \frac{C_1 C_2}{S_{CC}(0)} \tag{15}$$

with

$$D_{id} = a_1 D_M \frac{1}{\frac{\partial a_1}{\partial C_1}} \tag{16}$$

$$D_M = C_2 D_1 + C_1 D_2 \tag{17}$$

where D_1 and D_2 are the self-diffusion coefficients of pure components and a_1 is the activity of first component, Ag in binary melts.

RESULTS

The square well potential parameters of the pure components are used for the study of Ag-In melts at different compositions. The parameters taken from literature [16] and are given in Table 1. A necessary condition in the application of Lebowitz equations is $s_{22} > s_{11}$. Here s_{11} corresponds to the diameter of Ag and s_{22} refers to the diameter of In. The PSFs in long-wavelength-limit are obtained through eqns. (7) to (9) and are pre-

Table 1. Potential parameters for Ag-In alloy.

	σ (nm)	**ε/k$_B$ (Degree Kelvin)**	**λ**
Ag	0 .260	500.00	1.75
In	0 .283	173.86	1.70

Table 2. Computed values of PSFs and total structure factor S(0) in long-wavelength-limit at different atomic % of In in Ag-In liquid alloys.

% of In in Ag-In alloy	Temperature (K)	$S_{Ag\text{-}Ag}(0)$	$S_{In\text{-}In}(0)$	$S_{Ag\text{-}In}(0)$	S(0)
20	1123	0.515	1.153	-0.743	0.033
30	1023	0.908	1.197	-1.015	0.035
40	873	1.569	1.314	-1.409	0.036
50	873	1.679	0.948	-1.231	0.039
70	873	1.425	0.367	-0.682	0.041
80	873	1.260	0.206	-0.459	0.041
90	873	1.118	0.103	-0.271	0.040

Table 3. Computed values of chemical ordering parameters at different compositions of In in Ag-In liquid alloys.

% of In in Ag-In alloy	Coordination Number (Z)	$S^{id}_{cc}(0)$	$S_{cc}(0)$	$D_M \times 10^{-9}$ (m^2/s)	$D_{id} \times 10^{-9}$ (m^2/s)	α
20	12.5	0.09	0.110	0.9	1.309	-0.04
30	11.8	0.16	0.243	0.9	0.778	0.013
40	11.9	0.21	0.450	0.8	0.427	0.043
50	11.6	0.25	0.407	0.8	0.491	0.035
70	11.2	0.24	0.154	0.8	1.091	-0.030
80	10.8	0.21	0.065	0.9	2.215	-0.11
90	10.5	0.16	0.016	0.9	5.063	-0.27

sented in Table 2. The total structure factor in long-wavelength limit, S(0) was evaluated from equation (10) and are given in Table 2 and also presented as a function of concentration in Figure 1. The D_M values at different compositions are calculated by Venkatesh et al. [16] and therefore not repeated here but employed in the computation of D_{id} at the same compositions.

Computed values of ψ, $S_{CC}(0)$, D_M, D_{id} and α are listed in Table 3. Further, to understand the chemical ordering in the alloy, the ratio D_M/D_{id} and α are plotted as function of concentration in Figure 2.

Discussion

Unfortunately, there are no experimental values for partial structure factors (PSFs) in the long-wavelength limit and isothermal compressibility are available for comparison. Thus, it can be seen from Table 2 in the high composition region of Ag up to 50% Ag-Ag correlation in long-wavelength-limit is favourable whereas as In-In correlation is favourable at lower % of In. In high % of In cross correlation is favourable and this opinion can be supported by the observed $S_{CC}(0)$ values beyond 70% of In as presented in Table 2. Decrease in $S_{CC}(0)$ is an indication of compound formation between components of the alloy [8]. S(0) against % of In is plotted in Figure 1 it can be observed that this value also decreases between 35 to 40% of In and also beyond 70% of In.

Computed values of $S_{CC}(0)$ with their ideal values, i.e $S_{CC}^{ideal}(0)$, total coordination number, ψ and the CSRO, a at different atomic fraction

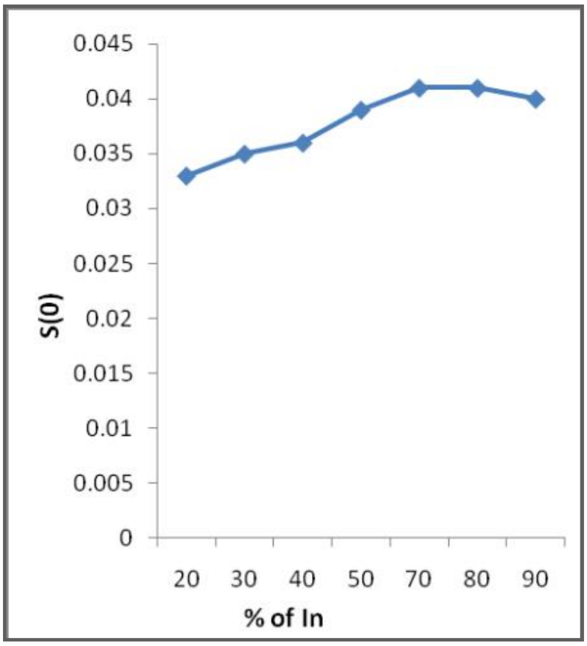

Figure 1. % of In in Ag-In alloy vs S(0)

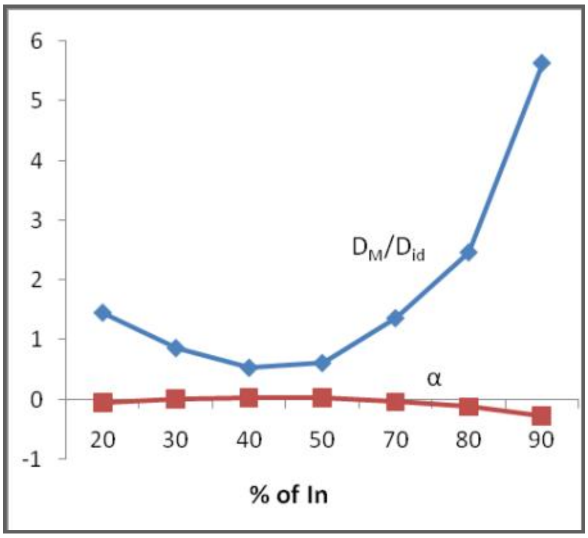

Figure 2. % of In in Ag-In alloy vs D_M/D_{id} and α

of In in liquid Ag – In liquid binary alloys are shown in Table 3. A liquid binary alloys can be classified on the basis of their concentration dependent $S_{CC}(0)$ data. If $S_{CC}(0) < S_{CC}^{ideal}(0)$ for those concentrations liquid metals components in binary melts show compound forming nature and exhibit some short range order while, $S_{CC}(0) > S_{CC}^{ideal}(0)$ at these concentrations components show demixing tendency.

D_{12}/D_{id} approaches 1 for an ideal mixing and less than 1 of this ratio shows phase separation and more than 1 indicates the compound formation tendency in binary mixtures. From Table 2 we confirm that the computed results of $S_{CC}(0)$ for 0.30 to 0.70 atomic fraction of In in Ag-In melts have higher values than their corresponding ideal values and this shows the segregation tendency of Ag and In atoms. This outcome is also supported by positive values of a and less than 1 values of D_{12}/D_{id} between this concentration range [10] as can be seen from Figure 2. The negative difference of $S_{CC}(0)$ from their corresponding ideal values and the condition $D_{12}/D_{id} > 1$ inform that there is complex formation below 0.30 and above 0.70 atomic fractions of In. The CSRO parameter varies between –1 to 1, with negative values indicating the short range atomic ordering in the melt and positive values indicating segregation of atomic constituents.

CONCLUSIONS

Considered alloys show compound forming nature between 0.7 to 0.3 atomic fractions of In, hence, there must be some ordering potential between components of binary alloys. The perturbation of hard sphere with square well interaction is suitable model for such calculations. Microscopic functions of the alloy were determined using potential parameters of pure components. There is no evidence for experimental results of $S_{CC}(0)$ from scattering properties of the alloys, however, experimentalist determine this function by analyzing experimental thermodynamic activity data so the purposed model calculation is very useful for understanding the chemical ordering in binary melts.

REFERENCES

1. Gopala Rao RV & Satpathy A (1990). Statistical-mechanical model in the evaluation of partial and total structure factors, atomic distribution functions, and diffusion coefficients of silver-tin liquids at various concentrations. *Phys Rev B*, **41**, 11938.
2. Anusionwu BC, & IIo-Okeke EO (2005). Segregation and surface properties of In-Zn liquid alloys. *Phys Chem Liq*, **43**, 25–36 .
3. Awe OE & Olawole O (2012). Correlation between bulk and surface properties in Cd-X (X=Hg,Mg) liquid alloys. *J Non-Cryst Sol,* **358**, 1491–1496.
4. Singh NKP, Singh RN & Choudhary RB (1991). Thermodynamic investigation of atomic order in AlMg liquid alloys. J Phys Condens Matter, **3**, 3635.
5. Gonz’alez DJ, Gonz´alez LE, Opez JML & Stott MJ (2005). Collective modes in liquid binary alloys. An ab initio molecular dynamics study of the LiMg and LiBa alloys. J Phys Condens Matter, **17**, 1429.
6. Mishra PP, Milanarunb M, Jha N & Mishra, AK (2002). Thermodynamic properties of liquid glass-forming Ca–Mg alloys. *J Alloys Compd,* **340**, 108.
7. Odusote YA (2008). Investigation of ordering phenomenon in Me-Pt (Me=Fe,Ni) liquid alloys. *Sci Technol Adv Mater,* **9**, 1–7.
8. Singh RN & Sommer F (1997). Segregation and immiscibility in liquid binary alloys. Rep Prog Phys, **60**, 57.
9. Khaeque MA, Bhuiyan GM, Sharmin S, Rashid RIMA & Rahman SMM (2002). Calculation of partial structure factors of a less-simple binary alloy. *European Phys J B,* **26**, 319.
10. Singh BP, Adhikari D & Jha IS (2012). Short range order in molten Al–Si alloys. *Phys Chem Liq,* 50, 697.
11. Mendelev MI (1998). An iterative procedure for the creation of computer models of non-crystalline materials from diffraction data. *J Non-Cryst Solids*, 223, 230.
12. Mendelev MI (1998). Computer simulation of Ag–In liquid alloys structure and self-diffusion coefficient calculations. *J Non-Cryst Solids*, **232**, 560.
13. Arai Y, Shirakawa Y, Tamaki S, Saito M & Waseda Y (1998). Structural properties of liquid Ag-In system. *Phys Chem Liq*, 35, 253.
14. Kes H, Dalgic SS & Dalgic S (2005). Structure of less simple liquid alloys: Ag_X-In_{1-X}, *J Optoelectron Adv Materials*, **7,** 2047–2057.
15. Bhuiyan GM, Ali I & Mujibur Rahman SM (2003). Atomic transport properties of AgIn liquid binary alloys. *Phys B: Condens Matter*, **334,** 147.
16. Venkatesh R, Mishra RK & Gopala Rao RV (2003). Structural, thermodynamics and other associated properties of partially ordered Ag-In alloy. *Phys Stat Sol B*, **240,** 549–560.
17. Lebowitz JL (1964). Exact solution of generalized Percus-Yevick equation for a mixture of hard spheres. *Phys Rev,* **133A**, 895.
18. Gopala Rao RV & Venkatesh R (1989). Computation of total and partial structure factors, coordination number, and compressibility with self- and mutual-diffusion coefficients of Hg-In alloy. *Phys Rev B*, **39**, 3563.
19. Mishra RK & Venkatesh R (2008). Theoretical evaluation of structural and various associated properties of Al–Si melts. *Chem Phys,* **354**, 112–117.