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

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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. 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.

A good number of experimental, theoretical and simulation results on structure, dynamic and thermodynamic properties of Ag-In melts 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 $S_{xx}(k)$, $S_{yy}(k)$ and $S_{xy}(k)$. 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 be by integrating $g_{xy}(r)$ and $g(r)$ functions in between first two minimum values of these functions.

In present paper, the direct correlation functions (DCFs) of liquid Ag-In alloys were determined using Lebowitz solution of Percus-
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 $S_{AgAg}(0)$, $S_{InIn}(0)$ and $S_{AgIn}(0)$ 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 $S_{eq}(0)$ were compute from long-wavelength-limit of PSFs. The ratio of mutual diffusion coefficients ($D_{ab}$) and inter-diffusion coefficients ($D_{ab}$) of components and chemical short range order parameter (CSRO), $\alpha$ 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 \(^{16}\)

\[
C_{xy}(r) = C_{xy}^0(r) - \frac{\epsilon_{xy}}{k_BT} r
\]  

(1)

where $C_{xy}^0(r)$ is the DCF in the hard sphere region, $0 < r < \sigma_{xy}$, obtained by Lebowitz \(^{17}\) for Percus-Yevick equation, $-\frac{\epsilon_{xy}}{k_BT}$ 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 $\sigma_{xx}$, $\epsilon_{xx}$ and $\sigma_{xy}$ ($\lambda_{xx}$) 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

\[
\begin{align*}
\sigma_{12} &= \frac{(\sigma_1 + \sigma_2)}{2} \\
\epsilon_{12} &= \left(\frac{\epsilon_{11} \epsilon_{22}}{\epsilon_{12}}\right)^{1/2} \\
\lambda_{12} &= \frac{\lambda_{11} \sigma_1 + \lambda_{22} \sigma_2}{2 \sigma_{12}}
\end{align*}
\]

(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 $k \to 0$, DCFs can be given as

\[
\rho_i C_{ii}(0) = -24 \eta_i \left[ \frac{a_i}{3} + \frac{b_i \sigma_i}{4} + \frac{d \sigma_i^3}{6} \right] + \frac{8 \eta_i \epsilon_{ii}(\lambda_{ii}^3 - 1)}{k_B T}
\]

(3)

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

(4)

\[
C_{12}(0) = -4\pi \epsilon_{12} \sigma_{12}^3 \left(\lambda_{12}^3 - 1\right) \frac{3}{k_B T} - 4\pi a_i \sigma_{12}^3 \frac{3}{3} - 4\pi \sigma_{12}^3 \left\{ \frac{b (\sigma_1 + 2 \sigma_2)}{12} + \lambda d \sigma_1 (3 \sigma_1 + 5 \sigma_2) \right \} + \frac{d \sigma_1^2 (2a_i + 3 \sigma_2)}{30}
\]

(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 $\rho_i C_{ii}(0)$ and $\rho_{12} C_{12}(0)$ as follows

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

(6)

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

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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 $C_{12}(0)$

$$S_{Ag-Ag}(0) = \left[ 1 - \rho_{Ag} C_{Ag-Ag}(0) \right]$$

$$- \frac{\rho_{Ag} \rho_{In} C_{Ag-In}(0)}{1 - \rho_{In} C_{In-In}(0)} \right]^{-1}$$

(7)

$$S_{In-In}(0) = \left[ 1 - \rho_{In} C_{Ag-In}(0) \right] S_{Ag-Ag}(0)$$

$$\frac{1 - \rho_{In} C_{In-In}(0)}{1}$$

(8)

$$S_{Ag-In}(0) = \frac{(\rho_{Ag} \rho_{In})^{1/2} C_{Ag-In}(0) S_{Ag-Ag}(0)}{1 - \rho_{In} C_{In-In}(0)}$$

(9)

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

$$S(0) = \left[ c_{Ag} f_{Ag}^2 S_{Ag-Ag}(0) \right] + c_{Ag} f_{In} S_{Ag-In}(0)$$

$$+ c_{In} f_{In}^2 S_{In-In}(0)$$

$$X \left[ c_{Ag} f_{Ag}^2 + c_{In} f_{In}^2 \right]^{1/2}$$

(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 wavelength limit and $S_{n}(0)$ and also be

$$S_{CC}(0) = \left[ c_{Ag} c_{In} S_{Ag-Ag}(0) \right] + c_{Ag} S_{In-In}(0)$$

$$- 2 \left( c_{Ag} c_{In} \right)^1 S_{Ag-In}(0)$$

(11)

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

$$\alpha = \frac{S_{CC}(0) - S_{CC}(0),id}{\Psi S_{CC}(0) - S_{t}}$$

(12)

Here

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

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

$$\Psi = 4 \pi \rho \int g(r) r^2 dr$$

(14)

Further, $D_M$ and $D_l$ can be given by Darken thermodynamic relation as

$$D_M = \frac{C_1 C_2}{S_{CC}(0)}$$

(15)

$$D_l = a_1 D_M \frac{1}{c_1}$$

(16)

$$D_M = C_2 D_1 + C_1 D_2$$

(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 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>
<thead>
<tr>
<th></th>
<th>$\sigma$ (nm)</th>
<th>$\epsilon/k_B$ (Degree Kelvin)</th>
<th>$\lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>0.260</td>
<td>500.00</td>
<td>1.75</td>
</tr>
<tr>
<td>In</td>
<td>0.283</td>
<td>173.86</td>
<td>1.70</td>
</tr>
</tbody>
</table>
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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.

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

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

<table>
<thead>
<tr>
<th>% of In in Ag-In alloy</th>
<th>Coordination Number (Z)</th>
<th>$S_{id}^{CC}(0)$</th>
<th>$S_{cc}(0)$</th>
<th>$D_m \times 10^{-9}$ (m²/s)</th>
<th>$D_{id} \times 10^{-9}$ (m²/s)</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>12.5</td>
<td>0.09</td>
<td>0.110</td>
<td>0.9</td>
<td>1.309</td>
<td>-0.04</td>
</tr>
<tr>
<td>30</td>
<td>11.8</td>
<td>0.16</td>
<td>0.243</td>
<td>0.9</td>
<td>0.778</td>
<td>0.013</td>
</tr>
<tr>
<td>40</td>
<td>11.9</td>
<td>0.21</td>
<td>0.450</td>
<td>0.8</td>
<td>0.427</td>
<td>0.043</td>
</tr>
<tr>
<td>50</td>
<td>11.6</td>
<td>0.25</td>
<td>0.407</td>
<td>0.8</td>
<td>0.491</td>
<td>0.035</td>
</tr>
<tr>
<td>70</td>
<td>11.2</td>
<td>0.24</td>
<td>0.154</td>
<td>0.8</td>
<td>1.091</td>
<td>-0.030</td>
</tr>
<tr>
<td>80</td>
<td>10.8</td>
<td>0.21</td>
<td>0.065</td>
<td>0.9</td>
<td>2.215</td>
<td>-0.11</td>
</tr>
<tr>
<td>90</td>
<td>10.5</td>
<td>0.16</td>
<td>0.016</td>
<td>0.9</td>
<td>5.063</td>
<td>-0.27</td>
</tr>
</tbody>
</table>

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. and therefore not repeated here but employed in the computation of $D_{id}$ at the same compositions.

Computed values of $\psi$, $S_{cc}(0)$, $D_m$, $D_{id}$ and $\alpha$ are listed in Table 3. Further, to understand the chemical ordering in the alloy, the ratio $D_m/D_{id}$ and $\alpha$ 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. $S(0)$ 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, $\psi$ and the CSRO, $\alpha$ at different atomic fraction
of In in liquid Ag–In 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 $\alpha$ and less than 1 values of $D_{12}/D_{id}$ between this concentration range 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.
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REFERENCES


