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Calculation of partial structure factors of a less-simple binary alloy

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Abstract. The partial static structure factors, using the Faber-Ziman (FZ) theory, have been calculated for Ag-In alloy. For 20% Ag at 623 K and 70% Ag at 973 K, the interionic pair potential based on the Bretonnet-Silbert (BS) formalism are calculated and the hard sphere diameters for the component elements are estimated from the potential profile using the linearised Weeks-Chandler-Andersen (LWCA) method. The average number densities are calculated on the assumption that the atomic volumes are simply additive. The calculated structure factors are compared with the experimental values. The partial structure factors for Ag-Ag at 20% Ag and In-In at 70% Ag appear to be slightly out of phase with the calculated values particularly in large *q*-region. From the calculations it appears that this discrepancy is related to the process of derivation of the experimental structure factors from the total one, and the Ag-In alloy can be described by a mixture of hard spheres.

PACS. 61.25.Mv Liquid metals and alloys – 61.20.-p Structure of liquids

1 Introduction

It has been known for quite a long time that for pure liquid metals, the structure factors resemble closely to those for hard spheres. Calculations of static and dynamic properties like entropy, specific heat, viscosity and resistivity on this hard sphere assumption have been found to be quite satisfactory [1–4]. Among many different theoretical approaches, the derivation of the interatomic pair potential based on the Bretonnet-Silbert (BS) assumptions [5] attracted attention for its simplicity in concept and effectiveness in accuracy. In the early nineties, BS proposed a model to describe interionic interactions mainly for liquid transition metals. This model treats the *sp*- and *d*-bands separately within the well established pseudopotential formalism. The *sp*-band is described in terms of the empty core model, while the *d*-band contribution is derived from the *d*-band scattering phase shift using inverse scattering approach. The resulting model pseudopotential thus reduces to a simple local form. As mentioned above, the BS model is not only simple in basic assumptions but it is found to be equally easy to handle numerically. One of the important advantages of it is that the local form allows one to extend this model to other liquid metals for which the effects of the *sd* hybridization are significant. In this way the model has proved successful for liquid transition metal calculations [6,7]. It may be noted that non-local pseudopotentials that conserve norm should be preferred for accurate calculation of physical properties. But there are evidences [8] that the local pseudopotentials describe physical properties, in some cases, more efficiently than the non-local ones.

Though the BS formalism [4,6,7] remains one of the best tools in calculating physical properties of single component metallic systems, it has not been applied in the case of two-component or binary systems. It is relevant to mention here that the properties of mixtures are very important for practical purposes. In addition, since these properties vary with composition and thermodynamic conditions, by their own right, they deserve attention. A recent work [9] based on X-rays diffraction experiment on a binary alloy (Ag-In) aroused interest in this particular mixture. This, therefore, becomes doubly fascinating to see how one component metallic approach can be extended and employed to two-component mixtures; the purpose of the present work is to pursue and develop this extension effectively. At the same time it would be exciting to observe how the BS potential works, in particular, for alloys in explaining physical properties.

The theoretical idea behind this BS formalism and its explicit forms used in the present attempt is briefly mentioned in the following section. In calculating different structure factors, the established formulas are mentioned along with the relevant references without going through its derivation. The paper ends with a discussion of the calculated results with a comparison of the experimentally derived values in Section 3.

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Table 1. Input parameters: Core radii: Rc_1, Rc_2; Softness parameters: a_1, a_2; Number densities: n_1, n_2; hard sphere diameters: σ_1, σ_2 for Ag and In, respectively. C_1 denotes the concentration of Ag.

T(K)	Rc_1(au)	a_1(au^{-1})	Rc_2(au)	a_2(au^{-1})	n_1(A^{-3})	n_2(A^{-3})	C_1	σ_1(A)	σ_2(A)
623.0	1.04	0.20	1.32	0.27	0.0553	0.0362	0.2	2.52	2.83
973.0	1.04	0.20	1.32	0.27	0.0535	0.0349	0.7	2.50	2.9

2 Theory

2.1 Pair potential

As mentioned above the local pseudopotential can be constructed by the superposition of *sp*- and *d*-band contributions [5] for a metallic system,

$$\begin{aligned} W(r) &= \sum_{m=1}^{2} B_m \exp(-r/ma) \qquad \text{if } r < R_C \\ &= -Z/r \qquad\qquad\qquad\qquad \text{if } r > R_C \end{aligned} \tag{1}$$

where a, R_C and Z stand for softness parameter, core radius and the effective s-electron occupancy number, respectively. The form inside the core is obtained from the concept of d-band inverse scattering approach. Outside the core it is the bare Coulomb interaction between an electron and an ion. The coefficients B_1 and B_2 for the components depend on their R_C, a and Z values. The unscreened form factor of equation (1) is:

$$W(q) = 4\pi n a^3 \left[\frac{B_1 J_1}{(1+a^2q^2)^2} + \frac{2B_2 J_2}{(1+4a^2q^2)^2}\right] - \frac{4\pi Z e^2 n}{q^2}\cos(qR_C) \tag{2}$$

where, $n(= z\rho)$ is the average number density and

$$\begin{aligned} J_m = 2 - \exp\left(-\frac{R_C}{ma}\right)\Bigg\{&\left[\frac{R_C}{ma}\left(1+m^2a^2q^2\right) + \left(1-m^2a^2q^2\right)\right]\frac{\sin(qR_C)}{maq} \\ &+ \left[2+\frac{R_C}{ma}\left(1+m^2a^2q^2\right)\right]\cos(qR_C)\Bigg\}\cdot \end{aligned} \tag{3}$$

The effective interionic potential for the two species may be written as:

$$V_{ij}(r) = \left(\frac{Z_iZ_j}{r}\right)\left[1 - \frac{2}{\pi}\int F_N(q)\frac{\sin(qr)}{q}\mathrm{d}q\right] \qquad i,j = 1,2 \tag{4}$$

where, $F_N(q)$ is the normalized energy wave number characteristics:

$$F_N(q) = \left(\frac{q^2 W(q)}{a\pi Z n}\right)^2 \left[1 - \frac{1}{\varepsilon(q)}\right]\left[\frac{1}{1-G(q)}\right]\cdot \tag{5}$$

Here $\varepsilon(q)$ and $G(q)$ denote the dielectric function and local field correction, respectively. These functions were taken from Ichimaru and Utsumi [10]. The values of core radii were taken from Harrison [11]. The interatomic pair potentials $V_{11}(r)$, $V_{12}(r)$ and $V_{22}(r)$ are calculated for average number density for different concentrations of the two component species. The input values for two concentrations are shown in Table 1.

2.2 Determination of HSD

The important parameters like the hard sphere diameters (HSD) of the constituent ions for these systems are found from the interatomic pair potential profiles using the linearized Weeks-Chandler-Andersen (LWCA) theory [12]. In accordance with the original WCA theory [13], the free energy of a system is expressed in terms of a functional Taylor expansion with a soft repulsive potential $\nu(r)$ and a hard repulsive potential $\nu_\sigma(r)$ related to the blip function $B(r)$ given by

$$B(r) = Y_\sigma(r)\left\{\exp\left[-\beta\nu(r)\right] - \exp\left[-\beta\nu_\sigma(r)\right]\right\} \tag{6}$$

where $\beta = (k_{\mathrm{B}}T)^{-1}$, k_{B} being the Boltzmann constant. The blip function $B(r)$ is a measure of the departure of the actual potential $\nu(r)$ from the HS reference potential $\nu_\sigma(r)$, and $Y_\sigma(r)$ is a cavity function given by

$$Y_\sigma(r) = g_0(r)\exp(\beta\nu_\sigma) \tag{7}$$

where $g_0(r)$ is the pair correlation function of the HS reference system.

In the LWCA [12], the Fourier transform of $B(r)$ is expanded in terms of the Bessel functions and then using the thermodynamic condition that for an effective hard sphere diameter, $B(q)$ vanishes, one arrives at:

$$\beta\nu(\sigma) = \ln\left\{\frac{-2\beta\sigma\nu'(\sigma) + S + 2}{-\beta\sigma\nu'(\sigma) + S + 2}\right\}\cdot \tag{8}$$

The solution of this transcendental equation (8) yields the hard sphere diameter σ for the alloy components under study. Values so obtained are listed in Table 1.

2.3 Structure factors

The Ashcroft and Langreth (AL) partial structure factors $S_{11}(q)$ (Ag-Ag), $S_{12}(q)$ (Ag-In) and $S_{22}(q)$ (In-In) are calculated in line with their original work [14]. The

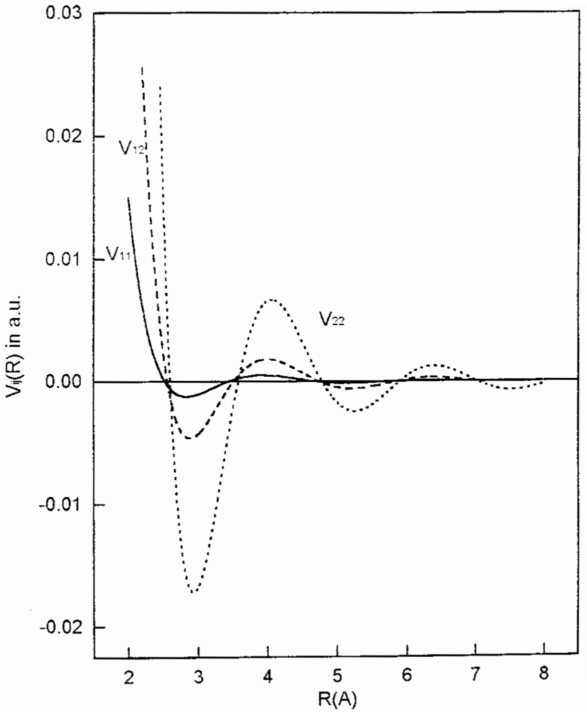

Fig. 1. Interatomic pair potentials for Ag-Ag (V_{11}), Ag-In (V_{12}) and In-In (V_{22}) for 20% Ag in Ag-In alloy at 623 K.

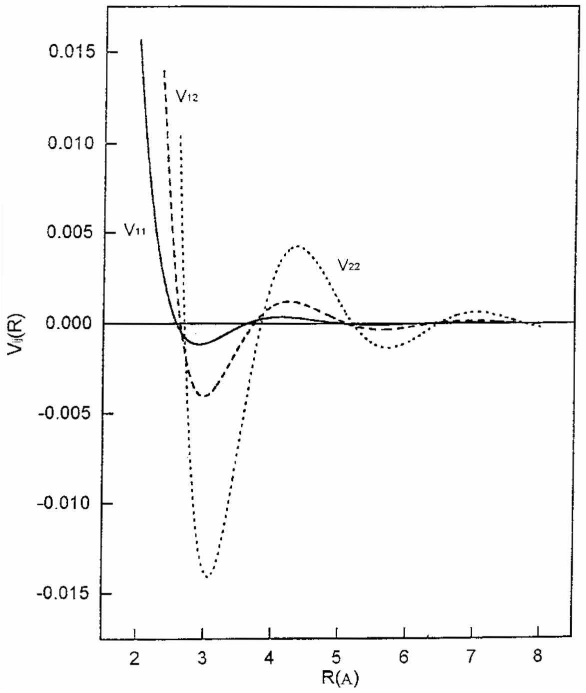

Fig. 2. Interatomic pair potentials for Ag-Ag (V_{11}), Ag-In (V_{12}) and In-In (V_{22}) for 70% Ag in Ag-In alloy at 973 K.

necessary inputs are the concentrations of the two spheres in the mixture and the hard sphere diameters. The total packing fraction η of the mixtures was found as:

$$\eta = \eta_1 + \eta_2 = \frac{\pi}{6}\left(C_1 n_1 \sigma_1^3 + C_2 n_2 \sigma_2^3\right) \tag{9}$$

where, C_1, C_2 and n_1, n_2 represent the concentrations and number densities of Ag and In, respectively. The final formulas for the AL partial structure factors are given in [14].

The Faber-Ziman (FZ) partial structure factors $A_{ij}(q)$ are calculated from the AL partial structure factors $S_{ij}(q)$ [15] and they are given by:

$$\begin{aligned}
A_{11}(q) &= \left[S_{11}(q) - C_2\right]/C_1 \\
A_{12}(q) &= \frac{S_{12}(q)}{\sqrt{(C_1 C_2)}} + 1 \\
A_{22}(q) &= \left[S_{22}(q) - C_1\right]/C_2.
\end{aligned} \tag{10}$$

3 Results and discussions

The interatomic pair potentials $V_{11}(r)$, $V_{12}(r)$ and $V_{22}(r)$ calculated from equation (4) for the two binary alloys near their melting points for different compositions are shown in Figures 1 and 2. The core radii Rc_1 and Rc_2 were taken from [11]. The values of the softness parameter a were found from the following process. The integral equation theory variational-modified-hypernetted-chain (VMHNC) was used to solve the Ornstein-Zernike (OZ) equation with a closure relation [16]

$$g(r) = \exp[h(r) - C(r) - \beta v(r) - B(r)]. \tag{11}$$

The softness parameter a for which the resulting structure factors matched closely with those of experimental values [15] of the elemental systems was finally adopted for further use in the present study of alloy. The number densities n_1 and n_2 of Ag and In at the two temperatures were found from Brandes [17]. These values used to calculate pair potentials are given in Table 1.

From Figures 1 and 2, it is evident that the depth of the primary potential well of $V_{22}(r)$ (In-In) is much deeper than that of $V_{11}(r)$ (Ag-Ag). Apparently, this seems to be largely due to the difference in the Z values (1.0 for Ag and 3.0 for In) for the two elements. For a better understanding probably one has to look into many body effects in the matrix. The hard sphere diameters σ_1 and σ_2 found from the potential profiles by using the linearised LWCA method [12] are also given in Table 1.

The Ashcroft-Langreth (AL) partial structure factors $S_{ij}(q)$ were first evaluated with the above hard sphere diameters and concentrations. These are then used to get the Faber-Ziman (FZ) partial structure factors $A_{11}(q)$, $A_{12}(q)$ and $A_{22}(q)$ corresponding to Ag-Ag, Ag-In and In-In structure factors respectively for 20% and 70% Ag concentrations; these are shown in Figure 3 and in Figure 4, respectively. The profiles of $A_{22}(q)$ for 20% Ag and $A_{11}(q)$ for 70% resemble very closely to that given in the above cited work. The profiles of $A_{11}(q)$ for 20% Ag and $A_{22}(q)$ for 70% Ag

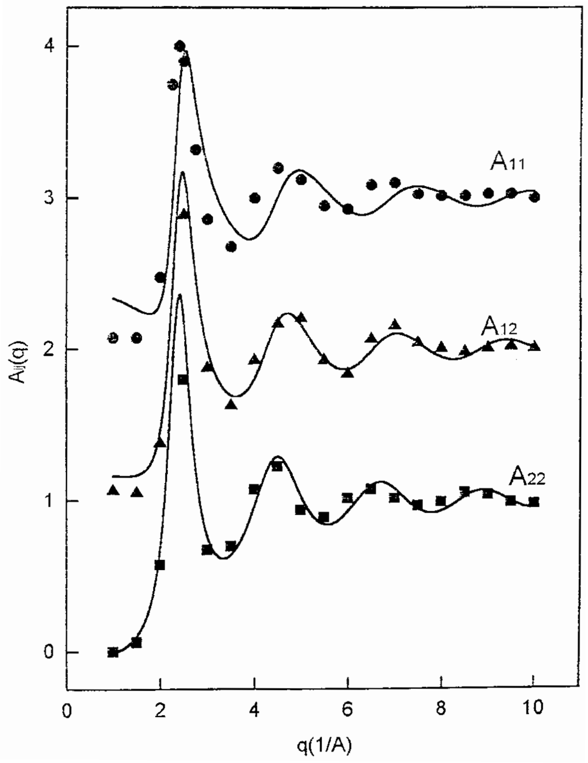

Fig. 3. Faber-Ziman [FZ] structure factors $A_{11}(q)$, $A_{12}(q)$ and $A_{22}(q)$ for 20% Ag at 623 K. Solid circles, triangles and squares are the corresponding experimental points from reference [9].

concentrations seem to be slightly out of phase in the high q-region. The primary peak position for In-In is located at a shorter q than those of other two components for both the concentrations. The peak position of $A_{11}(q)$ for 20% Ag is slightly lower than those of $A_{11}(q)$ in Arai *et al.* [9], but in both these concentrations the peak positions of $A_{11}(q)$, $A_{12}(q)$ and $A_{22}(q)$ appear in order of decreasing q-values. Mutatis mutandis, the general agreement between the experimental values and the calculated ones is pretty good. Any discrepancy observed between the experimental and calculated values is likely to result from the steps of the process in extracting the experimental values.

From the work presented here it may be concluded that the structure of an alloy at temperature near melting are that of the mixtures of two hard spheres of different sizes and charges. Presently the calculations of physical quantities of these binary alloys are in progress. If experimental and calculated quantities come out within the limit of experimental errors, the assumptions will have more solid base.

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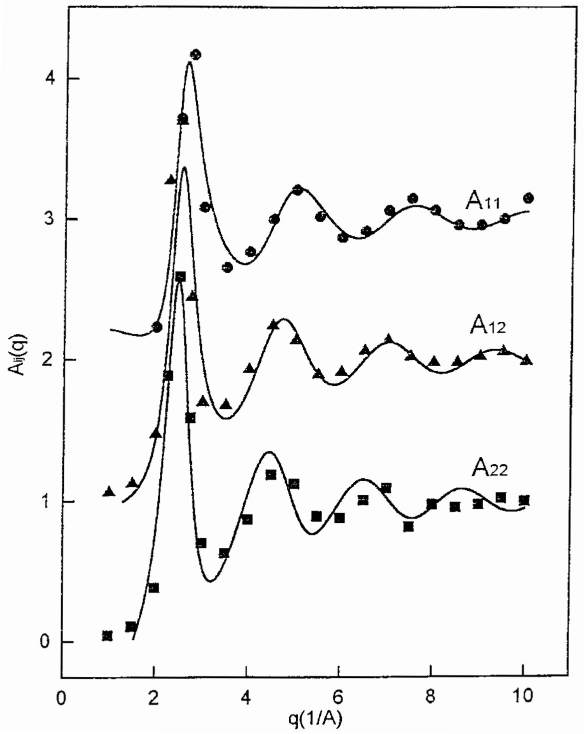

Fig. 4. Faber-Ziman [FZ] structure factors $A_{11}(q)$, $A_{12}(q)$ and $A_{22}(q)$ for 70% Ag at 973 K. Solid circles, triangles and squares are the corresponding experimental points from reference [9].

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