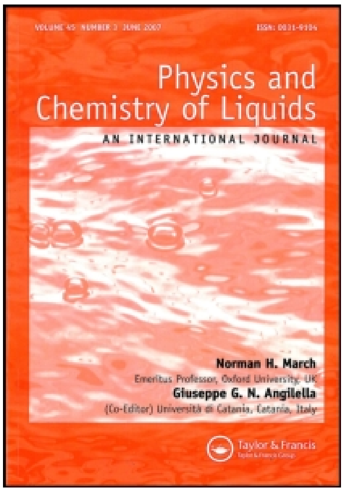

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On the Concentration Dependence of the Ordering Potential in Liquid Li–Pb Alloys

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By using the Gibbs–Bogoliubov variational method, Bhatia and Young have recently provided an improvement on the Flory model of mixtures. The expression for the free energy of mixing arising from the Bhatia and Young approach is used to study the concentration fluctuations $S_{cc}(0)$ of the liquid Li–Pb alloy. It is shown that the experimental behaviour of $S_{cc}(0)$ can be explained within the framework of this theory if the ordering potential is assumed to vary strongly with concentration near the stoichiometric composition Li_4Pb.

1 INTRODUCTION

The properties of the liquid Li–Pb alloy have been extensively studied by a number of workers (for recent reviews see Refs [1, 2]). In this system the thermodynamic excess functions, structure factors, electrical resistivities, thermopowers and magnetic susceptibilities all show pronounced deviations from ideality close to the stoichiometric

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composition Li_4Pb. Theoretical interpretations of the thermodynamic and structural properties of the liquid Li–Pb alloy have been given by Hoshino and Young[3] and by Hoshino[4,5] in terms of the compound-forming model introduced by Bhatia and coworkers.[6] This is a phenomenological model which assumes the existence of finite lifetime "chemical complexes" or "molecules" in the mixture. Alternatively, Copestake *et al.*[7], using the mean spherical and hypernetted chain approximations, have shown that a system of charged hard spheres with screened Coulomb interactions (and satisfying the requirement of local charge neutrality) allows good predictions of the concentration-concentration structure factor $S_{cc}(q)$ for Li_4Pb. This approach has recently been extended by Hafner *et al.*[8] to develop a theory for the structure and thermodynamic properties of Li-based liquid alloys.

In the present paper we shall focus attention on the long-wavelength limit ($q \to 0$) $S_{cc}(0) = N\langle(\Delta c)^2\rangle$, where $\langle(\Delta c)^2\rangle$ is the mean square fluctuation in concentration. $S_{cc}(0)$ is given in terms of the Gibbs free energy of mixing per atom by[9]

$$S_{cc}(0) = \frac{kT}{(\partial^2 \Delta G/\partial c^2)_{T,p}}, \qquad (1)$$

where k is the Boltzmann constant, T the temperature and p the pressure. The characteristic features of $S_{cc}(0)$ have been analysed by several workers for different classes of liquid alloys (see e.g. the review articles[6,10]) as well as for non-metallic systems.[11,13] In particular, for the liquid Li–Pb alloy $S_{cc}(0)$ presents a large dip at the stoichiometric composition[14,15] as a consequence of the tendency of this system for heterocoordination. A theoretical interpretation of this behaviour has been given by Bowles and Silbert[16] using the random-phase approximation.

The models we shall consider here are based on the ideas recently put forward by Bhatia and Young,[17] who by means of the Gibbs–Bogoliubov variational method[18,19] have provided a rationale for, and improved on, the Flory expression for the free energy of mixing of a binary fluid.[20,21] Their discussion is rather qualitative, however, and we shall attempt here to explore their theory more quantitatively. In particular, we shall show that within the framework of this approach the $S_{cc}(0)$ behaviour of the liquid Li–Pb alloy can be explained if the ordering potential is assumed to vary strongly with concentration as is in keeping with the observed thermodynamic and transport properties of this system. Our findings reinforce a similar conclusion reached by Bowles and Silbert in the paper cited above.

2 MODEL CALCULATIONS

Following Bhatia and Young,[17] we consider a binary mixture modelled by the Hamiltonian

$$H = H_{hs} + V, \tag{2}$$

where H_{hs} describes a hard sphere reference system and V is a perturbation providing a tail interaction between unlike atoms. The interactions are assumed to be pairwise additive. The free energy of mixing corresponding to the above Hamiltonian is given by perturbation theory as

$$\Delta G \simeq \Delta F = -T\Delta S_{hs} + c(1-c)n\omega_0, \tag{3}$$

where ΔS_{hs} is the entropy of mixing of the hard sphere reference system, n is the total number density, and ω_0 is defined by

$$\omega_0 = \int v_{12}(r) g_{12}^{hs}(r)\, d\mathbf{r}, \tag{4}$$

$v_{12}(r)$ being the pair interaction between unlike atoms and $g_{12}^{hs}(r)$ the radial distribution function for unlike hard spheres in the reference system. ΔG may be taken as approximately equal to ΔF, the Helmholtz free energy of mixing, because "zero-pressure" conditions are assumed. Since the hard-sphere formula for the entropy of mixing is superior to Flory's formula,[22,23] Eq. (3), which is the basic result of the paper by Bhatia and Young, is an improvement on the Flory model of mixtures.

On substituting (3) in (1), $S_{cc}(0)$ is given by

$$\frac{1}{S_{cc}(0)} = \frac{1}{S_{cc}^{hs}(0)} + \frac{1}{kT}\frac{\partial^2}{\partial c^2}[c(1-c)n\omega_0], \tag{5}$$

where $S_{cc}^{hs}(0) = kT/(\partial^2 \Delta G_{hs}/\partial c^2)_{T,p}$ is the concentration fluctuation of a hard sphere system, for which $\Delta G_{hs} = -T\Delta S_{hs}$. In what follows we describe several approaches to the calculation of the quantity ω_0 occurring in Eqs (3) and (5).

Firstly it may be noted that Eq. (4) can be written in the form

$$\begin{aligned}\omega_0 &= \int v_{12}(r)\, d\mathbf{r} + \int v_{12}(r)(g_{12}^{hs}(r) - 1)\, d\mathbf{r} \\ &= \tilde{v}_{12}(0) + \frac{1}{n(2\pi)^3[c(1-c)]^{1/2}} \int \tilde{v}_{12}(q) S_{12}^{hs}(q)\, d\mathbf{q},\end{aligned} \tag{6}$$

where $S_{12}^{hs}(q)$ is the hard-sphere Ashcroft–Langreth partial structure factor (whose expression is analytically available in the Percus–Yevick approximation[24,25]) and $\tilde{v}_{12}(q)$ is the Fourier transform of $v_{12}(r)$. The simplest approximation to ω_0 results from discarding all but the zero-wavenumber vector from (6), which thus reduces to

$$\omega_0 \simeq \tilde{v}_{12}(0) = \int v_{12}(r)\,d\mathbf{r}, \tag{7}$$

an expression which can also be obtained directly from (4) by neglecting correlations under the integral sign. If a better approximation to ω_0 is to be achieved, the full Eq. (6) must be used. In this article we present the results of using for $v_{12}(r)$ the simple model potential

$$v_{12}(r) = \begin{cases} \mu\varepsilon & (r < d_{12}) \\ \varepsilon & (d_{12} < r < \lambda d_{12}), \\ 0 & (\lambda d_{12} < r) \end{cases} \tag{8}$$

where μ and λ are real parameters and d_{12} is defined by $d_{12} = (d_1 + d_2)/2$, d_1 and d_2 being the hard-sphere diameters of the two components. Fourier transformation of (8) leads to

$$\tilde{v}_{12}(q) = \tfrac{4}{3}\pi d_{12}^3\varepsilon[(\mu - 1)f(qd_{12}) + \lambda^3 f(\lambda q d_{12})], \tag{9}$$

where

$$f(x) \equiv \frac{3(\sin x - x\cos x)}{3}. \tag{10}$$

In the particular case $q = 0$,

$$\tilde{v}_{12}(0) = \tfrac{4}{3}\pi d_{12}^3\varepsilon(\mu - 1 + \lambda^3). \tag{11}$$

Substitution of Eqs (9)–(11) in (6) allows the quantity ω_0 to be calculated in terms of the parameters λ, μ and ε.

In the next section we discuss the results of calculating $S_{cc}(0)$ for the Li–Pb system using the above two approximations for ω_0 (Eqs (7) and (6, 9–11)).

3 RESULTS AND DISCUSSION

In applying Eq. (5) to the liquid Li–Pb alloy we have firstly assumed that the ordering potential $\tilde{v}_{12}(0)$ (Eq. (7)) is independent of concentration. An analytical expression for $S_{cc}^{hs}(0)$ is available in the Percus–Yevick approximation (see e.g. Refs [25, 26]) and has been used throughout this paper. The hard-sphere diameters necessary for computing $S_{cc}^{hs}(0)$ were obtained by fitting d_1 and d_2 to the experimental entropies of the pure metals,[27] as in the method described by Hoshino and Young[3]; the appropriate densities at $T = 932\,\mathrm{K}$ are $\rho(\mathrm{Li}) = 0.461\,\mathrm{g\,cm^{-3}}$ and $\rho(\mathrm{Pb}) = 10.212\,\mathrm{g\,cm^{-3}}$.[28] In fitting the hard-sphere diameters we also took into account the electronic contribution (see e.g. Ref. [29]). The values thus obtained are $d(\mathrm{Li}) = 2.50$ Å and $d(\mathrm{Pb}) = 2.95$ Å. The total number density n was determined using the volume of mixing observed by Ruppersberg and Speicher.[28]

The results of the above calculations are represented by the curve A of Figure 1, which corresponds to the best fit of Eq. (5), with $\omega_0 = \tilde{v}_{12}(0) = \text{constant}$, to the experimental EMF data of Saboungi *et al.*[15] The value thus obtained for $\tilde{v}_{12}(0)/kT$ is -158 Å^3. The negative value obtained for the ordering potential reflects the attractive character of the tail interaction between unlike atoms, and its effect is to depress $S_{cc}(0)$ relative to hard sphere values, as required (see Figure 1). All this is in agreement with the tendency of the system for heterocoordination. The numerical results, however, do not produce a reasonably good fit to the experimental values of $S_{cc}(0)$.

In order to provide a better description of $S_{cc}(0)$ we have considered the full expression (6) for ω_0 using the model potential (8). In this case too, $\tilde{v}_{12}(0)$ (Eq. (11)) is assumed independent of concentration, but a concentration-dependent term appears in the expression of ω_0 (the integral term of (6)). To calculate this term we have used the analytical expression for $S_{12}^{hs}(q)$ in the Percus-Yevick approximation,[24,25] the actual integration having been performed by a modification of the Simpson method. We describe below several of the results obtained with this approach.

Figure 1 shows a representative sample of our calculations. The curves B and C give the optimal fits of Eq. (5) (with ω_0 given by (6), (9-11)) corresponding to two different values of $\lambda(\lambda = 1.1$ and $\lambda = 1.3$, respectively), μ being fixed ($\mu = 1$) and $\tilde{v}_{12}(0)$ being considered as the only freely adjustable parameter. The values of this parameter are $\tilde{v}_{12}(0)/kT\ (B) = -195$ Å^3 and $\tilde{v}_{12}(0)/kT\ (C) = -148$ Å^3 which correspond, according to (11), to the values $\varepsilon/kT\ (B) \approx -1.728$ and $\varepsilon/kT\ (C) = -0.795$. As can be seen in Figure 1, the effect of the integral term of Eq. (6) is to elevate the two peaks of $S_{cc}(0)$ relative to the values of the curve A, as required; the greater the value of λ, the smaller is this elevation, and for values around $\lambda = 1.9$ the difference is negligible. It should be noted, however, that no improvements are produced in the region around the minimum of $S_{cc}(0)$, doubtless due to a marked dependence of $\tilde{v}_{12}(0)$ on concentration in this area.

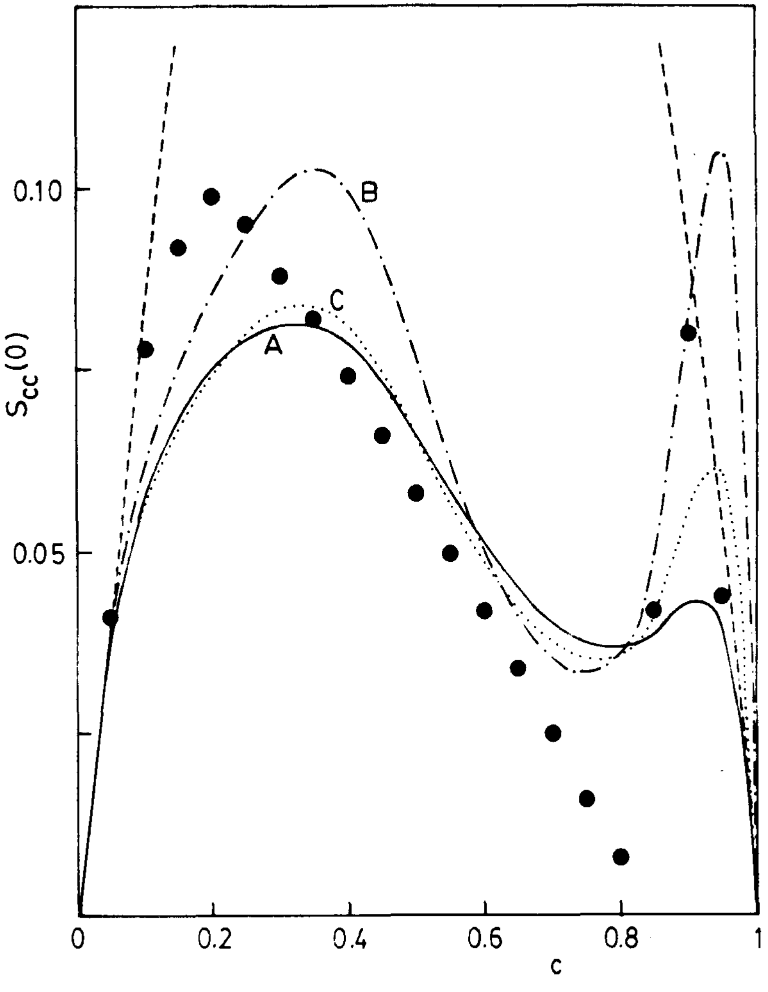

Figure 1 $S_{cc}(0)$ for the liquid Li-Pb alloy plotted against lithium concentration. The curves A, B and C correspond to the various approximations used (see text). The points show experimental results. For reference, the hard-sphere curve is also shown (— — —).

Figure 2 shows the $S_{cc}(0)$ curves obtained from Eq. (5) by assigning several constant values to $\omega_0 = \tilde{v}_{12}(0)$. It is clear from the figure that the values of $\tilde{v}_{12}(0)$ needed to fit the experimental $S_{cc}(0)$ data are indeed strongly dependent on concentration. Figure 3, which shows the curve of the values of $\tilde{v}_{12}(0)/kT$ which fit $S_{cc}(0)$ at each concentration when Eq. (7) is used, closely resembles that obtained by Bowles and Silbert[16] on the basis on the random-phase approximation, with the same striking dip at stoichiometry. A similar curve is obtained when the model potential (8) is used in the full expression for ω_0.

To sum up, the model for the free energy of mixing embodied in Eq. (3) accounts for the behaviour of $S_{cc}(0)$ in liquid Li-Pb alloys if the ordering potential is assumed to be concentration dependent. This is true both when ω_0 is approximated as in Eq. (7) and when the full expression (6) is used with the model potential (8). The concentration dependence of $\tilde{v}_{12}(0)$ would appear to be due[16] to the existence near

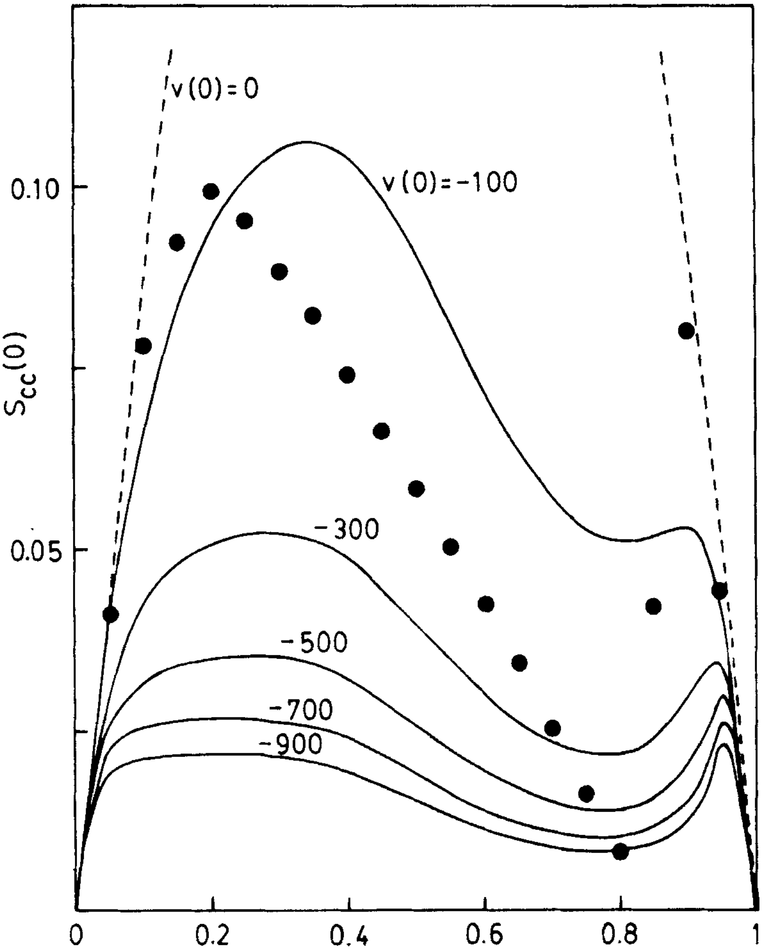

Figure 2 $S_{cc}(0)$ curves obtained for different values, in Å^3, of $v(0) \equiv \tilde{v}_{12}(0)/kT$ (see text). The value $v(0) = 0$ corresponds to the hard-sphere reference system. The points are the experimental $S_{cc}(0)$ data for Li-Pb.

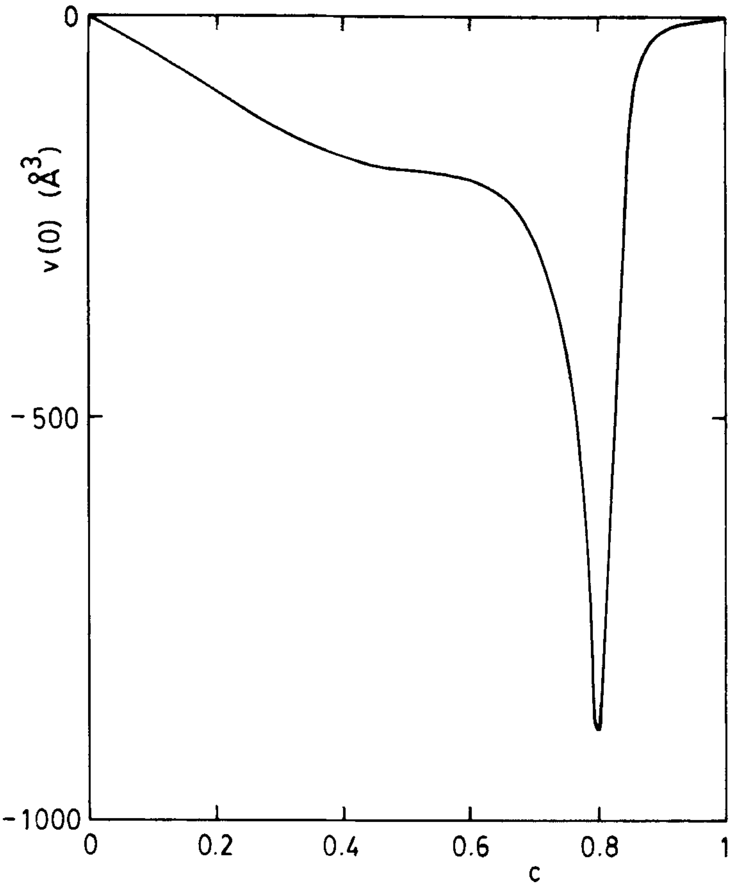

Figure 3 Required concentration dependence of the ordering potential $v(0) \equiv \tilde{v}_{12}(0)/kT$ for the system Li-Pb ($c \equiv c_{\mathrm{Li}}$).

stoichiometry of low-energy atomic configurations which result in increased effective interaction among the participating atoms.

Finally, we note that the applicability of Eq. (3) to the study of other thermodynamic properties of a strongly heterocoordinating system like Li-Pb could be questioned. The use of this equation implies, for example, that if ω_0 and n are assumed to be independent of temperature, then the entropy of mixing is simply the hard sphere expression ΔS_{hs}, so that possible ordering effects in the entropy of mixing are not taken into account. These effects, as well as the small electron-gas contribution, are considered in the treatment of Li-based alloys developed by Hafner *et al.*[8] However, as Young[30] has pointed out, the results of Hafner's treatment for the entropy of mixing of the system

Li-Pb are no better than those yielded by the simple hard sphere description used by Alblas *et al.*[31]

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