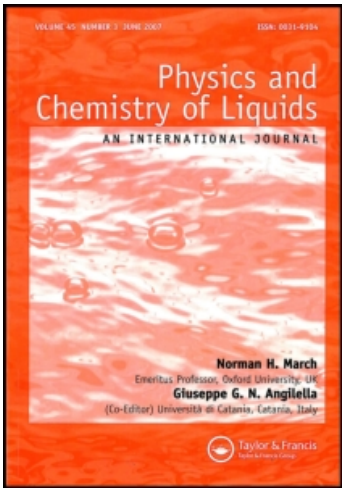

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A Correlation Between a Hard Sphere System and Liquid State Theory

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Letter

A Correlation Between a Hard Sphere System and Liquid State Theory

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Currently two theories viz the hard sphere system and liquid state theory are primarily used to understand the thermodynamical behaviour of liquid metal alloys. However, these two approaches have been pursued independently and little attempt has been made to correlate the two theories. The present work explores the possibility of finding the correlation between the two approaches. We take numerical examples of NaHg and LiPb, the compound forming alloys, and apply the hard sphere results in liquid state theory.

Recently Bhatia and Singh[1] developed a statistical mechanical model based on liquid state theory for compound forming alloys and explained several thermodynamical properties of liquid metal alloys. The model assumes the existence of appropriate chemical complexes $A_\mu B_\nu$ and that the energy of AA or BB bond depends on whether the bond is part of the complex or not. Further by applying the grand partition function technique, they developed various formulae for discussing both the thermodynamic properties and the short range order. We present the formulations of Bhatia and Singh[1] that are being employed in the present calculations. The Warren–Cowley short range order (S.R.O.) parameter $\alpha_1^{2,3}$, for the nearest neighbour sites can be defined by the probability $[B/A]$ that defines atom B exists at a site 2 which is nearest neighbour to site 1. A knowledge of SRO is useful in

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understanding many physical properties mainly for the calculation of structure factors.[4,5] Finally, Eq. (4.8) of Bhatia and Singh[1] can be written

$$\alpha_1 = \frac{\beta - 1}{\beta + 1} \tag{1}$$

where β is defined by [Eq. 2.23 of Ref. (1)]

$$\beta = \sqrt{1 + 4C(C-1)(\eta^2 - 1)} \tag{2}$$

which in turn is related with activity coefficients γ_A and γ_B and excess free energy of mixing G_M^{exc} by

$$\gamma_A = \left[\frac{\beta - 1 + 2C}{C(\beta + 1)}\right]^{Z/2}, \qquad \gamma_B = \left[\frac{\beta + 1 - 2C}{(1-C)(1+\beta)}\right]^{Z/2} \tag{3}$$

$$\frac{G_M^{exc}}{NK_BT} = C \ln \gamma_A + (1 - C) \ln \gamma_B \tag{4}$$

and

$$S_{cc}(0) = \frac{C(1-C)(1+\alpha_1)}{1 - (Z-1)\alpha_1} \tag{5}$$

Here η is a function related with interchange energy ω i.e. $\eta = \exp(\omega/ZK_BT)$. In the present work we assume that η is a function related with effective packing fraction of an alloy in hard sphere system. The notion does not seem unrealistic if we look to Eq. (5.19) of the work Chaturvedi *et al.*[6] who have defined interchange energy in terms of compressibility which in turn is related with packing fraction in Percus–Yevick approximation.[7] As the exact relation between compressibility and effective packing fraction of an alloy is not known, η is assumed to be the effective packing fraction of the alloys of interest. This is an approximate relation and may not be true for all alloys. We know in an alloy if unlike pairs are preferred over like pairs, α_1 becomes negative and vice-versa. The effective packing fractions at different concentrations employed in the present calculations are taken from our previous work.[8,9] Our model that calculates concentration dependent packing fraction and volume of mixing of an alloy is already discussed at length elsewhere[8,10] and needs no repetition. We interpret the observed behaviour of excess free energy of mixing G_M^{exc}, concentration fluctuations $S_{cc}(0)$, activity coefficients γ_A and γ_B and the short range order parameter (SRO) α_1, on the basis of hard sphere parameter η. The coordination number Z is the same as that quoted by Bhatia and Singh[1] for LiPb and obtained by fitting G_M^{exc}/NK_BT to its experimental value[11] at equiatomic concentration for NaHg system. Figure 1, showing the short range order parameter α_1(S.R.O.), reveals the existence of a privileged group of unlike

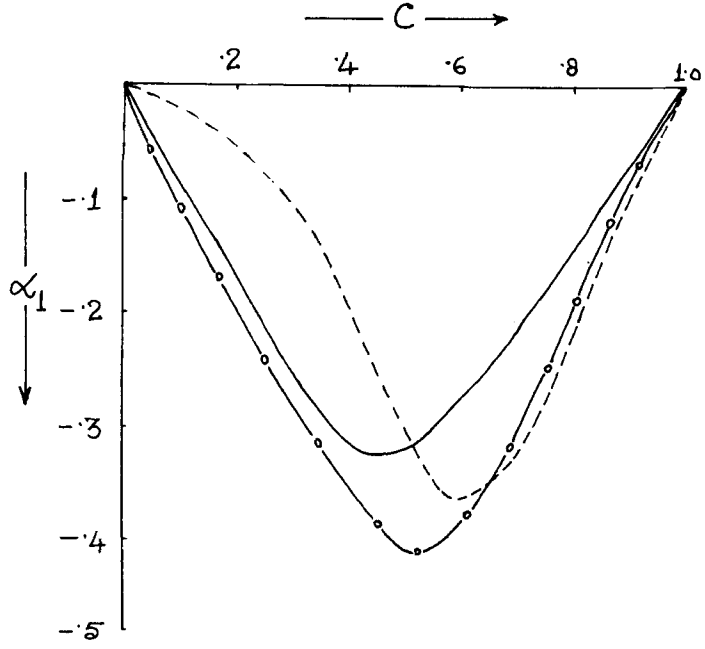

FIGURE 1 Short range order parameter α_1 versus concentration (a) NaHg (circle and dash —O—O—). (b) LiPb (full line) for the present calculations and dotted lines (.....) for LiPb due to Ref. 1. Same notations are used in all figures.

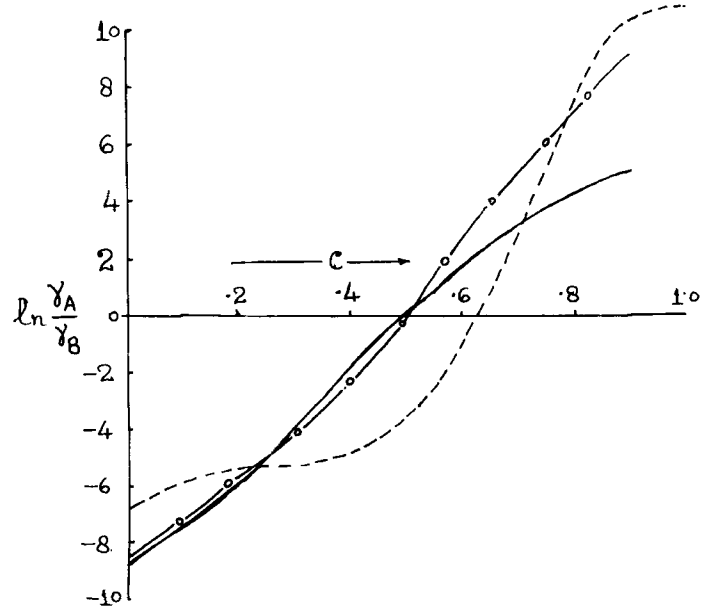

FIGURE 2 Concentration dependence of $\ln(\gamma_A \gamma_B)$. Notations are same as described in Figure 1. XX experimental points from Ref. 11.

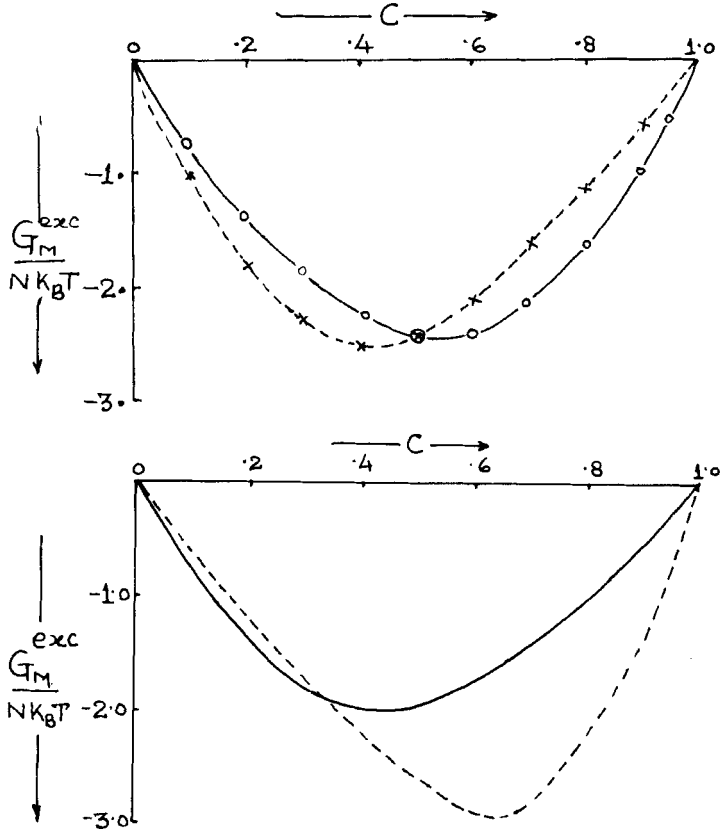

FIGURE 3(a and b) Concentration dependence of G_M^{exc}/NK_BT (a) NaHg (b) LiPb.

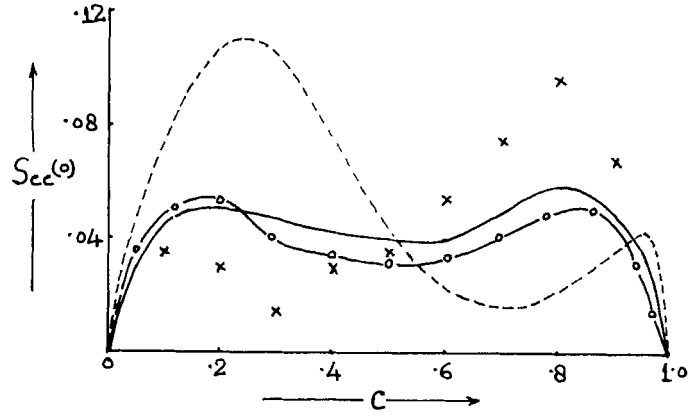

FIGURE 4 Concentrations dependence of $S_{cc}(0)$.

pair of the cluster in both the compound forming alloys. Figure 2 depicts the ratio of the activity coefficients $\gamma = \gamma_A/\gamma_B$. G_M^{exc} and $S_{cc}(0)$ are plotted versus concentration in Figures 3(a, b) and 4 respectively. The results are compared with the theoretical values of Bhatia and Singh[1] for LiPb and with the experimental values[11] for NaHg alloy. Though the exact compound forming compositions i.e. $NaHg_2$ and Li_4Pb are not predicted by our treatment, nevertheless the results, shown in Figures 1 to 4, are, in general, in reasonable agreement with available data particularly for NaHg system. Knowing that these properties particularly $S_{cc}(0)$ are very sensitive to input parameters, we can conclude that there is a possibility of finding a correlations between liquid state theory and the hard sphere reference system. However, more comprehensive efforts are clearly needed in this direction.

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References

1. A. B. Bhatia and R. N. Singh, *Phys. Chem. Liq.*, **11**, 285 (1982).
2. J. M. Cowley, *Phys. Rev.*, **77**, 667 (1950).
3. N. H. March, S. Wilkins and J. E. Tibballs, *Crys. Latt. Defects*, **6**, 253 (1976).
4. J. Bletry, *Z. Naturf.*, **33A**, 327 (1978).
5. M. Favre-Bonte, J. C. Joud, P. Hicter and P. Desre, *J. De. Physique*, C8–586 (1981).
6. D. K. Chaturvedi, M. Rovere, G. Senatore and M. P. Tosi *Physica*, **111B**, 11 (1981).
7. M. Shimoji, *Liquid Metals*, (1977), Academis Press p. 20.
8. K. N. Khanna and P. Singh, *Phys. Chem. Liq.*, **12**, 337 (1983).
9. K. N. Khanna, *J. Phys. F: Metal Physics* **14**, 1827 (1984).
10. K. N. Khanna and P. Singh, *Physica*, **114B**, 174 (1982).
11. R. Hultgren, P. D. Desai, D. T. Hawking, M. Gleiser and K. K. Kelley 1973. Selected values of the Thermodynamic Properties of Binary Alloys (*Metals Park, Ohio, Amm. Soc. Met.*).