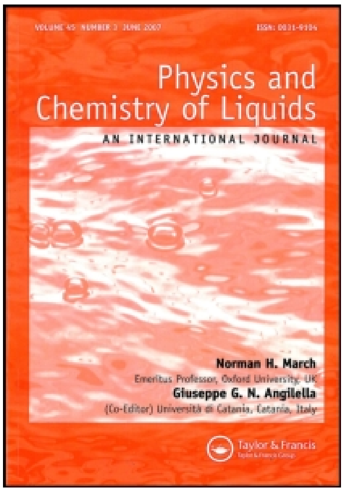

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Description of *S_{cc}*(0) in Liquid NaCs Alloys using The Bhatia-Young Model of Mixtures

R. J. Bowles[a]; L. J. Gallego[b]; M. Silbert[c]
[a] Research & Technology Centre, ICI Chemicals and Polymers, Cheshire, U.K. [b] Departamento de Física de la Materia Candensada, Facultat de Física, Universidad de Santiago de Compostela, Spain [c] School of Physics, University of East Anglia, Norwich, UK

To cite this Article Bowles, R. J. , Gallego, L. J. and Silbert, M.(1989) 'Description of *S_{cc}*(0) in Liquid NaCs Alloys using The Bhatia-Young Model of Mixtures', Physics and Chemistry of Liquids, 19: 2, 113 — 118
To link to this Article: DOI: 10.1080/00319108908028442
URL: http://dx.doi.org/10.1080/00319108908028442

Phys. Chem. Liq., 1989, Vol. 19, pp. 113-118
Reprints available directly from the publisher
Photocopying permitted by license only

DESCRIPTION OF $S_{cc}(0)$ IN LIQUID NaCs ALLOYS USING THE BHATIA-YOUNG MODEL OF MIXTURES

R. J. BOWLES*, L. J. GALLEGO** and M. SILBERT

School of Physics, University of East Anglia,
Norwich, NR4 7TJ, UK.

(Received 21 September 1988)

The Bhatia-Young expression for the free energy of mixing of a binary fluid has been used to study the concentration fluctuation in liquid NaCs alloys. This system has a strong tendency to homocoordination at sodium concentration near 0.8. In spite of this fact, good overall agreement with the experimental $S_{cc}(0)$ data is provided by assuming an ordering potential which is independent of concentration.

KEY WORDS: Concentration fluctuations, ordering potential, Flory model.

1 INTRODUCTION

Bhatia and Young[1] have proposed a simple model for the free energy of mixing of a binary fluid using hard spheres as a reference system and a tail interaction between unlike species. The model represents an improvement on the Flory expression for the free energy of mixing of a binary mixture.[2,3] Moreover, it provides an interpretation for the interchange energy parameter in terms of the asymptotic behaviour of the ordering potential.[4]

In this note we explore the Bhatia-Young formalism within the context of liquid metal alloys, following a similar approach to that used to study the system LiPb[5]. Specifically, we shall consider here the NaCs liquid alloy, a system which has been the subject of a large number of experimental and theoretical investigations (see (4) and references therein). The main features of the thermodynamic properties of this system are the tendency to homocoordination, as indicated by the concentration-concentration partial structure factor $S_{cc}(0)$[6,7], and an entropy of mixing which is almost ideal.[7,8] In this work we shall show from the study of $S_{cc}(0)$ that the ordering potential

---

* Present Address: Research & Technology Centre, ICI Chemicals and Polymers, P.O.B. 8 The Heath, Runcorn, Cheshire WA7 4QD, U.K.

** Permanent address: Departamento de Física de la Materia Candensada, Facultat de Física, Universidad de Santiago de Compostela, Spain.

for liquid NaCs alloy may be regarded as independent of concentration, in marked contrast to the behaviour found in LiPb.[5]

In the next section we write down the Bhatia-Young expressions for the free energy of mixing and the basic equations used in this work. In Section 3 we present and discuss the results of our $S_{cc}(0)$ calculations for the system NaCs.

2 THEORY

The Bhatia-Young expression for the Gibbs free energy of mixing per atom of a binary fluid reads[1]

$$\Delta G \simeq \Delta F = \Delta F_{\mathrm{hs}} + nc_1c_2\omega, \tag{1}$$

where ΔF_{hs} denotes the Helmholtz free energy of mixing of the hard sphere reference systen, n the number density, and $c_1 \equiv c$, $c_2 \equiv 1 - c$ the atomic concentrations. ω can be written as[4]

$$\omega = \tilde{v}_{12}(0) + \frac{1}{n(2\pi)^3(c_1c_2)^{1/2}} \int \tilde{v}_{12}(q)S_{12}^{\mathrm{hs}}(q)dq, \tag{2}$$

where $\tilde{v}_{12}(q)$ is the Fourier transform of $v_{12}(r)$, the interaction potential between unlike species, and $S_{12}^{\mathrm{hs}}(q)$ is the hard-sphere Ashcroft-Langreth partial structure factor, for which an analytical expression is available in the Percus-Yevick approximation.[9,10] In (1), ΔG may be taken approximately equal to ΔF because normal pressure conditions are assumed.

The simplest approximation for ω results from discarding all but the zero-wavenumber component in (2), which gives

$$\omega \simeq \tilde{v}_{12}(0) \equiv \int v_{12}(r)dr. \tag{3}$$

In principle, $\tilde{v}_{12}(0)$ is a function of the thermodynamic state of the system, i.e. $\tilde{v}_{12}(0) = f(n, c, T)$, as is the case for all effective pair potentials.[11] However, for the system considered in this paper, the alloy NaCs, we shall show that the experimental $S_{cc}(0)$ data at $T = 383$ K can be fairly well described with a constant value of $\tilde{v}_{12}(0)$.

In this work we shall use both the simple approximation (3) and the full Eq. (2) for ω. To illustrate the application of this latter equation, we shall consider here the simple model potential

$$v_{12}(r) = \begin{cases} \varepsilon & \text{for } r < \lambda\sigma_{12} \\ 0 & \text{for } r > \lambda\sigma_{12} \end{cases} \tag{4}$$

where $\sigma_{12} = (\sigma_1 + \sigma_2)/2$, σ_1 and σ_2 being the hard-sphere diameters of the two components, and λ a real parameter. Fourier transforming (4) gives

$$\tilde{v}_{12}(q) = \tfrac{4}{3}\pi\sigma_{12}^3\lambda^3\varepsilon f(\lambda q\sigma_{12}), \tag{5}$$

where

$$f(x) = \frac{3(\sin x - x\cos x)}{x^3} \tag{6}$$

If $q = 0$, Eq. (5) leads to

$$\tilde{v}_{12}(0) = \tfrac{4}{3}\pi\sigma_{12}^3\lambda^3\varepsilon. \tag{7}$$

Equations (5)-(7) can be substituted in (2) to obtain ω in terms of λ and ε.

The long wavelength limit of the concentration-concentration partial structure factor, $S_{cc}(0)$, can be obtained from[12]

$$S_{cc}(0) = \frac{k_B T}{\left[\dfrac{\partial^2 \Delta G}{\partial c^2}\right]_{T,P,N}} \tag{8}$$

where k_B is the Boltzmann constant. Using the Bhatia-Young expression for ΔG (Eq. (1)), we have

$$\frac{1}{S_{cc}(0)} = \frac{1}{S_{cc}^{\mathrm{hs}}(0)} + \frac{1}{S_{cc}^{\omega}(0)}, \tag{9}$$

where $S_{cc}^{\mathrm{hs}}(0)$ refers to the hard-sphere reference system, and $S_{cc}^{\omega}(0)$ gives the contribution of the tail interaction between unlike atoms. In the next section we discuss the results of our $S_{cc}(0)$ calculations for the system NaCs using Eq. (9) and the two above approximations for ω (Eqs (3) and (2, 5-7), respectively).

3 RESULTS

We have calculated $S_{cc}(0)$ for the system NaCs taking our reference data from the experimental work reported by Neale and Cusack at $T = 383$ K.[7] The hard sphere concentration fluctuations have been obtained using the long wavelength limit (see, e.g., Ref. 4)

$$\lim_{q\to 0} S_{cc}(q) = c_1 c_2 \lim_{q\to 0}\left[c_2 S_{11}(q) + c_1 S_{22}(q) - 2(c_1 c_2)^{1/2} S_{12}(q)\right], \tag{10}$$

which, for a hard sphere system, is available analytically in the Percus-Yevick approximation.[13] The hard-sphere diameters were obtained by fitting σ_1 and σ_2 to the experimental entropies of the pure elements,[14] as described in Ref. 15, and taking proper account of the electronic contribution.[16] The values thus obtained are $\sigma(\mathrm{Na}) = 3.2121$ Å and $\sigma(\mathrm{CS}) = 4.4832$ Å, which we have assumed to be unchanged on mixing. The number density, n, was calculated from the densities of the pure Na and Cs metals and the volume of mixing of the alloy reported by Neale and Cusack.[7] Finally, the integration in (2) was carried out using a modification of the Simpson method, and the subsequent differentiation, necessary to obtain the corresponding term $S_{cc}^{\omega}(0)$ of Eq. (9), was done numerically. Figure 1 shows our $S_{cc}(0)$ results using the approximation (3) and ω and assuming volume-independent forces. In this case ω is a constant. The best fit to the experimental data corresponds to the value $\omega/k_B T = 102.27$ Å^3. The positive value obtained for the ordering potential reflects the tendency of the liquid NaCs alloy to homocoordination. On the other hand, the good agreement with the experimental $S_{cc}(0)$ data confirms that the assumption of

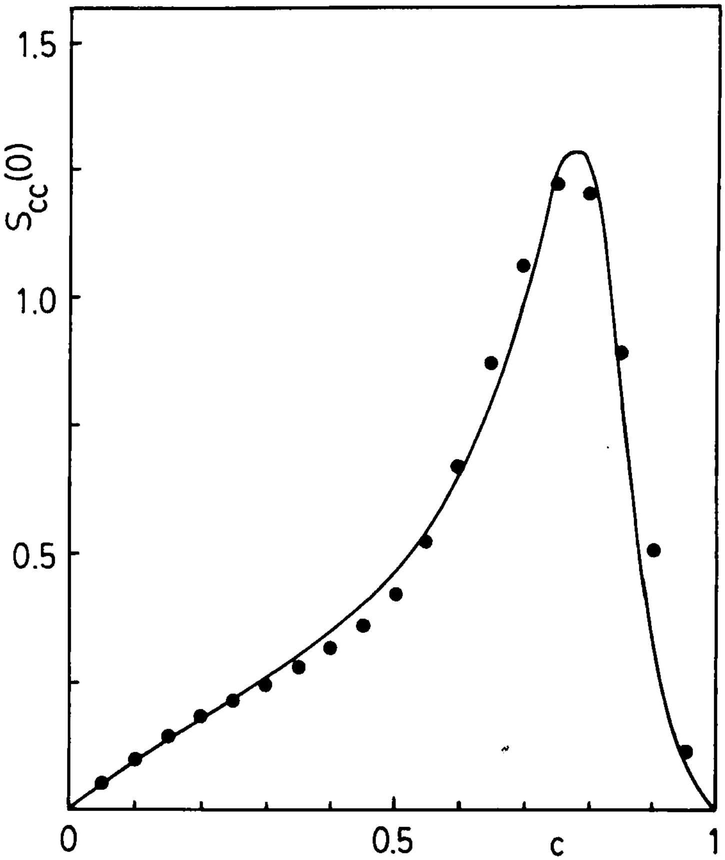

Figure 1 $S_{cc}(0)$ for the liquid NaCs alloy plotted against Na concentration. The curve corresponds to the calculations performed with Eq. (9) and taking for ω/k_BT the value 102.27 Å^3. The points show experimental results.[7]

concentration independence for the ordering potential is reasonable for this system. To further support this assumption we have plotted, in Figure 2, the required values of ω to fit $S_{cc}(0)$ at each concentration when Eq. (9) is used. The resulting concentration dependence of ω resembles the variation with composition of the interchange energy parameter obtained by Neale and Cusack.[17] It can be seen that ω is almost independent of composition over most of the concentration range, which contrasts with the behaviour found in LiPb.[5]

Figure 3 shows a representative sample of our calculations using the model potential (4). The curves A and B correspond to the values $\lambda = 1.5$, $\varepsilon/k_BT = 0.133$ and $\lambda = 1.7$, $\varepsilon/k_BT = 0.100$, respectively. The curve B, which corresponds to a weaker and longer range for the tail interaction between unlike atoms, gives better results than the curve A. The best overall agreement with experiment for this model is given by the curve C, which was obtained by taking the limit $\lambda \to \infty$, $\varepsilon \to 0$, with $\lambda^3\varepsilon$ = constant. This latter curve is the same as that of Figure 1, which was derived by assuming the

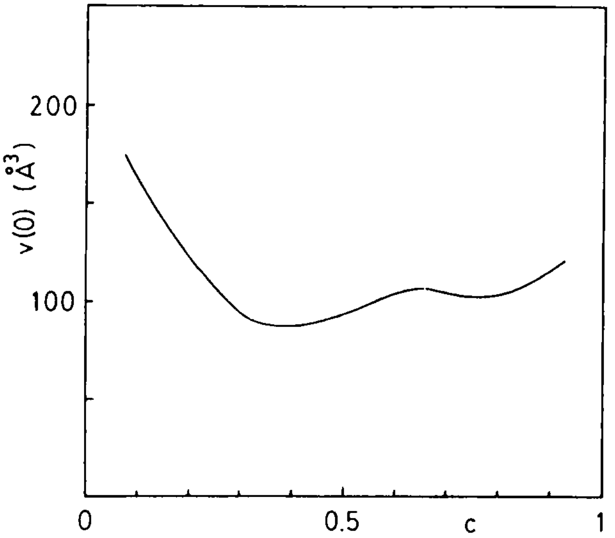

Figure 2 Required concentration dependence of the ordering potential $v(0) = \tilde{v}_{12}(0)/k_BT$ for the system NaCs (see text). c denotes the Na concentration.

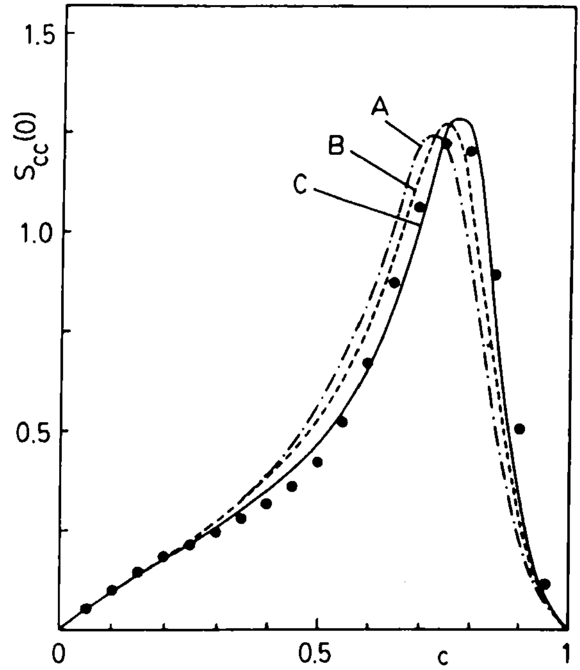

Figure 3 $S_{cc}(0)$ curves obtained for different values of the parameters λ and ε in the pair potential (4) (see text): curve A, $\lambda = 1.5$, $\varepsilon/k_BT = 0.133$; curve B, $\lambda = 1.7$, $\varepsilon/k_BT = 0.100$. The curve C corresponds to the limit $\lambda \to \infty$, $\varepsilon \to 0$, with $\lambda^3\varepsilon$ = constant. The points are experimental results.[7] c is the Na concentration.

approximation (3) for ω. This is because in such a limit the Fourier transform $\tilde{v}_{12}(q \neq 0)$ given by Eqs (5) and (6) is zero, so that the only contribution to ω in Eq. (2) is the zero-wavenumber component.

To sum up, the $S_{cc}(0)$ behaviour of the liquid NaCs alloy can be well described within the context of the Bhatia-Young formalism by assuming a concentration independent value of the ordering potential. For this description it appears, therefore, that the details of the potentials are not important. In spite of its simplicity, the description provided represents an improvement over the Flory model, which has been used by several authors[18,19] as a first approximation to describe the characteristic features of the NaCs system.

Acknowledgements

We thank Professor W. H. Young for helpful suggestions. One of us (LJG) is grateful to the British Council and the Xunta de Galicia of Spain for the financial support provided to visit the University of East Anglia during the course of this work. He also thanks the Dirección General de Investigación Científica y Técnia of Spain (Grant PB86-0654-CO2) for partial support.

References

1. A. B. Bhatia and W. H. Young, *Phys. Chem. Liq.*, **14**, 47 (1984).
2. P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).
3. E. A. Guggenheim, *Mixtures* (Oxford: Oxford U.P., 1952).
4. W. H. Young, *Can. J. Phys.*, **65**, 241 (1987).
5. L. J. Gallego, J. A. Somoza and J. A. Alonso, *Phys. Chem. Liq.*, **16**, 249 (1987).
6. K. Ichikawa, S. M. Granstaff and J. C. Thompson, *J. Chem. Phys.*, **61**, 4059 (1974).
7. F. E. Neale and N. Cusack, *J. Phys. F: Met. Phys.*, **12**, 2839 (1982).
8. J. A. Alonso and L. J. Gallego, *J. Phys. F: Met. Phys.*, **15**, L185 (1985).
9. N. W. Ashcroft and D. C. Langreth, *Phys. Rev.*, **156**, 685 (1967); see also erratum *Phys. Rev.*, **166**, 934 (1968).
10. Y. Waseda, *The Structure of Non-Crystalline Materials* (New York: McGraw-Hill, 1980).
11. J. S. Rowlinson, *Mol. Phys.*, **52**, 567 (1984).
12. A. B. Bhatia and D. E. Thornton, *Phys. Rev. B*, **2**, 3004 (1970).
13. J. E. Enderby and D. M. North, *Phys. Chem. Liq.*, **1**, 1 (1968).
14. R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelley and D. D. Wagman, *Selected Values of the Thermodynamic Properties of the Elements* (Metal Park, Ohio: American Society for Metals, 1973).
15. K. Hoshino and W. H. Young, *J. Phys. F: Met. Phys.*, **10**, 1365 (1980).
16. M. Silbert, I. H. Umar, M. Watabe and W. H. Young, *J. Phys. F: Met. Phys.*, **5**, 1262 (1975).
17. F. E. Neale and N. Cusack, *Phys. Chem. Liq.*, **14**, 115 (1984).
18. A. B. Bhatia and N. H. March, *J. Phys. F: Met. Phys.*, **5**, 1100 (1975).
19. R. N. Singh and A. B. Bhatia, *J. Phys. F: Met Phys.*, **14**, 2309 (1984).