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SIMPLE GENERALISED BHATIA–MARCH– FLORY FORMULA FOR CONCENTRATION FLUCTUATIONS IN LIQUID MIXTURES

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The Bhatia–March–Flory formula for S_{cc} describes concentration fluctuations in liquid binary mixtures in which the size ratio between the atoms is large. In this way, a successful application to Na–Cs has been achieved. On the other hand, Karaoglu and Young derived an expression for S_{cc} that is applicable when the size ratio is near to unity but when atomic couplings are concentration-dependent. Thereby, Li–Mg was successfully described. In the present work, the two descriptions are combined to produce a simple formula probably of considerable generality and Sn–Zn and Na–Cd are thus successfully described.

KEY WORDS: Concentration fluctuations, binary mixtures, size ratio.

1 INTRODUCTION

The concentration fluctuation function S_{cc} of Bhatia and Thornton¹ is the key to many thermodynamic properties of binary fluid mixtures. At the microscopic level, it tells us of the relative affinity of like and unlike atoms and macroscopically, therefore, it indicates the degree of tendency to phase separation (PS) or compound formation (CF).

The conformal model of Longuet–Higgins², also called the regular solution model in zeroth approximation³, provides a simple description of S_{cc} by introducing an ordering energy which quantifies the relative atomic affinity mentioned above. In particular, the size and sign of the ordering energy governs the general character (PS or CF tendency) of the system. In the original and simplest version of the theory, it was assumed that the ordering energy is concentration-independent. This is readily seen to imply that thermodynamic data are symmetrical about the equiatomic composition—an exceptional occurrence that points to the limited applicability of the model in this form.

But when the component atomic volumes are very different (and the thermodynamic data are asymmetrical) Bhatia and March⁴ showed that the conformal

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model could be suitably generalised using some early semi-empirical work due to Flory⁵. The resulting BMF theory may be viewed⁶⁻⁸ as providing concentration dependence to the ordering energy through that of the mean volume per atom. The liquid Cs—Na alloy system, where the volume ratio is 3, provides⁴ a successful application of the BMF S_{cc} formula.

However, there are other asymmetrical systems for which the volume ratio is near unity. Then, the concentration dependence of the atomic interactions (and therefore of the ordering energy) must arise by other means. In the case of simple liquid alloys, the obvious mechanism is through the free electron gas, the variation of which with density leads to a corresponding variation in the interatomic forces. This effect has been considered by Karaoglu and Young⁹ (KY for reference purposes below). They provided a simple illustration using Mg—Li, a system in which the ionic number density varies little across the composition diagram but where the mean valence electron density changes by a factor of 2.

In the work to be presented below, both the above features (the composition dependence of the BMF volume ratios and of the KY atomic coupling) are simultaneously incorporated into a single description of the ordering energy. A simple formula for S_{cc} is thus derived that should have quite wide applicability to simple liquid metal alloys.

2 THEORY

Consider a mixture of $c_1N = cN$ atoms of type 1 and $c_2N = (1 - c)N$ atoms of type 2. Then, if G is the Gibbs free energy[†], the concentration fluctuation function S_{cc} , as defined by Bhatia and Thornton¹, is given by

$$k_B TS_{cc}^{-1} = (\partial^2 G / \partial c^2)_{PTN} \quad (1)$$

The generalised conformal model, to be discussed in this paper, is founded on the assumption that the Gibbs free energy is describable through an equation of the form[‡]

$$G - G_{\text{ideal}} = \frac{1}{2\Omega} \sum c_i c_j g_{ij} \quad (2)$$

Here, Ω is the mean volume per atom, the g_{ij} are atomic coupling parameters and

$$G_{\text{ideal}} = -k_B T \sum c_i \ln \{c_i \Omega (M_i k_B T / 2\pi \hbar^2)^{3/2}\} \quad (3)$$

In the latter expression, M_1 and M_2 are the atomic masses.

[†] Per atom, here and for all other extensive thermodynamic quantities in this paper.

[‡] In his review of the present problem, Young⁸ used F and coefficients w_{ij} instead of G and g_{ij} . As $G - F = P\Omega$ and Ω is to be taken linear in c , F and G can be used interchangeably in Eq. (1). It seems more direct for present purposes to use G and g_{ij} .

In writing (2), it is assumed that the interaction energy of a type i atom with all its type j neighbours depends on the ambient macroscopic density of the latter. This is in the spirit of Van der Waals. Fortunately, we do not need to consider the g_{ij} individually; the focus of our interest will be on the combination

$$g = g_{11} - 2g_{12} + g_{22} \tag{4}$$

although, in general, the associated ordering energy g/Ω will be referred to a new base.

We now make two assumptions:

- (i) $\Omega =$ linear in $c = c_1\Omega_1 + c_2\Omega_2$, where Ω_1 and Ω_2 are the specific volumes of the pure liquids.
- (ii) $g_{ij} =$ linear in $c = c_1g_{ij}^1 + c_2g_{ij}^2$ where g_{ij}^k is the $i-j$ coupling parameter in the medium k limit. (In the present work, k is always equal to i or j , of course).

In view of (ii), we note that g , as defined by (4), is linear in c and so, therefore is

$$u = g - g_0 \tag{5}$$

where g_0 is any absolute constant for the system. Let us, therefore, write

$$u = c_1u^1 + c_2u^2 \tag{6}$$

where u^1 and u^2 are redefined ordering interactions in the pure liquid limits. The particular choice of g_0 required below is

$$g_0 = g_{11}^2 + g_{22}^1 - \frac{\Omega_2}{\Omega_1} g_{11}^1 - \frac{\Omega_1}{\Omega_2} g_{22}^2 \tag{7}$$

It takes four parameters to define this obscure expression but, mercifully, all we need to know about it, for present purposes, is that it is a constant, to be absorbed as indicated above.

Substitution of G , as given by (2), into (1), under the assumptions (i) and (ii), now yields

$$S_{cc}^{-1} - (c_1c_2)^{-1} = \frac{\Omega_1\Omega_2}{\Omega^3} \frac{\bar{u}}{k_B T} + \left\{ \frac{\Omega_1\Omega_2}{\Omega^3} \left(c - \frac{1}{2} \right) + \frac{(c_1^2\Omega_1 - c_2^2\Omega_2)}{\Omega^2} \right\} \frac{\Delta u}{k_B T} + \frac{(\Omega_1 - \Omega_2)^2}{\Omega^2} \tag{8}$$

where

$$\bar{u} = \frac{1}{2}(u^1 + u^2), \quad \Delta u = u^1 - u^2 \tag{9}$$

Below, we use the u 's of eqs. (6) and (9) but it is of some interest to note that if we analyse similarly the original g of Eq. (4), we obtain $\bar{u} = \bar{g} - g_0$ and $\Delta u = \Delta g$.

If we assume a concentration-independent ordering interaction u , so that $\Delta u = 0$, Eq. (8) reduces to the single-parameter BMF formula. Alternatively, if we suppose that the volume is independent of concentration, so that $\Omega_1 = \Omega_2$, Eq.(8) reduces to the KY result

$$S_{cc}^{-1} - (c_1c_2)^{-1} = [\bar{u} + 3(c - 1/2)\Delta u]/\Omega k_B T \quad (10)$$

Eq. (8), incidentally, can be alternatively written

$$S_{cc}^{-1} - (c_1c_2)^{-1} = \frac{\Omega_1\Omega_2}{\Omega^3} \frac{u}{k_B T} + \frac{(c_1^2\Omega_1 - c_2^2\Omega_2)}{\Omega^2} \frac{\Delta u}{k_B T} + \frac{(\Omega_1 - \Omega_2)^2}{\Omega^2} \quad (11)$$

This is somewhat more pleasing to the eye than the earlier expression but it has to be remembered that, in (8), \bar{u} and Δu are independent constants for the alloy system whereas, in (11), u depends on c (linearly, as in (6)) and Δu is defined in terms of its pure liquid limits (as in (9)). This alternative form of the result serves, however, to show explicitly that it is not correct to generalise the BMF formula in an 'obvious' way by merely allowing the interaction to vary with concentration. Such a procedure would lose the second term from the right of Eq. (11).

3 APPLICATIONS

We now discuss certain illustrative examples beyond the separate reaches of the BMF and KY approximations but that are adequately described by Eq. (8).

(a) Zn-Sn at 750 K

This system exhibits a marked asymmetry in S_{cc} and, as the volume ratio $\Omega_{Zn}/\Omega_{Sn} = 0.58$ is significantly different from unity, it is natural to investigate first the efficacy of the BMF formula. As Figure 1 shows, this produces some degree of success but, as the figure also indicates, the full flexibility of Eq. (8) is needed to obtain a completely satisfactory fit.

The valency of Zn is 2 and of Sn is 4, so the electronic volume ratio is 1.15 (twice the atomic volume ratio mentioned above). The rather small variation in electron density is matched by a correspondingly modest change in ordering interaction ($u_1/u_2 = 1.33$). This is in keeping with the expectation of Section 1 that the latter depends primarily on the former. By the same token, one should expect a large electronic volume ratio to signal a strong ordering interaction and therefore more dramatic behaviour of S_{cc} . This happens in the following example.

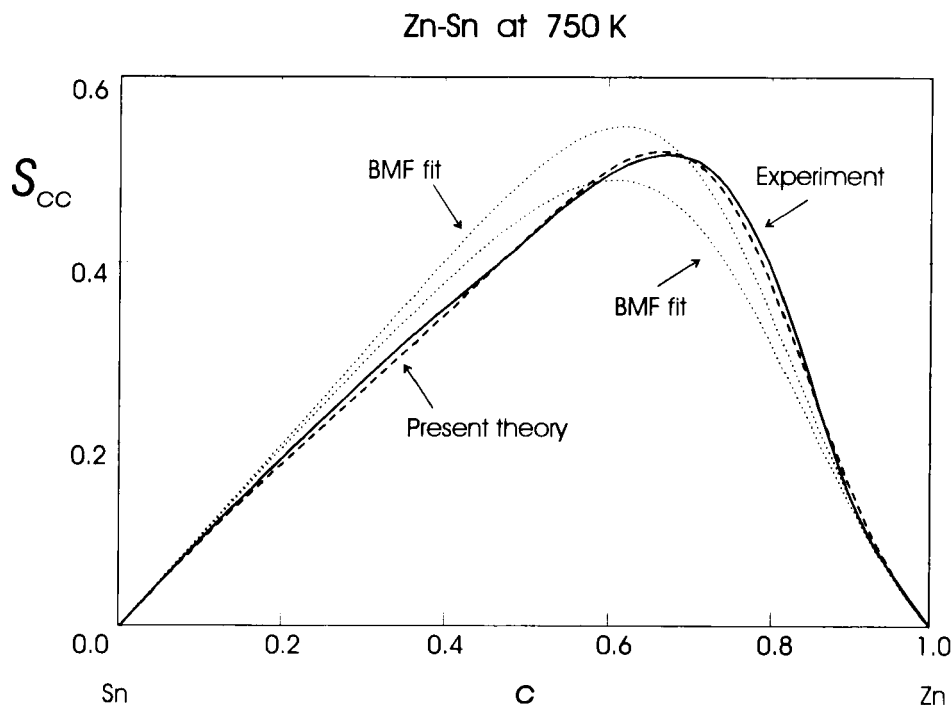


Figure 1 S_{cc} versus c for Zn, Sn_{1-c} at 750 K. The experimental curve (—) is deduced from the activity data of Hultgren *et al.*¹⁰. Use of the full Eq.(8) with $\bar{u}/k_B T = -331$, $\Delta u/k_B T = -93$ and, in atomic units a_0^3 of volume, $\Omega_1 \equiv \Omega_{Zn} = 112$, $\Omega_2 \equiv \Omega_{Sn} = 194$, yields a result (-----) barely distinguishable from experiment. The BMF formula (Eq.(8) with $\Delta u = 0$) is only partially successful in this respect; of the two attempted fits (.....), the higher corresponds to $\bar{u}/k_B T = -370$, the lower to -340 .

(b) *Na-Cd at 669 K*

In this case, the atomic volume ratio is $\Omega_{Cd}/\Omega_{Na} = 0.53$, which is much as in the previous example. Now, however, remembering that the valencies of Na and Cd are respectively 1 and 2, the corresponding electronic volume ratio is $\frac{1}{2} \times 0.53 = 0.26$. A variation in electron density by a factor of 4 can be expected to produce a large change in the ordering interaction and, thereby, strongly influence S_{cc} . This appears to be what occurs.

We should first remark that the BMF formula ($\Delta u = 0$ in Eq.(8)) is quite incapable of describing the measured S_{cc} (shown in Figure 2). This is because, to the extent that the ideal gas term $(\Omega_1 - \Omega_2)^2/\Omega^2$ is negligible in (8), the system has, at every concentration, either always a compound forming tendency ($S_{cc} > c_1 c_2$) or a phase separating tendency ($S_{cc} < c_1 c_2$). The presence of the gas term shifts the critical $c_1 c_2$ curve downwards by an insignificant amount (about 10% in the central region), so it follows that any attempt to describe the Na-rich region fails at the Cd-rich end and vice versa.

Na-Cd at 669 K

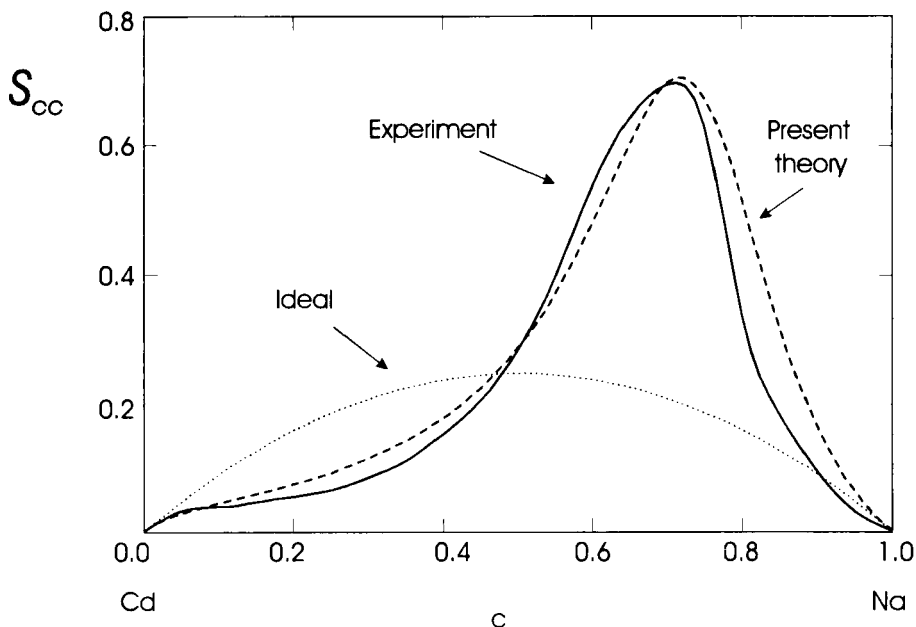


Figure 2 S_{cc} versus c for $\text{Na}_c\text{Cd}_{1-c}$ at 669 K. The experimental curve (—) is due to Harada *et al*¹¹; it agrees quite well with the earlier experimentally based result of Hoshino and Endo¹². The theoretical curve (-----) uses Eq.(8) with $\bar{u}/k_B T=0$ and $\Delta u/k_B T=-1420$ and, in atomic units a_0^3 of volume, $\Omega_1 \equiv \Omega_{\text{Na}} = 300$, $\Omega_2 \equiv \Omega_{\text{Cd}} = 158$. The ideal result $c_1 c_2$ (.....) is also shown.

By contrast, the full formula (8) is rather successful. In fact, ignoring the BMF term completely (by taking $\bar{u}=0$), but now invoking the new Δu term, reproduces (Figure 2) the qualitative features found by experiment.

4 CONCLUSIONS

The ordering energy of a conformal mixture can be written u/Ω , where Ω is the mean volume per particle and u incorporates the atomic couplings. In the BMF description, Ω varies linearly with composition and u is constant; in the KY description, u varies linearly and Ω is constant. The present work allows both effects to occur simultaneously and, as a result, a simple formula for S_{cc} is obtained that contains the BMF and KY expressions as special cases.

The linear variation of the coupling parameters suggests that the systems to which the formalism is applicable are in some sense simple. In the case of liquid alloys they should presumably be of nearly free electron type, without chemical complex formation. Zn-Sn (Figure 1) provides an example which might be safely assumed to be of this character.

A second kind of S_{cc} curve that is describable by the new formula is one in which there is a phase separating tendency ($S_{cc} \gtrsim c_1 c_2$) on one side of the composition diagram and a compound forming tendency ($S_{cc} \lesssim c_1 c_2$) on the other. Many such curves are found in the literature, one example being given in Figure 2.

A different mechanism, the pseudobinary one in which the existence of long-lifetime chemical complexes exist in the melt, can also explain¹¹ measured S_{cc} curves of Figure 2 type. It has been argued by the present authors¹³ on the basis of the entropy observations^{11,12} that Na–Cd, the system illustrated in Figure 2, is best viewed as a simple nearly free electron system without any significant degree of complex formation. The present study proceeds on that assumption and reaches conclusions consistent with it.

We have also analysed the Na–Ga and Na–In systems in the above way. These, like Na–Cd, have the asymmetric single peak feature of Figure 2, and qualitative fits to the respective measured data^{11,12,14} have been obtained. However, in Na–Ga, a good fit overall is marred by significant underestimation of S_{cc} at the Na-rich end whereas, in Na–In, the almost constant part of the curve in the In-rich region is not reproduced. It is an open question whether an entirely satisfactory fit can be obtained by further refinement of the present approach. For example, quadratic concentration-dependence of the volume and of the coupling parameters would seem to be not inappropriate generalisations for NFE systems; further study along these lines might help to resolve the undecided question⁸ of whether Na–Ga and Na–In do or do not form chemical complexes of associated atoms.

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