Generalised Bhatia-March formula for concentration fluctuations in binary liquid mixtures:

application to Na-Cs

Generalised Bhatia–March formula for concentration fluctuations in binary liquid mixtures: application to Na–Cs

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Abstract. A derivation, based on first principles, is provided of the Bhatia–March formula for $S_{cc}(0)$ of a binary fluid. A natural simple generalisation (a completion of the underlying van der Waals-like description) is then proposed. Finally, the application to Na–Cs is considered and the generalised formula is shown to provide a good description not only of $S_{cc}(0)$ but of the excess internal energy and entropy.

1. Introduction

Bhatia and March (1975; hereafter BM) introduced a formula for describing the concentration fluctuations of a binary mixture, and this has served well, over the years, as an aid to the interpretation of observed data. It has, however, a somewhat empirical (even obscure) basis, rooted as it is in lattice gas models (Longuet-Higgins 1951, Guggenheim 1952) and early polymer theory (Flory 1942). In section 2, however, we indicate a more fundamentally based approach to the problem and rederive the formula in a more compact form.

From the new standpoint, the BM formula appears to rely on an incomplete van der Waals model. When the latter is completed, a generalised BM result is obtained (section 3).

The liquid Na–Cs system is used for illustrative purposes in section 4 and a summary of our work is provided in section 5.

2. Derivation of the Bhatia–March formula

Consider a simple binary fluid containing $c_1 N \equiv cN$ atoms of type 1 and $c_2 N \equiv (1 - c)N$ atoms of type 2, all in a total volume Ω, at temperature T. Then the concentration–concentration fluctuation function $S_{cc}(0)$ is defined by

$$Nk_B T S_{cc}^{-1}(0) = (\partial^2 G/\partial c^2)_{P,T,N} \tag{1}$$

where, in standard notation, the Gibbs free energy is

$$G = E - TS + P\Omega. \tag{2}$$

The right-hand side of equation (1) is the Darken (1967) stability function, and its linkage

to fluctuation theory is due to Bhatia and Thornton (1970). We can substitute equation (2) into equation (1) to obtain

$$Nk_B T S_{cc}^{-1}(0) = (\partial^2 E/\partial c^2 - T \partial^2 S/\partial c^2 + P \partial^2 \Omega/\partial c^2)_{P,T,N} \tag{3}$$

and the various terms of this equation will be examined below.

Let us now consider the fluid microscopically. Suppose the atomic interactions are given by $v_{ij}(r)$ and the radial distribution functions by $g_{ij}(r)$. Then, if

$$w_{ij} = \int v_{ij}(r) g_{ij}(r) \, dr \tag{4}$$

the internal energy is[†]

$$
\begin{aligned}
E &= \tfrac{3}{2} N k_B T + (N^2/2\Omega)(c_1^2 w_{11} + 2 c_1 c_2 w_{12} + c_2^2 w_{22}) \\
&= \tfrac{3}{2} N k_B T - (N^2/2\Omega) c_1 c_2 w_{cc} + (N^2/2\Omega)(c_1 w_{11} + c_2 w_{22})
\end{aligned} \tag{5}
$$

where

$$w_{cc} = w_{11} - 2 w_{12} + w_{22}. \tag{6}$$

Unfortunately, we cannot write down an equally explicit and straightforward expression for the entropy. However, general theory tells us that

$$S = S_c + S_{gas}(\Omega) + S_{int} \tag{7}$$

where

$$S_c = -N k_B (c_1 \ln c_1 + c_2 \ln c_2) \tag{8}$$

and

$$S_{gas}(\Omega) = N k_B \{\tfrac{5}{2} + \ln[(\Omega/N)(m k_B T/2\pi\hbar^2)^{3/2}]\} \tag{9}$$

where $m = m_1^{c_1} m_2^{c_2}$, the m_i being the atomic masses. S_{int} arises from the interactions.

The terms of equation (3) may now be evaluated using equations (5) and (7) under the following assumptions:

(i) There is no excess volume of mixing, i.e. $\Omega = c_1 \Omega_1 + c_2 \Omega_2 \equiv \Omega_0$, where Ω_i ($i = 1, 2$) is the volume of N atoms of pure i at temperature T and pressure P.
(ii) S_{int} is, at most, linear in concentration, thus making no contribution to (3).
(iii) The w_{ij} are independent of concentration.

Thus, we obtain

$$S_{cc}^{-1}(0) = (N\Omega_1 \Omega_2/\Omega_0^3)(w/k_B T) + 1/c(1 - c) + (\Omega_1 - \Omega_2)^2/\Omega_0^2 \tag{10}$$

where

$$w = w_{cc} - (\Omega_2 - \Omega_1)(w_{22}/\Omega_2 - w_{11}/\Omega_1). \tag{11}$$

As invariably quoted and used, the BM formula appears more complicated than equation (10), but simple algebra shows that the two are, in fact, equivalent in form.

[†] We adhere to the convention invariably adopted in such work hitherto by considering insulators explicitly. In the case of metallic systems, we can expect the volume energy terms (Hasegawa and Watabe 1972) to contribute. Contributions linear in c do not affect any of the properties of subsequent interest ($S_{cc}(0)$, ΔE, ΔS), while higher-order contributions must be assumed absorbed into the w_{ij} of equation (5).

Equation (10) is somewhat more general in that only the first term of equation (11), namely w_{cc} (defined by equation (6)), can be identified with the 'interchange energy' parameter of the BM formula. The final part of (11) is new†. In practice, if we confine our attention to fitting a measured $S_{cc}(0)$ versus c curve, we fit w instead of w_{cc} and the same comparison with experiment is obtained.

Actually BM, on the basis of the then existing theories, thought that the Flory entropy expression and, therefore, their $S_{cc}(0)$ formula might be valid only for size ratios $\Omega_2/\Omega_1 \gtrsim 2$. The present discussion, however, gives all size ratios an equal theoretical status.

It is next instructive to examine the excess internal energy and the excess entropy, and we begin with the former. If assumption (iii) holds, and the w_{ij} are independent of concentration, then the pure liquid energies are

$$E_i = \tfrac{3}{2}Nk_B T + (N^2/2\Omega_i)w_{ii} \qquad (i = 1, 2). \tag{12}$$

Then, by equation (5), the excess energy is

$$\begin{aligned} \Delta E &\equiv E - c_1 E_1 - c_2 E_2 \\ &= -(N^2/2\Omega)c_1 c_2 w_{cc} + \tfrac{1}{2}N^2 c_1 w_{11}(1/\Omega - 1/\Omega_1) \\ &\quad + \tfrac{1}{2}N^2 c_2 w_{22}(1/\Omega - 1/\Omega_2) \end{aligned} \tag{13}$$

and so, on invoking assumption (i), we have

$$\Delta E = -(N^2/2\Omega_0)c_1 c_2 w. \tag{14}$$

The Flory excess energy term is obtained if we drop (unreasonably from the present point of view) the final two contributions to equation (13); then w_{cc} rather than w appears in the BM formula.

Turning next to the excess entropy and equation (7), we see that, if assumptions (i) and (ii) hold, then

$$\Delta S \equiv S - c_1 S_1 - c_2 S_2 = S_c + \Delta S_{gas}(\Omega_0) \tag{15}$$

where

$$\Delta S_{gas}(\Omega_0) = Nk_B\big(\ln(\Omega_0/N) - c_1 \ln(\Omega_1/N) - c_2 \ln(\Omega_2/N)\big). \tag{16}$$

As shown by Hoshino (1980) and Visser *et al* (1980), this expression is equivalent to the Flory excess entropy.

3. The generalised Bhatia–March formula

The treatment of the internal energy above, by taking w_{ij} constant, is very much in the spirit of van der Waals. In this way, we obtain an account of the strength of the interatomic potential tails. But, in a van der Waals approach, we should also incorporate the atomic core sizes (the excluded-volume effect) through the entropy. Clearly this has

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† In a recent paper, Gonzalez and Silbert (1988) present the results of numerical calculations of model binary alloys within the mean spherical approximation. The main conclusion of this work is that, whereas many structural aspects are sensitive only to the ordering potential, the thermodynamic properties and, specifically, $S_{cc}(0)$ are sensitive to all the potentials used. To the extent that w_{cc} can be identified with the integrated ordering potential (they are not exactly the same thing), the conclusions of that work and ours are similar.

not been done so far, and we need to take some account of S_{int} in equation (7). In doing so below, we justify more fully a method that has been introduced and exploited by Visser *et al* (1980), Neale and Cusack (1984) and Bhatia and Young (1984).

For entropy interpretation purposes, the hard-sphere model has proved useful in the past and we turn to it again here. In terms of the effective diameters, σ_1 and σ_2, an accurate expression for $S_{int} = S_{int}^{hs}(\Omega, \sigma_1, \sigma_2)$ is known (Young 1977)† and equation (7) becomes

$$S = S_c + S_{gas}(\Omega) + S_{int}^{hs}. \tag{17}$$

Note that the actual volume Ω, rather than the ideal volume Ω_0, appears in equation (17); experience has shown that the recognition of a non-zero excess volume is a vital matter.

The excess volume will also affect E and $P\Omega$ in equation (2). However, under normal circumstances ($P = 1$ atm) the correction to $P\Omega_0$ is completely negligible. In the former case, we already have a non-trivial description via the w_{ij} and it seems unreasonable, within the present very simplified context, to introduce a further refinement (and more disposable parameters; see equation (5)) at this point. We therefore adhere to the development of the previous section, except for the entropy.

With the above corrections inserted, we recalculate equation (3) and find

$$S_{cc}^{-1}(0) = [S_{cc}^{-1}(0)]_{BM} - [(\partial^2/\partial c^2)(\ln(\Omega/\Omega_0) + S_{int}^{hs}/Nk_B)]_{P,T,N} \tag{18}$$

the BM result being given by equation (10). The diameters are normally fitted to the experimentally deduced pure liquid entropies and assumed to be concentration independent. In this approximation, therefore, no new free parameters are introduced. But we require more measured input, namely the pure liquid entropies and the actual alloy volumes.

Finally, let us note for future reference, that the excess entropy of mixing can be written, on the basis of equation (17), as

$$\Delta S = (\Delta S)_F + Nk_B \ln(\Omega/\Omega_0) + \Delta S_{int}^{hs} \tag{19}$$

where $(\Delta S)_F$ is the Flory expression (15) and

$$\Delta S_{int}^{hs} = S_{int}^{hs}(\Omega, c, \sigma_1, \sigma_2) - c_1 S_{int}^{hs}(\Omega_1, \sigma_1, \sigma_1) - c_2 S_{int}^{hs}(\Omega_2, \sigma_2, \sigma_2). \tag{20}$$

4. Application to Na–Cs

It is useful to provide an illustrative example and we do so by considering Na–Cs. We consider only the most simple of approximations (constant w, constant σ_1, σ_2); for more sophisticated calculations, the reader is referred to Visser *et al* (1980) and Neale and Cusack (1984).

The relevant experimental work on liquid Na–Cs has been done by Ichikawa *et al* (1974), Huijben *et al* (1977, 1979) and Neale and Cusack (1982). The data are in broad agreement and we will, in the following, consider mainly the Neale–Cusack (NC) results, which are most complete for our purpose.

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† In the notation of that paper, to which the reader is referred for further details, $S_{int}^{hs} = S_\eta + S_\sigma + S_{elec}$.

Table 1. Na–Cs calculation input data[a].

Temperature, T	$= 383 \text{ K}$
Na specific volume, Ω_1	$= 41.3 \text{ Å}^3$
Cs specific volume, Ω_2	$= 123.3 \text{ Å}^3$
Energy parameter, w	$= -6.9 \text{ eV Å}^3$
Na core diameter, σ_1	$= 3.21 \text{ Å}$
Cs core diameter, σ_2	$= 4.48 \text{ Å}$

[a] The core diameters reproduce the experimentally determined pure liquid entropies, $S_1 = 7.893 N k_B$, $S_2 = 12.245 N k_B$ (Hultgren *et al* 1973). The volume data of figure 1 complete the input information.
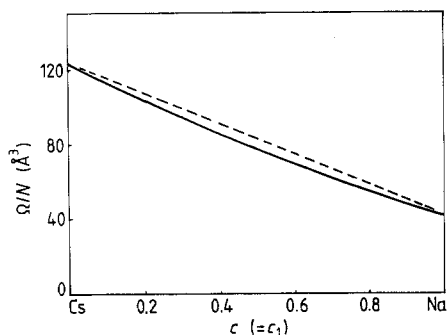

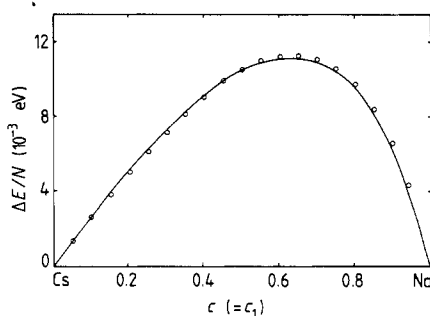**Figure 1.** Volume per atom versus concentration: ——, zero pressure (Neale and Cusack 1982); ----, zero excess volume.

Figure 2. Excess internal energy per atom versus concentration: ——, theory (equation (14) with $w = -6.9 \text{ eV Å}^3$); $\bigcirc$, experiment (Neale and Cusack 1982).

The input data to the present calculations are given in table 1 and figure 1. Table 1 contains w, the only free parameter of the theory, this having been judiciously chosen so as to achieve, in the following analysis, good overall agreement with experiment. Figure 1 shows the curve of absolute volume per atom. The departure from linearity is quite small, and indeed, for some purposes, it is negligible. But, as we will see, for the entropy it is necessary to include it.

With the above data, we now calculate the various thermodynamic curves and compare them with experiment. Figure 2 shows $\Delta E/N$, calculated using equation (14) with $w = -6.9 \text{ eV Å}^3$; it will be seen that the agreement with the measured data is good. The occurrence of a constant w, independent of concentration, is indicated by the work of Neale and Cusack (1984) as well as by that of Bowles *et al* (1989). Moreover, despite the rather different approach of the latter authors, very much the same value was obtained.

Figure 3 shows $\Delta S/N k_B$ calculated using equation (19) with σ_1 and σ_2 as in table 1, and here the agreement with experiment is also good. This is in contrast with the Flory result (equation (15), i.e. equation (19), first term). Clearly, the effect of the new entropy terms in this particular system is to cancel almost exactly the Flory term, $\Delta S_{gas}(\Omega_0)$, in equation (15), so that a near-ideal entropy is obtained, in agreement with experiment.
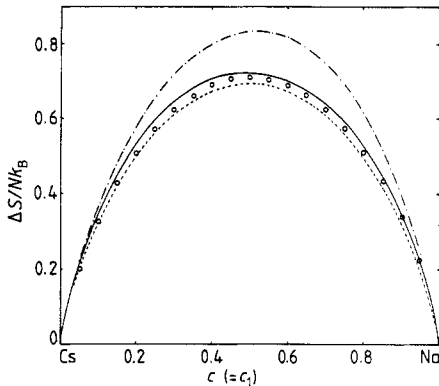
Figure 3. Excess entropy per atom versus concentration: ——, theory (equation (19) with σ_1, σ_2 as in table 1); —·—·—, Flory theory (equation (15), i.e. equation (19), first term); ----, ideal (equation (8)); O, experiment (Neale and Cusack 1982).
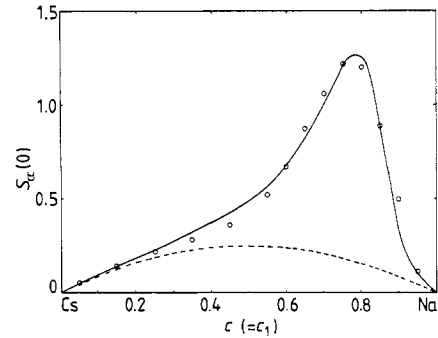
Figure 4. $S_{cc}(0)$ versus concentration: ——, theory (equation (18) with $w = -6.9$ eV Å^3 and σ_1, σ_2 as in table 1); ----, ideal $(= c(1 - c))$; O, experiment (Neale and Cusack 1982).

We finally consider $S_{cc}(0)$. With the same parameter, $w = -6.9$ eV Å^3, already used, equation (18) yields the theoretical curve shown in figure 4. There is a considerable measure of agreement with the experimentally deduced NC results.

Actually, if we use the unmodified Flory entropy (equation (15)) and thereby describe $S_{cc}(0)$ by the original BM formula (equation (10), i.e. equation (18), first term), we can achieve, as BM showed, a comparison between theory and experiment that is as good as that shown in figure 4. But this requires us to choose $w = -8.1$ eV Å^3, which provides via equation (14) excess energies that are about 17% too high (Neale and Cusack 1984).

It is, perhaps, appropriate at this point to remark that there is an existing refinement of the BM approach (Alblas *et al* 1983, Singh and Bhatia 1984) that can simultaneously achieve a satisfactory energy, entropy and $S_{cc}(0)$. This starts from the Gibbs free energy, formally defined by equations (2), (5) and (7), but now with T-dependent interaction parameters. We thus obtain terms in the separate energy and entropy contributions additional to those seen in equations (5) and (7). This development appears, however, to have little in common with that of the present paper.

5. Summary

We have, we believe, placed the BM formalism within a more rigorous framework. In doing so, we have identified it as of incomplete van der Waals type. By this, we mean that the internal energy is described suitably by a mean-field parameter, but the entropy takes no account of the atomic core sizes (the excluded-volume effect). When the latter effect is suitably incorporated, we obtain a generalised formalism that can provide, simultaneously, realistic internal energies, entropies and $S_{cc}(0)$ values.

The formalism is tested on Na–Cs and excellent accounts of the excess internal energy and entropy are obtained. The calculated and experimentally based $S_{cc}(0)$ are also found to be in rather satisfactory agreement.

Acknowledgments

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