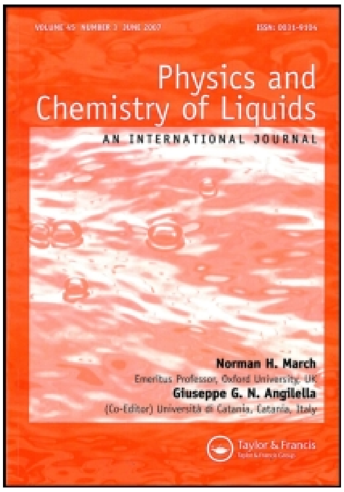

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Improved Flory Formula for the Excess Free Energy of a Binary Liquid Mixture

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A simple model for the free energy of mixing of a binary fluid is proposed using hard spheres as a reference system and a tail interaction between the unlike atoms. The model, firstly, provides an interpretation and rationale for the interchange energy parameter w and its temperature dependence occurring in the Flory formula and for a number of other current ideas. Secondly, it leads to a formula which appears to be a suitable next step in the refinement of the Flory model.

The Flory formula[1,2] for the Gibbs free energy‡ of mixing per atom of a binary fluid is

$$\Delta G = k_B T(c_1 \ln \phi_1 + c_2 \ln \phi_2) + c_1 \phi_2 w \tag{1}$$

where $c_1 \equiv c$ and $c_2 \equiv 1 - c$ are the atomic concentrations and ϕ_i are the volume fractions. The (c-independent) interchange parameter w was originally assumed to be independent of temperature and then, provided one neglects the possible small temperature dependence of ϕ_i due to volume expansion §, the two parts of Eq. (1) could be interpreted as the entropic and enthalpy terms. In this form, the formula has enjoyed some notable successes; for example, Bhatia and March[3] showed it gives a good account of $S_{CC}(0) \equiv k_B T(\partial^2 \Delta G/\partial c^2)_{T,P}$ for NaCs. Although it was already suggested

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‡ Eq. (1) is normally applied at low (1 atm.) pressure so that we will not distinguish between the Gibbs and Helmholtz free energies, although we adhere to the normal convention of using the symbol G in the Flory theory and F in the hard sphere formalism of Eqs. (5) and (8).

§ Effects due to temperature dependence of ϕ_i are neglected throughout the paper.

a long time ago[4] that there is nothing in the statistical mechanical derivation of (1) which makes it either necessary of justifiable to take w to be temperatue (and pressure) independent, it has only recently become clear that for a more quantitative analysis of the experimental data, significant T-dependence of w is on occasion indeed required (Alblas *et al.*[5] and references given there). When w is considered T-dependent, we can rewrite (1) as

$$\Delta G = T\left[k_B(c_1 \ln \phi_1 + c_2 \ln \phi_2) + c_1\phi_2 \frac{dw}{dT}\right] + c_1\phi_2\left(w - T\frac{dw}{dT}\right)$$
$$\equiv -T[\Delta S_f] + \Delta H_f \tag{2}$$

Remembering the standard thermodynamic formulae, one sees that ΔS_f and ΔH_f in (2) represent respectively the entropy and enthalpy of mixing. The subscript f has been added to indicate that they refer to the Flory expression. A theoretical evaluation of dw/dT, as of w, is of course outside the scope of Flory's work.

An alternative formulation of the problem uses a hard sphere reference system,[6,7] and we draw attention to two developments from this point of view. First, Ratti and Bhatia[8] showed that a hard sphere system, in which the unlike pairs are supplemented by a further interaction, is capable of describing $S_{CC}(0)$ in NaCs. Ratti and Bhatia used the random phase approximation (RPA) in which the direct correlation functions are written

$$c_{ii} = c_{ii}^{hs} \qquad (i = 1, 2)$$
$$c_{12} = c_{12}^{hs} - (k_B T)^{-1} v_{12}, \tag{3}$$

where v_{12} allows for non-additivity of the atomic tails. A second development in this area is the realisation[9–11] that the hard sphere description of the entropy contains physical features (packing, size difference) that the Flory expression is incapable of describing and that this description provides an apparently accurate picture of the entropy of real systems.[7,12] Visser *et al.*,[9] and Neale and Cusack[11] have, therefore, replaced the first term of Eq. (1) by a hard sphere form.

In this note, we describe a model system which coordinates the above and a number of related ideas and provides a rationale for what would appear to be the next stage in the refinement of the Flory formula. It also suggests that the Flory formula (1) is perhaps less inadequate than indicated in Refs. 9, 11, provided we identify the second term in (2) (rather than in (1)) with the enthalpy of mixing with similar identification for the entropy of mixing, as one should.

We begin by considering a binary mixture modelled by the Hamiltonian

$$H = H_{hs} + V; \quad V = \sum_{\text{unlike}} v_{12}. \tag{4}$$

Here H_{hs} describes a hard sphere reference system and V is a perturbation providing a tail interaction between unlike atoms. In anticipation of the connection between this equation and Eq. (3), we use the same symbol v_{12} in both cases.

The free energy corresponding to the above Hamiltonian is given by perturbation theory to be

$$F = F_{hs} + \langle V \rangle_{hs} = F_{hs} + c_1 c_2 \rho w_0 \tag{5}$$

where

$$w_0 = \int v_{12} g_{12}^{hs}\, d\mathbf{r}. \tag{6}$$

Here, ρ is the number density and g_{12}^{hs} the radial distribution function for unlike hard spheres in the reference system. The Gibbs–Bogoliubov variational method[6,7] gives the parameters (hard sphere diameters) of the reference system and the entropy S of the system is given by

$$S = -\left(\frac{\partial F}{\partial T}\right)_\rho \equiv S_{hs}. \tag{7}$$

S_{hs}, and likewise the entropy of mixing ΔS_{hs}, $(S - c_1 S_{hs}^{(1)} - c_2 S_{hs}^{(2)})$ below, will in general have some (implicit) temperature dependence through the variation of diameters. (See below). The free energy of mixing of the alloy corresponding to (5), in view of (7), is

$$\Delta F = \Delta F_{hs} + c_1 c_2 \rho w_0 = -T\Delta S_{hs} + c_1 c_2 \rho w_0, \tag{8}$$

where, in view of Eq. (7), the second term is the energy (enthalpy) of mixing and the first term the contribution to ΔF from entropy of mixing $\Delta S \equiv \Delta S_{hs}$.

Now first consider a simple approximation to w_0 (Eq. (6)) occurring in Eqs. (5) and (8). This is obtained by Fourier expanding each term in (6) and retaining only the zeroth components. The result is

$$w_0 \simeq \tilde{v}_{12}(0) \equiv \int v_{12}\, d\mathbf{r}, \tag{9}$$

which is an absolute constant for volume-independent forces.

Equation (9) amounts to the RPA in the present context and we show this by calculating the bulk modulus, $B \equiv \rho(d/d\rho)(\rho^2 d/d\rho)F$. This is found from Eqs. (5) and (9) to be

$$B = B_{hs} + 2c_1 c_2 \rho^2 \tilde{v}_{12}(0) \tag{10}$$

(assuming volume-independent forces). On the other hand, we can obtain the same result from Eq. (3) using the Kirkwood-Buff formula[13,2]

$$\frac{B}{\rho k_B T} = 1 - \rho[c_1^2 \tilde{c}_{11}(0) + 2c_1 c_2 \tilde{c}_{12}(0) + c_2^2 \tilde{c}_{22}(0)]. \tag{11}$$

For, substitution of Eq. (3) into the latter leads us immediately back to Eq. (10).

We thus regard the status and credibility of Eq. (9) as established in that it is compatible with the successful RPA approach of Ratti and Bhatia. In this connection it is of interest to note that, notwithstanding the remark following Eq. (9), Ratti and Bhatia found they could assume $\tilde{v}_{12}(0)$ was c-independent at fixed T.

Next we observe that

$$c_1\phi_2 \equiv c_1\left(\frac{c_2\Omega_2}{c_1\Omega_1 + c_2\Omega_2}\right) = c_1c_2\rho\Omega_2. \tag{12}$$

Hence, provided we can neglect the concentration dependence of Ω_2 which is generally not unreasonable, the concentration dependence of the second term in Eq. (1) or Eq. (2) is the same as that of the second term ($c_1c_2\rho w_0$) in (8) for density independent forces and w_0 given by (9). Since the latter term in (8) is by definition enthalpy of mixing we must identify it with the second term in (2), i.e., using (12),

$$c_1c_2\rho w_0 = c_1c_2\rho\Omega_2\left(w - T\frac{\mathrm{d}w}{\mathrm{d}T}\right). \tag{13}$$

In the RPA, the left hand side of (13) is independent of T, and hence w must have the form

$$w = a + bT; \qquad a = \frac{w_0}{\Omega_2} \tag{14}$$

and $b(=\mathrm{d}w/\mathrm{d}T)$ is a constant, not necessarily zero. Remembering Eq. (2), the expression for the entropy of mixing ΔS_f is

$$\Delta S_f = -k_B[c_1 \ln \phi_1 + c_2 \ln \phi_2] - bc_1\Phi_2 \tag{15}$$

which has different concentration dependence than the first term in (1). An estimate of "b" in terms of our hard sphere model is possible by equating ΔS_f to ΔS_{hs}. We hope to present concentration dependence of ΔS_f and ΔS_{hs} and estimates of "b" for different cases in a later communication.

In RPA (Eq. (9) for w_0 and Eq. (14) for w), the heat and entropy of mixing are both independent of temperature. Hence the excess specific heat

$$\Delta C_P = \left(\frac{\partial\Delta H}{\partial T}\right)_P = T\left(\frac{\partial\Delta S}{\partial T}\right)_P = \frac{d(c_1c_2\rho w_0)}{dT}, \tag{16}$$

is zero (Kopp's rule). Actually when the full expression (6) is used for w_0, the hard sphere diameters must be permitted to change with temperature in accordance with the Gibb–Bogoliubov variational method,[6,7] as mentioned earlier. w_0 then depends on temperature and $\mathrm{d}^2w/\mathrm{d}T^2 \neq 0$. It is of interest to enquire into an estimate of dw_0/dT or ΔC_P, which experience suggests will be, in general, small (Kopp's rule).

Equations (6) and (16) yield $\Delta C_P = \Delta C_P\,(\text{core}) + \Delta C_P\,(\text{tail})$, where

$$\Delta C_P\,(\text{core}) = -c_1c_2 4\pi\rho\sigma_{12}^3\left(\frac{\mathrm{d}\ln\sigma_{12}}{\mathrm{d}T}\right)v_{12}(\sigma_{12})g_{12}^{hs}(\sigma_{12}) \tag{17}$$

and

$$\Delta C_P\,(\text{tail}) = -c_1c_2\int_{\rho_{12}}^{\infty}\frac{\mathrm{d}}{\mathrm{d}T}(\rho v_{12}g_{12}^{hs})4\pi r^2\mathrm{d}r. \tag{18}$$

It is difficult to ascertain even the sign of the latter, but Eq. (17), by contrast, provides an unequivocal result which we tentatively take to be indicative of of ΔC_P as a whole. In that case the sign (positive or negative) is induced by the system's character, that is on whether its tendency is to phase separation or compound formation.

In the case of NaCs a rough numerical evaluation is possible from data in the literature. Ratti and Bhatia,[8] starting from Eq. (3), fitted $S_{CC}(0)$ at 383 K using a constant packing fraction of 0.45 and $v_{12}(\sigma_{12}) = 0.069\ k_BT$. In a separate study of pure liquid entropies and specific heats, Silbert *et al.*[14] found diameter temperature coefficients of about $-2 \times 10^{-4}K^{-1}$ associated with packing fractions of $\sim$0.43. The latter are reasonably compatible with Ratti and Bhatia's value and correspond[15] to a hard sphere radial distribution function value at contact of 4.2. One may reasonably interpolate these data across the phase diagram to obtain, from (17),

$$\Delta C_P\,(\text{core}) \approx -c_1c_2 4\pi(0.82)(-2 \times 10^{-4})(0.069 \times 383\ \mathrm{k}_B)(4.2)$$

which allows a maximum value of about 0.5 $\mathrm{JK}^{-1}\ \mathrm{mol}^{-1}$. This is compatible with the conclusion of Neale and Cusack[16] that $\Delta C_P < 1\ JK^{-1}\ \mathrm{mol}^{-1}$.

To summarize, Eq. (8) for ΔF is the basic result of this paper and we have provided some background theory to substantiate it. In the random phase approximation (Eq. (9) for w_0), the enthalpy of mixing in Eq. (8) (for density independent forces) has the same concentration dependence as the second term in Flory's expressions (1) or (2). The discussion shows that the enthalpy of mixing term in (8) should be identified with the second term in Flory's expression (2) (rather than in (1)), and similarly the entropy of mixing with the first term in (2). It also suggests that at a given T the simple concentration dependence of ΔG in Flory's formula (1), with appropriate w, is likely adequate to describe the activities and $S_{CC}(0)$ although more detailed calculations are necessary to fully substantiate this point. Finally, formula (8) would appear to be a suitable next step in the refinement of the Flory model and, indeed, Visser *et al.*[9] and Neale and Cusack,[11] in analysing their observed data, have already anticipated the RPA equivalent of it.

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