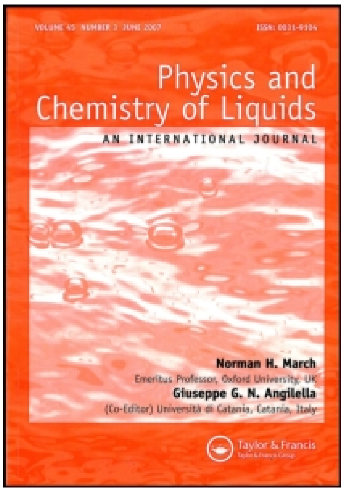

Physics and Chemistry of Liquids

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

Theory of Surface Tension in Liquid Mixtures

A. B. Bhatia[ab]; N. H. March[a]; M. P. Tosi[ac]
[a] Theoretical Chemistry Department, University of Oxford, Oxford, England [b] Department of Physics, University of Alberta, Edmonton, Canada [c] International Centre for Theoretical Physics, Trieste, Italy

To cite this Article Bhatia, A. B. , March, N. H. and Tosi, M. P.(1980) 'Theory of Surface Tension in Liquid Mixtures', Physics and Chemistry of Liquids, 9: 3, 229 — 244

To link to this Article: DOI: 10.1080/00319108008084779

URL: http://dx.doi.org/10.1080/00319108008084779

Phys. Chem. Liq., 1980, Vol. 9, pp. 229–244
0031-9104/80/0903-0229$04.50/0

Theory of Surface Tension in Liquid Mixtures

A. B. BHATIA,† N. H. MARCH, and M. P. TOSI‡

Theoretical Chemistry Department, University of Oxford,
1 South Parks Road, Oxford OX1 3TG, England

(*Received October 22, 1979*)

Equations determining the density profiles of a multicomponent liquid are first given in terms of the partial direct correlation functions in the presence of the surface. The fluctuation theory of surface tension is also generalized to liquid mixtures.

The density gradient procedure simplifies the above problem to knowledge of direct correlation functions in the bulk mixture. For the binary case, the density profile equations are then usefully written in terms of number-concentration correlation functions. The total density and surface segregation profiles are finally considered in a simplified model by utilizing the theory of conformal solutions. Such a model, though limited in practice, should apply, for example, to the Na–K alloy system.

1 INTRODUCTION

Two of us[1] have recently developed a phenomenological theory of the surface tension σ of a liquid binary alloy in terms of the alloy isothermal compressibility, the liquid surface thickness, the concentration fluctuations and a size factor.

In the present paper, we set out fully a first principles theory of the density profiles in a multicomponent system in terms of the partial direct correlation functions c_{ij} in the presence of a planar surface. This is discussed in section 2 below while in section 3 the surface tension of liquid mixtures is calculated.

Unfortunately, in practice, the required information on the partial direct correlation functions is unlikely to become available for some time yet. Therefore, in section 4, the simplified density profile equations resulting from

---

† Permanent address: Department of Physics, University of Alberta, Edmonton, Canada.

‡ Permanent address: International Centre for Theoretical Physics, Trieste, Italy.

a density gradient expansion[2,3] are expressed, for binary mixtures, in terms of number-concentration correlation functions. The relation to the phenomenology of Bhatia and March[1] is thereby established.

Finally, in section 5, the explicit form of these density profile equations is developed for the model of conformal solutions. Though this model is limited to systems where the size factor is not too large, it should apply to a liquid Na-K alloy, for example.

2 DENSITY PROFILE EQUATIONS IN TERMS OF DIRECT CORRELATION FUNCTIONS IN PRESENCE OF SURFACE

We first give below the argument of Lovett, Mou and Buff,[4] generalized to multicomponent mixtures, for the equations determining the density profiles.

Let $u_i(r)$ denote the dimensionless one-body potential per particle for species i

$$u_i(r) = \beta(\mu_i - U_i(r); \beta = (k_B T)^{-1} \tag{2.1}$$

Here $U_i(r)$ is the external potential for species i, while μ_i is its chemical potential.

The system is considered to be open and at constant V and T. The single particle densities are then

$$\rho_i(r) = \langle \hat{\rho}_i(r) \rangle \tag{2.2}$$

where $\langle \cdots \rangle$ denotes the ensemble average as usual.

Given all the $u_i(r)$, the various $\rho_j(r)$ are uniquely determined and vice-versa, at given V and T. Hence the quantities $u_i(r)$ can be regarded as functionals of the various $\rho_j(r)$ and vice versa. One has then

$$\frac{\delta \rho_i(r)}{\delta u_j(r')} = \langle \hat{\rho}_i(r) \hat{\rho}_j(r') \rangle - \langle \hat{\rho}_i(r) \rangle \langle \hat{\rho}_j(r') \rangle \tag{2.3}$$

and

$$\frac{\delta u_i(r)}{\delta \rho_j(r')} = \delta_{ij} \frac{\delta(r - r')}{\rho_i(r)} - c_{ij}(r, r') \equiv K_{ij}(r, r'), \tag{2.4}$$

$c_{ij}(r, r')$ being the direct correlation functions already mentioned above. If $u_i(r)$ is written as

$$u_i(r) = \ln(\rho_i(r)\Lambda_i^3) - C_i(r) \tag{2.5}$$

where $\Lambda_i = h(2\pi m_i k_B T)^{-1/2}$, then

$$c_{ij}(r, r') = \frac{\delta C_i(r)}{\delta \rho_j(r')}. \tag{2.6}$$

Now denoting the functional dependence of the quantity u_i by

$$u_i(r_1, [\rho_1(r), \rho_2(r) \cdots \rho_\nu(r)]) \equiv u_i(r_1) \text{ say} \tag{2.7}$$

then translational invariance implies:

$$u_i(r_1, [\rho_1(r+\delta) \cdots \rho_\nu(r+\delta)]) \equiv u_i(r_1+\delta). \tag{2.8}$$

Hence we find

$$u_i(r_1+\delta) - u_i(r_1) = \sum_{j=1}^{\nu} \int d^3r \frac{\delta u_i(r_1)}{\delta \rho_j(r)} (\rho_j(r+\delta) - \rho_j(r)) + \cdots$$

Taking the limit $\delta \to 0$ yields

$$\nabla u_i(r_1) = \sum_{j=1}^{\nu} \int d^3r \frac{\delta u_i(r_1)}{\delta \rho_j(r)} \nabla \rho_j(r) \tag{2.9}$$

$$= \sum_{j=1}^{\nu} \int d^3r\, K_{ij}(r_1, r) \nabla \rho_j(r) \tag{2.10}$$

where in Eq. (2.10) we have used Eq. (2.4).

If the external potential is now reduced to zero, i.e. $\nabla u_i(r) = 0$, then Eq. (2.10) becomes

$$\sum_{j=1}^{\nu} \int d^3r\, K_{ij}(r_1, r) \nabla \rho_j(r) = 0 \tag{2.11}$$

or using Eq. (2.4)

$$\frac{\nabla \rho_i(r_1)}{\rho_i(r_1)} = \sum_{j=1}^{\nu} \int d^3r\, c_{ij}(r_1, r) \nabla \rho_j(r) \tag{2.12}$$

These then are the basic equations determining the density profiles, the partial direct correlation functions c_{ij} being those in the presence of the surface.

3 SURFACE TENSION OF MIXTURES

Knowing the density profile and direct correlation function in a one-component liquid, the surface tension can be determined from a formula associated with the names of Yvon and of Triezenberg and Zwanzig[5] (TZ) The equivalence of this formula, for a liquid with pair interaction potentials, to the well known theory of Kirkwood and Buff[6] has recently been established by Schofield.[7] The generalization of the TZ argument to liquid mixtures is given below.

To calculate the surface energy and surface tension, consider that the equilibrium profiles ρ_i have gradient along the x-axis. Then the total energy depends on the cross-sectional area of the fluid perpendicular to the x-axis. We focus attention on that surface which satisfies Gibbs equimolar criteria with respect to the species i and locate the origin of the Gibbs surface at $(0, y, z)$. Then, if we take the system in the form of a cylinder of basal area a_0 we can write, for extension a from the Gibbs surface in phase I and extension b similarly in phase II:

$$a_0 \int_{-a}^{b} \rho_i(x)\mathrm{d}x = a_0[a\rho_i^{\mathrm{I}} + b\rho_i^{\mathrm{II}}] = N_i \tag{3.1}$$

where ρ_i^{I} and ρ_i^{II} are the densities of species i in the bulk phases I and II.

Let us write r for the two dimensional vector $\mathbf{r}(y, z)$. Now if there is a small fluctuation in the various $\rho_j(x)$, $j = 1, 2, 3, \ldots, \nu$, so that

$$\rho_j(x) \to \rho_j(x) + \Delta\rho_j(r, x) \tag{3.2}$$

and such that

$$\int \Delta\rho_j(r, x)\mathrm{d}^2r\,\mathrm{d}x = 0 \quad \text{for all } j \tag{3.3}$$

then the change in the Helmholtz free energy A is

$$\Delta A = \tfrac{1}{2} k_B T \sum_{ij} \int \Delta\rho_i(r_1x_1)\Delta\rho_j(r_2x_2)K_{ij}(r_1x_1, r_2x_2)\mathrm{d}^2r_1\,\mathrm{d}^2r_2\,\mathrm{d}x_1\,\mathrm{d}x_2 \tag{3.4}$$

We now Fourier analyze $\Delta\rho_j$ as

$$\Delta\rho_j(r_2x_2) = \sum_q \rho_j(q, x_2)\exp(iq\cdot r_2) \tag{3.5}$$

and remembering that $K_{ij}(r_1, x_1, r_2, x_2) \equiv K_{ij}(0, x_1, r_2 - r_1, x_2)$ we define

$$K_{ij}(q, x_1x_2) = \int K_{ij}(0, x_1, r_2 - r_1, x_2)e^{+iq\cdot(r_2-r_1)}\,\mathrm{d}^2(r_2 - r_1). \tag{3.6}$$

From a direct generalization of the TZ argument we have, using (2.4),

$$K_{ij}(q, x_1x_2) = \delta_{ij}\frac{\delta(x_1 - x_2)}{\rho_i(x_1)} - \hat{c}_{ij}(q, x_1x_2) \tag{3.7}$$

with

$$\hat{c}_{ij}(q, x_1x_2) = \int c_{ij}(0, x_1, r, x_2)e^{iq\cdot r}\,\mathrm{d}^2r. \tag{3.8}$$

Substituting (3.5) and (3.8) in (3.4) we then find

$$\Delta A = \tfrac{1}{2}a_0 k_B T \sum_{ij}\sum_{q} \int \rho_i^*(qx_1)\rho_j(qx_2)K_{ij}(q, x_1x_2)\mathrm{d}x_1\,\mathrm{d}x_2. \tag{3.9}$$

In this (quadratic approximation for ΔA) there is no mixing of different q, and we can consider the fluctuation of each q separately.

For small q

$$K_{ij}(q, x_1x_2) = K_{ij}^{(0)}(x_1x_2) + q^2K_{ij}^{(2)}(x_1x_2) + \cdots \tag{3.10}$$

$$K_{ij}^{(0)} = \delta_{ij}\frac{\delta(x_1 - x_2)}{\rho_i(x_1)} - \int c_{ij}(r_1 = 0, x_1, rx_2)\mathrm{d}^2r \tag{3.11}$$

$$K_{ij}^{(2)}(x_1x_2) = \tfrac{1}{4}\int c_{ij}(r = 0, x_1, r, x_2)r^2\,\mathrm{d}^2r \tag{3.12}$$

and (3.9) becomes (omitting the sum over q)

$$\begin{aligned}\Delta A = {} & \tfrac{1}{2}a_0 k_B T \sum_{ij} \int \rho_i^*(qx_1)\rho_j(qx_2)K_{ij}^{(0)}(x_1x_2)dx_1\,\mathrm{d}x_2 \\ & + \tfrac{1}{2}a_0 k_B T q^2 \sum_{ij} \int \rho_i^*(qx_1)\rho_j(qx_2)K_{ij}^{(2)}(x_1x_2)\mathrm{d}x_1\mathrm{d}x_2 \\ & + \cdots\end{aligned} \tag{3.13}$$

Now because of the fluctuation $\Delta\rho_i(r, x)$ in the density of species i, the location of the Gibbs surface also fluctuates. If $x_0(\mathbf{r})$ is the shift in the Gibbs surface at $\mathbf{r}$ we have

$$\int_{-a}^{b}[\rho_i(x) + \Delta\rho_i(r, x)]\mathrm{d}x = [a + x_0(r)]\rho_i^{\mathrm{I}} + [b - x_0(r)]\rho_i^{\mathrm{II}}$$

or

$$\int_{-a}^{b}\Delta\rho_i(r, x)\mathrm{d}x = x_0(r)[\rho_i^{\mathrm{I}} - \rho_i^{\mathrm{II}}] \equiv \Delta\rho_i x_0(r).$$

Thus

$$x_0(r) = \frac{1}{\Delta\rho_i}\int \Delta\rho_i(r, x)\mathrm{d}x \tag{3.14}$$

where $\Delta\rho_i = \rho_i^{\mathrm{I}} - \rho_i^{\mathrm{II}}$.

The area of the new surface is

$$a \doteq a_0 + \tfrac{1}{2}\int \mathrm{d}^2r\,|\nabla_r x_0(r)|^2 \tag{3.15}$$

where the integral is over the original area a_0.

With the Fourier expanison

$$x_0(r) = \sum_q x_0(q)\exp(iq \cdot r) \tag{3.16}$$

we can write

$$x_0(q) = \frac{1}{\Delta\rho_i}\int \rho_i(q, x)\mathrm{d}x \tag{3.17}$$

The change in area due to fluctuation is thus

$$a - a_0 = \tfrac{1}{2}a_0 \sum_q q^2 |x_0(q)|^2 \tag{3.18}$$

or for fluctuation of $\Delta\rho_i(r, x)$ of a given q

$$a - a_0 = \tfrac{1}{2}a_0 q^2 |x_0(q)|^2 \tag{3.19}$$

One can in principle determine $\rho_j(q, x)$ by minimizing (3.13) with respect to them, subject to a given change in the area of the surface, i.e. (3.19). According to TZ, this gives the same result as their heuristic procedure for a one-component system.

We follow the heuristic procedure again below for the multicomponent case. Consider that a small fluctuation $x_0(q)$ in the surface has occurred. For small q, this amounts to virtually a vertical shift. Then it is not unreasonable to suppose that the density profiles are all bodily shifted: i.e.

$$\rho_j(x) \to \rho_j(x - x_0(q)) \quad \text{for all } j$$

and hence

$$\rho_j(x, q) = -\frac{\mathrm{d}\rho_j(x)}{\mathrm{d}x}x_0(q) + 0((x_0(q))^2). \tag{3.20}$$

Substituting (3.20) in (3.13) we then obtain

$$\begin{aligned}\Delta A = \tfrac{1}{2}a_0 k_B T |x_0(q)|^2 \Bigg\{ & \sum_{ij}\int \frac{\mathrm{d}\rho_i}{\mathrm{d}x_1}\frac{\mathrm{d}\rho_j}{\mathrm{d}x_2}K_{ij}^{(0)}(x_1 x_2)\mathrm{d}x_1\,\mathrm{d}x_2 \\ & + \sum_{ij} q^2 \int \frac{\mathrm{d}\rho_i}{\mathrm{d}x_1}\frac{\mathrm{d}\rho_j}{\mathrm{d}x_2}K_{ij}^{(2)}(x_1 x_2)\mathrm{d}x_1\,\mathrm{d}x_2 + \cdots \Bigg\}.\end{aligned} \tag{3.21}$$

In the limit $q \to 0$ $\Delta a \to 0$ and $\Delta A = 0$. In other words we must have

$$\sum_{ij}\int \frac{\mathrm{d}\rho_i}{\mathrm{d}x_1}\frac{\mathrm{d}\rho_j}{\mathrm{d}x_2}K_{ij}^{(0)}(x_1 x_2)\mathrm{d}x_1\,\mathrm{d}x_2 = 0$$

or

$$\sum_i \int \frac{\mathrm{d}\rho_i}{\mathrm{d}x_1}\left(\int \sum_j \frac{\mathrm{d}\rho_j}{\mathrm{d}x_2}K_{ij}^{(0)}(x_1 x_2)\mathrm{d}x_2\right)\mathrm{d}x_1 = 0 \tag{3.22}$$

Sufficient conditions for (3.22) to be true are

$$\sum_j \int \frac{d\rho_j}{dx_2} K_{ij}^{(0)}(x_1 x_2) dx_2 = 0 \quad \text{for each } i(=1, 2 \cdots \nu). \tag{3.23}$$

These ν-equations are just the equations (2.12) for determining density profiles. Substituting the result (3.22) in (3.21), using (3.19) and noting that surface tension σ is given by

$$\sigma = \frac{\Delta A}{(a - a_0)} \tag{3.24}$$

we have

$$\sigma = k_B T \sum_{ij} \int \frac{d\rho_i}{dx_1} \frac{d\rho_j}{dx_2} K_{ij}^{(2)}(x_1 x_2) dx_1\, dx_2 \tag{3.25}$$

which is the desired generalization of the TZ formula to multi-component mixtures. The same result can also be obtained by generalizing the one-component treatment based on the pressure difference across a curved surface,[8] but we shall not go into details here.

4 DENSITY GRADIENT FORM OF PROFILE EQUATIONS

Though the density profile equations given in Eq. (2.12) are formally exact, it has been stressed that they require knowledge of the direct correlation functions in the presence of the surface. In the absence of such information, we turn to the density gradient expansion which leads to simplified Euler equations for the density profiles.[2,3]

These may be written in terms of chemical potentials μ_1 and μ_2 as

$$\left.\begin{aligned} \mu_1 &= \mu_1[\rho_1(x), \rho_2(x)] + F_1 \\ &\text{and} \\ \mu_2 &= \mu_2[\rho_1(x), \rho_2(x)] + F_2 \end{aligned}\right\} \tag{4.1}$$

Here $\rho_1(x)$ and $\rho_2(x)$ are the density profiles through the surface of components 1 and 2, as above, while F_1 and F_2 are given by, with spatial derivatives denoted by ρ_1' etc.,

$$F_1 = (\rho_1')^2\left(-\frac{1}{2}\frac{\partial A_{11}}{\partial \rho_1}\right) - \rho_1'\rho_2'\frac{\partial A_{11}}{\partial \rho_2} + (\rho_2')^2\left(\frac{1}{2}\frac{\partial A_{22}}{\partial \rho_1} - \frac{\partial A_{12}}{\partial \rho_2}\right) - (\rho_1'' A_{11} + \rho_2'' A_{12}) \tag{4.2}$$

and

$$F_2 = (\rho_1')^2\left(\frac{1}{2}\frac{\partial A_{11}}{\partial \rho_2} - \frac{\partial A_{12}}{\partial \rho_1}\right) - \rho_1'\rho_2'\frac{\partial A_2}{\partial \rho_1} + \tfrac{1}{2}(\rho_2')^2\frac{\partial A_{22}}{\partial \rho_2} - (\rho_1'' A_{12} + \rho_2'' A_{22}). \tag{4.3}$$

Finally, the quantities A_{ij} are given by

$$A_{ij} = \frac{k_B T}{6}\int \mathrm{d}^3 r\, r^2 c_{ij}(\mathbf{r}\{\rho\}) \tag{4.4}$$

where c_{ij} are bulk direct correlation functions.

Following Bhatia and Thornton,[9] it is helpful to work with the number N and concentration c direct correlation functions which we shall define through

$$c_{NN}(k) = \alpha_1^2 c_{11}(k) + \alpha_2^2 c_{22}(k) + 2\alpha_1\alpha_2 c_{12}(k)$$

$$c_{NC}(k) = \alpha_1\alpha_2[\alpha_1 c_{11}(k) - \alpha_2 c_{22}(k) + (\alpha_2 - \alpha_1)c_{12}(k)]$$

and

$$c_{cc}(k) = \alpha_1^2\alpha_2^2[c_{11}(k) + c_{22}(k) - 2c_{12}(k)] \tag{4.5}$$

Consistent with the above, we shall also work with the total density $\rho(x) = \rho_1(x) + \rho_2(x)$ and with the quantity, concentration c_1 and c_2 $(=1 - c_1)$,

$$\Delta(x) = c_2\rho_1(x) - c_1\rho_2(x) \tag{4.6}$$

which is a rather direct measure of the surface segregation ($\alpha_1 = \rho_1/\rho$, $\alpha_1 + \alpha_2 = 1$).

Using these quantities, we rewrite the Euler equations (4.1) in terms of A_{NN}, A_{NC} and A_{CC} defined as

$$\begin{aligned} A_{NN} &= c_1^2 A_{11} + 2c_1c_2A_{12} + c_2^2 A_{22} \\ &= -\tfrac{1}{2}k_B T\frac{\mathrm{d}^2}{\mathrm{d}k^2}c_{NN}(k)\bigg|_{k=0} + \cdots \end{aligned} \tag{4.7}$$

$$\begin{aligned} A_{NC} &= c_1A_{11} - c_2A_{22} + (c_2 - c_1)A_{12} \\ &= -\frac{1}{2}\frac{k_BT}{\alpha_1\alpha_2}\frac{\mathrm{d}^2}{\mathrm{d}k^2}c_{NC}(k)\bigg|_{k=0} + \cdots \end{aligned} \tag{4.8}$$

$$\begin{aligned} A_{CC} &= A_{11} - 2A_{12} + A_{22} \\ &= -\frac{1}{2}\frac{k_BT}{\alpha_1^2\alpha_2^2}\frac{\mathrm{d}^2}{\mathrm{d}k^2}c_{CC}(k)\bigg|_{k=0}. \end{aligned} \tag{4.9}$$

Then the Euler equations take the form

$$c_1\mu_1 + c_2\mu_2 = \frac{\partial\psi(\rho(x), \Delta(x))}{\partial\rho(x)} - A_{NN}\rho'' - A_{NC}\Delta'' - \frac{1}{2}\frac{\partial A_{NN}}{\partial\rho}\rho'^2 - \frac{\partial A_{NN}}{\partial\Delta}\rho'\Delta' + \left(\frac{1}{2}\frac{\partial A_{CC}}{\partial\rho} - \frac{\partial A_{NC}}{\partial\Delta}\right)\Delta'^2 \tag{4.10}$$

and

$$\mu_1 - \mu_2 = \frac{\partial\psi(\rho(x), \Delta(x))}{\partial\Delta(x)} - A_{NC}\rho'' - A_{CC}\Delta'' - \left(\frac{\partial A_{NC}}{\partial\rho} - \frac{1}{2}\frac{\partial A_{NN}}{\partial\Delta}\right)\rho'^2 - \frac{\partial A_{CC}}{\partial\rho}\rho'\Delta' - \frac{1}{2}\frac{\partial A_{CC}}{\partial\Delta}\Delta'^2 \tag{4.11}$$

Multiplying the first equation by $\rho'(x)$ and the second by $\Delta'(x)$ and summing we find

$$(c_1\mu_1 + c_2\mu_2)\rho' + (\mu_1 - \mu_2)\Delta' = \frac{\mathrm{d}\psi(\rho(x), \Delta(x))}{\mathrm{d}x} - \frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}x}[A_{NN}\rho'^2 + 2A_{NC}\rho'\Delta' + A_{CC}\Delta'^2). \tag{4.12}$$

This can be integrated to give the constant pressure P through the interface as

$$P = (c_1\mu_1 + c_2\mu_2)\rho(x) + (\mu_1 - \mu_2)\Delta(x) - \psi(\rho(x), \Delta(x)) + \tfrac{1}{2}[A_{NN}\rho'^2 + 2A_{NC}\rho'\Delta' + A_{CC}\Delta'^2] \tag{4.13}$$

For prescribed chemical potentials μ_1 and μ_2, Eqs. (4.10) and (4.11) must be solved simultaneously to determine the total density profile $\rho(x)$ and the surface segregation profile $\Delta(x)$. Substitution of these profiles in Eq. (4.13) then leads to the pressure P.

Since the Helmholtz free energy density $\psi(x)$ can be written[3] as

$$\Psi(x) = \psi(\rho(x), \Delta(x)) + \tfrac{1}{2}[A_{NN}\rho'^2 + 2A_{NC}\rho'\Delta' + A_{CC}\Delta'^2] \tag{4.14}$$

it follows from the fact that the total Helmholtz free energy is

$$\sum_i \mu_i N_i - PV + \sigma a_0 \tag{4.15}$$

that the surface tension is given by[3]

$$\sigma = \int_{-a}^{b} \mathrm{d}x[A_{NN}\rho'^2 + 2A_{NC}\rho'\Delta' + A_{CC}\Delta'^2]. \tag{4.16}$$

It should be noted that if $\Delta(x) = 0$, the first Euler equation reduces to that of a one-component liquid, which will be exploited below.

Furthermore, the approximation $F_1 = F_2$ in Eqs. (4.1), which leads back[3] to the phenomenology of Bhatia and March,[1] can be seen from Eq. (4.11) to involve putting A_{NC} and $\partial A_{NN}/\partial\Delta$ to zero in that equation, and Δ to zero in all but the first term on the right hand side.

5 MODEL OF CONFORMAL SOLUTIONS

Equations (4.10)–(4.12) take us as far as we can proceed generally with the density gradient theory of the surface segregation, which we can take to be the problem of determining $\Delta(x)$.

However, we shall see below that further progress can be made if we introduce into the density gradient theory the model of conformal solutions. This model assumes the existence of a monatomic reference liquid, with atoms interacting via a pair potential $\phi(r)$. The alloy pair potentials are then generated by

$$\phi_{ij}(r) = a_{ij}\phi(\lambda_{ij}r) \tag{5.1}$$

and the basic assumption of the theory is that the deviations of a_{ij} and λ_{ij} from unity are small. This allows perturbation theory based on the properties of the reference liquid as the unperturbed problem to be applied. The thermodynamic properties of conformal solutions are discussed fully by Longuet-Higgins.[10] The structural properties of a conformal solution are also known.[11,12]

5.1 Scaling of density profile and surface tension in a one-component liquid

Before going on to discuss the two-component liquid, our main interest here, let us consider what happens to the density profile of a one-component liquid when the pair potential $\phi(r)$ is changed to $a\phi(\lambda r)$.

We can use the scaling property of the pair correlation function[11] to go from a bulk direct correlation function in the reference liquid, say $c_0(r, T, \rho, z)$, z being the fugacity, to a new form $c_0(\lambda r; a\beta, \lambda^{-3}\rho, a^{3/2}z)$ under scaling of $\phi(r)$. One has also to use the scaling property of the chemical potential, first given by Longuet-Higgins as[10]

$$\mu(\beta, \rho) = a\mu_0(a\beta, \lambda^{-3}\rho) + \frac{3}{\beta}\ln\lambda. \tag{5.2}$$

From the Euler equation of the density gradient method it is easy to verify that the density profile scales as

$$\rho(x) = \lambda^3 \rho_0(\lambda x; a\beta, \lambda^{-3}\rho, a^{3/2}z), \tag{5.3}$$

the subscript zero always indicating the reference liquid property. Therefore the surface tension is given by

$$\sigma(\beta, \rho, z) = a\lambda^2 \sigma_0(a\beta, \lambda^{-3}\rho, a^{3/2}z). \tag{5.4}$$

We should note that, from a corresponding states argument, Guggenheim[13] had anticipated a result of this form.

It is worth noting that, for a liquid alloy with arbitrary a_{ij} and λ_{ij}, the assumption that $\Delta(x)$ is small would allow an approximation to the total density profile $\rho(x, c)$ in terms of the reference liquid profile $\rho_0(x; \beta, \rho, z)$ in Eq. (5.3). As will emerge in detail below, the natural scaling parameters are then the concentration dependent forms

$$a = 1 + \sum_{ij} c_i c_j (a_{ij} - 1) \tag{5.5}$$

and

$$\lambda = 1 + \sum_{ij} c_i c_j (\lambda_{ij} - 1). \tag{5.6}$$

However, in this situation we caution that the use of Eq. (5.4) with a and λ chosen as in (5.5) and (5.6) will not yield a complete description of the concentration dependence of σ because of terms of the same order which will arise from the surface segregation profile $\Delta(x)$. Therefore, using eqs (5.4)–(5.6) might be viewed as merely a relatively rough interpolation between the pure liquid surface tensions.

5.2 Euler equations for conformal solutions

We summarize in Appendix 1 the results we need in order to write expressions for the quantities A_{NN}, A_{NC} and A_{CC} appearing in the Euler eqs. (4.10) and (4.11) for the specific model of conformal solutions. These expressions are

$$\begin{aligned} A_{NN} &= A + (a-1)\mathscr{F}_1 + (\lambda - 1)\mathscr{F}_2 - 2(\Delta/\rho)A_{NC} - (\Delta/\rho)^2\, \mathrm{d}\mathscr{F}_c \\ A_{NC} &= -(a_{NC}H_1 + \lambda_{NC}H_2) - (\Delta/\rho)\,\mathrm{d}\mathscr{F}_c \\ A_{CC} &= \mathrm{d}\mathscr{F}_c \end{aligned} \tag{5.7}$$

where the concentration dependence has been made explicit through

$$\left.\begin{aligned} a_{NC} &= \alpha_1 a_{11} - \alpha_2 a_{22} + (\alpha_2 - \alpha_1)a_{12} \\ \lambda_{NC} &= \tfrac{1}{2}(\lambda_{11} - \lambda_{22}) \\ \text{and} \qquad \mathrm{d} &= 2a_{12} - a_{11} - a_{22} \end{aligned}\right\} \tag{5.8}$$

together with Eqs. (5.5) and (5.6). The other quantities in Eq. (5.7), which are functions only of the density, are defined in Appendix 1. Of course, when we use this model to calculate surface tension in the density gradient framework, the constant densities and concentrations appearing above become functions of position. In particular, we have explicitly

$$a_{NC}(x) = \bar{a}_{NC} - \frac{\Delta(x)d}{\rho(x)} \tag{5.9}$$

$$a(x) - 1 = \bar{a} - 1 + \frac{2\Delta(x)}{\rho(x)}\bar{a}_{NC} - \frac{\Delta^2(x)d}{\rho^2(x)} \tag{5.10}$$

and

$$\lambda(x) - 1 = \bar{\lambda} - 1 + \frac{2\Delta(x)}{\rho(x)}\lambda_{NC} \tag{5.11}$$

where $\bar{a}$ etc refer to the bulk concentrations. Here we have used[10] $\lambda_{12} = \frac{1}{2}(\lambda_{11} + \lambda_{22})$.

To the extent that the parameters $a_{ij} - 1$ and $\lambda_{ij} - 1$ are small, as is assumed in conformal solution theory, there are two types of parameter. In the first group are $\bar{a} - 1$ and $\bar{\lambda} - 1$ while in the second are $\bar{a}_{NC}$, λ_{NC} and d. Basically the first group determine the variation of the total density profile $\rho(x)$ from the reference liquid in lowest order, while the second group determine the surface segregation $\Delta(x)$ which is first order in these parameters. The detailed equations are lengthy and since they are differential equations which cannot be integrated generally we shall restrict ourselves to exhibiting their structure.

As discussed above for arbitrary a_{ij} and λ_{ij} again the total density profile is given in lowest order by scaling the reference liquid profile using Eqs. (5.3), (5.5) and (5.6). The same qualifications made above apply to the surface tension obtained in this approximation as can be made more explicit by calculating $d\sigma/dc$ in the alloy. The concentration dependence from the scaled form (5.4) is fully determined by the parameters $\bar{a}$ and $\bar{\lambda}$ whose concentration derivatives are proportional to $\bar{a}_{NC}$ and λ_{NC} respectively. If these quantities are different from zero, $\Delta(x)$ would not be zero and hence it can be seen that $\Delta(x)$ would contribute terms of the same order as those from the scaled reference liquid to the concentration dependence of the surface tension.

Of course, an objective of conformal solution theory must be to allow $\Delta(x)$ to be calculated. To do so, we must return to the Euler Eq. (4.11), and examine its dependence on the small parameters of the conformal solution model. As the parameters of the second group introduced above, namely $\bar{a}_{NC}$, $\bar{\lambda}_{NC}$ and d are allowed to go to zero, $\Delta(x)$ must clearly tend to zero. But in Eq. (4.11). there are individual terms which are an order of magnitude larger than those depending explicitly on Δ. Clearly all terms of this order must cancel, leaving a second-order linear differential equation to be solved for Δ. This equation reads

$$\frac{d}{dx}(\mathscr{F}_c\Delta') + G(\rho(x))\Delta = \frac{1}{d}\left[\mu_1 - \mu_2 - \frac{\partial\psi(\rho(x), \Delta(x))}{\partial\Delta(x)}\right]_2 \tag{5.12}$$

where the quantity on the right-hand side is the second-order term of the quantity inside the brackets after expansion in the small parameters of the conformal solution model. Here G is given by

$$G = \int \phi(r)g_0(r, \rho)d^3r + H_1\frac{\rho''}{\rho} - H_1\frac{\rho'^2}{\rho^2} + \mathscr{F}_1\frac{\rho'^2}{\rho^2} \tag{5.13}$$

While we think it of interest that Eq. (5.12) is eventually examined by numerical methods, we caution that the conformal solution calculation of A_{NN} etc may have to be taken to second-order in the small parameters to be totally consistent.

6 DISCUSSION AND SUMMARY

While a formally exact theory of surface segregation has been presented via the Euler eqs. (2.12), to implement this requires knowledge of the partial direct correlation functions in the presence of the surface; information not currently available.

Therefore, we have utilized a density gradient expansion of the Euler equations, which in terms of number-concentration correlation functions leads to the forms (4.10) and (4.11). These determine the total density $\rho(x)$ and the surface segregation profile $\Delta(x)$. But even their solution currently presents formidable difficulties and in particular requires knowledge of the bulk direct correlation functions c_{ij} for all bulk densities from the liquid values to those of vapour.

To make further progress, pair potential interactions in the liquid alloy have been assumed which scale from a monatomic reference liquid. It can then be demonstrated that the total density profile $\rho(x)$ is well described by concentration dependent scaling of the reference liquid profile, provided Δ is small compared with ρ. Even under the same conditions, Δ contributes significantly to the concentration dependence of the surface tension.

Finally, the simplification of this scaled potential model afforded by conformal solution theory is shown to lead to a linear second-order differential equation for $\Delta(x)$. It would be of interest if this equation could be solved; we expect the conformal solution assumptions, though rather restrictive, to apply to the Na–K liquid alloy system.

Acknowledgement

One of us (ABB) acknowledges the award of a Senior Visiting Fellowship by the Science Research Council during his stay in Oxford, and support from N.S.E.R.C., Canada.

Two of us (MPT and NHM) were helped by partial financial support from CNR, Italy, on a collaboration embracing the study of surfaces and interfaces.

Finally, we wish to thank Professor J. S. Rowlinson for a helpful discussion in the course of this work.

References

1. A. B. Bhatia and N. H. March, *J. Chem. Phys.*, **68**, 4651 (1978).
2. P. D. Fleming, A. J. M. Yang, and J. H. Gibbs, *J. Chem. Phys.*, **65**, 7 (1976).
3. A. B. Bhatia, N. H. March, and J. Sutton, *J. Chem. Phys.*, **69**, 2258 (1978).
4. R. Lovett, F. P. Buff, and C. Y. Mou, *J. Chem. Phys.*, **65**, 570 (1976).
5. D. G. Triezenberg and R. Zwanzig, *Phys. Rev. Lett.*, **28**, 1183 (1972).
6. J. G. Kirkwood and F. P. Buff, *J. Chem. Phys.*, **17**, 338 (1949).
7. P. Schofield, *Chem. Phys. Letts.*, **62**, 413 (1979).
8. R. Lovett, P. A. Dehaven, J. J. Vieceli Jr., and F. P. Buff, *J. Chem. Phys.*, **58**, 1880 (1973).
9. A. B. Bhatia and D. E. Thornton, *Phys. Rev.*, **B2**, 3004 (1970).
10. H. C. Longuet-Higgins, *Proc. Roy. Soc. London*, **A205**, 247 (1951).
11. M. Parrinello, M. P. Tosi, and N. H. March, *Proc. Roy. Soc.*, London, **A341**, 91 (1974).
12. See also N. H. March and M. P. Tosi, *Atomic Dynamics in Liquids* (Macmillan, London 1976).
13. E. A. Guggenheim, *J. Chem. Phys.*, **13**, 253 (1945).

Appendix 1

Kernels of surface tension formula for conformal solutions in the density gradient framework

We use the results of Parrinello *et al.*[11] to construct the partial structure factors of a conformal solution in the number-concentration representation.[9] The results can be written ($\alpha_1 = \rho_1(x)/\rho, \alpha_2 = 1 - \alpha_1$)

$$S_{NN}(k) = S_0(k) + (a-1)f_1(k) + (\lambda - 1)f_2(k) \tag{A1.1}$$

$$S_{NC}(k) = -\alpha_1\alpha_2[a_{NC}h_1(k) + \lambda_{NC}h_2(k)] \tag{A1.2}$$

and

$$S_{CC}(k) = \alpha_1\alpha_2 + \alpha_1^2\alpha_2^2\,\mathrm{d}f_c(k). \tag{A1.3}$$

The definitions of a, λ, a_{NC}, λ_{NC} and d have been given already in the main text. while $S_0(k)$ is the structure factor of the reference liquid. The other functions $\mathscr{F}_1$, $\mathscr{F}_2$, $\mathscr{F}_c$, H_1 and H_2 in Eqs. (5.7) are the Fourier transforms of the following properties of the reference liquid

$$f_1(r) = \beta \frac{\partial g_0(r)}{\partial \beta}\bigg|_\rho + \frac{3\rho}{2\beta}\frac{\partial g_0(r)}{\partial \rho}\bigg|_\beta \tag{A1.4}$$

$$f_2(r) = r\frac{\partial g_0(r)}{\partial r} - 3\rho \frac{\partial P}{\partial \rho}\bigg|_\beta \frac{\partial g_0(r)}{\partial P}\bigg|_\beta \tag{A1.5}$$

$$h_1(r) = \beta\left[\phi(r)g_0(r) + \rho\int \mathrm{d}s\, \phi(s)(g_3(\mathbf{r}, \mathbf{s}) - g_0(r)g_0(s))\right] \tag{A1.6}$$

$$h_2(r) = \beta\left[r\frac{\mathrm{d}\phi}{\mathrm{d}r}g_0(r) + \rho\int \mathrm{d}s\, s\frac{\partial \phi}{\partial s}(g_3(\mathbf{r}, \mathbf{s}) - g_0(r)g_0(s))\right] \tag{A1.7}$$

and

$$f_c(r) = \beta\phi(r)g_0(r). \tag{A1.8}$$

Here $g_0(r)$ is the radial distribution function of the reference liquid, while g_3 is the three-atom correlation function.

We also require the Pearson–Rushbrooke relations between the N–C direct correlation functions and the partial structure factors. These are

$$\rho c_{NN}(k) = 1 - \frac{S_{CC}}{S_{NN}S_{CC} - S_{NC}^2} \tag{A1.9}$$

$$\rho c_{NC}(k) = \frac{\alpha_1\alpha_2 S_{NC}}{S_{NN}S_{CC} - S_{NC}^2} \tag{A1.10}$$

and

$$\rho c_{CC}(k) = \alpha_1\alpha_2\left[1 - \frac{c_1c_2S_{NN}}{S_{NN}S_{CC} - S_{NC}^2}\right] \tag{A1.11}$$

To leading order, the explicit results for conformal solutions are

$$\rho c_{NN}(k) = c_0(k) + \frac{(a-1)f_1(k)}{S_0^2(k)} + \frac{(\lambda - 1)f_2(k)}{S_0^2(k)}. \tag{A1.12}$$

$$\rho c_{NC}(k) = -\alpha_1\alpha_2\left[a_{NC}\frac{h_1(k)}{S_0(k)} + \lambda_{NC}\frac{h_2(k)}{S_0(k)}\right] \tag{A1.13}$$

and

$$\rho c_{CC}(k) = \alpha_1^2\alpha_2^2\, \mathrm{d}f_c(k). \tag{A1.14}$$

The equations for A_{NN} etc in the main text follow immediately using Eqs. (4.7)–(4.9).

The following abbreviations have been used in writing (5.7):

$$A = -\frac{1}{2}\frac{k_BT}{\rho}\frac{d^2}{dk^2}c_0(k), \quad \mathscr{F}_1 = -\frac{1}{2}\frac{k_BT}{\rho}\frac{d^2}{dk^2}\left(\frac{f_1(k)}{S_0^2(k)}\right)$$

$$\mathscr{F}_2 = -\frac{1}{2}\frac{k_BT}{\rho}\frac{d^2}{dk^2}\left(\frac{f_2(k)}{S_0^2(k)}\right), \quad H_1 = -\frac{1}{2}\frac{k_BT}{\rho}\frac{d^2}{dk^2}\left(\frac{h_1(k)}{S_0(k)}\right)$$

$$H_2 = -\frac{1}{2}\frac{k_BT}{\rho}\frac{d^2}{dk^2}\left(\frac{h_2(k)}{S_0(k)}\right), \quad \mathscr{F}_c = -\frac{1}{2}\frac{k_BT}{\rho}\frac{d^2}{dk^2}f_c(k),$$

all derivatives being evaluated at $k = 0$.