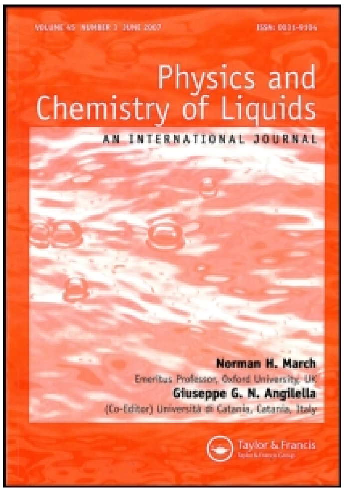

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Short Range Order and Concentration Fluctuations in Regular and Compound Forming Molten Alloys

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Short Range Order and Concentration Fluctuations in Regular and Compound Forming Molten Alloys[†]

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First, a statistical mechanical model is developed for compound forming molten alloys with the aim that it explains both the concentration dependence of the thermodynamic quantities – free energy of mixing G_M, concentration fluctuations $S_{CC}(0)$, etc. – and the short range order (SRO) parameter α_1 for the nearest neighbour shell obtained from neutron and X-ray scattering. The model assumes the existence of appropriate privileged groups or chemical complexes $A_\mu B_\nu$ (μ, ν small integers) and that the energy of an AB, AA or BB bond depends on whether that bond is part of the complex or not. The expression for G_M reduces to the well-known quasi-chemical expression for regular alloys when no complexes are formed.

The theory is next applied to discuss G_M, $S_{CC}(0)$, etc., for three compound forming alloys, MgBi, LiPb and AgAl.

The bond energies once chosen to explain thermodynamic data enable one to evaluate SRO α_1. The calculated α_1 are, in general, good agreement with the available data in both the compound forming and regular alloys. The theory also provides a natural explanation of change of α_1 on melting in such alloys as Cd–Mg.

1 INTRODUCTION

It is well known that the concentration fluctuation structure factor $S_{CC}(q)$ is intimately related to local order in a binary alloy.[1] In recent years $S_{CC}(q)$ and other structure factors and hence the Cowley–Warren short range order (SRO) parameter for the nearest neighbour shell has been estimated from

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neutron and X-ray scattering data in a number of molten alloys.[2–9] No theoretical discussion of these results on SRO seems to have been given to date. The present work attempts to remedy this lack and to interpret the SRO results in terms of some theoretical models of the alloys and the thermodynamic data. There is, of course, considerable literature on SRO in solid alloys where it was first introduced;[10–12] for recent excellent reviews see March *et al.*,[13] Fontaine.[14]

First, we recall the definition that an A–B alloy is said to be regular[15] if (1) A and B atoms are of approximately the same size so that the size effects can be neglected and (2) the free energy of mixing G_M (and hence also the concentration fluctuations $S_{CC}(0)$) is symmetric about the concentration $c = \frac{1}{2}$. For regular alloys, the simplest model which has been used to interpret[16] $S_{CC}(0)$ is the conformal solution model[17] or, what is essentially equivalent to, the regular solution model in the zeroth approximation.[15] These approximations, although they involve the interchange energy ω (defined precisely later) which describes whether the unlike atom pairs or the like atom pairs are energetically preferred as nearest neighbours, actually ignore the consequent local ordering in deriving the expressions for G_M.[15,18] The regular solution model in the next (called the first or the quasi-chemical) approximation, however as we shall see later, can be applied quite usefully to interpret the SRO results in a number of regular alloys.

The situation for asymmetric alloys, for example, LiPb, AgAl, CuSn, etc., is not quite so simple. These alloys (we will be concerned here with only those alloys where the size effect is not large enough to be the cause of asymmetry in G_M, as for example, it is in NaCs alloy[19]) have the characteristic that in the solid state they form compounds at one or more stoichiometric compositions. Bhatia and collaborators[20–22] developed a phenomenological model to explain the variation of G_M, activities, and $S_{CC}(0)$ with concentration, by assuming that if the binary A–B alloy in the solid state forms a compound at the composition $A_\mu B_\nu$ (μ, ν small integers), then in the liquid state the alloy consisted of a mixture of A atoms and B atoms and a number of "chemical complexes" $A_\mu B_\nu$ all in chemical equilibrium with one another. The model explains successfully the thermodynamic properties of a number of compound forming alloys[20–25] and more recently Gray[26] has elucidated the statistical mechanical foundation of the model. However, a discussion of SRO on its basis has not yet been given.

In this paper we therefore first present a formulation for calculating the concentration dependence of the various thermodynamic properties which at the same time is capable of yielding information on SRO. We assume the existence of "complexes" or privileged group of atoms $A_\mu B_\nu$ as in Refs. 20–22 (and other references quoted there)—but rather than determining their number by the condition of chemical equilibrium—we take a more microscopic approach. We characterize the existence of a privileged group by assuming that the energy of a given nearest neighbour bond (AB, BB or AA) is different if it belongs to the group than if it does not. It is then possible to set up the grand partition function for the problem which is treated essentially by the method proposed by Bethe[10] and Peierls[27] to treat SRO in solid alloys. Naturally here because of our lack of knowledge on structural information on $A_\mu B_\nu$ a number of additional simplifying assumptions have to be made to make the problem tractable; these are best described in Section 2 when we have set up the grand partition function. In the absence of the existence of the privileged groups, the method just reduces to that of Bethe and yields the same results as the quasi-chemical approximation for regular alloys referred to above.

Before proceeding further we need to mention the recent work of Cartier *et al.*[28,29] who have refined Bethe's method for regular alloys, and have[30] also calculated the conditional probabilities and the ratio of the activities of the two components for A_3B ($\mu = 3$, $\nu = 1$) type alloys by assuming that the atoms are located on the sites of a face-centered cubic lattice.

In Sections 2–4 we describe the formulation and develop the various formulae for discussing both the thermodynamic properties and the short range order. The interaction parameters occurring in the formula for SRO are the same as those occurring in the expressions for G_M, $S_{CC}(0)$, etc., and hence may be determined from the thermodynamic data. In Section 5 we use these formulae to interpret the observed behaviour of G_M, activities and $S_{CC}(0)$, and SRO for a number of compound forming molten alloys. This is followed by a discussion of SRO in regular alloys in Section 6. It is concluded that the theory is in good overall agreement with experiment and provides a useful link between the thermodynamic properties and SRO.

2 A QUASI-CHEMICAL APPROXIMATION FOR COMPOUND FORMING ALLOYS

2.1 The Method and Assumptions

As customary in most lattice models of an alloy we assume (1) the atoms are located on the sites of a lattice (2) each lattice site has z nearest neighbours (3) the interaction is of short range and effective between nearest neighbours only and (4) the partition function $q_A(T)$ of an A atom associated with the inner and translational degrees of freedom is the same wherever A is located —and similarly $q_B(T)$. The grand partition is then

$$\Xi = \sum_{E} q_A^{N_A}(T) q_B^{N_B}(T) e^{(\mu_A N_A + \mu_B N_B - E)/k_B T}, \tag{2.1}$$

where μ_A and μ_B are the chemical potentials of the two species A and B, E is the energy of the alloy for a given configuration of $N_A A$ atoms and $N_B B$ atoms due to the nearest neighbour interactions, and the sum is over all configurations and over all possible values for N_A and N_B subject to $N(=N_A + N_B)$ constant, the total number of lattice sites.

The essential steps of the method to be followed here are now as follows: Consider the whole set of lattice sites divided into a small cluster of just a few lattice sites and the remainder. Distinguishing the quantities referring to the cluster and the remainder by suffixes 1 and 2 respectively, we have

$$N_A = N_{1A} + N_{2A}, \qquad N_B = N_{1B} + N_{2B},$$
$$E = E_1 + E_2 + E_{12}. \tag{2.2}$$

The energy E_1 refers to configurations on a small set of sites and can be handled easily. E_{12} refers to the interaction energy due to atoms in the cluster interacting with the surrounding lattice sites and is replaced by an average value. (The philosophy being that the interactions within the cluster are of primary importance and the other terms in Ξ therefore can be treated approximately). Using (2.2) in (2.1), we can write

$$\Xi = \sum_{E_1, E_2, E_{12}} \zeta_A^{N_{1A}} \zeta_B^{N_{1B}} \zeta_A^{N_{2A}} \zeta_B^{N_{2B}} e^{-(E_1 + E_2 + E_{12})/k_BT}, \tag{2.3}$$

where we have abbreviated

$$\zeta_A = q_A(T) e^{\mu_A/k_BT}, \qquad \zeta_B = q_B(T) e^{\mu_B/k_BT}. \tag{2.4}$$

Defining the average value of E_{12} by

$$\Xi_2 e^{-\bar{E}_{12}/k_BT} = \sum_{E_2, E_{12}} \zeta_A^{N_{2A}} \zeta_B^{N_{2B}} e^{-(E_2 + E_{12})/k_BT}, \tag{2.5}$$

we can rewrite (2.3) as

$$\Xi = \Xi_1' \cdot \Xi_2, \tag{2.6}$$

where

$$\Xi_1' = \sum_{E_1} \zeta_A^{N_{1A}} \zeta_B^{N_{1B}} e^{-(E_1 + \bar{E}_{12})/k_BT}. \tag{2.7}$$

The term Ξ_1' which is the quantity of interest here is the grand partition function of the cluster—the prime on it denoting the fact that in writing it we have taken into account the interaction of the cluster with its surrounding.

So far the procedure is exact. Cartier *et al.*[28] (see also Fowler and Guggenheim[31]) have shown that $\bar{E}_{12}$ may be approximated to the form

$$e^{-\bar{E}_{12}/k_BT} \approx \phi_A^{\nu_A} \phi_B^{\nu_B}, \tag{2.8}$$

where ν_A is the number of lattice sites in domain 2 which are the nearest neighbours of the A atoms in the cluster. ϕ_A and ϕ_B are constants which as we shall see presently are eliminated from the final result. With (2.8), (2.7) becomes

$$\Xi_1' = \sum_{E_1} \zeta_A^{N_{1A}} \zeta_B^{N_{1B}} \phi_A^{\nu_A} \phi_B^{\nu_B} e^{-E_1/k_BT}. \tag{2.9}$$

From the definition of Ξ_1', the average values of A and B atoms in the cluster are given by

$$\langle N_{1A} \rangle = k_B T \frac{\partial \ln \sum_1'}{\partial \mu_A}, \ \langle N_{1B} \rangle = k_B T \frac{\partial \ln \sum_1'}{\partial \mu_B}, \tag{2.10}$$

or using (2.4)

$$\frac{\langle N_{1B} \rangle}{\langle N_{1A} \rangle} = \frac{c_B}{c_A} = \frac{\xi_B}{\xi_A} \frac{\partial \ln \sum_1'}{\partial \xi_B} \bigg/ \left(\frac{\partial \ln \sum_1'}{\partial \xi_A} \right). \tag{2.11}$$

$c_A = (1 - c_B)$ is the average concentration of A atoms in the cluster and must obviously be the same as the concentration c of A atoms in the alloy. Hence c_B/c_A is independent of the size of the cluster. One now uses two different sizes of cluster to evaluate (2.11) and hence eliminate ϕ_A, ϕ_B. The simplest case is, of course, when one takes clusters of just one and two lattice sites. We consider here the problem of compound forming alloys in this approximation.

2.2 Expression for Ξ_1' for clusters of one and two lattice sites

When the cluster consists of just one lattice site, there are no AA, AB or BB bonds in the cluster and hence $E_1 = 0$. Then since the site can be occupied by either an A atom or a B atom, and ν_A or ν_B in (2.8) is z, the coordination number of the lattice, one has

$$\Xi_1'^{(1)} = \zeta_A \phi_A^z + \zeta_B \phi_B^z, \tag{2.12}$$

where we have added the superscript (1) to indicate that this is the expression for Ξ_1' for the cluster of one atom.

For a cluster of two lattice sites, the cluster can have either two A atoms or two B atoms or an A and a B atom. Let $\varepsilon_{ij}(i, j = A$ or $B)$ denote the energy of an ij bond if the ij bond is a free bond, and let $\varepsilon_{ij} + \Delta\varepsilon_{ij}$ denote its energy if the ij bond is one of the bonds in the complex $A_\mu B_\nu$. Further let P_{ij} denote the probability that the ij bond in the cluster is part of the complex. Then, for example, if the cluster consists of two A atoms, the energy $E_1 = (1 - P_{AA})\varepsilon_{AA} + P_{AA}(\varepsilon_{AA} + \Delta\varepsilon_{AA}) = \varepsilon_{AA} + P_{AA}\,\Delta\varepsilon_{AA}$. The expression for $\Xi_1'^{(2)}$ can then be readily obtained from (2.9) as

$$\Xi_2'^{(2)} = \xi_A^2 \phi_A^{2(z-1)} \rho_{AA} + \xi_B^2 \phi_B^{2(z-1)} \rho_{BB} + 2\xi_A \xi_B \phi_A^{z-1} \phi_B^{z-1} \rho_{AB}, \quad (2.13)$$

where we have set

$$\rho_{ij} = e^{-(\varepsilon_{ij} + P_{ij} \Delta\varepsilon_{ij})/k_B T}, \; i, j = A, B. \quad (2.14)$$

To assign values of P_{ij}, consider first the AB pair in the cluster. We assume that around each lattice site, say that occupied by A, there are $\mu + \nu - 2$ nearest neighbour lattice sites such that if they are occupied by $\mu - 1$ A atoms and $\nu - 1$ B atoms, then these together with the AB pair of the cluster form the complex $A_\mu B_\nu$. Let P_0 denote the probability that on these lattice sites there are $\mu - 1$ A atoms and $\nu - 1$ B atoms. Obviously to a first approximation $P_0 \simeq c^{\mu-1}(1 - c)^{\nu-1}$. The various ways (and their probabilities) in which the AB pair can be part of the complex then are depicted in Table I. The total probability that the AB pair of the cluster belongs to a complex $A_\mu B_\nu$ is the sum of probabilities in the last column, i.e.

TABLE I

Table for evaluating P_{AB}

Around A atom	Around B atom	Probability of formation of $A_\mu B_\nu$
•	×	$P_0(1 - P_0)$
×	•	$P_0(1 - P_0)$
•	•	P_0^2
×	×	Zero

•, ×, represent, respectively, that complexes are being formed or not.

$$p_{AB} = P_0(2 - P_0) = c^{\mu-1}(1 - c)^{\nu-1}[2 - c^{\mu-1}(1 - c)^{\nu-1}]. \quad (2.15)$$

In exactly the same way one may obtain

$$P_{AA} = c^{\mu-2}(1 - c)^{\nu}[2 - c^{\mu-2}(1 - c)^{\nu}], \mu \geq 2, \quad (2.16)$$

$$P_{BB} = c^{\mu}(1 - c)^{\nu-2}[2 - c^{\mu}(1 - c)^{\nu-2}], \nu \geq 2. \quad (2.17)$$

P_{AA} and P_{BB} are zero respectively for $\mu < 2$ and $\nu < 2$. It will be realised that (2.15)–(2.17) represent rather a simplistic approximation to P_{ij}. But in the absence of specific assumptions regarding the structure of the complexes they are the only ones that seem possible. (For the special case $\mu = 3$, $\nu = 1$ the expression (2.15) reduces to that used by Cartier and Barriol.[32])

For this reason we cannot expect our method to give in general good results if the tendency to form complexes is very strong.† We also note that although in general all three $\Delta\varepsilon_{ij}$ may be required for detailed agreement with experiment, the crucial one is the energy $\Delta\varepsilon_{AB}$ connected with the AB bond.

If we now use in (2.11) the expressions (2.12) and (2.13) for Ξ'_1 successively we get

$$\frac{1-c}{c} = \frac{\xi_B}{\xi_A}\left(\frac{\phi_B}{\phi_A}\right)^Z = \frac{\xi_B^2\phi_B^{2(z-1)}\rho_{BB} + \xi_A\xi_B\phi_A^{z-1}\phi_B^{z-1}\rho_{AB}}{\xi_A^2\phi_A^{2(z-1})\rho_{AA} + \xi_A\xi_B\phi_A^{z-1}\phi_B^{z-1}\rho_{AB}}. \tag{2.18}$$

Setting

$$\sigma = \frac{\phi_B}{\phi_A}\left(\frac{\rho_{AA}}{\rho_{BB}}\right)^{1/2}, \tag{2.19}$$

and

$$\eta = \frac{(\rho_{AA}\rho_{BB})^{1/2}}{\rho_{AB}}, \tag{2.20}$$

we immediately obtain from (2.18) a quadratic equation for σ, which is,

$$c\sigma^2 + (1-2c)\sigma\eta^{-1} - (1-c) = 0, \tag{2.21}$$

whence

$$\sigma = \left(\frac{1}{2c\eta}\right)(2c - 1 + \beta), \tag{2.22}$$

where for later convenience we have set

$$\beta = \sqrt{1 + 4c(1-c)(\eta^2 - 1)} \tag{2.23}$$

and where the plus sign has to be taken in front of the square root so that $\sigma \to 1$ if $\eta \to 1$.

3 FORMULAE FOR ACTIVITIES AND FREE ENERGY OF MIXING

The connection with thermodynamics is now made by noting firstly that from (2.19) and the first equality in (2.18)

$$\frac{\xi_A}{\xi_B} = \frac{c}{1-c}\sigma^z\left(\frac{\rho_{BB}}{\rho_{AA}}\right)^{z/2} \tag{3.1}$$

---

† In terms of the work of Refs. 20, 22, tendency to form complexes is said to be strong if $|G_M(c_c)/Nk_BT| \gtrsim 3$, where $c_c = \mu/(\mu + \nu)$ is the compound forming concentration. For such G_M there are nearly as many complexes in the mixture at a given c as are possible from conservation of atoms at that c.

Secondly note that ξ_A and ξ_B are given by (2.4) and that the activity coefficients γ_A and γ_B of the two species are defined by

$$\mu_A = \mu_A^{(0)} + k_B T \ln[c\gamma_A],\ \mu_B = \mu_B^{(0)} + k_B T \ln[(1-c)\gamma_B], \tag{3.2}$$

where $\mu_A^{(0)}$ and $\mu_B^{(0)}$ are the chemical potentials of the respective pure species. Next remembering that $\mu_A^{(0)}$, $\mu_B^{(0)}$, $q_A(T)$, $q_B(T)$, and ε_{AA} and ε_{BB} in (2.13) are independent of concentration, we obtain for the ratio of the two activity coefficients $\gamma = \gamma_A/\gamma_B$, the expression

$$\ln\gamma = z\ln\sigma + (z/2k_B T)(P_{AA}\,\Delta\varepsilon_{AA} - P_{BB}\,\Delta\varepsilon_{BB}) + \mathscr{I}, \tag{3.3}$$

where $\mathscr{I}$ is a constant independent of concentration but may depend on temperature and pressure—its determination is discussed presently. For later convenience we note that by using (2.22) and (2.23) the first term in (3.3) may be written as

$$z\ln\sigma = \tfrac{1}{2}z\ln\frac{(1-c)}{c}\frac{\beta + 2c - 1}{\beta - 2c + 1}. \tag{3.4}$$

Now let G_M^{exc} denote the excess free energy of mixing:

$$G_M^{\text{exc}} = G_M - Nk_B T[c\ln c + (1-c)\ln(1-c)], \tag{3.5}$$

and abbreviate $f(c) = G_M^{\text{exc}}/Nk_B T$, then from standard thermodynamic definitions (see Appendix)

$$f'(c) = \ln\gamma;\ f'(c) \equiv df/dc. \tag{3.6}$$

Hence

$$\begin{aligned} f(c) &= G_M^{\text{exc}}/Nk_B T \\ &= z\int_0^c [\ln\sigma + (2k_B T)^{-1}(P_{AA}\,\Delta\varepsilon_{AA} - P_{BB}\,\Delta\varepsilon_{BB})]\,dc + \mathscr{I}c. \end{aligned} \tag{3.7}$$

Equation (3.7) already fulfills the condition that $f(0) = 0$, and the constant $\mathscr{I}$ in it is to be determined from the requirement on $f(c)$ that $f(c) = 0$ at $c = 1$ also. We may observe that for $c = \frac{1}{2}$, $\ln\sigma = 0$, and hence if $\Delta\varepsilon_{AA} = \Delta\varepsilon_{BB} = 0$, then from (3.3) $\mathscr{I}$ is also equal to the value of $\ln\gamma$ at $c = \frac{1}{2}$.

Lastly since the long wavelength limit of the concentration fluctuation structure factor is given by[1]

$$S_{CC}(0) = N\overline{(\Delta c)^2} = Nk_B T \Big/ \left(\frac{\partial^2 G_M}{\partial c^2}\right)_{T,P,N}, \tag{3.8}$$

we may obtain for $S_{CC}(0)$, using (3.3) and (3.6), the expression:

$$S_{CC}(0) = \frac{c(1-c)}{Y}, \tag{3.9}$$

where

$$Y = 1 + \tfrac{1}{2}z\left(\frac{1}{\beta} - 1\right) + \frac{zc(1-c)}{2\beta k_B T} \cdot \{2(1-2c)P'_{AB}\Delta\varepsilon_{AB}$$

$$+ (\beta - 1 + 2c)P'_{AA}\,\Delta\varepsilon_{AA} - (\beta + 1 - 2c)P'_{BB}\,\Delta\varepsilon_{BB}\}. \quad (3.10)$$

Here $P'_{AA} = dP_{AA}/dc$, etc.

The above expressions simplify considerably if there is no tendency to form chemical complexes, i.e. for a regular mixture. For this case $\Delta\varepsilon_{ij} = 0$ for all $i, j = A, B$. Now the general expression for η is, from (2.14) and (2.20)

$$\eta^2 = \exp\left[\frac{2\omega}{zk_BT}\right]\exp\left[\frac{2P_{AB}\Delta\varepsilon_{AB} - P_{AA}\Delta\varepsilon_{AA} - P_{BB}\Delta\varepsilon_{BB}}{k_BT}\right], \quad (3.11)$$

where for conformity with usage for regular mixtures we have introduced the interchange energy ω by

$$\omega = z(\varepsilon_{AB} - \tfrac{1}{2}\varepsilon_{AA} - \tfrac{1}{2}\varepsilon_{BB}). \quad (3.12)$$

Hence for a regular mixture $\eta(=\exp[\omega/zk_BT])$ is independent of concentration and β, defined in (2.23), is symmetric about $c = \frac{1}{2}$, while $\ln \sigma$ is antisymmetric about $c = \frac{1}{2}$. Hence it follows from (3.7) that the constant $\mathscr{I}$ is zero for this case, and one has from (3.3) and (3.7)

$$\ln \gamma = z \ln \sigma, \quad (3.13)$$

$$G_M^{\text{exc}}/Nk_BT = z\int_0^c \ln \sigma\, dc. \quad (3.14)$$

Expression (3.13) with σ given by (3.4) is identical with the well-known expression for $\ln \gamma$ for a regular mixture in the quasi-chemical approximation (for example, see Ref. 15—note x of Ref. 15 is $1 - c$ in our notation). Moreover—with η independent of c—Eq. (3.14) is readily integrable and one obtains just the expression for G_M^{exc} given in Ref. 15 (see also Section 6).

The expression (3.9) for $S_{CC}(0)$ also simplifies:

$$S_{CC}(0) = \frac{c(1-c)}{1 + \frac{1}{2}z(1-\beta)/\beta}, \text{(R.M.)} \quad (3.15)$$

where the letters R.M. are intended as a reminder for future reference that this expression refers to the regular mixture.

We may note in passing that for the case where AB complexes are formed ($\mu = \nu = 1$), $P_{AB} = 1$, $P_{AA} = P_{BB} = 0$. Hence, the mixture (in our approximation) behaves exactly like a regular mixture, with ω replaced by $\omega + z\Delta\varepsilon_{AB}$.

4 EXPRESSION FOR SHORT RANGE ORDER PARAMETER

First we deduce the following from the formulation of Section 2:

Let X_{AB} denote the probability that one lattice site of a nearest neighbour pair is occupied by an A atom and the other by a B atom. Similarly define X_{AA} and X_{BB}. Then from the definition of the grand partition function (2.13) for a cluster of two sites, it follows that

$$X_{AA} = \frac{\xi_A^2 \phi_A^{2(z-1)} \rho_{AA}}{\Xi_1'^{(2)}},$$

$$X_{BB} = \frac{\xi_B^2 \phi_B^{2(z-1)} \rho_{BB}}{\Xi_1'^{(2)}}$$

$$X_{AB} = X_{BA} = \frac{\xi_A \xi_B \phi_A^{(z-1)} \phi_B^{(z-1)} \rho_{AB}}{\Xi_1'^{(2)}} \tag{4.1}$$

From (4.1) and (2.20) one has

$$\frac{X_{AA} X_{BB}}{X_{AB}^2} = \eta^2. \tag{4.2}$$

Using the normalisation condition

$$X_{AA} + X_{BB} + 2X_{AB} = 1, \tag{4.3}$$

and Eqs. (4.1) and (2.18), we have

$$X_{AA} = c - X_{AB}, X_{BB} = (1 - c) - X_{AB}. \tag{4.4}$$

Substituting (4.4) in (4.2) and solving for X_{AB}, one obtains readily using (2.23)

$$X_{AB} = \frac{2c(1 - c)}{\beta + 1}. \tag{4.5}$$

Now the Warren–Cowley[11,12] short range order (SRO) parameter α_1 for the nearest neighbour sites is defined as follows: Given an atom A at the lattice site, say 1, let $[B/A]$ denote the probability that a B atom exists at a site 2 which is nearest neighbour to site 1. Then

$$\left[\frac{B}{A}\right] = c_B(1 - \alpha_1), c_B = 1 - c. \tag{4.6}$$

So defined, $\alpha_1 = 0$ for a random alloy since $[B/A]$ for this case is just c_B, the mean concentration of B atoms. If unlike pairs are preferred over like pairs in the alloy, then α_1 is negative and for the converse case α_1 is positive. From simple probabilistic considerations it follows that α_1 lies in the range

$$
\begin{aligned}
-\frac{c}{(1-c)} &\leq \alpha_1 \leq 1, c \leq \tfrac{1}{2}, \\
-\frac{(1-c)}{c} &\leq \alpha_1 \leq 1, c \geq \tfrac{1}{2}.
\end{aligned}
\tag{4.7}
$$

The conditional probability $[B/A]$ is related to X_{AB} simply by $X_{AB} = c[B/A]$, since c is the probability that a given site is occupied by an A atom. Hence from (4.6) and (4.5) we obtain

$$\alpha_1 = \frac{\beta - 1}{\beta + 1}, \tag{4.8}$$

which is the expression we wished to obtain. Thus if we know the interaction parameters ω/z and $\Delta\varepsilon_{ij}$—say from the thermodynamic data—we can estimate α_1 from Eq. (4.8).

For the special case of regular mixtures Eq. (4.8) has of course been noted either explicitly or implicitly previously.[33–35] For the sake of the unfamiliar reader we may mention that in the usual version of the *QC* theory,[15] the relation equivalent to (4.2) is obtained in terms of the numbers N_{AA}, N_{BB} and N_{AB} of *AA*, *BB* and *AB* bonds by a combinatorial method. To see the equivalence one has only to note that $N_{AA} = \frac{1}{2}NzX_{AA}$, $N_{BB} = \frac{1}{2}NzX_{BB}$, $N_{AB} = NzX_{AB}$.

Before discussing applications of Eq. (4.8) it is instructive to note that there is rather an interesting relation between $S_{CC}(0)$ and α_1 for regular mixtures (in *QCA*). Eliminating β between (4.8) and (3.15) one may obtain ($c_1 \equiv c$, $c_2 = 1 - c$)

$$\frac{S_{CC}(0)}{c_1 c_2} = \frac{1 + \alpha_1}{1 - (z - 1)\alpha_1} \tag{4.9}$$

$$= 1 + z\alpha_1 + z\alpha_1(z - 1)\alpha_1 + z\alpha_1((z - 1)\alpha_1)^2 + \cdots . \tag{4.10}$$

On the other hand, there exists an (exact) sum rule (for mixtures where size effects are negligible) between $S_{CC}(0)$ and SRO for different neighbour shells, namely[13,2]

$$\frac{S_{CC}(0)}{c_1 c_2} = 1 + z_1\alpha_1 + z_2\alpha_2 + \cdots + z_n\alpha_n + \cdots \tag{4.11}$$

where α_n is the SRO for the nth neighbour shell and z_n the number of atoms in that shell ($z_1 \equiv z$). Expansion (4.10) thus illustrates that QCA is necessarily an approximation to the true state of affairs. It also shows that the QCA expression for α_1 may be expected in general to be a good approximation if $|z_1\alpha_1| \ll 1$ and if $z_n\alpha_n \to 0$ rapidly with increasing n. It is of course known to be poor for temperatures below and near the critical transition temperature for solids with long-range order.[34,35] Equally we can expect it to be unsatisfactory (as similar approximations in all critical phenomena) near the critical temperature for phase separation. However for liquid mixtures with negative α_1, expression (4.8) may not be unreasonable even if $|z\alpha_1|$ is not much less than unity—it being unlikely that there be long-range order even in a strongly interacting liquid mixture (except ionic liquids).

5 COMPARISON WITH EXPERIMENT FOR COMPOUND FORMING MIXTURES

5.1 Thermodynamic properties

We apply the formulae of Section 3 to calculate the concentration dependences of G_M^{exc}, etc., for three liquid alloy systems: MgBi, LiPb and AgAl for which the complexes may be respectively taken as Mg_3Bi_2, Li_4Pb and Ag_3Al. The former two show strong tendency to form complexes while AgAl has relatively weaker tendency. In the actual calculation the coordination number z was fixed in advance and a reasonable choice of the relevant interaction parameters (4 for MgBi and 3 each for AgAl and LiPb since from (2.17) $P_{BB} \equiv 0$ if $\nu = 1$ in $A_\mu B_\nu$) was made from the experimental data on $S_{CC}(0)$ and G_M at a couple of concentrations. The constant $\mathscr{I}$ occurring in (3.3) and (3.7) is not an independent constant and was determined, as mentioned in Section 3, from the requirement that $f(c = 1) = 0$. The choice of z and the corresponding interaction parameters ω and $\Delta\varepsilon_{ij}$ are tabulated for the three systems in Table II, and G_M^{exc}, $\ln\gamma$ and $S_{CC}(0)$ are plotted versus c in Figures 1–3.

For one system namely, MgBi (Figure 1), the calculations were made for two values of z (8 and 10) to examine the effect of z. We see from the figure that the difference in z makes hardly any impact on the run of G_M^{exc}, $\ln\gamma$ and

TABLE II

Interaction energy parameters ω and $\Delta\varepsilon_{ij}$ for MgBi ($\mu = 3, \nu = 2$), LiPb ($\mu = 4, \nu = 1$) and AgAl ($\mu = 3, \nu = 1$) systems

System	T°K	z	ω/k_BT	$\Delta\varepsilon_{AB}/k_BT$	$\Delta\varepsilon_{AA}/k_BT$	$\Delta\varepsilon_{BB}/k_BT$
MgBi	975	8	−6.50	−1.40	−2.00	2.27
MgBi	975	10	−6.50	−1.40	−2.00	1.45
LiPb	932	10	−1.50	−1.40	+1.20	
AgAl	1173	12	−0.225	−0.338	+0.015	...

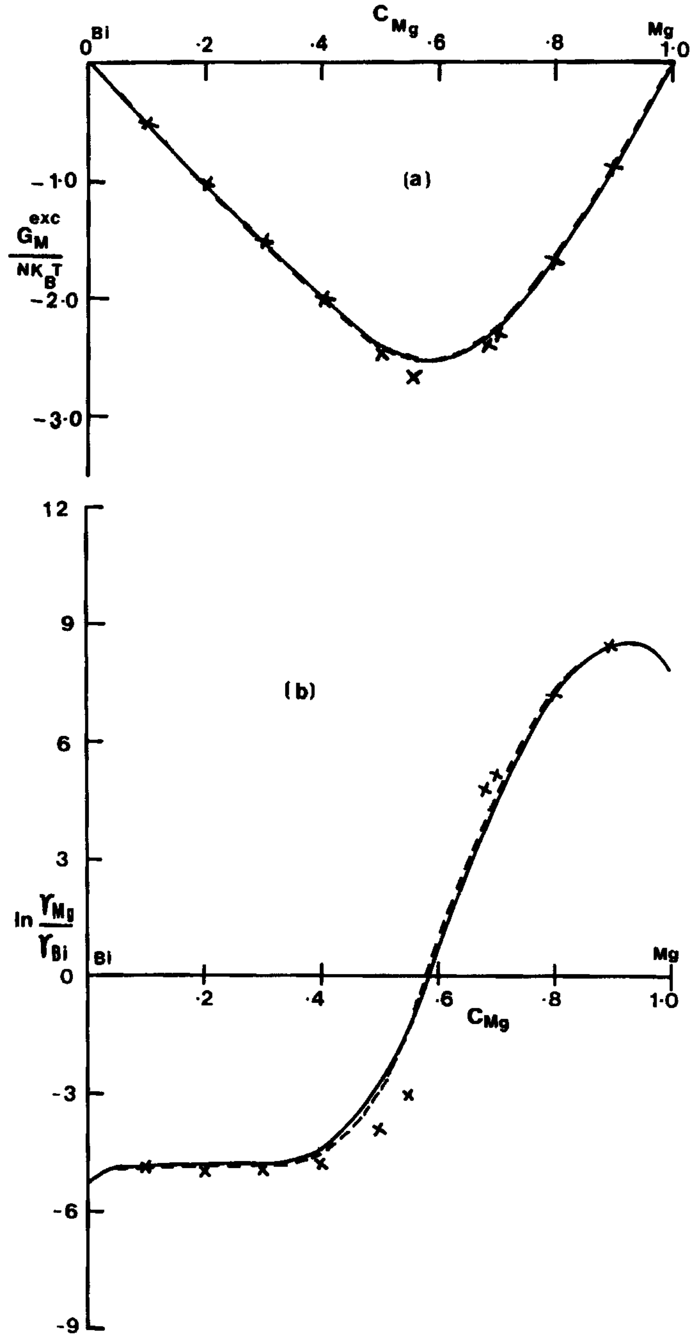

FIGURE 1 Thermodynamic quantities for Mg–Bi versus concentration (a) G_M^{exc}/Nk_BT, (b) $\ln(\gamma_{MG}/\gamma_{Bi})$ and (c) $S_{CC}(0)$. ——— theory with $z = 10$, - - - theory with $z = 8$. ×, experimental data from Ref. 36.

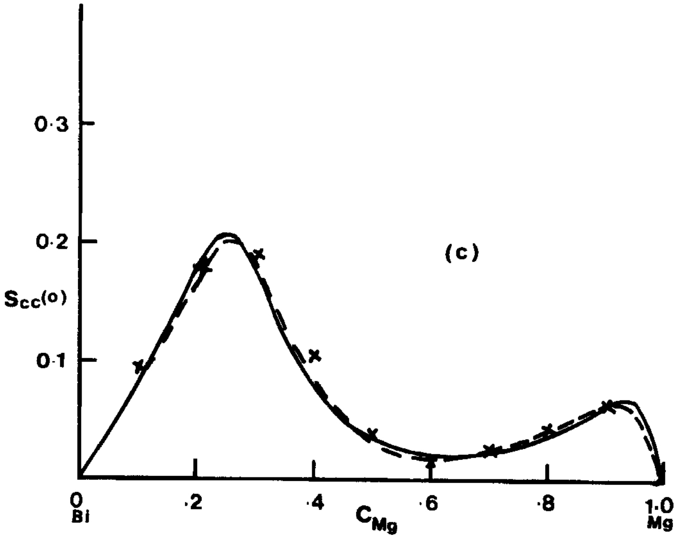

FIGURE 1c

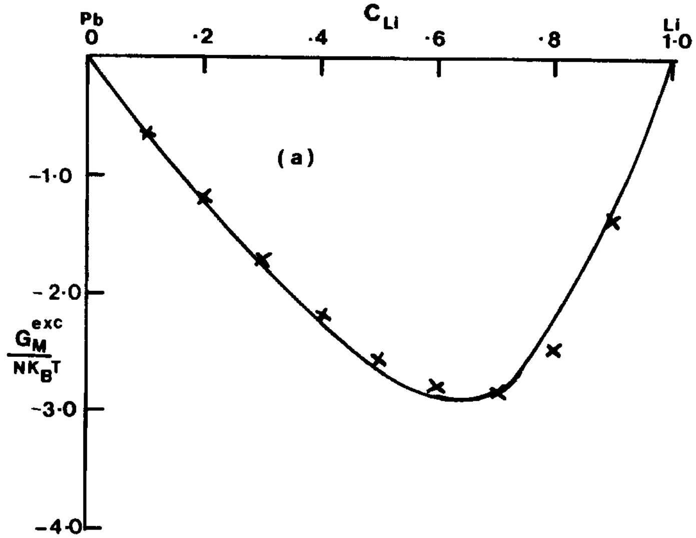

FIGURE 2 Thermodynamic quantities for Li–Pb versus concentration (a) G_M^{exc}/Nk_BT, (b) $\ln(\gamma_{Li}/\gamma_{Pb})$ and (c) $S_{CC}(0)$. ——— theory with $z = 10$. ×, experimental data from Ref. 37. ▮, experimental points for $S_{CC}(0)$ from Ref. 2.

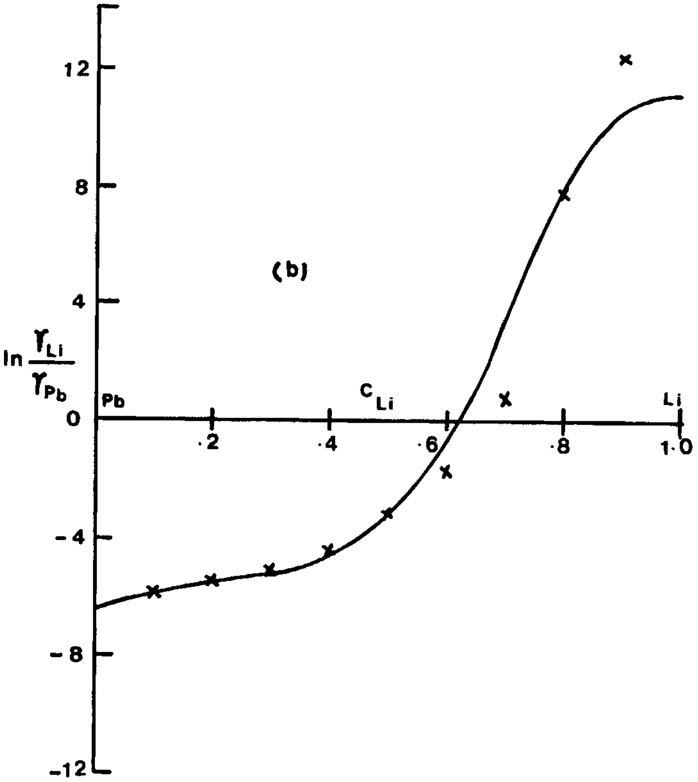

FIGURE 2b

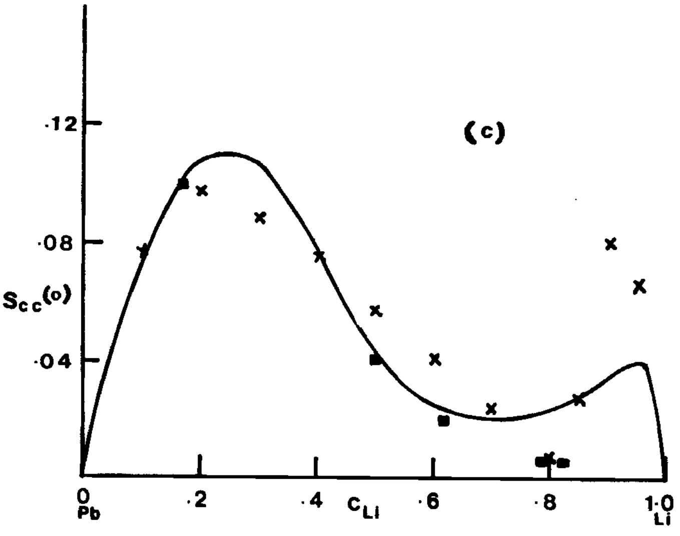

FIGURE 2c

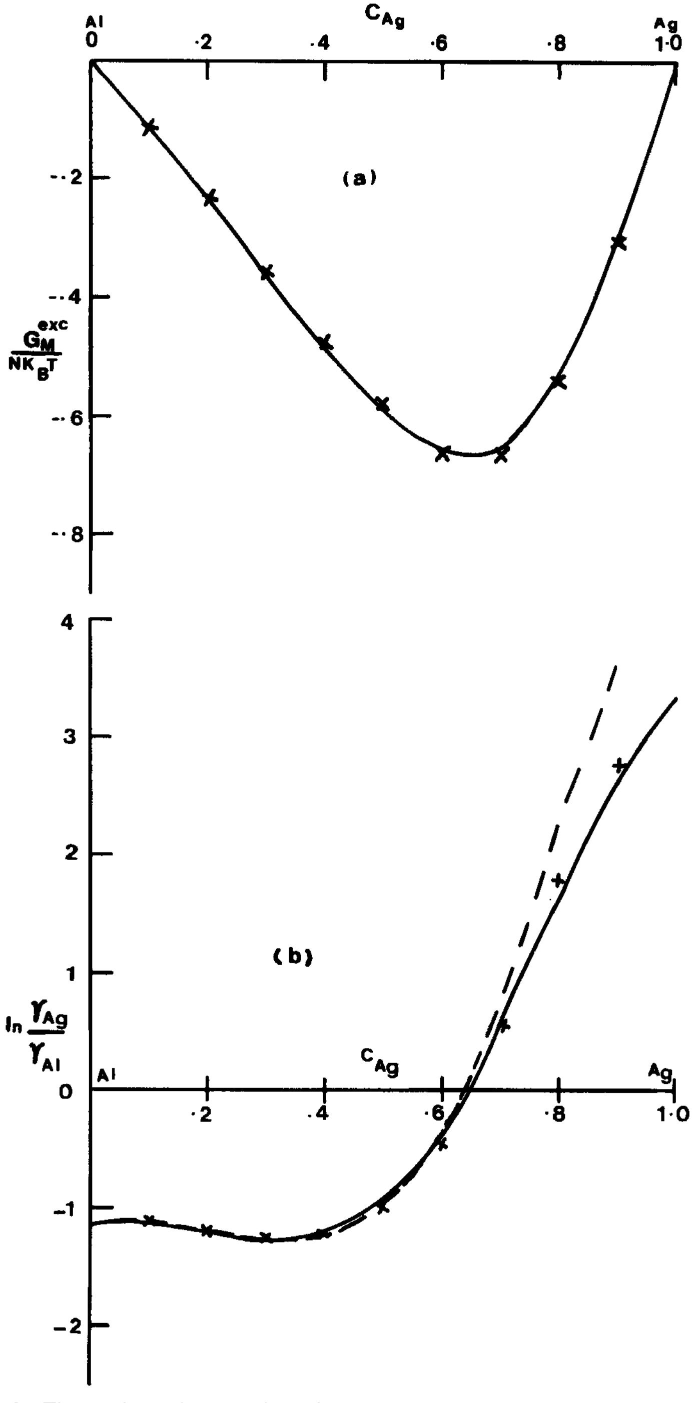

FIGURE 3 Thermodynamic quantities for AgAl versus concentration (a) G_M^{exc}/Nk_BT, (b) $\ln(\gamma_{Ag}/\gamma_{Al})$ and (c) $S_{CC}(0)$. —— theory with $z = 12$. (In Figure 3b, ---- theory of Ref. 30.) ×, experimental points from Ref. 44.

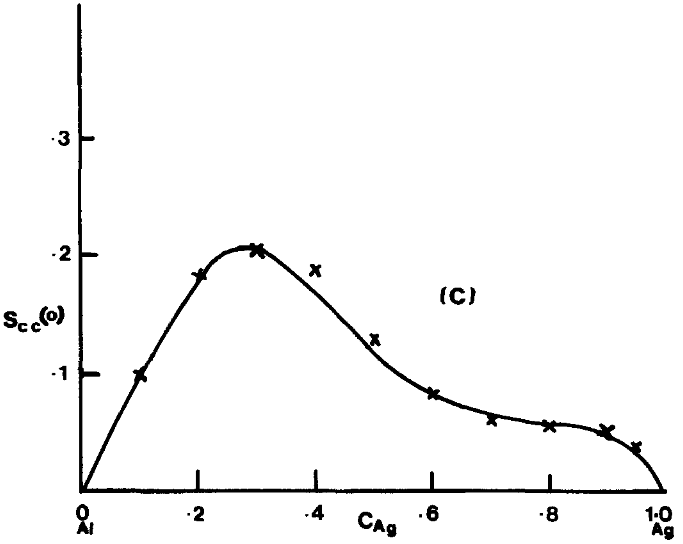

FIGURE 3c

$S_{CC}(0)$ so long as the interaction parameters are chosen appropriately. It will be seen later that this is in contrast with the case of SRO (α_1) which is found to be more sensitive to the choice of z (Figure 4a).

For reasons which will be apparent presently the results shown for LiPb and AgAl in Figure 2 and Figure 3 respectively were calculated taking $z = 10$ for LiPb and $z = 12$ for AgAl.

We see from Figures 1–3 that the computed values of G_M^{exc} in each case are in very good agreement with the experimental data and that the fit for $\ln \gamma$ and $S_{CC}(0)$† is also reasonable. As mentioned in the Introduction, Cartier and Barriol computed $\ln \gamma$ and the conditional probabilities $[B/A]$ for systems which form A_3B complexes. In the terminology of Section 2, they take clusters of one and four lattice sites on a face-centered cubic lattice ($z = 12$) which makes their calculations rather more intricate than ours. From their computed values of $\ln \gamma$ for AgAl, given in Figure 3b, we see that our calculations seem to be in as good an agreement with experiment as their values.

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† Experimental $S_{CC}(0)$ is inferred from the observed activities $a_i (= c_i \gamma_i)$, $i = A, B$, using $S_{CC}(0) = (1 - c_i)/d(\ln a_i)/dc_i$.

5.2 Short range order

With the parameters given in Table 2 the SRO α_1 are readily inferred from (4.8) using (2.23) and (3.11). These are plotted as a function of c in Figure 4a–c for the MgBi, LiPb and AgAl systems.

We note first from Figure 4 that α_1 is negative for each case, indicating that unlike atom pairs are preferred over the like atom pairs as nearest neighbours. Secondly we observe that the peak value of $|\alpha_1|$ is significantly larger for MgBi and LiPb than for AgAl. This is to be expected since the former two are much more strongly interacting systems than AgAl (peak values of $|G_M^{\text{exc}}/Nk_BT|$ being respectively, 2.69, 2.86 and 0.62). Apart from the peak values, the detailed concentration dependence of α_1 also depends on the interaction parameters and may vary markedly from one alloy to another. In particular, we note that $\alpha_1 - c$ curves are quite asymmetric (about $c = \frac{1}{2}$) for LiPb and AgAl but approximately symmetric for MgBi—even though G_M^{exc} and $S_{CC}(0)$ are asymmetric for all the three alloys. In Figure 4c for AgAl, we have also given for comparison the values of α_1 obtained from the conditional probability $[B/A]$ calculated in Ref. 30.

Coming to the experimental values of α_1 we first recall that for a binary alloy in which the size effects are negligible (or more precisely for which the N–C structure factor $S_{NC}(q) \equiv 0$), the Fourier transform of $S_{CC}(q)$ enables

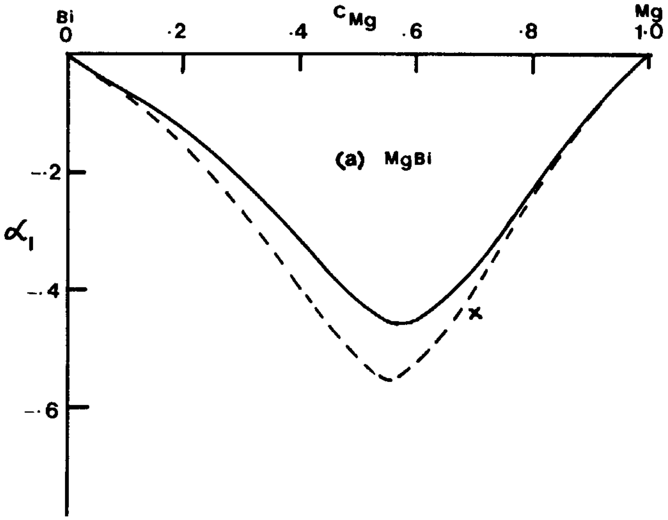

FIGURE 4 Short range order parameter α_1 versus concentration: (a) Mg–Bi, (b) Li–Pb, (c) Ag–Al. ——, – – – – theory with z values as explained in Figures 1–3. In Figures 4a, b, × experimental from Refs. 5 and 2 respectively. ▌ in Figure 4b due to Ref. 38, and —·—·— in Figure 4c due to Ref. 30 as explained in the text.

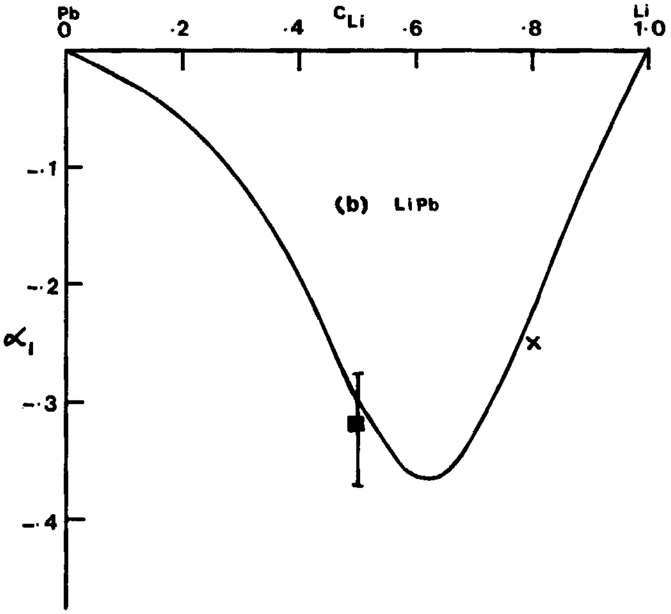

FIGURE 4b

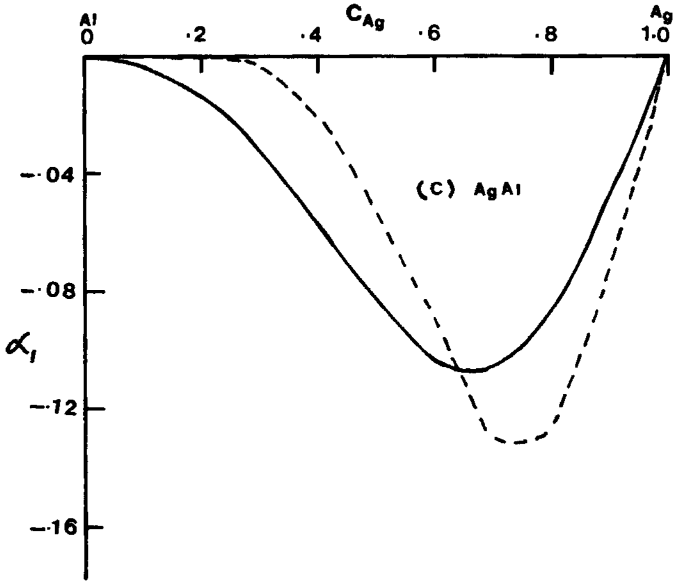

FIGURE 4c

one to evaluate $z\alpha_1$ (see Ruppersberg and Egger[2]). Further z may be evaluated from the Fourier transform of $S_{NN}(q)$. The actual determination of α_1 is quite a long and fine art[2–9] and the results are available only for few cases.

We note that in actual practice z (which may depend on concentration also) has not always deen determined from $S_{NN}(q)$ as indicated above. Since $S_{CC}(q)$ yields $z\alpha_1$, the inferred value of α_1 depends on the choice of z. It may be seen from the theoretical expression for α_1—see Figure 4a and discussion in Section 4.1—that the theoretical α_1 (for a given set of thermodynamic data)† also depends significantly on the choice of z. In making the comparison between the experimental and theoretical α_1, it is therefore advisable to take the same value of z for the two evaluations of α_1.

Boos and Steeb[5] have determined α_1 for MgBi system at $c_{\text{Mg}} = 0.7$. At this concentration they give $z = 7.8$. Their value $\alpha_1 = -0.44$ compares well with our theoretical value $\alpha_1 = -0.40$ for $z = 8$. (Note from (4.7) that α_1 cannot be less than $-3/7 = -0.43$ at $c = 0.7$). For LiPb system Ruppersberg and Egger[2] give at $c_{\text{Li}} = 0.8$, the value $\alpha_1 = -0.25$ and $z = 10$. Our calculated value for this case is $\alpha_1 = -0.22$. It is of interest to mention that Bletry[38] has recently given a formulation for calculating the structure factors where α_1 acts as a parameter. He infers that the experimental $S_{NN}(q)$ and $S_{CC}(q)$ for LiPb at $c_{\text{Li}} = 0.5$ imply that $\alpha_1 = -0.32 \pm 0.05$. This may be compared to our value in Figure 4b of $\alpha_1 = -0.29$ at this concentration.

6 SRO IN REGULAR ALLOYS

6.1 General remarks

We first record for convenience the well known QCA expressions[15,31] for the activity coefficients γ_A and γ_B and G_M^{exc} for the regular alloys. As already mentioned they may be deduced also as a special case of the formulae of Section 3 and are given by ($c \equiv c_A$):

$$\gamma_A = \left\{\frac{\beta - 1 + 2c}{c(\beta + 1)}\right\}^{\frac{1}{2}z}, \qquad \gamma_B = \left\{\frac{\beta + 1 - 2c}{(1 - c)(1 + \beta)}\right\}^{\frac{1}{2}z}, \tag{6.1}$$

$$G_M^{\text{exc}}/Nk_BT = c \ln \gamma_A + (1 - c) \ln \gamma_B. \tag{6.2}$$

The expression for $S_{CC}(0)$ is given by (3.15) and of course α_1 again by (4.8). In these expressions β is still given by (2.23) but η now in (2.23) is just $\eta = \exp[\omega/zk_BT]$ and is independent of the concentration.

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† It is instructive to mention that for the simple case of a regular mixture and $\omega/zk_BT \ll 1$, the expression for $G_M^{\text{exc}} \simeq Nc(1 - c)\omega$, while from (4.8) $\alpha_1 \simeq 2c(1 - c)(\omega/zk_BT)$. Thus for a given G_M^{exc}, $\alpha_1 \propto z^{-1}$ for this case.

Equations (6.1) and (6.2) for γ's and G_M^{exc} have been extensively discussed in the literature. For want of space we shall therefore not make comparison of these expressions with experimental data for individual cases, but confine our discussion to α_1 and to a lesser extent to $S_{CC}(0)$. Equations (6.1) and (6.2) will however be used, of course, to determine as appropriate the parameter η or the interchange energy ω from the experimental data. In this connection we note that at $c = \frac{1}{2}$, $\beta = \eta$ and

$$G_M^{\text{exc}}/Nk_BT = \tfrac{1}{2}z \ln \frac{2\eta}{\eta + 1}. \tag{6.3}$$

As the behaviour of $S_{CC}(0)$ on the basis of QCA does not seem to have been reported previously, it is of interest to examine it briefly. Figure 5 depicts the variation of $S_{CC}(0)$ with c evaluated from (3.15) for different values of ω/k_BT. The curves are drawn for $z = 8$. We observe that when ω is negative $S_{CC}(0)$ is less than its ideal ($\omega = 0$) value: $S_{CC}^{\text{id}}(0) = c(1 - c)$, while it is greater when $\omega > 0$. For small negative values of ω/k_BT, $S_{CC}(0)$ has just one peak, namely at $c = \frac{1}{2}$. However, as ω/k_BT becomes more negative [for $\omega/k_BT < -2.8$] $S_{CC}(0)$ has a minimum at $c = \frac{1}{2}$ with a peak on either side; the minimum of $S_{CC}(0) \to 0$ as $\omega/k_BT \to -\infty$. It is to be noted that this feature is in striking contrast with the behaviour of $S_{CC}(0)$ in the zeroth or conformal solution approximation[18] where $S_{CC}(0)$ has just one extremum value for all ω/k_BT, namely a maximum at $c = \frac{1}{2}$.

When ω is positive there is tendency for segregation of two types of atoms and the system remains in one phase at all concentrations only above the critical temperature T_c given by[15]

$$\frac{\omega}{k_BT_c} = z \ln \frac{z}{z - 2}. \tag{6.4}$$

As $T \to T_c$ from above it will be seen from (3.15) that $S_{CC}(0) \to \infty$ at $c = \frac{1}{2}$.

The variation of SRO (α_1) with c for different ω/k_BT is shown in Figure 6. As expected, α_1 is negative for negative values of ω. We may draw attention to the change in the nature of the curves as ω/k_BT becomes increasingly negative. This can be understood from the dilute limit expressions for α_1 given in the Appendix. Also, as may be verified from (4.8), for $\omega/k_BT \to -\infty$, α_1 tends to its minimal value given by (4.7), namely $\alpha_1 = -(1 - c)/c$ for $c > \frac{1}{2}$ and $\alpha_1 = -c/(1 - c)$ for $c < \frac{1}{2}$.

For positive values of ω/k_BT, α_1 is positive. A point to note here is that according to the QCA expressions (4.8) or (4.9) the largest positive value that α_1 can have is $\alpha_1 = 1/(z - 1)$, which occurs at $c = \frac{1}{2}$ and $T = T_c$. For any reasonable z this is considerably lower than the maximum allowed value of α_1, namely unity, according to (4.7). We may recall from our discussion of Section 4 that we expect the QCA expression for α_1 to be a good approximation only for $T \gg T_c$.

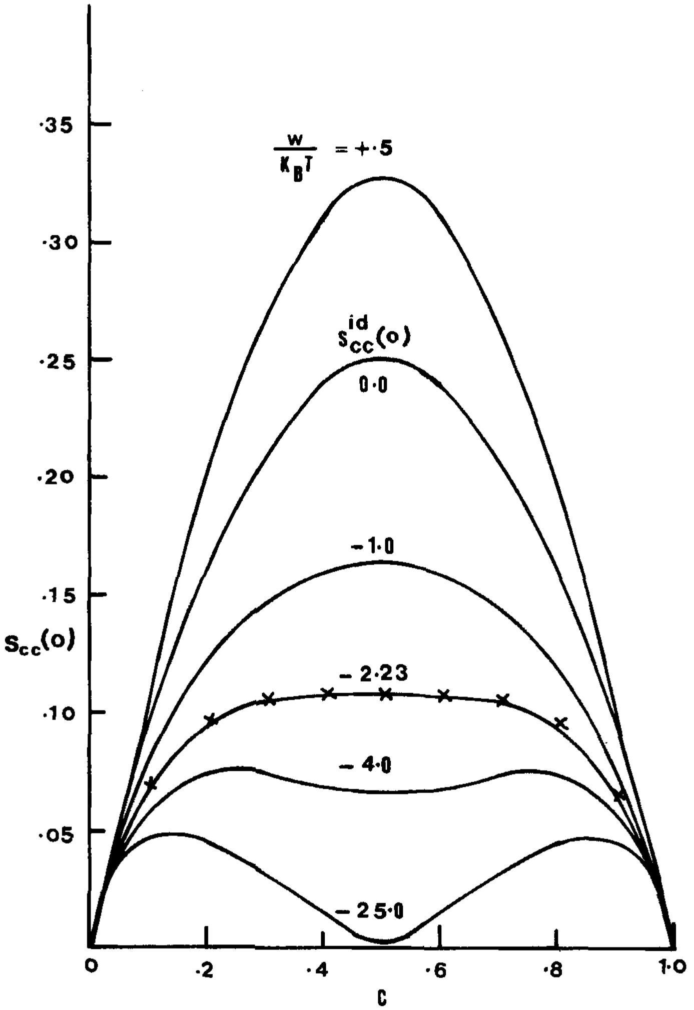

FIGURE 5 Concentration fluctuations $S_{CC}(0)$ versus concentration calculated for regular alloys for different values of the interchange energy ω/k_BT and $z = 8$. The value $\omega/k_BT = -2.23$ corresponds to Cd–Mg system and × denote experimental $S_{CC}(0)$ inferred from the activity data of Ref. 36.

6.2 Individual systems

Table III gives the experimental and calculated values of α_1 for five alloy systems. In the first four alloys unlike atoms are preferred over the like atoms as nearest neighbours (ω and α_1 negative) and in the fifth, LiNa, the reverse is the case. For each alloy the coordination number z as quoted in the reference measuring α_1 is also given. Using this coordination number ω was deduced from the available thermodynamic data on $G_M^{\rm exc}$ or γ and then

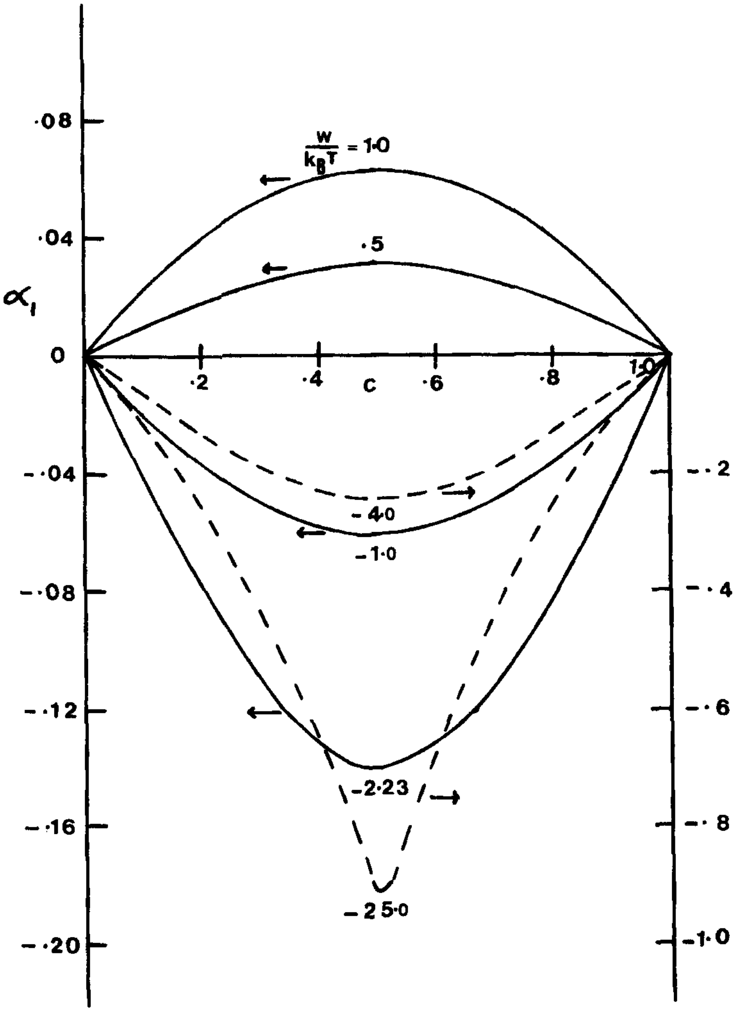

FIGURE 6 Short range order α_1 versus concentration calculated for regular alloys for different values of $\omega/k_B T$ and $z = 8$. Dashed curves refer to scale on the right.

α_1 calculated at the temperature of observation of α_1. For want of data ω was assumed to be independent of temperature.

We observe that for the first system listed in Table III, namely $Cd_{25}Mg_{75}$, the measured value (Boos and Steeb[6]) of α_1 agrees well with the theoretical value—ω was determined from the experimental[36] G_M^{exc}. As an illustrative example, the same value of ω was used to calculate $S_{CC}(0)$ at $T = 923$°K and is shown in Figure 5 together with the $S_{CC}(0)$ inferred from the activity data.[36] For $Li_{70}Mg_{30}$, we see from the Table that the experimental value of

TABLE III

Short range order parameter α_1 for a number of regular molten alloys

System	T °K	z	α_1(exp)†	α_1 (theory)	ω/k_B°K‡
$Cd_{25}Mg_{75}$	823	7	-0.13	-0.12	-2057[a]
$Li_{70}Mg_{30}$	887	10	-0.035	-0.044	-945[b]
$Li_{70}Mg_{30}$	887	10	-0.035	-0.094	-2091[a]
$Li_{72}Ag_{28}$	600	10	-0.15	-0.21	-3803[c]
$Ag_{50}Mg_{50}$	1093	10	-0.37	-0.22	-4498[a]
$Li_{61}Na_{39}$	590	10	$+0.5$	$\simeq +0.1$	$\sim +1316$†

† For references see text.
‡ Inferred from thermodynamic data from:
[a] Ref. 36. [b] Ref. 39. [c] Ref. 40

α_1 (Ruppersberg *et al.*)[41] agrees well with the calculated value when ω is inferred from the recent data on G_M^{exc} by Saboungi and Blander.[39] The older data on G_M^{exc} given in Ref. 36 differs significantly from that of Ref. 39, and as seen from Table III gives a substantially different α_1.

For LiAg system ω was determined from the activity data of Becker *et al.*[40] The calculated value $\alpha_1(= -0.21)$ for $Li_{72}Ag_{28}$ is about 40% higher than the corresponding experimental value (Reiter *et al.*[3]) of $\alpha_1 = -0.15$. These values may be compared with the value $\alpha_1 = -0.24 \pm 0.05$ inferred by Bletry[38]—already referred to—from his work on structure factors.

For the AgMg system ω was determined from the heat of mixing (H_M) data[36] using the QCA expression (for ω independent of T)

$$H_M = 2\omega(1+\beta)^{-1}c(1-c). \tag{6.5}$$

Bearing in mind the possible uncertainties in the H_M data the agreement between the calculated and experimental (Steeb and Hezel)[42] values of α_1 is not unreasonable.

The last system in the table, namely LiNa, shows tendency for segregation and has been included primarily to illustrate that, as already discussed, the QCA expression for α_1 cannot be expected to give reasonable agreement with experiment near the critical temperature for phase transition. (In the absence of thermodynamic data, ω was estimated from (6.4) using $T_C = 580$°K—ignoring the asymmetry exhibited[43] by the Li-Na system.) We note that the maximum possible value of α_1 in QCA for alloys showing segregation tendency is just $1/(z-1)$ or 0.11 if $z = 10$—while the experimental value is 0.5.

6.3 Change of α_1 on melting

Boos and Steeb[6] have found in the $Cd_{25}Mg_{75}$ alloy an interesting fact that the local order actually increases (α_1 becomes more negative) on melting.

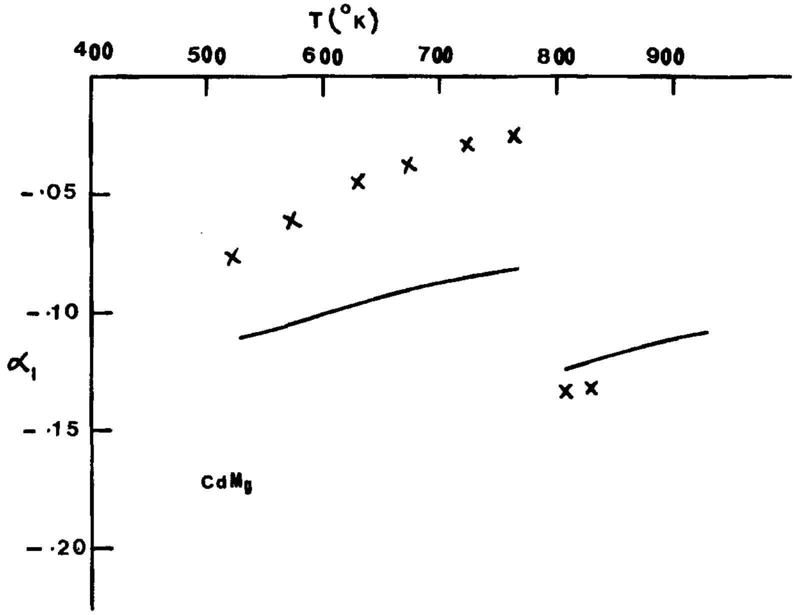

FIGURE 7 Temperature variation of α_1 across the melting for $Cd_{25}Mg_{75}$. —— theory; × experimental.[6]

Their results are plotted as a function of temperature in Figure 7. This behaviour has a ready explanation on the basis of our formulae and the fact that in the solid phase the coordination number[6] $z = 12$, while in the liquid phase $z = 7$. Then from the data[36] on G_M^{exc} in the solid phase we find $\omega_s/k_B = -2134$°K, compared to $\omega_l/k_B = -2057$°K in the liquid phase given in Table III. Although $\omega_s \simeq \omega_l$, the lower coordination number in the liquid phase implies from (4.8) that α_1 would become more negative on melting. From the theoretical values of α_1 given in Figure 7 it is apparent that our formulae explain satisfactorily the change in α_1 on melting. The actual numerical values of α_1 in the solid phase seem to indicate a somewhat lower numerical value of ω_s than deduced above from the existing data on G_M^{exc}.

7 CONCLUDING REMARKS

In this paper we have developed a model which provides a quantitative link between the various thermodynamic properties (G_M, $S_{CC}(0)$, etc.), and the short range order parameter α_1 in the compound forming and regular molten alloys. Once the interaction parameters of the theory have been set from the thermodynamic data at a few concentrations, one can determine

G_M, $S_{CC}(0)$, etc., as well as α_1 over the whole concentration range. A knowledge of $\alpha_1(c)$ is useful in understanding many physical properties—for example calculation of structure factors.[38,45] Since α_1 from scattering experiments is at present available only sparsely, the ready link of α_1 with the thermodynamic properties in our formalism is of added interest.

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Appendix

We give here the dilute limit ($c \ll 1$ and $1 - c \ll 1$) expressions for the activity coefficients γ_A and γ_B (and for $\gamma = \gamma_A/\gamma_B$) which are helpful in fixing the interaction parameters and in studying the dilute limit behaviour of $S_{CC}(0)$ and other structure factors.[16,21]

By definition, γ_A and γ_B are given by

$$k_B T \ln \gamma_A = \left(\frac{\partial G_M^{\mathrm{exc}}}{\partial N_A}\right)_{T,P,N_B}, \quad k_B T \ln \gamma_B = \left(\frac{\partial G_M^{\mathrm{exc}}}{\partial N_B}\right)_{T,P,N_A}. \tag{A.1}$$

Remembering the abbreviation $f(c) = G_M^{\mathrm{exc}}/Nk_BT$ and that $N = N_A + N_B$ and $c = N_A/N$, one has from (A.1)

$$\ln \gamma_A = f(c) + (1 - c)f'(c), \tag{A.2}$$

$$\ln \gamma_B = f(c) - cf'(c). \tag{A.3}$$

Hence $\ln \gamma = f'(c)$ which is the relation (3.6) used in the text.

Now if we write, for the limit $c \ll 1$,

$$\ln \gamma = a_0 + a_1 c + \mathcal{O}(c^2), \tag{A.4}$$

one obtains using (A.2) and (A.3)

$$\ln \gamma_A = a_0 + a_1 c + \mathcal{O}(c^2), \tag{A.5}$$

$$\ln \gamma_B = -\tfrac{1}{2}a_1 c^2 + \mathcal{O}(c^3). \tag{A.6}$$

(A.5) shows that the coefficient a_1 in (A.4) is just the well-known Wagner interaction parameter $a_1 = [(d \ln \gamma_A/dc)_{T,P}]_{c\to 0}$. In terms of a_1, the expression for $S_{CC}(0)$, using (3.5) and (3.8). is

$$S_{CC}(0) = c(1 - c) - a_1 c^2 + \mathcal{O}(c^3) \tag{A.7}$$

To determine a_0 and a_1 from the general expression (3.3) for γ, let y denote the exponent in the expression (3.11) for η^2, namely

$$y = \frac{\{2(\omega/z) + 2P_{AB}\,\Delta\varepsilon_{AB} - P_{AA}\,\Delta\varepsilon_{AA} - P_{BB}\,\Delta\varepsilon_{BB}\}}{k_B T} \tag{A.8}$$

and let $y(0)$ and $y'(0)$ denote respectively the value of y and dy/dc at $c = 0$ with similar meanings for $P_{AB}(0)$, $P'_{AB}(0)$, etc. Then using (2.23) the expansion of β, to order c^2, is

$$\beta = 1 + 2c(e^{y(0)} - 1) + 2c^2[1 - e^{y(0)} + y'(0)]e^{y(0)} + \cdots \tag{A.9}$$

Next using (A.9) in (3.4) and (3.3) one obtains for the coefficients a_0 and a_1 in the expansion (A.4) for $\ln \gamma$, $(c \ll 1)$, the expressions

$$a_0 = \mathscr{I} + z\left\{\frac{[(\omega/z) + P_{AB}(0)\Delta\varepsilon_{AB} - P_{BB}(0)\Delta\varepsilon_{BB}]}{k_B T}\right\}, \tag{A.10}$$

$$a_1 = z\left\{1 - e^{y(0)} + \frac{(P'_{AB}(0)\Delta\varepsilon_{AB} - P'_{BB}(0)\Delta\varepsilon_{BB})}{k_B T}\right\}. \tag{A.11}$$

For the limit $c \to 1$, the expansion for β is obtained from (A.9) by replacing $c \to 1 - c$, $y(0) \to y(1)$, the value of y at $c = 1$, and $y'(0) \to -y'(1)$. The expansion for $\ln \gamma$ then is, $(1 - c) \ll 1$,

$$\begin{aligned}\ln \gamma = \mathscr{I} &- z\left\{\frac{[(\omega/z) + P_{AB}(1)\Delta\varepsilon_{AB} - P_{AA}(1)\Delta\varepsilon_{AA}]}{k_B T}\right. \\ &+ z(1 - c)\left\{e^{y(1)} - 1 + \frac{(P'_{AB}(1)\Delta\varepsilon_{AB} - P'_{AA}(1)\Delta\varepsilon_{AA})}{k_B T}\right\} + \cdots.\end{aligned} \tag{A.12}$$

For $(\mu, \nu) = (3, 1), (4, 1)$ and $(3, 2)$—corresponding to the three compound forming alloys considered in the text—one has on using (2.15–17) in (A.10)

$$\ln \gamma = \mathscr{I} + \frac{\omega}{k_B T}, \quad (c = 0). \tag{A.13}$$

For $c = 1$, one has for $(\mu, \nu) = (3, 1)$ and $(4, 1)$

$$\ln \gamma = \mathscr{I} - \frac{(\omega + z\,\Delta\varepsilon_{AB})}{k_B T} \tag{A.14}$$

and for $(\mu, \nu) = (3, 2)$

$$\ln \gamma = \mathscr{I} - \frac{\omega}{k_B T}. \tag{A.15}$$

These expressions provided a check on the numerical results reported in Section 5.

Finally the dilute limit expressions for the SRO α_1 are also of interest. Using (A.9) in (4.8), one has, for $c \ll 1$,

$$\alpha_1 = c(e^{y(0)} - 1) + c^2[y'(0)e^{y(0)} - (e^{y(0)} - 1)(2e^{y(0)} - 1)] + \cdots. \tag{A.16}$$

The expansion for α_1 for $(1 - c) \ll 1$ may be obtained from (A.16) by replacing in it $c \to 1 - c$, $y(0) \to y(1)$ and $y'(0) \to -y'(1)$.

For the case of a regular mixture, $\Delta\varepsilon_{ij} \equiv 0$ and $y(0)$ in (A.16) is just $y(0) = [2\omega/zk_B T]$ while $y'(0) = 0$. Hence $(d^2\alpha_1/dc^2)_{c=0}$ changes sign at a value of ω given by $(\omega/zk_B T) = -\frac{1}{2} \ln 2$; this is reflected in the curvature of the $\alpha_1 - c$ curves of Figure 6 as discussed in Section 6.