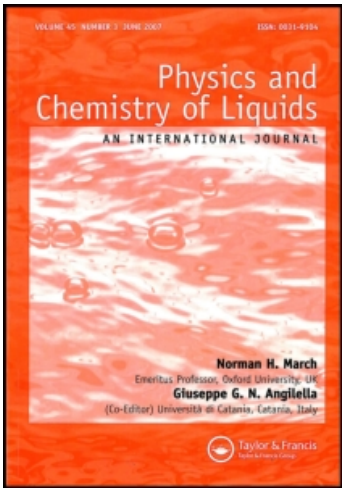

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

A Quasi-lattice Theory for Compound Forming Molten Alloys

A. B. Bhatia[a]; R. N. Singh[ab]
[a] Physics Department, University of Alberta Edmonton, Alberta, Canada [b] Department of Physics, Bhagalpur University, Bhagalpur, India

To cite this Article Bhatia, A. B. and Singh, R. N.(1984) 'A Quasi-lattice Theory for Compound Forming Molten Alloys', Physics and Chemistry of Liquids, 13: 3, 177 — 190
To link to this Article: DOI: 10.1080/00319108408080778
URL: http://dx.doi.org/10.1080/00319108408080778

Phys. Chem. Liq., 1984, Vol. 13, pp. 177–190
0031-9104/84/1303-0177$18.50/0

Printed in the United Kingdom

A Quasi-lattice Theory for Compound Forming Molten Alloys†

A. B. BHATIA and R. N. SINGH‡
Physics Department, University of Alberta Edmonton, Alberta, Canada, T6G 2J1

(*Received June 8, 1983*)

The complex formation model of Bhatia and Hargrove (BH) to explain the thermodynamic properties of compound forming A-B alloys is reformulated using a quasi-lattice picture. The formulation is explicitly carried out to an approximation where the pseudo-ternary alloy (of A and B atoms and $A_\mu B_\nu$ complexes (μ, ν small integers)), envisaged in BH, is treated in the quasi-chemical approximation. It is advantageous over BH in two major respects: Firstly, it gives useful insight into the two approximations used in BH, since these follow from it by simply going to a lower (zeroth) approximation and setting the coordination number z of the alloy to be $z = 2$ and $z = \infty$. Secondly, unlike the BH approach, it provides also an expression for the short range order parameter α_1 for nearest neighbours. The effect of varying z in the formulae is examined and a brief discussion of α_1 is given.

1. INTRODUCTION

In recent years a number of workers[1–9] have discussed characteristic features of concentration fluctuations and other thermodynamic properties of compound forming molten alloys using the complex formation model as proposed by Bhatia *et al.*[7–9] (for earlier references, see Ref. 7–9). A partial aim of this paper is to show that the results given in Ref. 7–9—particularly in Ref. 8, hereafter referred to as BH—can be derived as special cases of a more general formulation. The latter which we present below is based on the ideas underlying Guggenheim's[10] quasi-lattice theory of mixtures of polymers.

The aforementioned reformulation of BH model is desirable for several reasons: First, it provides a firmer statistical mechanical foundation for some of the approximations made in BH and points ways on how to improve

† Work supported in part by the Natural Sciences and Engineering Research Council of Canada.

‡ Present address: Department of Physics, Bhagalpur University, Bhagalpur-812007, India.

upon them. For reasons which will become clear in the text the formulation is actually carried out to an approximation higher than that necessary for relating it to BH work (§3, 4). Secondly, it makes clear the role of the coordination number z of the alloy—unlike the BH expressions which do not contain z (§5). Finally, unlike the earlier treatment, the present formulation yields also an expression for the short range order existing in the liquid alloy (§6)—a topic which has received considerable attention in the last few years both experimentally[11] and theoretically[12].

2. COMPLEX FORMATION MODEL

The essential assumption of the complex formation model[7-9] is that a liquid binary AB alloy consists of certain numbers of individual A and B atoms and of chemical complexes of the type $A_\mu B_\nu$ (μ, ν, small pairs of integers), all in chemical equilibrium with one another. The choice of μ, ν is usually, though not invariably, apparent from the concentration(s) at which the A–B alloy forms a stable compound in the solid phase. We shall here assume for simplicity that only one type of chemical complexes (one pair of μ, ν) are formed—the present treatment, as of BH (see Ref. 9), is readily generalisable to the case where several types of complexes are formed.

Let the binary alloy contain in all N atoms of which Nc are A atoms and $N(1-c)$ B atoms. If these exist in the molten alloy as n_1 individual A atoms, n_2 individual B atoms and n_3 complexes $A_\mu B_\nu$, then from the conservation of atoms

$$n_1 = Nc - \mu n_3, \qquad n_2 = N(1-c) - \nu n_3. \tag{2.1}$$

Now if $G_i^{(0)}$ denote the chemical potential, per atom, of the species $i (i = 1, 2, 3)$, in its pure state, then the free energy of mixing G_M of the binary A–B mixture can be written following BH as

$$G_M \equiv G - NcG_1^{(0)} - N(1-c)G_2^{(0)} = -n_3 g + G' \tag{2.2}$$

where G is the total Gibbs free energy of the mixture and

$$g = \mu G_1^{(0)} + \nu G_2^{(0)} - G_3^{(0)} \tag{2.3}$$

$$G' = G - (n_1 G_1^{(0)} + n_2 G_2^{(0)} + n_3 G_3^{(0)}). \tag{2.4}$$

The equilibrium value of n_3 (and hence of n_1 and n_2 via (2.1)) at a given temperature and pressure is given by

$$(\partial G_M / \partial n_3)_{T,P,N,c} = 0. \tag{2.5}$$

In (2.2), the first term $(-n_3 g)$ represents the lowering of the (free) energy due to the formation of the chemical complexes. The second term is the free

energy of mixing of a ternary mixture of fixed n_1, n_2, n_3 whose constituents A, B, and $A_\mu B_\nu$ are assumed to interact relatively weakly with one another—any strong bonding interaction between A and B atoms having been taken care of via the formation of the chemical complexes. The problem of determining G_M and hence other thermodynamic properties thus reduces to having an expression for G'. We next consider a quasi-lattice formulation for deriving an expression for G', postponing, for convenience, comment on the forms for G' used in BH.

3. QUASI-LATTICE FORMULATION FOR G'

In quasi-lattice models of liquid mixtures[10,13], all the atoms are assumed to be located on a set of equivalent lattice sites, each site having z nearest neighbours. If the size (volume) of the two types of atoms A and B differ by no more than forty or fifty percent, then each atom (of either type) can be taken to occupy just one lattice site[10]. Most compound forming alloys fall in this category and for simplicity we consider this important case only. The atoms of the complex $A_\mu B_\nu$ then occupy $\mu + \nu$ lattice sites, and the total number of lattice sites is just N, the total number of atoms in the alloy:

$$N = n_1 + n_2 + n_3(\mu + \nu). \tag{3.1}$$

Finally the interaction between the atoms is assumed to be of short range and is represented by nearest neighbour bond or contact energies.

3.1 Configurational energy E

The first step in obtaining an expression for the partition function and hence G' is to determine the form of the configurational energy E. Each individual A or B atom has z nearest neighbour contacts all of which contribute to E. Some of the contacts of an atom in a complex however are with other atoms of the same complex; these do not contribute to E as their contribution is included in the g-term of Eqn. (2.2). Let zq_3 denote the number of nearest neighbour pairs of sites of which one is occupied by a given complex and the other is not. The total number of contacts which contribute to E is then $\frac{1}{2}z\mathcal{N}$ where

$$\mathcal{N} = n_1 + n_2 + q_3 n_3. \tag{3.2}$$

We discuss the value of q_3 later. Next, in the sense explained below, we have to regard an A atom (or a B atom) belonging to the complex as though it were different from the individual A (or B) atom not belonging to the complex. We denote the contact between two individual A atoms as an AA contact with its energy as ω_{AA}, while if the contact is between an A atom belonging to a

complex and an individual A atom we denote it as an $A'A$ contact with its energy as $\omega_{A'A}$ ($=\omega_{AA'}$). Similarly we denote by $A'A'$ the contact between two A atoms belonging to two different complexes with its energy as $\omega_{A'A'}$. Finally if the numbers of different types of contacts, AA, $A'A$, AB etc. are n_{AA}, $n_{A'A}$($=n_{AA'}$), n_{AB}($=n_{BA}$) etc., then the configurational energy E equals:

$$E = n_{AA}\omega_{AA} + n_{BB}\omega_{BB} + n_{AB}\omega_{AB} + n_{AA'}\omega_{AA'} + n_{AB'}\omega_{AB'} + n_{BB'}\omega_{BB'} + n_{BA'}\omega_{BA'} + n_{A'B'}\omega_{A'B'} + n_{A'A'}\omega_{A'A'} + n_{B'B'}\omega_{B'B'}. \quad (3.3)$$

We simplify (3.3) as follows:

First we note that n_{AA} etc. are not all independent of one another. By straightforward counting from a given atom, one has

$$n_{AA} + \tfrac{1}{2}n_{AB} + \tfrac{1}{2}(n_{AA'} + n_{AB'}) = \tfrac{1}{2}zn_1, \quad (3.4)$$

$$n_{BB} + \tfrac{1}{2}n_{BA} + \tfrac{1}{2}(n_{BA'} + n_{BB'}) = \tfrac{1}{2}zn_2, \quad (3.5)$$

$$n_{A'A'} + \tfrac{1}{2}n_{A'A} + \tfrac{1}{2}n_{A'B} + \tfrac{1}{2}n_{A'B'} = \tfrac{1}{2}c_c q_3 z n_3, \quad (3.6)$$

$$n_{B'B'} + \tfrac{1}{2}n_{B'B} + \tfrac{1}{2}n_{B'A'} + \tfrac{1}{2}n_{B'A} = \tfrac{1}{2}(1 - c_c)q_3 z n_3, \quad (3.7)$$

where c_c is the compound forming concentration $c_c = \mu/(\mu + \nu)$.

Secondly, to make the problem more tractable, we assume that the complexes are randomly oriented. In other words, if n_{13}, for example, denote the total number of nearest neighbour pairs of sites such that one site is occupied by an individual A atom and another by an atom (A' or B') from the complex, then, because of assumed random orientations,

$$n_{AA'} = c_c n_{13}; \qquad n_{AB'} = (1 - c_c)n_{13}. \quad (3.8)$$

Similarly defining n_{23} and n_{33} one has

$$n_{BA'} = c_c n_{23}, \qquad n_{BB'} = (1 - c_c)n_{23}, \quad (3.9)$$

$$n_{A'A'} = c_c^2 n_{33}, \qquad n_{B'B'} = (1 - c_c)^2 n_{33}, \qquad n_{A'B'} = 2c_c(1 - c_c)n_{33}. \quad (3.10)$$

It follows, of course, from the definitions of n_{13} etc., that (irrespective of whether (3.8)–(3.10) are true or not)

$$n_{13} = n_{AA'} + n_{AB'}, \qquad n_{23} = n_{BA'} + n_{BB'}, \qquad n_{33} = n_{A'A'} + n_{B'B'} + n_{A'B'}. \quad (3.11)$$

Making for convenience a change of notation, $n_{AA} = n_{11}$, $n_{BB} = n_{22}$ and $n_{AB} = n_{12}$, equations (3.4) and (3.5) and the sum of (3.6) and (3.7) may be respectively written as, using (3.11)

$$n_{11} + \tfrac{1}{2}n_{12} + \tfrac{1}{2}n_{13} = \tfrac{1}{2}zn_1, \quad (3.12)$$

$$n_{22} + \tfrac{1}{2}n_{12} + \tfrac{1}{2}n_{23} = \tfrac{1}{2}zn_2, \quad (3.13)$$

$$n_{33} + \tfrac{1}{2}n_{13} + \tfrac{1}{2}n_{23} = \tfrac{1}{2}q_3 z n_3, \quad (3.14)$$

which we shall need presently.

Using now (3.8)–(3.10) the configurational energy (3.3) may be written as

$$E = \sum_{i=1}^{3} n_{ii}\omega_{ii} + \sum\sum_{i<j} n_{ij}\omega_{ij}, \tag{3.15}$$

where we have set $\omega_{11} = \omega_{AA}$, $\omega_{22} = \omega_{BB}$, $\omega_{12} = \omega_{AB}$ and

$$\begin{gathered}\omega_{13} = c_c\omega_{AA'} + (1 - c_c)\omega_{AB'}, \qquad \omega_{23} = c_c\omega_{BA'} + (1 - c_c)\omega_{BB'}, \\ \omega_{33} = c_c^2\omega_{A'A'} + (1 - c_c)^2\omega_{B'B'} + 2c_c(1 - c_c)\omega_{A'B'}.\end{gathered} \tag{3.16}$$

Finally, on using (3.12)–(3.14) in (3.15), one can write E as

$$E = \frac{1}{2}z[n_1\omega_{11} + n_2\omega_{22} + q_3n_3\omega_{33}] + [n_{12}\chi_{12} + n_{13}\chi_{13} + n_{23}\chi_{23}], \tag{3.17}$$

which is the form for E we wished to obtain. In (3.17), $2\chi_{12} = 2\omega_{12} - \omega_{11} - -\omega_{22}$, with similar definitions for χ_{13} and χ_{23}. The three χ_{ij}'s are the interchange energies with obvious physical interpretation. They alone enter the expression for the free energy of mixing G' of the ternary mixture—the remaining terms in (3.17), being linear in the n_i, do not contribute to G'.

3.2 The partition function and the expression for G'

The configurational partition function Ω is

$$\Omega = \sum_{E} g(E)e^{-E/k_BT}, \tag{3.18}$$

where $g(E)$ is the number of configurations having a given E, i.e. for a given set of n_{ij}. We treat Ω in the well-known quasi-chemical approximation (QCA) which is described in detail for binary mixtures of both monomers and polymers by Guggenheim[10]. Since the steps for a ternary mixture are similar, we give here only the final result. One has (for a given n_1, n_2, n_3)

$$\Omega \simeq W(n_1, n_2, n_3)\frac{F([n_{ij}^*])}{F([\bar{n}_{ij}])}e^{-E([\bar{n}_{ij}])/k_BT}, \tag{3.19}$$

where

$$F([n_{ij}]) = n_{11}!n_{22}!n_{33}!(\tfrac{1}{2}n_{12}!)^2(\tfrac{1}{2}n_{13}!)^2(\tfrac{1}{2}n_{23}!)^2,$$

$\bar{n}_{ij}$ are the solution of the three equations (3.12)–(3.14) and the three chemical equilibrium type relations:

$$\frac{(\frac{1}{2}\bar{n}_{ij})^2}{\bar{n}_{ii}\bar{n}_{jj}} = e^{-\chi_{ij}/k_BT}, \qquad (i, j = 1, 2, 3, i \neq j), \tag{3.20}$$

which are sufficient to determine all six $\bar{n}_{ij}$. n_{ij}^* are similarly determined, except that they obey, instead of (3.20),

$$(\tfrac{1}{2}n_{ij}^*)^2/n_{ii}^* n_{jj}^* = 1, \qquad (i, j = 1, 2, 3, i \neq j), \tag{3.21}$$

which correspond to as though the different constituents (A, B, $A_\mu B_\nu$) of the mixture were distributed at random ($\chi_{ij} \equiv 0$). Further, $E([\bar{n}_{ij}])$ is the configurational energy given by (3.17) but with n_{ij} replaced by $\bar{n}_{ij}$. Finally, $W(n_1, n_2, n_3)$ in (3.19), represents the number of ways in which $n_1 A$ atoms, $n_2 B$ atoms, and $n_3 A_\mu B_\nu$ complexes can be randomly arranged on N lattice sites.

Since each complex $A_\mu B_\nu$ occupies $(\mu + \nu)$ lattice sites, W depends also on the arrangement of atoms inside a complex. The evaluation of W however for complexes of arbitrary shape, even if it were known, can be difficult and we assume here that the atoms in a complex are arranged in open chains which may or may not be branched. Guggenheim[10] has investigated W for a multicomponent mixture of polymers whose molecules are all of the open chain type just described and hence W for our problem becomes just a special case of his Eqn. (10.10.2). Noting that for our case $r_1 = r_2 = 1, q_1 = q_2 = 1$ and $r_3 = \mu + \nu$, we have for W

$$W = \left(\frac{\rho_3}{\sigma_3}\right)^{n_3} \frac{N!}{n_1! n_2! n_3!} \left(\frac{\mathcal{N}!}{N!}\right)^{(1/2)z}, \tag{3.22}$$

where (ρ_3/σ_3) depends on the internal symmetry of the complex and does not enter into the expression for G'. $\mathcal{N}$ is already given in Eqn. (3.2)—the value of q_3 for open chained molecules being

$$q_3 = \mu + \nu - 2(\mu + \nu - 1)/z. \tag{3.23}$$

The configurational free energy F_c is related to Ω by $F_c = -k_B T \ln \Omega$. The free energy of mixing G' differs from F_c by appropriate linear terms[10] in n_i such that $G' \equiv 0$ when any two of n_1, n_2, n_3 equal zero. Making use of (3.22) in (3.19) one obtains finally for G' the expression

$$G' = G'_a + k_B T[y(\bar{n}_{ij}) - y(n_{ij}^*)] + (\bar{n}_{12}\chi_{12} + \bar{n}_{13}\chi_{13} + \bar{n}_{23}\chi_{23}), \tag{3.24}$$

where

$$y(n_{ij}) = n_{11}\ln n_{11} + n_{22}\ln n_{22} + n_{33}\ln n_{33} + n_{12}\ln(\tfrac{1}{2}n_{12}) + n_{23}\ln(\tfrac{1}{2}n_{23}) + n_{13}\ln(\tfrac{1}{2}n_{13}), \tag{3.25}$$

and G'_a arises from the W term:

$$G'_a = k_B T\left(n_1 \ln \frac{n_1}{N} + n_2 \ln \frac{n_2}{N} + n_3 \ln\left(\frac{(\mu + \nu)n_3}{N}\right) - \frac{1}{2} z q_3 n_3 \ln \frac{\mu + \nu}{q_3} - \frac{1}{2} z\mathcal{N} \ln \frac{\mathcal{N}}{N}\right), \tag{3.26}$$

and is the free energy of mixing which the mixture would have if its constituents were all non-interacting ($\chi_{ij} = 0$).

The work of this and the preceding section shows that the complex formation model for the compound forming binary alloys can be formulated within a quasi-lattice framework. When the expression (3.24) for G' is used in the expression (2.2) for G_M, we shall refer to it, for brevity, as G_M in the quasi-chemical approximation (QCA) for compound forming alloys†, the last three words being understood in the context. We shall not pursue a discussion of thermodynamic properties on the basis of QCA, our aim in this paper having been to demonstrate that the formulation based on complex formation model can be carried out to at least this approximation and to examine how it is related to BH work. We shall see later that for quantitative calculations of short range order the use of QCA would be necessary.

4. ZEROTH APPROXIMATION AND RELATION TO BH WORK

In the so-called zeroth approximation[10] the constituents of a mixture are assumed to be distributed at random. In our context this means taking $\bar{n}_{ij} \equiv n_{ij}^*$, despite the bias due to the non-zero interchange energies χ_{ij} implied by (3.20). We can obtain the expression for G' in the zeroth approximation from (3.24) by neglecting in it all terms higher than the first order in χ_{ij}. To this order of approximation one may verify that $y(\bar{n}_{ij}) - y(n_{ij}^*) = 0$ and hence

$$G' = G'_a + \sum_{i<j}\sum n_{ij}^* \chi_{ij}. \tag{4.1}$$

By direct counting or using (3.21) in Eqns. (3.12)–(3.14) one has

$$n_{11}^* = \frac{1}{2} z \frac{n_1^2}{\mathcal{N}}, \qquad n_{22}^* = \frac{1}{2} z \frac{n_2^2}{\mathcal{N}}, \qquad n_{33}^* = \frac{1}{2} z q_3^2 \frac{n_3^2}{\mathcal{N}},$$

$$n_{12}^* = z \frac{n_1 n_2}{\mathcal{N}}, \qquad n_{13}^* = z q_3 \frac{n_1 n_3}{\mathcal{N}}, \qquad n_{23}^* = z q_3 \frac{n_2 n_3}{\mathcal{N}}. \tag{4.2}$$

† The well-known QCA expression for G_M for a regular binary alloy is, of course, just the expression (3.24) for G' with $n_3 = 0$ (and hence also $n_{13} = n_{23} = n_{33} = 0$), while G_M for a regular ternary alloy is given by (3.24) with $\mu + \nu = 1 = q_3$. As far as we know the QCA expression (3.24) for G' for the free energy of mixing of a ternary alloy where one of the constituents (atoms, molecules) has different size has not been given before.

Substituting (4.2) in (4.1) and introducing for ease of comparison with BH:

$$z\chi_{12} = v_{12}, \qquad zq_3\chi_{13} = v_{13} \quad \text{and} \quad zq_3\chi_{23} = v_{23}, \tag{4.3}$$

one obtains

$$G' = G'_a + \mathcal{N}^{-1} \sum\sum_{i<j} n_i n_j v_{ij}. \tag{4.4}$$

In BH two approximations were used for G': the Flory's approximation[14] and the conformal solution[15] approximation. Both can be derived[14,15] without reference to a lattice model or the coordination number. However they can also be obtained as special cases of (4.4) as follows: First, as is well known for binary mixtures[10], the former approximation is equivalent to taking the limit $z \to \infty$. Setting $z \to \infty$ in (4.4) and remembering (3.26) and the definitions (3.2) and (3.23) for $\mathcal{N}$ and q_3 respectively, one finds for G' $(z \to \infty)$

$$G' = k_B T[n_1 \ln(n_1/N) + n_2 \ln(n_2/N) + n_3 \ln(\mu + \nu)n_3/N] + N^{-1} \sum\sum_{i<j} n_i n_j v_{ij}, \tag{4.5}$$

which is the expression for G' in Flory's approximation for the case where two of the constituents have the same volume V, say, and the third has the volume $(\mu + \nu)V$.

The other, namely, the conformal solution approximation for G' used in BH, strictly applies to only such liquid mixtures (as opposed to, less condense, gaseous mixtures) whose constituents all have comparable volumes. In our case this would mean taking $\mu + \nu = 1$ in (4.4) which is physically not the case if the complexes are formed. Interestingly enough, however, the conformal solution expression for G' is obtainable from (4.4) for any value of $\mu + \nu$ if we set $z = 2$ in it. Putting $z = 2$ in (3.26) and noting from (3.23) that now $q_3 = 1$ and hence $\mathcal{N} = n_1 + n_2 + n_3 = n$, say, Eqn. (4.4) becomes (for $z = 2$)

$$G' = k_B T \sum_{i=1}^{3} n_i \ln(n_i/n) + \sum\sum_{i<j} (n_i n_j/n)v_{ij}, \tag{4.6}$$

which is the standard conformal solution expression for the free energy of mixing of a ternary mixture[15].

Since neither $z \to \infty$ nor $z = 2$ are physically realistic coordination numbers it is of interest to examine how the thermodynamic quantities depend on z. Below we first give expressions for some of the thermodynamic quantities for a compound forming mixture, using for G' (4.4) in the expression (2.2) for G_M, and then examine the behaviour of one of them on z as an illustration.

5. EXPRESSIONS FOR THERMODYNAMIC QUANTITIES AND DEPENDENCE ON Z

5.1 Expressions for G_M, activity and concentration fluctuations

First, it is convenient to rewrite explicitly the expression (2.2) for G_M using (4.4) and (3.26) in it. One obtains

$$G_M = -n_3 g + k_B T\left\{n_1 \ln \frac{n_1}{N} + n_2 \ln \frac{n_2}{N} + n_3 \ln\left(\frac{(\mu + \nu)n_3}{N}\right)\right.$$
$$\left. - \frac{1}{2} z n_3(\mu + \nu - \gamma)\ln \frac{\mu + \nu}{\mu + \nu - \gamma} - \frac{1}{2} z\mathcal{N} \ln \frac{\mathcal{N}}{N}\right\} + \frac{1}{\mathcal{N}} \sum\sum_{i<j} n_i n_j v_{ij}, \tag{5.1}$$

where we have set for later convenience

$$\gamma = \mu + \nu - q_3 = 2(\mu + \nu - 1)/z. \tag{5.2}$$

Note that in terms of γ, $\mathcal{N} = N - \gamma n_3$. Applying the equilibrium condition (2.5), we obtain

$$n_1^{\mu} n_2^{\nu} = (n_3 \mathcal{N}^{\mu+\nu-1})\tilde{K} e^{X}, \tag{5.3}$$

where

$$\ln \tilde{K} = -(g/k_B T) + \ln(\mu + \nu) - \frac{1}{2} z(\mu + \nu - \gamma)\ln \frac{\mu + \nu}{\mu + \nu - \gamma}, \tag{5.4}$$

and

$$X = \frac{1}{\mathcal{N} k_B T}\left\{(n_1 - \mu n_3)v_{13} + (n_2 - \nu n_3)v_{23} - (\mu n_2 + \nu n_1)v_{12}\right.$$
$$\left. + \left(\frac{\gamma}{\mathcal{N}}\right) \sum\sum_{i<j} n_i n_j v_{ij}\right\}. \tag{5.5}$$

For given values of the interaction parameters g and v_{ij}, Eqn. (5.3) together with (2.1) determines the equilibrium values of n_1, n_2, n_3 at a given T, P and c of the binary A–B mixture. We continue for simplicity to denote these equilibrium values also by n_i, it being understood that in the following all n_i and their derivatives refer to equilibrium values.

The algebra for deriving the expressions for the activity etc. is similar to that in BH and we omit details. The activity a_A of the species A is found to be

$$\ln a_A = \ln \frac{n_1}{N} - \frac{1}{2} z \ln \frac{\mathcal{N}}{N} + \frac{1}{\mathcal{N} k_B T}(n_3 v_{13} + n_2 v_{12}) - \frac{1}{\mathcal{N}^2 k_B T} \sum\sum_{i<j} v_{ij} n_i n_j. \tag{5.6}$$

The tendency to form complexes is especially transparent in the behaviour of the long wavelength limit of the concentration fluctuation structure factor $S_{CC}(0)$.[16] Recalling that $S_{CC}(0)$ is given by

$$S_{CC}(0) = \frac{Nk_BT}{(\partial^2 G_M/\partial c^2)_{T,P,N}} = \frac{(1-c)}{d\ln a_A/dc}, \tag{5.7}$$

one may obtain for $S_{CC}(0)$, the expression

$$S_{CC}(0) = \frac{\vartheta_{CC}}{1 + \mathscr{D}\vartheta_{CC}}, \tag{5.8}$$

where

$$\vartheta_{CC} = N\left(\sum_{i=1}^{3} \frac{(n_i')^2}{n_i} - \frac{\frac{1}{2}z\gamma^2(n_3')^2}{\mathscr{N}}\right)^{-1} \tag{5.9}$$

$$\mathscr{D} = \frac{2}{N\mathscr{N}k_BT}\sum\sum_{i<j} v_{ij}\left(n_i'n_j' + \frac{\gamma n_3'}{\mathscr{N}}(n_i'n_j + n_in_j') + \frac{\gamma^2(n_3')^2}{\mathscr{N}^2}n_in_j\right), \tag{5.10}$$

where a prime denotes differentiation with respect to c. The expressions for other thermodynamic quantities, the entropy and heat of mixing and the volume of mixing, will not be given here for brevity; we may remind though that in deriving them g and v_{ij} should be considered for consistency as functions of temperature and pressure as emphasized in BH[7-9] and more recently in Alblas *et al*[17].

We note that for $z = 2$ and $z = \infty$, the various above expressions reduce to those given in BH under the labels of the conformal solution and Flory's approximation respectively as, of course, they should.

5.2 Effect of z on $S_{CC}(0)$ for a limiting case

We consider the limiting case where the tendency to form chemical complexes is very strong. This corresponds to having $\tilde{K} \ll 1$ in the equilibrium equation (5.3) and, in practice, it applies if the observed $|G_M(c_c)| > 3Nk_BT$. For $\tilde{K} \to 0$, one has†

$$n_3 \to Nc/\mu, \quad \text{for} \quad 0 < c \leq c_c[=\mu/(\mu+\nu)] \tag{5.11}$$

$$n_3 \to N(1-c)/\nu \quad \text{for} \quad c_c \leq c < 1. \tag{5.12}$$

† We note that the solutions (5.11) and (5.12) and hence the corresponding ϑ_{CC} expressions (5.13) and (5.14) are not valid, very close to $c = 0$, and $c = 1$ respectively. Near these end limits, eqn. (5.3) requires more detailed consideration.

When (5.11) holds, $n_1 \to 0$ and also $n_1' \to 0$ and $(n_1')^2/n_1 \to 0$. Hence using (2.1) and (5.11) in (5.9) one has, for $0 < c \leq c_c$,

$$\sigma_{cc}^{-1} = \frac{\mu + (\mu + \nu)(\mu + \nu - 1)c}{\mu c[\mu - (\mu + \nu)c]} - \frac{\gamma(\mu + \nu - 1)}{\mu(\mu - \gamma c)}. \tag{5.13}$$

Similarly for the case (5.12), $n_2 \to 0$, $n_2' \to 0$ and $(n_2')^2/n_2 \to 0$, and hence, for $c_c \leq c < 1$,

$$\sigma_{cc}^{-1} = \frac{\nu + (\mu + \nu)(\mu + \nu - 1)(1 - c)}{\nu(1 - c)[\nu - (\mu + \nu)(1 - c)]} - \frac{\gamma(\mu + \nu - 1)}{\nu(\nu - \gamma(1 - c))}. \tag{5.14}$$

The explicit expressions for $\mathscr{D}$ corresponding to (5.13) and (5.14) are readily obtained from (5.10) and are omitted here.

To illustrate the effect of varying z on $S_{CC}(0)$ we consider for simplicity that all the interchange energies $v_{ij} \equiv 0$. Then $\mathscr{D} = 0$ and $S_{CC}(0) = \sigma_{CC}$. Figure 1a depicts the variation of $S_{CC}(0)$ with concentration for three values of

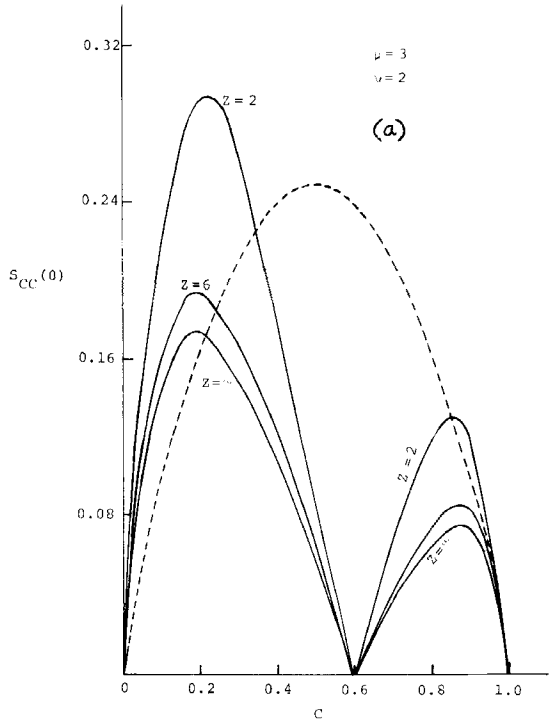

FIGURE 1a Concentration fluctuations $S_{CC}(0)$ versus concentration for different coordination number z, for an alloy with strong tendency to form $A_\mu B_\nu$ complexes and $v_{ij} \equiv 0$, and for $\mu = 3$, $\nu = 2$. For reference, the dotted curve shows $S_{CC}(0)$ for an ideal binary alloy.

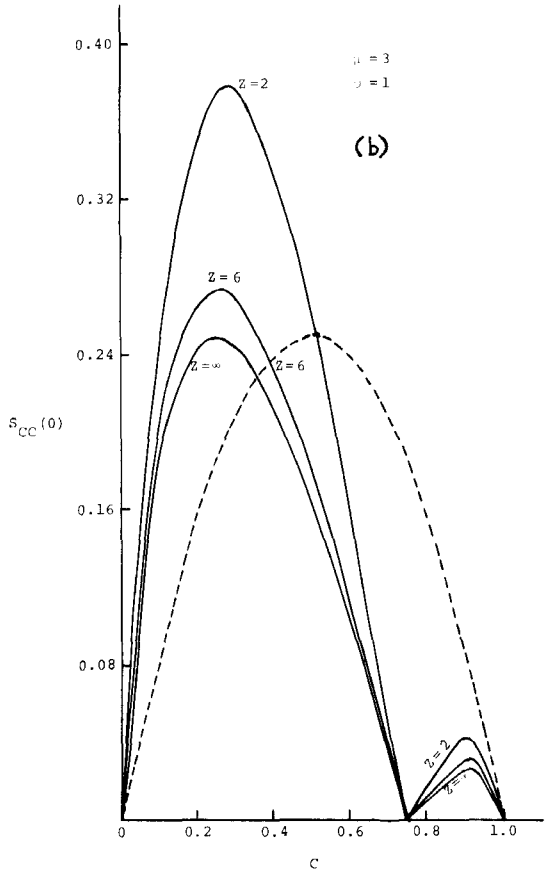

FIGURE 1b Concentration fluctuations $S_{CC}(0)$ versus concentration for different coordination number z, for an alloy with strong tendency to form $A_\mu B_\nu$ complexes and $v_{ij} \cong 0$, and for $\mu = 3, \nu = 1$. For reference, the dotted curve shows $S_{CC}(0)$ for an ideal binary alloy.

z (= 2, 6 and ∞) for the case $\mu = 3, \nu = 2$. Figure 1b depicts a similar variation for the case $\mu = 3$, $\nu = 1$. Curves for intermediate z, not shown in Figures, progressively tend towards the $z = \infty$ curve as z increases. We observe that for a given μ, ν, the curves for different z are all qualitatively similar. An important point is that the curve for $z = 6$ lies much closer to the $z = \infty$ curve than to the $z = 2$ curve. Since the coordination number z usually lies between six and twelve, one can expect that the Flory's approximation ($z \to \infty$) would in general agree better with experiment than the conformal solution approximation, as was actually found to be the case in the analyses of BH.

6. SHORT RANGE ORDER

The Cowley–Warren[18] short range order (SRO) parameter α_1 for nearest neighbours is defined by

$$N_{AB} = Nzc(1 - c)(1 - \alpha_1). \tag{6.1}$$

If there is overall preference for unlike atoms to be first neighbours, then α_1 is negative, while for random distribution of A and B atoms $\alpha_1 = 0$. As mentioned in the Introduction, α_1, originally introduced for solids, has been measured recently in a number of both regular and compound forming liquid alloys[11] and a theoretical interpretation of some of these results has been given by Bhatia and Singh[12]. For compound forming alloys these authors give a treatment which is likely applicable only to cases where there is not too strong a tendency to form chemical complexes. It is therefore not without interest to note here that the formulation of the present paper implies an expression for N_{AB} and hence for α_1.

In the notation of Sec. 3, N_{AB} is (a) the sum of all the contacts labelled there as AB, $A'B$, AB' and $A'B'$ plus (b) the number of AB *intracomplex* contacts. The total number of intracomplex contacts are, of course,

$$\tfrac{1}{2}zN - \tfrac{1}{2}z\mathcal{N} = \tfrac{1}{2}n_3\gamma z$$

and we assume that a fraction β of these are AB contacts. Then remembering Eqns. (3.8)–(3.10), we have for N_{AB}

$$N_{AB} = n_{12} + (1 - c_c)n_{13} + c_c n_{23} + 2c_c(1 - c_c)n_{33} + \tfrac{1}{2}n_3\gamma z\beta. \tag{6.2}$$

The actual calculation of (6.2) requires the knowledge of β, n_3 and n_{ij}.

As regards β, if the complexes formed are $AB(\mu = \nu = 1)$, then obviously $\beta = 1$. For other (μ, ν), in the absence of specific knowledge on the internal structure of the complexes, β has to be regarded as an adjustable parameter, although we can expect β to be close to unity since it is the unlike atom bonds which must have lower energy if the $A_\mu B_\nu$ complexes are to be formed.

Next, if the three interchange energies χ_{ij} are all zero (or if we work in the zeroth approximation), then $n_{ij} = n_{ij}^*$ and n_3 is given by the equilibrium Eqn. (5.3). Substituting for n_{ij}^*, from (4.2), in (6.2) and using (6.1) one has

$$z\alpha_1 = \frac{(\mu + \nu - 1)n_3}{Nc(1 - c)}\left\{-\beta + \frac{2[(1 - c)^2\mu + c^2\nu]}{\mu + \nu} + \frac{2\gamma n_3}{N - \gamma n_3}\frac{[\mu - (\mu + \nu)c]^2}{(\mu + \nu)^2}\right\}. \tag{6.3}$$

We observe that if there is no tendency to form chemical complexes ($n_3 = 0$) then $\alpha_1 = 0$ according to (6.3). This is to be expected since for this case

($n_3 = 0$ and $\chi_{12} = 0$), the A and B atoms in the alloy are distributed at random and hence $n_{12} = n_{12}^* = Nzc(1 - c)$.

Actually, the experimental evidence on $S_{CC}(0)$ and G_M for many alloys indicates that in general $v_{ij} \neq 0$, and, hence also, $\chi_{ij} \neq 0$ since z is non-infinite. The zeroth approximation expression (6.3) is then not likely to be a sufficiently good approximation for α_1 since it approximates $n_{ij} = n_{ij}^*$ and thus ignores the bias due to the interchange energies. The n_{ij} therefore have to be evaluated at least in the quasi-chemical approximation which involves solving for the six n_{ij}, the six Eqns. (3.12)–(3.14) and (3.20). When, however, the tendency to form chemical complexes is very strong and n_3 is given by (5.11) or (5.12), three of the n_{ij} tend to zero and the problem of solving for the remaining n_{ij} becomes more tractable.

We hope to present a fuller discussion of N_{AB} and α_1 and its comparison with experiment in a later communication.

References

1. S. Tamaki and N. E. Cusack, J. Phys. F *9*, 403 (1979).
2. P. Gray, N. E. Cusack, S. Tamaki and Y. Tsuchiya, Phys. Chem. Liq. *9*, 307 (1980).
3. P. Gray, J. de Physique C *8*, 577 (1981).
4. L. M. Pavlova and V. M. Glazov, Doklady Akad. Nauk SSSR *254*, 1162 (1980).
5. K. Hoshino and W. H. Young, J. Phys. F *10*, 1365 (1980).
6. S. Tamaki, Y. Waseda, S. Takeda and Y. Tsuchiya, J. Phys. F *12*, 1101 (1982).
7. A. B. Bhatia and W. H. Hargrove, Lett. Nuovo Cim. *8*, 1025 (1973).
8. A. B. Bhatia and W. H. Hargrove, Phys. Rev. B *10*, 3186 (1974).
9. A. B. Bhatia, W. H. Hargrove and D. E. Thornton, Phys. Rev. B *9*, 435 (1974).
10. E. A. Guggenheim, *Mixtures*, Oxford University Press, Oxford (1952).
11. For example, see H. Ruppersberg and H. Egger, J. Chem. Phys. *63*, 4095 (1975); A. Boos and S. Steeb, Z. Naturf. *32A*, 1279 (1977); H. Ruppersberg and H. Reiter, J. Phys. F *12*, 311 (1982) and references given there and in Ref. 12.
12. A. B. Bhatia and R. N. Singh, Phys. Chem. Liq. *11*, 255 (1982).
13. I. Prigogine, *The Molecular Theory of Solutions*, North-Holland New York (1957).
14. P. J. Flory, J. Chem. Phys. *10*, 51 (1942).
15. H. C. Longuet-Higgins, Proc. Roy. Soc. A 205, 247 (1951).
16. A. B. Bhatia and D. E. Thornton, Phys. Rev. B *2*, 3004 (1970).
17. B. P. Alblas, J. Dijkstra, W. van der Lugt and A. B. Bhatia, Phys. Chem. Liq. *12*, 255 (1983).
18. J. M. Cowley, Phys. Rev. *77*, 667 (1950).