Concentration fluctuations and partial structure factors of compound-forming binary molten alloys*

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The paper discusses some characteristic features of the concentration fluctuations S_{CC} and hence of the partial structure factors (in the zero-wave-vector limit) of compound forming solutions. The discussion is based on a phenomenological model: It is assumed that the binary mixture consists of A and B atoms and their chemical associations $A_\mu B_\nu$ (μ, ν small integers) in chemical equilibrium. The formulation is given in general terms, but the actual calculations are made here by assuming that (a) only one type of chemical association (one pair of μ and ν) are formed and (b) the mixture of A, B and $A_\mu B_\nu$ can be considered to be ideal. The theoretical results for S_{CC} for $(\mu, \nu) = (3, 2)$, $(3, 1)$, and $(2, 1)$ are compared with those determined from the measured thermodynamic activity data for the Mg-Bi, Ag-Al, and Hg-K systems, respectively. It is concluded that the agreement between the calculated and experimental values is not unsatisfactory, although for full quantitative agreement the simplifying assumptions (a) and (b) above are, in general, too crude. Finally it is shown that the concentration dependence of the partial structure factors in these solutions depends characteristically on the values of (μ, ν).

I. INTRODUCTION

Since the determination of the structure factors in the long-wavelength limit is difficult from x-ray- and neutron-scattering experiments, it is natural to turn to other considerations to have information on them (for a review, see Faber[1]). According to a recent work,[2,3] the calculation of the structure factors—the words "in the long-wavelength limit" are to be understood throughout unless stated otherwise—for a binary fluid mixture requires the knowledge of three thermodynamic quantities, namely, the volume, the compressibility, and the mean-square fluctuations, S_{CC}, in the concentration, as functions of composition. A discussion of S_{CC} on some simple theoretical models was given in Ref. 2, and more recently Bhatia *et al.*[4] have calculated the concentration dependence of the partial structure factors (defined below) using the model of conformal solutions of Longuet-Higgins.[5]

The structure factors may be determined from the measured thermodynamic data also.[6-8] In particular, McAlister and Turner[6] made such an evaluation for Na-K and K-Hg systems. The model of conformal solutions referred to above, explains the data on Na-K, but not on K-Hg, presumably because here the difference in forces between the two species is too large for this model to apply.[4,5]

Like the K-Hg system, there are other molten systems, for example, Na-Hg, Mg-Bi, Ag-Al, where the difference in the interactions between the two species is not small. This is evidenced by the fact, amongst others (magnitudes of molar free energies relative to RT etc.), that in the solid state they form intermetallic compounds at one or more well-defined stoichiometric compositions.

The present paper discusses, using an approximate model, some characteristic features of the concentration fluctuations S_{CC} and other structure factors in such compound-forming solutions.

For the calculation of structure factors, one needs a theory for the Gibbs free energy G. For the solutions under consideration, a first-principle calculation (from statistical mechanics) of G is difficult and does not seem to be available. We therefore use here a phenomenological model.

It is assumed that the mixture consists of the A and B atoms and chemical associations of the type $A_\mu B_\nu$, μ, ν small integers, in chemical equilibrium. The requirement that, at constant temperature and pressure, G be a minimum then gives the equilibrium number of different chemical species in terms of their chemical potentials. Although a general formulation is given, the actual calculations are made in this paper by making the simplifying assumption that the mixture of different chemical species can be considered as an ideal solution. For liquid mixtures (as opposed to gaseous) this assumption is albeit approximate. However, it does make the problem tractable and has been used in the past with a varying degree of semiquantitative success to understand a variety of properties, see for example, Bent and Hilderbrand,[9] and Darken,[10] where other references to the literature may be found.

In Sec. II, we collect together the relevant results on the structure factors. In Sec. III, the formal expressions for the concentration fluctuations S_{CC} are derived, which are then used to discuss specific cases of different μ and ν (Sec. IV). For comparison, S_{CC} as calculated from the measured thermodynamic data for the Mg-Bi, Ag-Al,

and Hg-K systems are also given here. Finally, in Sec. V, we apply these results to discuss the variation of partial structure factors with concentration.

II. STRUCTURE FACTORS AND THEIR LONG-WAVELENGTH LIMIT

For a binary system there are several equivalent sets of structure factors defined in the literature. A commonly used set is the set of the partial structure factors or the interference functions $a_{\alpha\beta}$ (q) defined by[1,11]

$$a_{\alpha\beta} (q) = 1 + (N/V) \int [g_{\alpha\beta}(r) - 1]$$
$$\times e^{i\vec{q}\cdot\vec{r}} d^3 r, \qquad (2.1)$$

where N is the total number of atoms in volume V, q is the wave number, and $g_{\alpha\beta}(r) = g_{\beta\alpha}(r)$, $\alpha, \beta = 1$, 2, are the pair distribution functions. In the long-wavelength limit, $a_{\alpha\beta}(q \to 0) \equiv a_{\alpha\beta}$ may be written in terms of certain thermodynamic quantities as[2]

$$a_{11} = \theta + (1/c^2 - 2\delta/c + \delta^2) S_{CC}$$
$$- (1-c)/c, \qquad (2.2)$$

$$a_{22} = \theta + [1/(1-c)^2 + 2\delta/(1-c) + \delta^2]$$
$$\times S_{CC} - c/(1-c), \qquad (2.3)$$

$$a_{12} = \theta + [\delta^2 - (1 - 2c)\delta/c(1-c) - 1/c(1-c)]$$
$$\times S_{CC} + 1, \qquad (2.4)$$

where c is the concentration of species 1 and

$$\theta = \frac{N}{V} k_B T \kappa_T, \quad \delta = \frac{1}{V}\left(\frac{\partial V}{\partial c}\right)_{T,P,N},$$

$$S_{CC} = N k_B T / (\ \frac{\partial^2 G}{\partial c^2}\ )_{T,P,N}. \qquad (2.5)$$

Here $\kappa_T = V^{-1}(\partial V/\partial P)_{T,c}$ is the isothermal compressibility at constant composition and G is the Gibbs free energy. δ simply represents the fractional change in the volume of the mixture with concentration and $S_{CC} \equiv N \langle (\Delta c)^2 \rangle$ is the mean-square fluctuations in the concentration.

The roles of θ, δ, and S_{CC} are somewhat more apparent in the structure factors S_{NN} $(\vec{q})$, S_{NC} $(\vec{q})$, and S_{CC} $(\vec{q})$, which are respectively associated with the (number) density-density, density-concentration, and concentration-concentration correlations.[2,3] $S_{NN}(\vec{q})$, etc., are linearly related to $a_{\alpha\beta}(\vec{q})$, and in the long-wavelength limit, for fluid mixtures,

$$S_{CC} (q \to 0) \equiv S_{CC}, \quad S_{NN} = \theta + \delta^2 S_{CC},$$
$$S_{NC} = -\delta S_{CC}. \qquad (2.6)$$

If $\delta = 0$, the fluctuations in density are independent of those in concentration and $S_{NC} = 0$. Further, S_{NN} is then θ, like the expression for the structure factor of a pure fluid.

III. EXPRESSIONS FOR G AND S_{CC}

A distinctive aspect of the molten mixtures under consideration is that in their respective solid state, they form compounds at one or more definite chemical compositions. It is therefore reasonable to assume that in the molten state of the mixture there is a strong tendency for the two types of atoms A and B to form chemical associations of the type $A_\mu B_\nu$, where μ, ν are small nonzero integers, the precise numerical values of μ and ν depending on the mixture under consideration.

To write down a phenomenological expression for G on the above basis, consider, for definiteness, 1 g mole of mixture of A and B atoms, the molar fraction of A atoms being c. Let at any instant these exist as n_1 g mole of A atoms, n_2 of B atoms, and n_α g mole of $A_{\mu_\alpha} B_{\nu_\alpha}$ molecules, where $\alpha = 3$, 4, $\ldots$, m, and μ_α and ν_α are again small nonzero integers. From the conservation of total number of A and B atoms, we have

$$n_1 = c - \sum_{\alpha=3}^{m} \mu_\alpha n_\alpha,$$
$$n_2 = 1 - c - \sum_{\alpha=3}^{m} \nu_\alpha n_\alpha, \qquad (3.1)$$

and

$$n \equiv \sum_{i=1}^{m} n_i = 1 - \sum_{\alpha=3}^{m} (\mu_\alpha + \nu_\alpha - 1) n_\alpha. \qquad (3.2)$$

If G_i denote the chemical potential per gm mole of the species i, $i = 1$, 2, $\ldots$, m, then the differential change in the free energy $G = \sum_i n_i G_i$ is given by (S, entropy)

$$dG = -S dT + V dP + \sum_{i=1}^{m} G_i \delta n_i. \qquad (3.3)$$

We can now regard n_α, $\alpha = 3$, 4, $\ldots$, m as order parameters whose equilibrium values are determined by the requirement that for equilibrium at constant T, P, and c, G is a minimum. Hence eliminating δn_1 and δn_2 from (3.1) and setting $(\partial G/\partial n_\alpha)_{T,P,c,n_{\alpha'}} = 0$, we obtain

$$\mu_\alpha G_1 + \nu_\alpha G_2 - G_\alpha = 0,$$
$$\alpha = 3, 4, \ldots, m. \qquad (3.4)$$

If G_i, $i = 1$, 2, $\ldots, m$, are known, Eqs. (3.4) together with (3.1) constitute m equations to determine the equilibrium values of n_1, n_2, $\ldots, n_m$ at a given T, P, and c.

It is convenient to write the chemical potentials in the form $(i = 1, 2, \ldots, m)$,

$$G_i = G_i^{(0)} + RT \ln(n_i/n)$$

$$+ RT \ln \gamma_i, \qquad (3.5)$$

where $G_i^{(0)}$ is a function of P and T only and is just the molar Gibbs free energy for the pure species

i (at the pressure and temperature of the mixture) and γ_i, by definition, is the activity coefficient of the species i. The γ_i's, in general, depend both on the various concentrations n_j/n and P and T. If the mixture of different chemical species can be considered to form an ideal solution, then all the $\gamma_i \equiv 1$. (This assumption, of course, does not imply that the molten system considered just as a mixture of A and B atoms forms an ideal solution.) Substituting (3.5) into (3.4), one has for the equilibrium values of n_i the equations

$$\frac{(n_1\gamma_1/n)^{\mu_\alpha}(n_2\gamma_2/n)^{\nu_\alpha}}{(n_\alpha\gamma_\alpha/n)}$$

$$= e^{-g_\alpha/RT} \equiv K_\alpha, \qquad (3.6)$$

where

$$g_\alpha = \mu_\alpha G_1^{(0)} + \nu_\alpha G_2^{(0)} - G_\alpha^{(0)} \qquad (3.7)$$

and the last equality defines K_α. Under the assumption of ideality ($\gamma_i \equiv 1$, $i = 1$, 2, ...,m), Eqs. (3.6) become the familiar equations for studying chemical reactions, K_α being known as the reaction constants. Note that, to avoid cumbersome notation, we have denoted in (3.6) the equilibrium value of a n_i also by n_i. In the equations that follow all n_i signify equilibrium values.

The Gibbs free energy may now be written as

$$G = \sum_i n_i G_i = cG_1^{(0)} + (1-c)G_2^{(0)}$$

$$- \sum_{\alpha=3}^{m} n_\alpha g_\alpha + RT \sum_{i=1}^{m} n_i \ln\frac{n_i}{n}$$

$$+ \sum_{i=1}^{m} n_i A_i, \qquad (3.8)$$

where $A_i = RT\ln\gamma_i$. Noting that g_α are independent of the concentration, we may then obtain by straightforward differentiations and use of (3.1), (3.2), (3.6), and the Gibbs-Duhem relations for A_i,

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,c} = cV_1^{(0)} + (1-c)V_2^{(0)}$$

$$- \sum_{\alpha=3}^{m} n_\alpha v_\alpha + \sum_{i=1}^{m} n_i\left(\frac{\partial A_i}{\partial P}\right)_{T,c} \qquad (3.9)$$

and

$$\frac{RT}{S_{CC}} = \left(\frac{\partial^2 G}{\partial c^2}\right)_{T,P} = RT\left(\sum_{i=1}^{m}\frac{(n_i')^2}{n_i} - \frac{(n')^2}{n}\right)$$

$$+ \sum_{i=1}^{m} n_i' A_i', \qquad (3.10)$$

where $v_\alpha = (\partial g_\alpha/\partial P)_{T,c}$, and a prime denotes differentiations with respect to c. Further, $V_1^{(0)}$ and $V_2^{(0)}$ are the molar volumes of the pure liquids A and B, respectively. The expressions for δ and κ_T may be obtained by differentiating (3.9) with re-

spect to c and P, respectively.

In order to apply Eqs. (3.6)–(3.10) to a particular system, we have to specify γ_i's and μ_α, ν_α. As already mentioned, the simplest approximation to γ_i results if one assumes that the mixture of different chemical species M_i ($M_i = A, B, A_{\mu_\alpha}B_{\nu_\alpha}$), is ideal, so that all $\gamma_i \equiv 1$. This is tantamount to assuming that there is no interaction between the different M_i. The next approximation to γ_i would then correspond to assuming pairwise interactions ω_{ij} between the different M_i which are sufficiently weak for the theory of conformal solutions to apply. For this case γ_i are given by[5]

$$\gamma_i = e^{A_i/RT} = \exp\left[\left(\sum_{j=1}^{m}\frac{n_j}{n}\omega_{ij}\right.\right.$$

$$\left.\left.- \sum_j\sum_{j<k}\frac{n_j}{n}\frac{n_k}{n}\omega_{kj}\right)\middle/RT\right], \qquad (3.11)$$

with $\omega_{ij} \equiv 0$, if $i = j$. The use of γ_i from (3.11), apart from adding a number of additional parameters (ω_{ij}), makes the problem of solving (3.6) immensely difficult. We shall here adopt the ideal solution approximation ($A_i \equiv 0$, $\gamma_i \equiv 1$) with the reservation that to obtain detailed quantitative agreement more sophisticated expressions for γ_i such as (3.11) will have to be employed.

There are a number of binary-alloy systems which, in the solid state, form compounds only at one stoichiometric composition, e.g., Mg-Bi at $c_{Mg} = \frac{3}{5}$, Ag-Al at $c_{Ag} = \frac{3}{4}$. In such cases one has to consider only one pair of values for μ, ν. The same is approximately true when the compounds are formed at more than one stoichiometric composition, provided one of these is considerably more stable than the others. For simplicity, and also since our main purpose in this paper is to discuss broad features of the concentration fluctuations and of the partial structure factors rather than consider one specific system in detail, we shall present here results of calculation assuming that only one type of chemical associations are formed in the molten mixture.

It is convenient next to rewrite some of the above formulas for the aforementioned simple case. We denote the single type of chemical association by $A_\mu B_\nu$ and its molar amount by n_3. Equations (3.1) and (3.2) then reduce to

$$n_1 = c - \mu n_3, \quad n_2 = 1 - c - \nu n_3,$$

$$n = 1 - (\mu + \nu - 1)n_3. \qquad (3.12)$$

Further, with $\gamma_1 = \gamma_2 = \gamma_3 = 1$, Eqs. (3.5)–(3.10) yield

$$\frac{(n_1/n)^\mu(n_2/n)^\nu}{n_3/n} = e^{-g/RT} \equiv K, \qquad (3.13)$$

with

$$g = - RT \ln K = \mu G_1^{(0)} + \nu G_2^{(0)} - G_3^{(0)}, \tag{3.14}$$

$$G = c G_1^{(0)} + (1 - c) G_2^{(0)} + n_3 RT \ln K + RT \sum_{i=1}^{3} n_i \ln \frac{n_i}{n}, \tag{3.15}$$

$$V = c V_1^{(0)} + (1 - c) V_2^{(0)} - n_3 v, \quad v = - RT \left(\frac{\partial \ln K}{\partial P} \right)_T, \tag{3.16}$$

$$\delta = \frac{1}{V} \left(\frac{\partial V}{\partial c} \right)_{T,P,N} = \frac{V_1^{(0)} - V_2^{(0)} - n_3' v}{c V_1^{(0)} + (1 - c) v_2^{(0)} - n_3 v}, \tag{3.17}$$

$$\theta = - \frac{RT}{V^2} \left(\frac{\partial V}{\partial P} \right)_{T,c} = \frac{RT}{V^2} \left[c V_1^{(0)} \kappa_T^{(1)} + (1 - c) V_2^{(0)} \kappa_T^{(2)} + \left(\frac{\partial}{\partial P} (n_3 v) \right)_{T,c} \right], \tag{3.18}$$

and

$$S_{CC} = \left(\sum_{i=1}^{3} \frac{(n_i')^2}{n_i} - \frac{(n')^2}{n} \right)^{-1}. \tag{3.19}$$

From (3.13),

$$n_1' = 1 - \mu n_3', \quad n_2' = - 1 - \nu n_3', \quad n' = - (\mu + \nu - 1) n_3'. \tag{3.20}$$

Hence remembering that K is independent of concentration, we have from (3.13),

$$n_3' = \frac{[(\mu + \nu) c - \mu] n n_3}{n_1 n_2 n_3 (\mu + \nu - 1)^2 - \mu^2 n n_2 n_3 - \nu^2 n n_1 n_3 - n n_1 n_2}. \tag{3.21}$$

Care has to be taken in using (3.21) at $c = 0$ and $c = 1$, since here n_3 and one of n_1 and n_2 simultaneously tend to zero.

Finally in evaluating θ one needs $(\partial n_3 / \partial P)_{T,c}$, which is given by, from (3.12) and (3.13),

$$\left(\frac{\partial n_3}{\partial P} \right)_{T,c} = \frac{v}{RT} \left(\frac{\mu^2}{n_1} + \frac{\nu^2}{n_3} + \frac{1}{n_3} \right.$$

$$\left. - \frac{(\mu + \nu - 1)^2}{n} \right)^{-1}. \tag{3.22}$$

We observe from the above equations that the determination of concentration fluctuations (S_{CC}) requires only the knowledge of the reaction constant K. An approximate value of K for a specific system may be inferred from (3.15) and the experimental data on the free energy of mixing

$$\Delta G = G - c G_1^{(0)} - (1 - c) G_2^{(0)}.$$

The determination of V and θ from Eqs. (3.16) and (3.18) requires the knowledge of v and $(\partial v / \partial P)_T$, respectively, which are related to the first and second derivatives of K with respect to pressure. In practice v may be inferred from the data on volume. θ is usually small (~ 0.03) and, in the absence of experimental data, may, to a first approximation, be linearly interpolated between its values for the two pure liquids.

IV. CONCENTRATION FLUCTUATIONS S_{CC} FOR DIFFERENT μ, ν

We now use Eqs. (3.13) and (3.19) to calculate the concentration fluctuations S_{CC} as a function of concentration and the reaction constant K for different pairs of values of μ and ν.

A. Limiting cases

If we eliminate n_1 and n_2, using (3.12), Eq. (3.13) becomes an algebraic equation of degree $\mu + \nu$ in n_3. Hence, except for the case $\mu = 1$ and $\nu = 1$, one has to solve (3.13) numerically and then obtain S_{CC}. Before presenting the numerical results it will be useful first to consider certain limiting cases.

$a.\ K \to \infty$. First, if $K = \infty$, one can readily see from (3.13) that $n_3 = 0$ and also $(n_3')^2 / n_3 = 0$. Then $n_1 = c$, $n_2 = 1 - c$, and one has from (3.19) and (3.20),

$$S_{CC}^{id} = c(1 - c), \tag{4.1}$$

where the superscript id on S_{CC} indicates that the binary mixture behaves like an ideal solution in this case.

$b.\ K \to 0$. The solutions in which molecular formations occur to a marked degree form the opposite case. Here $K \ll 1$, with typical values of 10^{-1}-10^{-4}. We therefore consider the limiting case $K = 0$, although physically K can never be zero as it corresponds to infinitely large negative free energy of mixing [cf. Eq. (3.15)]. We shall see presently that the simple expression for S_{CC} for $K = 0$ corresponds closely to the S_{CC} for a nonzero $K \ll 1$.

With $K = 0$, (3.13) implies that either $n_1 = 0$, so that $n_3 = c / \mu$, or $n_2 = 0$ so that $n_3 = (1 - c) / \nu$. Remembering that the maximum possible value of

n_3 is $n_3 = (\mu + \nu)^{-1}$, we have

$$n_3 = c/\mu \qquad \text{for } 0 < c \le \mu/(\mu + \nu), \qquad (4.2)$$

$$n_3 = (1 - c)/\nu \quad \text{for } \mu/(\mu + \nu) \le \ c < 1. \qquad (4.3)$$

The concentrations $c = 0$ and $c = 1$ are excluded from the ranges of c in (4.2) and (4.3). Here n_3 = 0 so that the left-hand side of Eq. (3.13) has the form 0/0 and it needs special consideration to which we come to presently.

When (4.2) is valid, one has

$$n_1 = 0, \quad n_2 = 1 - c - c\nu/\mu, \quad (n_1')^2/n_1 = 0,$$

$$n = 1 - (\mu + \nu - 1)c/\mu. \qquad (4.4)$$

Hence using (3.19) and (3.20) one obtains

$$S_{CC} = (c/\mu)[\mu - c(\mu + \nu)]$$

$$\times [\mu - (\mu + \nu - 1)c],$$

$$0 < c \le \mu/(\mu + \nu). \qquad (4.5)$$

Similarly when (4.3) is valid,

$$S_{CC} = [(1 - c)/\nu][\nu - (1 - c)(\mu + \nu)]$$

$$\times [\nu - (1 - c)(\mu + \nu - 1)], \quad \mu/(\mu + \nu) \le c < 1. \qquad (4.6)$$

Note that (4.6) may be obtained from (4.5) by replacing everywhere in (4.5) c by $1 - c$, μ by ν, and ν by μ. Since (4.5) is, in general, not valid at $c = 0$, it cannot be used to calculate the slope of S_{CC} at $c = 0$, and, in fact, gives incorrectly this slope except when $\mu = 1$ (see Eqs. (4.16) – (4.18) below). Similar remarks apply to (4.6) at $c = 1$.

c. $c \ll 1$, $K \ll 1$. To obtain S_{CC} and its slope near $c = 0$ and $c = 1$, let us go back to Eq. (3.13) with $K \ne 0$ and rewrite it in the form, using (3.12),

$$(c - \mu n_3)^\mu (1 - c - \nu n_3)^\nu$$

$$= K n_3 [1 - (\mu + \nu - 1)n_3]^{\mu + \nu - 1}. \qquad (4.7)$$

Consider first the case $c \ll 1$. Then noting that n_3 is necessarily less than or equal to c/μ, we have, to leading order in small quantities,

$$(c - \mu n_3)^\mu \simeq K n_3$$

or

$$y^\mu + K'y - c = 0, \qquad (4.8)$$

where

$$y = (\mu n_3)^{1/\mu}, \quad K' = (K/\mu)^{1/\mu}. \qquad (4.9)$$

For $\mu = 1$, (4.8) gives

$$y = n_3 \simeq c/(1 + K) \quad \text{for } \mu = 1. \qquad (4.10)$$

For $\mu \ge 2$, we can neglect, for sufficiently small c, the first term in (4.8) compared to the second term and hence

$$y \simeq c/K' \quad \text{or} \quad n_3 \simeq c^\mu/K, \quad \mu \ge 2. \qquad (4.11)$$

Equation (4.11) is clearly valid if $(c/K')^\mu \ll c$, or

$$c \ll (K/\mu)^{1/(\mu - 1)}. \qquad (4.12)$$

Noting that (4.10) and (4.11) are correct to the power of c exhibited in them, and using Eqs. (3.12), we can readily expand the expression (3.19) for $(S_{CC})^{-1}$ in powers of c. One finds, for $\mu = 1$,

$$S_{CC}^{-1} = c^{-1} + 1 + 2\nu/(1 + K) + O(c), \quad \mu = 1 \qquad (4.13)$$

$$S_{CC}^{-1} = c^{-1} + 1 - K^{-1}\mu(\mu - 1)c^{\mu - 2}$$

$$+ O(c^{\mu - 1}), \quad \mu \ge 2. \qquad (4.14)$$

For comparison,

$$(S_{CC}^{id})^{-1} = c^{-1} + 1 + c + c^2 + \dots. \qquad (4.15)$$

From (4.13) and (4.14), we have, to order c^2,

$$S_{CC} = c - c^2 - [2\nu/(1 + K)]c^2 + O(c^3), \quad \mu = 1 \qquad (4.16)$$

$$S_{CC} = c - c^2 + (2/K)c^2 + O(c^3), \quad \mu = 2 \qquad (4.17)$$

$$S_{CC} = c - c^2 + O(c^3), \quad \mu \ge 3. \qquad (4.18)$$

The expressions for S_{CC}^{-1} and S_{CC} near $c = 1$ are simply obtained from Eqs. (4.13)–(4.18) by replacing everywhere c by $1 - c$, μ by ν, and ν by μ.

B. Discussion and numerical results

Equations (4.13)–(4.18) show first that in every case as $c \to 0$, $S_{CC} \to c$, as it should. Second, as c increases from zero (but still $c \ll 1$), S_{CC} increases and lies below the ideal value if $\mu = 1$ and above it if $\mu \ge 2$. With further increase of c, Eq. (4.5) shows that S_{CC} has a maximum at some concentration, say, c_1 ($c_1 < \mu/\mu + \nu$), and then drops to zero at $c = \mu/\mu + \nu$. S_{CC} has a discontinuous slope at this point, since as c increases further, Eq. (4.6) takes over and S_{CC} rises again to a maximum, at the concentration c_2, say, and then decreases to zero, the limiting behavior near $c = 1$ being governed by whether $\nu = 1$ or $\nu \ge 2$ in accordance with equations similar to (4.13)–(4.18).

It is interesting to remark here that the fact that (for $K \to 0$), $S_{CC} = 0$ at $c = \mu/\mu + \nu$ and has a V-shaped variation with concentration near $c = \mu/\mu + \nu$ is similar to the behavior of the concentration fluctuations in a perfectly ordered solid alloy near the appropriate stoichiometric composition.[2,12] For the latter at the stoichiometric composition itself, of course, $S_{CC}(\vec{q}) = 0$ for all wave vectors $\vec{q}$ except for the spikes which correspond to Bragg reflections due to the formation of the superlattice. In a compound forming molten solution at the chemical composition, $S_{CC}(q)$ may then be expected to be

TABLE I. The positions (c_1 and c_2) and heights of the peaks in S_{CC} for the limiting case $K \to 0$ for some pairs of μ, ν. For comparison the value of $S_{CC}^{id} = c(1-c)$ at each of the concentrations is also given.

$\mu + \nu$	μ	ν	c_1	$S_{CC}(c_1)$	$S_{CC}^{id}(c_1)$	c_2	$S_{CC}(c_2)$	$S_{CC}^{id}(c_2)$
2	1	1	0.212	0.096	0.167	0.788	0.096	0.167
3	2	1	0.261	0.232	0.193	0.87	0.058	0.113
4	3	1	0.283	0.379	0.203	0.906	0.042	0.085
5	4	1	0.294	0.52	0.208	0.926	0.033	0.069
9	8	1	0.310	1.111	0.214	0.96	0.0174	0.038
5	3	2	0.221	0.295	0.172	0.853	0.131	0.125

much smaller than S_{CC}^{id} for small q, have a peak higher than S_{CC}^{id} at some higher q, and then oscillate about S_{CC}^{id} with progressively damped amplitude [see definition and sum rule on $S_{CC}(q)$ given in Ref. 2].

Returning to Eqs. (4.5) and (4.6), we may deduce from them that the positions c_1 and c_2 of the two maxima in S_{CC} and their heights are given by

$$c_1 = (\mu/y)f(y),$$

$$c_2 = 1 - (\nu/y)f(y), \tag{4.19}$$

$$S_{CC}(c_1) = (\mu/y)^2 f(y)(1 - f(y))$$

$$\times [y + f(y)(1-y)], \tag{4.20}$$

$$S_{CC}(c_2) = (\nu/\mu)^2 S_{CC}(c_1), \tag{4.21}$$

where $y = \mu + \nu$ and

$$f(y) = \frac{2y - 1 - (y^2 - y + 1)^{1/2}}{3(y-1)}. \tag{4.22}$$

We note that the heights of the two peaks are in general unequal being in the ratio $(\nu/\mu)^2$. Table I gives values of c_1, c_2 and the heights of the peaks for some values of μ and ν.

For a nonzero K, but $K \ll 1$, the position and heights of the peaks would still be roughly given by Eqs. (4.19)–(4.21), while the V-shaped behavior near $c = \mu/(\mu + \nu)$ will get rounded into a minimum. With further increase in K, the two maxima will gradually merge into each other in accordance with the limiting behavior $S_{CC}^{id} = c(1-c)$ for $K \to \infty$. These features are illustrated in Figs. 1–4, where we give the results of numerical calculations for S_{CC} for different values of K for the cases (μ, ν) = (1, 1), (3, 2), (3, 1), and (2, 1).

In Fig. 2, we also give the experimental values of S_{CC} for the Mg-Bi system which is known to form the compound Mg_3Bi_2 in the solid state. These were obtained from the data on the activities tabulated in Hultgren et al., [13] by noting that if γ_A is the activity coefficient of metal A (concentration c) in the binary solution, then [14]

$$S_{CC} = c(1-c) \Big/ \left[1 + c\left(\frac{\partial \ln \gamma_A}{\partial c}\right)_{T,P}\right]$$

$$= c(1-c) \Big/ \left[1 - (1-c)\left(\frac{\partial \ln \gamma_B}{\partial c}\right)_{T,P}\right]. \tag{4.23}$$
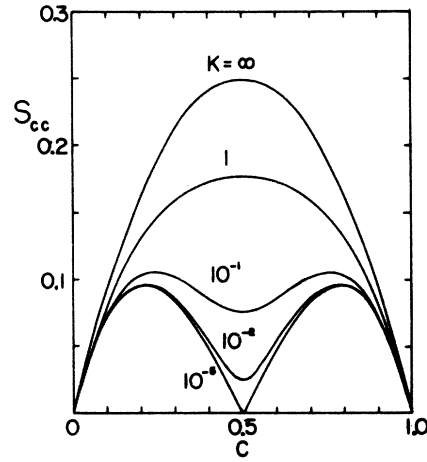

FIG. 1. Concentration fluctuations S_{CC} as a function of concentration in a binary mixture forming chemical associations of the AB type ($\mu = \nu = 1$). The different curves are for different values of the reaction constant K as marked; the curve $K = \infty$ represents $S_{CC} = S_{CC}^{id} = c(1 - c)$.

The data on free energy of mixing for this alloy at the temperature concerned suggests that $K \sim 10^{-6}$–10^{-4}. We see that the experimental S_{CC} has a minimum and two maxima at approximately the right concentrations and their heights are of the right orders of magnitude.

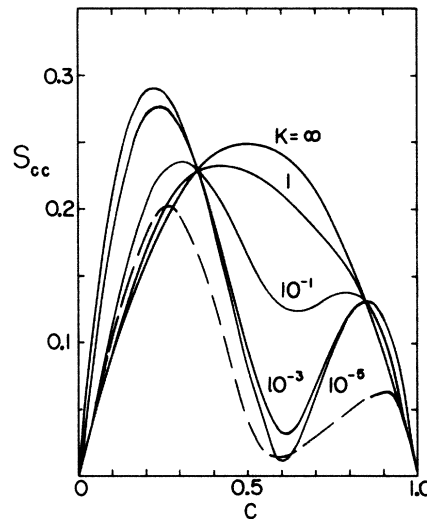Figure 3 similarly shows the experimental val-

FIG. 2. S_{CC} as a function of concentration c of A atoms in a binary mixture forming chemical associations of the A_3B_2 type ($\mu = 3$, $\nu = 2$). (—) theoretical for different values of the reaction constant K; (— —) experimental from data of Ref. 13 (see also Ref. 8) for the Mg-Bi system with $c = c_{Mg}$.
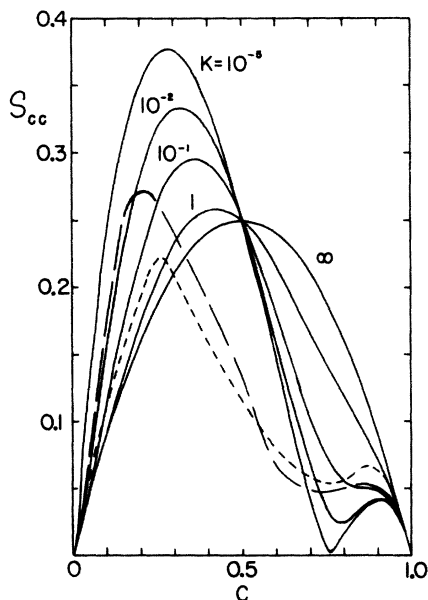
FIG. 3. S_{CC} as a function of concentration c of A atoms in a binary mixture forming chemical associations of the A_3B_1 type ($\mu=3$, $\nu=1$). (—) theoretical for different values of the reaction constant K; (— —) experimental from data of Ref. 13 for the Ag-Al system; (---) experimental from data of Ref. 15 for the Ag-Al system (see also Ref. 10) ($c = c_{Ag}$).

ues of S_{CC} for the Ag-Al system, which in the solid state forms the compound Ag$_3$Al. These were obtained from the data given in Ref. 13 and also that given by Wilder and Elliot. [15] For this system the free-energy data suggests $K \sim 10^{-2}$ and we see that the minimum at $c_{Ag} \simeq \frac{3}{4}$ is very shallow compared to that in the Mg-Bi system at $c_{Mg} = \frac{3}{5}$, as expected.

Finally, in Fig. 4 ($\mu=2$, $\nu=1$), the experimental values of S_{CC} for the Hg-K system are given. Here $K \sim 10^{-5} - 10^{-4}$. We see that the height and the position of the first peak, and the low values of S_{CC} near $c_{Hg} \simeq \frac{2}{3}$ are fairly well reproduced by the theoretical curves, but the experimental curve shows no second maximum. The experimental S_{CC} for Hg-Na is similar for $c_{Hg} \gtrsim \frac{1}{2}$, but the height of the first peak here is substantially less than that for the Hg-K system. These discrepancies are probably at least partly due to the fact that these solutions, in the solid state, form not only the compound Hg$_2 B$ ($B \equiv$ K or Na) but also HgB, Hg$_4 B$ and Hg$_3 B$, so that several pairs of (μ, ν) should be simultaneously taken into consideration [see Eq. (3.10)].

Finally, as a contrast to the behavior of S_{CC} depicted in Figs. 1–4, we may recall the variation of S_{CC} with concentration in a solution where the theory of conformal solutions[5] (or of regular

solutions in the zeroth approximation[16]) applies. Here[2,4]

$$S_{CC} = c(1-c) \Big/ \Big(1 + \frac{2\omega}{RT}c(1-c)\Big), \qquad (4.24)$$

where ω is an interaction energy independent of c. S_{CC} given by (4.24) is symmetric about $c = \frac{1}{2}$, has a maximum at $c = \frac{1}{2}$, and lies, for all c, either above $S_{CC}^{id} = c(1-c)$ or below S_{CC}^{id}, depending upon whether ω is negative or positive. For the former case the temperature $T_c = \omega/2R$ is the critical solution temperature below which the mixture separates into two phases.

From the above discussion, it is apparent that the simplified version of the model (on which the calculations are presented here) has reasonable applicability to at least some of the compound forming solutions, although in general other factors [more than one type of $A_\mu B_\nu$ and deviation from the assumption of ideality, see Eq. (3.10)] have to be considered for obtaining quantitative agreement.

V. VARIATION OF PARTIAL STRUCTURE FACTORS WITH CONCENTRATION

Knowing S_{CC}, it is relatively a simple matter to infer the concentration dependence of the partial structure factors a_{ij} or of the other two number-concentration structure factors S_{NN} and S_{NC} (see Sec. II).

For this purpose we require θ and δ. Of these, as mentioned earlier, θ is usually small (~ 0.03) and in the absence of experimental data may, to a first approximation, be assumed to vary lin-
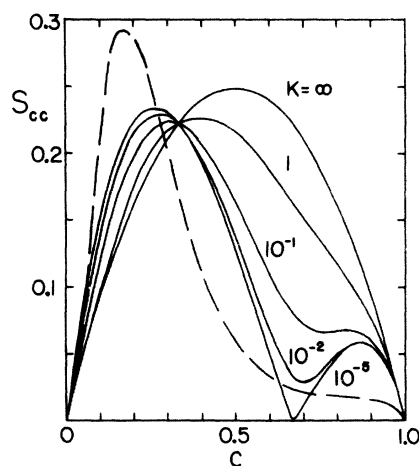

FIG. 4. S_{CC} as a function of concentration c of A atoms in a binary mixture forming chemical associations of the A_2B_1 type ($\mu=2$, $\nu=1$). (—) theoretical for different values of the reaction constant K; (— —) experimental from data of Ref. 13 for the Hg-K system with $c = c_{Hg}$.

early with c between the two pure metals. δ may be inferred from the data on volume as a function of concentration, which, if the simplified version of the model is valid, should be given by (3.16), in which we need only to fix the parameter v (and, of course, $V_1^{(0)}$ and $V_2^{(0)}$) from the observed data. In this connection we should note that according to (3.16), the excess volume ΔV, i.e., the actual volume of the mixture minus the volume obtained by linear interpolation between the values for the two pure liquids, is given by

$$\Delta V = V - c V_1^{(0)} - (1-c) V_2^{(0)} = -n_3 v .\qquad(5.1)$$

Hence $|\Delta V|$ is maximum when n_3 is maximum, that is, at the concentration $c = \mu/\mu + v$. For many cases $\Delta V/V$ is at most a few percent and we have not been able to verify this conclusion for lack of sufficient data. (In these cases, δ calculated by assuming the linear dependence of volume on c, forms a reasonable approximation). For the amalgams discussed earlier, HgK and HgNa, the observed maximum in $|\Delta V|$ ($\sim 0.24\,V$ and $0.18\,V$, respectively)[17,18] occurs near $c = \frac{1}{2}$. We have already mentioned the reasons why the simplified version of the model taking $\mu = 2$ and $v = 1$ is not quite adequate for these systems.

When the tendency to form chemical associations $A_\mu B_v$ is strong ($K \ll 1$), the variation of a_{ij} with concentration depends markedly on the values
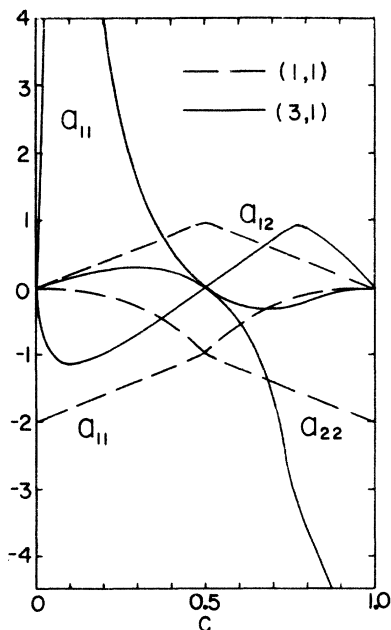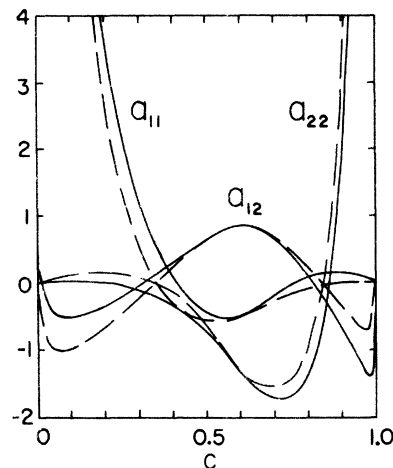

FIG. 6. Partial structure factors a_{ij} as a function of concentration c of A atoms in a binary mixture forming chemical associations of the type A_3B_2 ($\mu = 3$, $v = 2$). (— —) $\delta = 0$; (—) δ, as explained in the text. For values of a_{11} near $c = 0$ and of a_{22} near $c = 1$, not shown in the diagram, see text following Eq. (5.10).

of μ and v. To illustrate this feature and to see how this variation is affected by δ, we depict a_{ij} versus concentration curves for a few cases in Figs. 5–7. For simplicity we have throughout set $\theta = 0$ and drawn all the curves for $K = 10^{-3}$. As will
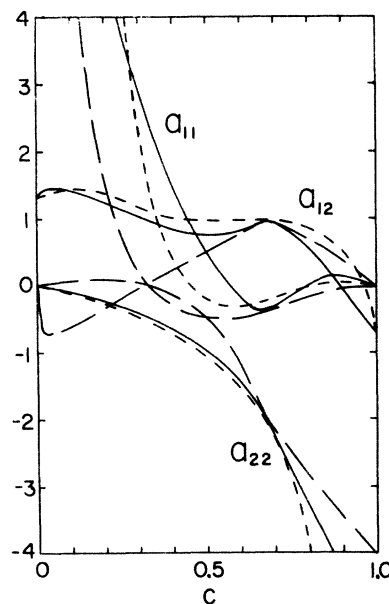

FIG. 5. Partial structure factors a_{ij} as a function of concentration c of A atoms in a binary mixture forming chemical associations of the $A_\mu B_v$ type. (— —) $\mu = v = 1$; (—) $\mu = 3$, $v = 1$. Both sets of curves are for $\delta = 0$ (equal partial molar volumes for the two species).

FIG. 7. Partial structure factors a_{ij} as a function of concentration c of A atoms in a binary mixture forming chemical association of the type A_2B_1 ($\mu = 2$, $v = 1$). (— —) theoretical with $\delta = 0$; (—) theoretical with δ as explained in the text; (- - -) experimental from Ref. 6 for the Hg-K system with $c = c_{Hg}$.

be clear from the inspection of Figs. 1–4 for S_{CC}, a smaller value of K does not affect the results qualitatively. (For $K \to \infty$, $S_{CC} \to S_{CC}^{id}$ $[=c(1-c)]$, and the concentration dependence of a_{ij} is quite different from that depicted in these figures; for example, if $\delta = 0$, then all $a_{ij} = \theta \sim 0.03$.)

Figure 5 gives the results for the cases (μ, ν) = (1, 1) and (3, 1) taking $\delta = 0$ (equal partial molar volumes for the two species at all c). The curves for $(\mu, \nu) = (1, 1)$ are qualitatively similar to those given in Faber.[19] The dashed curves in Fig. 6 show the concentration dependence of a_{ij} for $\mu = 3$, $\nu = 2$ case taking $\delta = 0$, while the smooth curves are drawn by assuming that the volume varies linearly between the volumes of the two pure constituents. The numerical values for the volumes were chosen appropriate to the Mg-Bi system, so that $\delta(c)$ varies monotonically with concentration from -0.29 at $c = 0$ to -0.4 at $c = 1$. These values of $\delta(c)$ should be correct to about 10% for this system since $\Delta V \simeq 0.02V$ at the composition Mg_3Bi_2.

Last, Fig. 7 gives the results for $\mu = 2$, $\nu = 1$ case. The curves with long dashes are again for $\delta = 0$, while the smooth curves are drawn using $\delta(c)$ obtained from the measured data on volumes for the K-Hg system.[17] $[\delta(c)$ first decreases from $\delta(0) \simeq -1.3$ to $\delta(\frac{1}{2}) = -1.5$ and then increases monotonically to $\delta(1) \simeq -0.7.]$ For comparison the values of a_{ij} obtained by McAlister and Turner[6] from the measured thermodynamic data are also given.

Considering the limitations of the model discussed earlier and the uncertainty in determining S_{CC} from the measured activity data,[14] the agreement between the two is not unsatisfactory.

The results presented above need two further comments. First, we observe that in Figs. 6 and 7 the dashed ($\delta = 0$) and smooth ($\delta \neq 0$) curves for each a_{ij} come very close to each other near the appropriate chemical composition. This is not surprising if we refer to Eqs. (2.2)–(2.4) for a_{ij} and consider the limiting case $K \to 0$. Then since now $S_{CC} = 0$ at the stoichiometric composition $c = \mu/\mu + \nu$, the partial structure factors become independent of δ at this composition, and are given by (with $\theta = 0$)

$$a_{11} = -\nu/\mu, \quad a_{22} = -\mu/\nu,$$

and

$$a_{12} = +1, \quad [c = \mu/(\mu + \nu)] . \tag{5.2}$$

The values of a_{ij} for $K = 10^{-3}$ given in Figs. 6 and 7 are close to these values at $c = \frac{3}{5}$ and $c = \frac{2}{3}$, respectively.

Second, it is of interest to give explicit expressions for the values of a_{ij} (c) at $c = 0$ and $c = 1$. If we substitute the expansions (4.16)–(4.18) for S_{CC} into the Eqs. (2.2)–(2.5) and take the limit $c \to 0$ (or $c \to 1$ as the case may be), we obtain $[a_{ij}(c = 0)$ $\equiv a_{ij}(0)$, etc.]

$$a_{11}(1) = \theta(1), \qquad a_{22}(0) = \theta(0) \qquad \text{for all } \mu \text{ and } \nu, \tag{5.3}$$

$$a_{12}(0) = \theta(0) - \delta(0), \qquad a_{12}(1) = \theta(1) + \delta(1) \qquad \text{for all } \mu \text{ and } \nu, \tag{5.4}$$

$$a_{11}(0) = \theta(0) - 2\delta(0) - 2\nu(1+K)^{-1} \qquad \text{for } \mu = 1, \tag{5.5}$$

$$= \theta(0) - 2\delta(0) + 2/K \qquad \text{for } \mu = 2 \tag{5.6}$$

$$= \theta(0) - 2\delta(0) \qquad \text{for } \mu \geq 3, \tag{5.7}$$

and

$$a_{22}(1) = \theta(1) + 2\delta(1) - 2\mu(1+K)^{-1} \qquad \text{for } \nu = 1, \tag{5.8}$$

$$= \theta(1) + 2\delta(1) + 2/K \qquad \text{for } \nu = 2, \tag{5.9}$$

$$= \theta(1) + 2\delta(1) \qquad \text{for } \nu \geq 3. \tag{5.10}$$

Thus, for example, in Fig. 6 ($\mu = 3$, $\nu = 2$), the dashed curve for a_{11} starts from zero and steeply rises with small increase in the concentration, has a large maximum (~ 33, not shown in the diagram) at $c \simeq 0.01$, and then follows the curve as in the diagram. In contrast, a_{22}, near $c = 1$, continues to rise to the value $a_{22}(1) \simeq 2/K \simeq 2000$ in accordance with (5.9). It may be seen[20] from Eqs. (2.4) and (2.5) that $a_{11}(0)$ and $a_{22}(1)$ depend on the curvature of S_{CC}, i. e., $d^2 S_{CC}/dc^2$, at $c = 0$ an $c = 1$, respectively, so that their determination from experimental S_{CC} is difficult. The limits given in Eqs.

(5.5) to (5.10) may therefore serve as useful guidelines where the model is applicable.

Note added in proof: Since the submission of the manuscript, two higher approximations have been applied to the calculation of S_{CC}, etc. These correspond to assuming that the mixture of A, B and $A_\mu B_\nu$ can be treated (i) in the conformal solution approximation, Eq. (3.11) for γ_i, and (ii) in Flory's approximation for mixtures of monomers and polymers. See A. B. Bhatia and W. H. Hargrove, Nuovo Cimento Lett. (to be published), and A. B. Bhatia and W. H. Hargrove (unpublished).

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[14]Alternatively, in terms of the activities $a_A = c\gamma_A$, $a_B = (1 - c)\gamma_B$,

$$S_{CC} = (1 - c)\left[\left(\frac{\partial \ln a_A}{\partial c}\right)_{T,P}\right]^{-1} = -c\left[\left(\frac{\partial \ln a_B}{\partial c}\right)_{T,P}\right]^{-1}.$$

We mention that, in certain ranges of concentration, a precise determination of the slopes of $\ln a$- or $\ln \gamma$-vs-c curves (and hence S_{CC}) requires more data than is presently available.

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