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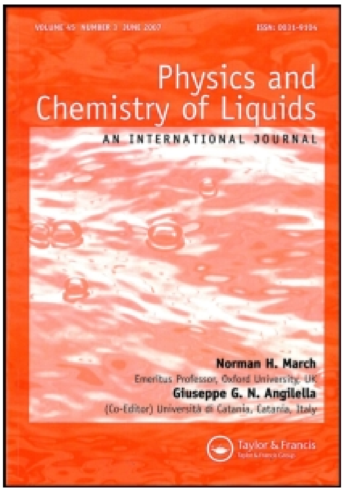

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Number-Concentration structure factors and their long wavelength limit in multicomponent fluid mixtures

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Number-Concentration Structure Factors and their Long Wavelength Limit in Multicomponent Fluid Mixtures†

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Structure factors, similar to the number-concentration structure factors of a binary alloy, are introduced for multicomponent mixtures. Expressions for the long wavelength limit of these (and hence of the related, more conventional) structure factors are derived in terms of the various thermodynamic quantities and their variation with concentrations for some special cases is discussed.

1 INTRODUCTION

The structure (and therefore scattering etc., by) of a mixture containing ν species of atoms is described, in general, by $\frac{1}{2}\nu(\nu + 1)$ independent structure factors. These are usually defined such that each structure factor is directly related to the corresponding atoms pair correlation function, for example, the well-known partial structure factors $a_{\alpha\beta}(q)$ or $S_{\alpha\beta}(q)$, $\alpha, \beta = 1, 2, \ldots, \nu$ [Faber and Ziman,[1] Ashcroft and Langreth[2] and Enderby and North[3]]. For a binary mixture, one may also introduce, following Bhatia and Thornton,[4] the number concentration (N–C) structure factors $S_{NN}(q)$, $S_{NC}(q)$ and $S_{CC}(q)$, which are respectively associated with the number–number (density), number–concentration and concentration–concentration correlations. Recently several authors[5–8] have found the N–C formalism useful in interpreting experimental data and it seems to be of interest to extend this formalism to multicomponent mixtures.

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In Section 2, we define the N-C structure factors for a multicomponent mixture and give some of their formal properties. The expressions for the long wavelength (wave number $q \to 0$) limit of these structure factors are given in Section 3, which, as for a binary alloy, are found to be simply related to the various thermodynamic quantities. Section 4 discusses the behaviour of these expressions for some simple models of the mixtures. Finally, in Section 5, the relationship between the N-C structure factors and the partial structure factors $a_{\alpha\beta}(q)$ is derived to obtain explicit expressions for $a_{\alpha\beta}(0)$.

2 THE NUMBER-CONCENTRATION STRUCTURE FACTORS

2.1 Notation and definition

Consider a ν-component mixture of volume V, containing N_α atoms of type α where α takes the values $1, 2, \ldots, \nu$. Let N denote the total number of atoms and let c_α be the average concentration of species α:

$$c_\alpha = \frac{N_\alpha}{N}, \qquad N = N_1 + N_2 + \cdots + N_\nu. \tag{2.1}$$

Now if $n_\alpha(\mathbf{r})$ denote the instantaneous number density of the species α, the deviation $\delta n_\alpha(\mathbf{r})$ from the mean is

$$\delta n_\alpha(\mathbf{r}) \equiv n_\alpha(\mathbf{r}) - \frac{N_\alpha}{V} = \sum_m \delta(\mathbf{r} - \mathbf{R}^\alpha_m) - \frac{N_\alpha}{V} \tag{2.2}$$

where $\mathbf{R}^\alpha_m$ is the position of the mth atom of type α. Making the Fourier expansion

$$\delta n_\alpha(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{q}} N_\alpha(\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{r}}, \tag{2.3}$$

$$N_\alpha(\mathbf{q}) = \int e^{i\mathbf{q}\cdot\mathbf{r}} \delta n_\alpha(\mathbf{r}) d^3 r$$

$$= \sum_m e^{i\mathbf{q}\cdot\mathbf{R}^\alpha_m} - N_\alpha \delta_{\mathbf{q},0}. \tag{2.4}$$

The reality of $\delta n_\alpha(\mathbf{r})$ requires that $N_\alpha(\mathbf{q}) = N^*_\alpha(-q)$.

Next let $N(\mathbf{q})$ denote the Fourier transform of the local deviation $\delta n(\mathbf{r})$ in the total number density $n(\mathbf{r}) = n_1(\mathbf{r}) + n_2(\mathbf{r}) + \cdots + n_\nu(\mathbf{r})$; then

$$N(\mathbf{q}) = \sum_{\alpha=1}^{\nu} N_\alpha(\mathbf{q}). \tag{2.5}$$

The local deviation in the concentration of the species α may be specified by

$$\delta c_\alpha(\mathbf{r}) = (N^{-1})(\delta n_\alpha(\mathbf{r}) - c_\alpha \delta n(\mathbf{r})) \tag{2.6}$$

so that if $\delta n_\alpha(\mathbf{r})/\delta n(\mathbf{r})$ is equal to the average concentration of the species α, namely c_α, then $\delta c_\alpha(\mathbf{r}) = 0$, as it should. Denoting the Fourier transform of $\delta c_\alpha(\mathbf{r})$ by $C_\alpha(\mathbf{q})$, one has

$$C_\alpha(\mathbf{q}) = \int \delta c_\alpha(\mathbf{r}) e^{i\mathbf{q}\cdot\mathbf{r}}\, \mathrm{d}^3 r = (N^{-1})(N_\alpha(\mathbf{q}) - c_\alpha N(\mathbf{q})). \tag{2.7}$$

Only $\nu - 1$ of $C_\alpha(\mathbf{q})$ are, of course, independent of one another since

$$\sum_{\alpha=1}^{\nu} C_\alpha(\mathbf{q}) = 0. \tag{2.8}$$

Making now the convention that the first $\nu - 1$ concentration variables are the independent ones, the N-C structure factors may be defined as $(i, j = 1, 2, \ldots, \nu - 1)$

$$S_{NN}(q) = \frac{1}{N} \langle N^*(\mathbf{q}) N(\mathbf{q}) \rangle \tag{2.9}$$

$$S_{NC_i}(\mathbf{q}) = \tfrac{1}{2} \langle N^*(\mathbf{q}) C_i(\mathbf{q}) + N(\mathbf{q}) C_i^*(\mathbf{q}) \rangle \tag{2.10}$$

$$S_{C_iC_j}(q) = \tfrac{1}{2} N \langle C_i^*(\mathbf{q}) C_j(\mathbf{q}) + C_i(\mathbf{q}) C_j^*(\mathbf{q}) \rangle \tag{2.11}$$

where $\langle \ldots \rangle$ denotes ensemble average. For a fluid mixture, from symmetry, $S_{NN}(q)$ etc. depend on the magnitude q of $\mathbf{q}$ only.

We observe that Eqs. (2.9)–(2.11) define, in all, $\frac{1}{2}\nu(\nu + 1)$ structure factors. Of these $S_{NN}(q)$ is similar to the structure factor $S(q)$ of a pure fluid, since it is, like $S(q)$, associated with the fluctuations in the number density of the atoms. The $\frac{1}{2}\nu(\nu - 1)$ structure factors $S_{C_iC_j}(q) = [S_{C_jC_i}(q)]$ are associated with the intercorrelations between the fluctuations in the $\nu - 1$ (chosen) independent concentration variables and the remaining $\nu - 1$ structure factors $S_{NC_i}(q)$, arise from the cross-correlations between the fluctuations in density and the concentrations. For a binary mixture $\nu = 2$, so that $i = j = 1$, and Eqs. (2.9)–(2.11) reduce to the definitions of the three N-C structure factors $S_{NN}(q)$, $S_{NC}(q)$ and $S_{CC}(q)$ introduced in Ref. 4. Further significance of the N-C structure factors will become apparent as we proceed.

We remark here that throughout the paper we denote, as above, an index by a Greek letter (α or β) when it runs from 1 to ν and by a Roman letter (i, j, etc.) when it refers to only from 1 to $\nu - 1$.

2.2 Sum rules and expression for scattering

Like the case of a binary mixture, $S_{NN}(q)$ etc. defined in (2.9)–(2.11) obey certain sum rules. The method for obtaining these is standard, for example, see Ref. 4. One obtains ($i, j = 1, 2, \ldots, \nu - 1$)

$$\frac{1}{(2\pi)^3}\int [S_{NN}(q) - 1]\mathrm{d}^3q = -\frac{N}{V} \tag{2.10}$$

$$\int S_{NC_i}(q)\mathrm{d}^3q = 0 \tag{2.11}$$

and

$$\int [S_{C_iC_j}(q) - \{c_i\delta_{i,j} - c_ic_j\}\mathrm{d}^3q = 0 \tag{2.12}$$

which show that as $q \to \infty$, $S_{NN}(q) \to 1$, $S_{NC_i}(q) \to 0$, $S_{C_iC_i}(q) \to c_i(1 - c_i)$ and $S_{C_iC_j}(q) \to -c_ic_j$ for $i \neq j$.

The scattering or X-rays or the coherent scattering of neutrons is essentially given by the scattering function $I(q)$:

$$I(q) = \frac{1}{N}\left\langle \left| \sum_{\alpha=1}^{\nu} W_\alpha N_\alpha(\mathbf{q}) \right|^2 \right\rangle \tag{2.13}$$

where W_α [$\equiv W_\alpha(q)$] is the appropriate form factor for the atoms of type α. Since from (2.5), (2.7) and (2.8)

$$N_i(\mathbf{q}) = c_iN(\mathbf{q}) + NC_i(\mathbf{q}), \qquad N_\nu(\mathbf{q}) = c_\nu N(\mathbf{q}) - N\sum_i C_i(\mathbf{q}) \tag{2.14}$$

one has on using (2.9)–(2.12),

$$I(q) = |\overline{W}|^2 S_{NN}(q) + \sum_i \{\overline{W}\Delta W_i^* + (\overline{W})^*\Delta W_i\} S_{NC_i}(q)$$
$$+ \frac{1}{2}\sum_{i,j}\sum \{\Delta W_i^*\Delta W_j + \Delta W_i\Delta W_j^*\} S_{C_iC_j}(q) \tag{2.15}$$

where

$$\overline{W} = \sum_{\alpha=1}^{\nu} c_\alpha W_\alpha \qquad \text{and} \qquad \Delta W_i = W_i - W_\nu. \tag{2.16}$$

In obtaining (2.15) we have set $\langle \mathrm{Im}\, N^*(\mathbf{q})C_i(\mathbf{q})\rangle = 0$ and $\langle \mathrm{Im}\, C_i^*(\mathbf{q})C_j(\mathbf{q})\rangle = 0$ (Im stands for the imaginary part), as expected in general on grounds of symmetry.[9] If all the W_α are real, or have the same phase, then (2.15) is true irrespective of whether these terms are zero or not.

3 LONG WAVELENGTH LIMIT OF STRUCTURE FACTORS

As in the case of a binary mixture,[4,10] for $q \to 0$, the N–C structure factors defined in (2.9)–(2.11) have the following physical meaning:

$$S_{NN}(0) = \frac{\langle(\Delta N)^2\rangle}{N}, \qquad S_{NC_i}(0) = \langle \Delta N \Delta c_i\rangle$$

and

$$S_{C_iC_j} = N\langle \Delta c_i \Delta c_j\rangle \tag{3.1}$$

where $\langle(\Delta N)^2\rangle$ is the mean square fluctuations in the number of particles in the volume V of the medium, $\langle(\Delta c_i)^2\rangle$ is the mean square fluctuation in the concentration of the ith species, Δc_i being defined by

$$\Delta c_i = \frac{\Delta N_i - c_i \Delta N}{N},$$

and $\langle \Delta N \Delta c_i\rangle$ and $\langle \Delta c_i \Delta c_j\rangle$, $i \neq j$, represent the correlations between the fluctuations ΔN and Δc_i and between Δc_i and Δc_j respectively. The expressions for $S_{NN}(0)$ etc., in terms of the various thermodynamic functions, may be derived from statistical thermodynamics. One finds, firstly, for the subgroup of structure factors $S_{C_iC_j}$ (the derivation is lengthy but similar to that given in Ref. 4 for a binary mixture and is omitted here for brevity)

$$S_{C_iC_j}(0) = \frac{N k_B T G^{ij}}{D} \tag{3.2}$$

where k_B is the Boltzmann constant, T the temperature, G^{ij} is the cofactor of the element G_{ij} of the $\nu - 1 \times \nu - 1$ matrix whose determinant is D:

$$D = \begin{vmatrix} G_{11} & G_{12} & \cdots & G_{1,\nu-1} \\ G_{21} & G_{22} & \cdots & G_{2,\nu-1} \\ \vdots & & & \\ G_{\nu-1,1} & & \cdots & G_{\nu-1,\nu-1} \end{vmatrix} \tag{3.3}$$

where

$$G_{ij} = \left(\frac{\partial^2 G}{\partial c_i \partial c_j}\right)_{N,T,P,c'} \tag{3.4}$$

G being the Gibbs free energy of the mixture and P the pressure. The subscript c' in (3.4) implies that during differentiation with respect to a c_i all other concentrations are held constant. Note that in differentiation with respect to a c_i, $c_\nu = 1 - c_1 - c_2, \ldots, c_{\nu-1}$ is to be regarded as a dependent variable.

For the simple case of a ternary mixture, (3.2) reads

$$S_{c_1c_1}(0) = \frac{Nk_BTG_{22}}{D}, \qquad S_{c_2c_2}(0) = \frac{Nk_BTG_{11}}{D},$$

$$S_{c_1c_2}(0) = -\frac{Nk_BTG_{12}}{D}.$$

with

$$D = G_{11}G_{22} - (G_{12})^2. \tag{3.5}$$

For a binary mixture, of course, one has only $S_{c_1c_1}(0)$, the expression for which is just $S_{c_1c_1}(0) = Nk_BT/G_{11}$, in agreement with the result of Ref. 4.

The $q \to 0$ limit of other structure factors $S_{NC_i}(q)$ and $S_{NN}(q)$, is given by

$$S_{NC_i}(0) = -\sum_{j=1}^{\nu-1} \delta_j S_{c_ic_j}(0) \tag{3.6}$$

$$S_{NN}(0) = \theta - \sum_{i=1}^{\nu-1} \delta_i S_{NC_i}$$

$$= \theta + \sum_{i,j=1}^{\nu-1}\sum \delta_i \delta_j S_{c_ic_j}(0) \tag{3.7}$$

where

$$\theta = \left(\frac{N}{V}\right)k_BT\kappa_T, \qquad \kappa_T = V^{-1}\left(\frac{\partial V}{\partial P}\right)_{T,N,c}$$

is the isothermal compressibility (at constant $c_1, c_2, \ldots, c_{\nu-1}$) and δ_i are the dilatation factors:

$$\delta_i = \frac{1}{V}\left(\frac{\partial V}{\partial c_i}\right)_{N,T,P,c'} = \frac{v_i - v_\nu}{v} \tag{3.8}$$

where $v(= \sum_{a=1}^{\nu} v_a c_a)$ is the molar volume, per atom, of the mixture, and a v_i, v_ν or v_a is the partial molar volume, per atom, of the species indicated by the subscript on v.

We observe from (3.6) and (3.8) that if all the partial molar volumes v_a are equal to one another, then all $\delta_i = 0$ and hence all $S_{NC_i}(0) = 0$, indicating that the fluctuations in ΔN and those in concentrations are independent of one another, as one might expect intuitively. A given $S_{NC_i}(0)$ can, of course, be zero, under less restrictive conditions on v_α depending on the behaviour of $S_{C_iC_j}(0)$. For example, for an ideal solution, for which $S_{C_iC_j}(0)$ are given by Eq. (4.5) below, it may be seen from (3.6) that $S_{NC_i}(0) = 0$ if $v_i = v$. As regards $S_{NN}(0)$, it may be noted that if all the $\delta_i = 0$, then $S_{NN}(0)$ has the form corresponding to a pure fluid, namely

$$S_{NN}(0) = \left(\frac{N}{V}\right) k_B T \kappa_T.$$

4 $S_{C_iC_j}(0)$ FOR SOME SPECIAL CASES

The Gibbs free energy G can be quite generally written as a sum of three terms:

$$G = N\left[\sum_{\alpha=1}^{\nu} c_\alpha G_\alpha^{(0)}\right] + G^{id} + G^E \tag{4.1}$$

where $G_\alpha^{(0)}$ is the molar free energy, per atom, of the species α in its pure state, G^{id} is the free energy of mixing for an ideal solution, namely it is just $(-T)$ times the entropy of random mixing:

$$G^{id} = Nk_B T \sum_{\alpha=1}^{\nu} c_\alpha \ln c_\alpha, \tag{4.2}$$

and G^E is the excess free energy. The first term in (4.1) is linear in c_α so that only the second and third terms contribute to G_{ij} and hence to $S_{C_iC_j}(0)$. (The volume, κ_T and δ_i of course depend on the first term and also, depending on its form, on G^E.)

Substituting (4.1) and (4.2) in (3.4) and introducing the notation:

$$X_{ij} = \frac{1}{Nk_B T}\left(\frac{\partial^2 G^E}{\partial c_i \partial c_j}\right)_{T,P,N,c'} \tag{4.3}$$

one has

$$G_{ij} = Nk_B T\left[\frac{1}{c_\nu} + \frac{1}{c_i}\delta_{i,j} + X_{ij}\right]. \tag{4.4}$$

For an ideal solution $G^E = 0$ and hence $X_{ij} = 0$, and it is a simple matter to evaluate the various determinants involved in the expression (3.2) for $S_{C_iC_j}(0)$. One obtains

$$S^{id}_{C_iC_i}(0) = c_i(1 - c_i)$$

$$S^{id}_{C_iC_j}(0) = -c_i c_j, \qquad i \neq j \tag{4.5}$$

where the superscript "*id*" has been added to indicate that these expressions refer to an ideal solution.

When the solution is not ideal ($X_{ij} \neq 0$), the explicit expressions for $S_{c_i c_j}(0)$ become, in general, progressively involved as ν increases. For a ternary mixture the expressions for $S_{c_i c_j}(0)$ are, using (4.4) in (3.5)

$$\begin{aligned} S_{c_1 c_1}(0) &= \frac{c_1[1 - c_1 + c_2 c_3 X_{22}]}{\mathscr{D}} \\ S_{c_2 c_2}(0) &= \frac{c_2[1 - c_2 + c_1 c_3 X_{11}]}{\mathscr{D}} \\ S_{c_1 c_2}(0) &= \frac{-c_1 c_2[1 + c_3 X_{12}]}{\mathscr{D}} \end{aligned} \tag{4.6}$$

where

$$\begin{aligned} \mathscr{D} = [1 &+ c_1(1 - c_1)X_{11} + c_2(1 - c_2)X_{22} - 2c_1 c_2 X_{12} \\ &+ c_1 c_2 c_3(X_{11}X_{22} - X_{12}^2)]. \end{aligned} \tag{4.7}$$

As an example, we examine here the behaviour of $S_{c_i c_j}(0)$ for the model of conformal solutions (or of regular solutions in the zeroth approximation) which has been frequently used[11-13] in discussions on thermodynamic properties of mixtures. The necessary conditions for the validity of the model are (a) that the various ratios v_α/v_β between the atomic volumes of the different species lie between $\frac{1}{2}$ and 2, as for an ideal solution, and (b) $|\omega_{\alpha\beta}/k_B T| < 2$, where $\omega_{\alpha\beta}$ are, appropriately defined, pairwise interchange energies ($\omega_{\alpha\beta} \equiv 0$, for $\alpha = \beta$). In terms of $\omega_{\alpha\beta}$, G^E for this model is given by

$$G^E = N \sum_{\alpha<\beta}\sum c_\alpha c_\beta \omega_{\alpha\beta} \tag{4.8}$$

so that

$$X_{ij} = (k_B T)^{-1}(\omega_{ij} - \omega_{i\nu} - \omega_{j\nu}) \tag{4.9}$$

remembering that $\omega_{ij} \equiv 0$, if $i = j$. For a ternary mixture, $\nu = 3$, and (4.9) gives

$$X_{11} = -\frac{2\omega_{13}}{k_B T}, \qquad X_{22} = -\frac{2\omega_{23}}{k_B T}$$

and (4.10)

$$X_{12} = \frac{(\omega_{12} - \omega_{13} - \omega_{23})}{k_B T}.$$

Substituting (4.10) in (4.6) one gets

$$
\begin{aligned}
S_{c_1c_1}(0) &= c_1\left[1 - c_1 - 2c_2c_3\left(\frac{\omega_{23}}{k_BT}\right)\right]\mathscr{D}^{-1} \\
S_{c_2c_2}(0) &= c_2\left[1 - c_2 - 2c_1c_3\left(\frac{\omega_{13}}{k_BT}\right)\right]\mathscr{D}^{-1} \qquad (4.11) \\
S_{c_1c_2}(0) &= -c_1c_2\left[1 + c_3\,\frac{(\omega_{12} - \omega_{13} - \omega_{23})}{k_BT}\right]\mathscr{D}^{-1}
\end{aligned}
$$

where

$$
\begin{aligned}
\mathscr{D} = 1 &- 2\,\frac{(c_1c_2\omega_{12} + c_1c_3\omega_{13} + c_2c_3\omega_{23})}{k_BT} \\
&- c_1c_2c_3\,\frac{(\omega_{12}^2 + \omega_{13}^2 + \omega_{23}^2 - 2\omega_{12}\omega_{13} - 2\omega_{23}\omega_{13} - 2\omega_{12}\omega_{23})}{(k_BT)^2}.
\end{aligned}
\tag{4.12}
$$

If in the above expressions we let $c_2 = 0$, $c_3 = 1 - c_1$, so that we have a binary mixture of species 1 and 3, then one has only $S_{c_1c_1}(0)$ and the expression for it becomes

$$
S_{c_1c_1} = \frac{c_1(1 - c_1)}{1 - 2c_1(1 - c_1)\omega_{13}/k_BT} \tag{4.13}
$$

which is just the well known expression for $S_{CC}(0)$ for a binary conformal solution.

There are, of course, other approximations to G^E available in the literature,[11–13] e.g. the well known Flory's approximation which is valid when ω_{ij} are small, as above, but v_α/v_β deviate considerably from unity. Since the calculations of $S_{c_ic_j}(0)$, once G^E is given, are straightforward, we do not pursue the matter further here.

Experimentally it is often the thermodynamic activities a_α, rather than G^E, which are directly measured. If $\gamma_\alpha = a_\alpha/c_\alpha$ denote the activity coefficient of species α, one has, by definition,

$$
k_BT \ln \gamma_\alpha = \left(\frac{\partial G^E}{\partial N_\alpha}\right)_{T,P,N'} \tag{4.14}
$$

where subscript N' indicates that all N_β $(\beta \neq \alpha)$ are held constant during differentiation. Hence, remembering that X_{ij} is given by (4.3), it is readily shown that†

$$X_{ij} = \left[\frac{\partial}{\partial c_j}\{\ln \gamma_i - \ln \gamma_\nu\}\right]_{T,P,c'} = \left[\frac{\partial}{\partial c_i}\{\ln \gamma_j - \ln \gamma_\nu\}\right]_{T,P,c'} \tag{4.15}$$

and conversely,

$$\left(\frac{\partial \ln \gamma_i}{\partial c_j}\right)_{T,P,c'} = X_{ij} - \sum_{r=1}^{\nu-1} c_r X_{rj}. \tag{4.16}$$

Note that $X_{ji} = X_{ij}$, but, in general, $d \ln \gamma_i/\partial c_j \neq \partial \ln \gamma_j/\partial c_i$. The various γ_α, of course, satisfy the usual Gibb-Duhem type relations

$$\sum_{\alpha=1}^{\nu} N_\alpha \left(\frac{\partial \ln \gamma_\alpha}{\partial N_\beta}\right)_{T,P,N'} = 0, \qquad \beta = 1, 2, \ldots, \nu, \tag{4.17}$$

which as most recently emphasized by Darken[14] provide useful checks on the internal consistency of measurements and (or) extrapolations. Using the fact that $\partial \ln \gamma_\nu/\partial N_\beta = \partial \ln \gamma_\beta/\partial N_\nu$, and changing the independent variables to c_i, Eq. (4.17) may be equivalently written as $(r, r' = 1, 2, \ldots, \nu - 1)$

$$\sum_r c_r \left(\frac{\partial \ln \gamma_r}{\partial c_i} - c_\nu \frac{\partial \ln \gamma_i}{\partial c_r} - \sum_{r'} c_{r'} \frac{\partial \ln \gamma_r}{\partial c_{r'}}\right) = 0 \tag{4.18}$$

with $i = 1, 2, \ldots, \nu - 1$ and

$$\sum_{\alpha=1}^{\nu} \sum_{r=1}^{\nu-1} c_\alpha c_r \frac{\partial \ln \gamma_\alpha}{\partial c_r} = 0 \tag{4.19}$$

where it is understood that $(\partial/\partial c_r) \equiv (\partial/\partial c_r)_{T,P,c'}$ etc. Equations (4.18)–(4.19) may be regarded as generalizations of the corresponding equations obtained by Darken[14] for a ternary mixture.

Finally, it is of interest to consider the mixture in the dilute solution limit, that is, where one of the components, say c_ν, tends to unity. For this case all $c_i \to 0$, $i = 1, 2, \ldots, \nu - 1$, and one obtains, to second order in c_i, the following expressions for $S_{c_i c_j}(0)$:

$$\begin{aligned} S_{c_i c_i}(0) &= c_i(1 - c_i) - \varepsilon_{ii} c_i^2 \\ S_{c_i c_j}(0) &= -c_i c_j(1 + \varepsilon_{ij}), \qquad i \neq j \end{aligned} \tag{4.20}$$

---

† Note that for any thermodynamic function

$$\left(\frac{\partial \psi}{\partial N_\beta}\right)_{T,P,N} = \left(\frac{\partial \psi}{\partial N}\right)_{T,P,\mathbf{c}} + \frac{1}{N}\sum_{i=1}^{\nu-1}\left(\frac{\partial \psi}{\partial c_i}\right)_{N,T,P,c'}(\delta_{i,\beta} - c_i)$$

where **c** implies all c_i are held fixed during differentiation and $(\partial\psi/\partial N)_{T,P,\mathbf{c}}$ is, of course, just (ψ/N) if ψ is an extensive variable and zero if it is an intensive variable.

where $\varepsilon_{ij} \equiv (X_{ij})_{c_\nu \to 1}$. The ε_{ij} $(= \varepsilon_{ji})$ are identical with the Wagner[15] interaction coefficients (ε_{ij}^{w}) well known in metallurgy. The latter are defined by

$$\varepsilon_{ij}^{w} = \left[\left(\frac{\partial \ln \gamma_i}{\partial c_j}\right)_{T,P,c'}\right]_{c_\nu \to 1} \tag{4.21}$$

so that one sees immediately from (4.16) that $\varepsilon_{ij}^{w} = \varepsilon_{ij}$. For a conformal solution X_{ij} are independent of the concentrations and the ε_{ij} are just given by (4.9). For a recent tabulation and list of references on experimental values of the Wagner-coefficients see Sigworth and Elliott.[16,17]

5 LONG WAVELENGTH LIMIT OF THE PARTIAL STRUCTURE FACTORS

The partial structure factors $a_{\alpha\beta}(q)$ are defined by[1]

$$a_{\alpha\beta}(q) = 1 + \frac{N}{V}\int [g_{\alpha\beta}(r) - 1]e^{iq\cdot r}\,\mathrm{d}^3r \tag{5.1}$$

where $g_{\alpha\beta}(r)$ is the conventional pair distribution function. An alternative set of structure factors[2,3] is $S_{\alpha\beta}(q)$ which are related to $a_{\alpha\beta}(q)$ by

$$S_{\alpha\beta}(q) = \delta_{\alpha\beta} + (c_\alpha c_\beta)^{1/2}(a_{\alpha\beta}(q) - 1) \tag{5.2}$$

and which, in our notation, are[4]

$$S_{\alpha\beta}(q) = (2N)^{-1}(c_\alpha c_\beta)^{-1/2}\langle N_\alpha^*(q)N_\beta(q) + N_\alpha(q)N_\beta^*(q)\rangle. \tag{5.3}$$

Remembering that $N_\alpha(q)$ are given by (2.14) and $S_{NN}(q)$ etc. by (2.11), one finds that $a_{\alpha\beta}(q)$ are related to $S_{NN}(q)$ etc. by $(i, j = 1, 2, \ldots, \nu - 1)$

$$\begin{aligned} a_{ij}(q) = S_{NN}(q) + 1 - (c_i^{-1})\delta_{i,j} + (c_i^{-1})S_{NC_i}(q) + (c_j^{-1})S_{NC_j}(q) \\ + (c_i c_j)^{-1})^{-1}S_{C_iC_j}(q) \end{aligned} \tag{5.4}$$

$$a_{i\nu}(q) = S_{NN}(q) + 1 + (c_i^{-1})S_{NC_i}(q) - (c_i c_\nu)^{-1}\sum_{j=1}^{\nu-1}(S_{C_iC_j}(q) + c_i S_{NC_j}(q)) \tag{5.5}$$

$$a_{\nu\nu}(q) = S_{NN}(q) + 1 - (c_\nu^{-1}) - (2c_\nu^{-1})\sum_{j=1}^{\nu-1} S_{NC_j}(q) + (c_\nu^{-2})\sum_{i,j=1}^{\nu-1}\sum S_{C_iC_j}(q) \tag{5.6}$$

and conversely

$$S_{NN}(q) = \sum_{\alpha,\beta=1}^{\nu}\sum c_\alpha c_\beta a_{\alpha\beta}(q) \tag{5.7}$$

$$S_{NC_i}(q) = c_i\left(\sum_{\alpha=1}^{\nu} c_\alpha a_{\alpha i}(q) - \sum_{\alpha,\beta=1}^{\nu}\sum c_\alpha c_\beta a_{\alpha\beta}(q)\right) \tag{5.8}$$

$$S_{C_iC_j}(q) = c_ic_j\left(a_{ij}(q) - \sum_{\alpha=1}^{\nu} c_\alpha(a_{i\alpha}(q) + a_{j\alpha}(q)) + \sum_{\alpha,\beta=1}^{\nu}\sum c_\alpha c_\beta a_{\alpha\beta}(q)\right)$$
$$+ c_i\delta_{i,j} - c_ic_j. \tag{5.9}$$

Since the above relations are valid at all q, Eqs. (5.4)–(5.6) may be used to evaluate the $q \to 0$ limit of $a_{\alpha\beta}$. For this one has only to remember that $S_{NC_i}(0)$ and $S_{NN}(0)$ are related to $S_{C_iC_j}(0)$ by (3.6) and (3.7) and that $S_{C_iC_j}(0)$ are to be determined as described in Section 4. Two special cases for which the expressions for $a_{ij}(0)$ simplify considerably may be noted here.

First, for an ideal solution $S_{C_iC_j}(0)$ are given by (4.6) and one finds

$$S_{NC_i}(0) = -c_i\Delta_i, \qquad S_{NN}(0) = \theta + \overline{\Delta^2} \tag{5.10}$$

and hence

$$a_{\alpha\beta}(0) = \theta + \overline{\Delta^2} - \Delta_\alpha - \Delta_\beta \tag{5.11}$$

where

$$\Delta_\alpha = \frac{v_\alpha - v}{v}, \qquad \overline{\Delta^2} = \sum_{\alpha=1}^{\nu} c_\alpha\Delta_\alpha^2. \tag{5.12}$$

If, in addition, the partial molar volumes of the different species are the same, then all $\Delta_\alpha = 0$ and $a_{\alpha\beta}(0) = \theta$ for all α and β. For this case, one, of course, expects that the various $a_{\alpha\beta}(q)$ will be the same also at all q.

Secondly, if we consider the solution in the dilute limit, taking $c_\nu \to 1$, then $S_{C_iC_j}(0)$ are given by (4.20). Using (4.20) and (3.6)–(3.7) in (5.4)–(5.6), one obtains, for $c_\nu \to 1$,

$$a_{ij}(0) = \theta - \delta_i - \delta_j - \varepsilon_{ij}, \qquad i, j = 1, 2, \ldots, \nu - 1, \tag{5.13}$$

$$a_{i\nu}(0) = \theta - \delta_i, \qquad a_{\nu\nu}(0) = \theta. \tag{5.14}$$

Equations (5.13) show that even in the dilute limit the $a_{ij}(0)$ depend both on the dilatation factors and on the deviation of the mixture from ideality, just as $a_{11}(0)$ does in a dilute (with $c_2 \to 1$) binary mixture as noted by Bhatia *et al.*[18] and, in terms of Wagner coefficient ε_{11}, by Bellissent and Desré.[19]

6 SUMMARY

In this paper we have defined and discussed some of the properties of the number-concentration (N-C) structure factors for multicomponent mixtures. In this (N-C) scheme, the $\frac{1}{2}\nu(\nu + 1)$ independent structure factors, required for the description of a ν-component mixture, consist of (1) a group of $\frac{1}{2}\nu(\nu-1)$ structure factors $S_{C_iC_j}(q)$ which are associated with correlations amongst the various $(\nu-1)$ concentrations, (2) $\nu-1$ structure factors, $S_{NC_i}(q)$, associated with the density-concentration correlations and (3) the structure factor $S_{NN}(q)$ associated with the density-density correlations. In the $q \to 0$ limit, the expressions for $S_{C_iC_j}(0)$ are completely determined if the free energy of mixing (or thermodynamic activities) is known as a function of concentrations. The determination of $S_{NC_i}(0)$ and $S_{NN}(0)$ involves a knowledge of $S_{C_iC_j}(0)$, compressibility and the dependence of volume on concentrations. The behaviour of $S_{C_iC_j}(0)$ for several special cases is examined. In particular, for the dilute solution limit $S_{C_iC_j}(0)$ are found to be simply related to the well known Wagner interaction coefficients. Finally, the relationship between the N-C structure factors and the partial structures $a_{\alpha\beta}(q)$ is given, which enables one to obtain convenient expressions for $a_{\alpha\beta}(0)$ in terms of thermodynamic quantities.

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