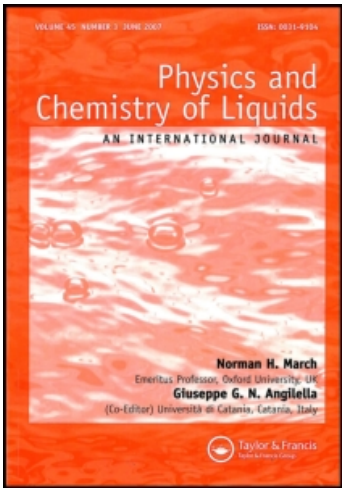

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

On the Zero Wavenumber Structure Factors of Binary Associating Mixtures

A. B. Bhatia[a]
[a] Department of Physics, University of Alberta, Edmonton, Alberta, Canada

To cite this Article Bhatia, A. B.(1984) 'On the Zero Wavenumber Structure Factors of Binary Associating Mixtures', Physics and Chemistry of Liquids, 13: 4, 241 — 253
To link to this Article: DOI: 10.1080/00319108408080783
URL: http://dx.doi.org/10.1080/00319108408080783

Phys. Chem. Liq., 1984, Vol. 13, pp. 241–254
0031-9104/84/1304–0241$18.50/0

Printed in the United Kingdom

On the Zero Wavenumber Structure Factors of Binary Associating Mixtures†

A. B. BHATIA

Department of Physics, University of Alberta, Edmonton, Alberta, Canada, T6G 2J1

(*Received August 19, 1983*)

By equating the appropriate scattering expressions, the structure factors (SF) $S_{CC}(0)$, $S_{NC}(0)$ and $S_{NN}(0)$ of a binary A-B alloy with tendency to form associates $A_\mu B_\nu$ (μ, ν small integers), are expressed in terms of the six SF $S'_{\alpha\beta}(0)$ of the ternary mixture of A, B and $A_\mu B_\nu$ and their concentrations x_α ($\alpha = 1, 2, 3$). When x_α satisfy the equilibrium condition for the reaction $\mu A + \nu B \rightleftharpoons A_\mu B_\nu$, these relations become thermodynamic identities; otherwise they determine $S_{CC}(0)$ etc. for the nonequilibrium situations. The difference between $S_{CC}(0)$ etc., when there is equilibrium and when the chemical degree of freedom is frozen in, say, by quenching, is discussed. The relations between the above $S_{CC}(0)$ etc. and the corresponding SF for a strongly associating mixture in the "chemical" scheme (system regarded as a binary mixture of $A_\mu B_\nu$ and A or B atoms) are also obtained.

1 INTRODUCTION

The thermodynamic properties of an $A - B$ mixture which has strong tendency to form associates $A_\mu B_\nu$ (μ, ν small integers), are often described by regarding it either as a binary mixture of A and B, or as a binary mixture of $A_\mu B_\nu$ and A or B, depending upon the relative concentrations of A and B in the system. The two descriptions are referred to as "elemental" and "chemical" respectively[1] and some examples of such mixtures are: alkali metal–alkali halide mixtures, metal-ammonia solutions (NH_3 or ND_3 regarded as a single unit) and compound forming molten alloys like Tl–Te, Mg–Bi.[1–7] The X-ray or neutron scattering, on the other hand, is generally expressed in the elemental scheme. Since the zero wave number ($q \to 0$)

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

limit of the structure factors $S_{ij}(0)$, obtained from scattering, is related to thermodynamic quantities, it is of interest to have relations between the appropriate $S_{ij}(0)$ in the two schemes. For the alkali metal–alkali halide mixtures ($\mu = \nu = 1$), the relation between one of the structure factors, namely concentration fluctuations, in the two schemes has been recently given by Yokokawa and Kleppa,[1] assuming that there is chemical equilibrium.

The problem is of interest in a broader context also, namely, how does the $q \to 0$ limit of scattering depend on whether the mixture is in equilibrium with respect to the chemical degree of freedom,

$$\mu A + \nu B \rightleftharpoons A_\mu B_\nu, \tag{1}$$

or not; the latter case being an idealised example of a "glass" with one degree of freedom frozen in. The purpose of this paper is to obtain relations between the $S_{ij}(0)$ in the two schemes formulating the problem with the above wider context in view.

The starting point of our work is the equivalence of the expressions for the scattering whether the mixture is regarded as a binary mixture of A and B or a ternary mixture of A, B and $A_\mu B_\nu$. This gives (Sec. 2) expressions for the three independent structure factors $S_{ij}(0)$ (or $S_{NN}(0)$, $S_{CC}(0)$, $S_{NC}(0)$) in terms of the six structure factors $S^t_{\alpha\beta}(0)$ of the ternary mixture (t, standing for ternary and $\alpha, \beta = 1, 2, 3$). Some thermodynamic considerations are given in Sec. 3, where it is also demonstrated that the above relations between $S_{ij}(0)$ and $S^t_{\alpha\beta}(0)$ become thermodynamic identities when the condition of chemical equilibrium is imposed, as they should. The case of strongly associating mixtures is considered in Sec. 4, where the relations between the number-concentration structure factors ($S_{CC}(0)$ etc.) in the elemental and chemical schemes are obtained. The question of difference between $S_{CC}(0)$ for equilibrium and non-equilibrium situations is discussed in Secs. 4.2 and 5.

2 EXPRESSIONS FOR SCATTERING

For a binary mixture consisting in all of N_A A atoms and N_B B atoms, the X-ray or the coherent neutron scattering function $I(q)$ is

$$I(q) = N[c_A b_A^2 S_{AA}(q) + c_B b_B^2 S_{BB}(q) + 2(c_A c_B)^{1/2} b_A b_B S_{AB}(q)], \tag{2}$$

where $N = N_A + N_B$, $c_A = N_A/N$, $c_B = 1 - c_A$, $S_{ij}(q)$ ($i, j = A, B$) are the structure factors defined by Enderby and North[8] or Ashcroft and Langreth,[9] and b_A and b_B are the X-ray form factors or the coherent neutron scattering lengths for the species A and B respectively. It is useful to introduce also the number concentration structure factors $S_{NN}(q)$, $S_{CC}(q)$, and $S_{NC}(q)$, which

respectively represent number-number (irrespective of atom type) correlations, concentration-concentration correlations and a cross term.[10] $S_{NN}(q)$ etc. are linearly related to $S_{ij}(q)$ and $I(q)$ in terms of them is given by[10]

$$I(q) = N[\langle b\rangle^2 S_{NN}(q) + 2\langle b\rangle \Delta b S_{NC}(q) + (\Delta b)^2 S_{CC}(q)], \tag{3}$$

where

$$\langle b\rangle = c_A b_A + c_B b_B, \Delta b = b_A - b_B. \tag{4}$$

Now suppose that the above mixture actually consists of n_1 free A atoms, n_2 free B atoms and n_3 chemical complexes (associates) $A_\mu B_\nu$. From conservation of atoms we have

$$n_1 = N_A - \mu n_3, n_2 = N_B - \nu n_3. \tag{5}$$

Since the scattering now depends also on the internal structure of $A_\mu B_\nu$, a general expression for $I(q)$ in terms of the correlations of A, B and $A_\mu B_\nu$ is far from trivial.[11,12] However, in the $q \to 0$ limit, a chemical complex may be considered as structureless with the scattering length $b_3 = \mu b_A + \nu b_B$. $I(0)$ is then just the $q \to 0$ limit of the usual expression for $I(q)$ of a ternary mixture of three atomic species with scattering lengths $b_A \equiv b_1$, $b_B \equiv b_2$ and b_3, namely,[8-9]

$$I(0) = n\left(\sum_{\alpha,\beta=1}^{3} (x_\alpha x_\beta)^{1/2} b_\alpha b_\beta S^t_{\alpha\beta}(0)\right), \tag{6}$$

where $n = n_1 + n_2 + n_3$, $x_\alpha = n_\alpha/n$, $\alpha = 1, 2, 3$, and where t has been added on $S^t_{\alpha\beta}(0)$ to distinguish them from the $S_{ij}(0)$, $i, j = A, B$ of the binary mixture.

The $q \to 0$ limit of (2) must equal (6). Hence, comparing the co-efficients of b_1 and b_2 (or setting $q \to 0$ in eqns. (2.15) of Ref. 11) we have

$$N_A S_{11}(0) = n[x_1 S^t_{11}(0) + 2(x_1 x_3)^{1/2} \mu S^t_{13}(0) + \mu^2 x_3 S^t_{33}(0)], \tag{7}$$

$$N_B S_{22}(0) = n[x_2 S^t_{22}(0) + 2(x_2 x_3)^{1/2} \nu S^t_{23}(0) + \nu^2 x_3 S^t_{33}(0)], \tag{8}$$

$$\begin{aligned}(N_A N_B)^{1/2} S_{12}(0) = n[&(x_1 x_2)^{1/2} S^t_{12}(0) + (x_1 x_3)^{1/2} \nu S^t_{13}(0) \\ &+ (x_2 x_3)^{1/2} \mu S^t_{23}(0) + x_3 \mu\nu S^t_{33}(0)].\end{aligned} \tag{9}$$

Similarly $S_{NN}(0)$ etc. are related to $S^t_{\alpha\beta}(0)$ by†

$$\begin{aligned}NS_{NN}(0) = n[&x_1 S^t_{11}(0) + x_2 S^t_{22}(0) + 2(x_1 x_2)^{1/2} S^t_{12}(0) \\ &+ 2(\mu + \nu)\{(x_1 x_3)^{1/2} S^t_{13}(0) + (x_2 x_3)^{1/2} S^t_{23}(0)\} + (\mu + \nu)^2 x_3 S^t_{33}(0)],\end{aligned} \tag{10}$$

† We may note that if one sets $x_3 = 0$ (and hence $x_1 = N_A/n$, $x_2 = N_B/n$) on the right hand sides of (10)–(12) one just gets, as one should, the usual linear relations[10,13] between $S_{NN}(0)$ etc. and the $S_{ij}(0)$, $i, j = A, B$ referred to above.

$$NS_{NC}(0) = n[c_B x_1 S^t_{11}(0) - c_A x_2 S^t_{22}(0) + (c_B - c_A)(x_1 x_2)^{1/2} S^t_{12}(0) + (c_B\mu - c_A\nu + c_B(\mu + \nu))(x_1 x_3)^{1/2} S^t_{13}(0) + (c_B\mu - c_A\nu - c_A(\mu + \nu)) \times (x_2 x_3)^{1/2} S^t_{23}(0) + (\mu + \nu)(c_B\mu - c_A\nu) x_3 S^t_{33}(0)], \quad (11)$$

$$NS_{CC}(0) = n[c_B^2 x_1 S^t_{11}(0) + c_A^2 x_2 S^t_{22}(0) - 2c_A c_B (x_1 x_2)^{1/2} S^t_{12}(0) + 2(c_B\mu - c_A\nu)\{c_B(x_1 x_3)^{1/2} S^t_{13}(0) - c_A(x_2 x_3)^{1/2} S^t_{23}(0)\} + (c_B\mu - c_A\nu)^2 x_3 S^t_{33}(0)]. \quad (12)$$

Equations (7)–(12) express $S_{ij}(0)$ or $S_{NN}(0)$ etc. in terms of the structure factors $S^t_{\alpha\beta}(0)$ and the concentrations of A, B and $A_\mu B_\nu$ of the ternary mixture. As they are derived from equating the appropriate scattering expressions they are equally true whether the binary atomic A–B mixture is in equilibrium with respect to the chemical degree of freedom or whether it is genuinely a ternary mixture (n_α, $\alpha = 1, 2, 3$, arbitrary except for the conservation of atom conditions (5)).

We next recall that for a m-component ($m = 2, 3, \ldots$) fluid mixture, which is in a state of thermodynamic equilibrium with respect to all its relevant degrees of freedom, $S^{(m)}_{\alpha\beta}(0)$ can be expressed in terms of the thermodynamic quantities[13–15] ($\alpha, \beta = 1, 2, \ldots m$)

$$(n_\alpha n_\beta)^{1/2} S^{(m)}_{\alpha\beta}(0) = \left(\frac{\partial n_\alpha}{\partial G_\beta}\right)_{T,V,G'} = \left(\frac{\partial n_\beta}{\partial G_\alpha}\right)_{T,V,G'}, \quad (13)$$

where G_β is the chemical potential of the species β and the subscript G' signifies that all G_α except the one with respect to which differentiation is being carried out are held constant. In our context, regarding the ternary mixture in a state of thermodynamic equilibrium, $S^t_{\alpha\beta}(0)$ are given by (13) with $m = 3$. Even so, the $S_{ij}(0)$ of the left hand side of eqns. (7)–(9) are not necessarily given by the thermodynamic expressions (13) with $m = 2$. However, as demonstrated below, if the condition of chemical equilibrium is imposed, then eqns. (7)–(9) (and hence also eqns. (10)–(12)) do indeed become thermodynamic identities. For the case where the chemical degree of freedom happens to be frozen in, eqns. (7)–(12) are to be regarded as a means of evaluating $S_{ij}(0)$ or $S_{NN}(0)$ etc. in terms of $S^t_{\alpha\beta}(0)$ and the concentrations x_α of the ternary mixture. (See Secs. 4.2 and 5).

3 THERMODYNAMIC CONSIDERATIONS AND CHEMICAL EQUILIBRIUM

In terms of the chemical potentials G_α of the ternary mixture the Gibbs free energy G is

$$G = n_1 G_1 + n_2 G_2 + n_3 G_3, \quad (14)$$

where, as before, the index 1 refers to free A atoms, index 2 to free B atoms and index 3 to $A_\mu B_\nu$. Regarded as a binary mixture of A and B atoms, with G_A and G_B their chemical potentials, G is also

$$G = N_A G_A + N_B G_B. \tag{15}$$

As here, we distinguish, where necessary, the quantities referring to binary A–B mixture by subscripts A, B and those referring to the ternary mixture by subscripts α, $\alpha = 1, 2, 3$. In (14), G/n and G_α are functions of pressure P and temperature T and two of the concentrations x_α, while in (15) G/N, G_A and G_B are functions of P and T and c_A or $c_B = 1 - c_A$. For future use we note that it follows from the definitions of the volume V of the mixture and of the partial molar volumes v_α, v_A and v_B that

$$V = n_1 v_1 + n_2 v_2 + n_3 v_3 = N_A v_A + N_B v_B. \tag{16}$$

Also the isothermal compressibility of the mixture

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial^2 G}{\partial P^2}\right)_{T,N,c_A} = -\frac{1}{V}\left(\frac{\partial^2 G}{\partial P^2}\right)_{T,n,x_1,x_2} \tag{17}$$

is the same in two schemes.

Now the condition for chemical equilibrium between A, B and $A_\mu B_\nu$ is that G be a minimum, i.e.

$$(\partial G/\partial n_3)_{T,P,N_A,N_B} = 0. \tag{18}$$

Remembering (14) and (5), (18) gives for the equilibrium condition

$$G_3 - \mu G_1 - \nu G_2 = 0. \tag{19}$$

With (19) and (5) the expression (14) for G reduces to $G = N_A G_1 + N_B G_2$ and a comparison with (15) shows that chemical equilibrium implies

$$G_1 \equiv G_A, G_2 \equiv G_B. \tag{20}$$

(19) and (20) imply also

$$v_1 \equiv v_A, v_2 \equiv v_B, v_3 (\equiv v_{A_\mu B_\nu}) = \mu v_A + \nu v_B. \tag{21}$$

With (19) and (20), it is now straightforward to show that eqns. (7)–(9) are thermodynamic identities. Consider, for example, eqn. (7) which on using (13) on its right hand side may be written as

$$\begin{aligned} N_A S_{11}(0) &= \left(\frac{\partial n_1}{\partial G_1}\right)_{T,V,G_2,G_3} + \mu\left(\frac{\partial n_1}{\partial G_3}\right)_{T,V,G_1,G_2} + \mu\left(\frac{\partial n_3}{\partial G_1}\right)_{T,V,G_2,G_3} \\ &\quad + \mu^2\left(\frac{\partial n_3}{\partial G_3}\right)_{T,V,G_1,G_2} \\ &= \left(\left(\frac{\partial}{\partial G_1}\right)_{T,V,G_2,G_3} + \mu\left(\frac{\partial}{\partial G_3}\right)_{T,V,G_1,G_2}\right)(n_1 + \mu n_3). \end{aligned} \tag{22}$$

Because of (19) the operator in the square bracket is just $(\partial/\partial G_1)_{T,V,G_2}$ or because of (20) just $(\partial/\partial G_A)_{T,V,G_B}$. Further $n_1 + \mu n_3 = N_A$. Hence (22) becomes

$$N_A S_{11}(0) = (\partial N_A/\partial G_A)_{T,V,G_B}, \tag{23}$$

which is just the thermodynamic expression for $S_{11}(0)$ for a binary A–B mixture as was to be demonstrated. The corresponding demonstration for $S_{12}(0)$ and $S_{22}(0)$ is similar. That (10)–(12) are also thermodynamic identities then of course follows since $S_{NN}(0)$ etc. are linearly related to $S_{ij}(0)$.

4 NUMBER-CONCENTRATION STRUCTURE FACTORS IN BINARY MIXTURES OF B AND $A_\mu B_\nu$

As mentioned in the Introduction, there are many binary A–B mixtures where the associative tendency is so strong that their properties are frequently described by regarding them as binary mixtures of the appropriate chemical complexes $A_\mu B_\nu$ and free A or B atoms. We consider for definiteness $c_A \leq c_c$ $[c_c \equiv \mu/(\mu + \nu)]$. (The results for $c > c_c$ follow by obvious transpositions in the discussion given below.) Then in the chemical scheme the mixture consists of B and $A_\mu B_\nu$. In this Section we first obtain the relations between the number-concentration structure factors in the chemical and elemental schemes from scattering considerations and then make some comments regarding chemical equilibrium.

4.1 Expressions

Denoting the concentration of $A_\mu B_\nu$ by x and of B by $(1 - x)$ and remembering from (5) that now $(c \equiv c_A)$

$$n_1 = 0, \qquad n_2 = N(1 - c) - N\nu c/\mu, \qquad n_3 = Nc/\mu, \tag{24}$$

we have for relations between x, c, N and n

$$c = \frac{x\mu}{1 + x\mathscr{A}}, \; x = \frac{c}{\mu - c\mathscr{A}}, \tag{25}$$

$$\frac{N}{n} = 1 + x\mathscr{A} = \frac{\mu}{\mu - c\mathscr{A}}, \; \mathscr{A} = \mu + \nu - 1. \tag{26}$$

Next let the $q \to 0$ limit of the number-concentration structure factors in the chemical scheme be denoted by $S_{nn}(0)$, $S_{nx}(0)$ and $S_{xx}(0)$. If the $n - x$ system is in a state of thermodynamic equilibrium, $S_{nn}(0)$ etc. are expressible

as usual in terms of thermodynamic quantities:[10]

$$S_{xx}(0) = \frac{nk_BT}{(\partial^2 G/\partial x^2)_{T,P,n}} = \frac{-x}{(\partial \ln a_2/\partial x)_{T,P}}, \tag{27}$$

$$S_{nx}(0) = -\delta_x S_{xx}(0), \tag{28}$$

$$S_{nn}(0) = (n/V)k_BT\kappa_T + \delta_x^2 S_{xx}(0), \tag{29}$$

where

$$\delta_x = \frac{1}{V}\left(\frac{\partial V}{\partial x}\right)_{n,T,P} = \frac{n}{V}(v_3 - v_2). \tag{30}$$

Again, as discussed in Section 2, since in the $q \to 0$ limit the structure of $A_\mu B_\nu$ plays no role in scattering, $I(0)$ is given, in terms of $S_{nn}(0)$ etc., by

$$I(0) = n[\langle b\rangle_x^2 S_{nn}(0) + 2\langle b\rangle_x(\Delta_x b)S_{nx}(0) + (\Delta_x b)^2 S_{xx}(0)], \tag{31}$$

where

$$\langle b\rangle_x = xb_3 + (1-x)b_B, \Delta_x b = b_3 - b_B, \tag{32}$$

with $b_3 = \mu b_A + \nu b_B$. In the elemental scheme, on the other hand, $I(q)$ is given by (3) for any q. Hence setting $q \to 0$ in (3) and comparing the coefficients of b_A and b_B in (3) and (31), one has

$$S_{CC}(0) = \mu^2\left(\frac{n}{N}\right)^3 S_{xx}(0) = \frac{S_{xx}(0)}{\mu}(\mu - c\mathscr{A})^3, \tag{33}$$

$$S_{NC}(0) = \frac{\mu n}{N}[S_{nx}(0) + \mathscr{A}\frac{n}{N}S_{xx}(0)], \tag{34}$$

$$S_{NN}(0) = \frac{n}{N}\left[\left(\frac{N}{n}\right)^2 S_{nn}(0) + 2\mathscr{A}\frac{N}{n}S_{nx}(0) + \mathscr{A}^2 S_{xx}(0)\right], \tag{35}$$

and, conversely, to (34) and (35)

$$S_{nx}(0) = \frac{N}{n\mu}\left[S_{NC}(0) - \frac{N}{n}\frac{\mathscr{A}}{\mu}S_{CC}(0)\right], \tag{36}$$

$$S_{nn}(0) = \frac{N}{n}\left[\left(\frac{n}{N}\right)^2 S_{NN}(0) - \frac{2n}{N}\frac{\mathscr{A}}{\mu}S_{NC}(0) + \frac{\mathscr{A}^2}{\mu^2}S_{CC}(0)\right]. \tag{37}$$

Before discussing the question of chemical equilibrium, we observe that if we formally define a quantity δ_c by, in analogy with δ_x of (28),

$$S_{NC} = -\delta_c S_{CC}(0), \tag{38}$$

we have, using (34), (28), (25) and (26),

$$\delta_c = (N/n\mu)[(N/n)\delta_x - \mathscr{A}], \tag{39}$$

and further from (35), (28) and (29)

$$S_{NN}(0) = (N/V)k_B T\kappa_T + \delta_c^2 S_{CC}(0), \tag{40}$$

which shows that in terms of δ_c and $S_{CC}(0)$, $S_{NC}(0)$ and $S_{NN}(0)$ have the same form as though the A–B system itself were in equilibrium with respect to all its degrees of freedom.[10]

Parenthetically, it is interesting to recall that eqns. (38) and (40) allow one to write from (3) the expression for $I(0)$ in an instructive form[3,10,16]

$$I(0) = N(N/V)k_B T\kappa_T\langle b\rangle^2 + N(\Delta b - \langle b\rangle\delta_c)^2 S_{CC}(0). \tag{41}$$

Similarly using (28) and (29) in (31)

$$I(0) = n(n/V)k_B T\kappa_T\langle b\rangle_x^2 + n(\Delta_x b - \langle b\rangle_x\delta_x)^2 S_{xx}(0). \tag{42}$$

These forms have the advantage that they exhibit the contribution to $I(0)$ from concentration fluctuations and from compressibility separately. One readily verifies, using the appropriate equations given above, that the compressibility term in (41) is equal to the compressibility term in (42) and similarly the second term in the two equations equals one another.

4.2 Equilibrium Condition, $S_{CC}(0)$ and δ_c

As follows from their derivation, the relations (33)–(37) between the $n - x$ and the N–C structure factors for the $B - A_\mu B_\nu$ system are true irrespective of thermodynamic considerations. If the $B - A_\mu B_\nu$ system is in a state of thermodynamic equilibrium then $S_{nn}(0)$ etc. are given by (27)–(29) and the relations (33)–(35) allow one to evaluate the structure factors $S_{NN}(0)$ etc. in the elemental scheme from the thermodynamic properties of the system in the chemical scheme. Further, if we assume that the $B - A_\mu B_\nu$ system is actually in equilibrium with respect to the chemical reaction (1), then, firstly, by virtue of (20), the activity a_2 of free B atoms in $B - A_\mu B_\nu$ system is identical to the activity a_B of B species in the A–B scheme. Hence, using (27) in (33)

$$S_{CC}(0) = \frac{(\mu - c\mathscr{A})^3}{\mu} \frac{(-x)}{(\partial \ln a_B/\partial x)_{T,P}}$$

$$= \frac{x(\mu - c\mathscr{A})^3}{c\mu} \frac{(-c)}{(\partial \ln a_B/\partial c)_{T,P}\, dc/dx},$$

or, since from (25),

$$dc/dx = (x/(c\mu))(\mu - c\mathscr{N})^3,$$

one gets

$$S_{CC}(0) = -\frac{c}{(\partial \ln a_B/\partial c)_{T,P}} = \frac{Nk_BT}{(\partial^2 G/\partial c^2)_{T,P,N}}, \tag{43}$$

which is the well-known expression for the $q \to 0$ limit of the structure factor $S_{CC}(q)$ for an A-B system which is in a state of thermodynamic equilibrium with respect to all its relevant degrees of freedom.[10] Secondly, using (21) in (39), the expression (39) for δ_c becomes

$$\delta_c = (N/V)(v_A - v_B) = V^{-1}(\partial V/\partial c)_{T,P,N}, \tag{44}$$

so that remembering (38) and (40), the expressions (33)–(35) formally reduce to the usual thermodynamic expressions[10] for $S_{CC}(0)$ etc. for the A–B system.

Conversely, the above paragraph shows that we could have derived relations (33)–(35) between $S_{xx}(0)$ etc., and $S_{CC}(0)$ etc., from thermodynamic relations alone by assuming chemical equilibrium, i.e. (20) and (21). As mentioned in the Introduction the relation (33) between $S_{CC}(0)$ and $S_{xx}(0)$ for the special case $\mu = \nu = 1$, namely, $S_{CC}(0) = (1 - c)^3 S_{xx}(0)$ has been recently derived by Yokokawa and Kleppa[1] in this way (note the difference in notation in Ref. 1).

For the assumption of chemical equilibrium to be valid, however, the values of n_α taken in (24) must be a solution of (5) and the equilibrium eqn. (19). The latter can be written in the form[17,18]

$$\frac{(n_1/n)^\mu (n_2/n)^\nu}{n_3/n} = K\beta, \tag{45}$$

where K, the reaction constant, is independent of the concentrations and $\beta(=\gamma_3/\gamma_1^\mu\gamma_2^\nu$, γ_α, activity coefficients) is a smoothly varying function of n_α whose form depends on the model taken for the ternary mixture (for an ideal mixture all $\gamma_\alpha = 1$). When the tendency to form associates is very strong† ($K \ll 1$, strictly $K\beta \ll 1$) the solution of (45) in most of the concentration range ($0 \leq c \leq c_c$) is indeed approximately that given by (24). However, near $c = c_c$ and near $c = 0$ (and similarly near $c = 1$ if one is in the range $1 \geq c \geq c_c$) this is not necessarily the case.

† We may recall[18] that a rough practical criterion for this is that $\ln K \lesssim -3(\mu + \nu)$ or $G_M(c_c)/RT \lesssim -3$, where $G_M(c_c)$ is the molar free energy of mixing of the binary A-B mixture at the compound forming concentration c_c.

First, near $c = 0$, the solution of (45) for $\mu = 1$ is $n_3 \simeq Nc/(1 + K')$, where $K' \equiv K(\beta)_{c=0}$, so that for this case with $K' \ll 1$, the solution (24) is approximately valid near $c = 0$ also. However, for $\mu \geq 2$, the solution of (45) is[17]

$$n_3 \simeq Nc^{\mu}/K', \text{ for } c \ll (K'/\mu)^{1/(\mu-1)}, \tag{46}$$

so that the system here is perforce a ternary mixture of A, B and $A_\mu B_\nu$ (rather than just binary of B and $A_\mu B_\nu$) if it is to be considered to be in chemical equilibrium. Because of this $S_{CC}(0)$ as evaluated from (33) exhibits the following anomalous feature.

A well-known property of the concentration fluctuation structure factor (in $q \to 0$ limit) for a binary solution which is in thermodynamic equilibrium with respect to all its degrees of freedom is that in the dilute limit, it equals the solute concentration.[17-19] For our case the equilibrium thus implies that for $x \ll 1$, and hence also for $c \ll 1$, $S_{xx}(0) \to x$ and $S_{CC}(0) \to c$. If we take $S_{xx}(0) = x$, (33), however, actually gives $S_{CC}(0) = \mu c$ in this limit, which is not equal to c unless $\mu = 1$. The reason, as already mentioned, is that (46), rather than (24), is the solution of the equilibrium eqn. (45). Once, of course, this equilibrium is present it follows from the general thermodynamic expression (43) that $S_{CC}(0) \to c$ for $c \to 0$. (A verification of this, using (46), for a special model of the ternary mixture is given in Sec. 5.) On the other hand, if for some reason the chemical degree of freedom is "frozen in", and the $B - A_\mu B_\nu$ is a genuine binary fluid mixture of B and $A_\mu B_\nu$ with $S_{xx}(0)$ given by (27), then $S_{CC}(0)$ for it would indeed be μc for $c \ll 1$.

In the other dilute limit of the $B - A_\mu B_\nu$ system, namely $x \to 1$, $S_{xx}(0) = 0$ at $x = 1$, and hence from (33) $S_{CC}(0) = 0$ at $c = c_c$. Actually one verifies from (45) that, except for the physically unrealistic case of $K\beta = 0$ which implies the free energy of mixing G_M to be infinite,[17] there is always some dissociation of the associates, i.e. n_1, n_2, n_3 have all to be taken non-zero at $c = c_c$. This has the consequence[1,17,18] that $S_{CC}(0)$, although much less than unity (for $K\beta \ll 1$) at and near $c = c_c$, $S_{CC} \neq 0$ at $c = c_c$, in contrast to that given by (33).

5 $S_{CC}(0)$ FOR EQUILIBRIUM AND NON-EQUILIBRIUM STATES: AN ILLUSTRATION

For given values of n_1, n_2, n_3 of A, B and $A_\mu B_\nu$ respectively, the number-concentration structure factors $S_{CC}(0)$ etc., in the elemental scheme are given by (10)-(12). Because of the conservation of atom conditions (5), for a given N_A and N_B, only one n_α, say n_3, is arbitrary; n_3 may be regarded as an order parameter associated with the chemical reaction (1). If the reaction

has proceeded to equilibrium at the temperature and pressure under consideration, n_3 has the value, say $\bar{n}_3$, obtained by solving the equilibrium equation (45). When $n_3 = \bar{n}_3$, then, as follows from Section 2, $S_{CC}(0)$ etc. may equally be evaluated from their thermodynamic expressions (43) etc. for the A–B system. One can, however, envisage a situation in which $n_3 \neq \bar{n}_3$ and the rate of reaction is so sluggish that for all practical purposes the chemical degree of freedom is "frozen in". This can occur, for example, if the mixture is quickly cooled from a higher temperature T_1 to a sufficiently lower temperature T_2. At T_2, then $n_3 \simeq \bar{n}_3(T_1)$ and the corresponding mixture may be genuinely regarded as a ternary mixture in a state of thermodynamic equilibrium. $S^t_{\alpha\beta}(0)$ in (10)–(12) may then be evaluated from the observed thermodynamic properties at T_2, using (13) or the more practical expressions given in Ref. 20 for the ternary and multi-component mixtures. The structure factors for the equilibrium and non-equilibrium situations can be significantly different from each other. To illustrate this as well as some general features of $S_{CC}(0)$ for strongly associating mixtures described in Section 4, we consider the simple substitutional alloy approximation[21] for $S^t_{\alpha\beta}(0)$ – in thermodynamic terms a necessary, but not sufficient, condition for this is that the mixture be ideal.

In the substitutional alloy approximation one has[21]

$$S^t_{\alpha\beta}(0) = (x_\alpha x_\beta)^{1/2}(n/V)k_B T\kappa_T + \delta_{\alpha\beta} - (x_\alpha x_\beta)^{1/2}, \tag{47}$$

where $\delta_{\alpha\beta}$ is the Kronecker delta. Substituting (47) in (10)–(12) one finds

$$S_{NN}(0) = (N/V)k_B T\kappa_T + \mathscr{A}^2(n_3/Nn)(N - (\mu + \nu)n_3), \tag{48}$$

$$S_{NC}(0) = (n_3/N)\mathscr{A}(\mu + \nu)(c_c - c), \tag{49}$$

$$S_{CC}(0) = c(1 - c) - (n_3/N)[\mu(1 - c)^2 + \nu c^2 - (\mu + \nu)^2(c_c - c)^2]. \tag{50}$$

It is obvious from (48)–(50) that the values of $S_{NN}(0)$ etc. depend markedly on the value of n_3. In particular, for $n_3 = 0$, (48)–(50) reduce to the expressions for $S_{NN}(0)$ etc. for a substitutional A–B alloy, namely,

$$S_{NN}(0) = (N/V)k_B T\kappa_T,\ S_{NC}(0) = 0 \text{ and } S_{CC}(0) = c(1 - c), \tag{51}$$

as they should. On the other hand, corresponding to strongly associating mixtures, if we take, as in Sec. 4, $n_3 = Nc/\mu$, for $0 \leq c \leq c_c$, then (48)–(50) give ($x \equiv x_3$)

$$\begin{aligned} S_{NN}(0) &= (N/V)K_B T\kappa_T + \mathscr{A}^2(n/N)x(1 - x), \\ S_{NC}(0) &= (n/N)^2\mathscr{A}\mu x(1 - x), \\ S_{CC}(0) &= (n/N)^3\mu^2 x(1 - x), \end{aligned} \tag{52}$$

Expressions for $S_{CC}(0)$ in (50) and (52) have been given earlier[11,17] in another context. Since for a "substitutional" alloy of B and $A_\mu B_\nu$,

$$S_{xx}(0) = x(1 - x),\ S_{nx}(0) = 0 \text{ and } S_{nn}(0) = (n/V)k_B T\kappa_T,$$

one verifies that (52) are in accordance with the relations (33)–(35) between $S_{NN}(0)$ and $S_{nn}(0)$ etc. obtained in Sec. 4.

As the expression (33) for $S_{CC}(0)$, so also the expression for $S_{CC}(0)$ in (52) gives in the dilute limit $c \to 0$, $S_{CC}(0) \to \mu c$, rather than $S_{CC}(0) \to c$, which $S_{CC}(0)$ would have if the A–B system was in equilibrium with respect to all its degrees of freedom. We immediately see that if we substitute for n_3 the equilibrium solution (46) in (50), then (50) gives $S_{CC}(0) \to c$.

Again, in the dilute limit $x \to 1$, (52), just as (33), gives $S_{CC}(0) = 0$ at $c = c_c$. As mentioned in Section 4 this is also due to the fact that $n_3 = Nc/\mu$ is not a good enough solution of (45) at $c = c_c$ even when $K \ll 1$. We can use (50) to make a rough estimate of $S_{CC}(0)$ at $c = c_c$. For $c = c_c$, (50) gives

$$S_{CC}(0) = c_c(1 - c_c)[1 - n_3/n_3^{(0)}] \tag{53}$$

where $n_3^{(0)}$ $(= N/(\mu + \nu))$ is the maximum possible value of n_3. Writing $n_3 = n_3^{(0)} - \Delta n_3$ in the equilibrium eqn. (45), noting that $\beta = 1$ in our example and using (5), one finds, for $K \ll 1$,

$$\frac{\Delta n_3}{n_3^{(0)}} \simeq K^{1/(\mu+\nu)}(\mu^\mu \nu^\nu)^{-(1/(\mu+\nu))},$$

provided $\Delta n_3/(n_3^{(0)}) \ll (\mu + \nu - 1)^{-2}$. Hence

$$S_{CC}(0) \simeq c_c(1 - c_c)K^{(1/(\mu+\nu))}(\mu^\mu \nu^\nu)^{-(1/(\mu+\nu))}, \tag{54}$$

which may be further related to $G_M(c_c)$ since, for $K \ll 1$, $R/T \ln K \simeq (\mu + \nu)G_M(c_c)$.[17] As an example, taking $\mu = 2, \nu = 1$, and $G_M(c_c)/RT = -3$— the value below which (24) is a reasonable solution of (45) except near $c = 0$ and $c = c_c - S_{CC}(0) \simeq 0.03\ c_c(1 - c_c)$ or about (1/30th) of the ideal value of $S_{CC}(0)$ at $c = c_c$.

To conclude, the above discussion shows that for associating mixtures the values of $S_{CC}(0)$ etc. (as, of course, of S_{CC} etc. at higher q) depend on whether or not there is equilibrium with respect to the chemical degree of freedom. It also suggests a way of calculating $S_{CC}(0)$ etc. for an associating alloy which is quickly quenched to a low enough temperature at which the chemical reaction cannot proceed to equilibrium. In a broader sense, the results of this paper may be of interest in the study of glasses. We recall that a glass is characterized by one or more order parameters which get "frozen in" at the glass transition temperature(s).[22,23] Quantitative specification of these parameters could thus provide clue to evaluation of $S_{CC}(0)$ etc. in the glassy state.

References

1. H. Yokokawa and O. J. Kleppa, *J. Chem. Phys.* **76**, 5574 (1982).
2. J. F. Jal, J. Dupuy and P. Chieux, *J. Phys. Colloque*, C-8 **41**, 257 (1980).
3. P. Chieux and P. Damay, *Chem. Phys Lett.*, **58**, 619 (1978).
4. J. C. Thompson, *Electrons in Liquid Ammonia*, Oxford University Press, 1976.
5. J. C. Thompson, K. Ichikawa and S. M. Granstaff,Jr., *Phys. Chem. Liq.*, **5**, 167 (1976).
6. Y. Nakamura and M. Shimoji, *Trans. Farad. Soc.*, **67**, 1270 (1971).
7. M. Shimoji, *Liquid Metals*, Academic Press, 1977.
8. J. E. Enderby and D. M. North, *Phys. Chem. Liq.*, **1**, 1 (1968).
9. N. W. Ashcroft and D. C. Langreth, *Phys. Rev.*, **156**, 685 (1967).
10. A. B. Bhatia and D. E. Thornton, *Phys. Rev.*, **B2**, 3004 (1970).
11. A. B. Bhatia and V. K. Ratti, *J. Phys. F: Metal Physics*, **6**, 927 (1976).
12. P. A. Egelstaff, D. I. Page and J. G. Powles, *Molec. Phys.*, **20**, 881 (1971).
13. N. H. March and M. P. Tosi, *Atomic Dynamics in Liquids*, MacMillan Press, 1976.
14. J. G. Kirkwood and F. Buff, *J. Chem. Phys.*, **17**, 338 (1951).
15. A. B. Bhatia and V. K. Ratti, *Nuovo Cim.*, **35B**, 77 (1976).
16. G. D. Wignall and P. A. Egelstaff, *J. Phys.*, **C1**, 1088 (1968).
17. A. B. Bhatia and W. H. Hargrove and D. E. Thornton, *Phys. Rev.*, **B9**, 435 (1974).
18. A. B. Bhatia and W. H. Hargrove, *Phys. Rev.*, **B10**, 3186 (1974).
19. A. B. Bhatia and R. N. Singh, *Phys. Chem. Liq.*, **11**, 285 (1982).
20. A. B. Bhatia and V. K. Ratti, *Phys. Chem. Liq.*, **6**, 201 (1977).
21. T. E. Faber and J. M. Ziman, *Phil. Mag.*, **11**, 153 (1965).
22. S. F. Edwards, *Polymer*, **17**, 933 (1976).
23. H. Ruppersberg, D. Lee and C. N. J. Wagner, *J. Phys.*, **F10**, 1645 (1980).