Intensity scattered by multicomponent compressible systems

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In this paper it is shown that the use of the volume fractions ϕ_i to characterize the composition of a system allows an easy evaluation of its scattered intensity at zero angle, even if it is compressible. If the volume fractions are independent of composition, the intensity can be split into two terms: the first corresponds to the density fluctuations of the medium at constant composition, the second is the composition fluctuations as already evaluated for an incompressible system. In a majority of cases these formulas can be generalized at any angle and for systems for which the volume fractions depend on composition and pressure. As an example the results of these calculations are expressed in terms of experimentally available quantities for a two component system studied either by light scattering or by neutron small angle scattering technique.

(Keywords: multicomponent systems; composition; volume fractions)

INTRODUCTION

Recently Benoit, Benmouna and Wu[1] proposed a general equation allowing the calculation of the scattered intensity at any angle by an incompressible medium composed of any number of polymers and copolymers. The thermodynamic part of this theory was based on the use of exchange chemical potentials. In this paper we would like to generalize these results to the case of compressible systems. In fact this problem has already been considered by many authors[2–4]. Recently des Cloizeaux and Jannink[5], using vectorial geometry analysis, a very elegant approach, gave a solution to this problem. Our purpose here is to show how it is possible to obtain these results very simply and to discuss their application to experimental situations.

THE SCATTERING PROBLEM

One knows that the intensity scattered at zero angle by a volume V made up of N identical molecules is described by the Einstein[6] equation:

$$I(0) \approx a^2\overline{\Delta N^2} \tag{1}$$

where, for neutron scattering a is the coherent scattering length (one assumes that the incoherent scattering has been suppressed). For light scattering a is equal to the polarizability of the molecules which are assumed to be isotropic. $\overline{\Delta N^2}$ is the average value of the fluctuations of the square of the number of molecules in the volume V. In fact one should introduce the necessary constants to replace $\approx$ by $=$ but, in order to have simpler formulas it will be assumed that these constants are unity and we shall discuss later their exact values.

Let us consider a system containing $p+1$ types of molecules and introduce the quantity P defined as:

$$P = \sum_{o}^{p} a_i N_i \tag{2}$$

where a_i is the value of the quantity a corresponding to the molecular species i. Equation (1) becomes:

$$I(0) = \overline{\Delta P^2} \tag{3}$$

or

$$I(0) = \sum_{i=o}^{p} a_i^2 \overline{\Delta N_i^2} + 2\sum_{i \neq k} a_i a_k \overline{\Delta N_i \Delta N_k} \tag{4}$$

This expression has now to be evaluated from the thermodynamic properties of the system.

Before doing so it is convenient to introduce new variables. Because density and composition fluctuations are of different nature it is important to use variables which separate them clearly. We shall therefore use the quantities N_i' defined as:

$$N_i' = N_i \frac{v_i}{v_0} = N_i z_i \tag{5}$$

where v_i and v_0 are the partial molar volumes of the molecules of species i and of species 0 respectively. The species 0 is arbitrarily called the solvent, and z_i is a thermodynamic quantity which can be defined as:

$$z_i = \frac{\left(\dfrac{\partial \mu_i}{\partial p}\right)_{V,N^k,T}}{\left(\dfrac{\partial \mu_0}{\partial p}\right)_{V,N^k,T}} \tag{6}$$

It will nevertheless be treated as a constant and the effect of its dependence on compression and composition will be discussed at the end of this paper. If one introduces also the quantity $N_T = \dfrac{V}{v_o} = \sum_{i=0}^{p} N_i z_i$ and the quantity $\phi_i = \dfrac{N_i z_i}{\sum N_i z_i}$ one obtains for P:

$$P = a_0 N_T + \sum_{i=1}^{p} \left[\frac{a_i}{z_i} - a_0\right] z_i N_i = a_0 N_T + \sum_{i=1}^{p} \left[\frac{a_i}{z_i} - a_0\right] N_i'$$

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$$= N_T\left[a_o + \sum_{i=1}^{p}\left[\frac{a_i}{z_i} - a_0\phi_i\right]\right] \tag{7}$$

This suggests the introduction of the quantities:

$$\bar{a}_i = \frac{a_i}{z_i} - a_0 \qquad \bar{a} = a_0 + \sum_{i=1}^{p} \bar{a}_i\phi_i \tag{8}$$

which are practically always used by experimentalists.

The value of the quantity $p = P/V$ becomes:

$$p = P/V = \bar{a}/v_0 = \frac{1}{v_0}\left[a_0 + \sum_{i=1}^{p} \bar{a}_i\phi_i\right] \tag{9}$$

where $\bar{a}$ is the average value of the a_i on the volume V.

One has therefore three possible expressions for the scattering intensity:

1. The expression given by equation (4) which gives the intensity as a function of the variables $N_0, N_1, \ldots, N_i, \ldots, N_p$.
2. If one uses the variables $N_T, N'_i, \ldots, N'_p$, one obtains, by differentiation of the first term of equation (7):

$$I(0) = a_0^2\overline{\Delta N_T^2} + 2\sum a_0\bar{a}_i\overline{\Delta N'_i\Delta N_T} + \sum\sum \bar{a}_i\bar{a}_k\overline{\Delta N'_i\Delta N'_k} \tag{10}$$

3. Finally, if one uses the variables $N_T, \phi_1, \ldots, \phi_p$ one obtains, by differentiation of equation (9):

$$I(0) = \bar{a}^2\overline{\Delta N_T^2} + 2N_T\sum_i \bar{a}\bar{a}_i\overline{\Delta N_T\Delta\phi_i}$$
$$+ N_T^2\sum_i\sum_k \bar{a}_i\bar{a}_k\overline{\Delta\phi_i\Delta\phi_k} \tag{11}$$

Equation (11), in which N_T and ϕ_i are the variables is evidently the most convenient because the three terms into which the scattering intensity is split have a simple physical meaning. The first one corresponds to fluctuations at constant composition. Through the variable N_T, it is the total number of molecules which varies, at constant composition, in the constant volume V and we are dealing with density fluctuations exactly as in a one component system.

The last term is due to the fluctuations of the volume fractions at constant N_T and constant volume. This is the term one would obtain assuming that the medium is incompressible. It has been evaluated recently^1.

The only problem left is the evaluation of the second term which corresponds to the coupling of density and composition fluctuations. This term has been shown to be zero^5. We shall give here another demonstration but before doing so, some classical results of thermodynamics will be summarized.

THE THERMODYNAMICS OF THE PROBLEM

If one uses the variables N_i for the definition of the Gibbs free energy one writes:

$$G = \sum_{i=0}^{p} N_i\mu_i \tag{12}$$

where μ_i is the chemical potential associated with the species i. If one uses the variables N_T and N'_i one has to use the exchange chemical potential $\bar{\mu}_i$ defined by the relation:

$$\bar{\mu}_i = \frac{\mu_i}{z_i} - \mu_0 \tag{13}$$

and to write:

$$G = N_T\mu_0 + \sum_{i=1}^{p} N'_i\bar{\mu}_i \tag{14}$$

or, using the variables N_T and ϕ_i:

$$G = N_T\left[\mu_0 + \sum_{i=1} \bar{\mu}_i\phi_i\right] \tag{15}$$

This leads to the definition of g, the free energy per volume of a solvent molecule:

$$g = \frac{G}{N_T} = \mu_0 + \sum_{i=1}^{p} \bar{\mu}_i\phi_i \tag{16}$$

g is only a function of the ϕ_i values. Because it is an intensive quantity it obeys the relations:

$$\bar{\mu}_i = \left[\frac{\partial g}{\partial\phi_i}\right]_{p,T} \tag{17}$$

One can also write for the volume the classical equation:

$$V = \sum_{i=0}^{p} v_iN_i$$

where the v_i values are, as before, the partial molecular volumes.

Deriving these equalities by the pressure p gives, assuming that z_i is a constant:

$$\left[\frac{\partial\bar{\mu}_i}{\partial p}\right] = \frac{1}{z_i}\frac{\partial\mu_i}{\partial p} - \frac{\partial\mu_o}{\partial p} = \frac{1}{z_i}v_i - v_0 = 0 \tag{18}$$

In the course of this paper the relation between the quantities $(\partial\mu_i/\partial N_k)v$ and $(\partial\mu_i/\partial N_k)p$ as well as the corresponding relations for the exchange potentials will be required. In the appendix the reader will be reminded that:

$$\left(\frac{\partial\mu_i}{\partial N_k}\right)_v = \left(\frac{\partial\mu_i}{\partial N_k}\right)_p + \frac{v_iv_k}{\beta V} \tag{19}$$

where β is the isothermal compressibility coefficient $(-1/v \times \mathrm{d}v/\mathrm{d}p)_T$ and v_i and v_k the volumes of the molecules of species i and k respectively. If one applies this relation to the exchange potentials one obtains evidently:

$$\left(\frac{\partial\bar{\mu}_i}{\partial N'_k}\right)_p = \left(\frac{\partial\bar{\mu}_i}{\partial N'_k}\right)_v \tag{20}$$

when i or k differs from zero. This quantity differs from 0 only if i and k are equal to 0. The chemical potential associated with N_T is μ_0 and one has:

$$\left(\frac{\partial\mu_0}{\partial N_T}\right)_p = \frac{v_0^2}{\beta V} \tag{21}$$

because $(\partial\mu_0/\partial N_T)_v = 0$ (μ_0 is, at constant pressure, independent of the total number of molecules).

THE QUANTITIES $\overline{\Delta X\Delta Y}$

This calculation can be made through the use of the grand partition function which can be defined as:

$$\Xi = \sum C\exp\frac{1}{kT}\left[\sum\mu_iN_i - U\right] \tag{22}$$

where C is a factor which, for this problem, can be considered as constant. The summation has to be extended, at V and T constant, over all the possible states of the system, each having the energy U. The classical method[7] to obtain average values of N_i is to take the derivative of $\ln \Xi$ with respect to μ_i:

$$\frac{\partial \ln \Xi}{\partial \mu_i} = \frac{1}{\Xi} \sum \frac{N_i}{kT} C \exp \frac{1}{kT} \left[\sum \mu_i N_i - U \right] = \frac{\bar{N}_i}{kT} \quad (23)$$

Multiplying the two terms of the right hand equality by $kT\Xi$ one obtains:

$$\sum N_i C \exp \frac{1}{kT} \left[\sum \mu_i N_i - U \right] = \Xi \bar{N}_i \quad (24)$$

Differentiating again with respect to μ_k and dividing by Ξ leads to:

$$\overline{N_i N_k} - \bar{N}_i \bar{N}_k = kT \frac{\partial N_k}{\partial \mu_i} = kT \frac{\partial N_i}{\partial \mu_k} = (\overline{\Delta N_i \Delta N_k})_{V,N_m} \quad (25)$$

where m represents all the indices, except i and k. (From now on, we shall omit the subscript T because all the derivatives are taken at constant temperature.)

The same procedure can be repeated if, instead of using as variables $N_0 \cdots N_p$, we use $N_T, N'_1 \cdots N'_p$. It suffices to replace the classical expression of G by equation (14). When N_T is kept constant i and k are different from o and one obtains:

$$(\overline{\Delta N'_i \Delta N'_k})_{V,N'_m} = kT \left(\frac{\partial N'_i}{\partial \bar{\mu}_k} \right)_{V,N_T,N_m} \quad (26)$$

Because in these derivations N_T is constant (i and k are different from o and T), one can write:

$$(\overline{\Delta \phi_i \Delta \phi_k})_{V,N_T,N_m} = \frac{kT}{N_T} \frac{\partial \phi_i}{\bar{\mu}_k} = \frac{kT}{N_T} \left(\frac{\partial \phi_k}{\partial \bar{\mu}_i} \right)_{V,N_T,N_m} \quad (27)$$

The case of the quantities $(\overline{\Delta N_T \Delta \phi_i})_{V,N_k}$ is more subtle because G is no more a linear function of these variables. If we use equation (15) for G and put it in the definition of Ξ, a first derivation with respect to $\bar{\mu}_i$ gives:

$$\frac{\partial \ln \Xi}{\partial \bar{\mu}_i} = \frac{1}{\Xi} \sum \frac{N_T \phi_i}{kT} C \exp \frac{1}{kT} \left[\mu_0 N_T + \sum \bar{\mu}_i N_T \phi_i - U \right]$$

$$= \frac{\overline{N_T \phi_i}}{kT} \quad (28)$$

or

$$\overline{N_T \phi_i} = kT \frac{\partial \ln \Xi}{\partial \bar{\mu}_i} \quad (29)$$

Classical thermodynamics tells us that:

$$kT \ln \Xi = G - A \quad (30)$$

where A is the Helmholtz free energy, and that:

$$\mathrm{d}(kT \ln \Xi) = N_T \, \mathrm{d}\mu_0 + N_T \sum_{i=1}^{p} \phi_i \, \mathrm{d}\bar{\mu}_i + V \, \mathrm{d}p - S \, \mathrm{d}t \quad (31)$$

which leads to:

$$N_T \phi_i = kT \frac{\partial \ln \Xi}{\partial \bar{\mu}_i} \quad (32)$$

where N_T and ϕ_i are the averages taken on the ensemble.

This shows that $\overline{N_T \phi_i} - N_T \phi_i = o$; therefore $\overline{\Delta N_T \Delta \phi_i} = 0$. This confirms that if one chooses the variables correctly there is no cross-term 'density–composition' in the expression of the scattering intensity.

The last term which has to be evaluated is the term $\overline{\Delta N_T^2}$ at ϕ_i constant. One obtains easily the classical result, known for pure liquids:

$$\overline{\Delta N_T^2} = kT \left(\frac{\partial N_T}{\partial g} \right)_{\phi,V} \quad (33)$$

CALCULATION OF THE SCATTERING INTENSITY

From the results of the preceding section it is evident that it is most convenient to use the variables N_T, ϕ_i ($1 \leqslant i \leqslant p$) because this eliminates all the cross terms of the form $\overline{\Delta N_T \Delta \phi_i}$. Returning to equation (11) one obtains:

$$I(0) = \bar{a}^2 kT \left(\frac{\partial N_T}{\partial g} \right)_{\phi,V} + N_T kT \sum_i \sum_k \bar{a}_i \bar{a}_k \frac{\partial \phi_k}{\partial \bar{\mu}_i} \quad (34)$$

The first term depends only on the variables N_T, because ϕ and V are constant and one obtains:

$$\left(\frac{\partial N_T}{\partial g} \right)_{\phi,V} = \frac{1}{\left(\frac{\mathrm{d}g}{\mathrm{d}N_T} \right)_{\phi,V}} \quad (35)$$

If one uses equation (20) in the case of a system with only one variable one sees that the term $(\partial g / \partial N_T)_p$ is equal to zero because g is independent of N_T and one obtains:

$$I(0) = \bar{a}^2 kT \left(\frac{\partial N_T}{\partial g} \right)_{\phi,V} = \bar{a}^2 kT \beta \frac{V}{v_0^2} \quad (36)$$

recovering the classical result for a homogeneous system.

The evaluation of the last term is classical. One has to express the $\partial \phi_k / \partial \bar{\mu}_i$ as functions of the $\partial \bar{\mu}_i / \partial \phi_k$. One writes the matrix $[\mathbf{H}]$ having $\partial \bar{\mu}_i / \partial \phi_k$ or $\partial^2 g / \partial \phi_i \partial \phi_k$ as the general term. This matrix has p rows and p columns and is symmetrical. The quantities $\partial \phi_k / \partial \bar{\mu}_i$ are the coefficient of the inverse matrix $[\mathbf{H}]^{-1}$, or the cofactors of the matrix $[\mathbf{H}]$ divided by its determinant. If one calls $[\mathbf{a}]$ the column vector made of the optical coefficient $\bar{a}_i$ defined in equation (10) and $[\mathbf{a}_T]$ its transpose or the row vector made of the $\bar{a}_i$ one obtains from equations (34) and (36) the final result

$$I(o) = V \left(\frac{a}{v_o} \right)^2 kT \beta + N_T kT [a_T][\mathbf{H}]^{-1}[a] \quad (37)$$

It is interesting to modify this formula in order to use quantities which are more familiar to the experimentalist. For this purpose one assumes that the free energy of the system can be put in the Flory–Huggins[8] form and writes:

$$\frac{1}{kT} \frac{\partial^2 g}{\partial \phi_i \partial \phi_k} = \frac{1}{\phi_0} + \chi_{ik} - \chi_{io} - \chi_{ko} = v_{ik} \quad (38)$$

$$\frac{1}{kT} \frac{\partial^2 g}{\partial \phi_i^2} = \frac{1}{z_i \phi_i} + \frac{1}{\phi_0} - 2\chi_{io} = v_{ii} \quad (38a)$$

where $\phi_0 = \sum_{i=1}^{p} \phi_i$; the χ_{ik} are the interaction coefficients, per volume of a solvent molecule, between species i and

k in the chosen solvent and the v_{ik} are the classical excluded volume parameters or the ratios of the excluded volume integral to the volume of the solvent v_o. These quantities do not have to be constant and can be defined for any system by the equations (38) and (38a). This allows one to rearrange the matrix $[\mathbf{H}]$ and write:

$$\frac{1}{kT}[\mathbf{H}] = [x_{ii}]^{-1} + [v_{ik}] \tag{39}$$

calling $[x_{ii}]$ the diagonal matrix having $x_{ii} = z_i\phi_i$ as elements along its principal diagonal and $[v_{ik}]$ the matrix of the excluded volume parameters. One obtains:

$$I(0) = V(a/v_o)^2 kT\beta + N_T[a_T][[x]^{-1} + [V]]^{-1}[a] \tag{40}$$

DISCUSSION

z_i is not a constant

Until now we have assumed that the z_i values were constant but, in the general case they could depend on pressure and composition being thermodynamical variables defined by equation (6). In order to extend our previous results we first note that equation (15) is valid, even if the z_i values are not constant. This follows from the fact that because G is a homogeneous function of the first order of the N_i' one can use the Euler theorem. In order to write equations (22) and (23) correctly one has to change the variables in the expression of G as well as in the integration volume. This means that one has to introduce the Jacobian of the transformation, i.e. the quantity:

$$\frac{\partial(N_0, N_1, N_2, \ldots, N_p)}{\partial(N_T, \phi_1, \phi_2, \ldots, \phi_p)} \tag{41}$$

If this Jacobian does not depend on the $\bar{\mu}_i$ or its derivatives equation (28) is valid and one recovers the basic equation of this paper $\overline{\Delta N_T \Delta\phi_i} = 0$.

This is obvious if the z_i values depend only on the pressure and are independent of the composition. Therefore differences between the compressibility of the solvent and the polymers do not alter the form of the results.

The case where the v_i or the z_i values depend on composition is more difficult. In order to verify that our equations are still valid in this case, we have used a straightforward but inelegant method. Starting from equation (26) one determines the quantities $\overline{\Delta N_i \Delta N_j}$ and evaluates the inverse of the determinant for general term $\partial\mu_i/\partial N_k + v_j v_k/\beta V$. For large values of p its calculation is tedious and we have only been able to show that the denominator is the product of two terms, one depending only on the compressibility of the system, the other on the free energy of mixing. This result is identical to the result obtained in the special case where the z_i values are constant. In order to evaluate $\overline{\Delta N_T \Delta\phi_i}$ we use the relation:

$$\overline{\Delta N_T \Delta\phi_i} = \frac{\phi_i}{N_i v_o}\sum_{k=0}^{p} v_k \overline{\Delta N_k \Delta N_i} - \frac{\phi_i}{\sum N_i v_i}\sum_{i,j}\overline{\Delta N_i \Delta N_j} \tag{41}$$

relating $\overline{\Delta N_T \Delta\phi_i}$ to the $\overline{\Delta N_i \Delta N_j}$. This has been done in the case of a two component system (see Appendix) and a three component system. In both cases one finds $\overline{\Delta N_T \Delta\phi_i} = 0$. It seems therefore that the equation (37) is more general than expected and valid for any solution.

The generalized spinodal

If one writes the complete matrix of $p+1$ rows and $p+1$ columns one sees that its determinant is simply the product of the compressibility term by the determinant of the matrix $[\mathbf{H}]$. This means that, even in the case of a system where the v_i values depend on pressure and composition, the scattering can become infinite only if the compressibility diverges or if the mixture goes to a critical point, even if these two points are near one from the other.

The number of functions $S_{ij}(q)$

One can write, quite generally, the scattering intensity as a function of the scattering vector $\mathbf{q}$, $|\mathbf{q}| = q = (4\pi/\lambda)\sin(\theta/2)$ where λ is the wavelength of the incident beam and θ the observation angle:

$$I(q) = \sum_i \sum_k \bar{a}_i \bar{a}_k S_{ik}(q) \tag{43}$$

and it has been claimed[10] that, because $S_{ik} = S_{kj}$, one needs for $p+1$ constituents $p(p+1)/2$ functions $S_{ik}(q)$ in the general case and $p(p-1)/2$ in the case of an incompressible system[9]. In fact, this is correct, at least for $q = 0$, for the incompressible media but not for the general case where the exact number is, following equation (40), $1 + p(p-1)/2$. This result is only valid for $q = 0$. In order to show that this remark is not always true let us consider the case of a diblock copolymer dissolved in a solvent: at zero angle two partial scattering factors only are required to describe its scattering, at finite angle, one needs the use of the partial structure factors $P_a(q)$, $P_b(q)$, $P_{ab}(q)$ to describe the system and four partial structure factors are needed.

The influence of the scattering angle

Another interesting problem is the evaluation of the scattering function at any angle. It is evident that, unless one is near to a critical point, the density fluctuation term is independent of the modulus of the scattering vector $\mathbf{a}$. This means that the first term of equation (40) is correct for any value of $\mathbf{q}$. Recently Benoît, Benmouna and Wu[1] proposed, without taking compressibility into account, an equation identical to the second part of the right hand side of equation (40) the only difference being that the term x_{ii} of the matrix $[\mathbf{x}]$ was given by:

$$x_{ii} = \phi_i z_i P_i(q) \tag{44}$$

$P_i(q)$ being the form factor of the molecules of the species i. A simple generalization of equation (40) is therefore obvious: it suffices to use for the x_{ii} the definition of equation (44) instead of the value $x_{ii} = z_i\phi_i$. One knows that the method used in reference 1 gives results identical to those obtained first by de Gennes[10] using a method which he called the random phase approximation. In this method it is assumed that the medium is incompressible but, because the same results can be obtained without making this hypothesis, one can conclude that the result is independent of this hypothesis.

Generalization to copolymers

Equation (40) was generalized to the case of copolymers by introducing in the matrix $[\mathbf{x}]$ cross-terms of the form:

$$x_{ik} = \Phi_c z_o u_i u_k P_{ik}(q) \qquad (45)$$

where Φ_c is the volume fraction of the copolymer with degree of polymerization z_c and volume fractions u_i and u_k of the species i and k in the copolymer molecule. Because these terms do not modify the zero angle result they can be introduced safely and allow one to write a general equation valid for every kind of mixture by generalization of the matrix [x]. Before closing this discussion it is important to realize that some of the conclusions which have been developed in these last paragraphs could be found to be incorrect in some special cases. They have to be used cautiously.

Up to now we have used volumes and volume fractions instead of masses which are always used by experimentalists. For instance we use the degree of polymerization z which depends on the solvent and on the nature of the other polymers in the case of a mixture of polymers and this is not an experimental quantity. In this last section we would like to use a more accessible language which expresses, as much as possible, these results in terms of experimentally available quantities in both cases: neutron and light scattering.

APPLICATION TO NEUTRON SCATTERING

As an example of the application of this formula let us consider the case of a binary mixture. Formula (34) becomes, if one uses $1/V\,\mathrm{d}\Sigma/\delta\Omega$, the differential cross-section per unit volume:

$$\frac{1}{V}\frac{\mathrm{d}\Sigma}{\delta\Omega} = \frac{\overline{\Delta P^2}}{V} = \left(\frac{\bar{a}}{v_o}\right)^2 kT\beta + \left[\frac{\bar{a}_i}{v_o}\right]^2 \frac{kTv_0}{\dfrac{\partial^2 g}{\partial\phi^2}} \qquad (46)$$

One sees first that the quantities a and $\bar{a}_1$ enter the formula through their ratio to the volume v_0. This leads, using equation (8), to

$$\begin{aligned} \bar{a}/v_0 &= a_0/v_0 + \phi_1(a_1/v_1 - a_0/v_0) \\ \bar{a}_1/v_0 &= a_1/v_1 - a_0/v_0 \end{aligned} \qquad (47)$$

where v_0 and v_1 are respectively the partial volumes of the solvent and of the solute respectively. If one knows the specific masses, ρ_0 and ρ_1, and the molecular masses, m_0 and m_1, one has:

$$\begin{aligned} \bar{a}/v_0 &= \phi_0\rho_0 a_0/m_0 + \phi_1\rho_1 a_1/m_1 \\ \bar{a}_1/v_0 &= \rho_1 a_1/m_1 - \rho_0 a_0/m_0 \end{aligned} \qquad (48)$$

calling ϕ_0 the volume fraction occupied by the solvent. Because for a polymer the quantity a_1/m_1 does not depend on the degree of polymerization one can take for a_1 and m_1 the values corresponding to the real monomer. If we assume that the system obeys Flory's law for its chemical potential, the scattering intensity will be:

$$\frac{1}{V}\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega} = \left(\phi_0\frac{\rho_0 a_0}{m_0} + \phi_1\frac{\rho_1 a_1}{m_1}\right)^2 kT\beta + \left(\frac{\bar{a}_1}{v_0}\right)^2 \frac{v_0}{\dfrac{1}{z\phi} + \dfrac{1}{(1-\phi)} - 2\chi} \qquad (49)$$

All the quantities (except z and χ) are experimentally available. At infinite dilution the second term of the scattering intensity takes the form:

$$\left(\frac{\rho_1 a_1}{m_1} - \frac{\rho_0 a_0}{m_0}\right)^2 z v_0 \phi = \left[\frac{a_1}{m_1} - \frac{\rho_0}{\rho_1}\frac{a_0}{m_0}\right]^2 \frac{M_1}{N} c_1 \qquad (50)$$

which is the well known form of the result if one calls M_1 the molecular weight of the solute, c_1 its concentration and N the Avogadro's number. Because v_0 and v_1 are partial quantities, ρ_1 and ρ_0 depend on concentration and should be measured carefully if one needs a great precision.

If, in the general case, one wishes to express all the terms of equation (49) as function of masses instead of volumes one writes $c = \rho_1\phi_1$ and $z_1 = M_1\rho_0/M_0\rho_1$, calling M_0 and M_1 respectively the molecular weight of the solvent and the solute. The generalization to many constituents is obvious.

THE CASE OF LIGHT SCATTERING

The case of light scattering is very similar to the case of neutrons but there are two difficulties related to the nature of the interactions between light and matter: first, one has to subtract from the total intensity the contribution of the fluctuations in orientation. This is well known[11] and formulas allowing the subtraction, from the total scattering, of the anisotropic < contribution have been developed a long time ago[11]. We shall therefore assume that this has been done or that the system has no orientation fluctuations.

The second difficulty comes from the fact that the values of a are no longer intrinsic properties of matter but are thermodynamic quantities related to the dielectric susceptibility ε or the index of refraction n of the system. If one writes the fundamental equation of electrostatic (in c.g.s. units)

$$\frac{\varepsilon - 1}{4\pi} = \frac{P}{E} \qquad (51)$$

one sees that the quantity p, defined in equation (9) is identical to p/E ($\bar{p} = P/E$). Because this quantity is an homogeneous function of the N_i, one can use equation (2). By differentiation, after replacing ε by the square of the index of refraction n one finds:

$$\frac{\bar{a}_i}{v_0} = \frac{n}{2\pi}\frac{\partial n}{\partial\phi_i} \qquad (52)$$

remembering that the $\bar{a}_i$ values are partial molar quantities. This shows that the $\bar{a}_i/v_0$ are well defined experimental quantities and are easy to measure. With these notations we shall now write the Rayleigh constant R of the system for unpolarized light (and isotropic molecules) at $q = 0$. One knows that:

$$R(o) = \frac{16\pi^4}{\lambda^4}\frac{1}{V}\overline{\Delta P^2} \qquad (53)$$

λ being the wavelength, *in vacuo*, of the incident beam. This expression can be divided in two terms which will be called R_d and R_ϕ and correspond to the density and composition fluctuations respectively.

The compressibility term R_d

Using the expressions of the first term of $\overline{\Delta P^2}$ defined in equation (34), one obtains for its first term, assuming following Coumou[12] that $\bar{a}$ does not depend on pressure:

$$\frac{1}{4\pi}\frac{\partial\varepsilon}{\partial p}=\frac{n}{2\pi}\frac{\partial n}{\partial p}=\bar{a}\left\{-\frac{\partial(1/v_o)}{\partial p}\right\}=\frac{\bar{a}}{v_o}\beta$$

or (54)

$$\frac{\bar{a}}{v_o}=\frac{n}{2\pi}\frac{\partial n}{\partial p}\frac{v_0}{\beta}$$

and using equation (40)

$$R_{\mathrm{d}}(o)=\frac{16\pi^4}{\lambda^4}\frac{1}{V}\frac{\bar{a}^2}{v_o^2}\overline{\Delta V^2}=\frac{4\pi^2 n^2 kT}{\lambda^4\beta}\left(\frac{\partial n}{\partial p}\right)^2 \tag{55}$$

where R_{d} is the part of the Rayleigh ratio due to the density fluctuations at $q=0$. (For $q\neq 0$ one has to multiply this result by the factor $((1+\cos^2\theta)/2)$ in the case of natural light. This is a classical expression for the scattering by a pure liquid. It assumes that the quantity $\bar{a}$ does not depend on pressure; this is questionable[10] but we do not want to enter into this discussion here.

The composition fluctuations term

Using equations (44) and (51) one writes immediately:

$$R_\phi(0)=\frac{4\pi^2}{\lambda^4}n^2\left(\frac{\partial n}{\partial\phi}\right)^2\frac{kTv_0}{\partial^2 g/\partial\phi^2} \tag{56}$$

calling R_ϕ the contribution to the Rayleigh ratio of the composition fluctuations at $q=0$.

One can also write this expression using the variables c and M_1 using the following transformations:

$$\frac{\partial n}{\partial\phi}=\frac{\partial n}{\partial(c/\rho_1)}=\rho_1\frac{\partial n}{\partial c} \tag{57}$$

$$\frac{\partial^2 g}{\partial\phi^2}=\rho_1^2\frac{\partial^2 g}{\partial c^2} \tag{58}$$

One uses also the Gibbs–Duhem relation to express $\partial^2 g/\partial\phi^2$ as function of $\partial\mu_0/\partial c$.

$$\frac{\partial^2 g}{\partial\phi^2}=\frac{\partial\bar{\mu}_1}{\partial\phi}=\frac{1}{z_1}\frac{\partial\mu_1}{\partial\phi}-\frac{\partial\mu_0}{\partial\phi}=\frac{-1}{\phi}\frac{\partial\mu_0}{\partial\phi}=\frac{-\rho_1^2}{c}\frac{\partial\mu_0}{\partial c} \tag{59}$$

Writing equation (54) as function of c one obtains:

$$R_\phi(0)=\frac{4\pi^2}{\lambda^4}n^2\left(\frac{\partial n^2}{\partial c}\right)^2\frac{kTv_0}{\partial^2 g/\partial c^2} \tag{60}$$

$$R_\phi=\frac{4\pi^2}{\lambda^4}n^2\left(\frac{\partial n}{\partial c}\right)^2\frac{kTv_0 c}{-(\partial\mu_0/\partial c)} \tag{61}$$

or, introducing the osmotic pressure $\bar{\omega}$ defined by:

$$\bar{\omega}vo=-(\mu_o-\mu_0^0) \tag{62}$$

$$R_\phi(q)=\frac{2\pi^2}{\lambda^4}n^2\left(\frac{\partial n^2}{\partial c}\right)^2\frac{kTc}{\partial\bar{\omega}/\partial c}(1+\cos^2\theta) \tag{63}$$

which is the classical formulation of the result for molecules with a form factor equal to unity.

CONCLUSIONS

All treatments, in which it is supposed that the system is incompressible, can be generalized to compressible media. One simply adds to the calculated value a second term which is the contribution of the density fluctuations of a medium of the same average density of coherent scattering length (or index of refraction) and the same compressibility. The variables we have used are natural variables; they allow a very simple derivation of the thermodynamic expressions for density and composition fluctuations. This should allow experimentalists to write correct formulas, especially when they use scattering experiments for the determination of thermodynamic quantities on low molecular weight substances[13,14].

In this paper we did not mention the effect of polydispersity which has been discussed extensively in reference 1. One has just to modify the definitions of the coefficient of the matrix [x] to take care of it.

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APPENDIX

Demonstration of equation (20)

From the theory of functions with more than one variable one writes:

$$\left(\frac{\partial\mu_i}{\partial N_k}\right)_{p,N}=\left(\frac{\partial\mu_i}{\partial N_k}\right)_{v,N}+\left(\frac{\partial\mu_i}{\partial p}\right)_N\left(\frac{\partial n}{\partial N_k}\right)_{v,N_m} \tag{A1}$$

where the index N_m means that all the N_i for $i\neq k$ are constant. Because one assumes that μ_i is taken at p constant one can write:

$$\mu_i=\left(\frac{\partial G}{\partial N_i}\right)_{N_{k,p}} \tag{A2}$$

Taking the derivative of $(\partial\mu_i/\partial p)_N$ with respect to p one can, changing the order of differentiation write:

$$\left(\frac{\partial\mu_i}{\partial p}\right)_N=\frac{\partial^2 G}{\partial p\partial N_i}=\left(\frac{\partial V}{\partial N_i}\right)_{N_m}=v_i \tag{A3}$$

since $\partial G/\partial p=V$. In order to evaluate the quantity

$(\partial p/\partial N_k)_{v,N}$ one writes:

$$\mathrm{d}V=\left(\frac{\partial V}{\partial N_k}\right)_p \mathrm{d}N_k+\left(\frac{\partial V}{\partial p}\right)_{N_k}\mathrm{d}p \tag{A4}$$

and this gives at constant volume ($\mathrm{d}V=0$):

$$\left(\frac{\partial p}{\partial N_k}\right)_v=-\frac{(\partial V/\partial N_k)_p}{(\partial V/\partial p)_{N_k}}=\frac{v_k}{\beta V} \tag{A5}$$

where v_k is the partial molar volume of component k and β the isothermal compressibility $(-1\partial v/v\partial p)$. Putting this value in equation (1A) one obtains the desired result, i.e.:

$$\left(\frac{\partial \mu_i}{\partial N_k}\right)_{v,N}=\left(\frac{\partial \mu_i}{\partial N_k}\right)_{p,N}+\frac{v_i v_k}{\beta V} \tag{A6}$$

The case of a two component system treated using the variables N_0, N_1

The matrix [**H**], after using equation (8) to transform the derivatives at constant V into derivatives at constant p, becomes:

$$[\mathbf{H}]=\begin{pmatrix}\left(\frac{\partial \mu_0}{\partial N_0}\right)_p+\frac{v_0^2}{\beta V^2} & \left(\frac{\partial \mu_0}{\partial N_1}\right)_p+\frac{v_1 v_0}{\beta V^2}\\ \left(\frac{\partial \mu_0}{\partial N_1}\right)_p+\frac{v_1 v_0}{\beta V^2} & \left(\frac{\partial \mu_1}{\partial N_1}\right)_p+\frac{v_1^2}{\beta V^2}\end{pmatrix} \tag{A7}$$

The determinant of this matrix can be evaluated easily using the Gibbs–Duhem relation:

$$N_0\frac{\partial \mu_0}{\partial N_i}+N_1\frac{\partial \mu_1}{\partial N_i}=0 \quad (i=0 \text{ or } 1) \tag{A8}$$

which enables one to express all the partial derivatives as function of one of them. One finds:

$$\mathrm{Det}=-\left(\frac{\partial \mu_0}{\partial N_1}\right)_p\frac{V}{\beta N_0 N_1} \tag{A9}$$

The cofactors are also easy to determine and one finds:

$$\frac{\overline{\Delta N_0^2}}{kT}=\frac{\beta N_0^2}{V}-\frac{N_0N_1v_1^2}{V^2}\left(\frac{\partial \mu_0}{\partial N_1}\right)^{-1} \tag{A10}$$

$$\frac{\overline{\Delta N_0\Delta N_1}}{kT}=\frac{\beta N_0N_1}{V}+\frac{N_0N_{1y}v_0v_1}{V^2}\left(\frac{\partial \mu_0}{\partial N_1}\right)^{-1} \tag{A11}$$

$$\frac{\overline{\Delta N_1^2}}{kT}=\frac{\beta N_1^2}{V}-\frac{N_0N_1v_0^2}{V^2}\left(\frac{\partial \mu_0}{\partial N_1}\right)^{-1} \tag{A12}$$

If one uses these variables one obtains, after rearrangement the following expression for $\overline{\Delta P^2}$.

$$\overline{\Delta P^2}=(a_0N_0+a_1N_1)^2\frac{kT\beta}{V}-\frac{N_0N_1(a_1v_0-a_0v_1)^2}{V^2}kT\left(\frac{\partial \mu_0}{\partial N_1}\right)_{N_2}^{-1} \tag{A13}$$

this expression is identical to equation (37) simplified for the case of two components because the quantity $(a_0N_0+a_1N_1)$ is equal to

$$(a_0N_0+a_1N_1)=N_T(a_0+\phi\bar{a}_1)=N_T\bar{a} \tag{A14}$$

and one knows that $(\partial\mu_0/\partial N_1)_{N_0}$ and $(\partial\mu_0/\partial\phi)$ obey the relation:

$$\left(\frac{\partial \mu_0}{\partial N_1}\right)_{N_0}=\left(\frac{\partial \mu_0}{\partial \phi}\right)\frac{\mathrm{d}\phi}{\mathrm{d}N_1}=\left(\frac{\partial \mu_0}{\partial \phi}\right)\frac{\phi(1-\phi)}{N_1} \tag{A15}$$

and that the quantity $a_1v_0-a_0v_1$ is given by:

$$a_1v_0-a_0v_1=v_1\left(a_1\frac{v_0}{v_1}-a_0\right)=v_1\bar{a}_1 \tag{A16}$$

One can also recover equation (32) writing the expressions of $\overline{\Delta N_\mathrm{T}^2}$, $\overline{\Delta N_\mathrm{T}\Delta\phi}$ and $\overline{\Delta\phi^2}$ as function of $\overline{\Delta N_0^2}$, $\overline{\Delta N_1^2}$ and $\overline{\Delta N_0\Delta N_1}$ because:

$$\Delta N_T=\Delta N_0+z_1\Delta N_1$$

$$\Delta\phi=\Delta\left(\frac{z_1N_1}{N_0+z_1N_1}\right)=\frac{1}{N_T}[z_1\Delta N_1-\phi(\Delta N_0+z_1\Delta N_1)] \tag{A17}$$

The calculation is tedious but straightforward. It is important to note that in this treatment we never made any differentiation of expressions containing z, except in the final statement in which we announce that formula (A13) is identical to equation (44) where we should introduce the derivative of z with respect to the composition. This means that, even if the ratio $z_i=v_i/v_0$ depends on pressure, equation (37) is correct in spite of being derived with z constant. This result which has been established in detail for a two component system can be extended to any number of constituents and should be used by experimentalists.