Some Remarks on the Scattering by Compressible Polymer Solutions and Blends

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Introduction. During the past few years many papers have been devoted to the scattering by polymer solutions and blends that try to take into account the compressibility of the system. This is motivated by the fact that, if one uses the theory of incompressible mixtures to explain scattering experiments, one obtains in some cases for the Flory[1] χ parameter values that are inconsistent with those obtained by other techniques. Since in his demonstration of the random phase approximation (RPA) de Gennes[2] assumes that the system is incompressible, it is tempting to attribute these discrepancies to the finite compressibility. The question that remains open is whether we have a theory that can explain the scattering by a multicomponent system at any angle or wave vector without making any assumption about its compressibility.

One can always[3] express the intensity scattered at zero scattering vector $I(0)$ in terms of the fluctuations of the quantity $\mathbf{P}$:

$$I(0) = \langle \delta \mathbf{P}^2 \rangle = \langle \delta \{ \sum_{i=1}^{p} n_i a_i \}^2 \rangle$$
$$I(0) = \sum_{i=1}^{p} \sum_{j=1}^{p} a_i a_j \langle \delta n_i \delta n_j \rangle \qquad (1)$$

where $I(0)$ is the intensity scattered at zero angle, n_i is the number of molecules of species i, and δn_i is the fluctuation of this number. $\mathbf{P} = \sum_{i=1}^{p} n_i a_i$ is what, for light scattering, would be the polarizability of the system but would have a different meaning for neutron or X-ray scattering. The double sum is extended to all the pairs of p molecular species and the brackets $\langle ... \rangle$ indicate a thermodynamical ensemble average.

We define partial structure factors by the relation

$$S_{ij}(q) = \frac{a_i a_j}{V} \sum_{i=1}^{p} \sum_{j=1}^{p} \langle \delta n_i(0)\ \delta n_j(r) \rangle \exp(-i \mathbf{q} \cdot \mathbf{r}) 4\pi r^2\ \mathrm{d}r \qquad (2)$$

where $\mathbf{q}$ is the scattering vector of modulus $(4\pi/\lambda)\sin(\theta/2)$, λ being the wavelength of the beam and θ the observation angle.

Equation 1 can also be written in matrix form:

$$I(0) = V[\mathbf{a}_i][\mathbf{S}_{ij}(0)][\mathbf{a}_j]^{\mathrm{T}} \qquad (3)$$

where $[\mathbf{a}_i]$ is a column vector, $[\mathbf{a}_j]^{\mathrm{T}}$ is its transpose, and $[\mathbf{S}_{ij}(0)]$ is the square matrix of the partial structure factors at $q = 0$.

Scattering at Zero Wave Vector, the Thermodynamic Limit. This will be a summary since this problem has already been solved by many authors.[4−8] Hill[7] has shown that the use of the grand canonical ensemble (at constant volume and temperature) allows us to write for $\mathbf{S}_{ij}(0)$ the following expression:

$$\mathbf{S}_{ij}(0) = \frac{1}{V} \langle \delta n_i \delta n_j \rangle_{T,n_{k \neq i \neq j}} = \frac{k_{\mathrm{B}} T}{V} \left(\frac{\partial n_i}{\partial \mu_j} \right)_{T,V,n_k} \qquad (4)$$

where k_{B} is the Boltzmann constant, T is the absolute temperature, and μ_i is the chemical potential of the species i, made of n_i molecules having as partial volume v_i, with $v_i = (\partial V/\partial n_i)_{T,p,n_k}$. The derivatives are taken at constant T, V, and n_k (with k different from i and j). From its definition, it is obvious that this matrix is symmetrical $\mathbf{S}_{ij}(0) = \mathbf{S}_{ji}(0)$ and that there are $p(p + 1)/2$ unknowns. But we also know that the quantities $(\partial n_i/\partial \mu_j)_{T,V,n_k}$ are not independent, since they are connected by Gibbs−Duhem relations. At constant $\mathbf{p}$ and T these relations give p equations relating the partial derivatives which means that the $p(p + 1)/2$ unknown functions are reduced to $p(p - 1)/2$. This relation is always used for incompressible systems. In the case of compressible systems one has, as we shall see later, to introduce an extra function, the compressibility, and the final result will be, as predicted, $[p(p - 1)/2] + 1$ independent $\mathbf{S}_{ij}(q = 0)$ functions.

What we intend to show is that it is always possible to write an expression for $I(0)$ depending only on $p(p - 1)/2 + 1$ unknown structure factors extending it later to any q. This has been obtained already by many authors, and we shall limit ourselves to the explanation of the principle of the method. In the Appendix we shall give the complete derivation in the simple case of two constituents.

Since the experimental meaning of the quantity $(\partial n_i/\partial \mu_j)_{T,V,n_k}$ is not very clear, it is more convenient to use the inverse function, $(\partial \mu_i / \partial n_j)_{T,\mathbf{p},n_k}$, which is obtained by taking the inverse of the matrix $\mathbf{S}_{ij}$ and by replacing one derivative by another following the well-known equation

$$\left(\frac{\partial \mu_i}{\partial n_j} \right)_{T,v,n_k} = \left(\frac{\partial \mu_i}{\partial n_j} \right)_{T,\mathbf{p},n_k} + \frac{v_i v_j}{\chi_T V} \qquad (5)$$

where v_i and v_j are the partial molecular volumes and the quantity χ_T is the isothermal compressibility $(-\mathrm{d} \ln V/\mathrm{d}\mathbf{p})_T$.

Without entering into details, one can simplify the presentation by introducing the quantity $(\partial^2 g_c/\partial \varphi_i \partial \varphi_j)_{T,\mathbf{p},n_k}$, where g_c is the free energy of mixing for a volume equal to the volume of one molecule (or a lattice cell, if you think in terms of a lattice) and φ_i is the volume fraction occupied by the species i in the mixture, i.e. the quantity $\phi_i = n_i v_i / \sum_{i=0}^{p-1} n_j v_j$, calling respectively n_i and v_i the number of molecules and the partial molecular volume of species i. We use as variables the total volume V and the φ_i's. We give also the index 0 to one species, which will be called the solvent. Inverting the matrix to write the coefficients $\partial \mu_j/\partial n_i$ instead of the $\partial n_i / \partial \mu_j$ one obtains, after some calculations which will not be presented here, the classical result:[9]

$$\frac{I(q{=}0)}{V} = \bar{a}^2 k_{\mathrm{B}} \mathrm{T} \chi_T + \frac{k_{\mathrm{B}} \mathrm{T}}{v_0} [\bar{a}_i] \left[\frac{\partial^2 g_{\mathrm{c}}}{\partial \varphi_i \partial \varphi_j} \right]^{-1} [\bar{a}_i]^{\mathrm{T}} \qquad (6)$$

where $\bar{a}$ is the average value of the scattering length of the sample and $\bar{a}_i$ is the contrast factor of the species,

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which are defined by the relations

$$\bar{a} = \sum_{i=0}^{p} \varphi_i a_i = a_0 + \sum_{1}^{p-1} \bar{a}_i \varphi_i$$
$$\bar{a}_i = \frac{a_i v_0}{v_i} - a_0 \qquad (7)$$

remembering that the matrix is now made of $(p-1)\cdot(p-1)$ terms. The result is clear: the number of unknown functions is what was presented in the last paragraph. One can also rewrite eq 6 by taking into account eq 3 and one obtains

$$I(q{=}0) = \bar{a}^2\langle\delta V^2\rangle + V[\bar{a}_i][\langle\delta\varphi_i\delta\varphi_j\rangle][\bar{a}_i]^{\mathrm{T}} \qquad (8)$$

which demonstrates that we always have $\langle\delta V\delta\varphi_i\rangle = 0$. This is an important result since it has to be obeyed in all cases. There are no correlations between the fluctuations of the total volume and those of the volume fractions of the constituents. The second term is, in fact, the same at constant pressure or constant volume, and this shows that if one wants to take compressibility into account, one has just to add to the classical term obtained for an incompressible system a term which is the scattering one would obtain for an average system having the same compressibility χ_T and where all the components have the average scattering length $\bar{a}$ per unit volume. This is an important result, obtained without any hypothesis about the nature of the system, which has to be verified by any theory of scattering by compressible systems (see the Appendix for the complete derivation in the case of a two-component system).

Scattering at Finite Wave Vector. At a finite wave vector q, the problem is more difficult because it is no longer a pure thermodynamical problem. We show here how the random phase approximation method proposed by de Gennes[2] can lead to a generalization of the zero angle result to compressible systems.

We introduce the densities $\rho_i = n_i/V$ instead of φ_i to avoid difficulties related to the possible changes of volume. The intensity scattered by a constant volume V is expressed, after changing slightly the conventions of the first part, as a function of the Fourier transforms of the density fluctuations $\delta\hat{\rho}_i(q)$ as

$$I(q) = \langle[\sum_i a_i\delta\hat{\rho}_i(q)]^2\rangle \qquad (9)$$

where the sign ^ indicates that we take the Fourier transform with respect to the distances r.

This gives for the partial structure factors $\mathrm{S}_{ij}(q)$

$$VS_{ij}(q) = \langle\delta\hat{\rho}_i(q)\ \delta\hat{\rho}_j(q)\rangle$$

The generalized compressibility of the system[12] at a finite wave vector q is directly related to the inverse of the density correlation matrix $\mathbf{S}_{ij}^{-1}$.

$$1/\hat{\chi}_T(q) = k_{\mathrm{B}}T\sum_{i,j}\mathbf{S}_{ij}^{-1}(q)\rho_i\rho_j \qquad (10)$$

We shall limit our discussion to the simple case of two constituents, leaving the general case till later.

As in the thermodynamic limit, the compressibility is the response function of the pressure due to a change of the total density at constant composition $\rho = \rho_2 + \rho_1$. We define $\chi_{T(q=0)}$ as the isothermal compressibility of the liquid mixture. The quantities $v_1 = \partial V/\partial n_1$ and $v_2 = \partial V/\partial n_2$ are the partial volumes at constant composition of the mixture in the limit of zero wave vector. The relation $\rho_1 v_1 + \rho_2 v_2 = 1$ is always valid.

In order to generalize the expression of the scattered intensity of eq 6 to finite wave vectors, we shall use, following Landau and Lifshitz,[10] as independent variables, instead of the two densities ρ_1 and ρ_2, the pressure $\mathbf{p}$ and the composition x of the system, which is not a volume fraction and is defined by $x = \rho_1/(\rho_1 + \rho_2) = n_1/(n_1 + n_2)$. Thus

$$\delta x = \frac{\rho_2\delta\rho_1 - \rho_1\delta\rho_2}{(\rho_1 + \rho_2)^2} \qquad (11)$$

The pressure fluctuation is related, at constant temperature, to the chemical potential fluctuations by the Gibbs–Duhem equation:

$$\delta\hat{\mathbf{p}} = \sum_i \rho_i\delta\hat{\mu}_i \qquad (12)$$

Using linear response theory,[2,12] which is the basis of the random phase approximation, the local fluctuations of the chemical potentials are written as

$$\delta\hat{\mu}_j(q) = k_{\mathrm{B}}T\sum_i \mathbf{S}_{ij}^{-1}(q)\ \delta\hat{\rho}_i(\mathrm{q}) \qquad (13)$$

where $\hat{\mu}_j(q)$ is the Fourier transform of the r-dependent chemical potential. One can then directly check that the two variables, pressure and composition, are not correlated and that at any wave vector $\langle\delta\hat{\mathbf{p}}(q)\ \delta\hat{x}(q)\rangle = 0$.

For this purpose it suffices to express the quantities $\delta\hat{P}(q)$ and $\delta\hat{x}(q)$ by utilizing eqs 11–13, to take their product, and to take its average value. One reaches immediately the conclusion that $\langle\delta\hat{x}\delta\hat{P}\rangle = 0$ regardless of the value of q. The scattered intensity can thus be written as in eq 6 as the sum of two terms, one proportional to the fluctuations of pressure and the other expressing the fluctuations of composition.

In a certain way this result is sufficient to prove what we wanted to show, i.e., that the scattering can always be written, by a correct choice of the variables, as the sum of two terms, one proportional to the fluctuations of pressure and the other one expressing the fluctuations of composition, a result already obtained by Benoît *et al.*[12] and Akcasu *et al.*,[13] who evaluated the scattering by RPA in the case of static scattering.

In order to have a complete formula, one has now to evaluate the quantities $\langle\delta\mathbf{p}^2\rangle$ and $\langle\delta x^2\rangle$. This can be done by the same method using eqs 11–13, and we give to the final result the form

$$I(q) = (\rho_1 a_1 + \rho_2 a_2)^2(\hat{\chi}_T)^2\langle\delta\hat{\mathbf{p}}(q)^2\rangle + \left[\frac{\rho_1\rho_2}{x(1-x)}\right]^2[a_1\hat{v}_2(q) - a_2\hat{v}_1(q)]^2\langle\delta\hat{x}(q)^2\rangle \qquad (14)$$

The pressure fluctuations can now be directly calculated by writing $[\delta\hat{\mathbf{p}}(q)^2\rangle = k_{\mathrm{B}}TV/\hat{\chi}_T(q)$. This allows us to write the scattered intensity in a form very similar to eq 6 or 8:

$$I(q) = (n_1a_1 + n_2a_2)_2k_{\mathrm{B}}T\hat{\chi}_T(q)/V + V\left[\frac{\rho_1\rho_2}{x(1-x)}\right]^2[a_2\hat{v}_1(q) - a_1\hat{v}_2(q)]^2S_{xx}(q) \qquad (15)$$

calling S_{xx} the partial structure factor obtained when one uses as a variable the composition x. If, instead of x, one uses the variable φ, one sees that, if φ does not depend on x, $\langle\delta\varphi(q)^2\rangle \approx \langle\delta x(q)^2\rangle$. This result is similar to a result obtained by Benoît, Benmouna, and Wu,[12] who evaluated the scattering by RPA without making any hypothesis about the compressibility of the system.

The only difficulty is the significance of the parameters $\hat{v}_1$ and $\hat{v}_2$ which, if one assumes that the ratio $\hat{v}_1/\hat{v}_2$ does not depend on **p**, take the form

$$\hat{v}_2(q) = [\rho_2 S_{11}(q) - \rho_1 S_{12}(q)]/[\rho_2{}^2 S_{11} + \rho_1{}^2 S_{22} - 2\rho_2\rho_1 S_{12}]$$

$$\hat{v}_1(q) = [\rho_1 S_{22}(q) - \rho_2 S_{12}(q)]/[\rho_2{}^2 S_{11} + \rho_1{}^2 S_{22} - 2\rho_2\rho_1 S_{12}] \quad (16)$$

or more simply

$$\hat{v}_2(q) = \frac{\rho_2 S_{22}{}^{-1} + \rho_1 S_{12}{}^{-1}}{S_{11}S_{22} - S_{12}{}^2}\hat{\chi}_T(q)$$

$$\hat{v}_1(q) = \frac{\rho_1 S_{11}{}^{-1} + \rho_2 S_{12}{}^{-1}}{S_{11}S_{22} - S_{12}{}^2}\hat{\chi}_T(q) \quad (17)$$

Both expressions reduce at $q = 0$ to the usual definitions $v_i = \partial V/\partial n_i = \partial\mu_i/\partial\mathbf{p}$ and this confirms the identity at $q = 0$ of eqs 14 and 6.

It is rather surprising to find such a q dependence of the partial volume of the constituents but, in fact, this effect must be very small and we are not sure that it could be detected in the classical conditions of neutron scattering by polymer mixtures or solutions.

Many experiments have been done on systems treated as incompressible, and people have seemed to detect a q dependence of χ. We know only two cases where this possibility has been envisaged: the first one is in the study of a polymer mixture next to the phase separation where scattering curves could not be interpreted without having values of χ depending of q.[14] The second is in a study by Hashimoto's[15] group where they explain the scattering around the glass transition by a q dependence of χ.

We have considered here only a system made of two components, but it is evident that the extrapolation of these results to systems with an arbitrary number of constituents should be straightforward, and we confirm that, regardless of the number of constituents, pressure and composition fluctuations are not coupled.

Discussion. In recent years a model which we shall call the void model was introduced in order to close the gap between the interpretation of the scattering by incompressible and compressible systems.[16-18] It was hoped that this model could explain the differences observed between the thermodynamic and the neutron scattering determination of the Flory χ.

We do not want here to enter into the details of these analyses but we just want to remember what are the conditions required by any model in order to be a possible candidate for the explanation of the results. The main condition is that the independence between pressure and composition fluctuations has to be respected because it is a general thermodynamical result. This means that, for a two-component system, the results have to be explained by two and only two independent partial structure factors, and that, in the general case, one needs no more than $p(p - 1)/2 + 1$ independent structure factors.

This seems not to be the case in the theories based on the void model, which means that these models are not complete and have to be improved. It is actually a challenge to understand why, at least in its actual state, the void model cannot be used without violating Hill's results. One idea is that a vacuum (or voids) cannot be treated as a thermodynamic constituent; its entropy of mixing is impossible to evaluate and it is difficult to apply the Gibbs–Duhem equation to a component with an unknown number of particles.

This discrepancy between thermodynamics and the void model has been already observed by Hammouda[18-20] who offers no reason for it. Taylor *et al.*[21] have also discussed this problem and confirm that, for their experiments, the correction due to the compressibility is so small that it is hardly larger than the noise and practically undetectable. This makes it impossible or very difficult to check experimentally the validity of one or the other point of view, but due to its simplicity and rigor, we are sure that Hill's results are correct.

Conclusion. As a conclusion we would like to ask people working in this field to verify if they can separate the effect of compressibility from the effect of composition fluctuations not only at $q = 0$ but also in the whole range of q values. If they are successful, this would simplify considerably the theoretical tools proposed to interpret these data.

Appendix: **Results for $q = 0$ When the Number of Constituents Is Equal to 2 ($p = 2$).** In order to show how eq can be obtained rigorously, we give the details of the calculation for $p = 2$. In this case eq 3 becomes

$$\frac{I(0)}{V} = \frac{k_{\mathrm{B}}T}{VD}\begin{bmatrix} a_1 \\ a_2 \end{bmatrix}\begin{Bmatrix} \dfrac{\partial\mu_2}{\partial n_2} & -\dfrac{\partial\mu_1}{\partial n_2} \\ -\dfrac{\partial\mu_2}{\partial n_1} & \dfrac{\partial\mu_1}{\partial n_1} \end{Bmatrix}[a_1 \quad a_2] \quad (A.1)$$

where

$$D = \frac{\partial\mu_1}{\partial n_1}\frac{\partial\mu_2}{\partial n_2} - \left(\frac{\partial\mu_1}{\partial n_2}\right)^2$$

and where the differentiations are made at constant V, T, and n_i.

In order to replace the variables **p** and T by V and T, we use the classical thermodynamic relation:

$$\left.\frac{\partial\mu_i}{\partial n_j}\right)_{V,T} = \left.\frac{\partial\mu_i}{\partial n_j}\right)_{p;T} - \frac{v_i v_j}{V\chi_T} \quad (A.2)$$

Using eq 4, one obtains after evaluation of the determinant and straightforward application of the Gibbs–Duhem relation

$$S_{11}(0) = \frac{\chi_T n_2{}^2}{V} - \frac{n_2 n_1 v_1{}^2}{V^2}\left(\frac{\partial\mu_2}{\partial n_1}\right)^{-1}$$

$$S_{21}(0) = \frac{\chi_T n_2 n_1}{V} + \frac{n_2 n_1 v_2 v_1}{V^2}\left(\frac{\partial\mu_2}{\partial n_1}\right)^{-1}$$

$$S_{11}(0) = \frac{\chi_T n_1{}^2}{V} - \frac{n_2 n_1 v_2{}^2}{V^2}\left(\frac{\partial\mu_2}{\partial n_1}\right)^{-1} \quad (A.3)$$

and

$$I(q{=}0) = (a_2n_2 + a_1n_1)^2\frac{k_BT\chi_T}{V} - \frac{n_2n_1(a_1v_2 - a_2v_1)^2}{V^2}k_BT\left(\frac{\partial\mu_2}{\partial n_1}\right)_{p,T}^{-1} \quad (A.4)$$

which is nothing but eq 6 written for a two-component system.

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