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Static Scattering from Multicomponent Polymer and Copolymer Systems

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ABSTRACT: Mathematical expressions for the scattering intensity of polymer solutions and of polymer blends are reviewed from both thermodynamic and mean-field points of view. A simple and general equation has been obtained that is equivalent to the classical Zimm equation. If one introduces the matrix [**S**] of the partial structure factors S_{ij}, the matrix [**x**] of the form factors and concentrations, and the matrix [**v**] of the excluded volume parameters one can write quite generally $[\mathbf{S}]^{-1} = [\mathbf{x}]^{-1} + [\mathbf{v}]$. This expression is valid for solutions of any copolymer and homopolymer mixtures, regardless of their structures, and can be easily transformed into expressions valid for polymer and copolymer blends. As an example, a formula has been developed (with the help of a computer program) for systems of polymers and copolymers containing three different types of monomers. This method allows us easily to obtain previous results and to predict new experimental possibilities.

Introduction

In recent years there has been extensive use of the random phase approximation (RPA) for studying various mixtures of homopolymers and copolymers in solution and in bulk.[1-5] These theories have been used to interpret results obtained by neutron scattering on mixtures of homopolymers and copolymers[2,6] in bulk and by light scattering on mixtures of homopolymers in solution.[7] The purpose of the present paper is to show that regardless of the number of constituents, it is possible to derive a general formula giving the scattered intensity at any angle θ or value of the parameter q $(=(4\pi/\lambda)\sin(\theta/2)$, where λ is the wavelength of the incident radiation). At $q = 0$, one recovers the classical results of the thermodynamics of multicomponent systems. In order to obtain these results we shall use the Ornstein-Zernike theory, which is equivalent to the RPA developed initially by de Gennes[8] or the method used by Olvera de la Cruz and Sanchez.[9] It should be pointed out that this theory, using a "mean-field" approximation, is unable to give a rigorous descripton of the scattering intensity when fluctuations are important. The theory, with the aforementioned restriction, is very useful for the interpretation of scattering data by experimentalists. More precise theories are certainly needed, but the present results will be kept as a basis for semiquantitative interpretation, just as the theory of regular solutions is very helpful to understand real solutions. In the first part of this paper, the results of the classical statistical theory of scattering by an incompressible multicomponent system at zero scattering angle ($q = 0$) will be briefly summarized and rewritten, in the frame of the classical Flory-Huggins theory, in a matrix form that is a generalization of the Einstein equation. In the second and the third parts, this matrix formulation will be extended to the case of polymer and copolymer solutions by using the Ornstein-Zernike equation. This shows that the scattering intensity can be written for any value of q and concentration in a compact form that corresponds to the matrix formulation of the Zimm equation. The results can be extended easily to polymers and copolymers in bulk. The last sections will be devoted to the study of the effect of polydispersity, and explicit results will be given in the case of three- and four-component systems.

I. Statistical Theory of Scattering by a Multicomponent System: Results in the Thermodynamic Limit at Zero Scattering Angle

The scattering at zero angle is given for a one-component system by the well-known Einstein[10] equation:

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

where $\overline{(\Delta N)^2}$ is the mean square of the fluctuations of the number of molecules N in the scattering volume V and a the scattering amplitude by a single molecule. In electromagnetic scattering, a is proportional to the dipole induced by the unit electric field. In order to avoid the use of cumbersome normalization factors that are discussed in many review articles,[11] we shall call a the polarizability of the molecules or the coherent scattering length and leave out normalization factors. If one deals with an incompressible multicomponent[12,13] system the generalization of this formula is straightforward. The scattering intensity is

$$I(0) = \sum_{ij=1}^{p} \bar{a}_i\bar{a}_j z_i z_j \overline{\Delta N_i \Delta N_j} = N_{\mathrm{T}} \sum_{ij=1}^{p} \bar{a}_i\bar{a}_j S_{ij}(0) \tag{2}$$

This formula corresponds to the intensity scattered by a system containing p different polymers in a solvent ($1 \le i \le p$, $1 \le j \le p$). N_{T} is the ratio of the scattering volume V to the volume of one solvent molecule v_0:

$$N_{\mathrm{T}} = V/v_0 \tag{3}$$

The quantities z_i are the ratio between the volume of one polymer molecule in the solvent to the volume of one solvent molecule; it is a kind of "degree of polymerization"

$$z_i = \frac{v_i}{v_0} \tag{4}$$

The $\bar{a}_j$ are defined in terms of the difference between the scattering by one monomer and the scattering by the

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solvent:

$$\bar{a}_i = \left(\frac{a_i}{z_i}\right) - a_0 \tag{5}$$

The average value

$$\overline{\Delta N_i \Delta N_j} = N_T S_{ij}(0)$$

is taken at constant N_T, temperature, and volume. Here $S_{ij}(0)$ is the value at $q = 0$ of the partial structure factor for the couple (i,j) defined at any q by

$$N_T S_{ij}(q) = \int_V \overline{\Delta N_i(0)\Delta N_j(\mathbf{r})} \exp(-i\mathbf{q}\cdot\mathbf{r})\, \mathrm{d}^3\mathbf{r} \tag{6}$$

In order to evaluate the $S_{ij}(0)$ one writes the free energy of mixing ΔG as

$$\Delta G = N_T \Delta g = N_T \mu_0 + \sum_{i=1}^{p} N_i z_i \bar{\mu}_i = N_T[\mu_0 + \sum_{i=1}^{p} \bar{\mu}_i \phi_i] \tag{7}$$

introducing Δg, the free energy of mixing per volume of a solvent molecule, ϕ_i, the volume fraction of the polymer species i, and the exchange chemical potential $\bar{\mu}_i$

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

Using the theory of fluctuations in a grand canonical ensemble,[14] one obtains the well-known result:

$$S_{ij}(0) = kT\frac{\partial \phi_i}{\partial \bar{\mu}_j} = kT\frac{\partial \phi_j}{\partial \bar{\mu}_i} \tag{8}$$

where i and j vary from 1 to p.

The evaluation of the quantities $\partial\phi_j/\partial\bar{\mu}_i$ is done by the following method: one writes the p linear equations ($1 \leq i \leq p$):

$$\mathrm{d}\bar{\mu}_i = \frac{\partial \bar{\mu}_i}{\partial \phi_1}\mathrm{d}\phi_1 + \frac{\partial \bar{\mu}_i}{\partial \phi_2}\mathrm{d}\phi_2 + \frac{\partial \bar{\mu}_i}{\partial \phi_3}\mathrm{d}\phi_3 + \cdots + \frac{\partial \bar{\mu}_i}{\partial \phi_p}\mathrm{d}\phi_p \tag{9}$$

This system can be written in a matrix form. One introduces the column vectors $[\mathbf{d}\bar{\mu}]$ and $[\mathbf{d}\varphi]$ and the $p \times p$ square matrix $[\mathbf{H}]$ whose elements are $\mathrm{d}\bar{\mu}_i$, $\mathrm{d}\phi_i$, and $\partial\bar{\mu}_i/\partial\phi_j$, respectively. Since

$$\partial\bar{\mu}_j/\partial\phi_j = \partial\bar{\mu}_i/\partial\phi_j = \partial^2\Delta g/\partial\phi_i\partial\phi_j \tag{10}$$

the matrix $[\mathbf{H}]$ is symmetric and eq 9 can be written as

$$[\mathbf{d}\bar{\mu}] = [\mathbf{H}][\mathbf{d}\varphi] \tag{11}$$

Multiplying both sides on the left by $[\mathbf{H}]^{-1}$ leads to

$$[\mathbf{H}]^{-1}[\mathbf{d}\bar{\mu}] = [\mathbf{d}\varphi] \tag{12}$$

This gives the solution of the problem:

$$[\mathbf{S}] = kT[\mathbf{H}]^{-1} \tag{13}$$

To proceed further, one needs an expression for the free energy of mixing Δg. We use the following equation:

$$\Delta g/kT = \phi_0 \ln \phi_0 + \sum_{i=1}^{p}\frac{\phi_i}{z_i}\ln \phi_i + \phi_0\sum_{i=1}^{p}\phi_i\chi_{i0} + \sum_{i\neq j}^{p}\phi_i\phi_j\chi_{ij} \tag{14}$$

If the interaction parameters χ_{ij} are constant, this equation is the classical Flory–Huggins[15] equation for p constituents. The calculation when the χ's depend on ϕ_i is tedious; we give the results when the χ_{ij}'s are functions of temperature only:

$$\frac{1}{kT}\frac{\partial^2\Delta g}{\partial\phi_i^2} = \frac{1}{z_i\phi_i} + \frac{1}{\phi_0} - 2\chi_{i0} \tag{15}$$

$$\frac{1}{kT}\frac{\partial^2\Delta g}{\partial\phi_i\partial\phi_j} = \frac{1}{\phi_0} - (\chi_{i0} + \chi_{j0} - \chi_{ij}) \tag{16}$$

(For this calculation ϕ_0 has to be replaced by $1 - \sum_{i=1}^{p}\phi_i$.) If the χ's depend on composition it is always possible by a new definition of the χ's to recover formulas 15 and 16.[16] It is a common practice to introduce the excluded volume parameters v_{ij}, which in the framework of the classical polymer solutions theory, are defined as

$$v_{ij} = \frac{1}{\phi_0} - (\chi_{i0} + \chi_{j0} - \chi_{ij}) \tag{17}$$

$$v_{ii} = \frac{1}{\phi_0} - 2\chi_{i0} \tag{18}$$

Using these quantities, one obtains for the matrix $[\mathbf{H}]$ in the case where $p = 3$:

$$[\mathbf{H}] = kT\begin{pmatrix} \dfrac{1}{z_1\phi_1} + v_{11} & v_{12} & v_{13} \\ v_{12} & \dfrac{1}{z_2\phi_2} + v_{22} & v_{23} \\ v_{13} & v_{23} & \dfrac{1}{z_3\phi_3} + v_{33} \end{pmatrix} \tag{19}$$

The matrix $[\mathbf{S}]$, which allows the calculation of the scattering intensity, is obtained from eq 13. The generalization of this matrix to any value of p is obvious.

It is possible to give to eq 19, and for the intensity of the scattered radiation, a more familiar aspect by writing: $[\mathbf{H}] = kT\{[1/\mathbf{z}\varphi] + [\mathbf{v}]\}$ calling $[\mathbf{v}]$ the matrix v_{ij} and $[1/\mathbf{z}\varphi]$ the diagonal matrix with elements $(z_i\phi_i)^{-1}$. This last matrix can also be written as $[\mathbf{z}\varphi]^{-1}$ and one writes

$$[\mathbf{S}]^{-1} = [\mathbf{z}\varphi]^{-1} + [\mathbf{v}] \tag{19'}$$

This is the generalization to a multicomponent system of the classical form due to Debye,[17] which has been established for one polymer in one solvent and can be written as

$$\frac{1}{S_{11}} = \frac{1}{\mathbf{z}\varphi} + v \tag{20}$$

with

$$S_{11} = \frac{I(0)}{N_T\bar{a}^2}$$

It is easy to show, starting from eq 1, that if the system is compressible and if Δg does not depend on pressure, one can take into account the effect of compressibility by subtracting from the total scattering the scattering due to density fluctuations in the medium.

II. Scattering at Any Angle: Application of the Ornstein–Zernike Method[18]

(a) Polymer–Solvent Mixtures. One can write for the scattering intensity of a solution made of N identical particles (small compared to λ):

$$I(q) = \bar{a}^2[N + N^2\langle\exp(-i\mathbf{q}\mathbf{r}_{12})\rangle] \tag{21}$$

where $\mathbf{q}$ is the scattering vector (its modulus is $(4\pi/\lambda)\sin(\theta/2)$). $\mathbf{r}_{12}$ is the vector joining molecules 1 and 2. When one evaluates the average value, denoted by the

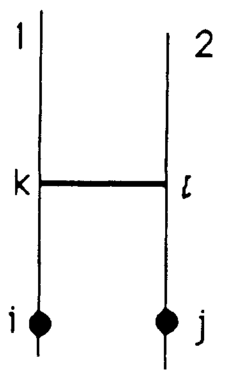

Figure 1. Illustration of the single contact approximation.

symbol ⟨ ⟩, one obtains

$$I(q) = \bar{a}^2 N\left(1 - N\int [1 - g(r)](\exp(-i\mathbf{qr}))\, \mathrm{d}^3\mathbf{r}\right)$$

$$I(q) = \bar{a}^2 N(1 - N\mathbf{v}) \tag{22}$$

where the quantity $\int [1 - g(\mathbf{r})] \exp(-i\mathbf{qr})\, \mathrm{d}^3\mathbf{r}$, which has been called the excluded volume parameter υ and has been defined in eq 17 and 18 for multicomponent systems, represents the interaction between two molecules (due to the short range of the intermolecular forces, it will be considered as independent of q). Ornstein and Zernike (OZ) have established a general equation connecting the direct interaction to what has been called the total interaction h

$$h = -\mathbf{v} - N\mathbf{v}h \quad \text{or} \quad h = \frac{-\mathbf{v}}{1 + N\mathbf{v}} \tag{23}$$

and proposed to replace in eq 22 the direct interaction $-\mathbf{v}$ by the total interaction h. This gives

$$\frac{N\bar{a}^2}{I(q)} = 1 + N\mathbf{v} \tag{24}$$

At low concentration ($N\upsilon$ small compared to unity) eq 22 and 24 are identical. The generalization of eq 24 to polymers has been made by Zimm[19] using what has been called the single-contact approximation. The interaction between molecules 1 and 2 (see diagram) can be considered as the sum of interactions between all monomers of molecules 1 and 2. To illustrate this approximation in a simple case, we consider the diagram in Figure 1. This allows one to write:

$$I(q)/\bar{a}^2 = Nz^2P(q) + N^2\sum_{ijkl}\langle \exp(-i\mathbf{q}(\mathbf{r}_{ik} + \mathbf{r}_{kl} + \mathbf{r}_{lj}))\rangle = Nz^2P(q) - C(q) \tag{25}$$

where, with the help of the diagram, one obtains[19,20]

$$C(q) = -\mathbf{v}N^2z^4P^2(q) \tag{26}$$

$P(q)$ is the form factor of the molecules, i.e., the quantity

$$P(q) = \frac{1}{z^2}\sum_{i}^{z}\sum_{j}^{z}\langle \exp(-i\mathbf{qr}_{ij})\rangle \tag{27}$$

where the points i and j belong to the same molecule. In order to apply the OZ equation (23) to this problem, we shall use the diagram in Figure 2. Equation 23 means that the total interaction (which can be called $H(q) = -hN^2z^4P^2(q)$) between i and j is made of two terms (see Figure 2): a direct interaction (equal to $-\mathbf{v}$) between chains 1 and 2 (horizontal line joining i and j) plus the product of a total interaction $H(q)$ between 1 and r (path i–i'–k–k') by the direct interaction between r and 2 (path k'–j'–j). When these terms are written one obtains

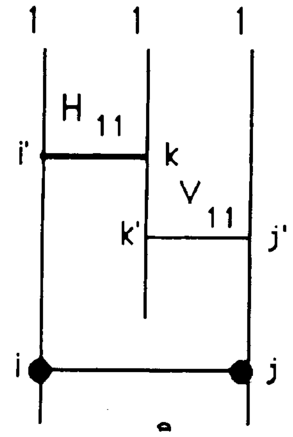

Figure 2. Illustration of the OZ equation for polymers.

$$H(q) = -\mathbf{v}N^2z^4P^2(q) - \mathbf{v}H(q)Nz^2P(q) \tag{28}$$

replacing $-\mathbf{V}$ by $C(q)$ and h by $H(q)$, eq 23 becomes

$$\frac{\bar{a}^2}{I(q)} = \frac{1}{Nz^2P(q)} + \mathbf{v} \tag{29}$$

This is the familiar Zimm equation, but now valid for any value of $\mathbf{v}$ since it depends on concentration (but not on q). By use of the intensity $i(q)$ and the excluded parameter υ per cell of the lattice or per volume of a solvent molecule

$$i(q) = I(q)/N_{\mathrm{T}} \qquad \upsilon = \mathbf{v}N_{\mathrm{T}} \tag{30}$$

transforms (29) into

$$\frac{\bar{a}^2}{i(q)} = \frac{1}{\phi zP(q)} + \upsilon \tag{29'}$$

where ϕ is the volume fract ion of polymer in the solution.

(b) Different Polymers in a Solvent. If one assumes the presence of p different species of polymers in the solution, one has to use eq 2, generalized to take the variable q into account, and write

$$I(q)/N_{\mathrm{T}} = i(q) = \sum_{i=1}^{p}\sum_{j=1}^{p}\bar{a}_i\bar{a}_jS_{ij}(q) \tag{31}$$

$S_{ij}(q)$ is made to two terms due to intramolecular and intermolecular contributions. One writes

$$S_{ii}(q) = x_{ii}(q) + H_{ii}(q) \quad \text{if} \quad i = j$$
$$S_{ij}(q) = H_{ij}(q) \quad \text{if} \quad i \neq j \tag{32}$$

where

$$x_{ii} = \phi_iz_iP_i(q)$$

characterizes the species i of "degree of polymerization" z_i, volume fraction ϕ_i, and form factor $P_i(q)$. $H_{ij}(q)$ contains all the interferences between macromolecules i and j. For one polymer, the OZ equation was written (eq 28) as

$$H_{11}(q) = -\upsilon_{11}{x_{11}}^2 - \upsilon_{11}x_{11}H_{11}(q)$$

For two polymers, one writes

$$H_{11}(q) = -\upsilon_{11}{x_{11}}^2 - \upsilon_{11}x_{11}H_{11}(q) - \upsilon_{12}x_{11}H_{12}(q) \tag{33}$$

This result is easily explained by using Figure 3, where the two possible interaction cases are represented. The

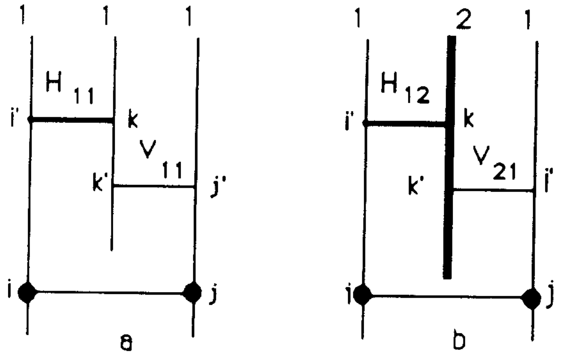

Figure 3. Illustration of the OZ equation for two polymers species.

same argument applies for H_{12}:

$$H_{12}(q) = -v_{12}x_{11}x_{22} - v_{12}x_{22}H_{11}(q) - v_{22}x_{22}H_{12}(q) \quad (34)$$

This gives in terms of S_{ij} and by application of eq 32:

$$S_{11}(1 + x_{11}v_{11}) + S_{12}x_{11}v_{12} = x_{11}$$
$$S_{12}(1 + x_{22}v_{22}) + S_{22}x_{22}v_{12} = 0 \quad (35)$$

The two other equations are obtained by exchanging the indices 1 and 2.

It is easy to generalize these equations to the case where one has an arbitrary number p of constituents. One obtains

$$H_{ij}(q) = -v_{ij}x_{ii}x_{jj} - \sum_{k=1}^{p} v_{ik}x_{ii}H_{kj}(q) \quad (36)$$

If one uses the S_{ij} instead of the H_{ij}, one obtains the following equations where we have made explicit the difference between the case where $i = j$ and $i \neq \theta$:

$$S_{ii}(1 + v_{ii}x_{ii}) + \sum_{k\neq i} v_{ik}S_{ik}x_{ii} = x_{ii} \quad \text{for } i = j$$
$$S_{ji}(1 + v_{ii}x_{ii}) + \sum_{k\neq j} v_{jk}S_{ik}x_{jj} = 0 \quad \text{for } i \neq j \quad (37)$$

The determination of S_{ij} requires the solution of this set of linear equations. This will be done as before by using matrix algebra. One defines the square matrix [S] by its elements S_{ij}, the square matrix [v] is defined by the v_{ij}, and the diagonal matrix [x] made of x_{ii}. It is easy to verify that eq 37 can be simply written as

$$[\mathbf{S}]([1] + [\mathbf{v}][\mathbf{x}]) = [\mathbf{x}]$$

or by simple arithmetic

$$[\mathbf{S}]^{-1} = [\mathbf{x}]^{-1} + [\mathbf{v}] \quad (38)$$

One recovers the classical Zimm equation in matrix form as well as the thermodynamical result eq 19′ in the $q = 0$ limit. This is very simple and remarkable since it unifies the results obtained by different methods.

(c) The Case of Copolymers of Arbitrary Architecture. In this last part it will be shown that eq 38 can be extended to copolymers of any architecture by a correct definition of the matrix [x]. Let us assume that we have for instance a copolymer made of three different monomers, 1, 2, and 3. This introduces six form factors $P_{11}(q)$, $P_{22}(q)$, and $P_{33}(q)$ and the cross terms $P_{12}(q)$, $P_{23}(q)$, and $P_{13}(q)$ and, therefore, six quantities x_{ij} leading to a 3 × 3 matrix. Using the volume fractions of part i of the copolymer ($f_i = z_i/z$, $z = \sum_{i=1}^{p} z_i$), one obtains for x_{ij}

$$x_{ij} = \phi z^2 f_i f_j P_{ij}(q) \quad (39)$$

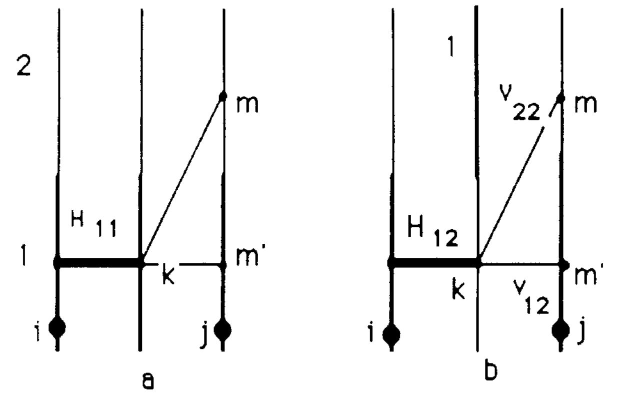

Figure 4. Illustration of the OZ equation for a two-component copolymer.

One has first to evaluate the quantities $C_{ij}(q)$ corresponding to the dilute solution term. This has been done[21] and we just recall the results for a two-component copolymer:

$$C_{11}(q) = -v_{11}x_{11}^{2} - 2v_{12}x_{11}x_{12} - v_{22}x_{11}^{2}$$
$$C_{12}(q) = -v_{11}x_{11}x_{22} - v_{12}(x_{11}x_{22} + x_{12}^{2}) - v_{22}x_{12}x_{22} \quad (40)$$

In order to evaluate the H's one may use Figure 4 corresponding to the interaction 1–1 for a two-component copolymer. There are four cases: two on diagram *a* and two on *b*. Summing them gives

$$H_{11} = C_{11} - H_{11}(v_{11}x_{11} + v_{12}x_{12}) - H_{12}(v_{12}x_{11} + v_{22}x_{12}) \quad (41)$$

One replaces now the H's by the S's remembering that, even for $i \neq j$, one has

$$S_{ij} = x_{ij} + H_{ij} \quad (42)$$

and using eq 41, one obtains

$$S_{11}(1 + v_{11}x_{11} + v_{12}x_{12}) + S_{12}(v_{12}x_{11} + v_{22}x_{12}) = x_{11} \quad (43)$$

The same calculation can be made for S_{12}:

$$S_{12}(1 + v_{22}x_{22} + v_{12}x_{12}) + S_{11}(v_{12}x_{22} + v_{11}x_{12}) = x_{12} \quad (43')$$

Two equivalent equations can be obtained by exchanging the indices 1 and 2. The solution of these equations will make use of the properties of matrices $[S_{ij}]$, $[v_{ij}]$, and $[x_{ij}]$. [1] is the diagonal unit matrix. This gives

$$[\mathbf{S}]([1] + [\mathbf{v}][\mathbf{x}]) = [\mathbf{x}] \quad (44)$$

which can also be written as

$$[\mathbf{S}]^{-1} = [\mathbf{x}]^{-1} + [\mathbf{v}] \quad (44')$$

This shows that the Zimm equation is quite general and gives a simple way to remember formulas that, if written explicitly, could be very lengthy. To end this paragraph we stress the fact that eq 44′ is quite general and can be used for copolymers of any architecture. The diagrams used do not mean that the results are restricted to linear block copolymers only.

(d) Applications to Polymers in Bulk. All these equations have been obtained for solutions. It would be interesting to derive similar formulas for copolymers in bulk. (Until now we have had no success writing this limit in a simple matrix form.) Nevertheless it is possible to eliminate the solvent in two different ways.

(i) One can decrease the solvent concentration toward zero. This concentration appears only in the parameters v_{ij} as an additional term $1/\phi_0$ (eq 18). Its elimination is not instantaneous since both numerator and denominator go to infinity but, nevertheless, it can be done, since the physics requires the existence of a signal linear in ϕ_0. What is also required is that all parameters like χ_{ii} and χ_{i0} cancel out; the only parameters left are the χ_{ij} (with $i \neq j$). Using this technique, one loses one constituent (the solvent) going from $p + 1$ to p constituents. This means that the number of $S_{ij}(q)$ required to describe the system goes from $p(p + 1)/2$ to $p(p - 1)/2$.

(ii) One can also replace the solvent by a polymer. At $q = 0$ this is evident, but in this case the "degree of polymerization", z_i looses its meaning (see eq 4). This fact has to be taken into account in the definition of the interaction parameters χ. At $q \neq 0$, one is tempted to replace $\phi_0 z_0$ by $\phi_0 z_0 P_0(q)$. It will be shown later that this is correct in all cases.

(e) Remarks Concerning Polydispersity. Since in all results that have been discussed previously the molecular characteristics of the samples were described by the quantities x_{ij}, the only effect of polydispersity is to modify their values. Assuming a distribution of degrees of polymerization and form factors we have to introduce the following quantities:

$$\langle x_{11} \rangle = \sum \frac{N_{1i} z_{1i}^2 P_{11i}(q)}{N_\mathrm{T}} \tag{45}$$

and

$$\langle x_{12} \rangle = \sum \frac{N_i z_{1i} z_{2i} P_{12i}(q)}{N_\mathrm{T}} = \sum \frac{N_i z_i^2 f_{1i} f_{2i} P_{12i}(q)}{N_\mathrm{T}} \tag{46}$$

Averages are taken over all polymers containing the species 1 or the couple 1–2. These averages are difficult to interpret and one prefers to write

$$\langle x_{11} \rangle = \Phi_1 z_{1w} \langle P_{11}(q) \rangle \quad \text{with} \quad \langle P_{11}(q) \rangle = \frac{\sum N_{1i} z_{1i}^2 P_{11i}}{\sum N_{1i} z_{1i}^2} \tag{47}$$

where Φ_1 is the volume fraction occupied by the constituent and z_{1w} its weight-average "degree of polymerization". Similarly

$$\langle x_{12} \rangle = \Phi_{12} z_w \langle f_1 f_2 \rangle \langle P_{12}(q) \rangle$$

with

$$\langle P_{12}(q) \rangle = \frac{\sum N_i z_i^2 f_{1i} f_{2i} P_{12i}(q)}{\sum N_i z_i^2 f_{1i} f_{2i}}$$

$$\langle f_1 f_2 \rangle = \frac{\sum N_i z_i^2 f_{1i} f_{2i}}{\sum N_i z_i^2} \tag{48}$$

where Φ_{12} is the volume fraction occupied by the copolymer components 1 and 2. These results can be useful for experimentalists, but they are interesting only when one deals with a concrete problem. Another more interesting aspect of polydispersity is the following: the above equations are written for any value of the polydispersity of the sample. If, for instance, the molecules of structure i are such that $f_{ki} = 0$ for $1 \leq k \leq p$, except $k = m$, then this copolymer i reduces to a homopolymer made only of monomers m. Furthermore, if f_{mi} and f_{ni} are both different from zero, this component is a copolymer containing only the monomers m and n. Since all these cases are taken into account in the definitions of x_{ij}, eq 44 describes any mixture containing p types of monomers distributed among homo- and copolymers of arbitrary composition and structure.

III. Application to Mixtures Made of Three Types of Monomers

(a) In a Solvent (Either Low Molecular Weight Compound or Homopolymer). One needs only to let $p = 3$ in eq 44 and write it in a form that can be used for practical purposes. This has been done with the help of a computer program (program MAPLE on the I.N.R.I.A. computer, in Sofia Antipolis, France). We shall give the final result with the notations used before. Let us first recall that the quantities x_{ij} and S_{ij} are functions of q and that v_{ij}, x_{ij}, and S_{ij} do not change when on exchanges the indices ($S_{ij} = S_{ji}$, $x_{ij} = x_{ji}$, $v_{ij} = v_{ji}$). Moreover, because the formulas are lengthy, we have introduced the symbol **C** with the following meaning. Circular symmetry requires that, to each term containing a combination of the indices 1, 2, and 3 must correspond another term containing the combinations 2,3,1 and 3,1,2. Therefore we define

$$\mathbf{C}f(1,2,3) = f(1,2,3) + f(2,3,1) + f(3,1,2) \tag{49}$$

The structure factors are written in the form

$$S_{ij} = \mathbf{s}_{ij}/\mathbf{D} \tag{50}$$

where **D** is the determinant of the matrix [1] + [**v**][**x**] (eq 44). The result is

$$\begin{aligned}\mathbf{D} = 1 + \mathbf{C}[x_{11}v_{11} + 2x_{12}v_{12} + (x_{11}x_{22} - x_{12}^2)(v_{11}v_{22} - v_{12}^2) + \\ 2(x_{12}x_{13} - x_{11}x_{23})(v_{11}v_{23} - v_{12}v_{13})] + [x_{11}x_{22}x_{33} + \\ 2x_{12}x_{23}x_{31} - \mathbf{C}(x_{33}x_{12}^2)][v_{11}v_{22}v_{33} + 2v_{12}v_{23}v_{31} - \mathbf{C}(v_{33}v_{12}^2)]\end{aligned} \tag{51}$$

One remarks that the the last two expressions in brackets are the determinents of the matrices [**x**] and [**v**], which will be called Det **x** and Det **v**.

$$\begin{aligned}\mathbf{s}_{11} = x_{11} + (x_{11}x_{22} - x_{12}^2)v_{22} + (x_{11}x_{33} - x_{13}^2)v_{33} + 2(x_{11}x_{23} - \\ x_{12}x_{13})v_{23} + (v_{22}v_{33} - v_{23}^2)\ \mathrm{Det}\ \mathbf{x}\end{aligned}$$

$$\begin{aligned}\mathbf{s}_{12} = x_{12} - (x_{11}x_{22} - x_{12}^2)v_{12} + (x_{12}x_{13} - x_{11}x_{23})v_{13} + (x_{12}x_{23} - \\ x_{22}x_{13})v_{23} + (x_{12}x_{33} - x_{13}x_{23})v_{33} + (v_{13}v_{23} - v_{12}v_{33})\ \mathrm{Det}\ \mathbf{x}\end{aligned} \tag{52}$$

Because of the circular symmetry, we do not have to write all the S_{ij} terms. The knowledge of $\mathbf{s}_{11}$ and $\mathbf{s}_{12}$ is sufficient for obtaining the other S's. All the cases that have been studied in detail so far[1,2,9,22] can be obtained from these results by making the necessary substitutions and simplifications.

(b) Ternary Copolymers in the Bulk. The majority of experiments that can be interpreted by these formulas are made by neutron scattering in bulk. Therefore, it is useful to obtain explicitly the limits of the previous results when the volume fraction of solvent goes to zero. This has been done with the help of the same MAPLE program. The scattering intensity depends only on three independent structure factors:

$$i(q) = (a_3 - a_2)^2 S_1^0(q) + (a_1 - a_3)^2 S_2^0(q) + (a_2 - a_1)^2 S_3^0(q) \tag{53}$$

We write again

$$S_i^0(q) = \frac{\mathbf{s}_i^0(q)}{\mathbf{D}^0} = \frac{-\mathbf{s}_{jk}^0(q)}{\mathbf{D}^0} \tag{54}$$

where $\mathbf{D}^0$ and $\mathbf{s}_i^0$ are the leading terms in the expansions of **D** and $\mathbf{s}_{jk}$ ($j \neq k$) as a function of $1/\phi_0$ when ϕ_0 goes to zero. The results are

$$\mathbf{D}^0 = \mathbf{C}[x_{11} + 2x_{12} - 2\{(x_{11}x_{22} - x_{12}^2)\chi_{12} + (x_{11}x_{23} - x_{12}x_{13})(\chi_{13} + \chi_{12} - \chi_{23})\}] - \mathrm{Det}\,\mathbf{x}\,\mathbf{C}(\chi_{12}^2 - 2\chi_{12}\chi_{23})$$

and

$$\mathbf{s}_{12}^0(q) = x_{12}^2 - x_{11}x_{22} + x_{13}(x_{12} - x_{22}) + x_{23}(x_{12} - x_{11}) + x_{33}x_{12} - x_{13}x_{23} + \mathrm{Det}\,\mathbf{x}\,[\chi_{13} + \chi_{23} - \chi_{12}] \quad (55)$$

For reasons of symmetry, $\mathbf{s}_2^0(q)$ and $\mathbf{s}_3^0(q)$ can be obtained by rotation of indices as explained earlier. In this case the comparison with known results is easier, since there are already a number of examples in the literature. The first one that will be considered is a mixture of homopolymers (all the x_{ij} for $i \neq j$ are zero). For two homopolymers one obtains the de Gennes formula.[8] For three homopolymers eq 55 gives

$$i(q) = \frac{\mathbf{C}[(a_1 - a_2)^2\{x_{11}x_{22} - x_{11}x_{22}x_{33}(\chi_{13} + \chi_{23} - \chi_{12})\}]}{\mathbf{C}[x_{11} - 2x_{11}x_{22}\chi_{12} - x_{11}x_{22}x_{33}(\chi_{12}^2 - 2\chi_{12}\chi_{23})]} \quad (56)$$

This expression can be written in a simpler manner:

$$i(q) = \frac{\mathbf{C}[(a_1 - a_2)^2K_3]}{\mathbf{C}[K_1K_2]} \quad (56')$$

where

$$K_1 = x_1^{-1} - \chi_1 \quad \text{with} \quad \chi_1 = \chi_{12} + \chi_{13} - \chi_{23} \quad (56'')$$

For copolymer 1–2 one recovers Leibler's result.[4,5] For a mixture of copolymer 1–2 and homopolymer 3, one obtains from eq 55

$$i(q) = \frac{\mathbf{C}[(a_1 - a_2)^2K'_3]}{\mathbf{C}[K'_1K'_2]}$$

with

$$K'_1 = \frac{x_2 + x_{12}}{x_{11}x_{22} - x_{12}^2} - \chi_1$$

$$K'_2 = \frac{x_1 + x_{12}}{x_{11}x_{22} - x_{12}^2} - \chi_2$$

$$K'_3 = x_3^{-1} - \frac{x_{12}}{x_{11}x_{22} - x_{12}^2} - \chi_3 \quad (57)$$

This result has already been obtained, transforming the solvent into a polymer and starting from eqs 51 and 52 written for only two species.[2] All the cases studied by Sanchez and Olvera de la Cruz[9] for star and graft polymers and by Ijichi and Hashimoto[22] are special cases of our general equation. As an example, let us consider the case of a star copolymer made of three branches of equal length and different natures. Only two form factors are needed: the first one is the structure factor of one branch, which will be called $P(q)$, the second one is the cross term between two branches, called $Q(q)$. If the chains are Gaussian, $P(q)$ and $Q(q)$ are given by

$$P(q) = 2\left[\frac{6}{q^2b^2z}\right]^2\left\{\frac{q^2b^2z}{6} - 1 + \exp\left(-\frac{q^2b^2z}{6}\right)\right\}$$

$$Q(q) = \left[\frac{6}{q^2b^2z}\left[1 - \exp\left(-\frac{q^2b^2z}{6}\right)\right]\right]^2 \quad (58)$$

All the x_{ii} are equal and given by

$$x_{11} = x_{22} = x_{33} = x = \frac{z}{3}P(q)$$

$$x_{12} = x_{23} = x_{13} = y = \frac{z}{3}Q(q) \quad (59)$$

In these expressions, z is, as before, the degree of polymerization in volume of one branch of the star and b the lenngth of the statistical element. Putting these values into eq 55 gives

$$i(q) = [\mathbf{C}(a_1 - a_2)^2\{(x - y)(x + 2y) - (x - y)^2(x + 2y)\mathbf{C}\chi_1\chi_2\}]/[3(x + 2y) - 2(x - y)(x + y)\mathbf{C}\chi_{12} + (x - y)y\mathbf{C}\chi_1 - (x - y)^2(x + 2y)\mathbf{C}\chi_1\chi_2] \quad (60)$$

The χ_i's have been defined in eq 56″.

This formula is rather simple. It shows that the shape of the scattering intensity ($i(q)$ versus q) does not depend on the relative magnitude of the scattering lengths a_i. The interactions affect $i(q)$ only through the symmetric combinations $\mathbf{C}\chi_1$, $\mathbf{C}\chi_{12}$, and $\mathbf{C}\chi_1\chi_2$. Even if two of the branches are highly incompatible, the system will remain in one phase if the third constituent is sufficiently compatible with the others. One will always see only one maximum as a function of q since the quantity responsible for its formation is $x - y$. The position of this maximum will probably be insensitive to the relative values of the χ parameters. It is interesting to see that if one adds an equal amount of three homopolymers of the species 1, 2, and 3 nothing will be changed, except the definitions of the quantities x. These results are very similar to those reported by Ijichi and Hashimoto.[22] The advantage of our procedure is that as soon as you know the system, the general formula eq 44 can be applied, and with standard algebra the desired results are obtained.

Conclusion

We describe in this paper the derivation of a simple and general equation for the scattering intensity of mixtures of polymers and copolymers in the presence of a solvent. This equation is based on the Ornstein and Zernike approximation, which is equivalent to other mean-field approximations. The interesting fact is that when written in a matrix form, this equation reduces to the classical Zimm formula for a one-component system. Moreover, at $q = 0$, it becomes the well-known thermodynamic equation for multicomponent systems. Despite the fact these results have been derived for solutions, we have shown that these formulas can be applied as well to pure polymers melts. The advantage of this equation is that it provides a universal description of polymer systems, regardless of architecture, composition, and concentration of the macromolecules. In the last part of the paper we give an explicit equation for the intensity scattered by homo- and copolymers containing three different kinds of monomers, in solution as well as in bulk. In order to illustrate how these formulas can be used, we have considered the case of a star polymer with three branches of equal length, each of them made with a different monomer. At first sight, the introduction of systems having more than two monomer constituents looks like a pure mathematical exercise: we belive that this is not the case. For example, a very simple case (which is of general interest) is the problem of the conformation of the two-block copolymer 1–2 mixed with homopolymer 1. The classical procedure to determine the conformation of a block copolymer is to use a mixture of deuterated and nondeuterated monomers, which we will call 1D and 1H. If, as has been strongly stressed by Bates,[23] one cannot neglect the χ interaction existing between D and H, eq 44 provides the appropriate theoretical basis for interpreting the experiments. More complicated systems are blocky terpolymers and even more complicated copolymers, which are extensively used in industry. These polymers or polymer mixtures can, if the blocks are sufficiently long, exhibit mesophase structures. Classical thermodynamics can predict only the behavior of these systems at $q = 0$. $\mathbf{D} = 0$ or $\mathbf{D}^0 = 0$ gives a generalized spinodal (function of q and volume fractions), which can be useful for the prediction of the appearance of such mesophases.

References and Notes

(1) Benoît, H.; Hadziioannou, G. *Macromolecules* **1988**, *21*, 1449.
(2) Benoît, H.; Wu, W.; Benmouna, M.; Moser, B.; Bauer, B.; Lapp, A. *Macromolecules* **1985**, *18*, 986.
(3) de Gennes, P.-G. *J. Phys. (Paris)* **1970**, *31*, 235.
(4) Leibler, L.; Benoît, H. *Polymer* **1981**, *22*, 195.
(5) Leibler, L. *Macromolecules* **1980**, *13*, 1602.
(6) (a) Warner, M.; Higgins, J. S.; Carter, A. J. *Macromolecules* **1983**, *16*, 1931. (b) Fischer, E. W. In *Scattering, Deformation and Fracture in Polymers*; Wignall, G. D., Crist, B., Russel, T. P.; Thomas, E. L., Eds.; Material Research Society: Pittsburgh, 1986; Vol. 79.
(7) Ould Kaddour, L.; Strazielle, C. *Polymer* **1987**, *28*, 459.
(8) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(9) Olvera de la Cruz, M.; Sanchez, I. *Macromolecules* **1986**, *19*, 2051.
(10) Einstein, A. *Ann. Phys.* **1910**, *33*, 1275.
(11) Ullman, R. Small Angle Neutron Scattering of Polymers. *Annu. Rev. Mater. Sci.* **1980**, *10*, 261.
(12) Stockmayer, W. H. *J. Chem. Phys.* **1950**, *18*, 58.
(13) des Cloizeaux, J.; Jannink, G. *Physica* **1980**, *102A*, 120.
(14) Hill, T. L. *Statistical Mechanics*; McGraw-Hill: New York, 1956.
(15) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1967.
(16) Sanchez, I. *Polymer* **1989**, *30*, 471.
(17) Debye, P. *J. Appl. Phys.* **1944**, *15*, 338.
(18) Ornstein, L. S.; Zernike, F. *Proc. Acad. Sci. Amsterdam* **1914**, *17*, 793.
(19) Zimm, B. *J. Chem. Phys.* **1948**, *16*, 1093.
(20) Benoît, H.; Benmouna, M. *Polymer* **1984**, *25*, 1059.
(21) (a) Benoît, H.; Benmouna, M. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1227. (b) Benoît, H.; Benmouna, M.; Strazielle, C.; Cesteros, C. Light scattering from mixtures of homopolymers and copolymers: Theoretical results and experimental examples. In *Physical Chemistry of Colloids and Macromolecules*; Ranby, B., Ed.; I.U.PA.C. Symposia, Blackwell Scientific Publications, 1987.
(22) Ijichi, L. Y.; Hashimoto, T. *Polymer Comm.* **1988**, *29*, 135.
(23) Bates, F. S.; Wignall, G. D. *Macromolecules* **1986**, *19*, 932.

Photoinduced Phase Transition of Gels

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ABSTRACT: Equilibrium swelling curves of copolymer gels of *N*-isopropylacrylamide and a photosensitive molecule, bis(4-(dimethylamino)phenyl)(4-vinylphenyl)methyl leucocyanide, were determined as a function of temperature under ultraviolet irradiation. Without ultraviolet irradiation the gels underwent a sharp, yet continuous, volume change, whereas upon ultraviolet irradiation they showed a discontinuous volume phase transition. For fixed appropriate temperatures, the gels discontinuously swelled in response to irradiation of ultraviolet light and shrank when the light was removed. The phenomena were caused by osmotic pressure of cyanide ions created by ultraviolet irradiation.

Introduction

Recently phase transitions and critical phenomena in polymer gels have attracted much attention because of their scientific interest and technological importance. Phase transitions accompanied by a reversible, discontinuous volume change as large as several hundred times, in response to infinitesimal changes in the environment condition, have been observed universally in various gels made of synthetic and natural polymers.[1-7] Variables that are known to induce a phase transition are temperature, solvent composition, pH, ionic composition, and small electric field.[8] Those findings have opened up a wide variety of possible applications of gels as sensors, chemomechanical transducers, switches, display units, memories, controllable drug delivery systems, and selective pumps.[1] For some of the applications, it will be clearly desirable if such a phase transition can be controlled by using light. The imposition of light can be done instantly, which is in contrast to other variables. For example, the temperature jump is limited by the thermal diffusion, and the pH change by ion diffusion. The electric field induced phase transition is also limited by the accompanying ion diffusion.

Recently, Irie and Kungwatchakun[11] reported a synthesis of photosensitive gels by incorporating photosensitive molecules, such as leucocyanide and leucohydroxide, into the gel network. These gels underwent volume changes upon irradiation and removal of ultraviolet light. However, a phase transition has not been observed in these synthetic gels because the condition at which the irradiation took place was far from the phase transition

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