Chapter 31 – **STRUCTURE FACTORS FOR POLYMER SYSTEMS**

Up to now, this book has focused on infinitely dilute systems only. Such systems are non-interacting and require solely the calculation of the form factor P(Q) for isolated particles. More concentrated (or interacting) systems require the calculation of the structure factor S(Q). Structure factors for fully interacting polymer systems are considered here. These apply to semi-dilute and concentrated polymer solutions and polymer blend mixtures in the homogeneous phase.

1. SCATTERING FROM INCOMPRESSIBLE SYSTEMS

Consider a system consisting of N "particles" of scattering length b_P occupying the sample volume V. The following would still hold if the word "polymers" were substituted for the word "particles". The scattering cross section is proportional to the density-density correlation function as follows:

$$\frac{d\Sigma(Q)}{d\Omega} = b_P{}^2 \frac{1}{V}\sum_{i,j}^{N} < \exp\left(-i\vec{Q}.\vec{r}_{ij}\right) >= b_P{}^2 \frac{1}{V} < n_P(-Q)n_P(Q) >. \qquad (1)$$

Here $n_P(Q)$ is the fluctuating particle density in Fourier space. The cross section for particles in solution is given by:

$$\frac{d\Sigma(Q)}{d\Omega} = b_P{}^2 \frac{1}{V} < n_P(-Q)n_P(Q) > + b_S{}^2 \frac{1}{V} < n_S(-Q)n_S(Q) >$$

$$+ 2b_P b_S \frac{1}{V} < n_P(-Q)n_S(Q) >. \qquad (2)$$

The subscripts P and S stand for particle and solvent respectively. For the sake of convenience, the following scattering factors are defined:

$$S_{PP}(Q) = \frac{v_P{}^2}{V} < n_P(-Q)n_P(Q) > \qquad (3)$$

$$S_{SS}(Q) = \frac{v_S{}^2}{V} < n_S(-Q)n_S(Q) >$$

$$S_{PS}(Q) = \frac{v_P v_S}{V} < n_P(-Q)n_S(Q) >.$$

The specific volumes v_P and v_S and scattering length densities $\rho_P = b_P/v_P$ and $\rho_S = b_S/v_S$ are defined for the polymer and the solvent respectively. To clarify, v_P is the

monomer volume and v_S is the volume of the solvent molecule. The scattering cross section becomes:

$$\frac{d\Sigma(Q)}{d\Omega} = \rho_P{}^2 S_{PP}(Q) + \rho_S{}^2 S_{SS}(Q) + 2\rho_P\rho_S S_{PS}(Q). \qquad (4)$$

Most scattering systems are incompressible. It is often convenient to make the following incompressibility assumption:

$$v_P n_P(Q) + v_S n_S(Q) = 0. \qquad (5)$$

This introduces the following simplification:

$$v_P{}^2 < n_P(-Q) n_P(Q) > = v_S{}^2 < n_S(-Q) n_S(Q) > \qquad (6)$$

$$= -v_P v_S < n_P(-Q) n_S(Q) >.$$

In other words:

$$S_{PP}(Q) = S_{SS}(Q) = -S_{PS}(Q) = -S_{SP}(Q) \qquad (7)$$

This simplifies the cross section to the following form:

$$\frac{d\Sigma(Q)}{d\Omega} = (\rho_P - \rho_S)^2 S_{PP}(Q) = \Delta\rho^2 S_{PP}(Q). \qquad (8)$$

This is reasonable since the contrast factor $\Delta\rho^2$ is always calculated relative to a "background" scattering length density value. Here, the solvent's scattering length density is taken to be that reference value.

2. INTER-PARTICLE INTERACTIONS

Consider a system consisting of N polymers of contrast factor $\Delta\rho^2$ occupying volume V. Each polymer comprises n monomers of volume v each so that the polymer volume is $v_P = nv$. Let us separate out the intra-polymer and the inter-polymer terms in the scattering cross section as follows:

$$\frac{d\Sigma(Q)}{d\Omega} = \Delta\rho^2 \frac{v^2}{V}\left[\sum_{\alpha=\beta}^{N}\sum_{i,j}^{n} < \exp\left(-i\vec{Q}.\vec{r}_{\alpha i \beta j}\right) > + \sum_{\alpha\neq\beta}^{N}\sum_{i,j}^{n} < \exp\left(-i\vec{Q}.\vec{r}_{\alpha i \beta j}\right) >\right]. \qquad (9)$$

The indices α and β run over the polymer chains and the indices i and j run over the monomers in a specific polymer chain. Consider a pair of polymer coils (called 1 and 2) and sum over all pairs.

$$\frac{d\Sigma(Q)}{d\Omega} = \Delta\rho^2 \frac{v^2}{V}\left[N\sum_{i,j}^{n} < \exp\left(-i\vec{Q}.\vec{r}_{1i1j}\right) > + N(N-1)\sum_{i,j}^{n} < \exp\left(-i\vec{Q}.\vec{r}_{1i2j}\right) > \right]. \quad (10)$$

Note that this formalism holds if the word "particles" were to be substituted for the word "polymers" assuming (of course) that the particles have internal structure (think monomers).

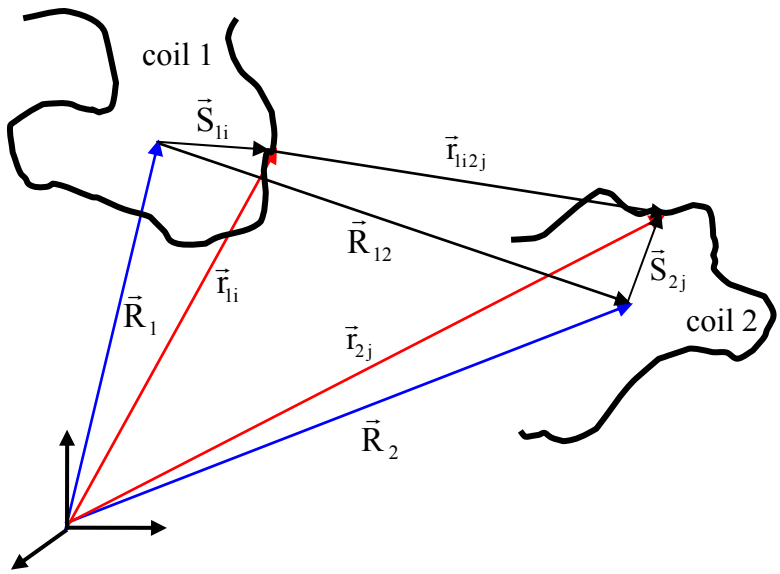

Figure 1: Schematic representation of the coordinate system showing a pair of scatterers that belong to two different polymer coils.

The inter-distance between the scattering pair $\vec{r}_{1i2j}$ can be expressed as $\vec{r}_{1i2j} = -\vec{S}_{1i} + \vec{S}_{2j} + \vec{R}_{12}$. and the inter-particle average can be split into the following parts:

$$< \exp\left(-i\vec{Q}.\vec{r}_{1i2j}\right) > = < \exp\left(i\vec{Q}.\vec{S}_{1i}\right) >< \exp\left(-i\vec{Q}.\vec{S}_{2j}\right) >< \exp\left(-i\vec{Q}.\vec{R}_{12}\right) > . \quad (11)$$

The first two averages are within single particles and the third average is across particles. The summations become:

$$\sum_{i,j}^{n} < \exp\left(-i\vec{Q}.\vec{S}_{1i2j}\right) > = < \exp\left(-i\vec{Q}.\vec{R}_{12}\right) > \sum_{i}^{n} < \exp\left(i\vec{Q}.\vec{S}_{1i}\right) > \sum_{j}^{n} < \exp\left(-i\vec{Q}.\vec{S}_{2j}\right) > . (12)$$

The form factor amplitude is defined as:

$$F(Q) = \frac{1}{n}\sum_{i}^{n} < \exp\left(-i\vec{Q}.\vec{S}_{1i}\right) > = \frac{1}{n}\sum_{j}^{n} < \exp\left(-i\vec{Q}.\vec{S}_{2j}\right) > . \quad (13)$$

The single-particle form factor itself is defined as:

$$P(Q) = \frac{1}{n^2}\sum_{i,j}^{n} < \exp\left(-i\vec{Q}.\vec{S}_{1i1j}\right) > . \qquad (14)$$

For uniform density particles, the following relation holds $P(Q) = |F(Q)|^2$. This is not true, however, for non-uniform density object such as polymer coils.

An inter-particle structure factor is defined as:

$$S_I(Q) = \frac{1}{N}\sum_{\alpha,\beta}^{N} < \exp\left(-i\vec{Q}.\vec{R}_{\alpha\beta}\right) > . \qquad (15)$$

The cross section can therefore be written as follows:

$$\frac{d\Sigma(Q)}{d\Omega} = \Delta\rho^2 \frac{v^2 n^2 N}{V}\left[P(Q) + |F(Q)|^2 \left(S_I(Q) - 1\right)\right]. \qquad (16)$$

Note that the statistical average $< \exp\left(i\vec{Q}.\vec{r}_{1i2j}\right) >$ involves integration over the following probability distribution $P(\vec{r}_{1i}, \vec{r}_{2j}, \vec{R}_{12})$ which can be split to show a conditional probability $P(\vec{r}_{1i}, \vec{r}_{2j}, \vec{R}_{12}) = P(\vec{r}_{1i}, \vec{r}_{2j} \mid \vec{R}_{12})P(\vec{R}_{12})$. For compact scatterers which do not interfere with each other's rotation $P(\vec{r}_{1i}, \vec{r}_{2j} \mid \vec{R}_{12})$ is independent of $\vec{R}_{12}$. $P(\vec{R}_{12})$ is the probability of finding the centers of mass of polymer coils 1 and 2 a distance $\vec{R}_{12}$ apart.

$$S_I(Q) = N < \exp\left(-i\vec{Q}.\vec{R}_{12}\right) > = \frac{N}{V}\int d\vec{R}_{12} P(\vec{R}_{12}) \exp\left(-i\vec{Q}.\vec{R}_{12}\right). \qquad (17)$$

The cross section for systems in this case is given by:

$$\frac{d\Sigma(Q)}{d\Omega} = \Delta\rho^2 \frac{v^2 n^2 N}{V} P(Q)\left[1 + \frac{|F(Q)|^2}{P(Q)}\left(S_I(Q) - 1\right)\right]. \qquad (18)$$

This result applies to systems with non-spherical symmetry and non-uniform density such as polymers. Polymer are, however, so highly entangled that an inter-chain structure factor $S_I(Q)$ is meaningless except for dilute solutions whereby polymer coils do not overlap. Inter-chain interactions for polymer systems are better handled using other methods described below.

Uniform density scatterers (such as particles) are characterized by $P(Q) = |F(Q)|^2$, so that:

$$\frac{d\Sigma(Q)}{d\Omega} = \Delta\rho^2 \frac{v^2 n^2 N}{V} P(Q) S_I(Q). \qquad (19)$$

Defining a particles' volume fraction as $\phi = Nnv/V$, the following result is obtained:

$$\frac{d\Sigma(Q)}{d\Omega} = \Delta\rho^2 S(Q) \qquad (20)$$
$$S(Q) = n\phi v P(Q) S_I(Q).$$

This is a well-known result. It is included here even-though it does not apply to polymer systems so that the derivation does not have to be repeated when covering scattering from particulate systems later. Note that the scattering factor S(Q) and the inter-particle structure factor $S_I(Q)$ should not be confused; S(Q) has the dimension of a volume whereas $S_I(Q)$ is dimensionless.

3. THE PAIR CORRELATION FUNCTION

Recall the definition for the inter-particle structure factor for a pair of particles (named 1 and 2):

$$S_I(Q) = N < \exp\left(-i\vec{Q}.\vec{R}_{12}\right) >= \frac{1}{N}\sum_{\alpha,\beta}^{N} < \exp\left(-i\vec{Q}.\vec{R}_{\varepsilon\beta}\right) > \qquad (21)$$
$$= \frac{1}{NV}\sum_{\alpha,\beta}^{N} \int d^3R_{\alpha\beta} \exp\left(-i\vec{Q}.\vec{R}_{\alpha\beta}\right) P(\vec{R}_{\alpha\beta}).$$

$P(\vec{R}_{\alpha\beta})$ is the probability of finding particle β in volume $d^3R_{\alpha\beta}$ a distance $\vec{R}_{\alpha\beta}$ away given that particle α at the origin. When the self term (α = β) is omitted, this result becomes:

$$S_I(Q) - 1 = \frac{1}{NV}\sum_{\alpha\neq\beta}^{N} \int d^3\vec{R}_{\varepsilon\beta} \exp\left(-i\vec{Q}.\vec{R}_{\alpha\beta}\right) P(\vec{R}_{\alpha\beta}) \qquad (22)$$
$$= \frac{N}{V}\int d^3\vec{R}_{12} \exp\left(-i\vec{Q}.\vec{R}_{12}\right) P(\vec{R}_{12}).$$

The probability $P(\vec{R}_{12})$ is referred to as the pair correlation function and is often called $g(\vec{R}_{12})$. Removing the forward scattering term yields the following well known result:

$$S_I(Q) - 1 = \frac{N}{V}\int d^3R_{12} \exp\left(-i\vec{Q}.\vec{R}_{12}\right)\left[g(\vec{R}_{12}) - 1\right] + (2\pi)^3\delta(Q). \qquad (23)$$

The last term (containing the Dirac Delta function) is irrelevant and can be neglected. This last equation shows that $S_1(Q)-1$ and $g(\vec{R}_{12})-1$ are a Fourier transform pair. Note that $g(\vec{R}_{12})$ peaks at the first nearest-neighbor shell and goes asymptotically to unity at large distances. The total correlation function is introduced as $h(\vec{R}_{12}) = g(\vec{R}_{12})-1$.

4. POLYMER SOLUTIONS

In the case of polymer solutions, the Zimm single-contact approximation (Zimm, 1946; Zimm, 1948) is a simple way of expressing the inter-polymer structure factor. Within that approximation, the first order term in a "concentration" expansion is as follows:

$$\sum_{i,j}^{n} < \exp\left(-i\vec{Q}.\vec{r}_{1i2j}\right) > = -\frac{v_{ex}}{V}\left(\frac{v^2}{V}n^2 P(Q)\right)^2 + \ldots \qquad (24)$$

v_{ex} is a dimensionless factor representing interactions. The cross section becomes an expansion:

$$\frac{d\Sigma(Q)}{d\Omega} = \Delta\rho^2\left[S_0(Q) - \frac{v_{ex}}{V}\left(S_0(Q)\right)^2 + \ldots\right]. \qquad (25)$$

This expansion can be resumed as follows $1 - x + x^2 \ldots = 1/(1+x)$ to yield:

$$\frac{d\Sigma(Q)}{d\Omega} = \Delta\rho^2 \frac{S_0(Q)}{1 + \frac{v_{ex}}{V}S_0(Q)}. \qquad (26)$$

The bare structure factor for non-interacting polymers has been defined as:

$$S_0(Q) = \frac{Nn^2v^2}{V}P(Q) = n\phi v P(Q). \qquad (27)$$

Resuming the series extends the single-contact approximation's applicability range to a wide concentration regime. The single-contact approximation applies best to semi-dilute solutions.

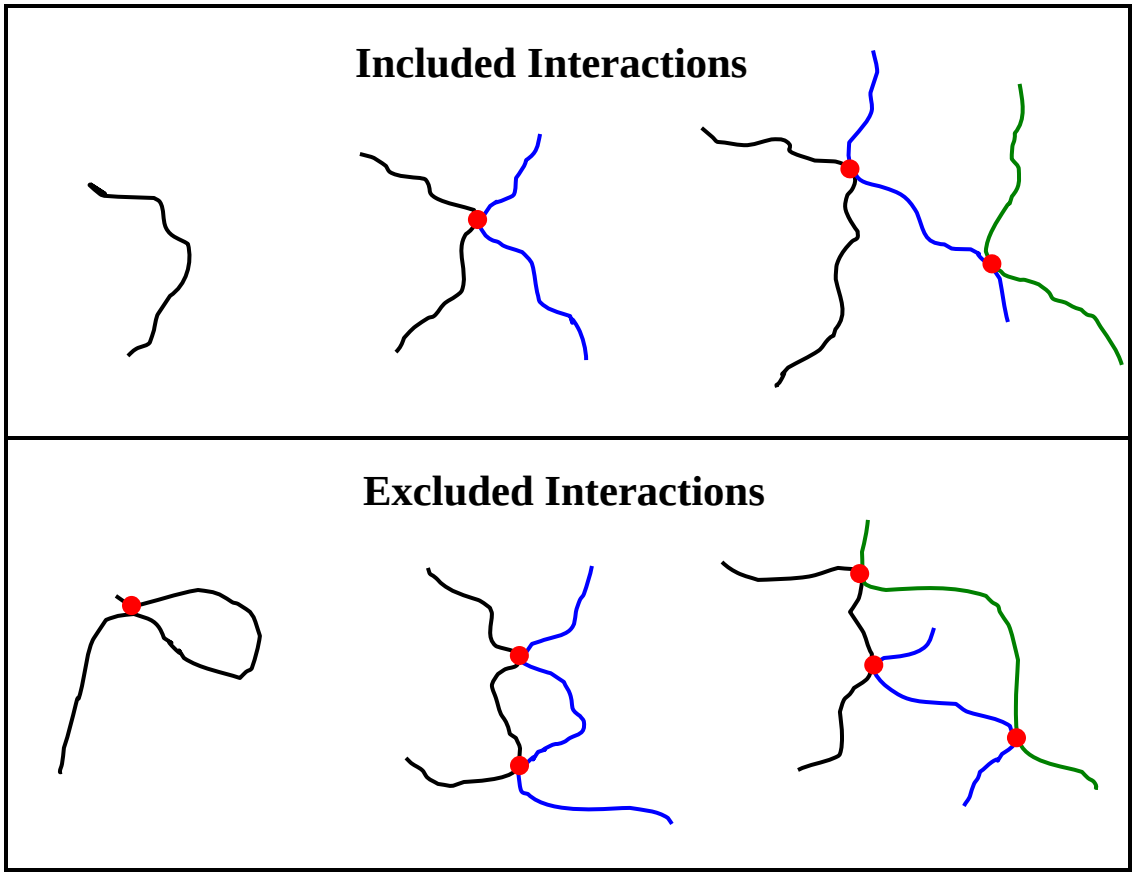

Figure 2: Typical interactions that are included and those that are excluded within the single-contact approximation.

5. THE ZERO CONTRAST METHOD

The zero contrast (or scattering length density match) method also called the high concentration method for polymer systems consists of using a mixture of deuterated and non-deuterated polymers and deuterated and non-deuterated solvents in order to isolate the single-chain form factor; i.e., in order to cancel out the inter-chain interaction terms. The scattering cross section for a polymer solution containing both deuterated and non-deuterated polymers is given by:

$$\frac{d\Sigma(Q)}{d\Omega} = \Delta\rho_D{}^2 S_{DD}(Q) + \Delta\rho_H{}^2 S_{HH}(Q) + 2\Delta\rho_D \Delta\rho_H S_{HD}(Q). \qquad (28)$$

The scattering length density differences between the deuterated (or hydrogenated) polymer and the solvent are:

$$\Delta\rho_D = (\rho_D - \rho_S) = \left(\frac{b_D}{v_D} - \frac{b_S}{v_S}\right) \tag{29}$$

$$\Delta\rho_H = (\rho_H - \rho_S) = \left(\frac{b_H}{v_H} - \frac{b_S}{v_S}\right).$$

The various partial scattering factors are split into single-chain parts and inter-chain parts as follows:

$$S_{DD}(Q) = n_D \phi_D v_D \left[P^S{}_D(Q) + \phi_D P^I{}_{DD}(Q)\right] \tag{30}$$

$$S_{HH}(Q) = n_H \phi_H v_H \left[P^S{}_H(Q) + \phi_H P^I{}_{HH}(Q)\right]$$

$$S_{HD}(Q) = \sqrt{n_H \phi_H v_H}\sqrt{n_D \phi_D v_D}\sqrt{\phi_H \phi_D}\, P^I{}_{HD}(Q).$$

Note that the inter-chain structure factors could be negative depending on the volume fraction. Assume that deuterated and hydrogenated polymers have the same degree of polymerization ($n_D = n_H = n_P$), and the same specific volume ($v_D = v_H = v_P$), and define the polymer volume fraction as $\phi_P = \phi_D + \phi_H$. The contrast match method consists in varying the relative deuterated to hydrogenated volume fraction but keeping the total polymer volume fraction constant.

Define the following "average of the square" and "square of the average" polymer contrast factors:

$$\left\{\Delta B_P{}^2\right\} = \left[\Delta\rho_D{}^2 \frac{\phi_D}{\phi_P} + \Delta\rho_H{}^2 \frac{\phi_H}{\phi_P}\right] \tag{31}$$

$$\left\{\Delta B_P\right\}^2 = \left[\Delta\rho_D \frac{\phi_D}{\phi_P} + \Delta\rho_H \frac{\phi_H}{\phi_P}\right]^2.$$

The scattering cross section becomes:

$$\frac{d\Sigma(Q)}{d\Omega} = \left\{\Delta B_P{}^2\right\} n_P \phi_P v_P P_S(Q) + \left\{\Delta B_P\right\}^2 n_P \phi_P v_P P_I(Q)$$

$$= \left(\left\{\Delta B_P{}^2\right\} - \left\{\Delta B_P\right\}^2\right) n_P \phi_P v_P P_S(Q) + \left\{\Delta B_P\right\}^2 n_P \phi_P v_P P_T(Q). \tag{32}$$

The following definition has been used:

$$P_T(Q) = P_S(Q) + \phi_P P_I(Q). \tag{33}$$

Note the following simplifications:

$$\left\{\Delta B_P{}^2\right\} - \left\{\Delta B_P\right\}^2 = \left(\rho_D - \rho_H\right)^2 \frac{\phi_D \phi_H}{\phi_P{}^2}. \tag{34}$$

$$\left\{\Delta B_P\right\} = \Delta\rho_D \frac{\phi_D}{\phi_P} + \Delta\rho_H \frac{\phi_H}{\phi_P} = \rho_D \frac{\phi_D}{\phi_P} + \rho_H \frac{\phi_H}{\phi_P} - \rho_S.$$

The final result follows:

$$\frac{d\Sigma(Q)}{d\Omega} = \left(\rho_D - \rho_H\right)^2 \frac{\phi_D \phi_H}{\phi_P{}^2} n_P \phi_P v_P P_S(Q) + \left(\rho_D \frac{\phi_D}{\phi_P} + \rho_H \frac{\phi_H}{\phi_P} - \rho_S\right)^2 n_P \phi_P v_P P_T(Q). \tag{35}$$

Setting the second contrast factor (between the polymer and the solvent) to zero cancels the second term containing $P_T(Q)$ leaving only the first term containing the single-chain form factor $P_S(Q)$. This zero contrast condition is therefore:

$$\rho_D \frac{\phi_D}{\phi_P} + \rho_H \frac{\phi_H}{\phi_P} = \rho_S. \tag{36}$$

Note that in general in order to achieve this condition, the solvent must also consist of mixtures of deuterated and non-deuterated solvents. Defining the following four indices DP, HP, DS, and HS for deuterated polymer, non-deuterated (hydrogenated) polymer, deuterated solvent and non-deuterated solvent, the contrast match condition becomes in the general case:

$$\rho_{DP} \frac{\phi_{DP}}{\phi_P} + \rho_{HP} \frac{\phi_{HP}}{\phi_P} = \rho_{DS} \frac{\phi_{DS}}{\phi_S} + \rho_{HS} \frac{\phi_{HS}}{\phi_S}. \tag{37}$$

Note that $\phi_{DP} + \phi_{HP} = \phi_P$, $\phi_{DS} + \phi_{HS} = \phi_P$ and $\phi_P + \phi_S = 1$.

6. THE RANDOM PHASE APPROXIMATION

The random phase approximation (de Gennes, 1979, Akcasu-Tombakoglu, 1990; Hammouda, 1993; Higgins-Benoit, 1994) is a simple mean-field approach used to calculate the linear response of a homogeneous polymer mixture following a thermodynamic fluctuation. Consider a binary mixture consisting of a mixture of polymers 1 and 2 with fluctuating densities $n_1(Q)$ and $n_2(Q)$. The interaction potentials between monomers 1 and 2 are W_{11}, W_{12}, W_{21} and W_{22}. Assume an external perturbation represented by potentials U_1 and U_2 and a constraint u that helps apply the incompressibility assumption. The parameter u can be thought of as a Lagrange multiplier in an optimization problem with constraints. The constraint here is the incompressibility condition. The linear response equations follow:

$$v_1 n_1(Q) = -S_{11}^0(Q)\left[\frac{U_1 + u + W_{11} v_1 n_1(Q) + W_{12} v_2 n_2(Q)}{k_B T}\right] \quad (38a)$$

$$v_2 n_2(Q) = -S_{22}^0(Q)\left[\frac{U_2 + u + W_{21} v_1 n_1(Q) + W_{22} v_2 n_2(Q)}{k_B T}\right] \quad (38b)$$

$$v_1 n_1(Q) + v_2 n_2(Q) = 0 . \quad (38c)$$

The last equation represents the incompressibility constraint. The non-interacting or "bare" structure factors $S_{11}^0(Q)$ and $S_{22}^0(Q)$ have been defined. These equations have assumed that no copolymers are present in the homogeneous mixture; i.e., that $S_{12}^0(Q) = S_{21}^0(Q) = 0$.

In order to solve the set of linear equations, we extract the perturbing potential u from the second equation and substitute it into the first equation to obtain:

$$v_1 n_1(Q) = -S_{11}^0(Q)\left[\frac{U_1 - U_2}{k_B T} + v_{11}(Q) n_1(Q)\right]. \quad (39)$$

This applies along with the following equation representing the response of the fully interacting system:

$$v_1 n_1(Q) = -S_{11}(Q)\left[\frac{U_1 - U_2}{k_B T}\right]. \quad (40)$$

The factor $v_{11}(Q)$ and the Flory-Huggins interaction parameter χ_{12} are defined as:

$$v_{11}(Q) = \frac{1}{S_{22}^0(Q)} - \frac{2\chi_{12}}{v_0} \quad (41)$$

$$\chi_{12} = \frac{W_{12}}{k_B T} - \left(\frac{W_{11} + W_{22}}{2 k_B T}\right).$$

Here v_0 is a reference volume (often taken to be $v_0 = \sqrt{v_1 v_2}$).

The RPA result for a homogeneous binary blend mixture follows:

$$\frac{1}{S_{11}(Q)} = \frac{1}{S_{11}^0(Q)} + \frac{1}{S_{22}^0(Q)} - \frac{2\chi_{12}}{v_0} \quad (42)$$

$$S_{11}^0(Q) = n_1\phi_1 v_1 P_1(Q).$$

$$P_1(Q) = \frac{2}{Q^4 R_{g1}^{\ 4}}\left[\exp(-Q^2 R_{g1}^{\ 2}) - 1 + Q^2 R_{g1}^{\ 2}\right]$$

R_{g1} is the radius of gyration. The incompressibility assumption yields the simplifying relations:

$$S_{11}(Q) = S_{22}(Q) = -S_{12}(Q) = S(Q). \qquad (43)$$

The scattering cross section is given by:

$$\frac{d\Sigma(Q)}{d\Omega} = (\rho_1 - \rho_2)^2 S(Q) \qquad (44)$$

$$\frac{(\rho_1 - \rho_2)^2}{\frac{d\Sigma(Q)}{d\Omega}} = \frac{1}{S_{11}^0(Q)} + \frac{1}{S_{22}^0(Q)} - \frac{2\chi_{12}}{v_0}.$$

This is the so-called de Gennes formula representing the scattering cross section for polymer blends in the single-phase (mixed phase) region. This is based on the Random Phase Approximation that applies for long degree of polymerizations (n_1>>1 and n_2>>2) and far from the phase boundary condition. This approach does not apply inside the demixed phase region.

This formalism also applies to polymer solutions by replacing one of the polymers (say component 2) by solvent; i.e., by setting $n_2 = 1$ and $P_2(Q) = 1$. In the case of polymer solutions, the excluded volume effect is included in the polymer form factor $P_1(Q)$. Note that the second virial coefficient can be defined for polymer solutions as $A_2 = v_{11}(Q=0)/2$.

The phase separation condition is achieved when the scattering intensity "blows up"; i.e., in the limit $S_{11}(Q=0) \to \infty$. This is achieved for

$$S_{11}^0(0) + S_{22}^0(0) - \frac{2\chi_{12}}{v_0} S_{11}^0(0) S_{22}^0(0) = 0. \qquad (45)$$

This is the so-called spinodal condition. Note that with the simplifying assumptions that $n_1 = n_2 = n$, $v_1 = v_2 = v_0$ and $\phi_1 = \phi_2 = 0.5$, the spinodal condition for polymer blends simplifies to $\chi_{12} n = 2$.

7. THE ISOTHERMAL COMPRESSIBILITY FACTOR

Most mixed polymer systems have finite compressibility. The scattering cross section consists of a Q-dependent coherent scattering term which is a good monitor of the structure, a Q-independent incoherent scattering term (mostly from hydrogen scattering), and another Q-independent "isothermal compressibility" term expressed as:

$$\left[\frac{d\Sigma}{d\Omega}\right]_{iso-comp} = \Delta\rho^2 \, k_B T \, \chi_T \, . \qquad (46)$$

Here $\Delta\rho^2$ is the contrast factor, $k_B T$ is the temperature in energy units and χ_T is the isothermal compressibility which is defined as:

$$\chi_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T . \qquad (47)$$

The isothermal compressibility term is usually small compared to the other terms. For example, $\chi_T = 4.57*10^{-4}$ cm^3/J for pure water at 25 ^oC and atmospheric pressure (Weast, 1984). χ_T is set equal to zero altogether for incompressible mixtures.

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QUESTIONS

1. What is the primary effect of the incompressibility assumption on the scattering cross section?
2. If an incompressible polymer solution is characterized by one (independent) structure factor, how many structure factors describe the equivalent compressible solution?
3. What is the Zimm single-contact approximation?
4. Does the inter-chain structure factor (with excluded volume) for dilute polymer solutions tend to increase or decrease the scattering intensity at low-Q?
5. What is the use of the zero contrast condition in concentrated polymer systems? What is the procedure to follow?
6. The Random Phase Approximation applies in what conditions?
7. What is the origin of monomer/monomer interactions in polymer mixtures?
8. Are polymer chains in mixed polymer blends characterized by excluded volume; i.e., are they swollen?
9. What is the pair correlation function g(r)?
10. Estimate $k_B T \chi_T$ (χ_T is the isothermal compressibility) for pure water for 25 ^oC and 1 atmosphere pressure.

ANSWERS

1. The primary effect of the incompressibility assumption is to simplify the scattering cross section from its full form $\frac{d\Sigma(Q)}{d\Omega} = \rho_P{}^2 S_{PP}(Q) + \rho_S{}^2 S_{SS}(Q) + 2\rho_P \rho_S S_{PS}(Q)$ (where P and S represent the polymer and the solvent respectively) to its simplified form $\frac{d\Sigma(Q)}{d\Omega} = (\rho_P - \rho_S)^2 S_{PP}(Q) = \Delta\rho^2 S_{PP}(Q)$. This is due to the incompressibility condition relating the various partial structure factors $S_{PP}(Q) = S_{SS}(Q) = -S_{PS}(Q) = -S_{SP}(Q)$.
2. An incompressible polymer solution is characterized by one structure factor $S_{PP}(Q)$. The equivalent compressible polymer solution is described by three structure factors: $S_{PP}(Q)$, $S_{SS}(Q)$ and $S_{PS}(Q)$.
3. The Zimm single-contact approximation assumes that inter-chain interactions occur only through single contacts or chains of single contacts. Double contacts within the same chain or between two different chains or higher order contacts are not included.
4. The inter-chain structure factor (with excluded volume) for dilute solutions decreases the scattering intensity at low-Q. Recall the negative sign in Zimm's single-contact approximation formula: $\frac{d\Sigma(Q)}{d\Omega} = \Delta\rho^2 \left[S_0(Q) - \frac{v_{ex}}{V} (S_0(Q))^2 + \ldots \right]$.
5. The contrast match method is a way to extract single-chain properties (such as the radius of gyration) from concentrated polymer systems. This method consists in using a mixture of deuterated and non-deuterated polymers and deuterated and non-deuterated solvents in the zero average contrast condition. This involves varying the deuterated to non-deuterated polymer fraction but keeping the total polymer fraction constant.

6. The Random Phase Approximation applies for high molecular weight polymers in the single-phase (mixed phase) region. It does not apply in the demixed phase region.
7. Monomers interact with each other and with organic solvent molecules due to Van der Waals interactions mostly. Hydrogen bonding dominates in water-soluble polymers.
8. Polymer coils follow random walk statistics in mixed polymer blends. They are not swollen like in polymer solutions. Their form factor is the well-known Debye function.
9. The pair correlation function g(r) is the probability of finding a scatterer at a radial distance r from another scatterer at the origin.
10. $k_BT = 1.38*10^{-23}$ [$J.K^{-1}$]*295 [K] = $4.112*10^{-21}$ [J] and $\chi_T = 4.57*10^{-4}$ cm^3/J so that $k_BT\ \chi_T = 1.879*10^{-24}$ cm^3.