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been considered in the present contribution but may be helpful for a more quantitative interpretation of the experimental findings. The work was kindly supported by Maizena Industrial Products, Hamburg, and the Deutsche Forschungsgemeinschaft within the scheme SFB 60.

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Theory of Dynamic Scattering from Ternary Mixtures of Two Homopolymers and a Solvent

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ABSTRACT: The random phase approximation technique, which has been used previously for static and some dynamical problems, is extended to the case of a mixture of two polymers in a solvent. The expressions of intermediate scattering functions obtained are valid at any concentration and for any mixture of monodisperse systems. The main result of this work is that there are two relaxation processes, which we have interpreted as cooperative and interdiffusion modes. The variations of amplitudes and decay rates of these modes with the composition are discussed. Two simple cases are considered in detail: (i) two interacting polymers of the same size but different contrast factors, (ii) a model for a bimodal molecular weight distribution obtained with two monodisperse polymers differing in molecular weight but otherwise identical. It is shown that it is possible to find conditions in which the two modes are identified.

I. Introduction

In recent years, there has been a growing interest in the scattering properties of ternary mixtures of two homopolymers and a solvent from both static[1,2] and dynamic[3-5] points of view. We have recently developed a theory of elastic scattering from such systems that is valid not only in the thermodynamic limit of forward scattering (i.e., zero angle) but also at any angle θ or wave vector $q = (4\pi/\lambda) \sin \theta/2$, where λ is the wavelength of the incident radiation. This theory predicts the essential features of the experimental data for mixtures of homopolymers in solution and, in certain cases, a reasonable quantitative agreement is obtained.[6] The present work attempts to generalize this theory for dynamical properties of such systems. First, we present the general formalism, which can be applied to an arbitrary mixture of homopolymers. Since it is difficult to extract the physical implications from general formulas, two particular practical examples are considered.

The first one is for a mixture of two polymers having the same molecular weight and dimensions but differing in their indices of refraction or contrast factors. We assume that we remain in the range of concentration and compatibility for which we have an homogeneous solution. In the second example, we investigate the effect of polydispersity for the case of two polymers with different molecular weights but otherwise identical. Both problems have been examined in the bulk limit[3] and in the dilute regime.[7] Here, we make an attempt to generalize these results at any concentration, within the framework of Ornstein–Zernike[8] theory or random phase approximation (RPA). The spirit of this approximation is to express the total intensity scattered by various species in the system, taking into account their interactions, in terms of the scattered intensity by the individual molecules. To make this clearer, let $S_{ii}(q)$ denote the static intensity scattered by the molecules of species i. $S_{ii}(q)$ is, in general, a sum of the intensity $S_{ii}^0(q)$ scattered by individual molecules and the contribution $Q_{ii}(q)$ due to the interactions between these molecules, i.e.

$$S_{ii}(q) = S_{ii}^0(q) + Q_{ii}(q) \tag{1}$$

Furthermore, interactions between different species i and j contribute to the total intensity through the quantity

$$S_{ij}(q) = Q_{ij}(q) \qquad (i \neq j) \tag{2}$$

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Similarly, the same formalism can be applied to inelastic scattering intensities or intermediate scattering functions. If we use the Kronecker delta function δ_{ij}, this can be written as

$$S_{ij}(q,t) = \delta_{ij}S_{ij}{}^0(q,t) + Q_{ij}(q,t) \tag{3}$$

$S_{ii}{}^0(q)$ and $S_{ii}{}^0(q,t)$ are referred to as the bare static structure factor and the bare intermediate scattering function, respectively. The total intermediate scattering function is

$$S(q,t) = \sum_i\sum_j a_i a_j S_{ij}(q,t) \tag{4}$$

This equation reduces to the static case by writing $t = 0$. a_i and a_j are contrast factors for neutrons and increments of refractive indices for light relative to polymers i and j, respectively. The RPA is used to express the Q_{ij}s in terms of the $S_{ii}{}^0$s.

II. Theoretical Formalism

A. Response Functions. In the dynamical version of the RPA, one introduces the dynamical response functions by expressing the time and q-dependent density fluctuations of the i-th polymer species $\delta\rho_i(q,t)$, as a response to an external excitation $\delta U_i(q,t)$. We use Fourier transforms because it is much more convenient to work in Fourier space than in real space. One proceeds in two steps. First, one writes density fluctuations in terms of bare response functions $\chi_{ii}{}^0(q,t)$

$$\delta\rho_i(q,t) = -\int_{-\infty}^{t} \mathrm{d}t'\, \chi_{ii}{}^0(q,t-t')[\delta U_i(q,t') + \sum_j v_{ij}\delta\rho_j(q,t')] \tag{5}$$

where $\chi_{ii}{}^0(q,t)$ are simply related to $S_{ii}{}^0(q,t)$ by[9]

$$kT\chi_{ii}{}^0(q,t) = -(\partial/\partial t)S_{ii}{}^0(q,t) \tag{6}$$

k is the Boltzman constant and T the absolute temperature. The second term on the right-hand side of eq 5 represents an internal potential due to the interactions between particles in the course of their rearrangements. v_{ij} are the familiar excluded volume parameters for pairs of monomers of type i and j. This potential was shown to act as a feedback mechanism in a closed-loop system (see Figure 1 of ref 3).

Taking the Laplace transform of eq 5 gives

$$\delta\rho_i(q,s) = -\chi_{ii}{}^0(q,s)[\delta U_i(q,s) + \sum_j v_{ij}\delta\rho_j(q,s)] \tag{7}$$

The next step consists of resolving these linear equations as

$$\delta\rho_i(q,s) = -\sum_j \chi_{ij}(q,s)\delta U_j(q,s) \tag{8}$$

which defines the response functions $\chi_{ij}(q,s)$ for the interacting system. These equations, for the case of an incompressible mixture of two polymers 1 and 2 in a solvent, yield

$$\chi_{11}(q,s) = \chi_{11}{}^0(q,s)[1 + v_{22}\chi_{22}{}^0(q,s)]/\{[1 + v_{11}\chi_{11}{}^0(q,s)] \times [1 + v_{22}\chi_{22}{}^0(q,s)] - v_{12}{}^2\chi_{11}{}^0(q,s)\chi_{22}{}^0(q,s)\} \tag{9}$$

$$\chi_{12}(q,s) = \chi_{21}(q,s) = -[v_{12}\chi_{11}{}^0(q,s)\chi_{22}{}^0(q,s)]/\{[1 + v_{11}\chi_{11}{}^0(q,s)][1 + v_{22}\chi_{22}{}^0(q,s)] - v_{12}{}^2\chi_{11}{}^0(q,s)\chi_{22}{}^0(q,s)\} \tag{10}$$

$\chi_{22}(q,s)$ can be deduced from $\chi_{11}(q,s)$ by interchanging indices 1 and 2. These equations are similar to those obtained in the static case,[2] replacing simply $\chi_{ij}(q,s)$ by $\chi_{ij}(q)$ and $\chi_{ii}{}^0(q,s)$ by $\chi_{ii}{}^0(q)$ and recalling the relationship between $S_{ij}(q)$ and $\chi_{ij}(q)$

$$S_{ij}(q) = kT\chi_{ij}(q) \tag{11}$$

Since these equations will be needed later, it is worthwhile to write them down explicitly

$$S_{11}(q) = \frac{S_{11}{}^0(q)[1 + v_{22}S_{22}{}^0(q)]}{[1 + v_{11}S_{11}{}^0(q)][1 + v_{22}S_{22}{}^0(q)] - v_{12}{}^2S_{11}{}^0(q)S_{22}{}^0(q)} \tag{12}$$

and

$$S_{12}(q) = S_{21}(q) = -\frac{v_{12}S_{11}{}^0(q)S_{22}{}^0(q)}{[1 + v_{11}S_{11}{}^0(q)][1 + v_{22}S_{22}{}^0(q)] - v_{12}{}^2S_{11}{}^0(q)S_{22}{}^0(q)} \tag{13}$$

$S_{22}(q)$ can be deduced from $S_{11}(q)$ by interchanging indices. Using classical thermodynamics,[10] one can show that, when the number of solvent molecules per unit volume N_s goes to zero (i.e., bulk limit), v_{ij} (redefined as v_{ij}/kT) can be replaced by $N_s{}^{-1}$ and $(v_{11}v_{22} - v_{12}{}^2)$ by $-2\chi v_s N_s{}^{-1}$, where v_s is the volume of a solvent molecule and χ the interaction parameter in the sense of Flory[11] (i.e., referring to the volume of a monomer unit having the same volume as the solvent molecule). Therefore, the bulk limit, which was the subject of an earlier investigation,[3] can be easily deduced from the above equations by letting N_s go to zero.

B. Intermediate Scattering Functions and Relaxation Modes. In light or neutron scattering experiments, one can choose properly the type of polymers and solvents or use an appropriate labeling procedure (for neutrons) to have access either to the partial dynamical functions $S_{ij}(q,t)$ or to the total scattering function $S(q,t)$ given by eq 4. Therefore it is interesting to be able to evaluate theoretically the relative contribution of each quantity separately, which leads us to introduce a matrix notation and define a dynamical scattering matrix $\mathbf{S}(q,t)$ as

$$\mathbf{S}(q,t) = \begin{bmatrix} S_{11}(q,t) & S_{12}(q,t) \\ S_{21}(q,t) & S_{22}(q,t) \end{bmatrix} \tag{14}$$

To proceed further, we assume that this matrix evolves over time following the simple exponential form

$$\mathbf{S}(q,t) = e^{-\Omega t}\cdot\mathbf{S}(q) \tag{15}$$

where $\Omega(q)$ is identified as the first cumulant matrix

$$\Omega(q) = -\lim_{t\to 0} \frac{\partial}{\partial t}\mathbf{S}(q,t)\cdot\mathbf{S}^{-1}(q) \tag{16}$$

This approximation, which consists of neglecting the memory matrix in the framework of the generalized Langevin equation satisfied by $\mathbf{S}(q,t)$, is well-known;[12,13] it is discussed at length in the references.

The resolution of eq 15 is straightforward. One obtains the following results:

$$S_{11}(q,t) = a_{\mathrm{I}}e^{-\Gamma_{\mathrm{I}}t} + a_{\mathrm{c}}e^{-\Gamma_{\mathrm{c}}t} \tag{17}$$

$$S_{21}(q,t) = b_{\mathrm{I}}e^{-\Gamma_{\mathrm{I}}t} + b_{\mathrm{c}}e^{-\Gamma_{\mathrm{c}}t} \tag{18}$$

where the amplitudes a_{I}, b_{I}, a_{c}, and b_{c} are

$$a_{\mathrm{I}} = \frac{(\Gamma_{\mathrm{I}} - \Omega_{22})S_{11}(q) + \Omega_{12}S_{21}(q)}{\Gamma_{\mathrm{I}} - \Gamma_{\mathrm{c}}} \tag{19}$$

$$a_{\mathrm{c}} = \frac{(\Gamma_{\mathrm{c}} - \Omega_{22})S_{11}(q) + \Omega_{12}S_{21}(q)}{\Gamma_{\mathrm{c}} - \Gamma_{\mathrm{I}}} \tag{20}$$

$$b_{\mathrm{I}} = \frac{(\Gamma_{\mathrm{I}} - \Omega_{11})S_{21}(q) + \Omega_{21}S_{11}(q)}{\Gamma_{\mathrm{I}} - \Gamma_{\mathrm{c}}} \tag{21}$$

$$b_c = \frac{(\Gamma_c - \Omega_{11})S_{21}(q) + \Omega_{21}S_{11}(q)}{\Gamma_c - \Gamma_I} \qquad (22)$$

Γ_I and Γ_c are the eigenvalues of $\mathbf{\Omega}$, i.e.

$$\Gamma_I = \Omega_{av} - (\Omega_{av}{}^2 - \Delta(\Omega))^{1/2} \qquad (23)$$

$$\Gamma_c = \Omega_{av} + (\Omega_{av}{}^2 - \Delta(\Omega))^{1/2} \qquad (24)$$

where $\Omega_{av} = (\Omega_{11} + \Omega_{22})/2$ and $\Delta(\Omega) = \Omega_{11}\Omega_{22} - \Omega_{12}\Omega_{21}$, and Ω_{ij} are the matrix elements of $\mathbf{\Omega}$. $S_{22}(q,t)$ and $S_{12}(q,t)$ are deduced from eq 17 and 18 by a proper interchange of indices.

All S_{ij}s are linear combinations of two exponentials characterized by the decay frequencies Γ_I and Γ_c. Therefore, regardless of the values of the contrast factors, the experimental results will depend on these modes. The different contrast factors will only modify the relative amplitudes of these modes. In the particular case where the two polymers have the same index of refraction (or contrast factors) $a_1 = a_2 = a$, and eq 4 can be written as

$$S(q,t) = a^2[S_{11}(q,t) + S_{22}(q,t) + S_{12}(q,t) + S_{21}(q,t)] = a^2[A_I e^{-\Gamma_I t} + A_c e^{-\Gamma_c t}] \qquad (25)$$

and we obtain for A_I and A_c the following expressions:

$$A_I = \{\Gamma_I[S_{11}(q) + S_{22}(q) + S_{12}(q) + S_{21}(q)] + [S_{11}(q) + S_{12}(q)][\Omega_{21} - \Omega_{22}] + [S_{22}(q) + S_{21}(q)] \times [\Omega_{12} - \Omega_{11}]\}/(\Gamma_I - \Gamma_c) \qquad (26a)$$

$$A_c = S_{11}(q) + S_{22}(q) + S_{12}(q) + S_{21}(q) - A_I \qquad (26b)$$

The relationship between dynamical responses and scattering functions is given by eq 6. In matrix form it becomes

$$kT\chi(q,t) = -(\partial/\partial t)\mathbf{S}(q,t) \qquad (27)$$

Combining this equation with the definition of the first cumulant matrix gives

$$\mathbf{\Omega} = \lim_{t\to 0} \chi(q,t)\cdot\chi^{-1}(q) \qquad (28)$$

and using the well-known Laplace limits theorem

$$\lim_{t\to 0} \chi(q,t) = \lim_{s\to\infty} s\chi(q,s)$$

one obtains

$$\mathbf{\Omega} = \lim_{s\to 0} s\chi(q,s)\cdot\chi^{-1}(q) \qquad (29)$$

One can write this equation in a standard form by defining the generalized mobility matrix $\mathbf{M}(q)$ as[13]

$$\mathbf{M}(q) = q^{-2} \lim_{s\to\infty} s\chi(q,s) \qquad (30)$$

Hence

$$\mathbf{\Omega} = q^2 kT\mathbf{M}(q)\cdot\mathbf{S}^{-1}(q) \qquad (31)$$

Therefore, since $\chi(q,s)$ and $\mathbf{S}(q)$ are known for this ternary mixture (see eq 9–13), we can calculate $\mathbf{\Omega}$ and thereby we can characterize completely the modes of relaxation of $\mathbf{S}(q,t)$.

C. Rouse Model. The substitution of eq 9 and 10 into eq 30 shows that the cross terms of the mobility matrix are zero (i.e.; $M_{12} = M_{21} = 0$) and that $M_{ii} = M_{ii}{}^0$ for $i = 1, 2$. This implies that the hydrodynamic interaction between different molecules has not been taken into account. Moreover, we assume that the Zimm type of hydrodynamic interactions are screened in the semidilute and concentrated regimes that are considered in this work. This is the reason that the dynamical motion of molecules in solution is described by the Rouse model.[14] This procedure implies that one neglects the intramolecular hydrodynamic interactions as well. One can easily remove this restriction by using the blob model, as suggested previously.[15] For simplicity all monomers are assumed to have the same friction coefficient denoted by ξ. With these restrictions, we obtain $M_{ii} = \phi_i/\xi$ and eq 31 simplifies significantly to

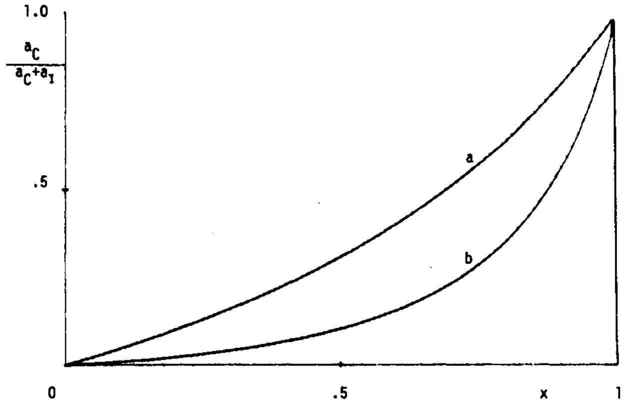

Figure 1. Variation of the relative amplitude of the cooperative mode $a_c/(a_c + a_I)$ as a function of the composition x of polymer 1 for a mixture of two interacting polymers at the $q = 0$ limit ($P(q) = P_1(q) = P_2(q) = 1$) where the constrast factor of polymer 2 is zero. The molecular weights of the two polymers are identical and $\chi/v = 5 \times 10^{-2}$: (a) $v\phi N = 1$; (b) $v\phi N = 5$.

$$\mathbf{\Omega} = q^2 \frac{kT}{\xi}\frac{1}{\Delta(S)}\begin{bmatrix} \phi_1 S_{22} & -\phi_1 S_{12} \\ -\phi_2 S_{21} & \phi_2 S_{11} \end{bmatrix} \qquad (32)$$

where $\phi_i = n_i N_i$ is the number of monomers per unit volume of type i, N_i the degree of polymerization of polymer i, and $\Delta(S)$ the quantity $S_{11}S_{22} - S_{12}S_{21}$. The results are illustrated below through two simple but practical examples.

III. Application to Two Special Cases

A. Two Interacting Polymers, One of Them Having No Contrast with the Solvent. The main result of the preceding section was to show that two relaxation modes characterize the time evolution of the dynamical scattering functions in the general case of a ternary mixture of two polymers and a solvent. This behavior is different from what is found in the case of a pure mixture of homopolymers where only one mode has been identified.[3] Therefore, it is useful to apply this theory to simple cases where experiments are possible and to check the existence of these modes. The first example we discuss here is one in which the two polymers have the same dimensions and molecular weights but differ in their scattering lengths or increments of refractive index, though they may have a nonzero interaction parameter χ. To simplify the problem further, we also assume that the quality of solvent is the same for both polymers and that the increment of refractive index or the scattering length of polymer 2 is matched by the solvent. The mixture PS–PMMA in toluene is an example of this situation. In these conditions, the intermediate scattering function reduces to $S_{11}(q,t)$, which is obtained as

$$S_{11}(q,t) = a_I e^{-\Gamma_I t} + a_c e^{-\Gamma_c t} \qquad (33)$$

a_I and a_c have been calculated, and the results are illustrated in Figure 1 where we have plotted $a_c/(a_c + a_I)$ as a function of x at $q = 0$, for $\chi/v = 5 \times 10^{-2}$ and $v\phi N = 1$ and 5. One should remember that in the standard notation $v\phi N = 2A_2Mc$, where A_2 is the second virial coefficient, c the concentration if g/mL, and M the molecular weight. To have an idea about what this parameter represents, one can define c^* as the concentration where the excluded volume between all the chains is equal to the volume of the solutions, i.e., $A_2Mc^* = 1$. This value c^* is not too far from the classical overlap concentration, which means that even for values of $v\phi N = 5$ the system is in the semidilute range. The frequencies Γ_I and Γ_c are

$$\Gamma_I = \Gamma_0(q)[1 - 2\phi\chi x(1 - x)NP(q)] \quad (34)$$

$$\Gamma_c = \Gamma_0(q)[1 + v\phi NP(q)] \quad (35)$$

Introducing the q-dependent critical interaction parameter

$$\chi^c(q) = [2\phi x(1 - x)NP(q)]^{-1} \quad (36)$$

one can rewrite Γ_I as follows:

$$\Gamma_I = \Gamma_0(q)\left[1 - \frac{\chi}{\chi^c(q)}\right] \quad (36')$$

$\Gamma_0(q)$ is the bare relaxation frequency characterizing the time decay of the bare scattering function $S^0(q,t)$. It is given by[12]

$$\Gamma_0(q) = q^2\frac{kT}{\zeta NP(q)} \quad (37)$$

where $P(q)$ is the form factor of a simple chain in the system and can generally be assumed to have the form of the Debye function, N is the number of monomers per chain, ζ is the friction coefficient which can depend on concentration, v is the excluded volume parameter, x is the fraction of polymer 1 in the system, and ϕ is the total segmental concentration in the system. In obtaining these results, we have assumed that χ/v is small compared to unity. In relatively dilute solutions, the quantity χ/χ^c is small when compared to 1; this means that the relaxation frequency Γ_I is practically unaffected by χ. We refer to this mode as an interdiffusion process. Furthermore, when $\chi = 0$, $\Gamma_I(q) = \Gamma_0(q)$ corresponds indeed to the diffusion of a single chain in the mixture. If the polymers are compatible and the solvent is good for both of them, $\chi/v \ll 1$, and the quantity $2\chi\phi Nx(1 - x)$ remains small compared to 1. In ref 3, which dealt with systems in bulk (mixtures of two homopolymers and pure monodisperse copolymers), we showed that the change of sign of χ did correspond simultaneously to the onset of dynamic unstability and to the crossing of the spinodal. Now, comparing eq 34–36 with the spinodal equation (which is given by letting the denominator D of eq 12 equal zero), we see that there is no identity between the two conditions. This means that this theory is only approximate. Nevertheless, these two conditions are not arbitrary and can be obtained from the general equation of the spinodal with very simple assumptions.

a. If one assumes that these two polymers, which have the same molecular weight and the same interaction parameter with the solvent $v_{11} = v_{22} = v$, have no incompatibility ($\chi = 0$), the equation of the spinodal can be written as

$$1 + v\phi N = 0$$

which is simply the bracket multiplying Γ_c in eq 35. In this case the spinodal corresponds to the separation between polymer and solvent. This justifies the cooperative term that has been given to this relaxation mode; it concerns the total concentration fluctuations of the two polymers.

b. If the concentration is high enough $v\phi N \gg 1$ and one can neglect unity in the equation of the spinodal, one finds

$$1 - 2\phi\chi Nx(1 - x) = 0$$

which is also the bracket of eq 34 defining Γ_I.

This part of the spinodal corresponds to the phase separation of two polymer solutions, one rich in polymer 1 and the second in polymer 2. Phase separation is due to the incompatibility of the polymers and Γ_I is related to the motions of one polymer with respect to the others. We refer to this as the interdiffusion mode.

One can also observe that, in the bulk limit, there is only one relaxation process Γ_I. The mode characterized by Γ_c disappears ($\Gamma_c \to \infty$). This is evident since we have assumed incompressibility of the system; there are no density fluctuations.

Suppose that we choose a concentration such that $v\phi N = 5$; the ratio Γ_c/Γ_I is about 6 and increases further if polymers are incompatible. This suggests a choice of experimental conditions close to the spinodal in order to have enough intensity in each of the two modes. Indeed, it is not sufficient to have a large value for the ratio Γ_c/Γ_I, but a_I and a_c should be of the same order of magnitude in order to be able to identify separately the cooperative and the interdiffusion modes. From Figure 1, it is evident that this can be achieved for approximately 0.8: these conditions are easy to obtain in an experiment.

We shall now summarize the discussion, making the following observations:

i. The interdiffusion mode describes the motion of individual chains with respect to each other; Γ_I goes to zero when we approach the phase separation between polymers. The decay rate of the cooperative mode depends on the excluded volume parameter, is insensitive to χ, and does not show any anomalous behavior when we approach the phase separation due to the incompatibility of the two polymers.

ii. In the bulk limit, v goes to infinity and thus Γ_c also. This implies that, as expected, the interdiffusion mode alone survives.

iii. In the small-q limit, one can define an interdiffusion coefficient D_I as $\Gamma_I = D_Iq^2$ and a cooperative diffusion coefficient D_c as $\Gamma_c = D_cq^2$. One expects D_c to increase and D_I to decrease with concentration. This is in fact what the present theory predicts and this can be seen in eq 34 and 35. As for D_c when $v\phi N \gg 1$, one obtains a very simple expression

$$D_c \approx \frac{kT}{\zeta}v\phi \quad (38)$$

iv. If one measures the initial slope of $S_{11}(q,t)$, one obtains a mean relaxation frequency which is a weighted average of Γ_I and Γ_c with respect to their relative amplitudes

$$\bar{\Gamma} = \frac{a_I\Gamma_I + a_c\Gamma_c}{a_I + a_c} \quad (39)$$

when the composition of component 1 goes to zero ($x \to 0$) keeping the total concentration constant, the mean frequency $\bar{\Gamma}$ tends to $\Gamma_I = \Gamma_0$ or the diffusion of a single chain in the system.

B. Bimodal Polymer Solutions. To simulate the effect of polydispersity, we consider the case of a solution containing two polymers differing in their molecular weights but otherwise identical. This implies that they have the same refractive index increment. We shall suppose for the sake of simplicity that they have also the same excluded volume parameter. This is not rigorous but does not affect our conclusions significantly. The measurable dynamic scattering function $S(q,t)$ is given by the sum of the three S_{ij}s. The calculations are performed following the general formalism described in the first part, by letting

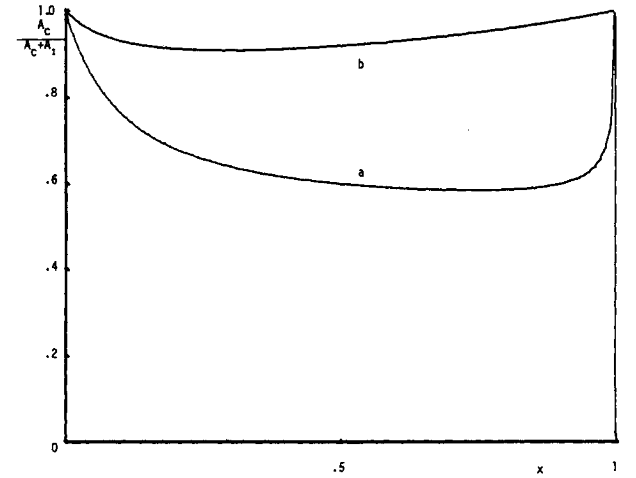

Figure 2. Variation of the relative amplitude of the cooperative mode $A_c/(A_c + A_I)$ as a function of x for a system at the $q = 0$ limit containing two polymers of different molecular weights (i.e., $y = N_1/N_2 = 10$) but otherwise identical: (a) $v\phi N = 1$; (b) corresponds to $v\phi N = 5$.

$S_{11}^0(q) = x\phi N_1P_1(q)$ and $S_{22}^0(q) = (1 - x)\phi N_2P_2(q)$, where N_1 and $P_1(q)$ are the degree of polymerization and the chain form factor of polymer 1, respectively. N_2 and $P_2(q)$ denote the same quantities for polymer 2. One obtains

$$a^{-2}S(q,t) = A_Ie^{-\Gamma_It} + A_ce^{-\Gamma_ct} \tag{40}$$

The amplitudes A_I and A_c are cumbersome functions of x, ϕ, N_1, N_2, $P_1(q)$, and $P_2(q)$ and are not reproduced explicitly here. Limiting values for $x = 0$ and 1 are given and plotted as a function of x (see Figure 2). Γ_I and Γ_c, however, are important quantities for the interpretation of scattering data, and, therefore, they are given explicitly

$$\frac{\Gamma_I}{q^2[(kT)/(N_2\zeta)]} = \frac{1}{2}\left[\frac{1}{yP_1} + \frac{1}{P_2} + v\phi N_2\right] - \frac{1}{2}\left[\left(v\phi N_2 + \frac{1}{P_2} - \frac{1}{yP_1}\right)^2 - 4xv\phi N_2\left(\frac{1}{P_2} - \frac{1}{yP_1}\right)\right]^{1/2} \tag{41}$$

$$\frac{\Gamma_c}{q^2[(kT)/(N_2\zeta)]} = \frac{1}{2}\left[\frac{1}{yP_1} + \frac{1}{P_2} + v\phi N_2\right] + \frac{1}{2}\left[\left(v\phi N_2 + \frac{1}{P_2} - \frac{1}{yP_1}\right)^2 - 4xv\phi N_2\left(\frac{1}{P_2} - \frac{1}{yP_1}\right)\right]^{1/2} \tag{42}$$

where $N_1 = yN_2$. It is interesting to observe the limits of these two modes, both their frequencies and amplitudes for $x = 0$ and $x = 1$. One obtains an expected result in both limits, namely, the cooperative diffusion due to concentration fluctuations in a solution of identical polymers

$$S(q,t) = A_ce^{-\Gamma_ct} \tag{43}$$

where for $x = 0$

$$A_c = \frac{\phi N_2P_2(q)}{1 + v\phi N_2P_2(q)}$$

$$\Gamma_c = q^2\frac{kT}{\zeta}\frac{1 + v\phi N_2P_2(q)}{N_2P_2(q)} \tag{44}$$

For $x = 1$, it is sufficient to replace the index 2 by 1 in this equation.

As x varies from 0 to 1, the cooperative diffusion mode shifts from the representation of a system of all identical chains of type 1 to that of another system of all identical chains of type 2. The amplitude of the interdiffusion mode A_I goes to zero in both limits, but its frequency is $q^2(kT/\zeta)[1/(N_1P_1(q))]$ at $x = 0$, and $q^2(kT/\zeta)[1/(N_2P_2(q))]$ at $x = 1$. The complete variation of the amplitudes and frequencies of the two modes as a function of x are given in Figures 2 and 3. Figure 2 shows the variation of $A_c/(A_c + A_I)$ as a function of x for two values of the concentration defined by $v\phi N_2 = 1$ and $v\phi N_2 = 5$. One notes that at high concentration the amplitude of the cooperative mode dominates and it becomes difficult to identify the second mode. If one wants to be able to observe both modes, one must choose a total concentration ϕ and a composition x such that the ratio $A_c/(A_c + A_I)$ is of the order of $^1/_2$, which means that A_c and A_I are of the same order of magnitude. Values of $v\phi N_2 = 1$ and $x = {}^1/_2$ seem to fulfill this condition approximately. One must also consider the relaxation frequencies Γ_I and Γ_c and choose conditions such that they can be distinguished easily. Figure 3, which gives the variations of $\Gamma_I/(q^2kT/N_2\zeta)$ and $\Gamma_c/(q^2kT/N_2\zeta)$ as a function of x for $v\phi N_2 = 1$ and 5 and $y = 10$, shows that the difference between Γ_I and Γ_c increases with the concentration. Therefore, one must choose $x \approx 0.5$ and a high concentration ϕ such that the amplitudes A_I and A_c are nearly equal. Figure 3 shows also the variation with x of the mean relaxation frequency $\bar{\Gamma}$ corresponding to the initial decay rate of $S(q,t)$ and defined by

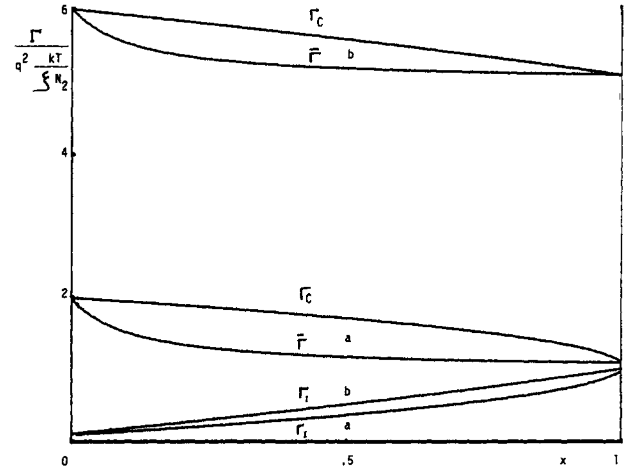

Figure 3. Variations with the composition x of the normalized relaxation frequencies $\Gamma_c/(q^2kT/N_2\zeta)$, $\Gamma_I/(q^2kT/N_2\zeta)$, and $\bar{\Gamma}/(q^2kT/N_2\zeta)$ for the same system as in Figure 2.

$$\bar{\Gamma} = \frac{A_I\Gamma_I + A_c\Gamma_c}{A_c + A_I} \tag{45}$$

The variation of $\bar{\Gamma}$ with x is close to that of Γ_c at different concentrations. In a previous paper,[7] in which hydrodynamic interaction was taken into account in the dilute regime, similar results were obtained. However, since these authors were interested only in the initial slope of $S(q,t)$ as a function of t, they did not try to identify the two modes. In the analysis of these examples, we did not discuss the influence of the value of the wave vector q on the results. It is evident by looking at eq 34–37 and 41–44 that the amplitudes and the frequencies of the modes are q dependent. Since in light scattering experiments one is practically always in the Guinier range ($qR_g < 1$), the functions $P(q)$ can be expanded by keeping only the first terms proportional to $q^2R_g^2$. This will give for the relaxation frequencies expressions of the form

$$\Gamma = Dq^2(1 + \alpha q^2R_g^2)$$

where the diffusion coefficient D and the coefficient α are easy to obtain. This could perhaps explain the experimental data of Hadgraft et al.[17]

Relations with Experiments. The former discussion shows that if we have only one relaxation mode for monodisperse systems there are two relaxation modes in the case of a bimodal distribution. Evidently these two modes are not always distinguishable depending on the experimental conditions. Since there are experimental results available (Nemoto et al.[18]), it is interesting to see if this theory can explain them. These authors have studied mixtures of polystyrene fractions in benzene in the semidilute regime. In one case, $M_{w1} = 775000$, $c_1 = 4.18 \times 10^{-2}$ g/g, $M_{w2} = 42800$, $c_2 = 2.58 \times 10^{-2}$ g/g, they obtain two relaxation times with a ratio 12.4 and a relative amplitude of the slow mode of 0.125. Knowing the second virial coefficient, one is able to evaluate these values with our model obtaining 11.4 and 0.06, respectively. Considering the precision, specially in the evaluation of the amplitude, the agreement is quite satisfactory. We did not try to show why in some other cases they report only one relaxation times since our purpose was just to show that this theory is able to explain the existence of two modes without being obliged to introduce sophisticated models.

IV. Conclusions

In this paper, we have investigated the dynamics of mixtures of homopolymers in a solvent using the RPA. We have given a general formalism that can be applied to mixtures having arbitrary properties of structure, concentration, thermodynamics, etc. The main point of this formalism is that it predicts two decay modes, which we have identified as cooperative and interdiffusion processes.

It seems that in some cases this theory can explain the results but much work remains to be done in order to see to what extent and with what precision this "mean-field" theory can describe the experimental data.

The same formalism can be readily applied to copolymer solutions, and this problem will be the subject of a forthcoming paper.

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Diffusion of Polymers in Semidilute Ternary Solutions. Investigation by Dynamic Light Scattering

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ABSTRACT: The dynamical behavior of a polystyrene/poly(methyl methacrylate)/toluene ternary mixture has been investigated by quasi-elastic light scattering in the semidilute range of concentration. According to theoretical calculations, two relaxation modes have been found. The slow motion is related to the relative motion of the two polymers (interdiffusion process). The fast motion is the classical cooperative motion of the physical network formed by the two polymers. The relative amplitude and the ratio of the frequencies of the two modes are in agreement with the theoretical predictions (Benmouna, M.; Benoit, H.; Duval, M.; Akcasu, Z. *Macromolecules*, preceding paper in this issue).

Introduction

The dynamical behavior of ternary systems containing two polymers and one solvent has been extensively studied by quasi-elastic light scattering (QELS). Two main groups of problems have been explored experimentally.

a. Two polymers, P1 and P2, differing in nature, are dissolved in a solvent that has the same index of refraction as P2. This implies that, from a scattering point of view, the system behaves like a quasi-binary mixture. Information on the motion of P1 entangled in P2 is obtained, and the concentration of P2 can be varied to see how the diffusion motion of P1 is affected.[1-8]

b. The second type of problem is a simple model of polydispersity. In the ternary mixture P1/P2/solvent, P1 and P2 have the same chemical nature but different molecular weights and relative concentrations.[9-11]

From these studies, it is seen that the correlation function of the scattered intensity $C(q,t)$ is usually not monoexponential; it has been sometimes analyzed as the sum of two exponentials. In both types of experiments when it is impossible to detect two relaxation phenomena, the experimentalists have analyzed $C(q,t)$ as if it was

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