Macromolecules **1994,** *27,* 5691-5696

Cooperative Diffusion and Interdiffusion in Polymer Solutions

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Received December 20, 1993; Revised Manuscript Received May 7, 1994®

ABSTRACT: It has been shown previously that collective diffusion as observed by dynamic light scattering from a binary polymer solvent system can be strongly influenced by longitudinal viscoelasticity. The formalism of ref 1 describing such a coupling is applied to a ternary system comprising either two types of homopolymers or one type of diblock copolymer in a solvent. It has to be distinguished between the decay of concentration fluctuations of the entire polymer subsystem, which is related to cooperative diffusion, and the decay of composition fluctuations, which is related to interdiffusion. Both, cooperative diffusion and interdiffusion, are found to couple to viscoelasticity. In addition, the interdiffusion process is affected by the total force exerted between the two species, which may create new effects.

1. Introduction

Dynamic light scattering from polymer solutions exhibit slow, viscoelastic modes in addition to a faster, diffusive mode. This type of slow mode becomes pronounced when lowering temperature, decreasing solvent quality, increasing polymer concentration, and increasing chain length.[2-9] Recent theoretical work provided new impulses on the understanding of the coupling between longitudinal viscoelasticity and collective diffusion.[1,10-12] According to ref 1, the mechanism behind these slow processes may be understood in the following way: Because diffusion of polymers is observed, the decay rate comprises a factor q^2, where $\mathbf{q}$ is the scattering vector. For a complete decay of fluctuations in polymer concentration, also internal rearrangement of individual polymers is necessary. This becomes more important with decreasing wavelength of the fluctuation and can theoretically be described by an additional q-dependent friction increasing as q^2. This results in slow, approximately q-independent modes on a time scale characteristic for internal polymer relaxations or viscoelasticity.

A ternary polymer solution containing two types of polymeric components in addition to the solvent is by itself more complicated. For homopolymers differing with respect to their monomeric units, or diblock copolymers combining two types of units on one chain, composition fluctuations arise in addition to fluctuations in the total polymer concentration. Whereas collective diffusion in a binary homopolymer solvent system has been studied extensively, there is less experimental knowledge on ternary systems.[13-16] When neglecting memory effects, two decay modes are predicted theoretically[17-21] and could also be detected experimentally.[13,14,16] Whereas these two modes are at least qualitatively understood, it is unknown which role the mechanisms creating viscoelastic modes in homopolymer solutions play here. This problem is addressed by applying the formalism of ref 1.

The paper is organized as follows: Section 2 briefly recapitulates the general results from ref 1 and sketches some simplifications. This provides the framework to introduce memory effects and viscoelasticity. Sections 3 and 4 consider a symmetrical system of two polymeric components in solution. This simplification has the advantage that the decay of fluctuations in polymer concentration and composition is decoupled and thus provides the possibility for a separate study of interdiffusion and cooperative diffusion. Section 3 describes the long-time limiting behavior, and section 4 discusses the time dependence of the decay of concentration and composition fluctuations.

2. General Theory

From dynamic light scattering experiments a dynamic scattering intensity can be deduced. Evidently, the result depends on the "visibility" of the polymeric components, or, more precisely, on the scattering contrast to the solvent. If the scattering lengths of both polymeric components are identical, fluctuations in the total polymer concentration can be studied, whereas under "zero-average contrast conditions"[13,21] the focus is on composition fluctuations. In general, the measured intensity can be expressed as a sum of partial scattering intensities weighted with appropriate scattering lengths, and these partial intensities are the subject of the theoretical investigation.

The system under consideration contains, in addition to the solvent, two types of polymer segments, and the index referring to the species is $\alpha = 1$ or 2. In the case of two different types of homopolymers, the segment concentrations are obtained from $c_\alpha = n_\alpha N_\alpha / V$, where n_α is the number of polymers belonging to species α in the volume V, and N_α is the number of statistical segments on a chain of species α. In a diblock copolymer system, the number of polymers containing segments of species 1 or 2 is $n_1 = n_2 = n$. The number of segments belonging to species α on each of these chains is N_α, and the entire chain comprises $N = N_1 + N_2$ segments. Within this notation, also the partial segment concentration in a diblock copolymer system is given by $c_\alpha = n_\alpha N_\alpha / V$, and the total segment concentration is $c = c_1 + c_2$.

The elements of the partial intensity matrix $\underline{I}(q,t)$ are defined in terms of the correlation functions of the partial densities $\rho_\alpha(\mathbf{q},t)$ in Fourier space by

$$I_{\alpha\beta}(q,t) = \langle \rho_\alpha(\mathbf{q},0)\, \rho_\beta(-\mathbf{q},t) \rangle \tag{1}$$

where the partial density of species $\alpha = 1$ or 2 is given by

$$\rho_\alpha(\mathbf{q},t) = V^{-1/2} \sum_i^{n_\alpha} \sum_l^{N_\alpha} \exp[-\mathrm{i}\mathbf{q}\cdot\mathbf{r}_{il}^{(\alpha)}(t)] \tag{2}$$

$\mathbf{r}_{il}^{(\alpha)}(t)$ denotes the position of segment l on polymer i belonging to species α at time t, and the summation in eq 2 is performed over all segments of species α.

In ref 1, the decay of the dynamic intensity matrix has been described by a generalized, time-dependent "fre-

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® Abstract published in *Advance ACS Abstracts*, September 1, 1994.

quency matrix" $\underline{\underline{\Omega}}(q,t)$ as

$$\frac{\partial}{\partial t}\underline{\underline{I}}(q,t) = -\underline{\underline{\Omega}}(q,t)\cdot\underline{\underline{I}}(q,t) \tag{3}$$

If this matrix is approximately constant in a certain time regime, characteristic rates referring to this time range are determined from the two eigenvalues of $\underline{\underline{\Omega}}$. To study the dynamics of ternary systems, $\underline{\underline{\Omega}}(q,t)$ has been approximated by its short-time limit[20]

$$\underline{\underline{\Omega}}(q,t\rightarrow 0) = \underline{\underline{\Omega}}^{(\mathrm{S})}(q) = q^2 k_{\mathrm{B}}T\begin{pmatrix} c_1/\xi_1^{(0)} & 0 \\ 0 & c_2/\xi_2^{(0)} \end{pmatrix}\cdot\underline{\underline{I}}^{-1}(q) \tag{4}$$

which depends on the segmental friction coefficients $\xi_\alpha^{(0)}$ and the static intensity matrix $\underline{\underline{I}}(q,t{=}0) = \underline{\underline{I}}(q)$ when neglecting hydrodynamic interaction. Equation 4 can explain the presence of two decay modes, but slow, nondiffusive modes as observed in a binary system are not included in such a description. To study these effects, the long-time limit of $\underline{\underline{\Omega}}(q,t)$ (eq 3) has to be considered.

In the long-time, Markovian limit, the generalized frequency matrix is related to the $z \rightarrow 0$ limit of the generalized friction matrix by[1]

$$\Omega_{\alpha\beta}(q,t\rightarrow\infty) = \Omega_{\alpha\beta}^{(L)}(q) = q^2 k_{\mathrm{B}}Tm_\alpha\sum_{\gamma=1}^{2}\frac{c_\gamma}{m_\gamma}[\underline{\underline{\tilde{\Xi}}}^{-1}(q,z\rightarrow 0)_{\alpha\gamma}[\underline{\underline{I}}^{-1}(q)]_{\gamma\beta} \tag{5}$$

m_α is the mass of a segment of species α, k_{B} is the Boltzmann constant, and T is the temperature. The generalized friction matrix $\underline{\underline{\tilde{\Xi}}}(q,z)$ has been introduced in Laplace space, and z is the Laplace variable. It determines directly the Laplace transform of the intensity matrix $\underline{\underline{\tilde{I}}}(q,z)$ as[1]

$$\underline{\underline{\tilde{I}}}(q,z) = [z + q^2\underline{\underline{m}}\cdot\underline{\underline{\tilde{\Xi}}}^{-1}(q,z)\cdot\underline{\underline{D}}(q)]^{-1}\underline{\underline{I}}(q) \tag{6}$$

in the overdamped limit. The elements of $\underline{\underline{D}}(q)$ are given by

$$D_{\alpha\beta}(q) = \frac{k_{\mathrm{B}}T}{m_\alpha}c_\alpha[\underline{\underline{I}}^{-1}(q)]_{\alpha\beta} \tag{7}$$

The diagonal matrix $\underline{\underline{m}}$ contains the segment masses m_α as its elements.

The formal expression for the generalized friction matrix was obtained as

$$\tilde{\Xi}_{\alpha\beta}(q,z) = \frac{1}{k_{\mathrm{B}}Tc_\beta}\frac{m_\beta}{m_\alpha}\langle\mathcal{F}_\alpha(\mathbf{q})\ Q_cQ_j[z + \mathcal{L}Q_cQ_j]^{-1}Q_cQ_j\mathcal{F}_\beta^*(\mathbf{q})\rangle \tag{8}$$

where the asterisk denotes complex conjugation. Q_c projects orthogonal to the partial densities, and Q_j, orthogonal to the currents. Further details are given in ref 1. The quantities $\mathcal{F}_\alpha$ depend on all forces $\mathbf{F}_{il,\mathrm{tot}}^{(\alpha)}$ exerted on segment il of species α, and the momenta $\mathbf{p}_{il}^{(\alpha)}$,

$$\mathcal{F}_\alpha^* = \frac{1}{\sqrt{V}}\sum_i^{n_\alpha}\sum_l^{N_\alpha}\left(\hat{\mathbf{q}}\cdot\mathbf{F}_{il,\mathrm{tot}}^{(\alpha)} + \frac{iq}{m_\alpha}(\hat{\mathbf{q}}\cdot\mathbf{p}_{il}^{(\alpha)})^2\right)\exp[i\mathbf{q}\cdot\mathbf{r}_{il}^{(\alpha)}] \tag{9}$$

In the limit of vanishing q, $\mathcal{F}_\alpha^*$ depends only on the total force exerted on species α, which is decomposed as

$$\sum_i^{n_1}\sum_l^{N_1}\mathbf{F}_{il,\mathrm{tot}}^{(1)} = \mathbf{F}^{(1-s)} + \mathbf{F}^{(1-2)} \tag{10}$$

for $\alpha = 1$. $\mathbf{F}^{(1-s)}$ is the force exerted by the solvent, and $\mathbf{F}^{(1-2)}$ is due to the presence of species 2. A corresponding decomposition is done for species 2. Interactions among segments of species 1 do not contribute to the sum in eq 10 because of pairwise cancelation of the related terms. The force on species 2 due to the presence of species 1, $\mathbf{F}^{(2-1)}$, is equal in magnitude to $\mathbf{F}^{(1-2)}$ but acts in the opposite direction.

As a simplification, forces due to the solvent, $\mathbf{F}^{(\alpha-s)}$, are assumed to be uncorrelated to the forces between polymer segments, $\mathbf{F}^{(1-2)}$, and relax on a quite fast time scale. When neglecting the correlation of forces due to the solvent acting on different segments, these types of correlations only influence the diagonal terms of the friction matrix (eq 8) and their contribution is described by chain length independent friction coefficients $\xi_\alpha^{(0)}$. If the time scales of solvent motion and polymer motion are well separated, only these terms are present for larger z in eq 8 and determine the short-time behavior.

To incorporate the interactions between the two polymeric species, the correlation function

$$\tilde{C}(z) = \frac{1}{k_{\mathrm{B}}TVc}\langle\mathbf{F}^{(1-2)}Q_cQ_j[z + \mathcal{L}Q_cQ_j]^{-1}Q_cQ_j\mathbf{F}^{(1-2)}\rangle \tag{11}$$

is introduced. The $q \rightarrow 0$ limit of the generalized friction matrix in eq 8 is determined by the correlations of $\mathbf{F}^{\alpha-s}$ and $\mathbf{F}^{1-2}$, and the approximations introduced above lead to

$$\tilde{\Xi}_{\alpha\beta}(q\rightarrow 0,z) = \xi_\alpha^{(0)}\delta_{\alpha\beta} + (-1)^{\alpha+\beta}\frac{cm_\beta}{c_\beta m_\alpha}\tilde{C}(z) \tag{12}$$

In contrast to the binary systems, not only forces between polymer and solvent but also the total force $\mathbf{F}^{(1-2)}$ acting between the two polymeric species included in $\tilde{C}(z)$ (eq 11) influence the $q \rightarrow 0$ limiting behavior. Especially close to the phase, or microphase separation, these forces may become strong and slowly relaxing, and therefore the second term in eq 12 is expected to be important then.

To treat the contribution to the generalized friction matrix in order q^2, $\mathcal{F}_\alpha$ is expanded to first order in q. In the resulting expression, only terms related to the more slowly relaxing interaction forces connecting the polymer chains are kept. These terms have the structure *force × position* and can therefore be regarded as a contribution to the stress. Within similar simplifications as described in ref 1, the contribution to $\tilde{\Xi}_{\alpha\beta}(q,z)$ can be expressed as a correlation function of partial stresses due to interactions between polymer segments and can be related to a partial longitudinal viscosity. This finally leads to the following form of the generalized friction matrix:

$$\tilde{\Xi}_{\alpha\beta}(q\rightarrow 0,z) = \xi_\alpha^{(0)}\delta_{\alpha\beta} + (-1)^{\alpha+\beta}\frac{cm_\beta}{c_\beta m_\alpha}\tilde{C}(z) + q^2\frac{\eta_{\alpha\alpha}(z)}{c_\alpha}\delta_{\alpha\beta} + O(q^4) \tag{13}$$

The longitudinal viscosity arising from the polymer subsystem is then given by

$$\eta_{\parallel}(z) = \eta_{11}(z) + \eta_{22}(z) \tag{14}$$

Equation 13 for the friction matrix contains several simplifications due to the neglect of some correlation functions. This makes the study of the dynamics including memory effects in such a quite complicated ternary system tractable. The intention here is to investiate if and how viscoelastic effects and forces between different species couple to cooperative diffusion and interdiffusion. The related terms describing such couplings are included in eq 13.

Equation 13 may be compared to results by Hess and Akcasu[22] investigating interdiffusion in a two-component polymer melt. They considered the $q \rightarrow 0$ limit, and their result is therefore independent of the viscoelastic term. Because the solvent is not present in their treatment, it corresponds to the case $\xi_\alpha^{(0)} = 0$. Then, eq 13 is entirely determined by the correlation function $\tilde{C}(z)$. They introduced a generalized friction matrix in a slightly different way which corresponds to $\underline{\underline{\Xi}}\cdot\underline{\underline{m}}^{-1}$ in this notation. When it is realized that in this simpler case the projectors Q_jQ_c in eq 11 may be replaced by unity in the limit $q \rightarrow 0$, their result can be recovered from eq 13.

The $z \rightarrow 0$ limit of eq 13 provides the basis to discuss the long-time limiting behavior. After some algebra, the frequency matrix in the long-time limit (eq 5) can be expressed in the suggestive form

$$\underline{\underline{\Omega}}^{(\mathrm{L})}(q) = q^2 k_{\mathrm{B}}T\begin{pmatrix} c_1/\tilde{\xi}_{11}(q) & c_2/\tilde{\xi}_{12}(q) \\ c_1/\tilde{\xi}_{21}(q) & c_2/\tilde{\xi}_{22}(q) \end{pmatrix}\cdot\underline{\underline{I}}^{-1}(q) \qquad (15)$$

where coefficients $\tilde{\xi}_{\alpha\beta}(q)$ are obtained as

$$\tilde{\xi}_{11} = \xi_1(q)\left(1 + \frac{\xi_2(q)\, c_2}{\xi_1(q)\, c_1}\,\frac{1}{[1 + \xi_2(q)\, c_2/(c\tilde{C}(z{=}0))]}\right) \qquad (16)$$

and

$$\tilde{\xi}_{12}(q) = \xi_2(q)\,\frac{c_2}{c_1}\left(1 + \frac{\xi_1(q)\, c_1}{\xi_2(q)\, c_2} + \frac{\xi_1(q)\, c_1}{c\tilde{C}(z{=}0)}\right) \qquad (17)$$

and $\xi_\alpha(q)$ is given by

$$\xi_\alpha(q) = \xi_\alpha^{(0)} + \frac{q^2}{c_\alpha}\eta_{\alpha\alpha}(0) \qquad (18)$$

The form of eq 15 may be compared to the result in the short-time limit (eq 4). The friction coefficients $\xi_\alpha^{(0)}$ in eq 4 are replaced by the q-dependent quantities $\tilde{\xi}_{\alpha\alpha}(q)$ in the long-time limit, and off-diagonal components $\tilde{\xi}_{12}(q)$ and $\tilde{\xi}_{21}(q)$ arise, indicating an additional dynamic coupling between the species. In the limiting case $\tilde{C}(0) \rightarrow 0$ and $\eta_{\alpha\alpha}(0) \rightarrow 0$, eq 15 reduces to the short-time result in eq 4.

From the comparison of eq 13 to the reuslts of Hess and Akcasu[22] treating a two-component melt, and the comparison of eq 15 to eq 4, which has provided the starting point to investigate the dynamics of multicomponent systems while neglecting memory effects,[17,20] it is evident that eqs 13 and 15 form a link between these quite different types of approaches.

3. Cooperative Diffusion and Interdiffusion

In this section, the decay rates typical for the long-time behavior as obtained from eq 15 are discussed. Interdiffusion is related to the decay of composition fluctuations, whereas cooperative diffusion describes the decay of concentration fluctuations. For a system comprising two polymeric components, $\underline{\underline{\Omega}}^{(\mathrm{L})}(q)$ has two eigenvalues specifying the relevant rates, and the decay of both, concentration or composition fluctuations, generally may contain contributions from both rates. Therefore, the eigenvalues of $\underline{\underline{\Omega}}^{(\mathrm{L})}(q)$ may in general not be interpreted as an interdiffusion and a cooperative mode.[19] Only under the special symmetry conditions

$$I_{11}(q,t) = I_{22}(q,t) \qquad (19)$$

$$\Omega_{11}^{(\mathrm{L})}(q) = \Omega_{22}^{(\mathrm{L})}(q) \qquad (20)$$

$$\Omega_{12}^{(\mathrm{L})}(q) = \Omega_{21}^{(\mathrm{L})}(q) \qquad (21)$$

concentration and composition fluctuations are decoupled, and one eigenvalue of $\underline{\underline{\Omega}}^{(\mathrm{L})}(q)$ determines the cooperative rate and the second eigenvalue is the interdiffusion rate. This special case is considered.

The conditions (19)–(21) require that interactions among segments of the same species are identical. When characterizing these interactions by excluded-volume parameters $\nu_{\alpha\beta}$, $\nu_{11} = \nu_{22}$ has to be fulfilled. Still, interactions between segments of different species may be somewhat larger due to a slight incompatibility, $\nu_{12} = \nu_{11} + \chi$, where χ is proportional to the Flory–Huggins interaction parameter. For the statics, this slight incompatibility is sufficient to create composition fluctuations as well as a phase, or microphase, separation.[21,23,24] In addition, segment concentrations have to be the same, $c_1 = c_2 = c/2$. In the case of diblock copolymers, this automatically implies $N_1 = N_2$. For homopolymers, the chains of both species are assumed to have the same length as well. These conditions on the segmental interactions, chain or block lengths, and segment concentrations guarantee that eq 19 is satisfied for $t = 0$. In order to be valid for all times, it is required that segments of different species are identical with respect to their dynamical properties as well. This means explicitly that the microscopic friction coefficients have to be identical, $\xi_1^{(0)} = \xi_2^{(0)} = \xi^{(0)}$. Also internal chain or block relaxations reflected in $\eta_{11}(z)$ and $\eta_{22}(z)$ have to be identical. Combining this last requirement with eq 14, this indicates $\eta_{11}(z)/c_1 = \eta_{22}(z)/c_2 = \eta_{\parallel}(z)/c$. In this case, also eqs 20 and 21 are satisfied.

Of course, a real system will never fulfill such conditions perfectly, but considerations on a symmetrical model system are expected to show the characteristic trends also present in a real system without obscuring the result by the presence of too many parameters. Such "ideal" systems have been investigated theoretically with respect to their dynamics while neglecting memory effects.[18,21]

Alternatively to the partial densities ρ_α referring to the species α, it is more convenient to express the structure functions in terms of the total polymer concentration,

$$\rho_c(\mathbf{q},t) = \rho_1(\mathbf{q},t) + \rho_2(\mathbf{q},t) \qquad (22)$$

and in terms of the composition,

$$\rho_x(\mathbf{q},t) = \frac{c}{c_1}\rho_1(\mathbf{q},t) - \frac{c}{c_2}\rho_2(\mathbf{q},t) \qquad (23)$$

Considering $\rho_c(\mathbf{q},t)$ and $\rho_x(\mathbf{q},t)$ to be the relevant variables, a structure factor $S_{cc}(q,t)$ accounting for fluctuations in the total polymer concentration,

$$S_{cc}(q,t) = \langle \rho_c(\mathbf{q},0)\, \rho_c(-\mathbf{q},t)\rangle = 2(I_{11}(q,t) + I_{12}(q,t)) \qquad (24)$$

a structure factor $S_{xx}(q,t)$ describing composition fluctuations,

$$S_{xx}(q,t) = \langle \rho_x(\mathbf{q},t)\, \rho_x(-\mathbf{q},0)\rangle = 8(I_{11}(q,t) - I_{12}(q,t)) \qquad (25)$$

and a coupling term,

$$S_{xc}(q,t) = \langle \rho_x(\mathbf{q},t)\, \rho_c(-\mathbf{q},0) \rangle = 0 \qquad (26)$$

can be introduced. The last equalities in eqs 24–26 only refer to symmetrical systems satisfying eq 19. From eq 26, the decoupling of concentration and composition fluctuations is evident.

When replacing $\underline{\underline{\Omega}}(q,t)$ in eq 3 by its long-time limit $\underline{\underline{\Omega}}^{(L)}(q)$ (eq 15), the decay of concentration fluctuations (eq 24) at long times can be expressed as

$$\frac{\partial}{\partial t} S_{cc}(q,t) = -[\Omega_{11}^{(L)}(q) + \Omega_{12}^{(L)}(q)] S_{cc}(q,t) \qquad (27)$$

and it is specified by the rate

$$q^2 D_{\mathrm{coop}}(q) = q^2 \frac{k_{\mathrm{B}}T}{\xi^{(0)} + q^2 \eta_{\parallel}(0)/c} \frac{c}{S_{cc}(q)} \qquad (28)$$

calculated from eqs 15 and 27. $S_{cc}(q)$ (or $S_{xx}(q)$) are the static values at $t = 0$ of the structure functions $S_{cc}(q,t)$ (or $S_{xx}(q,t)$). It may easily be verified that $q^2 D_{\mathrm{coop}}(q)$ is an eigenvalue of $\underline{\underline{\Omega}}^{(L)}(q)$. The result in eq 28 is formally identical to the result obtained for the long-time limit of the collective diffusion coefficient in ref 1, and the various considerations concerning the long-time behavior can also be applied to the cooperative diffusion process when replacing the dynamic intensity $I(q,t)$ considered in ref 1 by the correlation function of the total polymer density, $S_{cc}(q,t)$. The result in eq 28 is independent of the correlation function $\tilde{C}(0)$ related to the forces between the two species. For high viscosity and slow viscoelastic rates, $q^2 D_{\mathrm{coop}}(q)$ becomes independent of q if $S_{cc}(q)$ is approximately constant, whereas it reduces to the typical short-time result $(q^2 k_{\mathrm{B}}T)(c/S_{cc}(q))$ if viscoelastic effects are unimportant. The general behavior is expected to be very similar to the results for collective diffusion in a binary system.

The decay of composition fluctuations can be calculated from eqs 3, 15, and 25 leading to

$$\frac{\partial}{\partial t} S_{xx}(q,t) = -[\Omega_{11}^{(L)}(q) - \Omega_{12}^{(L)}(q)] S_{xx}(q,t) \qquad (29)$$

When inserting the explicit form of $\underline{\underline{\Omega}}^{(L)}(q)$ (eq 15) and employing eq 29, interdiffusion at long times is described by the rate

$$q^2 D_{\mathrm{int}}(q) = q^2 \frac{k_{\mathrm{B}}T}{\xi^{(0)} + 4\tilde{C}(0) + q^2 \eta_{\parallel}(0)/c} \frac{4c}{S_{xx}(q)} \qquad (30)$$

It may be verified that $q^2 D_{\mathrm{int}}(q)$ is the second eigenvalue of $\underline{\underline{\Omega}}^{(L)}(q)$. When letting $\tilde{C} \rightarrow 0$ and $\eta_{\parallel} \rightarrow 0$, while expressing $S_{xx}(q)$ within the random phase approximation it reduces to the known short-time result depending on chain length, on the single chain form configuration, and on the interaction parameter χ.[18,21] If the force correlation $\tilde{C}$ is important in eq 30 while $\eta_{\parallel}$ is small, the microscopic friction coefficient $\xi^{(0)}$ is replaced by a larger quantity $(\xi^{(0)} + \tilde{C}(0))$. This is expected to become important when the total force between the two species is large and slowly decaying, thus close to the phase or microphase transition. In the case that the viscoelastic contribution is high, the term proportional to q^2 in the denominator of eq 30 dominates the result, and the q-dependence of the rate in eq 30 drastically differs from $q^2/S_{xx}(q)$ typical for shorter times. This is the analogon of the slow viscoelastic modes encountered in collective diffusion.

From this analysis it is evident that two additional time scales are involved in the decay of composition fluctuations: typical viscoelastic times, which are also important for the decay of concentration fluctuations, and the typical time for the relaxation of the total force acting between the two species. The values of these times, the magnitude of the viscoelastic modulus, and the magnitude of the total force between the species then determine which of the various possible modes can be observed. Within a simple model, the characteristic features for the time dependence of $S_{cc}(q,t)$ and $S_{xx}(q,t)$ are discussed in the following.

4. Time Dependence of the Scattering Intensities

The aim of this section is the investigation of the time dependence of $S_{cc}(q,t)$ and $S_{xx}(q,t)$. Equations 6 and 7 can be expressed in terms of the Laplace transforms $\tilde{S}_{cc}(q,z)$ and $\tilde{S}_{xx}(q,z)$ of the time-dependent structure functions $S_{cc}(q,t)$ and $S_{xx}(q,t)$, respectively. In the symmetrical case under consideration, the resulting equations for $\tilde{S}_{cc}(q,z)$ and $\tilde{S}_{xx}(q,z)$ are decoupled and are obtained from eqs 6 and 7 as

$$\frac{\tilde{S}_{cc}(q,z)}{S_{cc}(q)} = \left[z + q^2 \frac{k_{\mathrm{B}}T}{\tilde{\Xi}_{cc}(q,z)} \frac{c}{S_{cc}(q)}\right]^{-1} \qquad (31)$$

and

$$\frac{\tilde{S}_{xx}(q,z)}{S_{xx}(q)} = \left[z + q^2 \frac{k_{\mathrm{B}}T}{\tilde{\Xi}_{xx}(q,z)} \frac{4c}{S_{xx}(q)}\right]^{-1} \qquad (32)$$

where

$$\tilde{\Xi}_{cc}(q,z) = \tilde{\Xi}_{11}(q,z) + \tilde{\Xi}_{12}(q,z) \qquad (33)$$

and

$$\tilde{\Xi}_{xx}(q,z) = \tilde{\Xi}_{11}(q,z) - \tilde{\Xi}_{12}(q,z) \qquad (34)$$

When employing the approximation (13) for the friction matrix, this simplifies to

$$\tilde{\Xi}_{cc}(q,z) = \xi^{(0)} + q^2 \eta_{\parallel}(z)/c \qquad (35)$$

and

$$\tilde{\Xi}_{xx}(q,z) = \xi^{(0)} + 4\tilde{C}(z) + q^2 \eta_{\parallel}(z)/c \qquad (36)$$

From eqs 31 and 35 it is evident that $\tilde{S}_{cc}(q,z)$ is independent of the correlation function $\tilde{C}(z)$. Therefore, $S_{cc}(q,t)$ is not directly affected by the forces between the species within the simplifications of eq 13. Equation 31 together with eq 35 is formally identical to the result obtained for the dynamic intensity $\tilde{I}(q,z)$ in a binary polymer solvent system, and all the results obtained for $I(q,t)$ in ref 1 can be generalized straightforwardly to $S_{cc}(q,t)$ when replacing $I(q)$ in ref 1 by $S_{cc}(q)$.

$\tilde{S}_{xx}(q,z)$ (eq 32) is influenced by viscoelastic effects and the additional interactions between the species, because $\tilde{\Xi}_{xx}(q,z)$ (eq 36) depends on $\eta_{\parallel}(z)$ and $\tilde{C}(z)$. To have a rough estimate on the qualitative effects, the viscoelastic behavior is characterized by a modulus G and a rate Γ_G,

$$\eta_{\parallel}(z) = \frac{G}{z + \Gamma_G} \qquad (37)$$

To describe $\tilde{C}(z)$, a similar simple ansatz is made,

$$\tilde{C}(z) = \frac{C_I}{z + \Gamma_I} \tag{38}$$

Combining eqs 32 and 36–38 leads to

$$\frac{\tilde{S}_{xx}(q,z)}{S_{xx}(q)} = \frac{1}{\Gamma_0(q)}\left[\frac{z}{\Gamma_0(q)} + \left\{1 + \frac{g}{z/\Gamma_0(q) + \Gamma_G/\Gamma_0(q)} + \frac{a}{z/\Gamma_0(q) + \Gamma_I/\Gamma_0(q)}\right\}^{-1}\right]^{-1} \tag{39}$$

where

$$\Gamma_0(q) = q^2 \frac{k_B T}{\xi^{(0)}} \frac{4c}{S_{xx}(q)} \tag{40}$$

is the decay rate obtained when neglecting memory effects. If $S_{xx}(q)$ becomes large, $\Gamma_0(q)$ shows critical slowing down. This feature has been discussed in ref 21 for two types of homopolymers and in ref 13 for diblock copolymers. The dimensionless quantities

$$g = \frac{G}{c k_B T} \frac{S_{xx}(q)}{4c} \tag{41}$$

and

$$a = \frac{C_1}{q^2 k_B T} \frac{S_{xx}(q)}{c} \tag{42}$$

determine the importance of the additional memory effects. Both are proportional to $S_{xx}(q)$, which implies their enhancement for large composition fluctuations. The coupling term a increases with decreasing q, which may qualitatively be understood when realizing that the total force exerted between the two species is a global feature.

The q-dependence of a does not lead to anomalies in eq 39, because also the rate $\Gamma_0(q)$ (eq 40) contains a factor q^2. In the small q limit, eq 39 simplifies to

$$\frac{\tilde{S}_{xx}(q,z)}{S_{xx}(q)} = \left[z + \frac{\Gamma_0(q)\,\xi^{(0)}}{\xi^{(0)} + 4\tilde{C}(z)}\right]^{-1} \tag{43}$$

when eq 38 is employed. When neglecting $\tilde{C}(z)$, the decay rate is $\Gamma_0(q)$, while the long-time limiting rate given in eq 30 is obtained when replacing $\tilde{C}(z)$ by $\tilde{C}(0)$. The q-dependence of both limiting rates are determined by $q^2/S_{xx}(q)$, and the only effect is that the microscopic friction $\xi^{(0)}$ is replaced by a larger friction when diffusion on a time scale $\Gamma_I t > 1$ is observed.

Interesting is the case of slow relaxations, $\Gamma_I \ll \Gamma_0(q)$ and $\Gamma_G \ll \Gamma_0(q)$. In ref 1 an approximate result for the decay of the dynamic intensity as a function of time could be obtained. Because $\tilde{S}_{xx}(q,z)$ in eq 39 depends on z in exactly the same way as $I(q,z)$ in ref 1, the calculation presented there can be carried out in the same way, finally leading to

$$\frac{S_{xx}(q,t)}{S_{xx}(q)} = \frac{\Gamma_0(q)}{\gamma(q)} \exp[-\gamma(q)t] + \frac{4C_I}{\xi^{(0)}\gamma(q)} \exp[-\Gamma_I t] + \frac{q^2 G}{\xi^{(0)} c \gamma(q)} \exp[-\Gamma_G t] \tag{44}$$

where

$$\gamma(q) = \Gamma_0(q) + q^2 \frac{G}{c\xi^{(0)}} + \frac{4C_I}{\xi^{(0)}} \tag{45}$$

Merely formally, $\gamma(q)$ corresponds to $q^2 D_c$ introduced in refs 1 and 10 and $\Gamma_0(q)$ corresponds to $q^2 D_\pi$. From eq 44, it can be seen that, in addition to viscoelastic modes, another q-independent mode of different origin characterized by the rate Γ_I may occur in the decay of composition fluctuations. Such a mode may be present on an intermediate q range. For large q, the amplitude as predicted from eq 45 is small, and for small q, eq 44 is not valid and eq 43 has to be applied.

In the case of diblock copolymers, $\Gamma_0(q)$ is constant for $q \rightarrow 0$, because $S_{xx}(q)$ vanishes as q^2.[23,24] The maximum of $S_{xx}(q)$ is located at $qR_G \sim 2$, where R_G is the radius of gyration. Close to the microphase separation, the critical slowing down of $\Gamma_0(q)$ is expected to be important for a finite value of q in the region around the maximum of $S_{xx}(q)$. If some quite immobile domains have already developed, the correlation function of the forces between the species may not fully relax on the time scale of observation. This implies a very small value of Γ_I. In such a case, eq 44 predicts that also $S_{xx}(q,t)$ cannot decay completely even for very small q where $\Gamma_0(q)$ is finite and viscoelastic effects are unimportant. Such a qualitative effect may be observable.

From this analysis it is evident that interdiffusion in the presence of large composition fluctuations can exhibit interesting but also quite complicated features.

5. Conclusion

The cooperative diffusion and interdiffusion in a ternary system of two types of polymeric components in a solvent have been addressed. As in the case of a binary polymer–solvent system, viscoelastic effects are expected if the viscosity increase due to the presence of polymers is high. This high viscosity is usually related to slow internal single chain relaxations. The general behavior of the decay of concentration fluctuations determining the cooperative diffusion process is expected to be very similar to the decay of the dynamic intensity in a binary polymer–solvent system.[1]

Interdiffusion is more complicated, because it is also influenced by the total forces acting between the species. This introduces a new time scale, which may be observed in dynamic light scattering. It has been shown that qualitatively new features may arise if this time is quite long, as is expected close to the phase or microphase separation.

Acknowledgment. This work has been supported by the Deutsche Forschungsgemeinschaft, SFB 262.

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