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Identification of Modes in Dynamic Scattering from Ternary Polymer Mixtures and Interdiffusion

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ABSTRACT: It is shown that the two exponential modes in dynamic scattering from ternary polymer mixtures cannot in general be identified with the interdiffusion and cooperative diffusion processes, contrary to recent suggestions in the literature. Conditions under which such an identification is possible are obtained. General expressions for the interdiffusion and cooperative diffusion coefficients associated with a given pair of components A and B in a ternary or in general in a multicomponent polymer mixture are obtained in terms of the partial mobilities $\mu_{\alpha\beta}$ and partial scattering functions $S_{\alpha\beta}(q)$ of the A and B homopolymers. When the latter are expressed in terms of the bare mobilities and static structure factors by the random phase approximation, a new expression of the interdiffusion coefficient in an incompressible ternary mixture of A and B homopolymers in a matrix of C homopolymers is found in terms of the tracer diffusion coefficients of the three components in the mixture. It is shown that the results of the controversial "fast mode" and "slow mode" theories are obtained as the two limits of this new expression as a function of the concentration and bare mobility of the matrix. The approach used in the paper is compared with the Onsager formalism.

I. Introduction

The intermediate scattering function $S_{aa}(q,t)$ of a labeled component A in a ternary incompressible mixture of polymers consisting of species A and B in a matrix of homopolymers C, or in a binary solution of A and B polymers, can be represented in the Markov limit by superposition of two exponentially decaying modes (bimodal relaxation) as

$$S_{aa}(q,t) = A_+ e^{-q^2 d_+ t} + A_- e^{-q^2 d_- t} \tag{1}$$

In the case of incompressible ternary mixtures, the bimodal relaxation is a consequence of the incompressibility constraint, which enables one to express the dynamics of one of the components, identified as the "matrix", in terms of the dynamics of the other two components. In the case of binary polymer solutions, the bimodal relaxation arises from the large difference between the relaxation times characterizing the dynamics of the solvent and the polymers. Since the solvent relaxes much faster than the polymers, one is allowed to invoke the Markov limit and to eliminate the dynamics of the solvent completely. In a ternary mixture, the relaxation time of the matrix, which plays the role of the solvent in a binary solution, is comparable to those of the other two components. In this sense, the ternary mixtures and binary solutions of polymers correspond to two opposite extreme limits, even though they both are described by bimodal relaxation.

A brief survey of the the literature relevant to the main theme of this paper is as follows:

The dynamics of binary polymer solutions was studied by Akcasu et al.,[1] in 1984, using the linear response theory in the Markov limit, and the expressions of the decay constants d_+ and d_-, as well as the amplitudes A_+ and A_-, were obtained. Both the partial structure factors $S_{\alpha\beta}(q)$ and the mobilities $\mu_{\alpha\beta}$, which are needed to calculate d_+ and d_-, were calculated in the lowest order in polymer concentrations in dilute solutions, including both inter- and intrachain hydrodynamic interactions. The results were then used to investigate the concentration dependence of the apparent diffusion coefficient, which is obtained from the first cumulant of the total dynamic scattering function $S(q,t) = S_{aa}(q,t) + S_{bb}(q,t) + 2S_{ab}(q,t)$, in the case of a binary solution of two components of the same species, differing only in their molecular weights. The same formalism was also used by Akcasu et al.,[2] in 1984, to study the dynamics of polyelectrolyte solutions, which also constitute a bimodal system. In this work a plasmon mode in the small-q limit is predicted. In 1987, Benmouna et al.,[3] recalculated the decay constants and the amplitudes in eq 1, ignoring the hydrodynamic interactions in the calculation of the mobilities, but using the random phase approximation in the calculation of the partial static structure factors. They identified the two modes in eq 1 as the cooperative and interdiffusion modes. This identification of the modes has later been used in the interpretation of several scattering experiments on binary polymer solutions, such as the recent work by Giebel et al.[4] and Brown and Zhou.[5]

The dynamics of binary polymer blends was studied by de Gennes,[6,7] Pincus,[8] Binder,[9] and Akcasu et al.,[10] using the random phase approximation. In the last reference, the dynamics of a melt of diblock copolymers was also considered, and specifically the first cumulant of the dynamic scattering function was investigated as a function of the wave vector q and the Flory interaction parameter. In a recent paper, Akcasu and Tombakoglu[11] studied the dynamics of polymer mixtures with an arbitrary number of components in a matrix of homopolymers, allowing the components to be homopolymers or parts of copolymers, stars, etc. They obtained, specifically, the expression of the mobility of a given component in the mixture, in terms of the "bare" system mobilities of all the components, and described the procedure to determine the dynamic scattering function in the interacting system in terms of the single-chain dynamic and static structure factors in the bare system.

This paper is concerned with the identification of the two modes in a bimodal system in general, which may be a binary polymer solution or a ternary polymer mixture. Specifically, it addresses the following question. Can the two modes be identified as the interdiffusion and cooperative diffusion modes? If not, how should the interdiffusion and cooperative diffusion modes be defined in a multicomponent mixture? How are the interdiffusion

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and cooperative diffusion coefficients related to the decay constants of the two modes? Under what conditions can the decay constants d_+ and d_- be identified as the cooperative and interdiffusion coefficients exactly?

Finally, is it possible to infer the interdiffusion and cooperative diffusion coefficient from a single dynamic scattering experiment on a labeled component, in which the decay constants d_+ and d_-, as well as the amplitudes A_+ and A_-, are extracted from the measured dynamic scattering function $S_{aa}(q,t)$ as a function of time at different wavenumbers q? In addition, the question of expressing the interdiffusion coefficient in terms of the tracer diffusion coefficients of the components in a ternary mixture is also addressed within the framework of the mean field theory, which, in the context of polymer dynamics, is often called the random phase approximation (RPA).

In the following several sections, we present the theoretical developments, and the answers to the above questions are summarized in the last section.

II. Theoretical Background

The theory of a multicomponent polymer solution was presented by Akcasu et al.,[1] in 1984, within the framework of the Zwanzig[12]–Mori[13] projection operator formalism. In order to introduce the concepts relevant to the present problem, and the notations, we briefly summarize the results of their work, in the case of a system with two components.

The number densities of the components are expressed as a column vector $\vec{\rho}(\vec{q})$ = colm $[\rho_A(\vec{q}),\rho_B(\vec{q})]$ where $\rho_\alpha(\vec{q})$ are the incremental number densities in Fourier space:

$$\rho_\alpha(\vec{q}) = \sum_{j=1}^{N_\alpha} \exp(i\vec{q}\cdot\vec{R}_j^\alpha) - N_\alpha \delta_{\vec{q}0}$$

Here $\vec{R}_j^\alpha$ is the position vector of the jth particle (or monomer) of kind α = (A, B), $\vec{q}$ is the wave vector, and N_α is the total number of particles (or monomers) of kind α in the system. The dynamic scattering matrix $\mathbf{S}(q,t)$ is then defined by

$$\mathbf{S}(q,t) = \langle \vec{\rho}(\vec{q},t)\vec{\rho}^\dagger(\vec{q})\rangle \tag{2}$$

where † denotes hermitian conjugation and the symbol $\langle ... \rangle$ implies thermal average. In the Markov limit,[12] the time evolution of $\mathbf{S}(q,t)$ is shown[1] to be governed by

$$\mathbf{S}(q,t) = e^{-q^2\mathbf{D}t}\mathbf{S}(q) \tag{3}$$

where $\mathbf{D}$ is the diffusivity matrix and $\mathbf{S}(q) \equiv \mathbf{S}(q,t{=}0)$ is the matrix of static structure factors. The diffusivity matrix is formally defined by

$$\mathbf{D} = \lim_{q\to 0} \frac{1}{q^2}[\Omega(q) - \int_0^\infty \mathrm{d}u\, \phi(q,u)] \tag{4}$$

where $\Omega(q)$ is the first cumulant matrix,[14] defined by

$$\Omega(q) = \langle \vec{\rho}(\vec{q})\mathcal{L}\vec{\rho}^\dagger(q)\rangle \mathbf{S}^{-1}(q) \tag{5}$$

and $\phi(q,t)$ is the memory matrix, defined by

$$\phi(q,t) = \langle \vec{f}(\vec{q},t)\vec{f}^\dagger(\vec{q})\rangle \mathbf{S}^{-1}(q) \tag{6}$$

In eq 5, $\mathcal{L}$ is an operator operating on the particle positions, and it governs the time evolution of $\vec{\rho}(\vec{q},t)$ through[14]

$$\vec{\rho}(\vec{q},t) = -\mathcal{L}\vec{\rho}(\vec{q},t) \tag{7}$$

In eq 6, $\vec{f}(\vec{q},t)$ is the random force appearing in the generalized Langevin equation, and its time evolution is governed by the modified operator $(1 - P)\mathcal{L}$, where P is the projection operator in the Zwanzig–Mori formalism. These details and explicit calculations of $\Omega(q)$ and $\phi(q,t)$ are not needed for the subsequent discussions. One of the reasons for introducing them here is to show that a microscopic expression of the diffusion matrix D in eq 3 is available, once an appropriate operator $\mathcal{L}$ for the system under consideration is specified. In the case of multicomponent polymer solutions $\mathcal{L}$ is conventionally chosen as the adjoint of Kirkwood's diffusion operator, which includes the hydrodynamic interactions through the Oseen tensor. In ref 1, the first cumulant and the mobilities were calculated by using this operator in eq 5.

In the case of incompressible ternary polymer mixtures, an explicit form of the $\mathcal{L}$ operator is not available, and here the above microscopic description is of little value from the computational point of view. Therefore, one resorts to the random phase approximation, which enables one to study the dynamics of polymer mixtures in terms of the dynamics of a single chain in the mixtures.[6-11]

The short-time behavior of $\mathbf{S}(q,t)$ is given[1,14] by

$$\mathbf{S}(q,t) = e^{-\Omega(q)t}\mathbf{S}(q) \tag{8}$$

which has the same form as its long-time behavior given in eq 3. Therefore, the following discussions are valid in both limits, by simply interchanging $\mathbf{D}$ and $\Omega(q)$.

We see from eqs 4 and 5 that $\mathbf{D}$ is in general not symmetric. However, it can be diagonalized by a similarity transformation

$$\mathbf{Q}\mathbf{D}\mathbf{Q}^{-1} = \mathbf{d} \tag{9}$$

where $\mathbf{d}$ = diag $[d_+,d_-]$. It can be shown that the eigenvalues are real. We assume, on physical grounds, that they are also positive. (These and other properties of the matrices $\mathbf{D}$ and $\mathbf{Q}$ are discussed in detail in Appendix A.) The eigenvalues are obtained by solving the quadratic equation

$$d^2 - 2D_{av}d + |\mathbf{D}| = 0 \tag{10}$$

where

$$D_{av} = \frac{1}{2}[D_{aa} + D_{bb}] \tag{11}$$

and

$$|\mathbf{D}| = D_{aa}D_{bb} - D_{ab}D_{ba} \tag{12}$$

The transformation $\mathbf{Q}$ is constructed in terms of the eigenvectors $\vec{\alpha}_+ = [1,\alpha_+]^\mathrm{T}$ and $\vec{\alpha}_- = [\alpha_-,1]^\mathrm{T}$ of $\mathbf{D}$, with eigenvalues d_+ and d_-, respectively, as

$$\mathbf{Q}^{-1} = \begin{bmatrix} 1 & \alpha_- \\ \alpha_+ & 1 \end{bmatrix} \tag{13}$$

where $\alpha_+ = (d_+ - D_{aa})/D_{ab}$ and $\alpha_- = D_{ab}/d_- - D_{aa})$. The particular normalization of $\vec{\alpha}_+$ and $\vec{\alpha}_-$ we have chosen in eq 13 is only for simplicity and has no physical content. Since $\mathbf{D}$ is not symmetric, the eigenvectors are not orthogonal. The left eigenvectors $\vec{\beta}_+$ and $\vec{\beta}_-$ are determined by $\vec{\beta}_j{}^\mathrm{T}\mathbf{D} = d_j\vec{\beta}_j{}^\mathrm{T}$ as $\vec{\beta}_+ = [1, -\alpha_-]^\mathrm{T}/(1 - \alpha_\pm\alpha_-)$ and $\vec{\beta}_- = [-\alpha_+,1]^\mathrm{T}/(1 - \alpha_+\alpha_-)$, and the eigenvectors $\vec{\alpha}_k$ form an orthonormal set, i.e., $\vec{\beta}_j{}^\mathrm{T}\vec{\alpha}_k = \delta_{jk}$. Expressing $\mathbf{D}$ as

$$\mathbf{D} = \sum_j d_j\vec{\alpha}_j\vec{\beta}_j{}^\mathrm{T} \qquad (j = +, -) \tag{14}$$

we obtain the modal expansion of the dynamic scattering function as

$$\mathbf{S}(q,t) = [\vec{\alpha}_+\vec{\beta}_+{}^\mathrm{T}e^{-q^2d_+t} + \vec{\alpha}_-\vec{\beta}_-{}^\mathrm{T}e^{-q^2d_-t}]\mathbf{S}(q) \tag{15}$$

In particular we find

$$S_{aa}(q,t) = \frac{S_{aa} - \alpha_- S_{ab}}{1 - \alpha_+\alpha_-} e^{-q^2 d_+ t} + \alpha_- \frac{S_{ab} - \alpha_+ S_{aa}}{1 - \alpha_+\alpha_-} e^{-q^2 d_- t} \qquad (16)$$

which was the starting equation of ref 1.

Before ending this section, we mention that the matrix $\mathbf{Q}$ introduced in eq 13 also diagonalizes, as shown in Appendix A, the static structure matrix $\mathbf{S}(q)$ by a congruent transformation

$$\mathbf{QSQ}^{\mathrm{T}} = \mathbf{s} \qquad (17)$$

where $\mathbf{s} = \mathrm{diag}\,[s_+,s_-]$, with positive diagonal elements s_j. The positivity of the s_j follows from the fact that the static structure factor is a positive definite matrix (Appendix A).

III. Normal Modes

In this section we discuss the nature of the two exponential terms in eq 1. Therefore we perform the following transformation on the number density vector $\vec{\rho}$

$$\vec{\xi}(t) = \mathbf{Q}\vec{\rho}(t) \qquad (18)$$

where the matrix $\mathbf{Q}$ is obtained directly from eq 13, as $\mathbf{Q}^{\mathrm{T}} = [\vec{\beta}_+,\vec{\beta}_-]$. Clearly, the components $\xi_+(t)$ and $\xi_-(t)$ are linear combinations of $\rho_a(t)$ and $\rho_b(t)$, i.e.

$$\xi_+(t) = \vec{\beta}_+{}^{\mathrm{T}}\vec{\rho}(t) = \frac{\rho_a(t) - \alpha_-\rho_b(t)}{1 - \alpha_+\alpha_-} \qquad (19)$$

$$\xi_-(t) = \vec{\beta}_-{}^{\mathrm{T}}\vec{\rho}(t) = \frac{\rho_b(t) - \alpha_+\rho_a(t)}{1 - \alpha_+\alpha_-} \qquad (20)$$

The important property of $\vec{\xi}(t)$ is that its correlation $\langle\vec{\xi}(\vec{q},t)\vec{\xi}^{\dagger}(\vec{q},0)\rangle$ is diagonal

$$\begin{aligned}\langle\vec{\xi}(t)\vec{\xi}^{\dagger}(0)\rangle &= \mathbf{Q}e^{-q^2Dt}\mathbf{SQ}^{\mathrm{T}} \\ &= \mathbf{Q}e^{-q^2Dt}\mathbf{Q}^{-1}\mathbf{QSQ}^{\mathrm{T}} \\ &= e^{-q^2dt}\mathbf{s}\end{aligned} \qquad (21)$$

where we have used eq 17 in the last step. The conclusion is that $\langle\vec{\xi}(t)\vec{\xi}^{\dagger}(0)\rangle$ is diagonal, i.e.

$$\begin{aligned}\langle\xi_+(t)\xi^*{}_+(0)\rangle &= e^{-q^2d_+t}s_1 \\ \langle\xi_-(t)\xi^*{}_-(0)\rangle &= e^{-q^2d_-t}s_2 \\ \langle\xi_+(t)\xi^*{}_-(0)\rangle &= 0\end{aligned} \qquad (22)$$

and $\xi_+(\vec{q},t)$ and $\xi_-(\vec{q},t)$ are the *eigenmodes of the system. They are statistically uncoupled at all times.* To elaborate on the last point, we consider the time evolution of the mean number densities within the linear response theory:

$$\dot{\bar{\vec{\rho}}}(t) = -q^2\mathbf{D}\bar{\vec{\rho}}(t) \qquad (23)$$

which is a set of two coupled diffusion equations, so that the time evolution of $\overline{\rho_a}(t)$ is always coupled to that of $\overline{\rho_b}(t)$. The mean values in eq 23, denoted by overbars, refer to the average over the realizations during the stochastic evolution of the system (in the Langevin sense), starting from a given initial condition $\vec{\rho}(0)$. The solution of eq 23, $\bar{\vec{\rho}}(t) = \exp[-q^2\mathbf{D}t]\vec{\rho}(0)$, can be written as a sum of two exponentials using the expansion of $\mathbf{D}$ in eq 14, in the same way as the expression of $\mathbf{S}(q,t)$ in eq 15. In fact, it can be written directly from eq 15, by replacing $\mathbf{S}(q)$ in it by $\vec{\rho}(0)$ and observing that $\vec{\beta}_+{}^{\mathrm{T}}\vec{\rho}(0) = \xi_+(0)$ and $\vec{\beta}_-{}^{\mathrm{T}}\vec{\rho}(0) = \xi_-(0)$ (cf. eqs 19 and 20):

$$\bar{\vec{\rho}}(t) = \xi_+(0)\vec{\alpha}_+e^{-q^2d_+t} + \xi_-(0)\vec{\alpha}_-e^{-q^2d_-t} \qquad (24)$$

The point of this result is that the *mean values* $\overline{\rho_a}(t)$ and $\overline{\rho_b}(t)$ of the number densities, and any linear combination of them, can be made to relax with a single exponential by adjusting their initial conditions represented by $\xi_+(0)$ and $\xi_-(0)$ in eq 24. For example, if we let $\xi_-(0) = 0$ by choosing

$$\rho_b(0) = \alpha_+\rho_a(0) \qquad (25)$$

then both $\overline{\rho_a}(t)$ and $\overline{\rho_b}(t)$ decay as $\exp[-q^2d_+t]$. The condition $\xi_-(0) = 0$ implies that the normal mode characterized by ξ_- is not excited in the mean. By multiplying eq 23 from the left by $\mathbf{Q}$, the time evolution of the *mean values* of the normal modes is obtained as

$$\dot{\bar{\vec{\xi}}}(t) = -q^2\mathbf{d}\bar{\vec{\xi}}(t) \qquad (26)$$

which is a set of two uncoupled diffusion equations for $\overline{\xi_+}(t)$ and $\overline{\xi_-}(t)$, with the diffusion constants d_+ and d_-, respectively. Hence, by setting one of the initial values $\xi_+(0)$ and $\xi_-(0)$ equal to zero, one excites only the other normal modes, as already pointed out above. The fact that the mean number densities can be made to decay with a single exponential by adjusting their initial conditions properly was used by Kehr et al.[15] and Jilge et al.,[16] in their computer studies of the transport properties of lattice gas models of alloys with two particle species.

As a final remark, we note that the flexibility one has in the choice of the initial conditions of the mean values does not exist in the case of the relaxation of correlation functions, described by the dynamic scattering matrix $\mathbf{S}(q,t)$ given in eq 15. In this case, the initial correlations are characterized by the static structure matrix $\mathbf{S}(q)$, which is not under our control. It is, however, still possible to make only one mode visible, by adjusting the excess scattering length a_j of the components in the total scattering function

$$\mathbf{I}(q,t) = \vec{a}^{\dagger}\mathbf{S}(q,t)\vec{a}$$

where $\vec{a} = [a_a,a_b]^{\mathrm{T}}$.

For example the mode corresponding to the decay constant d_- can be made invisible by choosing a_a and a_b such that $\vec{a}^{\mathrm{T}}\vec{\alpha}_-\vec{\beta}_-{}^{\mathrm{T}}\mathbf{S}(q)\vec{a} = 0$. In this case $\mathbf{S}(q,t)$ decays as $\exp[-q^2d_+t]$. This idea was suggested and implemented by Benoit.[17] It should be kept in mind, however, that the dynamics of the mixture, characterized by the decay constants d_+ and d_-, is not affected by which part of the system is made visible by adjusting the scattering lengths.

IV. Interdiffusion and Cooperative Diffusion

We now come to one of the main points of this paper: Can we identify the two normal modes as the interdiffusion and cooperative diffusion modes? To answer this question one must first define the interdiffusion and cooperative diffusion processes in a ternary mixtures, in fact, in a multicomponent mixture in general.

The interdiffusion process mediates the relaxation of thermal fluctuations in the relative local concentration of A and B molecules toward their equilibrium relative concentrations.[18-22] The A and B components may be dissolved into other components. The local relative concentration of the A component is defined by

$$c_a(\vec{r},t) = \frac{\rho_{a0} + \rho_a(\vec{r},t)}{\rho_{a0} + \rho_a(\vec{r},t) + \rho_{b0} + \rho_b(\vec{r},t)} \quad (27)$$

where $\rho_{j0} = (N_j/V)$ is the equilibrium number density of the jth component and $\rho_j(\vec{r},t)$ are the fluctuations about the mean. Clearly, $c_a(\vec{r},t) + c_b(\vec{r},t) = 1$. The concentration fluctuation δc_a about the mean $\rho_{a0}/(\rho_{a0} + \rho_{b0})$ is obtained from eq 27, in the linear approximation, as

$$\delta c_a(\vec{q},t) = x_a x_b \rho_-(\vec{q},t) \quad (28)$$

where $x_j = N_j/(N_a + N_b)$ is the relative fraction of the jth component, and

$$\rho_-(\vec{q},t) = \frac{1}{N_a}\rho_a(\vec{q},t) - \frac{1}{N_b}\rho_b(\vec{q},t) \quad (29)$$

$$\equiv \vec{E}^{\mathrm{T}}\vec{\rho}(\vec{q},t) \quad (30)$$

with

$$\vec{E}^{\mathrm{T}} = \left[\frac{1}{N_a}, -\frac{1}{N_b}\right] \quad (31)$$

Thus, the interdiffusion process is related to the relaxation of $\rho_-(\vec{q},t)$, which is the particular linear combination of the number densities $\rho_a(\vec{q},t)$ and $\rho_b(\vec{q},t)$, given in eq 29. This linear combination, however, is different from either of the two linear combinations, defining the normal modes as in eqs 19 and 20. Hence its dynamic scattering function

$$S_{--}(\vec{q},t) \equiv \langle \rho_-(\vec{q},t)\rho_-(\vec{q},0)\rangle \quad (32)$$

will be a linear superposition of the two pure modes. Explicitly, $S_{--}(q,t)$ can be calculated as

$$S_{--}(q,t) = \vec{E}^{\mathrm{T}}\mathbf{S}(q,t)\vec{E} \quad (33)$$

where $\mathbf{S}(q,t)$ is given in eq 15. In the case of a multicomponent mixture containing more than two components, the concentration fluctuation $\delta c_a(\vec{q},t)$ is still proportional to $\rho_-(\vec{q},t)$. In this case, ρ_- is still obtained from the density vector $\vec{\rho}$ as $\rho_- = \vec{E}^{\mathrm{T}}\vec{\rho}$, but now $\vec{E}^{\mathrm{T}} = [1/N_a, -1/N_b, 0, 0, ...]$. The dynamic scattering function $S_{--}(q,t)$ is also given by eq 33 with the extended $\vec{E}$. It is clear that $\mathbf{S}(q,t)$ in the general case will contain as many exponentials as the number of components.

Similarly, the cooperative diffusion process is related to the relaxation of the total number density of fluctuations of the A and B components toward the average total density $\rho_{a0} + \rho_{b0}$ as

$$\rho_+(\vec{q},t) = \rho_a(\vec{q},t) + \rho_b(\vec{q},t) \quad (34)$$

This combination is also different from those corresponding to the normal modes. Hence, we conclude that the two modes in dynamic scattering from bimodal systems cannot be identified, in general, as the interdiffusion and cooperative diffusion processes. It should be noted that, whereas the normal modes are independent of each other, the interdiffusion and cooperative modes are in general statistically coupled. There are, however, some special cases in which the latter two modes are uncoupled. We illustrate these cases with examples in the following section. Having unambiguously defined what is physically meant by the interdiffusion and cooperative diffusion processes, we now come to the definitions of the diffusion coefficients associated with them.

We first consider the interdiffusion coefficient, which is related to the relaxation of fluctuations in the local relative concentrations of a pair of components A and B, i.e., the relaxation of the dynamic scattering function $S_{--}(q,t)$ defined in eqs 32 and 33. If the interdiffusion process were a pure mode, $S_{--}(q,t)$ would relax with a single exponential as

$$S_{--}(q,t) = e^{-q^2 D_{\mathrm{in}} t} S_{--}(q) \quad (35)$$

where the static structure factor $S_{--}(q)$ is obtained from eq 33 explicitly as

$$S_{--}(q) = \frac{1}{{N_a}^2}S_{aa}(q) + \frac{1}{{N_b}^2}S_{bb}(q) - \frac{2}{N_a N_b}S_{ab}(q) \quad (36)$$

But it is not a pure mode, and its relaxation is bimodal, as shown in eq 33 or below, explicitly:

$$S_{--}(q,t) = \vec{E}^{\mathrm{T}} e^{-q^2 \mathbf{D} t}\mathbf{S}(q)\vec{E} \quad (37)$$

A natural definition of the interdiffusion coefficient emerges if we try to approximate the bimodal relaxation by a single exponential in eq 35. Hence, by matching the initial relaxations of eqs 35 and 37, we obtain

$$D_{\mathrm{in}} = \frac{\vec{E}^{\mathrm{T}}\mathbf{DS}\vec{E}}{S_{--}} \quad (38)$$

where $\mathbf{S}$ and S_{--} are the long-wave limits of $\mathbf{S}(q)$ and $S_{--}(q)$. It is convenient to introduce the mobility tensor μ through

$$\mathbf{D} = k_{\mathrm{B}}T\mu\mathbf{S}^{-1} \quad (39)$$

at this stage and express D_{in} as

$$D_{\mathrm{in}} = k_{\mathrm{B}}T\frac{\vec{E}^{\mathrm{T}}\mu\vec{E}}{S_{--}} \quad (40)$$

or explicitly

$$D_{\mathrm{in}} = k_{\mathrm{B}}T\frac{\dfrac{\mu_{aa}}{{N_a}^2} - 2\dfrac{\mu_{ab}}{N_a N_b} + \dfrac{\mu_{bb}}{{N_b}^2}}{\dfrac{S_{aa}}{{N_a}^2} - 2\dfrac{S_{bb}}{N_a N_b} + \dfrac{S_{bb}}{{N_b}^2}} \quad (41)$$

This is a novel definition of the interdiffusion coefficient in terms of the partial mobilities $\mu_{\alpha\beta}$ and partial structure factor $S_{\alpha\beta}$ of the A and B components in the mixture. It is valid in the case of both multicomponent polymer solutions and multicomponent mixtures of polymers. In the former case, microscopic definitions of the partial mobilities are available in eq 4. In the latter case, $\mu_{\alpha\beta}$ can be expressed in terms of the mobilities in the bare system within the framework of the random phase approximation, as we show in a later section.

We note that D_{in} in eqs 40 and 41 is expressed as a product of a kinetic factor

$$\Lambda_{\mathrm{in}} \equiv k_{\mathrm{B}}T\vec{E}^{\mathrm{T}}\mu\vec{E} \quad (42)$$

and a thermodynamic factor $(1/S_{--})$, as conventionally done in the literature.[18-21] In the conventional definition, the kinetic factor is given by the Green–Kubo formula

$$\Lambda_{\mathrm{in}} = \int_0^{\infty} \mathrm{d}t\, \langle J(t)J(0)\rangle \quad (43)$$

where $J(t)$ is the long-wave limit of the longitudinal interdiffusion current:

$$J(t) \equiv \frac{1}{N_a}\sum_{i=1}^{N_a} v_i^a(t) - \frac{1}{N_b}\sum_{j=1}^{N_b} v_j^b(t)$$

Here, $v_i^a(t)$ and $v_j^b(t)$ denote the longitudinal velocities of the particles (or monomers) belonging to components A and B. It is clear that the interdiffusion current is the relative velocity of the center of mass of the two components in the mixture. Since $J(t)$ can be written as

$$J(t) = \frac{\mathrm{d}}{\mathrm{d}t}Z_{\mathrm{in}}(t)$$

where $Z_{\mathrm{in}}(t)$ is the longitudinal component (e.g., the z-component) of the vector separation distance $\vec{R}_{\mathrm{in}}$ between the center of mass of components A and B, i.e.

$$\vec{R}_{\mathrm{in}} = \frac{1}{N_a}\sum_{i=1}^{N_a}\vec{R}_i^a - \frac{1}{N_b}\sum_{j=1}^{N_b}\vec{R}_j^b$$

where $\vec{R}_i^\alpha$ denotes the position vector of particle (or monomer) i of kind α, we have an alternative, and perhaps more physical, definition for the kinetic factor Λ_{in} as

$$\Lambda_{\mathrm{in}} = \lim_{t\to\infty}\frac{1}{6t}\langle|\vec{R}_{\mathrm{in}}(t) - \vec{R}_{\mathrm{in}}(0)|^2\rangle$$

in terms of the mean square displacement of the vector $\vec{R}_{\mathrm{in}}(t)$.

We now show that the conventional definition of the kinetic factor Λ_{in} in terms of the interdiffusion current correlation function, in fact, coincides with its present definition in eq 42. Starting from eq 43, we express Λ_{in} in Appendix B in terms of $S_{--}(q,t)$ as

$$\Lambda_{\mathrm{in}} = -\lim_{t\to\infty}\lim_{q\to 0}\frac{1}{q^2}\frac{\mathrm{d}S_{--}(q,t)}{\mathrm{d}t} \tag{44}$$

where the order of the limits is not interchangeable. This relation is derived from the Liouville equation and the time reversibility. Since eq 44 involves the large-time and small-q limit of $S_{--}(q,t)$, we use the expression of the latter given in eq 37, which is valid in the Markov limit, and obtain $\Lambda_{\mathrm{in}} = \vec{E}^{\mathrm{T}}\mathbf{D}\mathbf{S}\vec{E}$, i.e., the result in eq 42.

Before ending this discussion, we remark that the definitions of the interdiffusion coefficient for a given pair of components in a multicomponent solution or mixture of polymers is probably not unique. The particular definition we have proposed in this paper seems to be the most natural one and is consistent with the conventional definition. As shown in the later sections, it reduces to the unique definition in the case of our incompressible binary mixture, in which the interdiffusion becomes the only normal mode of the mixture in the Markov limit.

Another remark is about the distinction between the long- and short-time interdiffusion coefficients. If one uses in eq 37 the short-time approximation to $S_{--}(q,t)$ defined by

$$S_{--}(q,t) = \vec{E}^{\mathrm{T}}e^{-\mathbf{\Omega}(q)t}\mathbf{S}(q)\vec{E} \tag{45}$$

where $\mathbf{\Omega}(q)$ is the first cumulant matrix, instead of its Markov limit given in eq 37, to calculate the interdiffusion coefficient, one obtains the definition of the short-time interdiffusion coefficient:

$$\mathbf{D}_{\mathrm{in}}^{\mathrm{sh}} = \lim_{q\to 0}\frac{1}{q^2}\frac{\vec{E}^{\mathrm{T}}\mathbf{\Omega}(q)\mathbf{S}(q)\vec{E}}{S_{--}(q)}$$

Introducing the short-time mobility matrix $\mathbf{m}(q)$ through

$$\mathbf{\Omega}(q) = q^2k_{\mathrm{B}}T\mathbf{m}(q)\mathbf{S}^{-1}(q)$$

we obtain

$$\mathbf{D}_{\mathrm{in}}^{\mathrm{sh}} = k_{\mathrm{B}}T\frac{\vec{E}^{\mathrm{T}}\mathbf{m}\vec{E}}{S_{--}} \tag{46}$$

where $\mathbf{m}$ is the small-q limit of $\mathbf{m}(q)$. This is different from the long-time interdiffusion coefficient $\mathbf{D}_{\mathrm{in}}$ defined in eq 40 in terms of the long-time mobility matrix $\boldsymbol{\mu}$. In general, one defines the short-time diffusivity as

$$\mathbf{D}_{\mathrm{sh}} = \lim_{q\to 0}\frac{1}{q^2}\Omega(q)$$

(see eq 8), which is different from the long-time diffusivity matrix $\mathbf{D}$ because of the neglect of the memory term in eq 4. The latter involves the Markov limit of $\mathbf{S}(q,t)$ as $q\to 0$, $t\to\infty$ with a fixed q^2t, whereas eq 8 describes $\mathbf{S}(q,t)$ for short times. $\mathbf{D}_{\mathrm{in}}^{\mathrm{sh}}$ and $\mathbf{D}_{\mathrm{sh}}$ are often used in the study of the dynamics of polymer solutions[1] as an approximation to $\mathbf{D}_{\mathrm{in}}$ and $\mathbf{D}$, because of the difficulties in the calculation of the memory matrix in eq 4.

The cooperative diffusion process is responsible for the relaxation of the thermal fluctuations in the total number density of a given pair of A and B components toward its uniform equilibrium distribution. The diffusion coefficient D_{coop} associated with this process is obtained as the initial slope of $S_{++}(q,t) \equiv \langle\rho_+(\vec{q},t)\rho^*_+(\vec{q},t)\rangle$ where $\rho_+(\vec{q},t) = \rho_a(\vec{q},t) + \rho_b(\vec{q},t)$ is the total number density. Introducing $\vec{e}^{\mathrm{T}} = [1,1]$ so that $\rho_+(\vec{q},t) = \vec{e}^{\mathrm{T}}\vec{\rho}(\vec{q},t)$ and following the same arguments we used to define the interdiffusion coefficient, we obtain

$$D_{\mathrm{coop}} = k_{\mathrm{B}}T\frac{\vec{e}^{\mathrm{T}}\mu\vec{e}}{\vec{e}^{\mathrm{T}}\mathbf{S}\vec{e}} \tag{47}$$

or explicitly

$$D_{\mathrm{coop}} = k_{\mathrm{B}}T\frac{\mu_{aa} + \mu_{bb} + 2\mu_{ab}}{S_{aa} + S_{bb} + 2S_{ab}} \tag{48}$$

This formula was used by Akcasu et al.,[1] to calculate D_{coop} in the case of a dilute solution of A and B polymer chains differing from each other only in their molecular weights. They investigated the concentration dependence of D_{coop}, which they called the apparent diffusion coefficient, in the lowest order in concentration, including the effect of hydrodynamic interactions.

The dynamic scattering functions $S_{++}(q,t)$, $S_{--}(q,t)$, and

$$S_{+-}(q,t) = \langle\rho_+(\vec{q},t)\rho_-(-\vec{q},0)\rangle \tag{49}$$

are intimately related to the number–number (NN), concentration–concentration (CC), and number–concentration (NC) structure functions $S_{\mathrm{NN}}(q,t)$, $S_{\mathrm{CC}}(q,t)$, and $S_{\mathrm{NC}}(q,t)$ discussed by Bhatia et al.[23,24] These structure functions are defined as

$$S_{\mathrm{NN}}(q,t) = \frac{1}{N}\langle\delta N(\vec{q},t)\delta N(-\vec{q},0)\rangle \tag{50}$$

$$S_{\mathrm{CC}}(q,t) = \frac{1}{N}\langle\delta C(\vec{q},t)\delta C(-\vec{q},0)\rangle \tag{51}$$

$$S_{\mathrm{NC}}(q,t) = \frac{1}{N}\langle\delta N(\vec{q},t)\delta C(-\vec{q},0)\rangle \tag{52}$$

with $\delta N \equiv \rho_+$ and $\delta C \equiv Nx_ax_b\rho_- = N\delta c_a$. Then, the relations

$$S_{\mathrm{NN}}(q,t) = \frac{1}{N}S_{+\,+}(q,t) \tag{53}$$

$$S_{\mathrm{CC}}(q,t) = N(x_a x_b)^2 S_{-\,-}(q,t) \tag{54}$$

$$S_{\mathrm{NC}}(q,t) = x_a x_b S_{+\,-}(q,t) \tag{55}$$

are found. Here, $N = N_a + N_b$ and $x_a = N_a/N$; $x_b = 1 - x_a$. Notice that the Bhatia structure factors are intensive quantities. The analysis of neutron and X-ray scattering data from molten salts in terms of these structure factors has been proven to be quite useful.[25]

V. Simple Examples of Binary Mixtures

In the last section, the general concepts and definitions of the interdiffusion and collective diffusion processes in mixtures have been given. These concepts can now be discussed for a variety of systems. In this section we consider very simple examples of binary mixtures of spherical particles for which the diffusion coefficients can be obtained without approximations. This allows for a clear illustration of the general concepts. The following section is concerned with diffusion in polymer mixtures. For these complex systems, approximate schemes are needed for the calculation of the interdiffusion and cooperative diffusion coefficients. Such a scheme is the random phase approximation, which we will discuss in the following section.

Let us consider a binary mixture of spherical particles, such as aqueous suspensions of polystyrene spheres or silica particles dispersed in an organic solvent. In the Markov limit, the dynamics of a binary mixture is described by the matrix $\mathbf{S}(q,t) = \mathbf{A}_+ e^{-q^2 d_+ t} + \mathbf{A}_- e^{-q^2 d_- t}$ of dynamic partial structure factors. The matrix $\mathbf{S}(q,t)$ can be expressed in terms of the mobility matrix and the matrix $\mathbf{S}(q)$ of static partial structure factors as

$$\mathbf{S}(q,t) = \frac{1}{d_+ - d_-}\{[k_{\mathrm{B}}T\mu - d_-\mathbf{S}(q)]e^{-q^2 d_+ t} + [d_+\mathbf{S}(q) - k_{\mathrm{B}}T\mu]e^{-q^2 d_- t}\} \tag{56}$$

This equation can be obtained directly from the matrix equation (15), but it is easier to determine the amplitudes $\mathbf{A}_+$ and $\mathbf{A}_-$ by

$$\begin{gathered}\mathbf{S}(q) = \mathbf{A}_+ + \mathbf{A}_- \\ k_{\mathrm{B}}T\mu = d_+\mathbf{A}_+ + d_-\mathbf{A}_-\end{gathered} \tag{57}$$

The last equation follows from

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{S}(q,t)|_{t=0} = -q^2 k_{\mathrm{B}}T\mu \tag{58}$$

Equations 56 and 58 are quite useful in our further discussion. We discuss now successively four examples of binary mixtures.

a. Binary Mixture of Noninteracting A and B Particles. In this trivial example one readily obtains that $\mu_{\alpha\beta} = \delta_{\alpha\beta}N_\alpha D_\alpha^{\;0}/k_{\mathrm{B}}T$, $S_{\alpha\beta}(q) = N_\alpha\delta_{\alpha\beta}$, and $D_{\alpha\beta} = D_\alpha^{\;0}\delta_{\alpha\beta}$, where $D_\alpha^{\;0} = k_{\mathrm{B}}T/\xi_\alpha$ denotes the Stokes diffusion coefficient of a particle of kind α with friction coefficient ξ_α. From eq 3 follows

$$S_{\alpha\beta}(q,t) = \delta_{\alpha\beta}N_\alpha e^{-q^2 D_\alpha^{\,0} t} \tag{59}$$

which identifies the two decay constants d_+ and d_- as $d_+ = D_a^{\;0}$ and $d_- = D_b^{\;0}$. Not surprisingly, the two normal modes are identified as the tracer diffusion of the A and B particles, respectively.

The kinetic coefficient Λ_{in} is calculated with eq 42 as $\Lambda_{\mathrm{in}} = D_a^{\;0}/N_a + D_b^{\;0}/N_b$. The interdiffusion coefficient is obtained, using eq 40 and $S_{-\,-}(q) = 1/N_a + 1/N_b$, as the fast mode relation

$$D_{\mathrm{in}} = x_b D_a^{\;0} + x_a D_b^{\;0} \tag{60}$$

Using $S_{+\,+}(q) = N_a + N_b$ and $\Lambda_{\mathrm{coop}} \equiv k_{\mathrm{B}}T\hat{e}^{\mathrm{T}}\mu\hat{e} = N_a D_a^{\;0} + N_b D_b^{\;0}$, eq 48 gives the cooperative diffusion coefficient

$$D_{\mathrm{coop}} = x_a D_a^{\;0} + x_b D_b^{\;0} \tag{61}$$

as a weighted sum of the two tracer diffusion coefficients. It should be noted that both the probability density $P_{\mathrm{in}}(\vec{R}_{\mathrm{in}},t)$ of the relative vector $\vec{R}_{\mathrm{in}}$ between the center of masses of A and B particles and the probability density $P_{\mathrm{coop}}(\vec{R}_{\mathrm{c}},t)$ of the position vector

$$\vec{R}_{\mathrm{c}} = \frac{1}{N_a}\sum_{i=1}^{N_a}\vec{R}_i^{\,a} + \frac{1}{N_b}\sum_{j=1}^{N_b}\vec{R}_j^{\,b}$$

of the overall center of mass are solutions of the same diffusion equation

$$\frac{\partial}{\partial t}P(\vec{R},t) = \left(\frac{D_a^{\;0}}{N_a} + \frac{D_b^{\;0}}{N_b}\right)\nabla_{\vec{R}}^{\;2}P(\vec{R},t) \tag{62}$$

with $P = P_{\mathrm{in}}$ or $P = P_{\mathrm{coop}}$. Thus, the mean-squared displacement of $\vec{R}_{\mathrm{in}}$ and $\vec{R}_{\mathrm{c}}$ is given as

$$\langle[\vec{R}_{\mathrm{in}}(t) - \vec{R}_{\mathrm{in}}(0)]^2\rangle = \langle[\vec{R}_{\mathrm{c}}(t) - \vec{R}_{\mathrm{c}}(0)]^2\rangle = 6\Lambda_{\mathrm{in}}t \tag{63}$$

Equation 62 is obtained from the N-particle diffusion equation

$$\frac{\partial}{\partial t}P(\vec{R}^N,t) = \sum_{\alpha\epsilon\{\mathrm{A,B}\}} D_\alpha^{\;0}\sum_{i=1}^{N_\alpha}\nabla_{\vec{R}^{\alpha}_i}^{\;2}P(\vec{R}^N,t) \tag{64}$$

of noninteracting particles together with

$$P_{\mathrm{in}}(\vec{R}_{\mathrm{in}},t) = \int \mathrm{d}\vec{R}^N\, P(\vec{R}^N,t)\,\delta\left[\vec{R}_{\mathrm{in}} - \frac{1}{N_a}\sum_{i=1}^{N_a}\vec{R}_i^{\,a} + \frac{1}{N_b}\sum_{j=1}^{N_b}\vec{R}_j^{\,b}\right] \tag{65}$$

and a similar equation for $P_{\mathrm{coop}}(\vec{R}_{\mathrm{c}},t)$. Here, $\vec{R}^N = (R_1^a, ..., R_{N_a}^a; R_1^b, ..., \vec{R}_{N_b}^b)$. The dynamic scattering functions $S_{+\,+}$, $S_{-\,-}$, and $S_{+\,-}$ are also easily calculated as

$$S_{-\,-}(q,t) = \frac{1}{N_a}e^{-q^2 D_a^{\,0} t} + \frac{1}{N_b}e^{-q^2 D_b^{\,0} t} \tag{66}$$

$$S_{+\,+}(q,t) = N_a e^{-q^2 D_a^{\,0} t} + N_b e^{-q^2 D_b^{\,0} t} \tag{67}$$

$$S_{+\,-}(q,t) = e^{-q^2 D_a^{\,0} t} - e^{-q^2 D_b^{\,0} t} \tag{68}$$

Summarizing we have seen that the binary mixture of noninteracting particles provides a trivial example of a system where the two normal modes cannot be identified as interdiffusion and cooperative diffusion.

b. Binary Mixture without Interaction between Particles of Different Kinds. In such a mixture is $S_{ab}(q,t) \equiv 0$, i.e., the statics and dynamics of the A particles is completely decoupled from the dynamics of the B particles. Especially it is seen that the pair correlation function $g_{ab}(r)$ is identically equal to one. With the help of eq 58 it follows also that $\mu_{ab} = 0$. According to eq 39, the diffusivity matrix $\mathbf{D}$ is diagonal with components $D_{\alpha\beta} = \delta_{\alpha\beta}k_{\mathrm{B}}T\mu_{\alpha\alpha}/S_{\alpha\alpha}$, where $S_{\alpha\alpha}$ is the long-wavelength limit of $S_{\alpha\alpha}(q)$. This gives the main result

$$d_+ = k_{\mathrm{B}}T\frac{\mu_{aa}}{S_{aa}} \equiv D^a_{\mathrm{coop}} \tag{69}$$

$$d_- = k_B T \frac{\mu_{bb}}{S_{bb}} \equiv D^b_{\text{coop}} \qquad (70)$$

Here, D^a_{coop} denotes the cooperative diffusion coefficient of the system of α-particles, in which the presence of particles belonging to the other species is not felt. As expected, it is found that the mutually independent cooperative diffusion processes of A and B particles constitute the two normal modes.

The kinetic coefficient is found to be

$$\Lambda_{\text{in}} = k_B T \left(\frac{\mu_{aa}}{N_a^{\ 2}} + \frac{\mu_{bb}}{N_b^{\ 2}} \right)$$

and with eqs 40 and 48 follows

$$D_{\text{in}} = \frac{N_b^{\ 2} S_{aa} D^a_{\text{coop}} + N_a^{\ 2} S_{bb} D^b_{\text{coop}}}{N_b^{\ 2} S_{aa} + N_a^{\ 2} S_{bb}} \qquad (71)$$

and

$$D_{\text{coop}} = \frac{S_{aa} D^a_{\text{coop}} + S_{bb} D^b_{\text{coop}}}{S_{aa} + S_{bb}} \qquad (72)$$

The dynamic scattering functions are

$$S_{-\,-}(q,t) = \frac{S_{aa}(q)}{N_a^{\ 2}} e^{-q^2 D^a{}_{\text{coop}} t} + \frac{S_{bb}(q)}{N_b^{\ 2}} e^{-q^2 D^b{}_{\text{coop}} t} \qquad (73)$$

$$S_{+\,+}(q,t) = S_{aa}(q) e^{-q^2 D^a{}_{\text{coop}} t} + S_{bb}(q) e^{-q^2 D^b{}_{\text{coop}} t} \qquad (74)$$

$$S_{+\,-}(q,t) = \frac{S_{aa}(q)}{N_a} e^{-q^2 D^a{}_{\text{coop}} t} - \frac{S_{bb}(q)}{N_b} e^{-q^2 D^b{}_{\text{coop}} t} \qquad (75)$$

Thus, the interdiffusion and cooperative diffusion coefficient of the mixture are linear combinations of D^a_{coop} and D^b_{coop}, weighted with the long-wavelength static scattering functions $S_{\alpha\alpha}$. We have provided here another example of a system in which the two normal modes cannot be identified as interdiffusion and cooperative diffusion. Obviously, example (a) follows from (b) as a limiting case of vanishingly small number densities; i.e., for $N_\alpha / V \to 0$, $\alpha = a, b$, where $S_{\alpha\beta}(q) \to N_\alpha \delta_{\alpha\beta}$, $D^\alpha_{\text{coop}} \to D_\alpha{}^0$, and $\mu_{\alpha\beta} \to N_\alpha D_\alpha{}^0 \delta_{\alpha\beta} / k_B T$.

c. Binary Mixture of B Particles and a Vanishingly Small Amount of "Tracer" Particles A. A possible realization of such a mixture is an aqueous suspension of small polystyrene spheres in which a tiny amount of strongly scattering large spheres has been dissolved. The tracer diffusion in such samples has been studied quite recently both experimentally and theoretically.[26,27]

We assume that the influence of the few A spheres on the statics and dynamics of the B spheres is negligible. Thus, e.g., the pair correlation function $g_{bb}(r)$ describing the correlations of pairs of B spheres is essentially equal to the pair correlation function of a monodisperse system, in which all A particles have been removed. The pair correlation functions $g_{ab}(r)$ and $g_{aa}(r)$, however, are strongly dependent on the concentration and interaction parameters of the B spheres. Since $N_a \ll N_b$ it is found that $S_{+\,+}(q,t) \approx S_{bb}(q,t)$ and $S_{-\,-}(q,t) \approx G_a(q,t)/N_a$ where

$$G_a(q,t) = \langle \exp(i\vec{q}\cdot[\vec{R}_1^a(t) - \vec{R}_1^a(0)]) \rangle \qquad (76)$$

is the dynamic self-structure factor of an A sphere, say sphere 1. In the Markov limit, one finds

$$S_{+\,+}(q,t) = S_{bb}(q) \exp(-q^2 D^b_{\text{coop}} t) \qquad (77)$$

$$S_{-\,-}(q,t) = \frac{1}{N_a} \exp(-q^2 D^s_a t) \qquad (78)$$

Here, D^b_{coop} denotes the cooperative diffusion coefficient of the monodisperse solution of B spheres, where the few A spheres have been removed. The tracer diffusion coefficient of an A sphere in the mixture is denoted by D^s_a. From eqs 77 and 78 it is seen that $d_+ = D_{\text{coop}} = D^b_{\text{coop}}$ and $d_- = D_{\text{in}} = D^s_a$. Alternatively, we could have used the general expressions (41) and (48) to calculate the interdiffusion and tracer diffusion coefficient in the mixture. For example, it is readily found that $S_{-\,-}(q) = 1/N_a$ and with the Green–Kubo formula, eq 43, the result $N_a \Lambda_{\text{in}} = \int_0^\infty \mathrm{d}t \, \langle v_1^a(t) v_1^a(0) \rangle = D^s_a$ is obtained. Here, v_1^a is the longitudinal component of the velocity of a particle, say particle 1, of kind a. Equations 77 and 78 also follow from the results of example (b) in the limit $N_a/N_b \to 0$, provided that the A particles do not interact with B particles.

We have presented here a system where the two eigenmodes can in fact be identified with the cooperative diffusion process and the interdiffusion process. We will now give an example where this identification holds for arbitrary ratios N_a/N_b.

d. Binary Mixture of A and B Particles Which Differ Only in Labeling. In this case all $N = N_a + N_b$ particles are statistically equivalent and, especially, all three partial radial distribution functions are equal to each other; i.e., $g_{aa}(r) = g_{bb}(r) = g_{ab}(r)$. It easily follows that

$$S_{\alpha\beta}(q,t) = (\delta_{\alpha\beta} N_\alpha - x_\alpha x_\beta N) G(q,t) + x_\alpha x_\beta S_T(q,t) \qquad (79)$$

where $G(q,t) = \langle e^{i\vec{q}\cdot[\vec{R}(t) - \vec{R}(0)]} \rangle$ is the self-structure factor of a particle with position vector $\vec{R}$, with $G(q,0) = 1$, and

$$S_T(q,t) \equiv \sum_{i,j=1}^{N} \langle e^{i\vec{q}\cdot[\vec{R}_i(t) - \vec{R}_j(0)]} \rangle = S_{+\,+}(q,t) \qquad (80)$$

is the total dynamic structure factor of the statically and dynamically monodisperse system. The partial dynamic structure factors reduce in the Markov limit to

$$S_{\alpha\beta}(q,t) = (\delta_{\alpha\beta} N_\alpha - N x_\alpha x_\beta) e^{-q^2 D^s t} + x_\alpha x_\beta S_T(q) e^{-q^2 D_{\text{coop}} t} \qquad (81)$$

where D^s is the tracer diffusion coefficient of a particle and D_{coop} denotes the cooperative diffusion coefficient. Furthermore we find

$$S_{-\,-}(q,t) = \left(\frac{1}{N_a} + \frac{1}{N_b} \right) G(q,t) = \left(\frac{1}{N_a} + \frac{1}{N_b} \right) e^{-q^2 D^s t} \qquad (82)$$

$$S_{+\,+}(q,t) = S_T(q) e^{-q^2 D_{\text{coop}} t} \qquad (83)$$

$$S_{+\,-}(q,t) = 0 \qquad (84)$$

Thus, it follows the indentification $d_+ = D_{\text{coop}}$ and $d_- = D_{\text{in}} = D^s$. The eigenmode with decay constant d_+ can be identified as cooperative diffusion. The eigenmode with corresponding decay constant d_- describes the interdiffusion process, which, in this example, is identical with the self-diffusion process. That $D_{\text{in}} = D^s$ is to be expected since there is no correlation between fluctuations in the local total number density ρ_+ and fluctuations ρ_- in the local relative concentration of the two species, as stated by eq 84. Therefore, the particle exchange between the two species is driven only by tracer diffusion.

The general expression (41) can also be used to express D_{in} in terms of the mobilities and long-wavelength partial structure factors. With eq 58, the mobilities are obtained to be

$$\mu_{\alpha\beta} = \frac{1}{k_{\mathrm{B}}T}[(\delta_{\alpha\beta}N_\alpha - Nx_\alpha x_\beta)D^{\mathrm{s}} + x_\alpha x_\beta S_T D_{\mathrm{coop}}] \tag{85}$$

Also from eq 41 it follows that $D_{\mathrm{in}} = D^{\mathrm{s}}$ and with the Green-Kubo formula, eq 43, the result $D_{\mathrm{in}} = \int_0^\infty \mathrm{d}t\ \langle v(t)v(0)\rangle$ is obtained, where v is the longitudinal velocity of a particle.

The diffusivity matrix follows from eq 39 as

$$\mathbf{D} = \begin{pmatrix} x_a D_{\mathrm{coop}} + x_b D^{\mathrm{s}} & x_a(D_{\mathrm{coop}} - D^{\mathrm{s}}) \\ x_b(D_{\mathrm{coop}} - D^{\mathrm{s}}) & x_b D_{\mathrm{coop}} + x_a D^{\mathrm{s}} \end{pmatrix} \tag{86}$$

Obviously, $D_{ab} \neq D_{ba}$ unless $x_a = x_b = {}^1/_2$.

We have shown that for a mixture of two species of particles, which differ only in labeling, the two normal modes can be identified as coooperative diffusion and interdiffusion. The interdiffusion mode, however, is here identical with the tracer diffusion mode. In a later section we will show that this essentially constitutes the only system with $d_+ = D_{\mathrm{coop}}$ and $d_- = D_{\mathrm{in}}$, for arbitrary ratios N_a/N_b.

In this section, only mixtures of spherical particles were considered. The following section deals with the diffusion processes in ternary mixtures of homopolymers. The interdiffusion and tracer diffusion coefficients are calculated within the framework of the random phase approximation (RPA).

VI. Calculation of the Diffusion Coefficients with RPA

In this section we consider an incompressible ternary mixture of A and B homopolymers in a matrix of c homopolymers. It has been shown recently by Akcasu and Tombakoglu[11] that within the framework of the RPA the mobilities $\mu_{\alpha\beta}$ can be expressed in terms of the mobilities $\mu^0{}_{\alpha\beta}$ in the bare system as

$$\frac{1}{\mu_{aa}} = \frac{1}{\mu^0{}_{aa}} + \frac{1}{\mu^0{}_{bb} + \mu^0{}_{cc}} \tag{87}$$

$$\frac{1}{\mu_{ab}} = -\left[\frac{1}{\mu^0{}_{aa}} + \frac{1}{\mu^0{}_{bb}} + \frac{\mu^0{}_{cc}}{\mu^0{}_{aa}\mu^0{}_{bb}}\right] \tag{88}$$

with a similar expression for μ_{bb}. The "bare" system is defined[11] as the one in which the monomer-monomer interactions are not present, but the chain connectivity is maintained. The mobilities $\mu^0{}_{\alpha\beta}$ are related to the tracer diffusion coefficients in the bare system by

$$\mu^0{}_{\alpha\alpha} = \frac{N_\alpha D_\alpha}{k_{\mathrm{B}}T} \tag{89}$$

where N_α is the total number of particles (monomers) belonging to the αth component, $D_\alpha = k_{\mathrm{B}}T/\xi_\alpha$ is the tracer diffusion coefficient of a monomer (the segmental diffusion coefficient), and ξ_α is the friction coefficient of a monomer in the mixture. This result is obtained by adopting the Rouse model for the dynamics of a single Gaussian chain in the mixture.

The substitution of eqs 87 and 88 into eq 41 yields the kinetic factor Λ_{in} as

$$\Lambda_{\mathrm{in}} = \frac{D_a}{N_a} + \frac{D_b}{N_b} - \frac{(D_a - D_b)^2}{N_a D_a + N_b D_b + N_c D_c} \tag{90}$$

The D_αs in eqs 89 and 90 are, in principle, the tracer diffusion coefficients in the bare system, in which the monomer-monomer interactions are not present. But, in Rouse dynamics, the mobilities are related to the friction coefficients by $\mu^0{}_{\alpha\alpha} = N_\alpha/\xi_\alpha$ regardless of whether the monomer interactions are present or not. The friction coefficients ξ_α enter the Rouse dynamics as parameters that must be specified as an input from elsewhere. Hence, ξ_α and D_α are usually interpreted as the friction coefficient and the tracer diffusion coefficient of a monomer of the αth kind in the actual interacting mixture. They therefore depend implicitly on the composition and the temperature of the mixture. Experimentally, one measures the tracer diffusion coefficient $D^{\mathrm{P}}_\alpha = D_\alpha/p_\alpha$, where p_α is the number of monomers (or statistical segments) in a chain of kind α.

We now discuss the implications of eq 90, which is a new result. Perhaps the most interesting feature of this result is that it contains the results of both the slow mode[6-10] and fast mode theories,[18,19,28] as two limiting cases. The slow mode result follows when the matrix mobility $\mu^0{}_{cc}$ is much smaller than the sum of the mobilities of the other two components:

$$N_c D_c \ll N_a D_a + N_b D_b \tag{91}$$

Then, eq 90 yields

$$\frac{1}{\Lambda_{\mathrm{in}}} = N x_a x_b \left[\frac{x_b}{D_a} + \frac{x_a}{D_b}\right] \tag{92}$$

where $N = N_a + N_b$ and $x_a = N_a/(N_a + N_b)$. The condition in eq 91 is automatically satisfied when the matrix is removed, i.e., $N_c \rightarrow 0$, so that one is left with an incompressible mixture of the A and B components. The slow mode result was obtained initially for a binary incompressible mixture using the RPA. However, eq 90 indicates that the slow mode result is still valid even in the presence of a third component, i.e., the matrix, provided the unequality in eq 91 holds.

The fast mode result is obtained when the last term in eq 90 is negligible as compared to the sum of the first two:

$$\Lambda_{\mathrm{in}} = \frac{1}{N x_a x_b}[x_b D_a + x_a D_b] \tag{93}$$

The condition for the validity of this result can be obtained by comparing the magnitudes of the neglected term to that of the remaining ones.

$$\frac{1}{N_c D_c} \ll \frac{1}{N_a + N_b}\left(\frac{x_a}{D_a} + \frac{x_b}{D_b}\right) \tag{94}$$

This condition is satisfied when the number of the matrix particles is much larger than the total number of A and B particles, or when the friction coefficient ξ_c of the matrix particles is much smaller than the friction coefficients ξ_a and ξ_b of the A and B particles. This situation is similar to a solution of the A and B components, in which the solvent plays the role of the matrix in the ternary mixture. As we pointed out earlier in the introduction, the bimodal relaxation in such a solution is due to a clear separation of the relaxation times of the polymers and the solvent. The condition in eq 94 is indeed an expression of the qualitative requirement that the relaxation of the matrix is much faster than the relaxation times of the A and B components. Hence, when eq 94 is satisfied the incompressible ternary mixture behaves "like" a solution, and the fast mode result is valid when this solution-like behavior prevails.

The calculation of the thermodynamic factor $1/S_{--}$ in eq 38 requires the expressions of the partial structure factors $S_{\alpha\beta}(q)$ in the small-q limit (see eq 37), in the framework of the static RPA in terms of the single-chain static structure factors and the Flory interaction parameters. These calculations are standard[29-31] and will not be repeated here. We reproduce the necessary formulas in Appendix C and present the expression of D_{in} in the above two limiting cases. In the limit $N_cD_c \to 0$, we obtain the known result[9,10,29]

$$D_{\mathrm{in}} = \left[\frac{1}{x_ap_aD_a^{\mathrm{P}}} + \frac{1}{x_bp_bD_b^{\mathrm{P}}}\right]^{-1}\left(\frac{1}{x_ap_a} + \frac{1}{x_bp_b} - 2N\kappa_{ab}\right) \tag{95}$$

where D_α^{P} is the tracer diffusion coefficient of an αth polymer chain and κ_{ab} is the Flory interaction parameter normalized by the volume V of the system (see Appendix C). Hence $N\kappa_{ab}$ can be interpreted as the interaction parameter per segmental volume $v_{\mathrm{s}} = V/N$, assuming that the segmental volumes of the various species are the same.

In the limit $N_cC_c \to \infty$, the full expression of D_{in} including interactions among the polymer species is too lengthy to be written down here and is not essential for our discussion. Therefore, we only present the result in the absence of interactions

$$D_{\mathrm{in}} = \frac{x_bp_aD_a^{\mathrm{P}} + x_ap_bD_b^{\mathrm{P}}}{x_bp_a + x_ap_b} \tag{96}$$

which reduces to eq 60 when $p_a = p_b = 1$, i.e., in the case of point particles.

We not consider the cooperative diffusion coefficient defined in eq 48 in the case of an incompressible ternary mixture. Due to the local incompressibility constraint $\bar{\rho}_a + \bar{\rho}_b + \bar{\rho}_c = 0$, D_{coop} can be written as

$$D_{\mathrm{coop}} = k_{\mathrm{B}}T\frac{\mu_{cc}}{S_{cc}} \tag{97}$$

where S_{cc} is the long-wave limit of the static correlation function $S_{cc}(q)$ of the matrix and μ_{cc} is its mobility. In the RPA

$$\frac{1}{\mu_{cc}} = \frac{1}{\mu^0{}_{cc}} + \frac{1}{\mu^0{}_{aa} + \mu^0{}_{bb}} \tag{98}$$

and

$$S_{cc} = \frac{1}{\Delta}\left[\frac{1}{N_ap_a} + \frac{1}{N_bp_b} - 2\kappa_{ab}\right] \tag{99}$$

where

$$\Delta = \left(\frac{1}{N_ap_a} + v_{aa}\right)\left(\frac{1}{N_bp_b} + v_{bb}\right) - v_{ab}{}^2 \tag{100}$$

Notice that $S_{aa}S_{bb} - S_{ab}{}^2 = 1/\Delta$. We shall present the results again in the two limiting cases. In the bulk limit $N_cD_c \to 0$, we find $S_{cc} \to N_cp_c$ and $\mu_{cc} \to N_cD_c/k_{\mathrm{B}}T$ so that

$$D_{\mathrm{coop}} = D_c^{\mathrm{P}} \tag{101}$$

i.e., the cooperative diffusion coefficient approaches the tracer diffusion coefficient of a matrix molecule when the concentration of the matrix component becomes very small. It should be pointed out, however, that the amplitude of the mode, which coincides with the cooperative mode in the bulk limit, vanishes, and the dynamic scattering function relaxes exponentially as $\exp[-q^2D_{\mathrm{in}}t]$.

In the limit $N_cD_c \to \infty$, and again in the absence of interaction, i.e., $v_{\alpha\beta} = 0$, one easily obtains

$$D_{\mathrm{coop}} = \frac{x_ap_aD_a^{\mathrm{P}} + x_bp_bD_b^{\mathrm{P}}}{x_ap_a + x_bp_b} \tag{102}$$

which is the expected linear superposition of the tracer diffusion coefficients in solution when the chains do not interact with each other. We again observe that eq 102 reduces to eq 61 obtained for noninteracting Brownian point particles, when $p_a = p_b = 1$.

VII. Calculation of the Decay Constants with the RPA

The decay constants d_+ and d_- in eq 15 are the roots of the quadratic equation 10:

$$d_\pm = D_{\mathrm{av}} \pm (D_{\mathrm{av}}{}^2 - |\mathbf{D}|)^{1/2} \tag{103}$$

We first express d_+ and d_- in terms of the components of the mobility matrix μ and the static structure factor matrix $\mathbf{S}$ using $\mathbf{D} = k_{\mathrm{B}}T\mu\mathbf{S}^{-1}$. To compress writing, we absorb $k_{\mathrm{B}}T$ in μ as $\Lambda \equiv k_{\mathrm{B}}T\mu$. The components of Λ are the conventional Onsager coefficients. The elements of $\mathbf{D}$ are

$$D_a = \frac{1}{|\mathbf{S}|}[\Lambda_{aa}S_{bb} - \Lambda_{ab}S_{ab}]$$

$$D_{ab} = \frac{1}{|\mathbf{S}|}[\Lambda_{ab}S_{aa} - \Lambda_{aa}S_{ab}]$$

$$D_{ba} = \frac{1}{|\mathbf{S}|}[\Lambda_{ab}S_{bb} - \Lambda_{bb}S_{ab}]$$

$$D_{bb} = \frac{1}{|\mathbf{S}|}[\Lambda_{bb}S_{aa} - \Lambda_{ab}S_{ab}]$$

$$|\mathbf{S}| \equiv S_{aa}S_{bb} - S_{ab}{}^2 \tag{104}$$

As pointed out earlier, $\mathbf{D}$ is not symmetric. The D_{av} (see eq 11) and $|\mathbf{D}|$ appearing in eq 103 are

$$D_{\mathrm{av}} = \frac{1}{2|\mathbf{S}|}[\Lambda_{aa}S_{bb} + \Lambda_{bb}S_{aa} - 2S_{ab}\Lambda_{ab}] \tag{105}$$

$$|\mathbf{D}| = \frac{|\Lambda|}{|\mathbf{S}|} = \frac{\Lambda_{aa}\Lambda_{bb} - \Lambda_{ab}{}^2}{S_{aa}S_{bb} - S_{ab}{}^2} \tag{106}$$

Since $\Lambda_{\alpha\beta}$ and $S_{\alpha\beta}$ are expressed in the RPA in terms of the interaction parameters $\kappa_{\alpha\beta}$ and the bare system mobilities $\Lambda^0{}_{\alpha\beta}$ and structure factors $S^0{}_{\alpha\beta}$, the decay constants d_+ and d_- can be obtained from eqs 103–105 by simple but tedious arithmetic for an arbitrary incompressible ternary mixture. Here, we shall present the results only in the same limiting cases we considered above in the calculation of the diffusion constants.

In the bulk limit of $N_cD_c \to 0$ we find

$$|\Lambda| = N_cD_c\left[\frac{1}{N_aD_a} + \frac{1}{N_bD_b}\right]^{-1}$$

$$|\mathbf{S}| = N_cp_c\left[\frac{1}{N_ap_a} + \frac{1}{N_bp_b} - 2\kappa_{ab}\right]^{-1}$$

so that

$$|\mathbf{D}| = D_c^{\mathrm{P}}D_{\mathrm{in}}(\mathrm{bulk}) \tag{107}$$

where D_{in}(bulk) is the interdiffusion coefficient in the bulk limit, which was calculated in eq 95. The D_{av} is obtained in this limit as

$$D_{\mathrm{av}} = \frac{1}{2}[D_c^{\mathrm{P}} + D_{\mathrm{in}}(\mathrm{bulk})] \tag{108}$$

Substituting eq 107 and 108 into eq 103 yields the decay constants as $d_+ = D_c^{\mathrm{P}}$ and $d_- = D_{\mathrm{in}}$(bulk). Hence, in this limit the decay constants coincide with the cooperative and interdiffusion coefficients. As we pointed out earlier the amplitude of the mode corresponding to the cooperative mode vanishes, so that in a dynamic scattering experiment on an incompressible binary blend only the interdiffusion mode is present.

In the opposite limit $N_cD_c \to \infty$, and in the absence of interactions, $\Lambda_{\alpha\alpha} = \Lambda^0{}_{\alpha\alpha} = N_\alpha p_\alpha D_\alpha^{\mathrm{P}}$, $\Lambda_{\alpha\beta} = \Lambda^0{}_{\alpha\beta} = 0$, $S_{\alpha\alpha} =$

$S^0_{\alpha\alpha} = N_\alpha p_\alpha$, and $S_{\alpha\beta} = S^0_{\alpha\beta} = 0$, the calculations are simple and yield $2D_{\text{av}} = D^{\text{P}}_a + D^{\text{P}}_b$ and $|\mathbf{D}| = D^{\text{P}}_a D^{\text{P}}_b$. Hence, eq 103 yields $d_+ = D^{\text{P}}_a$ and $d_- = D^{\text{P}}_b$ (or vice versa), which implies that in this limit the two modes correspond to the relaxation of the components of A and B independently; i.e., $S_{\alpha\beta}(q,t) = \delta_{\alpha\beta}N_\alpha p_\alpha \exp[-q^2D^{\text{P}}_\alpha t]$. (This result becomes identical with that in eq 59 when $p_a = p_b = 1$.) Although this limit is trivial, it shows that the decay constants d_+ and d_- are not longer the same as the cooperative and interdiffusion coefficients we calculated in eqs 102 and 96, respectively. This observation brings us to the next question.

VIII. Conditions for the Identification of the Normal Modes as the Cooperative Diffusion and Interdiffusion Modes

In this section, we want to address one of the questions raised in the Introduction concerning the conditions on the dynamic and static properties of a ternary mixture under which the normal modes of the system coincide with the interdiffusion and cooperative diffusion modes. The normal modes are characterized by $\xi_+(q,t)$ and $\xi_-(q,t)$, which are defined in eqs 19 and 20, and by the interdiffusion and cooperative diffusion modes $\rho_-(\vec q,t)$ and $\rho_+(\vec q,t)$ introduced in eqs 29, 30, and 34. Hence, we want to find the conditions under which $\rho_+(\vec q,t)$ and $\rho_-(\vec q,t)$ are proportional to $\xi_+(\vec q,t)$ and $\xi_-(\vec q,t)$, respectively, for all t. Since the fluctuations of the normal modes are uncoupled in the sense that $\langle \xi_+(\vec q,t)\xi_-(\vec q,0)\rangle = 0$ holds for any t (see eq 22), the desired conditions are obtained from the requirement that $\langle \rho_+(\vec q,t)\rho_-(\vec q,0)\rangle = 0$ must hold at all times. Using $\rho_+(\vec q,t) = \vec e^{\text{T}}\vec\rho(\vec q,t)$ and $\rho_-(\vec q,0) = \vec E^{\text{T}}\vec\rho(\vec q,0)$, we rewrite this requirement as

$$\vec e^{\text{T}} e^{-q^2\mathbf{D}t}\mathbf{S}(q)\vec E = 0 \tag{109}$$

for all t. Evaluating eq 109 at $t = 0$, we obtain the condition on the static properties of the mixtures as $\vec e^{\text{T}}S(q)\vec E = 0$ or explicitly

$$\frac{S_{aa}(q) + S_{ab}(q)}{N_a} = \frac{S_{bb}(q) + S_{ab}(q)}{N_b} \tag{110}$$

which must hold for all q and any ratio of N_a/N_b. We shall investigate the physical implications of this condition on a polymer mixture presently. For a binary uncharged atomic fluid, it is easy to demonstrate that the long-wave limit of eq 110 implies equal thermodynamic partial molar volumes of both species.[25]

In order to obtain the condition on the dynamic properties we differentiate eq 109 with respect to time and evaluate the resulting equation at $t = 0$. The result is $\vec e^{\text{T}}\mathbf{DS}(q)\vec E = 0$, and in terms of the mobilities $\mathbf{D} = k_{\text{B}}T\boldsymbol{\mu}\mathbf{S}^{-1}$ this gives $\vec e^{\text{T}}\boldsymbol{\mu}\vec E = 0$. We note that we consider only the $q \to 0$ limit in the definition of the mobilities. In terms of the partial mobilities, $\vec e^{\text{T}}\boldsymbol{\mu}\vec E = 0$ becomes

$$\frac{\mu_{aa} + \mu_{ab}}{N_a} = \frac{\mu_{bb} + \mu_{ab}}{N_b} \tag{111}$$

which, also, must hold for any ratio N_a/N_b.

When the interdiffusion and cooperative diffusion modes coincide with the normal modes, i.e., when the conditions in eqs 110 and 111 are satisfied, we have $d_- = D_{\text{in}}$ and $d_+ = D_{\text{coop}}$. Hence, using these conditions in eqs 41 and 48, we obtain the following simplified expressions for $d_- = D_{\text{in}}$ and $d_+ = D_{\text{coop}}$ in a polymer mixture satisfying the conditions in eqs 110 and 111:

$$d_- = D_{\text{in}} = k_{\text{B}}T\left(\frac{\mu_{aa}}{N_a^{\ 2}} - \frac{\mu_{bb}}{N_b^{\ 2}}\right)\left(\frac{S_{aa}}{N_a^{\ 2}} - \frac{S_{bb}}{N_b^{\ 2}}\right)^{-1} \tag{112}$$

$$d_+ = D_{\text{coop}} = k_{\text{B}}T\frac{\mu_{aa} - \mu_{bb}}{S_{aa} - S_{bb}} \tag{113}$$

Using eqs 112 and 113, the diffusivity matrix $\mathbf{D}$ can be expressed in terms of D_{in} and D_{coop}. The result for $\mathbf{D}$ is given by eq 86, with D^{s} replaced by D_{in}. We point out that these results are not based on the RPA and are valid in any multicomponent solution or mixture of homopolymers.

In order to investigate the physical implications of the condition on the partial static structure factors given in eq 110, we write $S_{\alpha\beta}(q)$ for small q explicitly as

$$S_{\alpha\beta}(q) = N_\alpha\{p_\alpha P_{\text{D}}((qR_{G\alpha})^2)\delta_{\alpha\beta} + n_\beta\int d^3Re^{i\vec q\cdot\vec R}[g_{\alpha\beta}(R) - 1]\} \tag{114}$$

where $P_{\text{D}}(x)$ is the conventional Debye function and $g_{\alpha\beta}(R)$ is the pair correlation function of the center of masses of a pair of α and β chains with $\alpha,\beta = a$ or b. The n_β is the density of the monomers of kind β (we adopted Gaussian chain statistics in the calculation of the single-chain static structure factors, for simplicity). Using eq 114 in eq 110 and requiring that the resulting equality must hold for any q and any concentration of A and B polymers, we find that $p_a = p_b$, $R_{Ga} = R_{Gb}$ and $g_{aa}(R) = g_{bb}(R) = g_{ab}(R)$ must hold in order that the normal modes of the mixture coincide with the interdiffusion and cooperative diffusion modes. Physically, these conditions imply that the equilibrium properties of the chains of the A and B components must be identical.

The discussion of the physical implications of the condition on the dynamic properties given in eq 111 is more involved because it requires a model for the operator lsc in eqs 5 and 6, which governs the time evolution of the system. In the case of a binary polymer solution, $\mathcal{L}$ is customarily chosen as the adjoint of Kirkwood's generalized diffusion operator. In this case it is possible to show that the condition in eq 111 requires the friction coefficients ξ_a and ξ_b of the monomers of the components to be equal to each other, in addition to the static conditions we stated above. Since the derivations are somewhat involved, we prefer not to include them here.

In the case of incompressible ternary mixtures of polymers (without any solvent) a detailed microscopic description of the dynamics of the system in terms of an operator $\mathcal{L}$ does not seem to be feasible. Therefore, we resort to the random phase approximation to discuss the physical implications of the conditions in eqs 110 and 111 in such systems. Substituting the expressions of $\mu_{\alpha\beta}$ from eqs 87 and 88 into eq 111, we calculate the left-hand side of eq 111 as

$$\frac{\mu_{aa} + \mu_{ab}}{N_a} = \frac{\mu^0_{\ aa}}{N_a}\,\frac{\mu^0_{\ cc}}{\mu^0_{\ aa} + \mu^0_{\ bb} + \mu^0_{\ cc}}$$

The right-hand side of eq 111 is obtained by interchanging the subscripts a and b in this equation. By comparing both sides one obtains $\mu^0{}_{aa}/N_a = \mu^0{}_{bb}/N_b$. Since $\mu^0{}_{\alpha\alpha} = N_\alpha/\xi_\alpha$, the equality $\xi_a = \xi_b$ follows. The condition eq 109 in an incompressible ternary mixture can be shown with RPA to be $p_a = p_b$ and $v_{aa} = v_{bb} = v_{ab}$, by expressing $S_{\alpha\beta}$ in eq 109 in terms of $v_{\alpha\beta}$ and $S^0{}_{\alpha\beta} = N_\alpha p_\alpha\delta_{\alpha\beta}$ in the bare system (see Appendix C). This result is consistent with $g_{aa} = g_{bb} = g_{ab}$, which we found using eq 114. Indeed, v_{aa}

$= v_{bb} = v_{ab}$ implies (see Appendix C) $\kappa_{ac} = \kappa_{bc}$ and $\kappa_{ab} = 0$ for the Flory interaction parameters. If we require that the normal modes coincide with the interdiffusion and cooperative diffusion modes for a mixture of A and B in any matrix, then $\kappa_{ac} = \kappa_{bc}$ and $\kappa_{ab} = 0$ imply $W_{aa} = W_{bb} = W_{ab}$; i.e., the interaction potentials $W_{\alpha\beta}$ between the pairs of A and B monomers are the same.

It is interesting to calculate $d_+ = D_c$ and $d_- = D_{\text{in}}$ under these conditions in a ternary mixture using eqs 112 and 113. Using $p_a = p_b = p$, $v_{aa} = v_{bb} = v_{ab} = v$, and $\xi_a = \xi_b = \xi$, we find for $d_+ = D_c$:

$$d_+ = k_BT\frac{(N_c/\xi_c)(N/\xi)}{(N_c/\xi_c) + (N/\xi)}\left(\frac{1}{N_cp_c} + \frac{1}{N_p} - 2\kappa\right) \quad (115)$$

This result is identical with the interdiffusion coefficient of an incompressible binary mixture consisting of N chains with a polymerization index p and friction coefficient ξ, and N_c chains with p_c and ξ_c interacting with each other with the Flory interaction parameter κ. Hence, it could have been written down directly from eq 95 with a proper identification of the A and B components in it. In the solution limit $(N_c/\xi_c) \rightarrow \infty$, eq 115 reduces to $d_+ = D_c = (k_BT/\xi p)(1 - 2Np\kappa)$, and in the bulk limit $(N_c/\xi_c) \rightarrow 0$, it yields $d_+ = D_c = (k_BT/\xi_cp_c)$, which is the tracer diffusion coefficient of the matrix molecules.

For $d_- = D_{\text{in}}$ we obtain after some algebra $d_- = k_BT/\xi p$, which is the tracer diffusion coefficient of an A or B molecule in the mixture.

In conclusion, the normal modes d_+ and d_- can be identified as the cooperative and interdiffusion modes only when the A and B chains are identical and distinguished from each other only by their labeling. There is no restriction on the properties of the matrix molecules. Dynamically, such a system is equivalent to an incompressible interacting binary mixture, in which A and B molecules together constitute one component and the matrix C is the second component. Therefore, the cooperative diffusion coefficient of the A and B components becomes identical with the interdiffusion coefficient in the equivalent binary system, and the interdiffusion coefficient of the A and B components relative to each other reduces to the tracer diffusion coefficient of the individual molecules in the mixture. If all the A and B molecules are labeled in a dynamic scattering experiment on such a system, then the measured scattering function $S_T(q,t)$ will relax only with one exponential mode with $d_+ = D_c$, which corresponds to the interdiffusion in the binary mixture. If, on the other hand, only the A component is visible to the probing radiation, then the measured dynamic scattering function $S_{aa}(q,t)$ will contain two exponential terms with decay constants $D_+ = D_{\text{coop}}$ and $d_- = D_{\text{in}}$. In other words, the amplitudes of the modes depend on the labeling, but the relaxation frequencies are determined by the dynamics of the system, regardless of which part of it is visible to the scattered radiation.

IX. Connection with the Onsager Formalism

The transport properties of lattice gas models of alloys with two particle species and vacancies have been studied recently by Kehr et al.[15] and Jilge et al.[16] using the linear Onsager theory of transport and computer simulations. In this section we briefly point out the connection between the linear response theory used in our work and the Onsager formalism.

In both formalisms, one arrives at a bimodal description of the system by either eliminating the third component on the basis of local incompressibility or using the Markov limit when the third component relaxes much faster than the others. The diffusion equation for the mean values of the number densities is expressed as in eq 23, which is identical with the eq 2.25

$$\partial c_\alpha/\partial t = \sum_\beta D_{\alpha\beta}\nabla^2 c_\beta$$

in the work of Kehr et al.,[15] in which $c_\alpha(\vec{r},t)$ is the local concentration. Therefore, we have to compare the expressions for the components of the diffusivity matrix $\mathbf{D}$ in both formalisms. For the sake of comparison we reproduce the D_{aa} element (eq 2.24 of ref 15) obtained by Kehr et al. using the Onsager formalism

$$D_{\text{AA}} = \Lambda_{\text{AA}}\left[\frac{1}{c_{\text{A}}} + \frac{1}{c_{\text{V}}} + \chi_{\text{AA}} + \chi_{\text{VV}} - 2\chi_{\text{AV}}\right] + \Lambda_{\text{AB}}\left[\frac{1}{c_{\text{V}}} + \chi_{\text{AB}} + \chi_{\text{VV}} - \chi_{\text{AV}} - \chi_{\text{BV}}\right] \quad (116)$$

where c_{V} is the concentration of the vacancies and $k_BT\chi_{\alpha\beta}$ are the interaction potentials between a pair of particles. This has to be compared with

$$D_{aa} = \Lambda_{aa}\frac{S_{bb}}{\Delta} - \Lambda_{ab}\frac{S_{ab}}{\Delta} \quad (117)$$

given in eq 104 of this paper, where $\Delta = S_{aa}S_{bb} - S_{ab}^2$, and $S_{\alpha\beta}$ are the long-wave limits of the partial static structure factors. In the RPA, S_{bb} and S_{ab} are given by (see Appendix C)

$$\frac{S_{bb}}{\Delta} = \left(\frac{1}{N_ap_a} + v_{aa}\right) = \frac{1}{N_ap_a} + \frac{1}{N_cp_c} - \frac{1}{k_BT}[2W_{ab} - W_{aa} - W_{cc}]$$

and

$$\frac{S_{ab}}{\Delta} = -v_{ab} = -\frac{1}{N_cp_c} - \kappa_{ab} + \kappa_{ac} + \kappa_{bc} = -\frac{1}{N_cp_c} - \frac{1}{k_BT}[W_{ab} + W_{cc} - W_{ac} - W_{bc}]$$

In the case of particles, the polymerization indices are unity. Hence with the identification $N_a \rightarrow c_{\text{A}}$, $N_c \rightarrow c_{\text{V}}$, and $\chi_{\alpha\beta} = W_{\alpha\beta}/k_BT$, the two equations, 116 and 117, become identical. We may conclude that the expression of D_{aa} given in eq 117, based on the linear response theory, has a more fundamental basis than the one derived in the Onsager formalism. In the latter formalism, the static structure factors are already calculated in the framework of the mean field theory. The linear response theory used in this work also provides microscopic definitions of the Onsager coefficients $\Lambda_{\alpha\beta}$ (allowing extensions to q- and ω-dependent Onsager coefficients), whereas, in the phenomenological theory, they are introduced as parameters.

In conclusion, the two formalisms become identical once the mean field approximation is implemented in the microscopic theory.

X. On the Extraction of D_{in} and D_{coop} from Scattering Measurements

In this section we address the following question: Is it possible to extract D_{in} and D_{coop} from the measurement of the dynamic scattering function of a labeled component, i.e., $S_{aa}(q,t)$? To answer this question we rewrite $S_{aa}(q,t)$

from eq 1, using eq 56, as

$$S_{aa}(q,t) = \frac{1}{d_+ - d_-}\{[k_B T\mu_{aa} - d_- S_{aa}(q)]e^{-q^2 d_+ t} + [d_+ S_{aa}(q) - k_B T\mu_{aa}]e^{-q^2 d_- t}\} \quad (118)$$

The measurement of $S_{aa}(q,t)$ yields d_+, d_-, and the amplitudes. Equation 118 shows that we can only determine $S_{aa}(q)$ and μ_{aa}, at a given q, from the amplitudes, in addition to d_+ and d_-. The general expressions of D_{in} and D_{coop} in eqs 41 and 48, respectively, indicate that μ_{bb}, μ_{ab}, $S_{bb}(q)$, and $S_{ab}(q)$ are also needed for the calculation of D_{in} and D_{coop}. The knowledge of d_+ and d_- is not sufficient to determine these four unknowns, although it provides two relations among them, for d_+ and d_- are the eigenvalues of $\mathbf{D}$. Hence we conclude that the interdiffusion and cooperative diffusion coefficients cannot be extracted, in general, from the measurement of only $S_{aa}(q,t)$. If, in addition, $S_{bb}(q,t)$ is also measured on the same system, one can then determine μ_{bb} and $S_{bb}(q)$ form the amplitudes of $S_{bb}(q,t)$ (the decay constants d_+ and d_- are of course the same for both $S_{aa}(q,t)$ and $S_{bb}(q,t)$), and it may be possible to calculate μ_{ab} and $S_{ab}(q)$ from the knowledge of d_+ and d_- (eq 10) and infer D_{in} and D_{coop} from these two measurements.

In some special systems, however, one experiment may be sufficient. This is the case in an incompressible binary mixture of A and B homopolymers, where $\mu_{aa} = \mu_{bb} = -\mu_{ab}$ and $S_{aa} = S_{bb} = -S_{bb}$ holds. We have shown above (see the discussions following eq 108) that $d_+ = D_c^P = D_{coop}$, $d_- = D_{in}$ where D_{in} is given explicitly in eq 95, in this system. Furthermore, eq 41 yields in this case

$$D_{in} = k_B T\frac{\mu_{aa}}{S_{aa}} \quad (119)$$

When this information is used in eq 118, one finds that the amplitude of the d_+ mode vanishes, and $S_{aa}(q,t)$ becomes

$$S_{aa}(q,t) = S_{aa}(q)e^{-q^2 D_{in} t} \quad (120)$$

as we have already pointed out.

In the framework of the RPA, we can discuss the other extreme in which the parameters N_c and D_c of the matrix component satisfy the inequality in eq 94. In this limit the mobilities in the interacting system are approximated by the mobilities in the bare system (see eqs 87 and 88) so that $\mu_{aa} \approx \mu^0{}_{aa}$, $\mu_{bb} \approx \mu^0{}_{bb}$, and $\mu_{ab} \approx 0$. Although the number of the unknowns needed for the calculation of D_{in} and D_{coop}, is reduced from six to five, a single dynamic scattering experiment on only one labeled component is still not sufficient to extract D_{in} and D_{coop} from the measured amplitudes and decay constants. If the interaction between the A and B species can be ignored so that $S_{ab}(q) \approx 0$, then the measurement of $S_{aa}(q,t)$ only would be sufficient.

XI. Summary and Conclusions

We have shown in this paper that the two exponential modes observed in dynamic scattering experiments in the diffusive regime (Markov limit) on bimodal systems (i.e., a binary solution of A and B homopolymers or an incompressible ternary mixture of A and B homopolymers in a matrix of C homopolymers) cannot in general be identified as the interdiffusion and cooperative diffusion modes. We have arrived at this conclusion by first defining the interdiffusion (D_{in}) and the cooperative diffusion (D_{coop}) coefficients for a given pair of components A and B, in the presence of other components (or solvent). In these definitions, the two diffusion coefficients are expressed in terms of the relaxation frequencies of fluctuations in the local relative concentrations and in the total number density of the monomers belonging to A and B components. Furthermore, D_{in} and D_{coop} are related in these definitions to the mobilities μ_{aa}, μ_{bb}, and μ_{ab} and the partial structure factors $S_{aa}(q)$, $S_{bb}(q)$, and $S_{ab}(q)$ associated with the components A and B. We have then compared D_{in} and D_{coop} with the decay rates q^2d_+ and q^2d_- of the two modes, where d_+ and d_- are the eigenvalues of the diffusivity matrix $\mathbf{D}$, and found that d_+ and d_- are different from D_{coop} and D_{in} in general. This was illustrated by several examples of binary suspensions of spherical particles. We have, however, obtained conditions on $\mu_{\alpha\beta}$ and $S_{\alpha\beta}$ (α, β = a, b), under which $D_{coop} = d_+$ and $D_{in} = d_-$. The physical implication of these conditions is that the chains of the components must be identical, both dynamically and statistically, in the sense that the monomers must have the same friction coefficient, the chain lengths must be the same, and the pair correlation functions associated with the center of mass positions of a–a, b–b, and a–b, monomer pairs must be equal to each other. In other words, A and B chains must differ from each other only by their labeling. In this very special case, D_{in} becomes identical with the tracer diffusion coefficient.

We have also shown that D_{in} and D_{coop} cannot be in general inferred from the measurement of a single dynamic scattering function $S_{aa}(q,t)$. In such an experiment, the two amplitudes and the two relaxation frequencies are extracted from the data, thereby providing for four relations among the six unknowns $\mu_{\alpha\beta}$ and $S_{\alpha\beta}$ that are needed to calculate D_{in} and D_{coop}. One needs therefore another experiment, in which the second component is labeled, so that $S_{bb}(q,t)$ can provide the additional information for the calculation of D_{in} and D_{coop}.

The above conclusions are not based on the RPA and are applicable to both solutions and incompressible ternary polymer mixtures. More specific results have been obtained by expressing the mobilities $\mu_{\alpha\beta}$ and partial structure factors $S_{\alpha\beta}(q)$ in terms of their counterparts in the bare system, within the framework of RPA. Among other things, a new expression for the interdiffusion coefficient of the A and B components, in the presence of a matrix of C homopolymers, has been obtained in terms of the tracer diffusion coefficients of all the three components. This result contains, as two limiting cases, the results of both the "slow mode" and "fast mode" theories, in which D_{in} is expressed in terms of the tracer diffusion coefficients of A and B polymers only. The slow mode theory is recaptured in our treatment when the matrix component is gradually removed, resulting in an incompressible binary mixture of A and B polymers. The fast mode theory on the other hand emerges in the opposite limit of large matrix concentration or in the limit of large tracer diffusivity of the matrix molecules or both. This limit may be pictured physically either as a dilute solution of A and B polymers, in which the matrix corresponds to the solvent, or as a compressible mixture of A and B polymers, in which the matrix has a very high mobility, as would be the case with vacancies, for example. If, for qualitative interpretation of these two limits, the vacancies are treated as the matrix in a ternary mixture (by certainly stretching the validity of the RPA), then one would expect a gradual transition from the fast mode theory to the slow mode theory when the vacancy concentration, or the compressibility of the mixture, is reduced.[16]

In this paper we considered only mixtures of homopolymers. A solution of A–B block copolymers, or a ternary incompressible mixture consisting of A–B block copolymers in a homopolymer matrix, requires special attention because the relative motion of the parts of the block copolymers involves the internal modes of the entire copolymer chains and cannot be treated in the Markov limit. Although the procedure described in this paper is readily applicable to the identification of the modes in such systems also, by replacing the diffusivity matrix **D** by the first cumulant matrix $\Omega(q)$ there are still some new concepts to be introduced, such as the short-time and long-time mobilities, due to the difference in the relaxation times of the internal and external motions of the chains. We therefore postpone this topic to a future publication.

Appendix A. Properties of the Matrix Q

The matrix **Q**, which diagonalizes the diffusivity matrix **D** by a similarity transformation (see eq 9), also diagonalizes the static structure matrix **S** by a congruent transformation. The proof rests on the fact that $\mathbf{DS} = k_BT\mu$ is a symmetrix matrix, i.e.

$$\mathbf{DS} = \mathbf{SD}^{\mathrm{T}} \tag{A.1}$$

We note that **S** is symmetric but **D** is not. Bracketing both sides of eq A.1 by **Q** and $\mathbf{Q}^{\mathrm{T}}$, we find

$$\mathbf{QDSQ}^{\mathrm{T}} = \mathbf{QSD}^{\mathrm{T}}\mathbf{Q}^{\mathrm{T}}$$

or

$$\mathbf{QDQ}^{-1}\mathbf{QSQ}^{\mathrm{T}} = \mathbf{QSQ}^{\mathrm{T}}[\mathbf{Q}^{\mathrm{T}}]^{-1}\mathbf{D}^{\mathrm{T}}\mathbf{Q}^{\mathrm{T}}$$

Using $\mathbf{QDQ}^{-1} = \mathbf{d}$ and $\mathbf{QSQ}^{\mathrm{T}} = \mathbf{s}$ we arrive at

$$\mathbf{ds} = \mathbf{sd} \tag{A.2}$$

in which **d** is diagonal. In component form, eq A.2 reads $d_is_{ij} = s_{ij}d_j$, which proves that $s_{ij} = 0$ when $i \neq j$, provided that $d_i \neq d_j$, i.e., provided that the eigenvalues d_j are all distinct. The diagonal elements s_j are all positive for $\mathbf{QSQ}^{\mathrm{T}} = \mathbf{s}$ implies, with the usual sum convention, $Q_{ij}S_{jk}Q_{ik} = s_i$ and the static structure matrix **S** is positive definite. The latter property is expressed as $\tilde{y}^{\dagger}\mathbf{S}\tilde{y} > 0$ for any arbitrary column matrix $\tilde{y}$ with complex elements y_k, provided $\tilde{y} \neq 0$. Identifying y_k as Q_{ik} ($k = 1, 2, ..., n$), for each index i characterizing s_i, we arrive at $s_i > 0$. The positive definiteness of $\mathbf{S}(q) = \langle\vec{\rho}(\vec{q})\vec{\rho}^{\dagger}(\vec{q})\rangle$ follows from $\tilde{y}^{\dagger}\mathbf{S}(q)\tilde{y} = \langle|\tilde{y}^{\dagger}\vec{\rho}(\vec{q})|^2\rangle$. The right-hand side is always positive provided all the elements $\rho_j(\vec{q})$ of $\vec{\rho}(\vec{q})$ are finite. This is indeed the case because the $\rho_j(\vec{q})$s denote the number densities of the components, which are relevant to the physical problem.

In order to discuss the nature of the eigenvalues d_i of the diffusivity matrix **D**, we express **D** as (see eq 39) $\mathbf{D} = \Lambda\mathbf{S}^{-1}$ where the elements of Λ are the Onsager coefficients. It is $\Lambda = k_BT\mu$, where μ is the mobility matrix. We now have two real and symmetric $n \times n$ matrices Λ and **S**, and **S** is also positive definite and therefore nonsingular. According to a theorem in matrix algebra,[32] there is a nonsingular real square matrix **R** such that

$$\mathbf{RSR}^{\mathrm{T}} = \mathbf{I}$$

$$\mathbf{R}\Lambda\mathbf{R}^{\mathrm{T}} = \mathbf{d}$$

where $\vec{d} = \mathrm{diag}\,(d_1, ..., d_n)$ and **I** denotes the identity matrix. The diagonal elements d_j are the roots of the determinant equation $|\mathbf{dS} - \Lambda| = 0$. The latter can be written as $|\mathbf{dI} - \mathbf{D}||\mathbf{S}| = 0$. Since **S** is nonsingular it follows that $|\mathbf{dI} - \mathbf{D}| = 0$. Hence the d_js, $j = 1, 2, ..., n$ are also the eigenvalues of **D**. We see that the d_j are all positive provided that the mobility matrix μ is positive definite (see the proof of $s_i > 0$ given above). The symmetry of μ is a consequence of the self-adjointness of the time-evolution operator $\mathcal{L}$ introduced in eq 7, where the scalar product of two arbitrary dynamical variables A and B is taken to be the equilibrium average of the product AB^*. The modified operator $(1 - P)\mathcal{L}$, which determines the time evolution of the Langevin force $\vec{f}(\vec{q},t)$, is also self-adjoint in the complementary space of functions A satisfying $PA = 0$. The reality of the elements of μ, as well as those of the static structure matrix **S**, is a consequence of the symmetry of the mixture, i.e., of the fact that the equilibrium distribution $\psi_{\mathrm{eq}}(\vec{R}_{ij})$ of the vector distance $\vec{R}_{ij}$ between a pair of monomers depends only on $|\vec{R}_{ij}|$. The positive definiteness of μ, however, depends on the properties of the operator $\mathcal{L}$. For example, if the memory function in eq 4 is ignored, Λ is equal to the short-wave limit of $\langle\vec{\rho}(\vec{q})\mathcal{L}\vec{\rho}(\vec{q})^{\dagger}\rangle$, which is a common approximation often introduced in the explicit calculations of Λ or μ. In this case, the positive definiteness of Λ immediately follows from the positive definiteness of the Kirkwood diffusion operator $\mathcal{L}$, used in the description of the dynamics of polymer solutions, as proven by Doi and Edwards.[33] It may be possible to prove the positive definiteness of Λ also in the presence of the memory matrix in eq 4, by using the properties of the modified operator $(1 - P)\mathcal{L}$ in the complementary space. Since it is not directly relevant to the main point we want to make in this paper, we do not attempt to give here this proof. Instead, we simply assume that μ is positive definite on physical grounds, for the system is overdamped.

Appendix B. Derivation of Equation 44

The derivation can be presented quite generally for any density function $\rho(\vec{q})$ satisfying the continuity equation

$$\dot{\rho}(\vec{q},t) = iqJ(\vec{q},t) \tag{B.1}$$

where $J(\vec{q},t)$ is the longitudinal component of the current $\vec{J}(\vec{q},t)$ associated with $\rho(\vec{q},t)$ and the dot denotes differentiation with respect to time t. We are interested in the correlation function of $J(\vec{q},t)$ in the long-wave limit:

$$\begin{aligned}\langle J(t)J^*(0)\rangle &= \lim_{q\to0}\frac{1}{q^2}\langle\dot{\rho}(\vec{q},t)\dot{\rho}^*(\vec{q},0)\rangle \\ &= -\lim_{q\to0}\frac{1}{q^2}\frac{\partial^2S(q,t)}{\partial t^2}\end{aligned} \tag{B.2}$$

where $S(q,t) \equiv \langle\rho(\vec{q},t)\rho^*(\vec{q},0)\rangle$ and where we have used the property that for any dynamic variable

$$\langle\dot{A}(t)\dot{A}(0)\rangle = -\frac{\partial^2}{\partial t^2}\langle A(t)A(0)\rangle$$

The time integral of eq B.2 is

$$\int_0^t\mathrm{d}u\,\langle J(u)J^*(0)\rangle = -\lim_{q\to0}\frac{1}{q^2}\frac{\partial}{\partial t}S(q,t) \tag{B.3}$$

where

$$\frac{\partial S(q,t)}{\partial t}\Big|_{t=0} = 0$$

has been used. This is a consequence of the time reversibility, i.e., $\langle A(t)A(0)\rangle = \langle A(-t)A(0)\rangle$ for any dynamical variable obeying the Liouville equation. Hence, the long-time limit of eq B.3 is

$$\int_0^{\infty}\mathrm{d}u\,\langle J(u)J^*(0)\rangle = -\lim_{t\to\infty}\lim_{q\to0}\frac{1}{q^2}\frac{\partial S(q,t)}{\partial t} \tag{B.4}$$

which is used in eq 44. The right-hand side can be expressed in the Laplace domain as

$$-\lim_{z\to 0}\lim_{q\to 0}\frac{z}{q^2}[zS(q,z)-S(q)]$$

By introducing the q- and z-dependent diffusivity function $D(q,z)$ through

$$S(q,z)=\frac{S(q)}{z+q^2D(q,z)}$$

we find

$$\int_0^\infty \mathrm{d}u\ \langle J(u)J^*(0)\rangle=\lim_{z\to 0}\lim_{q\to 0}\left[\frac{zD(q,z)}{z+q^2D(q,z)}S(q)\right]$$
$$=D(q\to 0,z\to 0)S(q\to 0)$$

Appendix C. Results of the RPA in Multicomponent Mixtures

We summarize the results of the RPA for the calculation of the mobilities and the partial static structure factors in a mixture of polymers with an arbitrary number of components. These results have been obtained recently by Akcasu and Tombakoglu:[11] The RPA results for the mobilities are

$$\frac{1}{\mu_{aa}}=\frac{1}{\mu^0_{aa}}+\frac{1}{\mu^0_{bb}+\mu^0_{cc}+\mu^0_{dd}+\ldots}\tag{C.1}$$

$$\frac{1}{\mu_{ab}}=-\left[\frac{1}{\mu^0_{aa}}+\frac{1}{\mu^0_{bb}}+\frac{\mu^0_{cc}+\mu^0_{dd}+\ldots}{\mu^0_{aa}\mu^0_{bb}}\right]\tag{C.2}$$

The mobilities μ^0_{jj} in the bare system, i.e., a system of noninteracting chains without an incompressibility constraint, are given by

$$\mu^0_{jj}=\frac{N_j}{\xi_j},\quad \mu^0_{jk}=0\quad (j\neq k)\tag{C.3}$$

provided that the single-chain dynamics in the mixture is approximated by the Rouse dynamics. In eq C.3, N_j denotes the total number of the monomers belonging to the jth component, and ξ_j is the friction coefficient per monomer in the mixture. The latter is related to the tracer diffusion coefficient of a jth molecule by

$$D^{\mathrm{P}}_j=\frac{k_{\mathrm{B}}T}{\xi_jp_j}\tag{C.4}$$

where p_j is the index of polymerization. A remark about the normalization of the mobilities in eq C.3 is in order here. Since the physical relaxation frequencies involve the ratio of the mobilities to the static structure factors, one is free to choose their normalizations as long as they are consistent. The particular normalization used in eq C.3, which makes μ^0_{jj} an extensive quantity, is consistent with the normalization used in eq C.6 for $S^0_{jj}(q)$. Its choice is only for mathematical convenience. The RPA result for the static structure factor matrix is[34]

$$\frac{1}{\mathbf{S}(q)}=\frac{1}{\mathbf{S}^0(q)}+\mathbf{v}(q)\tag{C.5}$$

where the S^0_{jk} are the partial static structure factors involving a pair of chains belonging to the components j and k, respectively. If the pair of chains involves homopolymers, $S^0_{jk}(q)=0$ for $j\neq k$ and

$$S^0_{jj}(q)=N_jp_jP_{\mathrm{D}}((qR_{Gj})^2)\tag{C.6}$$

where $P_{\mathrm{D}}((qR_{Gj})^2)$ is the Debye function. The elements of the excluded volume matrix $\mathbf{v}(q)$ are given by

$$v_{jj}(q)=\frac{1}{S^0_{cc}(q)}-2\kappa_{jc}\quad (j\neq c)\tag{C.7}$$

$$v_{jk}(q)=\frac{1}{S^0_{cc}(q)}+\kappa_{jk}-\kappa_{jc}-\kappa_{kc}\quad (j\neq k\neq c)\tag{C.8}$$

$$\kappa_{ab}=\frac{1}{Vk_{\mathrm{B}}T}\left[W_{ab}(q)-\frac{1}{2}(W_{aa}(q)+W_{bb}(q))\right]$$
$$\text{(for any pair “}a\text{” and “}b\text{”)}\tag{C.9}$$

In these equations, the component "c" consists of homopolymers and is singled out as the "matrix" in the mixture. Hence the components of $\mathbf{S}(q)$ and $\mathbf{S}^0(q)$ in eq C.5 do not include the c component. Equation C.5 is an $(n-1)\times(n-1)$ matrix equation in a mixture of n components, because the matrix has been eliminated by using the incompressibility constraint. The Flory parameters κ_{ab} are related to the Fourier transforms $W_{ab}(q)$ of the pair interaction potential $W_{ab}(r)$ per monomer for a pair of a and b monomers. Due to the Fourier transform, $W_{ab}(q)$ has units of energy × volume, so that κ_{ab} is dimensionless. In eq C.8, $S^0_{cc}(q)$ is normalized such that $S^0_{cc}(q=0)=N_cp_c$, and hence the excluded volume parameters $v_{jk}(q)$ are also dimensionless. Finally, in the derivation of eqs C.8 and C.9, the segmental volumes are taken to be the same for all species (see the Appendix of ref 11).

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