to occur suddenly at an n_K of about 50.[3,11] Thus, we find that the subtle difference in crossover behavior has led to the above-mentioned considerable difference in n_{Kc} between the two polymers.

In conclusion, the combination of the YS theory and the DB equation accurately describes the dimensional behavior of flexible PIDP in NMP over a wide range of molecular weight. This combined theory seems to lack something important only for stiff chains, since it fails to explain the crossover behavior of PHIC, a typical stiff polymer, in hexane.

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Dynamics of Copolymer and Homopolymer Mixtures in Bulk and in Solution via the Random Phase Approximation[†]

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ABSTRACT: The dynamics of copolymer and homopolymer mixtures with an arbitrary number of components both in bulk and in solution is studied within the framework of the mean field theory, and an expression of the first cumulant of the dynamic scattering function of a labeled component is obtained in terms of the static and dynamic single-chain properties and the Flory interaction parameters. In particular, a new result is obtained to relate the mobility of the labeled chain to the mobilities of the other components, treating one of the homopolymer species as the "matrix" and using incompressibility. The case of polymers in solution is studied as a special case by treating the solvent as the matrix. The new results differ from the reported theoretical results for binary homopolymer and copolymer solutions, as well as copolymers in a homopolymer matrix. The origin of this discrepancy is explained.

Introduction

In this paper we formulate the dynamic random-phase approximation[1] (or the mean field theory) in matrix form so that it can readily be applied to mixtures of homopolymers and copolymers with an arbitrary number of components both in bulk and in solution and comment on its relation to the formulation based on the Zwanzig–Mori[2] projection operator technique. The work presented in this paper is an extension of our earlier work on the same topic in which we considered only binary polymer blends and copolymer melts.[3] Specifically, we calculate the dynamic scattering function of a labeled polymer species in the presence of others, treating one of the homopolymer component as the "matrix". We obtain the expression for the first cumulant and the relaxation frequencies of various modes in terms of the dynamic and static properties of a single chain and the Flory κ parameters. The results are extended to polymers in solution by treating the solvent as the matrix in the general formulation. When specialized to the case of binary homopolymer and copolymer solutions, our results differ from those reported earlier by Benmouna et al.[4,5] in the calculation of the mobilities and relaxation frequencies.

[†] Dedicated to Professor Walther Burchard on the occasion of his sixtieth birthday.

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Dynamic Mean Field Approximation

We consider a mixture of copolymers and homopolymers of different species. We refer to a species belonging to identical polymers as a "component". Homopolymers of a given species with different molecular weights are identified as different components. The species in identical copolymers are also identified as different components. For example, a mixture of AB copolymers in a matrix of A homopolymers is considered to be as a mixture of three components a, b, and c. The number density of the monomers in the jth component at a point $\mathbf{r}$ is denoted by $\rho_j(\mathbf{r})$. Let H be the Hamiltonian of the system and let $\mathbf{U}(\mathbf{r},t)$ denote an external time-dependent potential, which is coupled to the density of monomers, so that the total perturbation potential is given by

$$V(t) = \int \mathrm{d}\mathbf{r}\, \rho^{\dagger}(\mathbf{r})\mathbf{U}(\mathbf{r},t)$$

where $\rho(\mathbf{r}) = \mathrm{col}\,[\rho_1(\mathbf{r}), ..., \rho_j(\mathbf{r}), ...\, \rho_n(\mathbf{r})]$ and $\rho^{\dagger}(\mathbf{r})$ is the hermitian conjugate of $\rho(\mathbf{r})$. In the linear response theory,[6] the Fourier–Laplace transform of the time-dependent mean incremental density response to $\mathbf{U}(\mathbf{r},t)$ is expressed as

$$\delta\bar{\rho}(\mathbf{q},s) = -\chi(q,s)\mathbf{U}(\mathbf{q},s) \tag{1}$$

where $\chi(q,s)$ is the dynamic response matrix. The mean of the density is calculated with the time-dependent phase space distribution function in the perturbed system, which is characterized by the Hamiltonian $H + V(t)$. The time dependence of $\chi(q,s)$ and the equilibrium averages of the dynamical variables in the system are determined by using H in the Liouville equation.

Suppose the Hamiltonian H is split into two parts as $H = H_0 + H'$, where H' denotes the part of the Hamiltonian that we treat as perturbation. The response matrix in the unperturbed system is denoted by $\chi^0(q,s)$, which will henceforth be referred to as the "bare" response function, to distinguish it from the response function $\chi(q,s)$ in the original system with interaction H'. The time dependence of $\chi^0(q,s)$ and the equilibrium averages of the dynamical variables in the bare system are computed with H_0. We assume that H' can be written as

$$H' = \int \mathrm{d}\mathbf{r}\, \rho^{\dagger}(\mathbf{r}) \int \mathrm{d}\mathbf{r}'\, \mathbf{W}(\mathbf{r}' - \mathbf{r})\rho(\mathbf{r}') \tag{2}$$

where $W_{\mathrm{ab}}(r)$ denote the interaction potential per particle, or part of it, of a pair of "a" and "b" particles or monomers. In the mean field approximation, $\rho(\mathbf{r}')$ in eq 2 is replaced by its time-dependent mean $\bar{\rho}(\mathbf{r}')$, where the average is performed with the time-dependent perturbed distribution function that evolves in time according to the Liouville equation with $H_0 + H' + V(t)$. Treating

$$\mathbf{U}(\mathbf{r},t) + \int \mathrm{d}\mathbf{r}'\, \mathbf{W}(\mathbf{r}' - \mathbf{r})\bar{\rho}(\mathbf{r}') \tag{3}$$

as an external perturbation in the bare system characterized by H_0 and using the linear response theory,[6] we obtain from eq 1

$$\delta\bar{\rho}(\mathbf{q},s) = -\chi^0(q,s)[\mathbf{U}(\mathbf{q},s) + \mathbf{W}(\mathbf{q})\delta\bar{\rho}(\mathbf{q},s)] \tag{4}$$

The definition of the bare system and interaction matrix depends on the way we break up the Hamiltonian as an unperturbed part H_0 and a perturbation H'. Different choices of H_0 and H' lead to different bare response functions $\chi^0(q,s)$ and different interaction matrices $\mathbf{W}(\mathbf{q})$. However, the choice is interdepedent, since the choice of H_0 determines $\mathbf{W}(\mathbf{q})$ uniquely. The accuracy of the mean field approximation would improve by including as much information in H_0 as one can handle analytically. A convenient choice of H_0, which is often used in the applications because of its simplicity, is the one in which the dynamics of the bare system can be described by single-chain dynamics. In this case, H_0 contains only the chain connectivity. Although the dynamics and the equilibrium properties of the bare system are completely described by H_0, one may determine $\chi^0(q,s)$ approximately by, for example, using the Kirkwood–Riseman diffusion[7] equation rather than using the full Liouville description when the polymer mixtures is in solution. The point is that the mean field theory offers more flexibility than the way it has been used in the literature. For example, incompressibility is not an essential feature of the theory even though it has invariably been assumed in the applications.

The incompressibility constraint is included in the mean field theory[8] by introducing a fictitious external potential $u(\mathbf{r},t)$, which is coupled to all the monomers irrespective of their kind. The total potential energy associated with this interaction can then be written as

$$\int \mathrm{d}\mathbf{r}\, \rho(\mathbf{r})u(\mathbf{r},t)$$

where $\rho(\mathbf{r})$ is the total number density, i.e., $\rho(\mathbf{r}) = \rho^{\mathrm{T}}(\mathbf{r})\mathbf{E}$. Here $\mathbf{E}$ is a column matrix with elements "1". The potential $u(\mathbf{r},t)$ is to be determined such that the perturbed average of the total density will be zero (incompressibility). Again, treating $u(\mathbf{r},t)$ as an external potential we obtain

$$\delta\bar{\rho}(\mathbf{q},s) = -\chi^0(q,s)[\mathbf{U}(\mathbf{q},s) + u(\mathbf{q},s)\mathbf{E} + \mathbf{W}(\mathbf{q})\delta\bar{\rho}(\mathbf{q},s)] \tag{5}$$

subject to the boundary condition

$$\mathbf{E}^{\mathrm{T}}\delta\bar{\rho}(\mathbf{q},s) = 0$$

Here we assume for simplicity that the segment volumes of various species are the same (see the Appendix). Although it is possible to eliminate $u(\mathbf{q},s)$ and one of the components in the mixture by using this boundary condition in eq 5 as it is, we proceed assuming that the component to be eliminated, which we label as "c", is not coupled in the bare system to the other components; i.e., $\chi^0(q,s)_{\mathrm{cj}} = 0$ for $\mathrm{j} \neq \mathrm{c}$. This assumption necessarily implies that the component c consists of homopolymers. The results in this case are more readily interpretable and consistent with the conventional thermodynamic considerations. From eq 5 we obtain

$$\delta\bar{\rho}_{\mathrm{c}}(\mathbf{q},s) = -\chi^0(q,s)_{\mathrm{cc}}[U_{\mathrm{c}}(\mathbf{q},s) + u(\mathbf{q},s) + W_{\mathrm{cj}}(\mathbf{q})\delta\bar{\rho}_{\mathrm{j}}(\mathbf{q},s)] \tag{6}$$

First separating the term j = c in the summation over j in this equation, then solving it for $u(\mathbf{q},s)$, and substituting the latter into eq 5, one obtains

$$\delta\bar{\rho}(\mathbf{q},s) = -\chi^0(q,s)[\mathbf{U}(\mathbf{q},s)+k_{\mathrm{B}}T\mathbf{v}(q,s)\delta\bar{\rho}(\mathbf{q},s)] \tag{7}$$

where we have introduced the excluded volume parameters in a matrix form $\mathbf{v}(q,s)$, the component of which are

$$v_{\mathrm{aa}}(q,s) = \frac{\beta}{\chi^0{}_{\mathrm{cc}}(q,s)} - 2\kappa_{\mathrm{ac}}(q)$$

$$v_{\mathrm{ab}}(q,s) = \kappa_{\mathrm{ab}}(q) - \kappa_{\mathrm{ac}}(q) - \kappa_{\mathrm{bc}}(q) + \frac{\beta}{\chi^0{}_{\mathrm{cc}}(q,s)}$$

$$\kappa_{\mathrm{ab}}(q) = \beta\{W_{\mathrm{ab}}(q) - {}^1/{}_2[W_{\mathrm{aa}}(q) + W_{\mathrm{bb}}(q)]\} \tag{8}$$

In these equations $\kappa_{\mathrm{ab}}(q)$ are the usual Flory interaction parameters. It is noted that the dimension of the matrices in eq 7 is one less than the dimension of those in eq 5. Also, we observe that the s dependence of the excluded parameters $v_{\mathrm{ab}}(\mathbf{q},s)$ stems from the bare response function $\chi^0{}_{\mathrm{cc}}(q,s)$ of the component c, which is commonly the component forming the invisible matrix. Equation 7 can be solved for $\delta\rho(\mathbf{q},s)$ in the form of the eq 1 to obtain the response function in the interacting system as

$$\chi(q,s) \approx [\mathbf{I} + k_{\mathrm{B}}T\chi^0(q,s)\mathbf{v}(q,s)]^{-1}\chi^0(q,s) \qquad (9)$$

Equation 9 represents the basic equation of the mean field theory, in the sense that it expresses the dynamic response matrix $\chi(q,s)$ of interacting system in terms of the bare dynamic response matrix $\chi^0(q,s)$ and the excluded volume matrix $\mathbf{v}(q,s)$. The static response matrix $\chi(q) \equiv \chi(q,s{=}0)$ is also given by this equation in terms of the bare static response matrix $\chi^0(q)$ and $\mathbf{v}(q) \equiv \mathbf{v}(q,s{=}0)$ as discussed by Benoit et al.[9,10]

Calculation of the Scattering Functions

The remaining task in the application of the mean field theory for the interpretation of dynamic or static scattering experiments is to express the response matrices in terms of density correlation functions $\mathbf{S}(q,t) = \langle \delta\rho(\mathbf{q},t) \times \delta\rho^{\dagger}(\mathbf{q},0)\rangle$. The linear response theory[6] provides the desired relationship between them. For the static response function $\chi(q) = \chi(q,s{=}0)$, it yields

$$\chi(q) = (\beta/V)\mathbf{S}(q) \qquad (10)$$

where $\beta = 1/k_{\mathrm{B}}T$ and V is the volume of the system, which we set at $V = 1$ from now on, and where $\mathbf{S}(q) = \mathbf{S}(q,t{=}0)$ is the static scattering function. The same relationship holds also between $\chi^0(q)$ and $\mathbf{S}^0(q)$ in the bare system. Substitution of eq 10 into eq 9 leads to the well-known result due to Zimm[11] in matrix form

$$\mathbf{S}(q)^{-1} \approx \mathbf{S}^0(q)^{-1} + \mathbf{v}(q) \qquad (11)$$

The measured intensity $I(q)$ in a scattering experiment can easily be obtained by introducing a column vector $\mathbf{a}$ whose components denote the excess scattering powers of the different species in the mixture (see the Appendix), as

$$I(q) \approx \mathbf{a}^{\mathrm{T}}[\mathbf{S}^0(q)^{-1} + \mathbf{v}(q)]^{-1}\mathbf{a} \qquad (12)$$

Explicit forms of $I(q)$ for different combinations of homopolymer and copolymer mixtures both in bulk and in solution have been worked out by Benoit et al.[9,10]

The relationship between the dynamic response matrix $\chi(q,t)$ and the dynamic scattering matrix $\mathbf{S}(q,t)$ is more complicated:[6]

$$\chi(q,t) = -\beta\, \mathrm{d}\mathbf{S}(q,t)/\mathrm{d}t \qquad (13)$$

The same relation holds also between $\chi^0(q,t)$ and $\mathbf{S}^0(q,t)$. It proves more convenient[3] to introduce a frequency and q-dependent diffusion coefficient $\mathbf{D}(q,s)$ through the Laplace transform of $\mathbf{S}(q,t)$ as

$$\mathbf{S}(q,s) = [\mathbf{I}s + q^2\mathbf{D}(q,s)]^{-1}\mathbf{S}(q) \qquad (14)$$

In the Markov limit of $s \to 0$, $q \to 0$ with q^2/s = constant, $\mathbf{D}(q,s)$ reduces to the long-time diffusion matrix $\mathbf{D} = \mathbf{D}(0,0)$, and $\mathbf{S}(q,t)$ becomes $\mathbf{S}(q,t) = \exp(-q^2\mathbf{D}t) \times \mathbf{S}(0)$, i.e., the sum of exponentials with exponents determined[12] by the eigenvalues of $\mathbf{D}$. In general, $\mathbf{S}(q,t)$ is not an exponential function of time when $\mathbf{D}(q,s)$ depends on s. Using eq 14 in the Laplace transform of eq 13 yields

$$\chi(q,s) = \beta q^2\mathbf{D}(q,s)[\mathbf{I}s + q^2\mathbf{D}(q,s)]^{-1}\mathbf{S}(q) \qquad (15)$$

The same relationship holds also between $\chi^0(q,s)$, $\mathbf{D}^0(q,s)$, and $\mathbf{S}^0(q)$ in the bare system. Substituting these expressions of $\chi(q,s)$ and $\chi^0(q,s)$ into eq 9 yields one of the main contributions of this paper:

$$\mathbf{S}(q)^{-1}\mathbf{D}(q,s)^{-1} \approx \mathbf{S}^0(q)^{-1}\mathbf{D}^0(q,s)^{-1} + q^2\mathbf{v}'(q,s) \qquad (16)$$

or

$$\mathbf{D}(q,s) \approx [\mathbf{I} + q^2\mathbf{D}^0(q,s)\mathbf{S}^0(q)\mathbf{v}'(q,s)]^{-1}\mathbf{D}^0(q,s)[\mathbf{I} + \mathbf{S}^0(q)\mathbf{v}(q)] \qquad (17)$$

where we have introduced

$$\mathbf{v}'(q,s) = [\mathbf{v}(q,s) - \mathbf{v}(q)]/s \qquad (18a)$$

which can be calculated by using eq 8 as

$$\mathbf{v}'(q,s) = (\beta/s)[\chi^0{}_{\mathrm{cc}}(q,s)^{-1} - \chi^0{}_{\mathrm{cc}}(q,s{=}0)^{-1}]\mathbf{E}\mathbf{E}^{\mathrm{T}} \qquad (18b)$$

where $\mathbf{E}\mathbf{E}^{\mathrm{T}}$ is a square matrix with elements that are all equal to unity. A special case of eq 17 was presented earlier in a study of the dynamics of copolymer melts.[3] The Laplace transform of the dynamic scattering function of the interacting system follows from eq 14 by substituting $q^2\mathbf{D}(q,s)$ from eq 17. In principle the dynamic scattering function $\mathbf{S}(q,t)$ can be calculated in the time domain for all times if one knows, or models, the bare dynamic structure function $\mathbf{S}^0(q,t)$ and the excluded volume parameters represented by $\mathbf{v}(q,s)$. In cases when such detailed description is not feasible, one can still extract certain aspects of $\mathbf{S}(q,t)$ from the measurement and try to interpret it theoretically.[3] The first cumulant or the initial slope of $\mathbf{S}(q,t)$, defined by

$$\Omega(q) = -\lim\, \mathrm{d}\mathbf{S}(q,t)\mathbf{S}(q)^{-1}/\mathrm{d}t, \quad \text{as } t \to 0 \qquad (19)$$

has been customarily used for this purpose. Either using eq 19 directly or using $\Omega(q) = k_{\mathrm{B}}T\chi(q,t{\to}0)\mathbf{S}(q)^{-1}$, which follows from eq 13 and 19, one finds $\Omega(q) = q^2\mathbf{D}(q,\infty)$. Using this result in eq 17 yields

$$\Omega(q) \approx [\mathbf{I} + \Omega^0(q)\mathbf{S}^0(q)\mathbf{v}'(q,\infty)]^{-1}\Omega^0(q)[\mathbf{I} + \mathbf{S}^0(q)\mathbf{v}(q)] \qquad (20)$$

where $\Omega^0(q) = q^2\mathbf{D}^0(q,\infty)$ is the bare first cumulant defined by eq 19 with $\mathbf{S}^0(q,t)$. It is more convenient to work with mobilities rather than first cumulants, which are related to each other by $\mathbf{m}(q) = \beta\Omega(q)\mathbf{S}(q)/q^2$. From eq 20 and 11 we obtain

$$\mathbf{m}(q)^{-1} \approx \mathbf{m}^0(q)^{-1} + (q^2/\beta)\mathbf{v}'(q,\infty) \qquad (21)$$

where $\mathbf{v}'(q,\infty)$ can be calculated from eq 18b, using $\lim s\chi^0{}_{\mathrm{cc}}(q,s) = q^2m^0{}_{\mathrm{cc}}(q)$ as $s \to \infty$, as

$$\mathbf{v}'(q,s{\to}\infty) = \frac{\beta}{q^2}\frac{1}{m^0{}_{\mathrm{cc}}(q)}\mathbf{E}\mathbf{E}^{\mathrm{T}} \qquad (22)$$

In this equation, $m^0{}_{\mathrm{cc}}(q)$ denotes the mobility of the c component in the mixture, which is eliminated by using incompressibility. Substitution of eq 22 into eq 21 yields

$$\mathbf{m}(q)^{-1} \approx \mathbf{m}^0(q)^{-1} + [1/m^0{}_{\mathrm{cc}}(q)]\mathbf{E}\mathbf{E}^{\mathrm{T}} \qquad (23)$$

Inverting the right-hand side of eq 23 using the Sherman–Adams formula,[13] we obtain the main theoretical contribution of this paper:

$$\mathbf{m}(q) \approx \mathbf{m}^0(q) - \frac{\mathbf{m}^0(q)\mathbf{E}\mathbf{E}^{\mathrm{T}}\mathbf{m}^0(q)}{m^0{}_{\mathrm{cc}}(q) + \mathbf{E}^{\mathrm{T}}\mathbf{m}^0(q)\mathbf{E}} \qquad (24)$$

The novel feature of this equation is the presence of the second term, which seems to be missed in earlier attempts to extend the mean field theory to multicomponent mixtures in solution.[4,5] It is easier to first compute $\mathbf{m}(q)$

with eq 24 and then calculate the first cumulant $\Omega(q)$ by using $\Omega(q) = q^2\mathbf{m}(q)\mathbf{S}(q)^{-1}/\beta$ in which $\mathbf{S}(q)^{-1}$ is calculated with eq 11 than obtaining $\Omega(q)$ directly from eq 20. The calculation of $m^0{}_{cc}(q)$ and $\mathbf{m}^0(q)$ in the case of Rouse dynamics will be presented below.

Connection with the Langevin Equation Method

We now discuss the connection between the mean field theory and the generalized Langevin equation method based on Zwanzig–Mori projection operator technique.[2] In the latter approach, $\mathbf{D}(q,s)$ is given by[14]

$$q^2\mathbf{D}(q,s) = \Omega(q) - \mathbf{\Phi}(q,s) \qquad (25)$$

when the Kirkwood–Riseman diffusion operator is adopted to describe the dynamics of the interacting system. (The full Liouville operator can also be used for this purpose.) In eq 25, $\Omega(q)$ denotes the frequency matrix and is defined by[15]

$$\Omega(q) = \langle \delta\rho(\mathbf{q})L\delta\rho^{\dagger}(\mathbf{q})\rangle \mathbf{S}(q)^{-1}$$

The $\langle\cdots\rangle$ in this equation denotes the average with the equilibrium distribution Ψ_{eq}, and L denotes the adjoint of the Kirkwood–Riseman diffusion operator in the interacting system.[14,15] The explicit form of the memory matrix $\mathbf{\Phi}(q,t)$, which can be found elsewhere,[15,16] is not needed for our discussions. A comparison of eq 25 with eq 17 indicates that the mean field theory provides an approximate expression for $[\Omega(q) - \mathbf{\Phi}(q,s)]$ as a whole, which is easier to work with than the exact statistical mechanical definitions of $\Omega(q)$ and $\mathbf{\Phi}(q,s)$ in terms of the projection operators. Similarly, the mobility of the interaction system $\mathbf{m}(q) = \beta\langle\delta\rho(\mathbf{q})L\delta\rho^{\dagger}(\mathbf{q})\rangle/q^2$ is expressed approximately in eq 24 in terms of the mobility of the bare system $\mathbf{m}^0(q)$ and the mobility $m^0{}_{cc}(q)$ of the matrix. The dynamics of the bare system, also, can be described by the generalized Langevin equation by choosing an equilibrium distribution $\Psi^0{}_{eq}$, and an appropriate dynamical operator L^0, consistent with the choise of $\Psi^0{}_{eq}$, e.g., the adjoint of the Kirkwood–Riseman diffusion operator with $\Psi^0{}_{eq}$. Then, $\mathbf{D}^0(q,s)$ also can be written as $q^2\mathbf{D}^0(q,s) = \Omega^0(q) - \mathbf{\Phi}^0(q,s)$, where

$$\Omega^0(q) = \langle\delta\rho(\mathbf{q})L^0\delta\rho^{\dagger}(\mathbf{q})\rangle\mathbf{S}^0(q)^{-1} \qquad (26)$$

from which the mobility follows as

$$\mathbf{m}^0(q) = \beta\langle\delta\rho(\mathbf{q})L^0\delta\rho^{\dagger}(\mathbf{q})\rangle/q^2 \qquad (27)$$

The averages in the bare system are calculated with respect to $\Psi^0{}_{eq}$. Equation 27 yields the bare mobilities explicitly once L^0 is chosen.

Summary and Conclusions

(a) In the absence of hydrodynamic interactions (Rouse dynamics) $\mathbf{m}^0(q)$ follows from eq 27 as Diag $[n_jN_j/\xi_{j,j=1,2,...}]$, where n_j is the number of chains per unit volume, ξ_j is the friction coefficient per monomer, and N_j is the number of monomers per chain of type j. $m^0{}_{ab} = 0$ even when the components a and b constitute the two species in a copolymer when Rouse dynamics is used in eq 27. The mobility of the matrix $m^0{}_{cc} = n_cN_c/\xi_c$. The mobility $\mathbf{m}(q)$ of the interacting system follows from eq 24 as

$$m_{ij} \approx m^0{}_{ij}\delta_{ij} - \frac{m^0{}_{ii}m^0{}_{jj}}{m^0{}_{cc} + \sum_k^{n-1} m^0{}_{kk}} \qquad (28)$$

where $i, j = 1, 2, ..., n - 1$. It is noted $\mathbf{m}(q)$ is not diagonal even though $\mathbf{m}^0(q)$ is. The bulk limit follows from eq 28 with $m^0{}_{cc} = 0$. In the case of a melt of homopolymer species A and B, one obtains $m_{aa} = m_{bb} = -m_{ab}$, as must be true in an incompressible mixture, and the usual inverse superposition of mobilities:[17]

$$\frac{1}{m_{aa}} = \frac{1}{m^0{}_{aa}} + \frac{1}{m^0{}_{bb}} \qquad (29)$$

This results was also obtained by Akcasu et al.[3] in the study of the dynamics of binary homopolymer melts and copolymer melts. Equation 28 provides a generalization of this result to a multicomponent mixture in a matrix.

(b) The previous results can also be used when the polymers are in solution, by chosing the component c as the solvent and interpreting $\chi^0{}_{ss}(q)$ appropriately. For this purpose one treats the solvent "particles" as noninteracting "fictitious monomers", as is done in lattice models, with the same volume as that of the monomers of the chains. The static response function $\chi^0{}_{ss}(q)$ is obtained from eq 4 as βn_s, where n_s is the density of the solvent, because for noninteracting point particle $S^0{}_{ss}(q) = N_s$ where N_s is the total number of solvent particles. Benoit et al.[9,10] have calculated the static structure factor in homopolymer mixtures in solution, as well as copolymers in solution, using this identification, and showed that the bulk limit is correctly reproduced when the density n_s of the solvent is set equal to zero. The calculation of the dynamic response function $\chi^0{}_{ss}(q,s)$, however, requires closer attention. Using eq 13 and $S^0{}_{ss}(q,t) = N_s \exp(-q^2D_st)$ in it, which is the dynamic scattering function of the noninteracting solvent particles with a diffusion coefficient D_s, one obtains the response function of the solvent as $\chi^0{}_{ss}(q,s) = \beta n_s q^2 D_s/(s + q^2D_s)$ and its mobility as $m^0{}_{ss} = \beta n_s D_s$. Then, eq 28 becomes

$$m_{ab} \approx m^0{}_{ab}\delta_{ab} - \frac{m^0{}_{aa}m^0{}_{bb}}{\beta n_s D_s + \sum_j m^0{}_{jj}} \qquad (30)$$

The second term in this equation is missed in the study of the dynamics of binary homopolymer and copolymer solutions by Benmouna et al.[4,5] One may of course argue that the diffusion of the solvent "particles" is much faster than the diffusion of monomers of the chains, so that

$$\beta n_s D_s \gg \sum_j m^0{}_{jj} \qquad (31)$$

and hence the second term is negligible. However, in this case one would not be able to reproduce the bulk limit correctly as the limit $n_s \rightarrow 0$. If this approximation is indeed valid in solutions, then there should be a crossover concentration n_{sc}, determined with the equality sign in eq 31, such that the solution-like behavior prevails when $n_s > n_{sc}$ and the bulk behavior when $n_s < n_{sc}$. Hence, the use of eq 30 without the second term to calculate the relaxation frequencies, as was done by Benmouna et al.,[4,5] becomes questionable at concentrations near the bulk limit. This difficulty, which arises from the treatment of solvent particles as fictitious monomers, does not cause any problem in calculating static quantities as was done by Benoit et al.[9,10]

(c) The first cumulant is calculated by substituting eq 28 into $\Omega(q) = (q^2/\beta)\mathbf{m}(q)[\mathbf{S}^0(q)^{-1} + \mathbf{v}(q)]$. The elements of $\mathbf{v}(q)$ are determined from eq 8 with $\chi^0{}_{cc}(q) = \beta n_c N_c{}^2 P(x_c)$ where $P(x) = (2/x^2)[x - 1 + \exp(-x)]$ is the usual Debye function with $x = q^2R_g{}^2$. Since the Debye function is obtained from the static structure factor $S_s(q)$ for a single Gaussian chain in the q range where qa

$\ll 1$ (a = statistical segment length), $P(x)$ has to be replaced in the interpretation of neutron scattering experiments[18] involving large q values for which $qa \approx 1$ by the full expression[15,16] of $S_s(q)/N^2$:

$$P(x) = N^{-1}\{1 + 2(e^{\alpha} - 1)^{-1}[1 - (1 - e^{-N\alpha})/N(1 - e^{-\alpha})]\} \tag{32}$$

where $\alpha = q^2a^2/6 = x/N$. For $qa \gg 1$, $P(x)$ approaches asymptotically $1/N$, whereas the Debye function decreases as $2/x$.

(d) The calculation of the static structure factor $S^0(q)$ in the bare system is well-known for Gaussian chains: When the components a and b are homopolymers we have

$$S_{\mathrm{ab}}(q) = \delta_{\mathrm{ab}} n_{\mathrm{a}} N_{\mathrm{a}}{}^2 P_{\mathrm{a}}(x) \tag{33}$$

where $P_{\mathrm{a}}(x)$ is given by eq 32 with $N = N_{\mathrm{a}}$ and statistical length appropriate to a chains. When the components a and b are two species in a copolymer molecule we have

$$S_{\mathrm{ab}}(q) = (1/2)n_{\mathrm{cop}}(N_{\mathrm{a}} + N_{\mathrm{b}})^2[P_{\mathrm{T}}(x) - f_{\mathrm{a}}{}^2P_{\mathrm{a}}(x) - (1 - f_{\mathrm{a}})^2P_{\mathrm{b}}(x)] \tag{34}$$

where n_{cop} is the number density of the copolymers consisting of a and b, N_{a} and N_{b} are the number of monomers of each type in a copolymer molecule, and P_{T} is given by eq 32 with $N = N_{\mathrm{a}} + N_{\mathrm{b}}$. Here we assume for simplicity that both a and b chains have the same statistical length.

(e) The short-time behavior of $\mathbf{S}(q,t)$ is approximated in the framework of the mean field theory by

$$\mathbf{S}(q,t) \approx \exp\{-\mathbf{\Omega}(q)t\}\mathbf{S}(q) \tag{35}$$

or

$$\mathbf{S}(q,t) \approx \exp\{-(q^2/\beta)\mathbf{m}(q)\mathbf{S}(q)^{-1}t\}\mathbf{S}(q) \tag{36}$$

The initial slope ω_{aa} of $S_{\mathrm{aa}}(q,t)$ in a scattering experiment on a multicomponent system, in which only the a component is visible, is defined by $\omega_{\mathrm{aa}} = -\lim \mathrm{d}\ln S_{\mathrm{aa}}(q,t)/\mathrm{d}t$ as $t \to 0$. Its approximate form can be obtained from eq 36 and 28 as

$$\omega_{\mathrm{aa}}(q) \approx k_{\mathrm{B}}Tq^2 m^0{}_{\mathrm{aa}}\left[1 - \frac{m^0{}_{\mathrm{aa}}}{m^0{}_{\mathrm{cc}} + \sum_j m^0{}_{jj}}\right] S^{-1}{}_{\mathrm{aa}}(q) \tag{37}$$

The factor $S_{\mathrm{aa}}(q)$ is to be calculated from eq 11. All the quantities in eq 37 are now known in terms of single-chain properties and Flory κ parameters. *It is important to note that $\omega_{aa}(q)$ is not equal to $\Omega(q)_{aa} = [k_{\mathrm{B}}Tq^2 \times \mathbf{m}(q)\mathbf{S}(q)^{-1}]_{aa}$.* To clarify this point we not that the short-time behavior of $\mathbf{S}(q,t)$ is given by eq 35 so that $S_{\mathrm{aa}}(q,t) = \{\exp[-\mathbf{\Omega}(q)t]\mathbf{S}(q)\}_{\mathrm{aa}}$ and can be expressed as the sum of exponential functions of time with relaxation frequencies determined by the eigenvalues of $\mathbf{\Omega}(q)$. But its derivative at $t = 0$ is $\{\mathbf{\Omega}(q)\mathbf{S}(q)\}_{\mathrm{aa}}$, which is equal to $\omega_{\mathrm{aa}}(q) \times S_{\mathrm{aa}}(q)$. In other words, $\omega_{\mathrm{aa}}(q)$ is equal to a weighted average of the components of $\mathbf{\Omega}(q)$.

(f) It is often stated in the literature that the mean field theory is equivalent to neglecting the memory effects in the generalized Langevin equation description, i.e., $\mathbf{\Phi}(q,s)$, in eq 25. We think that this is not the case, at least in the present context, because in the random phase approximation $[\mathbf{\Omega}(q) - \mathbf{\Phi}(q,s)]/q^2$ in eq 25 is approximated as a whole by the right-hand side of eq 17. In fact, the memory effects can be included in the description of the bare system also, by applying the GLE technique to determine $q^2\mathbf{D}^0(q,s)$ as $q^2\mathbf{D}^0(q,s) = \mathbf{\Omega}^0(q) - \mathbf{\Phi}^0(q,s)$.

(g) The intrachain hydrodynamic interaction can be included in the calculation of $\mathbf{m}^0(q)$ through eq 27, if the c component is a solvent. We have not attempted to do so because this refinement does not seem to be needed in concentrated solutions, where the mean field approximation is expected to be valid and where the hydrodynamic interactions are screened. We think that the mean field theory is flexible enough to take into account not only the intra- but also the interchain hydrodynamic interactions, by allowing a part of the interspecies interactions to be included in the unperturbed Hamiltonian. In this case, the bare response matrix $\chi^0(q,s)$ is not diagonal even when the mixture contains only homopolymers, and the implementation of the mean field theory becomes cumbersome.

(h) Stühn and Rennie[18] have recently reported neutron scattering experiments on copolymers of A and B, in the matrix of A homopolymers. Only the A monomers in the copolymers were labeled. They have interpreted the data by extending the theoretical results of Akcasu et al.[3] for copolymer melts, to take into account the effect of the A matrix. Although their results reproduce the correct bulk limit, they are not consistent with the multicomponent description presented in this paper.

In conclusion, the theoretical results obtained in this paper in matrix form reduce the study of the dynamics of polymer mixtures with arbitrary number of component with RPA to straightforward matrix calculations.

Appendix. Chains with Different Segment Volumes

The intensity $I(q,t)$ for an n component system, before the incompressibility assumption is

$$I(q,t) = \sum_{i,j=1}^{n} a_i a_j \langle \delta\rho_i(\mathbf{q},\mathrm{t})\delta\rho_j{}^*(\mathbf{q},0)\rangle \tag{A1}$$

When the incompressibility constraint, which reads

$$\sum_{i=1}^{n} \nu_i \delta\rho_i(q,t) = 0 \tag{A2}$$

where the segment volumes υ_i are allowed to be different, is implemented, eq A1 becomes

$$I(q,t) = V\sum_{i,j=1}^{n-1}\left(\frac{a_i}{\nu_i} - \frac{a_n}{\nu_n}\right)\left(\frac{a_j}{\nu_j} - \frac{a_n}{\nu_n}\right)\bar{S}_{ij}(q,t) \tag{A3}$$

where V is the volume of the system and $\bar{S}_{ij}(q,t)$ is the volume fraction correlation function

$$\bar{S}_{ij}(q,t) = \frac{1}{V}\langle \delta\Phi_i(\mathbf{q},t)\delta\Phi_j{}^*(\mathbf{q},0)\rangle \tag{A4}$$

with $\delta\Phi_j = {}_{\nu_j}\delta\rho_j$, i.e., the volume fraction of the jth component. The component labeled $j = n$ in eq A1 has been taken to be the matrix (labeled "c" in the text) and has been eliminated in eq A3. The latter expresses $I(q,t)$ in terms of the "contrasts".

In order to include the effect of the difference in the segment volumes on the RPA calculations of $\bar{S}_{ij}(q,t)$ in eq A3 in terms of the bare correlation functions and interactions, it is convenient to start with the mean response equation

$$\delta\bar{\rho} = -\chi^0[\bar{\mathbf{U}} + u\nu\mathbf{E} + \mathbf{W}\bar{\rho}] \tag{A5}$$

which has the same form as eq 5 in the text except for the incompressibility term $u\mathbf{E}$ which now becomes $u\nu\mathbf{E}$

where υ is the diagonal matrix defined by $\upsilon = \delta_{ij}\nu_i$. We can express the volume fraction vector $\delta\mathbf{\Phi}$ in terms of the number density vector $\delta\rho$ as $\delta\mathbf{\Phi} = \upsilon\delta\rho$. Thus multiplying eq A5 by υ, we obtain for the mean response of $\delta\mathbf{\Phi}$

$$\delta\bar{\mathbf{\Phi}} = -\bar{\chi}^0[\bar{\mathbf{U}} + \bar{u}\mathbf{E} + \bar{\mathbf{W}}\delta\bar{\mathbf{\Phi}}] \tag{A6}$$

where $\bar{\chi}^0 = \upsilon\chi^0\upsilon$ is the bare response matrix for the mean volume fractions and $\bar{\mathbf{W}} = \upsilon^{-1}\mathbf{W}\upsilon^{-1}$ is the modified interaction matrix. In obtaining eq A6 we have used $\upsilon^{-1}\ \upsilon = \mathbf{E}$. The point of this transformation is that eq A6 has exactly the same form as that of eq 5, with the same incompressibility relation $\mathbf{E}^{\mathrm{T}}\delta\mathbf{\Phi} = 0$. Hence the various formulas obtained in the text, assuming the segment volumes to be the same, can be transcribed to the case of different segment volumes υ_i, by expressing the correlation functions in volume fractions and using the modified interaction matrix $\bar{\mathbf{W}} = \upsilon^{-1}\ \mathbf{W}\upsilon^{-1}$ in the calculation of the excluded volume matrix $\bar{\mathbf{v}}(q,s)$. Explicitely, we find

$$\upsilon_{ij}(q,s) = \frac{\beta}{\bar{\chi}^0{}_{nn}(q,s)} - 2\kappa_{in}(q)\delta_{ij} - [\kappa_{ij}(q) - \kappa_{in}(q) - \kappa_{jn}(q)](1 - \delta_{ij}) \tag{A7}$$

where

$$\kappa_{ij}(q) = \beta\left\{\bar{W}_{ij}(q) - \frac{1}{2}[\bar{W}_{ii}(q) + \bar{W}_{jj}(q)]\right\} \tag{A8}$$

and

$$\bar{\chi}^0{}_{nn}(q,t) = -\beta\frac{\mathrm{d}\bar{S}^0{}_{nn}(q,t)}{\mathrm{d}t} \tag{A9}$$

The bare mobilities become $m^0{}_{jj} = \nu_j{}^2 n_j N_j/\xi_j$.

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