

# Dynamics of Multicomponent Polymer Mixtures via the Random Phase Approximation Including Hydrodynamic Interactions

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**ABSTRACT:** A new and extended formulation of the random phase approximation (RPA) in the study of statics and dynamics of multicomponent polymer mixtures is presented. The new formulation simplifies the implementation of the RPA in both compressible and incompressible mixtures and allows the inclusion of hydrodynamic interaction in the dynamics of polymer melts in the RPA. The dynamics of copolymer melts with hydrodynamic interaction is studied in detail as an illustration of the extended formulation, and the variation of the first cumulant as a function of the wavenumber and interaction parameter is obtained.

## 1. Introduction

The implementation of the random phase approximation (RPA) in studying the statics and dynamics of multicomponent polymer mixtures with an arbitrary number of components has been presented recently by Akcasu and Tombakoglu<sup>1a</sup> and Akcasu.<sup>1b</sup> In these works, which henceforth we refer to as I, the polymer molecules with identical physical and chemical properties are identified as a "component". The molecules belonging to different components are allowed to be connected to each other to form copolymers, stars, etc. For example, a melt of copolymers of two chemical species is considered to be a two-component mixture in this description. Similarly, a mixture of polydisperse homopolymers is also treated as a multicomponent mixture in which the molecules in different components differ from each other only in their molecular weights. In the implementation of the RPA in incompressible multicomponent mixtures, one of the components, which is referred to as the "matrix" component in I, is eliminated by using the incompressibility constraint on the volume fractions of monomers in each component, and the system is described in terms of the densities of the remaining components. Although the introduction of incompressibility is not essential in the implementation of the RPA, it reduces the dimensionality of the response matrix, which is introduced to describe the linear response of the mean densities to external potentials, by one and thereby simplifies the calculation of the static structure factors and the dynamic scattering functions in mixtures with negligible compressibility. More importantly, the elimination of the matrix component enables one to express the results in terms of Flory interaction parameters, as shown in I. The elimination procedure was facilitated considerably by assuming that the molecules of the matrix component are not coupled in the bare system to the molecules of the other components. Mathematically, this assumption implies that in a mixture with  $n + 1$  components, the  $(n + 1)$ -dimensional dynamic response matrix  $\bar{\chi}^0(q,s)$  describing the mean incremental density response in the bare system to time-dependent external potentials, is block diagonal, i.e.,  $\chi_{j0}^0(q,s) = 0$ , for  $j = 1, \dots, n$ . Here, the subscripts "0" and  $j = 1, 2, \dots, n$  designate the matrix component and the remaining  $n$  components, respectively.

In this paper we present a generalization of the above elimination procedure by allowing the monomers of the matrix component to interact or to be connected with the monomers in other components, so that the assumption  $\chi_{j0}^0(q,s) = 0$ , for  $j = 1, \dots, n$  is no longer needed. This generalization not only simplifies the implementation of the RPA in incompressible multicomponent mixtures in which none of the components consists of homopolymers, such as in melts of copolymers, stars, etc., but also it allows more flexibility in the choice of the bare system in the implementation of the RPA, even in the case of homopolymer mixtures. For example, one can now allow hydrodynamic interactions among the monomers, which couples dynamically the matrix molecules to those of the remaining components, and use the full Kirkwood-Riseman diffusion equation to describe the dynamics of the bare system, rather than being restricted to the Rouse dynamics, as has been the case in the implementation of the RPA until now. The situation is similar to the implementation of the perturbation theory in quantum mechanics, in which one introduces an unperturbed system with a Hamiltonian  $H_0$  and a perturbation potential  $V$  such that the total Hamiltonian is  $H = H_0 + V$ . Putting more information into the unperturbed system, which corresponds to the bare system in the RPA, one can obtain increasingly more accurate results.

The formulation of the RPA in this extended form is presented in section 2. The derivations in this section are self-contained and are actually simpler than those presented in I, even though they are more general. A reader who is not interested in the derivations may skip this section, for the final results needed in applications which are summarized in section 3. Section 4 contains some applications illustrating the implementation of the RPA in its extended form. Discussions and conclusions are presented in section 5.

## 2. Derivations

We consider an  $(n + 1)$ -component polymer mixture and denote the Fourier transform of the local density of monomers  $\rho_j(\mathbf{r})$  belonging to the  $j$ th component by  $\rho_j(\mathbf{q})$ . We define an  $(n + 1)$ -component density vector  $\rho(\mathbf{q}) = \text{column}[\rho(\mathbf{q}), \rho_0(\mathbf{q})]$ , where  $\rho(\mathbf{q})$  is the density vector associated with the first  $n$  components and  $\rho_0(\mathbf{q})$  is the density of monomers belonging to the component chosen as the "matrix". The overbar will always imply  $(n + 1)$ -dimensional vectors and matrices. We now assume that

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the mixture is perturbed by applying time-dependent external potentials  $U_j(\mathbf{r}, t)$ ,  $j = 0, 1, \dots, n$ , which are coupled to the monomers in the  $j$ th component (see I) and collectively denoted by an  $(n + 1)$ -dimensional vector  $\bar{\mathbf{U}}(\mathbf{q}, s) = \text{column}[\mathbf{U}(\mathbf{q}, s), U_0(\mathbf{q}, s)]$  in the Fourier-Laplace domain. The mean value of the resulting perturbations in the monomer densities, measured from their equilibrium values, is also collectively denoted by a vector  $\langle \delta \rho(\mathbf{q}, s) \rangle = \text{column}[\langle \delta \rho(\mathbf{q}, s) \rangle, \langle \delta \rho_0(\mathbf{q}, s) \rangle]$ , which we refer to as the time-dependent incremental mean density response. The brackets  $\langle \dots \rangle$  denote the average with respect to the perturbed distribution function. According to the linear response theory,  $\langle \delta \rho(\mathbf{q}, s) \rangle$  is related to  $\bar{\mathbf{U}}(\mathbf{q}, s)$  in terms of an  $(n + 1) \times (n + 1)$  square dynamic response matrix  $\bar{\chi}(q, s)$  as

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

The dynamic response matrix is related to the dynamic scattering matrix in the equilibrium state by

$$\bar{\chi}(q, t) = -\frac{\beta}{V} \frac{d}{dt} \bar{\mathbf{S}}(q, t) \quad (2)$$

where  $\beta$  is the inverse temperature in energy units, i.e.,  $\beta = 1/k_B T$ , and  $V$  is the volume of the system. The elements of  $\bar{\mathbf{S}}(q, t)$  are defined as  $S_{jk}(q, t) = \langle \delta \rho_j(\mathbf{q}, t) \times \delta \rho_k(-\mathbf{q}, 0) \rangle_{\text{eq}}$ . Since  $\bar{\mathbf{S}}(q, t)$  is symmetric, so is  $\bar{\chi}(q, t)$ . The static response matrix, which characterizes the steady-state response of the mixture to a time-independent external potential, is obtained from eq 2 by integrating both sides in  $(0, \infty)$ :

$$\bar{\chi}(q) = \frac{\beta}{V} \bar{\mathbf{S}}(q) \quad (3)$$

The  $\bar{\chi}(q)$  is also equal to  $\bar{\chi}(q, s=0)$ , where  $\bar{\chi}(q, s)$  is the Laplace transform of  $\bar{\chi}(q, t)$ . Equations 2 and 3 are generic in the sense that they are valid regardless of the dimensionality, and both in the bare and interacting systems. When the mixture can be treated as incompressible, the total mean local density fluctuations must be zero. Here we assume for simplicity that monomeric volumes are the same for all components. The incompressibility condition is expressed mathematically as

$$\bar{\mathbf{E}}^T \langle \delta \bar{\rho}(\mathbf{q}, s) \rangle = 0 \quad (4a)$$

where  $\bar{\mathbf{E}} = \text{column}[1, 1, \dots, 1]$  with  $n + 1$  elements. Using  $\langle \delta \bar{\rho}(\mathbf{q}, s) \rangle = \text{column}[\langle \delta \rho(\mathbf{q}, s) \rangle, \langle \delta \rho_0(\mathbf{q}, s) \rangle]$ , one can express eq 4a as

$$\langle \delta \rho_0(\mathbf{q}, s) \rangle = -\mathbf{e}^T \langle \delta \rho(\mathbf{q}, s) \rangle \quad (4b)$$

where  $\mathbf{e} = \text{column}[1, 1, \dots, 1]$  with  $n$  elements. The elements of the dynamic response matrix in an incompressible mixture are not independent of each other. Indeed, multiplying eq 1 from the left by  $\bar{\mathbf{E}}^T$  and using eq 4a, one obtains  $\bar{\mathbf{E}}^T \bar{\chi}(q, s) \bar{\mathbf{U}}(\mathbf{q}, s) = 0$ . Since the latter must hold for any external potential, we must have  $\bar{\mathbf{E}}^T \bar{\chi}(q, s) = 0$ . The matrix  $\bar{\chi}(q, s)$  can be expressed in block diagonal form as

$$\bar{\chi}(q, s) = \begin{bmatrix} \chi(q, s) & \mathbf{X}(q, s) \\ \mathbf{X}^T(q, s) & \chi_{00}(q, s) \end{bmatrix} \quad (5)$$

where  $\mathbf{X}(q, s)$  is a column matrix with elements  $X_j(q, s) = \chi_{j0}(q, s)$ ,  $j = 1, \dots, n$ , and represents the coupling between the matrix and the other components. Substituting this form into  $\bar{\mathbf{E}}^T \bar{\chi}(q, s) = 0$  and using the symmetry of  $\bar{\chi}(q, s)$ , we obtain the following two conditions on the dynamic

matrix in incompressible mixtures:

$$\mathbf{X}(q, s) = -\chi(q, s) \mathbf{e} \quad (6a)$$

$$\chi_{00}(q, s) = -\mathbf{e}^T \mathbf{X}(q, s) \quad (6b)$$

Using eqs 1 and 6a, one can express the time-dependent incremental mean density response of the first  $n$  components in an incompressible mixture as

$$\langle \delta \rho(\mathbf{q}, s) \rangle = -\chi(q, s) [\mathbf{U}(\mathbf{q}, s) - U_0(\mathbf{q}, s) \mathbf{e}]$$

which can also be written as

$$\langle \delta \rho(\mathbf{q}, s) \rangle = -\chi(q, s) \mathbf{P}^T \bar{\mathbf{U}}(\mathbf{q}, s) \quad (7)$$

by introducing an  $(n + 1) \times n$  rectangular matrix  $\mathbf{P}$ , without the overbar for simplicity, as

$$\mathbf{P} = \begin{bmatrix} \mathbf{I} \\ -\mathbf{e}^T \end{bmatrix} \quad (8)$$

where  $\mathbf{I}$  is the  $n \times n$  identity matrix and  $\mathbf{e}$  was defined above. It is clear that  $\mathbf{P}^T \bar{\mathbf{U}}(\mathbf{q}, s) = [\mathbf{U}(\mathbf{q}, s) - U_0(\mathbf{q}, s) \mathbf{e}]$ . We note that  $\mathbf{P}^T \bar{\mathbf{U}}(\mathbf{q}, s)$  is a column vector with  $n$  components, whereas  $\bar{\mathbf{U}}(\mathbf{q}, s)$  has  $n + 1$  components. Introduction of the matrix  $\mathbf{P}$  greatly simplifies the later manipulations.

We mention in passing that the condition in eq 6b enables one to express  $\langle \delta \rho_0(\mathbf{q}, s) \rangle$  as

$$\langle \delta \rho_0(\mathbf{q}, s) \rangle = -\mathbf{X}^T(q, s) [\mathbf{U}(\mathbf{q}, s) - U_0(\mathbf{q}, s) \mathbf{e}]$$

which states the incompressibility constraint more explicitly. Since  $\langle \delta \rho_0(\mathbf{q}, s) \rangle$  is expressible in terms of the densities of the remaining  $n$  components, this expression is not needed in the following derivations.

The RPA provides an alternative, albeit approximate, expression for the time-dependent incremental mean density response  $\langle \delta \bar{\rho}(\mathbf{q}, s) \rangle$  as explained in I:

$$\langle \delta \bar{\rho} \rangle = -\bar{\chi}^0 [\bar{\mathbf{U}} + u \bar{\mathbf{E}} + \bar{\mathbf{W}} \langle \delta \bar{\rho} \rangle] \quad (9)$$

where  $\bar{\chi}^0(q, s)$  is the dynamic response matrix of the bare system,  $\bar{\mathbf{W}}(q)$  is the interaction matrix whose element  $W_{jk}(q)$  is the Fourier transform of the interaction potential  $W_{jk}(r)$  per monomer between a pair of monomers belonging to the  $j$ th and  $k$ th components, and  $u(q, s)$  is a fictitious potential (or Lagrange multiplier) added to maintain incompressibility, which will be eliminated using the incompressibility constraint in eq 4. In eq 9, we suppressed the arguments for simplicity. It is clear from eq 9 that the bare system is identical to the original system in all respects except for the absence of the interactions between monomers included in  $\bar{\mathbf{W}}(q)$  and the incompressibility. The effect of these on  $\langle \delta \bar{\rho}(\mathbf{q}, s) \rangle$  is included explicitly by the second and third terms in eq 9. The latter can also be written as

$$\left[ \frac{1}{\bar{\chi}^0} + \bar{\mathbf{W}} \right] \langle \delta \bar{\rho} \rangle = -\bar{\mathbf{U}} - u \bar{\mathbf{E}} \quad (10)$$

where  $1/\bar{\chi}^0$  is the inverse of  $\bar{\chi}^0$ . In a compressible mixture,  $u(q, s) = 0$ , and a comparison of eqs 1 and 10 yields

$$\frac{1}{\bar{\chi}(q, s)} = \frac{1}{\bar{\chi}^0(q, s)} + \bar{\mathbf{W}}(q) \quad (11a)$$

which is the RPA expression of the  $(n + 1) \times (n + 1)$  dynamic response matrix in compressible mixtures in terms of the bare system dynamic response matrix.

In an incompressible mixture, the potential  $u(q, s)$  in eq 10 is eliminated using the incompressibility constraint in eq 4b. One first expresses  $\langle \delta \bar{\rho} \rangle$  in eq 10 in terms of  $\langle \delta \rho \rangle$  as  $\langle \delta \bar{\rho} \rangle = \mathbf{P} \langle \delta \rho \rangle$  using eq 4b. Then one multiplies eq 10

from the left by  $\mathbf{P}^T$  and verifies that  $\mathbf{P}^T \bar{\mathbf{E}} = 0$ . The result reads

$$\mathbf{P}^T \left[ \frac{1}{\bar{\chi}^0} + \bar{\mathbf{W}} \right] \mathbf{P} \langle \delta \rho \rangle = -\mathbf{P}^T \bar{\mathbf{U}}$$

Comparing this expression with eq 7, we obtain

$$\frac{1}{\chi(q,s)} = \mathbf{P}^T \left[ \frac{1}{\bar{\chi}^0(q,s)} + \bar{\mathbf{W}}(q) \right] \mathbf{P} \quad (11b)$$

which expresses the  $n \times n$  dynamic response function in the original incompressible mixture in terms of the inverse of the  $(n+1) \times (n+1)$  dynamic response function  $\bar{\chi}^0(q,s)$  in the compressible bare system and the  $(n+1) \times (n+1)$  interaction matrix  $\bar{\mathbf{W}}(q)$ . This equation can be written in a more conventional form by introducing the Flory interaction matrix  $\kappa^F$  through  $\kappa^F(q) = (\beta/V) \mathbf{P}^T \bar{\mathbf{W}}(q) \mathbf{P}$  whose elements are related to the usual Flory interaction parameters  $\chi_{ij}^F(q)$ :

$$\kappa_{ij}^F = \chi_{ij}^F - \chi_{i0}^F - \chi_{j0}^F \quad (12a)$$

where

$$\chi_{ij}^F(q) = \frac{\beta}{V} \left\{ W_{ij}(q) - \frac{1}{2} [W_{ii}(q) + W_{jj}(q)] \right\} \quad (12b)$$

Since  $W_{ij}(q)$  has a dimension of energy-volume,  $\chi_{ij}^F(q)$  is dimensionless. In terms of  $\kappa^F(q)$  eq 11 reads

$$\frac{1}{\chi(q,s)} = \mathbf{P}^T \frac{1}{\bar{\chi}^0(q,s)} \mathbf{P} + \frac{V}{\beta} \kappa^F \quad (13)$$

which is one of the main results of the present derivation. It is possible to express the first term in eq 13 more explicitly by first finding the inverse of  $\bar{\chi}^0(q,s)$  using its block form given by

$$\bar{\chi}^0(q,s) = \begin{bmatrix} \chi^0(q,s) & \mathbf{X}^0(q,s) \\ \mathbf{X}^0(q,s)^T & \chi_{00}^0(q,s) \end{bmatrix}$$

(see Appendix A), where the block matrices are defined similar to those in eq 5, and then calculating  $\mathbf{P}^T (1/\bar{\chi}^0(q,s)) \mathbf{P}$ . We then obtain the following expression for  $\chi(q,s)^{-1}$  in terms of only  $n$ -dimensional matrices:

$$\frac{1}{\chi(q,s)} = \frac{1}{\chi^0(q,s)} + m \mathbf{Y} \mathbf{Y}^T + \frac{V}{\beta} \kappa^F(q) \quad (14)$$

where

$$\mathbf{Y}(q,s) = \chi^0(q,s)^{-1} \mathbf{X}^0(q,s) + \mathbf{e} \quad (15a)$$

$$m(q,s) = \frac{1}{\chi_{00}^0(q,s) - \mathbf{X}^0(q,s)^T \chi^0(q,s)^{-1} \mathbf{X}^0(q,s)} \quad (15b)$$

The form given in eq 13 was introduced by Akcasu et al.<sup>2</sup> in 1986 in the special case of a two-component mixture in their study of copolymer melts (see eq 34 of ref 2).

When the molecules in the matrix are not dynamically coupled to those in the remaining components so that the vector  $\mathbf{X}^0(q,s) = 0$ , which was assumed in I, eq 14 reduces to

$$\frac{1}{\chi(q,s)} = \frac{1}{\chi^0(q,s)} + k_B T \mathbf{v}(q,s) \quad (16)$$

where we have introduced

$$\mathbf{v}(q,s) = \beta \frac{\mathbf{e} \mathbf{e}^T}{\chi_{00}^0(q,s)} + V \kappa^F(q) \quad (17)$$

Equations 16 and 17 are identical to eqs 9 and 8 in I, respectively, in which  $\mathbf{v}(q,s)$  is referred to as the excluded volume matrix.

The remaining task is to present the procedure of calculating the static structure factors and dynamic scattering functions in the interacting system using eq 13 or 14 and point out the new features provided by the present extended formulation of the RPA. Since this procedure is the same as followed in I, we simply display the main steps.

In a compressible mixture, the static structure matrix follows immediately from eqs 3 and 11a as

$$\frac{1}{\bar{\mathbf{S}}(q)} = \frac{1}{\bar{\mathbf{S}}^0(q)} + \frac{\beta}{V} \bar{\mathbf{W}}(q) \quad (18a)$$

In an incompressible mixture, it follows from eqs 3 and 13 as

$$\frac{1}{\mathbf{S}(q)} = \mathbf{P}^T \frac{1}{\bar{\mathbf{S}}^0(q)} \mathbf{P} + \kappa^F(q) \quad (18b)$$

or, using the block form of the  $(n+1) \times (n+1)$ -dimensional static structure matrix  $\bar{\mathbf{S}}^0(q)$ , i.e.,

$$\bar{\mathbf{S}}^0(q) = \begin{bmatrix} \mathbf{S}^0(q) & \mathbf{s}^0(q) \\ \mathbf{s}^0(q)^T & S_{00}^0(q) \end{bmatrix}$$

where  $\mathbf{s}^0(q)_j = \mathbf{S}^0(q)_{j0}$ , and following the same steps leading from eq 13 to 14, one immediately finds

$$\frac{1}{\mathbf{S}(q)} = \frac{1}{\mathbf{S}^0(q)} + m \mathbf{Y} \mathbf{Y}^T + \kappa^F(q) \quad (18c)$$

with the new definitions of  $\mathbf{Y}(q)$  and  $m(q)$  as

$$\mathbf{Y}(q) = \mathbf{S}^0(q)^{-1} \mathbf{s}^0(q) + \mathbf{e} \quad (18d)$$

$$m(q) = \frac{1}{S_{00}^0(q) - \mathbf{s}^0(q)^T \mathbf{S}^0(q)^{-1} \mathbf{s}^0(q)} \quad (18e)$$

For example, in a binary mixture of A and B polymers, eqs 18 reduce to

$$\frac{1}{S(q)} = \frac{S_{\text{T}}^0(q)}{|\bar{\mathbf{S}}^0(q)|} - 2\chi^F \quad (19)$$

where  $S(q) = S_{\text{aa}}(q) = S_{\text{bb}}(q) = -S_{\text{ab}}(q)$ ,  $S_{\text{T}}^0(q) = S_{\text{aa}}^0(q) + S_{\text{bb}}^0(q) + 2S_{\text{ab}}^0(q)$ ,  $|\bar{\mathbf{S}}^0(q)| = S_{\text{aa}}^0(q)S_{\text{bb}}^0(q) - S_{\text{ab}}^0(q)^2$ , and  $\kappa_{\text{aa}}^F = \kappa_{\text{bb}}^F = -2\chi_{\text{ab}}^F = -2\chi^F$  have been used.

The generalized form in eq 18 greatly simplifies the calculation of the static structure factors when mixtures contain molecules with complicated architecture such as copolymers, stars, etc.<sup>3</sup> The partial structure factors  $S^0(q)_{\alpha\beta}$  in the bare system are to be calculated with the equilibrium distribution function, in which the interaction potentials  $W(q)_{\alpha\beta}$  are excluded in the Hamiltonian. For example, if all the interactions are included in  $W(q)_{\alpha\beta}$  in a mixture consisting of only homopolymers, then  $\mathbf{S}^0(q)$  is diagonal, and the diagonal elements are proportional to the single Gaussian-chain static structure factors in each component.

To calculate the dynamic scattering matrix  $\mathbf{S}(q,t)$ , we first express its Laplace transform as

$$\mathbf{S}(q,s) = \frac{1}{s\mathbf{I} + q^2 \mathbf{D}(q,s)} \mathbf{S}(q) \quad (20)$$

where  $\mathbf{D}(q,s)$  may be viewed as a generalized diffusivity matrix. Substitution of eq 20 into eq 2 yields

$$\frac{1}{\chi(q,s)} = \frac{V}{\beta} \left[ \frac{s}{q^2} \frac{\beta}{\mu(q,s)} + \frac{1}{\mathbf{S}(q)} \right] \quad (21)$$

where the mobility matrix  $\mu(q,s)$  is defined by

$$\mu(q,s) = \beta \mathbf{D}(q,s) \mathbf{S}(q) \quad (22)$$

The reason for introducing the mobility matrix is that it is a purely dynamic quantity. The relationships and definitions in eqs 20–22 are generic in the sense that they are valid in both the bare and interacting systems, irrespective of the dimensionality of the matrices.

In the case of a compressible mixture, one writes eq 21 for the  $(n+1) \times (n+1)$  dynamic response matrices, substitutes them into eq 11a, and makes use of eq 18a to obtain

$$\bar{\mu}(q,s) = \bar{\mu}^0(q,s) \quad (23a)$$

which relates the mobilities in the interacting and bare systems in the RPA.

In the case of an incompressible mixture, substitution of eq 21 into eq 13 and use of eq 18b in the resulting expression yield a simple relationship between the  $n \times n$  mobility matrix  $\mu(q,s)$  in the interacting system and the  $(n+1) \times (n+1)$  mobility matrix  $\bar{\mu}^0(q,s)$  in the bare system:

$$\frac{1}{\mu(q,s)} = \mathbf{P}^T \frac{1}{\bar{\mu}^0(q,s)} \mathbf{P} \quad (23b)$$

Introducing the block form

$$\bar{\mu}^0(q,s) = \begin{bmatrix} \mu^0(q,s) & \nu^0(q,s) \\ \nu^{0T}(q,s) & \mu_{00}^0(q,s) \end{bmatrix}$$

where  $\nu^0(q,s)_j = \mu^0(q,s)_{j0}$ , and following the same steps leading from eq 13 to 14, we obtain the following alternative expression for the inverse of  $\mu(q,s)$ :

$$\frac{1}{\mu(q,s)} = \frac{1}{\mu^0(q,s)} + m \mathbf{U} \mathbf{U}^T \quad (24a)$$

with a new definition of  $\mathbf{U}(q,s)$  and  $m(q,s)$  as

$$\mathbf{U}(q,s) = \mu^0(q)^{-1} \nu^0(q,s) + \mathbf{e} \quad (24b)$$

$$m(q,s) = \frac{1}{\mu_{00}^0(q,s) - \nu^0(q,s)^T \mu^0(q,s)^{-1} \nu^0(q,s)} \quad (24c)$$

In fact, using the Sherman–Morrison formula (Appendix A) to invert eq 24a, we obtain an expression for  $\mu(q,s)$ , rather than its inverse, as

$$\mu = \mu^0 - \frac{(\mu^0 \mathbf{e} + \nu^0)(\mathbf{e}^T \mu^0 + \nu^{0T})}{\mu_{00}^0 + \mathbf{e}^T \mu^0 \mathbf{e} + \nu^{0T} \mathbf{e} + \mathbf{e}^T \nu^0} \quad (25)$$

where we have suppressed the arguments  $(q,s)$  for simplicity. Equation 25 is also a new result. When the mobility matrix is block diagonal so that  $\nu^0(q,s) = 0$ , eq 25 reduces to

$$\mu(q,s) = \mu^0(q,s) - \frac{\mu^0(q,s) \mathbf{e} \mathbf{e}^T \mu^0(q,s)}{\mu_{00}^0(q,s) + \mathbf{e}^T \mu^0(q,s) \mathbf{e}} \quad (26)$$

which was given in I (eq 11 of ref 1b).

To display the new features of this result we consider a binary mixture of A and B species which may be homopolymers or copolymers. In this case, there is only one independent mobility in the interacting system because  $\mu_{AA} = \mu_{BB} = -\mu_{AB}$ , and it is given in terms of the mobilities  $\mu_{AA}^0$ ,  $\mu_{BB}^0$ , and  $\mu_{AB}^0$  in the bare system by

$$\mu_{AA} = \frac{\mu_{AA}^0 \mu_{BB}^0 - (\mu_{AB}^0)^2}{\mu_{AA}^0 + \mu_{BB}^0 + 2\mu_{AB}^0} \quad (27)$$

In the absence of coupling between the A and B compo-

nents so that  $\mu_{AB}^0 = 0$ , eq 27 reduces to the well-known inverse superposition rule of mobilities in incompressible binary mixtures:<sup>2,4-6</sup>

$$\frac{1}{\mu_{AA}} = \frac{1}{\mu_{AA}^0} + \frac{1}{\mu_{BB}^0}$$

This rule ceases to be valid when the mobility matrix in the bare system is not diagonal.

The short-time mobilities,  $\mathbf{m}(q)$  (not to be confused with  $m$  introduced in eqs 15b and 24c), defined in terms of the first cumulant matrix through<sup>7</sup>

$$\mathbf{m}(q) = \beta q^{-2} \Omega(q) \mathbf{S}(q) \quad (28)$$

are obtained from the generalized mobilities  $\mu(q,s)$  as the limit of the latter as  $s \rightarrow \infty$ .<sup>7</sup> Hence,  $\mathbf{m}(q)$  in the interacting system can be related to the bare system short-time mobilities  $\mathbf{m}^0(q)$  through eqs 23 or 25:

$$\mathbf{m} = \mathbf{m}^0 - \frac{(\mathbf{m}^0 \mathbf{e} + \mathbf{n}^0)(\mathbf{e}^T \mathbf{m}^0 + \mathbf{n}^{0T})}{m_{00}^0 + \mathbf{e}^T \mathbf{m}^0 \mathbf{e} + \mathbf{n}^{0T} \mathbf{e} + \mathbf{e}^T \mathbf{n}^0} \quad (29)$$

where the arguments  $(q)$  are suppressed and where  $n_j^0(q) = m_{j0}^0(q)$ . The mobilities in the bare system have usually been calculated by using Rouse dynamics, which does not take into account hydrodynamic interactions. One of the points we make in this paper is to show that both intra- and interchain hydrodynamic interaction can be included in the dynamics of the bare system, in the light of the new formulation of the dynamic RPA. The calculation of the mobilities in the presence of hydrodynamic interactions is standard (see, for example, refs 7–9):

$$m_{aa}^0(q) = N_a \left\{ \frac{1}{\xi_a} + \frac{1}{(2\pi)^3} \int d^3k \bar{T}_{33}(\mathbf{k}-\mathbf{q}) \left[ \frac{1}{N_a} S_{aa}^0(k) - 1 \right] \right\} \quad (30)$$

and

$$m_{ab}^0(q) = \frac{1}{(2\pi)^3} \int d^3k \bar{T}_{33}(\mathbf{k}-\mathbf{q}) S_{ab}^0(k) \quad (31)$$

where  $N_a$  is the total number of monomers in component A.  $\bar{T}_{33}(\mathbf{k})$  is the Fourier transform of  $T_{33}(\mathbf{R}) = \mathbf{q} \cdot \mathbf{T}(\mathbf{R}) \cdot \mathbf{q} / q^2$ , where  $\mathbf{T}(\mathbf{R})$  is the conventional Oseen tensor, i.e.,

$$\bar{T}_{33}(\mathbf{k}) = \frac{1}{\eta} \frac{1}{k^2} (1 - \cos^2 \theta_{\mathbf{k}}) \quad (32)$$

In eq 32,  $\theta_{\mathbf{k}}$  is the angle between vectors  $\mathbf{q}$  and  $\mathbf{k}$ , and  $\eta$  is the viscosity of the mixture, which we will discuss more in a later section. In eqs 30 and 31,  $S_{aa}^0(k)$  and  $S_{ab}^0(k)$  denote the partial static structure factors in the bare system and are defined as

$$S_{ab}^0(k) = \left\langle \sum_{\alpha=1}^{N_a} \sum_{\beta=1}^{N_b} e^{i\mathbf{k} \cdot \mathbf{R}_{\alpha\beta}} \right\rangle \quad (33)$$

The average  $\langle \dots \rangle$  refers to the equilibrium average in the bare system. Since there are no interactions among the monomers in the bare system except for those maintaining chain connectivity, the interchain correlations in eq 33 vanish. Hence, in eq 30 we have

$$S_{aa}^0(k) = N_a [S_A^S(k) + (2\pi)^3 n_a \delta(\mathbf{k})] \quad (34)$$

where  $n_a = N_a/V$  is the monomer density in component A, and  $S_A^S(k)$  is the single-chain static structure factor normalized as  $S_A^S(0) = p_a$ , where  $p_a$  is the polymerization index for an A molecule (number of monomers). Substitution of eq 34 into eq 30 and the use of  $\bar{T}_{33}(\mathbf{q}) = 0$  yield

$$m_{aa}^0(q) = N_a \left\{ \frac{1}{\xi_a} + \frac{1}{(2\pi)^3} \int d^3k \bar{T}_{33}(\mathbf{k}-\mathbf{q}) [S_A^S(k) - 1] \right\} \quad (35)$$

The above procedure leads to the conclusion that  $m_{ab}^0(q) = 0$  when the chains of components A and B are not connected to each other, but  $m_{ab}^0(q) \neq 0$  otherwise. For example, in the case of copolymer melts one finds

$$m_{ab}^0(q) = \frac{N_a}{(2\pi)^3} \int d^3k \bar{T}_{33}(\mathbf{k}-\mathbf{q}) S_{AB}^S(k) \quad (36)$$

where  $S_{AB}^S(k)$  is the correlation function between the two parts of a single A/B copolymer, normalized as  $S_{AB}^S(0) = (p_a p_b)^{1/2}$ . Since  $S_A^S(k)$  and  $S_{AB}^S(k)$  depend only on the magnitude of vector  $\mathbf{k}$ , the angular integration in eqs 35 and 36 can be performed:

$$m_{aa}^0(q) = N_a \left\{ \frac{1}{\xi_a} + \frac{1}{4\pi^2 \eta} \int_0^\infty dk Z(k/q) [S_A^S(k) - 1] \right\} \quad (37)$$

$$m_{ab}^0(q) = \frac{N_a}{4\pi^2 \eta} \int_0^\infty dk Z(k/q) S_{AB}^S(k) \quad (38)$$

where the function  $Z(x)$  denotes

$$Z(x) \equiv \frac{x}{2} (1 + x^2) \operatorname{Ln} \left| \frac{x+1}{x-1} \right| - x^2 \quad (39)$$

The  $S_A^S(k)$  and  $S_{AB}^S(k)$  in eqs 37 and 38 are obtained using Gaussian statistics. In the small- $q$  region where  $qa \ll 1$  holds, they are represented by the Debye function. Here " $a$ " denotes the statistical segment length of an A chain. Since neutron spin-echo scattering experiments are performed in the high- $q$  region, where  $qa$  can be of the order of unity, we need the full expression of  $S_A^S(k)$  and  $S_{AB}^S(k)$  valid for all  $q$ 's.<sup>10,11</sup> The former can be written as  $S_A^S(k) = p_a P(p_a, \alpha_a)$ , where

$$P(p_a, \alpha_a) = \frac{1}{P_a} \left\{ 1 + 2(e^{\alpha_a} - 1)^{-1} \left[ 1 - \frac{1 - e^{-p_a \alpha_a}}{p_a (1 - e^{-\alpha_a})} \right] \right\} \quad (40)$$

where  $\alpha_a = q^2 a^2 / 6$ . In the limit of  $a \rightarrow 0$  and  $p_a \rightarrow \infty$ , keeping  $R_{ga}^2 = p_a a^2 / 6$  constant,  $P(p_a, \alpha_a)$  reproduces the conventional Debye form:

$$P_D(x_a) = \frac{2}{x_a} (x_a - 1 + e^{-x_a}) \quad (41)$$

where  $x_a = p_a \alpha_a = (q R_{ga})^2$  and  $R_{ga}$  is the radius of gyration of an A chain. The difference between the full expression  $P(p_a, \alpha_a)$  and the Debye form  $P_D(x_a)$  is that the former behaves as  $1/p_a$  in the high- $q$  region where  $qa \gg 1$ , whereas the latter behaves as  $2/x_a$ .

We present the expression  $S_{AB}^S(k)$  in the case of diblock copolymer A-B, allowing the statistical segment lengths  $a$  and  $b$  of the two arms to be different. Writing  $S_{AB}^S(k)$  as  $S_{AB}^S(k) = p_b P_{ab}(p_a, p_b, \alpha_a, \alpha_b)$ , we obtain<sup>12,13</sup>

$$P_{ab}(p_a, p_b, \alpha_a, \alpha_b) = \frac{1}{p_a p_b} e^{-(\alpha_a + \alpha_b)/2} \left[ \frac{(1 - e^{-\alpha_a p_a})(1 - e^{-\alpha_b p_b})}{(1 - e^{-\alpha_a})(1 - e^{-\alpha_b})} \right] \quad (42)$$

Detailed calculation of  $P_{ab}$  for multiblock copolymers having different architectures can be found elsewhere.<sup>12</sup>

### 3. Interpretation of Dynamic Scattering Experiments on Polymer Melts

In this section we describe briefly the procedure to be followed for the interpretation of dynamic scattering experiments on multicomponent polymer mixtures using

the results of the previous section. We consider an  $(n + 1)$ -component mixture, in which one of the components (designated by A) is labeled. The dynamic scattering function  $S_{AA}(q, t)$  is measured as a function of time at different wavenumbers  $q$ , and its first cumulant  $\Gamma_{aa}(q)$  is extracted from the data as a function of  $q$ . The short-time behavior of the  $(n + 1)(n + 2)/2$  partial scattering functions  $S_{\alpha\beta}(q, t)$ ,  $\alpha, \beta = 1, \dots, n$ , are jointly described by a matrix equation

$$\bar{\mathbf{S}}(q, t) = e^{-\bar{\Omega}(q)t} \bar{\mathbf{S}}(q) \quad (43)$$

where the static structure factor  $\bar{\mathbf{S}}(q)$  is expressed as

$$\frac{1}{\bar{\mathbf{S}}(q)} = \frac{1}{\bar{\mathbf{S}}^0(q)} + \frac{\beta}{V} \bar{\mathbf{W}}(q) \quad (44)$$

in the RPA without incompressibility. The first cumulant matrix  $\bar{\Omega}(q)$  is related to the short-time mobility matrix  $\bar{\mathbf{m}}(q)$  through  $\bar{\Omega}(q) = k_B T q^2 \bar{\mathbf{m}}(q) \bar{\mathbf{S}}(q)^{-1}$ , in which  $\bar{\mathbf{m}}(q) = \bar{\mathbf{m}}^0(q)$  within the RPA without incompressibility (see eq 23a). The expressions of  $m_{\alpha\beta}^0(q)$  and  $S_{\alpha\beta}^0(q)$  are given by eqs 37–39 and 40–42. Thus, the calculation of  $\bar{\mathbf{S}}(q, t)$  is reduced to straightforward matrix manipulations. One finds for example that  $S_{AA}(q, t)$  can be expressed as a superposition of  $n + 1$  eigenmodes with relaxation frequencies  $\lambda_j(q)$  which are the eigenvalues of  $\bar{\Omega}(q)$ . Often, only the first cumulant  $\Gamma_{aa}(q)$  of  $S_{AA}(q, t)$  is analyzed in a scattering experiment which is given by

$$\Gamma_{aa}(q) = k_B T q^2 \frac{m_{aa}^0(q)}{S_{aa}^0(q)} \quad (45)$$

Note that  $\Gamma_{aa}(q)$  is not equal to any of the matrix elements of  $\bar{\Omega}(q)$ .

It is observed that in the absence of incompressibility the RPA requires specification of the partial structure factors  $S_{\alpha\beta}^0(q)$  in the bare system and the Fourier transform of the interaction potentials  $W_{\alpha\beta}(r)$  between pairs of monomers treated as perturbation. The accuracy of the RPA increasingly improves by including in  $W_{\alpha\beta}(r)$  smaller portions of the actual interaction potential. For example,  $W_{\alpha\beta}(r)$  may be chosen to include the long-range potential interactions among monomers and the short-range interchain excluded volume interactions. In this case the bare system consists of noninteracting chains, except for the chain connectivities, with intrachain excluded volume interactions. The latter must be included in the calculation of  $S_{\alpha\beta}^0(q)$ . The choice of  $W_{\alpha\beta}(r)$  affects the calculation of the bare system mobilities as well, through  $S_{\alpha\beta}^0(q)$  as indicated in eqs 37 and 38.

Implementation of the RPA in polymer melts, which can be treated as an incompressible mixture, is further simplified by making use of the incompressibility condition. The number of independent partial scattering functions  $S_{\alpha\beta}(q, t)$  is reduced from  $(n + 1)(n + 2)/2$  to  $n(n + 1)/2$ . The time evolution of these can be described by an  $n \times n$  matrix  $\mathbf{S}(q, t)$ . The short-time behavior of the latter is given by

$$\mathbf{S}(q, t) = e^{-\Omega(q)t} \mathbf{S}(q) \quad (46)$$

where the  $n \times n$  static structure matrix is to be calculated using eq 18 or equivalently eq 19. The  $n \times n$  first cumulant matrix  $\Omega(q) = k_B T q^2 \mathbf{m}(q) \mathbf{S}^{-1}(q)$  in eq 46 is evaluated by calculating the mobility matrix  $\mathbf{m}(q)$  from eq 29. The measured dynamic scattering function  $S_{AA}(q, t)$  contains  $n$  modes with relaxation frequencies  $\lambda_j(q)$ ,  $j = 1, \dots, n$ , which are the eigenvalues of  $\Omega(q)$ . In an incompressible mixture the total monomer density fluctuations, whose

relaxation is mediated by cooperative diffusion, vanish. Since the cooperative diffusion is not a pure normal mode of the mixture in general, the reduction in the number of modes from  $n + 1$  to  $n$  does not correspond to a simple deletion of one of the modes in the absence of incompressibility. The latter affects all the relaxation frequencies of the system.

In the calculation of the bare system mobilities and static structure factors in eqs 40–42 and 37–39, all the monomer–monomer interactions, except for those maintaining chain connectivities, are included in  $W_{\alpha\beta}(q)$ , so that the bare system consists of noninteracting Gaussian chains. Repetition is not taken into account explicitly in these calculations. It is usually included in the framework of the RPA through the bare mobilities such as discussed by Binder.<sup>6</sup>

#### 4. Dynamics of Block-Copolymer Melts with Hydrodynamic Interactions

Dynamics of block-copolymer melts were studied earlier<sup>2</sup> via the RPA in the small- and intermediate- $q$  regions without including hydrodynamic interaction. In this section, we consider this problem and include hydrodynamic interactions using the extended formulation of the RPA developed in the previous sections, as well as the high- $q$  region. The latter extension is needed in the interpretation of neutron spin-echo experiments. For simplicity, we consider symmetrical copolymers so that both the statistical segment lengths and the polymerization indices of the A and B blocks are the same, i.e.,  $p_a = p_b = p$  and  $\alpha_a = \alpha_b = \alpha = (qa)^2/6$ . Also  $N_a = N_b = N$ , where  $N$  is the total number of A or B monomers in the system. One can verify from eqs 40 and 42 that  $P_{ab} = 2P_T(q) - P_{1/2}(q)$ , where we have introduced  $P_T(q) = P(2p, \alpha)$  and  $P_{1/2}(q) = P(p, \alpha)$ , which are the static structure factors of a full Gaussian and a half-Gaussian chains, respectively. The static structure factor follows from eq 19 directly as  $S(q) = Np/Q(q)$ , where the thermodynamic factor  $Q(q)$  is defined by

$$Q(q) = \frac{1 - p\chi^F [P_{1/2}(q) - P_T(q)]}{P_{1/2}(q) - P_T(q)} \quad (47)$$

where we redefined the Flory interaction parameter to absorb  $2N$  so that now  $\chi^F$  is per segmental volume  $v_0 = V/2N$ . In eq 47, the expression of  $P_{1/2}(q)$  follows from eq 40 as

$$P_{1/2}(q) = \frac{1}{p} \left\{ 1 + \frac{2}{e^\alpha - 1} \left[ 1 - \frac{1 - e^{-p\alpha}}{p - e^{-\alpha}} \right] \right\} \quad (48)$$

with  $\alpha = q^2 a^2/6$ . The expression of  $P_T(q)$  is obtained by replacing  $p$  in eq 48 by  $2p$ . The above expression of  $S(q)$  reduces to eq 32 of ref 2, when  $P_{1/2}(q)$  and  $P_T(q)$  are replaced by the Debye function.

The calculation of the mobility  $m(q) = m_{aa}(q) = m_{bb}(q)$  in the interacting system in terms of the bare system mobilities is simplified in the case of symmetric copolymers because in this case  $m_{aa}^0(q) = m_{bb}^0(q)$ . From eq 29, one obtains  $m(q) = [m_{aa}^0(q) - m_{ab}^0(q)]/2$ . The expressions of  $m_{aa}^0(q)$  and  $m_{ab}^0(q)$  are given in eqs 37 and 38 with the modification  $N_a = N$  and  $\xi_a = \xi_b = \xi$ . Using  $P_{ab} = 2P_T(q) - P_{1/2}(q)$  in eq 38 and calculating the first cumulant  $\Gamma(q)$

Table I. Asymptotic Behavior of Various Quantities as a Function of  $q$

	small $q$ ( $qR_{gT} \ll 1$ )	intermediate $q$ ( $qR_{gT} \gg 1, qa \ll 1$ )	large $q$ ( $qa \gg 1$ )
$P_{1/2}(q)$	1	$12/(q^2 p a^2)$	$1/p$
$P_{1/2}(q) - P_T(q)$	$qR_{gT}/6$	$6/(q^2 p a^2)$	$1/(2p)$
$\Gamma_{1/2}^s(q)/q^2$	$D_{1/2}^s$	$(k_B T/16)(q/\eta)$	$k_B T/\xi$

$= \Gamma_{aa}(q) = \Gamma_{bb}(q)$  from eq 45, one finds

$$\frac{\Gamma(q)}{q^2 k_B T} = \left\{ \frac{1}{2p\xi} + \frac{1}{4\pi^2 \eta} \int_0^\infty dk Z(k/q) \left[ P_{1/2}(k) - P_T(k) - \frac{1}{2p} \right] \right\} Q(q) \quad (49)$$

which is also one of the contributions of this work. This equation can be cast to a more compact form as

$$\Gamma(q) = \{P_{1/2}(q)\Gamma_{1/2}^S(q) - P_T(q)\Gamma_T^S(q)\}Q(q) \quad (50)$$

where  $\Gamma_{1/2}^S(q)$  and  $\Gamma_T^S(q)$  are the half and full single-chain first cumulants, respectively, defined by

$$\Gamma_{1/2}^S(q) = q^2 k_B T \frac{1}{P_{1/2}(q)} \left\{ \frac{1}{p\xi} + \frac{1}{4\pi^2 \eta} \int_0^\infty dk Z(k/q) \left[ P_{1/2}(q) - \frac{1}{p} \right] \right\} \quad (51)$$

The advantage of the form in eq 50 is that the variations of the single-chain first cumulant are known and well documented. The asymptotic behavior of  $\Gamma(q)$  in various  $q$  regions can therefore be investigated easily in terms of the asymptotic expressions of  $\Gamma_{1/2}^S(q)$  and  $\Gamma_T^S(q)$ , as well as of those of  $P_{1/2}(q)$  and  $P_T(q)$ , which are presented in Table I.

In the small- $q$  region one finds

$$\Gamma(q \rightarrow 0) = \frac{6}{R_{gT}^2} [D_{1/2}^S - D_T^S] \quad (52)$$

where  $D_{1/2}^S$  is the translational diffusion coefficient of a single chain with a polymerization index  $p$  in a fluid with viscosity  $\eta$ , including hydrodynamic interaction:

$$D_{1/2}^S = k_B T \left\{ \frac{1}{p\xi} + \frac{1}{3\pi^2 \eta} \int_0^\infty dk \left[ P_{1/2}(k) - \frac{1}{p} \right] \right\} \quad (53a)$$

where we have used  $Z(x \rightarrow 0) = 4/3$ . Upon performing the indicated integral, one finds the well-known Zimm expression of translational diffusion coefficient for a Gaussian chain:

$$D_{1/2}^S = k_B T \left\{ \frac{1}{p\xi} + \frac{8}{3\pi(6\pi)^{1/2}} \frac{1}{a\eta p^{1/2}} \right\} \quad (53b)$$

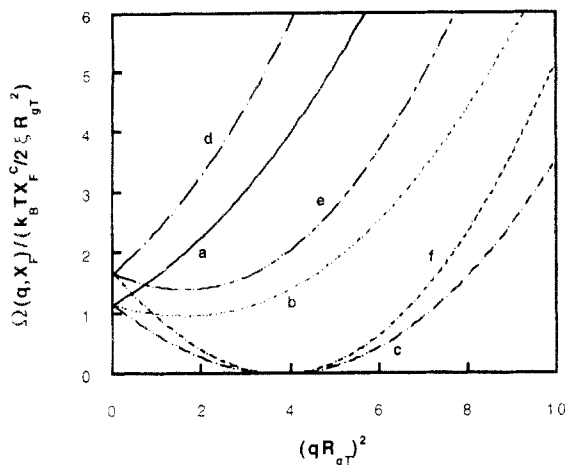
The constant frequency given in eq 52 corresponds to the structural mode characterizing the relaxation of the local inhomogeneities. Although it is related to the internal modes of the chain, it is sometimes loosely referred to as the interdiffusion coefficient. In the absence of hydrodynamic interaction, eq 52 reduces to  $3k_B T/p\xi R_{gT}^2$ , which is identical to eq 48 of ref 2.

In the intermediate- and high- $q$  regions one obtains

$$\Gamma(q) = \frac{1}{16} \frac{k_B T}{\eta} q^3 \left( 1 - 2\chi^F p \frac{1}{q^2 R_{gT}^2} \right), \quad \text{intermediate } q$$

$$= q^2 \frac{k_B T}{\xi} \left( 1 - \frac{1}{2}\chi^F \right), \quad \text{large } q \quad (54)$$

which are the same as the asymptotic behaviors of the first cumulant of a single chain in the presence of



**Figure 1.** Expected behavior of the first cumulant in copolymer melts as function of  $qR_{gT}^2$  when the Flory–Huggins interaction parameter  $X_F$  and the free draining parameter  $h^*$  are varied. Curves: (a)  $X_F/X_F^c = 0.0$ ,  $h^* = 0$ ; (b)  $X_F/X_F^c = 0.65$ ,  $h^* = 0$ ; (c)  $X_F/X_F^c = 1.0$ ,  $h^* = 0$ ; (d)  $X_F/X_F^c = 0.0$ ,  $h^* = 0.29$ ; (e)  $X_F/X_F^c = 0.65$ ,  $h^* = 0.29$ ; (f)  $X_F/X_F^c = 1.0$ ,  $h^* = 0.29$ .

hydrodynamic interactions. The additional factors represent the effect of interactions. Since  $p\chi^F \leq 5$  (see below) in the one-phase region, where  $Q > 0$ , the deviation of these factors from unity is negligible in these  $q$  regions. They are added only to indicate the trends with the interaction parameter.

The variation of  $\Gamma(q)$  with  $q$  between the above asymptotic  $q$  regions has to be calculated numerically using its full expression given in eq 49, as we have done in Figure 1 for a few values of the interaction parameter. We normalized  $\Gamma(q)$  as

$$\frac{\Gamma(q)}{k_B T \chi_c^F / 2 \xi R_{gT}^2} = \kappa \left[ \frac{1}{\eta(\kappa)} - \frac{\chi_c^F}{\chi_c^F} \right] \left[ 1 + \frac{3h^*}{(p\pi)^{1/2}} \int_0^\infty dx Z\left(\frac{x}{\kappa}\right) Y(x) \right] \quad (55)$$

where  $\kappa = q^2 R_{gT}^2$ ,  $\eta(\kappa) = [P_{1/2}(\kappa) - P_T(\kappa)] / [P_{1/2}(\kappa_c) - P_T(\kappa_c)]$ , and  $\chi_c^F = 1/p[P_{1/2}(\kappa_c) - P_T(\kappa_c)]$  is the critical value of the interaction parameter, at which  $Q(q)$  becomes zero (spinodal point) at a wavenumber  $\kappa_c$  that maximizes  $P_{1/2}(\kappa) - P_T(\kappa)$ . When the Debye forms of  $P_{1/2}(\kappa)$  and  $P_T(\kappa)$  are used, one finds<sup>2</sup>  $\kappa_c = 3.7984$  and  $[P_{1/2}(\kappa_c) - P_T(\kappa_c)] = 0.1906$ . With the full expression of  $P_{1/2}(\kappa)$  and  $P_T(\kappa)$ ,  $\kappa_c$  becomes slightly dependent on the chain length  $p$ . In eq 55,  $h^* = \xi/\eta a \pi (12\pi)^{1/2}$  is the usual draining parameter measuring the strength of the hydrodynamic interaction. The  $P_{1/2}(\kappa)$  and  $P_T(\kappa)$  are defined by

$$P_{1/2}(\kappa) = \frac{1}{p} \left\{ 1 + \frac{2}{e^{\kappa/2p} - 1} \left[ 1 - \frac{1 - e^{-\kappa/2}}{p(1 - e^{-\kappa/2p})} \right] \right\} \quad (56a)$$

$$P_T(\kappa) = \frac{1}{2p} \left\{ 1 + \frac{2}{e^{\kappa/2p} - 1} \left[ 1 - \frac{1 - e^{-\kappa}}{2p(1 - e^{-\kappa/2p})} \right] \right\} \quad (56b)$$

Since  $\kappa = q^2 R_{gT}^2$  is normalized with the radius of gyration of the full chain,  $P_T(\kappa)$  is not obtained from  $P_{1/2}(\kappa)$  by simply replacing  $p$  by  $2p$ . Finally,  $Y(x)$  in eq 55 denotes  $P_{1/2}(x) - P_T(x) - (1/2p)$ , or

$$Y(x) = \frac{e^{-x/2p}}{p(1 - e^{-x/2p})} \left\{ 1 - \frac{(1 - e^{-x/2})(3 - e^{-x/2})}{2p(1 - e^{-x/2p})} \right\} \quad (57)$$

Since  $Y(x \rightarrow \infty) = \exp(-x/2p)(1 - 3/2p)/p$ , the integration in eq 55 is convergent even though  $Z(x \rightarrow \infty) = 4/3$ . The

curves in Figure 1 are plotted with  $p = 100$  and  $h^* = 0.29$ . The latter corresponds approximately to the Flory value of 0.262 for the draining parameter in solution.<sup>14</sup> It is obtained treating statistical segments as a Gaussian chain and using preaveraged hydrodynamic interaction. This procedure may be used also in polymer melts to calculate the ratio of the friction coefficient per segment to the viscosity of the polymer mixture, i.e.,  $\xi/\eta a$ , at least as a first guess. We consider  $h^*$  as an adjustable parameter to be determined experimentally. The values 0, 0.65, and 1.0 for  $\chi^F/\chi_c^F$  are chosen for comparison with the curves in Figure 3 of ref 2, which are plotted with these values in the absence of hydrodynamic interaction, i.e., with  $h^* = 0$ , and using the Debye forms for  $P_{1/2}(\kappa)$  and  $P_T(\kappa)$ . The effect of hydrodynamic interaction in various  $q$  regions is clearly observable in Figure 1. It would be interesting to check these theoretical predictions experimentally and to assess the importance of hydrodynamic interactions in the dynamics of polymer melts.

## 5. Conclusions

We have presented in this paper a new formulation of the random phase approximation for the study of statics and dynamics of multicomponent polymer melts. This formalism allows interaction and connectivity of the monomers of the matrix component, which is eliminated on the basis of incompressibility, with the monomers of the remaining components and, thus, is particularly suitable to the study of melts of copolymers, stars, etc. The new elimination procedure used in this formalism elucidates the relationship between the Flory interaction parameters and the interaction potentials between monomer pairs, which is treated perturbatively, and enables one to include the effect of hydrodynamic interactions among the monomers in the study of dynamics of polymer melts. Hydrodynamic interactions were introduced earlier by Fredrickson<sup>15</sup> in the description of the dynamics of polymer mixtures by taking into account the coupling between the density and momentum fluctuations. The hydrodynamic interactions in Fredrickson's formulation enter in the functional Fokker–Planck equation for the distribution function of the order parameter, through the Oseen tensor with a renormalized macroscopic viscosity. The explicit results obtained in this paper for the first cumulant can also be obtained starting from this Fokker–Planck equation. Therefore, the viscosity of the mixture appearing in the results of this paper should also be interpreted as a renormalized macroscopic viscosity. The latter concept has also been introduced recently by Roby and Joanny<sup>16</sup> into dynamics of concentrated ternary polymer solutions.

Dynamics of copolymer melts with hydrodynamic interaction is presented in detail as an illustration of the new formalism, and the variation of the first cumulant is calculated with and without hydrodynamic interaction as a function of the wavenumber and interaction parameter. The effect of the hydrodynamic interaction is expressed in terms of a “free draining” parameter, as in the case of polymer solutions. Although hydrodynamic interactions are not expected to play a dominant role in the dynamics of polymer melts, the analytical results obtained in this paper may be used to assess their effect in the case of copolymer melts.

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**Appendix A. Inverse of a Block Matrix**

It can easily be verified that

$$\begin{bmatrix} \mathbf{A} & \mathbf{b} \\ \mathbf{b}^T & c \end{bmatrix}^{-1} = \begin{bmatrix} \mathbf{M} & \mathbf{n} \\ \mathbf{n}^T & m \end{bmatrix}$$

where  $\mathbf{A}$  is symmetric and  $\mathbf{M}$ ,  $\mathbf{n}$ , and  $m$  are

$$\begin{aligned} \mathbf{M}^{-1} &= \mathbf{A} - \frac{1}{c} \mathbf{b} \mathbf{b}^T \\ \mathbf{M} &= \mathbf{A}^{-1} + m \mathbf{A}^{-1} \mathbf{b} \mathbf{b}^T \mathbf{A}^{-1} \\ \mathbf{n} &= -m \mathbf{A}^{-1} \mathbf{b} \\ m &= \frac{1}{c - \mathbf{b}^T \mathbf{A}^{-1} \mathbf{b}} \end{aligned} \quad (\text{A1})$$

Equation A1 is known as the Sherman–Morrison formula.<sup>17</sup>

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