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Theory of Dynamic Scattering from Neutral and Weakly Charged Copolymers in Solution

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ABSTRACT: The dynamic scattering properties of neutral and weakly charged copolymers in solution are investigated. Symmetric diblocks are considered, and the physical meaning of various relaxation modes are discussed. It is shown that the two eigenmodes obtained in this case can be interpreted as the cooperative and interdiffusive modes even if the two blocks have a strong interaction, either of pure thermodynamic nature or of long-range electrostatic nature. In the case where one block is charged and the second neutral, the symmetry relationship leading to this simple interpretation is not valid but the modes retain qualitative similarities with the cooperative and interdiffusive processes. The analogy between copolymers and polyelectrolytes is also discussed. It is shown that the two effects are different and lead to different behaviors when changing the strengths of the electrostatic and thermodynamic interactions.

1. Introduction

To our knowledge, the efforts made to understand the dynamics of copolymers in solution are still insufficient. This is true at least if one compares it with the large attention paid to mixtures of homopolymers. A large body of experimental data[1-6] and theoretical models[7-10] describing the dynamics of mixtures of homopolymers is available, and, therefore, a good level of understanding of these properties has now been reached. It would be useful to see how these properties are modified if one introduces a mismatched composition within the chains and deals with copolymers. Few attempts in this direction were made for neutral polymers, and preliminary experiments have revealed interesting tendencies[11-13] which are not yet definitely understood. Therefore, more efforts are still needed to elucidate the dynamics of copolymers in solution from both theoretical and experimental points of view. This paper is an attempt in this direction where we examine some theoretical aspects of dynamic scattering from both neutral and weakly charged copolymers in solution. We consider only symmetric diblocks because of the important simplifications of the final results which help us to understand better the physical mechanisms underlying the dynamics of our systems. The identification of the eigenmodes characterizing the time evolution of various dynamical correlation functions is more apparent in the symmetrical case as suggested by Pusey et al.[9] and Akcasu et al.[7] This question of the identification of the modes is an important aspect of our discussions in this paper.

Of course, one of the main objectives of this paper is to discuss the effects of long-range electrostatic interactions on the dynamics of copolymers. Examples of these copolyelectrolytes are numerous and so are their applications. They can be encountered in various industrial activities, biology, medicine, etc. Amphiphilic molecules with a hydrophobic charged head and a hydrophilic neutral tail are a particular example of a copolyelectrolyte. Another example is given by polyampholyte molecules which contain both positively and negatively charged ions. Amphiphilic molecules in aqueous solutions were studied essentially above the critical micelle concentration where they form micelles, whereas polyampholyte molecules present interesting features due in particular to their special conformations which, under certain conditions, undergo a coil–globule transition.[14]

The present work is concerned with weakly charged copolymers that are dispersed to form a homogeneous solution. We assume that no complexes or superstructures such as micelles or aggregates are formed.

The time evolution of several dynamical correlation functions is considered. A special interest is focused on the variations of their relaxation frequencies with the wavenumber q. For a copolymer made of two monomer species in solution, it has been shown that all dynamic correlation functions evolve in time following a two-exponential function[7,15] with a different relative amplitude. The inverse characteristic relaxation times of these two exponentials are given by the eigenfrequencies Γ and Γ'. In addition to these two, other mean frequencies are also examined. Before introducing them, we note that the dynamic scattering function $S(q,t)$ which is directly measurable in the scattering experiments (neutron spin-echo or quasi-elastic light scattering) is defined quite generally in terms of the scattering lengths (neutron) or increments of refractive indices (light) which we denote in either case to be b_1 and b_2 and the partial dynamic structure factors $S_{ij}(q,t)$ as follows:

$$S(q,t) = b_1^2 S_{11}(q,t) + b_2^2 S_{22}(q,t) + b_1 b_2 [S_{12}(q,t) + S_{21}(q,t)] \quad (1)$$

The following experimental conditions may be considered:

(a) Only component 1 contributes to the scattering of radiation; this means that $b_2 = 0$, and one measures only $S_{11}(q,t)$. This function decays as

$$S_{11}(q,t) = a_{11} e^{-\Gamma t} + a'_{11} e^{-\Gamma' t} \quad (2)$$

Its initial slope is a weighted average of Γ and Γ' with respect to the amplitudes as shown by the definition

$$\Gamma_{11} = -\lim_{t \to 0} \frac{\partial}{\partial t} \log S_{11}(q,t) = \frac{a_{11}\Gamma + a'_{11}\Gamma'}{a_{11} + a'_{11}} \quad (3)$$

It is worth noting that $S_{11}(q,t)$ describes the relaxation in

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time of the density fluctuations of monomer 1:

$$S_{11}(q,t) = \langle \rho_1(q,t)\, \rho_1(-q) \rangle \tag{4}$$

The density $\rho(-q)$ without the time argument means that it is taken at $t = 0$.

(b) The scattering lengths or refractive indices of both polymers are equal, $b_1 = b_2$, and the measured $S(q,t)$ will be proportional to $S_T(q,t)$, the total dynamic correlation function:

$$S_T(q,t) = S_{11}(q,t) + S_{22}(q,t) + S_{12}(q,t) + S_{21}(q,t) \tag{5a}$$

We have written explicitly $S_{12}(q,t)$ and $S_{21}(q,t)$ separately to account for the possibility that these two dynamical functions may be different.

One sees that $S_T(q,t)$ represents the time correlation function of the total monomer density

$$\rho_T(q,t) = \rho_1(q,t) + \rho_2(q,t) \tag{5b}$$

and hence

$$S_T(q,t) = \langle \rho_T(q,t)\, \rho_T(-q) \rangle \tag{5c}$$

It can be shown that in general this function decays following a biexponential function:[15]

$$S_T(q,t) = a_T e^{-\Gamma t} + a'_T e^{-\Gamma' t} \tag{6}$$

Its initial slope Γ_T is the other mean frequency which will be studied in this paper. It is defined by

$$\Gamma_T = -\lim_{t \to 0} \frac{\partial}{\partial t} \log S_T(q,t) = \frac{a_T \Gamma + a'_T \Gamma'}{a_T + a'_T} \tag{7}$$

(c) The third experimental situation which will be invoked here corresponds to the case where the average scattering length (or average refractive index increment) is zero. It is sometimes loosely referred to as the "optical theta condition",[16] but we shall not use this terminology here. The zero average scattering length is expressed as

$$\phi_1 b_1 + \phi_2 b_2 = 0 \tag{8a}$$

or

$$x b_1 + (1 - x) b_2 = 0 \tag{8b}$$

where ϕ_1 and ϕ_2 are the concentrations in polymers 1 and 2, respectively; x is the composition of 1.

$$x = \phi_1/(\phi_1 + \phi_2) = N_1/(N_1 + N_2) \tag{9}$$

N_1 is the degree of polymerization of block 1 and $N \equiv N_1 + N_2$ the total degree of polymerization. For our symmetric diblock, we have $x = 1/2$. Substituting this condition into eq 1 yields

$$S(q,t) = b_1^{\,2} x^2 S_I(q,t) \tag{10a}$$

where $S_I(q,t)$, which we shall call the intermediate dynamic scattering function, is defined by

$$S_I(q,t) = \frac{S_{11}(q,t)}{x^2} + \frac{S_{22}(q,t)}{(1-x)^2} - \frac{S_{12}(q,t) + S_{12}(q,t)}{x(1-x)} \tag{10b}$$

This correlation function describes the time relaxation of the fluctuations in the quantity

$$\rho_I(q,t) = \rho_1(q,t)/x - \rho_2(q,t)/(1-x) \tag{10c}$$

which is commonly used as the order parameter in describing the microphase separation in copolymers and the kinetics of macrophase separation in blends.[17,18] One can show that

$$S_I(q,t) = \langle \rho_I(q,t)\, \rho_I(-q) \rangle \tag{10d}$$

and its relaxation in time is in general as follows:

$$S_I(q,t) = a_I e^{-\Gamma t} + a'_I e^{-\Gamma' t} \tag{11}$$

This work will also focus on the initial slope of this correlation function which is given by

$$\Gamma_I = -\lim_{t \to 0} \frac{\partial}{\partial t} \log S_I(q,t) = \frac{a_I \Gamma + a'_I \Gamma'}{a_I + a'_I} \tag{12}$$

The general formalism used as the basis for this investigation is summarized in section 2 where both dynamic and static properties are briefly reviewed. The application to a symmetric diblock is presented in section 3. The variations of the relaxation frequencies with the wavenumber q are examined in various cases of charge distributions including the neutral limit. We consider in particular the cases where monomers 1 and 2 are similarly charged, oppositely charged, or one is charged and the other is neutral.

2. General Formalism

The dynamic correlation matrix $\mathbf{S}(q,t)$ is known to satisfy the generalized Langevin equation[7]

$$\frac{\partial}{\partial t} \mathbf{S}(q,t) + \boldsymbol{\Omega} \cdot \mathbf{S}(q,t) - \int_0^t \mathrm{d}u\, \boldsymbol{\phi}(q,t-u)\, \mathbf{S}(q,u) = 0 \tag{13}$$

where $\boldsymbol{\Omega}$ is the first cumulant or initial slope of the matrix $\mathbf{S}(q,t)$, i.e.

$$\boldsymbol{\Omega} = -\lim_{t \to 0} \frac{\partial}{\partial t} \log \mathbf{S}(q,t) \tag{14}$$

and $\boldsymbol{\phi}(q,t)$ is the memory matrix. Since it is extremely difficult to calculate the memory term, we shall simply delete it and assume that the initial decay of $\mathbf{S}(q,t)$ is sufficient to characterize the dynamical properties of interest to us in this work. Therefore, the approximate solution of eq 13 without memory is

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

where $\mathbf{S}(q)$ is the static structure matrix

$$\mathbf{S}(q) = \mathbf{S}(q,t{=}0) \tag{16}$$

and $\boldsymbol{\Omega}$ can be written in terms of the structure matrix $\mathbf{S}(q)$ and the mobility matrix $\mathbf{M}(q)$ as

$$\boldsymbol{\Omega} = q^2 kT \mathbf{M}(q)\, \mathbf{S}^{-1}(q) \tag{17}$$

In the Rouse limit, $\mathbf{M}(q)$ has a simple form: All its elements are zero except the diagonal one which is equal to $M_i^{\,0} = \phi_i/\xi_i$, where ϕ_i and ξ_i denote the concentration and monomeric friction coefficient of species i, respectively. One observes that the short-time dynamics or first cumulant $\boldsymbol{\Omega}$ are completely determined by the knowledge of the static structure matrix $\mathbf{S}(q)$. The main properties of this matrix can be summarized as follows:

$\mathbf{S}(q)$ is given by an extension of the celebrated Zimm's formula which is written in the matrix form when dealing with a multicomponent polymer system.[7,19,20]

$$\mathbf{S}^{-1}(q) = \mathbf{S}_0^{\,-1}(q) + \mathbf{U} \tag{18}$$

For neutral polymers, the interaction matrix $\mathbf{U}$ coincides with the excluded-volume matrix $\mathbf{v}$. If monomers are charged, the matrix $\mathbf{U}$ becomes q-dependent because it includes the long-range electrostatic interactions. If this interaction is modeled by the Debye–Hückel potential, $\mathbf{U}$

becomes[21]

$$\mathbf{U} = \mathbf{v} + \alpha(q)\,\mathbf{F} \tag{19a}$$

where

$$\alpha(q) = \frac{4\pi l}{q^2 + k^2} \tag{19b}$$

and the elements of the square matrix **F** are

$$F_{ij} = \epsilon_{ij} f_i f_j \tag{19c}$$

f_i is the valence of the ion carried by monomer i, $\epsilon_{ij} = +1$ if charges i and j have the same sign and -1 otherwise; l is the Bjerrum length $l \equiv e^2/\epsilon kT$ where e is the electron charge, ϵ the dielectric constant, k the Boltzmann factor, and T the absolute temperature (e.g., for water at 15 °C, $l = 7$ Å). The Debye–Hückel screening length k^{-1} is defined by

$$k^2 = 4\pi l[\sum_i f_i\phi_i + \phi_{\text{salt}}] \tag{20}$$

where ϕ_{salt} is the salt concentration and includes both the concentration of counterions and co-ions (it is sometimes denoted by $2\phi_s$ for a 1:1 electrolyte, designating by ϕ_s the concentration of counterions only). The concentration of counterions of species i due to the polymer ionization is ϕ_{ci} and is equal to $\phi_i f_i$ because of the global electroneutrality condition. Furthermore, we assume that these counterions and eventually salt ions are pointlike particles and their role is limited to the screening of electrostatic interactions. This means that they have no specific contribution to the dynamical or to the structural properties of the system. This is an important simplification since it reduces the order of the matrices by one rank for each ionic species. However, should the small ions be included as full scattering components in this description, it would be a straightforward task to fulfill this requirement, but the algebra becomes tedious when one treats particular examples.

3. Case of a Symmetric Diblock Copolymer

It was shown starting from eq 15 that for a copolymer made of two monomer species in solution[8] the partial dynamical correlation functions $S_{ij}(q,t)$ decay following the biexponential function

$$S_{ij}(q,t) = a_{ij}e^{-\Gamma t} + a'_{ij}e^{-\Gamma' t} \tag{21}$$

where $S_{ij}(q,t)$ are the elements of the matrix $\mathbf{S}(q,t)$, Γ and Γ' are the eigenvalues of Ω, and the amplitudes a_{ij} and a'_{ij} can be expressed in general in terms of the elements of Ω and **S**. We shall be concerned here with the relaxation frequencies and will not discuss in detail the amplitudes. But the general expressions of a_{ij} and a'_{ij} are available and can also be examined without particular difficulty. The eigenvalues Γ and Γ' are defined by

$$\Gamma,\Gamma' = \Omega_{\text{av}} \pm [\Omega_{\text{av}}^2 - \Delta(\Omega)]^{1/2} \tag{22a}$$

with

$$\Omega_{\text{av}} = \frac{\Omega_{11} + \Omega_{22}}{2};\quad \Delta(\Omega) = \Omega_{11}\Omega_{22} - \Omega_{12}\Omega_{21} \tag{22b}$$

For a symmetric diblock, the matrix Ω reduces to

$$\Omega = q^2 D_0 \frac{\phi N}{2\Delta S}\begin{pmatrix} S_{11} & -S_{12} \\ -S_{12} & S_{22} \end{pmatrix} \tag{23}$$

where $\Delta S = S_{11}S_{22} - S_{12}^2$ and we have assumed that the monomer friction coefficients ξ_1 and ξ_2 are equal to ξ, and we introduced the Rouse diffusion coefficient

$$D_0 = kT/N\xi \tag{24}$$

Combining eqs 18 and 19, one can obtain the static structure factors $S_{ij}(q)$ as

$$\left(\frac{\phi N}{4}\right)^{-1}\mathcal{D}(q)\cdot S_{11}(q) = P_{1/2} + [v + \alpha(q) f_2^2]\phi N P_{\text{T}}(P_{1/2} - P_{\text{T}}) \tag{25}$$

$$\left(\frac{\phi N}{4}\right)^{-1}\mathcal{D}(q)\cdot S_{22}(q) = P_{1/2} + [v + \alpha(q) f_1^2]\phi N P_{\text{T}}(P_{1/2} - P_{\text{T}}) \tag{26}$$

$$\left(\frac{\phi N}{4}\right)^{-1}\mathcal{D}(q)\cdot S_{12}(q) = P_{12} - [v + \chi + \alpha(q)\epsilon f_1 f_2]\phi N P_{\text{T}}(P_{1/2} - P_{\text{T}}) \tag{27}$$

The common factor $\mathcal{D}(q)$ can be written as a sum of a neutral and an electrostatic part

$$\mathcal{D}(q) = \mathcal{D}_{\text{neutral}}(q) + \mathcal{D}_{\text{electrost}}(q) \tag{28a}$$

where the neutral part can be written in the factorized form

$$\mathcal{D}_{\text{neutral}}(q) = \left[1 - \frac{\chi}{2}\phi N(P_{1/2} - P_{\text{T}})\right]\left[1 + \left(v + \frac{\chi}{2}\right)\phi N P_{\text{T}}\right] \tag{28b}$$

and the electrostatic part is

$$\mathcal{D}_{\text{electrost}}(q) = \alpha(q)\,\phi N\left\{P_{1/2}\left(\frac{f_1 - \epsilon f_2}{2}\right)^2 + \epsilon f_1 f_2 P_{\text{T}} + v_{\text{e}}\phi N P_{\text{T}}(P_{1/2} - P_{\text{T}})\right\} \tag{29a}$$

and

$$v_{\text{e}} = v\left(\frac{f_1 - \epsilon f_2}{2}\right)^2 - \frac{\chi}{2}\epsilon f_1 f_2 \tag{29b}$$

In writing these results, we have used the standard notation which we briefly recall here: $P_{1/2}(q)$ and $P_{\text{T}}(q)$ are the form factors of a half-chain (i.e., one block) and the total chain, respectively; $P_{12}(q)$ is related to them by

$$2P_{\text{T}} = P_{1/2} + P_{12} \tag{29c}$$

We shall remove the q argument from all these quantities for convenience. Furthermore the excluded-volume parameters are assumed to satisfy the relationship

$$v_{11} = v_{22} = v;\quad v_{12} = v + \chi \tag{30}$$

which implies that the quality of solvent is the same for both monomers or that the interaction parameters between the polymers and the solvent are the same for both species; i.e., $\chi_{1S} = \chi_{2S}$. These two polymer species have a certain degree of incompatibility characterized by the interaction parameter χ which in the present case has a dimension of volume.[22] Substituting eqs 23 and 29 into eq 22 yields

$$\frac{\Gamma,\Gamma'}{q^2 D_0} = \frac{N\phi}{4\Delta S}\{S_{11} + S_{22} \pm [(S_{11} - S_{22})^2 + 4S_{12}^2]^{1/2}\} \tag{31}$$

The mean frequencies introduced earlier can also be expressed in terms of the static structure factors only. One can show, using the general expressions of a_{ij} in terms of S_{ij} and Ω_{ij} that these frequencies reduce to very simple forms.[7,8] We have from eq 3

$$\Gamma_{11}/q^2D_0 = \phi N/2S_{11}(q) \tag{32a}$$

where

$$S_{11}(q) = a_{11} + a'_{11} \tag{32b}$$

The total relaxation frequency Γ_T is given by eq 7 which can be reduced to the simple form

$$\Gamma_T/q^2D_0 = \phi N/S_T(q) \tag{33a}$$

where we have used

$$S_T(q) = a_T + a'_T \tag{33b}$$

Furthermore, noting that

$$S_T(q) = S_{11} + S_{22} + 2S_{12} \tag{33c}$$

and using eqs 25–29, one can write explicitly Γ_T as

$$\Gamma_T/q^2D_0 = \frac{\mathcal{D}(q)}{P_T\left\{1 - \left[\frac{\chi}{2} - \alpha\left(\frac{f_1 - \epsilon f_2}{2}\right)^2\right]\phi N(P_{1/2} - P_T)\right\}} \tag{34}$$

where the quantity $\mathcal{D}(q)$ is defined in eq 29.

The intermediate relaxation frequency Γ_I is defined in eq 12 and can be simplified as

$$\Gamma_I/q^2D_0 = 4\phi N/S_I(q) \tag{35a}$$

where we have used

$$S_I = a_I + a'_I = 4[S_{11} + S_{22} - 2S_{12}] \tag{35b}$$

The latter relaxation frequency can also be written explicitly if one uses eqs 25–29:

$$\Gamma_I/q^2D_0 = \frac{\mathcal{D}(q)}{(P_{1/2} - P_T)\left\{1 + P_T\left[\upsilon + \frac{\chi}{2} + \alpha\left(\frac{f_1 + \epsilon f_2}{2}\right)^2\right]\phi N\right\}} \tag{36}$$

We shall examine the variations of these frequencies with the wavenumber q in several cases of charge distributions. The first case to be studied is the neutral copolymer limit because it is not sufficiently known and is useful in identifying the effects of long-range Coulombic interactions and understanding the analogy between the copolymer effects and the polyelectrolyte effects which was mentioned by several authors[7,23] before.

3.1. Neutral Copolymer. The partial structure factors $S_{ij}(q)$ are obtained in this limit by letting $f_1 = f_2 = 0$ in eqs 25–29

$$S_{11} = S_{22} = S(q) = \frac{\phi N}{4}\frac{P_{1/2} + \upsilon\phi NP_T(P_{1/2} - P_T)}{\mathcal{D}_{\text{neutral}}(q)} \tag{37}$$

$$S_{12} = S_{21} = S'(q) = \frac{\phi N}{4}\frac{P_{12} - (\upsilon + \chi)\phi NP_T(P_{1/2} - P_T)}{\mathcal{D}_{\text{neutral}}(q)} \tag{38}$$

where the neutral denominator $\mathcal{D}_{\text{neutral}}(q)$ is given by eq 28b. The fact that $S_{11} = S_{22}$ results in important simplifications of the relaxation frequencies since, as shown by eq 31, the square root is equal to $2S_{12}(q) = 2S'(q)$, and, therefore, it is removed. This leads to the exact results:

$$\Gamma/q^2D_0 = N\phi/2(S - S') \tag{39}$$

$$\Gamma'/q^2D_0 = N\phi/2(S + S') \tag{40}$$

The interesting thing about these results is that they can be identified exactly with the mean frequencies Γ_I and Γ_T. Indeed, one can easily check that the structure factors $S_T(q)$ and $S_I(q)$ defined by eqs 33c and 35b become

$$S_T(q) = 2(S + S') \tag{41}$$

$$S_I(q) = 8(S - S') \tag{42}$$

Substituting these expressions into eqs 33a and 35a, one finds that

$$\Gamma \equiv \Gamma_I \tag{43}$$

$$\Gamma' \equiv \Gamma_T \tag{44}$$

This was already pointed out by Akcasu et al., but they concluded that $\Gamma = \Gamma_I$ and $\Gamma' = \Gamma_T$ *only* if the two blocks are identical *except* for their difference in the scattering lengths or the refractive indices. This was also the conclusion reached by Pusey et al.[9a] and Davies et al.[9b] on the basis of similar arguments. But the latter authors considered either mixtures of hard spheres[9a] or mixtures of Dextran molecules[9b] of different sizes. Here, we show that the identities in eqs 43 and 44 remain valid even if the two species are thermodynamically different by having an important interaction parameter χ. Indeed, combining eqs 37–40 and 28b, one arrives at the simple results:

$$(\Gamma, \Gamma_I)/q^2D_0 = 1/(P_{1/2} - P_T) - \chi\phi N/2 \tag{45}$$

$$(\Gamma', \Gamma_T)/q^2D_0 = 1/P_T + (\upsilon + \chi/2)\phi N \tag{46}$$

This means that these equations can be extended to ternary mixtures made of two different polymers and a solvent. Examples of such systems are PS–PMMA–solvent or PS–PDMS–solvent. Since these systems are extensively investigated by quasi-elastic light scattering,[3,5,6] the identification of Γ with Γ_I and Γ' with Γ_T can be extended to such experiments provided that the symmetry condition defined in eq 37 is fulfilled. In fact, we will show in later parts of this section that this identification remains valid for similarly and oppositely charged monomers where the interactions between species are not only much stronger but also long ranged. Note that in the literature mode I is called the *interdiffusive* mode and mode T the *cooperative* mode, and hence we shall use this terminology hereafter. Furthermore, unlike the case of homopolymers, the interdiffusive mode is essentially a *local* mode which results from the fact that the two polymer species are linked together by a chemical bond. As a consequence, the interdiffusive mode can be faster than the cooperative mode in a certain range of wavenumbers q and polymer concentrations ϕ. This behavior is in contrast with the case of homopolymers where the interdiffusive mode was found to be slower at all concentrations. The latter process is controlled by the *center of mass diffusion* and eventually by *reptation* if the conditions of this process are fulfilled.

It is also interesting to note that in the conditions where the symmetry relationship of eq 37 is satisfied $S_T(q,t)$ and $S_I(q,t)$ evolve in time following single-exponential functions, i.e.

$$S_T(q,t) = S_T(q)e^{-\Gamma_T t} \tag{46a}$$

and

$$S_I(q,t) = S_I(q)e^{-\Gamma_I t} \tag{46b}$$

This means that the amplitudes a_T and a'_I are zero. To illustrate the effects of concentration ϕ and interaction parameter χ on the frequencies defined above, we have plotted in parts a and b of Figure 1 the variations of $(\Gamma = \Gamma_I)/q^2D_0$ and $(\Gamma' = \Gamma_T)/q^2D_0$ as a function of qR_g for several values of the concentration and the interaction parameter, where R_g denotes the radius of gyration of the total polymer chain. Figure 1a represents the normalized interdiffusion frequency (or coefficient) as defined by eq 45. It shows that, for a small value of χ (i.e., $\chi = 0.1\upsilon$), the effect of concentration is weak. The curves corresponding to $\chi = 0.1\upsilon$ and high concentrations (i.e., $\upsilon\phi N = 5, 10$) are practically superimposed with curve 1 ($\upsilon\phi N = 1$). This is expected from eq 45 which shows that, if $\chi = 0$, the frequency $\Gamma_I = \Gamma$ is independent of the concentration. When the interaction parameter increases, the effect of concentration becomes more significant and one reaches a threshold limit at a wavenumber q_m where $\Gamma = \Gamma_I = 0$. This means that the fluctuations corresponding to scales on the order of q_m relax extremely slowly. Above this critical threshold, the system undergoes a microphase separation which is beyond the scope of the present work.[24,25] Figure 1b shows that $\Gamma' = \Gamma_T$ is quite sensitive to both the concentration and the interaction parameter, and this is of course expected as seen from eq 46. The following observations can also be made by comparison of the latter two figures. For small concentrations, essentially below the overlap concentration ϕ^* corresponding roughly to $\upsilon\phi^*N = 1$, if one assumes that υ is independent of ϕ, $(\Gamma = \Gamma_I)/q^2D_0$ is found to be larger than $(\Gamma' = \Gamma_T)/q^2D_0$ at any qR_g. This means that, unlike the homopolymer case, the interdiffusive mode is *faster* than the cooperative mode. When the concentration increases, one observes that, for high q's (i.e., $qR_g > 1$), the cooperative mode is increasingly faster as χ becomes larger. This can be understood by recalling that the cooperative mode reflects the total concentration fluctuations of length scales on the order of ξ (i.e., the concentration correlation length not to be confused with the monomer friction coefficient) which can be much shorter than R_g when ϕ increases. However, in the low q range (i.e., $qR_g < 1$) $\Gamma = \Gamma_I$ increases dramatically, much faster than $\Gamma' = \Gamma_T$ due to the inverse of internal structure factor $(P_{1/2} - P_T)^{-1}$ which goes to infinity when $q \to 0$. One notes in passing that the value $\chi = 0.1\upsilon$ was estimated by Ould-Kaddour and Strazielle[26] using static light scattering experiments on the ternary mixture PS–PMMA–solvent where polymers have molecular weights of about one million in the vicinity of ϕ^*.

The mean frequency Γ_{11} can be obtained by substituting eq 37 into eq 32a:

$$\Gamma_{11}/2q^2D_0 = [1 - \chi\phi N(P_{1/2} - P_T)/2][1 + (\upsilon + \chi/2)\phi NP_T]/\{P_{1/2} + \upsilon\phi NP_T(P_{1/2} - P_T)\} \tag{47}$$

The factor 2 in the denominator of the left-hand side is due to the fact that the diffusion coefficient of each block is $2D_0$ in the free-draining limit. The variation of $\Gamma_{11}/2q^2D_0$ as a function of qR_g is plotted in Figure 1c for the same concentrations and interaction parameters as in Figure 1a,b. Curves 1–3 correspond to $\chi/\upsilon = 0.1$ and the three concentrations $\upsilon\phi N = 1$, 5, and 10, respectively. Curves a–c correspond to $\chi/\upsilon = 1$ and the same concentrations, respectively. One observes that, if the concentration and the interaction parameter are kept small ($\upsilon\phi N = 1$; $\chi = 0.1\upsilon$), the curve is practically monotonically increasing as in the case of $\Gamma' = \Gamma_T$ in Figure 1b. If one increases the polymer concentration keeping the interaction parameter small, the curves shift upward and a minimum appears and becomes more pronounced as ϕ increases. If both the concentration and the interaction parameter are increased, the curves intersect each other and the minimum becomes deeper but its position q_m does not change. Furthermore, one may reach a critical threshold at q_m where $\Gamma_{11} \approx 0$ as observed in Figure 1a. In these conditions Γ_{11} shows essentially the features of $\Gamma = \Gamma_I$; Γ_{11} being a weighted average of $\Gamma = \Gamma_I$ and $\Gamma' = \Gamma_T$, it is reasonable to expect the identification of properties of both frequencies in its q dependence.

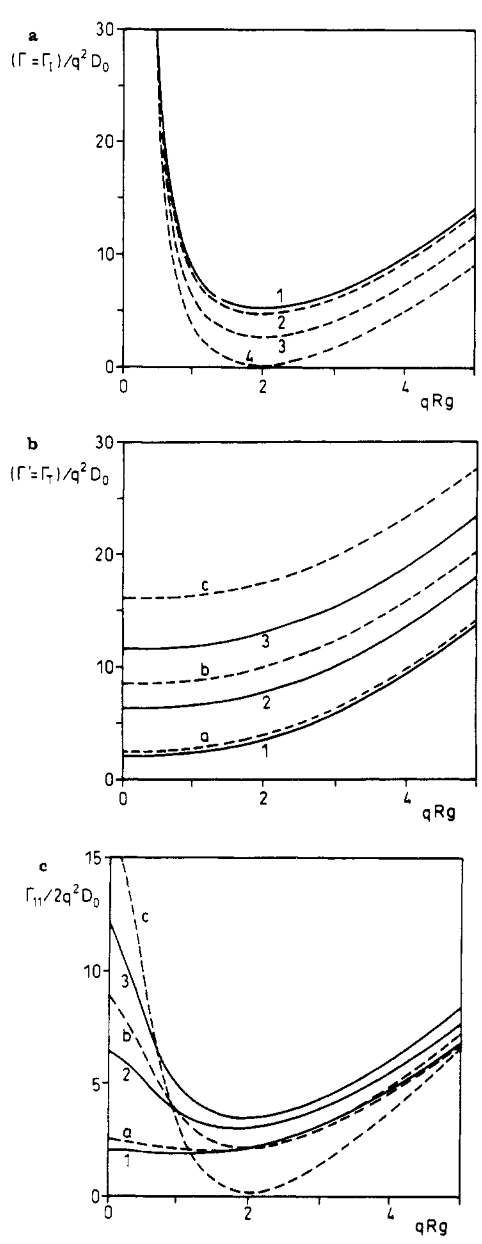

Figure 1. (a) Variations of $(\Gamma = \Gamma_I)/q^2D_0$ as a function of qR_g for a neutral copolymer as given by eq 45. Curve 1 corresponds to $\chi/\upsilon = 0.1$ and $\upsilon\phi N = 1$, 5, and 10. Curves 2–4 correspond to $\chi/\upsilon = 1$ and respectively $\upsilon\phi N = 1$, 5, and 10. (b) Variations of $(\Gamma' = \Gamma_T)/q^2D_0$ as in Figure 1a. Curves 1–3 correspond to $\chi/\upsilon = 0.1$ and $\upsilon\phi N = 1$, 5, and 10. Curves a–c correspond to $\chi/\upsilon = 1$ and $\upsilon\phi N = 1$, 5, and 10, respectively. (c) Variations of $\Gamma_{11}/2q^2D_0$ as in Figure 1b.

3.2. Charged Copolymer. We shall consider three examples of charge distributions and examine their consequences on the q dependence of the above frequencies. We still keep the assumption that the blocks have the same size (50/50 diblock copolymers), and this leads to the interesting identifications in eqs 43 and 44 and the physical interpretation of the eigenmodes, except in one case which we shall discuss below. In treating the effects of electrostatic interaction between the two blocks, we choose charge distributions that can either preserve the above simplifications or not.

(a) Similarly Charged Monomers ($f_1 = f_2 = f$; $\epsilon = +1$). By choosing $f_1 = f_2$, we intended to keep the symmetry property due to the equality of S_{11} and S_{22} still valid, and therefore the identifications of Γ with Γ_I and Γ' with Γ_T rigorously correct. First, one notes that the forms of the results obtained in the neutral limit are applicable to this case if one takes the precaution to replace v by an effective q-dependent excluded-volume parameter to account for the additional long-range electrostatic repulsion:

$$v_{\text{eff}}(q) = v + \alpha(q) f^2 \tag{48}$$

This means that

$$\Gamma'/q^2D_0 = \Gamma_T/q^2D_0 = P_T^{-1} + [v_{\text{eff}}(q) + \chi/2]\phi N \tag{49}$$

and since $\Gamma = \Gamma_I$ is independent of v as shown by eq 45, it remains unchanged when monomers are similarly charged. This implies that the onset of microphase separation is still governed by the thermodynamic parameter χ since the interaction between the two species does not seem to be affected by the Coulombic forces. It appears that only the excluded-volume interaction which acts on all monomers regardless of their nature is enhanced and becomes long ranged. Consequently, the interdiffusion process governed by the frequency $\Gamma_I = \Gamma$ is not modified by the electrostatic charges, but the cooperative diffusion process is strongly modified. In fact, the latter can be identified with the behavior one would obtain in ordinary polyelectrolyte systems.[23,27,28] This remark is of course expected because the distribution of charges is uniform along the chains and the polyelectrolyte nature dominates the copolymer nature in the cooperative relaxation process as clearly indicated by eq 49. These aspects are illustrated in Figure 2a where we have plotted ($\Gamma' = \Gamma_T)/q^2D_0$ as a function of qR_g for different values of f. One obtains the known behavior for an ordinary polyelectrolyte solution (see Figure 1 of ref 28). Even a small charge fraction such as $f = 0.01$ produces a dramatic increase of $\Gamma' = \Gamma_T$ at small q's. All the curves are shifted upward and the locations of their minima shifted to higher values of q_m when f increases. The other frequency $\Gamma = \Gamma_I$ is of course still given by Figure 1a as in the neutral limit. The interesting observation is that both types of frequencies $\Gamma = \Gamma_I$ and $\Gamma' = \Gamma_T$ show a significant rise at small q's, and hence a minimum at a certain wavenumber q_m. This *analogy* between *polyelectrolyte* and *copolymer* systems has already been pointed out before.[7,23] However, one should keep in mind that these *properties*, although *similar*, have *entirely different sources*. First, in the case of a copolymer the sharp increase at small q is essentially due to the internal structure since, as $q \to 0$, $P_{1/2} - P_T \to 0$ and its inverse which determines the internal relaxation frequency Γ_I goes to infinity. The effect of the interaction parameter χ is to change the deepness of the minimum at q_m and does not affect much the behavior at small q's. Furthermore, the latter interaction has a thermodynamic origin and measures the degree of incompatibility of the two species, and therefore it is very short ranged (essentially a delta function) which means that monomers interact essentially when they touch each other. This is in complete contrast with the electrostatic interaction which is long ranged and can be made ineffective when a salt is added and its concentration increased.

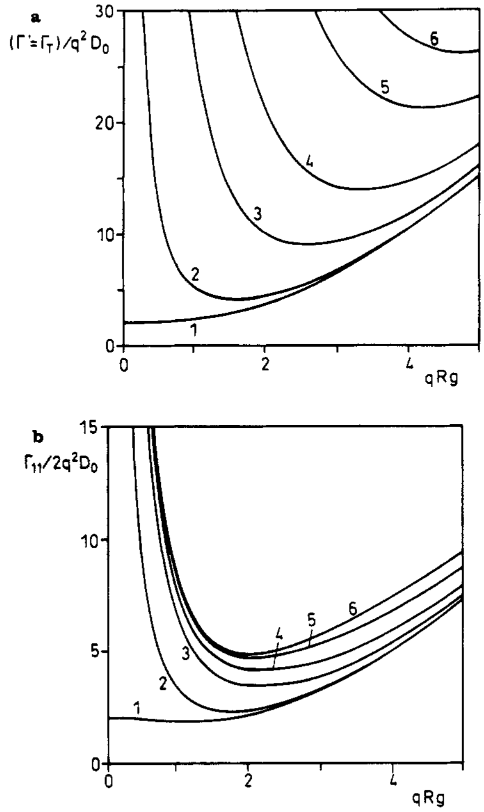

Figure 2. (a) Variations of ($\Gamma' = \Gamma_T)/q^2D_0$ as a function of qR_g for a diblock copolymer with similarly charged monomers ($f_1 = f_2 = f$; $\epsilon = +1$) and several values of f. Curves 1–6 correspond to f = 0, 0.01, 0.03, 0.05, 0.08, and 0.1, respectively. The other parameters are chosen as $v\phi N = 1$; $\chi/v = 0.1$ (eq 49). (b) Variations of $\Gamma_{11}/2q^2D_0$ as in Figure 2a.

Second, one can see from Figure 1a that when the polymer concentration and the interaction parameter χ are increased, the curves are shifted downward and the location of the minimum q_m is not changed. This is also in contrast with the polyelectrolyte behavior as shown in Figure 2a and discussed shortly before. Therefore, the analogy between the two systems is limited to the observation of a sharp increase at small q's and the emergence of a minimum in both cases, but the physical phenomena underlying these common features are entirely different. These properties are combined within the mean frequency Γ_{11} which is a weighted average of Γ_I and Γ_T. As pointed out earlier, one can show that Γ_{11} has the form of eq 47 which was obtained in the neutral limit, but the excluded-volume parameter must be replaced by $v_{\text{eff}}(q)$ as defined by eq 48; namely

$$\Gamma_{11}/2q^2D_0 = \frac{[1 - \chi\phi N(P_{1/2} - P_T)/2]\{1 + [v_{\text{eff}}(q) + \chi/2]\phi NP_T\}}{P_{1/2} + v_{\text{eff}}(q)\ \phi NP_T(P_{1/2} - P_T)} \tag{50}$$

The variation of this frequency with qR_g is illustrated in Figure 2b for several values of f. This figure together with Figure 1c illustrates clearly the differences between the copolymer behavior (Figure 1c) and the polyelectrolyte behavior (Figure 2b). For the small concentration and the interaction parameter that are chosen, it is reasonable to expect a monotonically increasing variation in the neutral limit (curve 1 of Figure 2b). As the charge parameter increases, there is a sharp rise at small q's, the curves are shifted upward, and their minima are moved to higher q_m values but with a much reduced rate as compared to Figure 2a. For $qR_g > 1$, the thermodynamic interaction tends to have an important effect (nearly neutral copolymer behavior) whereas, for $qR_g < 1$, it is the long-range electrostatic interaction that dominates the variation of Γ_{11} (polyelectrolyte effect).

(b) Oppositely Charged Monomers ($f_1 = f_2 = f$; $\epsilon = -1$). This is the case where the two blocks have charges of opposite signs which means that a polyanion and a polycation of the same size are linked together chemically. The two blocks may have a different chemical nature and therefore a certain degree of incompatibility in addition to their differences in the scattering power (i.e., $(\partial n/\partial c)$ or scattering lengths). To keep the symmetry relationship $S_{11} = S_{22}$ still valid, we assume that the valences of ions carried by monomers 1 and 2 are equal $f_1 = f_2 = f$ but $\epsilon = -1$ since they are of opposite signs. When this is substituted into eqs 25–29, one gets

$$S_{11} = S_{22} = S = \phi N[P_{1/2} + v_{\text{eff}}\phi NP_{\text{T}}(P_{1/2} - P_{\text{T}})]/4\mathcal{D}(q) \quad (51)$$

$$S_{12} = S_{21} = S' = \phi N[P_{12} - (v_{\text{eff}} + \chi_{\text{eff}})\phi NP_{\text{T}}(P_{1/2} - P_{\text{T}})]/4\mathcal{D}(q) \quad (52)$$

where $v_{\text{eff}}(q)$ is defined by eq 48 and $\chi_{\text{eff}}(q)$ is found as

$$\chi_{\text{eff}}(q) = \chi - 2\alpha(q)\,f^2 \quad (53)$$

$$\mathcal{D}(q) = [1 - \chi_{\text{eff}}\phi N(P_{1/2} - P_{\text{T}})/2]\left[1 + \left(v + \frac{\chi}{2}\right)\phi NP_{\text{T}}\right] \quad (54)$$

One observes that these expressions are similar to those obtained in the neutral case, but the excluded-volume and interaction parameters are replaced by the effective q-dependent parameters as defined above. Therefore, one can immediately write the final results

$$\Gamma/q^2D_0 = \Gamma_{\text{I}}/q^2D_0 = 1/(P_{1/2} - P_{\text{T}}) - \chi_{\text{eff}}(q)\ \phi N/2 \quad (55)$$

$$\Gamma'/q^2D_0 = \Gamma_{\text{T}}/q^2D_0 = 1/P_{\text{T}} + \left(v + \frac{\chi}{2}\right)\phi N \quad (56)$$

where we have used the fact that

$$v + \frac{\chi}{2} = v_{\text{eff}}(q) + \chi_{\text{eff}}(q)/2 \quad (57)$$

This fact shows that the situation is somewhat reversed as compared to the case of similarly charged monomers discussed in part a of this section. Indeed, one observes that the cooperative relaxation frequency $\Gamma' = \Gamma_{\text{T}}$ is not modified by the electrostatic attraction, which means that, during relaxation of the total concentration fluctuations, the enhancement of repulsive interaction due to the excluded volume within the same "family" is exactly compensated by the net effective attraction between the two families of monomers. This overall averaging to zero of the effective electrostatic interactions can be undestood by noting that Γ_{T}^{-1} describes the rate of relaxation of the total density fluctuations including the two species and this relaxation is rather slow as compared to the relaxation of the internal or interdiffusion mode if the polymer mean concentration is not too high. Equation 55 shows that the interdiffusion frequency $\Gamma_{\text{I}} = \Gamma$ is strongly modified through a dramatic reduction of the χ parameter due to a long-range attraction between the two oppositely charged blocks. This compatibilization of the two blocks is selective in space since it is more effective in the low q range. All these aspects are illustrated in Figure 3a where we have ploted $(\Gamma = \Gamma_{\text{I}})/q^2D_0$ as a function of qR_g for several values of f. This figure also presents a good example of the combination of polyelectrolyte and copolymer effects. There is a sharp increase at small q's and a minimum at a finite wavenumber q_m for all values of f including $f = 0$ in the neutral limit. In the latter limit, the rise of the curve 1 is due to the inverse structure factor $(P_{1/2} - P_{\text{T}})^{-1}$ as explained earlier (copolymer structure). When f increases, the polyelectrolyte effect emerges. This is illustrated by the shift of the curves upward and the shift of the location of their minimum q_m to higher values.

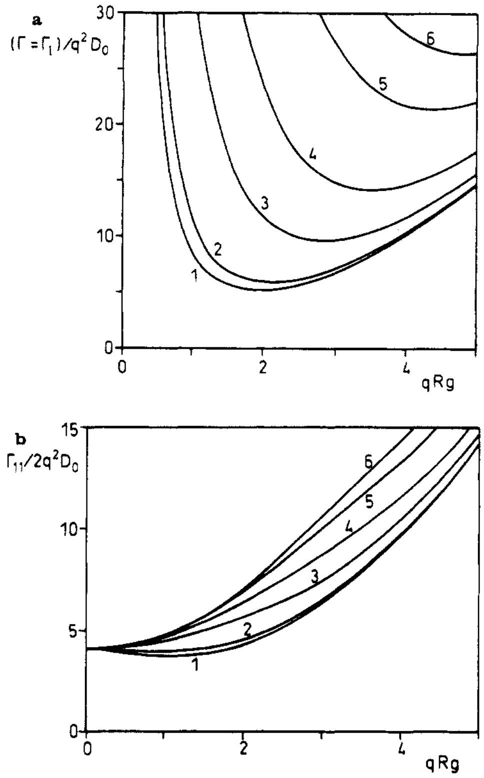

Figure 3. (a) Variations of $(\Gamma = \Gamma_{\text{I}})/q^2D_0$ as a function of qR_g for a diblock copolymer with oppositely charged monomers ($f_1 = f_2 = f$; $\epsilon = -1$) and several values of f. Curves 1–6 correspond to f = 0, 0.01, 0.03, 0.05, 0.08, and 0.1, respectively. The other parameters are $v\phi N = 1$ and $\chi/v = 0.1$ (see eq 55). (b) Variations of $\Gamma_{11}/2q^2D_0$ as in Figure 3a (see eq 58).

The mean frequency Γ_{11} can also be immediately written down if one takes the neutral result in eq 47 and replaces v and χ by $v_{\text{eff}}(q)$ and $\chi_{\text{eff}}(q)$, respectively. Therefore, the result can be deduced as

$$\Gamma_{11}/2q^2D_0 = \frac{[1 - \chi_{\text{eff}}(q)\ \phi N(P_{1/2} - P_{\text{T}})/2][1 + (v + \chi/2)]\phi NP_{\text{T}}}{P_{1/2} + v_{\text{eff}}(q)\ \phi NP_{\text{T}}(P_{1/2} - P_{\text{T}})} \quad (58)$$

First of all, one notes that, at $q = 0$, the limit of this expression is independent of the electrostatic interaction:

$$\lim_{q\to 0} \frac{\Gamma_{11}}{2q^2D_0} = 1 + (v + \chi/2)\phi N \quad (59)$$

Since this limit remains finite at $q = 0$, this means that

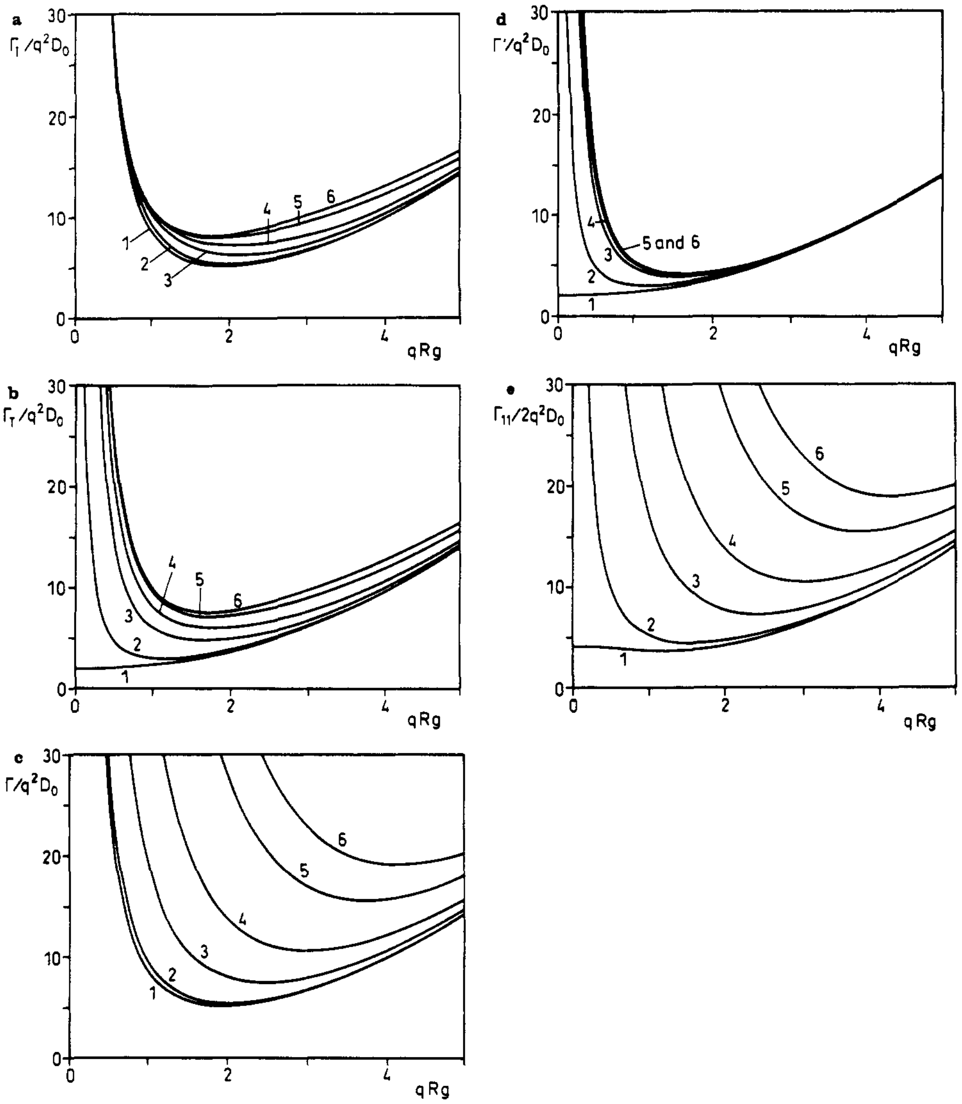

Figure 4. (a) Variations of Γ_I/q^2D_0 as a function of qR_g for a half-charged copolymer ($f_2 = 0$) and several values of f_1. Curves 1–6 correspond to $f_1 = 0$ (neutral copolymer), 0.01, 0.03, 0.05, 0.08, and 0.1, respectively. The other parameters are chosen as $v\phi N = 1$ and $\chi/v = 0.1$ (see eq 64). (b) Variations of Γ_T/q^2D_0 as in Figure 4a (see eq 65). (c) Variations of Γ/q^2D_0 as in Figure 4a (see eqs 31 and 60–63). (d) Variations of Γ'/q^2D_0 as in Figure 4a (curves 5 and 6 are superimposed). (e) Variations of $\Gamma_{11}/2q^2D_0$ as in Figure 4a (see eq 66).

the copolymer effect has been completely removed from Γ_{11} and all terms proportional to the copolymer structure factor ($P_{1/2} - P_T$) cancel out. The polyelectrolyte effect is also removed essentially because of the compensation indicated by eq 57. These aspects are illustrated graphically in Figure 3b where we represent the variation of $\Gamma_{11}/2q^2D_0$ as a function of qR_g for several values of f. The curves are monotonically increasing for all values of $f \neq 0$. In the neutral limit where $f = 0$, one obtains a very shallow minimum, indicating a small copolymer effect for the relatively small values of the concentration and interaction parameter chosen in these plots (i.e., $v\phi N = 1$ and $\chi/v = 0.1$). Therefore, it appears that the characteristics of $\Gamma' = \Gamma_T$ are dominant in the behavior of Γ_{11}. One knows that, although Γ_{11} describes the initial decay of the scattering function $S_{11}(q,t)$ due to one block only, the fact that the two blocks are linked together, the dynamics of one block is strongly coupled to the dynamics of the total chain. Nevertheless, the curves shown in Figure 3b are still quite sensitive to the electrostatic interaction, which means that the contribution of the interdiffusion process governed by $\Gamma = \Gamma_I$ is not negligible.

(c) Half-Charged Copolymer ($f_2 = 0$). This is the case where half of the chain is charged and the second half is neutral (e.g., like ampliphilic molecules). The partial structure factors can be immediately obtained from eqs 25–29 by letting $f_2 = 0$:

$$\left(\frac{\phi N}{4}\right)^{-1}\mathcal{D}(q)\cdot\mathbf{S}_{11} = P_{1/2} + v\phi N P_T(P_{1/2} - P_T) \qquad (60)$$

$$\left(\frac{\phi N}{4}\right)^{-1}\mathcal{D}(q)\cdot\mathbf{S}_{22} = P_{1/2} + [v + \alpha(q) f^2]\phi N P_T(P_{1/2} - P_T) \qquad (61)$$

$$\left(\frac{\phi N}{4}\right)^{-1}\mathcal{D}(q)\cdot\mathbf{S}_{12} = P_{12} - (v + \chi)\phi N P_T(P_{1/2} - P_T) \qquad (62)$$

The common factor $\mathcal{D}(q)$ becomes

$$\mathcal{D}(q) = \mathcal{D}_{\text{neutral}}(q) + \alpha(q) f^2\phi N[P_{1/2} + v\phi N P_T(P_{1/2} - P_T)]/4 \qquad (63)$$

The important thing to be noted first is that $S_{11} \neq S_{22}$, thereby removing the simplifications of the previous cases. This means that Γ and Γ' do not have a simple form since the quantity under the square root in eq 31 is not a complete square. This also means that Γ and Γ' cannot be identified exactly with Γ_I and Γ_T as before. These frequencies must be calculated separately and, in order to do it, one needs to put $f_2 = 0$ in eqs 36 and 34, respectively:

$$\Gamma_I/q^2D_0 = \frac{\mathcal{D}(q)}{(P_{1/2} - P_T)\left[1 + \left(\upsilon + \frac{\chi}{2} + \alpha f_1{}^2/4\right)\phi N P_T\right]} \qquad (64)$$

and

$$\Gamma_T/q^2D_0 = \frac{\mathcal{D}(q)}{P_T\left[1 - \left(\chi - \frac{\alpha}{2}f_1{}^2\right)\phi N(P_{1/2} - P_T)/2\right]} \qquad (65)$$

where $\mathcal{D}(q)$ is given by eq 63. Since these equations cannot be simplified further, we would like to proceed by presenting their variations with qR_g for different values of f_1. This is done in parts a and b of Figure 4, which give Γ_I/q^2D_0 and Γ_T/q^2D_0, respectively.

Figure 4a shows that the variation of Γ_I is dominated by the structure factor $(P_{1/2} - P_T)$ which appears in the denominator of eq 64. When the electrostatic interaction is introduced, the curves are only slightly modified. This is not the case of Γ_T which is completely changed when the electrostatic forces are switched on. This is illustrated in Figure 4b, which shows the quick transition from the neutral case where Γ_T/q^2D_0 is monotonically increasing to the case of a half-charged copolymer which is similar to the behavior of an ordinary polyelectrolyte system. Moreover, one observes that both frequencies do depend on electrostatic forces unlike the former cases discussed in parts a and b of this section, where one process was insensitive to these forces. The eigenfrequencies Γ and Γ' do not have a simple form as pointed out shortly before. Their variations with qR_g are plotted in parts c and d of Figure 4 for several values of f. One notes that the qualitative variations of Γ_I and Γ (parts a and c of Figure 4, respectively) on the one hand and Γ_T and Γ' (parts b and d of Figure 4, respectively) on the other hand are similar. Quantitatively, of course, these pairs of frequencies are different especially in the lower q range and for the pair (Γ_I, Γ). The reason is that the structural factor $(P_{1/2} - P_T)$ has an overwhelming contribution in determining the variation of Γ_I in the low q range. But, in spite of these numerical differences, one can ascertain that the pairs (Γ, Γ_I) and (Γ', Γ_T) describe similar dynamical processes. One must note that this is an extreme example of a nonsymmetric system where the comparison between the frequencies (Γ, Γ_I) and (Γ', Γ_T) is unfavorable. There are other examples of nonsymmetrical systems where (Γ, Γ_I) and (Γ', Γ_T) have much more similar behavior. Nonetheless, even with an extremely unfavorable case, the frequencies still retain qualitative similarities. Therefore, it is legitimate to interpret the physical processes underlying the dynamical behavior described by the frequencies Γ and Γ' as the interdiffusive and the cooperative modes, respectively. This interpretation appears to be quite general and is not necessarily restricted to the conditions where the symmetry relationship $S_{11} = S_{22}$ is strictly fulfilled.

The mean frequency Γ_{11} is obtained by substituting eq 60 into eq 32a:

$$\Gamma_{11}/2q^2D_0 = \mathcal{D}(q)/[P_{1/2} + \upsilon\phi N P_T(P_{1/2} - P_T)] \qquad (66)$$

Figure 4e represents the variation of $\Gamma_{11}/2q^2D_0$ as a function of qR_g for several values of f.

One observes that, for very weakly charged copolymers ($f_1 \leq 0.01$), Γ_{11} describes the process governed by Γ' which is only slightly sensitive to the electrostatic forces. But, for relatively highly charged copolymers, Γ_{11} shows a strong dependence of f which is reminiscent of the dynamical process described by Γ.

3.3. On the Effect of Hydrodynamic Interaction. The main conclusions of the above analysis are not modified by the introduction of hydrodynamic interaction. Using the Oseen tensor description, one can write the mobility matrix $\mathbf{M}(q)$ as a sum of two matrices. The first one $\mathbf{M}_0$ is the Rouse contribution already calculated in the above model. The second matrix is q-dependent and denotes the contributions of hydrodynamic interaction. One has[29]

$$\mathbf{M}(q) = \mathbf{M}_0 + \frac{1}{(2\pi)^2\eta_s}\int_0^\infty \mathrm{d}k\, f\left(\frac{k}{q}\right)\mathbf{S}(k) \qquad (67a)$$

where η_s is the solvent viscosity and $f(x)$ is given by

$$f(x) = x^2\left\{\left[\frac{x^2+1}{2x}\right]\log\left|\frac{x+1}{x-1}\right| - 1\right\} \qquad (67b)$$

Explicitly, the elements of $\mathbf{M}$ are

$$\mathbf{M}_{ii}(q) = \frac{\phi_i}{\xi_i} + \frac{1}{(2\pi)^2\eta_s}\int_0^\infty \mathrm{d}k\, f\left(\frac{k}{q}\right)\mathbf{S}_{ii}(k) \qquad (67c)$$

$$\mathbf{M}_{ij}(q) = \frac{1}{(2\pi)^2\eta_s}\int_0^\infty \mathrm{d}k\, f\left(\frac{k}{q}\right)\mathbf{S}_{ij}(k) \qquad (67d)$$

One observes that, in the symmetrical case where $S_{11}(q) = S_{22}(q)$ and $\xi_1 = \xi_2$, the mobilities satisfy also the symmetry relationship

$$M_{11} = M_{22} = M \quad \text{and} \quad M_{12} = M_{21} = M' \qquad (68a)$$

When these mobilities are used in the definitions of the elements of the first cumulant matrix $\mathbf{\Omega}$, one obtains the simple results

$$\Omega_{11} = \Omega_{22} = \Omega = q^2\frac{kT}{\Delta S}(MS - M'S') \qquad (68b)$$

$$\Omega_{12} = \Omega_{21} = \Omega' = q^2\frac{kT}{\Delta S}(M'S - MS') \qquad (68c)$$

with $\Delta S = (S - S')(S + S')$. Substituting eq 68b,c into the general expressions of the eigenfrequencies Γ and Γ'

$$\Gamma, \Gamma' = \Omega_{av} \pm [\Omega_{av}{}^2 - \Delta(\Omega)]^{1/2} \qquad (69a)$$

with

$$\Omega_{av} = \frac{\Omega_{11} + \Omega_{22}}{2}; \quad \Delta(\Omega) = \Omega_{11}\Omega_{22} - \Omega_{12}\Omega_{21} \qquad (69b)$$

one finds

$$\Gamma = \Gamma_T = q^2kT\frac{M + M'}{S + S'} \qquad (70)$$

$$\Gamma = \Gamma_I = q^2kT\frac{M - M'}{(S - S')} \qquad (71)$$

with

$$M = \frac{\phi}{2\xi} + \frac{1}{(2\pi)^2\eta_s}\int_0^\infty \mathrm{d}k\, f\!\left(\frac{k}{q}\right) S(k) \tag{72a}$$

$$M' = \frac{1}{(2\pi)^2\eta_s}\int_0^\infty \mathrm{d}k\, f\!\left(\frac{k}{q}\right) S'(k) \tag{72b}$$

The remaining task is to evaluate numerically these integrals knowing the values of $S(q)$ and $S'(q)$ corresponding to different cases and to evaluate the effect of hydrodynamic interaction. This effect is expected to be significant only in the dilute regime for concentrations below ϕ^* satisfying approximately the relation $v\phi^* N \approx 1$.

4. Conclusions

The purpose of this paper was to discuss the dynamic scattering properties of neutral and weakly charged copolymers in solution. The main conclusions of this study can be summarized in two parts:

First, the question of the identification of the eigenmodes in a solution of symmetric diblock copolymers was rediscussed. It was found that the identification of these two modes with the cooperative and interdiffusive modes required the symmetry relationship $S_{11} = S_{22}$. This was done using a slightly different argument as presented by Akcasu et al.[7] and some time ago by Pusey et al.[9] However, unlike their conclusions, it was shown that this identification remains valid even for different and incompatible species. In fact, the qualitative variations of (Γ, Γ_I) and (Γ', Γ_T) remain similar even when the symmetry relationship $S_{11} = S_{22}$ is not satisfied.

Second, this paper addressed the problem of weakly charged copolymers and focused on the analogy between the dynamical properties observed in neutral copolymers and those observed in polyelectrolyte solutions. It was shown that this analogy does not stem from a physical common basis. More specifically, the increase of the apparent diffusion coefficient in the small q range which is observed in both systems and, therefore, the emergence of a minimum have different physical sources. Moreover, the changes in the minimum go in opposite directions when one increases the charge parameter in the polyelectrolyte case and the thermodynamic parameter in the neutral copolymer case. The fact that we considered weakly charged copolymers produced interesting properties which combine the polyelectrolyte behavior and the copolymer behavior. The frequencies which were examined here illustrated in several cases interesting competing tendencies of these two effects.

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References and Notes

(1) Hanley, B.; Tirrell, M.; Lodge, T. *Polym. Bull.* **1985**, *14*, 137; *Chem. Eng. Commun.* **1983**, *24*, 93.
(2) Lodge, T.; Wheeler, L. M. *Macromolecules* **1986**, *19*, 2983.
(3) Nemoto, N.; Makita, Y.; Tsunashima, Y.; Kurata, M. *Macromolecules* **1984**, *17*, 2629.
(4) Aven, M. R.; Cohen, C. *Macromolecules* **1990**, *23*, 476.
(5) Giebel, L.; Borsali, R.; Fischer, E. W.; Meier, G. *Macromolecules* **1990**, *23*, 4054.
(6) Chu, B.; Wu, D. Q.; Liang, G. M. *Macromolecules* **1986**, *19*, 2665; **1987**, *20*, 93 and 1606.
(7) (a) Akcasu, A. Z.; Nägele, G.; Klein, R. *Macromolecules* **1991**, *24*, 4408. (b) Akcasu, A. Z. *Dynamic Light Scattering. The Method and Some Applications*; Brown, W., Ed.; Oxford University Press: Oxford, U.K., to appear in 1992.
(8) Benmouna, M.; Benoit, H.; Duval, M.; Akcasu, A. Z. *Macromolecules* **1987**, *20*, 1107.
(9) (a) Pusey, P. N.; Fijnaut, M. M.; Vrij, A. *J. Chem. Phys.* **1982**, *77*, 4270. (b) Davies, P.; Snook, I.; Van Megen, W.; Preston, B. N.; Compar, W. D. *Macromolecules* **1984**, *17*, 2376.
(10) Akcasu, A. Z.; Hammouda, B.; Lodge, T.; Han, C. C. *Macromolecules* **1984**, *17*, 759.
(11) Duval, M.; Picot, C.; Benoit, H.; Borsali, R.; Benmouna, M.; Lartigue, C. *Macromolecules* **1991**, *24*, 3185.
(12) Duval, M.; Haida, H.; Lingelser, J. P.; Gallot, Y. 27th EPS Meeting, Heraklion, Greece, Sept 1991.
(13) Borsali, R.; Fischer, E. W.; Benmouna, M. *Phys. Rev. A* **1991**, *43*, 5732.
(14) Higgs, P. G.; Joanny, J. F., to be published in *J. Chem. Phys.*
(15) Benmouna, M.; Benoit, H.; Borsali, R.; Duval, M. *Macromolecules* **1987**, *20*, 2620.
(16) (a) Fukuda, T.; Nagata, M.; Inagaki, H. *Macromolecules* **1984**, *17*, 548. (b) Ould-Kaddour, L.; Strazielle, C. *Polymer* **1987**, *28*, 459.
(17) Leibler, L. *Macromolecules* **1980**, *13*, 1602.
(18) Fredrickson, G. H.; Helfand, E. *J. Chem. Phys.* **1987**, *87*, 697.
(19) Benoit, H.; Benmouna, M.; Wu, W. *Macromolecules* **1990**, *23*, 1511.
(20) Vilgis, T. A.; Benmouna, M.; Benoit, H. *Macromolecules* **1991**, *24*, 4481.
(21) Benmouna, M.; Vilgis, T. A. *Macromolecules* **1991**, *24*, 3866.
(22) We use the same symbol χ for the interaction parameter with perhaps different dimensions (volume, energy, dimensionless, etc.).
(23) Vilgis, T. A.; Borsali, R. *Phys. Rev. A* **1991**, *43*, 6857.
(24) Vilgis, T. A.; Benmouna, M., in preparation.
(25) Rabin, Y.; Marko, J. F. *Macromolecules* **1991**, *24*, 2134.
(26) Ould-Kaddour, L. Ph.D. Thesis, University Louis Pasteur, Strasbourg, France, 1987; see also ref 16b.
(27) Joanny, J. F.; Leibler, L. *J. Phys. (Paris)* **1990**, *51*, 545.
(28) Benmouna, M.; Vilgis, T. A.; Hakem, F.; Negadi, A., to be published in *Macromolecules*.
(29) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press: Oxford, U.K., 1986.