Dynamic Scattering from Mixtures of Weakly Charged Polymers

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Received July 19, 1991; Revised Manuscript Received October 26, 1991

ABSTRACT: The dynamic scattering properties of mixtures of weakly charged polymers are investigated. The case of ternary mixtures of two charged polymers in solution is studied in detail. The time evolutions of the partial dynamic correlation functions are examined starting from the matrix equation $\mathbf{S}(\mathbf{q},t) = e^{-\Omega t}\mathbf{S}(\mathbf{q})$, where $\mathbf{S}(\mathbf{q})$ is the static structure matrix and Ω is the first-cumulant matrix. This quantity is expressed in terms of $\mathbf{S}(\mathbf{q})$ and the mobility matrix $\mathbf{M}(\mathbf{q})$ as $\Omega = q^2kT\mathbf{M}(\mathbf{q})\cdot\mathbf{S}^{-1}(\mathbf{q})$. The eigenvalues of Ω as well as other relevant relaxation frequencies are investigated in detail at various conditions of charge distribution. The model used here is based on three approximations: (i) an extension of the random phase approximation (RPA) to include the long-range electrostatic interaction in the calculation of the static structure matrix $\mathbf{S}(\mathbf{q})$, (ii) the Debye–Hückel approximation to describe the effects of Coulomb forces between charged particles, and (iii) the Rouse limit for chain dynamics. Furthermore, the small ions such as counterions and co-ions are assumed to be point particles, their dynamics is not accounted for explicitly, and, therefore, only the apparent diffusion of macroions is described.

1. Introduction

At present, only certain features of the dynamic scattering properties of polyelectrolyte solutions are reasonably well understood. Some progress has been made in developing theoretical models for spherical polyions[1–4] and semiflexible charged coils,[5–7] and certain predictions of these theories were verified by various scattering experiments using quasielectric light[8,9] or neutron spin-echo (NSE)[5,10] techniques. Of course, there are many aspects which are not yet well elucidated: the ordinary–extraordinary transition,[11] the electrolyte friction phenomenon and the effect of the polyion–polyion interactions on the friction forces, the condensation of counterions[12] for highly charged systems, etc., are examples of questions that still lack a conclusive answer at the present time. However, these issues are not raised in this work where we are interested in a somewhat different problem which is related to the dynamics of mixtures of weakly charged polymers in solution. Small ions such as counterions and co-ions either from the ionization of the polymers or from the added salt are assumed to be pointlike particles and structureless and their dynamics is completely omitted. We are interested only in effective, or apparent, dynamics of polyions, and we discuss the variations with the wave vector q of various relaxation frequencies that govern the time evolution of important and measurable dynamic correlation functions in different conditions of charge distributions. It is known that, in a ternary mixture of two polymers and a solvent, the dynamic correlation functions evolve in time following a two-exponential behavior[13–15] and the relaxation frequencies of these modes are given by the eigenvalues of the first-cumulant matrix Ω. Other frequencies are of particular importance and correspond to weighted averages of the former eigenvalues. Some of these frequencies will be examined here and their physical implications discussed in some detail in light of the recent papers by Akcasu.[14,15]

This paper is organized as follows: In the next section, we give a brief description of the general formalism in matrix notation which is valid for an arbitrary number of polymer components. In the following section, we discuss also briefly the case of a single polyion system in solution and recall the main aspects within the model presented here. This is useful if one wants to see how the known results for a single polyion system are modified by adding another polymer which may be neutral or charged with charges of the same or opposite signs. This is the subject of section 4 where we confine our description to a ternary mixture of polymer 1/polymer 2/solvent. We use the nomenclature solvent for a solution containing the actual solvent and small ions (counterions or salt ions) which are assumed to be poitlike and without any contribution to the scattering signal or to the dynamics of macromolecules. Section 5 is devoted to a brief discussion of some dynamic charge correlation functions.

2. General Formalism

The time evolution of the dynamic correlation functions can be investigated starting from the assumption that the dynamic scattering matrix $\mathbf{S}(\mathbf{q},t)$ decays in time following a single exponential which means that the memory effects are neglected. Therefore, we have

$$\mathbf{S}(\mathbf{q},t) = e^{-\Omega t}\mathbf{S}(\mathbf{q}) \qquad (1)$$

where the first-cumulant matrix Ω is defined in terms of the generalized mobility matrix $\mathbf{M}(\mathbf{q})$ and the static structure matrix $\mathbf{S}(\mathbf{q})$ as usual:

$$\Omega(\mathbf{q}) = q^2kT\mathbf{M}(\mathbf{q})\cdot\mathbf{S}^{-1}(\mathbf{q}) \qquad (2)$$

It is worth noting that a similar single-exponential decay of $\mathbf{S}(q,t)$ is obtained in the Markov limit where $t \rightarrow \infty$, $q \rightarrow 0$, and q^2t remains finite.[15] However, the decay rate includes a contribution from the integral of the memory function at all times which is very difficult if not impossible to evaluate except for very special cases. By neglecting memory effects, one excludes the possibility of the emergence of a hierarchy of relaxation times describing the internal modes of the chains. This implies that the nonexponential decay of the dynamic correlation function due to internal modes does not proceed to a significant extent in the time required for the eigenmodes of the mixture to be experimentally distinguished. This was the case for a series of QELS data reported on various ternary mixtures made of two polymers and a solvent.[13b,c] In all these experiments, only two exponential decay modes were observed and interpreted successfully using the formalism presented here. No indication of departure from these two exponentials which could be attributed to internal

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0024-9297/92/2225-1144$03.00/0

modes was detected. Nevertheless, such a good agreement is surprising in the sense that one would expect to see effects of internal dynamics or memory terms on the slow-mode component since the latter can take a relatively long time to relax completely, especially for high molecular weights and high concentrations. In his discussion of dynamic light scattering from nonideal systems made of either one-component or multicomponent mixtures of spheres, Schurr[16] has shown that, in the small q limit, $\mathbf{S}(q,t)$ decays in time following a single exponential provided that the concentration fluctuations are not strongly coupled to fluctuations in other slowly relaxing conserved quantities such as the energy.

Here, we adopt Rouse dynamics assuming that the hydrodynamic interaction is screened, and this assumption is valid above Φ^*, the overlap concentration. The main features of the dynamics are, however, preserved in the Rouse limit, and the effect of hydrodynamic interaction which introduces extra terms involving tedious numerical integrations of lengthy functions becomes important in the dilute regime and will be the subject of a future report. In this limit, $\mathbf{M}(\mathbf{q})$ is a diagonal matrix with the elements

$$M_i^0 = \Phi_i/\xi_i; \quad i = 1, 2, ... \tag{3}$$

ξ_i is the friction coefficient of a segment of type i, and Φ_i is the concentration of polymer i. For simplicity in the notations we shall use the same symbol Φ for the concentration regardless of its dimension (number concentration, weight concentration, etc.) unless specified explicitly otherwise. Because of the uncompressibility assumption, and assuming that Φ_i is expressed as the volume fraction occupied by the polymer species i, one writes $\Phi = \sum_i \Phi_i = 1 - \Phi_s$, where Φ_s is the volume fraction of the solvent. Therefore, the calculation of $\mathbf{\Omega}(\mathbf{q})$ and hence the matrix $\mathbf{S}(\mathbf{q},t)$ reduces to the calculation of the static structure matrix $\mathbf{S}(\mathbf{q})$. This was the subject of a recent paper,[17] where $\mathbf{S}(\mathbf{q})$ is obtained using the general formula

$$\mathbf{S}^{-1}(\mathbf{q}) = \mathbf{S}_0^{-1}(\mathbf{q}) + \mathbf{U}(\mathbf{q}) \tag{4}$$

A review of certain methods, including the RPA, which were used to derive this result can be found in ref 18. $\mathbf{S}_0(\mathbf{q})$ is the bare structure matrix whose elements are

$$S_i^0(\mathbf{q}) = \Phi_i N_i P_i(\mathbf{q}) \tag{5}$$

N_i and $P_i(\mathbf{q})$ are the number of segments and the form factor of polymer i, respectively. The interaction matrix $\mathbf{U}(q)$ is the sum of the ordinary excluded-volume matrix $\mathbf{V}$ and the electrostatic interaction matrix.

$$U = V + \alpha(\mathbf{q})\, \mathbf{f}\mathbf{f}^{\mathrm{T}} \tag{6a}$$

The elements of the matrix $\mathbf{v}$ are the usual excluded-volume parameters v_{ij} which can be written in terms of the Flory–Huggins interaction parameters χ_{ij} and Φ_s as

$$v_{ij} = 1/\Phi_s - 2\chi_{is} \tag{6b}$$

and

$$v_{ij} = 1/\Phi_s - \chi_{is} - \chi_{js} + \chi_{ij} \tag{6c}$$

The electrostatic part contains the quantity $\alpha(\mathbf{q})$ which is defined as

$$\alpha(\mathbf{q}) = \frac{4\pi l}{q^2 + \kappa^2} \tag{6d}$$

where

$$\mathbf{f} = \text{column } (f_1, \epsilon_{12} f_2, ...) \tag{6e}$$

$\mathbf{f}^{\mathrm{T}}$ is the transpose of $\mathbf{f}$, and $\epsilon_{12} \equiv \epsilon$ is a sign parameter; i.e., $\epsilon = +1$ if the charges on segments 1 and 2 are of the same sign, otherwise $\epsilon = -1$; $f_i e$ denotes the magnitude of the charge carried by segment i, e being the electron charge. We have

$$\alpha(\mathbf{q})\, \mathbf{f}\mathbf{f}^{\mathrm{T}} = \alpha(\mathbf{q}) \begin{pmatrix} f_1^2 & \epsilon f_1 f_2 \\ \epsilon f_1 f_2 & f_2^2 \end{pmatrix} \tag{6f}$$

Since we are dealing with weakly charged systems, f_i should be kept much smaller than 1. l is the Bjerrum length $l = e^2/\epsilon kT$ and is equal to 7 Å for water at 25 °C. κ^{-1} is the Debye–Hückel screening length and is defined by

$$\kappa^2 = 4\pi l[\sum_i f_i \Phi_i + \Phi_{\mathrm{salt}}] \tag{7}$$

$f_i\Phi_i = \Phi_{ci}$ is the concentration of counterions of species i because of the electroneutrality condition, and Φ_{salt} is the added salt concentration. We assume for simplicity that small ions from polymer ionization and the added salt carry the same charge $\pm e$ (1:1 electrolyte).

This formalism can be applied to an arbitrary number of polymer components, but we shall limit our discussions to ternary mixtures of two charged polymers and a solvent. In this case the rank of the matrices is two and $\mathbf{\Omega}$ has two eigenvalues Γ and Γ'. Solving eq 1, one finds that all partial dynamic correlation functions $S_{ij}(\mathbf{q},t)$ decay following the two-exponential form[13-15]

$$S_{ij}(\mathbf{q},t) = A_{ij} e^{-\Gamma t} + A'_{ij} e^{\Gamma' t} \quad (i, j = 1, 2) \tag{8}$$

where the amplitudes A_{ij} and A'_{ij} can be easily expressed in terms of S_{ij} and Ω_{ij},[19] and the frequencies Γ and Γ' are obtained as

$$\Gamma = \Omega_{\mathrm{av}} + (\Omega_{\mathrm{av}}^2 - \Delta(\Omega))^{1/2} \tag{9a}$$

$$\Gamma' = \Omega_{\mathrm{av}} - (\Omega_{\mathrm{av}}^2 - \Delta(\Omega))^{1/2} \tag{9b}$$

with

$$\Omega_{\mathrm{av}} = (\Omega_{11} + \Omega_{22})/2; \quad \Delta(\Omega) = \Omega_{11}\Omega_{22} - \Omega_{12}\Omega_{21} \tag{9c}$$

Ω_{ij} are the elements of the first-cumulant matrix.

In section 4, we shall examine the variations of Γ and Γ' as a function of the wave vector q at various conditions of charge distribution. But we must note that Γ and Γ' are not the only relaxation frequencies that govern the time evolution of dynamic correlation functions. Others are also important because they have special physical meanings and they correspond to particular weighted averages of Γ and Γ'.[15] We shall discuss three of them. The first one is Γ_1 and governs the initial decay of $S_{11}(\mathbf{q},t)$; the second one is Γ_{T} and corresponds to the initial decay of the total dynamic correlation function

$$S_{\mathrm{T}}(\mathbf{q},t) = S_{11}(\mathbf{q},t) + S_{22}(\mathbf{q},t) + S_{12}(\mathbf{q},t) + S_{21}(\mathbf{q},t) \tag{10}$$

The last one to be considered here is Γ_{I} and describes the initial relaxation of the intermediate scattering function $S_{\mathrm{I}}(\mathbf{q},t)$ which is defined as

$$\Phi^2 S_{\mathrm{I}}(\mathbf{q},t) = \frac{S_{11}(\mathbf{q},t)}{x^2} + \frac{S_{22}(\mathbf{q},t)}{(1-x)^2} - \frac{S_{12}(\mathbf{q},t) + S_{21}(\mathbf{q},t)}{x(1-x)} \tag{11}$$

where x is the composition of polymer 1, i.e., $x = \Phi_1/(\Phi_1 + \Phi_2)$. It is worth mentioning that these dynamical correlation functions are directly measurable by either quasielastic light scattering or neutron spin-echo techniques. To understand the conditions in which those functions are accessible, we recall that the measured dynamic correlation functions can be written in terms of

$S_{ij}(\mathbf{q},t)$ and the contrast factors $(a_i - s)$ or $(\delta n/\delta\Phi)_i$ as

$$S(\mathbf{q},t) = (a_1 - s)^2 S_{11}(\mathbf{q},t) + (a_2 - s)^2 S_{22}(\mathbf{q},t) + (a_1 - s)(a_2 - s)[S_{12}(\mathbf{q},t) + S_{21}(\mathbf{q},t)] \quad (12)$$

where a_i is the scattering length per monomer of type i and s the scattering length of a solvent molecule (occupying the same volume as a monomer segment); $(a_i - s)$ must be replaced by $(\delta n/\delta\Phi)_i$ for light scattering. If we choose a solvent such that $a_2 = s$, then $S(\mathbf{q},t)$ will be proportional to $S_{11}(\mathbf{q},t)$ as

$$S(\mathbf{q},t) = (a_1 - s)^2 S_{11}(\mathbf{q},t) \quad (13)$$

If the scattering lengths of both monomer segments are equal $a_1 = a_2$, $S(\mathbf{q},t)$ will be proportional to $S_{\mathrm{T}}(q,t)$, and if a_1, a_2, and the composition x are chosen such that the average constant is zero

$$(a_1 - s)x + (a_2 - s)(1 - x) = 0 \quad (14)$$

then $S(\mathbf{q},t)$ will be proportional to $S_{\mathrm{I}}(\mathbf{q},t)$ as

$$S(\mathbf{q},t) = (a_1 - s)^2 x^2 \Phi^2 S_{\mathrm{I}}(\mathbf{q},t) \quad (15)$$

where $S_{\mathrm{I}}(\mathbf{q},t)$ is defined by eq 11. Before turning to a detailed analysis of these dynamic correlation functions and their relaxation frequencies, let us first recall some important results concerning the dynamics of a single polyion system in solution consistent with the formalism presented in this section.

3. Case of a Single Polyion in Solution

In this case the matrix equations reduce to scalar equations and one has a single dynamic correlation function. This description implies that the counterions do not contribute to the scattering intensity (zero contrast with respect to the solvent) and their dynamics is completely omitted. Leaving out the contrast factor, we have

$$S(\mathbf{q},t) = S(\mathbf{q})\, e^{-\Omega t} \quad (16a)$$

where Ω is given in the Rouse limit by

$$\Omega = q^2 \frac{kT}{\xi} \frac{\Phi}{S(\mathbf{q})} \quad (16b)$$

and $S(q)$ is known, for example from ref 17 as

$$S(\mathbf{q}) = \frac{\Phi N P(\mathbf{q})}{1 + [v + \alpha(\mathbf{q})\, f^2]\Phi N P(\mathbf{q})} \quad (16c)$$

where v is the polymer excluded-volume parameter. Combining parts a–c of eq 16 gives the result for Ω which can be put in the form

$$\frac{\Omega}{D_0 q^2} = \frac{1 + [v + \alpha(\mathbf{q})\, f^2]\Phi N P(\mathbf{q})}{P(\mathbf{q})} \quad (17a)$$

where D_0 is the single-chain diffusion coefficient:

$$D_0 = kT/N\xi \quad (17b)$$

Equation 17a can be rewritten as

$$\frac{\Omega}{D_0 q^2} = \left[\frac{\Omega}{D_0 q^2}\right]_{\text{neutral}} + \alpha(\mathbf{q})\, f^2 \Phi N \quad (18a)$$

with

$$\left[\frac{\Omega}{D_0 q^2}\right]_{\text{neutral}} = \frac{1}{P(\mathbf{q})} + v\Phi N \quad (18b)$$

The variation of Ω/D_0q^2 as a function of qR_{g} is illustrated in Figure 1 for various values of the charge parameter f. In the neutral chain limit, $f = 0$ and one observes the known variation of Ω as a function of q; namely, when $q \to 0$, we have $\Omega/D_0q^2 = 1 + v\Phi N$ which in the numerical conditions of Figure 1 gives the value 2 since $v\Phi N = 1$. When q increases, the asymptotic behavior in the intermediate q range ($qR_{\mathrm{g}} \gg 1$) leads to the classical Rouse scaling law $\Omega \sim q^4$. For a charged polymer, Ω/q^2 increases when q decreases toward zero. This increase of Ω/q^2 is more pronounced for larger values of f. This behavior has already been pointed out by various authors before. But one notes that in the present model Ω/q^2 goes to a constant value when $q \to 0$ which implies that the dynamics of polyions is of diffusive nature unlike the earlier conclusions which attributed the increase of Ω/q^2 in the small q range to a plasmon mode. The reason for this behavior is because we have ignored the dynamics of the small ions. If the latter are introduced as full components in the mixture, and their dynamics is explicitly accounted for, one obtains a mode related to the relaxation of polyion concentration fluctuations and a charged plasmon mode whose frequency goes to a constant value when $q \to 0$. These aspects were discussed by several authors[5-11,16,20-22] before and we will not dwell more on this subject here. We could easily investigate the effects of the polymer concentration and added salt concentration on the variation of $\Omega(q)/q^2$ with the wave vector q within the present model. But these effects are well documented in the literature and, therefore, there is no need to go back to these discussions again. The question we want to answer here is to know how this behavior is changed when one adds another polymer which can be either neutral or charged. The first observation to be made in attempting to answer this question is that a second mode appears. In the next section, we discuss the variation of the two modes at various conditions of charge distribution.

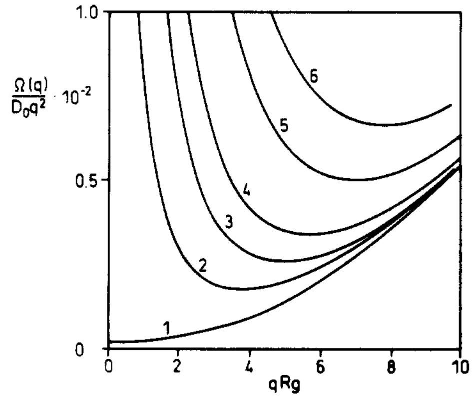

Figure 1. Variation of $\Omega(q)/D_0q^2$ for a single polyion system as a function of qR_{g} for various values of the charge parameter f. Curves 1–6 correspond to $f = 0$ (neutral polymer), 0.05, 0.075, 0.1, 0.15, and 0.2, respectively. The other parameters are chosen as $N = 10^4$, $l = 7$ Å, $R_{\mathrm{g}} = 135$ Å, $A_2 = 2.67 \times 10^{-4}$ cm³/g² ($v = 30$ Å³). Note that $\Omega(q)/D_0$ remains finite at $q = 0$ for all values of f.

4. Case of a Ternary Mixture of Two Polyions and a Solvent

4.1. Frequencies of the Eigenmodes Γ and Γ′. Combining eqs 2 and 9, one can easily verify that the eigenfrequencies Γ and Γ' take the forms

$$\Gamma, \Gamma' = q^2 \frac{kT}{2\Delta S}\{M_{11}S_{22} + M_{22}S_{11} \pm [(M_{11}S_{22} - M_{22}S_{11})^2 + 4M_{11}M_{22}S_{12}{}^2]^{1/2}\} \quad (19a)$$

where $\Delta S = S_{11}S_{22} - S_{12}{}^2$ and the mobilities are

$$M_{11} = x\Phi/\xi_1 \text{ and } M_{22} = (1 - x)\Phi/\xi_2 \quad (19b)$$

The static structure factors $S_{ij}(\mathbf{q})$ are defined by eqs 4–6.

Following the simplification we already described in ref 17, we assume without loss of generality that the thermodynamic parameters v_{ij} satisfy the condition

$$v_{11} = v_{22} = v; \quad v_{12} = v + \chi; \quad \chi \equiv \chi_{12} \tag{20a}$$

and the size parameters as such that

$$N_1 = N_2 = N; \quad P_1(\mathbf{q}) = P_2(\mathbf{q}) = P(\mathbf{q}) \tag{20b}$$

In these conditions $S_{ij}(\mathbf{q})$ become

$$S_{11}(\mathbf{q}) = \frac{x\Phi NP(\mathbf{q})\{1 + [v + \alpha(\mathbf{q}) f_2^{\,2}](1-x)\Phi NP(\mathbf{q})\}}{\mathcal{D}(\mathbf{q})} \tag{21a}$$

$$S_{22}(\mathbf{q}) = \frac{(1-x)\Phi NP(\mathbf{q})\{1 + [v + \alpha(\mathbf{q}) f_1^{\,2}]x\Phi NP(\mathbf{q})\}}{\mathcal{D}(\mathbf{q})} \tag{21b}$$

$$S_{12}(\mathbf{q}) = S_{21}(q) = -\frac{x(1-x)[v + \chi + \alpha(\mathbf{q})\epsilon f_1 f_2]\Phi^2N^2P^2(\mathbf{q})}{\mathcal{D}(\mathbf{q})} \tag{21c}$$

where the denominator $\mathcal{D}(\mathbf{q})$ is given by

$$\mathcal{D}(\mathbf{q}) = \mathcal{D}_{\text{neutral}} + \alpha(\mathbf{q})\,\{xf_1^{\,2} + (1-x)f_2^{\,2} + v_e x(1-x)\Phi NP(\mathbf{q})\}\Phi NP(\mathbf{q}) \tag{21d}$$

$$\mathcal{D}_{\text{neutral}} = 1 + \{v\Phi NP(\mathbf{q}) - \chi(2v + \chi)x(1-x)\Phi^2N^2P^2(\mathbf{q})\} \tag{21e}$$

$$v_e = v(f_1 - \epsilon f_2)^2 - 2\chi\epsilon f_1 f_2 \tag{21f}$$

If one assumes that the friction coefficients are the same, i.e., $\xi_1 = \xi_2 = \xi$, one can put the expressions of Γ and Γ' in the simple form

$$\frac{\Gamma, \Gamma'}{q^2D} = \frac{1}{P(\mathbf{q})}\left\{1 + \frac{\Phi NP(\mathbf{q})}{2}[xU_{11} + (1-x)U_{22} \pm [[xU_{11} - (1-x)U_{22}]^2 + 4x(1-x)U_{12}^{\,2}]^{1/2}]\right\} \tag{22a}$$

where U_{ij} are given by

$$U_{11} = v + \alpha(\mathbf{q})\, f_1^{\,2} \tag{22b}$$

$$U_{22} = v + \alpha(\mathbf{q})\, f_2^{\,2} \tag{22c}$$

$$U_{12} = v + \chi + \alpha(\mathbf{q})\,\epsilon f_1 f_2 \tag{22d}$$

It would be interesting to examine the variations of Γ and Γ' as a function of qR_g at various conditions of charge distribution. One notes a significant difference in the variations of the two frequencies. The frequency Γ' with a minus sign in front of the square root of eq 22a is practically independent of the charge distribution since the value of the square root is on the order of magnitude of the quantity $xU_{11} + (1-x)U_{22}$. Therefore the variation of Γ'/q^2D_0 as a function of qR_g is almost the same as that of the factor $1/P(\mathbf{q})$ as shown by eq 22a and illustrated in Figure 2a. This observation is true for the relatively small values of $v\Phi N$ and χ which are chosen in this plot. By taking higher concentrations and χ values, we observe a slight deviation from $1/P(\mathbf{q})$. But the important aspect is that this mode can be identified as the self-diffusion of a single chain in a matrix of other chains which was sometimes identified with the interdiffusion process.[13-15] A similar behavior will be found later in the discussion of the mean frequency $\Gamma_I(\mathbf{q})$. The other mode Γ corresponding to the plus sign in front of the square root of eq 22a is much more sensitive to the charge distribution as will be shown in the next plots. Figure 2b represents the variation of Γ/q^2D_0 as a function of qR_g for a mixture of neutral ($f_2 = 0$) and charged polymers ($f_1 \neq 0$) and various values of f_1. Curve 1 represents the case of a neutral mixture ($f_1 = 0$) and curves 2–6 correspond to increasing values of f_1. One notes that the variation of $\Gamma(\mathbf{q})$ is qualitatively similar to that of $\Omega(\mathbf{q})$ shown in Figure 1 for

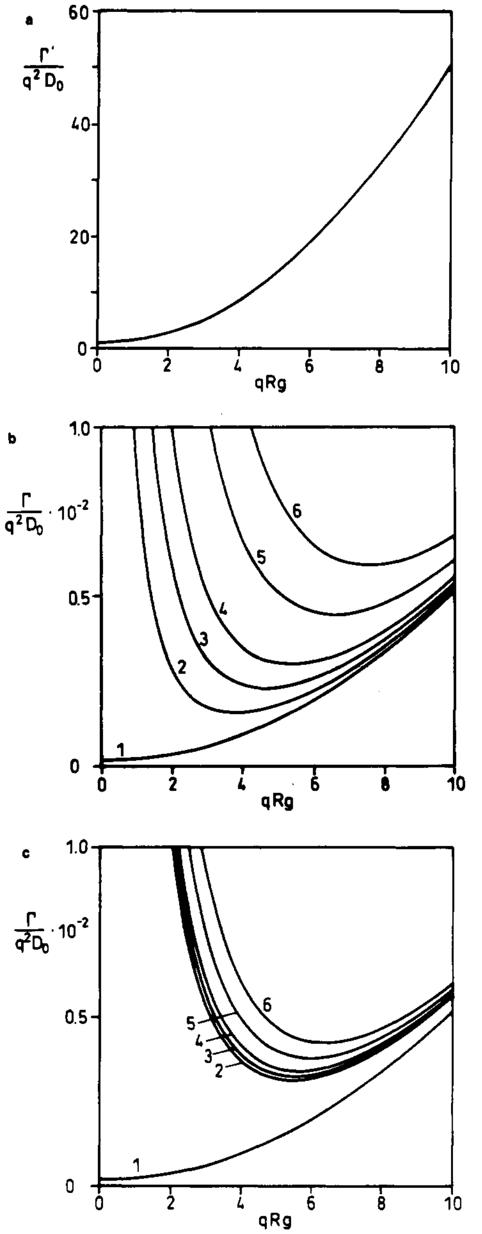

Figure 2. (a) Variation of Γ'/q^2D_0 as a function of qR_g for arbitrary values of f_1 and f_2. The other parameters are chosen as $v\Phi N = 1$, $x = 0.8$, and $\chi/v = 0.1$. This curve coincides practically with the variation of $1/P(\mathbf{q})$, the inverse of the Debye function. If χ and the concentration are chosen with higher values, a slight deviation from $1/P(\mathbf{q})$ would be observed. This frequency represents the self-diffusion of a single chain in the matrix of other chains. (b) Variation of Γ/q^2D_0 as a function of qR_g for a mixture of neutral ($f_2 = 0$) and charged polymers ($f_1 \neq 0$) for various values of f_1. Curves 1–6 correspond to $f_1 = 0$ (neutral mixture), 0.05, 0.075, 0.1, 0.15, and 0.2, respectively. The other parameters are chosen as $v\Phi N = 1$, $\chi/v = 0.1$, and $x = 0.8$ (no salt). (c) Variation of Γ/q^2D_0 as a function of qR_g for a mixture of two charged polymers with charges of the same ($\epsilon = +1$) or opposite signs ($\epsilon = -1$). Curve 1 corresponds to the neutral mixture ($f_1 = f_2 = 0$), and curves 2–6 correspond to $f_2 = 0.075$, 0.05, 0.01, 0.15, and 0.2, respectively; $f_1 = 0.1$ for all curves from 2 to 6, and $v\Phi N = 1$, $\chi/v = 0.1$, and $x = 0.8$ (no salt).

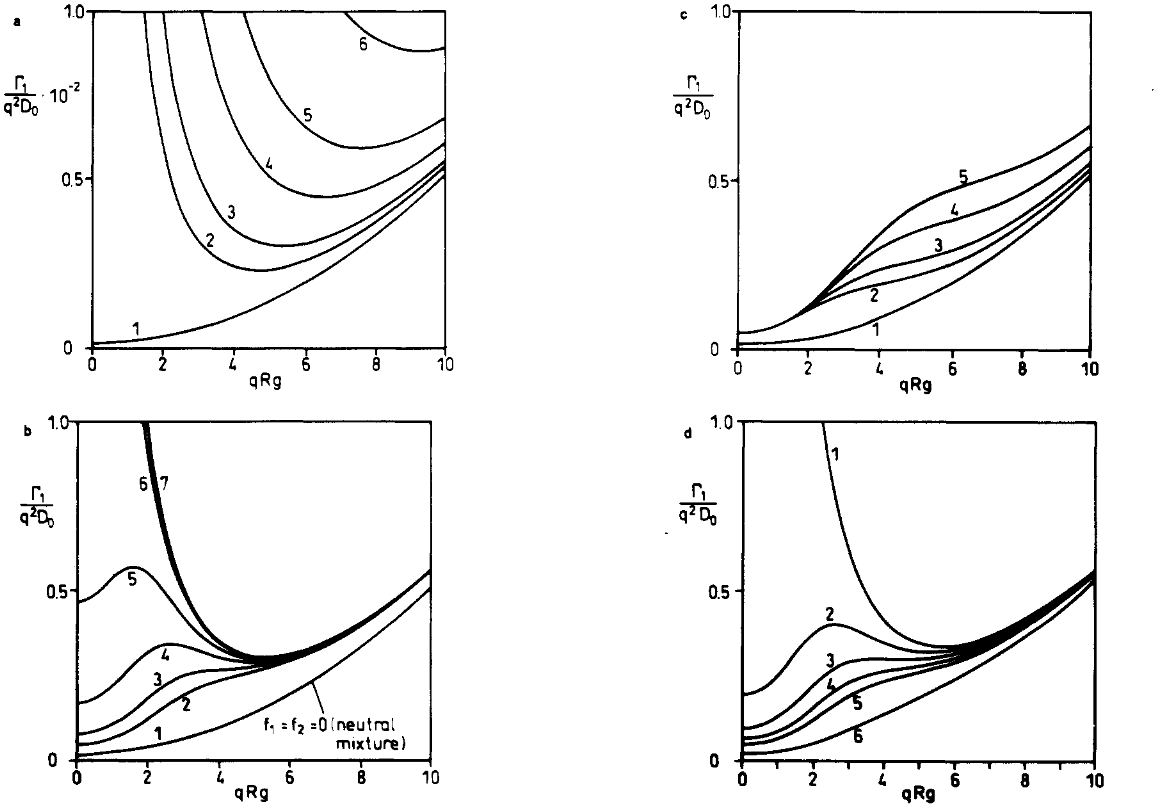

Figure 3. (a) Variation of Γ_1/q^2D_0 as a function of qR_g for a mixture of neutral ($f_2 = 0$) and charged polymers ($f_1 \neq 0$) for various values of f_1. Curves 1–6 correspond to $f_1 = 0$ (neutral mixture), 0.05, 0.075, 0.1, 0.15, and 0.2, respectively. The other parameters are as before: $v\Phi N = 1$, $\chi/v = 0.1$, $x = 0.8$, and no salt. (b) Variation of Γ_1/q^2D_0 as a function of qR_g for a mixture of polymers carrying charges of the same sign ($\epsilon = +1$). $f_1 = 0.1$ and curves 2–7 correspond to $f_2 = 0.1$, 0.075, 0.05, 0.03, 0.01, and zero, respectively. Curve 1 represents the neutral limit $f_1 = f_2 = 0$. The other parameters are chosen as before: $x = 0.8$, $v\Phi N = 1$, $\chi/v = 0.1$, and no salt. (c) Variation of Γ_1/q^2D_0 as a function of qR_g for a mixture of polymers carrying charges of the same sign ($f_1 = f_2 = f$; $\epsilon = +1$) and various values of f. Curves 1–5 correspond to $f = 0$ (neutral mixture), 0.075, 0.1, 0.15, and 0.2, respectively. The other parameters are chosen as $x = 0.8$, $v\Phi N = 1$; $\chi/v = 0.1$, and no salt. (d) Variation of Γ_1/q^2D_0 as a function of qR_g for $f_1 = f_2 = 0.1$ ($\epsilon = +1$) and various values of the composition x. Curves 1–6 correspond to $x = 1$ (single polyion system), 0.95, 0.9, 0.85, 0.8, and 0.5, respectively. The other parameters are chosen as usual: $v\Phi N = 1$, $\chi/v = 0.1$, and no salt.

a single polyion system. There is, in both cases, a strong increase of Γ/q^2 in the small q range which is even more enhanced when the charge parameter f_1 increases, and this supports our observation made earlier for neutral polymers[13] that this mode can be qualitatively identified as a cooperative diffusion mode.[14,15] Furthermore, the limit of Γ/q^2 is finite at $q = 0$ as opposed to the charged plasmon mode which gives Γ = constant for $q = 0$ for reasons that were explained shortly before. The variation of Γ/q^2D_0 when both polymers are charged is illustrated in Figure 2c by choosing $f_1 = 0.1$ and various values of f_2 ranging from 0.075 to 0.2. One observes that qualitatively the shape of the curves remains the same but quantitatively the effect of f_2 is significant. The important thing to be observed is that this figure is practically unchanged whether the polymers have charges of the same or opposite signs ($\epsilon = \pm1$). This can be understood easily by examining eq 22a and noting that the electrostatic contributions in U_{ij} are dominant and hence $U_{12}{}^2 = [v + \chi + \alpha(\mathbf{q})\ \epsilon f_1f_2]^2 \approx \alpha^2(\mathbf{q})\ f_1{}^2f_2{}^2$ is independent of the sign of ϵ.

4.2. Initial Slope of $S_{11}(\mathbf{q},t)$. If we choose the scattering length of monomer 2 equal to s or $(\delta n/\delta c)_2 = 0$, we obtain a dynamic scattering correlation function which is proportional to $S_{11}(\mathbf{q},t)$ whose time evolution is governed by the two modes:

$$S_{11}(\mathbf{q},t) = A_1e^{-\Gamma t} + A'_1e^{-\Gamma' t} \tag{23}$$

We shall not discuss the variations of the amplitudes A_1 and A'_1 and limit ourselves to the initial decay of $S_{11}(\mathbf{q},t)$ which is given by a weighted average of Γ and Γ' with respect to the amplitudes. We have

$$\Gamma_1(q) = -\frac{\partial}{\partial t}\ln S_{11}(\mathbf{q},t)|_{t=0} = \frac{A_1\Gamma + A'_1\Gamma'}{A_1 + A'_1} \tag{24a}$$

It can be easily shown that this frequency[13-15] is given by

$$\Gamma_1(\mathbf{q}) = q^2kT\frac{M_{11}(\mathbf{q})}{S_{11}(\mathbf{q})} \tag{24b}$$

Using eqs 19b and 21a, one obtains

$$\frac{\Gamma_1}{q^2D_0} = \frac{\mathcal{D}(\mathbf{q})}{P(\mathbf{q})\{1 + [v + \alpha(\mathbf{q})\ f_2{}^2](1-x)\Phi NP(\mathbf{q})\}} \tag{25}$$

where $\mathcal{D}(\mathbf{q})$ is given by eq 21d. Various limits can be considered, and one may expect Γ_1 to be highly dependent on the nature of the charge distributions. For a mixture of charged ($f_1 \neq 0$) and neutral ($f_2 = 0$) polymers eq 25 reduces to

$$\frac{\Gamma_1}{q^2D_0} = \left[\frac{\Gamma_1}{q^2D_0}\right]_{\text{neutral}} + \alpha(\mathbf{q})\ f_1{}^2x\Phi N \tag{26a}$$

where the neutral term is defined by

$$\left[\frac{\Gamma_1}{q^2D_0}\right]_{\text{neutral}} = \frac{\mathcal{D}_{\text{neutral}}}{[1 + v(1-x)\Phi NP(\mathbf{q})]} \tag{26b}$$

and $\mathcal{D}_{\text{neutral}}$ is written in eq 21e. This result has a similar form as in the case of a single polyion system (see eqs 18). Therefore, it is not surprising that the q dependence of Γ_1 would bear some similarity with $\Omega(\mathbf{q})$. This can indeed be noticed in Figure 3a where we have plotted Γ_1/q^2D_0 as a function of qR_g for various values of the charge parameter f_1 and $f_2 = 0$. The behavior of Γ_1 is dominated by Γ as one can see by comparison of Figures 2b and 3a.

Let us now examine the case where both polymers are charged with charges of either the same or opposite signs. In the case where these charges have the same sign $\epsilon = +1$, Γ_1 is still given by eq 25 but v_e takes the form (see eq 21f)

$$v_e = v(f_1 - f_2)^2 - 2\chi f_1 f_2 \tag{27}$$

The variation of Γ_1/q^2D_0 as a function of qR_g keeping f_1 constant ($f_1 = 0.1$) and giving various values to f_2 is illustrated in Figure 3b. One observes a drastic change in the curves from the behavior when $f_2 = 0$ (mixture of neutral and charged polymers). It is surprising to note that the increase of Γ_1/q^2 in the small q range tends to be reduced dramatically when f_2 increases and a tendency toward the behavior of a neutral mixture is observed. A close inspection of eq 25 shows that the electrostatic interaction is dominant both in the numerator and in the denominator which leads to a compensation of the strong electrostatic effect in the small q range. A special form of $\Gamma_1(\mathbf{q})$ is obtained in the particular case where $f_1 = f_2 = f$ ($\epsilon = +1$). One notes that $v_e = -2\chi f^2$ and Γ_1 has the same form as in the neutral limit but with a modified q-dependent excluded-volume parameter:

$$\frac{\Gamma_1}{q^2D_0} = \frac{1 + v_{\text{eff}}(\mathbf{q})\,\Phi NP(\mathbf{q}) - \chi[2v_{\text{eff}}(\mathbf{q}) + \chi]x(1-x)\Phi^2N^2P^2(\mathbf{q})}{P(\mathbf{q})\,[1 + v_{\text{eff}}(\mathbf{q})\,(1-x)\Phi NP(\mathbf{q})]} \tag{28a}$$

with

$$v_{\text{eff}}(\mathbf{q}) = v + \alpha(\mathbf{q})\,f^2 \tag{28b}$$

The variation of Γ_1/q^2D_0 as a function of qR_g given by eq 28 is represented in Figure 3c for several values of f from zero to 0.2. One observes that, although the effect of changing v to $v_{\text{eff}}(\mathbf{q})$ is not negligible, it is not comparable with the effect of electrostatic interaction in the case of a single polyion system or in the case of a mixture of charged and neutral polymers. One must also remember that we are looking at part of the dynamic scattering signal through $S_{11}(\mathbf{q},t)$ or its initial decay rate $\Gamma_1^{-1}(\mathbf{q})$. Therefore a significant effect of the composition x on the shape of the curves is expected. To understand this aspect a little better, we have plotted in Figure 3d the variation of Γ_1/q^2D_0 as a function of qR_g for $f_1 = f_2 = f = 0.1$ ($\epsilon = +1$) and various values of the composition x ranging from 1 (single polyion system) to 0.5. One observes that, as soon as x deviates slightly from 1, a drastic change in the variation of Γ_1/q^2D_0 appears in the low q range. A strong decrease is observed as $q \to 0$, and it is progressively enhanced when $x \to 0.5$.

We have mentioned earlier that Γ' is not sensitive to the effect of charges and Γ only weakly sensitive to their sign. This can be explained by the fact that the term depending on ϵ is squared and appears like $U_{12}^2 \sim \alpha^2(\mathbf{q})\,f_1^2f_2^2$. Therefore it is reasonable to expect that $\Gamma_1(\mathbf{q})$ may be only weakly dependent on the charge sign. This is indeed the case and one finds by plotting Γ_1/q^2D_0 for $\epsilon = -1$ qualitatively the same curves as the ones shown in parts b and c of Figure 3. Hence it is not necessary to reproduce these plots again. We may only note that, if $f_1 = f_2 = f$ and $\epsilon = -1$, one obtains an expression of $\Gamma_1(\mathbf{q})$ which is similar to the neutral case with a modified excluded-volume parameter $v_{\text{eff}}(\mathbf{q})$ and a Flory–Huggins interaction parameter $\chi_{\text{eff}}(\mathbf{q})$ as

$$\frac{\Gamma_1}{q^2D_0} = \frac{1 + v_{\text{eff}}(\mathbf{q})\,\Phi NP(\mathbf{q}) - \chi_{\text{eff}}(\mathbf{q})[2v_{\text{eff}}(\mathbf{q}) + \chi_{\text{eff}}(\mathbf{q})]x(1-x)\Phi^2N^2P^2(\mathbf{q})}{P(\mathbf{q})\,[1 + v_{\text{eff}}(\mathbf{q})\,(1-x)\Phi NP(\mathbf{q})]} \tag{29a}$$

where $v_{\text{eff}}(\mathbf{q})$ is defined in eq 28b and $\chi_{\text{eff}}(\mathbf{q})$ is given by

$$\chi_{\text{eff}}(\mathbf{q}) = \chi - 2\alpha(\mathbf{q})\,f^2 \tag{29b}$$

This may explain the fact that the curves for increasing values of f tend to approach (qualitatively) the shape of the curve in the neutral limit as shown by parts b and c of Figure 3.

4.3. Initial Slope of $S_T(\mathbf{q},t)$. The time evolution of $S_T(\mathbf{q},t)$ is also governed by the two modes of frequencies Γ and Γ'

$$S_T(\mathbf{q},t) = A_Te^{-\Gamma t} + A'_Te^{-\Gamma' t} \tag{30}$$

where A_T and A'_T can easily be described in terms of Ω_{ij} and S_{ij}. Our purpose however is to examine rather the mean frequency Γ_T which is a weighted average with respect to these amplitudes. This mean frequency coincides with the initial decay frequency of $S_T(q,t)$ as

$$\Gamma_T = -\frac{\partial}{\partial t}\ln S_T(\mathbf{q},t)|_{t=0} = \frac{A_T\Gamma + A'_T\Gamma'}{A_T + A'_T} \tag{31a}$$

which is shown[14,15] to be equal to

$$\Gamma_T = q^2kT\frac{M_T(\mathbf{q})}{S_T(\mathbf{q})} \tag{31b}$$

In the Rouse limit the total mobility M_T is

$$M_T(\mathbf{q}) = \Phi/\xi \tag{31c}$$

The total structure factor $S_T(\mathbf{q})$ can be obtained from eq 21a,b,c as

$$S_T(\mathbf{q}) = \frac{\Phi NP(\mathbf{q})\left\{1 - 2x(1-x)\Phi NP(\mathbf{q})\left[\chi - \frac{1}{2}\alpha(\mathbf{q})\,(f_1 - \epsilon f_2)^2\right]\right\}}{\mathcal{D}(\mathbf{q})} \tag{32}$$

and $\mathcal{D}(\mathbf{q})$ is given by eq 21d,e,f. Substituting eqs 31c and 32 into eq 31b yields

$$\frac{\Gamma_T}{q^2D_0} = \frac{\mathcal{D}(\mathbf{q})}{P(\mathbf{q})\left\{1 - 2\left[\chi - \frac{1}{2}\alpha(\mathbf{q})\,(f_1 - \epsilon f_2)^2\right]x(1-x)\Phi NP(\mathbf{q})\right\}} \tag{33}$$

In the case of a mixture of neutral ($f_2 = 0$) and charged polymers eqs 33 and 21 give

$$\frac{\Gamma_T}{q^2D_0} = \frac{\mathcal{D}_{\text{neutral}} + \alpha(\mathbf{q})\,xf^2[1 + v(1-x)\Phi NP(\mathbf{q})]}{P(\mathbf{q})\left\{1 + 2\left[\frac{\alpha(\mathbf{q})f^2}{2} - \chi\right]x(1-x)\Phi NP(\mathbf{q})\right\}} \tag{34}$$

Since the electrostatic terms are dominant in both the numerator and denominator of eq 34, one expects a compensation of these two contributions in the small q range and therefore the increase of Γ_T/q^2D_0 in this range should be reduced. This is indeed the case as shown by Figure 4a where we see that 20% of the neutral polymers are sufficient to decrease significantly the value of Γ_T/q^2D_0 in the small q range as opposed to the behavior shown by Figure 1 for example.

If the two polymers are similarly charged, the expression of Γ_T takes a particularly simple form. Letting $f_1 = f_2 = f$ and $\epsilon = +1$ in eqs 33 and 21f leads to

$$\frac{\Gamma_T}{q^2D_0} = \frac{\mathcal{D}_{\text{neutral}} + \alpha(\mathbf{q})\, f^2\{1 - 2\chi(1-x)x\Phi NP(\mathbf{q})\}\Phi NP(\mathbf{q})}{P(\mathbf{q})\{1 - 2\chi x(1-x)\Phi NP(\mathbf{q})\}} \tag{35a}$$

or in the more appealing form

$$\frac{\Gamma_T}{q^2D_0} = \left[\frac{\Gamma_T}{q^2D_0}\right]_{\text{neutral}} + \alpha(\mathbf{q})\, f^2\Phi N \tag{35b}$$

This equation has a form similar to that of eq 18a for the single polyion system and eq 26a giving $\Gamma_T(\mathbf{q})$ for a mixture of neutral and charged polymers. Therefore one expects that it leads to curves similar to those in Figures 1 and 3a. Figure 4b represents the variation of Γ_T/q^2D_0 as a function of qR_g for similarly charged polymers ($f_1 = f_2 = f$, $\epsilon = +1$) and various values of f. One observes a strong increase of Γ_T/q^2D_0 in the small q range which indicates a significant polyelectrolyte effect as shown by eq 35a or eq 35b. One can also examine the case where polymers are oppositely charged. We have observed earlier that the results are similar to those obtained in the neutral limit with modified expressions for $v_{\text{eff}}(\mathbf{q})$ and $\chi_{\text{eff}}(\mathbf{q})$ as defined by eqs 28b and 29b, respectively. Therefore one can easily verify that if $f_1 = f_2 = f$ and $\epsilon = -1$, eq 33 becomes

$$\frac{\Gamma_T}{q^2D_0} = \frac{1 + v_{\text{eff}}\Phi NP(\mathbf{q}) - \chi_{\text{eff}}(\mathbf{q})[2v_{\text{eff}}(\mathbf{q}) + \chi_{\text{eff}}(\mathbf{q})]x(x-1)\Phi^2N^2P^2(\mathbf{q})}{P(\mathbf{q})[1 - 2\chi_{\text{eff}}(\mathbf{q})\, x(1-x)\Phi NP(\mathbf{q})]} \tag{36}$$

One finds that the variation of Γ_T is not significantly changed from the neutral case and therefore there is no need to give its graphical representation here.

4.4. Initial Shape of $S_I(\mathbf{q},t)$. This is an interesting correlation function because it can be directly measured by scattering experiments (either light or neutron) in the zero-average contrast condition:

$$(a_1 - s)x + (a_2 - s)(1 - x) = 0 \tag{37}$$

One notes from eq 12 that $S(\mathbf{q},t)$ becomes proportional to $S_I(\mathbf{q},t)$:

$$S(\mathbf{q},t) = (a_1 - s)^2x^2\Phi^2S_I(\mathbf{q},t) \tag{38}$$

where $S_I(\mathbf{q},t)$ has been defined in eq 11; i.e.

$$\Phi^2S_I(\mathbf{q},t) = \frac{S_{11}(\mathbf{q},t)}{x^2} + \frac{S_{22}(\mathbf{q},t)}{(1-x)^2} - \frac{S_{12}(\mathbf{q},t) + S_{21}(\mathbf{q},t)}{x(1-x)}$$

One can show that $S_I(\mathbf{q},t)$ decays in time following the bimodal function[13,15]

$$S_I(\mathbf{q},t) = A_Ie^{-\Gamma t} + A'_Ie^{-\Gamma' t} \tag{39}$$

and its initial decay is governed by the frequency Γ_I

$$\Gamma_I = -\frac{\partial}{\partial t}\ln S_I(\mathbf{q},t)|_{t=0} = \frac{A_I\Gamma + A'_I\Gamma'}{A_I + A'_I} \tag{40a}$$

Using the general expressions of A_I, A'_I, Γ, and Γ' in terms of Ω_{ij} and S_{ij}, one obtains

$$\Gamma_I = q^2kT\frac{M_I(\mathbf{q})}{S_I(\mathbf{q})} \tag{40b}$$

where in general the intermediate mobility $M_I(\mathbf{q})$ is defined by[14,15]

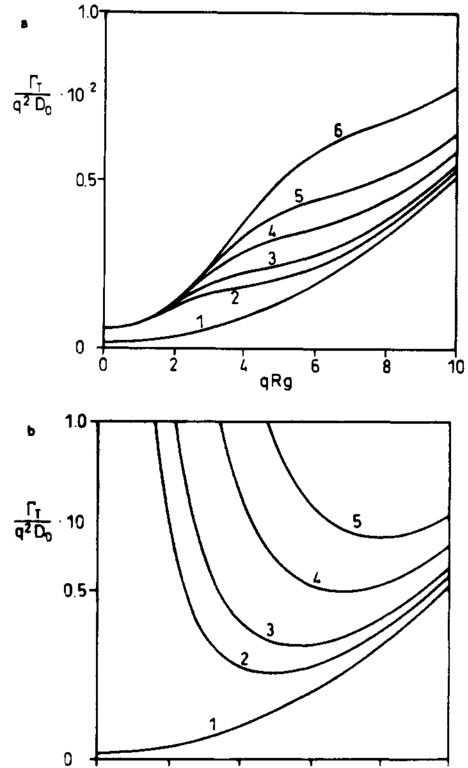

Figure 4. (a) Variation of Γ_T/q^2D_0 as a function of qR_g for a mixture of neutral ($f_2 = 0$) and charged polymers at different values of f_1. Curves 1–6 correspond to $f_1 = 0$ (neutral mixture), 0.075, 0.1, 0.15, 0.2, and 0.3, respectively. The other parameters are chosen as $x = 0.8$, $v\Phi N = 1$, $\chi/v = 0.1$, and no salt. (b) Variation of Γ_T/q^2D_0 as a function of qR_g for similarly charged polymers ($f_1 = f_2 = f$, $\epsilon = +1$) and several values of f. Curves 1–5 correspond to $f = 0$ (neutral limit), 0.05, 0.075, 0.1, and 0.2, respectively. The other parameters are chosen as $x = 0.8$, $v\Phi N = 1$, $\chi/v = 0.1$, and no salt.

$$\Phi^2M_I(\mathbf{q}) = \frac{M_{11}(\mathbf{q})}{x^2} + \frac{M_{22}(\mathbf{q})}{(1-x)^2} - \frac{[(M_{12}(\mathbf{q}) + M_{21}(\mathbf{q})]}{x(1-x)} \tag{40c}$$

and in the Rouse limit $M_I(\mathbf{q})$ simplifies greatly as

$$\Phi^2M_I = \frac{1}{\xi x(1-x)} \tag{40d}$$

Furthermore $S_I(\mathbf{q}) = S_I(\mathbf{q},t{=}0)$ can be obtained by substituting $S_{ij}(\mathbf{q})$ from eq 21 into eq 11 as

$$\Phi^2S_I(\mathbf{q}) = \frac{NP(\mathbf{q})\,\{1 + \mathcal{U}\Phi NP(\mathbf{q})\}}{x(1-x)\mathcal{D}(\mathbf{q})} \tag{40e}$$

where $\mathcal{D}(\mathbf{q})$ is defined in eq 21d and is given by

$$\mathcal{U} = x^2U_{11} + (1-x)^2U_{22} + 2x(1-x)U_{12} \tag{40f}$$

Substituting eq 22 into eq 40f yields

$$\mathcal{U} = v + 2x(1-x)\chi + \alpha(\mathbf{q})\,\{xf_1 + \epsilon(1-x)f_2\}^2 \tag{40g}$$

and substituting eq 40d,e,g into eq 40b leads to the following expression for Γ_T:

$$\frac{\Gamma_T}{q^2D_0} = \frac{\mathcal{D}(\mathbf{q})}{P(\mathbf{q})\,\{1 + [v + 2x(1-x)\chi + \alpha(\mathbf{q})\,(xf_1 + (1-x)\epsilon f_2)^2]\Phi NP(\mathbf{q})\}} \tag{41}$$

Without getting into a detailed investigation of the

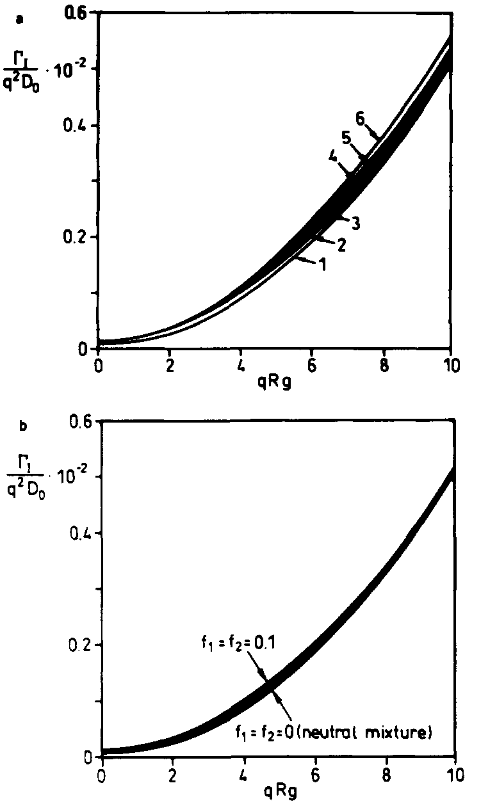

Figure 5. (a) Variation of Γ_I/q^2D_0 as a function of qR_g for a mixture of neutral ($f_2 = 0$) and charged polymers ($f_1 \neq 0$) for various values of f_1. Curves 1–6 correspond to $f_1 = 0$ (neutral mixture), 0.075, 0.1, 0.15, 0.2, and 0.3, respectively. The other parameters are chosen as $x = 0.8$, $v\Phi N = 1$; $\chi/v = 0.1$, and no salt. (b) Variation of Γ_I/q^2D_0 as a function of qR_g for a mixture of charged polymers ($\epsilon = +1$) keeping $f_1 = 0.1$ fixed and varying f_2 from zero (polymer 2 is neutral) to 0.1; the other values of f_2 used are 0.01, 0.03, 0.05, 0.075, and 0.1. The curves for all these values almost coincide with each other. The other parameters are chosen as in Figure 5a.

variation of Γ_I as a function of q, we mention that it is close to the behavior of Γ' discussed earlier. Indeed, this is shown in Figure 5a where we have plotted Γ_I/q^2D_0 as a function of qR_g for a mixture of neutral ($f_2 = 0$) and charged polymers ($f_1 \neq 0$) and various values of f_1. It shows a behavior similar to that in Figure 3a and a relatively small sensitivity to the charge parameter f_1. Figure 5b confirms this behavior since it represents a mixture of two charged polymers with $f_1 = 0.1$ fixed and various values of f_2 from zero to 0.1. The curves are practically the same which shows a very weak sensitivity to the charge parameters. These plots can be reproduced for other conditions of charge distribution with similar conclusions.

4.5. Dynamic Charge Correlation Functions. The charge density for a mixture of two polyions in solution is

$$z(\mathbf{q},t) = f_1e\rho_1(\mathbf{q},t) + f_2e\rho_2(\mathbf{q},t) \qquad (42)$$

where $\rho_1(\mathbf{q},t)$ and $\rho_2(\mathbf{q},t)$ are the densities of monomers 1 and 2, respectively. The dynamic charge correlation function can be defined as

$$S_z(\mathbf{q},t) = \langle z(\mathbf{q},t)\, z(-\mathbf{q},0)\rangle \qquad (43a)$$

where the symbol $\langle ...\rangle$ denotes the average with respect to the equilibrium distribution function. Substituting eq 42 into eq 43a yields

$$e^{-2}S_z(\mathbf{q},t) = f_1^{\,2}S_{11}(\mathbf{q},t) + f_2^{\,2}S_{22}(\mathbf{q},t) + \epsilon f_1f_2[S_{12}(\mathbf{q},t) + S_{21}(\mathbf{q},t)] \qquad (43b)$$

Therefore, the dynamic charge correlation function can be deduced from the knowledge of $S_{ij}(\mathbf{q},t)$ and its time evolution also governed by the eigenmodes of frequencies Γ and Γ', namely

$$S_z(\mathbf{q},t) = A_ze^{-\Gamma t} + A'_ze^{-\Gamma' t} \qquad (43c)$$

One notes that, if the charge parameters are chosen properly, one can have direct experimental access to certain dynamic charge correlation functions. For example, if $f_2 = 0$, the charge correlation function is proportional to $S_{11}(\mathbf{q},t)$:

$$e^{-2}S_z(\mathbf{q},t) = f_1^{\,2}S_{11}(\mathbf{q},t;f_2{=}0) \qquad (44a)$$

The time evolution of this function is completely characterized by the frequencies Γ, Γ', and Γ_1 for a mixture of charged and neutral polymers whose variations with q are displayed in Figures 3b, 2a, and 3a, respectively. If $f_1 = f_2 = f$ and $\epsilon = +1$, one finds that $S_z(\mathbf{q},t)$ is proportional to the total scattering function:

$$e^{-2}S_z(\mathbf{q},t) = f^2S_T(\mathbf{q},t;f_1{=}f_2{=}f;\epsilon{=}{+}1) \qquad (44b)$$

The frequencies governing the relaxation in time of this function are given by Γ, Γ', and Γ_T for a mixture of identically charged polymers and their variations with q are given for certain values of f in Figures 2a, 2c, and 4b, respectively. Finally, if $f_1 = f_2 = f$ and $\epsilon = -1$, eq 42 yields

$$e^{-2}S_z(\mathbf{q},t) = f^2[S_{11}(\mathbf{q},t) + S_{22}(\mathbf{q},t) - S_{12}(\mathbf{q},t) - S_{21}(\mathbf{q},t)] \qquad (44c)$$

The quantity inside the brackets can be identified with $S_I(\mathbf{q},t)$ in the case where the composition $x = 0.5$ (50/50 mixture). Γ_I describes the initial decay of $S_I(\mathbf{q},t)$, and its variation with qR_g is similar to the plots given in parts a and b of Figure 5.

5. Conclusions

In this paper, we have described the dynamics of weakly charged polymers in solution. We have considered in detail the case of ternary mixtures of two polymers in solution, but the general formalism presented in section 2 is valid for an arbitrary number of polymer components.[14,15] The solution is made of an ordinary solvent and all small ions such as the counterions due to the ionization of the polymers and salt ions. These small ions are described as pointlike, structureless and having no contribution to the scattering signal or to the interaction properties except for the screening of the electrostatic interaction and the overall electroneutrality condition. The dynamics of the small ions is completely omitted because we are interested in the apparent dynamics of the polyions. However, if one needs to introduce the dynamics of small ions explicitly in the model, one should include them as full components which increases the rank of matrices by one for each species. The present description does not mean that the coupling between the counterions and polyions is completely neglected. This coupling is present not only through the global electroneutrality condition but in the screening of the electrostatic interaction through the quantity $\alpha(\mathbf{q}) = 4\pi l/(q^2 + \kappa^2)$ which appears in the expressions of the relaxation frequencies. Furthermore, the electrostatic interaction between monomers is described by the Debye–Hückel model and is introduced in this work by assuming that the total interaction is a sum of the excluded volume and the electrostatic interactions (see eq 47). This description is used in the calculation of the static structure factors which are sufficient to describe the short-time dynamics of our system in the Rouse limit. In this description the internal chain structure and dynamics (internal modes) are fully expressed in the short time through the first cumulant $\mathbf{\Omega}$, its eigenvalues Γ and Γ' and hence the mean relaxation frequencies Γ_T and Γ_I. The variations with the wave vector q shown in various figures illustrate clearly the internal modes for $qR_g > 1$. Of course, these modes manifest themselves in the long-time limit by a deviation of the dynamic structure factor from a single exponential if the Markov limit is not reached or there is a strong coupling with other slowly varying variables. These aspects which are related to memory effects are ignored here because of their complexity as we have pointed out earlier. In the small q limit, the polyion shape is irrelevant since $P(q) = 1$ and one recovers the known results for point particles.[2,20] In particular the coupled mode theory results ignoring the dynamics of counterions are obtained.[25] The present study constitutes a generalization of the previous work[2,5,20,25] by including the effects of excluded-volume interaction and chain deformation although the dynamics of small ions has been omitted. The three basic assumptions used in this model are the random phase approximation for the calculation of the static structure matrix (eq 4), the Debye–Hückel approximation for the description of Coulombic interaction between charged monomers (eq 6) and the Rouse model neglecting hydrodynamic interaction (eqs 16b, 18, 25, 31c, and 40d). These approximations are reasonable in the concentration range above the overlap value Φ^* corresponding roughly to $v\Phi^*N = 1$. Indeed above Φ^*, one can assume that the RPA describes reasonably well the structural properties of the mixture in the absence of strong concentration fluctuations. Furthermore, the global electroneutrality condition requires that the concentration of small ions which ensures the screening of the electrostatic interaction increases proportionally to the polyion concentrations. Therefore, the screening becomes more effective and the Debye–Hückel approximation which is introduced as an additional interaction to the bare excluded volume is a reasonable approximation. Finally, it is known that, above Φ^*, the hydrodynamic interaction is screened and the Rouse model can be used to describe the dynamics of the mixture. We believe that, if the polymers remain weakly charged by maintaining the degree of ionization low and hence f small as compared to 1, one can still define a transition from the dilute to the semidilute regime which is not significantly different from the transition in the neutral case.[23,24] The possible connection of this transition with the so-called ordinary–extraordinary phase transition[11,16] is not clear to us and was not a subject of discussion here. One may be attempted to extrapolate the conclusions obtained in this work to the lower concentration range and present some speculations concerning the dilute regime. In this respect, it is known for neutral polymers that the RPA used in the calculation of $S(\mathbf{q})$ leads to the correct results in the dilute regime in spite of the presence of strong concentration fluctuations, since one recovers the single contact results as first derived by Zimm[26] for a binary polymer–solvent mixture. The Debye–Hückel approximation can always be used as long as the description is limited to weakly charged polymers. Perhaps, the most serious problem in the dilute regime arises when one neglects the hydrodynamic interaction. The extension of the present work to the dilute regime including the latter interaction is under preparation and will be the subject of a future paper.[27]

Another aspect which is neglected in the present work is connected with the memory effect in describing the time evolution of $\mathbf{S}(\mathbf{q},t)$. Our starting point is to assume that this dynamic matrix relaxes following a single-exponential form. The inclusion of memory effects is a more difficult problem to deal with and requires more attention if a further improvement of the dynamical description is needed.

Acknowledgment. We thank the reviewers for very useful comments and for pointing to our attention refs 11, 16, 21, 22, and 25. M.B. expresses his gratitude to Professor E. W. Fischer for kindly inviting him to the Max-Planck-Institut für Polymerforschung where this work was completed. Thanks are also due to Miss A. Negadi for help in computations.

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