Effect of Hydrodynamic Interaction on Diffusion in Polyelectrolyte Systems

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ABSTRACT: The short-time behavior of the collective diffusion of charged, flexible polymers is investigated theoretically. Electrostatic and hydrodynamic interactions are taken into account. The former determine the static correlations between the ionic constituents of the system, which are polyion segments, counterions, and co-ions from a monovalent electrolyte. Hydrodynamic interactions are treated in the Oseen approximation. Electrostatic interactions alone are known to enhance collective diffusion. In addition, two distinct effects are found to arise from hydrodynamic interactions: The magnitude of the short-time and long-wavelength limit of the collective diffusion function is increased, and the dependence on the scattering vector is altered in a characteristic way. We compare our results for the apparent diffusion function with experimental data.

1. Introduction

Static and dynamic scattering properties of polyelectrolyte systems have been the subject of intensive studies from both theoretical and experimental points of view. Systems containing charged spheres are very well understood, and recent theoretical work is successful in providing quantitatively correct descriptions. Flexible, charged polymers addressed here are much more complicated objects, because even a single polyion possesses many internal degrees of freedom. In addition, strong electrostatic repulsions between different polyions lead to a qualitatively different behavior as compared to neutral polymers.[1-9] Depending on polyion concentration, degree of polymerization, and salt concentration, several phases have been proposed.[3,10] Our present work refers to the isotropic phase. Dynamic properties of the type of system under investigation have been studied by neutron spin-echo techniques[7-9] and by light scattering.[6,11] The results are influenced by electrostatic interactions between the different ionic species and by their microscopic dynamical properties, which are expressed in terms of friction coefficients of the individual polymer segments and hydrodynamic interactions between them. Let us first comment on the description of static scattering properties, which, also on its own, is of high scientific interest.

Early interpretations of scattering properties are based on scaling arguments.[5,10,12] Since then, several theoretical investigations using various methods were aimed at a better understanding of these complicated systems.[13-18] For systems consisting of charged hard spheres, the Ornstein–Zernike equation is known to be the appropriate starting point. Recently, we proposed a model based on the extension of this equation to a multicomponent polymer system[14,15] and on the generalization of the excluded-volume interactions to include the long-ranged Coulomb potential between the ionic constituents. This scheme, which has been used to describe the correlations in a three-component system composed of charged, flexible polyions, counterions, and co-ions due to a 1:1 electrolyte, is employed here.

The general frame to describe the dynamics of a multicomponent system is based on projection operator techniques in a matrix formulation.[19-21] Application of this eigenmode expansion to salt-free polyelectrolyte systems of pointlike particles[20] revealed the emergence of two modes: One of them is an ordinary diffusive mode, whereas the second relaxation frequency approaches a finite value at vanishing q. The latter has been called a plasmon mode in analogy to the constant frequency of plasma oscillations. Under the assumption of vanishing hydrodynamic coupling between the different constituents the eigenmode expansion has already been applied by Genz[22] using the static model adopted here. A similar model was considered by Vilgis and Borsali.[17] Both approaches predict two modes in a salt-free system showing the typical polyelectrolyte features discussed above. If salt is present, a third mode appears characterizing essentially the diffusion of small ions.

However, it is well-known from many systems, including neutral polymers and charged spheres at moderate volume concentration, that neglect of hydrodynamic interaction may lead to a rather unsatisfactory description of dynamic properties.[23] Also experiments[1,6,8,9] on the type of polyelectroytes considered here give strong indications that the collective diffusion of polyions cannot be understood in terms of static quantities alone. Therefore, we consider the combined effect of long-ranged electrostatic interactions and hydrodynamic interactions on the first cumulant of the dynamic scattering intensity arising from polyion concentration fluctuations. This apparent diffusion function contains contributions from the different eigenmodes discussed above.

This paper is organized as follows: In section 2 we briefly review our approach to account for the static correlations. Section 3 presents the procedure to calculate the wave-vector-dependent apparent diffusion function, whereas section 4 gives the explicit results. Section 5 comments on the results in a wider context by discussing other possible influences on the measured collective diffusion function.

2. Static Scattering Properties

Small-angle neutron or X-ray scattering experiments, but also light scattering,[6,11] provide the current knowledge about the static properties of polyelectrolytes. The measured intensity, which depends on the scattering vector q, originates from scattering by all components constituting

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the system and can be decomposed as

$$I(q) = \sum_{\alpha,\beta} (a_\alpha - s)(a_\beta - s) I_{\alpha\beta}(q) \qquad (1)$$

where a_α is the scattering length of a monomer of species α and $(a_\alpha - s)$ gives the contrast to the scattering from the solvent. We consider a three-component system: $\alpha = 1$ refers to the monomers of the flexible, charged polyions with monomer concentration c_1 and degree of polymerization N. Co-ions, species 3, may be present if salt at a concentration c_3 is added to the solution, while counterions, species 2, are dissociated from polyions and salt ions. If the effective charge on a monomer of the polyion is denoted by $Z_{\text{eff}}e$ and the salt is a 1:1 electrolyte, the co-ion concentration follows from electroneutrality as

$$c_2 = Z_{\text{eff}} c_1 + c_3 \qquad (2)$$

As we are interested in the polyion properties it is sufficient to consider the polyion partial intensity $I_{11}(q)$, which we express in terms of the polyion form factor $P(q)$ and a partial structure factor $S_{11}(q)$ as

$$I_{11}(q) = Nc_1 P(q)\, S_{11}(q) \qquad (3)$$

Equation 3 should be regarded as a definition of a partial structure factor introduced in analogy to structure factors known for sphere systems. As a consequence, $S_{11}(q)$ depends on the polymer configuration. In the framework of a generalized multicomponent Ornstein–Zernike formalism, $S_{11}(q)$ was obtained[14,15] as

$$S_{11}(q) = [1 - Nc_1 P(q)\, c_{\text{eff}}(q)]^{-1} \qquad (4)$$

where $c_{\text{eff}}(q)$ plays the role of an effective direct correlation function between monomers on different polymer chains and is influenced by the presence of small ions. Following refs 15 and 22 $c_{\text{eff}}(q)$ can be expressed by direct correlation functions $c_{\alpha\beta}(q)$ between monomers of species α and β as

$$c_{\text{eff}}(q) = c_{11}(q) + \{c_2 c_{12}^{\,2}(q) + c_3 c_{13}^{\,2}(q) - c_2 c_3 A(q)\} B(q) \qquad (5)$$

with

$$A = c_{12}(q)[c_{12}(q)\, c_{33}(q) - c_{13}(q)\, c_{23}(q)] + c_{13}(q)[c_{13}(q)\, c_{22}(q) - c_{12}(q)\, c_{23}(q)] \qquad (6)$$

and

$$B = [1 - c_2 c_{22}(q) - c_3 c_{33}(q) + c_2 c_3 (c_{22}(q)\, c_{33}(q) - c_{23}^{\,2}(q))]^{-1} \qquad (7)$$

In principle, appropriate equations for $c_{\alpha\beta}(q)$, or related functions, should be solved. Victor[18] addresses this problem in a very recent publication and proposes a calculational strategy based on a generalized Poisson–Boltzmann equation. Instead, we approximate the direct correlation functions by corresponding functions known from the solution[24] of the mean spherical approximation (MSA) for a mixture of charged, hard, but unconnected spheres. The complete expressions can be found from ref 14, and explicit numerical results for the scattering intensity are given in refs 14, 15, and 22. We found that the general trends given by this model are suitable to describe the experimental results. As will become clear in section 4, the shape and general behavior of I_{11} determine the effect of hydrodynamic interactions.

3. Dynamic Scattering

Dynamic scattering experiments using quasielastic light scattering (QELS) or neutron spin–echo techniques are commonly interpreted in terms of the dynamic scattering intensity $I(q,t)$, which can be decomposed in analogy to eq 1 as

$$I(q,t) = \sum_{\alpha,\beta} (a_\alpha - s)(a_\beta - s) I_{\alpha\beta}(q,t) \qquad (8)$$

where $I_{\alpha\beta}(q,t{=}0) = I_{\alpha\beta}(q)$ are the static scattering intensities discussed in the preceding section. In general, $I(q,t)$ may be a complicated function of time. Often, the initial decay of this function is extracted from experimental data in order to obtain an effective, q-dependent diffusion function. From the theoretical point of view, an apparent diffusion function can be defined in terms of the first cumulant of $I(q,t)$ as

$$D_{\text{app}}(q) = -\frac{1}{q^2} \left. \frac{\partial \ln I(q,t)}{\partial t} \right|_{t \to \text{“}0\text{”}} \qquad (9)$$

where the limit $t \to$ “0” refers to a time scale, on which the fluid can be considered to be in local equilibrium with the (Brownian) particles, and the motion of macromolecules is overdamped. As can be seen from eq 8, $I(q,t)$, and therefore $D_{\text{app}}(q)$, depends on the scattering lengths of the constituents. Here, we restrict ourselves to the simple but experimentally important case where only the polyion motion is observed. In this case, the dynamic scattering intensity $I(q,t)$ is essentially given by $I_{11}(q,t)$, which can be expressed as

$$I_{11}(q,t) = \langle \rho_1(0)\, \rho_1^*(t) \rangle \qquad (10)$$

where

$$\rho_1(t) = \sum_{i=1}^{c_1/N} \sum_{m=1}^{N} \exp(i\vec{q}\cdot\vec{r}_{im}(t)) \qquad (11)$$

is a Fourier component of the polyion density, and $\langle ... \rangle$ denotes the equilibrium average. The position of monomer m on polymer i is denoted by $\vec{r}_{im}$. The dynamics of the whole system is described by an appropriate time-development operator $\mathcal{L}$. Thus, eq 10 can be rewritten as

$$I_{11}(q,t) = \langle \rho_1 \exp(-\mathcal{L}t) \rho_1^* \rangle \qquad (12)$$

The first time derivative of $I_{11}(q,t)$ is now expressed in terms of a generalized mobility M_{11}

$$-\left. \frac{\partial I_{11}}{\partial t} \right|_{t \to \text{“}0\text{”}} = \langle \rho_1 \mathcal{L} \rho_1^* \rangle = q^2 k_B T M_{11}(q) \qquad (13)$$

In the special case under consideration, $I(q,t) \sim I_{11}(q,t)$, eqs 9 and 13 lead to

$$D_{\text{app}}(q) = k_B T M_{11}(q) / I_{11}(q) \qquad (14)$$

To describe the time development in polymer and in macromolecular systems, the Kirkwood–Riseman or Smoluchowski operator[19,25] has been found to be appropriate. This operator contains so-called diffusion tensors describing hydrodynamic interactions. The quantity M_{11} defined in eq 13 then contains the contributions from hydrodynamic interactions between all monomers belonging to the polyion species. In principle, these diffusion tensors depend on the position and shape of all constituents in the system. As an approximation, only two-particle hydrodynamic interaction is considered, leading to diffusion tensors which depend only on the position of the respective particle pair. In addition, the polymer segments are regarded as pointlike disturbers of the velocity field in the fluid. Within this approximation, which is commonly employed in polymer physics, hydrodynamic interactions between polymer segments on the same or on different chains are described by the Oseen tensor **T**. Under these circumstances, eq 13 leads to[19]

$$M_{11}(q) = c_1/\zeta + \sum_{i,j}^{c_1/N} \sum_{n,m}^{N}{}' \langle \hat{q}\cdot\mathbf{T}(\vec{r}_{in} - \vec{r}_{jm})\cdot\hat{q} \times \exp[i\vec{q}(\vec{r}_{in} - \vec{r}_{jm})] \rangle \quad (15)$$

where the summation over identical monomers is excluded. The unit vector in the direction of $\vec{q}$ is written as $\hat{q}$, and ζ is the friction coefficient of a monomer. In the following section, we employ eqs 14 and 15 to evaluate the apparent diffusion function within the model described in section 2.

4. Effect of Hydrodynamic Interaction

To account for hydrodynamic interaction, $M_{11}(q)$, eq 15 has to be evaluated. It depends on static properties of the polyions and on dynamic properties. We represent the latter by the friction coefficient ζ of a monomer related to the monomer diameter d by

$$\zeta = 3\pi\eta d \quad (16)$$

and by the Oseen tensor

$$\mathbf{T}(\vec{r}) = \frac{1}{8\pi\eta r}\left(\mathbf{I} + \frac{\vec{r}:\vec{r}}{r^2}\right) \quad (17)$$

which has the Fourier transform

$$\mathbf{T}(\vec{k}) = \frac{1}{\eta k^2}\left(\mathbf{I} - \frac{\vec{k}:\vec{k}}{k^2}\right) \quad (18)$$

I is the unit matrix, and η is the solvent viscosity. Equation 15 is evaluated by expressing the Oseen tensor in r space in terms of its Fourier transform, eq 18, which leads to an integration in Fourier space. Summation over particles and equilibrium average can then be expressed by the static scattering intensity $I_{11}(q)$ or, using eq 3, by the form factor $P(q)$ and the structure factor $S_{11}(q)$. This leads to

$$M_{11}(q) = c_1 N\left(\frac{1}{N\zeta} + \frac{1}{(2\pi)^3}\int d^3k\, T(|\vec{q}-\vec{k}|)\, [P(k)\, S_{11}(k) - 1/N]\right) \quad (19)$$

where $T(|\vec{q}-\vec{k}|)$ denotes the component of the Oseen tensor along the q direction. Neglecting the term $1/N$ and using eq 18, the angular integration in eq 19, can be performed analytically

$$M_{11}(q) = c_1 N\left(\frac{1}{N\zeta} + \frac{1}{(2\pi)^2\eta}\int_0^\infty dk H\left(\frac{k}{q}\right) P(k)\, S_{11}(k)\right) \quad (20)$$

where the function $H(x)$ is given by

$$H(x) = \frac{x}{2}(x^2 + 1)\ln\left|\frac{x+1}{x-1}\right| - x^2 \quad (21)$$

Thus, structural properties influence the result for M_{11} through the term $P(k)\ S_{11}(k)$, which is proportional to $I_{11}(k)$. Although explicit results can only be found numerically, it is instructive to have a closer look at the analytic form of eqs 20 and 21. The function $H(x)$ has an asymptotic behavior as $(4/3)x^4$ for small x, has a pole without change in sign at $x = 1$, and decreases for large x to the asymptotic value $^4/_3$. For low salt content, $I_{11}(q)$ shows typically a broad maximum around $q_{\max}$. Let us now consider the integral in eq 20: For $q \gg q_{\max}$, the argument of $H, k/q$, is always small in the region of the maximum of $P(k)\ S_{11}(k)$, or $I_{11}(k)$, and it decreases with increasing q. Therefore, M_{11} decreases with increasing q as well. In the opposite limit, $q \rightarrow 0$, the argument of H is large in the important region around the maximum; thus, $H(k/q)$ is approximately constant there. Therefore, $M_{11}(q)$ approaches an approximately constant value at small q, which is much higher than the first term in eq 20, the Rouse limit. From this observation one might expect a decrease of $M_{11}(q)$ with increasing q, which becomes important at values of the order of magnitude of $q_{\max}$.

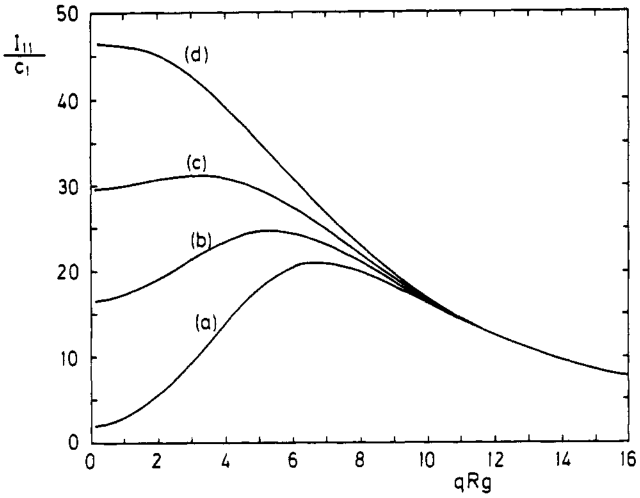

Figure 1. Effect of salt on I_{11} vs qR_G. Curves a–d refer to different salt concentrations: (a) no salt, (b) $c_3 = 0.166$ mol/L, (c) $c_3 = 0.332$ mol/L, (d) $c_3 = 0.582$ mol/L. The polyion concentration was assumed to be constant and given by $c_1 = 0.083$ monomol/L. Other parameters were taken for simplicity to be $Z_{\text{eff}} = 0.5$, $d = 2.5$ Å, $R_G = 32$ Å, and $N = 1000$.

To obtain explicit results, we employ a Debye form factor for $P(q)$

$$P(q) = \frac{2}{u^2}(\exp(-u) + u - 1), \quad u = (qR_G)^2 \quad (22)$$

where R_G denotes the radius of gyration of the polyions, and the results obtained in section 2. To get an idea about the static input, the results for the static scattering intensity are shown in Figure 1. For low salt content, a maximum is obtained, and the scattering at small angles rises strongly when the salt concentration is increased. This reflects the screening of electrostatic repulsion by salt ions. Figure 2 shows the corresponding results for $D_{\text{app}}(q)$ as obtained from eqs 14 and 20. Some comments are in order:

(i) The broken line shows results for a salt-free system in the Rouse limit, which neglects the second term in eq 20, and therefore hydrodynamic interactions. It should be compared to curve a, which contains this contribution. Evidently, just as in the case of neutral polymers the inclusion of hydrodynamic interaction predicts much higher values for $D_{\text{app}}(q)$, and for the mobility $M_{11}(q)$. Therefore, its influence on the magnitude cannot be considered as a small perturbation.

(ii) The effect of salt is illustrated in Figure 2 as well. Increase of salt concentration leads to a considerable decrease of $D_{\text{app}}(q)$ at small q values. This can be expected from the behavior of $I_{11}(q)$, see Figure 1 and eq 14. Results for higher salt content show much weaker variation with qR_G. Such a tendency has been found in experiments.[5] Similar results have recently been obtained by Ajdari et al.[28] using a different approach to describe the static structure.

In view of eq 14, many experimental data have been presented as a comparison between $I_{11}(q)$ and $D_{\text{app}}^{-1}(q)$.[1,6,8,9]

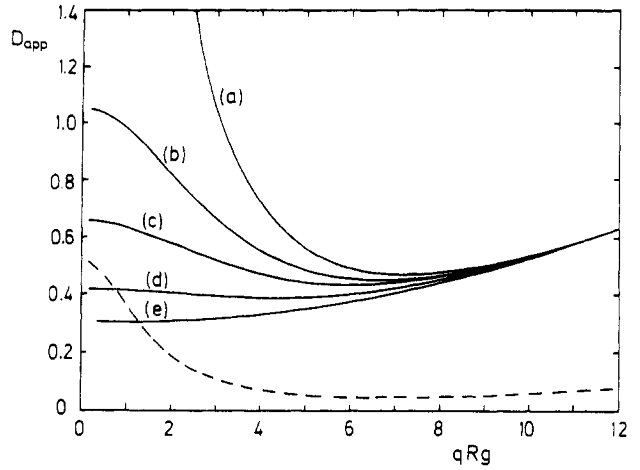

Figure 2. Apparent diffusion function calculated from the structural input used in Figure 1 in units of k_BT/ζ: (a) no salt, (B) $c_3 = 0.083$ mol/L, (c) $c_3 = 0.166$ mol/L, (d) $c_3 = 0.332$ mol/L, (e) $c_3 = 0.582$ mol/L. The broken line shows the Rouse limit in the salt-free case.

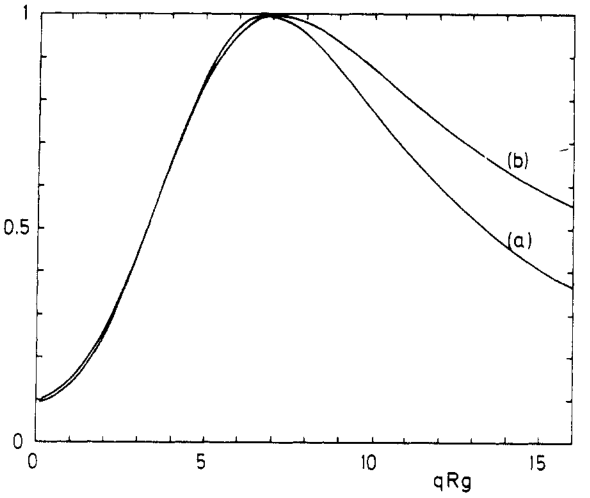

Figure 3. Shapes of $I_{11}(q)$, curve a, and $D_{app}^{-1}(q)$, curve b, vs qR_G compared in the salt-free case. $I_{11}(q)$ and $D_{app}^{-1}(q)$ are normalized to their maximum values.

This is especially suited to highlight intrinsically dynamic effects. In Figure 3 we present a similar comparison between the calculated function $D_{app}^{-1}(q)$ and the corresponding structural input $I_{11}(q)$. In the region $q < q_{max}$, the mobility function $M_{11}(q)$ appears to be approximately constant, which leads to the coincidence of D_{app}^{-1} and $I_{11}(q)$ in this kind of representation. For $q > q_{max}$, however, the decrease of $M_{11}(q)$ leads to values of $D_{app}^{-1}(q)$ lying above $I_{11}(q)$. Such a trend has been found in several experiments.[8,9] Thus, hydrodynamic interaction leads to two distinct effects: It increases strongly the magnitude of the collective diffusion function at small and intermediate q. But, since monomer friction coefficients are usually introduced in an empirical fashion, this consequence is difficult to extract from experiments. The second effect is a characteristic deviation of the q dependence of $D_{app}^{-1}(q)$, similar to the behavior found in several experiments.[8,9]

5. Other Influences on Collective Diffusion

Hydrodynamic interaction is not the only origin for a deviation between the experimentally determined collective diffusion function and the inverse of the scattering intensity. Therefore, let us comment on two additional effects, which can be important in the low-q limit and in the high-q limit, respectively.

It has already been mentioned in the Introduction that polyelectrolyte systems exhibit a so-called plasmon mode characterized by a finite decay rate in the limit $q \to 0$, whereas the decay rate of a diffusional mode vanishes as q^2 in this limit. In light scattering experiments one may come close to this limit, and it becomes a question of time resolution of the experimental setup and of the magnitude of the scattering vector, whether a contribution of this very fast decay mode is detectable. This point becomes more obvious when expressing the dynamic scattering intensity in an eigenmode expansion

$$I_{11}(q,t) = \sum_{i=1}^{3} b_i(q) \exp(-\Gamma_i(q)\, t) \qquad (23)$$

where three eigenmodes, $i = 1$–3, arise because a three-component system is considered. The procedure to obtain the decay rates $\{\Gamma_i(q)\}$ and the amplitudes $\{b_i(q)\}$ is well-known.[19-21] Comparison of eq 9 with eq 23 gives

$$D_{app}(q) = q^{-2} \sum_{i=1}^{3} \bar{b}_i(q)\, \Gamma_i(q) \qquad (24)$$

where $\bar{b}_i(q) = b_i(q)/(\sum_{i=1}^{3} b_i(q)) = b_i(q)/I_{11}(q)$. Due to the asymptotic behavior of the direct correlation functions introduced in section 2, $c_{ij}(q \to 0) \sim 1/q^2$, our model also predicts a plasmon mode characterized by $\Gamma_1(q)$. There are two cases which should be distinguished when eq 24 is used for a comparison with experimental results. In the first case we assume that the decay rate of the plasmon mode is sufficiently small so that the plasmon mode has not yet decayed on the time scale which is accessible in the experiment. Although $\Gamma_1(q \to 0)$ is a constant, whereas $\Gamma_{2,3}(q \to 0) \sim q^2$, one should realize that the first cumulant of eq 23 in the limit as $q \to 0$ does not have a nonzero value from which $\Gamma_1(q \to 0)$ can be directly determined. This fact follows because the amplitude $b_1(q)$ of the plasmon mode in eq 23 has to vanish as q^2 for $q \to 0$, since the expression for D_{app} in eq 24 has to coincide with the one given in eq 14. The latter is finite as $q \to 0$.

The other case is realized if the decay of the plasmon mode is too fast to be observed. Under this condition, $\Gamma_1^{-1} \ll t \ll \Gamma_{2,3}^{-1}$, the experimentally determined diffusion function is given by[21]

$$D_{eff}(q) = q^{-2} \sum_{i=2}^{3} \bar{b}_i(q)\, \Gamma_i(q) \qquad (25)$$

instead of $D_{app}(q)$ in eq 24. Obviously, $D_{eff}(q)$ is smaller than $D_{app}(q)$. Such an effect may contribute to deviations between the inverse diffusion function and the scattering intensity as found from light scattering experiments by Drifford et al.[6] When taking into account hydrodynamic coupling between all species of the system—polyions, counterions, and co-ions in this case—calculation of the eigenmodes and amplitudes is a formidable task, and questions about how to describe correctly the dynamics of small ions may arise. Therefore, we take an oversimplified point of view, neglect any hydrodynamic coupling between different species, and characterize the mobilities by diffusion constants D_1, D_2, and D_3 for the center-of-mass motion of the polyions, counterions, and co-ions, respectively. Neglecting an excluded-volume effect, which was found to give only a minor correction for low q, the limiting case $q \to 0$ corresponding to the model in section 2 has been treated analytically.[22] In the case that only polyions scatter radiation the effective diffusion coefficient introduced in eq 25 is given by

$$D_{\mathrm{eff}}(q \rightarrow 0) = D_1 \frac{2S + NZ_{\mathrm{eff}} + 1}{2S + 1} \frac{(1 + S)D_2 + SD_3}{NZ_{\mathrm{eff}}D_1 + (1 + S)D_2 + SD_3} \quad (26)$$

with

$$S = c_3/(c_1 Z_{\mathrm{eff}})$$

This expression reduces to the well-known Nernst–Hartley diffusion coefficient in the salt-free case, $S = 0$, while in the limit of high salt content, or more precisely, in the linear expansion of eq 26 for small $NZ_{\mathrm{eff}}^2 c_1/c_3$, the result already obtained by Lin, Lee, and Schurr[26] is reproduced. It is worthwhile to note that corresponding formulae in the two limiting cases mentioned above have been found useful in the interpretation of the fast diffusional mode observed by light scattering.[26,27] A qualitative similarity and quantitative discrepancy between experimental data and the limiting cases corresponding to eq 26 may well be due to the neglect of the indirect coupling of polyion and small-ion motion mediated via the solvent.

Also the high-q limit deserves some comments. The region, where the reciprocal wave vector is of the order of the monomer size, lies well inside the experimental range accessible for neutron scattering. From a general point of view, local properties should determine the dynamical behavior. When the fact that monomers have a certain minimum separation is taken into account, the limiting value for M_{11} from eq 15 is found to be c_1/ζ. This is not obvious from eqs 20 and 21. Because the form factor $P(q)$ has been introduced to describe a finite number of monomers, it approaches $1/N$. This term was neglected in eq 22. The limiting value of the structure factor $S_{11}(q)$ is unity, which may be seen from eq 4 or from refs 14 and 15. Combining these results gives $D_{\mathrm{app}}(q \rightarrow \infty) \rightarrow k_B T/\zeta$, independent of any more specific assumptions. Consideration of such a limit should include the q dependence of monomer scattering lengths, which was neglected in eq 1, and a more detailed description of local dynamic properties. Such effects may lead to values of $D_{\mathrm{app}}^{-1}(q)$ larger than those of $I_{11}(q)$ at very large q when presented in analogy to Figure 3. Although these effects point in the same direction as hydrodynamic effects described in Figure 3, the latter start to be important at the position $q_{\max}$ of the maximum in the scattering intensity. The maximum may occur, however, at considerably smaller values of q than those at which the monomer size is revealed.

6. Discussion

In this paper hydrodynamic effects on the diffusional behavior in a polyelectrolyte system are considered. The short-time behavior of the time-correlation function of the field scattered from flexible polyions can be measured by light and neutron scattering. Two effects determine the initial slope: electrostatic repulsion and hydrodynamic interaction. It is found that the apparent diffusion coefficient is enhanced due to both effects. Even in the Rouse limit the collective diffusion of polyions is faster than in a comparable neutral system.[17] The inclusion of hydrodynamic interaction increases further the diffusion. Hydrodynamic interactions between segments on the same polymer and on different polymers have opposite effects: They increase the mobility of a single polymer, because a correlated motion of segments in the same direction becomes easier when the velocity field of the surrounding fluid supports this motion. Qualitatively, one may understand this effect by considering a translational motion of the entire polymer. Without hydrodynamic interaction, every segment of the polymer experiences the same frictional force proportional to the difference between the velocity of the surrounding fluid and the polymer itself. Hydrodynamic interaction takes the alteration of the fluid velocity due to the presence of particles into account. While the outer polymer segments still experience a friction proportional to the difference between the polymer velocity and the fluid velocity outside the polymer coil, inner segments experience a weaker frictional force. A relative motion of particles with respect to one another is hindered by hydrodynamic interactions. This effect alone leads to a decrease of diffusivity and is well-known from systems of spherical particles. Both effects, enhancement of a correlated motion in the same direction and hindrance of uncorrelated motion, are incorporated in our treatment. In view of recent experiments,[8,9] we have studied the q dependence of the static scattering intensity $I_{11}(q)$ and of $D_{\mathrm{app}}^{-1}(q)$. Both quantities are found to be proportional to each other for q up to $q_{\max}$, where $q_{\max}$ is the scattering vector at maximum intensity, whereas at $q > q_{\max}$ we find $D_{\mathrm{app}}^{-1}(q)$ to exhibit a weaker dependence on q than $I_{11}(q)$. This change in behavior is due to hydrodynamic interactions and is at least in qualitative agreement with experiments.

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