Dynamics of Dense Polyelectrolyte Solutions

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ABSTRACT: We investigate a system of dense polyelectrolytes in solution. The Langevin dynamics of the system with linearized hydrodynamics is formulated in the functional integral formalism and a transformation made to collective coordinates. Within a dynamical random phase approximation (RPA) integration over the counterions and salt ions produces the Debye−Hückel-like screening of the Coulomb interactions with dependence on the frequency only as part of a more complicated coupling structure. We investigate the dynamics of the structure factor as well as the collective diffusion coefficient and comment upon the viscosity of the whole system of polymers with counterions and fluid in the simplest approximation. The coupling of the various components of the system produces nontrivial diffusive behavior. We draw conclusions about the relationship of the three length scales in the present system, i.e., the static screening length, the hydrodynamic screening length, and the Debye length.

I. Introduction

The statistical mechanics of polyelectrolytes has recently been the object of much research, of both analytical nature and simulations, ranging from a description of the flexible single-chain properties[1−7] to the properties of the dense melts in collective coordinates (refs 8−10 and references therein). The presence of the long-ranged Coulomb interactions makes such systems completely different from uncharged ones. Underlying many of these approaches is the electrostatic screened interaction according to Debye−Hückel, of the form

$$V_{DH}(\mathbf{r}) = k_B T \frac{\lambda_B}{|\mathbf{r}|} e^{-\kappa|\mathbf{r}|} \tag{1.1}$$

Here κ represents the screening parameter, or its inverse the Debye−Hückel screening length, and λ_B is called the Bjerrum length

$$\lambda_B = \frac{e^2}{4\pi\epsilon k_B T} \tag{1.2}$$

Here ϵ is the dielectric constant of the fluid, and $k_B T$ is the temperature multiplied by the Boltzmann constant. The parameter κ is proportional to the Bjerrum length and to the concentration of the counterions. Its inverse is the Debye screening length. The effective potential can be derived from the linearized Poisson−Boltzmann equation[11] or by utilizing collective density variables together with the random phase approximation in statistical mechanics (RPA) approach[8] and integration over salt and counterion degrees of freedom, which procedure again reproduces that form of effective screened interaction. In other models the mean spherical approximation (MSA) is used.[12] However, whether the Yukawa form of the pairwise potential is truly accurate for macromolecular systems still remains a debatable question, and even for the understanding of the critical behavior in the case of the simple electrolyte a debate concerning an appropriate minimal model exists (see, e.g., Levin and Fisher).[13]

On the statistical mechanical level, the properties of the single chain have been under much discussion as

to the precise dependence upon κ of the properties of the chain, which is expected to behave as with an enhanced persistence length due to the electrostatic interaction. Recent approaches to the problem are a treatment by Barrat and Joanny[2,10] and a renormalization treatment by Liverpool and Stapper.[1] On the level of systems of higher than extremely dilute concentrations, recent work by Muthukumar[14] has been based upon the assumption of an electrostatically altered effective, Gaussian step-length. As regards the implementation of the RPA, it has also been shown[8] that this approximation produces qualitatively correct results. It needs to be altered when strong, attractive interactions can cause complexation[15] or when the effects of the strength of the potential are such that the Gaussian assumption must fail.

The dynamics of polyelectrolytes has recently been addressed in a scaling−theoretical approach by Dobrynin et al.[16,17] An important experimental result in those dynamical considerations is the Fuoss law,[18] which states the proportionality of the viscosity and the inverse square root of the polyion concentration at sufficiently high densities. This was recently confirmed by Dobrynin, Rubinstein, and Colby.[16,17] Other treatments of this law have been by Witten and Pincus[19] and by Rabin.[20] Previously, a theoretical treatment[21,22] of the polyelectrolyte solution viscosity has been given by one of the authors by making use of the results of a mode−mode coupling approximation by Hess and Klein[23] in which a peak of the viscosity was derived. Recent experimental work by Isambert, Ajdari, Mitnuk, Viovy, and Prost[24] has highlighted a physical instability of a polyelectrolyte solution occurring when this solution is subjected to an external electric field.

In this paper we formulate the dynamics of a system of polyions with salt and counterions in the Langevin approach and couple the dynamics of these objects to a solvent which is assumed to be governed by linearized hydrodynamics. It is possible to bring the different length scales inherent to this problem, i.e., the charge screening length, the hydrodynamic screening, and the polymer length, into relation with each other. It is assumed that the system is sufficiently dense and the chain conformations close to the Gaussian ideal to

permit the use of a random phase approximation (RPA) in the context of the dynamics (see, e.g., ref 25).

Furthermore, it is assumed that linearized hydrodynamic properties of the solvent apply and that the investigation is limited to the semidilute regime in which the effects of entanglements of the macromolecular strands can be neglected. Importantly we find that this coupling of the dynamics produces results which are at variance with calculations where an effective Debye-screened potential was used straight away.

The paper is outlined as follows. Section II introduces the dynamical equations of the model system. These expressions are reformulated in terms of a set of collective variables and expressed through the formalism of Martin, Siggia, and Rose[26] and of Peliti and De Dominicis.[27] The subsequent sections and subsections under section III show the results for computations of the correlation functions: this is the dynamical structure factor from which we draw conclusions about the diffusional behavior. The final section recounts the results, discusses the hydrodynamic aspects, and concludes with a discussion on the interplay of the screening lengths.

II. The Model

A. The Langevin Equations. The model consists of the Edwards Hamiltonian for the flexible polyions with the excluded volume interaction written up to second virial order with the electrostatic potential containing the appropriate Bjerrum length, $\lambda_B = e^2/(4\pi\epsilon k_B T)$, for the solvent. The dielectric constant for the solvent is given by $\epsilon = \epsilon_r\epsilon_0$, $k_B T$ is the Boltzmann constant multiplied by the temperature, and e is the electronic charge (for the sake of simplicity only monovalent systems are discussed, although changing valences would present no significant problem in the formalism as used and approximated here.). Furthermore, counterions and salt ions occupy the solvent such that overall electrical neutrality is maintained. We label the four different species of molecule, i.e., polyion, counterion, and the two types of salt ion, by Greek subscripts $\alpha = 1, ..., 4$. There are exactly N_α identical ions of each species, with $N_3 = N_4$, which have position coordinates given by $r_{p\alpha}(s,t)$, where the contour length s is only a relevant variable for the macroions ($\alpha = 1$). Apart from this, no further internal degrees of freedom are associated with any of the system constituents. The complete Hamiltonian expresses the flexibility of the chains, the excluded volume contributions and the (unscreened) Coulomb interaction.

$$H = \frac{3}{2l}\sum_{p=1}^{N_1}\int_0^{L_\alpha}ds\left(\frac{\partial r_{p1}(s,t)}{\partial s}\right)^2 +$$

$$\frac{1}{2}\sum_{\alpha=1}^{4}\sum_{\beta=1}^{4}\sum_{p_\alpha=1}^{N_\alpha}\sum_{q_\beta=1}^{N_\beta}\int_0^{L_\alpha}\int_0^{L_\beta}ds_{p\alpha}ds_{q\beta}\left(w_{\alpha\beta}\delta(r_{p\alpha}(s_{i\alpha},t) - r_{q\beta}\right.$$

$$\left.(s_{j\beta}, t)) + M_{\alpha\beta}\frac{(1 - \delta_{\alpha\beta}\delta_{i_\alpha j_\beta}(1 - \delta_{1 i_\alpha}))}{|r_{p\alpha}(s_{i\alpha}, t) - r_{q\beta}(s_{j\beta}, t)|}\right) \quad (2.1)$$

The Kuhn length of the chains is given by l, and the numerator which contains Kronecker δ functions of the term expressing the Coulomb interaction is a technical description to exclude self-interaction by the point

particles. Formally, in order for the general form above to make sense, the lengths, L_α, of the counterions and salt ions are from one monomer. The Coulomb interaction is represented by the matrix $M_{\alpha\beta}$ of the appropriate interaction between the polymer and the counterions of the system:

$$M_{\alpha\beta} = \lambda_B k_B T\begin{pmatrix} f^2 & -f & +f & -f \\ -f & +1 & -1 & +1 \\ +f & -1 & +1 & -1 \\ -f & +1 & -1 & +1 \end{pmatrix} \quad (2.2)$$

The condition of electrical neutrality implies that $N_1 Lf - N_2 + N_3 - N_4 = 0$ must hold. The quantity f represents the constant, linear charge density of the polymer. The matrix $w_{\alpha\beta}$ represents the excluded volume interaction between the various components of the system. The Hamiltonian and the hydrodynamics then lead to the coupled, stochastic Langevin equations of the system for the chain molecules, the counterions, and the fluid velocity field.[28] When stick boundary conditions are employed the stochastic equations can be written as

$$L_p^\alpha \equiv -\frac{\partial}{\partial t}r_{p\alpha}(t) + v[r_{p\alpha}(t)] - \frac{1}{\zeta_\alpha}\frac{\delta H}{\delta r_{p\alpha}(t)} +$$

$$f_{p\alpha}(t) = 0 \quad (2.3)$$

$$L^v \equiv -\frac{\partial}{\partial t}v(x, t) +$$

$$\left\{\eta\nabla^2 v(x,t) - \sum_{p=1}^{N_1}\int_0^{L_1}ds\frac{\delta H}{\delta r_{p1}(s, t)}\delta(x - r_{p1}(s, t)) -\right.$$

$$\left.\sum_{\alpha=2}^{4}\sum_{p=1}^{N_\alpha}\frac{\delta H}{\delta r_{p\alpha}(t)}\delta(x - r_{p\alpha}(t)) + f_v(x, t)\right\}_\perp = 0 \quad (2.4)$$

The random forces, $f_{p\alpha}(s_{p\alpha},t)$ and $f_v(x,t)$ for the dynamics of the molecules and the fluid dynamics, respectively, are correlated as Gaussians and satisfy the fluctuation—dissipation theorem given by $\langle f_{p\alpha}(s_{p\alpha}, t)f_{q\beta}(s_{q\beta}, t')\rangle = (2/\zeta_\alpha)\delta_{\alpha\beta}\mathbf{1}\delta_{p_\alpha q_\beta}\delta(t - t')\delta(s_{p\alpha} - s_{q\beta})$ and $\langle f_v(x, t)f_v(x', t')\rangle = -2\eta\mathbf{1}\nabla_x^2\delta(x - x')\delta(t - t')$. We are also working in the case of the incompressible fluid continuum[28] and, hence, impose the transverse condition upon the velocity field of the fluid of bare viscosity η. The components have friction coefficients ζ_α which are in general different. The energy units above have been chosen such that $k_B T = 1$, and for subsequent sections, the distance units of the polymer will also be chosen such that the prefactor $^3/_2 l$ in the Hamiltonian vanishes.

B. Functional Integral Formalism. We now treat the set of coupled differential equations by using the functional integral approach of Martin, Siggia, and Rose[26] and follow the scheme of Fredrickson and Helfand[25] used for uncharged solutions of monodisperse polymers. Here we shall be concerned primarily with the collective behavior of the system dynamics, and, in following the work of Fredrickson and Helfand, we shall later ignore contributions in the collective variables which are of an order higher than two.

If use is made of causality and the fact that the Jacobian of the transformation then becomes unity,[29]

the functional integral expressions become

$$\left\langle \int \left\{ \prod_{\alpha=1}^{4} \prod_{p=1}^{N_\alpha} \mathcal{D}\hat{\mathbf{r}}_{p\alpha}(t)\, \mathcal{D}\hat{\mathbf{r}}_{p\alpha}(t) \right\} \mathcal{D}\mathbf{v}(\mathbf{x},\, t)\, \mathcal{D}\hat{\mathbf{v}}(\mathbf{x},\, t) \times \right.$$

$$\exp\{+i[\sum_{\alpha=1}^{4}\sum_{p=1}^{N_\alpha}\int_{-\infty}^{+\infty}\mathrm{d}t\int_0^{L_\alpha}\mathrm{d}s\,\hat{\mathbf{r}}_{p\alpha}(t)\cdot\mathbf{L}_p^\alpha +$$

$$\left. \int_{-\infty}^{+\infty}\mathrm{d}t\int_\Omega \mathrm{d}^3x\,\hat{\mathbf{v}}(x,\, t)\cdot\mathbf{L}^v]\}\right\rangle \quad (2.5)$$

Angular brackets indicate the averaging over Gaussian noise and Ω represents the volume. Following ref 25 we introduce collective variables in terms of collective density and response functions for each species α (with a number, N_α of molecules):

$$\rho_\alpha(\mathbf{k},\, t) = \sum_{p=1}^{N_\alpha}\int_0^{L_\alpha}\mathrm{d}s\,\exp(+i\mathbf{k}\cdot\mathbf{r}_{p\alpha}(s,\, t)) \quad (2.6)$$

$$\sigma_\alpha(\mathbf{k},\, t) = \sum_{p=1}^{N_\alpha}\int_0^{L_\alpha}\mathrm{d}s\,\hat{\mathbf{r}}_{p\alpha}(s,\, t)\,\exp(+i\mathbf{k}\cdot\mathbf{r}_{p\alpha}(s,\, t)) \quad (2.7)$$

$$\boldsymbol{\pi}_\alpha(\mathbf{k},\, t) = \delta_{\alpha1}(\mathbf{1}-\hat{\mathbf{k}}\hat{\mathbf{k}})\cdot\sum_{p=1}^{N_1}\int_0^{L_\alpha}\mathrm{d}s\left(\frac{\partial^2\mathbf{r}_{p1}(s,\, t)}{\partial s^2}\right)\times$$
$$\exp(+i\mathbf{k}\cdot\mathbf{r}_{p1}(s,\, t)) \quad (2.8)$$

Clearly, the $\boldsymbol{\pi}_\alpha$ has no meaning when it relates to pointlike salt or counterions in the system.

If one were to impose the additional condition that the whole system finds itself in a spatially varying, external field, which oscillates at a frequency $\tilde{\omega}$, such as $2\tilde{\mathbf{v}}(\mathbf{k})\cos\tilde{\omega}t$, the Langevin equations in the MSR formalism of eq 2.5 would have an additional contribution in the exponent of

$$\angle_{\text{ext}} = \sum_\alpha\sum_{\omega\mathbf{k}}\frac{i}{\zeta_\alpha}\tilde{V}(\mathbf{k})\mathbf{k}\cdot(\boldsymbol{\sigma}_\alpha(\mathbf{k},\,\omega+\tilde{\omega})+\boldsymbol{\sigma}_\alpha(\mathbf{k},\,\omega-\tilde{\omega}))$$
$$(2.9)$$

The linearized hydrodynamic formulation used here permits the integration over the fluid velocity fields to be performed exactly and enables the determination of the frequency−dependent structure factor of the molecular inclusions from which the diffusion coefficient of these components is derived. Consequently, one can write

$$Z = \int\left\{\prod\mathcal{D}\mathbf{r}\,\mathcal{D}\hat{\mathbf{r}}\right\}\exp(-\angle) \quad (2.10)$$

where $\angle = \angle_0 + \angle_1 + \angle_3$. The variables and integrals are all expressed in terms of their Fourier representations, the random forces have been integrated, and the functional integrals over the velocity fields, which occur

only to quadratic order, have been performed. The functions above are given by

$$\angle_0 = -i\int_\omega\left\{\sum_{p=1}^{N_1}\int_0^{L_1}\mathrm{d}s\,\hat{\mathbf{R}}_{p1}(s,\,\omega)\cdot\left[i\omega\mathbf{R}_{p1}(s,\,\omega)+\right.\right.$$
$$\left.\frac{1}{\zeta_1}\frac{\partial^2}{\partial s^2}\mathbf{R}_{p1}(s,\,\omega)+\frac{i}{\zeta_1}\hat{\mathbf{R}}_{p1}(s,\,\omega)\right]+$$
$$\left.\sum_{\alpha=2}^{4}\sum_{p=1}^{N_\alpha}\hat{\mathbf{r}}_{p\alpha}(\omega)\cdot\left[i\omega\mathbf{r}_{p\alpha}(\omega)+\frac{i}{\zeta_\alpha}\hat{\mathbf{r}}_{p\alpha}(\omega)\right]\right\} \quad (2.11)$$

$$\angle_\text{I} = i\sum_{\alpha=1}^{4}\sum_{\beta=1}^{4}\int_\mathbf{k}\int_\omega\frac{1}{\zeta_\beta}\rho_\alpha(-\mathbf{k},\,-\omega)[4\pi k^{-2}M_{\alpha\beta}+$$

$$w_{\alpha\beta}]i\mathbf{k}\cdot\boldsymbol{\sigma}_\beta(\mathbf{k},\,\omega)+\sum_{\alpha=1}^{4}\sum_{\beta=1}^{4}\int_\mathbf{k}\int_\omega(\mathbf{1}-\hat{\mathbf{k}}\hat{\mathbf{k}})\cdot\boldsymbol{\sigma}_\alpha(-\mathbf{k},\,-\omega)$$

$$\left[\frac{\eta k^2}{\omega^2+\eta^2 k^4}(\mathbf{1}-\hat{\mathbf{k}}\hat{\mathbf{k}})\cdot\boldsymbol{\sigma}_\beta(\mathbf{k},\,\omega)+\frac{1}{\omega+i\eta k^2}\boldsymbol{\pi}_\beta(\mathbf{k},\,\omega)\right]$$
$$(2.12)$$

$$\angle_3 = i\sum_{\alpha=1}^{4}\sum_{\beta=1}^{4}\sum_{\gamma=1}^{4}\int_{\mathbf{k}\mathbf{k}'}\int_{\omega\omega'}\frac{1}{\omega+i\eta k^2}(\mathbf{1}-\hat{\mathbf{k}}\hat{\mathbf{k}})\cdot\boldsymbol{\sigma}_\beta(-\mathbf{k},\,-$$
$$\omega)\cdot\mathbf{k}'\rho_\beta(\mathbf{k}',\,\omega)[M_{\beta\gamma}(\mathbf{k}')^{-2}+w_{\beta\gamma}]\,\rho_\gamma(\mathbf{k}-\mathbf{k}',\,\omega-\omega')$$
$$(2.13)$$

The friction coefficients for the polyion chain segments and the counterions are given by ζ_1 and ζ_2, respectively. The second term of $\angle_1$ and the contribution $\angle_3$ come from the coupling to the hydrodynamic medium with sticking boundary conditions.

Since we assume to be dealing with sufficiently dense systems below the onset of entanglement effects, we can make use of the approximation that the chains behave as Gaussians. The random phase approximation is implemented utilizing $\exp(-\angle_0)$ as the statistical measure for the collective variables as done by Fredrickson and Helfand.[25] The results are summarized in the appendix. Importantly, in the quadratic approximation the collective variables ρ_α and its dynamical conjugate field $\mathbf{k}\cdot\boldsymbol{\sigma}_\alpha$ decouple from $(\mathbf{1}-\hat{\mathbf{k}}\hat{\mathbf{k}})\cdot\boldsymbol{\sigma}_\alpha$ and $(\mathbf{1}-\hat{\mathbf{k}}\hat{\mathbf{k}})\cdot\boldsymbol{\pi}_\alpha$. This decoupling and the quadratic distribution also cause the cubic contribution $\angle_3$ to be a negligible contribution such that the hydrodynamics will not have any effect upon ρ_α and $\mathbf{k}\cdot\boldsymbol{\sigma}_\alpha$ when the interactions are considered at this order.

For the sake of simplicity, we perform the calculation for the system consisting of polyions and the counterions leaving the component labels $\alpha = 1$ and $\alpha = 2$ with concentrations given by ρ_1 and ρ_2, respectively. Extending the results for salt ions is straightforward. Investigating the properties of the structure factor requires the use of the collective variables which can be contained in a supervector

$$\underline{\psi}(\mathbf{k},\,\omega) = (\rho_1(\mathbf{k},\,\omega),\, \mathbf{k}\cdot\boldsymbol{\sigma}_1(\mathbf{k},\,\omega),\, \rho_2(\mathbf{k},\,\omega),\, \mathbf{k}\cdot\boldsymbol{\sigma}_2(\mathbf{k},\,\omega))$$
$$(2.14)$$

Averages concerning these quantities can now be expressed as follows:

$$\langle\mathbf{A}\rangle_\text{RPA} = \mathcal{N}\int\mathcal{D}\underline{\psi}\,\mathbf{A}\,\exp(-[\underline{\psi}^T(-\mathbf{k},\,\omega)\cdot\mathbf{T}\cdot\underline{\psi}(\mathbf{k},\,\omega)])$$
$$(2.15)$$

$$\mathbf{T} = \begin{vmatrix} 0 & \dfrac{i}{L\rho_1} + \dfrac{\zeta_1\omega}{\rho_1 k^2} + iv + \dfrac{i\lambda_{\mathrm{B}}f^2}{k^2} & 0 & -\dfrac{i\lambda_{\mathrm{B}}f}{k^2} \\[2ex] \dfrac{i}{L\rho_1} - \dfrac{\zeta_1\omega}{\rho_1 k^2} + iv + \dfrac{i\lambda_{\mathrm{B}}f^2}{k^2} \quad \dfrac{\zeta_1}{k^2\rho_1} & -\dfrac{i\lambda_{\mathrm{B}}f}{k^2} & 0 \\[2ex] 0 & -\dfrac{i\lambda_{\mathrm{B}}f}{k^2} & 0 & \dfrac{i}{\rho_2} + \dfrac{\zeta_2\omega}{\rho_2 k^2} + \dfrac{i\lambda_{\mathrm{B}}}{k_2} \\[2ex] -\dfrac{i\lambda_{\mathrm{B}}f}{k^2} & 0 & \dfrac{i}{\rho_2} - \dfrac{\zeta_2\omega}{\rho_2 k^2} + \dfrac{i\lambda_{\mathrm{B}}}{k_2} \quad \dfrac{\zeta_2}{k^2\rho_2} \end{vmatrix} \tag{3.1}$$

Here the matrix **T** contains the contributions from the RPA and the interaction term, $\angle_{\mathrm{I}}$. An explicit form of this matrix is given in the following section.

III. The Dynamic Structure Factor

After the interactions and the two coupled density fields which are not in the transverse direction, are included, the computation of the structure factor reduces to the identification of the appropriate elements of the inverse of the matrix **T** given below. The excluded volume interaction is assumed only between polyion chain segments, such that we take the matrix $w_{\alpha\beta}$ to be given by the expression $w_{\alpha\beta} = \delta_{1\alpha}\delta_{1\beta}v$. Here we consider the case of large length scales and large times. These conditions, $k R_{\mathrm{g}} \ll 1$ and $\omega\tau_r \ll 1$, where for the units which have been chosen, $R_{\mathrm{g}} = L/2$, and the Rouse time, $\tau_r = L^2\zeta_1\pi^{-2}$, lead to the matrix in the quadratic supervector formulation (eq 3.1). We shall be interested primarily in the diffusional behavior contained within this matrix. This requires only the consideration of the limits given above.

A. Expression for the Structure Factor. As a consequence we can write the polymer–polymer structure factor for the case $kR_{\mathrm{g}} \ll 1$. By recalling the definition of the matrix **T**, this must be the 1,1 element of the inverse, $\mathbf{T}^{-1}$

$$G_{11}(\mathbf{k}, \omega) = 2k^2\rho_1(\zeta_1 k^4 + 2\zeta_1 k^2\lambda_{\mathrm{B}}\rho_2 + \zeta_1\zeta_2{}^2\omega^2 +$$
$$\zeta_1\lambda_{\mathrm{B}}{}^2\rho_2{}^2 + \rho_1\lambda_{\mathrm{B}}{}^2 f^2\zeta_2\rho_2) \, L^2/(2k^6\lambda_{\mathrm{B}}f^2\rho_1 L + k^8 +$$
$$2Lk^8 v\rho_1 + \lambda_{\mathrm{B}}{}^2 f^4\rho_1{}^2 k^4 L^2 + \zeta_1{}^2\omega^2 k^4 L^2 + \zeta_1{}^2\omega^4\zeta_2{}^2 L^2 +$$
$$\lambda_{\mathrm{B}}{}^2 f^4\rho_1{}^2\zeta_2{}^2\omega^2 L^2 + 2vk^4\rho_1{}^2\lambda_{\mathrm{B}}{}^2\rho_2 f^2 L^2 +$$
$$2vk^6\rho_1{}^2\lambda_{\mathrm{B}}f^2 L^2 + \zeta_1{}^2\omega^2\lambda_{\mathrm{B}}{}^2\rho_2{}^2 L^2 + v^2 k^4\rho_1{}^2\zeta_2{}^2\omega^2 L^2 +$$
$$2\zeta_1{}^2\omega^2 k^2\lambda_{\mathrm{B}}\rho_2 L^2 + 2\zeta_1\omega^2\lambda_{\mathrm{B}}{}^2\rho_2 f^2\rho_1\zeta_2 L^2 +$$
$$2vk^2\rho_1{}^2\zeta_2{}^2\omega^2\lambda_{\mathrm{B}}f^2 L^2 + 2v^2 k^6\rho_1{}^2\lambda_{\mathrm{B}}\rho_2 L^2 +$$
$$v^2 k^4\rho_1{}^2\lambda_{\mathrm{B}}\rho_2{}^2 L^2 + v^2 k^8\rho_1{}^2 L^2 + 2k^2\zeta_2{}^2\omega^2\lambda_{\mathrm{B}}f^2\rho_1 L +$$
$$2k^4\lambda_{\mathrm{B}}{}^2\rho_2 f^2\rho_1 L + k^4\zeta_2{}^2\omega^2 + 2k^6\lambda_{\mathrm{B}}\rho_2 + k^4\lambda_{\mathrm{B}}{}^2\rho_2{}^2 +$$
$$2Lk^4\zeta_2{}^2\omega^2 v\rho_1 + 2Lk^4\lambda_{\mathrm{B}}{}^2\rho_2{}^2 v\rho_1 + 4Lk^6 v\rho_1\lambda_{\mathrm{B}}\rho_2) \tag{3.2}$$

Similar results hold for the cases of the other structure factors of the system. This is the structure factor of the polymers in the coupled systems of ions and counterions, where there is an excluded volume interaction between the polymer segments, a dynamic effective interaction, and dynamic alteration to the distribution of the polyions. When the limits $\rho_2 \to 0$, $\lambda_{\mathrm{B}} \to 0$ are taken, the expression becomes equivalent to that of Fredrickson and Helfand.[25]

Although this factor looks rather complicated, the form of the equation can be simplified significantly by noting the definition of the Debye parameter

$$\kappa^2 = \lambda_{\mathrm{B}}\rho_2 \tag{3.3}$$

and by introducing the quantity

$$\tilde{\xi}^{-2} = \rho_1 v \tag{3.4}$$

which differs from the conventional definition of the screening parameter by Edwards[30] by a factor of 4.

A plot of this structure factor is shown in Figure 1, where convenient values have been used for the parameters. The polyelectrolyte peak is clearly visible and moves to greater values of k with increasing frequency. The peak has already been discussed in the context of statistical mechanics by various authors.[8]

We find that broadening together with heightening in both k and ω directions of the polyelectrolyte peak is a result of either a decrease of the polyion charge density or of an increase of the Debye parameter.

B. Diffusional Behavior. By inspection of the fraction in eq 3.2, it is easy to identify that the numerator is a second-order polynomial in ω and the denominator, when expanded, is a polynomial of fourth order in the frequency. This suggests that the diffusion in the present approximation has two modes, which can be extracted by breaking the expression 3.2 into its partial fractions. The result of this manipulation is

$$G_{11} = \frac{A_1}{\Gamma_1 + \omega^2} + \frac{A_2}{\Gamma_2 + \omega^2} \tag{3.5}$$

where the modes associated with the amplitudes A_1 and A_2 have the following values which have been expanded to their lowest orders in k^2:

$$\sqrt{\Gamma_1}/k^2 \simeq \frac{\rho_1 f^2 + \rho_1\rho_2 v + L^{-1}\rho_2}{\zeta_1\rho_2 + f^2\rho_1\zeta_2} = D_{\mathrm{c}} \tag{3.6}$$

$$\sqrt{\Gamma_2} \simeq \frac{\lambda_{\mathrm{B}}}{\zeta_1\zeta_2}(f^2\rho_1\zeta_2 + \zeta_1\rho_2) \tag{3.7}$$

This behavior to is to be anticipated in a system where there are two components coupled by an interaction such as the Coulomb interaction, and it has been previously deduced within the context of a far simpler assumption about the dynamics of the polyelectrolyte system. The mode Γ_2 has already previously been identified as the plasmon mode. It is not proportional to k^2 at large length scales and agrees with that found by other methods.[8]
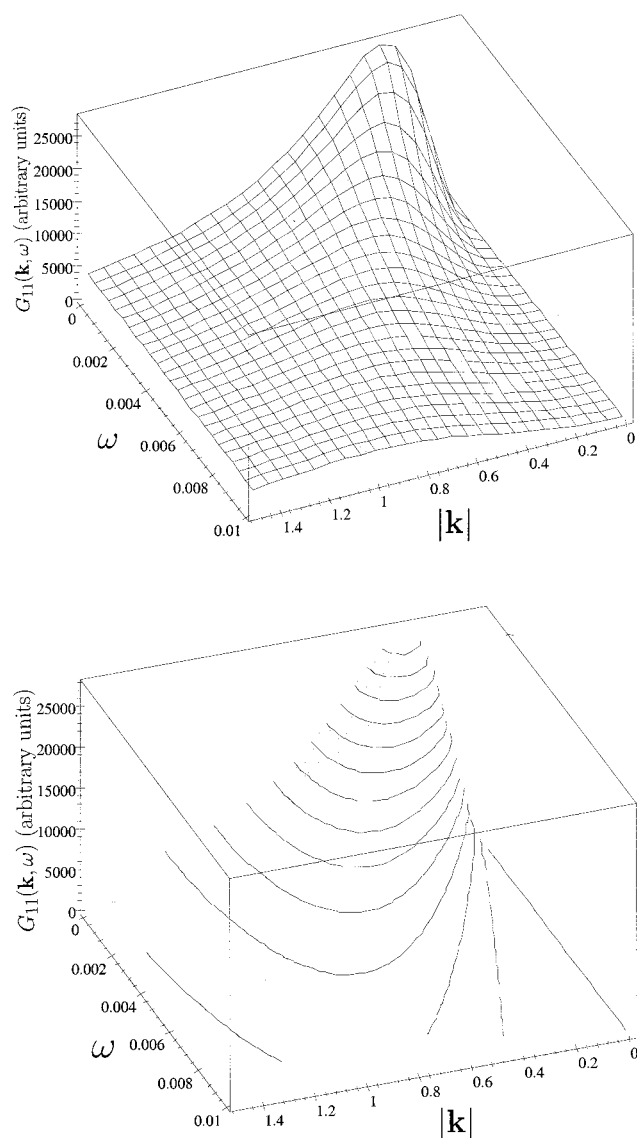
Figure 1. Dynamical structure factor plotted for $\zeta_1 = \zeta_2 = 1$, $\rho_1 = 1$, $f = 0.03$, $L = 100$, $v = 0$, $\kappa = 0.01$, and $\lambda_B = 1$. The graphs show clearly how the peak in the dynamic structure factor broadens in the ω-direction. The maximum width in ω occurs at a momentum transfer vector larger than the location of the scattering peak.

The cooperative diffusion coefficient is given by the expression 3.6. Here we see that this is also given as in the paper of Vilgis and Borsali,[8] with the limiting proportionality $v\rho_1 + 1/L$. This is the expected behavior. We note that in the present scheme of approximation the cooperative diffusion coefficient, D_c, depends on the interaction only through the linear charge density of the chains and the counterion concentration, whereas the plasmon mode is directly proportional to the Bjerrum length.

IV. Discussion

In the first scheme of integration of section II, the immediate integration over the fluid velocity field degrees of freedom leads directly to the nonlinear term in the polymer density, which is the only term coupling the nature of the interaction into the hydrodynamic description and vice versa. Under the RPA for the transversal components too, it is clear that this coupling term plays no contribution whatsoever, and then the

dynamics of this system would be exactly as in the case derived by Fredrickson and Helfand.[25] For frequencies $\omega L^2/\pi^2\zeta_1 \gg 1$ and at large length scales $kR_g \ll 1$ a macroscopic solution shear viscosity is found, $\eta' = \eta(1 + \rho_1[\eta]_R)$, with the intrinsic viscosity of the Rouse model $[\eta]_R = L\zeta_1 12\eta$.[25] At length scales below the radius of gyration, Fredrickson and Helfand find a hydrodynamic screening length $\xi^2 \propto \eta/\rho_1\zeta_1$, which screens the hydrodynamics such that at the smallest distances the viscosity is again η. This is completely *independent* of the nature of the interaction between the polymer segments, as it contains only terms due to the connectivity of the polyion chains.

However, the dynamic scattering intensity derived above can be implemented in an alternative computation of the reduced viscosity in the Rouse as well as the Zimm cases by making use of the results of Hess' and Klein's mode–mode coupling computations,[23] as has been done by Vilgis, Borsali, and Benmouna,[21,22] by implementation of the formula $\eta_r = (k_B T\rho_1^2/16\pi^3\eta c_p) \int_0^\infty dt \int_0^\infty dk \, S^2(\mathbf{k}, t)(k^2/S^4(k))(\partial H(k)/\partial\mathbf{k})$. The function $H(k)$ represents the particle–particle correlation function. Hitherto this formula could only be implemented by estimating the first cumulant frequency for the dynamical scattering intensity, but here we have already computed this from the more complete dynamical formalism. We have also shown that in the appropriate limits, the behavior of our more complicated system is like that derived by more conventional means, so we expect the occurrence of a viscosity peak to be qualitatively retained in this formalism.

It should be pointed out that the assumption of homogeneity of the separate constituents of charge and species in the solution, which are in no way correlated when the Gaussian approximation of the collective coordinates is made, provides the approximation which leads to the Debye–Hückel potential. This can also be derived in the other approximations, such as the linearization of the Poisson–Boltzmann equation. The RPA is valid for systems in which the temperature is high such that the various counterions can be understood to move almost independently and, and when the polymer density is high, such that the chains have a Gaussian end-to-end distribution. The success of this calculation has been tested in many and varied fields. As has been shown, the RPA can be applied to the dynamical case too, with the complicating factor of the occurrence of additional fields; however, these are also quadratic.

In polyelectrolytes the effect of the condensation of counterions on the chains has been known for some time (see refs 31 and 32 and references therein). The critical onset of this condensation for monovalent ions, which is derived from models of charged cylindrical objects, occurs in Manning's theory[31] when $\lambda_B f \geq 1$ (and at a lower clustering temperature in the case of solutions of rodlike polyelectrolytes; see Levin[33] and Levin and Barbosa)[34] such that we consider here the case of high temperature and low charge density. Indeed, this other regime of counterion condensation on flexible objects is less well understood and would necessitate a different treatment than the RPA.

First, it is noticed that the presence of the hydrodynamic interactions generates a term to third order in the density of the fields. Attempts to approximate this as a linear or quadratic contribution to the integrand are bound to fail. This is because of the decoupling in

the RPA of the fields relevant to the transverse and parallel **k** directions. The cubic term is responsible for the coupling of the hydrodynamic properties of the system to the remaining dynamic properties, and we can see how its neglect causes the diffusive motion not feature any properties of the solvent, except through the definition of the friction parameter, $\zeta = 6\pi\eta a$, where a represents the particle radius. To understand more fully the role of the coupling (not only that of the connectivity), in particular the nature of the interaction into the hydrodynamic properties, it becomes necessary to use an altered approach to the dynamics. This falls beyond the scope of this paper and will be discussed in a subsequent publication.[35]

We have given the dynamical structure factor of the system under discussion and shown that it reproduces the polyelectrolyte peak at sufficiently low frequencies. We have also discussed the diffusive behavior of the system, and reconfirmed the occurrence of the "plasmon" mode using the dynamical formalism.

Appendix: RPA Results

The RPA has been computed before by Fredrickson and Helfand.[25] Here we present the relevant results for the case $kR_g \ll 1$.

$$\langle \rho_1(-\mathbf{k}, -\omega)\rho_1(\mathbf{k}, \omega)\rangle_{\mathrm{RPA}} = \frac{2k^2\zeta_1}{\omega^2\zeta_1^2 + k^4L^{-2}} \quad (4.1)$$

$$\langle \rho_2(-\mathbf{k}, -\omega)\rho_2(\mathbf{k}, \omega)\rangle_{\mathrm{RPA}} = \frac{2k^2\zeta_2}{\omega^2\zeta_2^2 + k^4} \quad (4.2)$$

$$\langle \rho_1(-\mathbf{k}, -\omega)\mathbf{k}\cdot\boldsymbol{\sigma}_1(\mathbf{k}, \omega)\rangle_{\mathrm{RPA}} = \frac{2k^2}{\omega\zeta_1 + ik^2L^{-1}}\left(\frac{\zeta_1}{i}\right) \quad (4.3)$$

$$\langle \rho_2(-\mathbf{k}, -\omega)\mathbf{k}\cdot\boldsymbol{\sigma}_2(\mathbf{k}, \omega)\rangle_{\mathrm{RPA}} = \frac{2k^2}{\omega\zeta_2 + ik^2}\left(\frac{\zeta_2}{i}\right). \quad (4.4)$$

Apart from the nontrivial remaining averages $\langle \pi_\alpha\pi_\alpha\rangle$ and $\langle \pi_\alpha(1 - \hat{\mathbf{k}}\hat{\mathbf{k}})\sigma_\alpha\rangle$, all remaining pairwise correlations are zero.

References and Notes

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