PHYSICAL REVIEW E, VOLUME 64, 041802

# Dynamic charge-density correlation function in weakly charged polyampholyte globules

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(Received 15 October 2000; revised manuscripts received 30 May 2001; published 24 September 2001)

We study solutions of statistically neutral polyampholyte chains containing a large fraction of neutral monomers. It is known that such solutions phase separate at very low concentrations, even if the quality of the solvent with respect to the neutral monomers is good. The precipitate is semidilute if the chains are weakly charged. This paper considers $\theta$ solvents and good solvents, and we calculate the dynamic charge density correlation function $g(k,t)$ in the precipitate, using the quadratic approximation to the Martin-Siggia-Rose generating functional. It is convenient to express the results in terms of dimensionless space and time variables. Let $\xi$ be the blob size, and let $\tau$ be the characteristic time scale at the blob level. Define the dimensionless wave vector $q=\xi k$, and the dimensionless time $s=t/\tau$. In the regime $q<1$, corresponding to length scales larger than the blob size, and $1<s<q^{-4}$, corresponding to time scales in between the blob relaxation time and the relaxation time at scale $q^{-1}$, we find that the charge density fluctuations relax according to the power law $g(q,s)\sim q^2 s^{-1/2}$. This relaxation is qualitatively different from that of a neutral semidilute polymer solution. We expect our results to be valid for wave vectors $q>0.1$, where entanglements are unimportant.

DOI: 10.1103/PhysRevE.64.041802 PACS number(s): 61.25.Hq

## I. INTRODUCTION

A polyampholyte is a polymer chain that contains electrically charged monomers of both signs. Apart from the charged monomers, the chain may also contain neutral monomers. In this paper we study polyampholytes in which the neutral monomers are in the majority, so the chains are only weakly charged. The positive and the negative monomers are distributed with equal probability and without correlations along the chain, separated from each other by flexible neutral spacers. The chains are present in a solvent. We consider two situations; either the quality of the solvent with respect to the neutral monomers is good, or the solvent is under $\theta$ conditions.

It was shown in [1] that in both situations the system starts to phase separate already at very low concentrations. The precipitate resembles a semidilute solution, and is characterized by a correlation length that is independent of the chain length (provided that the chains are long enough). If the quality of the solvent is good, further collapse of the precipitate is prevented by the second order virial coefficient (also called the excluded volume parameter), whereas if the solvent is under $\theta$ conditions, further collapse is prevented by the third order virial coefficient [2]. The noncompact semidilute precipitate can be regarded as a dense melt of blobs. At length scales small compared to the blob size $\xi$, the electrostatic interaction is weak (relative to the entropy), and the system is indistinguishable from a single, neutral, noncollapsed polymer coil. In case of a good solvent, the chain conformation is a self-avoiding walk, whereas in case of a $\theta$ solvent, it is a random walk. On these short length scales, the charged monomers occupy random positions in space, and so the electrostatic interaction is unscreened. The importance of the electrostatic interaction relative to the entropy increases if one considers larger and larger length scales, and the break-even point is at the blob size. At length scales larger than the blob size the interaction is strong, and the charged monomers rearrange themselves spatially in order to minimize the energy. This leads to a screening of the interaction. A side effect of these rearrangements of the charges is an effective attraction, causing the system to appear collapsed on length scales larger than $\xi$. This physical picture, originally proposed in Ref. [2] for the case of an isolated collapsed polyampholyte chain, shows why the electrostatic screening length $\kappa^{-1}$ has to be equal to the blob size $\xi$, which is also equal to the hydrodynamic screening length, and to the static screening length of the excluded volume interactions in case of a good solvent. Since for weakly charged polyampholytes the blob size is much larger than the average distance between two charged monomers, Debye-Hückel theory [3] is applicable. An estimate for $\xi$ was given in [2]. If $b$ is the root-mean-square distance between two monomers neighboring along the chain, $f$ is the fraction of monomers that carries a charge, and $\ell=e^2/4\pi\epsilon k_B T$ is the Bjerrum length ($e$ is electron charge, $\epsilon$ is the electric permittivity of water, $k_B$ is Boltzmann's constant, and $T$ is the absolute temperature), then

$$\xi\sim\frac{b^2}{f\ell}. \tag{1}$$

As shown in [2], an isolated neutral polyampholyte chain will collapse into a spherical globule, whose interior is locally indistinguishable from the interior of the precipitate of a phase separated solution. However, if the isolated chain has a considerable net charge, there is the possibility that the formation of a spherical globule is prevented by the electrostatic repulsion. In that case the chain will attain the shape of a linear array of globules (also called pearls), connected to each other by long, thin strings (necklace model [4,5]). The critical net charge above which the spherical globular state is

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unstable against necklace formation is of the same order of magnitude as the typical excess charge of a ‘‘statistically neutral’’ chain. This means that in a representative ensemble, some chains will attain the shape of a sphere, while others will attain the shape of a necklace. The pearls are collapsed, and locally indistinguishable from the precipitate of a phase separated solution.

## II. METHOD AND REGION OF APPLICABILITY

We study the dynamics of the charge density fluctuations inside the collapsed phase (precipitate, globule or pearl), using the quadratic approximation to the Lagrange version [6,7] of the Martin-Siggia-Rose formalism [8]. We will follow closely the techniques of a paper by Fredrickson and Helfand [9]. Readers who wish to follows the details of our calculation are advised to study Ref. [9] first, especially its Appendix. First we will determine in what length scale regime this formalism is expected to give correct results. There are two important length scales in the system: the blob size $\xi$ and the entanglement length $\xi_e$. At length scales smaller than $\xi$, the thermal energy is larger than the electrostatic energy, and the system behaves as if it were a neutral single chain. Since in the past the dynamics of neutral chains have been studied extensively [10], and we are mainly interested in the influence of the electrostatic interaction, we will only consider length scales that are larger than $\xi$. When observed at these scales, the chain conformation is always a random walk, even if the quality of the solvent is good. This is due to a screening of the excluded volume interactions [10]. It means that the excluded volume parameter $v$ enters the physics at large length scales $>\xi$ only by fixing the blob size [2].

Another important length scale is the entanglement length $\xi_e$. It is very difficult to take the influence of entanglements on the dynamics into account, and we will not make an attempt to do so. This means that our results will not be valid on length scales large compared to the entanglement length $\xi_e$. One can obtain an estimate for $\xi_e$ in the following way. In a polymer melt, the number of monomers $N_e$ in between two entanglements is of the order $N_e \approx 200$ [11]. Since the polyampholyte precipitate can be regarded as a dense melt of blobs, it follows that the typical entanglement length is given by

$$\xi_e \sim \xi N_e^{1/2} \sim 10\xi. \tag{2}$$

At length scales that are large compared to $\xi_e$, it is to be expected that the dynamics occur via some kind of reptation, and on these scales the relaxation of charge density fluctuations probably becomes very slow (compare with Ref. [12], where systems with short range interactions are studied).

Next we discuss the hydrodynamic screening length $\xi_H$. It was argued in [13] that in a semidilute solution, $\xi_H$ has the same order of magnitude as the static correlation length $\xi$; both under $\theta$ conditions, and under good solvent conditions. This prediction was confirmed recently by extensive computer simulations [14]. It follows that at length scales smaller than the blob size $\xi$, the chain exhibits Zimm-like behavior, whereas at length scales larger than $\xi$, it exhibits Zimm-like behavior on time scales smaller than the blob relaxation time $\tau$, but Rouse-like behavior on time scales larger than $\tau$ [14]. Since it was shown in Ref. [9] that the quadratic approximation leads to the prediction of Rouse-like behavior, our analysis is only applicable if both the length scale is larger than $\xi$, and the time scale is larger than $\tau$. An expression for $\tau$ can be obtained by realizing that below the blob level, the system is indistinguishable from a single, neutral, noncollapsed chain. This leads to the estimate [10]

$$\tau \sim \frac{\eta \xi^3}{k_B T}, \tag{3}$$

where $\eta$ is the viscosity of water and $\xi$ is given by Eq. (1). Finally, we discuss the region of validity of the quadratic approximation. It entails expanding the effective Hamiltonian in powers of the charge density $\psi(\mathbf{r})$, and retaining only the second order term. This approximation can only be justified if the typical amplitude of $\psi(\mathbf{r})$ is small. At length scales smaller than $\xi$, the system is strongly fluctuating, and the amplitude of $\psi(\mathbf{r})$ is large. At length scales larger than $\xi$, the charge density fluctuations are strongly suppressed by the electrostatic interactions, and the amplitude of $\psi(\mathbf{r})$ is small. It follows that the quadratic approximation is acceptable at length scales larger than $\xi$, but not at length scales shorter than $\xi$.

Summarizing, the approximations made in this paper are expected to be reasonable if the length scale is larger than the blob size but smaller than the entanglement length, and the time scale is larger than the relaxation time at the blob level.

## III. CALCULATION OF THE DYNAMIC CHARGE CORRELATION FUNCTION

As mentioned in the introduction, we wish to describe the precipitate of a solution of weakly charged polyampholytes. The individual chains are assumed to be much longer than the minimum length required for an isolated chain to collapse into a globule. All chains have exactly the same number of charged monomers, and these monomers are placed at regular distances along the backbone. The last two assumptions, which are made in order to simplify the model, do not restrict the generality of our results. Let $N$ be the number of charged monomers per chain, $e$ the charge per monomer, $n_p$ the number of chains in the precipitate, and $V$ the volume of the precipitate. Note that $V$ cannot be chosen independently from $n_p$ and $N$, because the precipitate has a well-defined density [2]. Let the coarse grained conformation of chain $a$ be described by the three-dimensional vector $\mathbf{R}_a(\tau)$, where $\tau$ is a continuous parameter running along the backbone. It is defined such that for two charged monomers neighboring along the chain we have $\Delta\tau = 1$. We simplify the model by smearing out the electric charges along the chain, in such a way that $e\theta(\tau)d\tau$ is the amount of charge in between the points labeled by $\tau$ and $\tau + d\tau$, where $\theta(\tau)$ is a Gaussian random variable with first two moments

$$\langle \theta_a(\tau) \rangle = 0, \qquad \langle \theta_a(\tau)\theta_b(\tau') \rangle = \delta(\tau - \tau')\delta_{ab}. \tag{4}$$

Since we will work in the quadratic approximation, the fact that we switch to a Gaussian charge distribution has no effect on the final result. We will describe the system by means of the following effective Hamiltonian:

$$\frac{\mathcal{H}}{k_{\mathrm{B}}T}=\frac{3}{2\tilde{b}^2}\int_0^N \mathrm{d}\tau \sum_{a=1}^{n_{\mathrm{p}}}\left(\frac{\mathrm{d}\mathbf{R}_a(\tau)}{\mathrm{d}\tau}\right)^2 +\frac{\ell}{2}\sum_{a,b=1}^{n_{\mathrm{p}}}\int_0^N \mathrm{d}\tau \int_0^N \mathrm{d}\tau' \frac{\theta_a(\tau)\theta_b(\tau')}{|\mathbf{R}_a(\tau)-\mathbf{R}_b(\tau')|}, \quad (5)$$

where $\tilde{b}$ is the root-mean-square distance between two charged monomers neighboring along the chain. From now on, we will choose the units of length, mass, and time such that

$$\gamma=1, \qquad k_{\mathrm{B}}T=1, \qquad \tilde{b}^2=3, \quad (6)$$

where $\gamma$ is the effective friction coefficient per charged monomer. Ultimately, we are interested in how fluctuations in the charge density decay in space and over time. In terms of the annealed variables $\mathbf{R}_a(\tau)$ and the quenched variables $\theta_a(\tau)$, the charge density is given by $e\hat{\psi}(\mathbf{r},t)$, where[1]

$$\hat{\psi}(\mathbf{r},t)=\sum_a \int \mathrm{d}\tau \;\; \theta_a(\tau) \;\; \delta(\mathbf{r}-\mathbf{R}_a(\tau)). \quad (7)$$

In terms of $\hat{\psi}$, the Fourier transform of the dynamic charge density correlation function is given by

$$g_\theta(\mathbf{k},t)=\frac{e^2}{V}\langle \hat{\psi}(-\mathbf{k},t)\hat{\psi}(\mathbf{k},t)\rangle, \quad (8)$$

where the brackets denote an average over the annealed variables. Note that the correlation function depends explicitly on the disorder. The calculation is simplified considerably by making use of the fact that the correlation function is self-averaging, which means that $g_\theta(\mathbf{k},t)=\overline{g_{\theta'}(\mathbf{k},t)}$ with probability 1, where the bar denotes an average over the quenched variables $\theta'$. This means that in order to find $g_\theta(\mathbf{k},t)$ for a representative $\theta$ drawn from the Gaussian probability distribution Eq. (4) (which is what we are after), it suffices to calculate the average of this quantity over the disorder.

We will calculate $g(\mathbf{k},t):=\overline{g_{\theta'}(\mathbf{k},t)}$ by means of the Lagrange version [6,7] of the MSR (Martin-Siggia-Rose) formalism [8]. In the appendix we have provided a brief derivation of the MSR functional. It is convenient to introduce an external field $h(\mathbf{k},t)$ that couples to $\hat{\psi}(\mathbf{k},t)$. The dynamic charge correlation function can then be found by differentiating the logarithm of the MSR functional $Z[h]$ twice with respect to $h$. In principle, the average over the quenched disorder should be performed *after* the differentiation, but since $Z[h=0]=1$ is independent of the quenched variables (see the Appendix), the order of operations can be interchanged. This is a great simplification, and it makes the MSR formalism especially suitable for systems with quenched disorder.

Starting from Eqs. (A9) and (A10), and substituting the effective Hamiltonian Eq. (5) for the interaction energy, one arrives at the expression for the MSR functional. Since analogous calculations have been published before (see in particular Ref. [9]) we will not present the details, but just give the result. During the derivation, the following fields arise

$$\hat{\psi}_1(\mathbf{k},t)=\sum_a \int \mathrm{d}\tau\, \theta_a(\tau)\, \exp[i\mathbf{k}\cdot\mathbf{R}_a(\tau,t)],$$

$$\hat{\psi}_2(\mathbf{k},t)=\sum_a \int \mathrm{d}\tau\, \theta_a(\tau)\, \mathbf{k}\cdot\hat{\mathbf{R}}_a(\tau,t) \times \exp[i\mathbf{k}\cdot\mathbf{R}_a(\tau,t)]. \quad (9)$$

In the quadratic approximation, the final disorder averaged expression for $Z[h]$ is

$$Z[h]\propto \int \mathcal{D}\psi_1\mathcal{D}\psi_2\mathcal{D}\phi_1\mathcal{D}\phi_2 \times \exp\left[-\mathcal{L}+\int_\omega\int_{\mathbf{k}} h(-\mathbf{k},-\omega)\;\;\psi_1(\mathbf{k},\omega)\right], \quad (10)$$

where the Lagrangian $\mathcal{L}$ is given by (there are summations over the indices $i,j$)

$$\mathcal{L}=-\ell\int_\omega\int_{\mathbf{k}}\frac{4\pi}{k^2}\psi_1(-\mathbf{k},-\omega)\psi_2(\mathbf{k},\omega) -i\int_\omega\int_{\mathbf{k}}\phi_i(-\mathbf{k},-\omega)\psi_i(\mathbf{k},\omega) +\frac{c}{2}\int_\omega\int_{\mathbf{k}}V_{ij}(-\mathbf{k},-\omega)\psi_i(-\mathbf{k},-\omega)\psi_j(\mathbf{k},\omega). \quad (11)$$

$c=n_{\mathrm{p}}N/V$ is the density of charged monomers. The integral measures are defined by

$$\int_\omega :=\frac{1}{2\pi}\int \mathrm{d}\omega \qquad \int_{\mathbf{k}} :=\frac{1}{(2\pi)^3}\int \mathrm{d}^3\mathbf{k}. \quad (12)$$

Although in the full expression for the functional $Z[h]$ there are more fields present, in the quadratic approximation these fields couple neither to $\psi_i$, nor to $\phi_i$, and can therefore be omitted. Consequently, in the quadratic approximation the hydrodynamic interactions are not taken into account in the calculation of $g(\mathbf{k},t)$. Therefore, our results are only valid in the length scale and time scale regime where the dynamics are expected to be Rouse-like; which means length scales larger than the blob size, and time scales larger than

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[1] The hat on $\hat{\psi}$ denotes the dependence on the annealed variables $\mathbf{R}_a(\tau)$, and the quenched variables $\theta_a(\tau)$. This notation should not be confused with the notation in the MSR formalism, where the hat indicates conjugated variables (see Appendix A). We stick to these notations because of convention.

the blob relaxation time. The integrals over $\psi_i$ and $\phi_i$ in Eq. (10) are Gaussian and can be calculated explicitly, after which $g(\mathbf{k},t)$ can be obtained by differentiating the result twice with respect to the external field $h$. The result is

$$g(\mathbf{k},\omega)=\frac{cV_{11}(\mathbf{k},\omega)}{[1-\kappa^2k^{-2}V_{12}(\mathbf{k},\omega)][1-\kappa^2k^{-2}V_{21}(\mathbf{k},\omega)]}, \tag{13}$$

where $\kappa^2:=4\pi\ell c$ is the Debye-Hückel expression [3] for the inverse square screening length. The functions $V_{ij}$ are given by

$$V_{11}(\mathbf{k},t)=\frac{1}{N}\int \mathrm{d}\tau\langle\exp[i\mathbf{k}\cdot(\mathbf{R}(\tau,t)-\mathbf{R}(\tau,0))]\rangle_0,$$

$$V_{12}(\mathbf{k},t)=\frac{1}{N}\int \mathrm{d}\tau\langle\mathbf{k}\cdot\hat{\mathbf{R}}(\tau,t)\times\exp[i\mathbf{k}\cdot\{\mathbf{R}(\tau,t)-\mathbf{R}(\tau,0)\}]\rangle_0,$$

$$V_{21}(\mathbf{k},t)=-\frac{1}{N}\int \mathrm{d}\tau\langle\mathbf{k}\cdot\hat{\mathbf{R}}(\tau,0)\times\exp[i\mathbf{k}\cdot\{\mathbf{R}(\tau,t)-\mathbf{R}(\tau,0)\}]\rangle_0,$$

$$V_{22}(\mathbf{k},t)=-\frac{1}{N}\int \mathrm{d}\tau\langle\mathbf{k}\cdot\hat{\mathbf{R}}(\tau,t)\mathbf{k}\cdot\hat{\mathbf{R}}(\tau,0)\times\exp[i\mathbf{k}\cdot\{\mathbf{R}(\tau,t)-\mathbf{R}(\tau,0)\}]\rangle_0. \tag{14}$$

The average $\langle\cdots\rangle_0$ is calculated with respect to the single-chain Rouse Lagrangian $\mathcal{L}_0$, which is given by

$$\mathcal{L}=\int_\omega\int \mathrm{d}\tau\hat{\mathbf{R}}(\tau,-\omega)\cdot\hat{\mathbf{R}}(\tau,\omega)+\int_\omega\int \mathrm{d}\tau\omega\hat{\mathbf{R}}(\tau,-\omega)\cdot\mathbf{R}(\tau,\omega)-i\int_\omega\int \mathrm{d}\tau\hat{\mathbf{R}}(\tau,-\omega)\cdot\frac{\partial^2\mathbf{R}(\tau,\omega)}{\partial\tau^2}. \tag{15}$$

The calculation of the functions $V_{ij}$ in Eq. (14) can be simplified by making use of the fact that we are only interested in processes occurring at length scales of the order of the blob size $\xi$. As is usual for the semidilute regime, the blob size reaches a finite limit when the chain length approaches infinity. This limiting value is reached once the chain length exceeds the value necessary for an isolated neutral polyampholyte chain to collapse into a globule. It follows that for the processes occurring at length scale $\xi$ the limit $N\to\infty$ is meaningful, and approached easily in experimental situations. Therefore, we can safely assume that the wave vectors of interest satisfy $k\sim\xi^{-1}\gg N^{-1/2}$, which will simplify the calculations. Considering the time scale, it is clear that the processes occurring at length scale $\xi$ are much faster than those occurring at length scale $N^{1/2}$. Therefore, in the calculation of $V_{ij}(\mathbf{k},t)$ we can restrict ourselves to times satisfying $t\ll t_R$, where $t_R$ is the Rouse time [10] of a single chain. In this wave vector and time regime it is possible to find explicit and simple expressions for $V_{ij}(\mathbf{k},t)$. Those readers who are interested in the calculation leading to Eq. (16) are advised to study the Appendix of Ref. [9], where similar calculations are worked out in detail. The result is

$$V_{11}(k,t)=\exp[-k^2|t|^{1/2}],$$

$$V_{12}(k,t)=-\theta(-t)\frac{k^2}{|t|^{1/2}}\exp[-k^2|t|^{1/2}],$$

$$V_{21}(k,t)=-\theta(t)\frac{k^2}{|t|^{1/2}}\exp[-k^2|t|^{1/2}],$$

$$V_{22}(k,t)=0, \tag{16}$$

where $\theta(t)$ is the Heaviside step function. We omitted numerical constants of order unity. Although it is possible to find explicit expressions for the Fourier transforms $V_{ij}(k,\omega)$, the resulting expression for $g(k,\omega)$ would be rather complicated. Instead, it is much more useful to derive a transparent, albeit approximate, expression for $g(k,\omega)$. An additional advantage is that this simplified expression can easily be inverse Fourier transformed with respect to the frequency. Consider the frequency regime $\omega\gg k^4$. By substituting $z=-i\omega t$, distorting the integration contour back to the real axis, and expanding the integrand in powers of $zk^4/\omega$ [9], one arrives at the following approximate expressions for $V_{ij}(k,\omega)$:

$$|\omega|\gg k^4\Rightarrow\begin{cases}V_{11}(k,\omega)\approx|\omega|^{-3/2}k^2,\\ V_{12}(k,\omega)\approx\begin{cases}(-1+i)|\omega|^{-1/2}k^2 & \omega>0,\\ (-1-i)|\omega|^{-1/2}k^2 & \omega<0.\end{cases}\end{cases} \tag{17}$$

Combining Eqs. (13) and (17) one obtains

$$g(k,\omega)\propto\frac{k^2}{\ell|\omega|^{1/2}[(1+|\omega\kappa^{-4}|^{1/2})^2+1]}\qquad|\omega|\gg k^4. \tag{18}$$

There are two frequency regimes:

$$g(k,\omega)\approx\begin{cases}\ell^{-1}k^2\kappa^{-2}|\omega|^{-1/2} & |\omega|\ll\kappa^4\\ \ell^{-1}k^2\kappa^2|\omega|^{-3/2} & |\omega|\gg\kappa^4.\end{cases} \tag{19}$$

The critical frequency $\omega_c=\kappa^4$ that separates the two regimes in Eq. (19) corresponds to the inverse blob relaxation time in the Rouse model [use $\kappa^{-1}\sim\xi$; with the help of Eq. (6) one can restore the correct dimensions]. As discussed before, the formalism used can only be expected to describe the system correctly on time scales longer than the blob relaxation time, and therefore we should only consider the regime $|\omega|\ll\kappa^4$. Using the relations $\xi\sim\kappa^{-1}$ and $\kappa^2\sim c\ell$, one obtains that for $\xi/\xi_e<\xi k<1$ and $(\xi k)^4<\xi^4\omega<1$,

$$c^{-1}g(k,\omega)\approx(\xi k)^2|\xi^4\omega|^{-1/2}. \tag{20}$$

An inverse Fourier transform with respect to the frequency leads to

$$c^{-1}g(k,t)\approx(\xi k)^2|\xi^{-4}t|^{-1/2}, \qquad (21)$$

Equation (21) has a reduced form, the wave vector is rescaled with the inverse blob size, and the time is rescaled with the Rouse expression for the blob relaxation time. The time rescaling seems to be wrong, the real blob relaxation time is given by the Zimm expression[2] $\tau\sim\xi^3$, because below the blob level the hydrodynamic interactions are not screened. This incorrect result is due to the Gaussian approximation [9]. This does not mean that Eq. (21) breaks down completely, since at length scales larger than $\xi$ and time scales longer than $\tau$ the hydrodynamic interactions are screened and the chain *is* Rouse-like, Eq. (21) is valid, provided that one inserts the correct basic time scale $\tau$ at the blob level. Defining the dimensionless wave vector $q:=\xi k$ and the dimensionless time $s:=t/\tau$, we arrive at our final result

$$c^{-1}g(q\xi^{-1},s\tau)\approx q^2 s^{-1/2}, \qquad (22)$$

which is valid if both $0.1<q<1$ (corresponding to length scales in between the blob size and the entanglement length), and $1<s<q^{-4}$ (corresponding to times in between the relaxation time at the blob level, and the relaxation time at length scale $q^{-1}$). It would be interesting to test experimentally the power law decay in time.

## IV. DISCUSSION

In order to determine the role of the electrostatic interactions in the expression for the dynamic charge density correlation function, consider a system in which the electrostatic interactions between the charges are switched off. Physically, this could be achieved by immersing the polymer in a concentrated salt solution. Although in this case the chains would not collapse or phase separate, we will still assume that the system is semidilute, for instance by imposing a nonzero concentration. In this case, the charge density correlation function would follow immediately from Eqs. (13) and (16) by taking $\kappa=0$. It follows that when the electrostatic interactions are absent, the charge density correlations decay according to a stretched exponential $g\propto\exp(-\alpha t^{1/2})$, which is completely different from Eq. (22). We conclude that the appearance of the power law $g\propto s^{-1/2}$ must be due to the Coulomb interactions. In order to determine the influence of the polymeric bonds, we calculated for comparison the dynamic charge density correlation function of a salt solution, using the same formalism and approximations. The result is an exponential decay of the correlations over time:

$$c^{-1}g(k,t)=\frac{k^2}{k^2+\kappa^2}\exp[-\kappa^4 t] \qquad (23)$$

Again, the time dependence obtained is completely different from that of Eq. (22), meaning that the presence of the polymeric bonds has a large influence on the relaxation of charge density fluctuations.

The dynamic correlation function for the *total* density is qualitatively different from that for the charge density. To a first approximation, the presence of the charges does not have an influence on the dynamics of the total density. It follows that the dynamic correlation function for the total density is the same as in the case of a neutral semidilute polymer solution, which has been calculated within the quadratic approximation in Ref. [9]. On length scales that are small compared to the radius of gyration of the chains, but large compared to the correlation length $\xi$, the fluctuations in the total density decay *exponentially* with time [see Eq. (3.19) in Ref. [9]].

## ACKNOWLEDGMENT

H.J.A. is grateful to the NWO (Netherlands Organization for Scientific Research) for financial support.

## APPENDIX

In this appendix we present a brief derivation of the Martin-Siggia-Rose functional [8]. We will follow the method developed in Refs. [6,7]. Consider a system of $N$ interacting point particles in solution. Let $n=1,\ldots,N$ number the particles, let $\alpha=1,2,3$ denote a Cartesian coordinate, and let $R_{n\alpha}$ be the $\alpha$ component of the position of particle $n$. Let $\mathbf{R}$ denote the $3N$-dimensional vector with components $R_{n\alpha}$, and let $U[\mathbf{R}]$ denote the interaction energy. In case that $\mathbf{R}$ represents the coarse grained conformation of a polymer chain, entropic contributions have to be taken into account and one should replace $U$ by an effective Hamiltonian $\mathcal{H}$. The time evolution of the probability density $P[\mathbf{R},t]$ is governed by the Fokker-Planck equation [10,15]

$$\frac{\partial P}{\partial t}=\boldsymbol{\nabla}\cdot\mathbf{L}\cdot[k_{\mathrm{B}}T\boldsymbol{\nabla}P+P\boldsymbol{\nabla}U], \qquad (A1)$$

where $\boldsymbol{\nabla}$ represents the vector with components $\partial/\partial R_{n\alpha}$, and dots denote inner products. The mobility matrix $\mathbf{L}[\mathbf{R}]$ is given by [10]

$$L_{n\alpha,m\beta}=H_{\alpha\beta}(\mathbf{R}_n-\mathbf{R}_m) \qquad n\neq m,$$

$$L_{n\alpha,n\beta}=\frac{\delta_{\alpha\beta}}{\gamma}. \qquad (A2)$$

$H_{\alpha\beta}(\mathbf{r})$ is the Oseen tensor (see Ref. [10], Appendix 3 III) describing the hydrodynamic interaction, $\mathbf{R}_n$ denotes the position of particle $n$, and $\gamma$ is the friction coefficient per particle. In order to derive the Martin-Siggia-Rose functional it is convenient to switch first from the Fokker-Planck equation to the equivalent Langevin equation [15]. In the Stratonovich interpretation it is given by [6]

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[2] Use Eq. (3) in combination with Stokes relation $\gamma\sim\tilde{b}\eta$, and express the result in terms of the units defined by Eq. (6)

$$\frac{\partial \mathbf{R}}{\partial t} = -\mathbf{L}\cdot\nabla U + k_B T \nabla\cdot\mathbf{L} - \frac{1}{2}\mathbf{g}\cdot(\nabla\cdot\mathbf{g}) + \mathbf{g}\cdot\boldsymbol{\zeta}. \tag{A3}$$

The stochastic force $\zeta$ is a white Gaussian noise with first two moments

$$\langle \boldsymbol{\zeta}(t)\rangle = 0 \qquad \langle \boldsymbol{\zeta}(t)\boldsymbol{\zeta}(t')\rangle = \mathbf{I}\delta(t-t'). \tag{A4}$$

**I** is the $3N\times 3N$ identity matrix. The matrix **g** is related to the mobility matrix **L** by [6]

$$\mathbf{g}\cdot\mathbf{g}^{\mathrm{T}} = 2k_B T\mathbf{L}. \tag{A5}$$

Equation (A5) leaves some freedom in the choice of **g**, which can be used to impose the condition [6]

$$\nabla\cdot\mathbf{g} = 0. \tag{A6}$$

Using this, the Langevin equation simplifies to (it can be shown that $\nabla\cdot\mathbf{L}=0$)

$$\frac{\partial \mathbf{R}}{\partial t} = -\mathbf{L}\cdot\nabla U + \mathbf{g}\cdot\boldsymbol{\zeta} + \hat{\mathbf{h}}. \tag{A7}$$

The external force $\hat{h}_i(t)$ working on particle $i$ is introduced in order to be able to calculate response functions. This force will be set to zero afterwards. In Refs. [6,7] it is worked out in detail how one can derive, starting from a Langevin equation, the expression for the path probability distribution $\mathcal{P}[\mathbf{R}(t)]$. By introducing the so-called conjugated field $\hat{\mathbf{R}}(t)$, which is rather straightforward in the Lagrange formalism [7], one finds the expression

$$\mathcal{P}[\mathbf{R}(t),\hat{\mathbf{h}}] = \int \mathcal{D}\hat{\mathbf{R}}(t)\exp\left[-\mathcal{L}[\mathbf{R},\hat{\mathbf{R}}] + \int dt\,\hat{\mathbf{h}}(t)\cdot i\hat{\mathbf{R}}(t)\right], \tag{A8}$$

where the ''Lagrangian'' $\mathcal{L}[\mathbf{R},\hat{\mathbf{R}}]$ is given by

$$\mathcal{L}[\mathbf{R},\hat{\mathbf{R}}] = \int dt[k_B T\hat{\mathbf{R}}\cdot\mathbf{L}\cdot\hat{\mathbf{R}} + i\hat{\mathbf{R}}\cdot(\dot{\mathbf{R}} + \mathbf{L}\cdot\nabla U)]. \tag{A9}$$

The Martin-Siggia-Rose functional is defined by integrating the path probability over all possible evolutions $\mathbf{R}(t)$ of the system, in the presence of the external fields $\hat{\mathbf{h}}$ and **h**, where the field **h** couples to **R**. One obtains

$$Z[\mathbf{h},\hat{\mathbf{h}}] = \int \mathcal{D}\mathbf{R}(t)\int \mathcal{D}\hat{\mathbf{R}}(t)\exp\Big[-\mathcal{L}[\mathbf{R},\hat{\mathbf{R}}] + \int dt\,\mathbf{h}(t)\cdot\mathbf{R}(t) + \int dt\,\hat{\mathbf{h}}(t)\cdot i\hat{\mathbf{R}}(t)\Big]. \tag{A10}$$

It follows from Eq. (A8) that the correlation and response functions of the system described by the Langevin equation (A7) can be obtained from the MSR-functional Eq. (A10) by differentiation with respect to the external fields. However, the continuum expression for $Z$, as it is given here, is ill defined [16]. For instance, it is not possible to determine the value of the equal-time response function $\langle \mathbf{R}(t)i\hat{\mathbf{R}}(t)\rangle$. Retracing the derivation of Eq. (A10) one finds that the discretization underlying the integrals over time is such that the equal-time response functions are identically zero [16]. This extra information is sufficient to remove all ambiguity from Eq. (A10).

We discuss briefly the adequacy of the Langevin equation Eq. (A7) to describe the dynamics of polymer solutions. It has been argued [17] that Eq. (A7) would be inconsistent, in the sense that whereas the thermal fluctuations of the monomers are taken into account, the thermal fluctuations of the solvent velocity field are not (the Oseen tensor gives the *average* solvent velocity as a function of the forces). In order to obtain the same level of description for both the particles and the solvent, Oono and Freed [17] introduced a set of coupled Langevin equations. However, it seems to us that the only difference between these Oono-Freed equations and Eq. (A7) lies in the neglect of the solvent inertia in the latter, for the following reason. It was shown in Ref. [9] that if one derives the MSR functional from the Oono-Freed equations, the velocity and its conjugate appear quadratic in the Lagrangian, and so they can be integrated out explicitly. The resulting functional is identical to the one obtained from Eq. (A7), provided that one takes the solvent density to be zero. Since the effects of solvent inertia on the dynamics of polymer solutions are negligible anyway, we conclude that Eq. (A7) is equivalent to the Oono-Freed equations. As an illustration of the irrelevancy of the solvent inertia, consider the Zimm model. The characteristic frequency $\omega$ of fluctuations with wave vector $k$ is given by [10] $\omega = k_B T k^3/6\pi\eta$, where $\eta$ is the solvent viscosity. It follows from the Navier-Stokes equation that the solvent inertia is negligible if $\rho\omega \ll \eta k^2$, where $\rho$ is the solvent density. Taking the viscosity and the density of water one finds that the effects of the solvent inertia are negligible on length scales $L \gg 10^{-13}$ m. Nevertheless, if one is interested in the correlation and response functions of the solvent velocity field, the Oono-Freed equations are certainly useful [9].

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