Dynamic charge density correlation function in weakly charged polyampholyte globules

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Abstract

We study solutions of statistically neutral polyampholyte chains containing a large fraction of neutral monomers. It is known that, even if the quality of the solvent with respect to the neutral monomers is good, a long chain will collapse into a globule. For weakly charged chains, the interior of this globule is semi-dilute. This paper considers mainly $\theta$-solvents, and we calculate the dynamic charge density correlation function $g(k,t)$ in the interior of the globules, 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 $s = t/\tau$. We find that for $q < 1$, corresponding to length scales larger than the blob size, the charge density fluctuations relax according to $g(q,s) \sim q^2(1 - s^{1/2})$ at short times $s < 1$, and according to $g(q,s) \sim q^2 s^{-1/2}$ at intermediate times $1 < s < q^{-4}$. We expect these results to be valid for wave vectors $q > 0.1$, where entanglements are unimportant.

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 an isolated neutral chain collapses into a non-compact globule, provided that the chain length exceeds some critical value. For weakly charged chains the polymer concentration inside the globule is low. In case of a good solvent, further collapse is prevented by the second order virial coefficient (also called the excluded volume parameter), whereas in case of a $\theta$-solvent, further collapse is prevented by the third order virial coefficient \^[1]\]. The non-compact semi-dilute globule 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 neutral non-collapsed 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 chain to appear collapsed on length scales larger than $\xi$. This physical picture, originating from Ref. [1], shows why the electrostatic screening length $\kappa^{-1}$ has to be equal to the blob size $\xi$, which is also equal to the 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 [2] is applicable (see also Ref. [1]). If the chain has a net charge, there is the possibility that the formation of the globular state is prevented by the electrostatic repulsion, depending on the chain length and the magnitude of the excess charge. For the "statistically neutral" chains considered here, the typical excess charge is proportional to the square root of the chain length. It was shown in Ref. [3] that in this case the electrostatic repulsion is insufficient to prevent the formation of the globular state for long enough chains. The only effect of the presence of a relatively large excess charge is that the globule becomes elongated. In Ref. [4] multi-chain effects were studied. It was shown that solutions with non-zero concentration start to phase separate already at very low concentrations, even if the quality of the solvent with respect to the neutral monomers is good. The supernatant consists of isolated spherical globules floating in the solvent. These globules contain either a single neutral chain, or two chains whose excess charges cancel each other. The semi-dilute precipitate, which still has a low polymer concentration, is locally indistinguishable from the interior of the globules. In this paper we will concentrate on the dense (semi-dilute) phase.

II. METHOD AND REGION OF APPLICABILITY

We study the dynamics of the charge density fluctuations in the dense phase (precipitate or globule), using the quadratic approximation to the Lagrange version [5,6] of the Martin-Siggia-Rose formalism [7]. We will follow closely the techniques of a paper by Fredrickson and Helfand [8]. Readers who wish to follows the details of our calculation are advised to study Ref. [8] first, especially its appendix. First we will determine in what length scale regime this formalism is expected to give correct results. There are three important length scales in the system: the blob size $\xi$, the hydrodynamic screening length $\xi_H$, 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 has been studied extensively [8], 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 [3]. It means that the excluded volume parameter $v$ enters the physics at large length scales $> \xi$ only by fixing the blob size [1].

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 in the range $N_e \approx 50 - 500$. Since the interior of the polyampholyte globules can be regarded as a dense melt of blobs, it follows that the typical entanglement length is given by

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

(1)

At length scales that are large compared to $\xi_e$ it is to be expected that the dynamics occurs via some kind of reptation, and on these scales the relaxation of charge density fluctuations probably becomes very slow (compare with Ref. [10], where systems with short range interactions are studied).

Next we discuss the hydrodynamic screening length $\xi_H$. At length scales smaller than $\xi_H$, the chain exhibits Zimm-like behavior, whereas at length scales larger than $\xi_H$, it exhibits Rouse-like behavior. Since it was shown in Ref. [3] that the quadratic approximation leads to the prediction of Rouse-like behavior, our analysis is only applicable to length scales larger than $\xi_H$. We need an estimate of its value. According to Ref. [1],

$$\xi_H \sim \frac{1}{\rho b^2},$$  

(2)

where $\rho$ is the monomer number density, and $b$ is the statistical segment length of a monomer (NB in this paper the sign $\sim$ means: has the same order of magnitude). First consider the case of a $\theta$–solvent. According to Ref. [1] we have

$$\rho_\theta \sim \frac{f \ell}{b^4} \quad \xi_\theta \sim \frac{b^2}{f \ell},$$  

(3)

where $\ell := e^2/4\pi\epsilon k_B T$ is the Bjerrum length ($\ell = 0.7nm$ in water at room temperature), $\epsilon$ is the electric permittivity of water, $k_B$ is Boltzmann’s constant, $T$ is the temperature, and $f$ is the fraction of monomers that carries a charge. Combining Eqs. (1) and (2), we obtain

$$\xi_{H,\theta} \sim \xi_\theta.$$  

(4)

In a good solvent, characterized by excluded volume parameter $v$, we have [1]

$$\rho_g \sim \frac{f^2 \ell^2}{vb^5} \quad \xi_g \sim \left(\frac{vb^5}{f^3 \ell^3}\right)^{1/2}.$$  

(5)

Combining Eqs (1), (2) and (4), we obtain

$$\frac{\xi_{H,g}}{\xi_g} \sim \left(\frac{\rho_\theta}{\rho_g}\right)^{1/2} \gg 1.$$  

(6)
We conclude that under good solvent conditions the hydrodynamic screening length is larger than the blob size, whereas under $\theta-$conditions they are approximately equal.

Finally, we discuss the region of validity of the quadratic approximation. It entails expanding the effective Hamiltonian in powers of the charge density $\psi(r)$, and retaining only the second order term. This approximation can only be justified if the typical amplitude of $\psi(r)$ is small. At length scales smaller than $\xi$, the system is strongly fluctuating, and the amplitude of $\psi(r)$ is large. At length scales larger than $\xi$, the charge density fluctuations are strongly suppressed by the electrostatic interactions, and the amplitude of $\psi(r)$ 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 on length scales that are large compared to both $\xi$ and $\xi_H$, and small compared to $\xi_e$. In order to ensure that our region of applicability is not empty, we will henceforth assume that the solvent is under $\theta-$conditions, in which case $\xi_H \sim \xi$, and $\xi_e \sim 10\xi$.

Since in a $\theta-$solution the hydrodynamic interaction is screened beyond length scale $\xi$, its influence enters the physics on intermediate length scales $\xi < L < \xi_e$ in a trivial way via just one parameter, which is the characteristic time scale $\tau$ at the blob level. Since inside the blobs the influence of the electrostatic interactions is negligible and the chain is not collapsed, $\tau$ can be found by considering a single neutral ideal chain with hydrodynamic interaction (Zimm-model). This leads to the estimate [9]

$$\tau \sim \frac{\eta \xi^3}{k_B T}, \quad \xi \sim \frac{b^2}{f \ell},$$

(7)

where $\eta$ is the viscosity of water.

III. CALCULATION OF THE DYNAMIC CHARGE CORRELATION FUNCTION

As mentioned in the introduction, we wish to describe the (semi-dilute) precipitate of a solution of weakly charged polyaonphilites. 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 [1]. Let the coarse grained conformation of chain $a$ be described by the 3-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

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

(8)
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:

$$\frac{\mathcal{H}}{k_B T} = \frac{3}{2\tilde{b}^2} \int_0^N \mathrm{d}\tau \sum_{a=1}^{n_p} \left( \frac{\mathrm{d}R_a(\tau)}{\mathrm{d}\tau} \right)^2 + \frac{\ell}{2} \sum_{a,b=1}^{n_p} \int_0^N \mathrm{d}\tau \int_0^N \mathrm{d}\tau' \frac{\theta_a(\tau)\theta_b(\tau')}{|R_a(\tau) - R_b(\tau')|}, \quad (9)$$

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 $\gamma = 1$, $k_BT = 1$, $\tilde{b}^2 = 3$, (10)

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 $R_a(\tau)$ and the quenched variables $\theta_a(\tau)$, the charge density is given by $e\tilde{\psi}(r,t)$, where

$$\hat{\psi}(r,t) = \sum_a \int \mathrm{d}\tau \theta_a(\tau) \delta(r - R_a(\tau)). \quad (11)$$

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

$$g_\theta(k,t) = \frac{e^2}{V} \left\langle \hat{\psi}(-k,t)\hat{\psi}(k,t) \right\rangle, \quad (12)$$

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 the assumption that the correlation function is self-averaging, which means that $g_\theta(k,t) = g(k,t) := g_\theta(k,t)$ with probability 1, where the bar denotes an average over the quenched variables $\theta'$. This means that in order to find $g_\theta(k,t)$ for a representative $\theta$ drawn from the Gaussian probability distribution Eq. (8) (which is what we are after), it suffices to calculate the average of this quantity over the disorder.

We will calculate $g(k,t)$ by means of the Lagrange version of the MSR (Martin-Siggia-Rose) formalism. In the appendix we have provided a brief derivation of the MSR functional. It is convenient to introduce an external field $h(k,t)$ that couples to $\hat{\psi}(k,t)$. 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

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1 The hat on $\hat{\psi}$ denotes the dependence on the annealed variables $R_a(\tau)$, 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.
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. (9) for the interaction energy, one arrives at the expression for the MSR functional. Since analogous calculations have been published before (see in particular Ref. [8]) we will not present the details, but just give the result. During the derivation, the following fields arise:

\[ \hat{\psi}_1(k, t) = \sum_a \int d\tau \theta_a(\tau) \exp \left[ ik \cdot R_a(\tau, t) \right] \]

\[ \hat{\psi}_2(k, t) = \sum_a \int d\tau \theta_a(\tau) k \cdot \hat{R}_a(\tau, t) \exp \left[ ik \cdot R_a(\tau, t) \right] . \] (13)

In the quadratic approximation, the final disorder averaged expression for \( Z[h] \) is

\[ Z[h] \propto \int D\psi_1 D\psi_2 D\phi_1 D\phi_2 \exp \left[ -\mathcal{L} + \int \int h(-k, -\omega) \psi_1(k, \omega) \right] , \] (14)

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

\[ \mathcal{L} = -\ell \int \int \frac{4\pi}{k^2} \psi_1(-k, -\omega) \psi_2(k, \omega) - i \int \int \phi_i(-k, -\omega) \psi_i(k, \omega) \]

\[ + \frac{c}{2} \int \int V_{ij}(-k, -\omega) \psi_i(-k, -\omega) \psi_j(k, \omega). \] (15)

\( c = n_p N/V \) is the density of charged monomers. The integral measures are defined by

\[ \int_\omega := \frac{1}{2\pi} \int d\omega \quad \int_k := \frac{1}{(2\pi)^3} \int d^3k . \] (16)

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. One consequence of this is that in this approximation the hydrodynamic interactions do not have an influence on the dynamic charge density correlation function. Therefore, our results are only valid on length scales larger than the hydrodynamic screening length. The integrals over \( \psi_i \) and \( \phi_i \) in Eq. (14) are Gaussian and can be calculated explicitly, after which \( g(k, t) \) can be obtained by differentiating the result twice with respect to the external field \( h \). The result is

\[ g(k, \omega) = \frac{c V_{11}(k, \omega)}{(1 - \kappa^2 k^{-2} V_{12}(k, \omega))(1 - \kappa^2 k^{-2} V_{21}(k, \omega))} . \] (17)

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

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

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

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

\[ V_{22}(k, t) = -\frac{1}{N} \int d\tau \langle k \cdot \hat{R}(\tau, t) k \cdot \hat{R}(\tau, 0) \exp [ik \cdot (R(\tau, t) - R(\tau, 0))] \rangle_0 . \] (18)
The average $\langle \cdots \rangle_0$ is calculated with respect to the single-chain Rouse Lagrangian $\mathcal{L}_0$, which is given by

$$\mathcal{L} = \int_\omega \int d\tau \hat{\mathbf{R}}(\tau, -\omega) \cdot \hat{\mathbf{R}}(\tau, \omega) + \int_\omega \int d\tau \omega \hat{\mathbf{R}}(\tau, -\omega) \cdot \hat{\mathbf{R}}(\tau, \omega)$$

$$-i \int_\omega \int d\tau \hat{\mathbf{R}}(\tau, -\omega) \cdot \frac{\partial^2 \mathbf{R}(\tau, \omega)}{\partial \tau^2}. \quad (19)$$

Before starting to calculate $V_{ij}(\mathbf{k}, t)$, it is useful to determine what are the relevant length and time scales. As discussed in the introduction, we are interested in the processes occurring at length scales of the order of the blob size $\xi$. As is usual for the semi-dilute 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 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. The refore, we can safely assume that the wave vectors of interest satisfy $k \sim \xi^{-1} >> N^{-1/2}$, 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 $t << t_R$, where $t_R$ is the Rouse time $\mathbb{I}$ 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. (20) are advised to study the appendix of Ref. $\mathbb{8}$, where similar calculations are worked out in detail. The result is

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

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

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

$$V_{22}(\mathbf{k}, t) = 0, \quad (20)$$

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 $V_{ij}(\mathbf{k}, \omega)$, 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 $\omega >> k^4$. Further on we will see that the characteristic frequency at wave vector $k$ satisfies this criterion. By substituting $z = -i\omega t$, distorting the integration contour back to the real axis, and expanding the integrand in powers of $zk^4/\omega \mathbb{8}$, one arrives at the following approximate expressions for $V_{ij}(\mathbf{k}, \omega)$:

$$\begin{cases} V_{11}(\mathbf{k}, \omega) \approx |\omega|^{-3/2}k^2 & (\omega > 0) \\ V_{12}(\mathbf{k}, \omega) \approx \begin{cases} (-1 + i)|\omega|^{-1/2}k^2 & \omega > 0 \\ (-1 - i)|\omega|^{-1/2}k^2 & \omega < 0. \end{cases} \end{cases} \quad (21)$$

Combining Eqs. (17) and (21) one obtains
\[ g(k, \omega) \propto \frac{k^2}{\ell|\omega|^{1/2}\left[\left(1 + |\omega\kappa^{-4}|^{1/2}\right)^2 + 1\right]} \quad |\omega| >> k^4. \]  
\hfill (22)

There are two frequency regimes:

\[ g(k, \omega) \approx \begin{cases} 
\ell^{-1}k^2\kappa^{-2}|\omega|^{-1/2} & |\omega| << \kappa^4 \\
\ell^{-1}k^2\kappa^2|\omega|^{-3/2} & |\omega| >> \kappa^4.
\end{cases} \]  
\hfill (23)

As discussed before, the formalism used can only be expected to describe the system correctly at length scales larger than the blob size. Therefore, we will consider Eq. (23) only for \( k < \kappa \). In that case, both frequency regimes given in Eq. (23) lie within the range of validity \(|\omega| >> k^4\). Doing an inverse Fourier transform with respect to the frequency we find two regimes:

\[ c^{-1}g(k, t) \approx k^2\kappa^{-2} \times \begin{cases} 
1 - |\kappa^4t|^{1/2} & t < \kappa^{-4} \\
|\kappa^4t|^{-1/2} & \kappa^{-4} < t < k^{-4}
\end{cases} \]  
\hfill (24)

with the restriction \( \xi < k^{-1} < \xi_e \) on the wave vector. Note that, in accordance with the results of Ref. [1], the wave vector dependence of the static correlation function \( g(k, t = 0) \) coincides with the Debye-Hückel expression \( g \propto k^2/(k^2 + \kappa^2) \) in the regime \( k << \kappa \). Equation (24) predicts that charge density fluctuations decay with a wave vector independent initial rate \( \tau \sim \kappa^{-4} \sim \xi^4 \). The exponent 4 is characteristic for the Rouse model. Since at length scales smaller than \( \xi \) the hydrodynamic interactions are not screened, one would expect a rate \( \tau \sim \xi^3 \). The discrepancy is due to the Gaussian approximation [8]. This does not mean that Eq. (24) breaks down completely: since at length scales larger than \( \xi \) the hydrodynamic interactions are screened and the chain is Rouse-like, Eq. (24) is valid for \( k < \kappa \), provided that one inserts the correct basic time scale \( \tau \) at the blob level; see the discussion at the end of the introduction. Defining the dimensionless wave vector \( q := k/\kappa \) and the dimensionless time \( s := t/\tau \), we obtain for \( 0.1 < q < 1 \)

\[ c^{-1}g(q\kappa, s\tau) \approx q^2 \times \begin{cases} 
1 - |s|^{1/2} & s < 1 \\
|s|^{-1/2} & 1 < s < q^{-4}
\end{cases} \]  
\hfill (25)

with

\[ \tau \sim \frac{\eta\xi^3}{k_BT}. \]  
\hfill (26)

The expression for \( \tau \) reflects the Zimm behavior at small length scales, whereas the exponent 4 appearing in the condition \( s < q^{-4} \) reflects the Rouse behavior at longer length scales. The time dependence of the dynamic charge correlation function is schematically depicted in Fig. 1.

### 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 semi-dilute,
for instance by imposing a non-zero concentration. In this case, the charge density corre-
lation function would follow immediately from Eqs. (17) and (20) by taking $\kappa = 0$. It
follows that when the electrostatic interactions are absent, the charge density correlations
decay according to a stretched exponential $g(k, t) \sim k^2 \kappa^{-2} \exp \left[ - \left( \frac{t}{\tau'} \right)^{1/2} \right]$ for some $\tau'$.

Considering that the Taylor expansion of this function starts with $1 - \left( \frac{t}{\tau'} \right)^{1/2}$, one sees
from Eq. (25) that at short times an interacting system relaxes in qualitatively the same
way as a non-interacting system (though the decay rate is higher), but that at longer times
the relaxation is completely different. 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:

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

The time dependence of Eq. (27) is completely different from that of Eq. (25), 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. As an illustration, consider the correlation function for a semi-dilute
homopolymer solution, which has been calculated within the quadratic approximation in
Ref. [8]. 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. [8]). Experimentally, it would be interesting
to test the existence of the two frequency regimes in Eq. (23) by means of scattering
experiments.

**APPENDIX A:**

In this appendix we present a brief derivation of the Martin-Siggia-Rose functional [7].
We will follow the method developed in Refs. [5,6]. 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 [9,11]

$$\frac{\partial P}{\partial t} = \nabla \cdot \mathbf{L} \cdot [k_B T \nabla P + P \nabla U],$$

(A1)
where $\nabla$ represents the vector with components $\partial/\partial R_{\alpha}$, and dots denote inner products. The mobility matrix $L[\mathbf{R}]$ is given by

\begin{equation}
L_{n\alpha,m\beta} = H_{\alpha\beta}(\mathbf{R}_n - \mathbf{R}_m) \quad n \neq m
\end{equation}

\begin{equation}
L_{n\alpha,n\beta} = \frac{\delta_{\alpha\beta}}{\gamma}.
\end{equation}

$H_{\alpha\beta}(\mathbf{r})$ is the Oseen tensor (see Ref. [3], 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 [11]. In the Stratonovich interpretation it is given by

\begin{equation}
\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 \zeta.
\end{equation}

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

\begin{equation}
\langle \zeta(t) \rangle = 0 \quad \langle \zeta(t) \zeta(t') \rangle = I \delta(t - t').
\end{equation}

$I$ is the $3N \times 3N$ identity matrix. The matrix $\mathbf{g}$ is related to the mobility matrix $bf\mathbf{L}$ by

\begin{equation}
\mathbf{g} \cdot \mathbf{g}^T = 2k_B TL.
\end{equation}

Equation (A5) leaves some freedom in the choice of $\mathbf{g}$, which can be used to impose the condition [3]

\begin{equation}
\nabla \cdot \mathbf{g} = 0.
\end{equation}

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

\begin{equation}
\frac{\partial \mathbf{R}}{\partial t} = -\mathbf{L} \cdot \nabla U + \mathbf{g} \cdot \zeta + \hat{\mathbf{h}}.
\end{equation}

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. [5,6] 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 conjugate field $\mathbf{\hat{R}}(t)$, which is rather straightforward in the Lagrange formalism [3], one finds the expression

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

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

\begin{equation}
\mathcal{L}[\mathbf{R}, \mathbf{\hat{R}}] = \int dt \left[ k_B T \mathbf{\hat{R}} \cdot \mathbf{L} \cdot \mathbf{\hat{R}} + i\mathbf{\hat{R}} \cdot (\mathbf{\hat{R}} + \mathbf{L} \cdot \nabla U) \right].
\end{equation}

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 $\mathbf{\hat{h}}$ and $\mathbf{h}$, where the field $\mathbf{h}$ couples to $\mathbf{R}$. One obtains
\[ Z[\mathbf{h}, \mathbf{\hat{h}}] = \int D\mathbf{R} \int D\mathbf{\hat{R}}(t) \exp \left[ -\mathcal{L}[\mathbf{R}, \mathbf{\hat{R}}] + \int dt \mathbf{h}(t) \cdot \mathbf{R}(t) + \int dt \mathbf{\hat{h}}(t) \cdot \mathbf{i} \mathbf{\hat{R}}(t) \right]. \quad (A10) \]

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 [12]. For instance, it is not possible to determine the value of the equal-time response function \( \langle \mathbf{R}(t) i \mathbf{\hat{R}}(t) \rangle \). Retracking 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 [12]. 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 solutions. It has been argued [13] that Eq. (A7) is inconsistent, in the sense that whereas the thermal fluctuations of the particles 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 [13] 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. [8] 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 \( \omega = k_B T k^3 / 6 \pi \eta \), where \( \eta \) is the solvent viscosity. It follows from the Navier-Stokes equation that the solvent inertia is negligible if \( \rho \omega << \eta k^2 \), 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 \( L >> 10^{-13} \text{m} \). Nevertheless, if one is interested in the correlation and response functions of the solvent velocity field, the Oono-Freed equations are certainly usefull [8].

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FIGURE CAPTION

The dynamic charge density correlation function $g(q, s)$ as a function of the dimensionless time $s := t/\tau$ for fixed dimensionless wave vector $0.1 < q := k\xi < 1$, where $\xi$ is the blob size, and $\tau$ is the characteristic time scale at the blob level.
$g(q,s) \sim 1 - s^{1/2}$

$s = 1$

$s = t/\tau$

$s = q^{-4}$