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Polymeric Salts: Static and Dynamic Debye−Hückel Theory

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ABSTRACT: We study polymeric salts formed by connecting ionic end groups by a soluble polymeric backbone: this can be done either by linking similarly charged ions (anions and cations) and then mixing positively charged and negatively charged chains or by linking oppositely charged ions. This last case where the chains are globally neutral is of special interest: due to the connectivity constraint, the polymeric solution behaves as a dielectric at large length scales (in the absence of any small free ions) but it locally screens the electrostatic interactions such as a salt. In a suited range of end charge and chain length the strength of the macroscopic long-range interaction between test charges can be monitored by tuning the polymeric salt concentration. The relaxation of thermal fluctuations in the solution has three eigenmodes: a fast plasmon mode corresponding to the relaxation of charge fluctuations, and two modes independent of the strength of the electrostatic interaction, one being the cooperative mode found in usual semidilute solutions. The plasmon mode resembles that in free salt solutions except that the chain connectivity restricts the size of the charge fluctuations to the coil size.

1. Introduction

Charged polymers are widely used because they are usually water soluble and can be handled without the use of any organic solvent. Many properties of polyelectrolyte solutions, including their solubility, are controlled by the entropy of the free counterions.[1,2] Polyampholytes carry charges of both signs,[3] and in the absence of free ions they are usually insoluble[4] unless plus and minus charges are almost alternating along the polymer chain.[5] From the static point of view the free ions are effective in screening the electrostatic interactions in polyelectrolyte solutions at all scales while charges belonging to the chains only contribute weakly to the screening at intermediate length scales. From the dynamical point of view, polyelectrolyte solutions are conductors mainly due to the free ions. In a sense, dilute polyelectrolyte solutions behave as usual though very asymmetric salt solutions.

A different behavior is expected for polymeric salts where the charges of both signs are linked by polymeric chains and thus where there are no free ions (free ions remaining after the synthesis may be eliminated by dialysis). The polymeric backbones should be soluble by themselves and modified PEO chains could be good candidates. We consider two types of polymeric salts: ampholyte salts where each coil carries a plus charge at one end and a minus charge at the other end, and symmetric salts[6] where half of the chains carry a plus charge at both ends and half a minus charge[7] (Figure 1). We mainly focus on ampholyte salts for which a very specific behavior is awaited. As the chains are globally neutral they are not expected to act as charge carriers in conducting processes: the solution behaves thus as a dielectric at large length scales; more precisely at scales larger than the chain radius, any charge separation is prohibited. On the other hand at smaller scales the charges are almost free to organize and to participate to Debye screening. If the conditions are well chosen, the electrostatic interactions in the solution can thus be damped over several Debye lengths within one coil radius inside the semidilute solution and then cross over to the standard algebraic decay. The strength of the long-range interaction tail can be monitored by tuning the polymeric salt concentration.

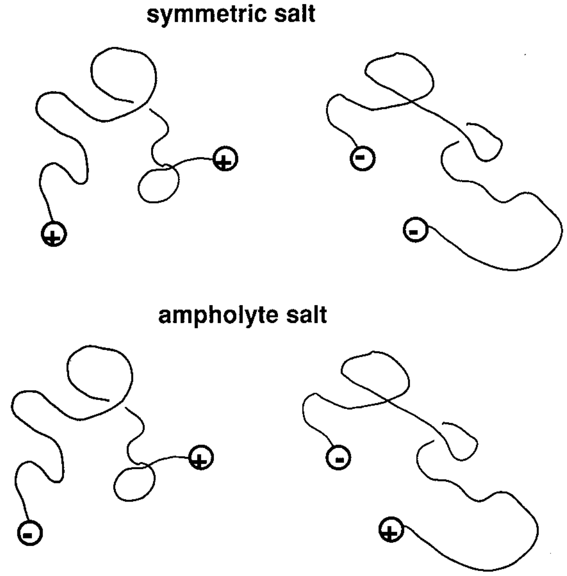

Figure 1. Symmetric salt and ampholyte salt.

Quasi-elastic light scattering experiments measure the relaxation of thermal fluctuations. They would help to refine our understanding of polymeric salt solutions. The relaxation of thermal fluctuations in weak polyelectrolyte solutions was calculated,[8,9] and the cooperative mode was measured.[10]

The fastest relaxation mode was found to be the plasmon mode associated with the electric charge relaxation. The relaxation frequency for a momentum transfer q is similar to that in usual salts $f_{\mathrm{pl}} \sim k_{\mathrm{B}}T(q^2 + \kappa^2)/\zeta$, with ζ a monomeric friction and κ the inverse Debye length associated with the small ions only. For ampholyte salts, in contrast, there are only charges bound to the backbones that can contribute to the screening, and an additional effect is expected when chain connectivity sets an upper bound to the spatial extension of charge fluctuations.

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In weak polyelectrolyte solutions, there is also an intermediate frequency corresponding to a local restoration of the Donnan equilibrium at the probed length scale $1/q$. As there are no free ions in polymeric salts, no Donnan mode is to be expected. The slowest mode corresponds to the relaxation of monomer concentration fluctuations and is diffusive. In weak polyelectrolytes, it shows a minimum at an intermediate lengthscale corresponding to the peak in the monomer/monomer structure factor, since in this q-range the restoring force is smallest.

In this paper, we examine theoretically both static screening and relaxation of thermal fluctuations in polymeric salts. The static structure factors and the dielectric constants are calculated in section 2 using the so-called random phase approximation (RPA) and the relaxation of thermal fluctuations in section 3. The last section presents some concluding remarks.

2. Static Structure Factor and Dielectric Constant

In the polymeric salt solution there are three independent fluctuating fields, say the cation concentration, the anion concentration, and the neutral monomer concentration (δC^+, δC^-, δC^n) or more conveniently the electric charge, the ionic strength, and the monomer concentration ($\delta\rho = \delta C^+ - \delta C^-$, $\delta I = \delta C^+ + \delta C^-$, $\delta C = \delta C^+ + \delta C^- + \delta C^n$). In the last representation the Coulomb interaction does not couple the fluctuations of the various fields.

When an external potential fluctuation $\delta\psi(q)$ is applied to the polymeric salt solution, it induces a charge fluctuation $\delta\rho(q)$ proportional to the potential fluctuation in the limit of linear response. The response function is the opposite of the charge/charge correlation $S_{z,z}$, and $\delta\rho_{\mathrm{ind}} = -S_{z,z}\delta\psi$. The external potential fluctuation can be attributed to an external charge fluctuation given by the Poisson equation $4\pi l_B \delta\rho_{\mathrm{ext}}/q^2 = \delta\psi$, with l_B the Bjerrum length (about 0.7 nm in water). The Maxwell equations for the electric field and the electric displacement field link the dielectric constant ϵ to the pure solvent dielectric constant ϵ_s (the solvent is considered here as a continuum) $\epsilon_s = \epsilon(\rho_{\mathrm{ext}} + \rho_{\mathrm{ind}})/\rho_{\mathrm{ext}}$. The dielectric constant of the solution depends thus only on that of the solvent and on the charge/charge structure factor (within linear response):

$$\epsilon = \frac{\epsilon_s}{1 - 4\pi l_B S_{z,z}/q^2} \qquad (1)$$

Within the random phase approximation the free energy density associated to concentration fluctuations is expanded to quadratic order: $F = (1/2)\, \mathbf{S}_{\alpha,\beta}{}^{-1}\, \delta\mathbf{C}_\alpha(\mathbf{q})\delta\mathbf{C}_\beta(-\mathbf{q})$ ($\alpha,\beta = +, -, \mathrm{n}$)

$$\mathbf{S}_{\alpha,\beta}{}^{-1} = \mathbf{S}^0{}_{\alpha,\beta}{}^{-1} + v_{\alpha,\beta} + 4\pi l_b z_\alpha z_\beta/q^2 \qquad (2)$$

where the superscript 0 denotes the Gaussian correlations, the second term on the right-hand side stands for short-range excluded volume interactions (at the mean-field level), and the last term accounts for Coulomb interactions z_α being the valency of species α. Throughout the paper we assume equal excluded volume interactions for all pairs of monomers regardless of their charge. As the charge fluctuations do not couple to the ionic strength fluctuations or to the monomer density fluctuations, the charge/charge structure factor reduces to $(S_{z,z})^{-1} = (S_{z,z}{}^0)^{-1} + 4\pi l_B/q^2$ and the dielectric constant eq 1 can be related to the Gaussian charge/charge structure factor

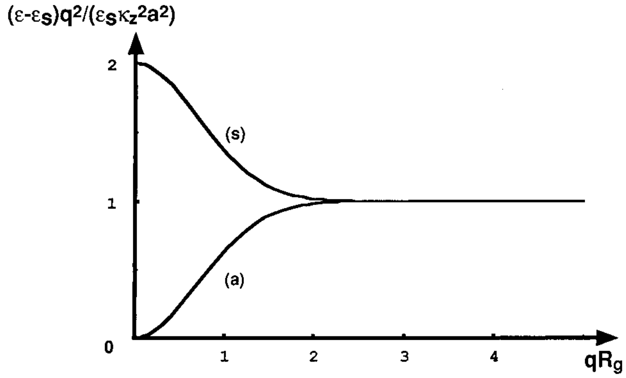

Figure 2. Relative increase of the dielectric constant as a function of q, for the symmetric salt (s) and ampholyte salt (a). Here κ_z is the inverse Debye length for the depolymerized salt.

$$\epsilon = \epsilon_s\,(1 + 4\pi l_B S_{z,z}{}^0/q^2) \qquad (3)$$

Details on Gaussian correlations are found in the Appendix. For the ampholyte salt the + and − charges are linked by the chain of N-2 neutral monomers, and $S_{z,z}{}^0 = S_{+,+}{}^0 + S_{-,-}{}^0 - 2S_{+,-}{}^0$ reduces to $S_{z,z}{}^0 = 2z^2(\phi/N)(1 - \exp(-Na^2q^2/6))$ whereas in the symmetric case the Gaussian correlations between opposite charges vanish and the Gaussian charge/charge structure factor simplifies to $S_{z,z}{}^0 = 4z^2(\phi/N)(1 + \exp(-Na^2q^2/6))$; in each case ϕ/N is the concentration of the equivalent z-valent (ampholyte case) or $2z$-valent (symmetric case) salt. The q-dependent dielectric constant reads thus

$$\epsilon = \epsilon_s\,(1 + 4\pi l_B z^2(2\phi/N)(1 - \exp(-Na^2q^2/6))/q^2) \qquad \text{(ampholyte salt)}$$

$$\epsilon = \epsilon_s\,(1 + 4\pi l_B z^2(4\phi/\mathrm{N})(1 + \exp(-Na^2q^2/6))/q^2) \qquad \text{(symmetric salt)} \quad (4)$$

The dielectric constant increment is plotted against the wave vector q in Figure 2. It is instructive to discuss the behavior of the dielectric constant at large scales, $qR_g \ll 1$, R_g being the Gaussian radius of gyration. For the symmetric salt $\epsilon = \epsilon_s(1 + \kappa^2/q^2)$ with $\kappa^2 = 8\pi l_B(2z)^2\phi/N$ as for a usual symmetric $2z$-valent salt. (Though the polymeric salt coils may strongly overlap, the charged chain ends remain dilute and no finite size effect of the ions is expected in contrast to concentrated conventional electrolytes.[11]) In contrast, for the ampholyte salt $\epsilon = \epsilon_s + (\phi/N)p^2/(3k_BT)$ as for an ideal gas of dipoles at concentration ϕ/N, each dipole carrying a moment $p = (e^2z^2Na^2)^{1/2}$ corresponding to the Gaussian polymer configuration. At large scales, a volume comprises as many + and − charges since they are linked by the polymeric chains and the total charge vanishes up to edge effects at the border of the volume. This means that the salt ampholytes act as dipoles that can align along the field. At short lengthscales however the connectivity plays no role and both the ampholyte salt and the symmetric salt behave as usual *z-valent* salts of concentration ϕ/N and $2\phi/N$, respectively. Thus the symmetric polymeric salt screens the electric interactions at all scales crossing over from the behavior of a $2z$-valent salt with a concentration ϕ/N at scales larger

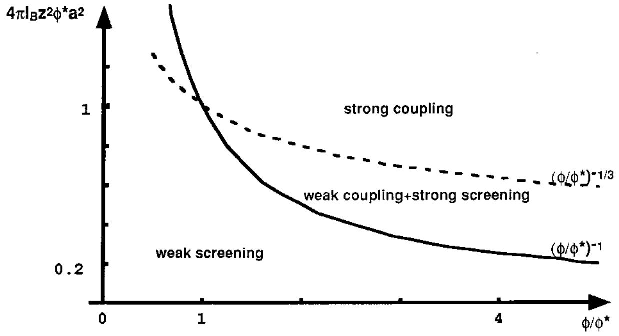

Figure 3. There exists a domain of weak coupling and strong screening for the ampholyte salt solution. The interaction parameter, $4\pi l_b z^2\phi^* a^2$ should be understood as $\alpha l_B z^2/R^{d-2}$, the interaction between two charges of the same polymer, d being the dimension of space.

than the coil size to the behavior of a z-valent salt with a concentration $2\phi/N$ at short scales, while the ampholyte salt screens the electrostatic intreractions at short scales and only increases the macroscopic dielectric constant at large scale. However, this short range screening is effective only if the Debye length is smaller than the coil size; this leads to the criterion $8\pi l_B z^2\phi a^2 > 1$, where Gaussian statistics has been assumed. For our calculation to be acceptable the coupling between charges needs to be weak enough: $4\pi l_B z^2(\phi/N)^{1/3} < 1$. As shown in Figure 3 there is a range of end charge z where these two constraints are satisfied provided that the concentration exceeds the Gaussian coil overlap concentration $\phi^* = a^{-3}/(8N)^{1/2}$, (here $l_B \sim a$ has been assumed).

The interaction $V(r)$ between two test charges immersed in the polymeric salt solution is calculated from the dielectric constant $\epsilon(q)$ as

$$V(r) = \frac{1}{(2\pi)^3}\int \frac{d^3q\, \exp(i\mathbf{q}\cdot\mathbf{r})}{q^2\epsilon(q)} \tag{5}$$

After performing the angular integrals, we obtain

$$V(x) = \frac{1}{4\pi\epsilon_s R}\frac{2}{\pi}\int_0^\infty \frac{\sin(ux)}{ux}\frac{du}{1 + \dfrac{\alpha^2(1 \pm \exp(-u^2))}{u^2}} \tag{6}$$

where the + sign and the − sign in the denominator correspond to the symmetric salt and to the ampholyte salt, respectively, $x = r/R$ being the reduced distance and $\alpha = \kappa R$ the "inverse" reduced screening strength, and κ is given by the Debye−Hückel formula for the equivalent nonpolymerized salt. In Figure 4 the potential is plotted together with the short range and macroscopic limits for $\alpha = 2$ for the polyampholyte salt. One sees how the local screening ensures the crossover from the microscopic Coulomb law in the pure solvent to the weaker macroscopic Coulomb law in the presence of the polymeric dipoles.

3. Relaxation of Thermal Fluctuations

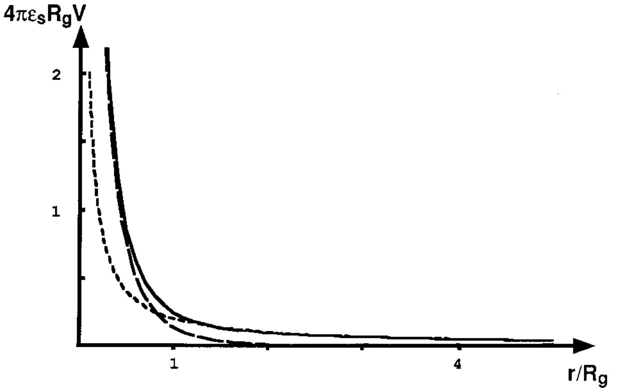

Figure 4. Interaction potential between unit test charges in an ampholyte salt solution in the case $\kappa R_g = 2$. The broken line corresponds to the potential with the screening length κ^{-1} that applies at short distance while the dashed line correspond to the macroscopic law.

As the polymeric salt solutions are stable systems, concentration fluctuations cost energy and relax. Close to equilibrium, the restoring forces can be described by linear response theory. The solvent is considered as a continuous viscous medium of viscosity η. We take hydrodynamic interactions between monomers into account through the Oseen tensor. Following Doi and Edwards,[12] the relaxation of the concentration fluctuations is then described by a Langevin equation

$$\frac{\partial\delta\mathbf{C}(\mathbf{q},t)}{\partial t} = -\Gamma(\mathbf{q})\cdot\delta\mathbf{C}(\mathbf{q},t) + \mathbf{R}(\mathbf{q},t) \tag{7}$$

where $\mathbf{R}(\mathbf{q},t)$ is a white noise and $\delta C(\mathbf{q},t) = \{\delta C_\alpha\}$ a vector whose components are the concentration fluctuations of the various species. The relaxation matrix $\Gamma(\mathbf{q})$ is given by a Kubo relation

$$\Gamma(\mathbf{q}) = k_BT\int \frac{d\mathbf{k}}{(2\pi)^3}\,\mathbf{S}(\mathbf{k}+\mathbf{q})\frac{q^2 - (\mathbf{q}\cdot\mathbf{k}/k)^2}{\eta k^2}\,\mathbf{S}^{-1}(\mathbf{q}) \tag{8}$$

The matrix $\mathbf{S}(\mathbf{q})$ of the equilibrium correlations has been discussed in the previous section. The mobility integral in the Kubo formula eq 8 can be carried out over the angles

$$\Gamma = \frac{k_BT}{\eta}\mathbf{K}(\mathbf{q})\mathbf{S}^{-1}(\mathbf{q})$$

$$\mathbf{K}(\mathbf{q}) = \frac{1}{4\pi^2}\int_0^\infty k^2 dk H(k/q)\mathbf{S}(k)$$

$$H(x) = \frac{x^{-1} + x}{2}\log\left|\frac{x+1}{x-1}\right| - 1 \tag{9}$$

where for large arguments $H(x \to \infty) \sim 4/3x^2$. It will turn out that hydrodynamic interactions are irrelevant for some local relaxation processes; for those cases, the results obtained from a Rouse model that does not include the hydrodynamic interactions are recovered.[13] In the Rouse formalism, the relaxation matrix reads

$$\Gamma = q^2k_BT\mathbf{M}(\mathbf{q})\mathbf{S}^{-1}(\mathbf{q}) \tag{10}$$

where the mobility matrix is diagonal, $\mathbf{M}(\mathbf{q}) = \{\delta(\alpha,\beta)C_\alpha/\zeta_\alpha\}$, ($\delta(\alpha,\beta)$ is the Kronecker symbol and ζ_α is the friction on species α).

There are three independent relaxation modes.

As the charge does not couple to the ionic strength or monomer fluctuations, charge relaxation is an eigenmode. This so-called plasmon mode is found to be the fastest relaxation mode. At larger time scales the relaxation is independent of the electrostatic interaction

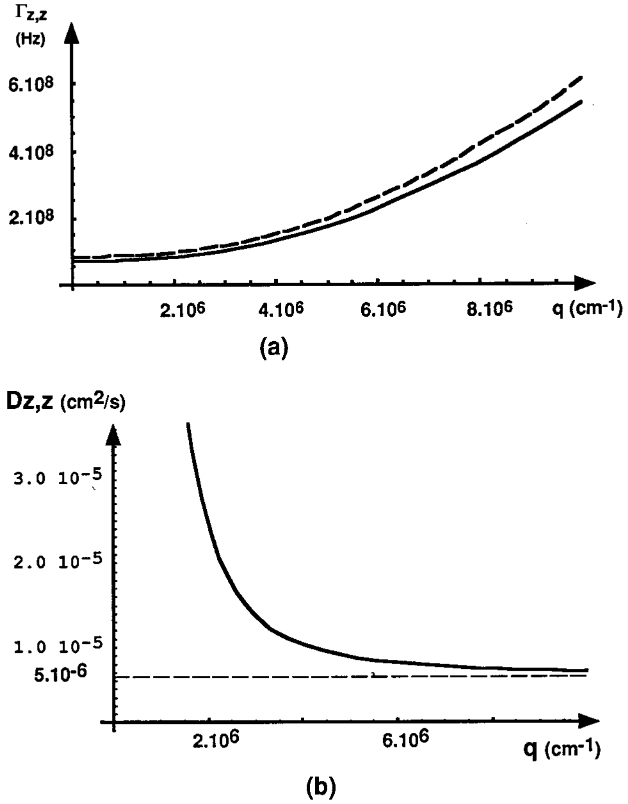

Figure 5. (a) Plasmon frequency for a ampholyte salt solution: $N = 10^3$, $a = b = 4 \times 10^{-8}$ cm, $l_B = 7 \times 10^{-8}$ cm, $z^2\Phi a^3/N = 4 \times 10^{-4}$ after eq 9. The broken line corresponds to eq 11. (b) The effective diffusion constant after eq 11; $D_{\rm eff} = \Gamma_{z,z}/q^2$ diverges as $q \to 0$.

and is diffusive. The chain ends carrying the charges then equilibrate (regardless of their charge), and finally the concentration of monomers has to equilibrate. The latter process is the slowest eigenmode and corresponds to the standard cooperative mode of the polymer solution (the breathing mode).

For the plasmon mode the integral in the mobility $K_{z,z}(q)$ as given by eq 9 is dominated by the upper bound and formally diverges. The mobility is dominated by the shortest (monomeric) scales. Introducing the cutoff $q_{\max} = \pi/2b$ and using the asymptotic form of $H(x)$ for large x to estimate the integral in $K_{z,z}(q)$, we obtain

$$\Gamma_{z,z} = \frac{k_B T}{6\pi\eta b}\left[\frac{q^2}{1 \pm \exp(-Na^2q^2/6)} + \kappa^2\right] \qquad (11)$$

where the +,− in the denominator correspond to the symmetric and the ampholyte salts, respectively, and the cutoff size b is of order the monomer size a. The plasmon frequency as given by eq 11 is plotted in Figure 5 together with the numerical result of eq 9, for given values of the parameters, and the agreement is fair. The mobility is dominated by the microscopic cutoff size b, and the results are identical to those of a Rouse model with a friction $\zeta = 6\pi\eta b$; hydrodynamic interactions do not play any role. (More precisely, long range hydrodynamic interactions do not play any role; the description in terms of the Oseen tensor does not correctly account for short length scales behavior; more generally, local correlations between monomers should also be considered more carefully; all these effects are hidden in the cutoff length b.) Also the chain connectivity plays no role. In the high q limit, the relaxation is diffusive as for a monomeric salt and the electrostatic interactions are irrelevant. In the low q limit, the symmetric salt behaves as a usual monomeric salt, the relaxation of charge fluctuations of size larger than κ^{-1} is driven by electrostatics, and $\Gamma_{z,z}(q \to 0) \sim (k_B T/6\pi\eta b)\kappa^2$. For the ampholyte salt, $\Gamma_{z,z}(q \to 0) \sim (k_B T/6\pi\eta b)(\kappa^2 + R_g^{-2})$. At low wave vector, the relevant length scale is the screening length κ^{-1} in the screened regime where charge fluctuations of size κ^{-1} may develop and the radius of gyration $R_g = (Na^2/6)^{1/2}$ at somewhat lower concentrations/valencies where the size of the charge fluctuations is limited by the chain size. The result that the friction on an ion is microscopic is somewhat surprising as a moving ion has to drag a chain section when it moves. The typical thermal charge fluctuation corresponds to a noncompensated central charge in a volume κ^{-3}, and its amplitude is about one charge. To invert the sign of the charge fluctuation, it is thus enough to remove one charge from the border, the motion being marginally driven by electrostatics. This charge is found in a small shell of microscopic thickness, and its motion outward over the shell thickness does not imply any motion of neutral chain sections.

The cooperative mode is identical to the cooperative mode of the corresponding neutral homopolymer solution.[12] The correlations of the concentration fluctuations, in the random phase approximation are given by $S_{\Phi,\Phi} = S^0{}_{\Phi,\Phi}/(1 + vS^0{}_{\Phi,\Phi})$ and the mobility $K_{\Phi,\Phi}$ is given by the Kawasaki−Ferell integral. Well inside the semidilute concentration range, the relaxation rate of the concentration fluctuations Γ_Φ reads

$$\Gamma_\phi = \frac{k{\rm B}T}{6\pi\eta_s\xi}\, q^2 F(q\xi)$$

$$F(x) = \frac{3}{4x^3}\,(x + (x^2 - 1)\arctan x)$$

$$F(x \to \infty) \sim 3\pi x/8 \qquad F(0) = 1 \qquad (12)$$

with the correlation length $\xi = a^2/12v\Phi_t$ associated to the total monomer concentration Φ_t. At small length scales ($q\xi \gg 1$), this relaxation frequency is proportional to q^3, and the relevant friction is proportional to the probed length scale q^{-1}; at large length scales ($q\xi \ll 1$), it is proportional to q^2/ξ and the relevant friction is proportional to the correlation length. For the polymeric salts, in the $\{\delta\rho, \delta I, \delta\Phi\}$ representation the charge fluctuations $\delta\rho$ do not couple to the two other fields. The correlation matrix **S** and its inverse consist of the diagonal charge/charge term and a 2 × 2 matrix. The same 2 × 2 matrix would describe a neutral polymer with labeled (though identical to the other monomers) ends. This (artificial) labeling does not change the relaxation of the overall concentration fluctuations that thus still corresponds to an eigenmode of relaxation rate Γ_Φ. As we now distinguish the chain ends, there is however an additional relaxation mode of relaxation rate $\Gamma_{\rm ec}$. This is obtained by subtraction of Γ_Φ from the trace of the 2 × 2 block in the Γ matrix.

$$\Gamma_{\rm ec} = \frac{k_B T}{\eta_s}\,(K_{I,I}S_{I,I}{}^{-1} + 2K_{I,\Phi}S_{I,\Phi}{}^{-1} + K_{\Phi,\Phi}(S_{\Phi,\Phi}{}^{-1} - 1/S_{\Phi,\Phi})) \qquad (13)$$

The values of the charges do not enter this frequency which is related to the existence of labeled chain ends and thus the ampholyte salt and the symmetric salt relax with the same frequency. The dominant contribution to Γ_{ec}, at both low and high momentum transfer, comes from the first term on the left-hand side of eq 13. After calculating the mobility integral $K_{I,I}$ which turns out to be dominated by the upper bound, we find that the relevant friction in Γ_{ec} is the friction on a monomer.

$$\Gamma_{ec} \approx \frac{k_B T}{6\pi\eta_s b} S^0_{I,I}(k\rightarrow\infty)\, q^2 \frac{S^0_{\Phi,\Phi}}{S^0_{I,I}S^0_{\Phi,\Phi} - (S^0_{I,\Phi})^2} \quad (14)$$

At large and small wavevectors, we obtain the following asymptotic behaviors:

$$\Gamma_{ec}(q\rightarrow\infty) = \frac{k_B T}{6\pi\eta_s b} q^2$$

$$\Gamma_{ec}(q\rightarrow 0) = \frac{k_B T}{6\pi\eta_s b}\left(\frac{3}{R_g^{\,2}} + \frac{q^2}{2}\right) \quad (15)$$

The relaxation is diffusive at high wave vectors; however the largest end/overall monomer fluctuation, is of size $\sim R_g$, the relaxation of fluctuations at larger length scales being driven by chain elasticity.

For the symmetric salt there is yet a fourth mode if the chains linking the positive and negative charges can be distinguished (for example by labeling the chains linking the positive ions). This extra mode is a composition mode driven by the electrostatic interactions and is thus a plasmon mode with a nonvanishing relaxation rate at zero wave vector. The relevant friction is the (mesoscopic) chain friction as illustrated by the following Rouse result:

$$\Gamma_c(q\rightarrow 0) = \frac{32z^2\pi k_B T l_B \Phi}{N^2\zeta} \quad (16)$$

with ζ a monomeric friction. This is the charge relaxation of a $2z$-valent salt at a concentration Φ/N with a Rouse friction $N\zeta$ per ion (i.e., per chain). We expect hydrodynamic interactions to change the ion (chain) friction into $\sim 6\pi\eta N\, a^2/\xi$ where Gaussian statistics is again assumed and where entanglements between chains are ignored.

4. Conclusions

We have presented a theoretical study of polymeric salt solutions consisting of water soluble chains (e.g., P.O.E) terminated by charged groups. Two cases were considered: ampholyte salts with all chains carrying a + charge at one end and a − charge at the other end, and symmetric salts with half of the chains carrying a plus charge at both ends and the other half carrying a − charge at both ends. These polymeric salt solutions are free of small ions (except those coming from water dissociation), we suggest that they could be used rather than usual salt for some applications.

We analyzed the dielectric constant of polymeric salt solutions. Symmetric salts behave very much as usual salts composed of small anions and cations. This is not the case of polyampholyte salts. As the chains are neutral and cannot act as charge carriers, the large scale behavior ($qR_g < 1$) is dielectric and each chain acts as a dipole that can align along the external field. At short scales ($qR_g > 1$) in contrast, charges can rearrange to screen the electrostatic interaction as in ordinary salts, this screening can be effective over the chain radius in a suited range of end charge and concentration (for chains composed of about 100−300 monomers, concentrations higher than the overlap concentration and end charges of two to three elementary charges seem appropriate). The dielectric constant goes then from the local value of the pure solvent to the higher macroscopic value through the screened crossover regime. As a solvent, the ampholyte salt solution retains thus some properties of ordinary salt solutions at short scales (a few nanometers); on the other hand, not being a conductor, it can sustain high electric fields. Such materials could perhaps be useful in separation experiments under electric fields where the polymer solutions could at the same time play the role of the transient network (for that purpose long alternating polyampholytes could also be used).

We also discussed the relaxation of thermal fluctuations in polymer salt solutions. The fastest relaxation mode is the so-called plasmon mode describing the relaxation of the charge fluctuations. It is rather similar to the plasmon mode of monomeric salts except that chain connectivity confines charge fluctuations within the coil size for ampholyte salts. This is the only mode driven by electrostatic interactions. On an almost comparable time scale, the chain end concentration relaxes toward its average value. In practice a similar mode should be seen in usual polymer solutions whenever the chain ends are different from the other monomers. These two fast modes are diffusive at small scales, and their frequency reaches a macroscopic limit at large scales. The sometimes defined apparent diffusion coefficient $D_{eff} = \Gamma/q^2$ diverges for those modes as $q \rightarrow 0$.

For the symmetric polymeric salt, if the cationic and anionic chains can be distinguished, there is an additional composition mode driven by electrostatics (at large scales); this mode is formally of the plasmon-type, with a polymeric friction. In practice one can label the anionic chain (say). With the relaxation time being much longer than the plasmon relaxation time of monomeric salt (which are in general to fast to be observed), this suggests a scattering experiment where a plasmon mode could be measured in the $q \rightarrow 0$ limit.

The slowest mode is the so-called cooperative mode of concentration fluctuations. As we assumed the same excluded volume for all monomers regardless of their charges, we obtain the usual Kawasaki−Ferell relaxation rate proportional to q^3 at low scales and to q^2/ξ at large scales ($\xi^{-1} > q > R_g^{-1}$) where the diffusion coefficient of a correlation volume drives the relaxation.

Our analysis is based on a mean-field theory restricted to linear response.

The mean-field excluded volume treatment applies to polymers in marginal solvent where $vN^{1/2} < 1$, a situation which is not unusual especially for the fairly short chains that we have in mind. A mean field as such gives a fair description of polymers in a *θ-solvent,* all results are unaffected up to the excluded volume dependence mainly showing up in the cooperative mode. There the excluded volume v can in a first approximation be replaced by $w^2\Phi$ and accordingly the correlation length is then proportional to $1/\Phi$. For polymers swollen in a good solvent, excluded volume correlations must be taken into account. At the scaling level this is straightforward: the coil radius becomes $R_g \sim N^\nu$ in a dilute solution and $R_g \sim N^{1/2}\Phi^{(2\nu-1)/2(1-3\nu)}$ in a semidilute solution, and the correlation length is $\xi \sim \Phi^{\nu/(1-3\nu)}$, where ν is the Flory swelling exponent; if entanglements are not taken into account, the friction per chain becomes $\sim N(\Phi a^3)^{(\nu-1)/(1-3\nu)}\eta b$; in an entangled semidilute solution, the chain friction obtained from reptation theory should be used.

The perturbative approach to the electrostatic interaction supposes weak interactions. A criterion in the case of the polymeric salt is that the interactions between charges at the average distance is weak; this has been discussed in section 2 and leads to $4\pi l_B(\Phi/N)^{1/3} < 1$, and this criterion also demands that there are ions within a Debye length. In Figure 3 we show that this requirement is compatible with strong screening ($\kappa R_g > 1$), basically because the distance between charges is smaller than the radius in the semidilute regime. The relevant variables are the interaction between two charges linked by an isolated chain and the reduced concentration Φ/Φ^*; they have to satisfy $(\Phi/\Phi^*)^{-\alpha} <$ *interaction* $< (\Phi/\Phi^*)^{-\beta}$. This conclusion holds true in a good solvent ($\alpha = 3/4$, $\beta = 1/3$), in a *θ-solvent* ($\alpha = 1$, $\beta = 1/3$), and in a marginal solvent ($\alpha = 1$, $\beta = 1/2$). (Here, to be consistent, the interaction is to be taken in four-dimensional space and decays as $1/R^2$.) For periodic polyelectrolytes carrying a fraction f of charged monomers on a Gaussian backbone $\Phi a^3 > f^{2/3}(l_b/a)^{1/3}$ ensures that electrostatic interactions are irrelevant in the semidilute polyelectrolyte blob. Under this condition RPA is expected to be accurate even for fairly strong polyelectrolytes. In the polymeric salt case the main limitation rather comes from the formation of neutral domains of higher ionic strength; this leads to the criterion $\kappa\xi < 1$, which also allows for higher charge at higher concentrations but turns out to be always less constraining than the previous weak interaction criterion.

The perturbative RPA treatment of electrostatics neglects higher order terms such as ion/dipole or dipole/dipole interactions. The latter clearly becomes important in less polar solvents close to the crossover from soluble polyelectrolytes to ionomers.

Finally, our dynamical study has been limited to short time scales where the decays are exponential and has ignored entanglements. Long chains are usually entangled[12,14] at high concentrations, and reptation dynamics is expected provided that $N(a/\xi)^{1/\nu} > 10^{1/\nu d-1}$. (We assume that chains are entangled if one chains shares space with about 10 other chains.) The dynamics of fluctuations in concentrated high molecular weight polymer solutions is beyond the scope of the present work.

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Appendix. Gaussian Correlations

The unit volume comprises Φ/N and $2\Phi/N$ uncorrelated Gaussian chains in the case of the ampholyte and the symmetric salts, respectively. It is thus sufficient to calculate the Gaussian correlations per chain. We further consider monovalent end charges; the extension to higher valencies is straightforward. Introducing the charge $C_+ - C_-$ and the ionic strength $C_+ + C_-$ (the factor $4\pi l_B$ being omitted), the Gaussian charge/charge correlation reads $S_{z,z}{}^0 = S_{+,+}{}^0 + S_{-,-}{}^0 - 2S_{+,-}{}^0$ and the ionic strength/ionic strength correlation $S_{I,I}{}^0 = S_{+,+}{}^0 + S_{-,-}{}^0 + 2S_{+,-}{}^0$. In the ampholyte salt case $S_{+,+}{}^0 = S_{-,-}{}^0 = \Phi/N$, $S_{+,-}{}^0 = \Phi/N \exp(-(N-1)q^2a^2/6)$, whereas in the symmetric salt case $S_{+,+}{}^0 = S_{-,-}{}^0 = \Phi/N2(1 + \exp(-(N-1)q^2a^2/6))$ and $S_{+,-}{}^0 = 0$. We thus write:

$$\begin{aligned} \text{ampholyte:}\quad & S^0_{z,z} = 2\Phi/N(1 - \exp(-q^2R_g^{\,2})) \\ & S^0_{I,I} = 2\Phi/N(1 + \exp(-q^2R_g^{\,2})) \\ \text{symmetric:}\quad & S^0_{z,z} = 4\Phi/N(1 + \exp(-q^2R_g^{\,2})) \\ & S^0_{I,I} = 4\Phi/N(1 + \exp(-q^2R_g^{\,2})) \end{aligned} \tag{1}$$

For both the ampholyte and the symmetric salts, the Gaussian cross correlations $S_{z,\Phi}{}^0 = S_{+,\Phi}{}^0 - S_{-,\Phi}{}^0$ and $S_{z,I}{}^0 = S_{+,+}{}^0 - S_{-,-}{}^0$ vanish by symmetry under charge inversion. The Gaussian correlation matrix **S°** thus reduces to a diagonal charge/charge term and a 2 × 2 ionic strength/concentration block.

The concentration/concentration correlation is given by the usual Debye function $f_D(u) = (2/u^2)(\exp(-u) + u - 1)$

$$\begin{aligned} \text{ampholyte:}\quad & S^0_{\Phi,\Phi} = N\Phi f_D(q^2R_g^{\,2}) \\ \text{symmetric:}\quad & S^0_{\Phi,\Phi} = 2N\Phi f_D(q^2R_g^{\,2}) \end{aligned} \tag{2}$$

The cross correlation $S_{I,\phi}{}^0 = S_{+,\phi}{}^0 + S_{-,\phi}{}^0$ is the same per chain in both cases, we obtain

$$\begin{aligned} \text{ampholyte:}\quad & S^0_{I,\Phi} = 2\Phi/N\,\frac{1 - \exp(-q^2R_g^{\,2})}{1 - \exp(-q^2a^2/6)} \\ \text{symmetric:}\quad & S_{I,\Phi}{}^0 = 4\Phi/N\,\frac{1 - \exp(-q^2R_g^{\,2})}{1 - \exp(-q^2a^2/6)} \end{aligned} \tag{3}$$

where the exponential in the denominators can be expanded in the physical range $qa < 1$. The inverse structure factor matrix involves the determinant of the 2 × 2 block, $\Delta = S_{I,I}{}^0\, S_{\Phi,\Phi}{}^0 - (S_{I,\Phi}{}^0)^2$. The following expansions proved useful in calculating the relaxation frequencies (we give the expression in the ampholyte case)

$$\begin{aligned} \Delta(q\to\infty) &= \frac{4\Phi^2}{q^2R_g^{\,2}} \\ \Delta(q\to 0) &= \frac{2}{3}\Phi^2q^2R_g^{\,2}\left(1 - \frac{q^2R_g^{\,2}}{2}\right) \end{aligned} \tag{4}$$

Inverting the correlation matrix preserves its block structure. Furthermore implementing the RPA only adds the electrostatic interaction to the z,z term and the excluded volume v to the Φ,Φ term of the inverse Gaussian correlation matrix. It is easily seen that the $S_{\Phi,\Phi}$ term retains its classical value $S^0{}_{\Phi,\Phi}/(1 + vS^0{}_{\Phi,\Phi})$ and so does $K_{\Phi,\Phi}$.

References and Notes

(1) Förster, F.; Schmidt, M. *Adv. Polym. Sci.* **1995**, **120**, 51.
(2) Barrat, J.-L.; Joanny, J.-F. *Adv. Chem. Phys.* **1996**, XCIV, 1.
(3) Candau, F.; Joanny, J.-F. Synthetic polyampholytes in aqueous solutions. In *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996.
(4) Everaers, R.; Johner, A.; Joanny, J.-F. *Macromolecules* **1997**, *30*, 8478.

(5) Wittmer, J.; Johner, A.; Joanny, J.-F. *Europhys. Lett.* **1993**, *24*, 263.
(6) Brereton, M.-G.; Vilgis, T.-A. *Macromolecules* **1990**, *23*, 2044. They analyze the statics of mixtures of monovalent chains.
(7) Antonietti, M.; Heyne, J.; Silescu, H. *Makromol. Chem.* **1991**, *192*, 3021. They describe a similar chemistry though with a non polar backbone.
(8) Ajdari, A.; Leibler, L.; Joanny, J.-F. *J. Chem. Phys.* **1991**, *95*, 4580.
(9) Borsali, R.; Vilgis, T.-A. *Phys. Rev. A* **1991**, *43*, 6857. This reference gives the corresponding Rouse dynamics.
(10) Moussaid, A.; Munch, J.-P.; Schosseler, F.; Candau, S.-J. *J. Phys. II* **1991**, *6*, 637.
(11) Lovett, R.; Stillinger, F.-H. *J. Chem. Phys.* **1968**, *48*, 3869.
(12) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Oxford University Press: Oxford, 1986.
(13) de Gennes, P.-G. *Physica* **1959**, *25*, 825.
(14) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithica, 1991.

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