

Influence of salt on the structure of polyelectrolyte solutions: An integral equation theory approach

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We investigate the influence of monovalent saltions on the structural properties of polyelectrolyte solutions using an integral equation theory. In this approach all species of the solution (polyions, counterions, and positively and negatively charged saltions) are treated explicitly leading to a four-component system. The polymer-reference-interaction-site model for this system, together with the reference-Laria–Wu–Chandler closure is solved numerically. We demonstrate that addition of salt leads to a screening of the Coulomb interaction, which is well captured by the Debye–Hückel potential with a salt density-dependent screening length, by discussing various correlation functions. Furthermore, we show that for an appropriate range of parameters, such as density or Bjerrum length, a shell of equally charged saltions exists in the vicinity of the polyion. The effective potential between two monomers reflects attraction among the equally charged polyions with a pronounced dependence on the salt concentration. © 2003 American Institute of Physics.

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I. INTRODUCTION

Polyelectrolytes are a special class of polymers which usually contain a large number of charged groups. The charges on the chain are compensated by oppositely charged counterions making the whole chain electrical neutral. Dissolving polyelectrolytes in a polar solvent, such as water, leads to the dissociation of the counterions, leaving a charged object, the so-called polyion, behind. The counterions and polyions are now subject to the long-range Coulomb interaction leading to a rich variety of effects which are not found in solutions of neutral polymers. The study of polyelectrolyte solutions has therefore been an outstanding problem in polymer science for the last decades from an experimental as well as a theoretical point of view.^{1–5} The interest in polyelectrolytes is easy to understand, since they play a fundamental role in everyday life. For example, most of the biopolymers such as DNA or RNA as well as almost all proteins are polyelectrolytes. On the other hand, synthetic polyelectrolytes are used in a very wide range of technical applications such as water purification, stabilization of gels, or superabsorbers.^{1,2,5–7} Despite significant theoretical and experimental efforts, many properties of polyelectrolyte solutions are still poorly understood compared to those of solutions of neutral polymers.^{5,8–12}

From the experimental point of view, trace impurities and very low excess scattering intensities in dilute solutions cause major problems in all scattering experiments (light,

x-ray, and neutron scattering). Therefore, scattering experiments and measurements of the radius of gyration are almost always done in semidilute solutions^{5,13–21} so that experimental data for the properties of dilute solutions or even single chains are still not very common. Moreover, often controversial results are reported when using different experimental methods.⁵

From the theoretical point of view, the main problem is the long-range character of the Coulomb potential. The existence of more than one typical length scale, caused by long-range (Coulomb) and short- to medium-range (excluded volume) interactions, makes the application of renormalization group theories and scaling ideas, which already proved to be very successful for describing neutral systems, difficult to apply for polyelectrolyte solutions.^{22–24}

On the other hand, computer simulations of polyelectrolyte solutions require large computational efforts due to the special techniques, such as the Ewald summation,²⁵ needed for the adequate treatment of the long-range Coulomb interaction. Therefore, computer simulations are even today often performed for short chains and/or dilute solutions only,^{26–30} but nevertheless provide very detailed information about the properties of polyelectrolyte solutions.

A different method for studying polyelectrolyte solutions is a liquid state theory approach based on the polymer-reference-interaction-site model (PRISM),^{31,32} which allows one, in contrast to computer simulations, to calculate the properties of systems at high densities containing very long chains. Yethiraj and Shew significantly contributed to the understanding of polyelectrolyte solutions applying the

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PRISM approach to rodlike as well as flexible polyelectrolytes.^{33–37} In particular, they demonstrated that the results of this approach are usually in good agreement with the results of computer simulations or experiments, e.g., for the static structure factor or the pair correlation function.

In a theoretical description of polyelectrolyte solutions the small ions, i.e., the counter- and saltions, can be treated in many different ways. The simplest approach is the treatment of all small ions in a mean-field manner leading to a one-component model containing only polyions interacting via the Debye–Hückel potential.^{34,38,39} In this model all information about the small ions is lost since they are assumed to be distributed spherical symmetric around the polyions. Therefore, important effects such as counterion condensation cannot be addressed by this approach. Nevertheless, results for quantities regarding polyions only, such as the monomer–monomer structure factor or correlation functions, are in excellent agreement with the results of more sophisticated approaches.⁴⁰ However, the growing interest in the distribution of the counterions with respect to a chain and especially counterion condensation requires the counterions to be treated explicitly, leading to a two-component model containing polyions and counterions. In the case of salt-free solutions the counterions and polyions interact via the unscreened Coulomb potential. In this model added salt may be treated again in a mean-field manner, leading to a Debye–Hückel potential between the counterions and polyions with a salt density-dependent screening length. Many important properties of polyelectrolyte solutions were successfully discussed within this model.^{35,37,41,42} Computer simulations as well as liquid state theories have mainly focused on these two approaches (one- and two-component model) in the past. Despite the great successes of these two models, it is nevertheless important to study the properties of polyelectrolyte solutions when all species of the solutions are treated explicitly, because experiments have shown that many results are sensitive to the kind of charged particles in the solution.^{43–46} Moreover, the distribution of the positively and negatively charged saltions can only be studied within such a model. All particles of the four-component system, positively charged polyions, negatively charged counterions, and positively and negatively charged saltions, interact via an unscreened Coulomb potential.

In this paper we address the influence of added salt on the structural properties of polyelectrolyte solutions by investigating the various pair correlation functions for different values of important parameters such as Bjerrum length, monomer density, and/or salt density. In particular, we will demonstrate that added salt leads to a screening of the Coulomb potential which is well captured by the Debye–Hückel potential. Furthermore, we will show that for large Bjerrum lengths and/or high salt densities a shell of oppositely charged saltions is found immediately outside the condensed counterion shell, as it was already predicted theoretically for spherical polyions.⁴³ Moreover, we will demonstrate that addition of salt can lead to a stronger effective attraction between the monomers of two polyions than in the case of salt-free solutions.⁴⁷

The paper is organized as follows: In Sec. II the model for the polyions and the basics of the PRISM theory are presented. In Sec. III we discuss the various correlation functions of the four-component system and compare them with the results of one- and two-component models based on a Debye–Hückel potential. In Sec. IV we calculate the effective potential and address the influence of added salt on such a potential. Finally, Sec. V summarizes our results.

II. PRISM AND MODEL

The PRISM theory is a liquid state theory for molecular systems and can be obtained by an extension of the well-known Ornstein–Zernike equation,⁴⁸ taking the connectivity of the chain molecules into account explicitly. The Ornstein–Zernike equation, as well as the PRISM theory, connects the total correlation function $h(r)$ with the so-called direct correlation function $c(r)$ and, in the case of molecular systems, with the intramolecular distribution function $\omega(\mathbf{r})$. The total correlation function $h(r)$ is related to the pair correlation function $g(r) = 1 + h(r)$ and the static structure factor $S(k)$, which can be expressed via $S(k) = \omega(k) + \rho h(k)$, where $\omega(k)$ is the intramolecular structure factor. In the case of the four-component system there are 16 different total correlation functions which will be denoted by $h_{ij}(r)$ ($i, j \in \{m, c, -, +\}$), where the index m refers to monomers of different polyions, c to counterions, $-$ to the negatively charged saltions, and finally $+$ to the positively charged saltions. For symmetry reasons, the correlation functions h_{ij} and h_{ji} are equal for all combinations of i and j ; hence, the number of different correlation functions immediately reduces to nine. The different correlation functions are all coupled by the PRISM equations, which can be written conveniently in Fourier space as

$$\mathbf{h}(k) = \boldsymbol{\omega}(k)\mathbf{c}(k)\boldsymbol{\omega}(k) + \boldsymbol{\omega}(k)\mathbf{c}(k)\boldsymbol{\rho}h(k), \quad (1)$$

where \mathbf{h} and \mathbf{c} are the matrices containing the different total and direct correlation functions. The matrices $\boldsymbol{\omega}$ and $\boldsymbol{\rho}$, respectively, are composed of the intramolecular structure factors $\omega_{ij} = \omega_i \delta_{ij}$ and the various particle densities $\rho_{ij} = \rho_i \delta_{ij}$. In this formulation all monomers of the chain are considered to be equivalent, i.e., chain end effects are neglected, and hence only one monomer correlation function for the whole polyion has to be considered. Otherwise, if all monomers of the polyion would be treated explicitly, we would obtain a vast number of different correlation functions, leading to intractable numerical problems especially for longer chains. The correlation functions can only be calculated when additional relations are provided between the direct correlation functions, the total correlation functions, and the intermolecular potential. In contrast to the PRISM equation (1), the so-called closure relations cannot be calculated exactly for all systems. Therefore, many different closures, depending on the approximation, have been proposed in the literature.^{32,49–52} For molecular systems with hard-core interaction, the reference–Laria–Wu–Chandler closure

$$\begin{aligned}
&\omega_i(r) * c_{ij}(r) * \omega_j(r) \\
&= \omega_i(r) * (c_{o,ij}(r) - \beta v_{ij}(r)) * \omega_j(r) + h_{ij}(r) \\
&\quad - h_{o,ij}(r) - \ln \left(\frac{g_{ij}(r)}{g_{o,ij}(r)} \right), \quad r > \sigma_{ij}, \\
&\quad g_{ij}(r) = 0, \quad r < \sigma_{ij}, \\
&\quad i, j \in \{m, c, +, -\},
\end{aligned} \quad (2)$$

proved to be very successful for the one- and two-component system.³⁴ Here, the index 0 denotes reference functions obtained for a pure hard-core system at the same density using the PY closure. The asterisks denote convolution integrals, and $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ is the average of the diameters σ_i of the different particle species in the solution. When the intramolecular structure factors ω_i are known, the PRISM equations (1) together with the closure relations (2) can easily be solved numerically using a Picard iteration scheme.⁴⁸

Model

The polyions are modeled as a linear sequence of N touching hard spheres of diameter σ_m and charge $Z_m e$. Since we assume that the polyions remain in a rodlike conformation for all parameter variations, the intramolecular structure factor is known and given by

$$\omega_m(k) = 1 + \frac{2}{N} \sum_{j=1}^{N-1} (N-j) \frac{\sin(jk\sigma_m)}{jk\sigma_m}. \quad (3)$$

The counterions and saltions are also modeled as charged hard spheres with diameters σ_c , σ_- , and σ_+ and charges $Z_c e$, $Z_- e$, and $Z_+ e$, respectively. Hence, the intramolecular structure factors of the counterions and saltions are all equal and given by $\omega_c(k) = \omega_+(k) = \omega_-(k) = 1$. Charge neutrality of the system relates the charges and densities of the different particle species with each other, i.e., $Z_m \rho_m + Z_c \rho_c + Z_+ \rho_+ + Z_- \rho_- = 0$. Treating the solvent as a dielectric continuum with a dielectric constant ϵ the intermolecular potential is given by

$$\beta v_{ij}(r) = \beta v_{ij}^{\text{HC}}(r) + Z_i Z_j \frac{l_B}{r}; \quad i, j \in \{m, c\}, \quad (4)$$

where $v_{ij}^{\text{HC}}(r)$ is the hard-core potential and $l_B = \beta e^2 / \epsilon$ is the Bjerrum length.

The results presented in the following sections have been obtained for systems with monovalent ions, i.e., $Z_m = Z_+ = 1$ and $Z_c = Z_- = -1$. Furthermore, we assume that all ions are of the same size, i.e., we set $\sigma = \sigma_m = \sigma_c = \sigma_- = \sigma_+$. As a consequence, the negatively charged saltions and counterions are indistinguishable and the same correlation functions are obtained for these two species. Therefore, it is possible to reduce the four-component system to a three-component system containing only polyions, positively charged saltions, and negatively charged ions (counterions and negatively charged saltions) without any loss of information about the system.

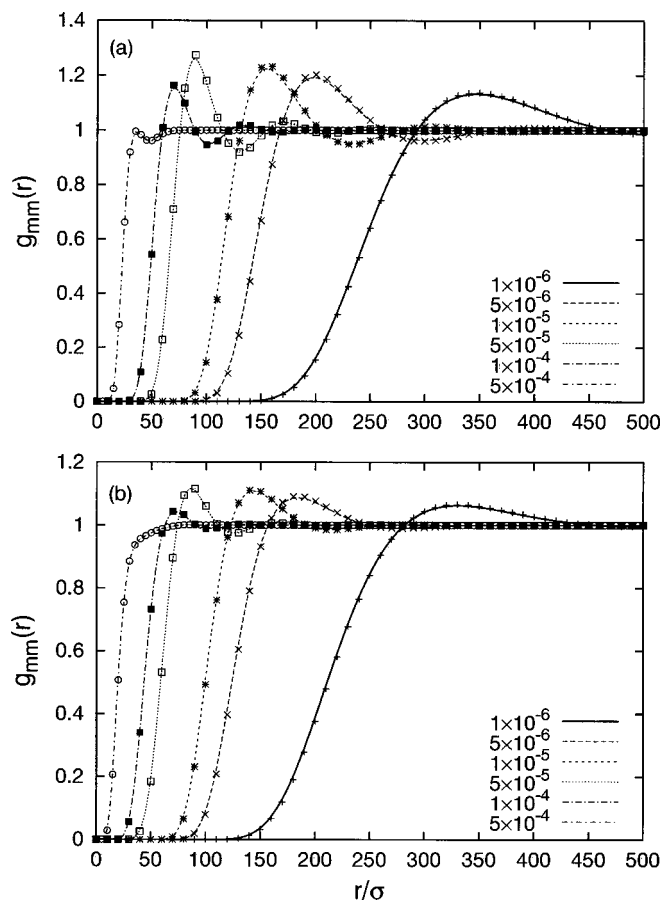


FIG. 1. Comparison between the monomer-monomer pair correlation functions $g_{mm}(r)$ of the one-component model with Debye-Hückel potential (dots) and the multicomponent model with the bare Coulomb potential (lines) for various monomer densities η_m . The Bjerrum length is $l_B = 0.6\sigma$ and the chain length is $N = 80$. The salt densities are $\eta_+ = \eta_m$ (a) and $\eta_+ = 4\eta_m$ (b), respectively.

III. CORRELATION FUNCTIONS

The structure of polyelectrolyte solutions in the presence of counterions has been determined in Refs. 34, 37, and 47. Due to the Coulomb interaction, the monomer-monomer correlation function exhibits a long-range liquidlike order in such systems. Addition of salt leads to a screening of the Coulomb interaction among the various charges. As a consequence, the liquidlike structure more and more disappears with increasing salt concentration. The qualitative features of the monomer-monomer correlation function can be deduced from studies with a pure Debye-Hückel potential.³⁴ Studies with an explicit treatment of counterions and saltions provide good agreement between measurements and theory for a system of tobacco mosaic viruses.⁴²

In the following sections, we will compare the correlation functions calculated within the three component system and various reduced systems. In addition, aspects of salt-salt and counterion-salt correlations will be discussed, which have not been addressed in the references above.

A. Monomer-monomer correlation

Figure 1 displays monomer-monomer correlation functions for various monomer packing fractions ($\eta = \pi \rho \sigma^3 / 6$)

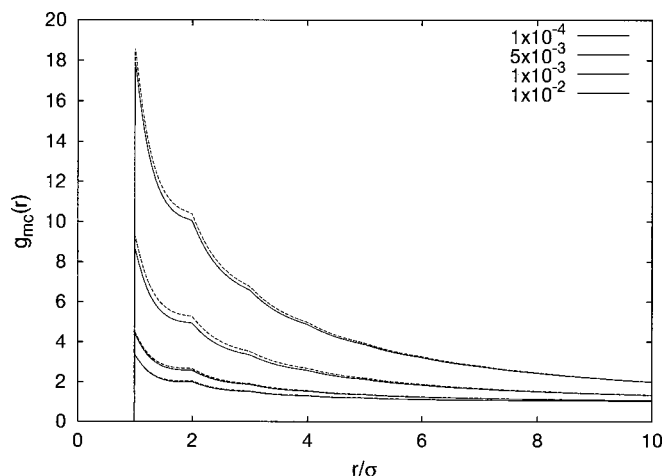


FIG. 2. Comparison between the monomer-counterion pair correlation functions $g_{mc}(r)$ of the two-component model with Debye-Hückel potential (dashed lines) and the multicomponent model with bare Coulomb potential (solid lines) for various salt densities η_+ . The Bjerrum length is $l_B = 0.6\sigma$, the chain length $N=80$, and $\eta_m = 10^{-4}$.

and salt densities. The Bjerrum length is $l_B = 0.6\sigma$ and the chain length is $N=80$. As is obvious from the figure, a higher salt content leads to a stronger screening of the Coulomb interaction. This is obvious from the fact that the peaks of the correlation functions at higher salt concentration are smaller and shifted to smaller distances r . This is consistent with the expectations from a one-component Debye-Hückel model. In the case of systems with added salt, the Debye screening length $\lambda_D = 1/\sqrt{4\pi l_B(\rho_c + \rho_- + \rho_+)}$ of the Debye-Hückel potential of a reduced one-component systems of polyions only, depends not only on the counterion density, but also on the salt concentration. Here, the screening length increases with increasing salt concentration. The comparison of the correlation functions of the four-component model and the one-component system exhibits excellent agreement even for very high salt concentrations (cf. Fig. 1). Hence, the Debye-Hückel approach is a valid method when one is interested in the distribution of the polyions only.

We would like to point out that a significant influence of salt appears for densities $\rho_- = \rho_+ \gtrsim \rho_c$ only.

B. Monomer-counterion correlation

The distribution of the counterions with respect to a polyion is described by the monomer-counterion correlation function $g_{mc}(r)$. As has been demonstrated for salt-free solutions,^{37,47} the counterions accumulate in the vicinity of a polyion at sufficiently high Bjerrum lengths, leading to a strongly peaked monomer-counterion correlation function at $r=\sigma$, whose height increases rapidly with the Bjerrum length. Figure 2 shows that this also applies to systems with added salt. Similarly to the monomer-monomer-correlation function, addition of salt leads to a decrease in the peak height. Since we interpret the large concentration of counterions close to a monomer as a manifestation of counterion condensation,⁴⁷ we find that the number of condensed counterions on a polyion is smaller than for salt-free systems.

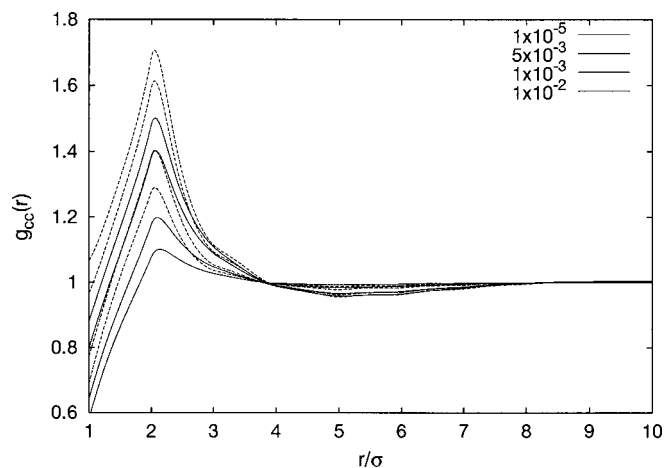


FIG. 3. Comparison between the counterion-counterion pair correlation functions $g_{cc}(r)$ of the two-component model with Debye-Hückel potential (dashed lines) and the multicomponent model with bare Coulomb potential (solid lines) for various salt densities η_+ . The Bjerrum length is $l_B = 2.0\sigma$, the chain length $N=80$, and $\eta_m = 10^{-2}$.

Hence, addition of salt leads to a release of condensed counterions. A similar effect, i.e., a decrease of the peak height in $g_{mc}(r)$, is achieved in salt-free solutions by decreasing the Bjerrum length. Since counterions and negatively charged saltions are indistinguishable in our system, we have to take into account all negatively charged ions, and not only the counterions, when we discuss counterion condensation. We then find that the number of condensed negatively charged ions in the system with added salt is actually higher than in a salt-free solution. This has significant consequences on the monomer-monomer interaction on very small length scales, and will be discussed in detail in Sec. IV. Thus, two effects contribute to screening in polyelectrolyte solutions: On the one hand, screening is caused by changes of the salt density, which changes the Debye screening length. On the other hand, negatively charged saltions partially replace condensed counterions and condense themselves.

Figure 2 exhibits a very good overall agreement between the correlation functions of the four-component system and a reduced two-component system (polyions and counterions) which takes into account the saltions by a Debye-Hückel potential with a salt density-dependent screening length. Small differences appear for distances $\lesssim 3\sigma$. For such distances counterions and saltions condense on the polyions, which are not captured by the Debye-Hückel approach.

C. Counterion-counterion correlation

A more detailed picture of counterion condensation is obtained from the counterion-counterion correlation function $g_{cc}(r)$. Counterion condensation causes the accumulation of counterions in the vicinity of the polyions. As a consequence, counterions closely approach each other despite the strong repulsive Coulomb interaction between them. Therefore, in salt-free solution the counterion-counterion correlation function displays a peak at $r=2\sigma$ for high Bjerrum lengths, and the height of this peak increases rapidly with Bjerrum length.^{37,47}

Figure 3 displays the counterion-counterion correlation

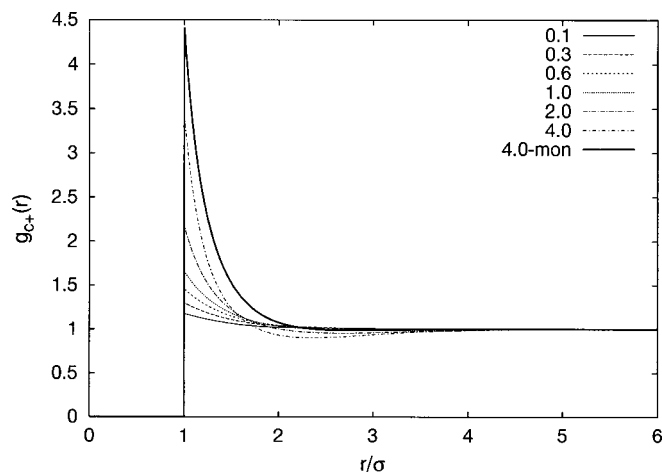


FIG. 4. Counterion-salt pair correlation functions $g_{c+}(r)$ for various Bjerrum lengths l_B and $N=80$. The densities are $\eta_m = \eta_+ = 10^{-2}$. The bold solid line (4.0-mon) is for a polymer of length $N=1$.

function for various salt concentrations. The Bjerrum length $l_B = 2\sigma$ was chosen because, for this value, g_{cc} exhibits a well-pronounced peak for a salt-free solution. Addition of salt leads to a decrease $g_{cc}(r)$. Hence, an increase of the salt concentration produces the same qualitative behavior as a decrease of the Bjerrum length in salt-free solutions. With respect to condensed counterions, a decreasing correlation function corresponds to a decrease of the amount of condensed counterions. This is of course in perfect agreement with the decreasing peak height in g_{mc} . Again, this expresses the release of condensed counterions by addition of salt and is a manifestation of screening. However, as pointed out before, we have to keep in mind that aside from counterions, negatively charged saltions are present in the solution and hence the total number of negatively charged ions, i.e., salt- and counterions, near a given negatively charged ion is actually higher than in the salt-free case.

Comparing the correlation functions of a four-component system with those of the two-component system containing polyions and counterions only, that interact via a Debye-Hückel potential, we find good agreement for distances larger than 3σ (Fig. 3). For smaller separations, the peak height is severely overestimated in the two-component model. Again, the deviations appear in a regime where counterions condense on the polyions, and it is not to be expected that the Debye-Hückel potential reproduces all the features of the correlation function on this length scale.

D. Counterion-salt correlation

As already mentioned above, for the set of parameters used in this paper the counterions and negatively charged saltions are equivalent. Therefore, all correlation functions regarding the negatively charged saltions are identical to those of the counterions, i.e., we have $g_{--} = g_{cc}$, $g_{m-} = g_{mc}$, and $g_{+-} = g_{c+}$. The remaining correlation functions to be addressed are the correlation functions between counterions and the positively charged saltions. Figure 4 shows correlation functions $g_{c+}(r)$ which exhibit the same behavior as $g_{mc}(r)$ with a peak at $r = \sigma$ whose height increases

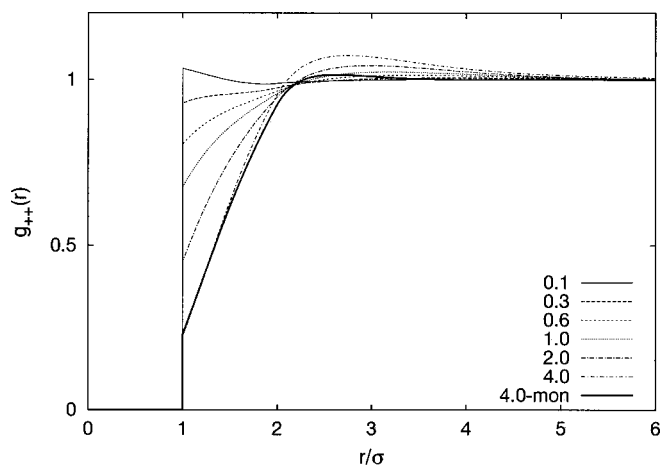


FIG. 5. Salt-salt pair correlation functions $g_{++}(r)$ for various Bjerrum lengths l_B and $N=80$. The densities are $\eta_m = \eta_+ = 10^{-2}$. The bold solid line (4.0-mon) is for a polymer of length $N=1$.

rapidly with the Bjerrum length. However, the height of the peaks for the two correlation functions is significantly different. Hence, counterion-salt pairs are formed. The number of saltions included in such pairs is however much smaller than the number of counterions condensed on a polyion.

Computer simulations²⁸ and our previous PRISM calculations⁴⁷ suggest that the amount of condensed counterions depends on chain length. To gain insight into the influence of the polymer aspect on the correlation among the counterions and positive saltions, we calculated $g_{c+}(r)$ for a polymer of length $N=1$, which corresponds to a solution of ions only. Figure 4 displays for this system a higher counterion-salt peak than for the polymer system. The reason is an effective reduction of the number of free counterions in the polymer system by counterion condensation. For a polymer system, there is a smaller number of counterions available to form counterion-saltion pairs.

E. Salt-salt correlations

Significant differences are observed between the counterion-counterion correlation functions and the salt-salt correlation functions $g_{++}(r)$. As shown in Fig. 5, we obtain a strong correlation hole for small distances. Moreover, only for large interaction strength a small and broad peak appears at $r \approx 3\sigma$. Hence, the correlation between the (+)-saltions is much less pronounced than the one between the counterions. The peak, however, indicates a shell of positively charged saltions in the vicinity of the polyion in contrast to the studies of Ref. 42. A similar structure was already found theoretically for spherical polyions.⁴³ The correlation function $g_{m+}(r)$ between monomers and saltions exhibits a strong correlation hole for $r < 2\sigma$, but distinct peaks are formed at distances $\geq 2.5\sigma$ for sufficiently large interaction strengths. Thus, $g_{m+}(r)$ supports the idea of a salt layer adjacent to a polyion.

Comparing g_{++} for the chain of length $N=80$ with the correlation function of a chain of length $N=1$, i.e., a system of saltions only, we find less pronounced correlations for the

latter system. Hence, the bonds and the linear (rodlike) molecular structure are responsible for the observed distribution of counterions and saltions.

It should be noted that the peak in g_{++} and therefore the saltion shell appears at large Bjerrum lengths. Because of numerical problems, particularly at low densities, we could not reach sufficiently large Bjerrum lengths for all densities to observe the positively charged ion cloud.

IV. EFFECTIVE POTENTIAL

An effective potential between two monomers or between two counterions, respectively, provides deeper insight into the system behavior on small length scales. In the following, we will briefly address the effective potential between two monomers under the influence of added salt. Further important properties of the effective potentials will be discussed in more detail in a separate article.

We define the effective potential such that the same pair correlation function is obtained in a reduced one-component system containing only polyions or counterions, respectively, as in the multicomponent system with the original intermolecular potential. The effective potential can be calculated within the PRISM theory in a straightforward manner, and is in good approximation given by

$$\beta v_{ii,\text{eff}}(r) = \beta v_{ii}(r) + (c_{ii}(r) - c_{ii,\text{eff}}(r)), \quad i \in \{m, c\}, \quad (5)$$

where $c_{ii,\text{eff}}$ is the direct correlation function of the effective one-component system. The effective potential is given by the bare intermolecular potential modified by the difference between the direct correlation function of the one- and multicomponent system. More details of the calculation of the effective potential can be found in Ref. 47.

The effective monomer–monomer potential is presented in Fig. 6 for various Bjerrum lengths. The chain length is $N=80$ and the salt density is $\eta_+ = 10^{-2}$. The monomer densities are $\eta_m = 10^{-2}$ (a) and $\eta_m = 10^{-4}$ (b), respectively. The effective potential exhibits the same qualitative behavior as in a salt-free solution.⁴⁷ For small Bjerrum lengths the potential is purely repulsive, but for large Bjerrum lengths a minimum appears at $r=2\sigma$ whose depth increases with the Bjerrum length. As a consequence, we find an effective attraction between two polyions at small distances despite the purely repulsive Coulomb interaction. A detailed examination shows that the minimum of $v_{mm,\text{eff}}$, for the same Bjerrum length and monomer density, is significantly deeper in the case of the system with added salt compared to a system without salt. According to Figs. 6(a) and 6(b), the minimum of the effective potential is deeper for lower monomer densities. As a consequence, the effective attraction between the polyions increases with increasing salt concentration of the solution. At a first glance, this behavior seems to contradict the results of the previous sections, which indicate a screening of the Coulomb interaction by the addition of salt. As already pointed out in Sec. III B, however, screening effects take place on length scales larger than a few monomer diameters, whereas the attraction between two polyions is only present on very short length scales.

The stronger attraction between the polyions in the sys-

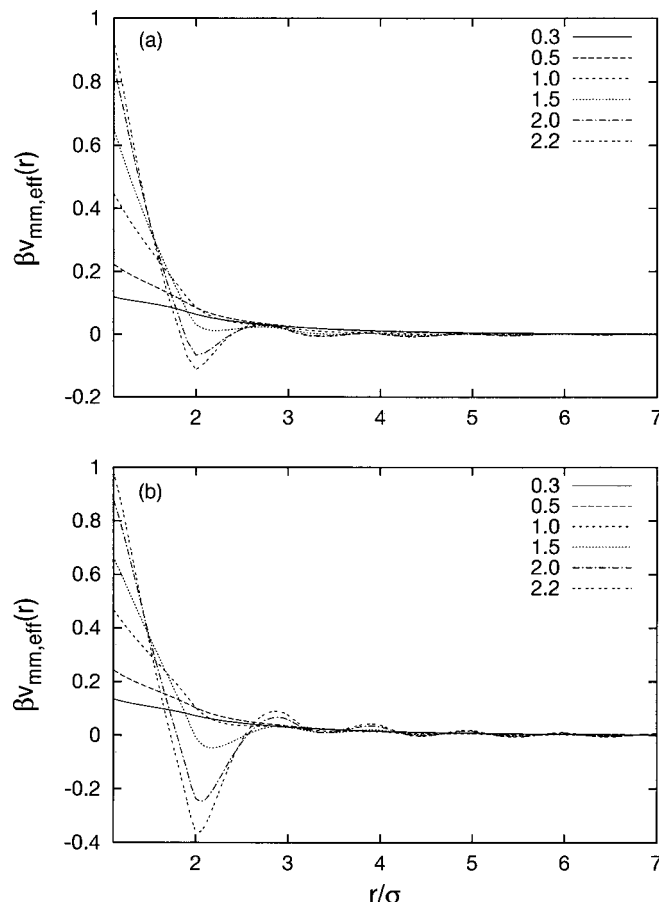


FIG. 6. Effective potential between two monomers for various Bjerrum lengths l_B , the salt density $\eta_+ = 10^{-2}$, and the chain length $N=80$. The monomer densities are $\eta_m = 10^{-2}$ (a) and $\eta_m = 10^{-4}$ (b), respectively.

tem with added salt can be explained by two different effects. For the salt-free case the attraction between two polyions was explained as a pure electrostatic effect where the condensed counterions attract the oppositely charged monomers of another polyion by Coulomb interaction. As discussed in Sec. III B for the system with added salt, there are in total more negatively charged ions adjacent to a polyion, leading to a stronger attractive interaction. On the other hand, the depletion interaction^{53,54} has to be taken into account too. As is well known, depletion causes an attractive interaction between the large particles in a solution of small and large particles, and the strength of the interaction increases with increasing density of the small particles. Since there are more negatively charged ions in the vicinity of a polyion in the system with added salt, the local density of ions in this region is higher than in the salt-free case, which may lead to a depletion interaction. A detailed analysis of the individual contributions will be presented elsewhere.

It should be noted that the attraction between two polyions for the parameters used in Fig. 6(b) is so strong that it can even be seen in the monomer–monomer correlation function of the four-component system displayed in Fig. 7. For large Bjerrum lengths a peak in $g_{mm}(r)$ appears at $r = 2\sigma$ in agreement with the position of the minimum in the effective potential. However, the peak cannot be observed in

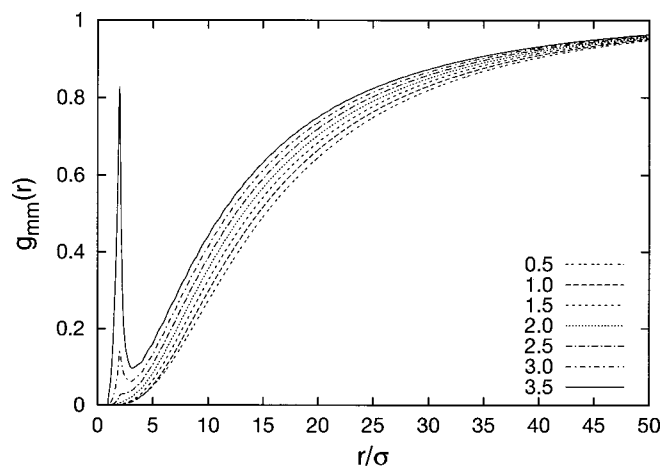


FIG. 7. Monomer-monomer pair correlation functions $g_{mm}(r)$ for various Bjerrum lengths l_B . [Parameters as in Fig. 6 (b).]

the monomer-monomer structure factor $S_{mm}(k)$, where it should appear at $k\sigma \approx \pi$; hence, the effect cannot be found in experiments measuring the structure factor.

V. CONCLUSION

We have studied the structural properties of polyelectrolyte solutions with added salt using the PRISM integral equation theory approach. The positively charged polyions, negatively charged counterions, and positively and negatively charged saltions have been taken into account explicitly. The polyions are modeled as charged rigid rods, which remain in their straight conformation for all variations of the relevant parameters. The solvent is treated as a continuous dielectric background. The intermolecular interactions among the various kinds of particles are given by the unscreened Coulomb potential and the hard-core potential. The effect of added salt on the structural properties of the solution is studied using various pair correlation functions.

We find that addition of salt leads to a screening of the Coulomb interaction beyond a few monomer diameters. As a consequence, the characteristic peaks in the monomer-monomer correlation function decrease with increasing salt concentration, and for very high salt concentrations g_{mm} is almost equivalent to the correlation function of an uncharged system. The monomer-counterion and counterion-counterion correlation functions also exhibit a decrease of the typical peak structure—the peaks appear due to counterion condensation—with increasing salt concentration. A detailed examination reveals that there are indeed fewer counterions condensed on a polyion, but the total number of adjacent negatively charged ions is actually larger than in the salt-free case. Hence, addition of salt leads to a release of condensed counterions. The absolute amount of condensed ions, however, is larger than in a salt-free solution, because saltions condense on a polyion. We observe strong correlation effects among the charged particle next to a polyion. This is reflected by a shell of positively charged saltions formed around the condensed counterions at large Bjerrum lengths.

In addition, we have demonstrated that the various correlation functions can be well approximated by correlation functions of reduced systems containing a smaller number of components, e.g., only polyions, and using a Debye-Hückel potential with a salt density-dependent screening length.

An extracted effective potential between polyions reflects the attractive interaction among the equally charged macroions for sufficiently large interaction strengths. Addition of salt leads to an enhancement of the attraction. For certain parameter combinations, the attraction is very strong and can even be detected in the monomer-monomer correlation function.

The results of this paper demonstrate that the PRISM integral equation theory approach captures the main aspects of the structure of polyelectrolyte solutions not only in salt-free systems but also for systems with added salt. The next step should be the inclusion of the conformational changes of flexible and semiflexible chains by a self-consistent integral equation method. Calculations along that line are under way.

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