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Structure of Polyelectrolyte Solutions: Influence of Salt and Chain Flexibility

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Summary: The structural properties of polyelectrolyte solutions with and without added salt are investigated using an integral equation theory approach. For rodlike systems, all components of the solution (polyions, counterions, anions, and cations) are treat explicitly. Solutions of flexible polyelectrolytes are investigated using the Debye-Hückel model. The Polymer-Reference-Interaction-Site model for the multicomponent system together with the Reference-Laria-Wu-Chandler closure is solved numerically. It is show that the Coulomb interaction leads to a long-range liquid like structure. Addition of salt causes screening of the interaction and the structure disappears at very high salt concentrations. Comparison of the correlation functions of the multicomponent systems with those obtained by a one-component Debye-Hückel model exhibits good agreement. Moreover, for an appropriate range of parameters, such as density or Bjerrum length, a shell of equally charged saltions exists in the vicinity of a polyion. The effective potential between two monomers displays attraction among the equally charged polyions. The strength of the attraction increases with increasing salt concentration.

Keywords: correlation function; effective potential; polyelectrolytes; PRISM; salt

Introduction

Polyelectrolyte solutions have attracted considerable attention over the last few decades but they are still one of the least understood colloidal systems both from the theoretical as well as experimental point of view. Understanding of the basic properties of such solutions is desirable, since polyelectrolytes play a fundamental role in many industrial applications and they are elementary for biological systems.[1–6] The coupling of various length scales introduced by the long-range nature of the Coulomb interaction, counterion condensation, and screening effects render polyelectrolytes difficult to study. Computer simulations provide valuable insight into the structural prop-

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erties of polyelectrolyte solutions but require special techniques to treat the long-range Coulomb interaction, e.g., Ewald summation, and hence are often limited to small systems with short chains and/or low densities.[7–9] Liquid state theory based upon the Polymer-Reference-Interaction-Site model (PRISM)[10] offers another theoretical approach to polyelectrolyte solutions. PRISM theory is an extension of the Ornstein-Zernike equation[11] of atomic systems to molecular systems by taking the connectivity of the sites of a molecule into account by the chain structure factor. Polyelectrolytes cover the whole range of stiffnesses from flexible to rodlike polymers depending on the chain length or the solution properties like the salt concentration. As a consequence, the structure of a solution and the conformations of the polyelectrolyte chains are strongly coupled. To account for this coupling, the solutions of the PRISM equations and the corresponding conformations of the polyelectrolytes have to be determined simultaneously. This is achieved by a recently developed extension of the PRISM theory.[12–22] Here, the non-pairwise intermolecular many chain interactions of a particular chain are cast into an effective pairwise intramolecular solvation potential which is determined self-consistently. This so called medium induced potential can be expressed by correlation functions calculated with the PRISM theory.[23–26]

In this paper we discuss the structural properties of polyelectrolyte solutions with and without added salt 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, it will be shown 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.[27] 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.[28] Flexible chains in solution exhibit significant conformational changes with increasing density.[29] This leads to shifts in the characteristic peaks of the monomer-monomer pair correlation functions, particular at higher packing fractions.

Prism and Model

The PRISM theory is a liquid state theory for molecular systems and can be obtained by an extension of the well-know Ornstein-Zernike equation[11] taking the connectivity of the chain molecules into account explicitly. The Ornstein-Zernike equation as well as the PRISM theory connect the total correlation function $h(r)$ with the so called direct correlation function $c(r)$ and, in case of molecular systems, with the intramolecular distribution function $\omega(r)$. 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 ten. The different correlation functions are all coupled by the PRISM equations which can be written conveniently in Fourier space as

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

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 a 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 approximations, have been proposed in the literature.[10,24,30–32] For molecular systems with hard core interaction, the Reference-Laria-Wu-Chandler closure

$$\omega_i(r) * c_{ij}(r) * \omega_j(r) \quad = \quad \omega_i(r) * (c_{o,ij}(r) - \beta v_{ij}(r)) * \omega_j(r)$$

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

proved to be very successful for the one- and two-component system.[33] 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.[11]

For rodlike chains, the polyions are modelled 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

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

The counterions and saltions are also modelled 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

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

where $v_{ij}^{\mathrm{HC}}(r)$ is the hard core potential and $l_B = \beta e^2/\epsilon$ is the Bjerrum length ($\beta = 1/k_B T$). 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.

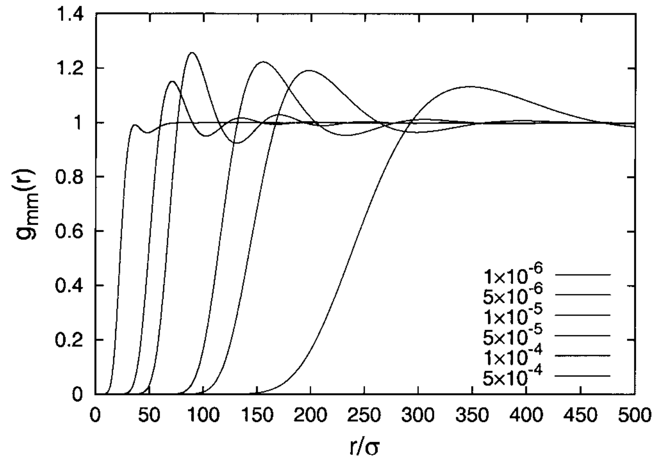

Figure 1. Monomer-monomer pair correlation functions $g_{mm}(r)$ for various monomer densities $\eta_m = \pi\rho_m\sigma^3/6$. The Bjerrum length is $l_B = 0.6\sigma$, the chain length is $N = 80$, and the salt densities are $\eta_+ = \eta_m$.

Correlation Functions of Rodlike Polyelectrolytes

Polyelectrolyte solutions exhibit a liquid-like order in dilute solution which diminishes at hight concentrations (cf. Figure 1). At infinite dilution $g_{mm}(r)$ has a value close to zero at small separations and monotonically increases to its asymptotic value of one at large separations. At low concentrations of polymer and salt, a peak appears on the length scale which is determined by the polyelectrolyte density. As the concentration is increased further, the liquid-like order first becomes more pronounced and then disappears at sufficiently high concentrations. This behavior has been obtained before by PRISM[33] and has been confirmed by computer simulations.[34] At fixed polymer concentration the structure disappears with increasing salt concentration as shown in Figure 2. However, significant changes are observed only, when the salt concentration exceeds the monomer concentration. For salt concentrations $\rho_+ > \rho_m$, further addition of salt leads to a strong screening of the Coulomb interaction, where the screening length decreases with increasing salt concentration, and the peak in the correlation function shifts to smaller length scales. Thus, the structure of the solution is no longer solely dependent on the polyelectrolyte concentration for salt concentrations exceeding such values.

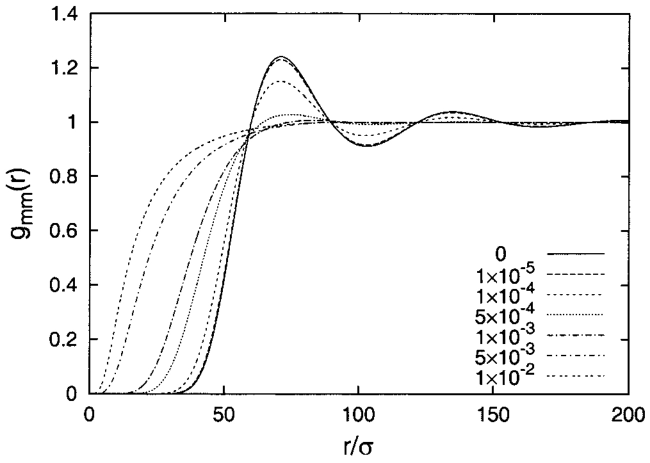

Figure 2. Monomer-monomer pair correlation functions $g_{mm}(r)$ for various salt concentrations η_+. The Bjerrum length is $l_B = 0.6\sigma$, the chain length is $N = 80$, and the monomer density is $\eta_m = 10^{-4}$.

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[17,28] 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. This also applies to the system with added salt, but there are pronounced quantitative differences. In the system with added salt the height of the peak of $g_{mc}(r)$ is much smaller than in the salt free system at the same Bjerrum length. A close examination shows that the peak height decreases when the salt concentration is increased. Since we interpret the large concentration of counterions close to a monomer as a manifestation of counterion condensation,[28] we find that the number of condensed counterions on the polyions is smaller than for systems without added salt. 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. Hence, addition of salt leads to a release (and/or exchange) of condensed counterions. 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,

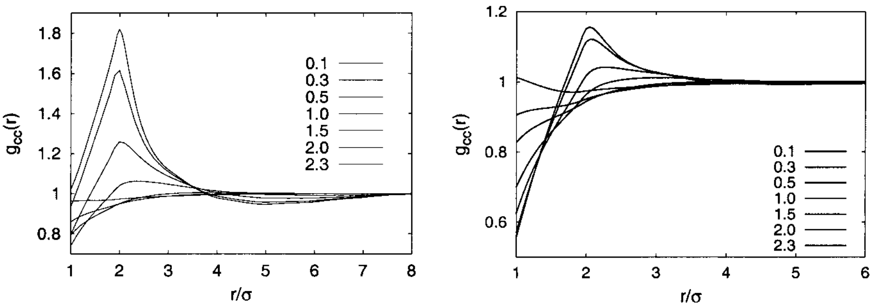

Figure 3. Counterion-counterion pair correlation functions for various Bjerrum lengths for a salt free system (left) and a system with added salt (right). The interaction strength decreases from top to bottom. The chain length is $N = 80$, the packing fraction of monomers $\eta_m = 10^{-2}$, and the packing fraction of saltions $\eta_+ = 10^{-2}$.

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. 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, despite the decreasing correlation function with increasing salt concentration, the absolute amount of condensed ions increases with increasing salt concentration and the number of condensed charges in salt systems exceeds that of salt free systems. This has significant consequences on the monomer-monomer interaction.

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[17,28] (cf. Figure 3). From Figure 3 we see that addition of salt leads to a decrease of the counterion-counterion correlation function. 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}, because less counterions near the polyion are equivalent with less counterions close to each other.

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 function to be addressed is the correlation function between counterions and the positively charged saltions. Since the two species are oppositely charged, they closely approach each other for large Bjerrum lengths resulting in a peak of $g_{c+}(r)$ at $r = \sigma$ similar to the behavior found for $g_{mc}(r)$. Thus, not only counterions start to condense on the polyions for large Bjerrum lengths, but also positively charged saltions condense on the counterions. However, we find pronounced quantitative differences in the behavior of g_{mc} and g_{c+}. The peaks of the latter correlation function are much smaller for the same Bjerrum length. If we interpret this in terms of condensation, there are less positively charged saltions condensed on the counterions than counterions on the polyions for a given Bjerrum length. This behavior is in agreement with results found for counterion condensation in salt free solutions, where the number of condensed counterions per monomer decreases with decreasing chain length.[8,28] When we consider a positively charged saltion as a polyion of chain length $N = 1$, it is perfectly clear why there are less counterions in the vicinity of saltions than in the vicinity of polyions.

Finally, we address the correlation function $g_{++}(r)$ between the positively charged saltions. As discussed above, for sufficiently large Bjerrum lengths the positively charged saltions condense on the counterions. Thus, there should be a shell of positively charged saltions in the vicinity of a polyion just outside the condensed counterions/saltions as already found theoretically for spherical polyions.[27] Figure 4 displays the correlation function $g_{++}(r)$ for the same set of parameters as in Figure 3. In contrast to Ref. [35], we indeed find a broad peak between $r = 3\sigma$ and $r = 4\sigma$, which increases with increasing Bjerrum length, indicating the saltion shell discussed above. In addition, we added the cation-cation correlation function for a monomeric system, i.e., a chain of length $N = 1$ at the same densities. It is obvious from Figure 4 that there is a pronounced chain length effect. With larger chain lengths more cations are condensed on the aggregate of polyion and counterions/anions than for shorter chains. (More details are presented in Ref. [36]).

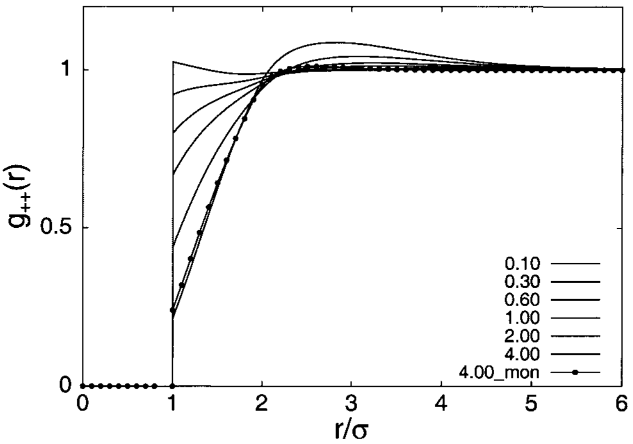

Figure 4. Salt-salt pair correlation functions $g_{++}(r)$ for various Bjerrum lengths l_B. l_B increases at $r = \sigma$ from top to bottom (parameters as in Figure 3). The line marked with dots corresponds to a solution of monomers (chain length $N = 1$) at the same densities.

Effective Potential for Rodlike Polyelectrolytes

Deeper insight into the consequences of counterion condensation is gained by an effective monomer-monomer and counterion-counterion potential, respectively.[28,37] The idea is to reduce the multicomponent system (macromolecules + counterions + salt) to effective one-component systems (macromolecules or counterions, respectively). We define the simplified model in such a way that the effective potential between the counterions or monomers, respectively, of the new system yields exactly the same correlation function (g_{cc}, g_{mm}) as found in the multicomponent case at the same density. Starting from the correlation function g_{cc} – respectively g_{mm} – of the multicomponent model we calculate an effective direct correlation function c_{eff} via the one-component Ornstein-Zernike equation. An effective potential is then obtained from the RLWC closures of the one- and multicomponent models.[28] For low and moderate densities the effective potential is well approximated by

$$\beta v_{ii,\text{eff}}(r) = \beta v_{ii}(r) + (c_{ii}(r) - c_{ii,\text{eff}}(r)) \ , \qquad (5)$$

where $i \in \{m, c\}$. Hence, the effective potential is equal to the bare potential plus a modification given by the correlation functions of the multicomponent and one-component model.

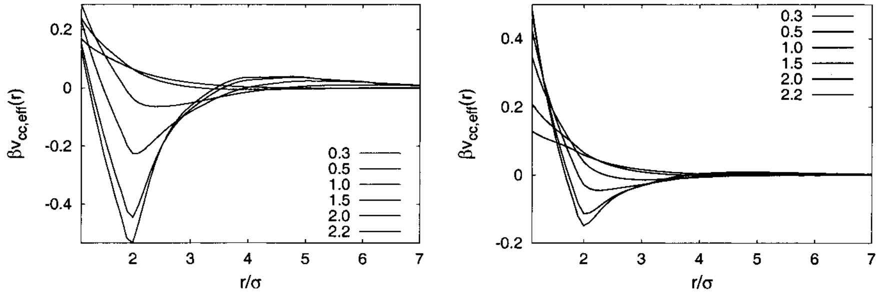

Figure 5. Effective potential between two counterions for various Bjerrum lengths for a salt free system (left) and a system with added salt (right). The interaction strength increases from top to bottom ($r \approx 2\sigma$). The chain length is $N = 80$, the packing fraction of monomers $\eta_m = 10^{-2}$, and the packing fraction of saltions $\eta_+ = 10^{-2}$.

Figure 5 (left) displays the effective counterion-counterion potential of a salt free system for various Bjerrum lengths. As is obvious from this figure, the effective potential is purely repulsive for low values of l_B and can very well be approximated by the bare Coulomb potential between the counterions. With increasing Bjerrum length the potential becomes negative for distances larger than a certain critical distance leading to an attractive force between two counterions. For even larger values of l_B, the effective potential exhibits a distinct minimum at a distance of about $r = 2\sigma$ in agreement with the position of the peak in g_{cc}. In systems with added salt, the qualitative structure of the effective counterion-counterion potential is similar to the salt free situation. However, the counterion attraction is weaker than in the salt free case. This can be considered a consequence of the screening of the Coulomb interaction among the counterions.

Similar to the effective counterion-counterion potential, we observe a minimum in the effective monomer-monomer potential at $r \approx 2\sigma$. Thus, also the oppositely charged polyions attract each other for sufficiently large interaction strengths. Comparing the potential for the salt free case (Figure 6 (left)) with the one of a system with added salt, we find a deeper minimum in the effective potential for the system with saltions, in contrast to the effective counterion potential. At a first glance, this behavior seems to contradict the results discussed in the previous section, which indicate a screening of the Coulomb interaction by addition of salt. Screening effects, however, take place on length scales larger than a few monomer diameters, whereas the attraction between

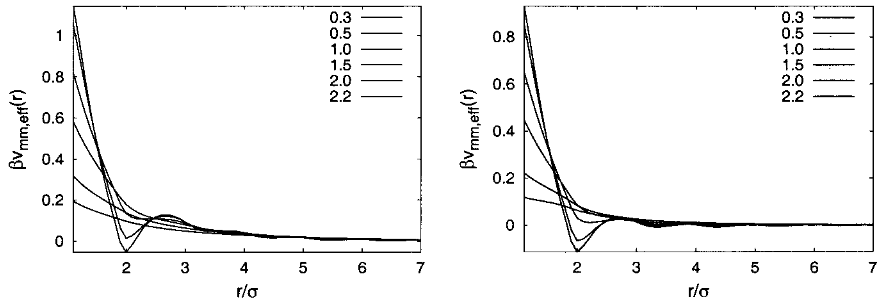

Figure 6. Effective potential between two monomers for various Bjerrum lengths for a salt free system (left) and a system with added salt (right). The interaction strength decreases from top to bottom ($r = \sigma$). The chain length is $N = 80$, the packing fraction of monomers $\eta_m = 10^{-2}$, and the packing fraction of saltions $\eta_+ = 10^{-2}$.

two polyions is only present on very short length scales.

The stronger attraction between the polyions in the system with added salt can be explained by two different effects. For the salt free case the attraction between two polyions is explained as a pure electrostatic effect, where the condensed counterions attract the oppositely charged monomers of another polyion by Coulomb interaction. As discussed in the previous section, 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[38,39] 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. The correlation functions for non-charged systems at the same densities display only a very weak depletion effect. Hence, the observed effect seems to be dominated by the Coulomb interaction.

It should be noted that for the parameters used in Figure 6 (right), the attraction between two polyions is so strong that it can even be seen in the monomer-monomer correlation function.[36] 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 the monomer-

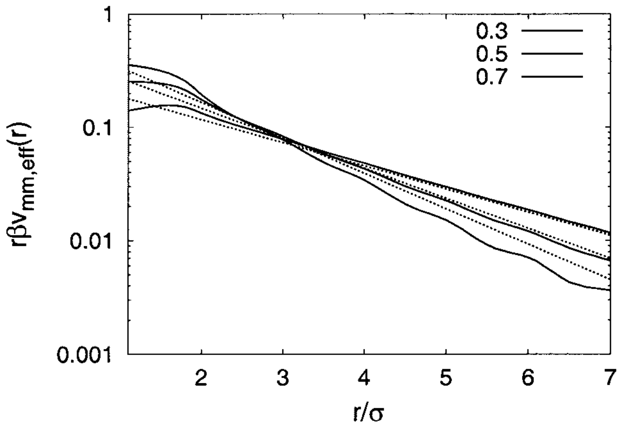

Figure 7. Scaled effective potential between two monomers for various Bjerrum lengths at the salt density $\eta_+ = 10^{-2}$. The interaction strength increases from top to bottom ($r = 7\sigma$). The chain length is $N = 80$ and the packing fraction of monomers $\eta_m = 10^{-2}$.

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.

The quantitative comparison of the obtained effective monomer-monomer potential with the Debye-Hückel potential exhibits excellent agreement for both, the dependence of the potential on the screening length as well as the dependence on the interaction strength. This applies for salt free systems[28] as well as for systems with added salt. Figure 7 shows the scaled effective potential for a system with added salt at various Bjerrum lengths. The dashed curves represent the Debye-Hückel potential $\beta v_{\mathrm{DH}} = l_B \exp\left(-\kappa r\right)/r$, where $\kappa = \sqrt{4\pi l_B[\rho_c Z_c^2 + 2\rho_+ Z_+^2]}$ is the inverse Debye screening length. Significant deviations form the Debye-Hückel potential are observed at monomer separations smaller than $r \approx 2\sigma$. This is not surprising, because at such small length scales the detailed shape of the interacting particles (monomers and counterions) matters. Naturally, further deviations are obtained at higher Bjerrum lengths due to counterion condensation.

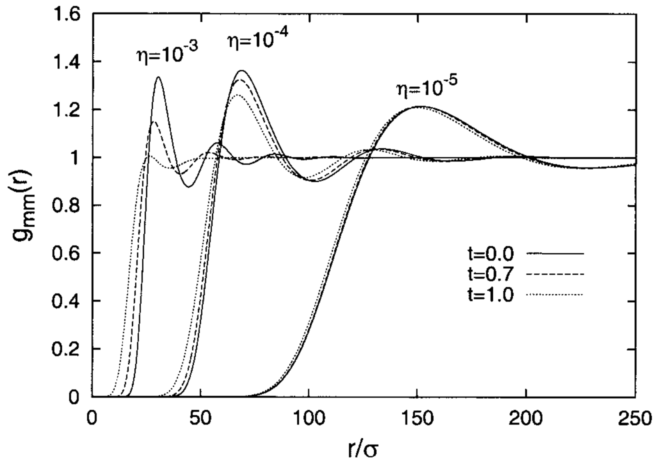

Figure 8. Monomer-monomer pair correlation functions of semiflexible chains of various stiffnesses t and densities η_m. The chain length is $N = 63$ and the Bjerrum length is $l_B = 0.5\sigma$.

Correlation Functions of Flexible Polyelectrolytes

To study the structural properties of solutions of flexible polyelectrolytes, we consider a one-component system of flexible chains interacting via the Debye-Hückel potential. As discussed in the last section, the Debye-Hückel potential provides an excellent description of multicomponent rodlike systems, thus, we expect it to capture the essential features of a system of flexible chains too. In studies of other systems the Debye-Hückel potential proved to be useful already.[33,40]

In order to adequately characterize the structural properties, possible changes in chain conformations have to be taken into account. As a consequence, the structure of a solution and the conformations of the polyelectrolyte chains are strongly coupled. To account for this coupling, the solutions of the PRISM equations and the corresponding conformations of the polyelectrolytes have to be determined simultaneously. This is achieved by a recently developed extension of the PRISM theory.[12–22] Here, the non-pairwise intermolecular many chain interactions of a particular chain are cast into an effective pairwise intramolecular solvation potential which is determined self-consistently. This so called medium induced potential (W) can be expressed by correlation functions calculated with the PRISM theory.[23–26] The total intramolecular potential V is then given by

$$V(\mathbf{r}) = \sum_{i=0}^{N} \sum_{j=i+1}^{N} \left[l_B \frac{e^{-\kappa|\mathbf{r}_i - \mathbf{r}_j|}}{|\mathbf{r}_i - \mathbf{r}_j|} + \beta W_{i,j}(|\mathbf{r}_i - \mathbf{r}_j|) \right] , \qquad (6)$$

where $\beta W_{i,j}(k) = -\rho c(k) S(k) c(k)$ is the Fourier transformed medium induced potential. To analytically calculate the conformational properties of the semiflexible polyelectrolyte chain, we resort to the approximation scheme proposed by Edwards and Singh.[41] The details of the method are described in Ref. [29]. Here we will only present some of the results obtained by this approach.

Figure 8 depicts monomer pair correlation functions for various densities and chain stiffnesses ranging from flexible chains ($t = 0$) to rodlike chains ($t = 1$), respectively. The chain length is $N = 63$ and the Bjerrum length is $l_B = 0.5\sigma$. The semiflexible chains exhibit a similar liquid-like order as rodlike chains (cf. Figure 1). For the lowest density ($\eta = 10^{-5}$) the peak position and the peak height are almost independent from the chain stiffness despite the fact that the chain size is very sensitive to the stiffness in this density range as discussed in Ref. [29]. This is explained by the fact that the structure of the liquid in this density range is dominated by electrostatic interactions and not packing effects, which would depend on the chain size. With increasing density the peak sharpens and its height changes. Moreover, the peak height decreases with increasing stiffness. Therefore, an effect of the chain size should only be noticed for densities where packing effects have to be taken into account, i.e, for densities close and above to the overlap density. For flexible chains, the peak maximum is always located at larger distances than for stiffer chains. At the same density, the coils of the flexible chains exhibit a smaller overlap and hence a stronger Coulomb interaction. The comparison of the correlation functions for various Bjerrum lengths shows that the shift of the peaks and the increase of the peak height as a function of stiffness is less pronounced in the system with larger Bjerrum lengths, especially for low and moderate densities. This follows from the rodlike structure even of flexible chains at large Bjerrum lengths. Hence, the stiffness dependence of the correlation function disappears with increasing Bjerrum length. However, this applies only as long as the screening length, which increases with increasing density, is not too small. The chains behave like uncharged chains for small screening lengths and hence exhibit again a dependence on the chain stiffness.

Conclusions

We have studied the structural properties of polyelectrolyte solutions composed of rodlike and flexible linear chain molecules, respectively. In particular, the influence of salt has been considered. 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. A detailed examination of the monomer-counterion and counterion-counterion correlation functions, respectively, reveals that there are less counterions condensed on a polyion, but the total number of adjacent negatively charged ions is actually larger than in the salt free case. 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 well be 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.

Chain flexibility influences the structural properties of a polyelectrolyte solution. Considering the pair correlation function, we find that semiflexible chains exhibit the same qualitative behavior as rodlike chains, but the characteristic peaks are shifted to larger distances and the height of the peaks increases with increasing density and decreasing chain stiffness due to conformational changes of the chains caused by the increasing density. This effect is more pronounced for lower densities and smaller Bjerrum lengths. There are various other aspects with respect of conformational changes of semiflexible chains, which have not been discussed in this article. Details of such systems can be found in Ref. [29].

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