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Density Inhomogeneities of Highly Charged Polyelectrolyte Solutions Confined between Uncharged and Nonadsorbing Walls

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Monte Carlo simulations are used to study the density profile of dilute and semidilute solutions of highly charged polyelectrolytes confined between uncharged and nonadsorbing walls. We find that the density profile displays oscillations whose wavelength corresponds to that of correlations in bulk polyelectrolyte solutions. The amplitude of the oscillations increases with chain molecular weight. The density oscillations observed cannot be attributed to the confining walls, poor backbone solubility, colloidal-like ordering, or nonuniform distribution of counterions. We conclude that the correlations in polyelectrolyte solutions must be due to a balance between the segment–segment electrostatic interactions and the chains' translational entropy.

Introduction

Interest in polyelectrolytes, that is, polymer chains carrying ionizable groups, is prompted by their widespread use: The food and cosmetic industries utilize polyelectrolytes as stabilizers and thickening agents, and water absorbent materials consist of charged polymers. While the behavior of uncharged polymer solutions is well understood, polyelectrolyte solutions still present experimental and theoretical challenges. This is due to the coupling between long-range Coulombic interactions and the innately complex nature of polymeric molecules.^{1,2} One of the most unique features of polyelectrolyte solutions, in bulk, is the existence of a peak in the scattering function.^{3,4} Such a peak indicates short-range order in the solution and is absent in equivalent solutions of uncharged (neutral) polymer chains.

What is the source of these correlations? In dilute solutions, the individual coils do not overlap. They repel each other, in a manner similar to that of charged colloidal suspensions.⁵ The correlation length is related to the concentration of particles or coils.^{3,5} As the polymer concentration increases and the chains overlap, one might expect this type of ordering to be suppressed and, therefore, the density profile to become uniform. That is not the case, although the scaling of the correlation wavelength with polymer concentration changes around the overlap concentration,^{3,4} indicating thereby that another mechanism is at work.

The density correlations in semidilute solutions of chains where the fraction of charged segments is low may be attributed to low backbone solubility in water.^{6–8} In a manner reminiscent of block copolymer microphase separation in a selective solvent,⁹ the insoluble segments may form microdomains surrounded by the charged segments.

To date, however, there is no satisfactory explanation for the density correlations observed in semidilute solutions of highly charged polyelectrolytes.³ The term "highly charged" is used here to describe chains where the fraction of charged units approaches unity but where the distance between neighboring charges is larger than (or equal to) the Bjerrum length.⁵

In this paper we investigate confined solutions of highly charged polyelectrolytes, in the absence of added salt. The confining walls are uncharged and nonadsorbing. We find that these solutions exhibit density oscillations as a function of distance from the confining walls. The wavelength of the oscillations is similar to that of density correlations in bulk polyelectrolyte solutions of equal concentration.^{3,4} The amplitude of the oscillations increases with chain molecular weight.

We show that the density oscillations are not due to colloidal-like ordering of individual coils. Neither can they be attributed to poor backbone solubility,⁶ the confining walls,⁸ or a nonuniform distribution of counterions.³ We suggest that the electrostatic interactions between segments¹⁰ favor density inhomogeneities, which are countered by the chains' translational entropy.

Methods

In the simulations presented here, we model the polyelectrolyte chain as a pearl necklace of N freely jointed hard spheres (beads), where each bead carries a unit charge. We use either $N = 32$ or $N = 64$. These chain lengths ensure a polyelectrolyte behavior¹¹ but are still short enough to allow an intensive computer study. The bead diameter σ was chosen to be 4 Å, and the separation between them was taken to be $l_0 = 7.14$ Å.

The solvent is modeled as a continuous dielectric medium of relative dielectric constant $\epsilon = 78$, corresponding to water at room temperature. Under these conditions, the Bjerrum length for our model is $\lambda_B = \beta e^2 / (4\pi\epsilon\epsilon_0) \approx 7.14$ Å, where β^{-1} is the Boltzmann's constant multiplied by the absolute temperature and ϵ_0 is the vacuum permittivity. The bead separation was chosen to match the Bjerrum length, so that we need not consider counterion condensation.¹²

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The surfaces are taken to be hard walls which are impenetrable to the beads forming the chains. Since we examine uncharged walls, no electrical or other (attractive or repulsive) interaction between the polymer beads and the surfaces is considered. The material outside the pore has the same dielectric constant as the solvent (water).

The Debye-Hückel approximation is used to describe the electrostatic interactions between the chain beads. In this approach, the effects of the small ions in the system are represented through a screened effective interaction between the chain beads. The interaction energy between two beads is then given by $\beta u_{ij} = \lambda_B e^{-\kappa r_{ij}} / r_{ij}$, with κ^{-1} being the screening length and r_{ij} the distance between particles. We consider only salt-free solutions, so that the concentration of counterions is directly coupled to the average polymer concentration: $\kappa = (4\pi\lambda_B\rho)^{1/2}$, where ρ is the total monomer density.

Using molecular dynamics, Stevens and Kremer³ have shown that the Debye-Hückel models yield results that are within 5% of both the chain dimensions and the osmotic pressure values obtained by allowing a free distribution of counterions. This agreement has been explained recently by the calculations of Donley et al.,¹⁰ which show that the wavelength dependence of the screening length is mainly due to the chain conformations and not to fluctuations in the counterion distribution.¹⁰ This dependence is automatically incorporated in a simulation such as ours, where the chain conformations and the interactions between the chain ions are specifically calculated.

The Monte Carlo simulations are performed in the canonical ensemble: the number of molecules, the volume, and the temperature are kept constant. The simulation cell is a rectangular parallelepiped with the two walls placed on the yz plane at $x = -L/2$ and $x = L/2$. Periodic boundary conditions are applied in the directions parallel to the walls, namely the y and z directions.

At least $n_c = 8$ chain molecules in the simulation box were considered in all the cases presented here. To test the effect of the size of the system, simulations of a particular case ($n = 64$, $L = 300$, and $\kappa^{-1} = 18$ Å) were made with $n_c = 4$ and $n_c = 16$ producing practically identical results. Every step consisted of two movement attempts: one with the reptation algorithm and another with the crankshaft algorithm.¹³ The new configurations were accepted or rejected following the Metropolis criteria.¹⁴ The initial configurations were randomly generated.

The equilibration run consisted of at least 10 000 cycles, where a cycle is defined as Nn_c steps. Finally, the average density profile was taken over at least 150 000 cycles. As a control, the analog neutral system was also simulated.

The average size of the isolated chain in free space was calculated in a separate simulation. In this infinitely dilute limit, the Coulombic interactions are unscreened and $1/\kappa = \infty$. The radius of gyration of the isolated chain $R_{g,0}$ was found to be 46 Å (71 Å) for a chain of length $N = 32$ ($N = 64$). In comparison, the radius of gyration of the neutral counterpart is much smaller: $R_{g,n} = 21$ Å (35 Å). We consider several different values for the wall separation, ranging from order 4 to 10 times $R_{g,0}$.

Results and Discussion

Figure 1 shows the polymer density profile for a very dilute solution of polyelectrolytes (solid line) and neutral chains (dotted line). The difference between the two systems is striking. The neutral chains are distributed almost uniformly, except for a depletion layer characteristic of polymers near uncrossable walls.¹⁵ The polyelectrolyte depletion zone (a) is much narrower and is followed by a large density enhancement zone (region b). In the middle of the pore (c) the polyelectrolyte concentration is low. This profile is similar to that calculated by Dahlgren and Leermakers,¹⁶ using a mean-field model, for polyelectrolyte solutions near a single uncharged surface.

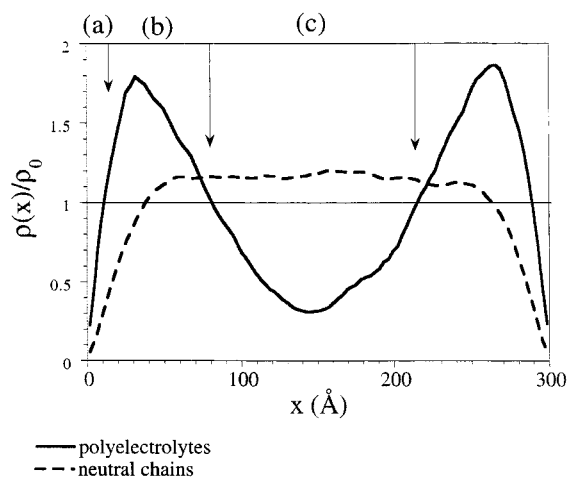


Figure 1. Polymer density profile of a polyelectrolyte and a neutral polymer solution. The chain length is $N = 32$ in both cases. The monomer density is $\rho_0 = 4.2 \times 10^{-6}$ Å⁻³, and the separation between the walls is $L = 300$ Å. The corresponding screening length for the charged chains is $\kappa^{-1} = 58$ Å. Region a denotes the polyelectrolyte depletion zone where the density is lower than ρ_0 . Region b is the polyelectrolyte enhancement zone, and region c is the intermediate zone.

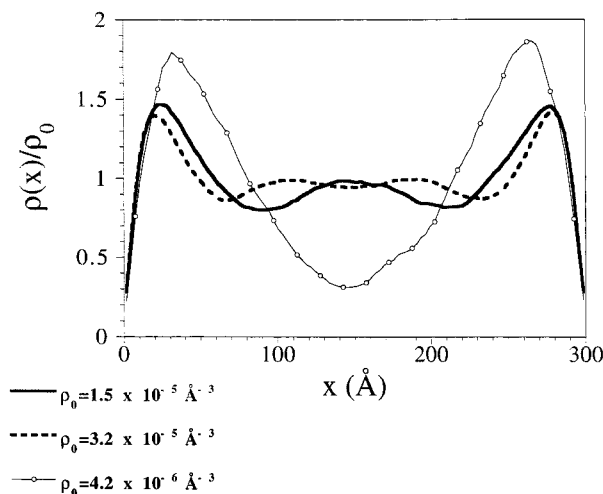


Figure 2. Polyelectrolyte density profile at three different concentrations, for the wall separation $L = 300$ Å and $N = 32$. The screening lengths decrease with increasing polymer concentration and are $\kappa^{-1} = 58$ Å, $\kappa^{-1} = 27$ Å, and $\kappa^{-1} = 18$ Å, respectively. The reduced density profile of uncharged (neutral) chains at these densities is similar to that plotted in Figure 1.

It is interesting to note that the polyelectrolyte density profile shown in Figure 1 is also similar to the profile calculated (using a mean-field model) by Borukhov et al.¹⁷ for polyelectrolyte solutions confined between *charged* surfaces. Borukhov et al.¹⁷ attributed this type of distribution to the long-range effect of surface charges, but our results show that the nonuniform distribution of polyelectrolyte chains confined between surfaces is an inherent property of the polyelectrolyte chains themselves.

In Figure 2 we show the effect of the average polyelectrolyte concentration on the density profile. The screening lengths corresponding to the increasing polymer densities are 58, 27, and 18 Å, respectively. We see that increasing the overall polymer concentration leads to more pro-

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nounced inhomogeneities in the density profile. At the intermediate concentration, a peak develops in the middle of the pore. At higher concentrations, this peak splits into two, producing an *oscillatory* profile.

Bulk polyelectrolyte solutions show a similar trend; both experiments⁴ and molecular dynamic simulations³ show a well-defined peak in the scattering function of polyelectrolyte solutions, both below and above the overlap concentration. This peak indicates the existence of density correlations in the system.

In dilute solutions (i.e., isolated chains) below overlap, the individual chains order and the peak position varies as the cube root of the polymer concentration. Above the overlap concentration where ordering of individual chains cannot occur, the peak in the scattering persists. The density correlations scale then with the square root of the polymer concentration.^{3,4}

Calculating the wavelength of the density oscillations for the intermediate concentration,¹⁸ we find a value of 70 Å, which is within 5% of that obtained by Stevens and Kremer³ for a bulk solution. This agreement suggests that the oscillations we observe are not likely to be the product of confinement but are related to bulk density correlations.

The crossover concentration from dilute to semidilute solutions c^* is not as well defined for polyelectrolytes as it is for neutral chains. This is due to the nonspherical chain configurations induced by the charge-charge interactions.³ In Figure 3a we compare the density profiles of $N = 32$ and $N = 64$ long chains. We see that the wavelength of the oscillations is unaffected by chain length. This indicates that even the shorter chains ($N = 32$) are well within the semidilute regime at this concentration. Also, it is interesting to note that the amplitude of the oscillations *increases* with chain molecular weight, thereby indicating a dependence on entropy. Looking at a typical system configuration (Figure 3b), we see that at this density the chains clearly overlap and that a single chain may contribute segments to several high-density areas.

The effect of wall spacing on the polyelectrolyte density profile is shown in Figure 4. The depletion layer and enhancement zone are unaffected by the wall separation. Confinement is only manifested in the number of intermediate density peaks. The fact that the wavelength we calculate agrees with that of the equivalent bulk solution³ and that the spacing does not change the wavelength indicates that (outside the depletion and enhancement zones) the walls do not affect the correlations in the system.

In Figure 5 we plot the segment density profile, the location of the chain center of mass, and the average radius of gyration of the chains. As may be expected, peaks in the density profile correspond to the center of mass peaks; high-density areas indicate high density of chains, and vice versa. However, the average radius of gyration profile is *out of phase* with the center of mass profile. This means that, on average, the radius of gyration of chains located in high-density areas is smaller than that of chains located in low-density areas. Since the radius of gyration of a polyelectrolyte chain decreases with increased screening,³ this may indicate that chains located in high-density areas experience stronger screening than those in low-density areas.

In summary, we have shown that semidilute solutions of highly charged, flexible polyelectrolytes confined be-

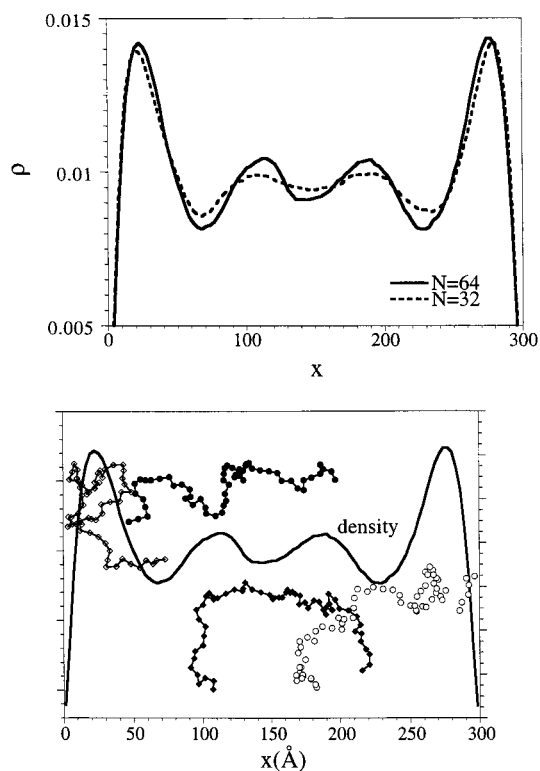


Figure 3. (a, top) Effect of chain length on the density profile of polyelectrolyte chains. $\rho_0 = 3.2 \times 10^{-5} \text{ Å}^{-3}$, so that $\kappa^{-1} = 18 \text{ Å}$. (b, bottom) Distribution of chain segments. We show the projection of the location of the chains' segments in one characteristic configuration. The solid line denotes the density profile. The various symbols describe the position of segments belonging to some of the 16 chains simulated. Note that the chains denoted by filled symbols span the density peaks. $N = 64$ and $\rho_0 = 3.2 \times 10^{-5} \text{ Å}^{-3}$.

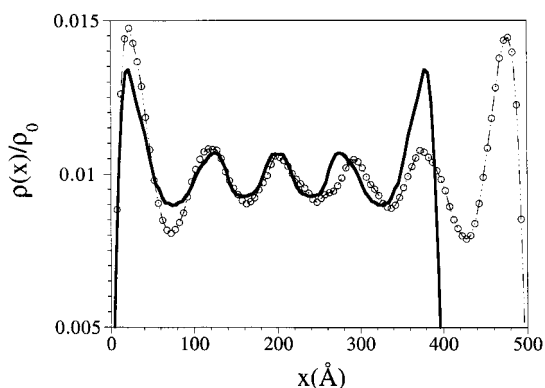


Figure 4. Polyelectrolyte density profile at two different wall separations. $\rho_0 = 3.2 \times 10^{-5} \text{ Å}^{-3}$ and $N = 64$.

tween non-interacting walls display density correlations whose wavelength is similar to that of equivalent bulk solutions. But what is the driving force for these density correlations? Clearly, they are not due to confinement. Neither can they be attributed to local phase separation of an insoluble backbone⁶ or to colloidal-like ordering of domains. Moreover, our use of a uniform Debye-Hückel screening length is equivalent to the (inaccurate) assumption that the counterions are uniformly distributed in the system. Thus, the density oscillations cannot be due to inhomogeneities in the counterion distribution (although those, when allowed, may enhance the oscillation amplitude).^{10,19}

We suggest that the density correlations in polyelectrolyte solutions are due to segment-segment electrostatic

(18) At $\rho = 3.2 \times 10^{-5} \text{ Å}^{-3}$ the distance between peaks is approximately $\lambda = 70 \text{ Å}$. To compare it to the data of Stevens, Kremer,¹¹ we translate λ to a wavevector by using l_0 as the unit length.

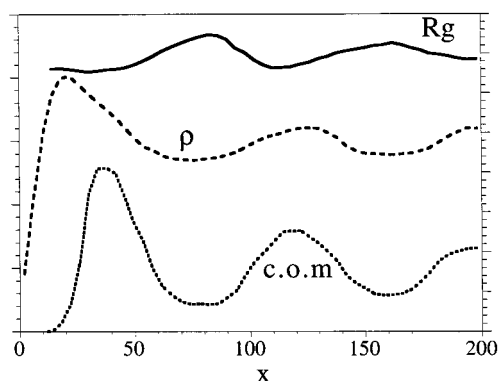


Figure 5. Chain characteristics as a function of distance from the wall: ρ is the density profile, c.o.m. is the fraction of chains whose center of mass is located at that x , and R_g is the (average) radius of gyration of the chains whose center of mass is located at that point. $N = 64$, $\kappa^{-1} = 14$ Å, and the wall separation is $L = 400$ Å. The scales of the three plots are shifted for clarity.

interactions. These favor a nonuniform profile.²² In small-ion systems, entropy dominates and uniform density ensues. However, when the molecular weight of a macroion increases, the translational entropy per charge

(segment) decreases, and density inhomogeneities emerge. This is consistent with our observation that the amplitude of the oscillations increases with chain molecular weight.

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(21) The Debye–Hückel approximation used here should reduce inhomogeneities, since it enforces a uniform distribution of the counterions. If the counterion distribution was allowed to fluctuate, charge neutrality would drive the counterions concentration to match the polymer profile, enhance oscillations. Recent simulations¹⁹ calculations¹⁰ show that counterion fluctuations may even lead to *attractive* interactions between rigid polyions.

(22) Using the Poisson eq, the electric field of a system⁵ is given by the integral over the density of charged units. The energy density is equal to the square of the electric field, the overall system energy is given by the integral of this energy density. For illustration purposes, we take an arbitrary segment profile of the form $\rho(x) = a + b \cos[\alpha x]$ (note that a cannot be zero, since the integral over the segment density must be equal to the total number of segments in the system). If the electrostatic energy favored uniform distribution, we expect that the energy would be minimal when the oscillation amplitude b is zero. However, we see that the energy is minimized at a finite oscillation amplitude (or, conversely, at a finite wavelength).

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