End-effects of strongly charged polyelectrolytes - a molecular dynamics study

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Abstract

We investigate end-effects in the ion distribution around strongly charged, flexible polyelectrolytes with a quenched charge distribution by molecular dynamics simulations of dilute polyelectrolyte solutions. We take the counterions explicitly into account and calculate the full Coulomb interaction via an Ewald summation method. We find that the free counterions of the solution are distributed in such a way that a fraction of the chain charges is effectively neutralized. This in turn leads to an effective charge distribution which is similar to those found for weakly charged titrating polyelectrolytes that have an annealed charge distribution. The delicate interplay between the electrostatic interactions, the chain conformation and the counterion distribution is studied in detail as a function of different system parameters such as the chain length $N_m$, the charge fraction $f$, the charged particle density $\rho$, the ionic strength and the solvent quality. Comparisons are made with predictions from a scaling theory.

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I. INTRODUCTION

“Polyelectrolytes are polymers bearing ionizable groups, which, in polar solvents, can dissociate into charged polymer chains (macroions) and small counterions.” The combination of macromolecular properties and long-range electrostatic interactions results in an impressive variety of phenomena which makes these systems interesting from a fundamental as well as from a technological point of view.

A thorough understanding of polyelectrolytes has become increasingly important in biochemistry and molecular biology. This is due to the fact that virtually all proteins, as well as the DNA, are polyelectrolytes.

Unfortunately, the theoretical understanding of polyelectrolytes is less developed than the understanding of the properties of neutral polymers. The presence of long-range interactions renders the application of renormalization group techniques and scaling ideas much more difficult than in the neutral case. This is due to the fact that many new length scales appear that are not well separated and therefore can influence each other in a complicated fashion.

The degrees of freedom of the counterions contribute largely to the entropy. Their equilibrium distribution is strongly influenced by the immobile charges on the macroion. However, this distribution is strongly coupled to the conformation of the macroion itself, resulting in a complex interplay of chain conformation and ion distribution. In the following we will present a systematic investigation of the spatial counterion distribution around strongly charged flexible polyelectrolytes by means of computer simulations.

In this work we will treat the case of quenched strongly charged polyelectrolytes in both good and poor solvent for the backbone which possess a fixed charge distribution along the polymer backbone that is usually fixed through the initial chemistry. This is the case, for example, for the often studied polystyrene sulfonate. Strong means here that the average charge separation on the backbone is on the order of the Bjerrum length so that we are in the regime were some of the counterions are in close proximity to the macroion, a phenomenon that is usually called counterion condensation.

Through molecular dynamics simulations (MD) we will demonstrate explicitly that the counterion distribution around a quenched strongly charged polyelectrolyte shows the appearance of an “end-effect”, namely that the distribution of counterions around the ends is significantly different from that around the inner part of the chain. A similar situation has been analyzed theoretically in a recent work by Castelnovo et al. for annealed weakly charged polyelectrolytes. Annealed means that the degree of ionization of the macroion can depend on the pH of the solution, so that the ionization sites of the backbone can move along the chain. In their paper they show that the electrostatic field of the polyelectrolyte alters the degree of ionization along the backbone, thus leading to an “end-effect” in the charge distribution. This effect has already been found by numerical simulations for polyelectrolyte chains interacting via a Debye-Hückel potential. It could be of some relevance for systems where end-effects are known to be important, like adsorption on charged surfaces, or self-assembly of weakly charged linear micelles.

We will show that a totally flexible, strongly charged polyelectrolyte system with a quenched charge distribution shows qualitatively the same behavior. We argue that this follows from
the fact that the positions of the counterions are “annealed”. Thus the distribution of all charges along the chain (fixed monomer charges and mobile ions) appears to be annealed. The result is again an “end-effect” that originates physically in the electrostatic field of the polyelectrolyte. We thus demonstrate that the qualitative picture of the charge distribution which emerges out of the scaling theory is even correct for strongly charged polyelectrolytes in a regime where the blob picture ceases to be meaningful, because for the highly charged case the electrostatic blobs are of the order of one monomer.

The paper is organized as follows: First we describe our model and the simulation technique. Then we present our approach to analyze the end-effects. Afterwards we show our results for systems of flexible polyelectrolyte chains in good solvent with explicit counterions in the dilute concentration regime, and investigate the influence of the chain length, the charge parameter, the density and the ionic strength on the charge inhomogeneity along the chain contour length. The last section treats the case of a poor solvent chain, and we end with some conclusions.

II. MODEL AND SIMULATION TECHNIQUE

Our model of a polyelectrolyte solution consists of $N_p$ flexible bead-spring-chains with $N_m$ monomers, $N_c$ counterions and in some cases $N_s$ pairs of salt ions which are located in a simulation box of length $L$ with periodic boundary conditions (3D torus). A fraction $f$ of the $N_m$ monomers is monovalently charged ($v = 1$). The number $N_c$ of monovalent counterions ($v = -1$) is then chosen such that the overall system is electrically neutral. If we have $N_q = N_m f$ charges on a polymer chain, then the number of counterions is given by $N_c = N_p N_q$, and the total number of charged particles in the system is $N_{tq} = 2(N_c + N_s)$, giving rise to a charged particle density $\rho = \frac{N_{tq}}{L^3}$.

The interaction between monomers is described via a standard Lennard-Jones potential of the form:

$$U_{LJ}(r) = \begin{cases} 4 \cdot \epsilon_{LJ} \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 - c(R_c) \right] : \text{for } r \leq R_c \\ 0 : \text{for } r > R_c \end{cases} \quad (1)$$

The function $c(R_c)$ is chosen as $c(R_c) = \left( \frac{\sigma}{R_c} \right)^{12} - \left( \frac{\sigma}{R_c} \right)^6$ to give a potential value of zero at the cutoff. For the good solvent case all chain monomers interact only via the repulsive part of the Lennard-Jones potential, hence $R_c = 2^{1/6} \sigma$. For the poor solvent case we set $R_c = 2.5 \sigma$, which gives the chain monomers a short range attraction. The discontinuity at $R_c$ is small compared to the applied random forces and causes therefore no problems for the stability of the simulation. In this case the depth of the potential minimum can be tuned by $\epsilon_{LJ}$.

For both cases we assume that all ions do not have any short range attractive parts in the Lennard-Jones interaction, as it is reasonable for alkali metals.

The chain monomers are in addition connected along the chain by the FENE (finite extensible nonlinear elastic) bond potential,

$$U_{FENE}(r) = -\frac{1}{2} k R_0^2 \ln \left( 1 - \frac{r^2}{R_0^2} \right) \quad (2)$$
with spring constant $k = \frac{7k_BT}{\sigma^2}$ and finite extension $R_0 = 2\sigma$. All charged particles interact in addition via full Coulombic interaction

$$E_c(r_{ij}) = \lambda_B k_B T \frac{v_i v_j}{r_{ij}}, \quad (3)$$

where $v_i$ is the valence of the $i^{th}$ charged particle in units of the elementary charge $e$ and $\lambda_B = \frac{e^2}{4\pi\varepsilon_0\varepsilon_r k_B T}$ is the Bjerrum length characterizing the strength of the electrostatic interaction.

The electrostatic energy of the box is calculated with the P3M (Particle-particle particle-mesh) algorithm which is based on the Ewald summation method. Details of this method can be found in Deserno and Holm\textsuperscript{11,12}.

In our molecular dynamics (MD) simulations we had no explicit solvent molecules. However, we implicitly take the polarizability of the medium into account through an effective relative permeability $\varepsilon_r$, which we take to be that of water at room temperature, $\varepsilon_r = 80$.

The (MD) method employed in the present work is similar to the one used in Ref.\textsuperscript{13}. To simulate a constant temperature ensemble, the particles are coupled to a heat bath. The motion of the $i^{th}$ particle is given by the Langevin equation:

$$m \ddot{r}_i = -\nabla V_{tot}(\{r_j\}) - m\Gamma \dot{r}_i \tau - \vec{f}_i(t),$$

where $m$ (chosen as unity) is the mass of the particles, $V_{tot}$ is the total potential force made up of the above described Lennard-Jones, FENE and Coulomb terms, which are all pairwise additive, $\Gamma$ denotes the friction coefficient, and $\vec{f}_i$ is a random force. The two last quantities are linked by the dissipation-fluctuation theorem $<\vec{f}_i(t) \cdot \vec{f}_j(t')> = 6m\Gamma k_BT \delta_{ij} \delta(t-t')$. We used a damping constant $\Gamma = \tau^{-1}$, with time step 0.015$\tau$ at constant temperature $k_B T = 1\epsilon$.

The number of MD steps was chosen such that the typical observables like the end-to-end distance $R_e = \sqrt{\langle \vec{R}_e^2 \rangle}$ or the radius of gyration $R_g$ had sufficiently relaxed, which happened usually after 500 000 up to 2 000 000 MD steps. We normally performed between 5 000 000 and 10 000 000 MD steps to take measurements. Some basic parameters and observables of the investigated systems are summarized in Table I. The charge parameter $\xi$, often referred to as Manning parameter, is defined as the number of unit charges along the chain contour per Bjerrum length. Since the chains are flexible we have also given an effective charge parameter $\xi_{R_e}$ which gives the number of unit charges per Bjerrum length when the whole chain is mapped on a rod of length $R_e$. For more information about chain extension in such systems see e.g. Stevens and Kremer\textsuperscript{14}.

### III. DATA ANALYSIS OF THE EFFECTIVE CHARGE

Our strongly charged polyelectrolyte chains have a charge parameter $\xi$ of the order of unity, hence some fraction of the counterions are located closely to the chain (they would be Manning condensed, if the chain was infinitely long\textsuperscript{15}). The main idea of defining an effective charge is that the chain charges can be effectively neutralized by the close proximity of an oppositely charged counterion, which is basically the concept of charge renormalization\textsuperscript{15}. Our definition of the effective charge which we will explain in this paragraph is meant as a straightforward practical approach. This is due to the difficulty of defining this quantity...
in a rigorous theoretical framework. Thus we do not fix the effective charge by fitting the asymptotic distribution to a Debye-Hückel distribution of a renormalized spherical charge distribution as in Ref. \[13\], nor do we actually require the ions to obey some Manning condensation criterion since that is only defined for infinite rod-like polyelectrolytes.\[4\]\[16\].

To investigate the proximity between a free ion \(i\) and a polyelectrolyte chain we introduce \(d_i(j)\), the distance between this ion and the charged monomer \(j\) that is closest in space. \(C_j\) is then the set of all ions \(i\) which are closest to monomer \(j\). To enhance statistics we sometimes average over neighboring monomers.

A snapshot of a polyelectrolyte and the counterions in its vicinity illustrating the definition of their smallest distance \(d_i(j)\) is shown in Fig. \[4\]. For a reasonably stretched charged polymer the ions are located inside an approximately cylindrical space and are assigned to every charge along the contour length of the polyelectrolytes. The average ion charge \(n_q(r, j)\) located at a distance \(r\) from the charged monomer \(j\) is then given by

\[
n_q(r, j) = \left\langle \sum_{i \in C_j} v_i \delta(r - d_i(j)) \right\rangle
\]  

(4)

Here \(\delta(x)\) is the Dirac delta function. The brackets indicate the canonical average which is taken over all chains and configurations.

By integrating \(n_q(r, j)\) from zero to \(r\) we obtain

\[
P(r, j) = \int_0^r dr' \ n_q(r', j)
\]

(5)

which is the local ion charge contained in the interval \([0, r]\). We are now able to define the local effective charge

\[
q_{\text{eff}}(r, j) = (1 + P(r, j))
\]

(6)

as a function of monomer \(j\) and distance \(r\).

The concept of an effective charge applied to the entire polyelectrolyte instead of each charged monomer yields the effective charge as a function of radius alone. The average ion charge \(n_q(r)\) located at a distance \(r\) from the polyelectrolyte is then calculated via equation (4) by taking the sum over all charged monomers. Via equation (4) and (5) we can define also the integrated counterion charge \(P(r)\) and the effective charge \(q_{\text{eff}}(r)\) for the polyelectrolyte. Later we will need those quantities normalized to the chain charge \(N_q\),

\[
\bar{q}_{\text{eff}}(r) = \frac{1}{N_q} q_{\text{eff}}(r) \quad \text{and} \quad \bar{P}(r) = \frac{1}{N_q} P(r)
\]

(7)

Of course there is a difficulty in choosing for \(r\) an appropriate cut-off radius \(r_c\). For our purposes it is not necessary to require that the ions are condensed in the physical sense of Manning, which is rigorously applicable anyhow only for the case of infinitely long rods (see for example the discussion in Ref. \[13\]). It is well known that the concept of an effective
charge for macromolecules is difficult to define both theoretical and experimental and that it depends on the properties which one considers\textsuperscript{17-19}. Since we are interested in the deviation of the effective charge along the chain backbone from its mean value we found that the qualitative result is rather independent from the way the effective charge is defined. Thus we have chosen a simple operational definition and investigate in the next paragraph how different cut-off radii influence the end-effects.

In Fig. 2 the relative effective charge \( q_{\text{eff}}(r_c, j)/\bar{q}_{\text{eff}}(r_c) \) is shown for three different values of \( r_c = 3.16\sigma, 5.01\sigma, 7.94\sigma \) (see System 1 in Table I). One observes that the qualitative form is independent from the exact value of \( r_c \), although \( \bar{q}_{\text{eff}}(r_c) \) changes slowly from 0.72 over 0.64 to 0.57 with increasing \( r_c \), simply because more counterions are accounted for. More pronounced is the decrease of the relative effective charge at the very ends with increasing \( r_c \) due to the increasing geometrical artifacts, namely the pole-caps become larger. Another good reason to choose a small \( r_c \) is the need to look at the chain as a rodlike object, as is explained more clearly in the next paragraph, and the fact that \( r_c \) should be smaller than the Debye screening length \( \lambda_D^2 = 4\pi\ell_B(c_{ci} + 2c_s) \) which is especially important at high densities (high counterion concentrations \( c_{ci} \)) and high salt concentrations \( c_s \). In the case considered in Fig. 2 the screening length assumes the value \( \lambda_D = 23.0\sigma \). The advantages of a larger cut-off are that more counterions are found within \( r_c \), which enhances the statistics. However, as can be seen from the scattering of the data points, the statistical error is quite constant for the three values of \( r_c \). For most of our data analysis we have decided to fix \( r_c = 5.01\sigma \), thus dropping the \( r_c \) dependence from our notation.

In the following discussion of the results we characterize the curves for the relative effective charges \( q_{\text{eff}}(r_c, j)/\bar{q}_{\text{eff}}(r_c) \) with help of some basic quantities. The first, which we call amplitude, is the maximal difference of \( q_{\text{eff}}(r_c, j)/\bar{q}_{\text{eff}}(r_c) \) between an end and the middle of the chain. Here we want to remark that the maximal value of \( q_{\text{eff}}(r_c, j) \) is often not achieved at the outermost monomers due to the above mentioned geometrical artifacts. The amplitude contains information about the strength of the end-effect. The second is the penetration depth of the end-effect, which is defined through the occurrence of a plateau of \( q_{\text{eff}}(r_c, j)/\bar{q}_{\text{eff}}(r_c) \) in the middle of the chain. For example, in Fig. 4, this plateau extends approximately from \( j = 25 \) to \( j = 80 \) which corresponds to a penetration depth of 25 monomers along the contour. Using \( R_c \) this contour length can be rescaled to a length in space. In our example the contour length of 25 monomers corresponds to a real extension of 10.8\( \sigma \). One should keep in mind, however, that the absolute values are weakly varying functions of the chosen cut-off \( r_c \).

\section*{IV. RESULTS}

In this section we will discuss our main results for the ion distribution and its inhomogeneities around flexible polyelectrolytes under various conditions. First we will compare our results with analytical theory. Then we will have a closer look on the influence of various parameters such as the chain length, the charge parameter, the density, the salt concentration and the solvent quality. We will also investigate conformational inhomogeneities which can be seen in the bond energy distribution.
A. Connection to the Cell Model

Even though we want to focus on the inhomogeneities of the counterion distribution around polyelectrolytes we first look at the integrated ion charge $P(r)$ itself. This quantity can be exactly computed within mean-field Poisson-Boltzmann theory for the cell model ($CM$) of an infinitely long charged rod, and the solution is characterized by the three parameters, namely the rod of radius $r_0$, the charge parameter $\xi_{CM}$, and the enclosing cylindrical cell of radius $R_C$. A recent discussion of this model and comparisons with computer simulations can be found, for example, in the work of M. Deserno.

If the counterions are monovalent, and we are dealing with a salt-free solution, then $|\bar{P}(r)|$ also has the meaning of an integrated probability distribution function for finding an ion at distance $r$. In Fig. 3 we have plotted $|\bar{P}(r)|$ together with $\bar{q}_{\text{eff}}(r)$ as a function of $\log(r)$ (see System 1 in Table 1). $|\bar{P}(r)|$ has two inflection points, the first is in the inner region near the polyelectrolyte ($r < R_g$) the second further out ($r > R_g$). Because only the inner region has an approximately cylindrical symmetry the outer region cannot be compared to the cell model. For comparison we have plotted the integrated distribution function obtained from the cell model for an infinitely long charged rod at the same concentration with a value of $\xi_{CM} = 1.65$. This value was determined from the location of the first inflection point of the simulated $|\bar{P}(r)|$, $(R_M, |\bar{P}(R_M)|)$, where the so-called Manning radius $R_M$ is the $r$ value of the inflection point. Our simulation data yielded $(6.9\sigma \pm 1.0\sigma, 0.39 \pm 0.03)$, and leads to a charge parameter via $\xi_{CM} = \frac{1}{1-|\bar{P}(r)|}$. The other two parameters of the cell model $r_0$ and $R_C$ are fixed through the particle size $\sigma$ and the concentration. The good agreement of the cell model curve with our simulated data for $r < R_g$ suggests that the overall ion distribution is mainly governed by the central part of the polyelectrolyte where we have a cylindrical symmetry in the vicinity of the chain. Also the $r$ value of the inflection point of the fitted curve $R_M = 6.67\sigma$, the so called Manning radius, is in good agreement with the simulated data even though this value is fixed and not fitted. For $r > R_g$ the difference to the cell model is due to the loss of the cylindrical symmetry in the simulated solution. This is especially reflected by the occurrence of a second inflection point for $|\bar{P}(r)|$ which is not present in the solution of the cell model for the salt-free case.

However, we want to remark that the results for $|\bar{P}(r)|$ are neither consistent with what one would expect inside the cell model from the bare line charge parameter $\xi = 0.98$ nor an effective line charge parameter $\xi_{Re} = \ell_B N_q / R_e = 2.4$ determined by the chain extension. This is probably due to the complex geometrical situation around a flexible polymer. From far away the polyelectrolyte can be seen as a rodlike object of length $R_e$ with an effective line charge parameter $\xi_{Re}$ but for closer distances the local chain structure is important with an upper bound of $\xi$ for the line charge parameter characteristic for that region. Thus it is not surprising that the fitted simulation result $\xi_{CM}$ is in between the two extreme values of the line charge parameter. We believe that this is due to several differences between the simulated system and the cell model. First the length of the polyelectrolyte is of the same order than the cell radius, thus chain end-effects will play an important role. Second the configurations of the polyelectrolyte can only roughly be approximated by a cylindrical stiff object. And last the solution of the cell model on the level of the Poisson-Boltzmann equation neglects correlations between the particles. The inhomogeneities of the ion distribution along
the polyelectrolytes backbone which we will discuss from now on in this paper can not be compared to the cell model since they are excluded from this theory by definition. A more detailed analysis of the applicability of the cell model to flexible polyelectrolytes will be left for future investigations.

B. Qualitative Comparison with Scaling Theory

As already mentioned above, a strongly charged polyelectrolyte with a fixed charge distribution with mobile counterions can be looked upon like a titrating polyelectrolyte with an annealed charge distribution where the counterions together with their ability to neutralize a fraction of the chain charges, play the “annealed” part. We will demonstrate that our strongly charged polyelectrolytes regarding the inhomogeneity of the effective charge behaves qualitatively the same way as scaling theory predicts for titrating polyelectrolytes. We will also show in the following subsections that the dependence of this inhomogeneity from system parameters are in good agreement. One of the observable effects is the accumulation of counterions in the middle parts of the chain, as can be inspected in Fig. 2. Towards the end of the chain, the effective charge increases which is equivalent to a decrease in the counterion concentration. The reason for this behavior is the difference in the electrostatic potential created by the charges of the polyelectrolyte, which is stronger in the middle than at the ends. In a simplified picture one can say that an ion close to the middle part of the chain is attracted by more chain charges than an ion sitting at the chain end. This effect as well as the electrostatic field of a charged flexible chain itself has been analytically described by Castelnovo et al. for titrating polyelectrolytes.

Apart from this common origin of the inhomogeneity and the similarity of the results there are some important differences between the two systems which restricts the comparison. The strength of the electrostatic interaction in the theory and in the simulation is quite different. Thus, the blob picture used in the scaling theory, is not applicable for our simulations. In the scaling theory of the titrating polyelectrolytes the charge fraction \( f \) fixes both, the electrostatic field of the chain and the number of charges subject to this field. This is different from our system, where \( f \) fixes the quenched charge distribution, and thereby the electrostatic field of the chain, but the number of considered charges subject to this field is determined by the number of ions inside the cut-off distance \( r_c \). At first sight there is also a difference in the origin of the charge inhomogeneity. In the case of a titrating polyelectrolyte, the inhomogeneity is due to a repulsion between the mobile charges on the chain. In our system, the inhomogeneity is due to the attraction of the free counterions to the fixed chain charges. When, however, the free ions close to the chain and the chain charges are considered together as an “effective charge”, then it is again the repulsion between the effective charges of the chain which causes the inhomogeneity.

The comparison between scaling theory and our simulations can only be qualitative because the compared systems are physically different. Thus qualitative means that the predictions of the scaling theory about the end-effect and its parameter dependencies can be confirmed. Although the functional form of the end-effect is very similar between the two systems we cannot perform a quantitative comparison, e.g. fitting the results of the scaling theory to
our data, due to the different meaning of the charge fraction \( f \) of the scaling theory and our effective charges.

The result of charge accumulation at the end is also in agreement with results from simulative studies of both flexible and rigid weakly charged titrating polyelectrolytes where the electrostatic interactions are treated on the Debye-Hückel level.

C. Chain length

Because of the already mentioned influence of the surrounding geometry it is first of all interesting to look at the chain length dependence of the end-effect. In Fig. 4 the inhomogeneity of the effective charge is shown for different chain length \( N_m \), varying from \( N_m = 36 \) to \( N_m = 288 \) (systems 2,3,4, and 5 in Table [1]). The qualitative form, the accumulation of charge at the ends of the chain, does not change with chain length. However, one observes a slight increase of the amplitude of the end-effect from 0.11 over 0.16, 0.17 to 0.18 with increasing chain length. For the longest chains with \( N_m \geq 144 \) one can see a plateau, which indicates a finite penetration depth of the end-effect. The amplitude depends on the difference of the electrostatic field of the chain and on the number of annealing ions with distance \( r \) smaller than \( r_c \). The slight increase of the amplitude points to a saturation of both quantities already for chains with length \( N_m \geq 72 \). An estimation for the case \( N_m = 288 \) gives a penetration depth of 65 monomers along the contour length which corresponds to a length of approximately 45\( \sigma \) in real space. This penetration depth is in agreement with the extension of the other chains. One has to compare the penetration depth with \( R_e/2 \) which is 11.5\( \sigma \), 24\( \sigma \), 49.5\( \sigma \), and 97.5\( \sigma \) for our chains with increasing length. This explains why there is no plateau visible for the shorter chains. Our observed penetration depth of 45\( \sigma \) fits well in magnitude to the Debye-length \( \lambda_D = 39.9 \sigma \), which was calculated assuming the same ion concentration and an isotropic electrolyte solution. However, our limited precision does not allow us to study further corrections to the screening length due to the inhomogeneity of our systems.

We are aware that the system with \( N = 288 \) is on the edge to the semi-dilute regime where the chains counterion clouds start to overlap but the influence on the chain extension and the local structure is so small that it does not influence our results significantly. The simulation time for the longest chains was roughly 8 CPU days on a 600MHz workstation with a Compaq EV6 chip. Due to limited CPU time and thus large statistical errors for long chains we use shorter chains for the investigation of the other parameters.

D. Charge parameter \( \xi \)

In this section we vary \( \xi \) from 1 over 0.5 to 0.25 by changing the charge fraction \( f \) and keeping the chain length \( N_m = 72, 71 \) and 69 respectively roughly constant (Systems 3, 6, and 7 in Table [1]). Lowering \( \xi \) yields a dramatic decrease of the end-effect as can be seen in Fig. 3. The amplitude diminishes drastically from 0.16 over 0.044 to 0.016 with decreasing \( \xi \). This result is again in good qualitative agreement with results from scaling
theory (compare Fig.2 in Ref.9). One reason of the observed behavior can be traced to the diminished electrostatic potential difference of the chain along its contour that allows the counterions to distribute more and more uniformly along the chain. Not only the difference responsible for the end-effect is getting smaller but also the electrostatic field of the chain itself becomes weaker, thereby allowing the counterions to move further away from the chain. This in turn yields fewer counterions which can play the annealed part, and also results in a reduced amplitude of the end-effect. We therefore conclude that the concept of an annealed charge distribution mediated by the free ions is not applicable to weakly charged chains with $\xi \ll 1$. The increase of the effective charge $\bar{q}_{\text{eff}}$ from 0.83$e$ over 0.93$e$ to 0.96$e$ which corresponds almost to the bare charge of the chain underlines our argument.

As is well known the charge parameter influences also the chain conformation. With decreasing $\xi$ (and less repulsion between the chain charges) the chain shrinks from $R_e = 48\sigma$ over $R_e = 34\sigma$ to $R_e = 23\sigma$. This slows also down the decrease of the effective charge parameter $\xi_{R_e} = l_B N_q/R_e$, which is lowered from 1.5 over 1.0 to 0.75, and thus is only half as large for the first system, whereas the bare $\xi$ has been reduced to a quarter. However, it is for all systems still close to the critical value 1. As we have described in section IV A, $\xi_{R_e}$ gives a better estimate for the counterion attraction at large distances than $\xi$ itself. But the reduced decrease of $\xi_{R_e}$ can not prevent the loss of counterions into the bulk solution, which again gives less possibilities of annealing, and results in a large variation of the end-effect.

E. Polymer concentration and added salt

In this section we investigate the influence of the polymer concentration and added salt on the end-effect. The results for systems 1, 8, 9 and 10 are shown in Fig 6. With decreasing density the amplitude of the end-effect is decreasing from 0.25 for $\rho = 10^{-4}\sigma^{-3}$ over 0.19 for $\rho = 10^{-5}\sigma^{-3}$ to 0.12 for $\rho = 10^{-6}\sigma^{-3}$. Also the penetration depth is decreasing with increasing concentration. This can be seen from the formation of a plateau region for the higher densities. The decrease of the amplitude is due to the effect that with decreasing polymer concentration the counterions will explore the larger accessible volume, or more technical spoken, they will gain more translatorial entropy, and thus more counterions will be found at larger distances. Thus less counterions can feel the inhomogeneity of the electrostatic field of the chain which makes the end-effect less pronounced. This is reflected in an increase of $\bar{q}_{\text{eff}}$ upon dilution from $\bar{q}_{\text{eff}} = 0.65e$ for $\rho = 10^{-4}\sigma^{-3}$ to $\bar{q}_{\text{eff}} = 0.88e$ for $\rho = 10^{-6}\sigma^{-3}$. But also the decrease of $\xi_{R_e}$ from 2.4 at $\rho = 10^{-4}\sigma^{-3}$ to 1.9 at $\rho = 10^{-6}\sigma^{-3}$ coming from the slight increase of the chains extension adds to the decrease of the amplitude. The decrease of the penetration depth with increasing density can be explained by the better screening at higher ionic strength. We have chosen a smaller value for the cutoff $r_c = 3.01\sigma$ for the data in Fig. 3 in order to have a smaller cutoff radius than one Debye-length. An addition of salt to system 1 keeps the polyelectrolyte density fixed, but enhances the charge density further to $\rho = 6 \cdot 10^{-4}\sigma^{-3}$, and we observe the same trends as before, namely that the amplitude is increased from 0.25 to 0.29.

The results depicted in Fig. 3 might at first sight appear puzzling, because for a smaller Debye-length one would expect a decrease of the amplitude of the end-effect due to the
fact that then each ion can ‘see’ only a smaller part of the chain, thus making the difference between a location at the middle and the end of a chain weaker. The reason for this somewhat unexpected behavior is that the dominating factor for the amplitude of the end-effect is not the change of the screening length $\lambda_D$ but the change in the number of annealing ions.

To investigate the influence of the screening length and to be able to test the predictions of the scaling theory we have done the data analysis also for constant $\bar{q}_{\text{eff}}$ instead of constant cutoff radius $r_c$. The scaling theory predicts for this case a decrease of the amplitude of the end-effect with decreasing screening length (compare Fig. 3. in Ref. 6). This can also be confirmed by our data, compare Fig. 7, where all systems have the same average effective charge $\bar{q}_{\text{eff}} = 0.85e$ and thus different values for $r_c$ ranging from $1.5\sigma$ to $14\sigma$. Here the amplitude of the end-effect changes from $0.18$ at $\rho = 10^{-6}\sigma^{-3}$ to $0.16$ at $\rho = 10^{-5}\sigma^{-3}$ to $0.12$ at $\rho = 10^{-4}\sigma^{-3}$ and $0.09$ for the salt case which is the predicted behavior. The changes in the penetration depth can also be observed more clearly in Fig. 7 and yield the same values as those derived from Fig. 6.

F. Effects on the conformation

Besides the inhomogeneity of the local effective charge there is also an inhomogeneity in the local conformation of a strongly charged polyelectrolyte. This inhomogeneity has different origins. Here we are interested in effects caused by the electrostatic interaction of the charged particles. The same inhomogeneity in the electric field that causes the free ions to distribute inhomogeneously also acts on the fixed charges of the polyelectrolyte. This gives rise to different stretching of the bonds along the contour length. One can see this effect by measuring the energy stored in the bonds. The relative bond energy $E_B(j)/\bar{E}_B$ is shown in Fig. 8 for two different chain length (Systems 2 and 3 in Table 1). Here $E_B(j)$ is the energy stored in the bond between the monomers $j$ and $j + 1$ coming from the Lennard-Jones and FENE potentials as defined in equations 1 and 2 and $\bar{E}_B$ is the average of $E_B(j)$ for the whole chain.

From a theoretical point of view it is interesting to know something about the tension along the chain, since the chain under tension model is the basis for the electrostatic blob picture used in scaling theory. Thus we have measured the bond energy along the contour length of the chain. The energy and thus the tension is lower at the ends of the chain. This yields in the blob picture a bigger electrostatic blob size at the ends than in the middle. This causes the polyelectrolyte to appear in a trumpet like shape.4

There are at least two reasons why we are not able to see this effect in a more direct fashion. The first one is that with our strongly charged chains we are far away from the region were the blob picture is applicable. Since for strongly charged chains an electrostatic blob would contain roughly only one monomer we can not measure the blob size directly via, e.g., the scaling of local distances. It is also impossible to relate the transversal extension of the chain perpendicular to its main axis (defined for instance by the principle axis of inertia) to the inhomogeneity of the electrostatic field of the chain. This is because already for neutral chains it is known, that the transversal fluctuations have different magnitudes along the chain, namely they are larger at the ends of the chain than in the middle.22
G. Poor solvent condition

In the case of polyelectrolytes under poor solvent conditions the additional short range attraction between the backbone monomers of the chains makes the already impressing variety of phenomena known from the good solvent case even richer and more interesting. Due to the balance of attractive and repulsive forces so-called necklace structures occur\cite{23,27}. Here we have simulated a system with $\epsilon_{LJ} = 1.75$ which is deep in the poor solvent regime\cite{26,27}. For the system (No. 11 in Table I) under investigation we find an interesting coexistence between structures with four and five pearls. Fig. 9 shows a snapshot of a necklace with five pearls. The question of the stability of these structures for strongly charged systems will be investigated in a future publication. Here we concentrate only on the difference in the counterion distribution around the strings and pearls. In order to see the relation between a particular necklace conformation and the local effective charge we restrict the data analysis to configurations with five pearls. The number of pearls in a configuration is calculated via a cluster algorithm which is adapted for linear chains\cite{28}. It is clearly visible in Fig. 10 that the end-effect in this case is smeared out almost uniformly over the end pearls. There is a sharp decrease in the effective charge in the region of the first string. In this gap between two pearls we find an accumulation of counterions and thus an enhanced decrease of the effective charge. The necklace structure in the middle part of the chain is also visible in the modulation of the effective charge along the backbone. Fig. 10 shows the effective charge along the contour length together with the effective charge of the five pearls.

However, with our method of measuring the effective charge it is not possible to answer the question whether the strings or the pearls in such a structure have different effective charges as it is proposed in\cite{6}. The difficulty is due to the limited size of the strings, and the difficulty to decide for the counterions between two pearls, if they belong to one of the pearls or to the string between them.

V. CONCLUSION

In this paper we looked at the spatial distribution of the counterions around strongly charged polyelectrolytes by means of MD simulations. We demonstrated that by partially neutralizing the quenched charged distribution on the chain backbone the inhomogeneous distribution of counterions lead to the same qualitative effects that are observed in weakly charged polyelectrolytes with an annealed charge distribution.

We have discussed the difficulty in defining the effective charge through the cut-off radius, because this radius also fixes the average charge fraction, but have also shown that the qualitative appearance of the end-effect is rather independent from its definition. The comparison of the simulated ion distribution with the Poisson-Boltzmann solution of the cell model of an infinitely extended charged rod has shown that the description of our polyelectrolytes as rodlike objects is valid which allows a description of the inhomogeneities along the contour of the chain in the presented way. We made a qualitative comparison with the results obtained for weakly charged titrating polyelectrolytes via scaling theory by Castelnovo et al.\cite{6}. We discussed the common underlying physical mechanism, namely the differences in
the electrostatic field of the chain along its backbone, and showed that this assumption is compatible with our results. The agreement between predictions of the scaling theory and our simulations was also confirmed for the qualitative dependencies of the end-effect from the investigated parameters chain length, charge fraction and ionic strength. We found a saturation of the end-effect for long chains, when the chain extension, namely $R_e$, is at least twice as large as the Debye screening length. A simple Debye-length criterion appears to be sufficient to explain the penetration depth of the end-effect. However, when we looked at the amplitude dependency on density and ionic strength of the solution, we found that in this case both parameters, the number of annealing ions and the ionic strength of the solution, influence the end-effect and that the first one dominates. We therefore fixed the number of annealing counterions to investigate the ionic strength dependence. This enabled us also to observe the expected decrease of the end-effect with increasing ionic strength. The amplitude of the end-effect was shown to depend strongly on the charge parameter $\xi$. The definition of such an end-effect via close mobile counterions can not be made for an effective charge $\xi << 1$. We observed the same conformational inhomogeneities that are found for weakly charged annealed polyelectrolytes.

Even though the chain conformation is very different in the poor solvent case the end-effect is qualitatively the same, namely the counterions are more likely to be found at the middle of the chain than at the ends. We could also clearly see the necklace structure by looking at the effective charge along the contour length. However the string length was too short to show any charge difference in pearls and strings as has been predicted in Ref.6 Overall we can conclude that the charge distribution of strongly charged polyelectrolytes (with or without annealing) behaves like that one of weakly charged titrating polyelectrolytes. This is due to the presence of the mobile partially neutralizing counterions, which results in an annealed backbone charge distribution. We hope that this work stimulates the future development of theories for strong polyelectrolyte solutions as well as for inhomogeneous electrostatic systems in general.

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### TABLES

| System | $N_p$ | $N_m$ | $N_q$ | $\rho$ | $R_e$ | $R_g$ | $\ell_B$ | $\xi$ | $\xi_{R_e}$ | $\bar{q}_{\text{eff}}$ |
|--------|------|------|------|------|------|------|--------|------|--------|----------|
| 1      | 8    | 106  | 36   | $10^{-4}$ | 46   | 16   | 3.0    | 0.98 | 2.4     | 0.65     |
| 2      | 7    | 36   | 36   | $10^{-4}$ | 23   | 8    | 1.0    | 0.98 | 1.6     | 0.87     |
| 3      | 5    | 72   | 72   | $10^{-4}$ | 48   | 16   | 1.0    | 0.98 | 1.5     | 0.83     |
| 4      | 3    | 144  | 144  | $10^{-4}$ | 99   | 31   | 1.0    | 0.98 | 1.4     | 0.80     |
| 5      | 3    | 288  | 288  | $10^{-4}$ | 195  | 62   | 1.0    | 0.98 | 1.5     | 0.79     |
| 6      | 5    | 71   | 36   | $10^{-4}$ | 34   | 12   | 1.0    | 0.49 | 1.0     | 0.93     |
| 7      | 5    | 69   | 18   | $10^{-4}$ | 23   | 8    | 1.0    | 0.25 | 0.75    | 0.96     |
| 8      | 8    | 106  | 36   | $10^{-5}$ | 52   | 17   | 3.0    | 0.98 | 2.1     | 0.77     |
| 9      | 8    | 106  | 36   | $10^{-6}$ | 56   | 18   | 3.0    | 0.98 | 1.9     | 0.88     |
| 10     | 4    | 106  | 36   | $6 \cdot 10^{-4}$ | 35   | 13   | 3.0    | 0.98 | 3.1     | 0.42     |
| 11     | 5    | 382  | 128  | $10^{-5}$ | 46   | 17   | 1.5    | 0.49 | 4.2     | 0.59     |

**TABLE I.** Some basic observables for the used systems: $N_p$ Number of polymers in simulation box, $N_m$ chain length (number of monomers), $N_q$ charge of polyelectrolyte, $\rho$ charged particle density in $\sigma^{-3}$ (number of charged particles divided by the box volume), $R_e$ end-to-end distance, $R_g$ radius of gyration, $\xi$ charge parameter along the contour (average bond length is $1.02\sigma$), $\xi_{R_e}$ charge parameter regarding $R_e$, $\bar{q}_{\text{eff}}(r_c = 5.01)$ effective charge in $[e]$ of a monomer and its ions closer than $r_c$. All length are given in units of $\sigma$. The statistical error of the measured quantities is less than 3%.
FIG. 1. Snapshot of a polyelectrolyte chain of system 1. The Figure shows the geometrical situation in the vicinity of the chain. The method of measuring the distance of free ions to the chain and their assignment to individual monomers is illustrated by the connections between the ions and their closest monomer.

FIG. 2. Inhomogeneity of the effective charge along the contour length: Qualitative independence from the cutoff radius $r_c$. System 1. As throughout the paper the fitted lines are thought as a guide to the eye.
FIG. 3. Ion charge distribution $|\bar{P}(r)|$ (+) and effective charge $\bar{q}_{\text{eff}}(r)$ (∗) as a function of the radius $r$. The dotted line is a fit to the cell model. The first inflection point of $|\bar{P}(r)|$ is marked with a □. For detailed parameters see system 1 in Table I.

FIG. 4. Effective charge along the contour length $q_{\text{eff}}(j)$ for different chain length $N_m$. Systems 2, 3, 4, 5 with increasing length. $j^*$: Here we have shifted the monomer index $j$ such that the innermost monomer has $j = 0$. 
FIG. 5. Effective charge along the contour length $q_{\text{eff}}(j)$ for different values of the charge parameter $\xi$. Systems 3, 6, 7 with decreasing $\xi$.

FIG. 6. Effective charge along the contour length $q_{\text{eff}}(j)$ (here with a cutoff radius $r_c = 3.14\sigma$) for different densities and salt concentration. Systems 1 ($\rho = 10^{-4}$), 8 ($\rho = 10^{-5}$), 9 ($\rho = 10^{-6}$) and system 10 ($\rho = 6 \cdot 10^{-4}$) with salt.
\[ \lambda_D = 6.9\sigma \]
\[ \lambda_D = 23.0\sigma \]
\[ \lambda_D = 72.8\sigma \]
\[ \lambda_D = 230.3\sigma \]

**FIG. 7.** Effective charge along the contour length \( q_{\text{eff}}(j) \) (here with constant \( \bar{q}_{\text{eff}} = 0.85 \)) for different densities and salt concentration as in Fig. [1].

**FIG. 8.** Configurational inhomogeneity: Relative bond energy \( E_B(j)/\bar{E}_B \) along contour length \( j \) for different chain length \( N_m \). Systems 2 and 3.
FIG. 9. Typical necklace conformation. Chain with charged (black) and neutral (grey) monomers, pearl extension (transparent grey), counterions (light grey). System 11.

FIG. 10. Effective charge along the contour length $q_{\text{eff}}(j)$ for the poor solvent case (pearl necklace structure). Pluses and solid line shows the data. The dotted horizontal lines indicate the location and the effective charge of the substructures (only pearls). System 11.