

Dynamics and Distribution of Counterions in the Vicinity of a Flexible Polyelectrolyte

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ABSTRACT

Using molecular dynamics simulations, we investigated the dynamics and the distribution of the counterions within the Bjerrum layer of a polyelectrolyte with the degree of ionization spanning a range covering the counterion condensation transition point. We found that, during the condensation process, individual counterions enter and leave the vicinity of the polyelectrolyte molecule independently and randomly on a time scale comparable to the diffusion time across a Debye layer, and that the distribution of the counterions along the polyelectrolyte is not uniform. Instead, these counterions form clusters and that, within a cluster, they are packed with short range orientation order. Our simulations provide information on the detailed arrangement of the condensed counterions along a flexible polyelectrolyte, which is useful in understanding the electrophoretic behavior of these molecules, as well as the interaction between them.

Keywords: electrophoresis, transport properties, counterions, polyelectrolyte, molecular dynamics

1 INTRODUCTION

The transport properties of polyelectrolytes in solution, such as their electrophoretic mobilities, are strongly related to the distribution of the counterions in the vicinity of such macromolecules, which, in turn, is controlled by the electrostatic interaction between the polyelectrolyte and the counterions, as well as by the interaction among the ions in the solution. When the charge density of the polyelectrolyte is high enough, its effective charge is lower than its nominal value due to the coupling between the polyelectrolyte and its surrounding counterions. The classical theory of Manning [1] hypothesized that a counterion condensation transition will occur when the linear charge density of the polyelectrolyte reaches a critical value. In this theory, the polyelectrolyte is viewed as a stationary, infinitely long straight line carrying equally charged groups of charge $-z_p e$ separated by a distance b . The condensation is controlled by a phenomenological parameter $\xi = z_p z_c l_B / b$, which also depends on the valence of the counterions, z_c , plus the Bjerrum length $l_B = e^2 / (\epsilon_r k_B T)$. Here ϵ_r is the

dielectric constant of the medium and $k_B T$ is the thermal energy. If the Manning parameter ξ is less than 1, all the counterions can escape to infinity; whereas, for $\xi > 1$, a finite amount of counterions become bound to, or are condensed on, the polyelectrolyte, and the charge of which is then partially neutralized. The amount of charge condensed per unit length is $z_p e (1 - 1/\xi) / (z_c b)$ so that the effective linear charge density of the polyelectrolyte is lowered to the critical value $-z_p e b^{-1} / \xi$. The condensed charge is then assumed to be distributed uniformly along the molecule, whereas the unbound ions in the solution are treated by the Debye-Hückel approximation.

Although Manning's theory succeeds quite well in elucidating the thermodynamic properties of polyelectrolyte solutions in equilibrium, very little is known about the spatial and temporal variations of the distribution of the counterions around the polyelectrolyte backbone which, besides being of fundamental interest, govern the electrostatic interaction of a polyelectrolyte with other molecules at the local level. In this context, we investigated, therefore, the distribution and association of the counterions along the polymer backbone within a distance of one Bjerrum length from a polyelectrolyte molecule by using molecular dynamics (MD) simulations. The Bjerrum length is the relevant length scale here because, within this range, the electrostatic interaction between a counterion and the polyelectrolyte dominates over Brownian motion thereby implying that any counterions inside this range can be considered as being bound to the molecule.

2 SIMULATION METHODS

The MD simulations that we performed used a model of a flexible polyelectrolyte suspended in a solvent, with or without added salt [2]. The major feature of our model is that the solvent atoms are represented explicitly, so that all hydrodynamic interactions are included naturally, with no ad hoc assumptions being introduced. Our model employs a simple molecular model for a solvent based on atoms interacting via the Lennard-Jones potential [3]. The polyelectrolyte molecule is modeled as a group of N beads joined linearly in a freely-jointed chain using the FENE potential [4], and carries a to-

tal charge $-Z_p e$ distributed uniformly along the chain. All dissolved ions are monovalent and the counterions from the salt and the polyelectrolyte are identical. Accordingly, the system includes N_- coions of charge $-e$ and $N_+ = (N_- + Z_p)$ counterions of charge $+e$ so as to maintain electro-neutrality. The charges interact via the Coulomb potential, with the dielectric constant ϵ_r chosen to be that of water. Other interactions between the polyelectrolyte, solvent atoms, and ions are incorporated using the Lennard-Jones potential. We keep the temperature in the simulations constant at $T = 1.0\epsilon/k_B$ and set $l_B = 1.854\sigma$, where ϵ is the depth of the potential well and σ is the core size in the Lennard-Jones potential. This value of l_B corresponds to $T = 300\text{K}$ and assumes that σ is comparable to the size of a water molecule, which is about 0.4nm . This model enables us to consider the coupling of hydrodynamic and electric effects in the polarization of a macromolecule subject to strong electric fields. The number of coions N_- is chosen such that the salt concentration is approximately 0.073M . Our simulations were conducted for the regime $\sigma < l_B < \lambda_D < R_g$, where λ_D is the Debye screening length and R_g is the radius of gyration of the polyelectrolyte. This is the usual regime in which experimental studies are performed. We vary the polyelectrolyte charge and length, Z_p and N , such that the Manning parameter, ξ , for our system with $b = \sigma$, $z_c = 1$ and $z_p = Z_p/N$, spans a range above and below the critical value 1.

3 COUNTERION DYNAMICS AND AVERAGE CHARGE DISTRIBUTION

In order to investigate the instantaneous distribution of the ions around a meandering polyelectrolyte, we constructed N spheres of fixed radius r centered at each of the beads and then quantified the relative distribution, along the chain, of the coions and counterions which were located inside these spheres. In particular, $r = 0$ corresponds to the chain backbone. Such calculations were conducted over a broad range of r/σ . We found that “counterion condensation” is a dynamic process in which individual ions enter and leave the vicinity of the polyelectrolyte independently and randomly on a time scale comparable to the diffusion time (τ_D) for a single counterion to diffuse across a Debye layer. On the other hand, the distribution of the counterions along the polyelectrolyte for $r \sim l_B$, being averaged over sufficiently long time scales, is found to be spatially uniform as was assumed in Manning’s theory. As an example, the curves in Fig. 1 illustrate the time-averaged total charge of the ions around the polyelectrolyte as a function of r/σ , both in the absence of an electric field (solid curve for $E = 0$), and when the polyelec-

trolyte is drifting under the action a DC electric field (dashed curve) of strength $E = 1$ measured in MD units $\epsilon/(e\sigma) \sim 67\text{kV/mm}$. The curves are plotted for $Z_p=40$ and 60 , corresponding to $\xi=1.483$ and 2.225 , respectively. The positions of the Bjerrum and the Debye lengths relative to the chain backbone are also indicated in the figure. It can be seen that, in the absence of an electric field, the time-averaged total charge of the ions within the Bjerrum layer, $r = l_B$, correlates well with the prediction of the Manning theory. Moreover, the number of the coions within this layer is found to be negligibly small as was assumed in Manning’s theory. Furthermore, the slopes of the solid curves for $E = 0$ in Fig. 1 for the polyelectrolytes of different charges, $Z_p=40$ and 60 , become similar for $r = \lambda_D$ to over several units of λ_D , i.e. within the Debye layer. This fact is qualitatively consistent with Manning’s assumption to neglect the effect of the polyelectrolyte charge on the time-averaged behavior of the “unbounded ions” and treat them within the framework of the linear Debye-Hückel theory.

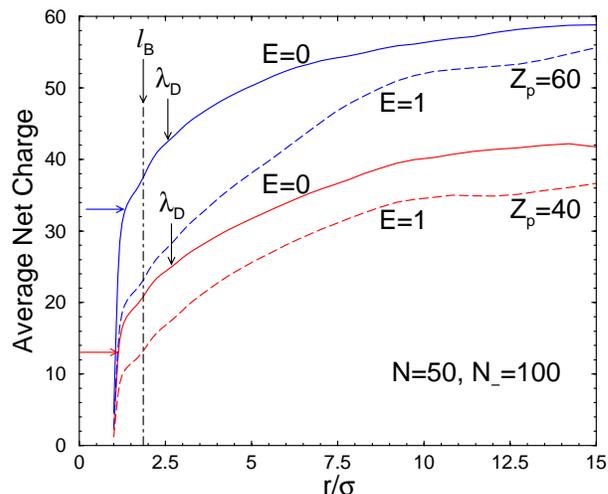


Figure 1: Charge distribution around a polyelectrolyte molecule for two different values of Z_p and for $E=0$ and $E=1$. The horizontal arrows mark the amount of condensed charge predicted by Manning’s theory.

However, in the presence of an external electric field, the charge in the vicinity of the polyelectrolyte is greatly reduced compared to its value when $E = 0$ (see Fig. 1) which in fact is reached only at a distance much further out. This is because some of the condensed counterions are stripped away from the region next to the polyelectrolyte and is in contrast with Manning’s theory for the electrophoresis of polyelectrolytes for $\xi > 1$ [5] and its generalizations [6]-[9], which assume that these counterions are not affected by the drift of the polyelectrolyte in an electric field. Shown in Fig. 2, is the dependence of the average steady state drift velocity, V , on the field

strength E for polyelectrolytes of different charges and chain lengths. In the range of the field strengths considered, V increases at a rate faster than E , hence, the mobility $\mu = V/E$ is an increasing function of E instead of being constant. But since the counterions which had accumulated on the polyelectrolyte are washed out by the field, the effective charge of the polyelectrolyte increases with E . In fact, if we define the effective charge Q_e of the polyelectrolyte as the difference between the bare polymer charge Z_p and the average net ionic charge accumulated inside the Bjerrum layer, we find that a plot of V/Q_e versus E is linear and that the ratio μ/Q_e is roughly equal to a constant to within about 2-3%. This indicates that the nonlinear behavior in the electrophoretic mobility is mainly due to the variation in the effective charge of the polyelectrolyte rather than to a change in the structure or orientation of the molecule under the action of the electric field, in contrast to the models in [5]-[9] which assume the opposite.

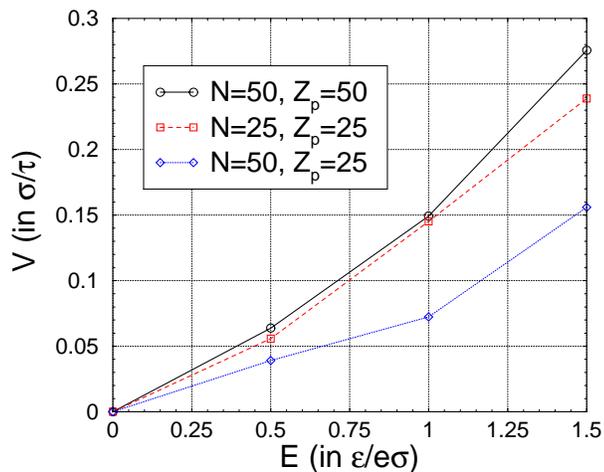


Figure 2: The field dependence of the polyion velocity, V , for different Z_p and N .

On a time scale comparable to or shorter than the diffusion time τ_D , the amount of charge in the vicinity of the molecule is wildly fluctuating. We analyzed the time fluctuations of the ions by calculating the average time correlation of the net ionic charge within the Bjerrum and the Debye layers of the polyelectrolyte at two different times, for polyelectrolytes with charge in the range $0 \leq Z_p \leq 60$, which corresponds to $0 \leq \xi \leq 2.225$. We found that the auto-correlation functions decay and reach values close to zero after a time shift of about a few τ_D , regardless of the charge of the polyelectrolyte and the strength of the electric field. Interestingly, we found that this time scale for the net charge inside the Bjerrum layer to become uncorrelated is the same as the corresponding time scale for the charge within the Debye layer. The fact that the charge inside the Bjerrum

layer is uncorrelated after a time of about τ_D indicates that, on this time scale, individual ions enter or leave the vicinity of the polyelectrolyte independently of one another.

4 SPATIAL CORRELATION OF COUNTERIONS

Although the counterions in the vicinity of the polyelectrolyte are distributed uniformly along the chain backbone on the long time scale, they form clusters on this molecule on a time scale shorter than or comparable to τ_D . We consider a counterion to be condensed whenever it lies within a distance l_B from the polyion and associate each condensed counterion to its nearest bead in the polymer chain which we term a bead-ion pair. We found that these bead-ion pairs are strongly correlated at short length scales. Specifically, to characterize the orientation correlation of the bead-ion pairs, we construct a triangular plane defined by a condensed counterion and its two nearest beads in the polymer chain, and obtain the angle θ between the normals of any two planes defined in this way. Then we compute the average value of $\cos \theta$ for polyions with charge in the range $0 \leq Z_p \leq 60$ as a function of the separation between two condensed counterions. Our analysis shows that the orientations of the bead-ion pairs are strongly correlated at short distances up to $4-5\sigma$, and that condensed counterions separated by larger separations are independent. We also found that an external electric field has very little effect on the spatial correlation for field strengths in the range $0 \leq E \leq 1$, showing that the interaction between the bead-ion pairs is much stronger than the interaction with the electric field, despite the fact that the maximum field strength that we used is much stronger than in typical experiments.

5 SUMMARY

Although the distribution of counterions around a polyion plays an important role in determining the properties of polyelectrolyte solutions, only very few studies have focused on the dynamics of counterion condensation and the distribution of counterions at the local level. Using MD simulations, we investigate, apparently for the first time, the dynamics of counterion condensation on a wandering flexible polyelectrolyte in equilibrium as well as drifting in an external electric field, when the Manning parameter spans from well below to well above the condensation transition for $\xi > 1$. We observe that strong electrostatic interactions cause counterions to form clusters around the polyelectrolyte within which they are packed with short range orientational order. This counterion clustering appears to be robust to changes in the degree of ionization as well as to the application of an external electric field.

Our simulations provide information concerning the detailed arrangement of the condensed counterions along a flexible polyelectrolyte, which is useful in understanding the electrophoretic behavior of these molecules, as well as the interaction between these molecules and other small molecules at the local level and for short time scales.

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