Unfolding polyelectrolytes in trivalent salt solutions using dc electric fields: A study by Langevin dynamics simulations

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We study the behavior of single linear polyelectrolytes condensed by trivalent salt under the action of electric fields through computer simulations. The chain is unfolded when the strength of the electric field is stronger than a critical value. This critical electric field follows a scaling law against chain length, and the exponent of the scaling law is $-0.77(1)$, smaller than the theoretical prediction, $-3\nu/2$ [R. R. Netz, Phys. Rev. Lett. **90**, 128104 (2003)], and the one obtained by simulations in tetravalent salt solutions, $-0.453(3)$ [P.-Y. Hsiao and K.-M. Wu, J. Phys. Chem. B **112**, 13177 (2008)]. It demonstrates that the scaling exponent depends sensitively on the salt valence. Hence, it is easier to unfold chains condensed by multivalent salt of a smaller valence. Moreover, the absolute value of chain electrophoretic mobility increases drastically when the chain is unfolded in an electric field. The fact that the mobility depends on electric field and on chain length provides a plausible way to impart chain-length dependence in free-solution electrophoresis via chain unfolding transition induced by electric fields. Finally, we show that, in addition to an elongated structure, a condensed chain can be unfolded into a U-shaped structure. The formation of this structure in our study is purely a result of the electric polarization, not of the elastohydrodynamics dominated in sedimentation of polymers. © 2009 American Institute of Physics.
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I. INTRODUCTION

To understand well the properties of charged macromolecules in electric fields, including the conformation and mobility, is very important in many domains of research, such as polymer science, biophysics, and microfluidics, because of the large variety of applications.¹ Applying electric fields is at the center of techniques to manipulate charged macromolecules. It can also be used as a tool to separate molecules by sizes. However, for the latter case, experiments are usually performed in a sieving matrix, such as in gel instead of in a solution.¹⁻³ This is because the free draining effect in an electrolyte solution produces an electrophoretic mobility independent of the chain length of macromolecules under a typical electrophoretic condition.⁴ Nevertheless, researchers continue to devote their efforts to finding ways for size separation in free solutions because of its high throughput and applications in microfluidics.

In 2003, Netz^{5,6} proposed a new strategy to achieve this goal by unfolding condensed polyelectrolytes (PEs) in electric fields. He predicted that the chain mobility increases when a condensed PE chain unfolds in an electric field and that the critical electric field to unfold a chain, E^* , depends on the chain length N , following the scaling law $E^* \sim N^{-3\nu/2}$, where ν is the chain swelling exponent. Therefore, longer chains will be unfolded and separated out earlier when the applied electric field slowly increases. His idea has been recently verified by simulations⁷ in which PE

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chains were condensed into globules by tetravalent salts and then stretched in electric fields. A more general form of the scaling law has been proposed in the study, and reads as $E^* \sim V^{-1/2}$, where V is the ellipsoidal volume calculated from the three eigenvalues of the chain gyration tensor. According to the scaling law obtained by the simulations, an electric field of 2 kV/cm should be applied to unfold collapsed PEs of chain length of the order of 10^6 . This electric field is relatively strong.

For practical reasons, we wish E^* to be as small as possible. One way to reduce E^* is to make the condensed chain structure less compact. This aim can be achieved, for example, by increasing temperature, by performing experiments in high-dielectric solutions, or by using a weak condensing agent to collapse PEs. In this paper, we choose the latter method using trivalent salt as the condensing agent and study the static and dynamic properties of chains and the unfolding electric field. Since the electrostatic interaction with trivalent salt is 25% weaker than that with tetravalent salt, some unexpected situations may take place. A key question is to know if E^* still follows the same scaling law of the strong condensation, as shown in the studies of Netz^{5,6} and Hsiao and Wu.⁷ The rest of this paper is organized as follows. In Sec. II, we describe our model and simulation setup. In Sec. III, we present our results. The discussed topics include the degree of unfolding, the critical electric field to unfold a chain, the electrophoretic mobility, the distribution of condensed trivalent counterions on a chain, and the chain conformation after unfolding. We give our conclusions in Sec. IV.

II. MODEL AND SIMULATION SETUP

Our simulation system contains a single PE and trivalent salt placed in a rectangular box with periodic boundary condition. The PE dissociates into a polyion chain and many counterions. The polyion is modeled by a bead-spring chain consisting of N beads; each bead carries a $-e$ charge, where e is the elementary charge unit. The counterions are modeled by spheres; each carries a $+e$ charge. The trivalent salt dissociates into trivalent cations (counterions) and monovalent anions (coions); these ions are also modeled by charged spheres. The solvent is treated as a uniform dielectric medium with a dielectric constant equal to ϵ_r . Three kinds of interactions are considered: the excluded volume interaction, the Coulomb interaction, and the bond connectivity. The excluded volume interaction is modeled by a purely repulsive Lennard-Jones potential

$$U_{\text{ex}}(r) = \begin{cases} 4\epsilon_{\text{LJ}}[(\sigma/r)^{12} - (\sigma/r)^6] + \epsilon_{\text{LJ}} & \text{for } r \leq 2^{1/6}\sigma \\ 0 & \text{for } r > 2^{1/6}\sigma, \end{cases} \quad (1)$$

where r is the distance between two particles, ϵ_{LJ} is the interaction strength, and σ denotes the diameter of a particle. We assumed that all the beads and spheres have identical ϵ_{LJ} and σ . We set $\epsilon_{\text{LJ}} = k_B T / 1.2$, where k_B is the Boltzmann constant and T is the temperature. The Coulomb interaction is

$$U_{\text{Coul}}(r) = \frac{Z_i Z_j \lambda_B k_B T}{r}, \quad (2)$$

where Z_i and Z_j are the valences of the two charges and $\lambda_B = e^2 / (4\pi\epsilon_r\epsilon_0 k_B T)$ is the Bjerrum length, at which two unit charges have the Coulomb interaction tantamount to the thermal energy $k_B T$. We set λ_B to be 3σ to simulate highly charged PEs, such as polystyrene sulfonate. U_{Coul} was calculated by the particle-particle particle-mesh (PPPM) Ewald method. Two adjacent beads (monomers) on the chain are connected by the bond connectivity, modeled by a finitely extensible nonlinear elastic potential,

$$U_{\text{bond}}(b) = -\frac{1}{2} k_b b_{\text{max}}^2 \ln \left(1 - \frac{b^2}{b_{\text{max}}^2} \right), \quad (3)$$

where b is the bond length, b_{max} is the maximum bond extension, and k_b is the spring constant. We set $b_{\text{max}} = 2\sigma$ and $k_b = 5.8333 k_B T / \sigma^2$. The average bond length under this setup is about 1.1σ . An

external uniform electric field $\vec{E}$ is applied toward the x direction. The equation of motion of a particle is described by the Langevin equation,

$$m_i \ddot{\vec{r}}_i = - \frac{\partial U}{\partial \vec{r}_i} - m_i \gamma_i \dot{\vec{r}}_i + Z_i e E \hat{x} + \vec{\eta}_i(t), \quad (4)$$

where m_i is the mass of particle i , $\vec{r}_i$ is its position vector, $m_i \gamma_i$ is the friction coefficient, and $\vec{\eta}_i$ simulates the random collision by solvent molecules. $\vec{\eta}_i(t)$ has zero mean over time and satisfies the fluctuation-dissipation theorem,

$$\langle \vec{\eta}_i(t) \cdot \vec{\eta}_j(t') \rangle = 6k_B T m_i \gamma_i \delta_{ij} \delta(t - t'), \quad (5)$$

where δ_{ij} and $\delta(t - t')$ are the Kronecker and the Dirac delta functions, respectively. The temperature control is incorporated according to this theorem. We assumed that the particles have the same mass m and damping constant γ . We set $\gamma = 1 \tau^{-1}$, where $\tau = \sigma \sqrt{m / (k_B T)}$ is the time unit. We know that the dynamics of polymers in dilute solutions is described by the Zimm model.⁸ However, when an electric field is applied in a typical electrophoretic condition, the hydrodynamic interaction is largely canceled out due to the opposite motions of the ions in the electrolyte solution.^{1,9,10} Therefore, in this study, we neglected the hydrodynamic interaction. Hydrodynamic interaction is important only when the chain length is very short.^{11,12}

We varied the chain length (or the number of monomers) from 24 to 384 and studied the static and dynamic properties of PE under the action of an electric field up to a field strength of $E = 2.0 k_B T / (e\sigma)$. We set the monomer concentration to $C_m = 0.0001 \sigma^{-3}$. In order to keep C_m constant, the size of the simulation box needs to be changed with N . Instead of using a cubic simulation box, we chose a rectangular parallelepiped of $1.6N\sigma \times 79.06\sigma \times 79.06\sigma$, where the box size in the field direction is linearly proportional to N to prevent overlap with itself under periodic boundary condition when the chain unfolds. The added salt concentration was fixed at $C_s = C_m/3$, the equivalence point (C_s^*). It has been shown that at this salt concentration, the chain collapsed into a compact globule structure in the absence of an electric field,^{13,14} with its effective chain charge almost being neutralized. We performed Langevin dynamics simulations¹⁵ with an integrating time step equal to $\Delta t = 0.005 \tau$. We first ran 10^6 – 10^7 time steps to bring the system to a steady state and then ran 10^8 time steps to accumulate data for analysis. To simplify the notation, we assign in the following text, that σ , m , and $k_B T$ are the units of length, mass, and energy, respectively. Therefore, the concentration will be described in units of σ^{-3} , the strength of the electric field in units of $k_B T / (e\sigma)$, and so forth.

III. RESULTS AND DISCUSSIONS

A. Degree of unfolding

We start by studying the chain conformation under the action of an electric field. The degree of unfolding, defined as the ratio of the end-to-end distance R_e of a chain over chain contour length $L_c = (N-1)b$, is used to characterize the conformation. The results are plotted in Fig. 1 as a function of E .

Each curve in the plot denotes the variation in R_e/L_c for a given chain length N . We can see that when the electric field is weak, the ratio is a constant. This indicates an unperturbed conformation of the chain, and the chain remains in a collapsed structure. An abrupt increase appears when E is increased over some critical value E^* . R_e can become as large as 90% of L_c if the applied field is very strong. This indicates a structural transition from a collapsed structure to an elongated structure. We noticed that the value of E^* depends on the chain length. The longer the chain length is, the smaller the E^* will be. Moreover, this structural transition happens in an interval of E . The size of the interval decreases with increasing chain length. Although the transition becomes sharper when the chain length is long, R_e increases in a continuous way with E , which suggests a second-order transition.

FIG. 1. R_e/L_c as a function of E at $C_s=C_s^*$ for different chain lengths N . The symbol $\times$ denotes the inflection point of the curve.

B. Critical electric field E^*

The dependence of the critical electric field E^* on the chain length N has been investigated in salt-free^{5,6} and in tetravalent salt solutions.⁷ Both of these studies showed that E^* scales as $N^{-0.5}$ to unfold a condensed chain. It is now important to know if this scaling law is valid for a PE chain condensed by trivalent counterions. To verify it, we first follow the method proposed by Netz:^{5,6} E^* is calculated by equating the polarization energy $U_{\text{pol}}=\vec{p}\cdot\vec{E}/2$ and the thermal fluctuation energy $k_B T$. Here $\vec{p}$ is the dipole moment of the PE-ion complex induced by the electric field and calculated by $\vec{p}=\sum_i Z_i e(\vec{r}_i-\vec{r}_{\text{cm}})$, where $\vec{r}_i$ is the position vector, running over all the particles inside the complex, and $\vec{r}_{\text{cm}}$ is the center of mass of the PE. The complex is considered as a set of particles, including monomers and ions, inside the region of a worm-shaped tube, which is the union of the jointed spheres with a radius of $r_t=3$, centered at each monomer center. The component of $\vec{p}$ at the field direction, p_x , is plotted against the field strength E in Fig. 2.

As seen in the log-log plot, p_x increases linearly with E with a slope equal to 1, when E is small. This is the well-known linear response of a dielectric object, $p_x=\alpha E$, which has been reported in the previous studies.^{6,7} However, different from the previous studies, we found that this linear region terminates before intersecting with the dotted line that denotes the relation $p_x E/2=k_B T$, especially when the chain is long. This is simply because the binding force to condense the PE chain in the trivalent salt solutions is weaker than that in the tetravalent salt.⁷ For the system studied by Netz,^{5,6} the chains were strongly condensed because of the unrealistically strong Coulomb coupling chosen by him. Therefore, his method can be used only as a rough estimation of E^* for the case of strong condensation but it is not suitable for the case of weak condensation. If we are going to continue with his method and calculate the intersection between the extended linear region and the dotted line, we will find that E^* scales as $N^{-0.463(4)}$. [See the open circles in Fig. 3(a).] This scaling law seems to follow the prediction of Netz, $N^{-3\nu/2}$, because the chain swelling exponent in zero electric field is $\nu=0.321(2)$ for this case [cf. Fig. 3(b)]. Nevertheless, E^* obtained by this method is actually overestimated, going much over the linear response region, especially when the chain is long.

To give a more accurate estimation of E^* , we follow here the definition of the unfolding electric field by simply taking the electric field at the inflection point of the curve R_e/L_c versus E . The inflection point on each curve in Fig. 1 is indicated by the symbol “ $\times$.” The scaling law

FIG. 2. p_x as a function of E for different chain lengths N . The dotted line denotes the equation $p_x E / 2 = k_B T$.

obtained by this method reads as $E^* \sim N^{-0.77(1)}$. [See the closed squares in Fig. 3(a).] The exponent $-0.77(1)$ is significantly smaller than the one obtained by Netz's method. Therefore, this E^* is smaller than Netz's prediction when chain is long. Moreover, we found that it is easier to unfold a PE chain in trivalent salt solutions than in tetravalent salt solutions. For example, for a chain of the length of 10^6 , E^* is 1.76×10^{-4} according to the scaling law. This E^* corresponds to about 185 V/cm, much smaller than 2 kV/cm predicted for the chains condensed by tetravalent salt in simulations.⁷ Our results show that the valence of the condensing agent plays an important role in the determination of the scaling law. There must exist a more complicated mechanism to polarize and to unfold a PE chain in an electric field discussed here. This mechanism will be investigated in detail in the future.

FIG. 3. (a) E^* vs N where the open circles denote data obtained by Netz's method and the closed squares denote data obtained from the inflection points. (b) Radius of gyration R_g vs N in zero electric field.

FIG. 4. μ_{PE} as a function of E for different chain lengths N .

C. Electrophoretic mobility and ion condensation

We now study the electrophoretic mobility μ_{PE} of a PE chain in electric fields with different strengths and show how μ_{PE} changes with E when the chain is unfolded to an elongated structure. μ_{PE} was calculated by v_{PE}/E , where v_{PE} is the velocity of the center of mass of the chain in the field direction. The results are shown in Fig. 4.

In weak electric fields μ_{PE} is nearly zero, indicating that the PE chain is effectively charge neutral, as reported in experiments.¹⁶ While E is increased over E^* , μ_{PE} turns to be negative and the chain starts to drift opposite of the field direction, which suggests a negative effective chain charge. We found that the stronger the field, the faster the chain will drift. For a long chain μ_{PE} shows, furthermore, a plateau region when $E > E^*$. The dependence of μ_{PE} on the electric field and the chain length gives a plausible way to electrophoretically separate PE chains by size in free solutions by means of a chain unfolding transition.⁷

The variation in μ_{PE} can be related to the ion condensation on the chain under the action of the electric field. Therefore, we studied here the number of the condensed trivalent ions on the chain by counting the ions inside the worm-shaped tube with a radius of $r_t=3$ around the chain. The results for $N=384$ in different strengths of electric field are plotted in Fig. 5 against the monomer index ι , rescaled from 0 to 1, where $\iota=0$ denotes the first monomer heading toward the field direction and $\iota=1$ denotes the last monomer of the other chain end.

We saw that $N_c(\iota)$ is flat when the applied field is small, $E \leq 0.007$, which shows a uniform distribution of the condensed trivalent ions along the chain. There is about 0.33 trivalent counterions, condensed on each monomer, which indicates the neutralization of the negatively charged chain backbone by these condensed counterions. If we further increase the electric field, these condensed ions distribute nonuniformly on the chain where fewer ions condensed near the heading end ($\iota=0$) than the tailing end ($\iota=1$). When $0.07 < E < 0.2$, $N_c(\iota)$ looks similar to an inclined line and the slope increases with E , resulting in a decrease in the total number of the condensed trivalent counterions on the chain. Therefore, $|\mu_{PE}|$ increases with E due to this partial detachment of the condensed ions by the electric field. At this moment, the PE-ion complex is polarized in a way that the condensed trivalent counterions are bound, basically immobile, on the chain. For the higher electric field, $0.2 < E < 1.0$, $N_c(\iota)$ becomes a horizontal sigmoidal curve and the value in the middle chain region is independent of E . The appearance of this horizontal region reflects the fact that the condensed trivalent counterions are now gliding on the chain. These ions can be stripped

FIG. 5. $N_c(l)$ obtained in different field strengths. The value of E is indicated near each curve.

off the chain by the strong electric field and the other ions in the bulk solution then condense onto it, establishing a steady state. The total number of the condensed trivalent counterions is approximately a constant in this electric field, which results in the plateau region of μ_{PE} against E . For an even stronger electric field, such as $E=2.0$, the base line of the horizontal sigmoidal curve moves downward. The condensed trivalent ions are stripped off the chain even more. The effective chain charge is thus more negative and $|\mu_{PE}|$ increases.

D. Conformation of an unfolded PE chain

In our simulations, the PE chains were unfolded for most of the time to an extended structure, similar to a straight line, aligned parallel to the field direction [see Fig. 6(a)]. Nonetheless, we sometimes observed that they were unfolded to a U-shaped structure in the electric fields. The open side of the U shape can point opposite and toward the chain drifting direction, as shown in Fig. 6(b) and 6(c), respectively.

This U-shaped structure has been observed experimentally in electrophoresis of microtubules¹⁷ and has also been shown in simulations of the elastic uncharged/charged chains in Stokes flows or in electric fields.^{18–21} These studies showed that a combination of the elastic and the hydrodynamic effects results in the bending of a rigid chain into a horseshoe shape, oriented perpendicular to the direction of motion.^{18,21} If chains are charged and the driving force is an electric field, another effect, the electric polarization of the PE complex, will play a role that favors parallel orientation to the electric field and competes with the elastohydrodynamic effect.¹⁹ In our simulations, the PE chains are flexible and the hydrodynamic interaction is neglected. Therefore, a different mechanism drives the chains to form U-shaped structures where the field-induced dipole moments on the two branches of a U-shaped chain establish equilibrium. This phenomenon can be seen by plotting in Fig. 7 the distribution of the condensed trivalent counterions $N_c(l)$ for the two U-shaped chains from Figs. 6(b) and 6(c), respectively.

The symmetry of $N_c(l)$ with respect to the middle point of the chain ($l=0.5$) shows that an equilibrated polarization was established on the two branches of the U chain in the electric field. The existence of two pointing directions of the open side of the U chain is a feature especially for the electric polarization. It is distinguishable from the elastohydrodynamic effect where only the U-shaped structure with the open side opposite to the moving direction is produced. Moreover, we noticed that the electrophoretic mobility of a U-shaped chain is approximately equal to that of an elongated chain of half of the chain length. For example, μ_{PE} is $-0.209(4)$ in Fig. 6(b), close to

FIG. 6. Snapshots of unfolded PE chains in electric fields. The yellow, white, red, and green spheres represent the monomers, monovalent counterions, trivalent counterions, and coins, respectively. The chain length, electric field, field direction, and chain drifting direction are indicated in the figure.

the mobility of the elongated chain of $N=96$, $-0.225(3)$. Furthermore, we verified the stability of these U-shaped chains and found that they can persist through the whole simulation period corresponding to, at least, the order of microseconds. However, by introducing some perturbations such as ac electric fields, the U-shaped structure can be transferred into the elongated chain structure but the inverted direction of transfer cannot be realized. Therefore, the U-shaped structure is probably metastable. We have calculated the total energy of the system for the U-shaped chain structure and also for the extended-chain structure. We found that the former energy is, at

FIG. 7. $N_c(t)$ for the two U-shaped chains in Figs. 6(b) and 6(c), respectively.

least, 5% higher than the latter. Moreover, the U-shaped chain has a slower electrophoretic mobility than the extended chain, which implies a larger number of counterions condensed on the U-shaped chain to decrease the effective chain charge; consequently, fewer ions are presented in the bulk solution, and the entropy of the solution is small compared to the one where the chain displays an extended structure. Therefore, the free energy of the system is lower for the extended chain than for the U-shaped chain. This estimation supports that the U-shaped structure is metastable. Since the open side of the U-shaped chain can point to one of the two directions, along or against the field direction, we predict the existence of other metastable states, due to polarization, in which the chain shows many bends, such as S- or W-shaped structures, in electric fields.

IV. CONCLUSIONS

We have studied the behavior of single PEs condensed by trivalent salt under the action of a uniform electric field by means of Langevin dynamics simulations. We found that the chains unfolded, while the strength of the electric field is stronger than some critical value E^* , similar to the previous study where the chains were condensed by tetravalent salt.⁷ E^* shows scaling-law dependence on the chain length N that reads as $E^* \sim N^{-0.77(1)}$. The exponent in the scaling law is different from the prediction by Netz^{5,6} and from the simulations in tetravalent salt solutions,⁷ which demonstrated the importance of the salt valence on the exponent. Therefore, the weaker the condensing agent, the larger the absolute value of the exponent and the easier the unfolding of a condensed chain. We showed that the electrophoretic mobility of chain $|\mu_{PE}|$ drastically increases while the chain is unfolded. The distribution of the condensed counterions on the chain was studied and related to the change in the mobility in different regions of the electric field. The dependence of μ_{PE} on the chain length and the electric field enables us to devise a way to impart chain-length dependence in free-solution electrophoresis through chain unfolding mechanism in electric fields. Finally, we pointed out the possibility of unfolding a condensed PE chain into a U-shaped structure in electric fields, in addition to the elongated structure, with the open side of the U heading or tailing the chain drifting direction. This structure is a result of purely electric polarization, different from the formation of the horseshoe-shaped chains in sedimentation experiments caused by elastohydrodynamics.

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