Influence of higher valent ions on flexible polyelectrolyte stiffness and counter-ion distribution

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We investigate the influence of counter-ion valency on the flexibility of highly charged flexible polymer chains using molecular dynamics simulations that include both salt and an explicit solvent. As observed experimentally, we find that divalent counter-ions greatly reduce the chain persistence length, $l_p$, in comparison with monovalent counter-ions. On the other hand, polyelectrolyte chains having trivalent counter-ions adopt a much more compact conformation than polyelectrolytes having monovalent and divalent counter-ions. We demonstrate that the tendency of polyelectrolyte chains to become deformed by proximal high valence counter-ions is due to chain “coiling” around the counter-ions. In particular, we find that the number of contacts that the proximal counter-ions have with the polyelectrolyte dictates the extent of chain coiling. This ion-binding induced coiling mechanism influences not only the conformational properties of the polyelectrolyte, but also the counter-ion distribution around the chain. Specifically, we find that higher valent counter-ions lead both to a counter-ion enrichment in close proximity to the polyelectrolyte and to a significant reduction in the spatial extent of the diffuse counter-ion cloud around the polyelectrolyte. [http://dx.doi.org/10.1063/1.4947221]

I. INTRODUCTION

A microscopic understanding of solution properties of highly charged polyelectrolytes is required for diverse manufacturing applications involving water soluble polymers and for understanding many biological processes. However, a theoretical understanding of solutions of these molecules has been slow to develop due to the complex coupling between the conformation of the polyelectrolyte chain and the structure of the ionic species in solution due to the long range Coulomb interactions between themselves and with the polyelectrolyte. Mean-field and other approximate theories\textsuperscript{1–8} and various experimental techniques\textsuperscript{9–14} have qualitatively indicated a “two-zone” picture describing the counter-ion distribution around the polyelectrolyte; a fraction of the counter-ions strongly associates with the chain backbone on a scale of the order of the chain segment size, while a significant fraction of a counter-ions form a diffuse “cloud” around the chain due to residual unscreened polyelectrolyte charge. However, the impact of charge valence on the counter-ion concentration in these zones and the impact of counter-ions on the chain conformational properties and, by extension the polyelectrolyte solution properties, are not yet well understood.

The bending and flexibility of polyelectrolyte chains, such as DNA and polystyrene sulfonate, is generally characterized by its persistence length, $l_p$, which is the sum of two contributions in the often cited Odijk, Skolnick, and Fixman theory:\textsuperscript{15,16} the first contribution reflects the “bare” or intrinsic chain stiffness, $l_p^0$, and the second derives from the electrostatic repulsion between the polyelectrolyte segments, $l_{ep}$, mediated by the counter-ions. Measurements have shown that the introduction of higher valence counter-ions can lead to large changes of the polyelectrolyte rigidity,\textsuperscript{17–21} as measured by $l_p = l_p^0 + l_{ep}$, an effect that is strongly correlated with the high frequency dynamics (picosecond range) of the polyelectrolyte measured by neutron scattering measurements.\textsuperscript{20} According to this theory, the electrostatic contribution is always positive, $l_{ep} > 0$, and higher valent counter-ions reduce the electrostatic repulsion and $l_p$. However, experiments clearly show that under certain conditions electrostatics can enhance the chain flexibility resulting in a negative contribution, $l_{ep} < 0$.\textsuperscript{17,22,23} Attempts to account for this effect have been made by considering how the distribution of counter-ions surrounding the polyelectrolyte couples to the chain conformation. This coupling has been described in the terms of counter-ion fluctuations\textsuperscript{24–26} or it is assumed that some of the counter-ions are loosely bound so that they reduce the effective polyelectrolyte charge,\textsuperscript{3,7,26,27} as in the Manning model of charge condensation.\textsuperscript{28,29}

Measurement advancements in recent years have allowed experiments to probe counter-ion structure in polyelectrolyte solutions at a nanometer scale. Small angle neutron and x-rays scattering studies indicate that the counter-ions are strongly spatially correlated with the molecular conformation.\textsuperscript{30–33} At the same time, the spatial extent of the divalent counter-ion distribution is found to be smaller than in the case of monovalent counter-ions.\textsuperscript{34–37} This local enrichment of divalent counter-ions in the proximity of the chain backbone coincides with drastic changes in the conformational properties,\textsuperscript{17,19,21} indicating that there is strong coupling between the polyelectrolyte and the distribution of counter-ions.\textsuperscript{38} However, the microscopic mechanism of this coupling

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as well as the quantification of the counter-ion distribution remains an open question.

We investigate the microscopic mechanism by which higher valence counter-ions influence the average molecular shape and flexibility of our model polyelectrolyte chain having high charge density in an explicit solvent solution with added salt that also interacts with the polyelectrolyte chain. We use molecular dynamics (MD) simulations of a coarse-grained bead-spring chain model with an explicit solvent. This coarse-grained model seems suitable since the change in the stiffness with counter-ion valence is a generic effect seen in semiflexible polyelectrolytes ranging from DNA, and RNA, to polystyrene sulfonate.

We calculate $l_0$ of the polyelectrolyte chain in different ionic environments with higher valent counter-ions while keeping the relevant electrostatic length scales fixed. To better understand from the observed stiffness variation, we also quantify the distribution of counter-ions, both at close proximity to the polyelectrolyte chain and at longer length scales corresponding to counter-ions that are diffusely associated with the polyelectrolyte. Based on these results, we rationalize the resulting effects of the counter-ions on the polyelectrolyte chain flexibility.

Our paper is organized as follows. Section II contains details of the model and simulation methods. Results of the characterization of the shape and flexibility of the polyelectrolytes at different ionic solvents are presented in Section III. Section IV concludes the paper.

II. MODEL AND METHODOLOGY

We employ a bead-spring model of Lennard-Jones (LJ) segments bound by stiff harmonic bonds suspended in explicit LJ solvent particles, some of which are charged to represent counter-ions and ions from added salt. The particular model incorporates minimal aspects of real polyelectrolyte solution while at the same time it allows for equilibrated molecular dynamics with an explicit solvent. The added cost in computational time required by inclusion of an explicit solvent is necessary to fully capture the polyelectrolyte structural and dynamical behavior, as indicated by a series of studies.

Moreover, simulation of the competitive binding of the solvent and counter-ions to the polyelectrolyte backbone, an essential feature of these molecules, requires an explicit solvent. Competitive binding of the molecular spaces to macromolecules is known to greatly alter the phase behavior of polymer solutions, leading to often counter-intuitive phase behavior. Even greater complexity can be expected when associated species have long range interactions.

All macro-ion segments, dissolved ions, and solvent particles are assigned the same mass $m$, size $\sigma$, strength of interaction $\varepsilon$, and all dissolved ions are monovalent. We set $\varepsilon$ and $\sigma$ as the units of energy and length; the cutoff distance for LJ interaction potential is $r_c = 2.5 \sigma$. Polyelectrolyte molecular mass ranges from $M_w = 11$ to 101 segments carrying a total charge $-Z_e \varepsilon$ distributed uniformly along the molecular structure, where $\varepsilon$ is the elementary charge. The charge per macro-ion segment is labeled as $\lambda$.

The bonds between polymer segments are connected via a stiff harmonic spring, $V_B(r) = k(r - l_0)^2$, where $l_0 = \sigma$ is the equilibrium length of the spring, and $k = 1000 \varepsilon/\sigma^2$ is the spring constant. All charged particles interact via the Coulomb potential, and the particle-particle particle-mesh method is used. The operating conditions are typical of the LJ liquid state: density $\rho = 0.8$ and reduced temperature $k_B T/\varepsilon = 1$, the latter condition maintained by a Nosé-Hoover thermostat.

The system is composed of a total of 64,000 solvent particles in a periodic cube of side $L$. The system includes $N_c$ ions of charge $-e$ and valence $z_c = 1$ and $N_+ = (z_+ N_c + Z_p) / z_c$ counter-ions, where $z_c$ is the counter-ion valence with $z_+ = 1, 2, \text{and} 3$; all systems have neutral total charge. The strength of electrostatic interactions with respect to the thermal fluctuations is determined by the Bjerrum length, $l_B = e^2/\varepsilon k_B T$ ($\varepsilon$ is the solvent dielectric constant, $T$ is the temperature, and $k_B$ is Boltzmann’s constant) and in our simulations we have $l_B/\sigma = 1.85$. Aside from the Bjerrum length, the other key length parameter for an ionic solution is the Debye screening length: $\lambda D = \left[4\pi \rho_s \left(\frac{z_+^2 \rho_s + z_-^2 \rho_s}{2}\right)\right]^{1/2}$, where $\rho_s = N_c/L^3$ are the ion densities. Simulations are conducted for $l_B/\sigma = 1.85$ and $\lambda_D/\sigma \approx 2.4$. The number of ions for each case is presented in Table I. Typical simulations equilibrate for 2000 $\tau$ and data are accumulated over a 7500 $\tau$ interval, where $\tau = \sigma (m/\varepsilon)^{1/2}$ is the MD time unit.

III. RESULTS

To quantify the change in polyelectrolyte rigidity with counter-ion valence, we use the worm-like chain (WCL) model, which treats polymers in solution as an ensemble of smoothly bending space curves in which the correlation in tangential direction is exponential.
Here, $s_1$ and $s_2$ denote the unit tangent vectors at any two points along the chain contour. The total contour length of the chain is $M_w$. In this model, there are two extremes: rod-like polymers with $M_w \sigma \ll l_p$, and random coils in another, $M_w \sigma \gg l_p$, while all other cases lie in between these two extremes. From the WLC model, one can derive, from Eq. (1), an expression for the radius of gyration, $R_g$:

$$R_g = \left[-\frac{y^2}{3} + 2y^3 - 2y^4(1 - e^{-1/y})\right]^{1/2}, \tag{2}$$

where $y = l_p/(M_w \sigma)$. We then calculate $R_g$ in our model (Fig. 1) and utilize Eq. (2) to estimate $l_p$. For chains without charges, $l_p$ is comparable with the segmental size, $l_p / \sigma \approx 1$, Fig. 1. For monovalent counter-ions, polyelectrolyte chains indeed stretch considerably due to the repulsion between macro-ion segments, so that $l_p / \sigma > 1$, consistent with the experimental expectation that charges enhance the molecular conformation; for our model we find $l_p / \sigma \approx 3.4$. On the other hand, higher valent counter-ions lead to a reduction of the chain size relative to monovalent counter-ions, see Fig. 1. Specifically, $l_p \approx 1.4$ for divalent case, which is smaller by factor of two with respect to monovalent counter-ions, a finding in good accord with experiments for DNA, RNA, and polystyrene sulfonate.\textsuperscript{17,20,21} Additionally, the persistence length obtained for divalent counter-ion is comparable to the persistence length for neutral chains. Similar simulation results (not shown here) are obtained in the case of salt-free solvents. For trivalent counter-ions, we find $R_g$ and $l_p \approx 0.6$ to be smaller than neutral chains, indicating that the polyelectrolyte is significantly more compact than worm-like conformation found for monovalent and divalent counter-ions.

The molecular conformations in linear chains with a uniformly distributed charge reflect a balance between the repulsion of charged segments of the macro-ion and the covalent bonds between the chain segments. In a mean field approximation, the main contribution comes from the Coulomb repulsive interactions between the segments, and the strength of these repulsive interactions is mediated by the density of the ions in the solvent. Since these interactions are expected to be repulsive then it is also expected for the polyelectrolyte to adopt rod-like molecular conformations. To determine to what degree a polyelectrolyte chain resembles a rod-like polymer or a random coil, we compare its shape to a chain with stiff bending potential and a chain without any charges. We use the ratio of the hydrodynamic radius over the radius of gyration, $R_h/R_g$, which is useful descriptor to quantify the shape of polymers:\textsuperscript{46,49} the calculation of $R_h$ is based on the friction coefficient of an arbitrary shaped Brownian particle. The values of $R_h/R_g$ for a smooth sphere are $1.29$, for a random walk are $0.79$, and this ratio approaches to zero for infinite long rod-like objects.\textsuperscript{46,47} Unlike rigid rods, polymers exhibit flexible molecular conformation, meaning that we need to calculate the time average molecular shape, i.e., $\langle R_h/R_g \rangle$. As we showed in a previous study,\textsuperscript{50} for monovalent counter-ions the linear chains become more anisotropic as $M_w$ increases. However, it is clear that polyelectrolyte chains have a relatively stretched “worm-like” configuration with respect to chains having no charges, but nonetheless their shape is quite distinct from a rod (see Fig. 2 for screenshots and Fig. 1(a)), consistent with experimental observations.\textsuperscript{51} For divalent counter-ions, this ratio is comparable to the neutral polymer chains ($\lambda = 0$), which is consistent with our $R_g$ discussion above. For trivalent counter-ions, $\langle R_h/R_g \rangle \approx 1$ signifying a more compact molecular conformation with respect to a random coil in ideal

**FIG. 1.** (a) Screenshots of the molecular conformation of a polyelectrolyte chain having molecular mass $M_w = 101$ at different counter-ion solvents. The particle colors correspond to polyelectrolyte chain (red), counter-ions (blue), and the coion (orange). (b) Radius of gyration, $R_g$, of a polyelectrolyte chain as function of $M_w$. Results for neutral chains are also presented. The dashed lines represent fits to worm-like chain model, Eq. (2), with the persistence length $l_p/\sigma \approx 3.4, 1.4$, and $0.6$ for monovalent, divalent, and trivalent counter-ions, respectively. The error bars correspond to two-standard deviations.

**FIG. 2.** Time average ratio of the hydrodynamic radius over the radius of gyration, $R_h/R_g$, for macromolecules (with charge per segment, $\lambda = 1$, and no charge, $\lambda = 0$) as function of molecular mass, $M_w$. Results for different counter-ion valance are also presented. The error bars indicate two standard deviations. The arrows correspond to the reference values of reference objects, for a smooth sphere is $1.29$, for the rod approaching infinite length their ratio is approaching $0$, while self-avoiding walks in $\theta$-solvent equals $0.79$.\textsuperscript{46,47}
conditions. However, we cannot characterize the molecular conformations as “collapsed”, as this would indicate that the shape would be closed to smooth sphere limit.

Why would the chain contract in size resulting in to a more compact molecular conformation for higher valence counter-ions? A more compact molecular conformation than that of a random coil suggests a negative contribution to the persistence length from the electrostatic interactions. This feature is not predicted within the OSF theory. This propensity of the persistence length to be reduced by the counter-ion valence has been noted in previous theoretical work. A possible interpretation is that the molecular structure is coupled to its ionic environment. The propensity of the counter-ions to localize in the proximity of the chain backbone for polyelectrolytes of sufficient charge density reduces the effective charge along the polyelectrolyte chain. To better understand the mechanism of how the persistence length of flexible polyelectrolytes is influenced by higher valent counter-ions, a microscopic picture is needed. To probe this question, we examine the distribution of the counter-ions in close proximity to the polyelectrolyte, as well as, at larger length scales.

The counter-ions in close proximity to the polyelectrolyte should have a particularly large effect on the chain conformation, so we first focus on the counter-ions close to the macro-ion chain backbone, i.e., at a distance \( r < 1.1 \sigma \). The particular distance is based on a consideration of the average distance of counter-ions defining the first coordination shell of the polymer. By using this definition, we exclude the counter-ions that are in close proximity but which are not physically direct contact with the polyelectrolyte chain. These “interfacial” counter-ions are transiently bound (i.e., correlated in position in a time-averaged sense) with the chain backbone where their number fluctuates around an average value, \( \langle n_{\text{int}} \rangle \), see Fig. 3(a). For the range of \( M_w \) values that we have explored, we do not find \( \langle n_{\text{int}} \rangle / M_w \) saturating as we increase \( M_w \). Moreover, we observe a non-trivial behavior where \( \langle n_{\text{int}} \rangle / M_w \) is higher for divalent counter-ions. These results, regarding \( \langle n_{\text{int}} \rangle / M_w \), are in contrast to the assumption taken in Manning condensation model that for given conditions, a fixed amount of counter-ions condenses on a rod-like polyelectrolyte. Rod-like polyelectrolytes have only one possible molecular conformation, thus any models that rely on the above mentioned assumption do not capture the molecular conformation changes in response to the condensed counter-ions.

Due to the close proximity to polyelectrolyte, these interfacial counter-ions screen a significant portion of the bare charge; we calculate an effective polyelectrolyte charge as \( Q_{\text{macro}} = Z_p - z_e \langle n_{\text{int}} \rangle \). Higher valent counter-ions are more effective at screening the polyelectrolyte charge. Fig. 3(b). This behavior provides an explanation as to why a higher value of \( \langle n_{\text{int}} \rangle / M_w \) is observed for divalent counter-ions rather than for trivalent counter-ions. A smaller number of trivalent counter-ions are needed to fully screen the bare polyelectrolyte charge than in the case of divalent counter-ions, since trivalent counter-ions have more charge than the divalent counter-ions. On the other hand, \( R_g \) for monovalent counter-ions is quite large with respect to higher valent counter-ions, meaning that the local polyelectrolyte charge density is low, thus the population of monovalent counter-ions is small leading to a small screening of the bare polyelectrolyte charge. This enhancement of the screening effect is generally appreciated in the polyelectrolyte field, and we next dig deeper into the molecular mechanism by which higher valent ions decrease chain rigidity.

The average charge found in the interfacial layer is highest for trivalent case and \( \langle n_{\text{int}} \rangle \) is higher in the divalent

![FIG. 3.](image-url)
case than in the other cases; see Fig. 3(b), suggesting a non-trivial relation between \( \langle n_{\text{int}} \rangle \) and screening of the bare charge. How do these interfacial counter-ions interact with the polyelectrolyte and regulate its size? We calculated the time average number of contacts these interfacial counter-ions have with the polyelectrolyte chain, \( \langle n_{\text{cont}} \rangle \), as can be seen in Fig. 3(c). Moreover, to quantify the trends of \( \langle n_{\text{cont}} \rangle \) with \( M_w \), we fit the data points to the following relation:

\[
\frac{\langle n_{\text{cont}} \rangle}{M_w} = n_{\text{cont}}^\infty \text{erf}(M_w^{1/2}/c),
\]

where \( n_{\text{cont}}^\infty \) is the number of contacts for \( M_w \to \infty \), \( c \) is a parameter set as \( c = 5 \), and erf is the error function. From fitting Eq. (3), we find \( \langle n_{\text{cont}} \rangle/M_w \) to sharply increase for higher valent counter-ions with \( n_{\text{cont}}^\infty \approx 0.38, 1.43, \) and 1.57 for monovalent, divalent, and trivalent counter-ions, respectively. This result suggests that there is an increase in \( n_{\text{cont}} \), but this trend does not necessarily mean that there is an increase in the number of contacts per interfacial counter-ion, since an increase of \( n_{\text{int}} \) would also increase \( n_{\text{cont}} \). To probe this issue, we calculated the probability distribution of the number of contacts that an individual interfacial counter-ion has \( p(n_{i,\text{cont}}) \), where \( \sum_{i=1}^{n_{\text{int}}} n_{i,\text{cont}} = n_{\text{cont}} \).

The resulting probability distributions are presented in Fig. 4. It is clear that the probability of finding a counter-ion with a large number of contacts increases significantly. For example, for \( n_{i,\text{cont}} = 5 \) the probability \( p(n_{i,\text{cont}} = 5) \) increases by a factor of approximately 35 times for trivalent counter-ions in comparison to monovalent counter-ions, as illustrated in Fig. 4. This substantial increase in the number of contacts per interfacial counter-ion can only mean one thing: the polyelectrolyte chain are evidently coiling around the interfacial counter-ions.

What drives this coiling behavior? Due to the strong attractive Coulomb interactions between the counter-ions and the polyelectrolyte, one may assume that the polyelectrolyte chain has the tendency to maximize these interactions. Let us first tentatively assume that this is an enthalpy driven effect. The maximization of the number of contact interactions between the interfacial counter-ions and the polyelectrolyte can be done in two ways. The first way involves maximizing the number of interfacial counter-ions and the second way of maximizing the number of contacts over a small number of interfacial counter-ions. However, there are other interactions that need to be considered. Maximization of the number of interfacial counter-ions along the polyelectrolyte chain would lead to an unfavorable state due to the repulsive interactions between the interfacial counter-ions. If on the other hand the polyelectrolyte chains maximize the number of contacts with the interfacial counter-ions, then the molecular state also becomes unfavorable because the chain coiling results in a more compact molecular conformation, thus enhancing the strong repulsive interactions between the polyelectrolyte charged segments. Thus, at equilibrium a polyelectrolyte chain coils around the interfacial counter-ions by balancing the number of interfacial counter-ions and the number of contacts. As discussed above, \( \langle n_{\text{int}} \rangle \) displays a non-trivial behavior both with higher valent counter-ions, as well as, with \( M_w \). Evidently, this coiling behavior is both an enthalpic and entropic driven process.

The coiling of the polyelectrolyte chain around the interfacial counter-ions is in line with the proposed two-stage mechanism of DNA bending by proteins, where the proteins bind first and then DNA bends around the protein.\(^\text{52}\) Rouzina and Bloomfield\(^\text{18}\) have likewise argued that the strong binding of the higher valent ion to the duplex DNA leads to an elastic distortion of the chain through a “bending polaron” mechanism.\(^\text{18}\) Our simulations show that the double helix structure of the polymer is not required to observe this chain kinking effect, and, indeed, higher valent ions are observed to reduce \( l_p \) in other polymers than duplex DNA molecules, such as sulfonate polystyrene.\(^\text{20}\)

The chain coiling of the polyelectrolyte chain not only influences the persistence length but also the short-ranged interactions of the polyelectrolyte chain with the solvent. Since we explicitly model the solvent, we can quantify how these interactions are affected by the chain coiling. We then calculate the probability distribution of the number of solvent particles in the interfacial layer, \( p(n_{\text{sol}}) \) based on the definition of the interfacial layer described above. In Fig. 5, we present the distributions \( p(n_{\text{sol}}) \) for a polyelectrolyte chain with \( M_w = 41 \) at different ionic solutions. Evidently, there is a significant reduction in the number of solvent particles in the interfacial layer in the case of higher valent counter-ions. This reduction in \( n_{\text{sol}} \) is strongly correlated with an increase in \( n_{\text{cont}} \), as illustrated in Fig. 5. We then have unequivocal evidence that the chain coiling, induced by the increase of ion-polymer contacts, significantly influences the competitive binding between the counter-ions and the solvent. We next consider the dynamical implications of this competitive binding process.

From the above discussion, it is clear that the higher valent counter-ions reduce the persistence length of the polyelectrolyte chain by causing the chain to coil around the counter-ions, suggesting that the segmental dynamics should also reflect this phenomenon. We then calculated the mean-square displacement, \( \langle r^2(t) \rangle \) for the polyelectrolyte segments and for the interfacial counter-ions. The “fast” dynamics probed by neutron scattering correspond to picosecond time.
scale ($t/\tau < 10$, where $\tau \approx 1$ ps) and the Debye-Waller factor is time by measurement of $\langle r^2 \rangle$ at this time scale. We see that the interfacial divalent counter-ions have higher “mobility” (i.e., larger $\langle r^2 \rangle$) than monovalent counter-ions, Fig. 6. This higher mobility is reflected in the segmental dynamics. Exactly this behavior has been observed in neutron scattering measurements on sulfonate polystyrene$^{20}$ and RNA$^{55}$ when the monovalent counter-ions are replaced with divalent ions. On the other hand, the dynamics of the solvent (neutral) particles near the chain backbone in our model is found to be nearly independent of the ionic environment (results not shown).

The coiling of the chain around the interfacial counter-ions then leads to a non-trivial behavior for both the segmental and counter-ion fast dynamics. In the monovalent case, the interfacial counter-ions have a limited range of mobility pathways; an interfacial monovalent counter-ion either it will move away from polyelectrolyte chains by escaping from interfacial layer or can move along polyelectrolyte chain. The latter motion is quasi-one-dimensional since the polyelectrolyte chain has a stretched molecular conformation, see Figs. 1(a) and 6(c). Divalent counter-ions have stronger interactions with the polyelectrolyte segments, meaning that there is a higher barrier for the counter-ions to escape from the interfacial layer. On the other hand, the molecular conformation of the polyelectrolyte resembles that of a random coil, as discussed above, and thus a divalent counter-ion exhibits a range of mobility pathways without losing the enthalpic contributions coming from their contacts with the polyelectrolyte chain. This leads to an overall enhancement in the fast dynamics of both the segmental and counter-ion dynamics, see Figs. 1(a) and 6(c). For trivalent counter-ions, the polyelectrolyte chain becomes collapsed, where the chain coiling creates an effective tight cage around a fraction of the interfacial trivalent counter-ions, see Figs. 1(a) and 6(c). This localization of the interfacial counter-ions leads to a significant slowing down of the counter-ion dynamics in this case, as illustrated in Fig. 6.

As mentioned in the Introduction, previous studies have suggested that the counter-ion distribution can be characterized by a two zone binding to the polyelectrolyte.$^{5,54}$ The first zone corresponds to counter-ions in close proximity to the chain, as anticipated by the Manning condensation theory and discussed above. The second zone corresponds to a diffuse counter-ion cloud located at larger distances from the polyelectrolyte, where the counter-ions are still spatially correlated with the polyelectrolyte. While extensive studies have investigated the interfacial counter-ions, the factors that influence the spatial extent of the “diffuse” counter-ion cloud are not well understood.

To characterize the diffuse counter-ion cloud in our model polyelectrolyte, we need to devise an appropriate approach for defining this scale. A common practice in polyelectrolyte studies is to calculate the average charge density of counter-ions as function of the distance from a polyelectrolyte chain, as seen in the inset of Fig. 7. This approach offers a detailed picture of the structure at short length scales, but...
At larger length scales the structural information is “diluted” by the small but not negligible amount of charge at larger distances — at larger distances, the volume of spherical shell is large. In other words, this creates a bias towards short length scale features. Since we are interested in measuring the diffuse counter-ions that may located at larger distances, we calculate the ion distribution surrounding the polyelectrolyte without normalizing by the volume of spherical shell. This description provides all the necessary information about the amount of charge at a given distance from a polyelectrolyte segment without being biased, as illustrated in Fig. 7.

At the beginning of our discussion, we discussed the role of the interfacial counter-ions so we examine how these interfacial counter-ions distribute around the polyelectrolyte chain, $q_b$, see Fig. 8. $q_b$ follows the distribution of the polyelectrolyte segments, $q_p$, but always corresponds to a smaller amount of charge, since the counter-ions at the interfacial layer only partially screen the polyelectrolyte bare charge. For comparison, we also present in Fig. 8 the counter-ion distribution $q_f(r)$ and the co-ion distribution $q_c(r)$. Evidently, at distances larger than $l_B$ and $\lambda_D$, but smaller than the size of the polyelectrolyte chain, there is a significant deviation between the $q_c$ and $q_f$. This suggests that $q_b$ is insufficient metric for accounting the whole impact of counter-ions near the polyelectrolyte. To better quantify the distribution of counter-ions around the polyelectrolyte, we calculate the average net charge, $q(r)$, as function of distance from the polyelectrolyte segments, which is simply the sum of $q_i$ and $-q_-$. Evidently, $q(r)$ represents both the counter-ions at the interfacial layer and the counter-ion cloud that is loosely associated with the polyelectrolyte, Fig. 8. Now we can define the relevant length scales. We expect $q(r) \approx 0$ for distances $r > R_b$, where $R_b$ corresponds to the location of the boundary between the counter-ion cloud around the polyelectrolyte and the bulk solvent, i.e., $q_+ = q_-$. For distances $r < R_b$, there is an excess counter-ion charge and a depletion of co-ion charges, meaning that $q(r) > 0$. The latter regime apparently embodies what has been described in the literature as the “diffuse counter-ion cloud”. We refer to $q(r)$ as the counter-ion distribution of the diffuse ionic cloud (including the counter-ions in the interfacial layer) and focus on characterizing the spatial extent of this distribution.

Typical $q(r)$ distributions as function of distance from a macro-ion segment for different valence counter-ions are presented in Fig. 7. To better characterize these distributions, we take a cue from previous work based on Poisson-Boltzmann calculations for rod polyelectrolytes suggesting that the size of the diffuse counter-ion cloud can be defined from the inflection point in the net ionic charge $Q(r) = \int_0^r q(x)dx$ at a distance $r$ from macro-ion segments. As expected, $Q(r)$ increases at long distances from the polyelectrolyte and saturates for large $r$ to $Q(r)/Z_p \approx 1$, as illustrated in Fig. 9. It is evident also that the higher counter-valence leads to a significant contraction of the size of the diffusely bound counter-ion cloud and so the net charge saturates at shorter distances, which is in good agreement with previous studies. We also find that the $Q(r)$ curves collapse onto a single master curve with the following empirical

FIG. 7. Average net charge, $q(r)$, as function of distance from a polyelectrolyte segment for a polyelectrolyte chain having $M_w = 41$. Inset: Average density net charge, $\rho_{net}(r)$, as function of distance from a polyelectrolyte segment for a polyelectrolyte chain having $M_w = 41$. The arrows highlight $r/\sigma = 5$ for comparison between $\rho_{net}(r)$ and $q(r)$.

FIG. 8. Distribution of the ionic net charge, $q(r)$, of monovalent counter-ion as well as the relevant distributions of the counter-ions $q_+$ and co-ions $q_-$. around a linear chain with molecular mass, $M_w = 41$. The distribution of the polymeric segments, $q_p(r)$, as well as the distribution of counter-ions located in the interfacial layer, $q_b(r)$, is also presented.

FIG. 9. Cumulative net charge, $Q(r) = \int_0^r q(x)dx$, for a polyelectrolyte chain having $M_w = 41$ as function of distance for different counter-ion valencies. The dotted lines represent fits of Eq. (4).
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WCL model is no longer strictly applicable. Higher valent counter-ions lead to a substantial increase of counter-ion concentration near the polyelectrolyte, which leads to not only to a more effective screening of the bare charge but also to a charge inversion in the trivalent counter-ion case. These conformational changes with counter-ion valency are associated with a drastic increase of the number of contacts the counter-ions have at the interface with polyelectrolyte, an effect associated with polyelectrolyte chain “coiling” around the counter-ions. Additionally, we find that higher counter-ion valence reduces the size of diffusely bound counter-ion cloud and when the size of this cloud becomes smaller than $\lambda$ then there is an effective charge inversion effect. For monovalent counter-ions, the size of the diffuse counter-ion cloud remains comparable to the chain size, i.e., $\alpha \propto R_g$.

IV. CONCLUSIONS

In summary, we have investigated the impact of monovalent, divalent, and trivalent counter-ions on the coupling between the polyelectrolyte’s persistence length and the average molecular shape. We also studied the influence of counter-ion valence on the dynamics at picosecond time scale. Divalent counter-ions reduce the persistence length of flexible chains approximately by factor of two and trivalent counter-ions lead to a partially collapsed chain so that the functional form:

$$Q(r) = Z_p \tanh^2 \left( \frac{r}{\alpha} \right),$$

where $\alpha$ characterizes the average scale of the diffusive bound counter-ions and the values are presented in Table I. The collapse of the $Q(r)$ curves indicates that the counter-ion distribution is coupled with the molecular conformation. Indeed, by plotting the ratio of $(\alpha - \lambda_D)/R_g$ as function of $M_w$, we find a wide range of behaviors, as illustrated Fig. 10. For divalent and trivalent counter-ions, the diffuse cloud is highly sensitive to $R_g$ and $M_w$ of the polyelectrolyte chain. For example, we find $\alpha < \lambda_D$ for trivalent counter-ions and $M_w < 20$, which suggests that the diffuse ionic cloud collapses when $\alpha$ becomes comparable to $\lambda_D$. This condition apparently coincides with charge inversion in the effective ionic cloud charge, see Fig. 3(b). On the other hand, the size of ionic cloud scales linearly with the size of the polyelectrolyte, i.e., $\alpha \propto R_g$ for monovalent counter-ions. Remarkably, this relation still holds for variable molecular architectures, e.g., stars, rings, and trefoil knots.

The diffuse counter-ion cloud must greatly influence the polarizability of the polyelectrolyte chain and providing a mechanism for chain clustering in solution due to the resulting long range interactions. Thus, the $\alpha$ parameter provides insights into the range of these interactions mediated via the diffuse counter-ions between polyelectrolytes. Future work will focus in understanding these long range interactions and they influence the self-assembly or phase behavior of polyelectrolyte solutions.