I. INTRODUCTION

Polyelectrolyte gels consist of charged polymers associated with each other in solution by either physical or chemical bonds, where the polymer-polymer interactions that govern the structure of such material are mediated by counter-ions and solvent. Cross-linking gels have attracted considerable technological and scientific attention due to their capacity to swell in volume by several orders of magnitude compared to their dry volume. Such gels can then be used as superadsorbants in hygiene products, as charged hard spheres and the solvent enters the model through its influence on the permittivity of the continuous medium surrounding the charged species. This is a natural extension of the Debye-Hückel theory of ionic solutions, where the charged species are non-polymeric. In variations of the primitive model (for example see the following Refs. for polyelectrolyte solutions and Refs. for polyelectrolyte cross-linking gels) the solvent may influence the properties of the polyelectrolyte systems via the effective short-range interactions between the polymer segments, thus mimicking the solvent quality. However, the influence of the solvent interactions for the ionic species in the polyelectrolyte solutions and gels are neglected with this type of continuum solvent models. To illustrate the importance of these interactions, we offer the following example. For typical electrostatic conditions in dilute polyelectrolyte concentrations, a fraction of the counter-ions are condensed along the polyelectrolyte backbone while the rest of the counter-ions are located at larger distances, but they remain associated with the polyelectrolyte chain in the form of an ionic cloud surrounding the chains. These two counter-ions “states” are transient and there is constant dynamic exchange of counter-ions between them. This two-state concept for counter-ions is widely accepted in the literature (theoretical and experimental studies) and we have repeatedly observed that solvation influences the structure and dynamics of polyelectrolyte solutions, and by extension, the swelling capacity and response of polyelectrolyte gels. According to the “primitive polyelectrolyte model” and its variations, the solvation of the polyelectrolyte chain is the result of a balance between the tendency of the counter-ions to condense along the polyelectrolyte backbone and residual electrostatic interactions between the counter-ions. However, this balance can be disturbed if the solvent particles have strong enough attractive interactions for the counter-ions in compari-
son to the electrostatic interactions between the counter-ions and polyelectrolyte segments; this effect reduces the number of condensed counter-ions along the chain backbone. This simple observation is missing from the previous theoretical frameworks of polyelectrolyte solutions and gels, and it is expected to become prominent at conditions where the long-ranged electrostatic interactions between charged species are equivalent to the short-ranged dispersion interactions between the solvent and charged species. In other words, polyelectrolyte and ion solvation results from a balance between the competitive associative interactions of three species, namely the counter-ions, the polyelectrolyte segments, and the solvent molecules. Competitive binding of molecular species to macromolecules is known to greatly alter the phase behavior of polymer solutions, leading to often counter-intuitive phase behavior and an even greater complexity is to be expected when associated species have long range interactions.

Why does the solvation of ionic species matter so much in polyelectrolyte solutions and gels? We momentarily shift our focus to the relative “simple” case of electrolyte solutions (with no polyelectrolyte chains) to underscore the significance of solvent-ion interactions. It is well known that in electrolyte solutions having different salts one gets a wide spectrum of changes in solution properties, such as the density, viscosity, and surface tension; these changes in solution properties are typically classified in terms of the Hofmeister series. Recent observations of Collins, and theoretical arguments by Ninham et al., suggest the importance of ion-size on the extent of ion-solvation and the dispersion interaction between ions and water, respectively, in understanding the trends of polymer solubility, i.e., the Hofmeister series. Indeed, the ion solvation energy effectively reflects a combination of Coulombic and dispersion interaction contributions between the ions and the solvent particles surrounding the ions. Motivated by these observations, we explored an explicit electrolyte solvent model in which the water-ion dispersion interaction parameter was determined by the ion solvation energy through the application of Born theory of ionic solvation. We found that molecular dynamics simulations utilizing this model captured semi-quantitatively observed changes in solution viscosity and water diffusion coefficient on ion type, an effect that classical coarse-grained pair-potential models fail to reproduce. Recent calculations of the same model reveal that several other thermodynamic properties, including the density, isothermal compressibility, and surface tension, can be understood via the solvent-ion interactions, suggesting that the Hofmeister series is closely related to ion solvation. Thus, if the solvent interactions with the ionic species plays such a crucial role in modulating the electrolyte solution properties, then it is logical to expect analogous effects in polyelectrolyte solutions and gels.

To probe and quantify the influence of the solvent interactions with the ionic species, we focus on the simplest case of polyelectrolyte solution systems, an isolated polyelectrolyte chain in solution corresponding to a highly dilute polymer concentration. Our motivation is also drawn from our previous work, where we have shown that counter-ion solvation can lead to effective long range attractive interchain interactions in salt-free polyelectrolyte solutions that can also greatly influence thermodynamic and dynamic properties of these polymer solutions. The choice of this type of system allows us to examine the solvent effects independently of the polymer network architecture and/or polymer concentration effects. We utilize a computational model that 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 due to fully capture the polyelectrolyte structural and dynamical behavior, as indicated by a series of studies. In particular, an explicit solvent is necessary in order to study the variation of the solvent interactions with different ionic species. In particular, we focus on the changes in the conformational properties of the polyelectrolyte chain and the distribution of the counter-ions surrounding the polymer for two types of solvent affinity namely the solvent affinity for the counter-ions and the solvent affinity for the polyelectrolyte chain.

Our paper is organized as follows. Section II contains details of the model and simulation methods. Results of the conformational properties of the polyelectrolyte chain and the characterization of the spatial distribution of the counter-ions surrounding the polyelectrolyte chain are presented in Section III. Section IV concludes the paper.

II. MODEL AND COMPUTATIONAL METHODS

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. The system is composed of a total of $N = 64,000$ particles in a periodic cube of side $L$ and volume $V$. The system includes a single polyelectrolyte chain having a molecular mass of $M_w = 41$ and a total charge $-Z_p e$. The bonds between polymer segments are connected via a stiff harmonic spring, $V_H(r) = k(r - l_0)^2$, where $l_0 = \sigma$ is the equilibrium length of the spring, and $k = 1000 \varepsilon / \sigma^2$ is the spring constant. The system also includes $N_-$ co-ions of charge $-e$ and $N_+ = N_- + Z_p$ counter-ions of charge $+e$ so that the system of interest has neutral total charge.

All macro-ion segments, dissolved ions, and solvent particles are assigned the same mass $m$, size $\sigma$, strength of interaction $\varepsilon$. We set $\varepsilon$ and $\sigma$ as the units of energy and
length; the cutoff distance for LJ interaction potential is \( r_c = 2.5 \sigma \). The size and energy parameters between \( i \) and \( j \) particles are set as \( \sigma_{ii} = \sigma_{jj} = \sigma_{ij} = \sigma \) and \( \varepsilon_{ii} = \varepsilon_{jj} = \varepsilon_{ij} = \varepsilon \), except for two energy interaction parameters: the first interaction parameter is between the solvent particles and the polyelectrolyte segments \( \varepsilon_{ps} \) and the second one is between the solvent particles and the positive ions \( \varepsilon_{cs} \). Variation of the interaction energy parameters between different types of particles reflect the degree of chemical incompatibility between the polymer parameters between different types of particles reflect the nature of electrostatic interactions and thus we tune them explicit solvent into our model, it does not influence the degree of chemical incompatibility between the polymer repeating units. For the purpose of our study, we focus on characterizing the effects of the variation of one interaction parameter separately. For example, when we state that \( \varepsilon_{cs}/\varepsilon = 4 \) then \( \varepsilon_{ps}/\varepsilon = 1 \). All charged particles interact via Coulomb potential (with a cut-off distance \( 10\sigma \)) and a relatively short range Lennard-Jones potential.

The systems were equilibrated at constant pressure and constant temperature conditions, i.e., reduced temperature \( k_B T/\varepsilon = 0.75 \) (where \( k_B \) is Boltzmann’s constant) and reduced pressure \( \langle P \rangle \approx 0.02 \), and the production run were performed at constant temperature constant volume, maintained by a Nosé-Hoover thermostat. The Bjerrum length was set equal to \( l_B = e^2/(\varepsilon k_B T) = 1.85 \sigma \), where \( \varepsilon \) is the dielectric constant of the solvent. We note that while we have introduced a LJ fluid as our explicit solvent into our model, it does not influence the nature of electrostatic interactions and thus we tune them via the dielectric constant. The Debye screening length: \( \lambda_D = [4\pi l_B (\rho_+ + \rho_-)]^{-1/2} \approx 2.4 \), where \( \rho_{ \pm} = N_{ \pm}/L^3 \) are the ion densities. Typical simulations equilibrate for \( 4000 \tau \) and data is accumulated over a \( 10 \times 10^3 \tau \) interval, where \( \tau = \sigma (m/\varepsilon)^{1/2} \) is the MD time unit and the time step \( \delta t = 0.005 \tau \). Typical screenshots for different types of solvent affinities are presented in Fig. 1. For comparison, we also consider an implicit solvent model at the same volume and temperature as our explicit solvent model, except that there is no solvent and all LJ interactions are described by Weeks-Chandler-Andersen potential.

III. RESULTS & DISCUSSION

Before we begin discussing the conformational properties of the polyelectrolyte chain, we briefly examine the spatial correlations between the counter-ions at different types of affinity solvent. The static structure factor, \( S(q) \), is a suitable property for this purpose and describes the mean correlations in the positions for a collection of point particles (in our case the positions of all the counter-ions), \( S(q) \):

\[
S(q) = \frac{1}{N_+} \left\langle \sum_{j=1}^{N_+} \sum_{k=1}^{N_+} \exp \left[ -i \mathbf{q} \cdot (\mathbf{r}_j - \mathbf{r}_k) \right] \right\rangle, \tag{1}
\]

where \( i = \sqrt{-1} \), \( q = |\mathbf{q}| \) is the wave number, \( \mathbf{r}_j \) is the position of particle \( j \), \( \langle \rangle \) denote the time average. For a solvent having no preferential affinity \( (\varepsilon_{cs}/\varepsilon = \varepsilon_{ps}/\varepsilon = 1) \), we find that \( S(q) \approx 1 \) for \( q \sigma > 1 \), which means that for these length scales there is no spatial correlation between the counter-ions, see Fig. 2. For \( q \sigma < 0.8 \), there is an upturn in \( S(q) \), which means that there are significant density fluctuations in these length scales. Typically, a significant excess scattering in low \( q \)-regime means two things: either a macrophase separation is taking place or the formation of clusters in the system. A visual inspection of the system (Fig. 1) clearly indicates that the...
latter is taking place rather than the former. The $S(q)$ behavior between solvents having no preferential affinity and the case of implicit solvent is very similar, indicating that the spatial correlations of the ions in these two cases are very similar. For solvents having strong affinity for the polyelectrolyte segments, we find that there is a small oscillatory behavior at length scales on the order of the chain size and no correlations at $q \sigma > 1$ similar to the no solvent affinity solvents. We interpret this behavior as follows. An increase in $\varepsilon_{ps}$ leads to the formation of a more compact solvation layer surrounding the polyelectrolyte chain, thus inhibiting its mobility. This localization of polyelectrolyte segments influences the localization of nearby counter-ions as observed in $S(q)$. For solvents having a strong affinity for the counter-ions, we find that there are fluctuations in all length scales. In particular, we find that there is a significant excess scattering compared to the other two types of solvent affinities in the low $q$-regime. Moreover, for $q \sigma > 1$, there is a sinusoidal-like behavior suggesting the existence of charge density waves that become damped at large distances similar to the local ordering in dense fluids. We interpret all these observations as follows: the strong counter-ion solvation leads to the formation of counter-ion clusters having liquid-like structure, while there are large ion density fluctuations at length scales larger than the cluster size. We note that these features in counter-ion affinity solvents exist even in the absence of polyelectrolyte chains and the presence of the polyelectrolyte chains influences the structure of the counter-ions at low $q$-region as seen in Fig. 2. We thus see a significant deviation from the physical picture indicated by the polyelectrolyte primitive model once we explicitly consider the solvent and its differential interaction with the different ionic species.

Now that we have a basic understanding on how the different types of solvent affinities influence the structure of the ions in an electrolyte solution, we focus on the characterization of the interfacial layer around the polyelectrolyte backbone. Theoretically, correlations between the counter-ions and the polyelectrolyte chains are usually described based on the classical counter-ion condensation theory of Manning and subsequent revisions of this classic model of polyelectrolytes$^{56-58}$. According to this theory, the counter-ions from their uniform distribution in the solution start to "condense" on the chain backbone, when the electrostatic interactions become comparable to thermal energy. This instability takes place when $\xi = \lambda l_B > 1$, ($\lambda$ is the polyelectrolyte charge per length). However, Manning theory models polyelectrolytes as infinitely long charged straight threads, while, real polyelectrolytes have a finite chain length and can be relatively flexible. The existence of a flexible backbone raises basic and theoretically unresolved questions about how the polyelectrolyte conformation affects the distribution of counter-ions distributed these polymers and about how the counter-ions, in turn, influence polymer conformation.

We set the interfacial layer based on an arbitrary distance criterion in which any counter-ion that is located at shorter distances than $1.1 \sigma$ are taken to be part of the interfacial region. This particular value, i.e., $1.1 \sigma$, is chosen in order to discriminate between the counter-ions that are in contact with the polyelectrolyte from the remaining counter-ions. Based on our model, we find that the interfacial counter-ions exhibit a rich spectrum of behaviors for the different molecular topologies$^{27}$ and counter-ion valance$^{52}$. Now that we have defined the interfacial region for our model, we calculate the time average number of interfacial counter-ions, $\langle n_{\text{inter}} \rangle$, for different values of $\varepsilon_{pc}$. As seen in Fig. 3, $\langle n_{\text{inter}} \rangle$ decreases as
the strength of the solvent affinity for counter-ions and for the polyelectrolyte segments, e.g., for solvents having either $\varepsilon_{\text{cs}}/\varepsilon > 4$ or $\varepsilon_{\text{ps}}/\varepsilon > 4$ we find $\langle n_{\text{inter}} \rangle \approx 0$. In other words, both type of solvent affinity for the charged species result in the effect, the solvent particles are effectively “kicking out” the counter-ions from the polyelectrolyte backbone. We also note that these interfacial counter-ions screen a significant portion of the bare charge of the polyelectrolyte due to their close proximity to polyelectrolyte. We calculate the effective polyelectrolyte charge, $Q_{\text{macro}} = Z_p - \langle n_{\text{inter}} \rangle$, and, as expected, the decrease of the number of interfacial counter-ions leads to the ionization of the chain backbone, as seen at the inset of Fig. 3. These two types of solvent affinity exhibit approximately the same trends from the standpoint of interfacial counter-ions, and thus it leads us to consider the question whether they are any qualitative differences between these two solvent affinities.

We now focus on the spatial distribution of counter-ions in relation to the position of the polyelectrolyte segments. Previously, we developed an approach for quantifying the spatial distribution of the counter-ions surrounding a polyelectrolyte chains and we briefly outline this approach.$^{27,52}$ In particular, we calculate the average net charge $q(r)$ as function of distance from the polyelectrolyte segments. This calculation is based on constructing a histogram of calculating the time average ion charge (counter-ions and co-ions) as function of distance from the polyelectrolyte segments; the histogram includes information from all polyelectrolyte segments. As shown in Fig. 4a, $q(r)$ is simply the difference of the counter-ion distribution $q_+(r)$ and the co-ion distribution $q_-(r)$, meaning that $q(r)$ contains information for both the counter-ions that are located in the interfacial layer (defined as any particle being at a distance $r/\sigma \leq 1.1$ from any polyelectrolyte segment) as well as in the diffuse counter-ion cloud. This approach$^{27,52}$ allows us to determine the size of the cloud of the diffuse counter-ions ($R_{\text{cloud}}$) associated with the polyelectrolyte chain, since the boundary between this cloud and the bulk is at $q(r=R_{\text{cloud}}) = q_+(r) - q_-(r) = 0$. An example illustrating these charge distributions is presented in Fig. 4a. For a weak dispersion interaction strength, $\varepsilon_{\text{cs}}/\varepsilon = 1$, a fraction of counter-ions have a small tendency to “condense” along the polyelectrolyte backbone. However, as we increase the solvent affinity for either the counter-
ions or the polyelectrolyte segments, we decrease the average number of condensed counter-ions along the polyelectrolyte backbone, thus altering the $q(r)$ distribution, as illustrated in Fig. 4b. The newly dissolved counter-ions continue to interact with the polyelectrolyte chain at relative large distances $2 < r/\sigma < 6$, leading to an enrichment of the diffuse counter-ion cloud surrounding the polyelectrolyte chain. While the $(\eta_{\text{water}})$ trends where approximately the same between the the two different types of solvent affinities, the $q(r)$ curves exhibit qualitative deviations from each other. These differences are related to the different molecular conformation of the polyelectrolyte chain is adopting, which we discuss in more detail below.

To better characterize these charge distributions, we consider the cumulative net charge, $Q(r) = \int_0^r q(x)dx$ at a distance $r$ from macro-ion segments. As we have discussed in previous work\textsuperscript{27,52}, $Q(r)$ quantifies the net ionic distribution around a polyelectrolyte chain. A basic feature of $Q(r)$ is that it starts from 0 at short distances $r/\sigma < 1$ and progressively increases at long distances until it saturates, i.e., $Q(r)/Z_p \approx 1$, see Fig. 5. The rate at which $Q(r)/Z_p$ reaches unity seems to follow the approximately universal functional form:

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

where $\alpha$ and $\mu$ are fitting parameters. The values of the $\mu$ parameter are of the order unity, where $\mu$ indicates the location at which $Q(r)$ starts to progressive increase. This suggests that $\mu$ is associated with the amount of charge in close proximity to the polyelectrolyte backbone. For the purpose of our study, we focus on the size $\alpha$, since $\alpha$ determines the overall size of the diffuse counter-ion cloud. We note that we previously found that the functional form of Eq. 2 held for polyelectrolytes having different molecular architectures\textsuperscript{27}, and this relation held even for for different counter-ion valence\textsuperscript{52}, suggesting that the rate of charge saturation is generally coupled to the structure of the polyelectrolyte chains and the charge carried by the counter-ions. Moreover, for monovalent counter-ions, the size of ionic cloud is directly coupled to the size of the polyelectrolyte chain, as quantified by the radius of gyration, $R_g$\textsuperscript{27}. Here, we extend this type of calculation to polyelectrolyte chains having different degrees of solvent affinity. For each value of the strength of the solvent affinity parameter $\varepsilon_{ps}$ or $\varepsilon_{cs}$, we expect to influence the value of the time average $R_g$ of the polyelectrolyte chain. Thus the question, does the size of the ionic cloud coupled...
by the changes in the size of the polyelectrolyte chains induced by the changes in the strength of the solvent affinity? By plotting the time average $\langle R_g \rangle$ as function of $\alpha$, we find that the average size of the polyelectrolyte chain with is again found to scale with the $\alpha$-parameter as we vary with the solvent affinity for the ionic species; see Fig. 6. This finding agrees with our observations from our previous study where we examined the role of molecular architecture on the size of the counter-ion cloud. It is worth pointing out that while we find $\langle R_g \rangle \sim \alpha$ to hold for both types of solvent affinities, the parameters of this linear relation are different between the two solvent affinities. Similar deviations from the monovalent counter-ions were also found for divalent and trivalent counter-ions, where the trend was amplified due to the stronger coupling between the counter-ions with the conformational properties of the polyelectrolyte chain, leading to a non-trivial dependence between the size of the ionic cloud and $R_g$. Thus, the solvation layer around different charged species influences this coupling in a non-trivial way.

Our findings regarding the relation between $R_g$ and $\alpha$, suggest that we examine the dependence of $R_g$ on solvent affinity. We find qualitatively similar trends from a quick look at the resulting average values of $R_g$ with variation of the strength of the different types of solvent affinities. Nevertheless, a quantitative comparison reveals additional differences between the different type of solvent affinity. In particular, we find that while an increase from $\varepsilon_{cs}/\varepsilon = 1$ to 2 leads to an increase in $R_g$, a stronger degree of swelling occurs if $\varepsilon_{ps}$ increases by the same amount. While the time average $R_g$ remains approximately constant for solvents having a counter-ion affinity ($2 < \varepsilon_{cs}/\varepsilon < 6$), for solvents having polyelectrolyte affinity there is monotonic decrease of $\langle R_g \rangle$ with $\varepsilon_{ps}$. Even while the time average value of $R_g$ ($\langle R_g \rangle$) is approximately the same for both two solvent affinities, i.e., solvent having $\varepsilon_{cs}/\varepsilon = 4$ and solvent having $\varepsilon_{ps}/\varepsilon = 4$, the variance of $R_g$, labeled as $X(R_g)$, between these solvents is significantly different, see inset of Fig. 7. Specifically, $X(R_g)$ for polyelectrolyte affinity solvents having $\varepsilon_{ps}/\varepsilon = 4$ is larger than counter-ion affinity solvents having $\varepsilon_{cs}/\varepsilon = 4$ by a factor of two. In other words, while the time average $R_g$ is approximately the same, the fluctuations can be significantly different, reflecting the influence of the solvent between the charged species.

A closer examination at the solvation layer is required to better understand the similarities and differences in $R_g$ in Fig. 7. For this reason, we calculate the time average number of interfacial solvent particles $\langle n_{solv} \rangle$ that are in contact with the polyelectrolyte backbone. A solvent particle is in contact with a polyelectrolyte segments if it is located at a distance $r \leq 1.1 \sigma$. The results are presented in Fig. 8. In particular, we find that for weak solvent affinity for the charged species (solvents having $\varepsilon_{cs}/\varepsilon \lesssim 1$) and for solvents having $\varepsilon_{ps}/\varepsilon \lesssim 1$) the $\langle n_{solv} \rangle$ values are similar. The same trend is found for strong solvent affinity for the charged species (solvents having $\varepsilon_{cs}/\varepsilon \gtrsim 6$ and for solvents having $\varepsilon_{ps}/\varepsilon \gtrsim 6$). However, for intermediate strength of solvent affinity, we find considerable differences between the two types of solvents. Specifically, solvents having $1 < \varepsilon_{ps}/\varepsilon < 6$ have significantly more solvent particles than solvents having $1 < \varepsilon_{cs}/\varepsilon < 6$. This is not surprising since by enhancing the cross energy interaction parameter between solvent particles and polyelec...
polyelectrolyte segments, it results in a "tight and sticky" packing of the solvent particles around the polyelectrolyte segments. This effect is more noticeable in the comparison between a solvent having $\varepsilon_{ac}/\varepsilon = 4$ and a solvent having $\varepsilon_{ps}/\varepsilon = 4$ because the $R_g$ is approximately the same, see Fig. 7. Nevertheless, we anticipate that the differences in the solvent packing at and near the interfacial layer between the different solvent affinities for the charged species to be responsible for the differences observed in the fluctuations in $R_g$ and shrinkage of polymer size for strong solvent affinity for the charged species.

So far, we have investigated the conformational properties of the polyelectrolyte chain and the spatial distribution of the counter-ions separately from each other. While we have demonstrated that the conformational properties of the polyelectrolyte chains are correlated with the distribution of the counter-ions, we have not yet directly examined the nature of this correlation. The simplest way to probe their correlation is to plot the time series of $R_g$ and $q(r)$ at different distances from the polyelectrolyte segments. From Fig. 9, it is clear that $R_g$ fluctuates at a lower frequency than $q(r)$. We anticipate this behavior since the polyelectrolyte chain is a larger and slower relaxing molecular species than the smaller and more mobile ions. In the example presented in Fig. 9, it is evident that the net charge at $r = \langle R_g \rangle/2$ follows closely the changes observed in $R_g$, which means that they are positively correlated. However, at larger distances $r = \langle R_g \rangle$, $R_g$ exhibits the opposite trends than the net charge, meaning that they are anti-correlated. However, these correlation effects are not always obvious, as in the example shown in Fig. 9. We thus need to better metrology for this phenomenon.

Now that we have determined the average size of the diffuse ionic cloud associated with the polyelectrolyte chain in solution, we can probe the following phenomenon. Past literature studies have generally assumed that salt is evenly distributed between polyelectrolyte gel or a polyelectrolyte complex coacervate in contact with an aqueous phase even though the asymmetry in salt concentration between the polymer rich and the solvent rich phases was known since the original work of Voorn-Overbeek. This asymmetry can be understood at least conceptually from a rough calculation based on our model. We calculate the density of the ions that are within diffuse counter-ion cloud as we defined it above (see also Fig. 5), assuming that overall domain is spherical with a radius, $R_{\text{cloud}} = 5a/2$ and compare it with the corresponding ion density of an electrolyte solution with the same $\lambda_D$ and $\lambda_B$ parameters. While a more precise characterization of the volume of the ionic cloud is required for a precise comparison, we find that ion density in ionic cloud associated with the polyelectrolyte chain is an order of magnitude larger than in the corresponding electrolyte solution, as expected.

We quantify these correlations using the Pearson correlation coefficient. In particular, we quantify the correlation between the values of $R_g$ and the net ionic charge $q(r)$ at different distances from the polyelectrolyte segments. Pearson correlation coefficient is a measure of the strength of the association between two discrete variables $x_i$ and $y_i$ and it is defined as,

$$R_{x,y} = \frac{\sum_{i=1}^{n} (x_i - \langle x \rangle) (y_i - \langle y \rangle)}{\left[\sum_{i=1}^{n} (x_i - \langle x \rangle)^2\right]^{1/2} \left[\sum_{i=1}^{n} (y_i - \langle y \rangle)^2\right]^{1/2}},$$

where the $\langle \rangle$ denote the mean. It has a value between +1 and -1, where 1 is highest positive correlation, 0 is no linear correlation, and -1 is highest negative correlation, i.e., an anti-correlation. The counter-ions exhibit different correlations with $R_g$ at different distances, Fig. 10. At short distances, we find that $R_{g,R_g}$ is positive, meaning that as $R_g$ increases there is then an increase in $q(r)$, a trend that is observed for all type of solvents that we have explored here. This trend can be understood as follows: when the polyelectrolyte chain...
is in the process of swelling, i.e., there is an increase in $R_q$, it makes “space” for counter-ions to approach the polyelectrolyte backbone leading to an increase in $q(r)$. At larger distances, we find that $R_{q,R_g}$ becomes negative and reaches a minimum. In other words, as the polyelectrolyte chains swells then the amount of net charge at larger distances decreases significantly. This is understandable because the process of swelling includes two competing effects that occur simultaneously to give rise to this anti-correlation effect. First, a fraction of counter-ions from the diffuse counter-ion cloud approach the chain at shorter distances as we described above. Second, as the chain swells, the charge density of the chain becomes reduced, resulting in a smaller repulsion for counter-ions in the bulk which can approach the polyelectrolyte chain at shorter distances. This effect reduces $q(r)$ at distances on the order of the chain size. In this second regime, where the $q(r)$ is anti-correlated with $R_g$, we find that different types of solvent result in different trends. For example, a polyelectrolyte implicit solvent model tends to have $R_{q,R_g}$ values close to 0, meaning that there is little or no correlation between these two quantities. However, for solvents having strong affinity for the counter-ions we observe the sharpest variations in $R_{q,R_g}$. Specifically, we find that at short distance there is a strong positive correlation $R_{q,R_g}(r = \frac{1}{2}(R_g)) \approx 0.8$, but at largest distances it changes to strong anti-correlation with $R_{q,R_g}(r = (R_g)) \approx -0.8$.

We observe that the counter-ion distribution for solvent having no affinity and the case of implicit solvent have approximately the same distribution, but $R_{q,R_g}$ in implicit solvent case are smaller than solvents having no affinity. The results presented in Fig. 10 highlight that the dispersion of interaction of the solvent with the charged species influence the coupling between the distribution of counter-ions and the conformational properties in subtle ways. These results, as well as the results presented in our study, further reinforce the viewpoint that an explicit solvent in the modeling of polyelectrolyte solutions and gels is necessary to capture the solution properties of polyelectrolyte solutions.

For the purposes of our study, the results in Fig. 10 provide a qualitative picture of how solvation can influence the dynamical coupling between the ionic cloud surrounding the polyelectrolyte chains and its conformation. While additional work is required to fully understand the nature of the relation between the solvation and this coupling, our findings point to one conclusion. One can view the changes in the polyelectrolyte chain conformation as the cause of the changes in the distribution of the ions surrounding the polyelectrolyte chain, but at the same time the reverse is also valid, i.e., changes in the distribution of the ions influence the polyelectrolyte conformations. Based on our model, we believe that each side, i.e., polyelectrolyte conformation and the ionic cloud surrounding the polymer, are continuously interacting each other in a dynamic fashion. Thus, the coupling becomes similar to one of the causality dilema ‘which came first: chicken or the egg’, where each side can be considered the cause and the effect. Our simulation observations reveal that the solvation of the charged species is an important factor in probing basic and theoretically unresolved questions about how the polyelectrolyte conformation affects the distribution of counter-ions distributed around these polymers and about how the counter-ions, in turn, influence polymer conformation.

IV. CONCLUSIONS

In summary, we have investigated the influence of the solvent affinity for the ionic species on the conformational properties of flexible polyelectrolytes. Specifically, we focus on differences between the interactions between the solvent particles and the counter-ions, and the interactions between the solvent particles and the polyelectrolyte segments. We find that an enhancement of the solvent for either these two ionic species results in qualitatively similar trends in the impact of the polyelectrolyte chain size and the radius of gyration of the polymer remains correlated with the size of the counter-ion cloud that surrounds the polymer chain. A quantitative comparison, however, indicates significant deviations. This effect was clearly revealed by considering the Pearson correlation coefficient between the radius of gyration of the polyelectrolyte chain and the net ionic charge at a given distance from the polyelectrolyte segments. In particular, we find that the Pearson correlation coefficient is positive at short distance, but at larger distances becomes negative. Between the two types of solvent affinity the...
Pearson correlation changes significantly, suggesting that the explicit description of the solvent in the theoretical treatment of polyelectrolyte solvents and gels is necessary. We conclude that the solution of ions and polymer chains significantly affect the resulting distributions of ionic species and polymer conformational properties in solution, implying that a realistic modeling of polyelectrolytes must include an explicit solvent.

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