Impact of Monovalent Counter-ions on the Conformation of Flexible Polyelectrolytes Having Different Molecular Architectures

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ABSTRACT

We explore the impact of monovalent counter-ions on the molecular conformation of highly charged flexible polyelectrolytes for a range of molecular topologies (linear chains, stars, and unknotted and trefoil rings) by molecular dynamics simulations that include an explicit solvent having short range interaction with the polyelectrolyte. In particular, we investigate how the counter-ions near the polyelectrolytes with variable mass influence the average molecular shape. We also characterize the interfacially "bound" counter-ions by calculating the time-averaged number of interfacial counter-ions, as well as the degree to which the polyelectrolytes wrap around the counter-ions by calculating the number of contacts between the counter-ions and the polyelectrolyte.

INTRODUCTION

Polyelectrolytes are an important class of polymeric molecules that carry charged groups that release counter-ions to an extent that depends on their conformation and charge density when dissolved in polar solvents. Examples include sulfonated polystyrene and polyacrylic acid, as well as, many biological molecules such as DNA and proteins. Insights from the study of these polymers have potential significance in numerous applications, e.g., biomedical implant materials and encapsulating material pharmaceutical drug delivery systems [1, 2]. However, the modeling of synthetic and biological polyelectrolyte solutions is theoretically complicated due to the strong coupling between the counter-ion distribution of and polyelectrolyte conformation [3].

Theoretically, correlations between the counter-ions distribution and the polyelectrolyte are usually described based on the classical counter-ion condensation theory of Manning and subsequent revisions of this classic model of polyelectrolytes [4-7]. According to this theory, when the electrostatic interactions become comparable to thermal energy the counter-ions from their uniform distribution in the solution start to "condense" on the chain backbone, thus largely screening the backbone charge. In the original theory [4, 5], this instability takes place when $\xi = \lambda\, l_B > 1$, (λ is the polyelectrolyte charge per length, and $l_B = e^2 / (\varepsilon_r\, k_B T)$ is the Bjerrum length and ε_r being the solvent dielectric constant). 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. Simulation studies [8-14] of flexible polyelectrolytes in solution have indicated deviations from the theoretical predictions of Manning theory and emphasize that the counter-ions and polymer conformation are coupled. We can also expect this coupling to be altered by chain topology and solvation (i.e., binding by the solvent to the polymer) that

competes with ion association with the polymer. The study of this phenomenon is clearly of practical and fundamental importance.

In the absence of a predictive fundamental theory, we investigate computationally the interdependency between the interfacial counter-ions and the polymer conformational properties of an isolated macro-ion having a range of molecular topologies as a natural starting point for understanding polyelectrolytes. For these model polymers, we quantify the how molecular topology alters the chain conformational properties and determine the average number of counter-ions interfacially associated and contacting the macro-ion. These quantities are generally distinct because individual counter-ions can have multiple contacts with the polyelectrolyte segments. We examine four molecular topologies: linear chains, stars, unknotted rings, and rings with trefoil knots, and we also vary the polymer molecular mass. The simulations are performed with an explicit solvent where the polyelectrolytes are constrained to have a relatively large polymer charge density.

METHODOLOGY

We employ molecular dynamics (MD) simulations based on a bead-spring model of Lennard-Jones (LJ) segments bound by stiff harmonic bonds suspended in explicit LJ solvent, some of which are charged to represent counter-ions and ions from added salt. All macro-ion segments, dissolved ions, and solvent particles are assigned the same mass m, diameter σ, strength of interaction ε, and all dissolved ions are monovalent. We set ε and σ as the units of energy and length and the cutoff distance for LJ interaction potential is $r_c = 2.5\ \sigma$. Polyelectrolyte molecular mass ranges from $M_w = f\ M + 1 = 11$ to 161 segments, where f is the number of arms and M is the number of segments per arm ($f = 2$ for all molecular architecture except for stars). A polyelectrolyte carries a total charge $-Z_p\ e = -\lambda\ M_w\ e$ distributed uniformly along the molecular structure. The 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. To model finite size rods, we use the same model as with flexible chains, but a bending potential is used, $U_{bend}\ (\theta) = k_{bend}\ (\theta - \theta_0)^2$; where $\theta_0 = 180°$ and $k_{bend} = 1000\ \varepsilon\ /\ rad^2$. All charged particles interact via the Coulomb potential and the particle-particle particle-mesh method is used.

The system is composed of a total of 64 000 solvent particles in a periodic cube of side L. The system includes N_- coions of charge $-e$ and $N_+ = N_- + Z_p$ counter-ions of charge $+e$ so that the system of interest has neutral total charge. Aside from l_B that specifies the strength of the Coulomb interaction, the other key length parameter for an ionic solution is the Debye screening length: $\lambda_D = [4\pi\ l_B\ (\rho_+ + \rho_-)]^{-1/2}$, where $\rho_\pm = N_\pm\ /\ L^3$ are the ion densities. Simulations are conducted for $l_B\ /\ \sigma = 1.85$ and $N_+ = 300$, which results to $\lambda_D\ /\ \sigma \approx 2.5$. The operating conditions are typical of the LJ liquid state: density $\rho\ \sigma^3 = 0.8$ and reduced temperature $k_B\ T\ /\ \varepsilon = 1$, the latter maintained by a Nosé-Hoover thermostat. Typical simulations equilibrate for 2000 τ and data is accumulated over a 7500 τ interval, where $\tau = \sigma\ (m\ /\ \varepsilon)^{1/2}$ is the MD time unit.
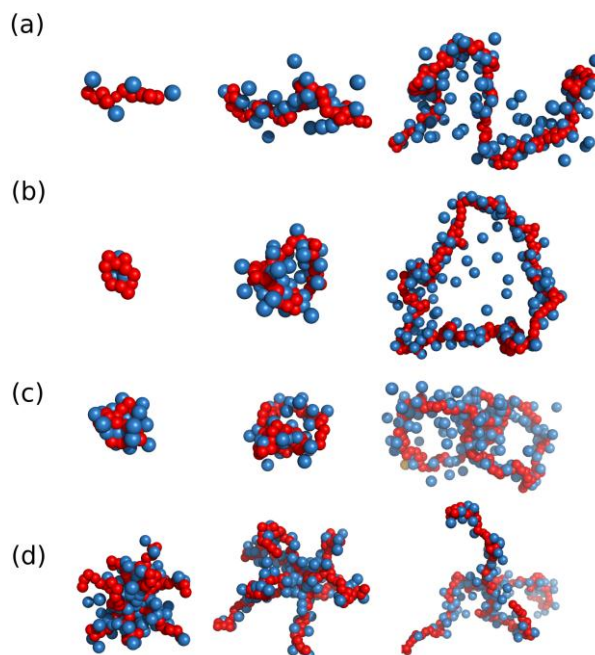
Fig. 1: Screenshots of typical molecular configurations of (a) linear chains; (b) unknotted rings; (c) rings with the trefoil knot; (d) star polymer with f M = 160. The solvent and the majority of the ions are rendered invisible for clarity. For (a-c) and from left to right the molecular mass increases and for (d) the chain functionality decreases with fixed molecular mass.

DISCUSSION

Isolated linear chains with a uniformly distributed charge might be expected to adopt rod-like molecular conformations. Based on this presumed picture, a series of studies have focused on solving Poisson-Boltzmann equation in a cylindrical geometry to estimate the counter-ion distribution [18-20]. However, the chain conformations in real polymer solutions reflect a balance between the repulsion of charged segments of the macro-ion and the covalent bonds between the chain segments so that chain only adopts a rod configuration in an ideal zero-temperature limit where thermal fluctuations can be neglected. 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 an often used descriptor to quantify the shape of arbitrary objects; the calculation of R_h is based on the friction coefficient of an arbitrary shaped Brownian particle [21, 22]. The values of R_h / R_g for a smooth sphere is 1.29, for a random walk is 0.79, and for an infinite long rod is 0 [15, 16]. In all cases, the linear chains become more anisotropic as M 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. 1b for screenshots and Fig. 2), consistent with experimental observations [17]. With respect to the neutral polymers ($\lambda = 0$) the ratio decreases for all molecular topologies and range of molecular mass explored. For small M, the polyelectrolytes become more spherical and symmetric since for $M_w \to 1$ there would be only a single sphere.
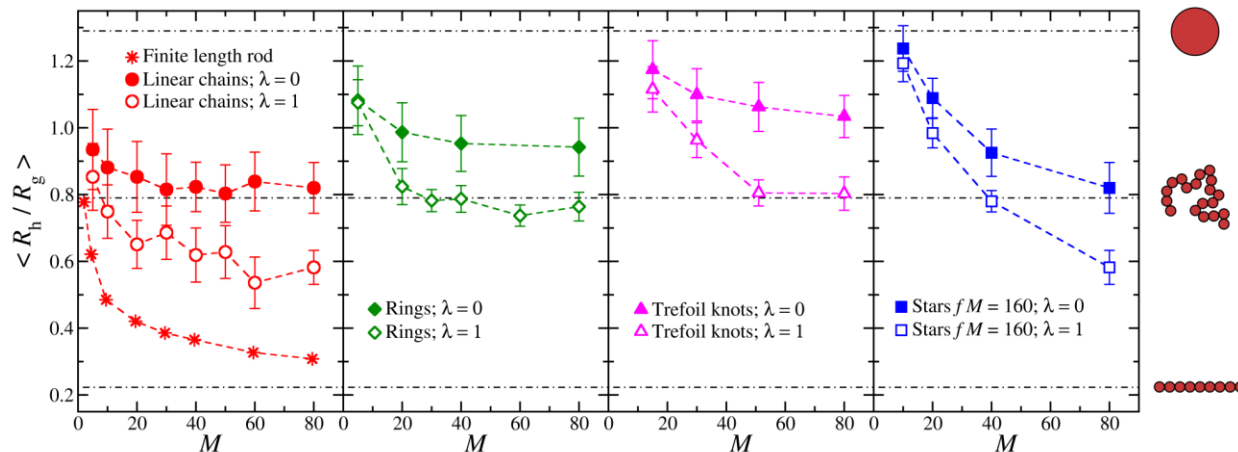
Fig. 2: Ratio of the hydrodynamic radius over the radius of gyration, R_h / R_g, for macromolecules (with charge per segment, $\lambda = 1$, and no charge, $\lambda = 0$) as function of M. Results for different molecular topologies are also presented. The error bars indicate two standard deviations. The dot-dashed lines correspond to the reference values of primary objects, for a smooth sphere is 1.29, for the rod with an aspect ratio of $A = 1550$ is 0.22 (see Figure), and for self-avoiding walks in θ-solvent is 0.79 [15, 16].

It is evident from Fig. 1 that the shape (as quantified by R_h / R_g) of our model polyelectrolyte molecules in solution is greatly influenced by molecular topology. For example, the rings resemble "donuts" rather than a rod-like structures. Thermal fluctuations give rise to deviations from this circular loop shape, as seen in Fig. 1b, but overall polyelectrolyte rings retain their donut configuration. Small rings evidently take a more spherical and symmetric shape, Figs. 1 and 2. Note that knotting further enhances this effect (trefoil knot is a unique prime knot with three crossings [23]). As M increases, however, the effect of the topological constraints evidently diminishes. Topological constraints counter-balance the chain stretching caused by the repulsion between the macro-ion charges. The mass dependence of polyelectrolyte trefoil knots reaches a plateau at M ≈ 50 where $R_h / R_g ≈ 0.8$, which is curiously close to that of a self-avoiding random walk [16]. We also consider stars, which are molecules having f arms of mass M emanating from the molecular core. By keeping the molecular mass, M_w, of the star polyelectrolytes fixed, $M_w = f M + 1 = 161$ and by varying the number of arms, f, we obtain significant changes in R_h / R_g corresponding to a shape from the limit of smooth spheres to flexible chain polyelectrolytes ($f = 2$), as indicated in Fig. 1e and Fig. 2. Molecular topology evidently greatly alters molecular conformation in highly charged polyelectrolytes; in addition, there are clear differences in terms of shape between charged flexible polyelectrolytes with rod-like structures and with neutral polymers. We next shift our attention to the counter-ions, which largely drive these conformational changes.

The counter-ions "bind" to the polyelectrolyte backbone, which is equivalent to Manning type condensation. The number of interfacial counter-ions with the polyelectrolyte, n_{int}, fluctuates over time reflecting a dynamical binding process. To identify the interfacial counter-ions near the interface, we have used a distance criterion of l_B from any macro-ion segment. Evidently n_{int} is neither independent of molecular mass nor molecular architecture, Fig. 3. This is not surprising given that polyelectrolytes under investigation have a flexible backbone, while in the Manning theory the polyelectrolytes are considered rigid slender needles. Nevertheless, the

prediction of Manning theory for the fraction counter-ions that would condense on a charged rod in salt-free case is $1 - 1/\xi$, which is qualitatively consistent with our findings despite obvious differences between the polyelectrolyte systems. The impact of molecular topology is more pronounced for small M, where polyelectrolytes with higher molecular complexity have the tendency to have a higher n_{int} resulting to a more efficient screening of the bare charge. There is evidently a much higher local charge "condensation" on the star and knotted ring polyelectrolytes, which can be attributed to the fact that these structures tend to be more particle-like than chain-like [24]. The molecular topology effect on the charge binding gradually disappears at higher M.
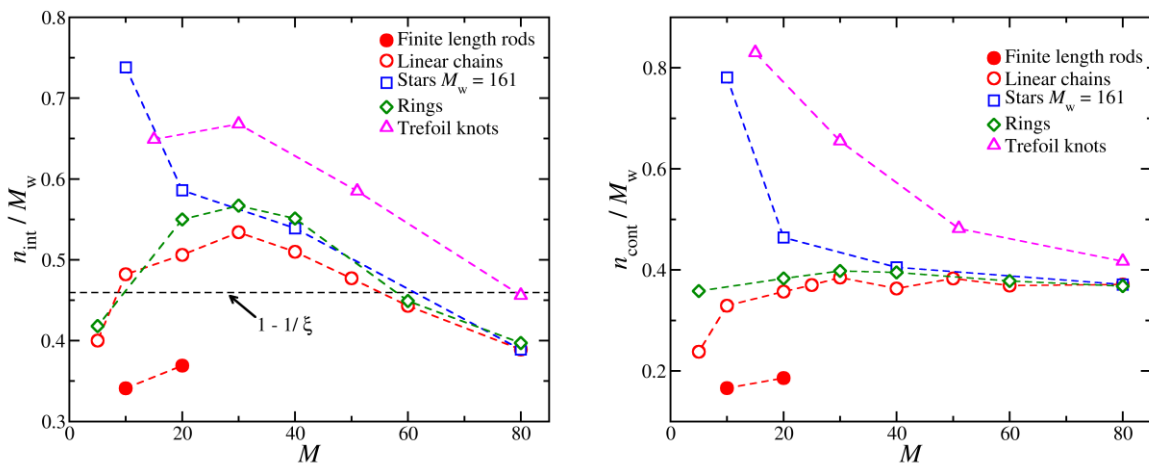

Fig. 3: (Left) Number of interfacial counter-ions, n_{int}, normalized with molecular mass, M_w, as function of the arm molecular mass, M. (Right) Number of contacts the interfacial counter-ions have with the polyelectrolyte, n_{cont}, normalized by M_w, as function of M.

We now focus on the following question: If the fraction of counter-ions do not remain fixed as in Manning theory, then which (if any) quantity remains invariant in this binding process? To probe this question, we narrow down the definition of interfacial counter-ions by considering only counter-ions being whose distance from a macro-ion segment is less or equal to $1.1\ \sigma$. We calculated the average number of contacts the interfacial counter-ions have with the polyelectrolyte chain, n_{cont}. While we find similar features as in the case of n_{int}, n_{cont} approaches to the same saturation level $n_{cont}/M_w \approx 0.37$ for all molecular topologies, which reflects the degree of chain "coiling" around counter-ions. In other words, this suggests that higher molecular mass polyelectrolyte chains become more flexible and adopt molecular conformations that coil around the counter-ions. Moreover, for chains we observe conformational transition at about $M \approx 30$. A similar conformational transition between rod-like conformations and flexible coil was recently discussed for the charged bipolymer DNA [25] and even unentangled linear alkane chains [26]. Ring polyelectrolytes exhibit similar trends for n_{int} and n_{cont}, but stars and trefoil knots attract more counter-ions and at the same time coil more efficiently.

CONCLUSIONS

In summary, we investigated the impact of monovalent counter-ions around polyelectrolytes having a range of topologies. While we find a well-defined fraction of counter-ions near the surface of the polyelectrolyte as anticipated by the Manning condensation theory,

this fraction is significantly influenced by molecular topology, a phenomenon that Manning theory cannot address. In particular, an increase in the molecular complexity leads to an increase of the number of interfacial counter-ions resulting to a more efficient screening of the bare charge. We expect that this effect should have a large influence on the propensity of the polyelectrolytes to undergo supramolecular assembly into large scale domains, a ubiquitous, but theoretically unexplained property of many synthetic and biological polyelectrolytes [27]. We also find that the chain contacts the interfacial counter-ions remains remarkably invariant, suggesting that the backbone chain "coils" around these counter-ions. This phenomenon should be even more prevalent for higher valent counter-ions and can be expected to influence the rigidity of the polyelectrolyte. We plan to investigate this effect in future work.

AKNOWLEDGEMENTS

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