

Abstract

An investigation of the structure of a polyelectrolyte solution interacting with an attractive wall has been carried out through molecular dynamics simulations. Total charge density along the polymer backbone was varied while density profiles and radius of gyration distributions were measured. Additionally, counterions were systematically localized to a single surface to study counterion charge location dependence of polymer position. Increasingly attractive surfaces result in polymers locating closer to the surface. This dependence weakens with lesser charge density on polymer. Average radius of gyration of polyelectrolyte is found to decrease with increasing charge concentration on backbone, in accordance with known scaling laws.

Introduction and Methods

The interaction of a charged polymer with an oppositely charged surface is not only of interest as a fundamental problem in polymer physics, but has increasing relevance in biophysics and materials science applications, such as biosensors and adhesive coatings.[1]

Here we have studied a simplified system of a semi-dilute polymer electrolyte solution and its behavior near an oppositely charged surface using molecular dynamics (MD) simulations. Polymers were simulated as 6-12 Lennard-Jones monomers connected via a bead-spring potential (spring constant $k = 3000$). Negative charges were distributed evenly along the neutral polymer backbone according to the polymer charge fraction, c_p , which was varied from 0 to 0.5. All simulations were performed under neutral charge conditions by introducing positively charged counterions as single monomer "polymers." The force between charged monomers was modeled as a screened coulomb potential,

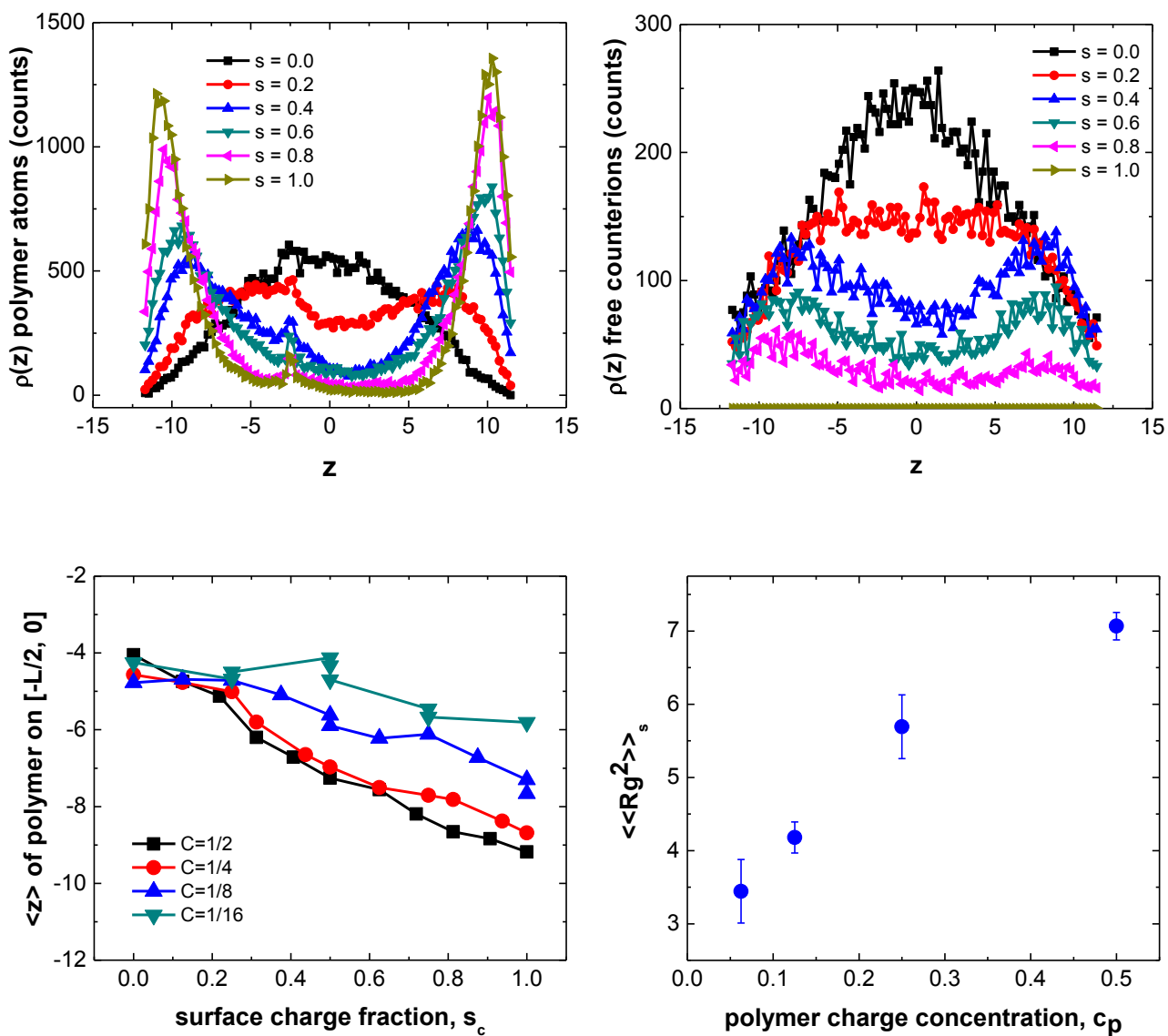
$$U = \frac{hq_iq_j}{r} e^{-\kappa r}$$

where r is the distance between atoms i and j , q is the respective atom charge, κ is the inverse debye screening length, a metric of the range of the electrostatics, and h is the "strength" of the electrostatic interaction. Like κ , h is dependent on such factors as the background dielectric, temperature, and ionic strength. κ was chosen to be 0.001, $h = 0.5$, $T = 1.0$, and $|q| = 1$ (0 for neutral species). An attractive wall was introduced by enforcing that a certain fraction of counterions was held at $z = -L/2$. This surface charge fraction, s_c , was varied from 0 to 1. Each simulation was run with 4 polymer chains, varying chain length M , and box size L the meets $\rho = N/L^3 = 0.005$. A hard wall with elastic collisions was enforced at $z = L/2$ and $z = -L/2$. Periodic boundary conditions were used in x and y .

Polymers were initially distributed along a perturbed lattice and 'free' counterions (those not bound to the bottom surface) were randomly distributed throughout the cell. Surface counterions were randomly distributed on $Z = -L/2$ according to a 10×10 grid. The initial configuration was minimized by conjugate gradient and then equilibrated at temperature using velocity rescaling for 20,000 steps. Positions were evolved according to the Velocity-Verlet algorithm. Each simulation was run in production for 100,000 steps and the polymer and counterion positions were recorded every 1000 steps for determining density and radius of gyration (R_g) distributions. For the data discussed below, all simulations were run at least 5 times, newly randomly seeded, and $M = 16$.

Results and Discussion

Histograms of the polymer and unbound counterion positions as a function of z (distance from box center to wall) are shown in Figures 1 and 2, respectively. For these simulations, $c_p = 0.5$ (i.e. every 2nd monomer is charged), and surface charge was varied from 0 (all counterions are free) to 1 (all counterions are in the wall).



Top Left: Figure 1 - density distribution of polymeric monomers as a function of surface counterion fraction (Polymer charge concentration = 0.5). Top Right: Figure 2 - density distribution of unbound counterions as a function of surface counterion fraction. (Polymer charge concentration = 0.5). Bottom Left: Figure 3 - average z -position of polymers as a function of surface counterion fraction and polymer charge density. Bottom Right: Figure 4 - average radius of gyration as a function of charge density on polymer.

As the fraction of counterions in the wall increase, the polymers tends to migrate towards the wall (at $|z|=12$). If the wall is neutral, the polymers are generally found towards the center. The unbound counterions are also distributed about the center of the box when the wall is neutral. As the charge in wall increases, the counterions also migrate towards the wall, This is consistent in that the counterions still prefer to associate with the polymer, which is located closer to the wall. However, the counterions are on average spaced further from the wall as they undergo repulsive interactions. The density profile of the counterions is subject to greater error since fewer counterions than polymer atoms have been simulated.

The migration of the polymer towards the attractive wall as the surface charge fraction is increases can also be seen in Figure 3, in which the average polymer position (on $-L/2$ to 0) varies with surface charge fraction for multiple polymer charge concentrations. When the polymers are highly charged, they are more likely to be associated with the wall, and are closer to the wall on average as more counterions are bound. For low charge concentrations on polymer, there are far fewer electrostatic interactions, and the average polymer position shows weak to no dependence on the fraction of bound or free counterions. In Figure 4, the average of the simulation average $\langle Rg^2 \rangle$ is given as calculated from multiple simulation trials. Like average polymer distance, $\langle Rg^2 \rangle$ has little dependence on surface charge fraction (result not shown). However, there is a clear power law dependence of $\langle Rg^2 \rangle$ on surface charge fraction, which is consistent with known scaling laws.[2] As a greater fraction of monomers become charged, the polymer backbone becomes increasingly stiff. Overall, these simulations demonstrate that even moderate a charge concentration on the surface can greatly change the polymer distributions, pulling the polymers to the surface if the interaction becomes attractive. However, there remains some anomalous behavior. For example, the upper wall at $z=L/2$ is hard but neutral, and thus one would not expect the observed accumulation of polymers near this surface. This might be due to the idiosyncrasies of the imposed hard wall interaction or calculation errors.

Further Improvements/'Future' Work

As mentioned above, the hard wall condition in z is not a very accurate representation of molecular interactions with a surface. Particularly, when we wish to study surface absorption and other local effects, the hard wall would likely overwhelm many subtler details. Thus improvements could be made by using an alternative potential for the wall, such as a 9-3 Lennard-Jones or other weaker repulsive potential. Additionally, increasing the box height would help reduce any finite size effects.

It is known that polyelectrolyte behavior varies strongly with solvent quality. Thus, investigating variations in the electrostatic strength and debye screening length would provide a better handle for relating this model to experimental systems.

Finally, polymer architectures are becoming increasingly complex, and modeling them would be worthwhile. Small changes such as changing the distribution of charges along the polymer from evenly spaced to random or even block copolymer could have effects on the results. More interestingly, replacing single monomer counterions with oppositely charged polymers could provide greater detail for real systems.

Movie Caption

Trajectory of a polyelectrolyte chain near a charged surface. Negatively charged monomers on polymer are highlighted in red. Negatively charged counterions are shown in blue, and are distributed on localized positions in the surface and freely in the simulation box. Additional polymer chains present in the box have been hidden for ease of viewing. The polyelectrolyte chain is seen to associate both with the surface and with the free counterions.

References

[1] L. Wang, L. Wang, and Z. Su. *Soft Matter*. 7:4851,2011.

[2] P.G. De Gennes, P. Pincus, R. M. Velasco, and F. Brochard. *J. Phys. France*. 37:12, 1976.