

Constant pH Simulations of Weak Polyelectrolytes

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I. Abstract

The interplay of charging environment and complexation of weak polyelectrolytes is nontrivial. Here, constant pH Monte Carlo simulations, which allow the titration of monomers, were utilized for a model system consisting of oppositely charged bead-spring polymers in an implicit salt solution. The salt concentration, set by the Debye length, and charging tendency are varied to probe the extent of complexation and the cooperativity of charging. At low salt conditions where the electrostatic interaction is long-ranged, a charged polymer promotes the charging of the chain of opposite charge. This is supported by the drop in the potential energy as the salt concentration decreases.

II. System and forcefield

A model system consists of a pair of interacting weak polyacid and weak polybase in an implicit salt solution. The diameter of monomers σ , their mass m , charge q , and thermal energy $k_B T$ set the dimensionless units of the system. The polyelectrolytes are modeled as bead-spring polymers where the bonded potential is

$$u_{bond}(r) = \frac{3}{2} k_B T \frac{r^2}{b_o^2}$$

where b_o is the bare average bond length which was set to 1.1σ . The Lennard-Jones potential with ϵ_{LJ} set to be $1k_B T$ is used to prevent core overlap,

$$u_{LJ}(r) = 4\epsilon_{LJ} \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right) - 4\epsilon_{LJ} \left(\left(\frac{\sigma}{r_{cut}} \right)^{12} - \left(\frac{\sigma}{r_{cut}} \right)^6 \right) \text{ for } r \leq 2\frac{1}{6}\sigma \\ = 0 \text{ elsewhere.}$$

The electrostatic interaction between charged monomers is modeled through the screened Coulomb potential,

$$u_{coul}(r) = k_B T l_B \frac{q_i q_j}{r} e^{-\kappa r},$$

where l_B is the Bjerrum length which is a measure of the strength of the electrostatic interaction (the electrostatic interaction energy of two ions is comparable to the thermal energy when they are l_B distance apart), κ is the inverse Debye length which set the length scale of the interaction. Here, l_B is set to 1.0σ . The inverse Debye length is related to the ion concentration,

$$\kappa^2 = 4\pi l_B \sum_i z_i^2 n_{i_o},$$

where n_{i_o} is the average number concentration of the i^{th} ion and z_i is its valency. Value κ is between 0.1 and $6.0\sigma^{-1}$, corresponding to low and high screening. At infinitely large κ , this model approaches the limit where charged monomers only interact through the bonded and the Lennard-Jones pair interactions.

In reality, the ionization state of weak polyelectrolytes fluctuates and has a strong pH dependence. This model of two bead-spring polyelectrolytes chains, schematic shown in Fig.1, tries to capture the titration behavior by allow protonation and deprotonation of monomers. The charge of ionized monomers is $-e$ for the polyacid $+e$ for the polybase. The total potential energy for this system is

$$U = \sum_{(i,j) \text{ bonded}} u_{bond}(r_{ij}) + \sum_{i < j} [u_{LJ}(r_{ij}) + u_{coul}(r_{ij})].$$

III. Simulation Methods

The titration behavior of weak polyelectrolytes was studied using hybrid Monte Carlo (HMC) simulations. The move set consists of short MD simulations and MC titration moves. The titration move (charging or discharging) of a random monomer is proposed with the acceptance probability

$$P_{acc} = \min(1, \exp(-\beta\Delta U \pm \beta\mu)),$$

where ΔU is the change in the total potential energy and μ associates with the chemical potential of protons. High μ corresponds to high charging tendency. For each type of the polyelectrolytes, μ has the form

$$\begin{aligned} \mu &= \mu_{PA} = k_B T \ln 10 (pH - pK_{a,PA}) \text{ for polyacid} \\ \mu &= \mu_{PB} = k_B T \ln 10 (pK_{a,PB} - pH) \text{ for polybase.} \end{aligned}$$

The charging ($e^{+\beta\mu}$) and discharging ($e^{-\beta\mu}$) move is equally likely. Here, it is assumed that the pK_a is independent of the monomer position on the chain and the ionization state of neighboring monomers. This is not true in reality.

For every 20 MC moves, polymer conformations are sampled by performing a short molecular dynamics (MD) simulation of 1000 steps. The time step δt was 0.05τ , where the timescale $\tau = \sigma \sqrt{m \epsilon_L^{-1}}$. The Langevin thermostat with the damping constant of $100 \delta t$ was used to maintain constant temperature at 1.0 in dimensionless unit. The box side length is 100σ and the electrostatic interaction was cut off at 50σ . The chain length of both polyelectrolytes is 60 unless otherwise noted. An equilibration of $10^5 \delta t$ with the initial ionization fraction of 0.5 is followed by a production run of 10^6 total proposal moves consisting of the described MD and MC titration moves.

IV. Results

a. Constant pH simulations

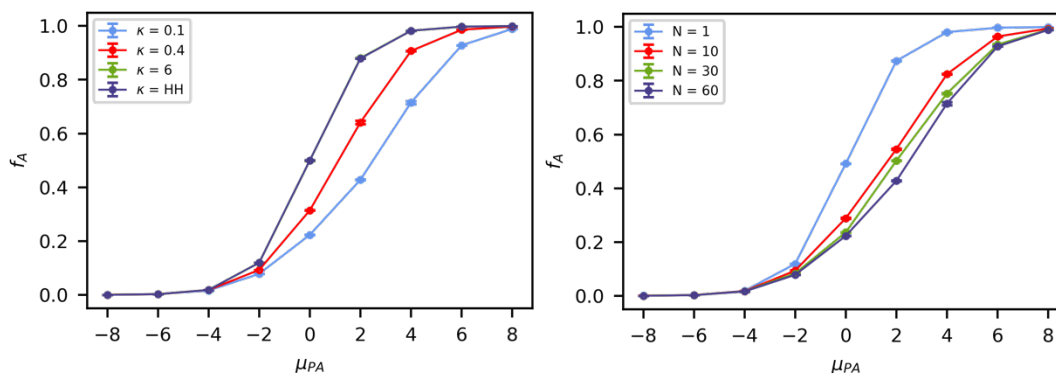


Figure 2: Titration curves of a single polyacid as a function of a) κ and b) chain length with $\kappa = 0.1$. System approaches the Henderson-Hasselbalch (HH) limit at with increased κ and decreasing chain length. $\kappa = 6$ curve collapses onto the HH curve.

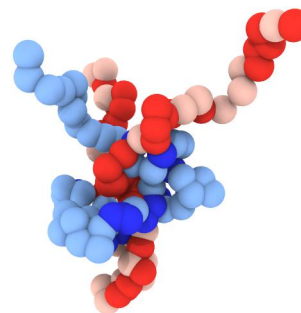


Figure 1: A polyacid and a polybase interacting. Light blue and light red beads represent the neutral polybase and polyacid monomers while dark blue and dark red beads are the charged polybase and polyacid monomers.

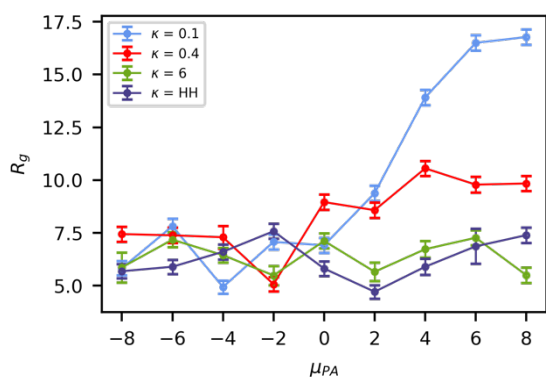


Figure 3: Radius of gyration of a single polyacid as a function of κ . The radius of gyration is insensitive to μ_{PA} at high κ where charge monomers weakly interact but increases with μ_{PA} at low κ due to intramolecular repulsion.

It is informative to first investigate the charging tendency through the titration of an isolated polyacid chain. The ionization fraction of the chain is defined as the number of charged monomers divided by the degree of polymerization. Fig. 2a shows the titration curves as a function of κ . The curves shift to the left and approaches the Henderson-Hasselbalch (HH) limit as screening increases. This is the limit where the titration of monomer is independent of the interactions with neighboring monomers such that the ionization fraction is 0.5 when $pH = pK_a$. Similar trend was observed by varying the chain length, N . Here, $N = 1$ case follows the HH behavior since monomers are free to move and there are minimal interactions of neighboring monomers. The titration curve shifts to the right as N increases (Fig. 2b). In high salt conditions, the ionized polyelectrolyte is not stretched due to the screening of the long-ranged

electrostatic interactions (Fig. 3). In low salt conditions, the chain extends due to the repulsive interactions between charged monomers. This demonstrates that charging of an isolated chain is penalized by repulsive electrostatic interactions.

The titration of a system of a polyacid and a polybase is expected to be cooperative due to the attraction of oppositely charged monomers. In low salt condition ($\kappa = 0.1$), interaction with the polybase of high charge tendency ($\mu_{PB} = +8$) promotes the charging on the polyacid when it is unfavorable for an isolated polyacid to be ionized ($\mu_{PA} = -2$). f_A increases from ~ 0.2 at $\kappa = 6$, which is close to the HH limit as shown in Fig. 2, to ~ 0.4 at $\kappa = 0.1$ (Fig.4). This cooperativity diminishes as κ increases since the electrostatic interaction becomes short-ranged.

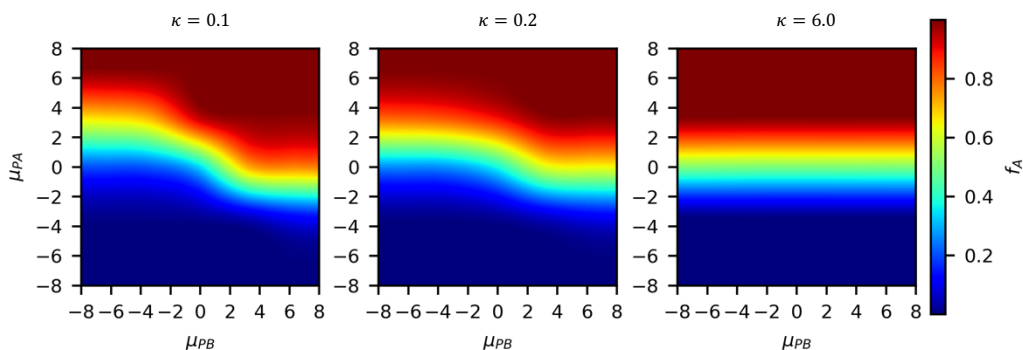


Figure 4: Associative charging at low κ as evident from the increase in the charge on the polyacid in the presence of a polybase with high charging tendency.

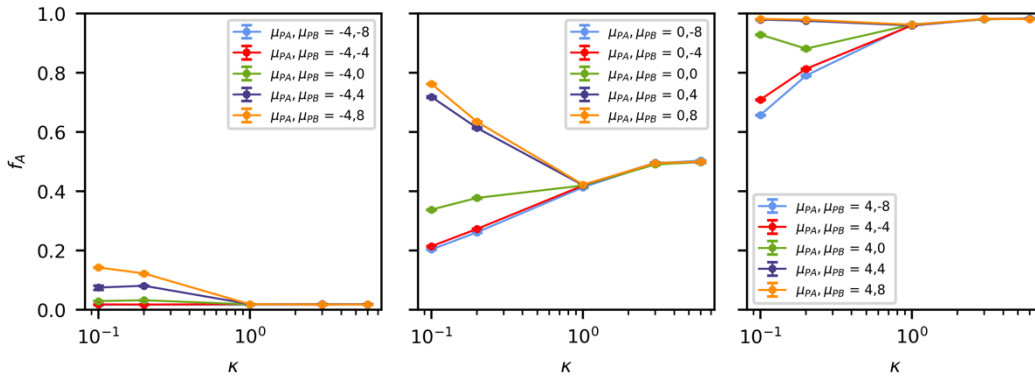


Figure 5: Ionization fraction of the polyacid as a function of κ , μ_{PA} and μ_{PB} . Figures correspond to $\mu_{PA} = -4, 0, 4$. The curves collapse on each other at $\kappa > 1$, which indicates the diminishing of associative charging at high salt concentration.

Similar conclusions can be inferred from plotting the ionization fraction of the polyacid as a function of κ , μ_{PA} and μ_{PB} (Fig. 5). At low κ , the charging of the polyacid is more favorable at high μ_{PB} . At $\kappa = 1$, all the curves collapse onto each other, indicating the absence of associative charging.

The associative charging effects can also be studied by investigating the potential energy, U . As shown in Fig. 6, κ has nonmonotonic effect on U . The increase in the potential energy with screening could be due to the reduced electrostatic attractions between oppositely charged monomers while the contributions from intramolecular repulsion is increased. The potential energy decreases with further increase in κ . At large κ , the contributions from the potential energy comes solely from core repulsions and bonded interactions

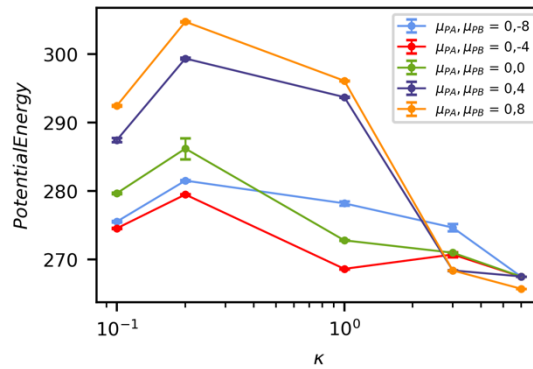


Figure 6: Nonmonotonic change in the potential energy with κ indicates the transition from associative charging dominated regime to intramolecular repulsive dominated regime.

b. Titration curve from multiple histogram reweighting

Multiple histogram reweighting method can be utilized to produce a continuous titration curve. This was demonstrated for a system of a single polyacid of 60 monomers at $\kappa = 0.1$. Simulations were performed for 17 values of μ_{PA} , equally spaced between -8 and 8. This is necessary in order to get sufficient overlap of the configurational distributions. WHAM was used to calculate the entropy and the Helmholtz free energy. Iterations were performed until the average residuals were less than 10^{-4} .

Even with 17 simulation points, the overlap between the configurational distributions is just enough for reasonable statistics (Fig. 7). The average bin count is about 400. More simulation time is needed to reduce the statistical errors of reweighting. Fig.8 shows the reweighted titration curve in comparison with the simulated data points.

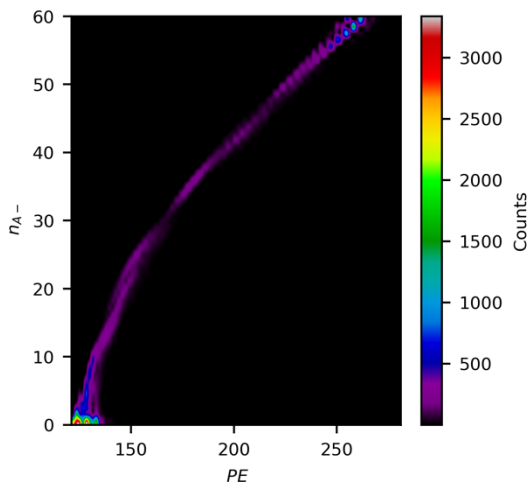


Figure 7: Histogram bin counts as a function of U and n_{A^-} . There is some overlap of U and n_{A^-} between simulations.

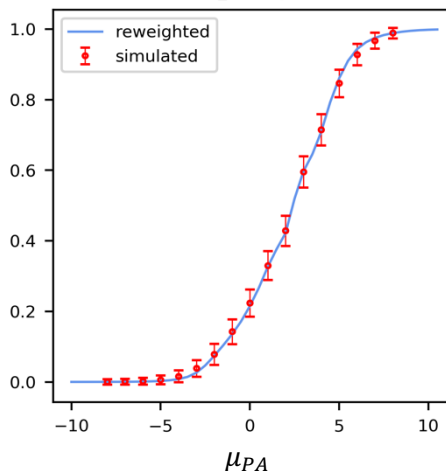


Figure 8: Comparison of the reweighted titration curve and the simulated data points

V. Conclusions

Simulations of a simple model of bead-spring polyelectrolytes demonstrate the associating charging effects through the ionization fraction and the potential energy landscape. In the presence of a charged polybase, the charging of a polyacid is promoted even in conditions where it is unfavorable for an isolated chain to be charged. As screening increases, the favorable electrostatic interactions between oppositely charge monomers are screened. This simple test case replicates common observations in experiments: complexes formed by weak polyelectrolytes are destabilized upon adding salt.

It was demonstrated that the titration curve could be obtained from multiple histogram reweighting method. However, the number of simulations required for the sufficient overlap is about 20, as shown in Fig.7. This is expensive and defeat the purpose of reweighting.

VI. Deficiencies of the model and improvements

This model relies on the assumption that the pK_a of a monomer on the polyelectrolyte is the same as that of a free monomer. This is not realistic since the ionization state of neighboring monomers can have large effects on the charging tendency. The contributions of solvent and ions to the titration can be studied by having explicit solvent molecules and ions. This requires a more complicated move set, for example relaxation of the solvent molecules after a titration move. In addition, more frequent MD move would improve the sampling of chain conformations and the statistics of the radius of gyration.

VII. Description of movie

Movie of interacting polyacid and polybase every 200 MC sweep shows changes in conformations and ionization states.