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Fundamentals of Polyelectrolyte Bridging

Abstract

Polyelectrolyte bridging occurs in systems of macroions with oppositely charged polyelectrolytes. Attractive forces between the like-charged macroions are induced by the polyelectrolytes, which can adsorb to two macrions and form a "bridge" between them. These interactions are important in many biological systems (Podgornik 2006). In this study, two positively charged macroions and one negatively charged polyelectrolyte were modeled to explore the fundamentals of polyelectrolyte bridging. The model used was able to produce bridging phenomena. Shorter polyelectrolyte chains were able to induce a greater attractive force at small macroion separations, but longer chains were able to maintain the force at larger macroion separations.

Background

Polyelectrolyte bridging has been proposed as an explanation for the attractive force induced between two like-charged macroions by an oppositely charged polyelectrolyte. Experimental, theoretical, and computational evidence suggests that the polyelectrolyte chain adsorbs to the surface of both macromolecules, causing the polyelectrolyte to stretch between them (see Figure 1). This bridging effect has been shown to cause an attractive force between the macroions, which would otherwise repel each other (Podgornik 2006).
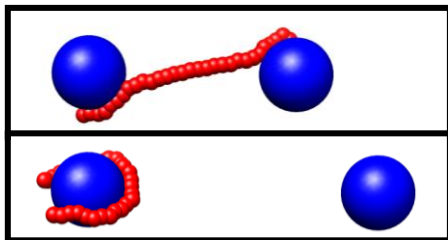

Figure 1: Diagram demonstrating polyelectrolyte bridging.

Evidence of polyelectrolyte bridging has been observed in many different systems. For example, flocculation in certain colloidal systems has been attributed to polyelectrolyte bridging. This type of interaction has also been used to explain behavior in biological systems (Podgornik 2006). Recently, computer simulations have suggested that polyelectrolyte bridging is important in the condensation and folding of nucleosomes, which comprise the chromosomes of the DNA of eukaryotic cells (Korolev 2006). Further investigation of the mechanisms and thermodynamics of polyelectrolyte bridging will allow for a deeper understanding of many processes, including those within the nuclei of cells.

The purpose of this project was to determine whether polyelectrolyte bridging can be modeled using a generic model with simple but fundamental interactions. The system was modeled by two large spheres of like charge fixed at a specified separation distance, with an oppositely charged polyelectrolyte between them. The hypothesis was that the polyelectrolyte would stretch between the two colloids, inducing an attractive force between the macromolecules. The bridging was predicted to occur until the distance between the colloids neared the length of the polyelectrolyte. After this critical distance, the polyelectrolyte was expected to jump completely onto one of the colloids, terminating the bridging effect.

Methods

In order to investigate the most fundamental aspects of the system, a simple model was chosen. Two colloids of positive charge were held at a fixed separation distance. A negatively charged polyelectrolyte was initially placed between the two colloids, and was then allowed to move freely according to Newtonian dynamics. The polyelectrolyte was modeled as a series of bonded spherical monomers, and the macroions were modeled as large spheres. The interactions between the various particles in the system were described by the following potential energy function:

$$U_{total} = U_{bonded} + U_{LJ} + U_{charged}$$

where the total potential energy is comprised of that from interactions between bonded monomers, Lennard-Jones (LJ) interactions between non-bonded particles, and electrostatic interactions between non-bonded particles. In the model, all energies and distances were non-dimensionalized according to the

LJ ε and σ of the monomer, respectively. For the interactions between bonded monomers, a Lennard-Jones chain model was used as follows:

$$U_{bonded} = \sum_{i<j,ij\ bonded} \frac{k}{2}(r_{ij} - r_0)^2$$

where r_{ij} is the distance between particles i and j, k is 3000, and r_0 is 1. The Lennard-Jones 6-12 potential with a cut and shift was used for the steric interactions. The equation describing the potential was:

$$U_{LJ} = \sum_{i<j,ij\ not\ bonded} 4\left(\left(\frac{\sigma_{rat}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{rat}}{r_{ij}}\right)^6\right) - 4\left(\left(\frac{\sigma_{rat}}{r_c}\right)^{12} - \left(\frac{\sigma_{rat}}{r_c}\right)^6\right) for\ r_{ij} < r_c$$

where r_c is the cutoff distance beyond which no LJ interactions occur (10 for this simulation). The term σ_{rat} is 1 if particles i and j are both monomers, 5 if particles i and j are a colloid and a monomer, and 9 if particles i and j are both colloids. The σ_{rat} term determines the relative sizes of the particles. The LJ interactions of the two colloids were not considered in the coded model because their positions are fixed at distances greater than the cutoff distance. Lastly, the equation for the screened electrostatic interactions between the particles was:

$$U_{charged} = \sum_{i<j,ij\ not\ bonded} \eta \frac{q_i q_j}{r_{ij}} e^{\frac{-r_{ij}}{\lambda}}$$

where q is the charge of the particle (in electron units), λ is the Debye screening length, and η is a combination of parameters that encompass the non-dimensionalized electrostatic strength. In this simulation, the Debye screening length was set so that the potential energy between the two colloids at their maximum separation distance was 0.01. The factor η was taken as 100 because this value produced the desired bridging behavior.

This study was completed within the canonical ensemble (constant number of particles, volume, and total energy). The simulation was performed using molecular dynamics with the Verlet integrator. The time step was 0.0001 for all simulation runs. To keep the temperature at the desired set point, the Andersen thermostat was employed. The massive collision version of the thermostat was used, with a collision occurring every 500 steps. The thermostat was turned off for the production runs to ensure that the simulation had constant total energy. For this study, the non-dimensionalized temperature was set at 10.0.

Each simulation run included a 500000 step equilibration phase, another 500000 step equilibration phase, and then a 1000000 step production phase. At the end of the second equilibration phase, the velocities were rescaled so the total energy equaled the average total energy from the run. The graphs of potential energy versus time were checked to make sure that the system had reached equilibrium before the start of the production phase.

Results and Discussion

There were two measures used to indicate that successful polyelectrolyte bridging had occurred. One metric was the mean end to end distance of the polyelectrolyte chain. When bridging occurred, the mean end to end distance increased as the colloids were moved further apart, indicating that the polyelectrolyte was being stretched between the two macroions. When the macroion separation distance neared the length of the polyelectrolyte, the entire chain then jumped onto one of the macroions. This break from bridging was indicated by a sudden drop in the mean end to end distance. Figure 2 shows this pattern for several polyelectrolyte chain lengths.
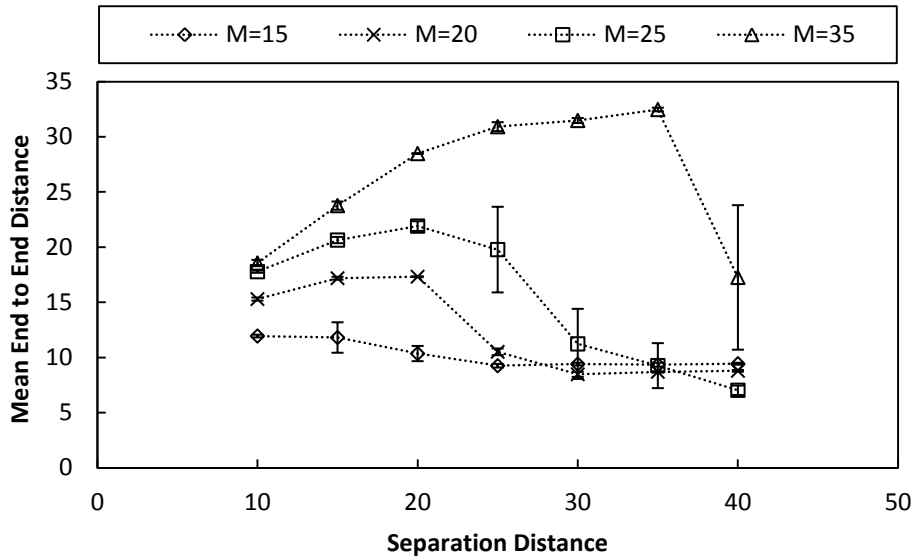
Figure 2: Mean end to end distance of the polyelectrolyte chain as a function of colloid separation distance. The error bars represent the standard deviation over 3 trials.

As was expected, longer polyelectrolyte chains maintained bridging at further colloid separation distances than shorter polyelectrolyte chains. Similar results were obtained by Podgornik, et al. in their 1993 study using a Monte Carlo simulation.

The other metric that indicated successful bridging was the mean force required to hold each colloid at a fixed position. Only the force along the axis on which the colloids were placed was tracked. Without the presence of the polyelectrolyte, the force between the colloids would be purely repulsive. Figure 3A shows the mean force on each colloid versus separation distance for 4 different polyelectrolyte lengths.
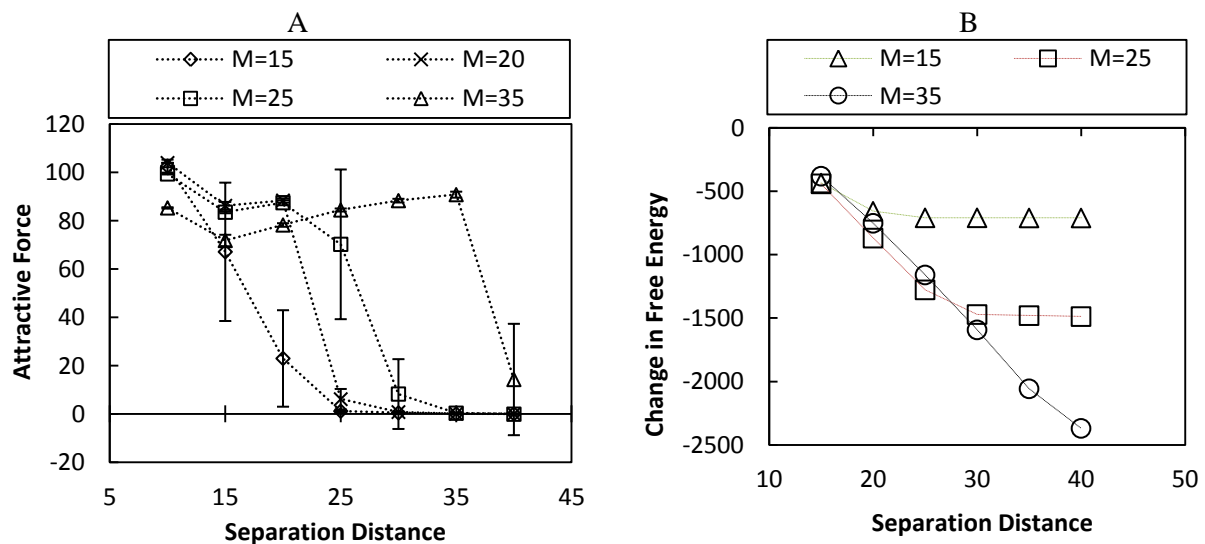

Figure 3: Attractive force on the colloid (A) and change in free energy (B) as a function of colloid separation distance. The error bars in (A) represent the standard deviation over 3 trials.

As can be seen from the graph, an attractive force was induced between the colloids by polyelectrolyte bridging. When the bridging ceased after the critical separation distance, the attractive force between the colloids became much smaller. The trend on the graph shows that shorter polyelectrolyte chains were able

to induce a larger attractive force at short distances, but the longer polyelectrolyte chains were able to maintain the attractive force at longer distances.

Thermodynamic integration was used to generate a plot of free energy versus colloid separation distance for three of the polyelectrolyte lengths tested. The following equation was used for the thermodynamic integration.

$$\Delta F(r) = F(r_1) - F(r_0) = -\int_{r_0}^{r_1} <f_r> dr$$

where F is the free energy of colloid separation, r is the separation distance, and f_r is the force along the direction of separation. In this study, r_o was 10, and all free energies are represented as the difference between the free energy at the specified separation distance and the free energy at r_o. Figure 3B shows the free energy, which decreased as the colloids were moved further apart. The longer polyelectrolyte lengths had a larger value of free energy at larger separation distances. The free energy leveled off once the polyelectrolyte jumped to one colloid and the bridging interactions ceased. This trend makes sense because the system is not at equilibrium while bridging is occurring due to the large force acting on the colloids. At distances where bridging stops, the system is at a minimum free energy because there is no net force on the colloid.

Conclusions

This fundamental model was able to capture bridging phenomena between two positively charged macroions and a negatively charged polyelectrolyte. The end to end distance of the polyelectrolyte increased as the distance between the macroions was increased, indicating that the polyelectrolyte was being stretched. During this stretching period, an attractive force was induced between the macroions. When the colloids were separated past a critical distance that scaled with the polyelectrolyte length, the bridging interaction ceased as the polyelectrolyte jumped onto one of the macroions. After this critical distance, the attractive force on the colloid dropped to zero. The free energy of colloid separation was large when the colloids were close, and decreased to a minimum once bridging was no longer occurring.

Future Studies

There are several improvements that could be made to the model used in this study to make it more realistic and robust. The screened electrostatics potential used in this study is a highly approximate, short-ranged model that may not capture all of the interactions present in polyelectrolyte bridging. Also, this study isolated two colloids and a single polyelectrolyte to focus on the interactions between these three bodies. In reality, there would be many colloids and polyelectrolytes interacting in solution. To study a more realistic system, an Ewald summation could be used to capture long-ranged Coulombic interactions.

In addition, there are many more simulations that could be run with the existing model to explore the fundamentals of polyelectrolyte bridging. The parameters used in this study were chosen to represent a generic system and to generate a desired qualitative behavior. These parameters could be changed to represent a specific colloid and polyelectrolyte pair of interest. Also, the charges of the polyelectrolyte and colloids could be varied to determine at what types of charges bridging occurs.

References

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