

# A Coarse Grain Model for the Interactions Between Oppositely Charged Polymers in Polar Dense Fluid Phases as a Function of Charge Density and Polymer Stiffness

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## **Abstract**

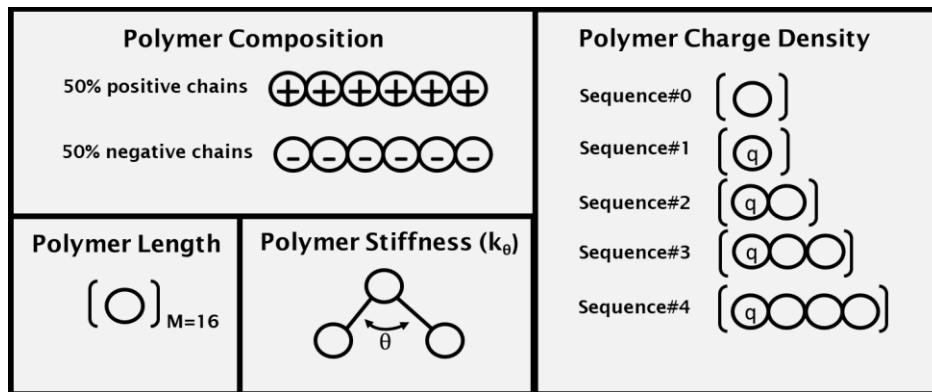
Complexation of oppositely charged conjugated polyelectrolytes has recently emerged as a promising route to achieve aqueous dispersions of conjugated polymers.<sup>1</sup> Despite these recent developments, further investigation is required to understand how the optical and transport properties of these polymer systems is effected by the charge interactions and by the increased polymer persistence length brought by the backbone conjugation. Here, the complexation of oppositely charged polymers in dense fluid phase is investigated via a simple molecular dynamics model. The properties of the materials in the dense fluid phase are investigated with varied chain stiffness and charge distribution. The radius of gyration and the polymer self-diffusion are monitored as rough proxies for the optical properties and the transport properties of the material. The radius of gyration is found to increase with charge density on the backbone, and the polymer self-diffusion is found to decrease as the charge density on the backbone is increased. Furthermore, a stiffer polymer backbone is shown to decrease the polymer self-diffusion rate.

## **Introduction**

Conjugated polymers are a useful class of materials, owing to their unique optical properties and ability to transport ionic and electronic carriers. Recent work has shown that complexation of oppositely charged conjugated polyelectrolytes can be used to form solution processible formulations of conjugated polymers.<sup>1</sup> While this approach has shown clear benefits for polymer processing, the effects of complexation on the material properties, namely the optical properties and the transport properties, remain largely unknown. Here, a rough molecular dynamics model for this complexation process is developed, where the optical properties and transport properties are emulated using the radius of gyration and the polymer self-diffusion coefficient respectively. The effect of the polymer stiffness, and charge density along the backbone is investigated.

## Results and Discussion

### Model detail



**Figure 1.** Schematic illustrating the simulated system along with the some of the key parameters in the model

A simple linear atomic chain model based loosely off the work of Reis et. al.<sup>2</sup> was chosen to model the behavior of oppositely charged polymer mixtures in the dense fluid phase. For the non-bonded interactions in the system, a Lennard Jones potential (see **Equation 1**) with a shift at a distance  $r_c=2.5$  was used so that the potential is zero at  $r_c$ . Additionally, a screened coulombic potential (see **Equation 2**) was utilized to model the interactions between charged groups on the polymers. Here the main parameter is the screening length  $\lambda$ . A sensitivity analysis was used to choose a value of  $L$  for this parameter (See SI).

$$U(r_{ij}) = 4(r_{ij}^{-12} - r_{ij}^{-6}) \quad (\text{E1})$$

$$U(r_{ij}) = \frac{(q_i q_j)}{r_{ij}} e^{-\frac{r_{ij}}{\lambda}} \quad (\text{E2})$$

For the bonded interactions, a simple harmonic bonding potential was used to model the behavior of harmonic bonds between adjacent atoms, where  $k$  is chosen to be 3000 (see **Equation 3**). Additionally, to model the effect of polymer stiffness, a bond angle potential was also incorporated into the model (see **Equation 4**). Here, a cosine harmonic potential was chosen over a standard angle harmonic potential for model simplicity, which is common for this type of system.<sup>3</sup> Here, the force can be obtained with the chain rule via  $F_i = -\frac{\partial U}{\partial r_i} = -\frac{\partial U}{\partial \cos\theta} \frac{\partial \cos(\theta)}{\partial r_i}$  where  $\cos\theta = \frac{r_{ji} \cdot r_{jk}}{r_{ji} r_{jk}}$  and similarly  $F_k = -\frac{\partial U}{\partial r_k}$ , and  $F_j = -F_i - F_k$ .

$$U(r_{ij}) = \frac{k}{2}(r_{ij} - r_0)^2 \quad (\text{E3})$$

$$U(\theta_{ijk}) = k_\theta (\cos(\theta_{ijk}) - \cos(\theta_0))^2 \quad (\text{E4})$$

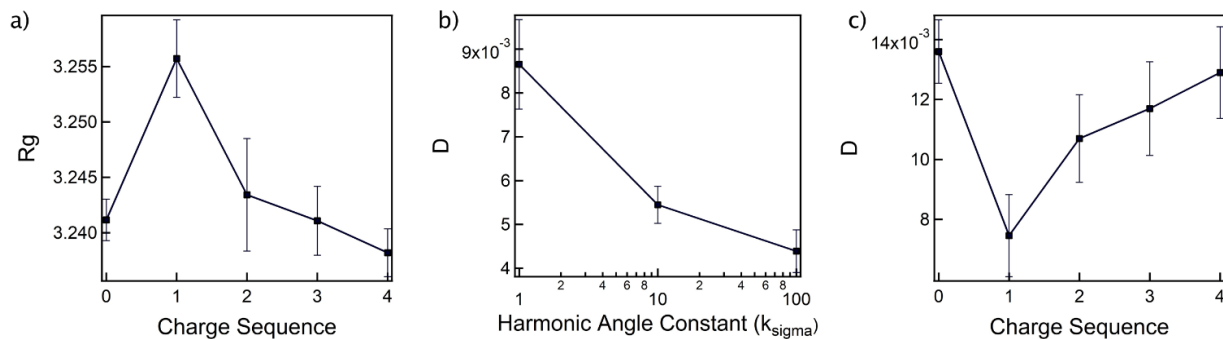
Here, the  $k_\theta$  parameter is tuned to control the stiffness of the polymer

### Simulation Algorithm

For all simulations, a reduced density of 0.8 was chosen with a total number of particles,  $N$ , equal to 240 to emulate a dense fluid phase. The simulation box size was thus chosen to be  $(N/\rho)^{1/3}$  with periodic boundary conditions. Time steps of 0.001 were utilized, and the velocity Verlet integrator was used for numeric integrations. All atoms were initiated on a cubic lattice and subsequently energy minimized using the conjugate gradient method prior to the MD run. For each simulation, two equilibration steps were first implemented. During the first equilibration step, the temperature was rescaled to a target temperature  $T=1.0$  every 1000 steps for a total of 10,000 steps. A second equivalent equilibration step was then implemented, and the energy was averaged throughout this period. The instantaneous velocity was then rescaled to set the instantaneous energy to the average energy over the second equilibration step. All properties were then computed during a proceeding production run in which no velocity rescaling was used. The diffusion coefficients were estimated using the slope of the mean squared displacement from the initial position with time via  $D = \frac{1}{6} \lim_{n \rightarrow \infty} \frac{d}{dt} \langle |\mathbf{r} - \mathbf{r}_0|^2 \rangle$  (see SI for more detail). Further, the radius of gyration ( $R_g$ ) was estimated by averaging the instantaneous  $R_g$  for all polymers and then averaging this value over the entire production period, where the  $R_g$  was calculated via  $R_g = \sqrt{\frac{1}{N} \sum |r_i - r_{COM}|^2}$ .

## Results

One important issue in mixtures of oppositely charged polymers is the effect of charge interactions on the conformation of the polymer. Charge repulsion along the polymer backbone can lead to stiffening of the polymer chain. Previous studies have also shown that the process of complexation between oppositely charged polymers can lead to increased persistence lengths.<sup>1</sup> Here, the average radius of gyration was calculated as a function of the charge density on the polymer backbone (**Figure 2a**). Simulations reveal that as the charge density is increased, the radius of gyration increases. This indicates that polymers are adopting a more extended conformation as the charge density increases. This is likely due to charge repulsion along the backbone. Some degree of polymer-polymer interaction/complexation could also be playing a role here.



**Figure 2.** a) Plot of the radius of gyration as a function of the charge sequence with no harmonic bond potential. b) Plot of the diffusion constant as a function of the harmonic angle constant  $k_{\theta}$  with charge sequence #1 c) Plot of the diffusion coefficient as a function of the charge sequence with no harmonic bond potential. All simulations were performed with  $M=16$ . Each plot represents the average of three simulations, and the standard error is represented using error bars.

The mobility in these polymer systems is also of interest, particularly when considering the transport properties. Here, the self-diffusion of polymer chains was calculated as a function of the polymer stiffness (via changing the harmonic angle constant  $k_{\theta}$ ) and the charge sequence. **Figure 2d** shows that the rate of polymer diffusion decreases as the chain stiffness increases. This trend is expected because as the stiffness increases, the polymer will adopt a more extended conformation, leading to a large average “particle diameter”. As a result, the polymer will experience slower diffusive dynamics. **Figure 2c** shows the polymer self-diffusion constant as a function of the charge density on the backbone. As expected, as the charge density on the backbone is increased, the self-diffusion constant decreases. This is likely because as the number of charged groups per polymer is increased, the polymers interact to a greater extent. These attractive interactions between polymers likely slow the polymer dynamics. Furthermore, as displayed by **Figures 2a and 2b**, increasing the charge density along the polymer backbone will increase the radius of gyration of the polymer and lead to a more extended conformation. This can in turn slow the diffusion rate, as shown by **Figure 2b**

### *Conclusions*

The results in this study have interesting implications for the properties of oppositely charged conjugated polyelectrolyte mixtures. In such polymer systems, the optical properties are often dependent on the conformation of the backbone, because polymers with more extended conformations often have a higher degree of conjugation. This study suggests that charged polymer mixtures have a more extended conformation when compared to their neutral counterparts. This is favorable in conjugated polymer mixtures because it indicates that the conjugation length will increase.

Another important consideration in conjugated polyelectrolyte mixtures is the transport properties, particularly the transport of charge in the form of ions and electrons. While the transport of ions and electrons is difficult to model and requires more detailed simulation, the mobility of the polymer chains themselves was calculated here to reveal some information about dynamics. Simulations reveal that the chain dynamics decreases as the charge density along the backbone increases. Since ion diffusion in polymer systems is often closely correlated to the polymer chain dynamics, we postulate that conjugated polyelectrolyte mixtures have slower ion dynamics than their neutral counterparts. On the contrary, the longer polymer conformation (increase conjugation length) and the decreased polymer dynamics observed in these mixtures could lead to improved electronic transport characteristics.

### *Future Work*

While this simple polymer model was enlightening, future improvements to the model could help elucidate more detailed properties of the system. In this work, a screened coulombic potential was used for ease of simulation. Future simulations could include explicit counter ions and a more accurate representation of Coulomb’s law to better emulate the interactions and dynamics in bulk polymer mixtures. The polymer lengths, simulation times, and overall number of particles were also unrepresentatively small, and should be increased to better represent real systems. Lastly, future work with these simulations should include a thermostat, such as the Anderson thermostat, in order to achieve simulations in the canonical ensemble. This would support the calculation of properties such as entropy, free energy, and radial distribution functions that are applicable to real world observations.

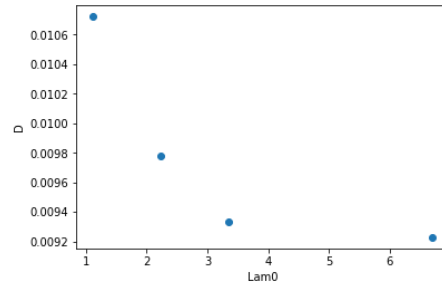
**Movie Caption**

The attached movie shows the evolution of the system after initialization for  $M=16$  and  $k_{\theta}=0$ , in which charge sequence #1 is utilized. The movie shows the first two equilibration steps and the production step together. Oppositely charge polymers are given different colors to enable observation of the interaction and mixing of oppositely charge polymer species

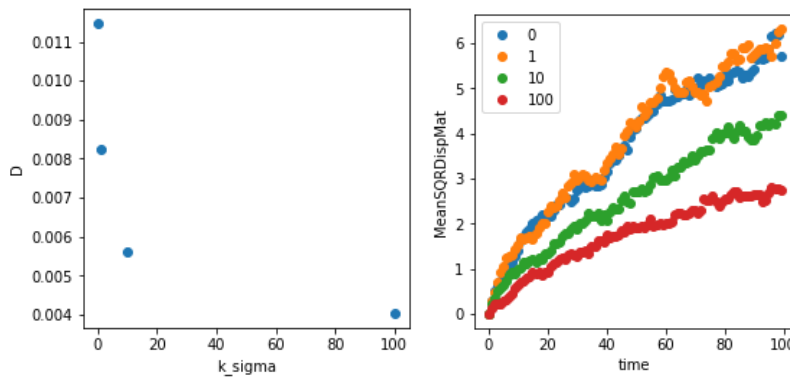
**References**

- (1) Danielsen, S. P. O.; Nguyen, T. Q.; Fredrickson, G. H.; Segalman, R. A. Complexation of a Conjugated Polyelectrolyte and Impact on Optoelectronic Properties. *ACS Macro Lett.* **2019**, *8* (1), 88–94.
- (2) Reis, R. A.; Silva, F. C.; Nobrega, R.; Oliveira, J. V.; Tavares, F. W. Molecular Dynamics Simulation Data of Self-Diffusion Coefficient for Lennard-Jones Chain Fluids. *Fluid Phase Equilib.* **2004**, *221* (1–2), 25–33.
- (3) Bulacu, M.; Goga, N.; Zhao, W.; Rossi, G.; Monticelli, L.; Periole, X.; Tieleman, D. P.; Marrink, S. J. Improved Angle Potentials for Coarse-Grained Molecular Dynamics Simulations. *J. Chem. Theory Comput* **2013**, *9*, 3292.

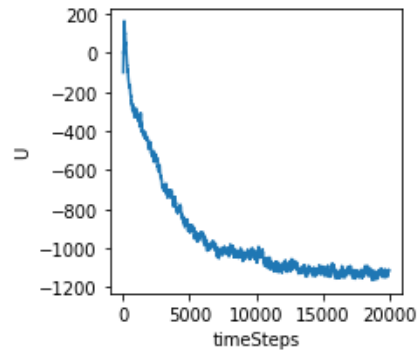
Supporting Information



**Figure S1:** Diffusion coefficient as a function of the screening length. Here, a screening length of  $L$  was chosen for simulations



**Figure S2:** Representative diffusion plots showing how the diffusion coefficient is calculated from the slope of the mean squared displacement



**Figure S3:** Plot of the potential energy as a function of time steps after initiation for charge sequence #1.