Entanglements and Dynamics of Polyelectrolytes in Concentrated Solutions and Complexes

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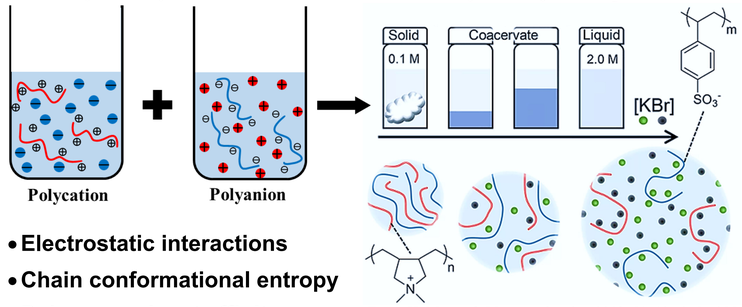
ABSTRACT

We performed coarse-grained molecular dynamics simulations of polyelectrolyte solutions and mixtures of oppositely charged chains with different degrees of polymerization. Analysis of the simulation results for the mean-square displacement of the monomers belonging to the central part of the chain and the chains' centers of mass shows that the chains' dynamics is a combination of constraint release and chain reptation in the confining tube. The constraint release appears to play a dominant role in mixtures of positively and negatively charged chains with intermediate and low degrees of polymerization. The degree of polymerization between entanglements N_e of the tube and super tube in systems of charged chains scales with solution concentration as $N_e \sim \rho^{-2}$ and has corresponding packing number P_e = 18.45±0.93. This is qualitatively different from the behavior of similar composition mixtures of neutral chains where in addition to $N_e \sim \rho^{-2}$ scaling dependence, the degree of polymerization between entanglements for the super tube demonstrates a $N_e \sim \rho^{-4/3}$ concentration dependence with corresponding packing number P_e = 6.64±0.19.

ION-CONTAINING POLYMERS IN SOLUTIONS

Polyelectrolyte Solutions **Polyelectrolyte Complexes**



- **Electrostatic interactions**
- **Chain conformational entropy**
- **Polymer−solvent affinity**

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MODEL AND SIMULATION DETAILS

Kremer-Grest Model:

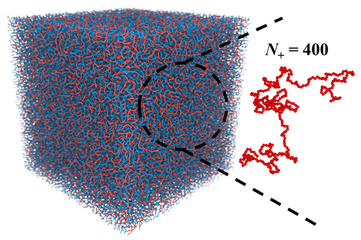
• Lennard-Jones (LJ) Potential + FENE

$$U_{LJ} = \begin{cases} 4\varepsilon_{LJ}\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6} - \left(\frac{\sigma}{r_{cut}}\right)^{12} + \left(\frac{\sigma}{r_{cut}}\right)^{6}\right] & r \le r_{cut} \\ 0 & r > r_{cut} \end{cases}$$

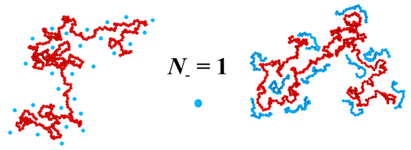
$$U_{FENE}(r) = -\frac{1}{2}k_{spring}R_{max}^2 \ln\left(1-\frac{r^2}{R_{max}^2}\right)$$

• Coulomb Potential

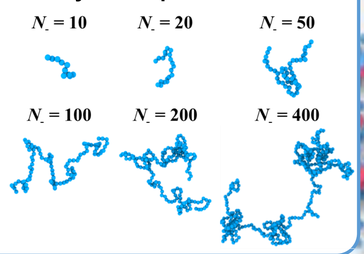
$$U_{Coul}(r) = k_B T \frac{l_B z_i z_j}{r}$$



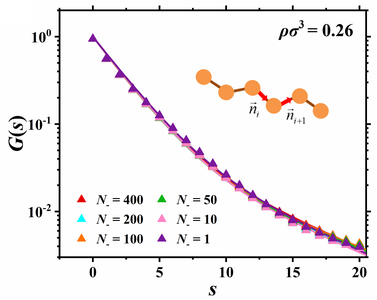
Polyelectrolyte Solutions



Polyelectrolyte Complexes



CHAIN SIZE AND KUHN LENGTH



Bond-Bond Correlation

$$G(s) = \frac{1}{n_b - s}\sum_{i=1}^{n_b - s}\langle(\vec{n}_i \cdot \vec{n}_{i+s})\rangle$$

•Fit by approximated function:

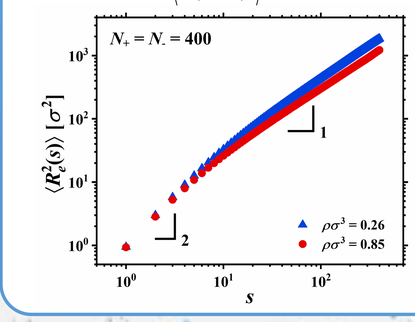
$$G(s) = (1-\alpha)e^{-|s|/\lambda_1} + \alpha e^{-|s|/\lambda_2}$$

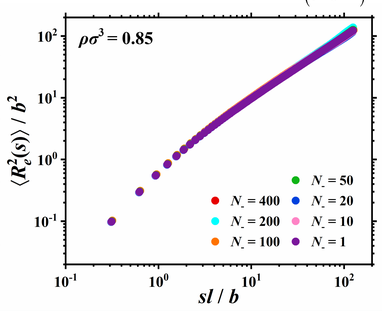
Kuhn Length

$$b = \left.\frac{\langle R_e^2(s)\rangle}{sl}\right|_{s\to\infty} \approx l\left((1-\alpha)h(\lambda_1) + \alpha h(\lambda_2)\right), \text{ where } h(\lambda) = \frac{1+e^{-1/\lambda}}{1-e^{-1/\lambda}}$$

Mean-Square End-to-End Distance

$$\langle R_e^2(s)\rangle = \frac{1}{N-s}\sum_{i=1}^{N-s}\left\langle l^2\left(\sum_{j=i}^{i+s-1} n_j\right)^2\right\rangle = l^2\left((1-\alpha)g(\lambda_1, s) + \alpha g(\lambda_2, s)\right), \text{ where } g(\lambda, s) = s\frac{1+e^{-1/\lambda}}{1-e^{-1/\lambda}} - 2e^{-1/\lambda}\frac{1-e^{-s/\lambda}}{\left(1-e^{-1/\lambda}\right)^2}$$





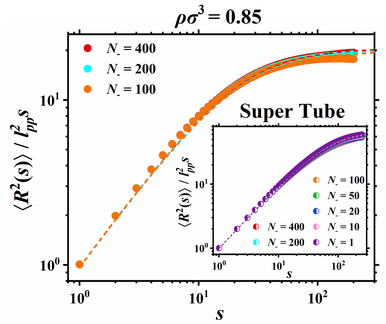
ENTANGLEMENTS OF CHARGED POLYMERS

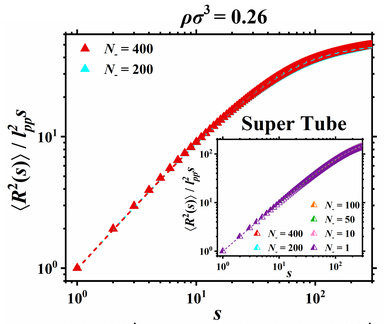
The number of overlapping entangled strands P_e inside a confinement volume d_T^3:

$$P_e \approx \rho d_T^3 / N_e \approx \rho(bl)^{3/2} N_e^{1/2}, \text{ where } d_T \approx \sqrt{blN_e}$$

The degree of polymerization between entanglements, $N_{e,+}$, for the longer chains forms a super tube.

$$N_{e,+} \approx (\rho/\rho_+)^2 N_e \Rightarrow N_{e,+} \approx 4N_e$$





Primitive Path Analysis (PPA)

$$\langle R_e^2(s)\rangle = s l_{pp}^2\left(\frac{1+\langle\cos\theta\rangle}{1-\langle\cos\theta\rangle} - \frac{2\langle\cos\theta\rangle}{s}\frac{1-\langle\cos\theta\rangle^s}{\left(1-\langle\cos\theta\rangle\right)^2}\right)$$

$$N_e = b_{pp}/l_{pp} = \left(1+\langle\cos\theta\rangle\right)/\left(1-\langle\cos\theta\rangle\right)$$

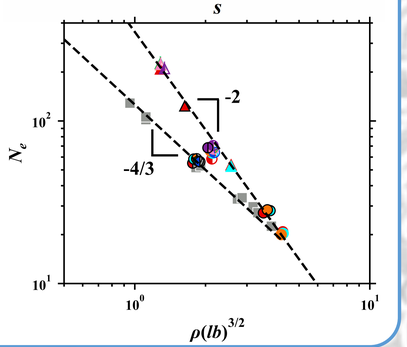
Dilution of Tube and Super Tube

Tube and super tube follow

$$N_e \sim \left(\rho(lb)^{3/2}\right)^{-2}$$

Super tube dilution in θ-solvent follows

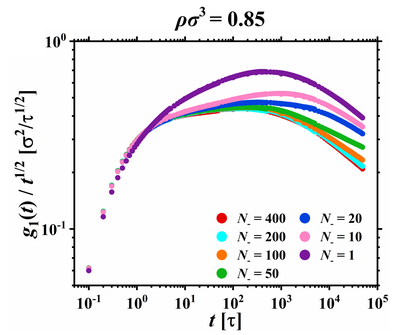
$$P_e \approx \left(\rho l^3 (b/l)^{3/4}\right)^{2/3} N_e^{1/2}$$

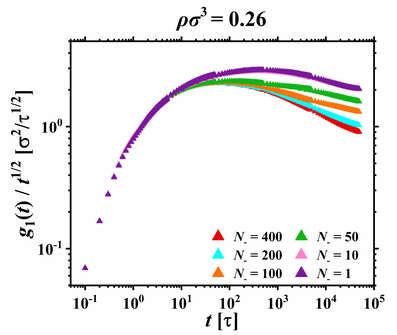


DYNAMICS OF CHARGED POLYMERS

Mean square displacement (MSD) of monomers belonging to positively charged chains:

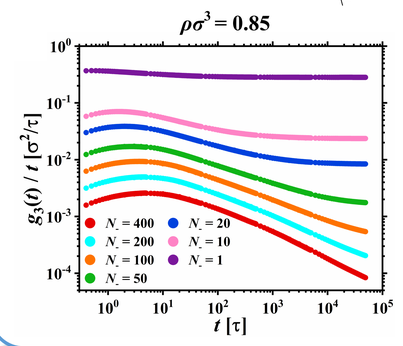
$$g_1(t) = \left\langle\left[\mathbf{r}_i(t+\Delta t) - \mathbf{r}_i(\Delta t)\right]^2\right\rangle$$

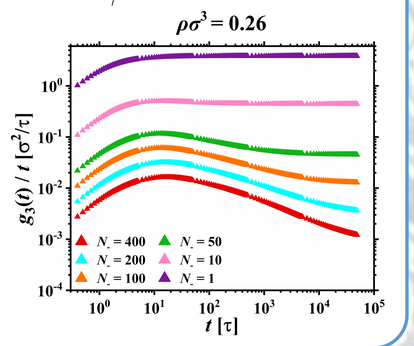




Mean square displacement (MSD) of the center of mass of "counterion" chains with different degrees of polymerization:

$$g_3(t) = \left\langle\left[\mathbf{r}_{cm}(t+\Delta t) - \mathbf{r}_{cm}(\Delta t)\right]^2\right\rangle$$





CONCLUSIONS

- For studied monomer concentrations, the electrostatic interactions are manifested in a weak renormalization of the chain Kuhn length and a moderate increase of the chain size.
- The increasing degree of polymerization of the negatively charged chains increases the concentration of entanglements per chain due to the decrease of N_e.
- The constraint release shown in the mixtures of chains with two different degrees of polymerization shortens the reptation time of the longer chains.
- The effect of the electrostatic interactions on chains' dynamics can be reduced to renormalization of the monomeric friction coefficient and Kuhn length.

AKNOWLEDGEMENTS

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