Self-Consistent Field Calculations of Polyelectrolyte Systems

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1. Polyelectrolytes (PE)

PE are charged polymers

PE are important materials

• Can be soluble in water
• Can be adsorbed onto charged surfaces

PE are difficult to study

• Both long-range (Coulomb) and short-range (excluded volume) interactions present in the system

2. Theoretical Formulism

Model PE System

Charge distributions:

• Smoothen: each segment carries a fraction of e'
• Annealed: each segment has a probability of carrying e'

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\begin{align*}
p &= A, B, \ldots \\
\rho &= 0, 1, 2, \ldots \\
\eta &= 0, 1, 2, \ldots
\end{align*}
\]

PE are charged polymers

PE have no volume

Monovalent system

All P segments have the same density \( \rho_0 \) as S

All P segments have the same statistical segment length \( a \)

3. Interface of a Phase-Separated PE Solution

N=100, \( p=0.05 \), \( \bar{d}_p=0.34 \), \( x_{SA}=1 \), \( f=29.4 \) (in units of \( R_g^A \), \( \kappa=1, c_i=0 \) (by default)

4. Behavior of PE Brushes

N=100, \( p=0.1 \), \( x_{A}=0.25, \epsilon=98.0 \) (in units of \( R_g^A \), \( \epsilon=0.012, x_{SA}=0.476, p=0.5 \) (annealed), \( c_i=0 \) (by default)

5. Lamellae of Symmetric Diblock PE

\( N_A=N_B=N/2=200, \bar{d}_p=0.8, x_{SA}=x_{SB}=0 \), \( c_i=0 \), \( x_{A}=x_{B}=1 \)

6. Phase Behavior of Symmetric PE Blends

\( N_A=N_B=N/2=200, p=0.02 \) (annealed), \( \bar{d}_p=0.8, x_{SA}=x_{SB}=0 \), \( c_i=0 \)

RPA: \( T > \beta (G_r^{AA}+G_r^{BB}) \) for microphase separation, where the Debye function is approximated by \( (1+h^2)^{-1} \).

7. Current Work: Towards Biosensors

PE adsorption and multilayer formation on charged surfaces

• Complex formation and charge inversion
• Insights into sensor surface / biomolecule interaction

Conformation of a single PE chain tethered to a surface

• 3D calculations including fluctuation effects
• Parameter tuning for multi-scale modeling

8. Summary

• A self-consistent field theory (SCFT) is developed for inhomogeneous polyelectrolyte (PE) systems, where both the smeared and the annealed charge distributions are considered, and the dielectric constant of the system is treated as position-dependent.
• We have applied the SCFT to several PE systems, including the interface of a phase-separated PE solution, lamellar of symmetric diblock PE, phase behavior of PE blends, and behavior of PE brushes.
• Further work on strongly charged PE on sampling fluctuations of the system is undergoing.

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\begin{align*}
f_i &= \text{free energy per chain} \\
P_{\text{MD simulations}} &= \text{Preliminary MD results}
\end{align*}
\]