Effect of Chain Rigidity on Ordering of Diblock Copolymers

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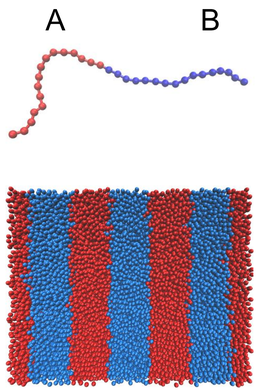
Motivation



- Semiflexible polymers exhibit behavior that depends strongly on chain stiffness
- Stiffness influences both individual chain conformations and collective ordering
- How rigidity affects phase behavior in diblock copolymers remains an open question
- Simulations provide a controlled way to isolate and study these effects

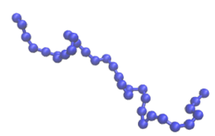
Background

- Continuous semiflexible polymer model
- Bending energy penalizes curvature
- Characterized by persistence length ℓ_p

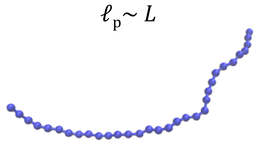
$$\ell_p = \frac{1}{\ell}\sum_{j=1}^{N}\langle \vec{l_0}\cdot\vec{l_j}\rangle$$

Persistence length measures how strongly bond directions along a chain remain correlated. When successive bonds tend to align in the same direction, the persistence length is large; when their orientations change rapidly, it is small.

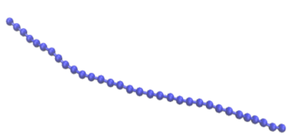
$\ell_p \ll L$



$\ell_p \sim L$



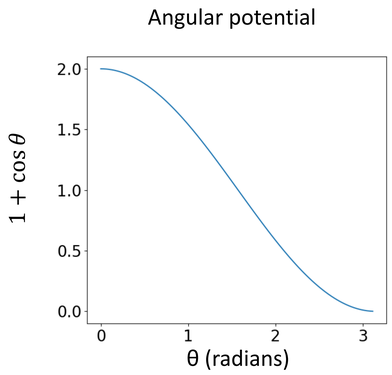
$\ell_p \gg L$



Simulation Methods

- Used HOOMD blue to run polymer simulations
- Bead-spring diblock copolymer model
- Used finitely extensible non-linear bonds (FENE)
- Lennard-Jones potential was used to model excluded volume
- Angular potential for modeling chain rigidity

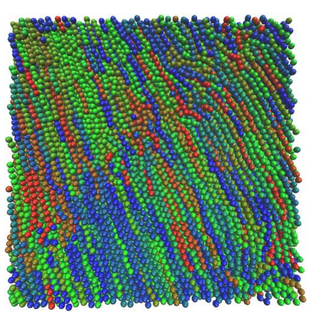
$$U_\theta = \varepsilon(1+\cos\theta)$$



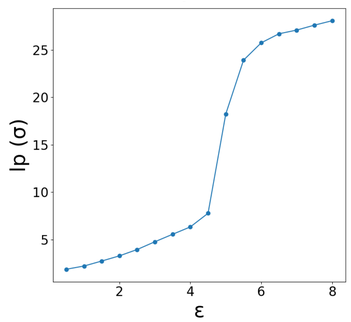
Varying Bending Rigidity

- Simulated at fixed concentration c = 0.85 $\frac{\text{particles}}{\sigma^3}$
- Varied strength of angular potential ε
- Measured persistence length

ε = 7



ℓ_p vs ε

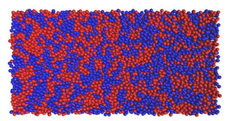


- Observed liquid crystal phase transition around ε = 5
- Suspected to be driven largely by concentration rather than strictly ε

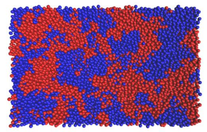
Lamellar Stability Under Varying A–B Interaction Strength

- Initialized system in a lamellar phase
- Removed bending rigidity to isolate interaction-driven effect
- Varied A–B exclusion interaction strength (ε_{AB})
- Identified a transition from ordered to disordered structure between ε_{AB} = 2 and ε_{AB} = 3

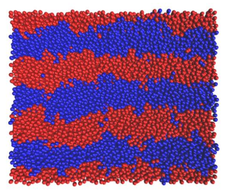
$\varepsilon_{AB} = 1$



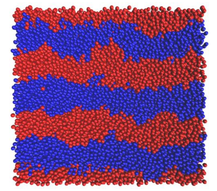
$\varepsilon_{AB} = 2$



$\varepsilon_{AB} = 3$



$\varepsilon_{AB} = 4$



Results and Next Steps

- Quantified how bending rigidity controls persistence length
- Identified transitions to ordered structures when bending rigidity and A–B interaction strength are considered separately
- Next: combine both effects to determine how they jointly control the onset of order

References

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