Field-Theoretic Monte-Carlo Simulations of Ternary Blends
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Introduction
Mixing polymers helps tune properties.
Adding diblocks promotes mixing.
Applications require understanding phase behavior of ternary blends.

MC-FTS worked well describing the limiting cases of pure homopolymer and pure diblock copolymer.
MC-FTS was able to study the behavior of a homopolymer blend, probing the disordered phase and precisely locating the critical point for various polymer lengths.

Pure diblocks microphase separate.
Pure homopolymers macrophase separate.

Bicontinuous microemulsions form between extremes.
Bicontinuous microemulsions are of technological and fundamental interest.

We start with pure copolymer or homopolymer. Then move on to ternary blends and bicontinuous microemulsions.

Theory for Binary Blends

Particle-based

\[ Z \sim \exp\left(\frac{-U}{k_BT}\right) \prod \phi_A + \phi_B - 1 \int P[\phi_A,\phi_B] \exp \left\{ -\frac{1}{2k_BT} \int d^3r\left( \phi_A \phi_B \hat{A} \right) \right\} \]

Field-based

\[ Z \sim \int \exp\left(\frac{H_{W_1}}{k_BT}\right) \prod W_1 \exp \left\{ -\frac{1}{2k_BT} \int d^3r\left( \phi_A \phi_B \hat{A} \right) \right\} \]

Use Monte Carlo to solve integrals exactly.
Treat incompressibility using mean-field theory.
Extension to ternary blends is straightforward.

Diblock Copolymer Results

MC-FTS successfully found the structure function. Results deviate from RPA, Renormalized one loop calculation and results by Fredrickson and Helfand.

Simulate a melt starting from order or disorder at various \( T \).
Hysteresis loops allow us to bracket the ODT in small region.

ODT was found for various \( N \).
Results are consistent with those of particle simulations.

Homopolymer Blend Results

MC-FTS successfully found the structure function. Results consistent with RPA.

Fourth-order cumulant method allows us to precisely locate the critical point, accounting for finite size effects.

Demixing is suppressed by fluctuations.
Suppression scales as \( N^{-1/2} \).
Suppression is less than predicted by ROL.

MC-FTS was able to study the behavior of a homopolymer blend, probing the disordered phase and precisely locating the critical point for various polymer lengths.

Ternary Blend – Future Work

MC-FTS worked well describing the limiting cases of pure homopolymer and pure diblock copolymer.
Moving on to ternary blends, below are snapshots of simulations varying homopolymer concentration.

The techniques used for simple cases can be extended to the full ternary blend phase diagram, to locate the bicontinuous microemulsion channel.
MC-FTS can then be used to study the nature of bicontinuous microemulsions.

This work was funded by NSF under the Center for Sustainable Polymers (CHE-1413862), and computational resources were provided by SHARCNET.