Field-Theoretic Monte-Carlo Simulations of Ternary Blends

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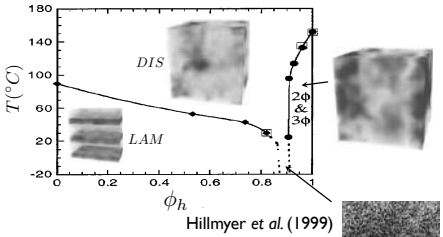
Introduction

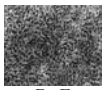
Mixing polymers helps tune properties.
Adding diblocks promotes mixing.
Applications require understanding phase behavior of ternary blends.

$\phi_h \quad 1-\phi_h$

Pure diblocks microphse separate.
Pure homopolymers macrophase separate.



Hillmyer *et al.* (1999)

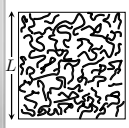


Bicontinuous microemulsions form between extremes.
Bicontinuous microemulsions are of technological and fundamental interest.

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

Theory for Binary Blends

Particle-based



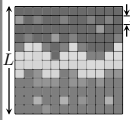
$$Z \sim \int \exp(-U/k_BT)\delta[\hat{\phi}_A + \hat{\phi}_B - 1] \prod_{\alpha=1}^{n} P[\vec{r}_\alpha]\mathcal{D}\vec{r}_\alpha$$

$$-\frac{U}{k_BT} = \frac{\chi_b N}{V}\int \hat{\phi}_A\hat{\phi}_B d\vec{r}$$

$$P[\vec{r}_\alpha] \propto \exp\left\{-\frac{3}{2Na^2}\int ds \left|\frac{d}{ds}\vec{r}_\alpha(s)\right|^2\right\}$$

$\Downarrow$ exact transformation

Field-based



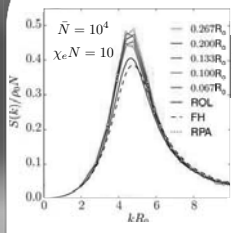
$$Z \sim \int \exp\left(\frac{H[W_-,W_+]}{k_BT}\right)\mathcal{D}W_-\mathcal{D}W_+$$

$$\frac{H[W_-,W_+]}{k_BT} = -\frac{1}{2}\ln Q_A Q_B + \frac{1}{V}\int\left(\frac{W_-^2(\vec{r})}{\chi_b N} - W_+(\vec{r})\right)d\vec{r}$$

W_- field couples to $\hat{\phi}_A(\vec{r}) - \hat{\phi}_B(\vec{r})$
W_+ field couples to $\hat{\phi}_A(\vec{r}) + \hat{\phi}_B(\vec{r})$
$Q_{A/B}$- single chain partition function

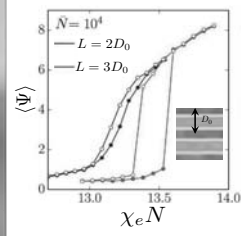
Use Monte Carlo to solve W_- integral exactly.
Treat incompressibility using mean-field theory.
Extension to ternary blends is straightforward.

Diblock Copolymer Results

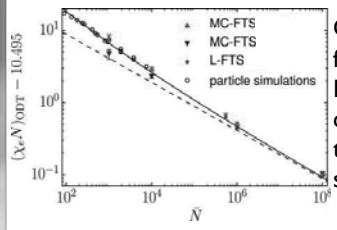


MC-FTS successfully found the structure function.
Results deviate from RPA, Renormalized one loop calculation and results by Fredrickson and Helfand.

ROL: Qin and Morse (2009)
FH: Fredrickson and Helfand (1987)



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

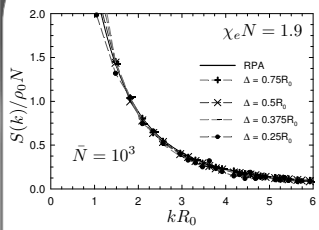


ODT was found for various $\bar{N}$.
Results are consistent with those of particle simulations.

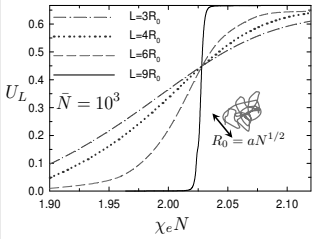
MC-FTS was able to examine the behavior of a diblock copolymer melt, probing the disordered phase and locating the ODT for various polymer lengths.

Vorselaars and Matsen (2015)

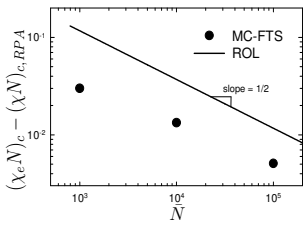
Homopolymer Blend Results



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.

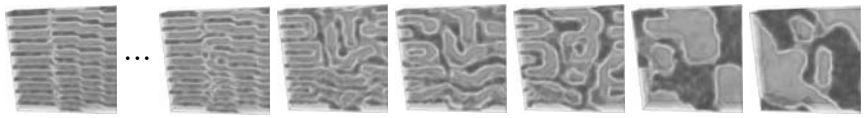


Demixing is suppressed by fluctuations.
Suppression scales as $\bar{N}^{-1/2}$.
Suppression is less than predicted by ROL.

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.



$\chi_e N_c = 15$
$N_c/N_h = 5$

$\phi_h \quad 0 \quad 0.6 \quad 0.7 \quad 0.8 \quad 0.85 \quad 0.9 \quad 1$

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.

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