Title: Monte Carlo Field-Theoretic Simulations Applied to Block Copolymer Melts

Date: Dec 05, 2013 09:15 AM

URL: http://pirsa.org/13120009

Abstract: Monte
Carlo field-theoretic simulations (MC-FTS) are performed on melts of symmetric
diblock copolymer for invariant polymerization indexes extending down to
experimentally relevant values of N=10⁴. The simulations are
performed with a fluctuating composition field, W₋(r), and a pressure
field, W₊(r),
that follows the saddle-point approximation. Our study focuses on the
disordered-state structure function, S(k),
and the order-disorder transition (ODT). Although short-wavelength fluctuations
cause an ultraviolet (UV) divergence in three dimensions, this is readily
compensated for with the use of an effective Flory-Huggins interaction
parameter, c_e. The resulting S(k)
matches the predictions of renormalized one-loop (ROL) calculations over the
full range of c_eN and N
examined in our study, and agrees well with Fredrickson-Helfand (F-H) theory
near the ODT. Consistent with the F-H theory, the ODT is discontinuous for
finite N and the shift in (c_eN)_{ODT}
follows the predicted N^{-1/3} scaling over our range of N.

Monte Carlo Field-Theoretic Simulations Applied to Block Copolymer Melts

Mark W. Matsen

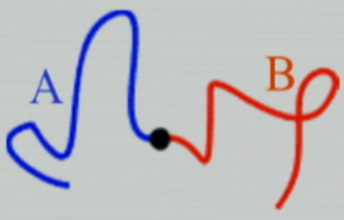
Waterloo Institute for Nanotechnology (WIN)
Department of Chemical Engineering
Department of Physics and Astronomy

Outline

- phase behaviour of diblock copolymer melts
- self-consistent field theory (SCFT)
- Fredrickson-Helfand fluctuation theory (1987)
- field-theoretic simulations (FTS)

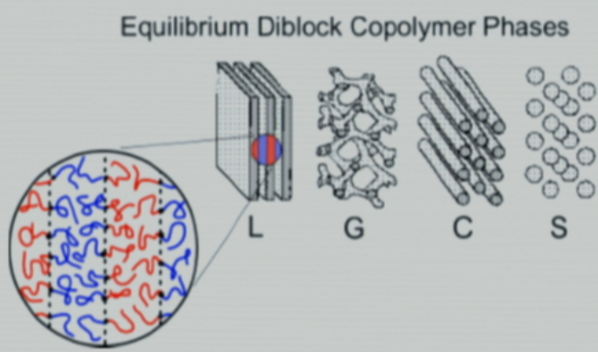
Diblock Copolymer Melts

N = total number of segments
f = fraction of segments that are of type A (i.e., blue)
χ = interaction strength between A and B segments



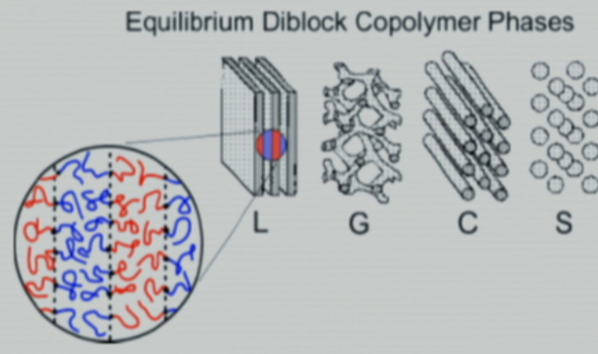
Diblock Copolymer Melts

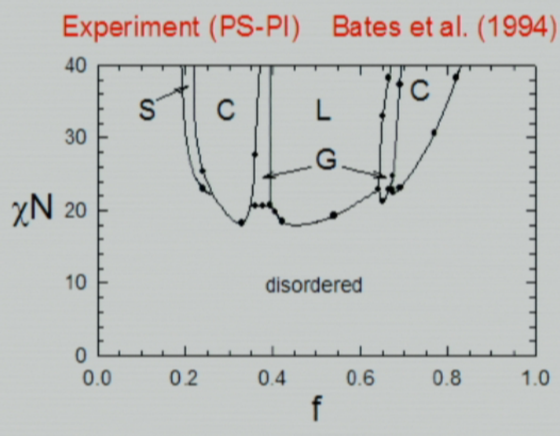
N = total number of segments
f = fraction of segments that are of type A (i.e., blue)
χ = interaction strength between A and B segments



Diblock Copolymer Melts

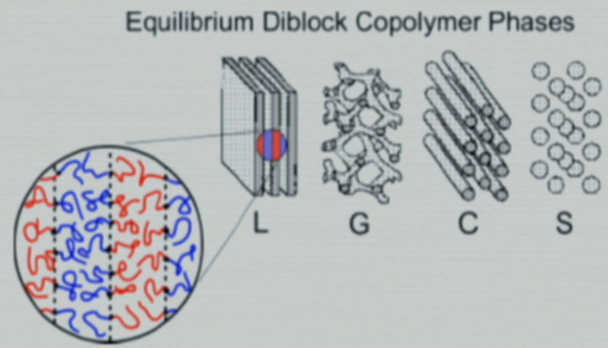
N = total number of segments
f = fraction of segments that are of type A (i.e., blue)
χ = interaction strength between A and B segments

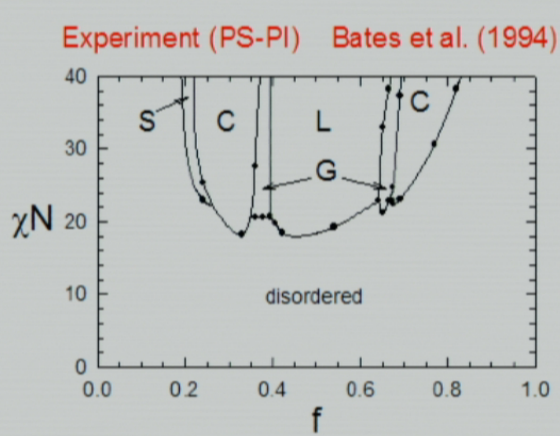


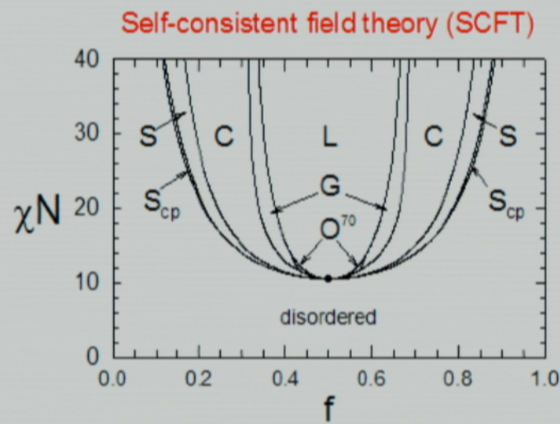


Diblock Copolymer Melts

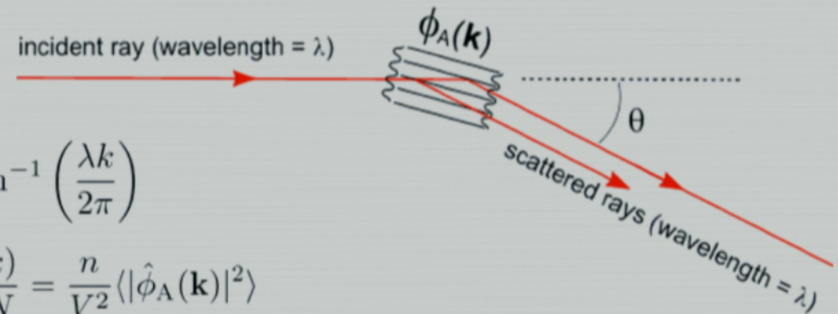
N = total number of segments
f = fraction of segments that are of type A (i.e., blue)
χ = interaction strength between A and B segments







Disordered-State Structure Function, S(k)

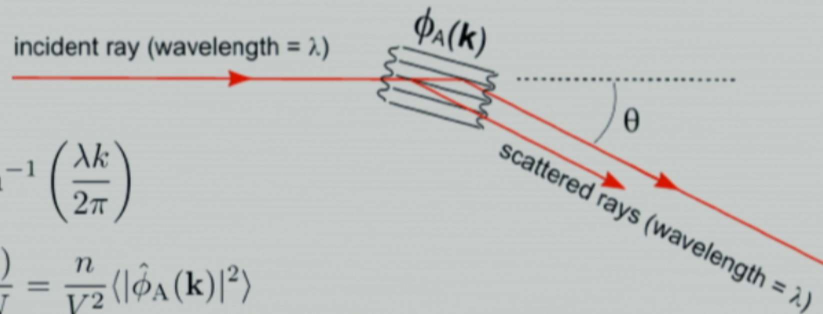


Bragg equation: $\theta = 2\sin^{-1}\left(\frac{\lambda k}{2\pi}\right)$

Scattering amplitude: $\frac{S(k)}{\rho_0 N} = \frac{n}{V^2}\langle|\hat{\phi}_{\mathrm{A}}(\mathbf{k})|^2\rangle$

where $\hat{\phi}_{\mathrm{A}}(\mathbf{k})$ is the Fourier transform of the A-segment concentration, $\hat{\phi}_{\mathrm{A}}(\mathbf{r})$.

Disordered-State Structure Function, S(k)



Bragg equation: $\theta = 2\sin^{-1}\left(\frac{\lambda k}{2\pi}\right)$

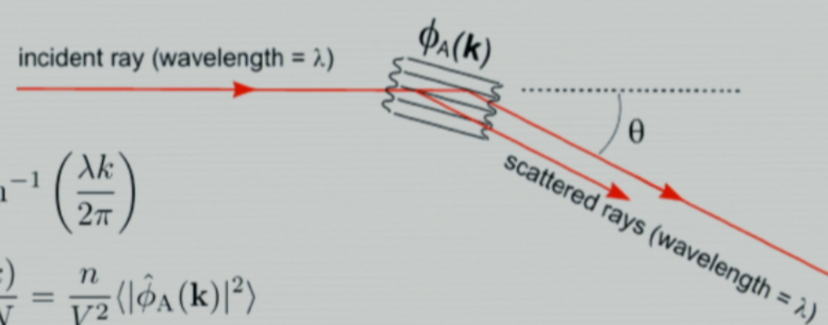
Scattering amplitude: $\frac{S(k)}{\rho_0 N} = \frac{n}{V^2}\langle|\hat{\phi}_{\rm A}(\mathbf{k})|^2\rangle$

where $\hat{\phi}_{\rm A}(\mathbf{k})$ is the Fourier transform of the A-segment concentration, $\hat{\phi}_{\rm A}(\mathbf{r})$.

Mean-field or "random-phase" approximation (RPA) by Leibler (1985)

$$\frac{F}{nk_BT} = \frac{F_0}{nk_BT} + \frac{1}{2}\sum_{\mathbf{k}} S^{-1}(k)|\phi_A(\mathbf{k})|^2 + \cdots$$

Disordered-State Structure Function, S(k)



Bragg equation: $\theta = 2\sin^{-1}\left(\frac{\lambda k}{2\pi}\right)$

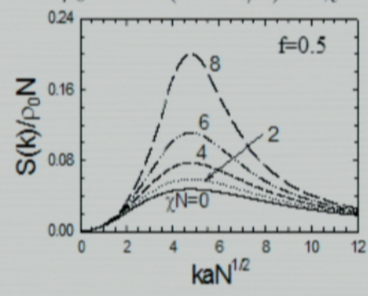
Scattering amplitude: $\frac{S(k)}{\rho_0 N} = \frac{n}{V^2}\langle|\hat{\phi}_{\mathrm{A}}(\mathbf{k})|^2\rangle$

where $\hat{\phi}_{\mathrm{A}}(\mathbf{k})$ is the Fourier transform of the A-segment concentration, $\hat{\phi}_{\mathrm{A}}(\mathbf{r})$.

Mean-field or "random-phase" approximation (RPA) by Leibler (1985)

$$\frac{F}{nk_BT} = \frac{F_0}{nk_BT} + \frac{1}{2}\sum_{\mathbf{k}} S^{-1}(k)|\phi_A(\mathbf{k})|^2 + \cdots$$

$$\frac{S(k)}{\rho_0 N} = \frac{1}{F(k^2a^2N/6) - 2\chi N}$$



Fredrickson-Helfand Theory

$$\frac{S(k)}{\rho_0 N} = \frac{1}{F(k^2a^2N/6) - 2\chi N + 256.8/\sqrt{\bar{N}\tau}}$$

where $\tau = 2(10.495 - \chi N) + \frac{256.8}{\sqrt{\bar{N}\tau}}$ and $\bar{N} = a^6\rho_0^2 N$

- Fluctuation shift of ODT for f = 0.5: $(\chi N)_{\mathrm{ODT}} = 10.495 + 41\bar{N}^{-1/3}$
- Assumptions valid for $\bar{N} \gtrsim 10^{10}$
- Typical experimental values: $\bar{N} \sim 10^3$-10^4

Fredrickson-Helfand Theory

$$\frac{S(k)}{\rho_0 N} = \frac{1}{F(k^2a^2N/6) - 2\chi N + 256.8/\sqrt{\bar{N}\tau}}$$

where $\tau = 2(10.495 - \chi N) + \dfrac{256.8}{\sqrt{\bar{N}\tau}}$ and $\bar{N} = a^6\rho_0^2 N$

- Fluctuation shift of ODT for f = 0.5: $(\chi N)_{\mathrm{ODT}} = 10.495 + 41\bar{N}^{-1/3}$
- Assumptions valid for $\bar{N} \gtrsim 10^{10}$
- Typical experimental values: $\bar{N} \sim 10^3$-10^4

Fredrickson-Helfand Theory

$$\frac{S(k)}{\rho_0 N} = \frac{1}{F(k^2a^2N/6) - 2\chi N + 256.8/\sqrt{\bar{N}\tau}}$$

where $\tau = 2(10.495 - \chi N) + \dfrac{256.8}{\sqrt{\bar{N}\tau}}$ and $\bar{N} = a^6\rho_0^2 N$

- Fluctuation shift of ODT for f = 0.5: $(\chi N)_{\mathrm{ODT}} = 10.495 + 41\bar{N}^{-1/3}$
- Assumptions valid for $\bar{N} \gtrsim 10^{10}$
- Typical experimental values: $\bar{N} \sim 10^3$-10^4

Renormalized One-Loop

- Diagrammatic expansion evaluated to lowest order
- Makes improved predictions for S(k)
- Difficult to apply to ordered phases

Ultra-Violet (UV) Divergence

- The Landau-Ginzburg free to quadratic order in fluctuations about the disordered phase is $\dfrac{F}{nk_BT} = \dfrac{F_0}{nk_BT} + \dfrac{1}{2}\sum_{\mathbf{k}} S^{-1}(k)|\phi_A(\mathbf{k})|^2 + \cdots$

- The free energy for fluctuations of wavevector **k** (ignoring constants) is

$$\frac{F_{\mathbf{k}}}{nk_BT} = -\ln\left\{\int \exp\left(\frac{n}{2}S^{-1}|\phi_A|^2\right) d\phi_A\right\} = -\ln\sqrt{S(k)} = -\frac{3lU}{2\pi^3k^2} \quad \text{as } k\to\infty$$

- The integrated free energy up to a cutoff, $|\mathbf{k}|<\Lambda$, is

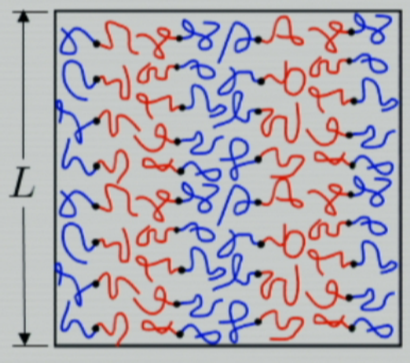
$$\sum_{\mathbf{k}} \frac{F_{\mathbf{k}}}{nk_BT} = -\frac{3lU}{2\pi^3}\int\frac{d\mathbf{k}}{k^2} = -\frac{6}{\pi^2}l\Lambda U\,, \qquad \text{where } U \propto \chi\int \hat{\phi}_A\hat{\phi}_B d\mathbf{r}$$

- This divergence can be accommodated for by defining an effective interaction parameter:

$$\chi_e = \chi\left(1 - \frac{6}{\pi^2}l\Lambda\right)$$

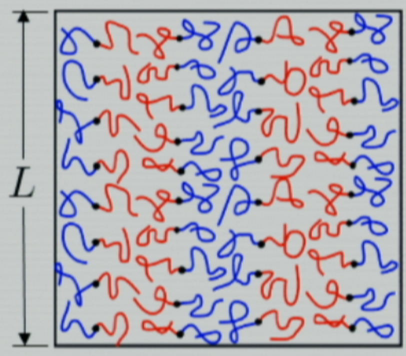
Transformation to Field-Based Model

Particle-Based Model



Transformation to Field-Based Model

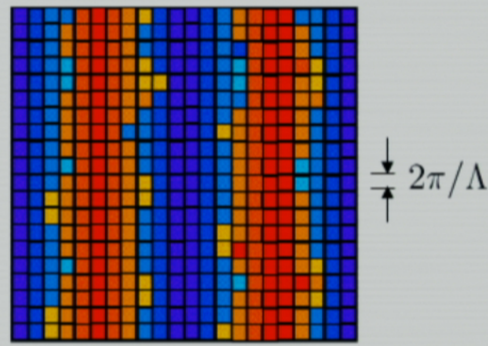
Particle-Based Model



Exact Mathematical Transformation

(Fredrickson et al., Macromolecules, 2002)

Field-Based Model



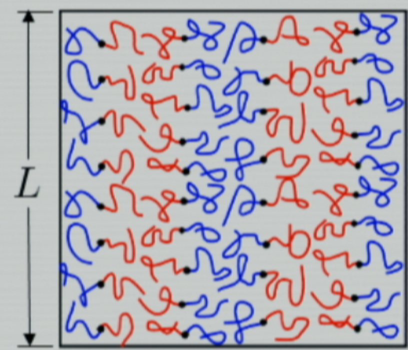
The partition function transforms to $Z \sim \int \exp\left(\frac{H[W_-, W_+]}{k_B T}\right) \mathcal{D}W_- \mathcal{D}W_+$,

where $\frac{H[W_-, W_+]}{n k_B T} = -\ln Q + \frac{1}{V}\int \left(\frac{W_-^2(\mathbf{r})}{\chi N} - W_+(\mathbf{r})\right) d\mathbf{r}$ is an effective Hamiltonian,

and Q is a partition function for a single diblock in the external fields, $W_-(\mathbf{r})$ and $W_+(\mathbf{r})$.

Transformation to Field-Based Model

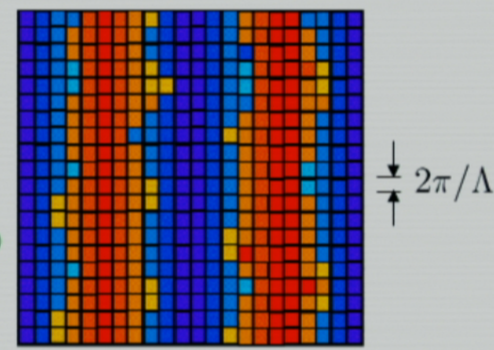
Particle-Based Model



Exact Mathematical Transformation

(Fredrickson et al., Macromolecules, 2002)

Field-Based Model



The partition function transforms to $Z \sim \int \exp\left(\frac{H[W_-, W_+]}{k_B T}\right) \mathcal{D}W_- \mathcal{D}W_+$,

where $\frac{H[W_-, W_+]}{nk_B T} = -\ln Q + \frac{1}{V}\int \left(\frac{W_-^2(\mathbf{r})}{\chi N} - W_+(\mathbf{r})\right) d\mathbf{r}$ is an effective Hamiltonian,

and Q is a partition function for a single diblock in the external fields, $W_-(\mathbf{r})$ and $W_+(\mathbf{r})$.

The composition" field $W_-(\mathbf{r})$, which couples to $\hat{\phi}_A(\mathbf{r}) - \hat{\phi}_B(\mathbf{r})$, is real valued,

but the "pressure" field $W_+(\mathbf{r})$, which couples to $\hat{\phi}_A(\mathbf{r}) + \hat{\phi}_B(\mathbf{r})$, is imaginary.

Thus the Boltzmann weight is no longer positive-definite, and we can't apply normal statistical mechanics.

Saddle-Point Approximation for the Pressure Field

- Fredrickson et al. overcome this by performing complex Langevin simulations
- An alternative proposed by Schmid et al. 10 years ago is to apply the saddle-point approximation to the pressure field.

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

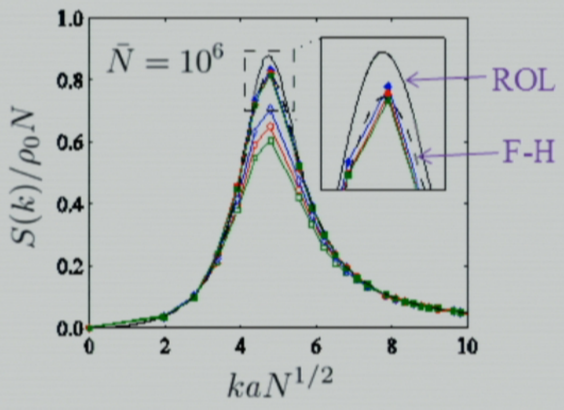
$w_+(\mathbf{r})$ is the value of $W_+(\mathbf{r})$ such that $\phi_A(\mathbf{r}) + \phi_B(\mathbf{r}) = 1$ at the mean-field level

- Because $w_+(\mathbf{r})$ is real-valued, the Hamiltonian is also real-valued and we can perform conventional Monte Carlo techniques to calculate:

Structure function: $$\frac{S(k)}{\rho_0 N} = \frac{n}{(V\chi N)^2}\langle |W_-(\mathbf{k})|^2\rangle - \frac{1}{2\chi N}$$

Order parameter: $$\Psi \equiv \frac{1}{V^2}\left\langle \max_{\mathbf{k}} |W_-(\mathbf{k})|^2 \right\rangle$$

S(k) for Symmetric (f=0.5) Diblocks



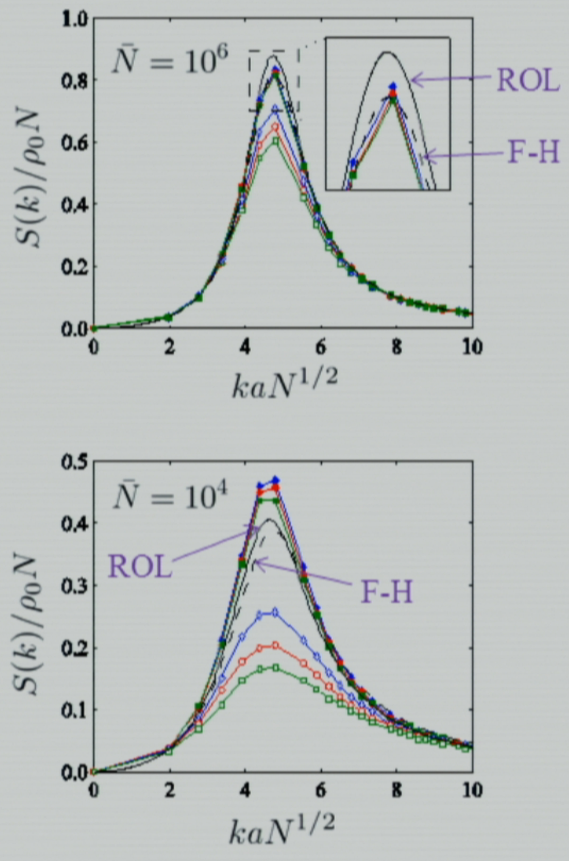
m = 16, 24, 32

open symbols: χN=10

closed symbols: χ_eN=10

$$\chi_e = \chi\left(1 - \frac{6}{\pi^2} l\Lambda\right)$$

S(k) for Symmetric (f=0.5) Diblocks



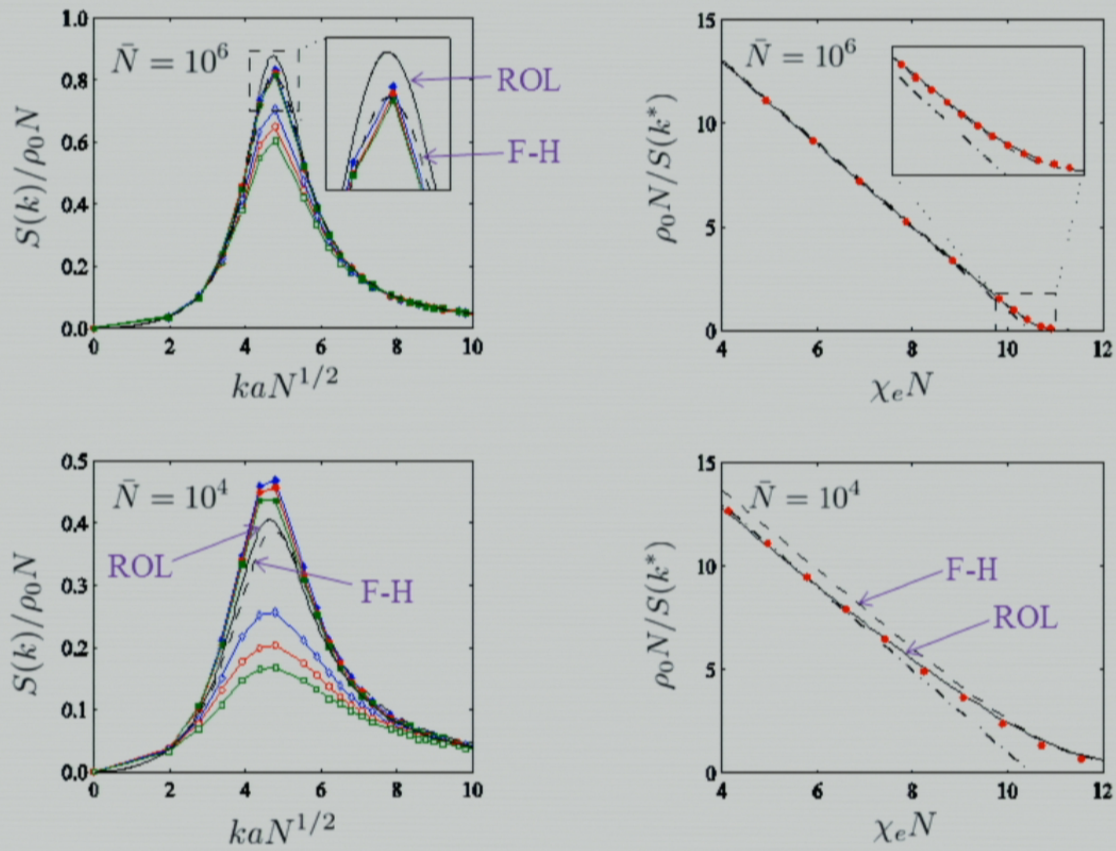
m = 16, 24, 32

open symbols: $\chi N=10$

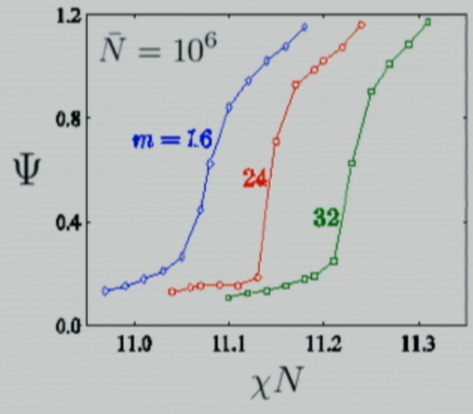
closed symbols: $\chi_e N=10$

$$\chi_e = \chi \left(1 - \frac{6}{\pi^2} l \Lambda \right)$$

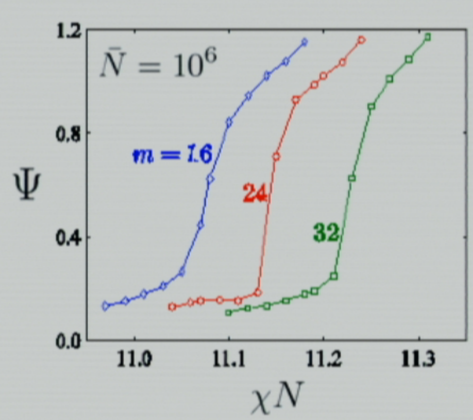
S(k) for Symmetric (f=0.5) Diblocks

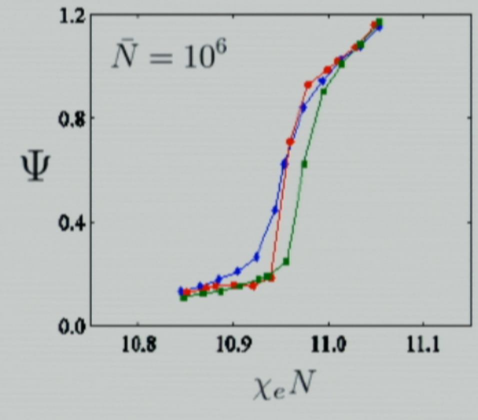


ODT for symmetric f=0.5 diblocks

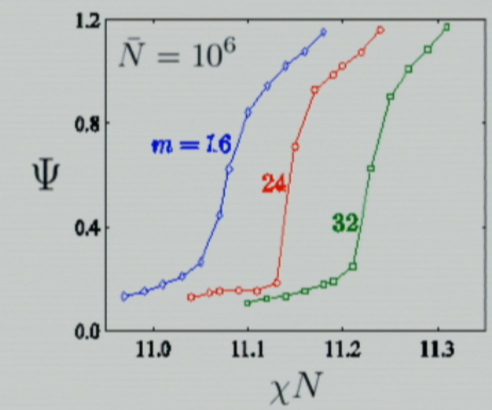


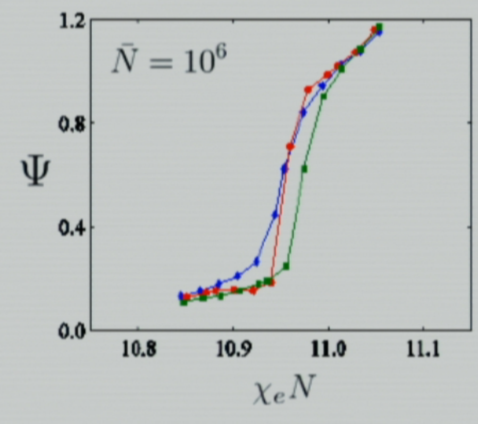
ODT for symmetric f=0.5 diblocks

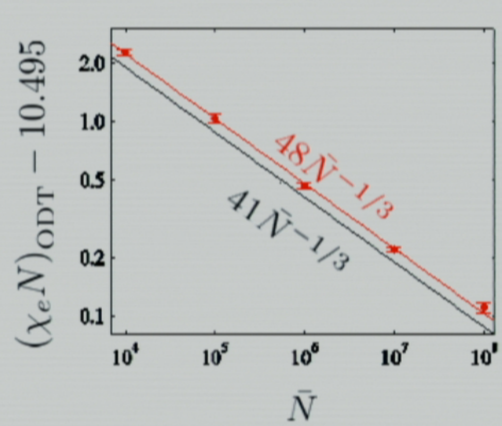




ODT for symmetric f=0.5 diblocks







The predicted $\bar{N}^{-1/3}$ scaling of F-H extends to experimentally relevant molecular weights!!

Summary

- 3D MC-FTS are numerically feasible
- UV divergence occurs, but can be handled by renormalization of χ
- MC-FTS predict consistent results with ROL
- $N^{-1/3}$ scaling for $(\chi N)_{ODT}$ holds down to $N=10^4$

Future work

- Program MC-FTS on GPUs
- Correction for saddle-point approximation (with Dave Morse)
- Wang-Landau sampling and finite-size analysis to locate ODT more accurately

Acknowledgements

- Pawel Stasiak – postdoc on this project
- University of Reading
- EPSRC – UK funding
- SHARCNET – computer resources