Introduction to Self-Consistent Field Theory Calculations

Edward H. Feng

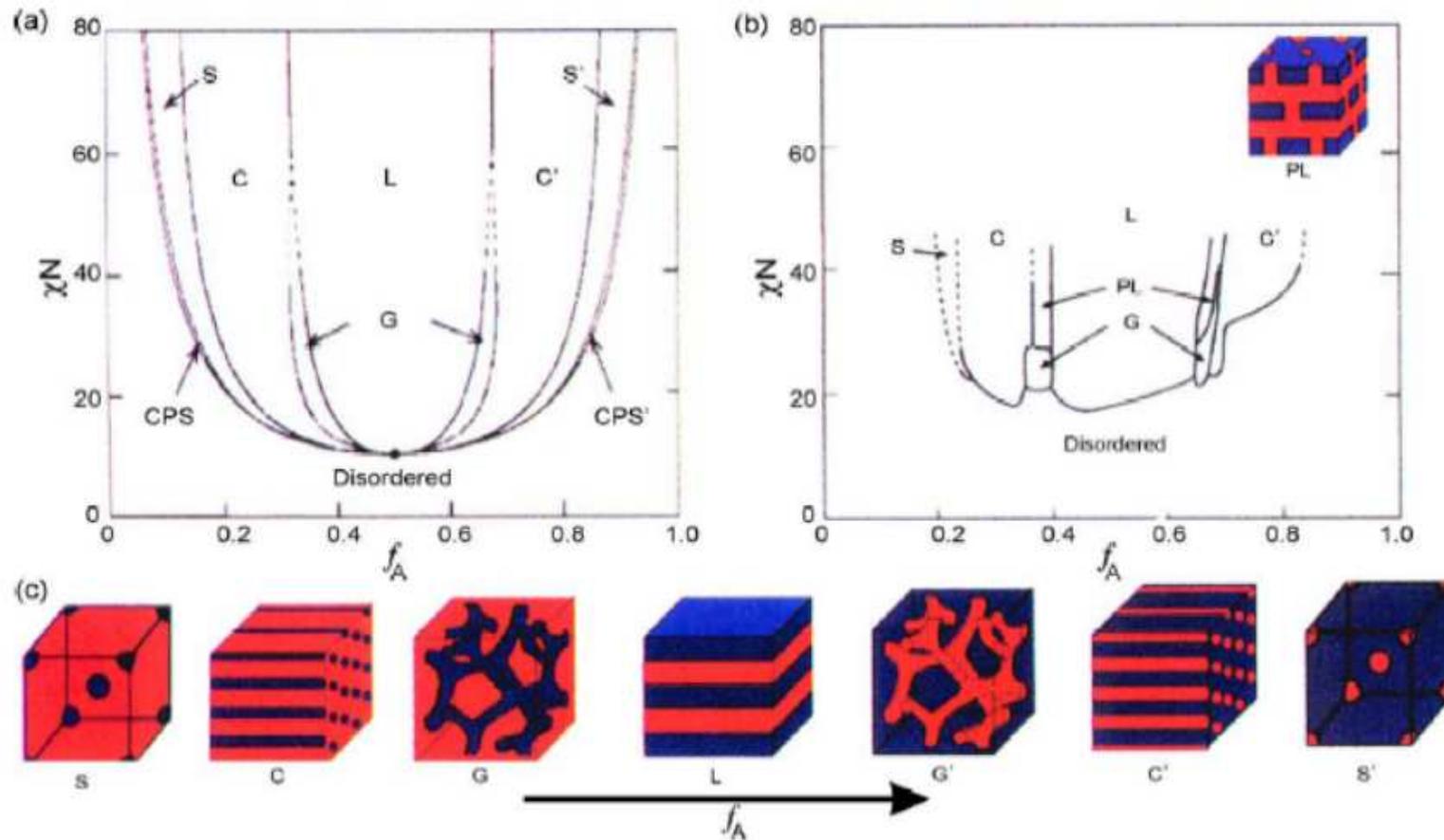University of California, Berkeley

Block copolymer self-assembly

Fig. 1. Diblock copolymers are predicted to self-assemble according to a phase diagram predicted by self-consistent mean field theory (a) and proven experimentally (b). A variety of constant-radius geometries are observed as a function of relative lengths of the two blocks (c). Reproduced with permission from *Physics Today* [2].

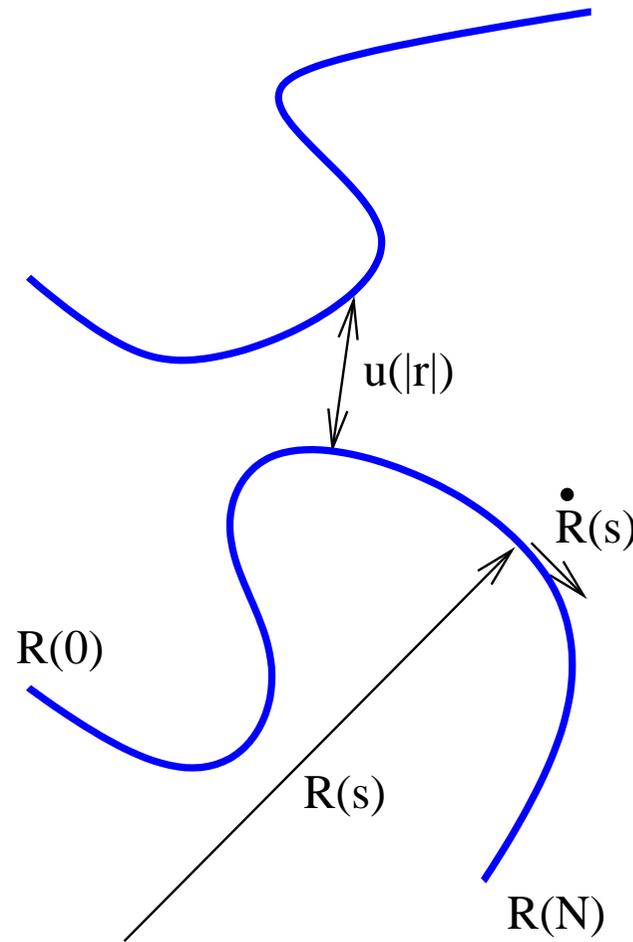What is this SCFT that we compare with experiments?

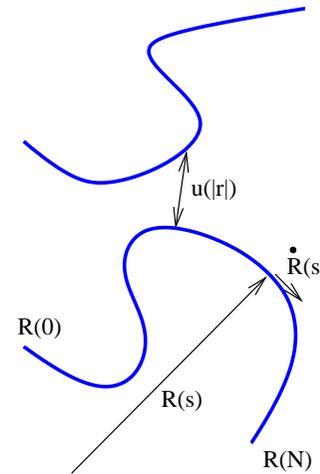# Rod-Coil Block Copolymers are Inhomogeneous
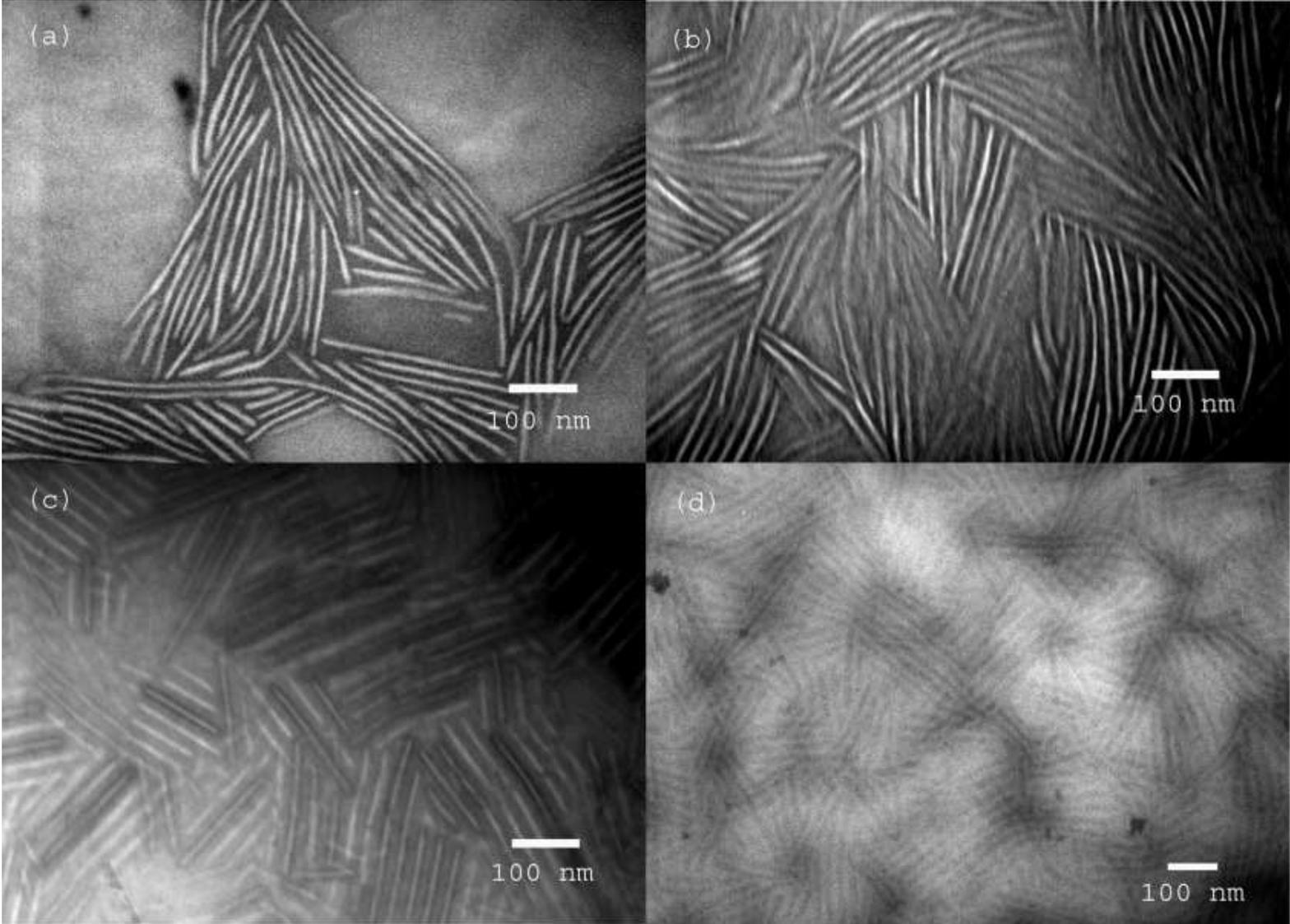
Field-Theoretic Model for Polymers

coarse grain model for polymers as continuous space curves

interested in meso-scale behavior

$\dot{R}(s)$ is a measure of chain stretching

u(|r|)

$\dot{R}(s)$

R(0)

R(s)

R(s)

R(N)

Model for Homopolymers in Good Solvent:

- Gibbs told us that the probability of a state is proportional to $\exp(-\beta E(x))$ where $\beta = 1/(kT)$ and $E(x)$ is the energy of state x
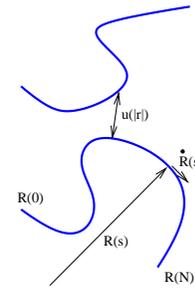
- continuous Gaussian chain model

$$Z(n, V, T) = \int \mathcal{D}\mathbf{R}^n \exp\left(-\beta U_0[\mathbf{R}^n] - \beta U_1[\mathbf{R}^n]\right)$$

where $\mathbf{R}^n \equiv \mathbf{R}_1(s), \mathbf{R}_2(s) \dots \mathbf{R}_n(s)$ denote the space curves of the n polymers

- first energetic contribution comes from stretching of each chain

$$U_0[\mathbf{R}^n] = \frac{3kT}{2b^2} \sum_{i=1}^{n} \int_0^N \left|\dot{R}_i(s)\right|^2 ds$$

this is Gaussian in the variable $\dot{\mathbf{R}}(s)$

Model for Homopolymers in Good Solvent:

$$Z(n, V, T) = \int \mathcal{D}\mathbf{R}^n \exp\left(-\beta U_0[\mathbf{R}^n] - \beta U_1[\mathbf{R}^n]\right)$$

- second energy contribution comes from the effective repulsion of polymer segments in good solvent

- if the density from the polymers is

$$\widehat{\rho}(\mathbf{r}) = \sum_{i=1}^{n} \int_0^N \delta(\mathbf{r} - \mathbf{R}_i(s))ds$$

then the repulsion between chains is

$$U_1[\mathbf{R}^n] = \int d\mathbf{r}d\mathbf{r}'\widehat{\rho}(\mathbf{r})u(|\mathbf{r} - \mathbf{r}'|)\widehat{\rho}(\mathbf{r}')$$
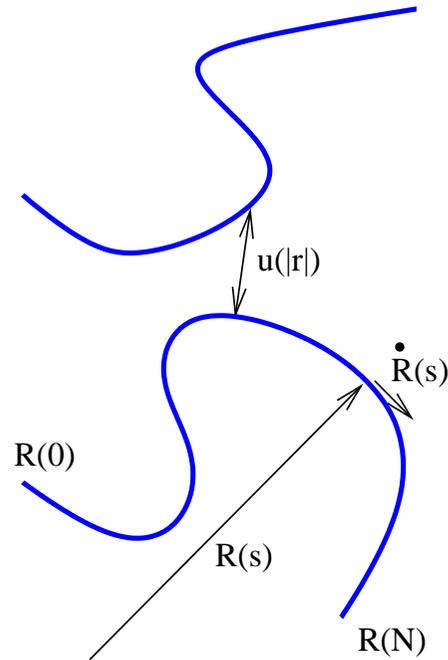
- assume a delta function interaction

$$u(|\mathbf{r} - \mathbf{r}'|) = kTu_0\delta(\mathbf{r} - \mathbf{r}')$$

so the interaction energy becomes

$$\beta U_1[\mathbf{R}^n] = \frac{1}{kT}\int d\mathbf{r}d\mathbf{r}'\widehat{\rho}(\mathbf{r})u(|\mathbf{r} - \mathbf{r}'|)\widehat{\rho}(\mathbf{r}') = u_0 \int d\mathbf{r}\widehat{\rho}(\mathbf{r})^2$$
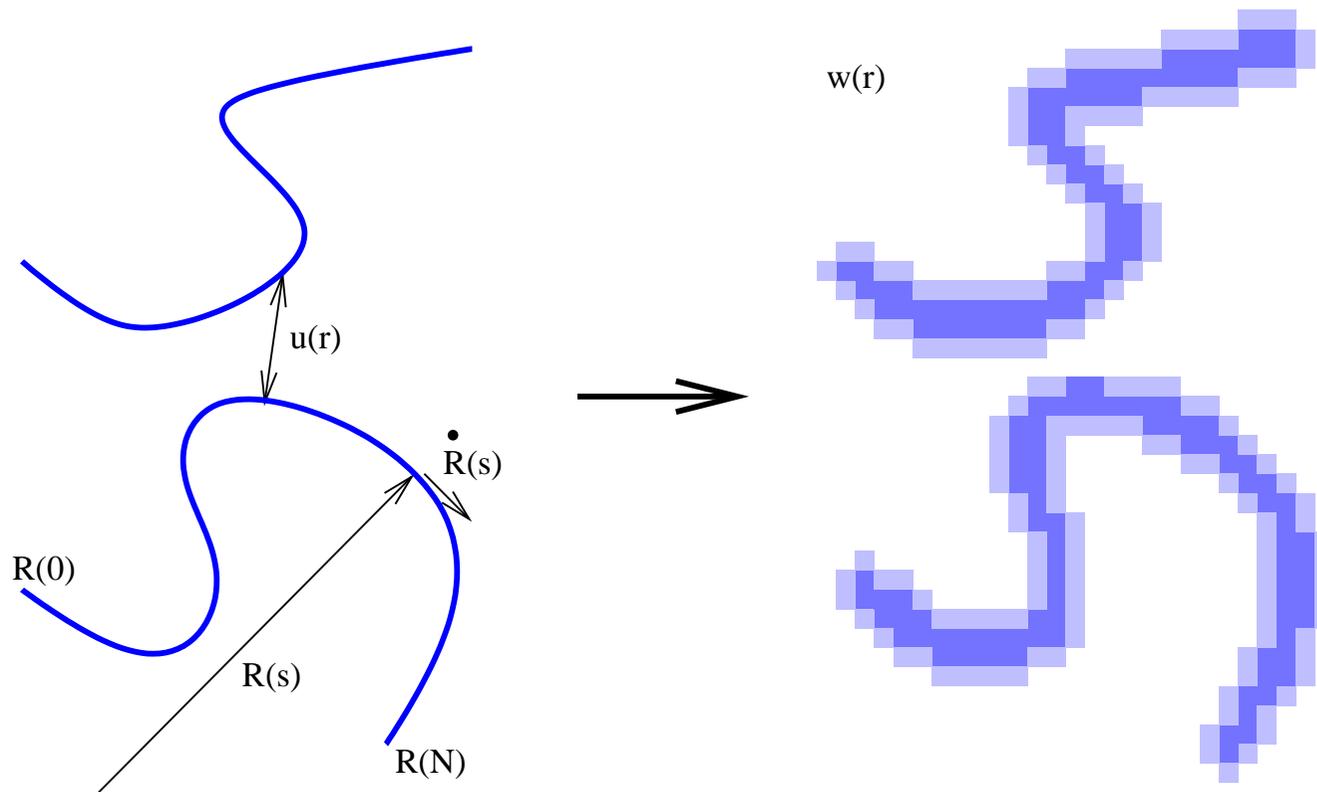
Model for Homopolymers in Good Solvent:

- partition function becomes

$$Z(n,V,T) = \int \mathcal{D}\mathbf{R}^n \exp\left(-\frac{3}{2b^2}\sum_{i=1}^{n}\int_0^N |\dot{\mathbf{R}}_i(s)|ds - u_0\int \hat{\rho}(\mathbf{r})^2 d\mathbf{r}\right)$$

Particle to Field Transformation

w(r)

$w(\mathbf{r})$ is a field conjugate to the density; in general, this is a complex field

$$Z(n, V, T) = \int \mathcal{D}w \, e^{-\mathcal{H}[w]}$$

$$\mathcal{H}[w_\pm] = \frac{1}{2u_0} \int w(\mathbf{r})^2 d\mathbf{r} - n \ln Q[iw]$$

math involves doing Gaussian integrals

Single Chain Partition Function

$$\mathcal{H}[w_\pm] = \frac{1}{2u_0} \int w(\mathbf{r})^2 d\mathbf{r} - n \ln Q[iw]$$

- to determine the single chain partition function $Q[iw]$ for an arbitrary field $w(r)$, we solve for a propagator that satisfies a modified diffusion equation:

$$\frac{\partial}{\partial s} q(\mathbf{r}, s; [iw]) = \frac{b^2}{6} \nabla^2 q(\mathbf{r}, s; [iw]) - iw(\mathbf{r}) q(\mathbf{r}, s; [iw])$$

for the initial condition $q(\mathbf{r}, 0; [iw]) = 1$
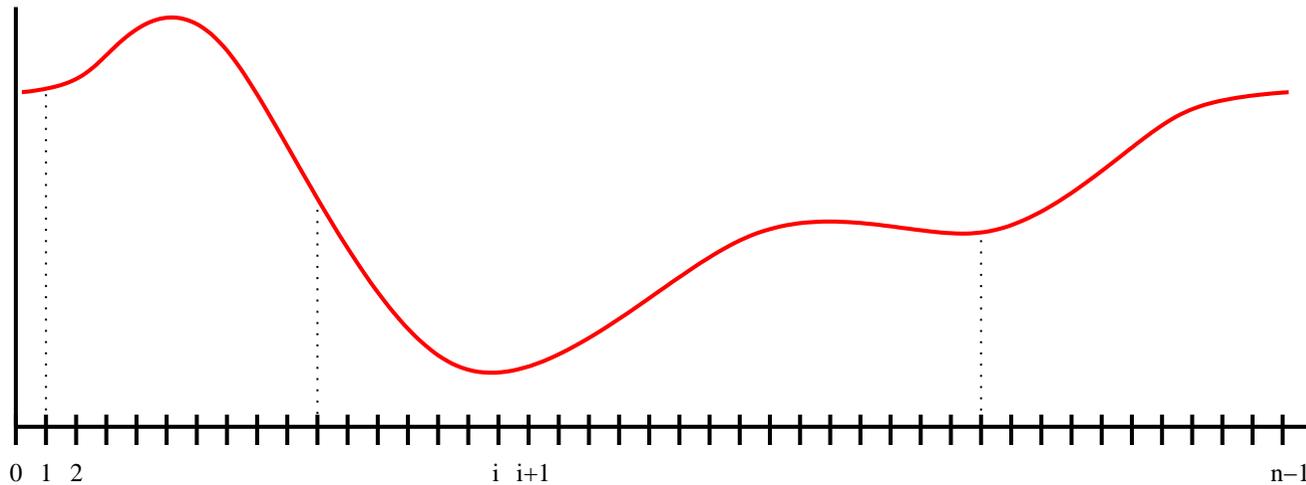
- one can show that

$$Q[iw] = \frac{1}{V} \int q(\mathbf{r}, N; [iw]) d\mathbf{r}$$

$$\rho(\mathbf{r}; [iw]) = \frac{n}{VQ[iw]} \int_0^N q(\mathbf{r}, s; [iw]) q(\mathbf{r}, s; [iw]) ds$$

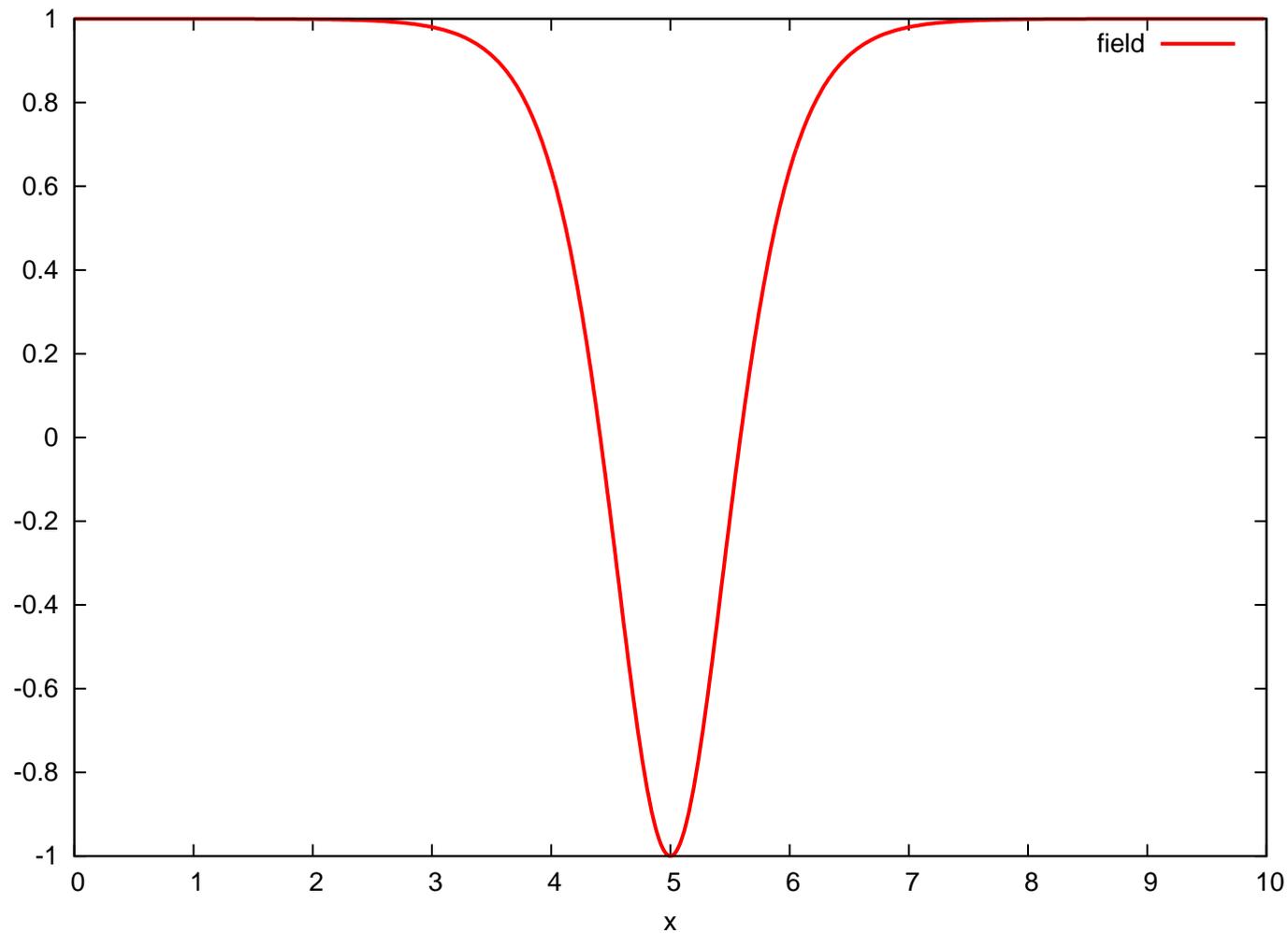is the density of the polymers in an external field $iw(\mathbf{r})$

- solving for $q(\mathbf{r}, s; [iw])$ is the majority of computational work

One Dimensional Example

- vector $\mathbf{r}$ becomes scalar r

- represent continuous periodic function by discretizing the interval

- $w(r)$, $q(r, 2; [iw])$, $\rho(r; [iw])$ are all functions which are discretized
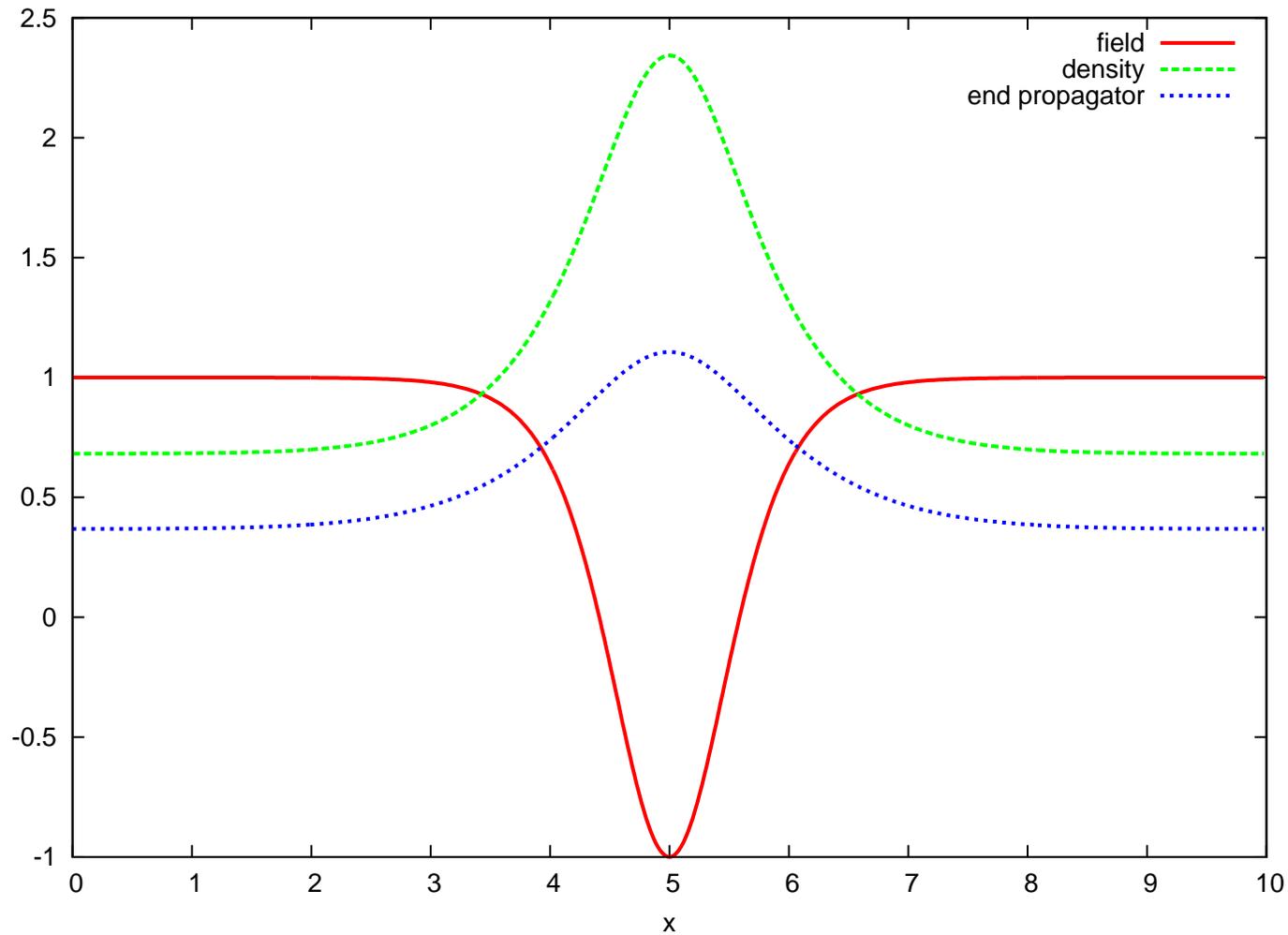
One Dimensional Example continued

$$\frac{\partial}{\partial s}q(r, s; [iw]) = \frac{b^2}{6}\nabla^2 q(r, s; [iw]) - iw(r)q(r, s; [iw])$$

where $iw(r)$ is the field above

Results for sample potential

end propagator is $q(r, N)$, the probability density for the end of the chain

this is obtained by solving the modified diffusion equation

Mean-Field Equations

$$Z(n, V, T) = \int \mathcal{D}w\, e^{-\mathcal{H}[w]}$$

$$\mathcal{H}[w_\pm] = \frac{1}{2u_0} \int w(\mathbf{r})^2 d\mathbf{r} - n \ln Q[iw]$$

- instead of attempting to calculate the integral over $w(\mathbf{r})$, we invoke the mean-field approximation asks for the *one* field $w^*(\mathbf{r})$ that minimizes $\mathcal{H}[w]$

$$\frac{\delta\mathcal{H}[iw]}{\delta iw(\mathbf{r})} = -\frac{iw(\mathbf{r})}{u_0} + \rho(\mathbf{r}; [iw]) = 0$$

$$\rho(\mathbf{r}; [iw]) = \frac{n}{VQ[iw]} \int_0^N q(\mathbf{r}, s; [iw]) q(\mathbf{r}, s; [iw]) ds$$
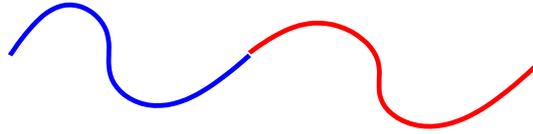
- for this model of homopolymer in good solvent, the mean-field solution is

$$w^*(\mathbf{r}) = -iu_0\rho_0$$

where $\rho_0 = nN/V$ is the average density of polymers

  - this solution does not depend on $\mathbf{r}$, so it is *homogeneous*

  - this solution is an imaginary number

Model for Coil-Coil Diblock Copolymer:

- continuous Gaussian chain model

$$Z(n, V, T) = \int \mathcal{D}\mathbf{R}^n \delta(\hat{\rho}_A(\mathbf{r}) + \hat{\rho}_B(\mathbf{r}) - \rho_0) \exp\left(-\beta U_0[\mathbf{R}^n] - \beta U_1[\mathbf{R}^n]\right)$$

$$U_0[\mathbf{R}^n] = \frac{3kT}{2b^2} \sum_{i=1}^{n} \int_0^N \left|\dot{R}_i(s)\right|^2 ds$$
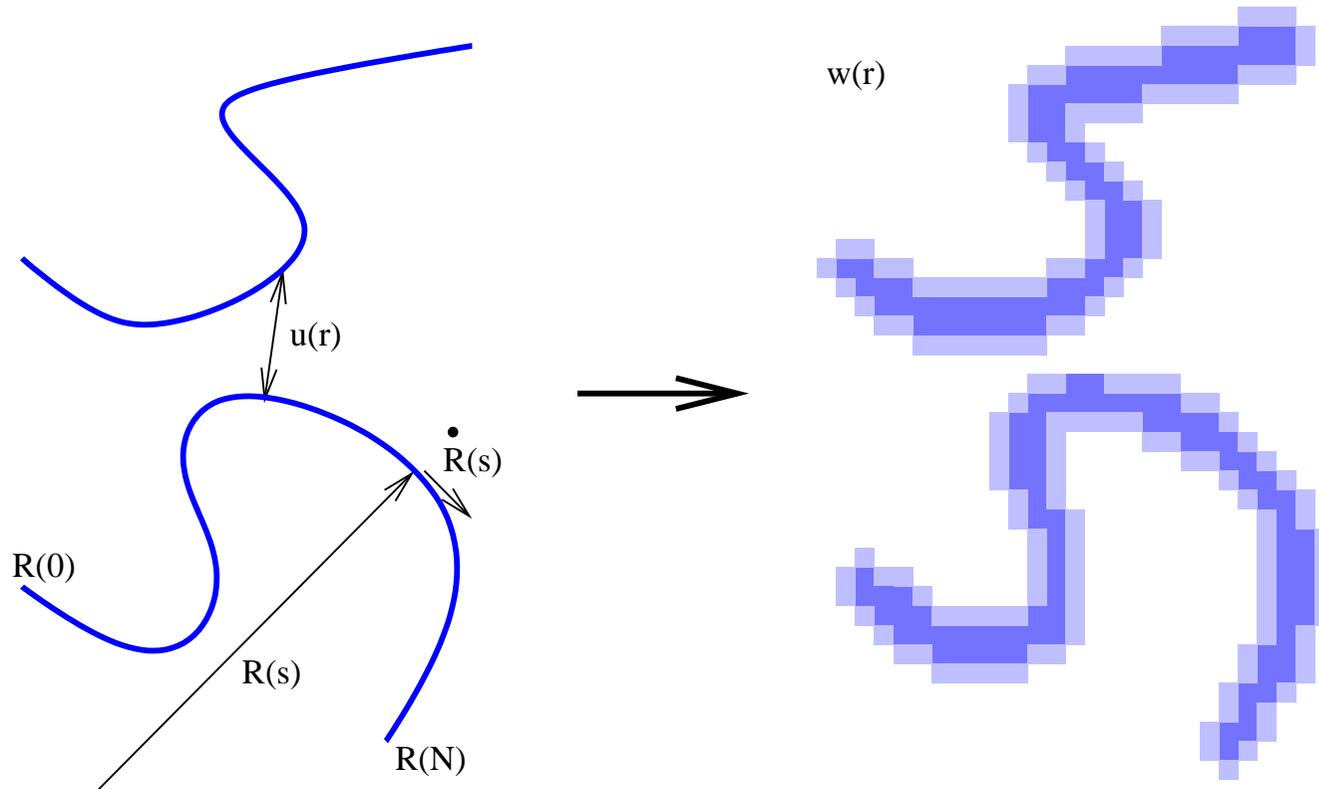
$$U_1[\mathbf{R}^n] = \int d\mathbf{r} d\mathbf{r}' \hat{\rho}_A(\mathbf{r}) u(\mathbf{r} - \mathbf{r}') \hat{\rho}_B(\mathbf{r}') = \rho_0^{-1} \chi kT \int d\mathbf{r} \hat{\rho}_A(\mathbf{r}) \hat{\rho}_B(\mathbf{r})$$

$$\hat{\rho}_A(\mathbf{r}) = \sum_{i=1}^{n} \int_0^{fN} \delta(\mathbf{r} - \mathbf{R}_i(s)) ds$$

  where f is volume fraction of A block

- χ is Flory-Huggins parameter in units of kT

- new physics is the density is fixed at ρ_0 for each $\mathbf{r}$

Particle to Field Transformation

$$Z(n, V, T) = \int \mathcal{D}w_{\pm} e^{-\mathcal{H}[w_{\pm}]}$$

$$\mathcal{H}[w_{\pm}] = \frac{\rho_0}{\chi} \int w_-(\mathbf{r})^2 d\mathbf{r} - \rho_0 \int i w_+(\mathbf{r}) d\mathbf{r} - n \ln Q[w_{\pm}]$$

Single Chain Partition Function

$$\mathcal{H}[w_\pm] = \frac{\rho_0}{\chi} \int w_-(\mathbf{r})^2 d\mathbf{r} - \rho_0 \int i w_+(\mathbf{r}) d\mathbf{r} - n \ln Q[w_\pm]$$

$$\frac{\partial}{\partial s} q(\mathbf{r}, s; [w_\pm]) = \frac{b^2}{6} \nabla^2 q(\mathbf{r}, s; [w_\pm]) - \psi(\mathbf{r}, s) q(\mathbf{r}, s; [w_\pm])$$

$$\psi(\mathbf{r}, s) = \begin{cases} i w_+(\mathbf{r}) - w_-(\mathbf{r}) & s \in (0, f) \\ i w_+(\mathbf{r}) + w_-(\mathbf{r}) & s \in (f, 1) \end{cases}$$

$$Q[w_\pm] = \frac{1}{V} \int q(\mathbf{r}, N; [w_\pm]) d\mathbf{r}$$

- partition function of a single chain in external fields

- use efficient method for calculating $q(\mathbf{r}, s)$

Mean-Field Equations

$$\mathcal{H}[w_\pm] = \frac{\rho_0}{\chi} \int w_-(\mathbf{r})^2 d\mathbf{r} - \rho_0 \int iw_+(\mathbf{r}) d\mathbf{r} - n \ln Q[w_\pm]$$

$$\frac{\delta \mathcal{H}[w_\pm]}{\delta iw_+(\mathbf{r})} = \rho_A(\mathbf{r}; [w_\pm]) + \rho_B(\mathbf{r}; [w_\pm]) - \rho_0 = 0$$

$$\frac{\delta \mathcal{H}[w_\pm]}{\delta w_-(\mathbf{r})} = \frac{2\rho_0}{\chi} w_-(\mathbf{r}) - \rho_A(\mathbf{r}; [w_\pm]) + \rho_B(\mathbf{r}; [w_\pm]) = 0$$

$$\rho_A(\mathbf{r}; [w_\pm]) = \frac{\rho_0}{Q[w_\pm]} \int_0^{fN} q(\mathbf{r}, s; [w_\pm]) q^\dagger(\mathbf{r}, N - s; [w_\pm])$$

$$\rho_B(\mathbf{r}; [w_\pm]) = \frac{\rho_0}{Q[w_\pm]} \int_{fN}^N q(\mathbf{r}, s; [w_\pm]) q^\dagger(\mathbf{r}, N - s; [w_\pm])$$

- find fields $w_+(\mathbf{x})$ and $w_-(\mathbf{x})$ that satisfy these equations

- usually work in scaled fields $W_\pm \equiv N w_\pm \sim O(1)$, so χN is relevant parameter

How do we compute the mean field solution?

- start with randomize fields $w_+(\mathbf{r})$ and $w_-(\mathbf{r})$

- calculate the densities and subsequently mean-field equations:

$$\frac{\delta\mathcal{H}[w_\pm]}{\delta i w_+(\mathbf{r})} = \rho_A(\mathbf{r}; [w_\pm]) + \rho_B(\mathbf{r}; [w_\pm]) - \rho_0$$

$$\frac{\delta\mathcal{H}[w_\pm]}{\delta w_-(\mathbf{r})} = \frac{2\rho_0}{\chi} w_-(\mathbf{r}) - \rho_A(\mathbf{r}; [w_\pm]) + \rho_B(\mathbf{r}; [w_\pm])$$

- update the fields:

$$w_+^{j+1}(\mathbf{r}) = w_+^j(\mathbf{r}) + \lambda\frac{\delta\mathcal{H}[w_\pm]}{\delta w_+(\mathbf{r})}$$

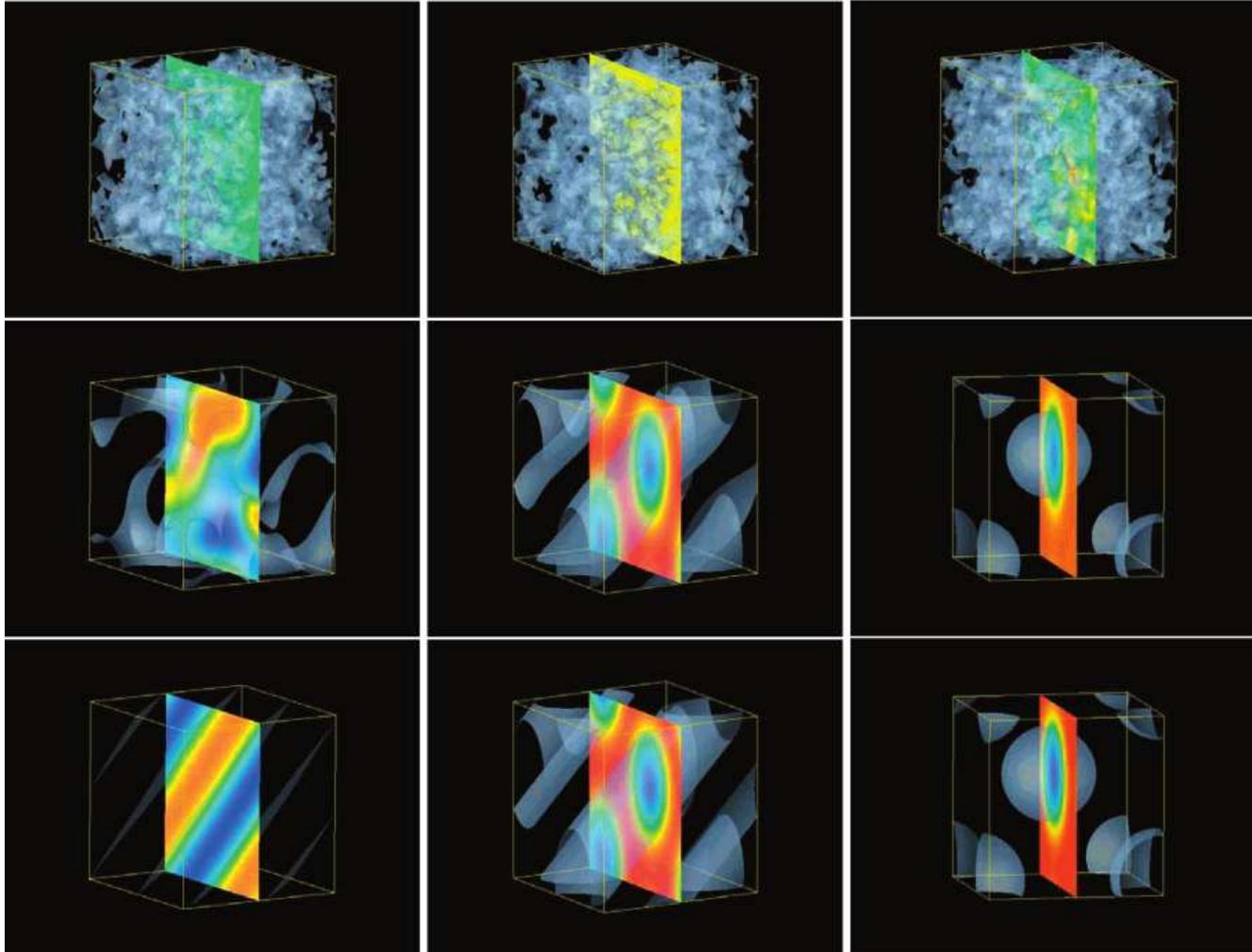$$w_-^{j+1}(\mathbf{r}) = w_-^j(\mathbf{r}) - \lambda\frac{\delta\mathcal{H}[w_\pm]}{\delta w_-(\mathbf{r})}$$

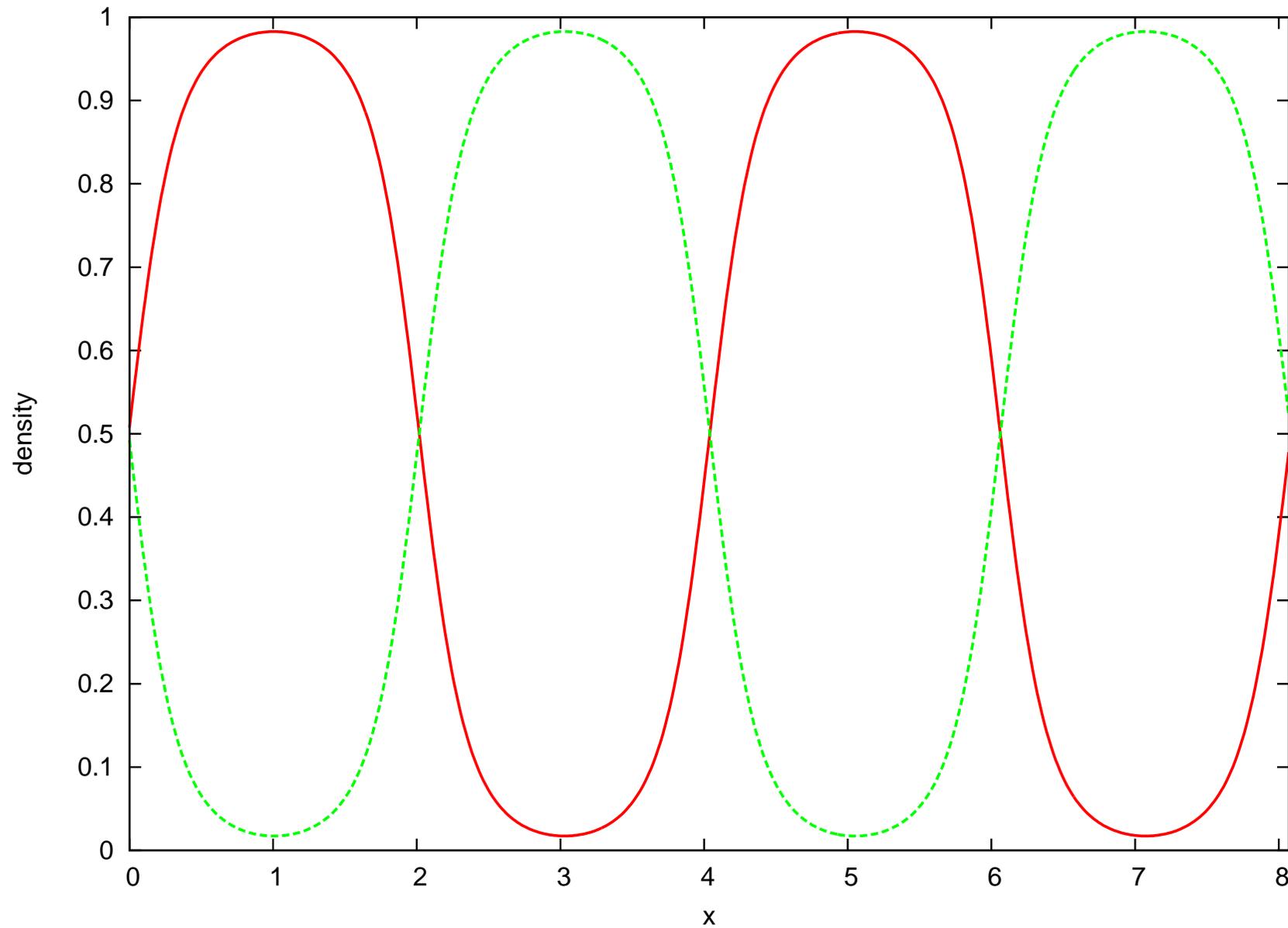- iterate until mean-field equations are satisfied

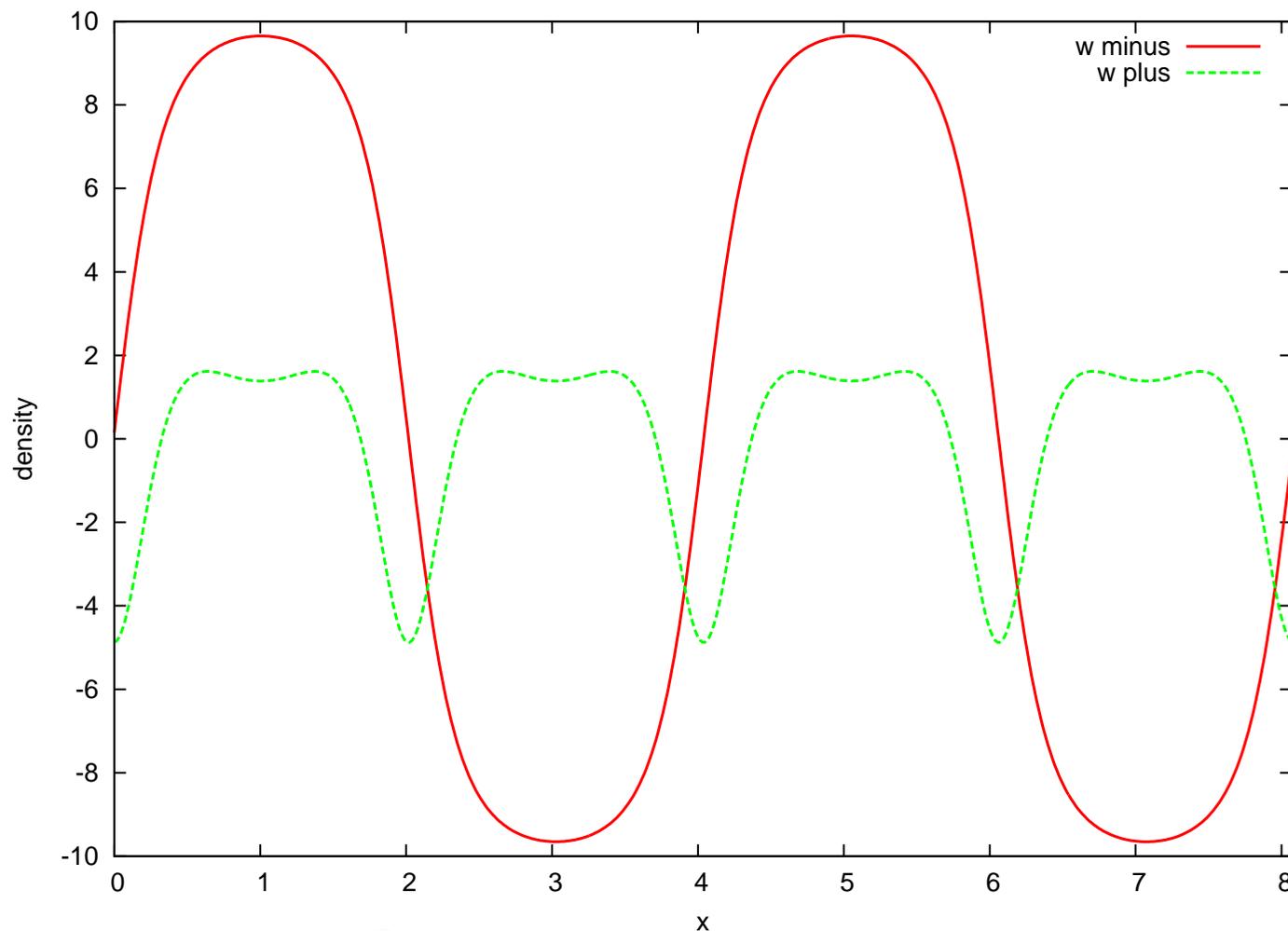# What does this look like?

time evolution from top to bottom

Closer look at Lamellar Phase

$f = 0.5,\ \chi N = 20$

Closer look at Lamellar Phase

$f = 0.5,\ \chi N = 20$

$$\frac{2}{\chi N}W_-(x) - \phi_A(x) + \phi_B(x) = 0$$

$$\phi_A(x) + \phi_B(x) - 1 = 0$$

finally, we can understand Justin's slide :)

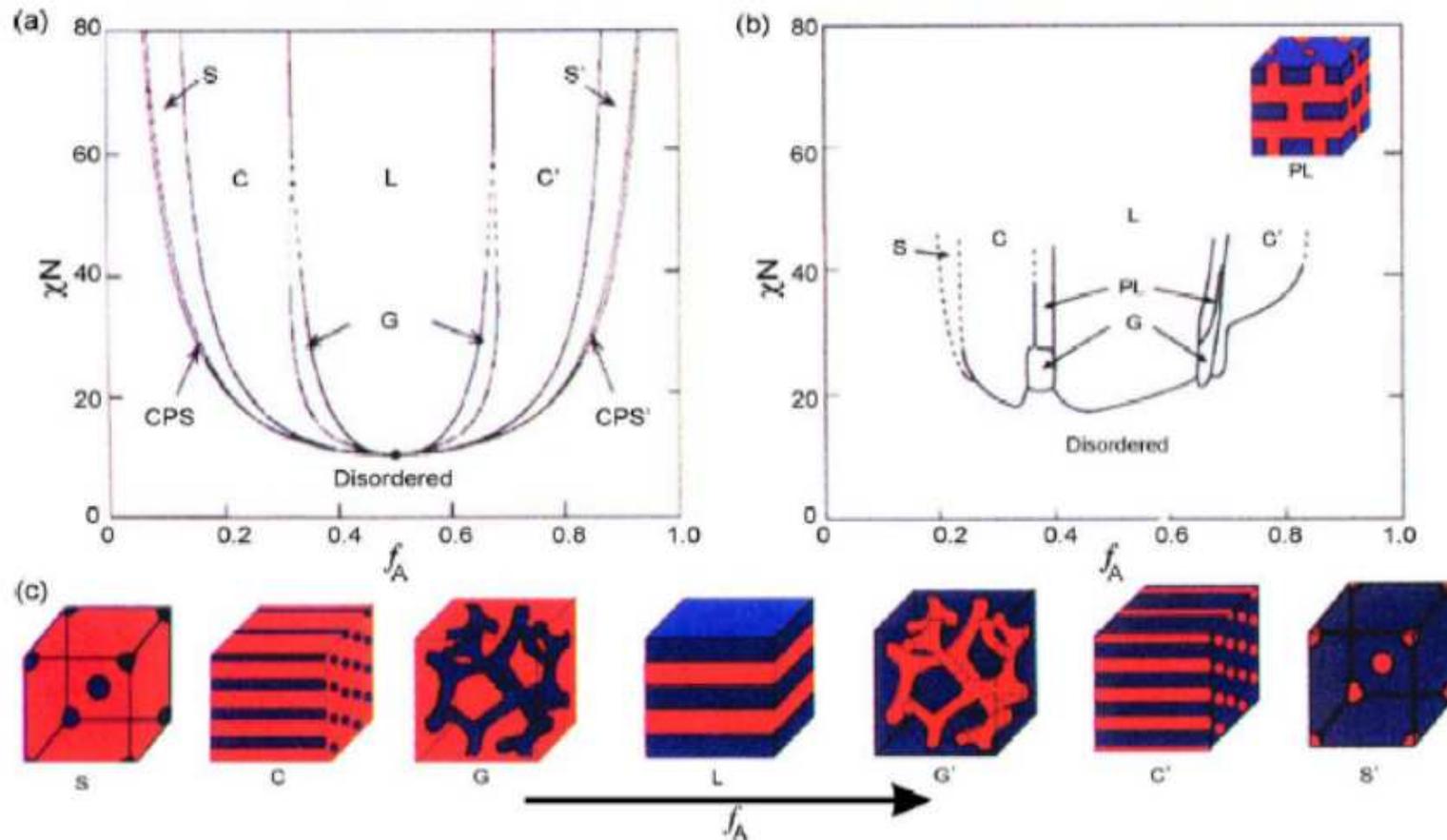# Block copolymer self-assembly

Fig. 1. Diblock copolymers are predicted to self-assemble according to a phase diagram predicted by self-consistent mean field theory (a) and proven experimentally (b). A variety of constant-radius geometries are observed as a function of relative lengths of the two blocks (c). Reproduced with permission from *Physics Today* [2].

Newest Phase Diagram

gyroid phase persists to $\chi N = 100$;

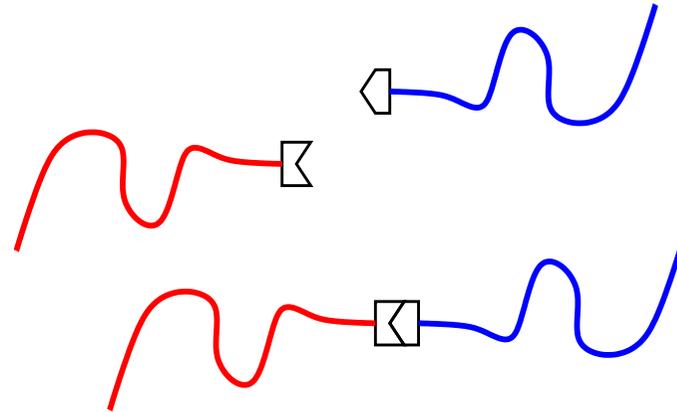E. Cochran et. al., *Macromolecules*, **39**, 2449-2451.
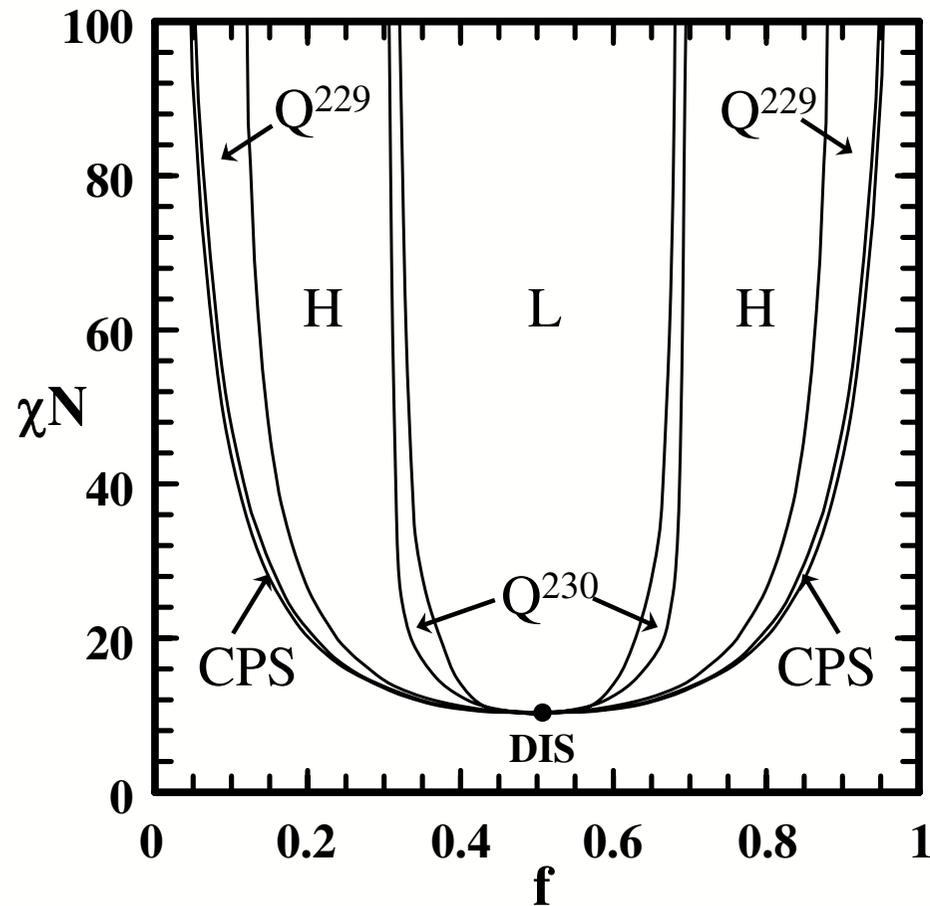
Grand Canonical Ensemble

$$\Xi(\mu, V, T) = \frac{1}{n!} \sum_{n=0}^{\infty} e^{\mu n} Z(n, V, T)$$

$$= \frac{1}{n!} \sum_{n=0}^{\infty} \int \mathcal{D}w_{\pm} e^{-\rho_0 \chi^{-1} \int w_-(\mathbf{r})^2 d\mathbf{r} + \rho_0 \int i w_+(\mathbf{r}) d\mathbf{r} + n \ln Q[w_{\pm}]} e^{\mu n}$$

$$= \int \mathcal{D}w_{\pm} e^{-\rho_0 \chi^{-1} \int w_-(\mathbf{r})^2 d\mathbf{r} + \rho_0 \int i w_+(\mathbf{r}) d\mathbf{r}} \frac{1}{n!} \sum_{n=0}^{\infty} (e^{\mu} Q[w_{\pm}])^n$$

$$= \int \mathcal{D}w_{\pm} e^{-\rho_0 \chi^{-1} \int w_-(\mathbf{r})^2 d\mathbf{r} + \rho_0 \int i w_+(\mathbf{r}) d\mathbf{r} + z Q[w_{\pm}]}$$

where $z \equiv e^{\mu}$ is the activity of the diblock copolymer

$$\mathcal{H}[W_{\pm}] = \frac{\rho_0}{\chi} \int w_-(\mathbf{r})^2 d\mathbf{r} - \rho_0 \int i w_+(\mathbf{r}) d\mathbf{r} - z Q[w_{\pm}]$$

Supramolecular Diblock

- z_A, z_B: activities of the two polymer species

- $f = N_A/N$: fraction of diblock that consists of A species (N is length of diblock)

- χ: Flory-Huggins parameter

- F_b: free energy of bonding

- incompressible melt conditions

Theoretical Results

parameters: z_A, f, χ, and h.

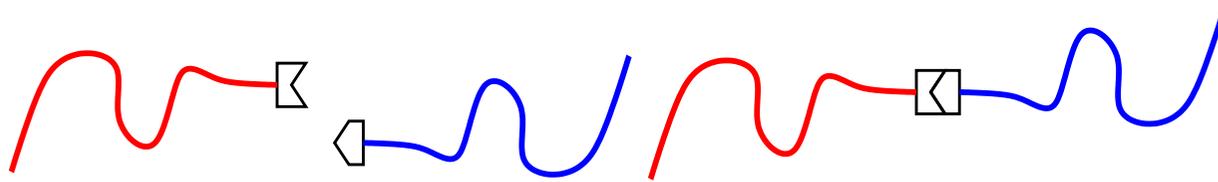$$\mathbf{x} \equiv \mathbf{r}/R_{g0}^3; \ W_\pm(\mathbf{x}) = Nw_\pm(\mathbf{x}).$$

- most natural to work in grand canonical ensemble for reacting systems; GCE partition function:

$$\Xi(z_A, V, T) = \int \mathcal{D}W_\pm e^{-\mathcal{H}[W_\pm]}$$

$$\mathcal{H}[W_\pm] = \frac{1}{\chi N}\frac{1}{V}\int d\mathbf{x}W_-^2(\mathbf{x}) - \frac{1}{V}\int d\mathbf{x}iW_+(\mathbf{x})$$
$$- z_A e^{-F_b - \ln N}Q_{AB}[W_\pm] - z_A Q_A[W_\pm] - Q_B[W_\pm]$$

- theory depends on *both* χN and N

- for each choice of parameters, there is a corresponding ternary blend system
  Jannert, Schick, *Macromolecules.* **30**:137 , '97. **30**:3916, '97.

Symmetric System: f=0.5, $z_A = 1$

- homopolymers of equal length, equal chemical potential for both species

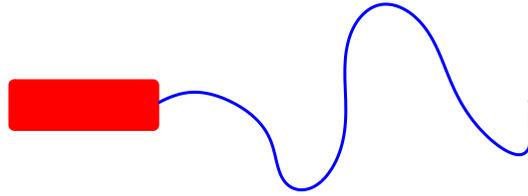- expect only disordered, macrophase separation and lamellar phases
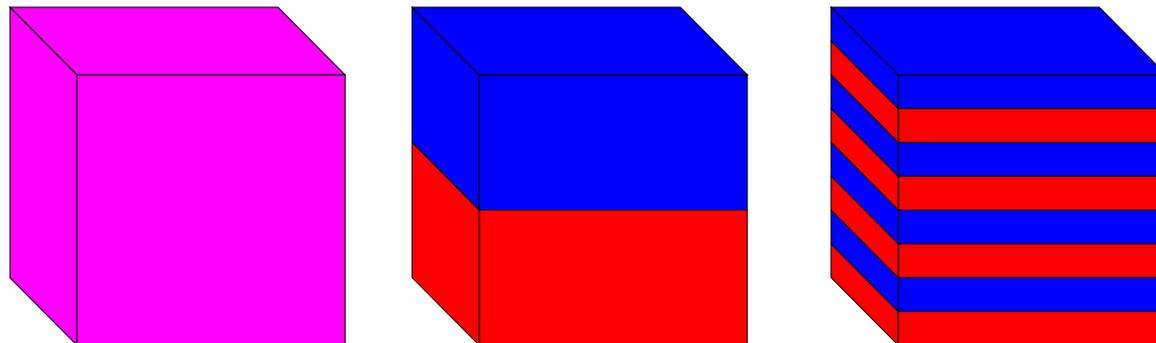
Three energy scales in the problem

- thermal energy: kT

- bonding energy $\sim h(kT)$

- chemical energy $\sim \chi N(kT)$

- scale everything by chemical energy:

  - dimensionless temperature $= 1/\chi N$

  - dimensionless bonding energy $= h/\chi N$

Phase Diagram with Re-entrant Behavior
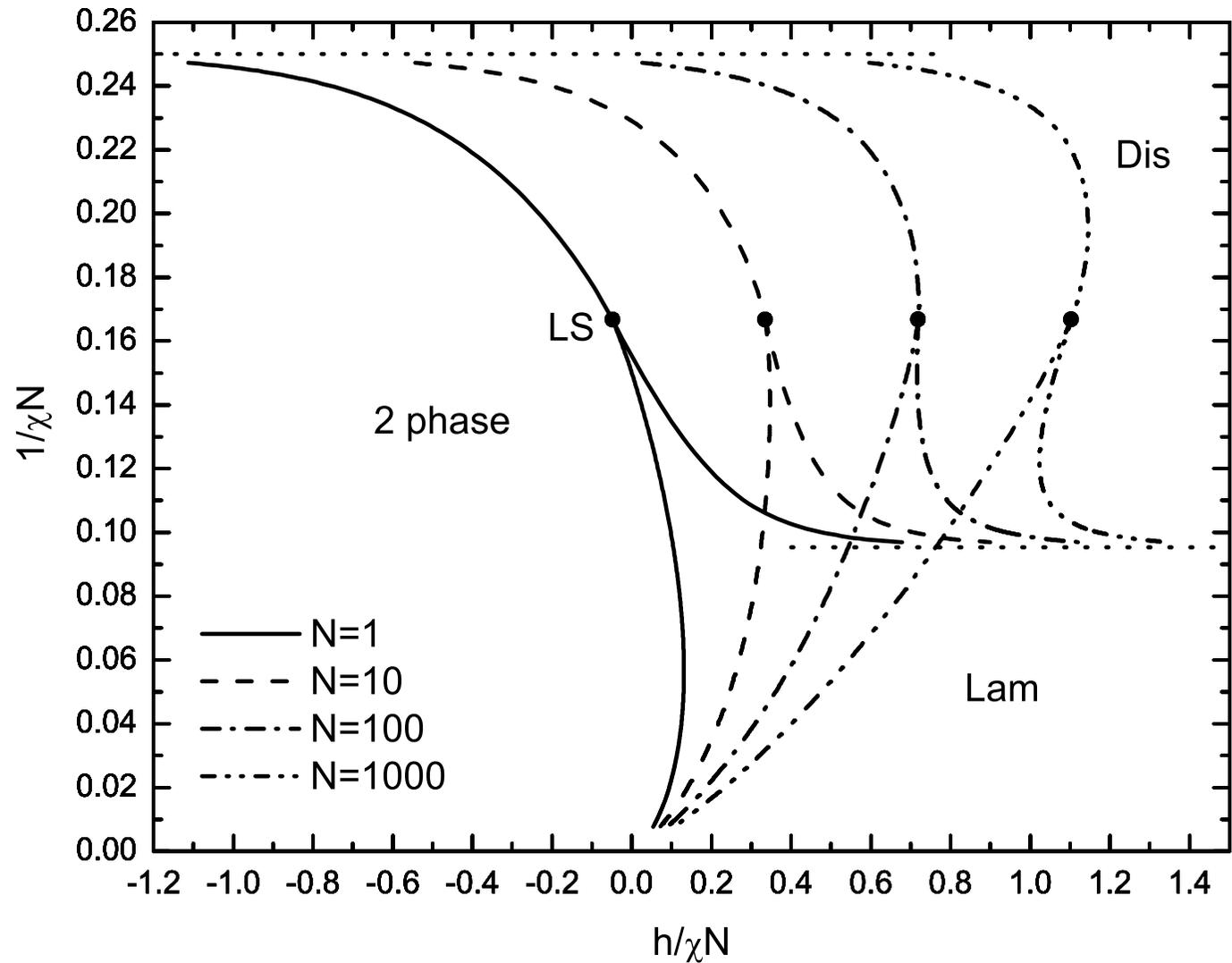
Model for Rod-Coil Diblock Copolymer:

- continuous Gaussian chain model for coil A block, stiff rod for B block

$$Z(n, V, T) = \int \mathcal{D}\mathbf{R}^n d\mathbf{u}^n \delta(\widehat{\rho}_A(\mathbf{r}) + \widehat{\rho}_B(\mathbf{r}) - \rho_0)$$

$$\times \exp\left(-\beta U_0[\mathbf{R}^n] - \beta U_1[\mathbf{R}^n\mathbf{u}^n] - \beta U_2[\mathbf{R}^n\mathbf{u}^n]\right)$$

where $\mathbf{u}^n = \mathbf{u}_1 \ldots \mathbf{u}_n$ denotes orientation of rods

$$\widehat{\rho}_B(\mathbf{r}) = \sum_{\alpha=1}^{n} \int_0^{(1-f)N} \delta(\mathbf{r} - (\mathbf{R}_\alpha(fN) + as\mathbf{u}_\alpha))ds$$

a is a length scale associated with the rod

$$U_2[\mathbf{R}^n\mathbf{u}^n] = -\frac{\mu}{2\rho_0}\int \widehat{S}_{ij}(\mathbf{r})\widehat{S}_{ij}(\mathbf{r})d\mathbf{r}$$

- $\widehat{S}_{ij}$ is the orientational order parameter

$$\widehat{S}_{ij}(\mathbf{r}) = \sum_{\alpha=1}^{n} \int_0^{(1-f)N} \left(u_{\alpha,i}u_{\alpha,j} - \frac{\delta_{ij}}{3}\right)\delta(\mathbf{r} - (\mathbf{R}_\alpha(fN) + as\mathbf{u}_\alpha))ds$$
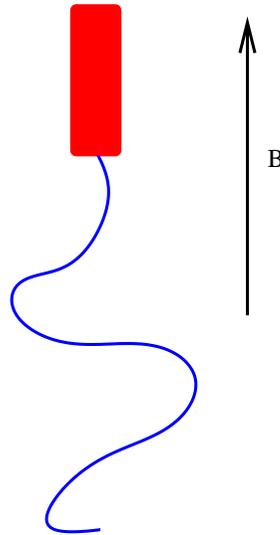
Rod-Coil Diblock Copolymers

- after analogous integral transformations, the partition function is

$$Z(n,V,T) = \int \mathcal{D}W_\pm \mathcal{D}M_{ij} e^{-\mathcal{H}[w_\pm]}$$

$$\mathcal{H}[W_\pm]$$
$$\sim \frac{1}{\chi N} \int W_-(\mathbf{r})^2 d\mathbf{r} - \int iW_+(\mathbf{r})d\mathbf{r} - V \ln Q[W_\pm, M_{ij}]$$
$$+ \frac{1}{2\mu N} \int M_{ij}(\mathbf{r})M_{ij}(\mathbf{r})d\mathbf{r}$$

Rod-Coil Diblock Copolymers in a Field

$$\mathcal{H}[W_\pm]$$

$$\sim \quad \frac{1}{\chi N} \int W_-(\mathbf{r})^2 d\mathbf{r} - \int iW_+(\mathbf{r}) d\mathbf{r} - V \ln Q[W_\pm, M_{ij}]$$

$$+ \frac{1}{2\mu N} \int M_{ij}(\mathbf{r}) M_{ij}(\mathbf{r}) d\mathbf{r} - \int d\mathbf{r} \Delta\chi^d B(\mathbf{r}) \frac{1}{2} (\mathbf{u}(\mathbf{r}) \cdot \mathbf{e} - 1)$$

- add term to free energy that accounts for alignment of rods in field, $\Delta\chi^d \equiv \chi_\parallel - \chi_\perp$, χ are the diamagnetic suspectibilities

- but we have to solve Maxwell's equations

$$\nabla \times B = \frac{j}{\epsilon_0 c^2} \ , \ \nabla \cdot B = 0$$

in addition to normal SCFT equations. . .

more details on the theory