Introduction to Self-Consistent Field Theory Calculations

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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

\[ \dot{R}(s) \text{ is a measure of chain stretching} \]
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

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

where \( R^n \equiv R_1(s), R_2(s) \ldots R_n(s) \) denote the space curves of the \( n \) polymers

- first energetic contribution comes from stretching of each chain

\[
U_0[R^n] = \frac{3kT}{2b^2} \sum_{i=1}^{n} \int_{0}^{N} |\dot{R}_i(s)|^2 \, ds
\]

this is Gaussian in the variable \( \dot{R}(s) \)
Model for Homopolymers in Good Solvent:

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

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

- if the density from the polymers is

\[ \hat{\rho}(r) = \sum_{i=1}^{n} \int_0^N \delta(r - R_i(s)) ds \]

then the repulsion between chains is

\[ U_1[R^n] = \int d\mathbf{r} d\mathbf{r}' \hat{\rho}(\mathbf{r}) u(|\mathbf{r} - \mathbf{r}'|) \hat{\rho}(\mathbf{r}') \]

- assume a delta function interaction

\[ u(|\mathbf{r} - \mathbf{r}'|) = kT u_0 \delta(\mathbf{r} - \mathbf{r}') \]

so the interaction energy becomes

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

\[ Z(n, V, T) = \int \mathcal{D}R^n \exp \left( -\frac{3}{2b^2} \sum_{i=1}^{n} \int_0^N |\dot{R}_i(s)|ds - u_0 \int \hat{\rho}(r)^2 dr \right) \]
$w(r)$ is a field conjugate to the density; in general, this is a complex field

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

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

Math involves doing Gaussian integrals
Single Chain Partition Function

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

- 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:

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

for the initial condition \( q(r, 0; [iw]) = 1 \)

- one can show that

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

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

is the density of the polymers in an external field \( iw(r) \)

- solving for \( q(r, s; [iw]) \) is the majority of computational work
One Dimensional Example

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

where \( iw(r) \) is the field above
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

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

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

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

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

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

- for this model of homopolymer in good solvent, the mean-field solution is

\[ w^*(r) = -iu_0 \rho_0 \]

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

- this solution does not depend on \( r \), so it is homogeneous

- this solution is an imaginary number
Model for Coil-Coil Diblock Copolymer:

- continuous Gaussian chain model

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

\[
U_0[R^n] = \frac{3kT}{2b^2} \sum_{i=1}^{n} \int_{0}^{N} |\dot{R}_i(s)|^2 ds
\]

\[
U_1[R^n] = \int d\mathbf{r} d\mathbf{r}' \hat{\rho}_A(\mathbf{r}) u(\mathbf{r} - \mathbf{r}') \hat{\rho}_B(\mathbf{r}') = \rho_0^{-1} \chi kT \int d\mathbf{r} \hat{\rho}_A(\mathbf{r}) \hat{\rho}_B(\mathbf{r})
\]

\[
\hat{\rho}_A(\mathbf{r}) = \sum_{i=1}^{n} \int_{0}^{fN} \delta(\mathbf{r} - \mathbf{R}_i(s)) ds
\]

where \( f \) is volume fraction of A block

- \( \chi \) is Flory-Huggins parameter in units of \( kT \)

- new physics is the density is fixed at \( \rho_0 \) 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

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

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

\[ \psi(r, s) = \begin{cases} 
  iw_+(r) - w_-(r) & s \in (0, f) \\
  iw_+(r) + w_-(r) & s \in (f, 1) 
\end{cases} \]

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

- partition function of a single chain in external fields
- use efficient method for calculating \( q(r, s) \)
Mean-Field Equations

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

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

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

\[ \rho_A(r; [w_\pm]) = \frac{\rho_0}{Q[w_\pm]} \int_{0}^{fN} q(r, s; [w_\pm]) q^\dagger(r, N - s; [w_\pm]) \]

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

- find fields \( w_+(x) \) and \( w_-(x) \) that satisfy these equations

- usually work in scaled fields \( W_\pm \equiv Nw_\pm \sim O(1) \), so \( \chi N \) is relevant parameter
How do we compute the mean field solution?

- start with randomize fields \( w_+ (r) \) and \( w_- (r) \)

- calculate the densities and subsequently mean-field equations:

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

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

- update the fields:

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

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

- iterate until mean-field equations are satisfied
What does this look like?

time evolution from top to bottom
Closer look at Lamellar Phase

\( f = 0.5, \chi N = 20 \)

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

\[ \phi_A(x) + \phi_B(x) - 1 = 0 \]
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 $\chi^N = 100$;

Grand Canonical Ensemble

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

$$= \frac{1}{n!} \sum_{n=0}^{\infty} \int Dw_{\pm} e^{-\rho_0 \chi^{-1}} \int w_-(r)^2 dr + \rho_0 \int iw_+(r) dr + n \ln Q[w_{\pm}] e^{\mu n}$$

$$= \int Dw_{\pm} e^{-\rho_0 \chi^{-1}} \int w_-(r)^2 dr + \rho_0 \int iw_+(r) dr \frac{1}{n!} \sum_{n=0}^{\infty} (e^{\mu Q[w_{\pm}]})^n$$

$$= \int Dw_{\pm} e^{-\rho_0 \chi^{-1}} \int w_-(r)^2 dr + \rho_0 \int iw_+(r) dr + zQ[w_{\pm}]$$

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

$$\mathcal{H}[W_{\pm}] = \rho_0 \int w_-(r)^2 dr - \rho_0 \int iw_+(r) dr - zQ[w_{\pm}]$$
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)
- $\chi$: Flory-Huggins parameter
- $F_b$: free energy of bonding
- Incompressible melt conditions
Theoretical Results

parameters: $z_A$, $f$, $\chi$, and $h$.

$x \equiv r/R_0^3$; $W_\pm(x) = N w_\pm(x)$.

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

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

$$\mathcal{H}[W_\pm] = \frac{1}{\chi N V} \int dx W_-^2(x) - \frac{1}{V} \int dx iW_+(x)$$

$$-z_A e^{-F_b - \ln N} Q_{AB}[W_\pm] - z_A Q_A[W_\pm] - Q_B[W_\pm]$$

- theory depends on both $\chi N$ and $N$

- for each choice of parameters, there is a corresponding ternary blend system

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

![Phase Diagram with Re-entrant Behavior](image-url)
Model for Rod-Coil Diblock Copolymer:

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

\[ Z(n,V,T) = \int D\mathbf{R}^n d\mathbf{u}^n \delta(\hat{\rho}_A(\mathbf{r}) + \hat{\rho}_B(\mathbf{r}) - \rho_0) \]
\[ \times \exp \left( -\beta U_0[\mathbf{R}^n] - \beta U_1[\mathbf{R}^n \mathbf{u}^n] - \beta U_2[\mathbf{R}^n \mathbf{u}^n] \right) \]

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

\[ \hat{\rho}_B(\mathbf{r}) = \sum_{\alpha=1}^n \int_0^{(1-f)N} \delta(\mathbf{r} - (\mathbf{R}_\alpha(fN) + a\mathbf{u}_\alpha)) ds \]

$a$ is a length scale associated with the rod

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

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

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

- after analogous integral transformations, the partition function is

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

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

\[ + \frac{1}{2 \mu N} \int M_{ij}(r) M_{ij}(r) dr \]
Rod-Coil Diblock Copolymers in a Field

\begin{align*}
\mathcal{H}[W_{\pm}] & \sim \frac{1}{\chi N} \int W_-(r)^2 dr - \int iW_+(r) dr - V \ln Q[W_\pm, M_{ij}] \\
& \quad + \frac{1}{2\mu N} \int M_{ij}(r) M_{ij}(r) dr - \int \nabla \chi^d B(r) \frac{1}{2} (u(r) \cdot e - 1)
\end{align*}

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

- but we have to solve Maxwell’s equations

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

in addition to normal SCFT equations...
more details on the theory