

Polymer Self-Consistent Field

Today: Theory (user's perspective)

Thurs: hands on use of PSCF

Focus: (today)

- physical approximation
- input parameters and outputs

What do we mean by

"self-consistent field"

or "mean-field"

approximation?

Characteristics:

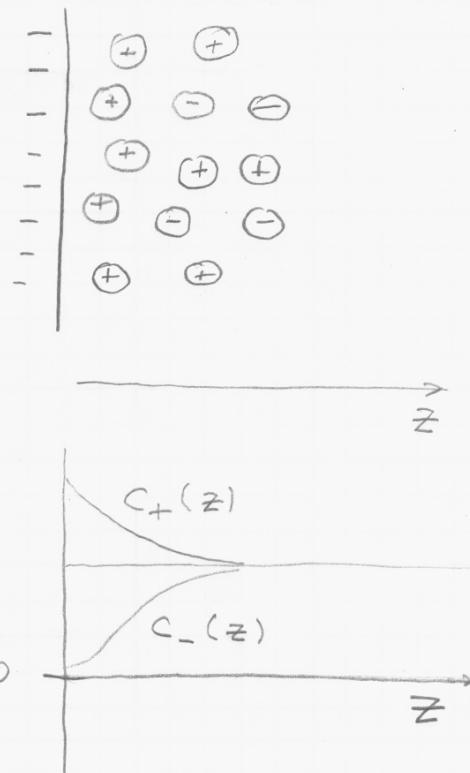
① Approximate reduction of a many molecule problem to a one-molecule problem.

② The one-molecule problem describes a molecule in an effective field,

"Self-consistency" - the effective field depends on solution to the one-molecule problem.

Example: Poisson-Boltzmann Theory

Typical problem: electrolyte solution near a charged surface.



$C_{\pm}(z)$ = mean cation/anion concentrations

$\rho(r)$ - mean charge density [C/m³]

$$\rho(r) = ze [C_+(r) - C_-(r)]$$

$\psi(r)$ - mean electric potential [V]

$$\epsilon_0 \nabla^2 \psi(r) = \rho(r)$$

Mean-field approximation

$$c_{\pm}(\underline{r}) \propto e^{-W_{\pm}(\underline{r})}$$

$$W_{\pm}(\underline{r}) \equiv \pm z e \psi(\underline{r}) / k_B T$$

→ non-dimensional mean-field/ion for cations or anions

Why is this not exact?

- Ignores electrostatic correlations



- Ignores steric/excluded volume interactions. (changes model for realism).

Characteristics:

- Effective single-ion problem

$$c_{\pm}(\underline{r}) \propto e^{-t^{\pm} z \psi(\underline{r}) / kT}$$

- Self-Triviality problem

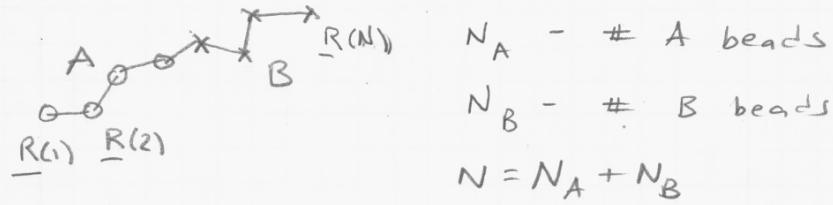
- Self-consistency condition (Poisson)

$$\epsilon_0 \nabla^2 \psi(\underline{r}) = z e [c_+(\underline{r}) - c_-(\underline{r})]$$

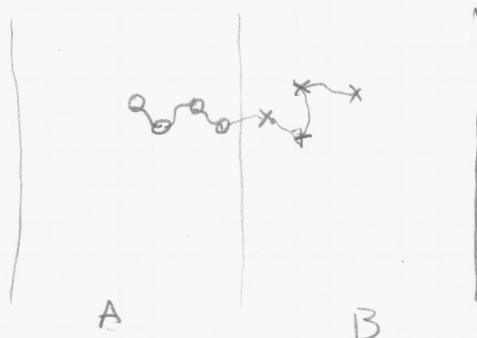
⇒ Requires an iterative solution
of self-consistency equation.

Polymer Self-Consistent Field Theory

Example: Diblock copolymer melt



Lamellar phase



Question:

What is the single-chain probability distribution $P(R(1), \dots, R(n))$?

(Probability of any specific conformation)?

Given this we can also compute

$$c_{A,B}(r) - \left\{ \begin{array}{l} \text{average concentration} \\ \text{of A/B monomers} \end{array} \right\}$$

"Mean-field" approximation:

Approximate by solution of a chain
in a pair of fields $w_A(\underline{r}), w_B(\underline{r})$

$$kT w_i(\underline{r}) - \left\{ \begin{array}{l} \text{excess chemical potential} \\ \text{for placing a monomer} \\ \text{of type } i \text{ at position } \underline{r} \end{array} \right\}$$

Incompressibility approximation:

Assume:

- Every monomer occupies a fixed volume ν
- $\nu(c_A(\underline{r}) + c_B(\underline{r})) = 1/\phi$
- Define volume fraction fields

$$\phi_i(\underline{r}) \equiv \nu c_i(\underline{r}) \quad i = A \text{ or } B$$

\uparrow
volume
fraction

\uparrow
average
concentration

Physical assumption: Free energy penalties for overall compression are much larger than those for segregation at fixed total density. Replace penalty by constraint.

Flory-Huggins approximations for fields:

General: e monomer types $i=1, \dots, e$

$$w_i(\underline{r}) = \sum_{j=1}^e \chi_{ij} \phi_j(\underline{r}) + \xi(\underline{r})$$

χ_{ij} - binary Flory interaction parameter
(dimensionless, defined per monomer)

$\xi(\underline{r})$ - Lagrange multiplier field

that imposes the incompressibility constraint

$$\nu \sum_{i=1}^e c_i(\underline{r}) = \sum_{i=1}^e \phi_i(\underline{r}) = 1$$

at every position \underline{r}

Analogy: Like pressure in
incompressible Navier-Stokes
equation.

Elements:

- Solution of single-chain-in-field

↓
monomer concentrations $c_i(r)$

(Trick: Modified Diffusion Egn.)

- Iterative solution of self-consistent field equations

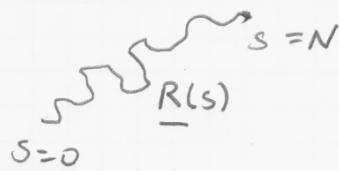
$$w_i(r) = \sum_{j=1}^e \chi_{ij} \phi_j(r) + g(r)$$

$$\mathbf{1} = \sum_{j=1}^e \phi_j(r)$$

loop iteration

Single-Chain Problem (briefly)

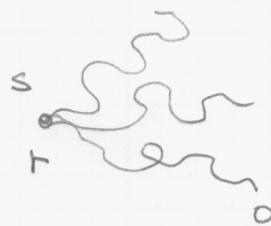
Use a continuous representation of chain



(assume that discrete chemical structure is irrelevant at length scales of interest)

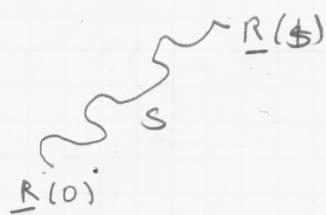
For simplicity, consider homopolymer in a single field $w(\underline{r})$

Define a statistical weight $g(\underline{r}, s)$



$g(\underline{r}, s) \propto \left\{ \begin{array}{l} \text{partition function of} \\ \text{a chain segment of length} \\ s \text{ with } \underline{R}(s) \text{ constrained} \\ \text{to position } \underline{r}. \end{array} \right\}$

In absence of a field, the polymer undergoes a random walk, like diffusion of Brownian particle.



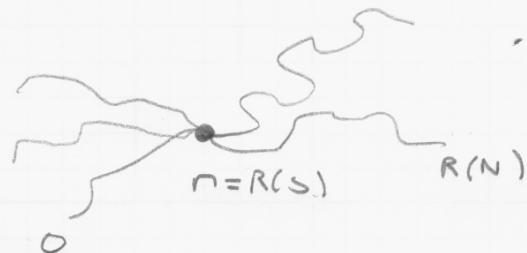
polymer conformation
or
Brownian trajectory
($s \rightarrow \text{time}$)

Theorem (without proof):

The statistical weight $g(r,s)$ obeys a modified diffusion equation (MDE)

$$\frac{\partial g}{\partial s} = - \left[-\frac{b^2}{6} \nabla^2 + w(r) \right] g$$

Given $g(r,s)$, we can compute monomer concentrations.

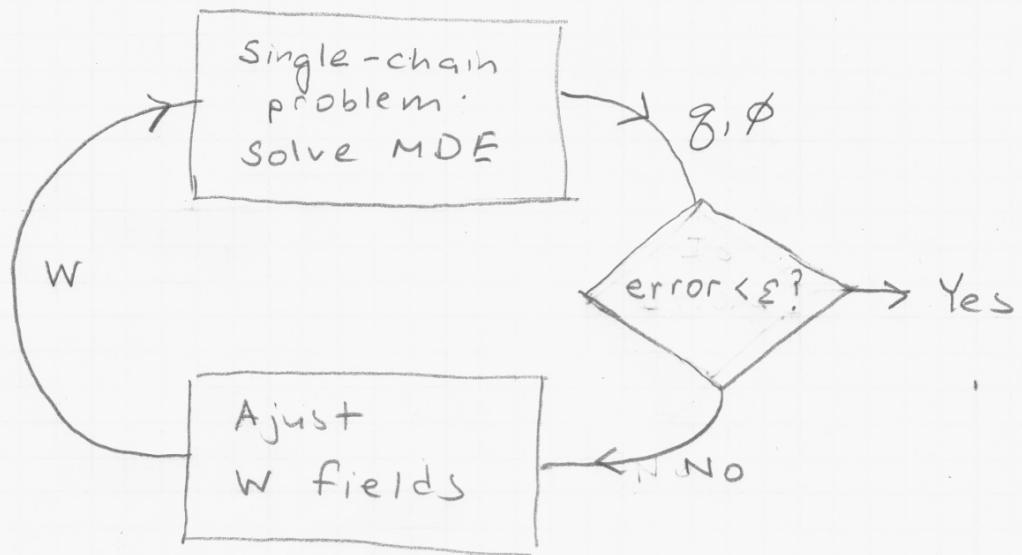


$$c(r,s) \propto g(r,s) g(r, N-s)$$

$\propto \left\{ \begin{array}{l} \text{partition function of a} \\ \text{chain with } R(s) \text{ constrained to } n \end{array} \right\}$

[Generalization to block copolymers is straightforward.]

SCF Algorithm (simplified)

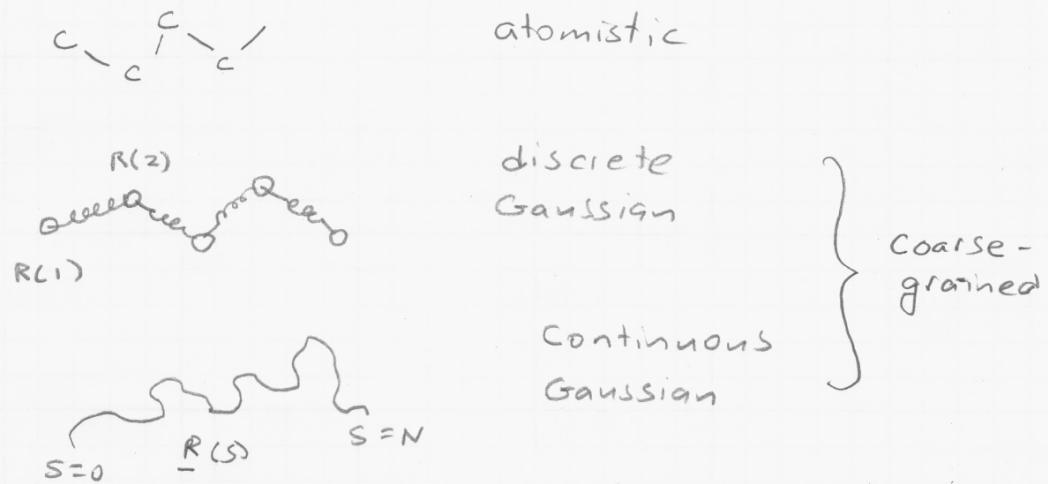


Key numerical algorithms:

- MDE solver
 - pseudo-spectral method
 - * Dominates computational cost
- Iterator to adjust w
 - Subtle, but relatively cheap
 - Anderson-mixing algorithm

Flexible definition of "Monomer"

Consider three related models for polyethylene



Definition of monomer is flexible even for atomistic model

(e.g., $(CH_2)_n$ or $(CH_2 - CH_2)_{n/2}$)

In discrete model we can add beads (increase N) or regroup (decrease N).

In continuous model, N need not be an integer.

Relationship with statistics: For a free chain

$$\langle |R(s) - R(s')|^2 \rangle = |s - s'| b^2$$

Physical properties of a segment of length N

$$R_e^2(N) \equiv \langle |\underline{R}(N) - \underline{R}(0)|^2 \rangle = Nb^2$$

$$V(N) = N\omega \quad (\text{steric volume})$$

where

b - statistical segment length

ω - monomer volume

Values of b, ω depend on definition of "monomer".

So do Flory-Huggins parameters. Note:

$X_{ij}N$ - cost of immersing segment
of i in j .

Rescaling:

If we change $N \rightarrow N/\lambda$

$$\text{then } \omega \rightarrow \lambda \omega$$

$$b \rightarrow \sqrt{\lambda} b$$

$$X_{ij} \rightarrow \lambda X_{ij}$$

So that $N\omega, Nb^2$, and NX_{ij} are unchanged.

Constraint: Monomer reference volume

ω must be the same for all monomer types.

'Experimentalist' Units:

Choose a monomer reference volume v

e.g., $v = 100 \text{ \AA}^3$ or volume per unit of specific species, etc.

ρ - density of homopolymer [g/cm^3]

m - mass per "monomer" [g/mol]

$$m = \rho [\text{g/cm}^3] v [\text{\AA}^3] \frac{10^{-24} \text{ cm}^3}{\text{\AA}^3} \times N_{Av} [\text{mol}^{-1}]$$

$$N_{Av} = 6.02 \times 10^{23} \text{ mol}^{-1}$$

For a chain segment of molecular weight M

$$N = \frac{M}{m} \leftarrow \begin{array}{l} \text{total M.W} \\ \leftarrow \text{M.W. per monomer} \end{array}$$

If b is known for a statistical segment (e.g., a chemical repeat unit) of mass m_0 , then

$$b \rightarrow \sqrt{\frac{m}{m_0}} b$$

Similarly if χ is known for such a unit

$$\chi \rightarrow \left(\frac{m}{m_0} \right) \chi$$

"Theorist" Units:

Consider a block polymer melt.

Chains of length N in experimentalist units.

Choose: $N = 1$ (one "monomer")

For each monomer type α

$$b_\alpha \rightarrow \sqrt{N} b_\alpha$$

$$\chi \rightarrow \chi N$$

For AB diblock, $b_A = b_B$, input parameters are:

block lengths \rightarrow block fractions

statistical segment lengths $\rightarrow \sqrt{N} b$

χ parameters $\rightarrow \chi N$

In a mixture, you choose reference volume to be volume/molecule of a particular species.

\Rightarrow Block "lengths" in PSCF are actually given by ~~the~~ ratio

volume of block / volume of monomer

$$\text{block length} = \frac{\text{(block volume)}}{\text{(monomer volume } w)}$$

Input and output variables in PSCF:

- Energies are in "thermal units" in which $k_B T = 1$
- All variables involving length must use the same units, can be Å, nm, or can set some physical length to 1.

e.g., if for a diblock copolymer melt I set $N=1$ and $b=1$, then $R_e = \sqrt{N} b = 1$ by definition.

- Free energy and pressure are output in intensive form

$$\tilde{f} = \frac{F\bar{v}}{k_B T V} \quad F - \text{total Helmholtz free energy}$$

V - total volume

$$\tilde{P} = \frac{P\bar{v}}{k_B T}$$

PSCF Software

Package with several SCFT implementations

→ pscf-fd: 1 dimensional finite difference

(useful for interfaces, spherical
and cylindrical micelles.)

→ Programs for periodic structures

pscf-pc → CPU

pscf-pg → GPU (Nvidia graphics card)

Model (common to all)

- Mixture of polymer and solvent species.
- Polymers can be linear or acyclic branched block polymers.
- Assumes incompressibility.
- Flexible statistical ensemble
 - (Volume fraction ϕ - μ)
 - or
 - chemical potential μ

Inputs

Chemical parameters:

For each monomer type

statistical segment length

For each polymer

block lengths

block monomer types

connectivity (if branched)

species ϕ or κ

For each solvent

solvent size (volume)

solvent type

Flory-Huggins parameters χ_{ij}

Algorithmic Parameters:

Spatial mesh (# grid points)

Contour step size ds

Crystallography

Lattice system (hex, cubic, orthorhombic etc)

Space Group (3D-230 choices)

Initial Guesses:

w fields

Unit cell parameters