1 Self-Consistent Field (SCF) Theory

In self-consistent field (SCF) formulation\(^1\), the average interaction between segments are treated as an mean-field, external field that a single segment feels. The self-consistency comes from assuming the local concentration \(c(\mathbf{r})\) and the mean-field potential \(U_{MF} \propto c(\mathbf{r})\) and solving for the new concentration and potential, \(c'(\mathbf{r})\) and \(U_{MF}'\), respectively, until a self-consistent solution can be found.

1.1 SCF – Single Chain Configuration

Before, a chain of length \(L = NA\) (\(A \equiv\) Kuhn length) was described by a lattice description. In the absence of segment-segment interactions (or an external field), the partition function \(Z_N \simeq z^N\) where \(z\) is the coordination number for the lattice.

In an external field each segment “feels” a potential \(u(\mathbf{r})\). Each \(i^{th}\) step needs to be weighted by a Boltzmann factor \(e^{-u(\mathbf{r}_i)/k_BT}\) so that the partition function becomes

\[
Z_N \simeq \sum_{\text{all config}} z^N \exp \left[ -\sum_{i=1}^{N} \frac{u(\mathbf{r}_i)}{k_BT} \right]
\]

Consider only the paths with fixed ends\(^2\), \(i.e., \mathbf{r}_1 = \mathbf{r}'\) and \(\mathbf{r}_N = \mathbf{r}\). The statistical weighted sum for this case is

\[
G_N(\mathbf{r}', \mathbf{r}) = \int g(\mathbf{r}_1, \mathbf{r}_2)g(\mathbf{r}_2, \mathbf{r}_3) \ldots g(\mathbf{r}_{N-1}, \mathbf{r}_N)\delta(\mathbf{r}' - \mathbf{r}_1)\delta(\mathbf{r} - \mathbf{r}_N)d\mathbf{r}_1d\mathbf{r}_2 \ldots d\mathbf{r}_N
\]

\(^1\)This approach is often called the Edwards’ approach because he was the first to make explicit the analogy between polymeric configuration and the paths of a nonrelativistic particle.

\(^2\)A complete discussion can be found in P.-G. de Gennes, *Scaling Concepts in Polymer Physics*, chapter 9.
where $g$’s are “bond” functions, i.e., $g \equiv e^{-U/k_BT}$. If another is added to this path, the corresponding sum is

$$G_{N+1}(r', r) = \frac{1}{z} \sum_{r''} G_N(r', r'') e^{U(r'' - r)/k_BT}$$

where we are now summing over all neighbors of the extra monomer at $r$.

For slowly varying $G$, the function $G_N(r', r'')$ can be expanded about $r'' = r$ as a Taylor series.

For a cubic lattice,

$$G_{N+1}(r', r) \approx G_N(r', r) e^{-U(r)/k_BT} + \frac{A^2}{6} \nabla^2 G_N(r', r)$$

or

$$-\frac{\partial G_N}{\partial N} \approx -\frac{A^2}{6} \nabla^2 G_N + \frac{U(r)G_N}{k_BT}$$

The above equation looks remarkably similar to the time-dependent Schrödinger equation.

Why do we care?

We can use this homomorphism between the “path” of the polymer and the path of an electron; we can use already available solutions from quantum mechanics! For example, the problem of polymer confinement in a tube or between plates is exactly like the particle-in-a-box problem in quantum mechanics.

However, there are some drawbacks. We’ve assumed short-ranged and weak interactions in the development of the formalism. For longer-ranged segment-segment interactions, e.g., electrostatic interactions, the formalism needs to be adapted or we need to look elsewhere.

2 Primer on Electrostatics

2.1 Poisson-Boltzmann (PB) Equation

Consider a charged surface with counterions in water (dielectric constant $\epsilon$).
The equilibrium condition that the chemical potential of the counterions $\mu$ is the same throughout the solution.

$$\mu = zeψ + k_B T \log ρ$$

where $z$ is the valence of the ions, $e$ is the unit charge, $ψ$ the electrostatic potential, and $ρ$ the density of counterions.

The equilibrium condition dictates then

$$\frac{d\mu}{dx} = ze \left( \frac{dψ}{dx} \right) + \frac{k_B T}{ρ} \frac{dρ}{dx} = 0$$

or

$$\frac{dρ}{dx} = -ρ \frac{ze}{k_B T} \left( \frac{dψ}{dx} \right)$$

The solution to the above equation is

$$ρ = ρ_0 e^{-zeψ/k_B T}$$

a Boltzmann distribution.

Poisson equation for valence $z = 1$ is

$$\nabla^2 ψ = -\frac{4π(ερ)}{ε}$$

with the Boltzmann counterion distribution becomes the Poisson-Boltzmann (PB) equation.

$$\nabla^2 ρ_0 e^{-εψ/k_B T}$$
2.2 Debye-Hückel (DH) Equation

With added (1:1) salt, PB equation becomes

\[ \nabla^2 \psi = -\frac{4\pi e}{\epsilon} \sum_i \rho_{0,i} e^{-e\psi/k_BT} \]

For weak potentials, i.e., \( e\psi/k_BT \ll 1 \), \( e^{-e\psi/k_BT} \approx 1 - e\psi/k_BT \), and the equation can be rewritten

\[ \nabla^2 \psi = 4\pi e^2 \frac{e\psi}{\epsilon k_BT} \left( \sum_i \rho_{0,i} \right) \psi \]

or

\[ \nabla^2 \psi = \kappa^2 \psi \]

The above is the Debye-Hückel equation.

The Debye parameter (or inverse screening length) \( \kappa \) is defined as

\[ \kappa^2 = \frac{4\pi e^2 c_s}{\epsilon k_BT} = 8\pi l_B c_s \]

where \( c_s \) is the total bulk salt concentration (in M) and \( l_B \) is the Bjerrum length. The Bjerrum length is defined as the length at which two unit charges feel each other with energy \( k_BT \).

3 Polyelectrolytes

3.1 Counterion Condensation\(^3\)

Consider a stiff polyelectrolyte with linear charge density \( \lambda = -e/b \) where \( b \) is the distance between the charges, and de-condensed counterion (ionized monomer) fraction \( f \). We can also define a dimensionless charge density (often called the Manning parameter) \( \xi = l_B/b \).

The Debye-Hückel potential for \( \kappa r \ll 1 \) (low salt) can be written

\[ \frac{e\psi(r)}{k_BT} = -2\psi f \ln(\kappa r) \]

\(^3\)Manning, 1969; Oosawa, 1968
which results in the ion distribution being

\[ \rho = \rho_0 (\kappa r)^{-2\xi_f} \]

We can now look at the total number of counterions per unit length \( P(R) \) within any given radius \( R \).

\[
P(R) = \int_0^R 2\pi r \rho(r) \, dr = 2\pi \rho_0 \kappa^{-2\xi_f} \int_0^R r^{(1-2\xi_f)} \, dr
\]

For \( \xi_f \ll 1 \), there is no condensation around the polyelectrolyte!

\[
\int_0^R r^{(1-2\xi_f)} \, dr \approx \int_0^R r \, dr \rightarrow \frac{1}{2} R^2
\]

For \( \xi_f \geq 1 \), there is condensation around the polyelectrolyte. For example, for \( \xi_f = 2 \),

\[
\int_0^R r^{(1-2\xi_f)} \, dr = \int_0^R \frac{1}{r^3} \, dr
\]
Counterions condense until $\xi_f = 1$ or $\xi_{eff} = 1$.

Physical explanation: Distribution of counterions around the polyelectrolyte needs to minimize both the counterion entropy, and the electrostatic energies of the polyelectrolyte and the counterions. In other words, for highly charged polyelectrolytes, the counterions will condense and lose entropy to lower the electrostatic repulsions between the charged monomers.

### 3.2 Polyelectrolyte Conformations

Let us assume the polyelectrolyte can be thought of as a flexible chain with free energy

$$
\frac{F}{k_B T} \approx \frac{R^2}{N b^2} + \frac{(f N)^2 l_B}{R}
$$

The coil size that corresponds to the minimum in the free energy is

$$
R^* \approx (\xi f^2)^{1/3} Nb
$$
We can now move to a less simple picture – “Blob” theory. Instead of one coil, consider many blobs of diameter $\xi_e$, each blob containing $g$ number of monomers. Then $N/g$ is the number of blobs and $\xi_e^2 \simeq gb^2$.

Flory-type free energy for these electrostatic blobs is then

$$\frac{F}{k_BT} \simeq \frac{N}{g} \left[ \frac{\xi_e^2}{gb^2} + \frac{(gf)^2l_B}{\xi_e} \right]$$

The “blob” size that corresponds to the minimum in this free energy is

$$\xi_e^* \simeq g \left( \frac{f^2l_B}{b} \right)^{1/3} b$$

Since this model is valid for weakly-charged polyelectrolytes, i.e.,

$$\frac{(gf)^2l_B}{\xi_e} \approx 1$$

The “blob” size can be written

$$\xi_e^* \simeq \left( \frac{\xi_e}{f^2l_B} \right)^{1/2} \left( \frac{f^2l_B}{b} \right)^{1/3} b \simeq \left( \frac{b}{f^2l_B} \right)^{1/3} b$$

And the number of monomers within each blob is independent of $N$ and depends purely on the electrostatics.

$$g \simeq \left( \frac{b}{f^2l_B} \right)^{2/3}$$

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\(^4\)de Gennes, Pincus, Velasco, and Brochard 1976
The number of blobs

\[
\frac{N}{g} \simeq N \left( \frac{f^2 l_B}{b} \right)^{2/3} = fN(f\xi)^{1/3}
\]

What happens with increase in the charge density of the polyelectrolyte, \textit{i.e.}, as \( f\xi \) increases? The number of blobs \( N/g \) increases...

You can be even more careful and allow for “linkers” between the blobs (necklace/cascade models).

Aside: Just as the path of a weakly interacting polymer is analogous to the path of an electron, the polyelectrolyte “blobs” are analogous to the droplets that form in Rayleigh instability.

### 3.3 Adsorption: Charge Reversal

We might expect two oppositely and singly charged objects to complex in solution to form “electroneutral” species. But what happens for multivalent ions in solution? Specifically what happens to polyelectrolytes in the presence of oppositely charged objects?

The reference (uncomplexed) state free energy for the polyelectrolyte is non-zero and positive since the charges along the chain cannot avoid one another. Since the chain always pays a high free energy cost, there is a \textit{stronger} drive for complexation than charged objects that carry one or two charges.

This leads to “overcharging” or charge reversal of complexes in solution and allows for the formation of polyelectrolyte multilayers\(^5\).

\(^5\)See for example many papers by the Rubner group.