Introduction into Theory and Simulations of Polyelectrolytes - The cylindrical cell model

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Overview

• charged polymers (= Polyelectrolytes)

• theoretical concepts

• mean-field cell model

• mean-field Poisson-Boltzmann theory

• some basics about simulations and

• departures from mean-field behavior

• poor solvents PE
What are polyelectrolytes?

Charged macromolecules which dissociate charges in solution
(⇒ water soluble !)

<table>
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<tr>
<th>synthetic examples:</th>
<th>biological examples:</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly-acrylic acid</td>
<td>cell membranes</td>
</tr>
<tr>
<td>sulfonated polystyrene</td>
<td>DNA, RNA, proteins</td>
</tr>
</tbody>
</table>

Applications:
- super-absorber
- viscosity modifiers,
- additives to detergents
- paper industry, waste management

Useful for:
- gene transfer mechanisms
- understanding biological functions,
- DNA packing

Large tendency to self-assemble in nanostructures !!
1. Example: hydrogel
Nano-Structures made of Like-Charged Objects

Structure formations of charged semi-flexible polymers

synthetic (PPPs) vs. biological semi-flexible PEs (fd, DNA)

morphologies, thermodynamics vs kinetics
2. Example: T5 bacteriophage
PEs possess many length scales: $R_e, \xi, L_p, \lambda_D, \ell_B \ldots$

$e$: unit electronic charge, $\epsilon_r$: relative dielectric permittivity. Electrostatic interaction energy: $\frac{e^2}{4\pi\epsilon_0\epsilon_rr}$.
The Bjerrum length $\ell_B$ is defined via $k_B T = \frac{e^2}{4\pi \epsilon_0 \epsilon_r \ell_B}$

$$\ell_B = \frac{e^2}{4\pi \epsilon_0 \epsilon_r k_B T}$$

For water at room temperature we find

$$\ell_B = \frac{(1.6 \cdot 10^{-19} C)^2}{4\pi \cdot 8.85 \cdot 10^{-12} \frac{C}{Vm} \cdot 78.5 \cdot 1.38 \cdot 10^{-23} \frac{J}{K} \cdot 298 K} \approx 7.13 \text{Å}$$

The electrostatic interaction of two charges $Q_1$ and $Q_2$ separated by $r$ is

$$E/k_B T = \ell_B \frac{Q_1 Q_2}{r}.$$

The electrostatic energy of a homogeneously charged $(Q)$ sphere of radius $R$ is

$$E/k_B T = \ell_B \frac{Q^2}{2R} \approx \ell_B \frac{Q^2}{R}.$$
Flory argument for chain extension

The Hamiltonian of a Gaussian chain is given by

\[ H_0 = \frac{3k_B T}{2b^2} \sum_{i=1}^{N}(\vec{r}_{i+1} - \vec{r}_i)^2 \]

\[ \implies R = b\sqrt{N} \quad \text{(RW), N monomers of size } b, \ f: \text{ fraction of charged monomers. The Flory energy of a PE chain is} \]

\[ E_F = k_B T \left( \frac{R^2}{Nb^2} + \frac{(Nf)^2\ell_B}{R} \right) \]

\[ \frac{\partial E_F}{\partial R} = 0 \implies \frac{2R}{Nb^2} - \frac{(Nf)^2\ell_B}{R^2} = 0 \]

\[ \implies R \sim N\ell_B^{1/3}f^{2/3}b^{2/3} \]

Chain growth linear in N, electrostatic interactions swell the chain \( R = N^{1/\nu} \), PE has \( \nu = 1 \), as opposed to RW (\( \nu = 2 \)) or SAW (\( \nu = 5/3 \))
1. Simplification

complex interaction: ion distribution $\leftrightarrow$ polymer conformation

stiff, stretched polymer conformation $\rightarrow$ uniformly charged rod.
Onsager argument for condensation

\[ \lambda = \frac{e_0}{b} \quad \ell_B := \frac{e_0^2}{4\pi \varepsilon k_B T} \]
\[ \phi(r) \approx \frac{\lambda}{2\pi \varepsilon} \ln(r) \]

question: \( \Delta F = \Delta E - k_B T \Delta S \) ?

\[ \Delta E \sim e_0 \frac{\lambda}{2\pi \varepsilon} \ln \frac{R}{r} \quad \Delta S \sim \ln \frac{V_R}{V_r} \sim 2 \ln \frac{R}{r} \]

\[ \Rightarrow \Delta F = \left( \frac{\ell_B}{b} - 1 \right) 2k_B T \ln \frac{R}{r} \]

\( \xi := \frac{\ell_B}{b} < 1 \), entropy dominated, \( \xi := \frac{\ell_B}{b} > 1 \), energy dominated

\[ \Rightarrow \text{The charged plane is energy dominated} \]

\[ \Rightarrow \text{The charged sphere is entropy dominated} \]
Successive approximation stages to go from a solution of many macromolecules to a cell model of **one** macromolecule

Factorization of the many-body partition function into a product of one-particle partition functions
The Restricted Primitive Model in the cell (RPM)

\[ U_{ij}(r_{ij}) = \begin{cases} \frac{-z_i z_j}{4 \pi \epsilon r_{ij}} & \text{if } 0 < r_{ij} \\ \infty & \text{otherwise} \end{cases} \]

\[ r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| \]

RPM

implicit solvent \( \varepsilon \)

charges interact via \( \frac{1}{r} \) + hard sphere potential \((\sigma_i, \sigma_j)\)
Sloppy *Motivation* of the Poisson-Boltzmann Equation. Start with the Poisson Equation:

\[ \nabla^2 \psi(\vec{r}) = -\frac{e}{\epsilon} (v^+(n^+(\vec{r}) + v^-(n^-(\vec{r})) \]

The electrochemical potential of each ion is \( \mu^{(i)} = ev^{(i)}\psi + k_B T \ln n^{(i)} \Rightarrow \)

Boltzmann populations \( n^{(i)} = n_0^{(i)} e^{-ev^{(i)}\psi/k_B T} \Rightarrow \)

**Poisson-Boltzmann Equation**

\[ \nabla^2 \psi(\vec{r}) = -\frac{e}{\epsilon} (v^+(n^+_0) e^{-ev^+(\psi)/k_B T} + v^+(n^-_0) e^{-ev^-(\psi)/k_B T}) \]

For an 1:1 electrolyte

\[ n_0 = n_0^+ = n_0^- \]

\[ \nabla^2 \psi(\vec{r}) = \frac{2e}{\epsilon} n_0 \sinh(e\psi/k_B T) \]

the linearized equation is called the Debye-Hückel approximation:
\[ \nabla^2 \psi(\vec{r}) = 8\pi \ell_B n_0 \psi(\vec{r}) = \lambda_D^{-2} \psi(\vec{r}) = \kappa \psi(\vec{r}) \]

with an exponentially screened solution

\[ \psi(r) = Ae^{-\kappa r} \]

where \( \kappa \) is called screening parameter, and \( \kappa^{-1} = \lambda_D^2 = (8\pi \ell_B n_0)^{-1} \). \( \lambda_D \) is called Debye-Hückel screening length (\( \approx \) range of the electrostatic interaction). Its value has a \( 1/\sqrt{n_0} \) salt dependence:

- 3 Å for 1 Mol NaCl
- 10 Å for 100 mMol (1:1) salt (physiological conditions)
- 1 \( \mu \)m for pure water \( (n_0 \approx 10^{-7} \text{ Mol due to autoionization of water into } H^+ \text{ and } OH^-) \).
Cell model for the rod and Poisson-Boltzmann theory

Bjerrum length: \( \ell_B := \frac{e_0^2}{4\pi \varepsilon k_B T} \)

Manning parameter: \( \xi := \lambda \ell_B / e_0 \)

potential: \( y(r) := \frac{e_0 \psi(r)}{k_B T} \)

\[
\begin{align*}
y'' + \frac{1}{r} y' &= 4\pi \ell_B n(r) \quad ; \quad y'(r_0) = -2\xi/r_0 \\
n(r) &= n(R) e^{y(r)} \quad ; \quad y'(R) = 0
\end{align*}
\]

\[
y(r) = -2 \ln \left\{ \frac{r}{R} \sqrt{1 + \gamma^{-2} \cos \left( \gamma \ln \frac{r}{R_M} \right)} \right\}
\]

The integration constants \( \gamma \) and \( R_M \) follow from the boundary conditions
The integration constants $\gamma$ and $R_M$ are found numerical from

$$\gamma \ln \frac{r_0}{R_M} = \arctan \frac{1-\xi}{\gamma}; \quad \gamma \ln \frac{R}{R_M} = \arctan \frac{1}{\gamma}$$

Linearizing the Boltzmann exponential yields the Debye-Hückel approximation with an exponential screened potential:

$$y(r) \approx A \frac{\exp -\kappa r}{r} \quad \text{with} \quad \kappa^2 := 4\pi \ell_B v^2 n$$

Screening constant $\kappa$ or Debye length $\lambda_D = \kappa^{-1/2}$
Counterion distribution and Manning condensation

the fraction of counterions within a distance \( r \in [r_0, R] \) is given

\[
f(r) = 1 - \frac{1}{\xi} + \frac{\gamma}{\xi} \tan \left( \frac{\gamma}{R_M} \ln \frac{r}{R_M} \right)
\]

Manning condensation at \( \xi > 1 \):

\[
f < 1 - \frac{1}{\xi} \iff \lim_{R \to \infty} r(f) < \infty
\]

Inflection point criterium:

\[
\left. \frac{d^2 f}{d(\ln r)^2} \right|_{r=R_M} = 0 \ \Rightarrow \ R_M
\]
Manning condensation

The (Manning–) fraction \( f(R_M) = 1 - 1/\xi \) is a critical limit, because (for \( \xi > 1 \)) we find:

\[
\lim_{R \to \infty} f(r) < 1 - \frac{1}{\xi} \quad \implies \quad r < \infty
\]

\[
\lim_{R \to \infty} f(r) = 1 - \frac{1}{\xi} \quad \implies \quad r = R_M \sim \sqrt{R} \to \infty
\]

\[
\lim_{R \to \infty} f(r) > 1 - \frac{1}{\xi} \quad \implies \quad r \sim R \to \infty
\]

\[
y(r) - y(r_0) = -2 \ln(r/r_0) + O(\ln \ln \frac{r}{r_0})
\]

Rod with charge parameter \( \xi = 1 \)

\[
\lim_{R \to \infty} \frac{n(R)}{n(r)} = \lim_{R \to \infty} \frac{1 + \gamma^2}{2\xi} = \frac{1}{2\xi} = \frac{P}{P_{ig}} = \hat{p}
\]
Condensation with added salt

Ion fraction $\rightarrow$ charge fraction

more salt $\rightarrow$ more screening

condensed layer contracts

$\xi = 2.1$

addition of salt causes an exchange of the relevant length scales: $R_M \rightarrow \ell_D$. The crossover can be quantified through the inflection point criterion. At $\ell_D \lesssim R_M$ condensation loses its meaning!

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Scheme of a typical computer simulation

\[ F = m \cdot a \]

- Electrostatics
- "Hard core"
- Periodic boundary conditions
- Langevin thermostat
- Friction
- Noise
- Development:
  - P⁴M-Algorithm
    (Mesh-Ewald)
  - Hexagonal cell
counterion condensation is stronger than in the Poisson-Boltzmann theory

product $\xi v$ no longer universal.

discrepancy increases with valence.

theoretical description through a local correction to the PB free energy functional possible.

Poisson-Boltzmann neglects correlations. These enhance counterion condensation, especially for multivalent counterions.
Overcharging in the presence of salt

\[ \xi = 4; \text{2:2-Salt}; \bar{n} = 2.1 \times 10^{-2} \sigma^{-3}. \]

the charge of the rods gets repeatedly over-compensated.

reversed charged layers.

charge oscillations are exponentially damped.

Poisson-Boltzmann fails qualitatively for strongly charged systems

better: integral equations, i.e. "hypernetted-chain" (HNC).
Entropic and Electrostatic Forces $F(\ell_B)$ on Two Rods

Parameter:

- $v = 3$
- $d_{\text{rod}} = 6\sigma$
- $d_{\text{surf}} = 2.5\sigma$
- $\lambda = 6.5e_0/\sigma$

PB theory gives always repulsion.

<table>
<thead>
<tr>
<th>$\ell_B/\sigma$</th>
<th>0.03</th>
<th>0.06</th>
<th>0.5</th>
<th>3</th>
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</thead>
<tbody>
<tr>
<td>Total Force</td>
<td></td>
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<td>Hardcore Force</td>
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<tr>
<td>Electrostatic Force</td>
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Graph showing the relationship between $\ell_B/\sigma$ and force components.
Validity of the Implicit Water Model- PMF

look at the NaCl (aq) pair potentials using an explicit water simulation containing 1000 SPC water molecules
Polyelectrolytes in poor solvents

Carbon backbone (oil) is poorly soluble in water!

Early cigar model (Khokhlov 1981)

Rayleigh instability (1882):
(charged oil drop)

\[ \frac{q^2}{4\pi\varepsilon R} = \gamma R^2 \]

pearl-necklace model

Kantor, Kardar - 1994: Polyampholyte

Dobrynin, Rubinstein, Obukhov - 1996: Polyelectrolytes
Mapping procedure for the Computer Model

Example: NaPSS
sulfonated polystyrene

\[ \varepsilon \]
beads with charge fraction \( f \)
nonlinear springs
dielectric background \( \varepsilon \)
effective bead–bead interaction

Monomers, ions
bond potential
solvent
solvent quality \( \tau \)

Mapping onto a bead–spring model
Varying $f$ and $f^2 \ell_B$ - validity of scaling
Relax and see the movie . . .
All newer simulation results were . . .

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