Polyelectrolytes

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Outline

1. Electrostatic interactions, counterion distribution
2. Dilute solutions – solvent quality
3. Semi-dilute solutions – chain conformations

What are polyelectrolytes?

Polyelectrolytes are polymers with ionizable groups.

**Common polyelectrolytes:**

Poly(styrene sulfonate)

![Chemical structure of poly(styrene sulfonate)](image1)

Poly(methacrylic acid)

![Chemical structure of poly(methacrylic acid)](image2)

Biopolymers – DNA

![Biopolymer structure](image3)
Terminology

**Polyelectrolytes** – chains with charged groups of the same sign (e.g. polystyrene sulfonate, polylysine)

![Polyanion and Polycation Diagram](image)

**Counterions** – small charges that dissociate from polyelectrolytes with the sign opposite to that of polyelectrolytes (e.g. Na\(^+\) for PSS)

Polyelectrolytes can be strong (constant charge) or weak (with pH-dependent charge) depending on the pKa of charged groups.

**Polyampholytes** – chains with charged groups of both signs (e.g. proteins).

In addition to polyelectrolytes (polyions) and counterions solution may contain small ions – salt (e.g. Na\(^+\), Cl\(^-\), Ca\(^{2+}\), H\(^+\))
Classes of Charged Systems

- Ionic solution (simple salt)
- Polyelectrolyte solution
- Solution of oppositely charged polyelectrolytes

Polyampholytes
- Random
- Block

Ionomers

Polyampholytes and ionomers are classes of charged systems based on their structure and charge distribution.
Basic Concepts

**Coulomb law** – electrostatic interaction energy in medium with dielectric constant $\varepsilon$

$$ U = \frac{q_1 q_2}{\varepsilon r} $$

**Interplay of electrostatic energy** $U$ and **thermal energy** $kT$ is the main theme of the course.

E.g. two elementary charges $q_1=q_2=e$ separated by $r=7\text{Å}$ in water (dielectric constant $\varepsilon=80$) interact with energy $U=kT$ (at room $T$)

**Bjerrum length** $l_B = \frac{e^2}{\varepsilon kT}$ is $7\text{Å}$ in water at room $T$.

For $r > l_B$ electrostatics between two elementary charges is weak and thermal energy wins. For $r < l_B$ electrostatics wins.

In non-polar medium $\varepsilon$ is smaller (e.g. $\varepsilon = 2$) and electrostatic interactions are much stronger. This prevents dissociation of charges. Most charges stay associated in dipoles and multipoles (e.g. **ionomers**).
Lecture 1

Small Ions

Simple Salt and Counterions
**Debye Length**

Consider a dissociated 1-1 salt solution with concentration $c_s$

$n_+ \sim c_s r^3$ is the average number of positive charges in volume $r^3$ with radius $r$

If electrostatics is not important – fluctuations of local charge concentrations are random ($n_+ \approx n_-$)

Net valence of this volume $|n_+ - n_-| \sim \sqrt{n_+}$

Electrostatic energy of this volume $U \approx \frac{e^2 (n_+ - n_-)^2}{\varepsilon r} \approx \frac{e^2 c_s r^3}{\varepsilon r} \approx \frac{e^2 c_s r^2}{\varepsilon}$

If this energy $U \approx kT$ concentration fluctuations become correlated

\[ r_D = \frac{1}{\sqrt{8\pi l_B c_s}} \]  E.g. $r_D = 1 \, \text{nm}$ in $0.1M$ solution and $r_D = 10 \, \text{nm}$ in $10^{-3} \, M$
Fluctuations on Length Scales Larger than Debye Length

On length scales larger than Debye length, neighboring Debye volumes have opposite charge (are correlated) leading to slower growth of net charge.

The energy of charge fluctuations on length scales larger than Debye length saturates at thermal energy $kT$. 
For $r > r_D$ electrostatics dominates and fluctuations of Debye volumes are correlated, leading to screening at Debye length.

Slightly more negative Debye volumes surround a positive probe charge, screening its field.

A second probe charge several $r_D$ away "feels" a significantly screened field of the first charge.

\[ U = \frac{q_1 q_2}{\varepsilon r} \exp \left( -\frac{r}{r_D} \right) \]

For $r >> r_D$ electrostatic interactions are completely screened.
For $r << r_D$ electrostatic interactions are pure Coulomb $U = q_1 q_2 / (\varepsilon r)$.

Electro-neutrality of screening volume is needed for complete (exponential) screening.

$r_D = 3 \text{ nm in } 10^{-2} \text{ M solution}$
and $r_D = 30 \text{ nm in } 10^{-4} \text{ M}$
Counterions

Solution is overall electroneutral.

In order for solutes (polymers, colloids, etc.) to be charged, oppositely charged counterions need to be dissolved in solution.

Electric field around charged objects controls the distribution of counterions.

Distribution of counterions depends on the symmetry of the field and is determined by the balance of electrostatic energy of counterions and the entropic part of their free energy.
Counterion Distribution

Plane-like charge

Electrostatic potential

\[ U \sim r \]

Entropy of free counterions \( S \sim \ln r \)

Energy wins: most counterions are bound and stay near charged surface within Gouy-Chapman length.

Line-like charge

Electrostatic potential

\[ U \sim \ln r \]

Balance depends on coefficient Onsager-Manning counterion condensation at high linear charge density.

Point-like charge

Electrostatic potential

\[ U \sim 1/r \]

Entropy wins: at low concentrations (large \( r \)) counterions unbind.
Counterions near Charged Plane

$\sigma$ – number of charges per unit area e.g. $\sigma = 1 \text{ nm}^{-2}$

$E_0 \approx e \sigma / \varepsilon$ – electric field due to charged plane

$V = E z \approx z e \sigma / \varepsilon$ – electrostatic potential near charged plane

Electrostatic attraction of a counterion to the plane $U = eV$ is on the order of thermal energy $kT$ at Gouy-Chapman length $\lambda$.

$\lambda e^2 \sigma / \varepsilon \approx kT \quad \lambda \approx 1 / (l_B \sigma)$ for $\sigma = 0.1 \text{ nm}^{-2}$ $\lambda = 2.3 \text{ nm}$

To screen part of surface charge $\sigma$ within $\lambda$

counterion concentration near the plane ($z < \lambda$) is $c_0 \lambda \approx \sigma$

$c_0 \approx \sigma / \lambda \approx \sigma^2 l_B \approx 1 / (l_B \lambda^2)$

Relation between Gouy-Chapman length and $c_0$

$\lambda \approx 1 / \sqrt{l_B c_0}$

is the same as between Debye length and $c_s$

$r_D \approx 1 / \sqrt{l_B c_s}$

At high salt concentrations ($c_s > c_0$) surface is screened by salt ($r_D < \lambda$).

At low salt concentrations ($c_s < c_0$) it is screened by counterions ($r_D > \lambda$).
**PFH: Self – Similar Solution**

Field is screened by counterions on all length scales $\geq \lambda$.

Screening length at distance $z > \lambda$ from the surface is $

\lambda

Counterion concentration $c(z) \approx 1/(l_B z^2)$

ear the surface $c \approx c_0 \approx 1/(l_B \lambda^2)$, $z < \lambda$

At all distances $c = \frac{1}{l_B (\lambda + z)^2} = c_0 \left( \frac{\lambda}{z + \lambda} \right)^2$

Electric field $E = \frac{e \sigma_{\text{eff}}}{\varepsilon} = \frac{e}{\varepsilon} \left( \sigma - \int_0^z c(z')dz' \right) = E_0 \frac{\lambda}{z + \lambda}$

Far from the plane ($z > \lambda$) distribution of counterions $c \approx 1/(l_B z^2)$

and electric field $E \approx e/(\varepsilon l_B z)$ is independent of the surface charge $\sigma$

Effective charge density “seen” from distance $z$ is $\sigma_{\text{eff}} \approx 1/(l_B (z+\lambda)) \sim E(z)$
Gouy-Chapman Distribution of Counterions

\[ \lambda = \frac{1}{2\pi l_B \sigma} \]

Near the plane \((z < \lambda)\)

\[ E \approx E_0 \approx \frac{e \sigma}{\varepsilon} \]

For \(\sigma = 1 \text{ nm}^2\), \(E_0 = 2 \times 10^7 \text{ V/cm}\)

Half of counterions are within G-C layer.

**Counterion concentration**

\[ c = c_0 \left( \frac{\lambda}{z + \lambda} \right)^2 \]

**Electric field.**

\[ E = E_0 \frac{\lambda}{z + \lambda} \]

Electrostatic potential increases logarithmically

\[ V = \int E dz = \frac{e}{l_B \varepsilon} \ln(1 + z / \lambda) \]

due to balance of energy \(eV\) and entropy \(k \ln z\) of counterions.
Counterion Distribution near the Surface

Assumption – no correlations between counterion positions.

Average distance between counterions at concentration $c_0$

$$r \approx c_0^{-1/3} \approx \sigma^{-2/3} l_B^{-1/3}$$

has to be larger than $l_B$ and smaller than $\lambda$.

$$r \gtrsim l_B \quad \text{and} \quad r \lesssim \lambda$$

$$\sigma < \frac{1}{l_B^2}$$

For counterions with valence $q$ this condition is

$$\sigma < \sigma_{WC} \approx \frac{1}{(l_B^2 q^3)}$$

Therefore multivalent counterions adsorb onto a charged plane with $\sigma > \sigma_{WC}$, forming strongly correlated “Wigner liquid”.

charged surface

Wigner lattice

multivalent counterions
Onsager-Manning Counterion Condensation

$\Gamma$ – number of charges per unit length  
  e.g. $\Gamma = 4 \text{ nm}^{-1}$

$E_0 \approx e\Gamma/(\varepsilon r)$ – electric field due to charged cylinder

Electrostatic potential around a charged cylinder

$$V = -\int_{r_0}^{r} E(r')dr' \approx -(e\Gamma/\varepsilon)\ln(r/r_0)$$

Entropic part of free energy of a counterion localized within a cylinder of radius $r$ is $\sim kT\ln r$.

Electrostatic energy $eV$ is balanced by $kT\ln r$ for all $r>r_0$ at $\Gamma_{OM} = kT\varepsilon/e^2 = 1/l_B$ – one charge per Bjerrum length.

If electrostatic energy $eV$ is higher than $kT\ln r$ if ($\Gamma > \Gamma_{OM}$) entropy cannot stabilize attraction at any $r>r_0$.

Counterions condense onto polyion reducing its charge density to the “universal” value $\Gamma_{OM}$. 
Effective charge of the particle $Q_{\text{eff}}$
(or polymer as observed from distance $r>R$)

$V = \frac{Q_{\text{eff}}}{\varepsilon R}$ – potential at $r \sim R$
(work to move a counterion from surface to distance $r$)

$e\frac{Q_{\text{eff}}}{\varepsilon R} \approx kT$ – up to logarithmic ($\ln c$) corrections

$Q_{\text{eff}} \approx e \frac{R}{l_B}$ – similar to Manning $Q_{\text{eff}}/(eR) \approx 1/l_B$

E.g. for $R=35$ nm effective charge of a particle is $Q_{\text{eff}} \approx 50e$

In order to significantly increase particle charge one needs to exponentially dilute particles (or add salt).
Two-Zone Model of Dilute Polyelectrolyte Solutions

Deshkovski et al ‘01

\[ \gamma_0 = \Gamma_0 l_B \]

\[ \gamma_R = \Gamma_R l_B \]

\( \gamma_0 \) – dimensionless linear charge density along the macroion

= number of charges per Bjerrum length

\( l_B = \frac{e^2}{\varepsilon kT} \)

\( \gamma_R \) – dimensionless linear charge density of the cylindrical zone at \( R = L/2 \)

Cylindrically-symmetric zone near polyion

Some counterions escape into the outer zone far from polyion.

Cylindrical zone has net charge (not electro-neutral).
Counterions leave cylindrical zone upon dilution increasing $\gamma_R$

I. Polyion charge density $\gamma_0$ is too low to localize counterions.

II. Polyion charge density $\gamma_0$ is high. Counterions condense to reduce electrostatic energy.

III. Entropy wins at very low concentrations and counterions leave polyions (even those with high $\gamma_0$).

There are phase transitions between different regimes.
Counterions distribution in the cylindrical zone $c(r) \sim r^{-2\gamma_0}$ is dominated by the outer regions ($\gamma_0 < 1$).

Changes of $\gamma_R$ only change the prefactor of $c(r) \sim r^{-2\gamma_0}$, $\gamma_{R_1} < \gamma_{R_2} < \gamma_{R_3}$.

MD of 16 rod-like polymers with $N=97$ and $l_B=3\sigma$.

$I. Weakly Charged Polyions$

$\gamma_0=0.5$

Liao et al '03
II. Saturated Condensation

Counterions are distributed self-similarly throughout the whole cylindrical zone.

Effective charge density of a polyion together with condensed counterions is constant.

Two-zone model predicts $c(r) \sim r^{-2}$

Onsager-Manning condensation

Liao et al ‘03
III. Unsaturated Condensation

At $\gamma_R = 1$ there is a transition to the unsaturated condensation regime with polyion starving for more counterions.

Two-zone model predicts $c(r) \sim r^{-2\gamma_R}$

$Liao$ et al ‘03

$\gamma_{R_1} < \gamma_{R_2} < 1 < \gamma_{R_3}$

$L_0 = 1.5$

$-2.36 \pm 0.06$
Challenge Problem
Particle with a crew-cut polyelectrolyte layer

Particle $R = 70 \text{ nm}$
150 chains 40K PSS
$L = 20 \text{ nm} - \text{chain length}$
$N = 200 \text{ monomers}$
(each charged)

Estimate:
(i) bare particle charge $Q_{\text{bare}}$;

(ii) uncondensed charge $Q_{\text{manning}}$;

(iii) effective surface charge $Q_{\text{surf}}$ of crew-cut layer of thickness $L$;

(iv) effective particle charge as seen from $r > 2R$

Assume salt concentration $c_s \sim 10^{-6} \text{ M}$ and particle concentration $\sim \mu \text{m}^{-3}$
Bjerrum length – determines electrostatic interaction strength between monovalent ions

\[ l_B = \frac{e^2}{(\varepsilon k T)} \approx 7 \text{ Å} \]

Debye length – determines screening of electrostatic interactions due to salt

\[ r_D = \frac{3 \text{ Å}}{[c_s]^{1/2}} \]

Note that multivalent ions lead to stronger screening

\[ r_D^{-2} = 4\pi l_B(q^2c_+ + q^{-2}c_-) \]

Gouy-Chapman length – determines counterion distribution at charged surface

\[ \lambda = \frac{1}{2\pi l_B \sigma} \]

Onsager-Manning condensation – linear charge density is reduced to one charge per Bjerrum length \( l_B \) by condensed counterions

General rule for charged objects – effective charge is \( eR/l_B \) (if \( R < r_D \)) up to \( ln c \) corrections