Polyelectrolytes

Michael Rubinstein (UNC-CH)

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Outline

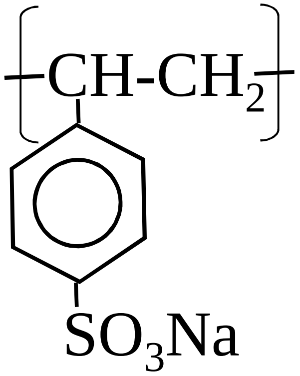
1. Electrostatic interactions, counterion distribution
2. Dilute solutions – solvent quality
3. Semi-dilute solutions – chain conformations

What are polyelectrolytes?

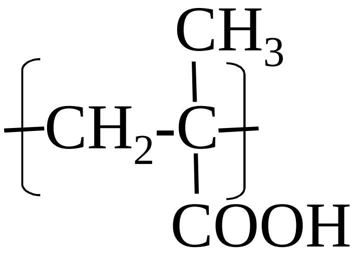
Polyelectrolytes are polymers with ionizable groups.

Common polyelectrolytes:

Poly(styrene sulfonate)

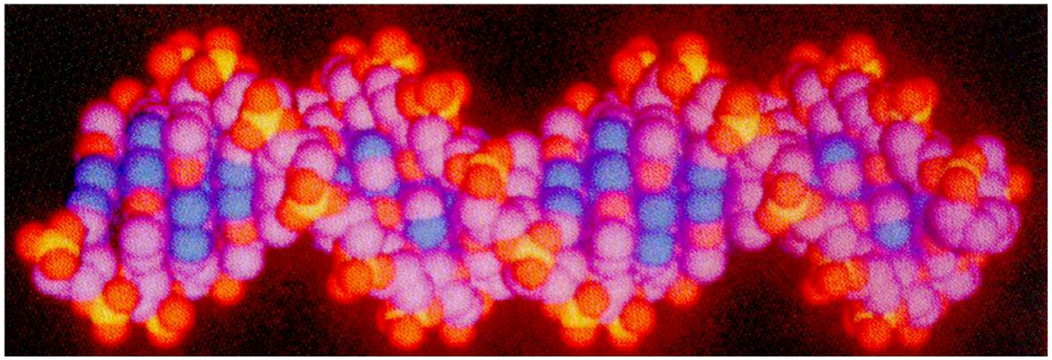


Poly(methacrylic acid)



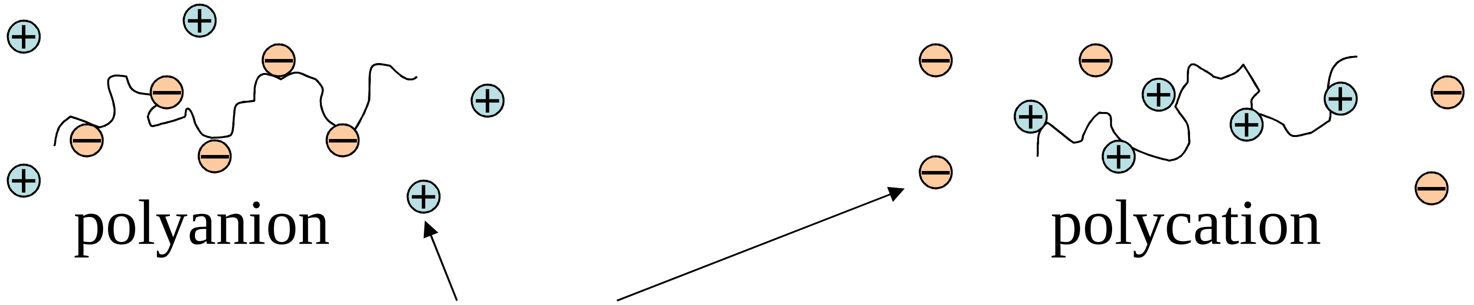
$$\left[CH_2-\overset{CH_3}{\underset{COOH}{C}} \right]$$

Biopolymers – DNA



Terminology

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

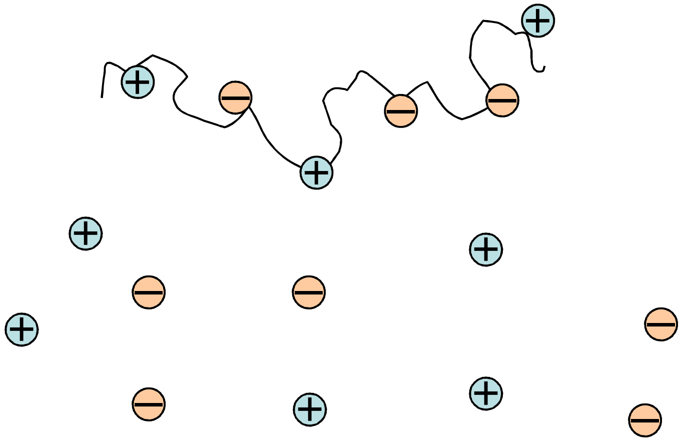


Counterions –small charges that dissociate from polyelectrolytes with the sign opposite to that of polyelectrolytes (e.g. Na^+ for PSS)

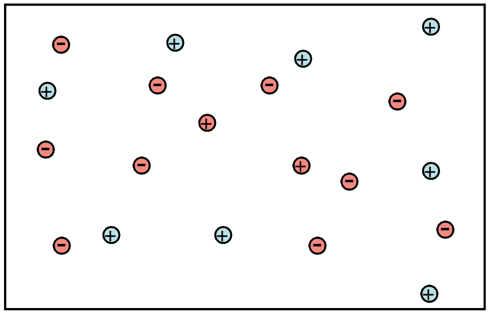
Polyelectrolytes can be strong (constant charge) or weak (with pH-dependent charge) depending on the pKa of charged groups.

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

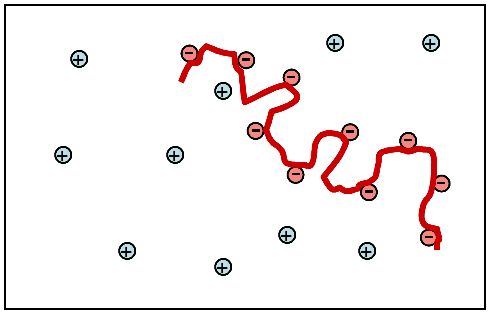
In addition to polyelectrolytes (polyions) and counterions solution may contain small ions – salt (e.g. Na^+, Cl^-, Ca^{2+}, H^+)



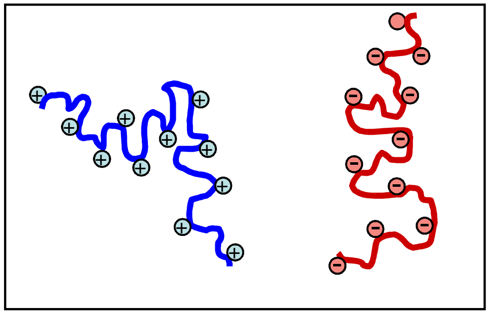
Classes of Charged Systems



ionic solution
(simple salt)

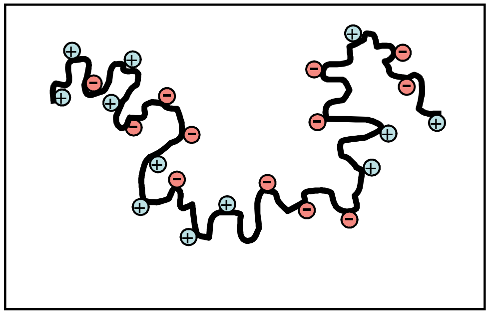


polyelectrolyte
solution

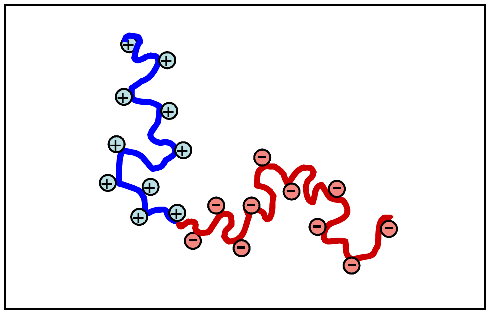


solution of
oppositely charged
polyelectrolytes

Polyampholytes

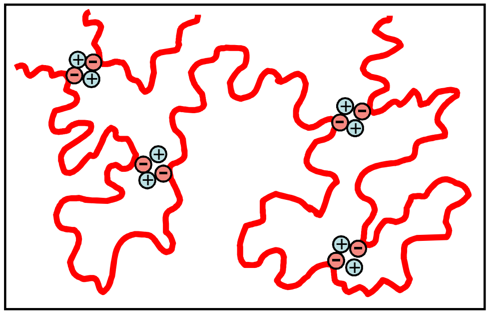


random



block

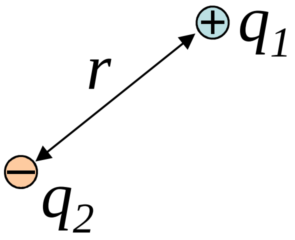
Ionomers



Basic Concepts

Coulomb law – electrostatic interaction energy in medium with dielectric constant ε

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



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 $r=7Å$ in water (dielectric constant $\varepsilon=80$) interact with energy $U=kT$ (at room T)

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

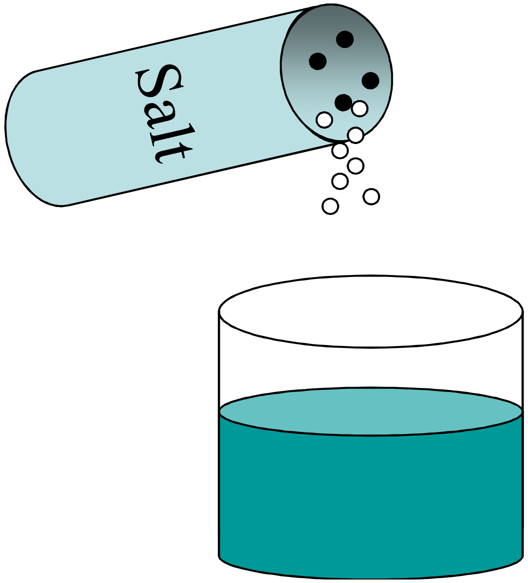
For $r > l_B$ electrostatics between two elementary charges is weak and thermal energy wins. For $r < l_B$ electrostatics wins.

In non-polar medium ε 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

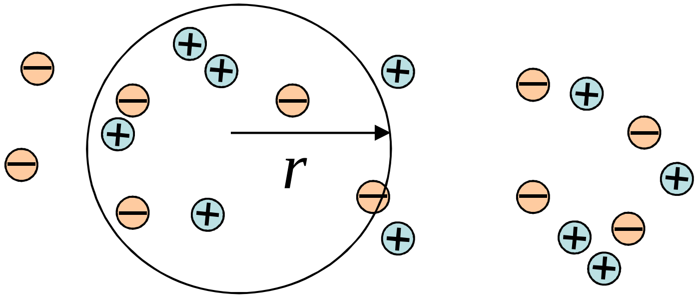
Simple Salt
and
Counterions



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

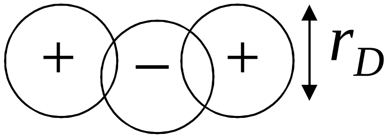


If electrostatics is not important –
fluctuations of local charge concentrations are random ($n_+ \approx n_-$)

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

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

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



Debye length

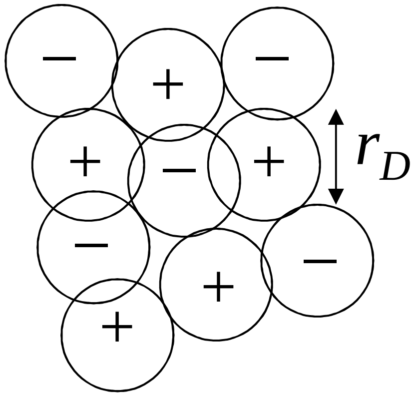
$$\frac{e^2 c_s r_D^2}{\varepsilon} \approx kT \longrightarrow l_B r_D^2 c_s \approx 1 \longrightarrow r_D \approx \frac{1}{\sqrt{l_B c_s}}$$

$$r_D = \frac{1}{\sqrt{8\pi l_B c_s}}$$

E.g. $r_D = 1\ nm$ in $0.1M$ solution and $r_D = 10\ nm$ in $10^{-3}\ M$

Fluctuations on Length Scales Larger than Debye Length

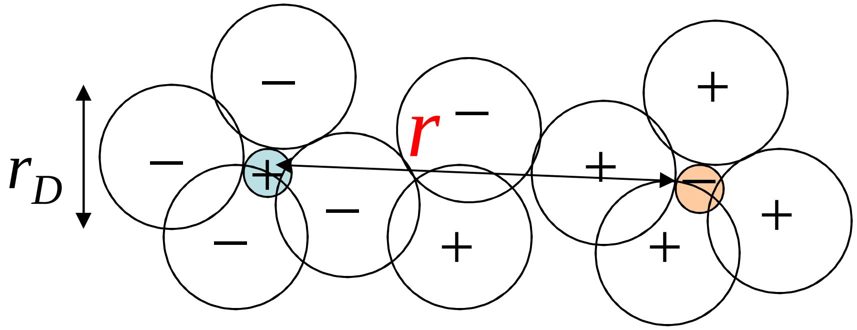
On length scales larger than Debye length
neighboring Debye volumes
have opposite charge (are correlated)
leading to slower growth of net charge



The energy of charge fluctuations
on length scales larger than Debye length
saturates at thermal energy kT.

Electrostatic Screening

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.

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

Counterions

Solution is overall electroneutral.

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

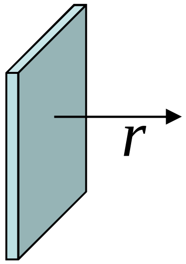
Electric field around charged objects controls the distribution of counterions.

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

Entropy of free counterions $S \sim \ln r$

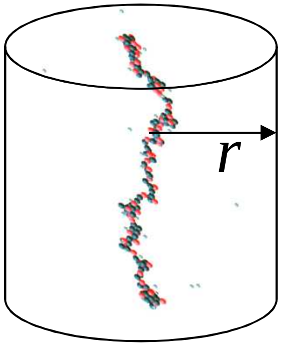


Electrostatic potential

$U \sim r$

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

Line-like charge

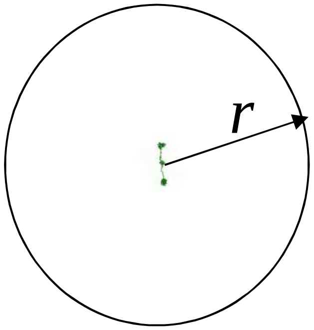


Electrostatic potential

$U \sim \ln r$

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

Point-like charge

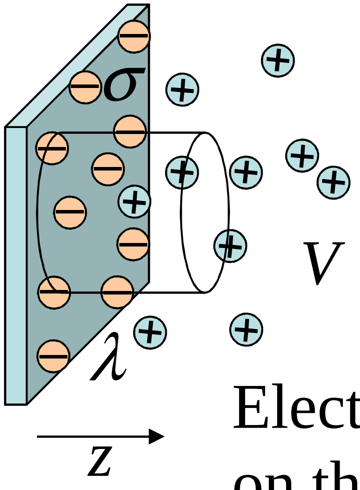


Electrostatic potential

$U \sim 1/r$

Entropy wins: at low concentrations (large r) counterions unbind.

Counterions near Charged Plane



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

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

$V = Ez \approx ze\sigma/\varepsilon$ – 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 λ.

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

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

To screen part of surface charge σ within λ counterion concentration near the plane ($z < \lambda$) is $c_0\lambda \approx \sigma$

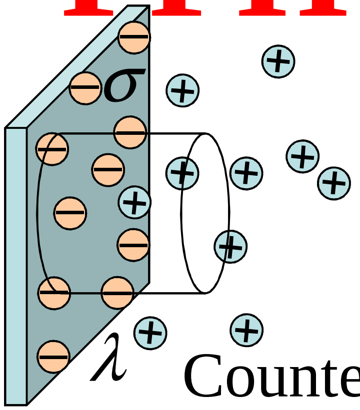
Relation between Gouy-Chapman length and c_0 is the same as between Debye length and c_s

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

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

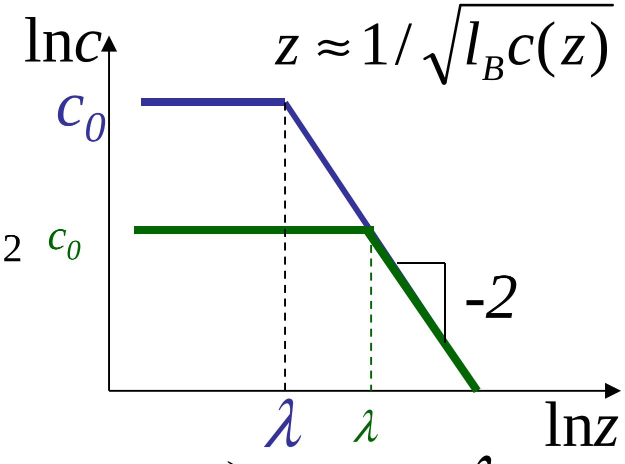
At high salt concentrations ($c_s > c_0$) surface is screened by salt ($r_D < \lambda$).
At low salt concentrations ($c_s < c_0$) it is screened by counterions ($r_D > \lambda$).

PFH: Self – Similar Solution



Field is screened by counterions on all length scales ≥ λ

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

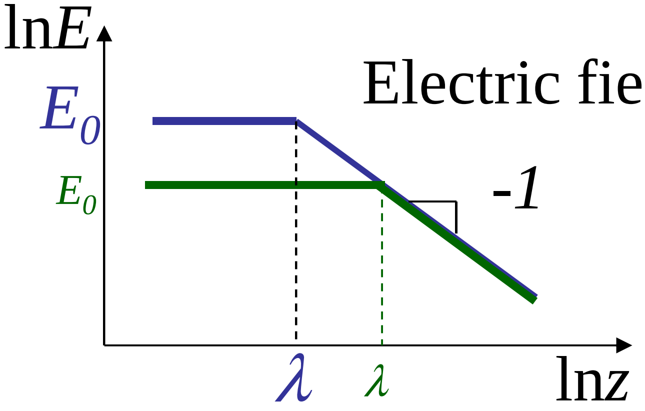


$$z \approx 1/\sqrt{l_B c(z)}$$

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

near the surface $c \approx c_0 \approx 1/\left(l_B \lambda^2\right) \quad z < \lambda$

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



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

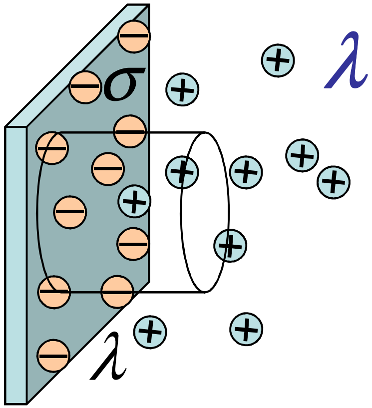
Far from the plane ($z > \lambda$)

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 σ

Effective charge density “seen” from distance z is $\sigma_{eff} \approx 1/(l_B(z+\lambda)) \sim E(z)$

Gouy-Chapman Distribution of Counterions



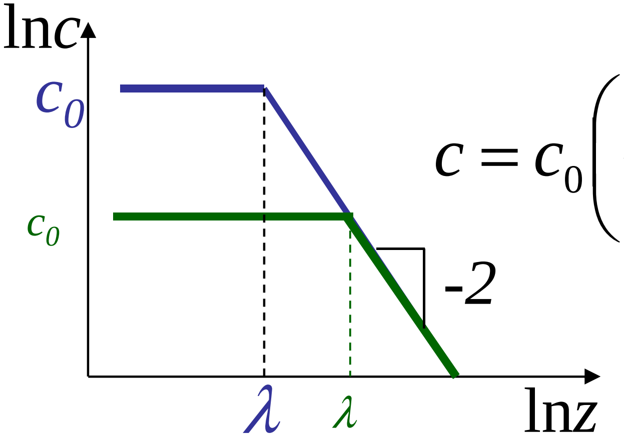
$\lambda = 1/(2\pi l_B \sigma)$

Near the plane ($z < \lambda$) $E \approx E_0 \approx e\sigma/\varepsilon$

For $\sigma = 1\ nm^{-2}$ $E_0 = 2\times 10^7\ V/cm$

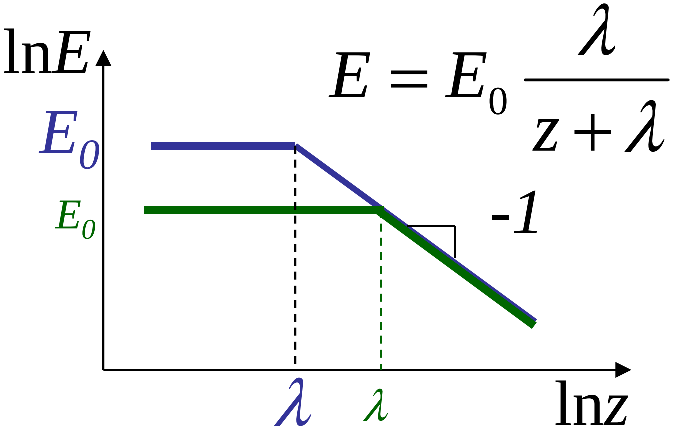
Half of counterions are within G-C layer.

Counterion concentration



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

Electric field.



$$E = E_0\frac{\lambda}{z+\lambda}$$

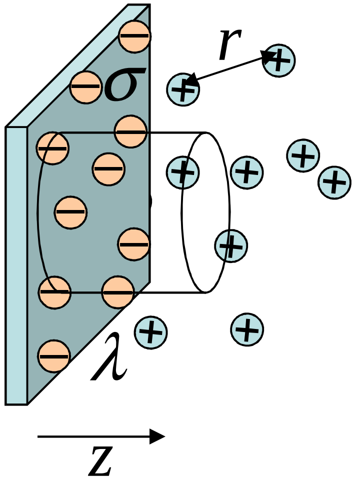
Electrostatic potential increases logarithmically

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

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 λ.

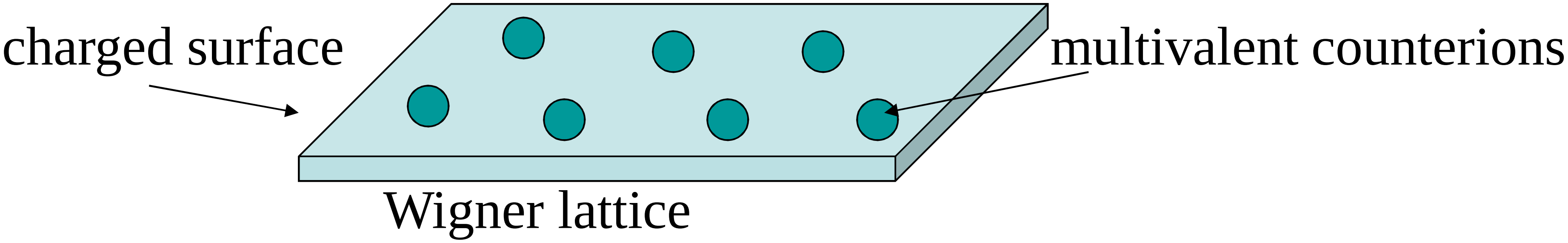
$r > l_B$ →

$r < \lambda$ →

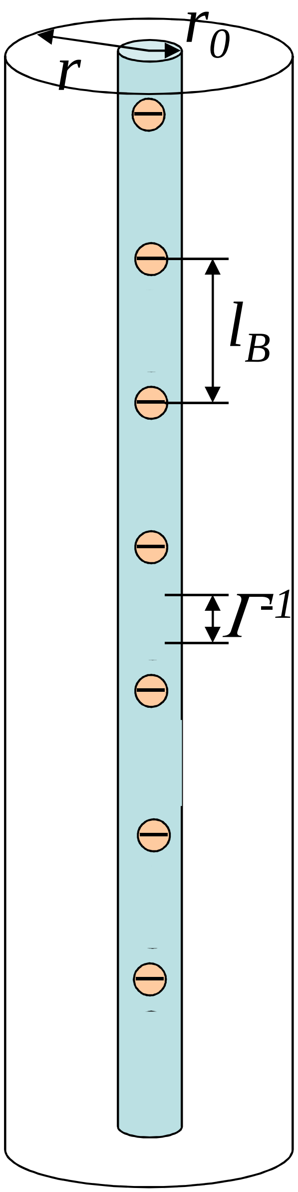
$\sigma < 1/l_B^2$

For counterions with valence q this condition is $\sigma < \sigma_{WC} \approx 1/(l_B^2 q^3)$

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



Onsager-Manning Counterion Condensation



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

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

Electrostatic potential around a charged cylinder

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

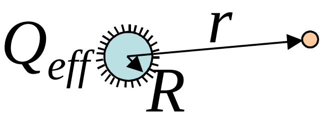
Entropic part of free energy of a counterion localized within a cylinder of radius r is $\sim kT\,lnr$.

Electrostatic energy eV is balanced by $kT\,lnr$ 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 $kT\,lnr$ 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 Γ_{OM}.

Spherical Regime – Poor Man's Version



Effective charge of the particle Q_{eff}

(or polymer as observed from distance $r>R$)

$V = Q_{eff}/(\varepsilon R)$ – potential at $r \sim R$

(work to move a counterion from surface to distance r)

$eQ_{eff}/(\varepsilon R) \approx kT$ – up to logarithmic ($ln\ c$) corrections

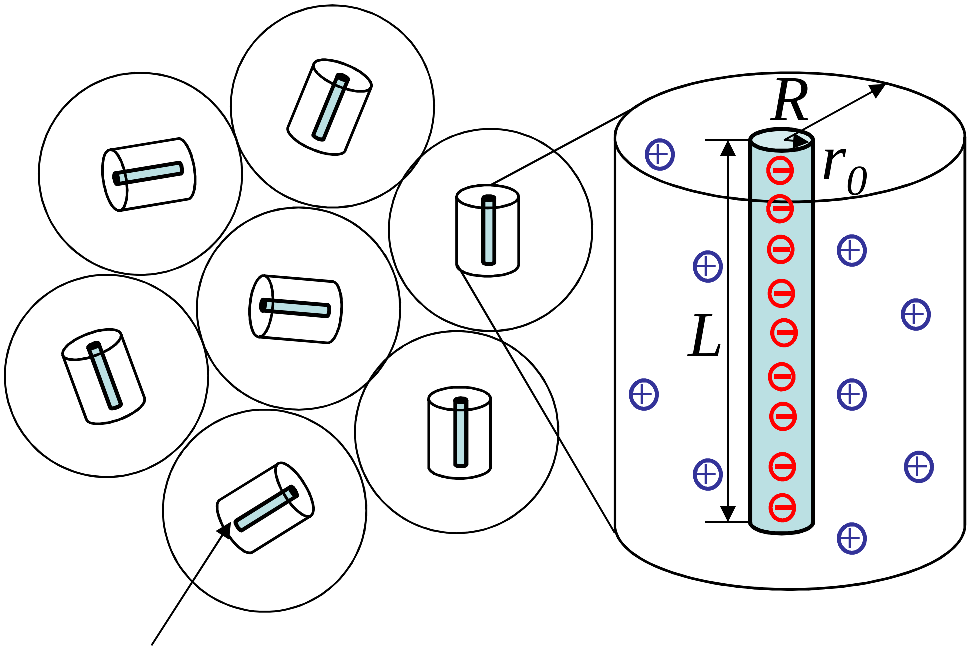
$\mathbf{Q_{eff} \approx e\ R/l_B}$ –similar to Manning $Q_{eff}/(eR) \approx 1/l_B$

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

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



γ_0 – dimensionless linear charge density along the macroion = number of charges per Bjerrum length $l_B = e^2/(\varepsilon kT)$

$$\gamma_0 = \Gamma_0 \, l_B$$

Γ_0 – number of charges per unit length

Cylindrically-symmetric zone near polyion

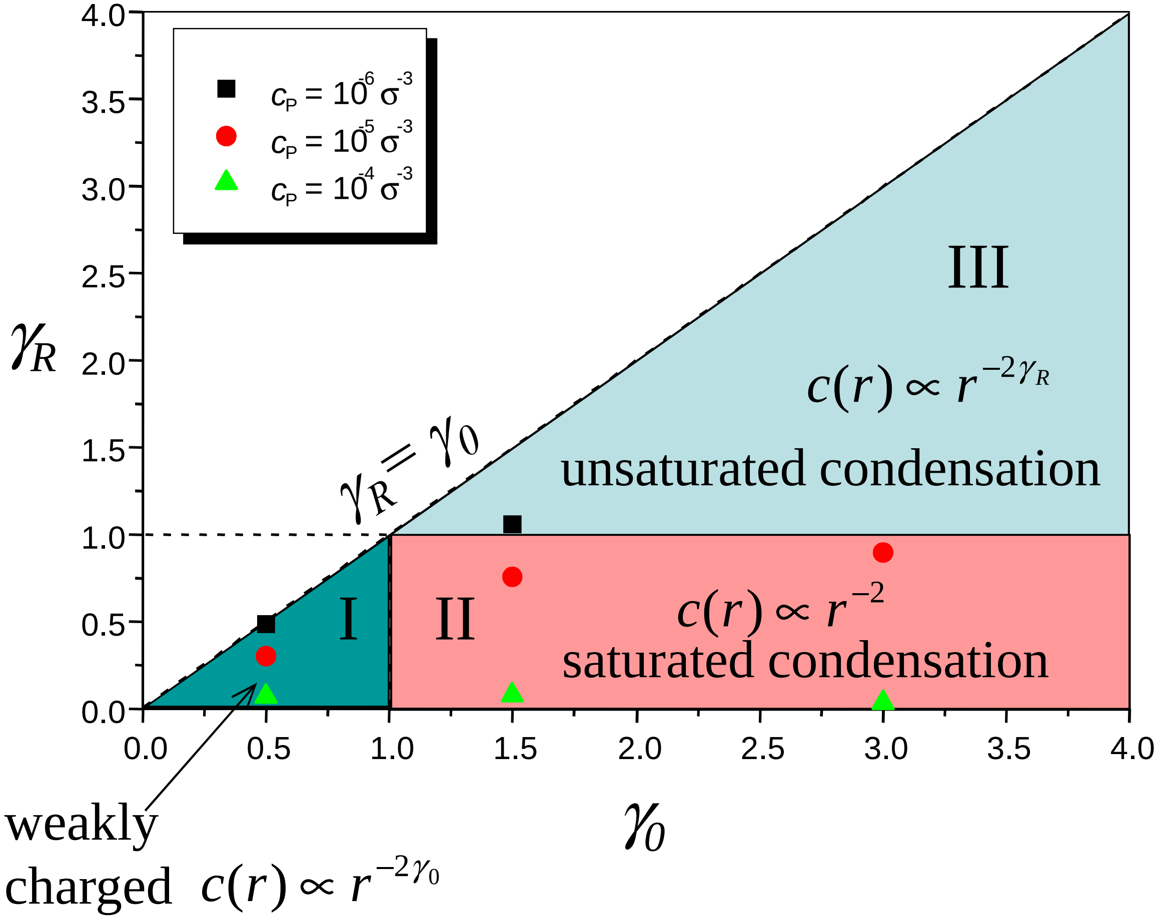
Some counterions escape into the outer zone far from polyion.

Cylindrical zone has net charge (not electro-neutral).

γ_R – dimensionless linear charge density of the cylindrical zone at $R=L/2$

$$\gamma_R = \Gamma_R \, l_B$$

Diagram of Phases



Deshkovski et al ‘01

Counterions leave cylindrical zone upon dilution increasing γ_R

I. Polyion charge density γ_0 is too low to localize counterions.

II. Polyion charge density γ_0 is high. Counterions condense to reduce electrostatic energy.

III. Entropy wins at very low concentrations and counterions leave polyions (even those with high γ_0).

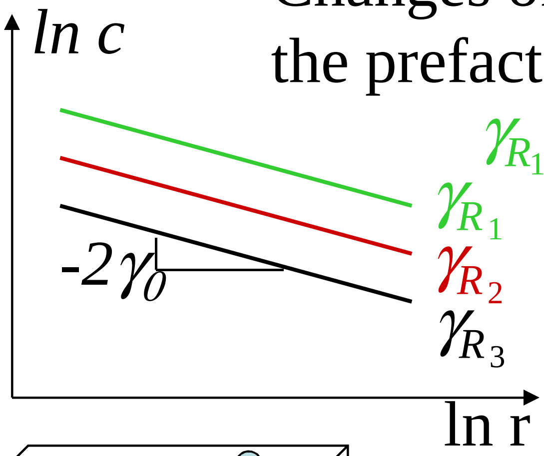
There are phase transitions between different regimes.

I. Weakly Charged Polyions

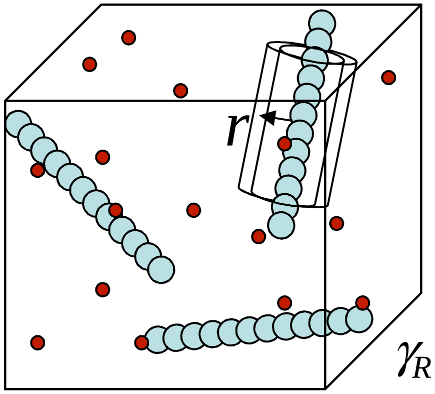
Counterions distribution in the cylindrical zone $c(r) \sim r^{-2\gamma_0}$ is dominated by the outer regions ($\gamma_0<1$).

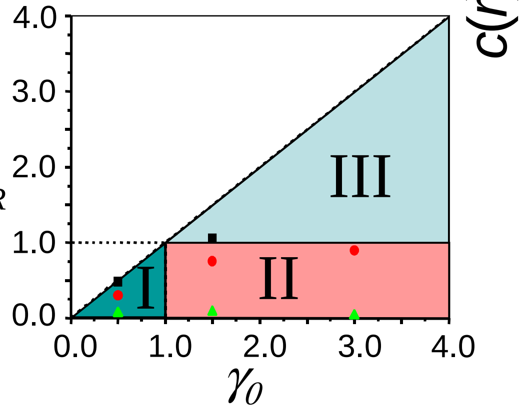
Changes of γ_R only change the prefactor of $c(r) \sim r^{-2\gamma_0}$

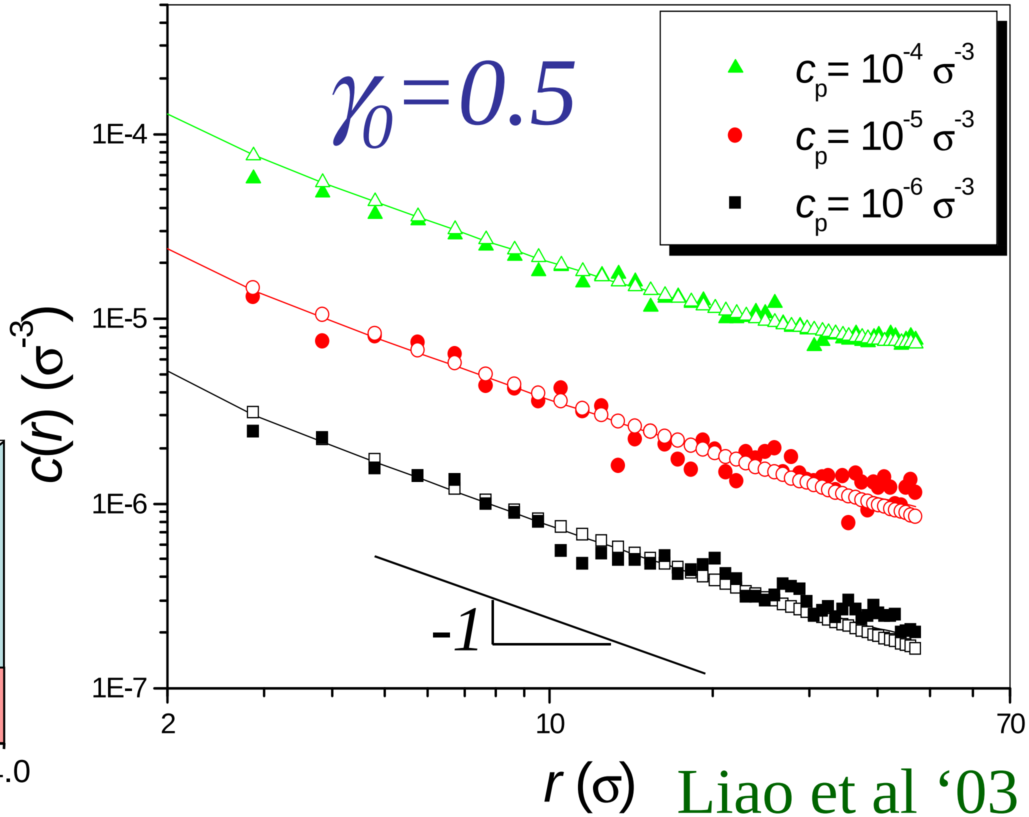
$\gamma_{R_1} < \gamma_{R_2} < \gamma_{R_3}$



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







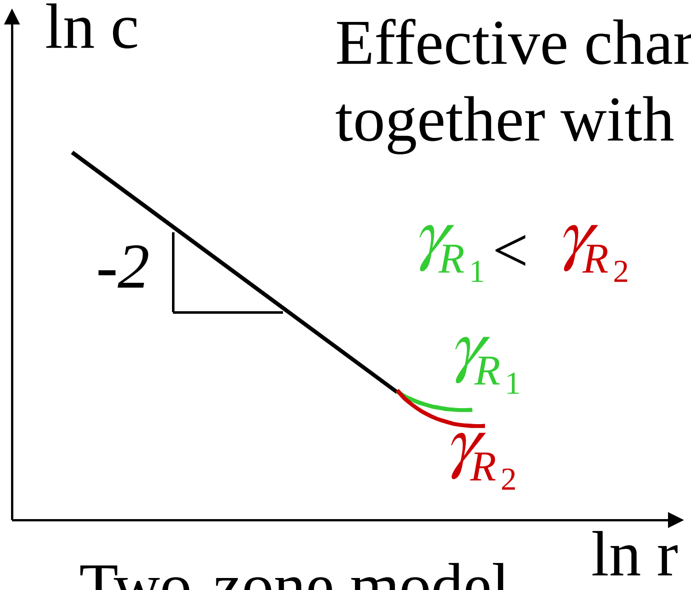
Liao et al ‘03

II. Saturated Condensation

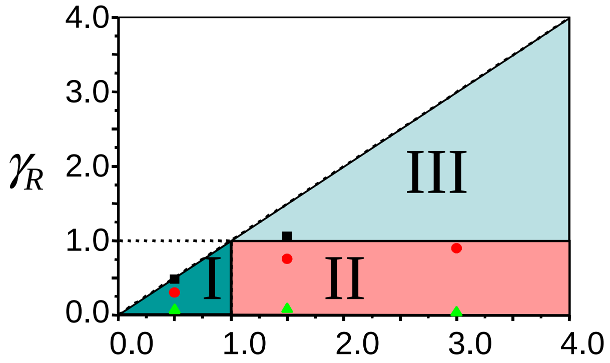
Counterions are distributed self-similarly throughout the whole cylindrical zone.

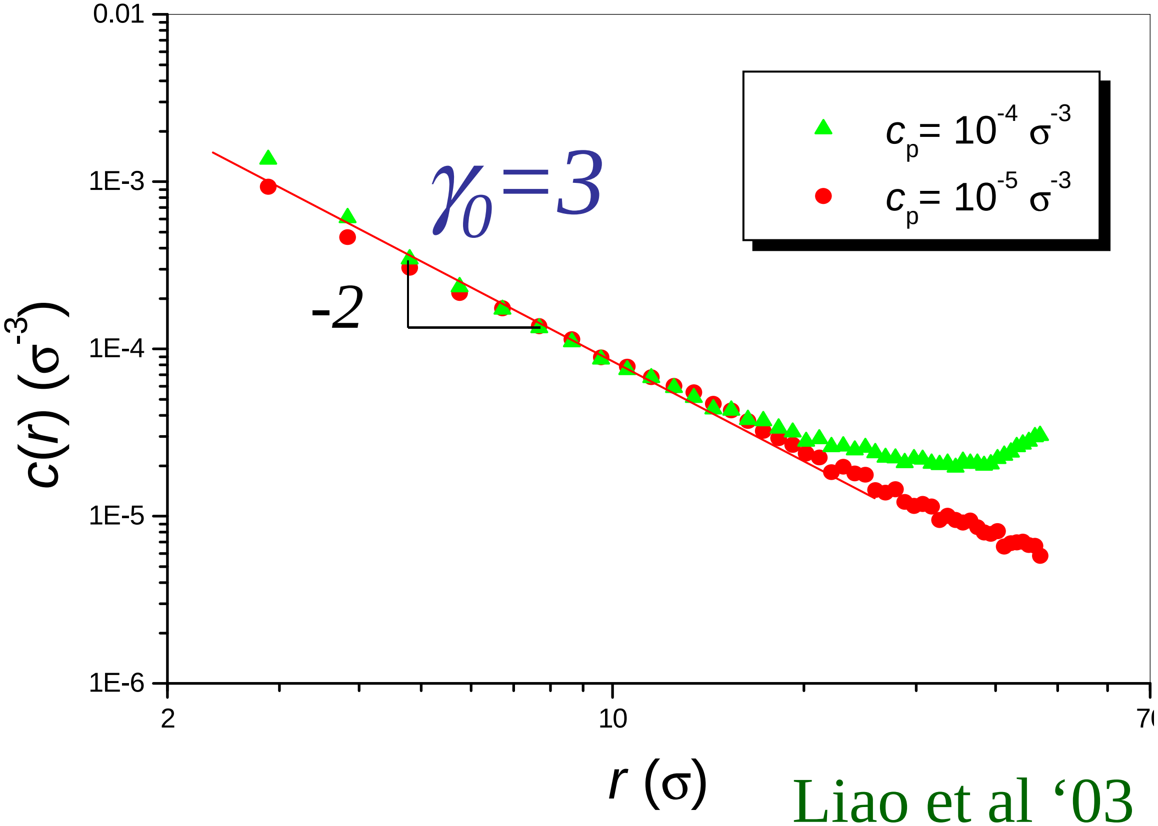
Onsager-Manning condensation

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



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

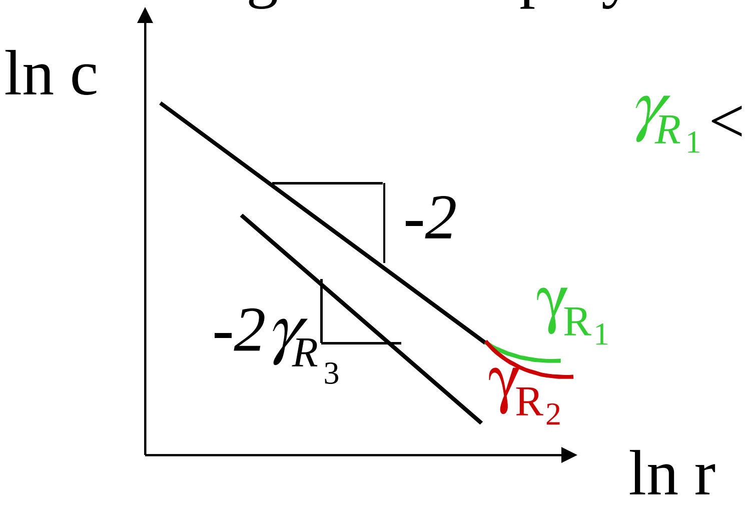




Liao et al ‘03

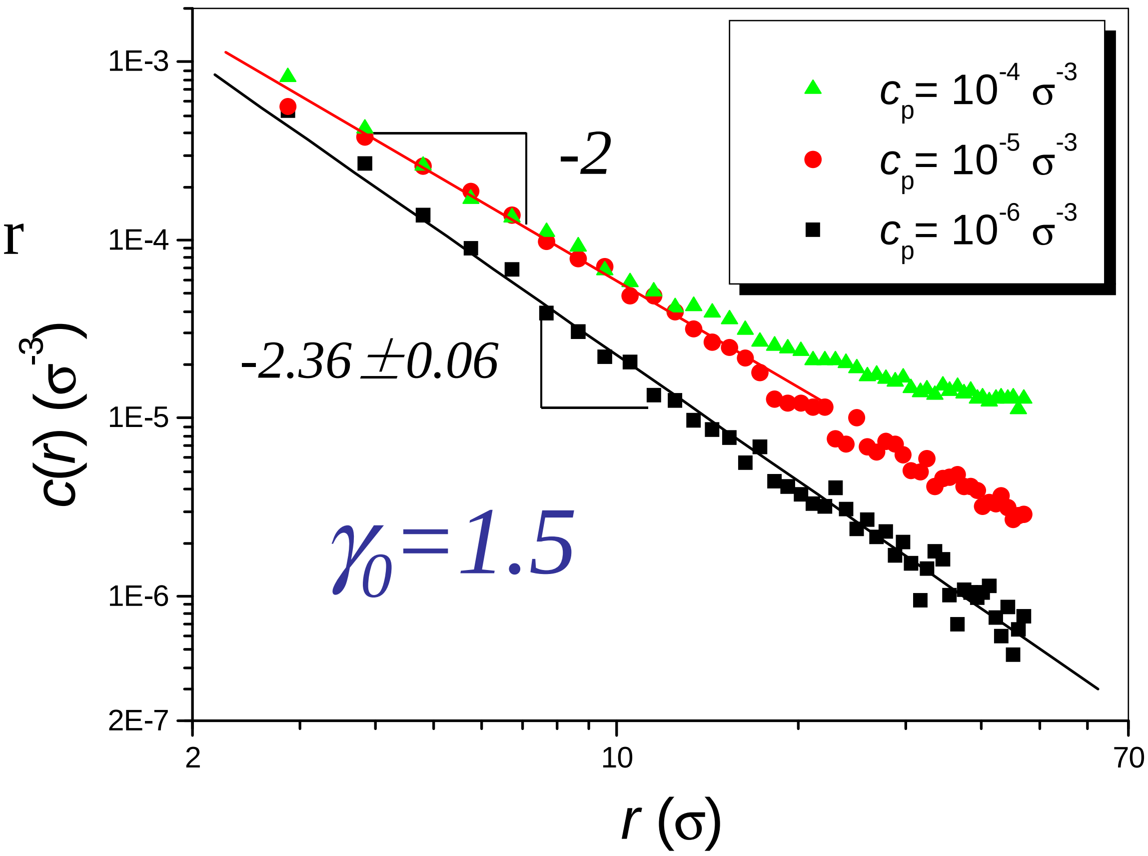
III. Unsaturated Condensation

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

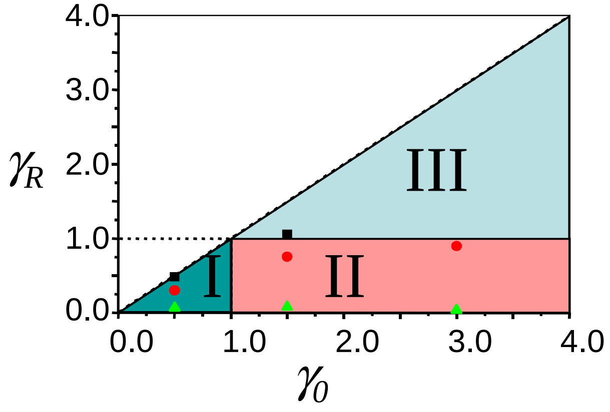


$\gamma_{R_1} < \gamma_{R_2} < 1 < \gamma_{R_3}$

Liao et al '03

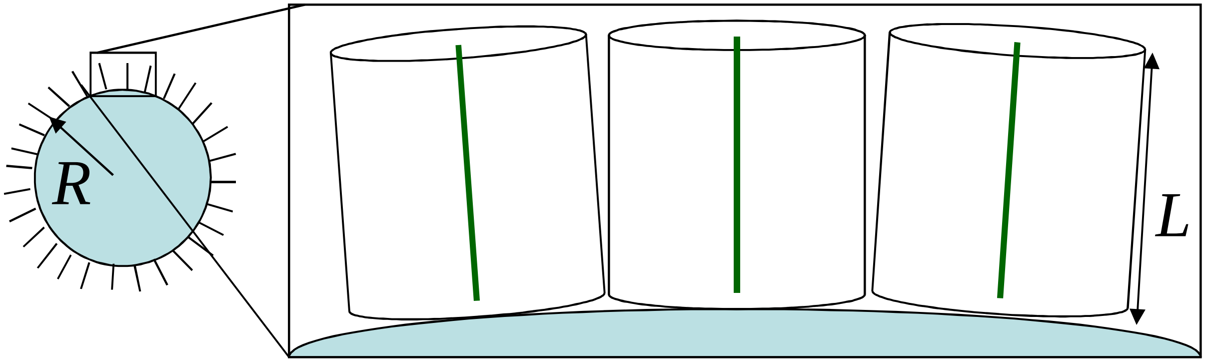


Two-zone model predicts $c(r) \sim r^{-2\gamma_R}$



Challenge Problem

Particle with a crew-cut polyelectrolyte layer



Particle $R = 70\ nm$

150 chains 40K PSS

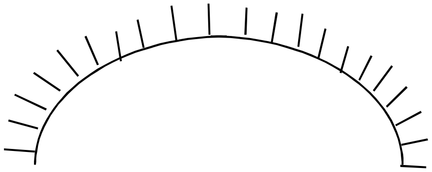
L = 20 nm – chain length

N = 200 monomers
(each charged)

Estimate:

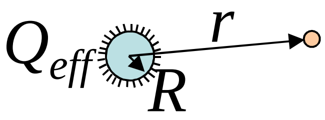
(i) bare particle charge Q_{bare};

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



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

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



Assume salt concentration $c_s \sim 10^{-6}\ M$ and particle concentration $\sim \mu m^{-3}$

Lecture 1 - Things to Remember

Bjerrum length – determines electrostatic interaction strength between monovalent ions $l_B = e^2/(\varepsilon kT) \approx 7\ \text{Å}$

Debye length – determines screening of electrostatic interactions due to salt $r_D = 3\ \text{Å}/[c_s]^{1/2}$

Note that multivalent ions lead to stronger screening

$$r_D^{-2} = 4\pi l_B(q_+^2 c_+ + q_-^2 c_-)$$

Gouy-Chapman length – determines counterion distribution at charged surface $\lambda = 1/(2\pi l_B \sigma)$

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