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Polyelectrolyte Theory:

1.1. Intro

- difficult to apply scaling or RG theories since there is no clear separation of length scales. Many scales are simultaneously present

size of polymer	R
correlation length	ξ
persistence length	L_p
Debye length (electrostatic screening length)	λ_D
Bjerrum length	l_B

Details of local chain structure are important and can control counterion condensation an. effect that happens for strong electrostatic chain & counterion interactions.

Especially the appearance of "counterions" (to counterbalance the charges on the chain backbone) is a new entity not present in neutral polymer solutions, and the possibility to

- change the degree of dissociation with pH
- change the strength of electrostatic interactions by changing the background salt concentration or the solution ϵ_r (relative dielectric const)

Qualitative Difference of PEs to uncharged polymers

- ① The crossover from dilute to semi-dilute solution regimes occur at much lower polymer concentrations (PE's are stretched)
- ② There is a well-pronounced peak in $S(q)$ for homogeneous PE solutions ($\sim \xi$)

the wave vector corresponding to increases with $c^{1/2}$
- ③ the osmotic pressure of PEs in salt-free solution exceeds the osmotic pressure of neutral polymers by several orders of magnitude.

\Rightarrow osmotic pressure $\sim c$, result of counterion contribution (ideal gas approximation)
- ④ The viscosity η of PE solutions goes like

$$\eta \sim c^{1/2} \text{ (Fuoss law)} \quad (\eta \sim c \text{ for uncharged polymers})$$
- ⑤ PEs in the semi-dilute regime follow unentangled dynamics in a much wider concentration range

1.2. Flory theory

Minimization of the free energy of a single chain (infinite dilution limit).

For a chain with N monomers

$$H = H_0 + \frac{1}{2} k_B T \sum_{k=1}^N \sum_{j \neq i} \frac{l_B z_i z_j}{|\vec{r}_i - \vec{r}_j|} \quad (1.2.1)$$

Free energy of neutral chain (Gaussian model)

$$H_0 = \frac{3 k_B T}{2 b^2} \sum_{i=1}^{N-1} (\vec{r}_i - \vec{r}_{i+1})^2, \quad b: \text{monomer size}$$

$$R_0^2 = N b^2 \quad (\text{Gaussian chain extension})$$

The Flory energy for a chain of size R is

ignoring prefactor of $\mathcal{O}(\text{unity})$

$$E_{\text{Flory}} = k_B T \left(\frac{R^2}{N b^2} + \frac{(N f)^2 l_B}{R} \right) \quad (1.2.2)$$

f : fraction of charged monomers $\rightarrow N f \approx Q$ total charge of the chain

$$\frac{\partial E_{\text{Flory}}}{\partial R} = 0 = k_B T \left(\frac{2R}{N b^2} - \frac{(N f)^2 l_B}{R^2} \right)$$

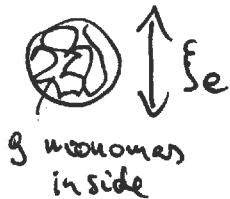
$$\hookrightarrow R^3 = \frac{(N f)^2 \cdot N b^2 \cdot l_B}{2}$$

$$(1.2.3) \quad \hookrightarrow R \sim N f^{2/3} (l_B b^2)^{1/3} \quad \text{linear in } N!$$

Rem Gauss $N^{1/2}$
SAW $N^{3/5}$ (in Flory approximation)

1.3. The Blob picture

Electrostatic blobs : a chain subunit within which the electrostatic interactions are a weak perturbation.



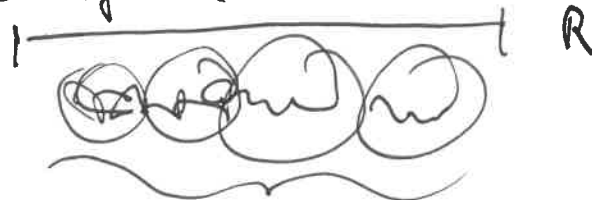
$$\hookrightarrow \frac{(f_e)^2 l_B}{f_e} = 1 \quad (1.3.1)$$

The chain statistics inside each blob is Gaussian on the scale $f_e \rightarrow f_e^2 = g_e b^2 \quad (1.3.2)$

From these 2 equations I find $f_e \sim b (f_e^2 l_B / b)^{-1/3} \quad (1.3.3)$

$$g_e \sim (f_e^2 l_B / b)^{-2/3} \quad (1.3.4)$$

The size of the whole chain is the

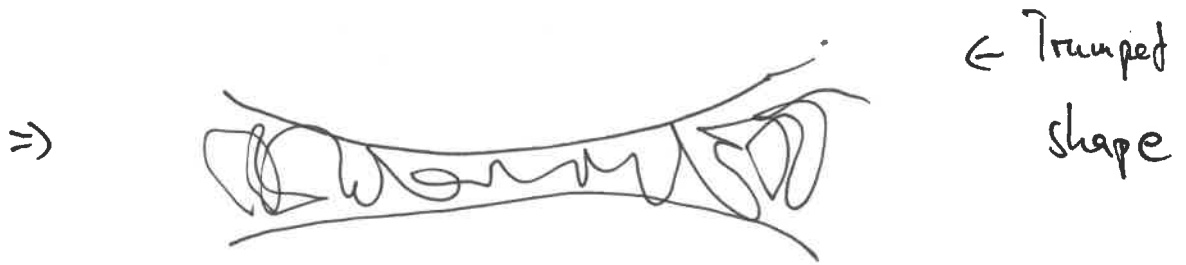


$$\begin{aligned} \leadsto R &\sim \left(\frac{N}{g_e}\right) f_e \sim N b (f_e^2 l_B / b)^{-1/3} \cdot (f_e^2 l_B / b)^{2/3} \\ R &\sim N b (f_e^2 l_B / b)^{1/3} = N f_e^{2/3} (l_B b^2)^{1/3} \quad (1.3.5) \end{aligned}$$

(exactly like the Flory argument)

Rem: A PE chain ^{does} is not here frozen like a shape

- fluctuations along the chain and in the transverse direction.
- transverse fluctuations random $R_{\perp} \sim \sqrt{N} b$
- include the ^{long-range} interaction of monomers for a cylinder of length R and radius ξ_e
 \Rightarrow extra factor $\log^{1/3}(N/g)$ (is of $O(1)$ and does not change anything in scaling)
- tension is not const along the chain
 electrostatic potential is higher in the middle than at the end



1.4 Poor solvent PE's

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$$\Theta = T$$

Gaussian statistics

$$T < \Theta$$

poor solvent conditions

$$f^2 l_B / b \ll 1$$

weakly charged (monomer-monomer interaction small)

Strength of attraction between monomers due to poor solvent is measured by reduced temperature

$$\tau = \frac{\Theta - T}{T} \quad (1.4.1)$$

The interaction part of the free energy of a neutral chain

$$\frac{F_{int}}{k_B T} \approx NB\tau + NCP^2 \quad (1.4.2)$$

2nd 3rd virial coefficient

$$B(T) \sim \tau b^3 \quad (\text{for a LJ pot.}) \quad \underline{\text{attractive}}$$

$$C(T) \sim b^6 \quad (b \sim \sigma) \quad \underline{\text{repulsive}}$$

In a poor solvent neutral polymers have the shape of a globule with density ρ_g .

This can be calculated by balancing the two-body attraction $-\tau b^3 \rho_g^2 N$ with the 3-body repulsion $b^6 \rho_g^3 N$

$$\Rightarrow \rho_g \sim \tau b^{-3} \quad (1.4.3)$$

The 2-body attraction becomes important if it is larger than the thermal energy; i.e.

The threshold is ^(1.4.4) $\tau b^3 \rho_g N \sim 1$ or $\tau > b^{-3} N^{-1} \rho_g^{-1}$

This sets an important length scale, ~~the number of~~ ξ_T , called the thermal blob size, which can be calculated as follows:

Let us ~~call~~ ^{denote} the number of monomers within one thermal blob of size ξ_T as g_t

then from (1.4.4) $\rho N = \frac{N^2}{V}$

$$\tau b^3 \frac{g_t^2}{\xi_t^3} = 1 \quad (1.4.5)$$

and below ξ_t are the fluctuations Gaussian, hence we have the unperturbed chain statistics

$$\xi_t^2 = g_t b^2 \quad (1.4.6)$$

Solving both equations yield

$$\xi_t \approx b \tau^{-1/2} \quad \wedge \quad g_t \approx \tau^{-2} \quad (1.4.7)$$

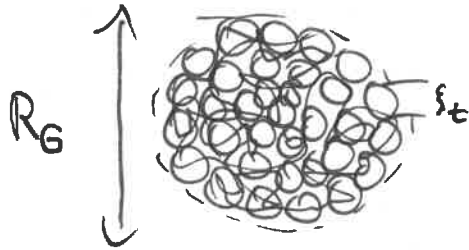
The whole size R_g of the polymeric globule is given by either (1.4.3) or by (1.4.7)

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Yielding R_G $R^3 = \frac{N}{\rho}$

$R = N^{1/3} b^2 R \sim N^{1/3} b$
* of kernel blobs

$$R_G \sim \left(\frac{N}{\rho} \right)^{1/3} \sim \xi_t \left(\frac{N}{g_t} \right)^{1/3} \sim b N^{1/3} \tau^{-1/3} \quad (1.4.8)$$



The free energy of the globule is $\approx k_B T$ per thermal blob

$$\frac{F_{int}}{k_B T} \sim - \frac{N}{g_t} \propto - N \tau^2 \quad (1.4.9)$$

to pull out a kernel blob will cost $\approx k_B T$, leading to a surface ^{energy} tension $F_{surf} \approx k_B T \frac{S}{\xi_t^2} \propto \gamma S$ with S being the surface, leading to

$$\gamma \propto \frac{k_B T}{\xi_t^2} \quad (1.4.10)$$

What changes now, if we charge up the droplet?

\Rightarrow Rayleigh Instability of charged droplet

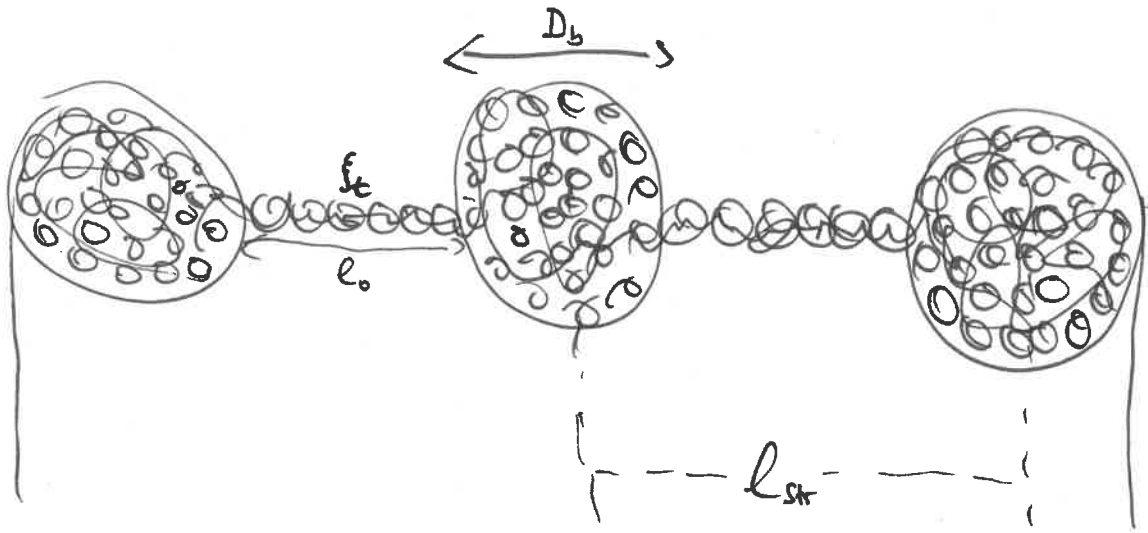
Electrostatic energy $\sim \frac{Q^2}{\epsilon R_{drop}}$

surface energy $\sim \gamma R_{drop}^2$

\hookrightarrow critical charge $Q_{crit} \sim (\gamma \epsilon)^{1/2} R_{drop}^{3/2} \quad (1.4.11)$

then the droplet breaks up into two smaller droplets, and so on...

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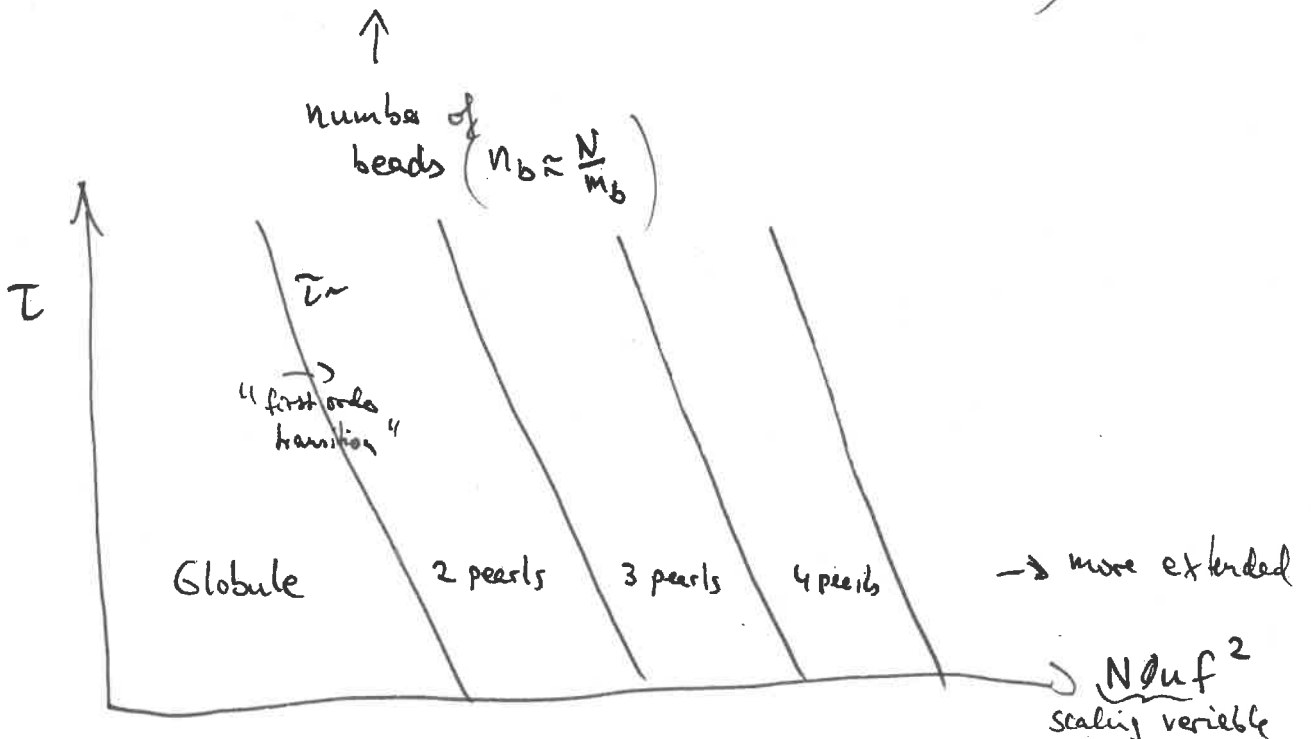
Schematics of a necklace-like PE chain

the critical charge per monomer for the split is

(1.4.12) $f_{crit} \sim \left(\frac{\Gamma}{uN} \right)^{1/2}$ $u = \frac{l_0}{b}$ electr. Coupl.

The length of necklace is approximated by

$$L_{nec} \approx n_b l_{str} \approx b f N \sqrt{\frac{u}{\Gamma} \ln \left(\frac{N u f^2}{|\Gamma|} \right)}$$



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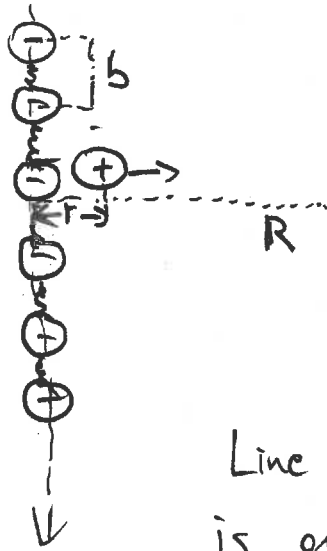
2. Describing Counterion distributions

2.1. The Onsager Argument for Counterion Condensation.

The PE is extended due to electrostatic repulsion of backbone charges.

Simplify: Assume a rodlike conformation:

^ infinite extension



Q: What is the change in free energy ΔF if I displace a counterion from a place r to R ?

Line charge density of the rigid PE is given by $\lambda = \frac{e_0}{b}$ (2.1.1)

The electrostatic potential ϕ of a homogeneously charged infinitely long charged rod is given by

$$\phi(r) \approx \frac{\lambda}{2\pi\epsilon} \ln(r) \quad (2.1.2)$$

$$\Delta F = \Delta E - k_B T \Delta S \quad (2.1.3)$$

$$\Delta E = e_0 \frac{\lambda}{2\pi\epsilon} \ln R - \ln r = e_0 \frac{\lambda}{2\pi\epsilon} \ln \frac{R}{r} \quad (2.1.4)$$

$$\Delta F \approx \ln \frac{V_R}{V_r} \sim 2 \ln \frac{R}{r} \quad (2.1.5)$$

Inserting (2.1.4) and (2.1.5) into (2.1.3)

yields

$$\begin{aligned} \Delta F &= \frac{q_b}{4\pi\epsilon} \left[\frac{e_0 \lambda}{2\pi\epsilon} - 2k_B T \right] \ln \frac{R}{r} \\ &= \left[\frac{e_0^2}{4\pi\epsilon b} - 1 \right] 2k_B T \ln \frac{R}{r} \\ &= (u - 1) 2k_B T \ln \frac{R}{r} \end{aligned} \quad (2.1.6)$$

Manning parameter u

For $u < 1$ $\Delta F < 0$ the ion can escape to infinity \leadsto entropy dominated

For $u > 1$ the ion wants to stay at the rod \leadsto energy dominated,

this effect is known as counterion condensation

two-state model:

The ion is either free or condensed, depending on the value of the Manning parameter u .

From the pure r -dependence of the electrostatic potential, we can draw important conclusions

A: infinite charged plane, $\phi(r) \sim r$, \leadsto energy dominated, a plane always condenses counterions

B: charged sphere, (i.e. a charged colloid), $\phi(r) \sim 1/r \leadsto$ entropy dominated
For a sphere the counterions always go away if V is large enough

2.2. The Poisson - Boltzmann equation

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Poisson: $\nabla^2 \psi(\vec{r}) = -\frac{e}{\epsilon} [n^+(\vec{r}) + n^-(\vec{r})]$ (2.2.1)

↑
Charge density of
positive and negative ions

The electrochemical potential of each ion is

$$\mu^{(i)} = e^i \psi + k_B T \ln n^{(i)} \quad \left[\begin{array}{l} \text{For monovalent ions} \\ v^i = |1| \end{array} \right]$$

(2.2.2) $\Rightarrow n^{(i)} = n_0^{(i)} e^{-e^i \psi / k_B T}$

Boltzmann distributed

(2.2.1) + (2.2.2) yield the PB - equation:

For a 1:1 electrolyte $v^+ = 1, v^- = -1$

$$n_0^+ = n_0^- \equiv n_0$$

$$\nabla^2 \psi(\vec{r}) = -\frac{2e}{\epsilon} n_0 \left[e^{-\frac{e}{k_B T} \psi} - e^{\frac{e}{k_B T} \psi} \right]$$

$$\nabla^2 \psi(\vec{r}) = \frac{2e}{\epsilon} n_0 \cdot \sinh\left(\frac{e}{k_B T} \psi\right) \quad (2.2.3)$$

This is a non-linear pde. Difficult to solve in general.

Therefore first simple approximation: for small $\frac{e}{k_B T} \psi$

linearize: $\sinh(x) \sim x$ for $x \ll 1$

$$\nabla^2 \psi(\vec{r}) = 2 \frac{e^2}{\epsilon k_B T} n_0 \psi = 8 \pi n_0 l_B \psi(\vec{r}) \quad (2.2.4)$$

$$= \lambda_D^{-2} \psi(\vec{r}) = \kappa^2 \psi(\vec{r})$$

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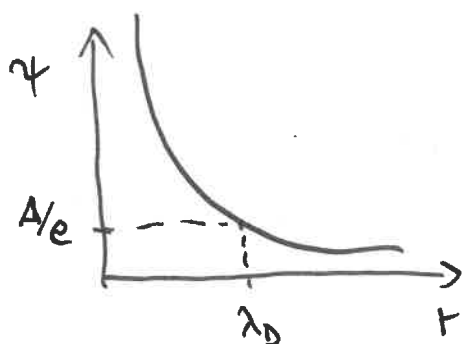
Here we have defined the Debye ^{screening} length λ_D and the screening parameter κ .

$$\kappa^{-1} = \lambda_D = (8\pi l_B n_0)^{-1/2} \quad (2.2.5)$$

λ_D measures approximately the length over which electrostatics is noticeable

(2.2.4) has an exponentially screened solution

$$\psi(r) \approx A e^{-\kappa r} \quad (2.2.6)$$



λ_D decreases as $1/\sqrt{n_0}$ with ion concentration
 \Rightarrow adding salt screens electrostatic interactions

Remember one value:

$$\lambda_D \sim 10 \text{ \AA} = 1 \text{ nm} \quad \text{for } 100 \text{ mM salt (physiological conditions)}$$

$$1 \text{ Mol salt } (= 10 \cdot 100 \text{ mM}) \rightarrow \lambda_D \sim \frac{1}{\sqrt{10}} \cdot 1 \text{ nm} \sim 3 \text{ \AA}$$

$$1 \text{ mM salt } (= \frac{1}{100} \cdot 100 \text{ mM}) \rightarrow \lambda_D \sim 10 \text{ nm}$$

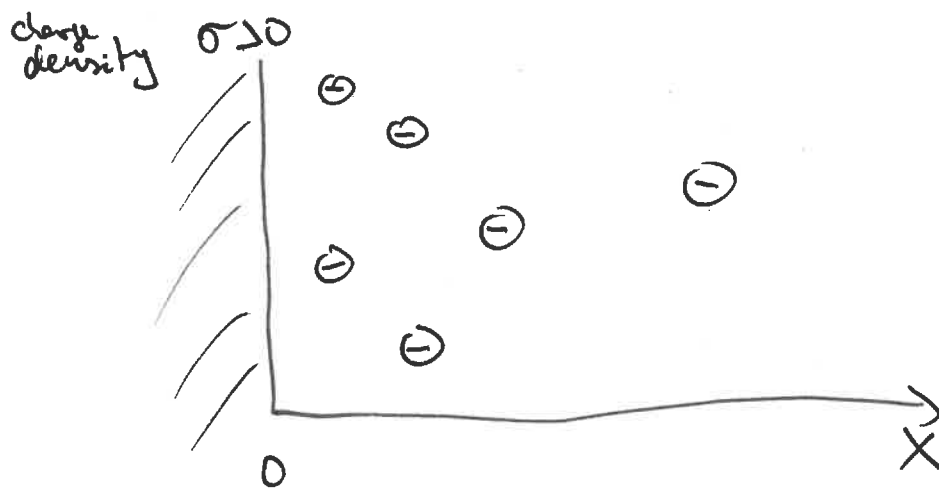
$n_0 \sim 10^{-7}$ (lowest salt concentration of pure water due to auto-ionization)

$$\hookrightarrow \lambda_D \sim 1 \text{ \mu m}$$

2.3. Analytic solution of PB

- Gouy - Chapman (1910) solution
- Chapman (1913)

salt-free solution (only counterions) of a charged infinite plane in half-space



only negative counterions present with valence z

The Lap form of the Laplacian depends on dimensionality:

$$\Delta(\Phi) = \frac{\partial^2}{\partial r^2} + (2-D) \frac{\partial}{\partial r}$$

plane $D=2$
rod $D=1$
sphere $D=0$

Therefore we need to solve the equation

$$\psi''(x) = \frac{ze}{\epsilon} n(0) e^{\beta ze \psi(x)} \quad (2.3.1)$$

where $n(0) = \frac{1}{2\pi l_B z^2 \lambda_{GC}^2}$ with $\lambda_{GC} = \frac{\epsilon}{2\pi l_B z \sigma}$ (2.3.2)
Gouy - Chapman length

(2.3.1) is a second-order diff. equation.

We need two boundary conditions.

1. BC : $\psi'(0) = -\frac{\sigma}{\epsilon} \rightsquigarrow$ field at $x=0$,
 $\psi'(0) = \vec{E}(0)$
 that of a charged plane

2. BC : $\lim_{x \rightarrow \infty} \psi'(x) = 0$
 Field vanishes at infinity
 (consequence of being charge neutral. I have as many counterions as there are charges on the plane)

Define the dimensionless potential $y(x) = \beta z e \psi(x)$

\Rightarrow (2.3.1) can be rewritten as

$$y'' = \frac{2}{\lambda_{GC}^2} e^y$$

the solution is $y(x) = -2 \ln\left(1 + \frac{x}{\lambda_{GC}}\right)$ (2.3.3)

the ion distribution is then given by

$$n(x) = n(0) e^{y(x)} = n(0) (x + \lambda_{GC})^{-2} \lambda_{GC}^2$$

$$= \frac{1}{2\pi l_B z^2} (x + \lambda_{GC})^{-2} \quad (2.3.4)$$

shows an algebraic decay

It is instructive to look at the integrated ion distribution:

$$\begin{aligned}
 P(x) &= \frac{ze}{\sigma} \int_0^x d\bar{x} n(\bar{x}) = \frac{ze}{\sigma} \underbrace{\frac{1}{2\pi l_B z^2}}_{\lambda_{GC}} \left[-(x + \lambda_{GC})^{-1} \right]_0^x \\
 &= \lambda_{GC} \left[-(x + \lambda_{GC})^{-1} + \lambda_{GC}^{-1} \right] = 1 - \left(1 + \frac{x}{\lambda_{GC}} \right)^{-1} \quad (2.3.5)
 \end{aligned}$$

From this we can compute

$$P(\lambda_{GC}) = 1 - \left(1 + \frac{\lambda_{GC}}{\lambda_{GC}} \right)^{-1} = \frac{1}{2}$$

This means, 50% of all counterions are located within the interval $[0, \lambda_{GC}]$

What are typical values for λ_{GC} ?

Exp: $\sigma \sim \frac{1e}{100 \text{ \AA}^2}$ (typical for membranes, glass plates or charged colloids)

in water at $T \sim 20^\circ\text{C}$, $l_B \sim 7 \text{ \AA}$

$$\hookrightarrow \lambda_{GC} \sim 2 \text{ \AA}$$

This is very small and demonstrates again, that a charged plane shows a strong localization of ions!

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It is instructive to solve the Debye-Hückel linearized PB equation

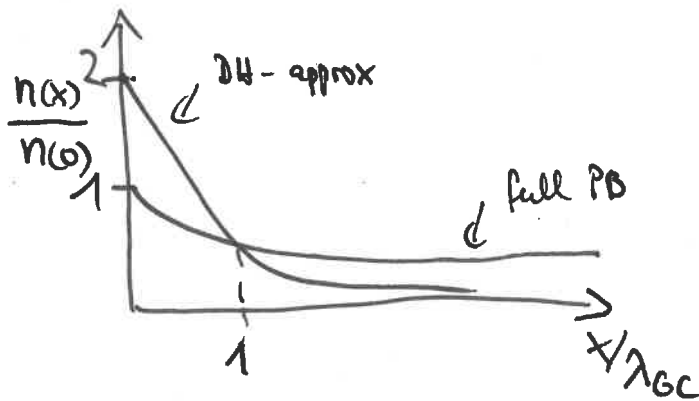
$$y'' = \frac{2}{\lambda_{GC}^2} e^y \xrightarrow{\text{linear}} y_{DH}'' = \frac{2}{\lambda_{GC}^2} (1 + y_{DH})$$

Solution is $y_{DH}(x) = e^{-2x/\lambda_{GC}} - 1$
 and $n_{DH}(x) = \frac{1}{\pi l_B z^2 \lambda_{GC}^2} e^{-2x/\lambda_{GC}}$ } exponential decay

For the contact density we find

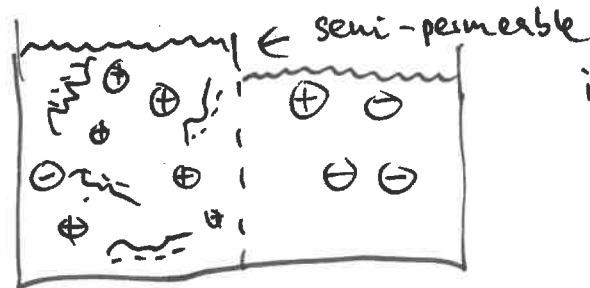
$$n_{DH}(0) = \frac{1}{\pi l_B z^2 \lambda_{GC}^2} = 2 n(0)$$

- This is indep. of the charge density always off by a factor of 2



2.4 Donnan Potential

There is an important effect for compartments that are in contact with a salt reservoir



ions + water can pass through

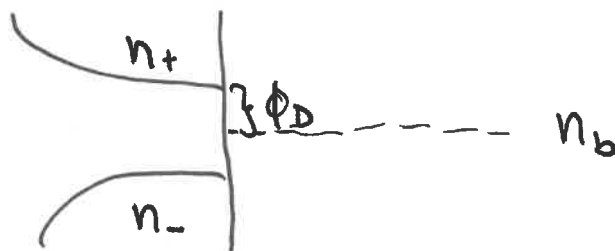
each compartment is charge neutral

The ions tend to go into the less crowded environment

each ion density is Boltzmann distributed

$$n_i = n_{0i} e^{-\beta z_i e \psi(x)}$$

At the membrane we find a discontinuity of ion densities! This gives rise to a potential to maintain this, called Donnan potential



n_{\pm} : cations/anions density at the cell boundary

n_b : bulk salt density

ϕ_D : Donnan potential

In equilibrium, the chemical potential on each side is equal

$$\begin{array}{ccc} \text{left} & \vdots & \text{right} \\ k_B T \ln n_{\pm} & = & k_B T \ln n_b \pm \Phi_D \\ \Rightarrow & & n_{\pm} = n_b e^{\pm \beta e \Phi_D} \end{array} \quad (2.4.1)$$

This equation gives rise to

$$n_+ n_- = n_b^2$$

solving for $\beta e \Phi_D = \frac{1}{2} \ln \frac{n_+}{n_-} = \ln \frac{n_+}{n_b}$

shows that Φ_D diverges for $n_b \rightarrow 0$

Note: the excess osmotic pressure $\beta P = n_+ + n_- - 2n_b$

can be written as

$$\beta P = (\sqrt{n_+} - \sqrt{n_-})^2 \geq 0$$

is always positive