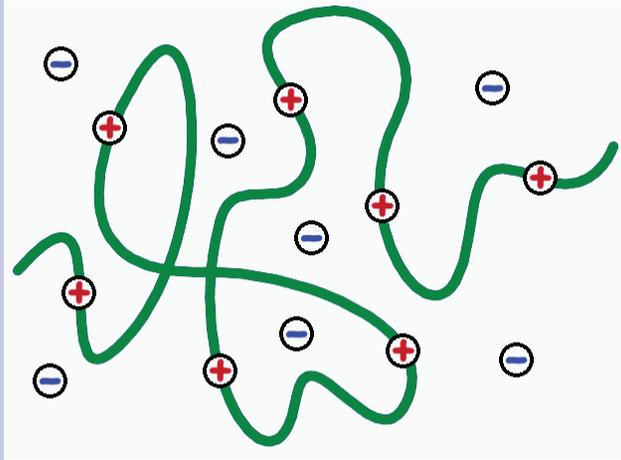


Statistical Physics of Polyelectrolytes.

Polyelectrolytes.



A schematic picture of a polyelectrolyte molecule.

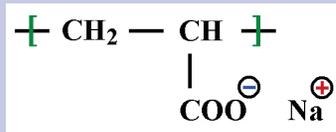
Macromolecules containing charged monomer units are called **polyelectrolytes**. Charged monomer units appear as a result of dissociation reaction:



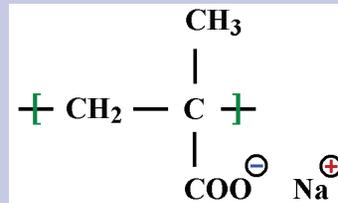
Thus, **counter ions are always present** in polyelectrolyte systems. The number of counter ions equals the number of charged monomer units.

The most important polyelectrolytes are biological macromolecules: DNA, RNA and proteins.

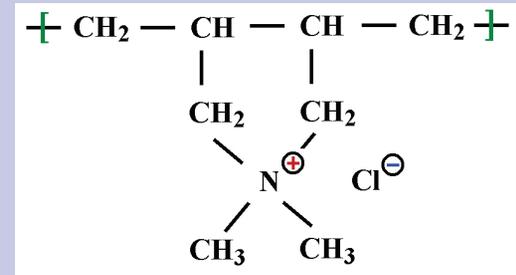
Typical Monomer Units for Polyelectrolytes.



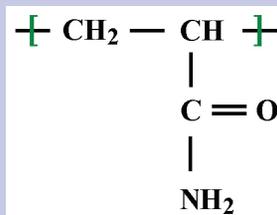
(a)
sodium
acrylate



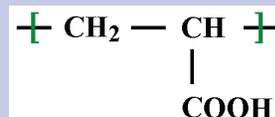
(b)
sodium
metacrylate



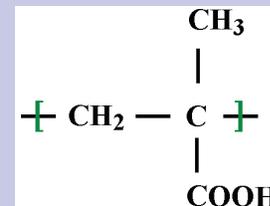
(c)
diallyldimethylammonium
chloride



(d)
acrylamide



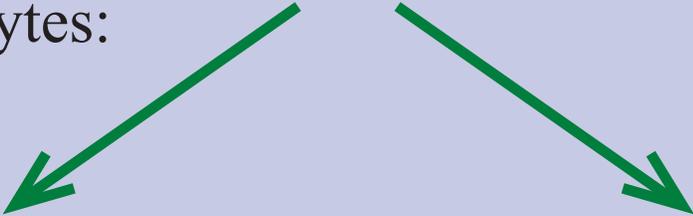
(e)
acrylic
acid



(f)
methacrylic
acid

Strongly and Weakly Charged Polyelectrolytes.

It is important to distinguish **strongly** and **weakly** charged polyelectrolytes:



**strongly charged
polyelectrolytes**

large fraction of links is charged, Coulomb interactions dominate the thermodynamics of these systems.

**weakly charged
polyelectrolytes**

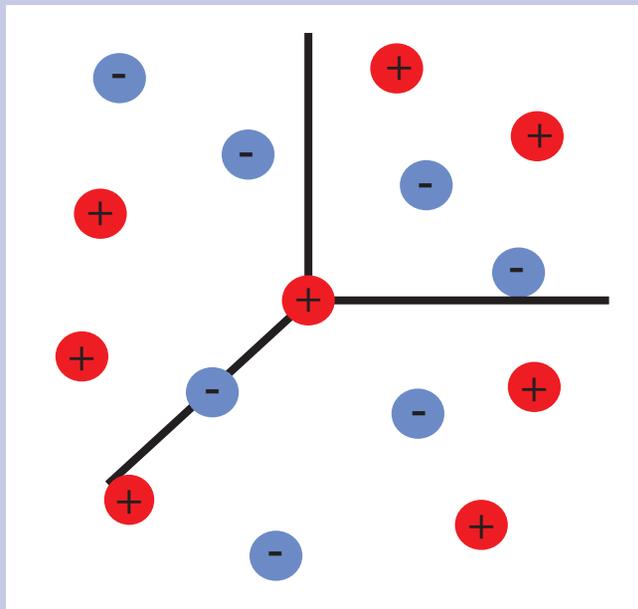
small fraction of links is charged; Coulomb interactions interplay with Van-der-Waals interactions of the uncharged links.

Before discussing the special polyelectrolyte features, let us remind the basic fact of the theory of **low-molecular electrolyte solutions**, namely the fact that the Coulomb interactions are **screened** at some distance, called **the Debye-Huckel radius**.

Debye-Huckel Theory.

An important feature of the electrolyte solutions is the **screening** of the Coulomb interactions. We consider first the classical theory of screening by the point-like charges developed in 1920s by P. Debye and E. Huckel.

Consider an electroneutral **plasma** (or **electrolyte solution**) consisting of n sorts of ions, the i -th sort having concentration c_i and charge $e_i = z_i e$. We fix now a **single charge $+e$** at the origin and calculate the equilibrium potential $\varphi(\vec{r})$ and charge distributions $c_i(\vec{r})$ around it.



This system is governed by two equations: the **Poisson equation** defines the potential in terms of the charge density, while the **Boltzmann equation** defines the equilibrium charge distribution if the potential is given. Combined they compose a **self-consistent** system.

Debye-Huckel Theory.

Poisson equation: $\Delta\phi = -\frac{4\pi\rho}{\epsilon}$ (ρ is the total charge density)

$$\Delta\phi = -4\pi\frac{e}{\epsilon}\delta(\vec{r}) - \frac{4\pi}{\epsilon}\sum_i ez_i\delta c_i(\vec{r})$$

Boltzmann equation: $c(\vec{r}) \sim \exp(-E(\vec{r})/kT)$

$$\delta c_i(\vec{r}) = c_i(\vec{r}) - \bar{c}_i = \bar{c}_i \left[\exp\left(-\frac{ez_i\phi}{kT}\right) - 1 \right]$$

where the mean density \bar{c}_i and the local variation of density $\delta c_i(\vec{r})$ due to the presence of a fixed charge are introduced.

Combining these two equations we get the **Poisson-Boltzmann equation:**

$$\Delta\phi = -4\pi\frac{e}{\epsilon}\delta(\vec{r}) - \frac{4\pi}{\epsilon}\sum_i ez_i\bar{c}_i \left[\exp\left(-\frac{ez_i\phi}{kT}\right) - 1 \right]$$

Generally, it is not analytically solvable, but if the field is weak enough one can **linearize** it to get the **Debye-Huckel approximation.**

Debye-Huckel Theory.

Debye-Huckel linearized equation:

$$\Delta\varphi = -4\pi \frac{e}{\varepsilon} \delta(\vec{r}) - \frac{4\pi e^2}{\varepsilon kT} \left(\sum_i z_i^2 \bar{c}_i \right) \varphi$$

Note, that the coefficient before the linear term on the right hand side is a constant of order *(length)⁻²*, so one can rewrite this equation as follows:

$$\Delta\varphi = -4\pi \frac{e}{\varepsilon} \delta(\vec{r}) - \frac{1}{r_D^2} \varphi$$

where

$$r_D = \left(\frac{\varepsilon kT}{4\pi e^2 \left(\sum_i z_i^2 \bar{c}_i \right)} \right)^{1/2}$$

is the so-called **Debye-Huckel radius**. This radius characterizes the typical distance at which the charge at the origin is screened by the other charges.

Debye-Huckel Theory.

$$\Delta\varphi = -4\pi \frac{e}{\varepsilon} \delta(\vec{r}) - \frac{1}{r_D^2} \varphi$$

To solve this equation take a **Fourier transform**:

$$\varphi_{\vec{k}} = \int \varphi(\vec{r}) e^{-i\vec{k}\vec{r}} d^3r$$

Then

$$-k^2 \varphi_{\vec{k}} = -\frac{4\pi e}{\varepsilon} + r_D^{-2} \varphi_{\vec{k}}$$

and

$$\varphi_{\vec{k}} = \frac{4\pi e/\varepsilon}{k^2 + r_D^{-2}}$$

Taking the inverse Fourier transform one gets the final answer:

$$\varphi(\vec{r}) = \frac{e}{\varepsilon r} \exp\left(-\frac{r}{r_D}\right), \text{ i.e., indeed, the potential is effectively cut off at the distance } r_D \text{ from the origin.}$$

Why is Polyelectrolyte Theory Complicated?

Main complications of the theory of **polyelectrolyte** solutions as compared with the theories of **neutral polymer solutions**:

1. Additional parameters (linear charge density, salt concentration, pH, etc.)
2. Coulomb interactions are generally not short-ranged, i.e. they give rise to an additional typical length scale - that of Debye-Huckel radius, which can be comparable with, for example, the persistent length.
3. An interplay between Coulomb and Van-der-Waals interactions in weakly charged polyelectrolytes.

as compared with the theories of **low-molecular electrolytes**:

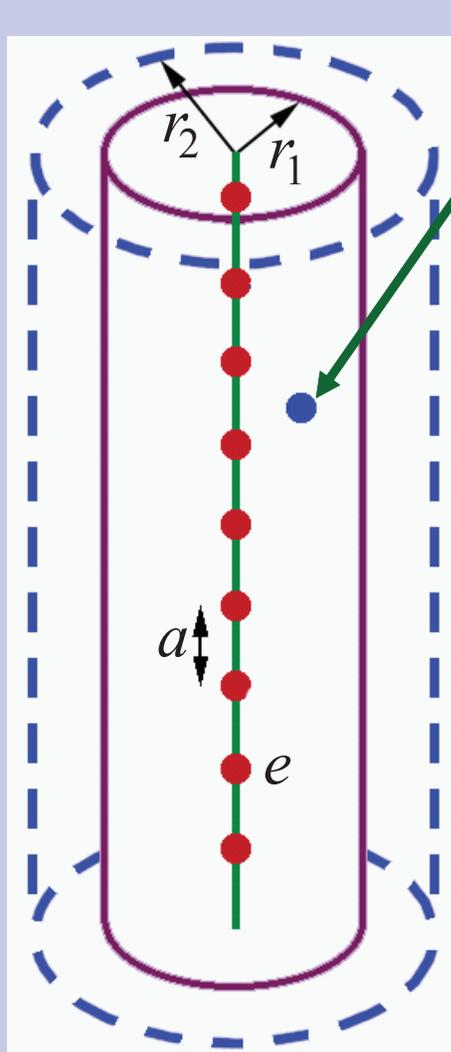
1. Additional parameters (chain length, persistent length, fraction of charged links, etc.)
2. Screening is due to both small ions and polymer chains.

Moreover, remember that generally the **Coulomb interactions are not weak** and the Debye-Huckel linearization is not always valid.

Some Basic Phenomena of the Polyelectrolyte Statistics.

1. Counter ion condensation.
2. Electrostatic persistent length.
3. Charge screening by the non-point objects.
4. Translational entropy of the counter ions, and the osmotic pressure coupled to it.

Counter Ion Condensation.



counter ion

Consider a **strongly charged polyelectrolyte** chain in a **salt-free** solution. In such a system an important phenomenon may take place, namely a **counter ion condensation**.

Let us find the equilibrium mean distance between a counter ion and a charged polymer chain in a set up shown in the figure.

To do that we estimate the free energy change due to the change of the counterion-polymer distance from r_1 to r_2 .

Counter Ion Condensation.

The gain in the entropy of translational motion is

$$\Delta F_1 \sim kT \Delta S \sim kT \ln \frac{V_1}{V_2} \sim kT \ln \frac{r_2}{r_1}$$

The decrease in the average energy of attraction of a counter ion to the charged line is

$$\Delta F_2 \sim -e\Delta\phi \sim -e \frac{\rho}{\epsilon} \ln \frac{r_2}{r_1} \sim -\frac{e^2}{\epsilon a} \ln \frac{r_2}{r_1}, \text{ where } \rho = e/a \text{ is the linear density of the charge.}$$

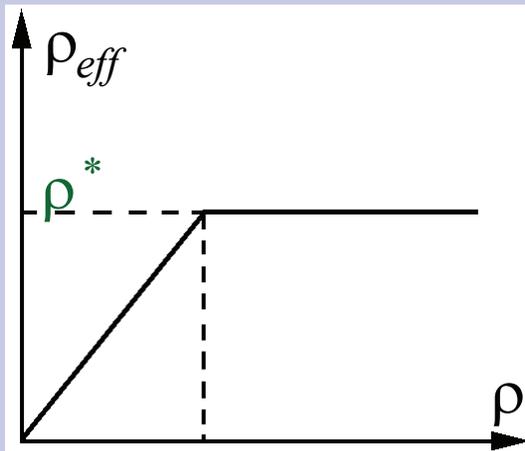
We see that both contributions (ΔF_1 and ΔF_2) are proportional to $\ln(r_1/r_2)$. Therefore, only two results are possible:

If $u \equiv \frac{e^2}{\epsilon a kT} < 1$ then $\Delta F_1 > |\Delta F_2|$, i.e., the gain in entropy is more important; the **counter ion goes to infinity**.

On the other hand, if $u \equiv \frac{e^2}{\epsilon a kT} > 1$ then $\Delta F_1 < |\Delta F_2|$ and the counter ion approaches the charged line and **“condenses”** on it.

Counter Ion Condensation.

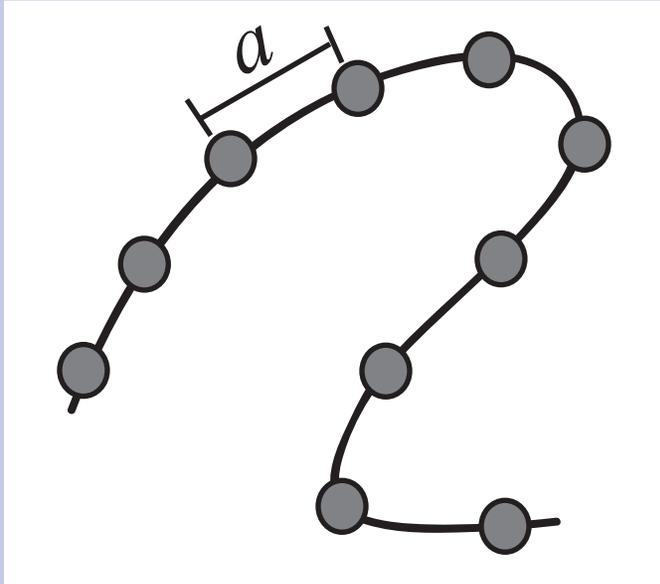
Now let us add charges gradually - the second, the third, etc. Considering the newly added charges in the same way, we see that charging the line is possible only up to the linear density $\rho^* = \epsilon kT/e$ and any counter ions added on top of it, will **condensate on the line** preventing any more increase in the effective charge. Note, that **condensation of the counter ions stops** immediately after the **critical concentration** is reached, all the remaining counter ions still float in the solution.



The dependence of the effective charge on the line as a function of its initial charge.

Thus, in the presence of counter ions there is a threshold ρ^* such that it is impossible to have a charged line with linear charge density above this threshold.

Electrostatic Persistent Length.



If $a \ll r_D \ll l$, where l is the properly renormalized (see below) persistent length, it is possible to separate the short-range and long-range effects of the Coulomb interactions. Putting it in other words, one can separate the electrostatic interactions along the chain, which manifest themselves in the

increase of the chain stiffness, and the electrostatic interactions on the long scale which give some additional contribution to the volume interactions (Odijk, Skolnick, Fixman, 1977).

Thus, the **persistent length** of a polyelectrolyte chain in this case can be written down as follows:

$$l = l_0 + l_{el}$$

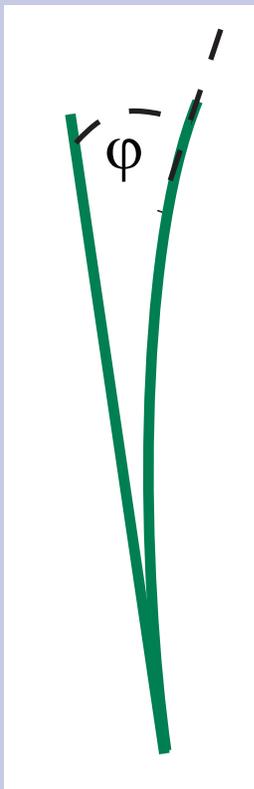
where l_0 is the “bare” persistent length of a non-polyelectrolyte chain, and l_{el} is the electrostatic contribution to the stiffness we are now to calculate.

Electrostatic Persistent Length.

The **internal elastic energy** of an uncharged wormlike (persistent) chain can be written down as follows:

$$E_{elast} = \frac{1}{2} b \int_0^L \rho^2(s) ds$$

where $\rho(s) = \left| \partial^2 \vec{r}(s) / \partial s^2 \right|$ is the **local curvature** of the chain, and b - some coefficient.



For small φ the curvature is of order $\rho \sim \frac{\varphi}{L}$

and thus, the energy $E_{elast} \sim \frac{1}{2} b \frac{\varphi^2}{L}$

One can define the **persistent length** as the length at which the thermal energy is large enough to substantially bend the chain:

$$E|_{L \sim l, \varphi \sim 1} \sim kT$$

We get therefore for the bare persistent length

$$l_0 \sim b/kT$$

Electrostatic Persistent Length.

If the polymer chain is **charged** there is additional **repulsion** between the monomers, the corresponding energy reads

$$u_{ij} = \frac{e^2}{\epsilon r_{ij}} \exp(-r_{ij}/r_D)$$

where r_{ij} is the distance between i -th and j -th monomer.

This energy is minimal when the chain is **rectilinear**, so in the vicinity of the rectilinear conformation one can **expand** the energy to get

$$E = E_{elast} + E_{el}; \quad E_{el} \sim \frac{1}{2} b_{el} \frac{\phi^2}{L}$$

which gives rise to an **electrostatic contribution** into the persistent length: $l_{el} \sim b_{el}/kT$, the total persistent length being the sum $l = l_0 + l_{el}$

The final result for this electrostatic contribution within the domain of applicability of the OSF theory (i.e., for $a \ll r_D \ll l_0$) reads

$$l_e = \frac{ur_D^2}{a}$$

where $u = \frac{e^2}{\epsilon akT}$ is the counter ion condensation parameter.

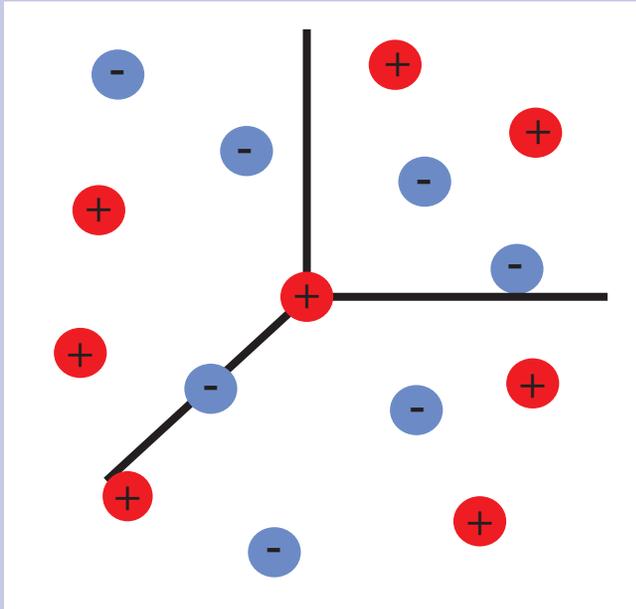
Electrostatic Persistent Length.

$$l_e = \frac{ur_D^2}{a}$$

Note, that

- if $u > 1$ (i.e., the **counter ion condensation** takes place), the condensed ions participate neither in the electrostatic energy nor in the screening of charges, so the effective values of $u_{eff} = 1$, $a_{eff} = l_B = e^2 / \epsilon kT$ (the so-called **Bjerrum length**) and c_{eff} (the concentration of counter ions) are to be used allowing for the condensation effect.
- $l_e \gg r_D$, i.e., the chain **stiffening occurs on a scale much larger than the Debye-Huckel radius.**

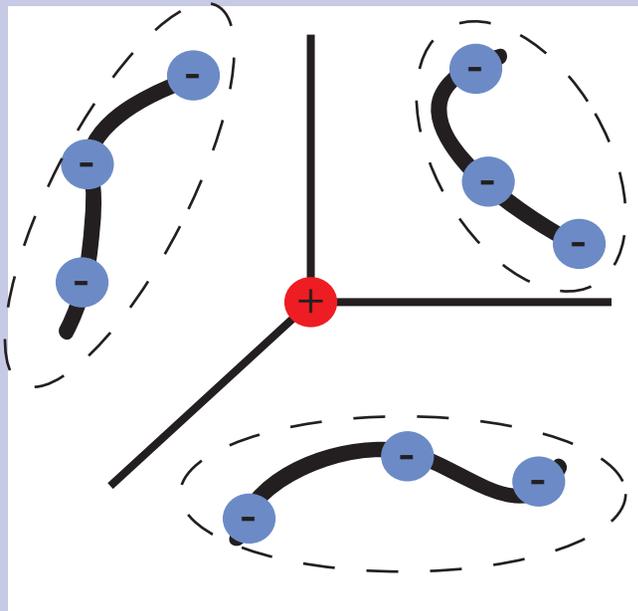
Screening by the Non-Point-Like Objects.



For the screening by **point-like** charges we have

$$\varphi(\vec{r}) = \frac{e}{\epsilon r} \exp\left(-\frac{r}{r_D}\right)$$

$$r_D = \left(\frac{\epsilon kT}{4\pi e^2 z^2 c}\right)^{1/2}$$



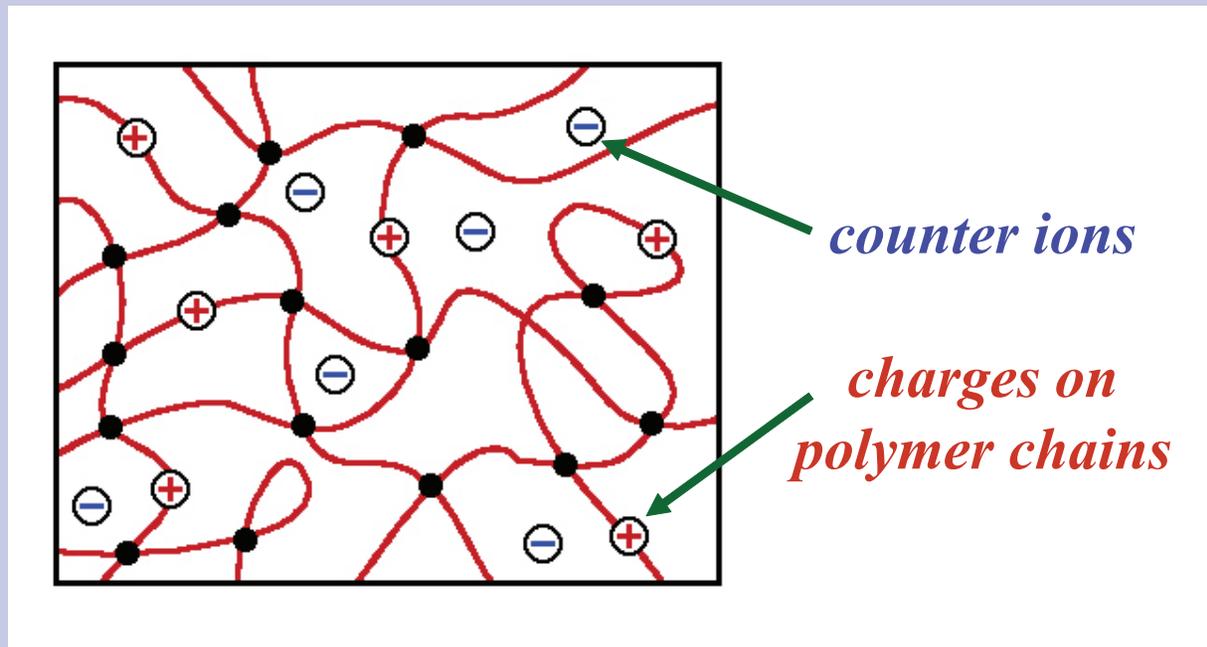
For the screening by the **charges connected into a chain**

$$r_D = \left(\frac{\epsilon kT}{4\pi e^2 z_{eff}^2 c}\right)^{1/2}$$

where z_{eff} is the total charge (in the e units) within a sphere of radius ξ , ξ being the **correlation length** of the solution.

Superabsorbing Properties of the Polyelectrolyte Gels.

As an example of a crucial role of the counter ions osmotic pressure consider swelling and collapse of a **polyelectrolyte gel**.



Schematic picture of a polyelectrolyte gel

We know that typical values of the swelling coefficient α for **regular gels** lies in the interval 1.2 - 2.5, which corresponds to a **15-fold** increase of the volume of the gel upon swelling in the maximum. On the other hand, **polyelectrolyte gels** normally increase their volume in water **several hundred times**. This property is due exactly to the **osmotic pressure of counter ions**.

Superabsorbing Properties of the Polyelectrolyte Gels.

Indeed, it is thermodynamically advantageous for the counter ions to abandon the gel and travel in the whole external volume, because in this way they gain significant **entropy of translational motion**. However, this is impossible, because this would violate the condition of **macroscopic electroneutrality** of the gel and lead to enormously large electrostatic energy of the system. The counter ions are therefore forced to be **confined within the gel**, and they produce a significant **osmotic pressure** in the gel. This osmotic pressure induces a very essential gel swelling: in this way there is more space for the translation motion of each counter ion.

This property is used for the design of **superabsorbing polymer systems**. The superabsorbing properties of polyelectrolyte gels in water are quite **universal**: they are observed for any gel, independently of its chemical structure, provided that the gel contains monomer units which **dissociate in water** to provide charged counter ions.