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## 09. Ionic soft matter I

Gerhard Müller

University of Rhode Island, gmuller@uri.edu

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# Ionic Soft Matter: Dissociation Equilibrium [pln61]

Soft materials may contain ionic groups that dissociate in water environment:

- charged colloids (with charges spread across surface),
- charged polymers (poly-electrolytes),
- charged micelles (with charges on headgroups of amphiphiles).

Ions attached to macro-molecules or aggregates become immobile macro-ions. In a macro-electrolyte, a significant fraction of ions are bound, unlike in a normal electrolyte. The absence/presence of bound charges matters.

The state of ionic soft matter is controllable in three principal ways:

- pH ( $H^+$  concentration),
- salinity (concentration of salts with ionic bonds dissociated),
- electric field.

## Dissociation equilibrium in normal electrolyte:

Equilibrium condition for  $AB \rightleftharpoons A^+ + B^-$  governed by chemical potentials:

$$\mu_{AB} = \mu_{A^+} + \mu_{B^-}. \quad (1)$$

Dependence of chemical potentials  $\mu_i$  on (scaled) molar densities  $n_i$ , assuming all three solute components to be dilute (see pln30):<sup>1</sup>

$$\mu_i = \mu_i^{(0)}(T, p) + k_B T \ln(n_i/n_0). \quad (2)$$

Using the notation  $n_i/n_0 \doteq [i]$ , we infer from (1) and (2) the mass action rule,

$$\frac{[A^+][B^-]}{[AB]} = K_{AB}, \quad K_{AB} \doteq e^{\beta(\mu_{AB}^{(0)} - \mu_{A^+}^{(0)} - \mu_{B^-}^{(0)})}, \quad (3)$$

where  $K_{AB}$  is the dissociation constant. The associated pK value is

$$\text{pK}_{AB} \doteq -\log_{10} K_{AB}. \quad (4)$$

## Level of pH:

For the case of dissociation of the solvent (water) molecules,



the unit  $n_0$  is chosen such that  $[H_2O] = 1$ .

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<sup>1</sup>The customary unit is  $n_0 = 1\text{mol/dm}^3$ .

The simplified mass action rule reads

$$[\text{H}^+][\text{OH}^-] = K_w = (10^{-7})^2, \quad (5)$$

with  $[\text{H}^+] = [\text{OH}^-]$  for pure water. The pK of water,  $\text{pK}_w = 14$ , is an empirical constant.

The level of pH is associated with the (scaled) number density  $[\text{H}^+]$ :

$$\text{pH} \doteq -\log_{10}[\text{H}^+] \quad \left\{ \begin{array}{l} > 7 : \text{alkaline} \\ = 7 : \text{neutral} \\ < 7 : \text{acidic} \end{array} \right. \quad (6)$$

- Adding hydrochloric acid to water, where it partially dissociates,



forces an increase in  $[\text{H}^+]$ . Condition (5) forces a decrease in  $[\text{OH}^-]$ . The pH is lowered in the process. Charge neutrality is maintained as  $\text{OH}^-$  ions are being replaced by  $\text{Cl}^-$  ions.

- Adding sodium hydroxide (lye) to water, where it partially dissociates,



forces an increase in  $[\text{OH}^-]$ . Condition (5) forces a decrease in  $[\text{H}^+]$ . The pH is raised in the process. Charge neutrality is maintained as  $\text{H}^+$  ions are being replaced by  $\text{Na}^+$  ions.

Saturation effect: lowering pH increasingly suppresses dissociation of acid.

Equilibrium conditions:

$$\frac{[\text{H}^+][\text{Cl}^-]}{[\text{HCl}]} = K_{\text{HCl}} = 10^{-\text{pK}_{\text{HCl}}}, \quad [\text{H}^+] = 10^{-\text{pH}}. \quad (7)$$

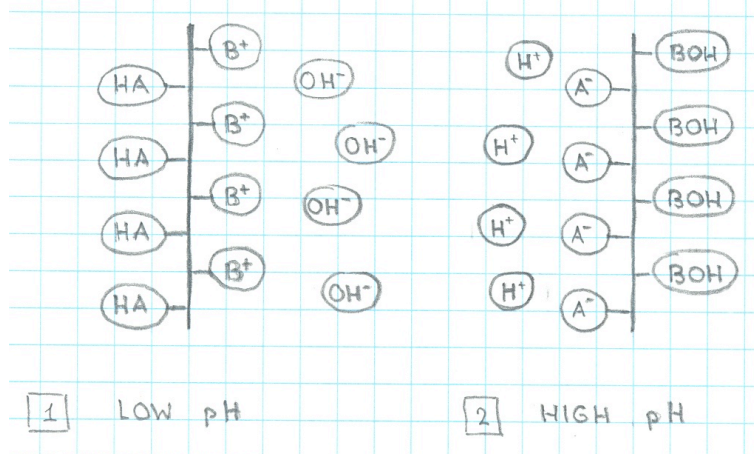
Probability of dissociated acid:

$$P_{\text{Cl}^-} = \frac{[\text{Cl}^-]}{[\text{Cl}^-] + [\text{HCl}]} = \frac{1}{1 + \frac{[\text{HCl}]}{[\text{Cl}^-]}} = \frac{1}{1 + \frac{[\text{H}^+]}{K_{\text{HCl}}}} = \frac{1}{1 + 10^{\text{pK}_{\text{HCl}} - \text{pH}}}. \quad (8)$$

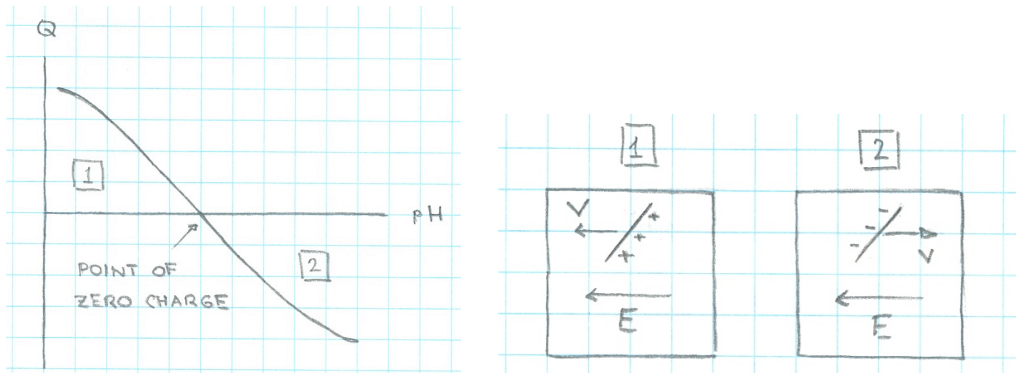
The rate of dissociation is 50% when  $\text{pH} = \text{pK}_{\text{HCl}}$ . In like manner, the dissociation of lye is increasingly suppressed as the pH rises.

### Dissociation equilibrium in macro-electrolyte:

Consider a macro-electrolyte with both acidic groups HA and alkaline groups BOH. We now know that a low pH increasingly suppresses dissociation of the former and a high pH increasingly suppresses dissociation of the latter.



In consequence, the charge  $Q$  on the macromolecules changes gradually from positive to negative with increasing pH, crossing a point of zero charge at a specific level of pH. In a uniform and constant electric field  $\vec{E}$ , a change in pH may switch the direction in which such macromolecules drift.



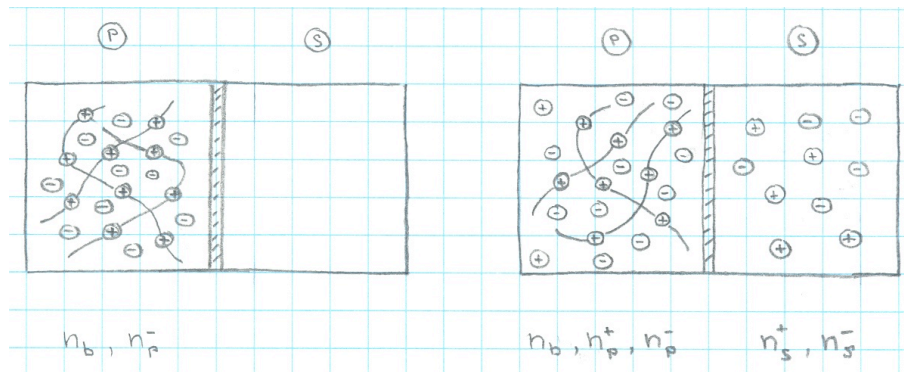
In the presence of macro-electrolytes (e.g. poly-electrolytes) the dissociation equilibrium condition deviates from (3). Dissociation of nearby acidic or alkaline groups is inhibited by electrostatic effects. Dissociation along the poly-electrolyte is strongly correlated over a characteristic length, named Bjeruum length, which is just under 1nm in water at room temperature.

[gleaned from Doi 2013]

# Donnan Equilibrium [p1n62]

Here we investigate the chemical equilibrium in a region that contains a solvent on one side, possibly with salt in dilute solution, and a poly-electrolyte on the other side. The inhomogeneity is maintained by a semipermeable wall.

Within the space occupied by the poly-electrolyte, the bound charges are taken into account in the form of a continuous background. The Donnan equilibrium is being established by the mobility of small counter-ions and co-ions.



## Situation depicted on the left:

Container with two chambers of equal volume separated by semi-permeable membrane.

- (s) contains solvent with no significant ion content,
- (p) contains a poly-electrolyte solution.

Positive charges are bound to polymers:<sup>1</sup>  $n_b, e_b^+$ . Negative charges are carried by small, mobile ions:  $n_p^-, e_p^-$ . Membrane is permeable to small ions only.

Local charge density:<sup>2</sup>  $\rho_p(\mathbf{r}) = n_b(\mathbf{r})e_b^+ + n_p^-(\mathbf{r})e_p^-$ ,  $\rho_s(\mathbf{r}) = n_s^-(\mathbf{r})e_s^-$

Charge neutrality condition:  $\rho_p(\mathbf{r}) = \rho_s(\mathbf{r}) = 0$

- ▷ Charge neutrality constraint prevents small ions from migrating through membrane in significant numbers.
- ▷ Osmotic pressure,  $\pi = n_b k_B T$ , depends on the density of ionic groups, which is much larger than the density of polymers.

<sup>1</sup>Scaled number density and charge of bound ionic groups or of small mobile ions.

<sup>2</sup>Averaged over suitably chosen mesoscopic distances.

### Situation depicted on the right:

Salt is added to the solution and partially dissociates. Now small, mobile ions with positive or negative charges are present left (p) and right (s). These ions are free to migrate through the membrane until the (chemical) Donnan equilibrium is established.

Equilibrium condition:<sup>3</sup>  $\mu_0 + k_B T \ln n_p^\pm + e_p^\pm \psi_p = \mu_0 + k_B T \ln n_s^\pm + e_s^\pm \psi_s$ .

Charge neutrality condition implies  $n_p^+ + n_b = n_p^-$ ,  $n_s^+ = n_s^- \doteq n_s$ .

Results describing Donnan equilibrium, all expressed in terms of  $n_b$  (poly-electrolyte attribute) and  $n_s$  (controllable by salt concentration):

- density of mobile ions in the chamber with poly-electrolyte [pex56]:

$$n_p^\pm = \frac{1}{2} \left[ \sqrt{n_b^2 + 4n_s^2} \mp n_b \right],$$

- Donnan potential:

$$\Delta\psi \doteq \psi_p - \psi_s = \frac{k_B T}{e_0} \ln \left( \sqrt{1 + \left[ \frac{n_b}{2n_s} \right]^2} + \frac{n_b}{2n_s} \right),$$

- osmotic pressure:

$$\Delta\pi = k_B T \left[ \sqrt{n_b^2 + 4n_s^2} - 2n_s \right].$$

[gleaned from Doi 2013]

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<sup>3</sup>The simplifying assumption  $\mu_0^{(p)} = \mu_0^{(s)} \doteq \mu_0$  neglects the fact that the presence of polymers affects the chemical potential via a change in dielectric constant

[pex56] **Donnan equilibrium between ionic polymer and solvent**

Consider ionic polymers in solution confined to one chamber (p) of a container separated from a chamber (s) with solvent by a semi-permeable wall as shown. The polymer contains positive ionic groups and salt has been added to the solvent. All ions except the polymers are free to migrate between compartments. The number density of (positive) bound charges is  $n_b$ . The mobile ions in chamber (p) have number densities  $n_p^+$ ,  $n_p^-$  and those in chamber (s)  $n_s^+$ ,  $n_s^-$ . At thermal equilibrium, charge neutrality is established (on some mesoscopic length scale),

$$n_p^+ + n_b = n_p^-, \quad n_s^+ = n_s^- \doteq n_s,$$

as well as an electric potential difference and an osmotic pressure between the chambers:

$$\Delta\psi \doteq \psi_p - \psi_s, \quad \Delta\pi \doteq k_B T [n_p^+ + n_p^- - 2n_s].$$

The condition of chemical equilibrium for the mobile ions can then be stated as follows:

$$\mu_0 + k_B T \ln n_p^\pm \pm e_0 \psi_p = \mu_0 + k_B T \ln n_s^\pm \pm e_0 \psi_s,$$

where we assume monovalency and equal reference values in both chambers.

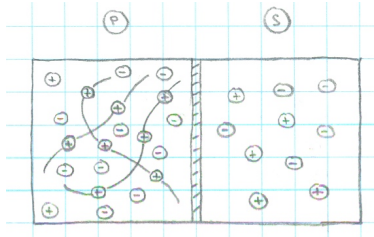
(a) Convert this relation into

$$n_p^\pm = n_s \exp(\mp \beta e_0 \Delta\psi),$$

where  $e_0$  is the elementary charge and  $\beta \doteq 1/k_B T$ .

(b) Use these ingredients to derive the following expressions for the densities  $n_p^\pm$ , the Donnan potential  $\Delta\psi$ , and the osmotic pressure  $\Delta\pi$ , all as functions of  $n_b$  and  $n_s$  (see [pln62]).

(c) Simplify all results for the cases  $n_s \ll n_b$  and  $n_s \gg n_b$  of low and high salt concentrations, respectively.



[adapted from Doi 2013]

**Solution:**



# Poly-Electrolyte Gel [pln66]

In [pln65] we have investigated the swelling equilibrium of a polymer gel and expressed it as the balancing of osmotic pressure acting as an expanding force and gel elasticity acting as a restoring force. For uncharged polymers in a solvent with negligible amounts of ions we have derived the following expression for the osmotic pressure:

$$\pi_{\text{sol}}(\phi) = \frac{k_{\text{B}}T}{v_{\text{c}}} \left[ -\ln(1 - \phi) - \phi - \chi\phi^2 \right].$$

In [pln62] we have investigated the Donnan equilibrium of a poly-electrolyte in contact with a solvent containing mobile ions. We have found that the Donnan equilibrium features an ionic contribution to the osmotic pressure,

$$\pi_{\text{ion}}(n_b, n_s) = k_{\text{B}}T \left[ \sqrt{n_b^2 + 4n_s^2} - 2n_s \right],$$

where  $n_b$  is the number density of bound charges in ionic groups on the poly-electrolyte molecules and  $n_s$  is the number density of mobile ions in pure solvent.

When we investigate the swelling equilibrium of a poly-electrolyte gel we must take into account both contributions to the osmotic pressure. An approximate implementation of this requirement just adds the two contributions. The modified swelling equilibrium then becomes

$$G_0 \left( \frac{\phi}{\phi_0} \right)^{1/3} = \pi_{\text{sol}}(\phi) + \pi_{\text{ion}}(\hat{n}_b, n_s),$$

where  $\hat{n}_b = n_b(\phi/\phi_1)$  reflects the change in the number density of bound charges due to swelling.

A more accurate implementation would start from the free-energy density with all contributions included and then determine the equilibrium from the extremum condition.

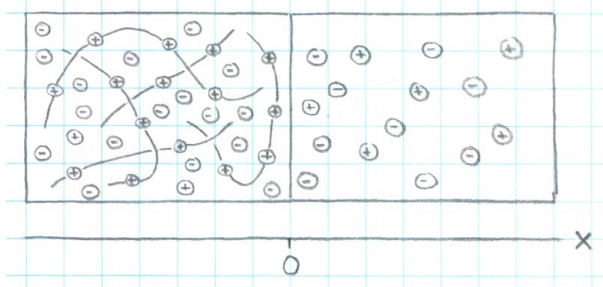
Given the known shape of  $\pi_{\text{sol}}(\phi)$  and the weak dependence of  $\pi_{\text{ion}}(\hat{n}_b, n_s)$  on  $\phi$  it is readily concluded that the presence of ions has an enhancing effect on the swelling.

[extracted in part from Doi 2013]

## Charge Density Profile Near Interface [pln67]

The relation between densities  $n_p^\pm, n_s, n_b$  of free and bound ions as described in [pln62] and worked out in [pex56] for the Donnan equilibrium between two chambers reflect bulk properties sufficiently far from the interface.

Near the interface the densities and the electric potential acquire profiles that deviate from the bulk values in characteristic ways:



- bound charges:  $n_b(x) = n_b \theta(-x)$  (step function),
- mobile charges:  $n_+(x), n_-(x)$ ,
- electric potential:  $\psi(x)$ ,
- Donnan potential:  $\Delta\psi = \psi(-\infty) - \psi(+\infty)$ ,
- charge density:  $\rho_e(x) = e_0[n_b(x) + n_+(x) - n_-(x)]$ ,

Charge neutrality condition:  $\int_{-\infty}^{+\infty} dx \rho_e(x) = 0$ .

Electric dipole moment:  $P_e = \int_{-\infty}^{+\infty} dx x \rho_e(x)$ .

Poisson equation:  $\epsilon \frac{d^2\psi}{dx^2} = -\rho_e(x)$ ,  $\epsilon \doteq \epsilon_r \epsilon_0$ .

Solution of Poisson equation [pex57]:

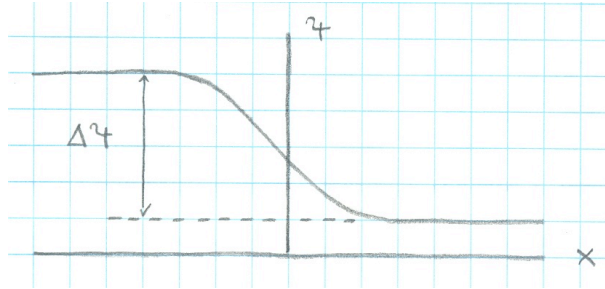
$$\psi(x) = -\frac{1}{2\epsilon} \int_{-\infty}^{+\infty} dx' |x - x'| \rho_e(x'). \quad (1)$$

Donnan potential from electric dipole moment via charge density [pex57]:

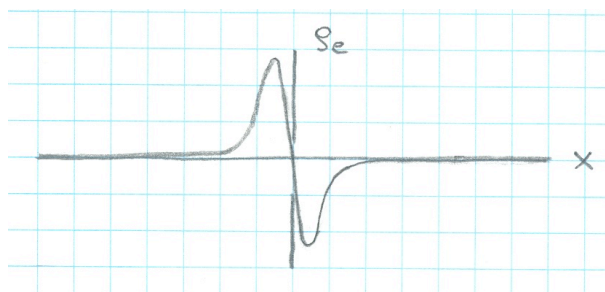
$$\Delta\psi = -\frac{P_e}{\epsilon}. \quad (2)$$

At this stage of the analysis we can infer the charge density profile  $\rho_e(x)$  from a model profile  $\psi(x)$  for the electric potential or vice versa. The quantitative analysis of a two-parameter model is part of [pex57].

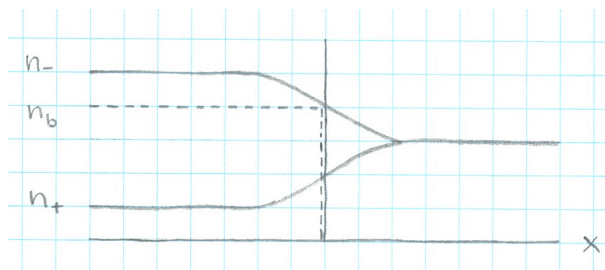
A model electric potential  $\psi(x)$  of the shape



will result in a charge density  $\rho_e(x)$  in the shape of a double layer:



Further ingredients and assumptions are needed for a quantitative analysis of the densities  $n_+(x)$ ,  $n_-(x)$  of mobile ions. However the qualitative shapes of those profiles are no mystery:



[extracted in part from Doi 2013]

## [pex57] Poly-electrolyte gel: double layer of charges at interface

Consider a gelled polymer with ionic groups immersed in a polyelectrolyte solution. We focus on a region near the interface between gel and solution. Suppose the interface is flat and the  $x$ -axis perpendicular to it with the gel at  $x < 0$  and the solution at  $x > 0$ . This setup represents an application of [pex56], somewhat generalized. The number densities of (positive) bound charges, and mobile ions have specific profiles:  $n_b(x), n_+(x), n_-(x)$ , which, in turn, determine the profile of the charge density:  $\rho_e(x) = e_0[n_b(x) + n_+(x) - n_-(x)]$ .

(a) The electric potential  $\psi(x)$  and the charge density  $\rho_e(x)$  are then related via the following 1D rendition of the Poisson equation:

$$\epsilon \frac{d^2\psi}{dx^2} = -\rho_e(x),$$

where  $\epsilon \doteq \epsilon_r \epsilon_0$  is the permittivity constant (assumed uniform). Show that this relation can be inverted as follows:

$$\psi(x) = -\frac{1}{2\epsilon} \int_{-\infty}^{+\infty} dx' |x - x'| \rho_e(x').$$

(b) Given the charge neutrality condition and the definition of the electric dipole moment,

$$\int_{-\infty}^{+\infty} dx \rho_e(x) = 0, \quad P_e = \int_{-\infty}^{+\infty} dx x \rho_e(x),$$

show that the Donnan potential,  $\Delta\psi \doteq \psi(-\infty) - \psi(+\infty)$ , is related to  $P_e$  as follows:

$$\Delta\psi = -\frac{P_e}{\epsilon}.$$

(c) Consider the model potential  $\psi(x) = c[1 - b \tanh(ax)]$  with adjustable parameters  $a, b, c$ . Infer the corresponding model charge density  $\rho_e(x)$  and plot the profiles of both functions for judicious choices of the parameters. Explain any features that have to do with double layers of charges and electric dipole moment.

[adapted from Doi 2013]

**Solution:**

## [pex10] Poly-electrolyte gel: profiles of ion densities

In order to extend part (c) of [pex57] to the density profiles  $n_{\pm}(x)$  of positive and negative mobile ions near the interface between gel and solution we must take into account the chemical equilibrium condition,

$$\mu_0 + k_B T \ln n_{\pm}(x) \pm e_0 \psi(x) = \mu_0 + k_B T \ln n_s,$$

with the assumption that far away from the bound charges of the gel we have  $n_+(x) = n_-(x) = n_s = \text{const}$  enforced by the charge neutrality condition.

(a) Show that the profiles become

$$n_{\pm}(x) = n_s e^{\mp \beta e_0 \psi(x)}.$$

(b) Plot the profiles of  $n_+(x)$  and  $n_-(x)$  over the same range of  $x$  with the same parameters as in [pex57]. Choose the values for  $n_s$ ,  $\beta e_0$ , and  $\psi(+\infty)$  judiciously.

**Solution:**

# Poisson-Boltzmann Equation for $\psi(x)$ [pln68]

What is the source of model profiles for the electric potential  $\psi(x)$  such as used in [pex57]? Consider a scenario with a given profile of bound charges,  $n_b(x)$ , and the presence of several species  $i = 1, 2, \dots$  of small, mobile ions with yet unknown profiles  $n_i(x)$  and charges  $e_i$ .

From the condition of chemical equilibrium for each species,

$$\mu_i^{(0)} + k_B T \ln n_i(x) + e_i \psi(x) = \mu_i^{(0)} + k_B T \ln n_i^{(s)}, \quad (1)$$

in slight generalization of [pex10] we infer that

$$n_i(x) = n_i^{(s)} e^{-\beta e_i \psi(x)}, \quad (2)$$

where the  $n_i^{(s)}$  are uniform ionic densities far away from the bound charges, where  $\psi(x) \rightarrow 0$ . They satisfy the charge neutrality condition,  $\sum_i e_i n_i^{(s)} = 0$ .

The charge density,

$$\rho_e(x) = e_b n_b(x) + \sum_i e_i n_i(x), \quad (3)$$

slightly generalized from [pln67], substituted into the Poisson equation (see [pln67]) with  $n_i(x)$  from (2) yields the Poisson-Boltzmann equation for the profile of the electric potential,

$$\epsilon \frac{d^2}{dx^2} \psi(x) = -e_b n_b(x) - \sum_i e_i n_i^{(s)} e^{-\beta e_i \psi(x)}, \quad (4)$$

which has a unique physical solution for given profile  $n_b(x)$ , asymptotic densities  $n_i^{(s)}$ , and boundary conditions  $\psi(+\infty) = \psi'(+\infty) = 0$ .

## Debye approximation:

The nonlinear nature of (4) puts an analytic solution out of reach. In the Debye approximation we write  $e^{-\beta e_i \psi(x)} \simeq 1 - \beta e_i \psi(x)$ , linearizing (4). The linearized Poisson-Boltzmann equation can be brought into the form

$$\frac{d^2}{dx^2} \psi(x) - \kappa^2 \psi(x) = -\frac{1}{\epsilon} e_b n_b(x), \quad \kappa^2 \doteq \frac{\beta}{\epsilon} \sum_i e_i^2 n_i^{(s)}. \quad (5)$$

[gleaned from Doi 2013]

### [pex9] Electric potential near thin layer of bound charge

Consider a thin layer of bound charge,

$$n_b(x) = n_l \delta(x), \quad (1)$$

with charge per unit area  $e_l$  immersed in a monovalent, ionic solvent with asymptotic densities  $n_{\pm}^{(0)} = n_0$ , consistent with charge neutrality. Show that the profile of the electric potential is of the exponential form,

$$\psi(x) = \frac{n_l e_l}{2\kappa\epsilon} e^{-\kappa|x|}, \quad \kappa^{-1} = \sqrt{\frac{\epsilon k_B T}{2n_0 e_0^2}}, \quad (2)$$

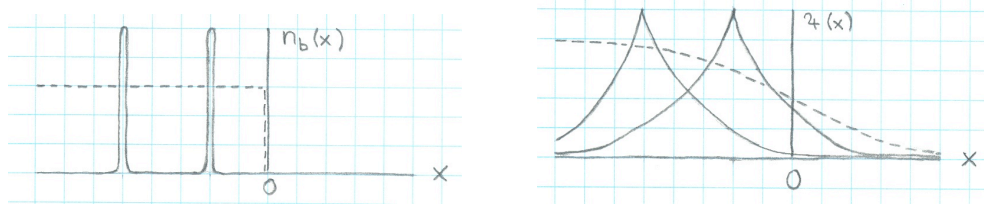
where  $\kappa^{-1}$  is the Debye screening length (see also [pex25]). The most expedient way to carry out this task is by confirmation that the function (2) is a solution of the linearized Poisson-Boltzman equation from [pln68] with  $n_b(x)$  from (1).

[adapted from Doi 2013]

**Solution:**

## [pex8] Electric potential near interface to poly-electrolyte gel I

Here we invoke the principle of superposition to construct from the solution  $\psi_l(x)$  of [pex9] for a thin layer of bound charge the solution  $\psi_c(x)$  for a semi-infinite poly-electrolyte gel with a uniform density of bound charge and a flat interface at  $x = 0$ . The superposition principle is exact for any linear ODE. Here we use it for the linearized Poisson-Boltzmann equation.



The sketch shows (on the left) how we build up the bound charge from thin layers and (on the right) the potential for the continuum from the exponentially decaying potentials of thin layers. Carry out the integral below to find

$$\sum_{x_i < 0} \psi_l(x_i) \rightarrow \psi_c(x) = \int_{-\infty}^0 dx' \psi_l(x - x') = \frac{e_l n_l}{2\kappa^2 \epsilon} [e^{-\kappa x} \theta(x) + (2 - e^{\kappa x}) \theta(-x)].$$

The associated bound-charge density,

$$\sum_{x_i < 0} n_l \delta(x_i) \rightarrow n_b(x) = n_l \theta(-x),$$

will be confirmed in [pex7].

**Solution:**



## [pex7] Electric potential near interface to poly-electrolyte gel II

(a) Take the potential  $\psi_c(x)$  worked out in [pex8] via the superposition principle from the potential  $\psi_l(x)$  worked out in [pex9] and substitute it into the linearized Poisson-Boltzmann equation from [pln68] to show that the associated distribution of bound charges is

$$n_b(x) = n_l \theta(-x).$$

(b) In [pex57] we have used a model potential  $\psi_m(x) = c[1 - b \tanh(ax)]$  to describe the same situation. Find the optimized model parameters  $a, b, c$  in  $\psi_m(x)$  that best represent the potential  $\psi_c(x)$  found in [pex8]. Plot the two functions in the same graph using suitably scaled variables.

**Solution:**

## Solution of P.-B. Eq. via Fourier Transform [pln69]

For certain distributions of bound charges,  $n_b(x)$ , it is convenient to solve the linearized Poisson-Boltzmann equation from [pln68],

$$\frac{d^2}{dx^2}\psi(x) - \kappa^2\psi(x) = -\frac{e_b}{\epsilon}n_b(x), \quad \kappa^2 \doteq \frac{\beta}{\epsilon} \sum_i e_i^2 n_i^{(s)}, \quad (1)$$

via Fourier transform.<sup>1</sup>

Fourier transforms of electric potential and distribution of bound charge:

$$\bar{\psi}(k) \doteq \int_{-\infty}^{+\infty} dx e^{ikx} \psi(x), \quad \bar{n}_b(k) \doteq \int_{-\infty}^{+\infty} dx e^{ikx} n_b(x). \quad (2)$$

Solution of (1) in reciprocal space:

$$\bar{\psi}(k) = \frac{e_b}{\epsilon} \frac{\bar{n}_b(k)}{k^2 + \kappa^2}. \quad (3)$$

One application, worked out in [pex6], considers a layer of bound charge with exponential profile of variable thickness. In the limit of a very thin layer, the result of [pex9] arrived at via a different method, can thus be reproduced.

Solution of Poisson equation for charge density  $\rho_e(x)$  from [pln67] via Fourier transform:

$$\bar{\rho}_e(k) = \epsilon k^2 \bar{\psi}(k) = e_b n_b(k) \frac{k^2}{k^2 + \kappa^2} \xrightarrow{|k|/\kappa \rightarrow 0} 0. \quad (4)$$

Charge neutrality is satisfied at sufficiently long wavelengths. The characteristic length scale on which charge neutrality becomes accurate is the Debye screening length  $\kappa^{-1}$ .

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<sup>1</sup>This method also works when the quantities of interest vary in more than one spatial direction.

### [pex6] Layer of bound charge of exponential profile and variable thickness

Consider a layer of bound charges (as realized in a poly-electrolyte gel) with exponential profile,

$$n_b(x) = \frac{n_l}{2a} e^{-|x|/a},$$

immersed in an ionic solvent. The width of the layer is controlled by the parameter  $a$ .

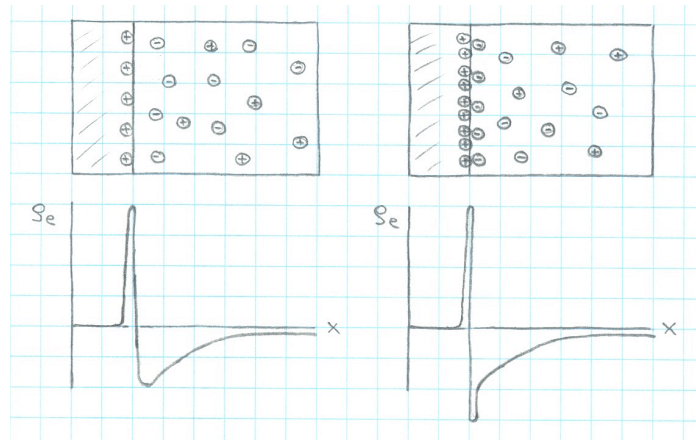
- (a) Solve the linearized Poisson-Boltzmann equation via Fourier transform as described in [pln69].
- (b) Show that in the limit  $a \rightarrow 0$  the result of [pex9] emerges.
- (c) Plot  $n_b(x)$  and  $\psi(x)$  versus  $x$  for the cases  $a = 1.5, 0.5, 0.1, 0.0001$  (four curves each in two frames). Set  $e_b, \epsilon, \kappa, n_l$  all equal to unity for the purpose of graphical representation.

**Solution:**

# Ion Densities Near Charged Surface [p1n70]

Consider the plane interface between a solid with surface charge and a liquid with dissociated molecules. The (positive) surface charge causes an accumulation of counter-ions and a deficiency of co-ions in the vicinity.

The profile of the resulting charge density near the interface is sketched below for the cases of a weakly charged (left) and a strongly charged (right) surface.



## Analysis for weakly charged surface:

- surface charge density:  $\sigma$ ,
- ionic density in bulk:  $n_0$ ,
- monovalent ionic charge:  $e_0$ ,
- dielectric constant:  $\epsilon$ ,
- electric field near (conducting) surface:  $E = \sigma/\epsilon$ ,
- Debye screening length:  $\kappa^{-1} = \sqrt{\epsilon k_B T / 2n_0 e_0^2}$ .

Poisson equation in liquid (at  $x > 0$ ):  $\frac{d^2}{dx^2}\psi(x) - \kappa^2\psi(x) = 0$ .

One-parameter solution:  $\psi(x) = \psi(0) e^{-\kappa x}$ .

Boundary condition:  $\psi'(0) = -\kappa\psi(0) = -E = -\frac{\sigma}{\epsilon}$ .

Physically relevant solution:  $\psi(x) = \frac{\sigma}{\epsilon\kappa} e^{-\kappa x}$ .

Ion densities:  $n_{\pm}(x) = n_0 \exp\left(\mp \frac{e_0\psi(x)}{k_B T}\right)$  (from [p1n68]).

Charge density:  $\rho_e(x) = e_0[n_+(x) - n_-(x)]$ .

[extracted from Doi 2013]

# Electric Force Between Charged Plates I [pln71]

## Parallel plates in vacuum:

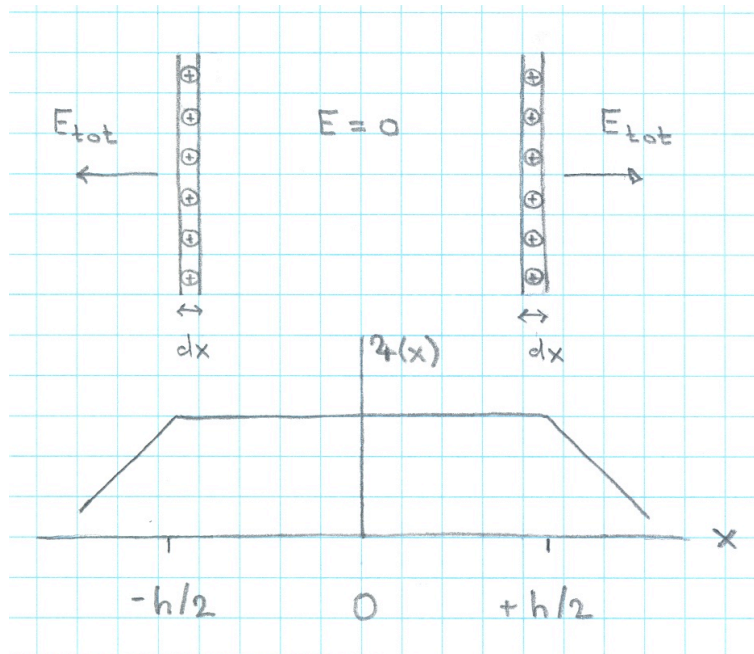
Consider two parallel plates of infinitesimal thickness  $dx$  and equal (positive) charge per unit area  $\sigma = \rho dx$  on them. The plates are positioned at a distance  $h$  from each other as shown.

Each plate generates a uniform electric field  $E_p = \sigma/2\epsilon_0$  pointing away from it. This ignores perimeter effects. The total field then vanishes between the plates. On the outside, the field is uniform with magnitude  $E_{tot} = \sigma/\epsilon_0$  and pointing away.

The electric potential  $\psi(x)$  is constant between the plates and descends from that values on the outside at the rate  $|d\psi/dx| = |E_{tot}| = \sigma/\epsilon_0$ .

The force between the plates is repulsive and independent of distance. Its magnitude per area is determined as follows:

$$f \doteq \frac{F}{A} = \sigma E_p = \frac{\sigma^2}{2\epsilon_0} = -\frac{\epsilon_0}{2} \left( \frac{d\psi}{dx} \right)_{-h/2} \left( \frac{d\psi}{dx} \right)_{+h/2}.$$



[adapted from Doi 2013]

## Electric Force Between Charged Plates II [pln72]

### Parallel plates immersed in electrolyte solution:

The number densities of  $n_{\pm}(x)$  of mobile ions assume equal values  $n_0$  far away from the plates, thus satisfying charge neutrality.

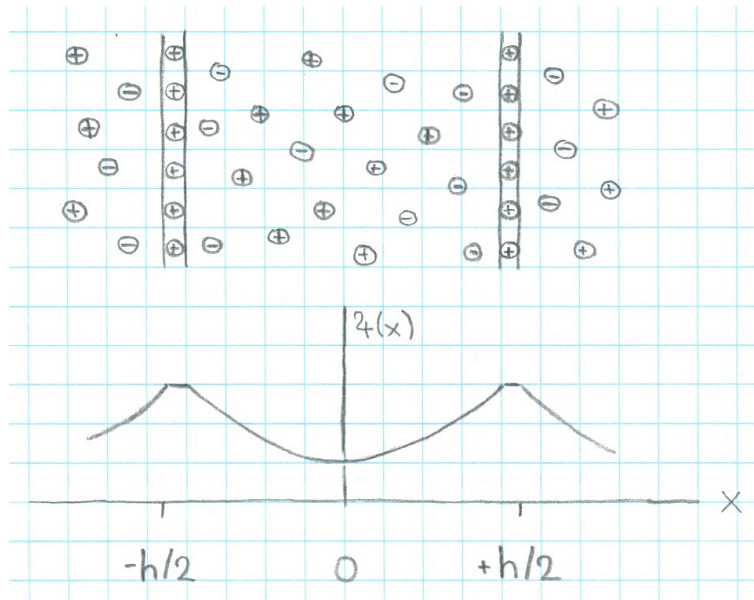
In the region  $-h/2 < x < +h/2$  the counter-ions are being pulled toward one or the other plate whereas the co-ions are being pushed away from either plate and, in part, out of the region between the plates. The electric field  $E(x)$  between the plates is directed inward with decreasing strength toward the center ( $x = 0$ ), where it vanishes.

The electric potential  $\psi(x)$  assumes reflection-symmetric profile as sketched. The charge density  $\rho_e(x)$  is related to the potential  $\psi(x)$  via the Poisson equation,

$$\frac{d^2\psi}{dx^2} = -\frac{1}{\epsilon} \rho_e(x), \quad (1)$$

making it negative throughout the region but more so near the plates than at the center.

The presence of the electrolyte has the effect of weakening the repulsive force between the plates as analyzed in the following.



The force per unit area has an electrostatic contribution and an osmotic contribution:  $f = f_{el} + f_{os}$ .

The *osmotic force* (per unit area) is caused by the inhomogeneous ionic densities in the region between the plates:

$$f_{\text{os}}(x) = \Delta\pi(x) = k_{\text{B}}T \sum_{\pm} \Delta n_{\pm}(x), \quad \Delta n_{\pm}(x) = n_0 [e^{\mp\beta e_0\psi(x)} - 1]. \quad (2)$$

The *electrostatic force* (per unit area) is calculated as the Coulomb force between charges to the left and to the right of a fictitious plane at position  $x$  between the plates. We use the same strategy as in [pln71] for plates with charge densities  $\sigma = \rho dx$ :

$$\begin{aligned} f_{\text{el}}(x) &= \frac{1}{2\epsilon} \int_{-h/2}^x dx_1 \rho_e(x_1) \int_x^{+h/2} dx_2 \rho(x_2) \\ &= \frac{\epsilon}{2} \int_{-h/2}^x dx_1 \frac{d^2\psi}{dx_1^2} \int_x^{+h/2} dx_2 \frac{d^2\psi}{dx_2^2} = -\frac{\epsilon}{2} \left( \frac{d\psi}{dx} \right)^2 + \text{const.} \end{aligned} \quad (3)$$

The total force,

$$f = f_{\text{os}}(x) + f_{\text{el}}(x) = k_{\text{B}}T \sum_{\pm} \Delta n_{\pm}(x) - \frac{\epsilon}{2} \left( \frac{d\psi}{dx} \right)^2, \quad (4)$$

is independent of  $x$ ,  $df/dx = 0$ , by virtue of the fact that the potential  $\psi(x)$  must satisfy the Poisson-Boltzmann equation,

$$\epsilon \frac{d^2\psi}{dx^2} = -e_0 [n_+(x) - n_-(x)], \quad n_{\pm}(x) = n_0 e^{\mp\beta e_0\psi(x)}. \quad (5)$$

The force  $f$  is thus most conveniently calculated for  $x = 0$  where  $d\psi/dx = 0$  for symmetry reason. Here we have

$$f_{\text{int}} \doteq f(0) = k_{\text{B}}T n_0 [e^{-\beta e_0\psi(0)} + e^{\beta e_0\psi(0)} - 2]. \quad (6)$$

We find the potential  $\psi(x)$  via the linearized Poisson-Boltzmann equation,

$$\frac{d^2\psi}{dx^2} - \kappa^2\psi = 0, \quad \kappa^2 = \frac{2e_0^2 n_0}{k_{\text{B}}T\epsilon}, \quad (7)$$

with the physical boundary conditions,

$$\left. \frac{d\psi}{dx} \right|_{\pm h/2} = \pm \frac{\sigma}{\epsilon}, \quad (8)$$

where  $\sigma$  is the charge density on each plate.

Resulting (symmetric) profile of electric potential between the plates:

$$\psi(x) = \frac{\cosh(\kappa x)}{\epsilon \kappa \sinh(\kappa h/2)}. \quad (9)$$

Substitution of (9) into (6) with the exponential expanded yields

$$f_{int} = \frac{1}{2} \epsilon \kappa^2 [\psi(0)]^2 = \frac{\sigma^2}{2\epsilon \sinh^2(\kappa h/2)}. \quad (10)$$

With plate separation  $h$  increasing, the force  $f_{int}$  weakens exponentially fast on the scale of the Debye screening length  $\kappa^{-1}$ .

[adapted from Doi 2013]



# Electric Force Between Charged Plates III [pln78]

## Parallel plates with unequal charge densities:

For this generalization of [pln72] we change the coordinate system as shown. We are looking for a solution of the linearized Poisson-Boltzmann equation,

$$\frac{d^2\psi}{dx^2} - \kappa^2\psi = 0, \quad \kappa^2 = \frac{2e_0^2 n_0}{k_B T \epsilon}, \quad (1)$$

with boundary conditions  $\psi(0) = \psi_A$ ,  $\psi(h) = \psi_B$ . These boundary values are related to the charge densities on the plates via Gauss' law:  $\psi'(0) = -\sigma_A/\epsilon$ ,  $\psi'(h) = \sigma_B/\epsilon$ . The solution as worked out in [pex4] reads

$$\psi(x) = \frac{\psi_A \sinh(\kappa h - \kappa x) + \psi_B \sinh(\kappa x)}{\sinh(\kappa h)}, \quad (2)$$

with

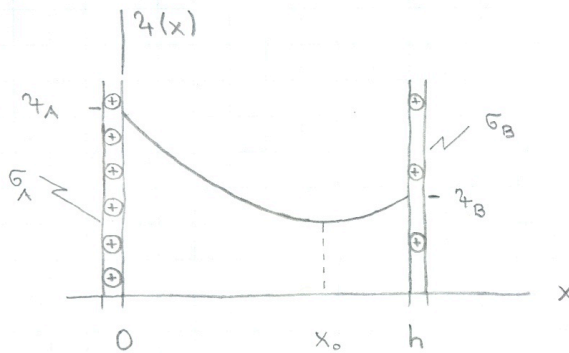
$$\psi_A = \frac{\sigma_A \cosh(\kappa h) + \sigma_B}{\kappa \epsilon \sinh(\kappa h)}, \quad \psi_B = \frac{\sigma_B \cosh(\kappa h) + \sigma_A}{\kappa \epsilon \sinh(\kappa h)}. \quad (3)$$

In generalization of [pln72] we obtain for the (repulsive) interaction force (per unit area) between the plates the expression

$$f_{\text{int}} = \frac{1}{2} \epsilon \kappa^2 [\psi(x_0)]^2, \quad \left. \frac{d\psi}{dx} \right|_{x_0} = 0. \quad (4)$$

This expression is evaluated in [pex3] and reads<sup>1</sup>

$$f_{\text{int}} = \frac{1}{2} \epsilon \kappa^2 \frac{2\psi_A \psi_B \cosh(\kappa h) - \psi_A^2 - \psi_B^2}{\sinh^2(\kappa h)}. \quad (5)$$



[adapted from Doi 2013]

<sup>1</sup>Positive charge densities,  $\sigma_A \geq \sigma_B > 0$  constrain this expression to be positive. Hence the force will always be repulsive albeit weakened by the electrolyte.

[pex4] Electric potential between charged plates immersed in electrolyte

Consider two conducting plates with uniform charge densities  $\sigma_A$  and  $\sigma_B$  positioned as shown.

(a) Solve the linearized Poisson-Boltzmann equation,

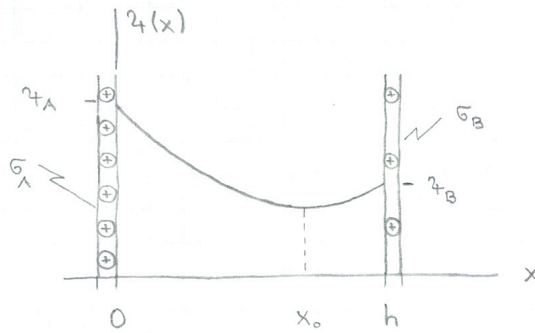
$$\frac{d^2\psi}{dx^2} - \kappa^2\psi = 0 \quad \kappa^2 = \frac{2e_0^2 n_0}{k_B T \epsilon}, \quad (1)$$

with boundary conditions  $\psi(0) = \psi_A$ ,  $\psi(h) = \psi_B$ , using the ansatz  $\psi(x) = ae^{-\kappa x} + be^{\kappa x}$ .

(b) Use Gauss' law,

$$\psi'(0) = -\frac{\sigma_A}{\epsilon}, \quad \psi'(h) = \frac{\sigma_B}{\epsilon}, \quad (2)$$

to express the boundary values of  $\psi_A, \psi_B$  of the potential in terms of the charge densities  $\sigma_A, \sigma_B$  on the plates and the distance  $h$  between the plates. The results of both parts are stated in [pln78].



[adapted from Doi 2013]

**Solution:**

**[pex3] Electric force between charged plates immersed in electrolyte**

Consider two conducting plates with uniform charge densities  $\sigma_A$  and  $\sigma_B$  positioned as shown.

(a) Show that the electric potential as calculated in [pex4] has a minimum at position  $x_0$ , where

$$\tanh(\kappa x_0) = \frac{\psi_A \cosh(\kappa h) - \psi_B}{\psi_A \sinh(\kappa h)}. \quad (1)$$

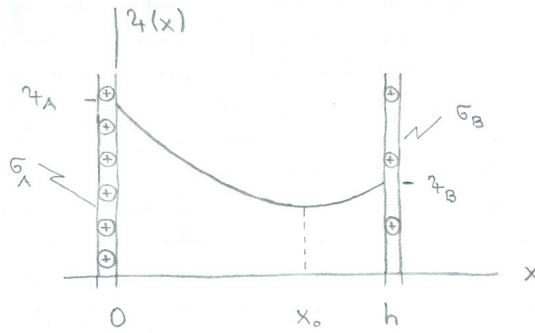
(b) Calculate the interaction force (per unit area) between the plates, using the relation,

$$f_{\text{int}} = \frac{1}{2} \epsilon \kappa^2 [\psi(x_0)]^2, \quad \left. \frac{d\psi}{dx} \right|_{x_0} = 0, \quad (2)$$

justified in [pln78], arriving at the result

$$f_{\text{int}} = \frac{1}{2} \epsilon \kappa^2 \frac{2\psi_A \psi_B \cosh(\kappa h) - \psi_A^2 - \psi_B^2}{\sinh^2(\kappa h)}. \quad (3)$$

with the dependence of  $\psi_A, \psi_B$  on  $\sigma_A, \sigma_B$  as determined in [pex4] and stated in [pln78].



[adapted from Doi 2013]

**Solution:**