Electrostatics light: vacuum ($\varepsilon = \varepsilon_0$)

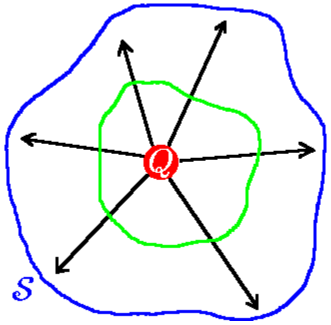
Force to charge q caused by charge Q: $\vec F = \dfrac{1}{4\pi\varepsilon_0}\dfrac{qQ}{r^2}\dfrac{\vec r}{r}$

Field intensity: $\vec{\mathcal{E}} = \dfrac{\vec F}{q} = \dfrac{1}{4\pi\varepsilon_0}\dfrac{Q}{r^2}\dfrac{\vec r}{r}$

El. potential: $\phi = \dfrac{1}{4\pi\varepsilon_0}\dfrac{Q}{r}$, it holds $\vec\nabla\phi \equiv \dfrac{\partial}{\partial\vec r}\phi \equiv \mathrm{grad}\,\phi \equiv \left(\dfrac{\partial}{\partial x}, \dfrac{\partial}{\partial y}, \dfrac{\partial}{\partial z}\right)\phi = -\vec{\mathcal{E}}$

Electric flux through an r-sphere: $\displaystyle\int_{\text{sphere}} \vec{\mathcal{E}}\cdot\mathrm{d}\vec s = \frac{Q}{\varepsilon_0}$

The number of field lines is conserved
($\int$ does not depend on r nor surface direction)

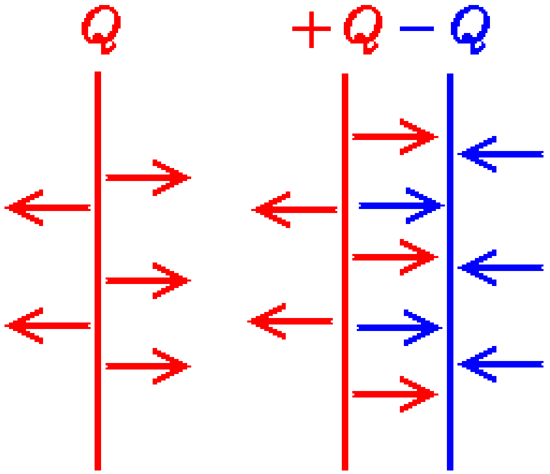


⇒ for charge **inside** surface S it holds: $\displaystyle\frac{Q}{\varepsilon_0} = \oint_S \vec{\mathcal{E}}\cdot\mathrm{d}\vec s$

Field intensity close to a capacitor: $\mathcal{E} = \dfrac{Q}{2\varepsilon_0\mathcal{A}}$

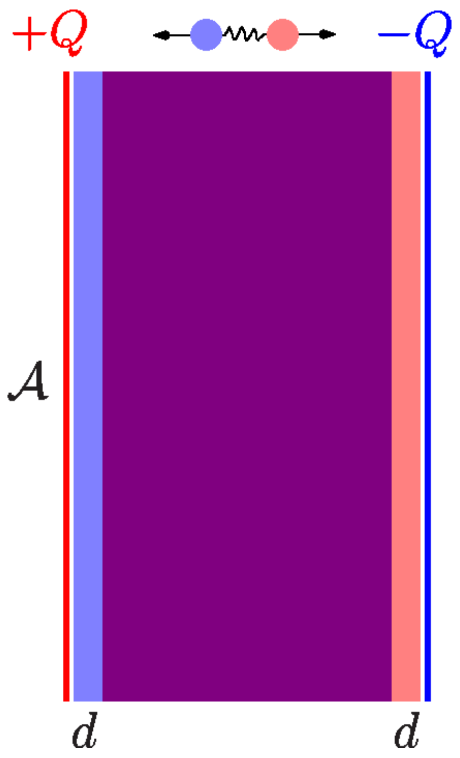
Field intensity between plates: $\mathcal{E} = \dfrac{Q}{\varepsilon_0\mathcal{A}}$

($\mathcal{A}$ = plate area, $S = 2\mathcal{A}$)



Electrostatics light: dielectrics

Dielectric = "positive charge (density $+\rho$) + negative charge ($-\rho$)"



In a field in capacitor $Q_\oplus || -Q$ charges displaced by d

The *screening charge* left is $-Q_\text{s}$, right $+Q_\text{s}$, $Q_\text{s} = d\mathcal{A}\rho$

Effective charge reduced by $1/\varepsilon_\text{r}$ (= *definition* of ε_r):

$$Q - Q_\text{s} = Q/\varepsilon_\text{r} \qquad \text{(screening charge} = -Q_\text{s},\ Q_\text{s} > 0)$$

The field intensity (∝ force) is reduced in the same ratio:

$$\mathcal{E} = \frac{Q}{\mathcal{A}\varepsilon_\text{r}\varepsilon_0} = \frac{Q}{\mathcal{A}\varepsilon} \qquad (\text{def. } \varepsilon = \varepsilon_\text{r}\varepsilon_0)$$

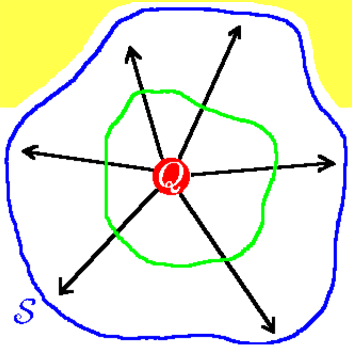
Volume density of the dipole moment (= *polarisation*) in V is $(V\rho d)/V = \rho d = P$. Total:

$$Q_\text{s} = d\mathcal{A}\rho = \mathcal{A}P = Q - \frac{Q}{\varepsilon_\text{r}}, \quad \text{i.e. } Q = \frac{Q}{\varepsilon_\text{r}} + Q_\text{s} = \frac{Q}{\varepsilon_\text{r}} + \mathcal{A}P$$

divide by $\mathcal{A}$, ⇒ *define* el. displacement: $D \equiv \frac{Q}{\mathcal{A}} = \frac{Q}{\mathcal{A}\varepsilon_\text{r}} + P = \varepsilon_0\mathcal{E} + P$

Capacitance: $C = \frac{Q}{\phi} = \frac{\mathcal{A}D}{\phi} = \frac{\mathcal{A}\epsilon\mathcal{E}}{\phi} = \frac{\mathcal{A}\epsilon}{\text{distance of plates}}$

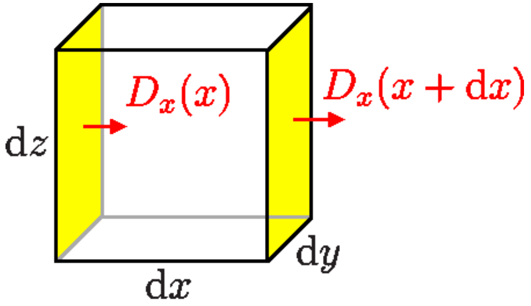
Poisson equation



"Number of displacement lines" (flux) is conserved:

$$Q = \oint_{\mathcal{S}} \vec{D} \cdot \mathrm{d}\vec{s}, \quad \vec{D} = \epsilon \vec{\mathcal{E}}$$

Let $\mathcal{S}$ = cube $\mathrm{d}x \times \mathrm{d}y \times \mathrm{d}z$:



$$\begin{aligned}\mathrm{d}Q = \mathrm{d}V\rho = \oint_S \vec{D} \cdot \mathrm{d}\vec{s} &= \mathrm{d}y\mathrm{d}z[D_x(x+\mathrm{d}x) - D_x(x)] \\ &+ \mathrm{d}x\mathrm{d}z[D_y(y+\mathrm{d}y) - D_y(y)] \\ &+ \mathrm{d}x\mathrm{d}y[D_z(z+\mathrm{d}z) - D_z(z)]\end{aligned}$$

$$= \mathrm{d}x\mathrm{d}y\mathrm{d}z\left(\frac{\partial D_x}{\partial x} + \frac{\partial D_y}{\partial y} + \frac{\partial D_z}{\partial z}\right) = -\mathrm{d}V\epsilon\left(\frac{\partial^2\phi}{\partial x^2} + \frac{\partial^2\phi}{\partial y^2} + \frac{\partial^2\phi}{\partial z^2}\right)$$

where $\rho = \mathrm{d}q/\mathrm{d}V$ = charge density and the permittivity is constant.

Laplace operator: $\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) \equiv \nabla^2 \equiv \Delta$

here we will not use symbol Δ not to confuse with $\Delta\phi = \phi^{\text{right}} - \phi^{\text{left}}$

Poisson equation: $\boxed{\nabla^2\phi = -\frac{\rho}{\epsilon}}$ or in 1D $\frac{\mathrm{d}^2\phi}{\mathrm{d}x^2} = -\frac{\rho}{\epsilon}$

Electric double layer

Different affinities of ions to an interface s or g / ionic solution ⇒ **surface charge**:

- ionisation (dissociation/protonization) of groups
  (-COOH → ⊖, -NH_2 → ⊕)
- preferential disolution or adsorption of ions (AgCl in ⊙ NaCl → ⊖)
  Paneth–Fajans[–Hahn] rule:
  Ions are adsorbed at a surface if they make an insoluble crystal with the co-ion
- preferential adsorption of a surfactant (soap on water is negative)
- isomorfic substitution (Al^{3+}/Si^{4+} at clay)
- crystal cleaving

Question: what happens in the solution?

Electric double layer: Not this way!

Let's have ⊙ NaCl between electrodes (plates). El. field intensity = $\mathcal{E}$.
Ions do not interact with the plates.
Concentration of Na^+ a Cl^- between the plates?

Naïve solution:

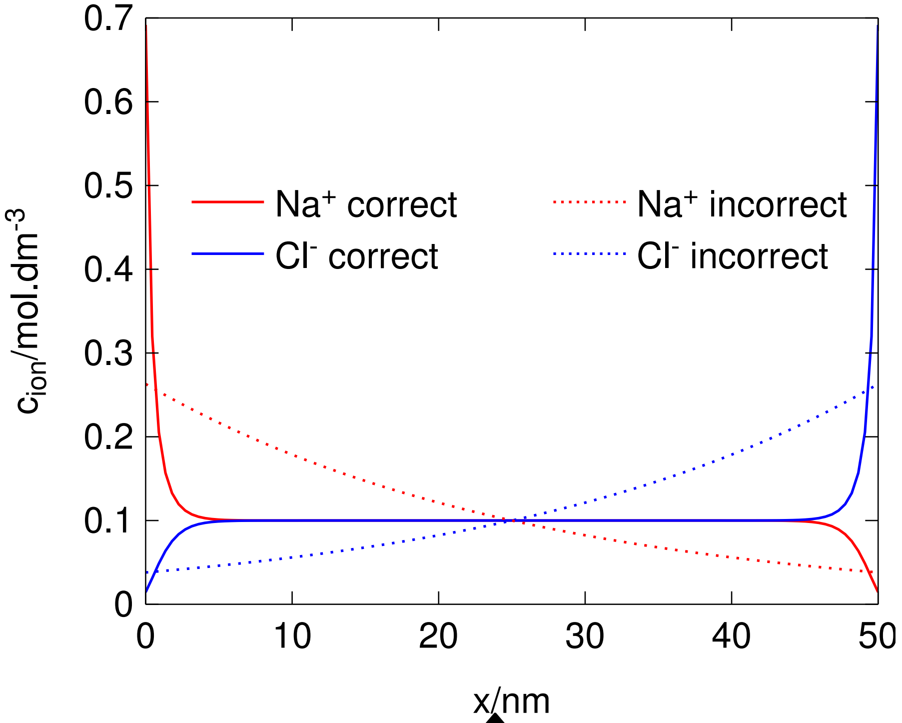
~~elst. potential = $\phi(x) = \mathcal{E}x$~~

~~cation pot. energy = $e\phi(x)$~~
~~probability:~~

~~$$\exp[-e\phi(x)/k_BT] = \exp(-e\mathcal{E}x/k_BT)$$~~

~~anion pot. energy = $-e\phi(x)$~~
~~probability:~~

~~$$\exp[-e\phi(x)/k_BT] = \exp(e\mathcal{E}x/k_BT)$$~~



Example. 0.1 M ⊙ NaCl, plate distance = 50 nm, voltage = 50 mV ↑

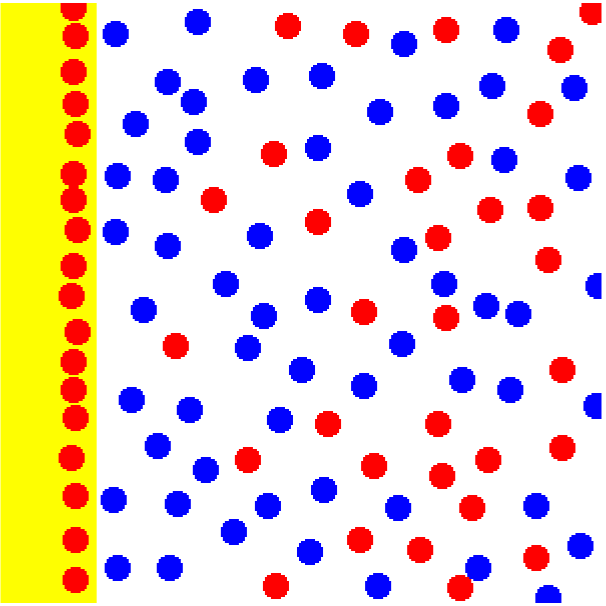
Neutral (zero potential) in the middle

1 eV = 96 485 J/mol

— : correct

····· : the naïve solution is in disagreement with the electroneutrality of the bulk

Diffuse layer: Gouy-Chapman



- el. potential in the bulk is $\phi(\infty) = 0$
- el. potential at the electrode is ϕ_0
  (now we do not care about its origin)
- ions = charged points, electrode = hard wall
- no interaction/adsorption of ions at the electrode
- ion concentrations replaced by an averaged charge density (no ion-ion correlation)
- solvent is a dielectric continuum (permittivity = $\varepsilon = \varepsilon_r \varepsilon_0$)
- simplification: 1:1 salt (NaCl) at concentration c

Poisson equation: $\dfrac{d^2\phi}{dx^2} = -\dfrac{\rho}{\varepsilon}$

Charge density: $\rho = \sum_i z_i \rho_i = \rho_+ - \rho_-$, where

$$\rho_+ = cF \exp\left[-\frac{\phi(x)e}{k_B T}\right] \qquad \rho_- = cF \exp\left[\frac{\phi(x)e}{k_B T}\right]$$

Poisson–Boltzmann equation for the potential: $\dfrac{d^2\phi}{dx^2} = \dfrac{cF}{\varepsilon}\left[e^{\phi e/k_B T} - e^{-\phi e/k_B T}\right]$

Diffuse layer: Gouy-Chapman

The Poisson–Boltzmann equation:

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}x^2} = \frac{cF}{\varepsilon}\left[\mathrm{e}^{\phi e/k_\mathrm{B}T} - \mathrm{e}^{-\phi e/k_\mathrm{B}T}\right], \quad \phi(0) = \phi_0,\ \phi(\infty) = 0$$

- Linearisation = approximate solution for weak potentials ($\phi e/k_\mathrm{B}T \ll 1$, tj. $\phi \ll 26$ mV for $298\,\mathrm{K}$):

$$\exp(x) \approx 1 + x \quad \Rightarrow \quad \frac{\mathrm{d}^2\phi}{\mathrm{d}x^2} = \frac{2cF}{\varepsilon}\frac{\phi e}{k_\mathrm{B}T} \quad \Rightarrow \quad \phi = \phi_0\mathrm{e}^{-x/\lambda}$$

$$\lambda = \sqrt{\frac{\varepsilon k_\mathrm{B}T}{2cFe}} = \sqrt{\frac{\varepsilon RT}{2cF^2}} = \textbf{Debye screening length} \quad \text{mixture: } \lambda = \sqrt{\frac{\varepsilon RT}{2I_cF^2}}$$

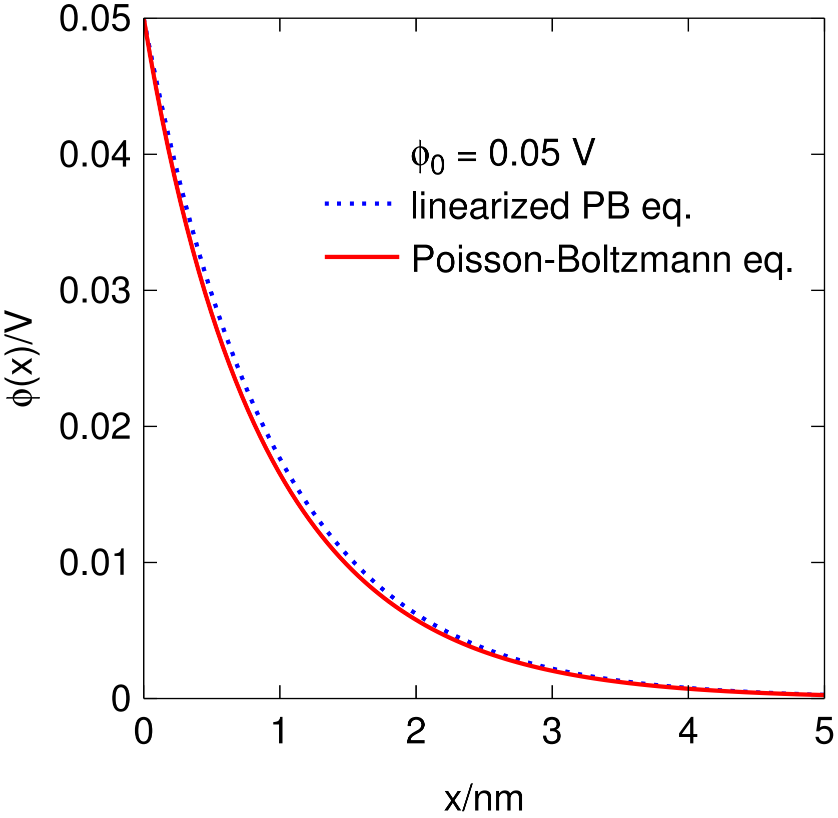
Example. NaCl in water, $c = 0.1\,\mathrm{mol\,dm^{-3}}$, $25\,°\mathrm{C} \Rightarrow \lambda = 0.96$ nm
($\varepsilon = \varepsilon_\mathrm{r}\varepsilon_0$, $\varepsilon_\mathrm{r} = 78.4$, $\varepsilon_0 = 8.854\times10^{-12}\,\mathrm{F\,m^{-1}}$)

For comparison:

- averaged O–O separation in water = 0.28 nm $\Rightarrow$ 120 $\mathrm{H_2O}$ in a λ-sphere
- Bjerrum length : $\lambda_\mathrm{B} = \dfrac{e^2}{4\pi\epsilon k_\mathrm{B}T} \overset{\text{water}}{\approx} 0.7\,\mathrm{nm}$ (energy of a pair of univalent ions = $k_\mathrm{B}T$)

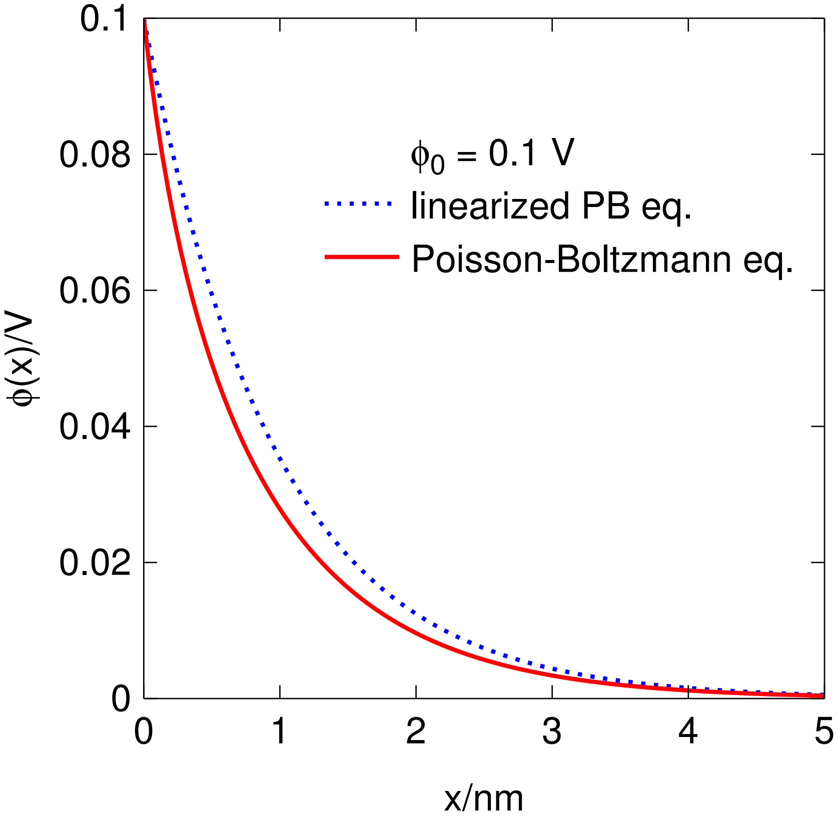
Diffuse layer: Gouy-Chapman

$\phi_0 = 50$ mV



1:1 electrolyte, $c = 0.1\,\mathrm{mol\,dm^{-3}}$

$\phi_0 = 100$ mV



The potential as a function of the distance from a charged surface decays exponentially as a consequence of screening (by counterions)

Called **diffuse layer**, because can be explained by an equilibrium between diffusion and attraction to a charged surface

Electric double layer

Charged surface attracts **counterions**.

Gouy-Chapman

charged surface

diffusion layer gradually screens the charge

neutral solution

Helmholtz

charged surface

adsorbed counterions screen the total charge

neutral solution

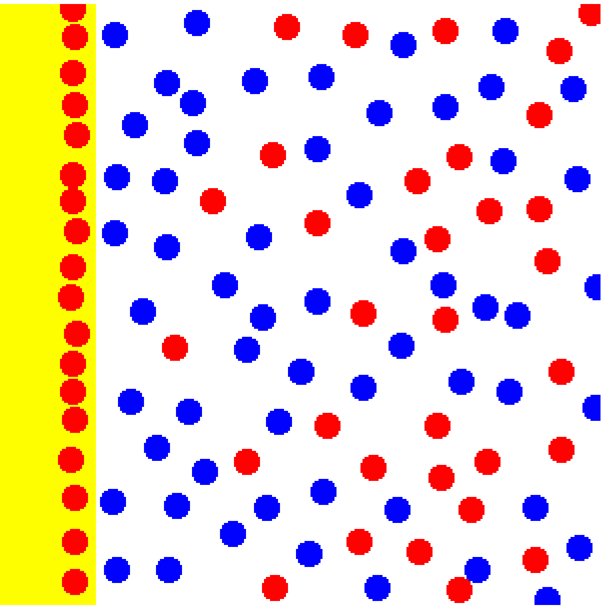
Stern

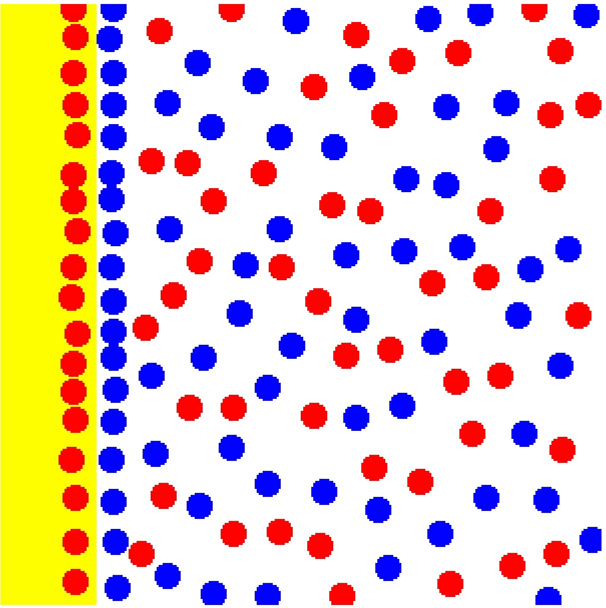
charged surface

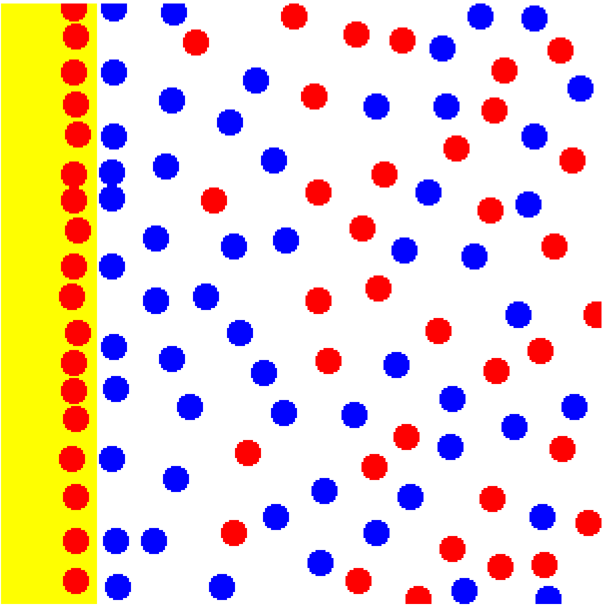
adsorbed counterions screen a portion of the charge

the diffusion layer gradually screens the rest

neutral solution







Surface charge

(surface charge) = − (charge of the Gouy–Chapman layer)

$$\sigma = -\int_0^\infty (\rho_+ - \rho_-)\mathrm{d}x = -\int_0^\infty cF\left\{\exp\left[-\frac{\phi(x)e}{k_\mathrm{B}T}\right] - \exp\left[\frac{\phi(x)e}{k_\mathrm{B}T}\right]\right\}\mathrm{d}x$$

Using the linearized theory, $\exp(x) \approx 1 + x$, because $\phi(x)e/k_\mathrm{B}T \ll 1$

$$\sigma \approx \int_0^\infty 2cF\frac{\phi(x)e}{k_\mathrm{B}T}\mathrm{d}x = 2\lambda cF\phi_0\frac{e}{k_\mathrm{B}T} = \frac{\varepsilon}{\lambda}\phi_0 \tag{1}$$

Capacitance of the Gouy–Chapman double layer (as a capacitor):

$$\frac{C}{\mathcal{A}} = \frac{\sigma}{\phi_0} = \frac{\varepsilon}{\lambda}$$

Usually the differential capacitance is measured, $\mathrm{d}\sigma/\mathrm{d}\phi$, because $\sigma \not\propto \phi$

Example. A molecule of soap covers about $a = 0.2\,\mathrm{nm}^2$. Counterions on average $\lambda = 1$ nm apart in a 0.1 M solution.

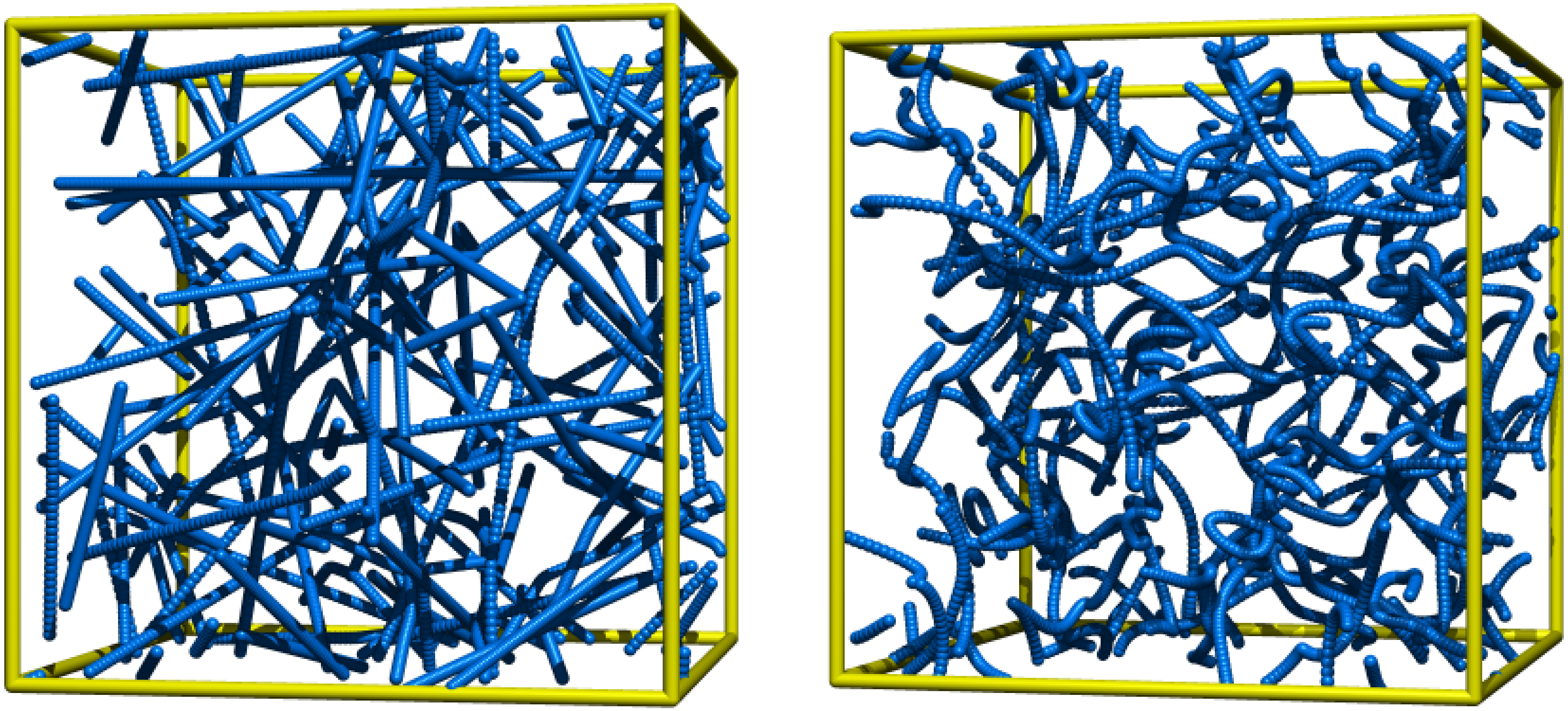
a) What is the surface charge?
b) What is the capacitance (per m^2)? ($\varepsilon_\mathrm{r} = 78.$)
c) What is the potential of the surface?

a) $-0.8\,\mathrm{C\,m^{-2}}$, b) $0.7\,\mathrm{F\,m^{-2}}$, c) -1.1 V (really less)

Ions

Plasma, electrolyte solutions:

- charge–charge interaction decays slowly ($u \propto 1/r$)
- non-ideal behavior
- there is no B_2



helium T=300 K helium T=10 000 K

Debye–Hückel theory of electrolyte solutions

Simplifications:

- solvent = homogeneous dielectric continuum
- ions (several kinds of) = charged hard spheres of diameter σ; other than electric interactions neglected)
- distribution of ions described in terms of charged density (or probability of finding an ion); ion–ion correlations neglected
- it holds $ze\phi \ll k_\mathrm{B}T$ – for “most ions”
  – for 1:1 $c < 0.1\,\mathrm{mol\,dm^{-3}}$ needed
  – for $|z| > 1$ even more dilute solutions needed

Ionic strength:

$$I_c = \frac{1}{2}\sum_i z_i^2 c_i$$

often using molality: $I = \frac{1}{2}\sum_i z_i^2 \underline{m}_i$

the sum is over all ions in the solution

Debye–Hückel theory of electrolyte solutions

Results (screened Coulomb or Yukawa potential):

screening

$$\phi(r) = \frac{1}{4\pi\varepsilon}\frac{ze}{r} \qquad \rightarrow \qquad \phi(r) = \frac{1}{4\pi\varepsilon}\frac{ze}{r}\exp(-r/\lambda)$$

Debye (screening) length (radius of the ionic atmosphere):

$$\lambda = \sqrt{\frac{\varepsilon RT}{2I_\mathrm{c}F^2}} \qquad (\approx 1\,\mathrm{nm} \text{ for } 1{:}1,\ c = 0.1\,\mathrm{mol\,dm^{-3}})$$

Activity coefficients of ions:

$$\boxed{\ln\gamma_i = -Az_i^2\frac{\sqrt{I_\mathrm{c}}}{1+a\sqrt{I_\mathrm{c}}}} \overset{\sigma=0}{\approx} -Az_i^2\sqrt{I_\mathrm{c}}$$

point charges
(limiting law)

$$A = \frac{e^3N_\mathrm{A}^2\sqrt{2}}{8\pi(\varepsilon RT)^{3/2}} \qquad (= 1.176\,\mathrm{dm^{3/2}\,mol^{-1/2}} \text{ for water } 25\,°\mathrm{C})$$

$$a = \sqrt{\frac{2F^2}{\varepsilon RT}}\,\sigma \qquad (\doteq 1\,\mathrm{dm^{3/2}\,mol^{-1/2}} \text{ pro } \sigma = 0.3\,\mathrm{nm})$$

- Applicability to $\sim I_\mathrm{c} = 0.1\,\mathrm{mol\,dm^{-3}}$ (univalent); bivalent etc. are problematic

Strong electrolyte solution

$$\mathrm{Al_2(SO_4)_3} \;\rightarrow\; 2\,\mathrm{Al}^{3+} + 3\,\mathrm{SO}_4^{2-}$$

In general:

$$\mathrm{C}_{\boldsymbol{\nu}_\oplus}\mathrm{A}_{\boldsymbol{\nu}_\ominus} \;\rightarrow\; \boldsymbol{\nu}_\oplus \mathrm{C}^{z_\oplus +} + \boldsymbol{\nu}_\ominus \mathrm{A}^{z_\ominus -}$$

Electroneutrality ($z_\oplus > 0$, $z_\ominus > 0$):

$$\boldsymbol{\nu}_\oplus z_\oplus = \boldsymbol{\nu}_\ominus z_\ominus$$

⇒ $\gamma_\oplus$ a $\gamma_\ominus$ cannot be determined by classical electrochemistry approaches

Mean chemical potential (1 = solvent, 2 = salt)

$$\mu_{2\pm} = \frac{\boldsymbol{\nu}_\oplus \mu_\oplus + \boldsymbol{\nu}_\ominus \mu_\ominus}{\boldsymbol{\nu}_\oplus + \boldsymbol{\nu}_\ominus}$$

Mean activity ($\nu = \boldsymbol{\nu}_\oplus + \boldsymbol{\nu}_\ominus$)

$$a_{2\pm} = \sqrt[\boldsymbol{\nu}]{a_\oplus^{\boldsymbol{\nu}_\oplus} a_\ominus^{\boldsymbol{\nu}_\ominus}}$$

Ionic strength for a salt of molarity c (use electroneutrality):

$$I_c = \frac{1}{2} z_\ominus z_\oplus (\boldsymbol{\nu}_\ominus + \boldsymbol{\nu}_\oplus) c$$

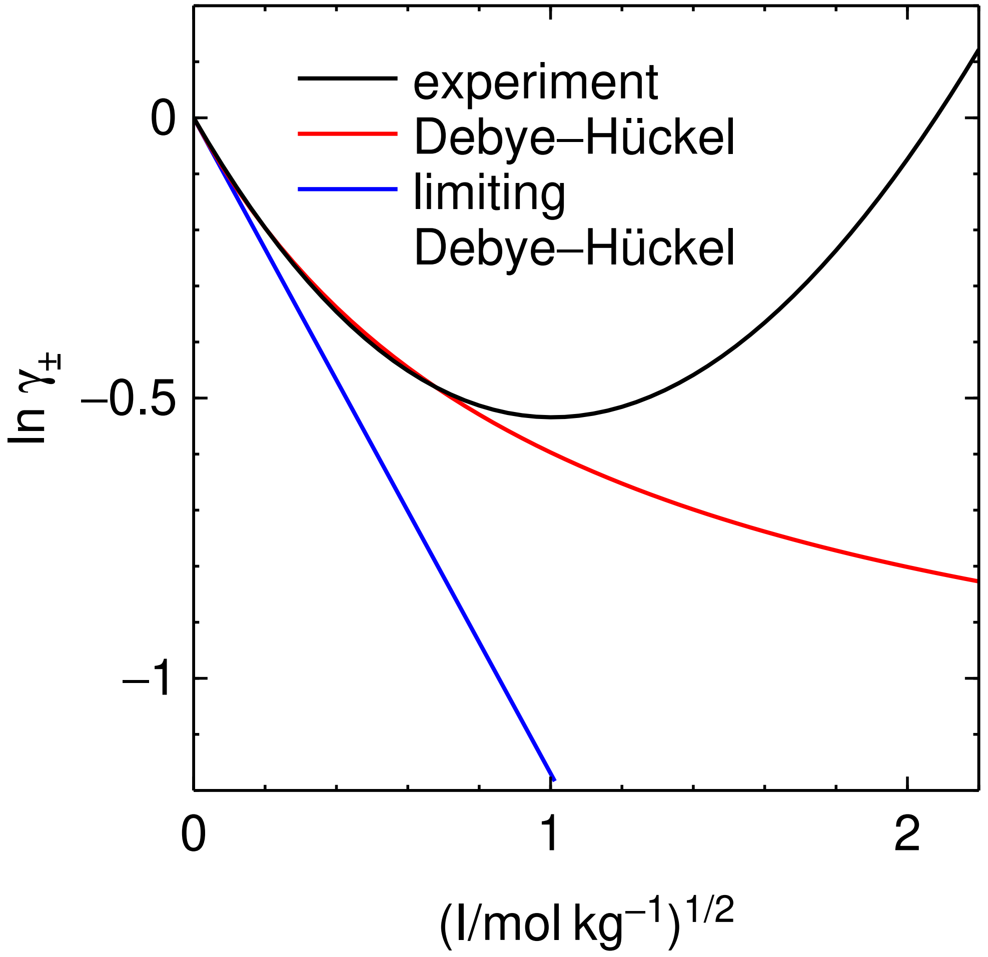
Strong electrolyte solution

Mean activity coefficient

$$\gamma_{2\pm} = \sqrt[\nu]{\gamma_{\oplus}^{\nu_{\oplus}}\gamma_{\ominus}^{\nu_{\ominus}}}$$

$$\ln \gamma_{2\pm} \overset{\text{Debye–Hückel}}{=} -z_{\ominus} z_{\oplus} A \frac{\sqrt{I_c}}{1 + a\sqrt{I_c}}$$

$A = 1.176\,\mathrm{dm^{3/2}\,mol^{-1/2}}$,
$a = 1\,\mathrm{dm^{3/2}\,mol^{-1/2}}$



Test for ⊙ NaCl

Activity coefficients of ions

Calculate:

- mean activity coefficient of ions in ⊙ $CaCl_2$, $c = 0.01\,\mathrm{mol\,dm^{-3}}$

0.71

- mean activity coefficient in ⊙ CH_3COOH, $c = 0.1\,\mathrm{mol\,dm^{-3}}$, dissociation degree $= \alpha = 0.013$

0.960

- activity coefficient of protons in ⊙ H_2SO_4, $c = 0.01\,\mathrm{mol\,dm^{-3}}$, ionized 100% to the 1st degree, 60% to the 2nd degree

0.859

Solubility of an insoluble salt (e.g., $BaSO_4$):

- drops in a ⊙ containing one of the ions (e.g., $Ba(NO_3)_2$ or Na_2SO_4)
- increases in presence of other (noninteracting) ions, because the activity coefficient of Ba^{2+} and $SO_4{}^{2-}$ decrease

Example. The solubility product of barium sulfate is 1.0×10^{-10}. Calculate the solubility $BaSO_4$ a) in pure water, and b) in 0.01 M ⊙ of NaCl.

$10\,\mu\mathrm{mol\,dm^{-3}}$, $15\,\mu\mathrm{mol\,dm^{-3}}$

- may change due to pH change in case of hydrolysis (calcium oxalate in oxalic acid, calcium carbonate and carbon dioxide)