Electrostatics light—vacuum \((\varepsilon = \varepsilon_0)\)

force to charge \(q\) caused by charge \(Q\): 
\[
\vec{F} = \frac{1}{4\pi\varepsilon_0} \frac{qQ}{r^2} \frac{\vec{r}}{r}
\]

field intensity: 
\[
\vec{E} = \frac{\vec{F}}{q} = \frac{1}{4\pi\varepsilon_0} \frac{Q}{r^2} \frac{\vec{r}}{r}
\]

potential: \(\phi = \frac{1}{4\pi\varepsilon_0} \frac{Q}{r}\), it holds 
\(\nabla \phi \equiv \frac{\partial}{\partial \vec{r}} \phi \equiv \text{grad } \phi \equiv \left( \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right) \phi = -\vec{E}\)

Electric flux through an \(r\)-sphere: 
\[
\int_{\text{sphere}} \vec{E} \cdot d\vec{s} = \frac{Q}{\varepsilon_0}
\]

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

\(\Rightarrow\) for charge inside surface \(S\) it holds: 
\[
\frac{Q}{\varepsilon_0} = \int_S \vec{E} \cdot d\vec{s}
\]

Field intensity close to a capacitor: 
\[
\vec{E} = \frac{Q}{2\varepsilon_0 A}
\]

Field intensity between plates: 
\[
\vec{E} = \frac{Q}{\varepsilon_0 A}
\]

\((A = \text{plate area}, \ S = 2A)\)
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 $-Q_s$, right $+Q_s$, $Q_s = dA \rho$

Effective charge reduced by $1/\epsilon_r$ (≡ definition of $\epsilon_r$):

$$Q - Q_s = Q/\epsilon_r$$

(screening charge = $-Q_s$, $Q_s > 0$)

The field intensity ($\propto$ force) is reduced in the same ratio:

$$\mathcal{E} = \frac{Q}{A\epsilon_r \epsilon_0} = \frac{Q}{A\epsilon}$$

(def. $\epsilon = \epsilon_r \epsilon_0$)

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

$$Q_s = dA \rho = AP = Q - \frac{Q}{\epsilon_r}, \text{ i.e. } Q = \frac{Q}{\epsilon_r} + Q_s = \frac{Q}{\epsilon_r} + AP$$

divide by $A$, ⇒ define el. displacement: $D = \frac{Q}{A} = \frac{Q}{A\epsilon_r} + P = \epsilon_0 \mathcal{E} + P$

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

“Number of displacement lines” (flux) is conserved:

\[ Q = \oint_S \vec{D} \cdot d\vec{s}, \quad \vec{D} = \epsilon \vec{\varepsilon} \]

Let \( S = \) cube \( dx \times dy \times dz \):

\[
\begin{align*}
\mathrm{d}Q &= \int_S \vec{D} \cdot d\vec{s} \\
&= \int_S \left[ D_x(x + dx) - D_x(x) \right] dydz \\
&+ \int_S \left[ D_y(y + dy) - D_y(y) \right] dxdz \\
&+ \int_S \left[ D_z(z + dz) - D_z(z) \right] dxdy \\
&= \int_S \left( \frac{\partial D_x}{\partial x} + \frac{\partial D_y}{\partial y} + \frac{\partial D_z}{\partial z} \right) \mathrm{d}x \mathrm{d}y \mathrm{d}z \\
&= -\int_S \left( \frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} + \frac{\partial^2 \phi}{\partial z^2} \right) \mathrm{d}V \epsilon \\
&= -\int_S \frac{\partial^2 \phi}{\partial \xi^2} \mathrm{d}V \epsilon
\end{align*}
\]

where \( \rho = dq/dV = \) charge density and the permittivity is constant.

Laplace operator:

\[
\left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \equiv \nabla^2 \equiv \Delta
\]

Poisson equation:

\[
\nabla^2 \phi = -\frac{\rho}{\epsilon}
\]

or in 1D \( \frac{d^2 \phi}{dx^2} = -\frac{\rho}{\epsilon} \)
Electric double layer

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

- ionisation (dissociation/protonization) of groups
  (-COOH → ⊙, -NH₂ → ⊕)

- preferential dissolution 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)

- isomorphic substitution (Al³⁺/Si⁴⁺ at clay)

- crystal cleaving

**Question: what happens in the solution?**
Let’s have $\circ \text{NaCl}$ between electrodes (plates). Elst. intensity $= \mathcal{E}$. Ions do not interact with the plates.

Concentration of $\text{Na}^+$ a $\text{Cl}^-$ between the plates?

**Naïve solution:**

- elst. potential $= \phi(x) = \mathcal{E}x$
- cation pot. energy $= e\phi(x)$
  - probability: $\exp[-e\phi(x)/k_B T] = \exp(-e\mathcal{E}x/k_B T)$
- anion pot. energy $= -e\phi(x)$
  - probability: $\exp[-e\phi(x)/k_B T] = \exp(e\mathcal{E}x/k_B T)$

**Example.** 0.1 M $\circ \text{NaCl}$, plate distance $= 50$ nm, voltage $= 50$ mV

Neutral (zero potential) in the middle

--- : correct

----- : the naïve solution is in disagreement with the electroneutrality of the bulk phase

$1 \text{ eV} = 96 485 \text{ J/mol}$
Diffuse layer: Gouy-Chapman

- 1:1 salt (NaCl) at concentration \( c \)
- electric pot. \( \phi \) far away is \( \phi(\infty) = 0 \)
- electric pot. at the electrode is \( \phi_0 \)

  (now 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 = \( \epsilon = \epsilon_r \epsilon_0 \))

Poisson equation: 
\[
\frac{d^2\phi}{dx^2} = -\frac{\rho}{\epsilon}
\]

Charge density: 
\[
\rho = \sum_i z_i \rho_i = \rho_+ - \rho_-
\]

  where

  \[
  \rho_+ = cF \exp \left( -\frac{\phi(x)e}{k_BT} \right) \quad \rho_- = cF \exp \left( \frac{\phi(x)e}{k_BT} \right)
  \]

Poisson–Boltzmann equation for the potential: 
\[
\frac{d^2\phi}{dx^2} = \frac{cF}{\epsilon} \left[ e^{\phi e/k_BT} - e^{-\phi e/k_BT} \right]
\]
The Poisson–Boltzmann equation:
\[
\frac{d^2 \phi}{dx^2} = \frac{cF}{\varepsilon} \left[ e^{\phi e/k_BT} - e^{-\phi e/k_BT} \right], \quad \phi(0) = \phi_0, \quad \phi(\infty) = 0
\]

Linearisation, or approximate solution for weak potentials
($\phi e/k_BT \ll 1$, tj. $\phi \ll 26 \text{ mV for } 298 \text{ K}$):

\[
\exp(x) \approx 1 + x \quad \Rightarrow \quad \frac{d^2 \phi}{dx^2} = \frac{2cF \phi e}{\varepsilon k_BT} \quad \Rightarrow \quad \phi = \phi_0 e^{-x/\lambda}
\]

\[
\lambda = \sqrt{\frac{\varepsilon k_BT}{2cFe}} = \sqrt{\frac{\varepsilon RT}{2cF^2}} = \text{Debye screening length} \quad \text{mixture: } \lambda = \sqrt{\frac{\varepsilon RT}{2IcF^2}}
\]

**Example.** NaCl in water, $c = 0.1 \text{ mol dm}^{-3}, 25 \text{ °C} \Rightarrow \lambda = 0.96 \text{ nm}
($\varepsilon = \varepsilon_r \varepsilon_0, \varepsilon_r = 78.4, \varepsilon_0 = 8.854 \times 10^{-12} \text{ F m}^{-1}$)

- averaged O–O separation in water = 0.28 nm $\Rightarrow 120 \text{ H}_2\text{O} \text{ in a } \lambda\text{-sphere}$
- Bjerrum length (energy if a pair of univalent ions = $k_BT$):

\[
\lambda_B = \frac{e^2}{4\pi\varepsilon k_BT} \text{ water} \approx 0.7 \text{ nm}
\]
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.
Charged surface attracts **counterions**.

<table>
<thead>
<tr>
<th><strong>Gouy-Chapman</strong></th>
<th><strong>Helmholtz</strong></th>
<th><strong>Stern</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>charged surface</td>
<td>charged surface</td>
<td>charged surface</td>
</tr>
<tr>
<td>diffusion layer gradually screens the charge</td>
<td>adsorbed counterions screen the total charge</td>
<td>adsorbed counterions screen a portion of the charge</td>
</tr>
<tr>
<td>neutral solution</td>
<td>neutral solution</td>
<td>the diffusion layer gradually screens the rest</td>
</tr>
<tr>
<td></td>
<td></td>
<td>neutral solution</td>
</tr>
</tbody>
</table>

[Images of charged and neutral solutions with red and blue dots represent the counterions and the solution respectively.]
Surface charge

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

\[ \sigma = - \int_0^\infty (\rho_+ - \rho_-)dx = - \int_0^\infty cF \left\{ \exp \left[ -\frac{\phi(x)e}{k_BT} \right] - \exp \left[ \frac{\phi(x)e}{k_BT} \right] \right\} dx \]

Using the linearized theory, \( \exp(x) \approx 1 + x \), because \( \phi(x)e/k_BT \ll 1 \)

\[ \sigma \approx \int_0^\infty 2cF\frac{\phi(x)e}{k_BT}dx = 2\lambda cF\phi_0 \frac{e}{k_BT} = \frac{\varepsilon}{\lambda} \phi_0 \]  

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

\[ \frac{C}{A} = \frac{\sigma}{\phi_0} = \frac{\varepsilon}{\lambda} \]

Usually the differential capacitance is measured, \( d\sigma/d\phi \), because \( \sigma \propto \phi \)

**Example.** A molecule of soap covers about \( a = 0.2 \text{ nm}^2 \). Counterions on average \( \lambda = 1 \text{ nm} \) apart in a 0.1 M solution.

a) What is the surface charge?
b) What is the capacitance (per m\(^2\))? (\( \varepsilon_r = 78 \).)
c) What is the potential of the surface?
Ions

Plasma, electrolyte solutions:

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

helium $T=300 \, \text{K}$

helium $T=10,000 \, \text{K}$
Debye–Hückel theory of electrolyte solutions

Simplifications:

- solvent = homogeneous dielectric continuum
- ions (several kinds of) = charged hard spheres of diameter $\sigma$; 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 $ze\phi \ll k_B T$ – for “most ions”
  - for $1:1$ c $< 0.1$ 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: $I = \frac{1}{2} \sum_i z_i^2 m_i$

the sum is over all ions in the solution
Debye–Hückel theory of electrolyte solutions

Results (screened Coulomb or Yukawa potential):

\[ \phi(r) = \frac{1}{4\pi \varepsilon} \frac{ze}{r} \quad \rightarrow \quad \phi(r) = \frac{1}{4\pi \varepsilon} \frac{ze}{r} \exp(-r/\lambda) \]

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

\[ \lambda = \sqrt{\frac{\varepsilon RT}{2I_cF^2}} \quad (\approx 1 \text{ nm for } 1:1, \ c = 0.1 \text{ mol dm}^{-3}) \]

Activity coefficients o ions:

\[ \ln \gamma_i = -Az_i^2 \frac{\sqrt{I_c}}{1 + a\sqrt{I_c}} \quad \sigma=0 \approx -Az_i^2 \sqrt{I_c} \quad \text{point charges} \]

\[ A = \frac{e^3 N_A^2 \sqrt{2}}{8\pi(\varepsilon RT)^{3/2}} \quad (= 1.176 \text{ dm}^{3/2} \text{ mol}^{-1/2} \text{ for water } 25 \degree \text{C}) \]

\[ a = \sqrt{\frac{2F^2}{\varepsilon RT} \sigma} \quad (\doteq 1 \text{ dm}^{3/2} \text{ mol}^{-1/2} \text{ pro } \sigma = 0.3 \text{ nm}) \]

Applicability to about \( I_c = 0.1 \text{ mol dm}^{-3} \) (univalent), bivalent even less, trivalent problematic
Strong electrolyte solution

\[ \text{Al}_2(\text{SO}_4)_3 \rightarrow 2\text{Al}^{3+} + 3\text{SO}_4^{2-} \]

In general:

\[ \nu_\oplus A_\oplus \rightarrow \nu_\oplus K_\oplus + \nu_\ominus A_\ominus \]

Electroneutrality \((\nu_\oplus > 0, \nu_\ominus > 0)\):

\[ \nu_\oplus z_\oplus = \nu_\ominus z_\ominus \]

\[ \Rightarrow \gamma_\oplus a \gamma_\ominus \text{ cannot be determined by classical electrochemistry approaches} \]

Mean chemical potential \((1 = \text{solvent}, 2 = \text{salt})\)

\[ \mu_{2\pm} = \frac{\nu_\oplus \mu_\oplus + \nu_\ominus \mu_\ominus}{\nu_\oplus + \nu_\ominus} \]

Mean activity \((\nu = \nu_\oplus + \nu_\ominus)\)

\[ a_{2\pm} = \sqrt{a_\oplus a_\ominus} \]
Mean activity coefficient

\[
\gamma_{2\pm} = \sqrt[2]{\gamma_+ \gamma_-}
\]

\[
\ln \gamma_{2\pm} = -z_+ z_- \Lambda \frac{\sqrt{I_c}}{1 + a \sqrt{I_c}}
\]

where \( \Lambda = 1.176 \text{ dm}^{3/2} \text{ mol}^{-1/2} \), \( a = 1 \text{ dm}^{3/2} \text{ mol}^{-1/2} \)

Test for ⊙ NaCl:
Activity coefficients of ions

Calculate:

- mean activity coefficient of ions in \( \textcircled{\text{CaCl}}_2 \), \( c = 0.01 \text{ mol dm}^{-3} \)
- mean activity coefficient in \( \textcircled{\text{CH}_3\text{COOH}} \), \( c = 0.1 \text{ mol dm}^{-3} \), dissociation degree = \( \alpha = 0.013 \)
- activity coefficient of protons in \( \textcircled{\text{H}_2\text{SO}_4} \), \( c = 0.01 \text{ mol dm}^{-3} \), ionized 100% to the 1st degree, 60% to the 2nd degree

Solubility of an insoluble salt (e.g., \( \text{BaSO}_4 \)):

- drops in a \( \textcircled{\text{Ba(NO}_3)_2 \text{ or Na}_2\text{SO}_4} \)
- increases in presence of other (noninteracting) ions, because the activity coefficient of \( \text{Ba}^{2+} \) and \( \text{SO}_4^{2-} \) decrease

**Example.** The solubility product of barium sulfate is \( 1.0 \times 10^{-10} \). Calculate the solubility \( \text{BaSO}_4 \) a) in pure water, and b) in 0.01 M \( \textcircled{\text{Cl}} \) of NaCl.

- \( 10 \mu\text{mol dm}^{-3} \), \( 15 \mu\text{mol dm}^{-3} \)

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