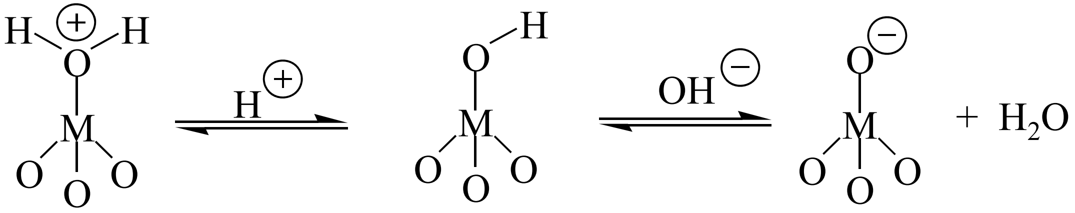
Lecture 3

Charged interfaces

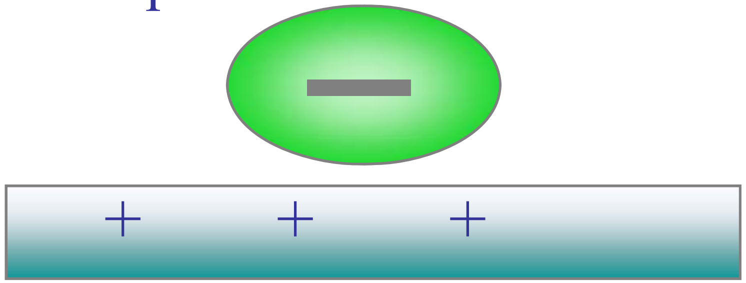
Origin of Surface Charge

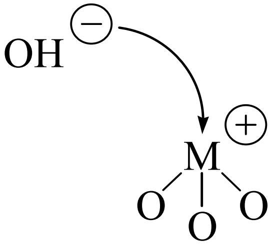
Immersion of some materials in an electrolyte solution. Two mechanisms can operate.

(1) Dissociation of surface sites.



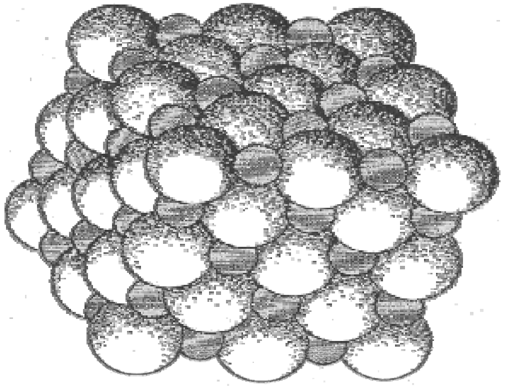
(2) Adsorption of ions from solution.



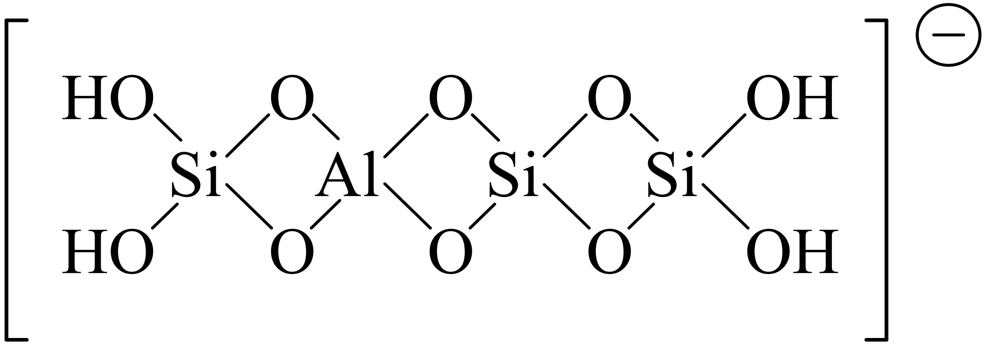


Origin of Surface Charge

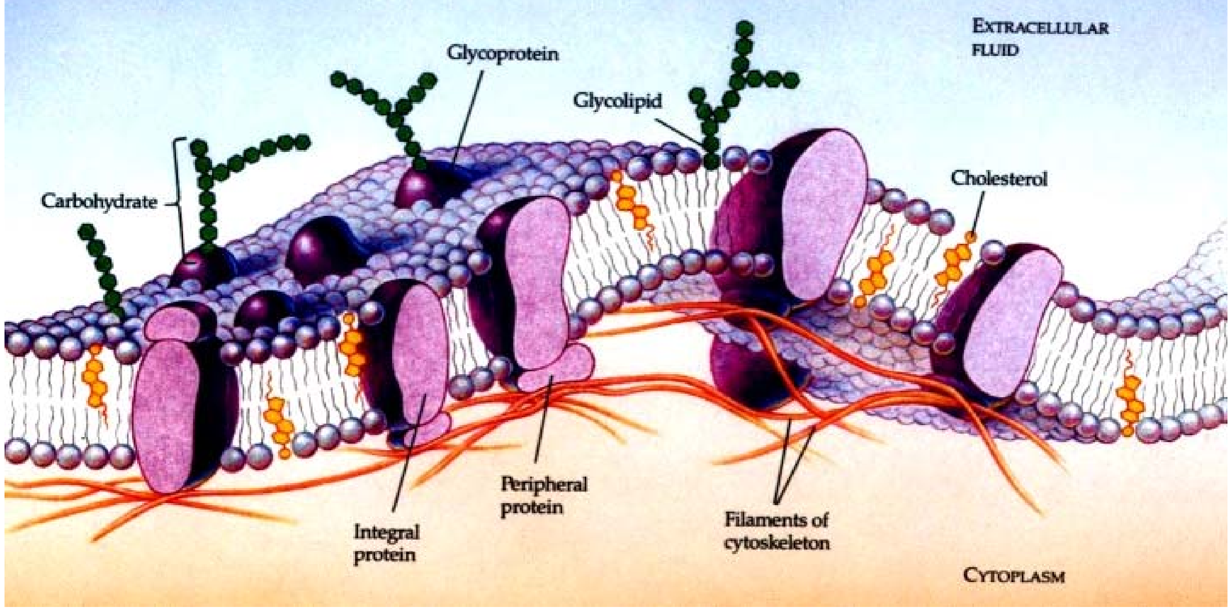
(3) Some ionic crystals have a slight imbalance in number of lattice cations or anions on surface, *eg*. AgI, $BaSO_4$, CaF_2,NaCl, KCl



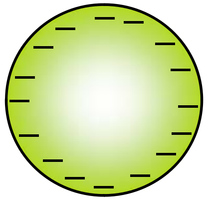
(4) Surface charge due to crystal lattice defects, *eg*. lattice substitution in kaolin



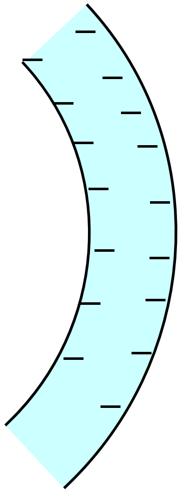
Origin of Surface Charge



The bacteria membrane is made of a self organizing lipid bi-layer. Most of the lipids head-groups are negative charged.



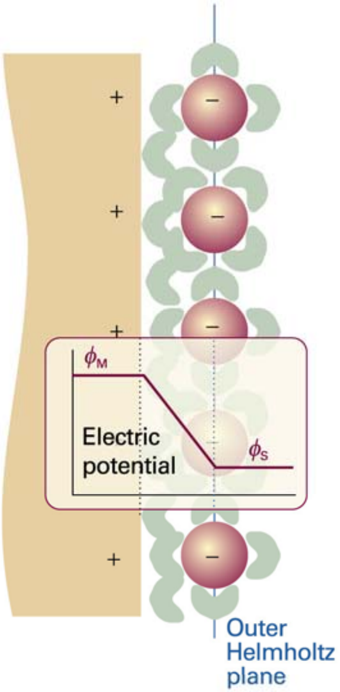
Oil droplets develop negative charge.

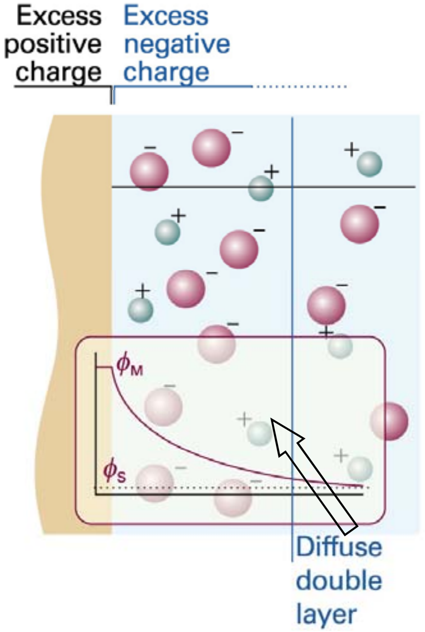


Bubbles develop negative charge since cationic species are more mobile, than anionic species and accumulate to the interface.

Electric Double Layer

- Surface charge and counter ions attracted from the solution form “electric double layer”





<u>Helmholtz layer model:</u>

•Simplest model,

• electric field is limited to an approx. molecular layer,

• cannot explain capacitance of the EDL

Gouy-Chapman model

• includes diffuse layer

• a continuum theory

• agrees with the experiment in the most cases

Poisson-Boltzmann theory

- Let’s find the electric potential near a charged interface:
- Poisson equation: $\nabla^2\phi = \frac{\rho_e}{\varepsilon\varepsilon_0}$
- As the ions can freely move their distribution will be described by Boltzmann equation: $c_i = c^0{}_i \exp\left(-W_i/kT\right)$

$$\nabla^2\phi = \frac{c^0 e}{\varepsilon\varepsilon_0}\left[\exp\left(e\phi/kT\right) - \exp\left(-e\phi/kT\right)\right]$$

Poisson-Boltzmann theory

- For a planar surface:

$$\frac{d^2\phi}{dx^2}=\frac{c^0 e}{\varepsilon\varepsilon_0}\left[\exp\left(e\phi/kT\right)-\exp\left(-e\phi/kT\right)\right]$$

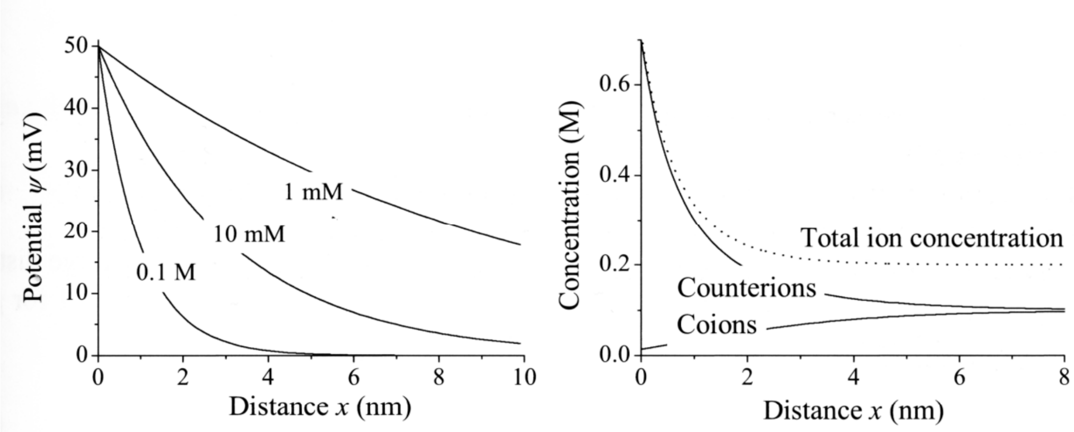
- For low potentials:

$$\frac{d^2\phi}{dx^2}=\frac{c^0 e}{\varepsilon\varepsilon_0}\left[1+e\phi/kT+\ldots-1+e\phi/kT-\ldots\right]\approx\frac{c^0 e^2}{\varepsilon\varepsilon_0 kT}\phi$$

- The solution:

$$\phi=C_1\exp\left(-x/\lambda_D\right)+C_2\exp\left(x/\lambda_D\right)$$

$$\lambda_D=\sqrt{\frac{\varepsilon\varepsilon_0 kT}{2c^0 e^2}}$$



- for multivalent ions $I=\sum_i c_i^0 Z_i^2$

Poisson-Boltzmann theory

- if the potential is high

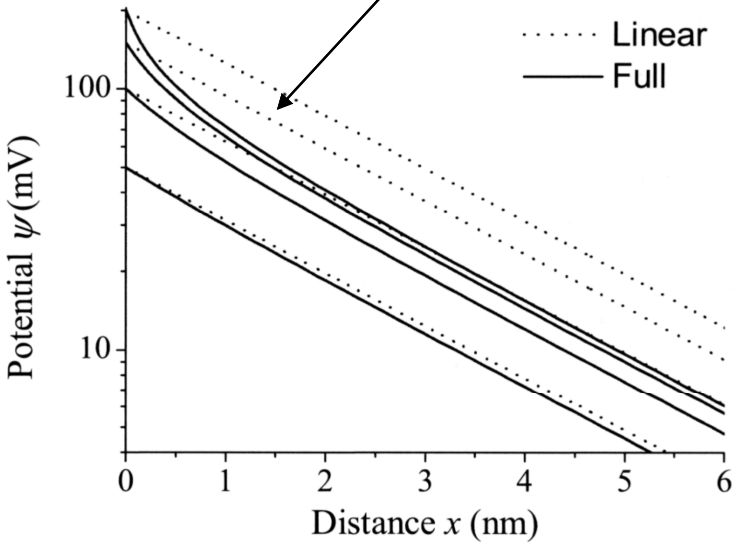
$$\frac{d^2\phi}{dx^2} = \frac{c^0 e}{\varepsilon\varepsilon_0}\left[\exp\left(e\phi/kT\right) - \exp\left(-e\phi/kT\right)\right]$$

$$\frac{d^2 y}{dx^2} = \kappa^2 \sinh y$$

- solution:

$$e^{y/2} = \frac{e^{y_0/2} + 1 + \left(e^{y_0/2} - 1\right)\cdot e^{-\kappa x}}{e^{y_0/2} + 1 - \left(e^{y_0/2} - 1\right)\cdot e^{-\kappa x}}$$

y_0 – dimensionless potential at the surface



full solution leads to lower potentials

The Graham Equation

- If we know the surface charge (e.g. density of charged groups on a functionalized surface) we can find the surface potential

- From electroneutrality, the surface charge should be equal to the total charge of all ions in the double layer

$$\sigma = \int_0^\infty \rho_e dx = \int_0^\infty \frac{d^2\psi}{dx^2} dx = \varepsilon\varepsilon_0 \left.\frac{d\psi}{dx}\right|_{x=0}$$

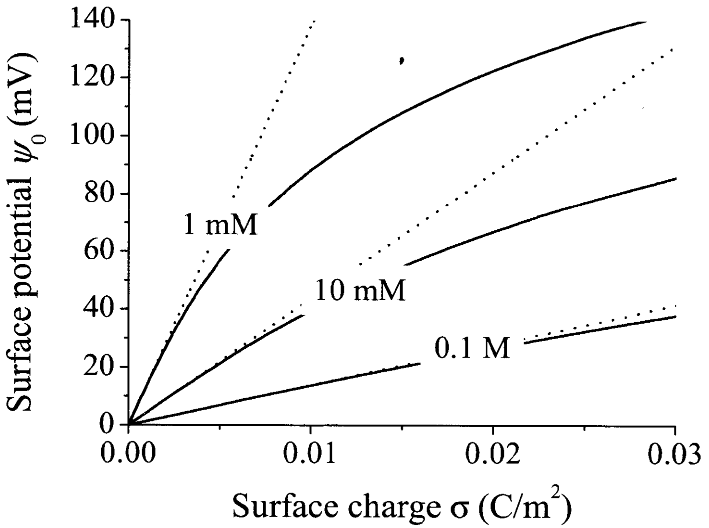
far away from the interface potential approaches 0, so its derivative approaches 0 as well

The Graham Equation

- If we know the surface charge (e.g. density of charged groups on a functionalized surface) we can find the surface potential

- Graham equation:

$$\sigma = \sqrt{8c_0\varepsilon\varepsilon_0 k_B T}\,\sinh\left(\frac{e\psi_0}{2k_B T}\right)$$



- at low potentials:

$$\sigma \approx \sqrt{8c_0\varepsilon\varepsilon_0 k_B T}\cdot\frac{e\psi_0}{2k_B T} = \frac{\varepsilon\varepsilon_0\psi_0}{\lambda_D}$$

Capacitance of the double layer

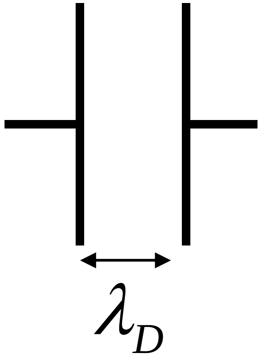
- The differential capacitance can be calculated from the Graham equation:

$$C = \frac{d\sigma}{d\psi_0} = \sqrt{\frac{2e^2 c_0 \varepsilon\varepsilon_0}{k_B T}} \cosh\left(\frac{e\psi_0}{2k_B T}\right) = \frac{\varepsilon\varepsilon_0}{\lambda_D} \cosh\left(\frac{e\psi_0}{2k_B T}\right)$$

- at low potentials:

$$C = \frac{d\sigma}{d\psi_0} \approx \frac{\varepsilon\varepsilon_0}{\lambda_D}$$

compare: plate capacitor



- capacitance raises with the increasing salt concentration

Limitation of Poisson-Boltzmann theory

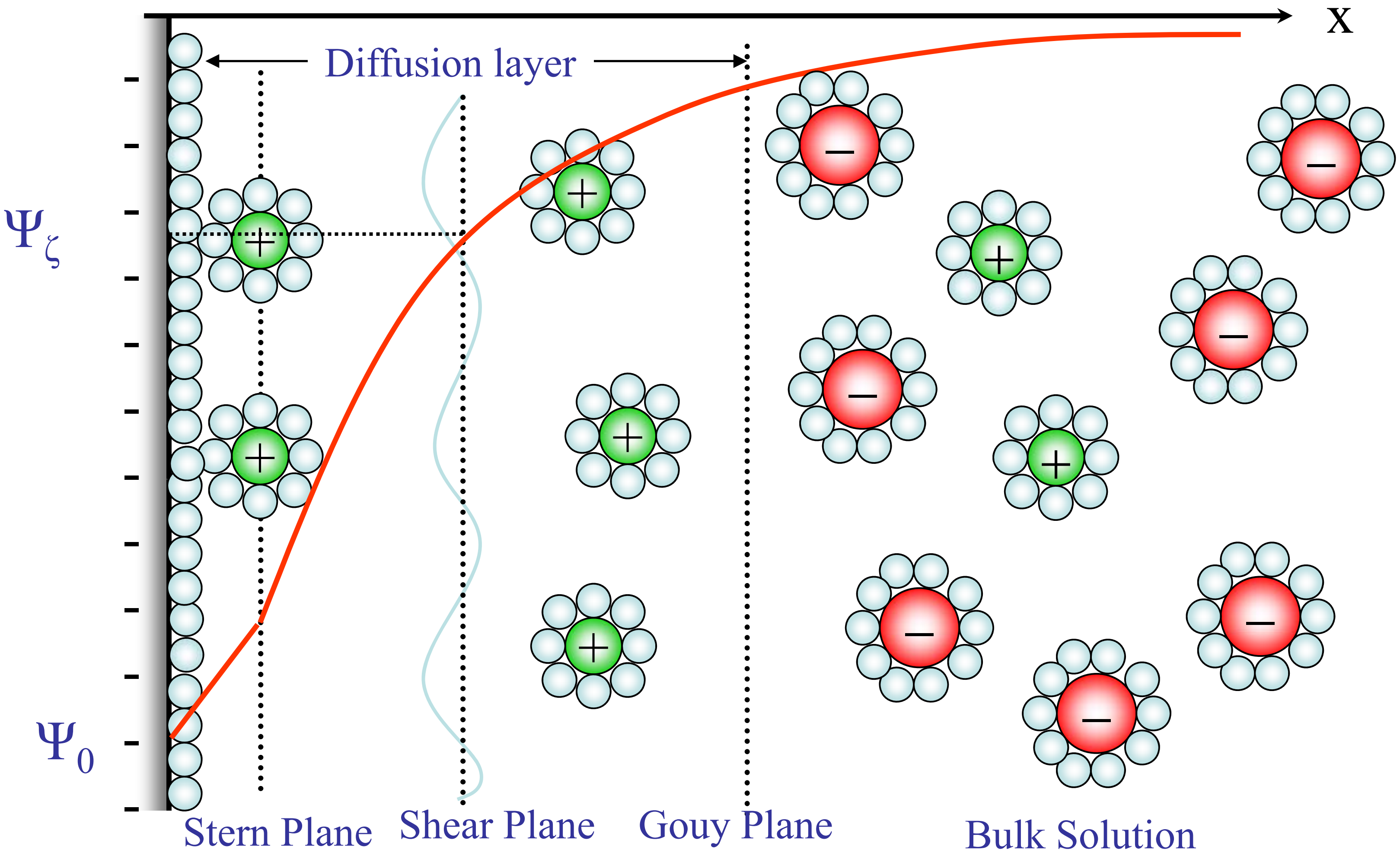
- Finite size of ions is neglected,
  - e.g. at the 100mV potential we expect a counterion concentration increase by a factor of 50. If the bulk concentration is 0.1M, we have 5M on the surface corresponding to 1nm ion-ion distance
- Ionic correlations are neglected,
  - ions might coordinate their mutual arrangement
- Discrete charge of ions is neglected
- Non-Coulombing interactions are neglected (e.g. interaction of hydration shells)
- Solvent assumed to be continuous (assumed to be a media with a constant dielectric constant)
- Surfaces assumed to be flat on molecular scale

Comments on the use of Poisson-Boltzmann theory

- Poisson-Boltzmann theory describes the double layer surprisingly well as the errors compensate each other
- The range: monovalent salt concentration up to 0.2M and potentials below 50-80 mV. Large deviations expected for 2- and 3-valent ions due to charge quantization and at curved interfaces (biological membranes)
- Improvements are not so easy. Can be done by modelling and statistical mechanic approach

Stern layer model

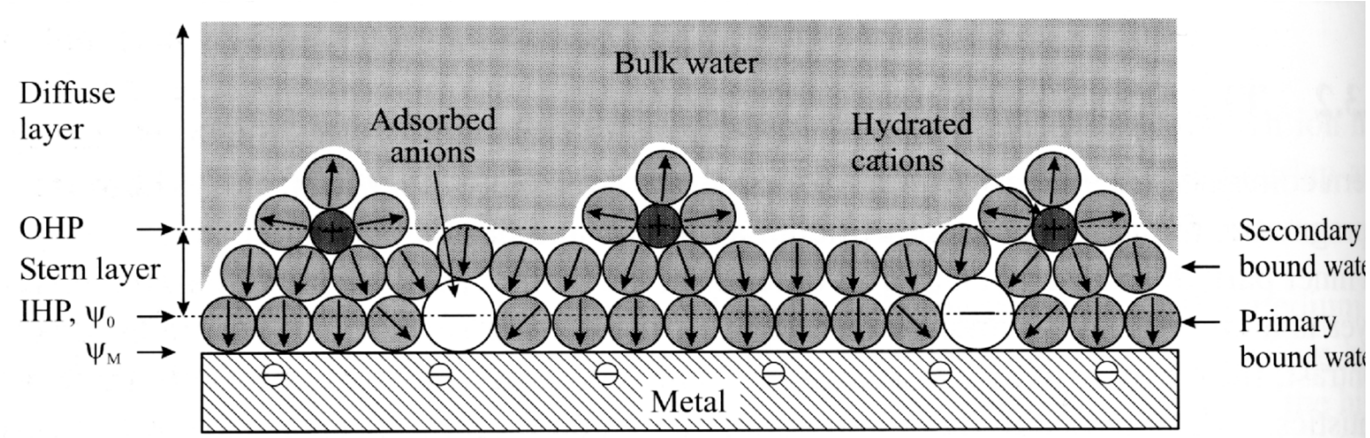
- semi empirical extension to Gouy-Chapman theory to take into account the layer of ions adsorbed on the surface:



- the potential where the bound layer of ions (Stern layer) ends is the zeta-potential.

Stern layer model

- The metal solution interface:
  - potential is constant up to the surface due to high conductivity
  - water molecules show preferential orientation (hence reduced permettivity, down to ~6)



- capacitance at the interface

$$\frac{1}{C^A} = \frac{1}{C_{St}{}^A} + \frac{1}{C_{GC}{}^A}$$

$$C_{St}{}^A = \frac{2\varepsilon_{St}\varepsilon_0}{r_{ion}}, \qquad \varepsilon_{St} \approx 6-32 \quad \text{for water}$$

typically 10-100 $\mu F/cm^2$

Gibbs free energy of the double layer

- Formation of the DL involves three processes:
  - formation of a charge on the surface (chemical forces driven dissociation or specific adsorption of ions)

$$\Delta G = -\sigma\psi_0$$

  - formation of counterion DL driven by electrstatic forces

$$\Delta G = -\int_0^\sigma \psi_0' d\sigma'$$

  - diffusion due to thermal fluctuations (entropy gain and electrostatic energy increase compensate)

$$\Delta G = 0$$

Gibbs free energy of the double layer

- Total Gibbs free energy

$$\Delta G = -\sigma\psi_0 + \int_0^{\sigma} \psi_0' d\sigma' = -\int_0^{\psi_0'} \sigma' d\psi_0'$$

  - using Graham’s equation

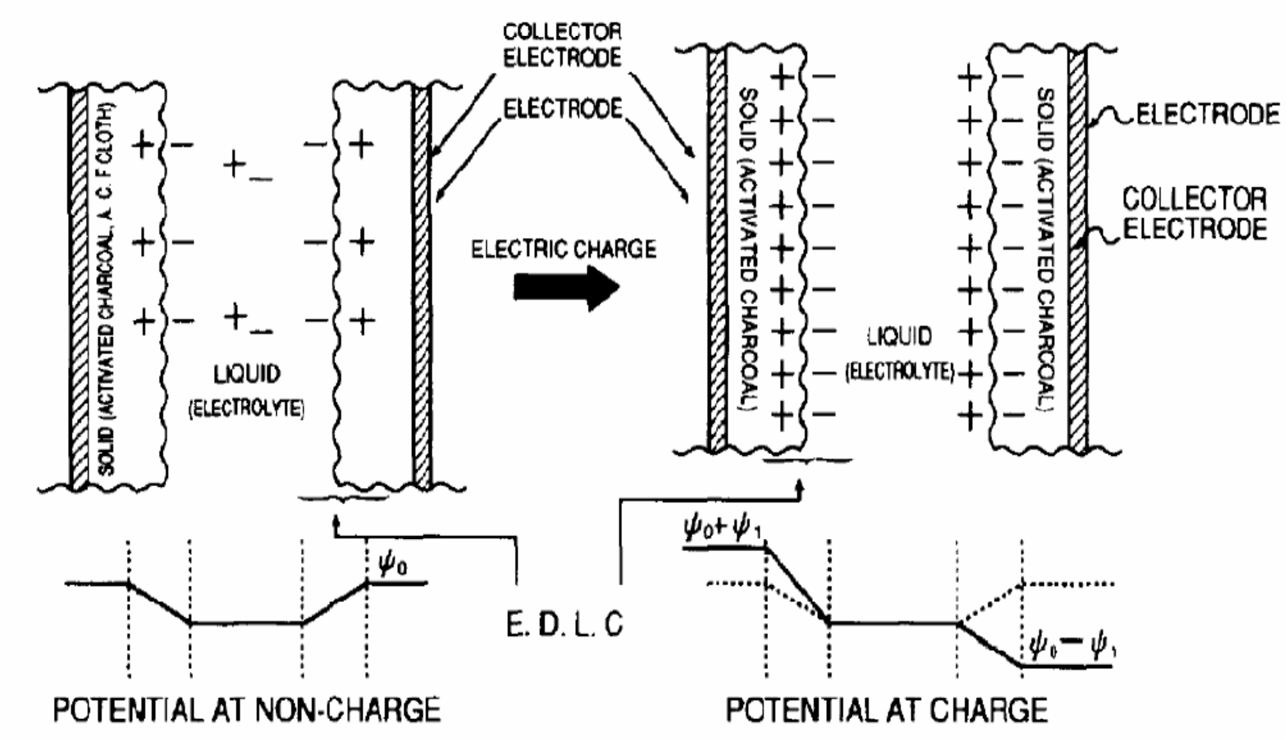
$$\Delta g = -\int_0^{\psi_0'} \sqrt{8c_0\varepsilon\varepsilon_0 k_B T}\,\sinh\left(\frac{e\psi_0}{2k_BT}\right) d\psi_0' =$$

$$= 8c_0k_BT\lambda_D \cosh\left(\frac{e\psi_0'}{2k_BT}\right)\Bigg|_0^{\psi_0} = 8c_0k_BT\lambda_D\left[\cosh\left(\frac{e\psi_0}{2k_BT}\right) - 1\right]$$

  - for low potentials

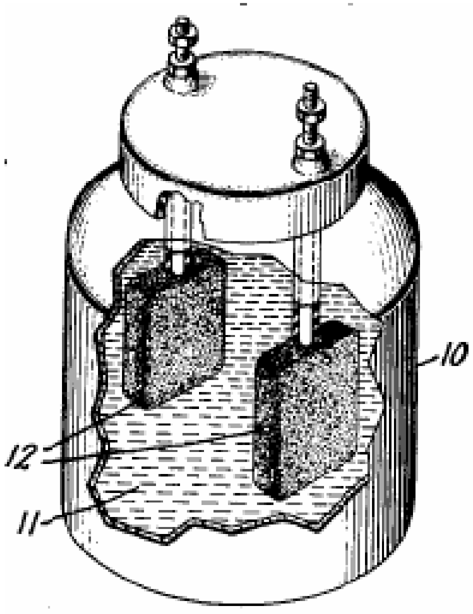
“Super Capacitors”

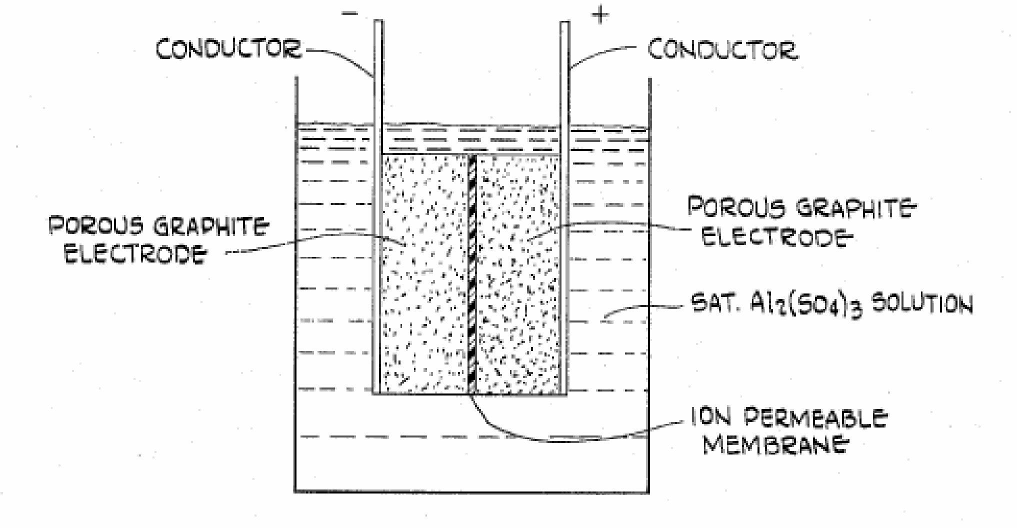
- EDLCs store electrical charge at the interface between the surface of a conductor and an electrolytic solution. The accumulated charges hence form an electric double-layer, the separation of each layer being of the order of a few Angstroms and therefore leading to very high capacitance per unit area.

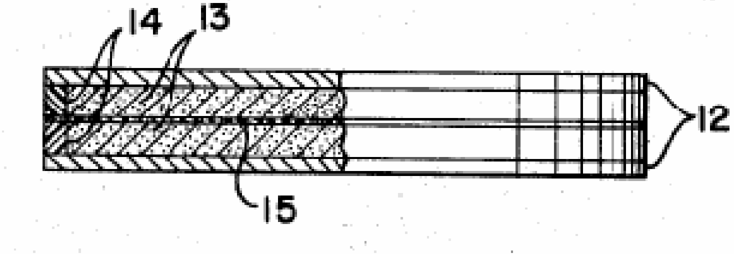


“Super Capacitors”: history

- First EDLC was patented in 1957 by General Electric using porous carbon electrodes. It was noted that the capacitor exhibited an “exceptionally high capacitance.”
- In 1966, The Standard Oil Company, Cleveland, Ohio (SOHIO) patented a device that stored energy in the double layer interface “the double-layer at the interface behaves like a capacitor of relatively high specific capacity”.
- In 1970 SOHIO patented a disc-shaped capacitor utilising a carbon paste soaked in an electrolyte.
- Commercially produced from 1980s







Problems

- **Ch.4.1** Compare the Debye length of 0.1 mM NaCl solution of water and ethanol ($\epsilon = 25.3$).
- **Ch.4.2** Plot the potential versus distance for surface potentials of 60 mV, 100 mV, and 140 mV using the solution of the linearized and the full Poisson-Boltzmann equation for an aqueous solution with 2 mM KCl.
- **Ch.4.3** For an electrophysiological experiment you form an electrode from a 5 cm long platinum wire (0.4 mm diameter) by bending it in the shape of a spiral. Calculate the total capacitance of the diffuse electric double layer for aqueous solutions of a monovalent salt at concentrations of 0.1 and 0.001 M. Assume a low surface potential.
- **Ch.4.4** Silicon oxide has a typical surface potential in an aqueous medium of —70 mV in 50 mM NaCl at pH 9. Which concentration of cations do you roughly expect close to the surface? What is the average distance between two adjacent cations? What is the local pH at the surface?