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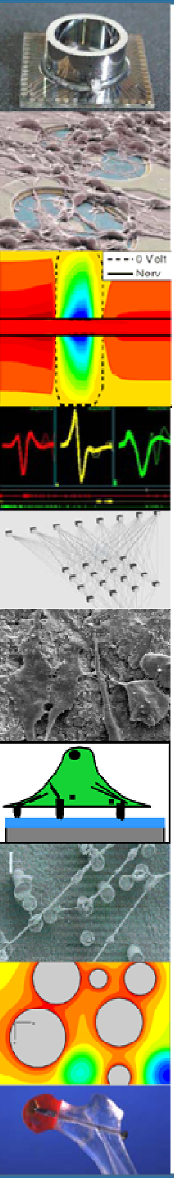

Classical Models of the Interface between an Electrode and Electrolyte

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Outline

Motivation

Electrical Double Layer (EDL)

EDL Models

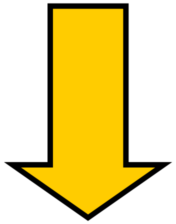
- **Classical Models**

EDL Capacitance Comparison

Future Goals

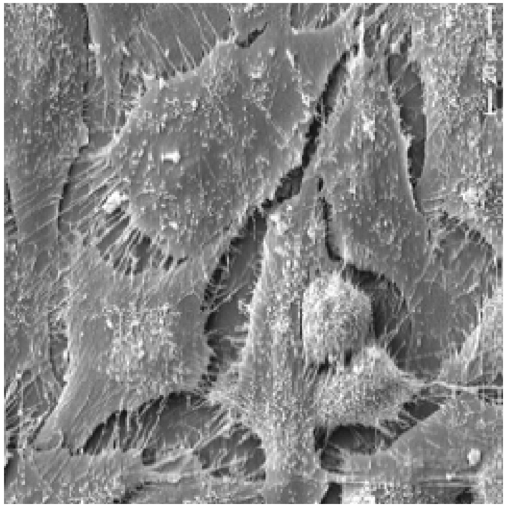
Motivation

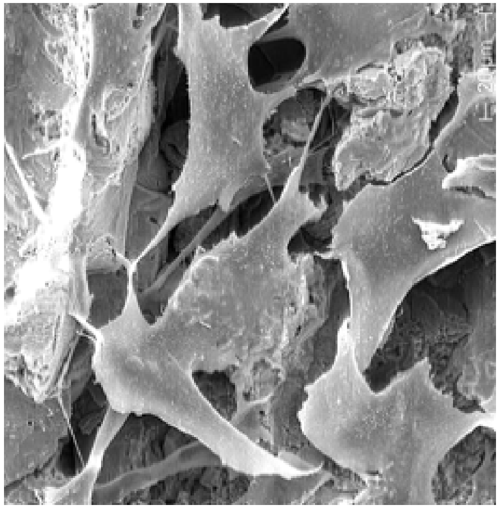
Implant & Body Fluids



Electrical

Double Layer





Source: Lüthen et al. (2005), Biomaterials 26

Electrical Double Layer (EDL)

- **What?**

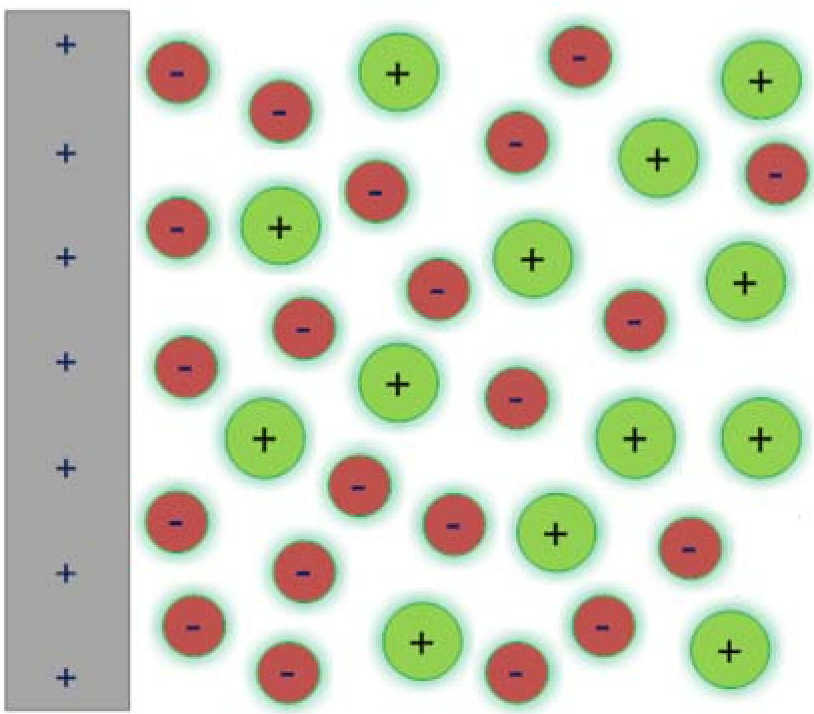
  The interface between a charged surface and an electrolyte

- **How big?**

  Thickness: 0.1 - 100 nm (~ ionic strength of the solution)

- **Where?**

  Implant´s surface
  Electrolyte battery
  In microsystems, around charged nanoparticles (biomolecules, latex beads…)
  Aurora, solar corona, pulsars

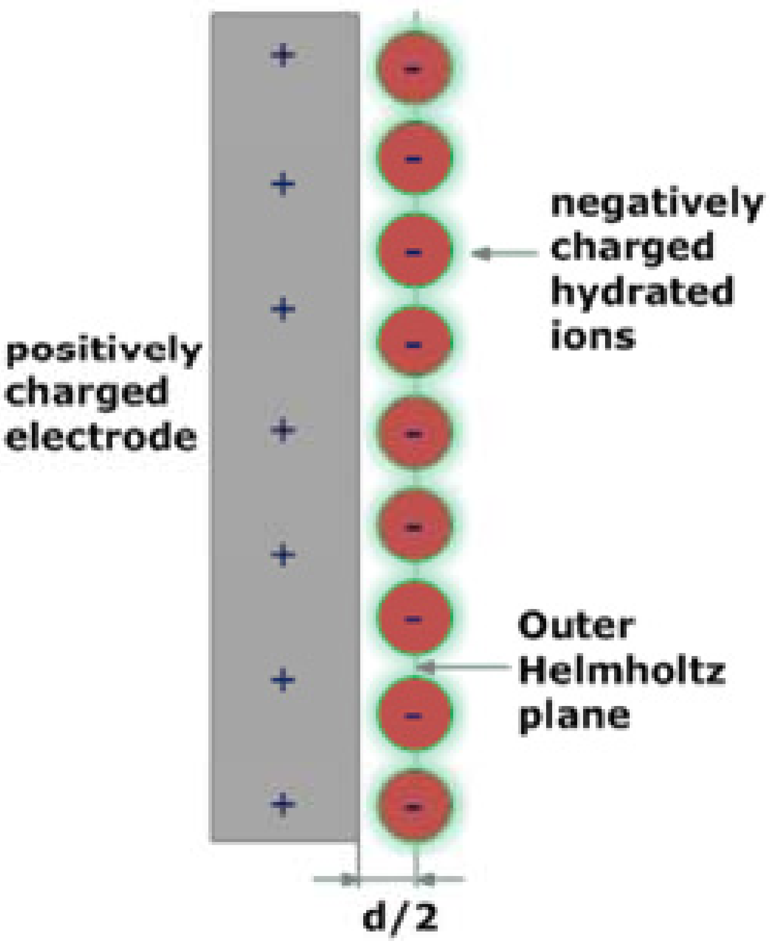


Distribution of Ions

Determined by three factors:

- electrostatic (Coulombic) forces
- diffusion
- specific interactions

Helmholtz Model

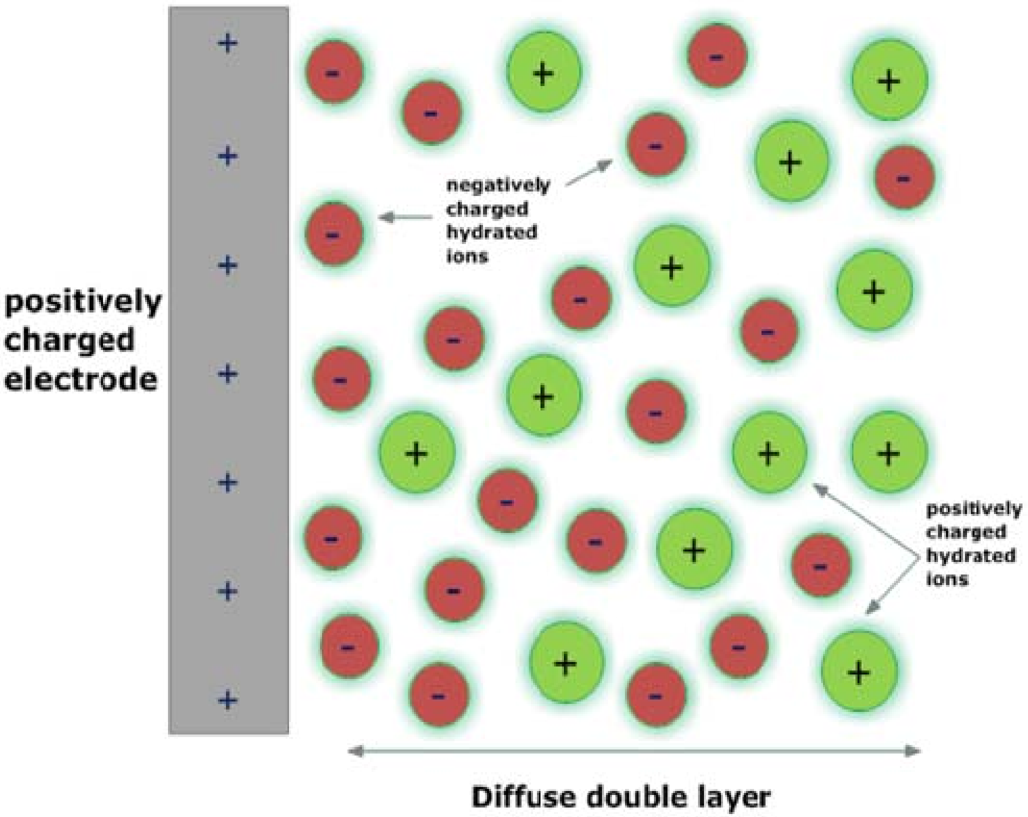


Potential profile determined by Poisson’s equation:

$$\frac{d^2\varphi}{dx^2} = -\frac{\rho}{\varepsilon_r \varepsilon_0} \quad \Rightarrow \quad \frac{d^2\varphi}{dx^2} = 0$$

ε_r	relative permittivity of medium
ε_0	permittivity of free space
ρ	space charge density
φ	electric potential
x	distance tangential to the electrode‘s surface
d	diameter of the solvated counter ion

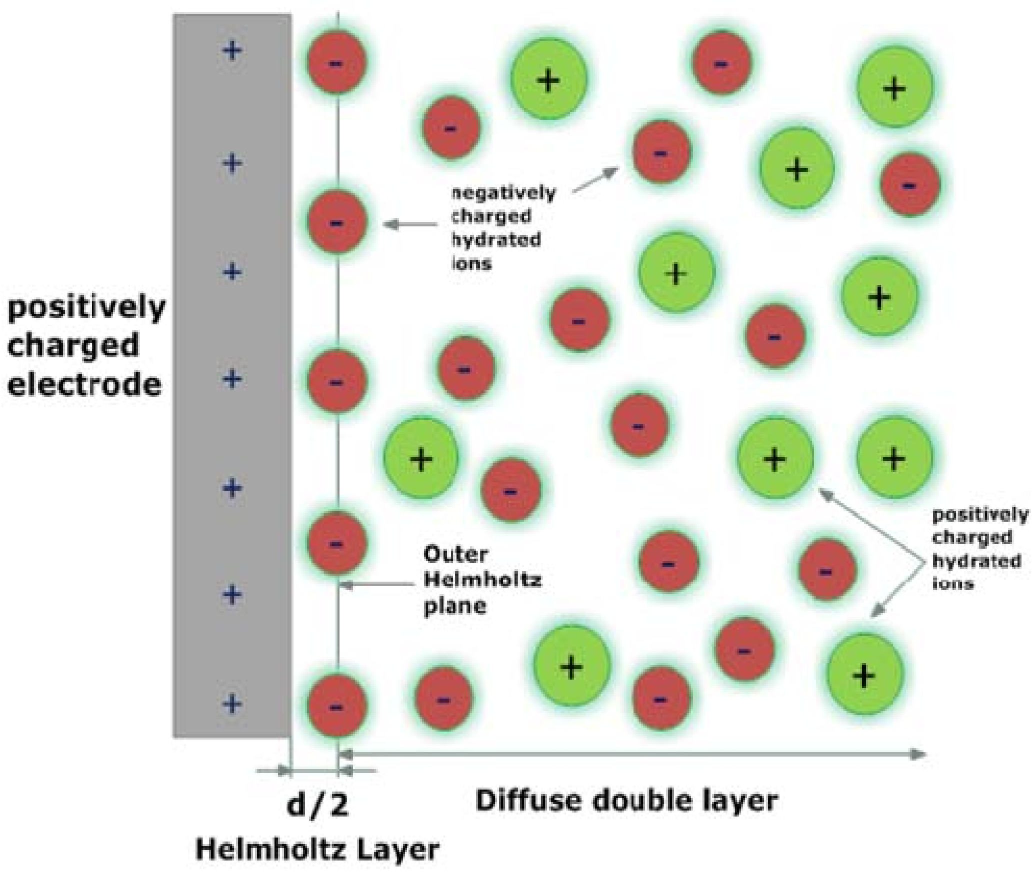
Gouy-Chapman Model



Assumptions:

- **ions as point-like charges**
- **dilute ionic solution**
- **continuum dielectric solvent**

Stern Model



Helmholtz layer

+

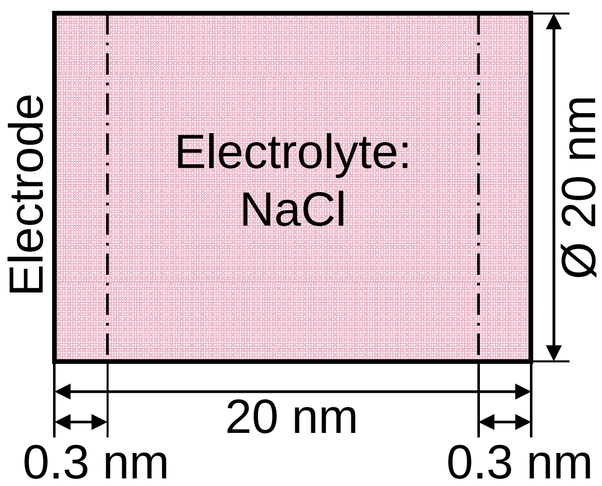
Diffuse double layer

Total capacitance:

C_H and $C_{diffuse}$ in series:

$$\frac{1}{C_d} = \frac{1}{C_H} + \frac{1}{C_{diffuse}(\varphi_0)}$$

- Geometry and Subdomain Settings



Helmholtz Model:

Poisson Equation: $$\frac{d^2\varphi}{dx^2} = 0$$

Gouy-Chapman Model:

Linearized Poisson-Boltzmann Equation:

$$\frac{\partial\varphi}{\partial x} = \left(\frac{8kTn^0}{\varepsilon_r\varepsilon_0}\right)^{1/2} \sinh\left(\frac{ze\varphi}{2kT}\right)$$

where

k	**Boltzmann constant**
e	**unit charge**
z_i	**ion *i* charge number**
c_i	**concentration of ion *i***
T	**temperature**
n_i^0	**number of ion *i* in bulk**

Numerical Simulation (2)

<u>Stern Model:</u>

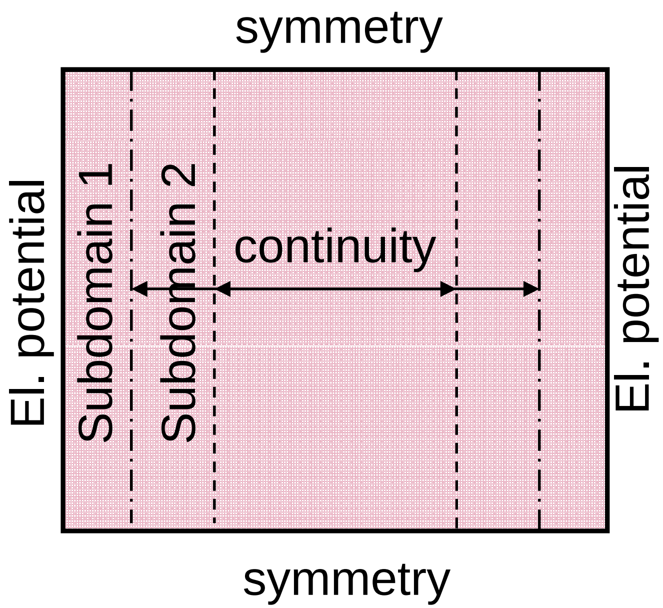
Subdomain 1:

$$\frac{d^2\varphi}{dx^2} = 0$$

Subdomain 2:

$$\frac{\partial\varphi}{\partial x} = \left(\frac{8kTn^0}{\varepsilon_r\varepsilon_0}\right)^{1/2} \sinh\left(\frac{ze\varphi}{2kT}\right)$$

- Boundary conditions



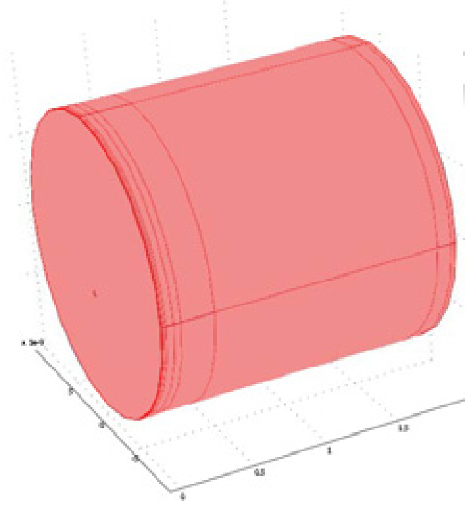
Postprocessing

- Capacitance computation

$$Q = \oint_{\Gamma_i} D_0 \cdot n dA$$

$$C = \frac{Q}{\Delta\varphi}$$

where
Q – free electric charge
dA - vector representing an infinitesimal element of area
D_0 - electric displacement field



	Helmholtz Model	Gouy-Chapman Model	Stern Model	Experiment
C_{dl} [μF/cm^2] analytical	231.41	77.16	57.92	6
C_{dl} [μF/cm^2] numerical	231.69	77.03	57.61	6

Classical Models – an overview

Assumptions:

- ions as point-like charges
- dilute ionic solution
- continuum dielectric solvent

Advantages:

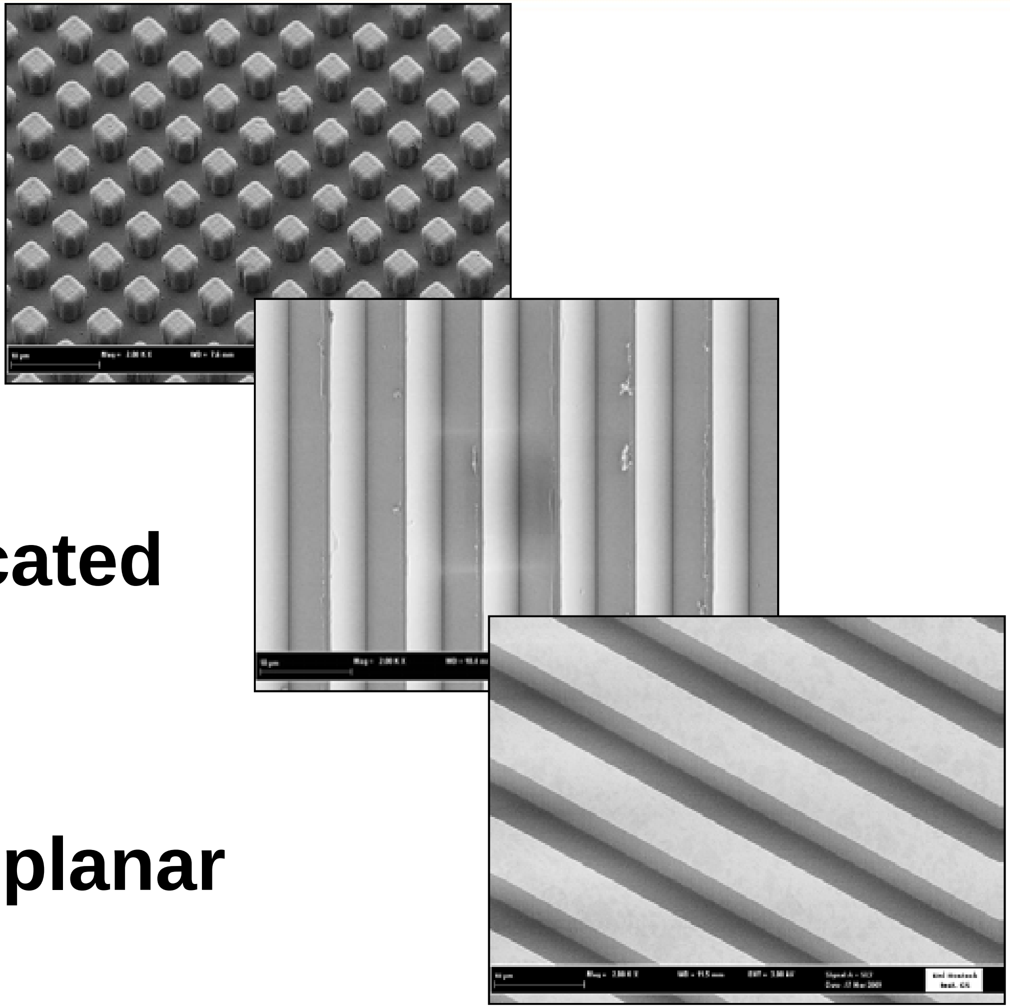
- Simple implementation
- Analytical solution

Disadvantages:

- ions treated as point charges
- only significant interactions - Coulombic ones
- constant electrical permittivity
- not time-dependent
- infinite concentration of counter-ions near the charged surface
- inhomogeneity of the charge distribution not included
- finite size & shape anisotropy of molecules not incorporated
- distorted structure by steric effect & hydration force not included
- overlapping problem

Summary & Outlook

- **Importance of EDL**
- **Classical Models**
- **Need of a Sophisticated Model**
- **Modelling of a non-planar electrode‘s surface**



Source: Lange, R. et al (2009), Material and cell biological investigations on structured biomaterial surfaces with regular geometry, IBI 2009