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Zelenograd, Moscow

Nanobiotechnology and Biosensors



**Solid
Liquid
Interface**

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Content

I. Motivation

II. Introduction

III. Theoretical Approach

IV. Experiment

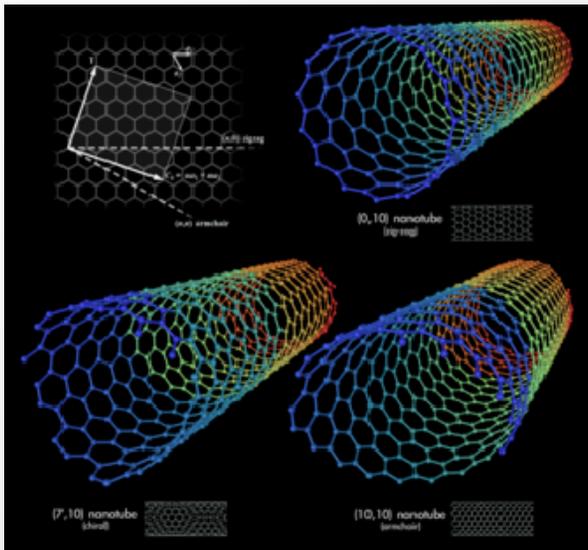
V. Simulation

VI. Application

VII. Review

Motivation

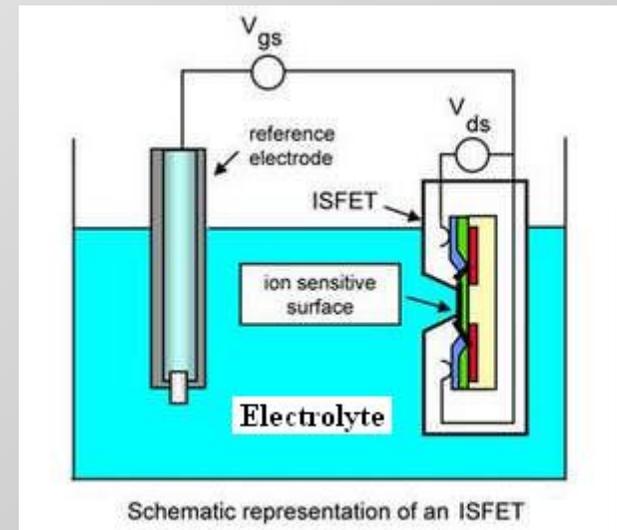
Understanding of Solid/Liquid-Interface is inevitable for applications in the field of Nanobiotechnology and Biosensors



- Nanotubes – solid tubes with liquid inside

- Electrokinetics & microfluidics

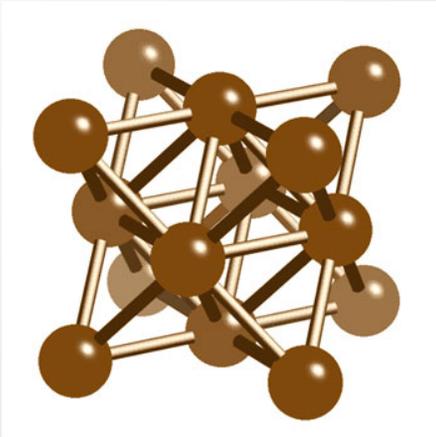
- Biosensors – metal/electrolyte-contact
e.g. ISFET:



Introduction

Solid

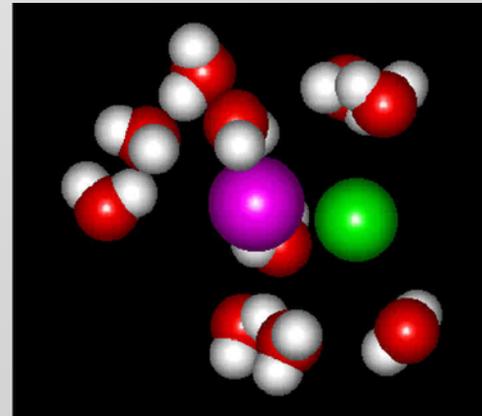
- Dominant forces: covalent bonding
- Structure: crystalline grid
- Smallest unit: unit cell → *immobile*



Conductance: electronic

Liquid

- Dominant forces: ionic and hydrogen bonds
 - special: hydration, surface tension
- Structure: no particular order
- Smallest unit: atoms and molecules → *mobile*



Conductance: ionic

Concept of the „Electric double layer“

• The Helmholtz layer:

charged surface

→ electric field

→ attraction of counterions

→ arrangement of *plate-capacitor* with molecular size

Capacitance per unit area:

$$C_H^A = \frac{\varepsilon \cdot \varepsilon_0}{d}$$

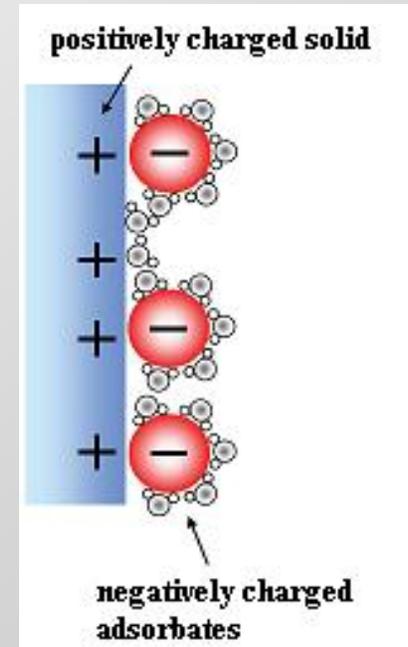
d - half diameter of solvated ion
 ε - dielectric constant of water

Potential - Poisson equation (PE):

$$\nabla^2 \psi = -\frac{\rho}{\varepsilon \varepsilon_0}$$

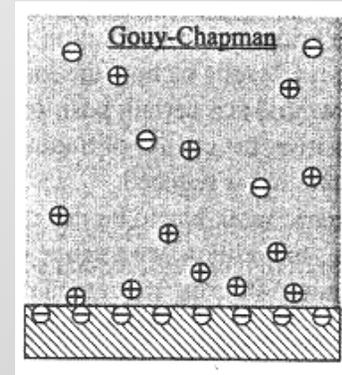
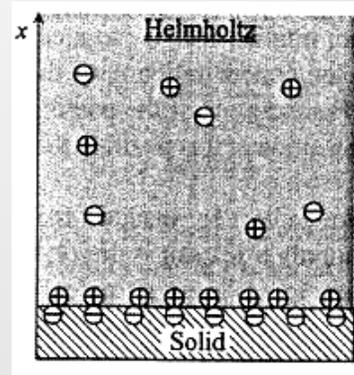
→
 $\rho = 0$

linear potential drop



• Gouy-Chapman Theory (GCT):

thermal fluctuations of charge carriers
 → „diffuse electric double layer“



Boltzmann equation (BE):

$$c_i = c_i^0 \cdot \exp\left(\frac{-W_i}{k_B T}\right) \longrightarrow \rho = e(c^+ - c^-) = ec_0 \cdot \left[\exp\left(-\frac{e\psi(x, y, z)}{k_B T}\right) - \exp\left(\frac{e\psi(x, y, z)}{k_B T}\right) \right]$$

use for local charge density

Poisson-Boltzmann equation (PBE = PB + BE):

$$\nabla^2 \psi = \frac{c_0 e}{\epsilon \epsilon_0} \cdot \left(e^{-\frac{e\psi}{k_B T}} - e^{\frac{e\psi}{k_B T}} \right)$$

assumptions made:

- 1:1 salt; otherwise: $e \rightarrow z_i \cdot e$
- only electric work done

Applying PBE to a planar surface:

simplifications: • $x, y, z \rightarrow x$

• $e|\psi| \ll k_B T \Rightarrow \frac{e|\psi|}{k_B T} \rightarrow 0 \rightarrow$ series expansion

result:

$$\frac{d^2\psi}{dx^2} = \frac{2c_0 e}{\epsilon\epsilon_0 k_B T} \cdot \psi$$

\rightarrow linearized PBE or
Debye-Hückel approximation



boundary conditions

$$\psi = \psi_0 \cdot e^{-\kappa x}$$

with:

general case

$$\kappa \equiv \sqrt{\frac{2c_0 e^2}{\epsilon\epsilon_0 k_B T}} = \sqrt{\frac{e^2}{\epsilon\epsilon_0 k_B T} \sum_i c_i^0 z_i^2}$$

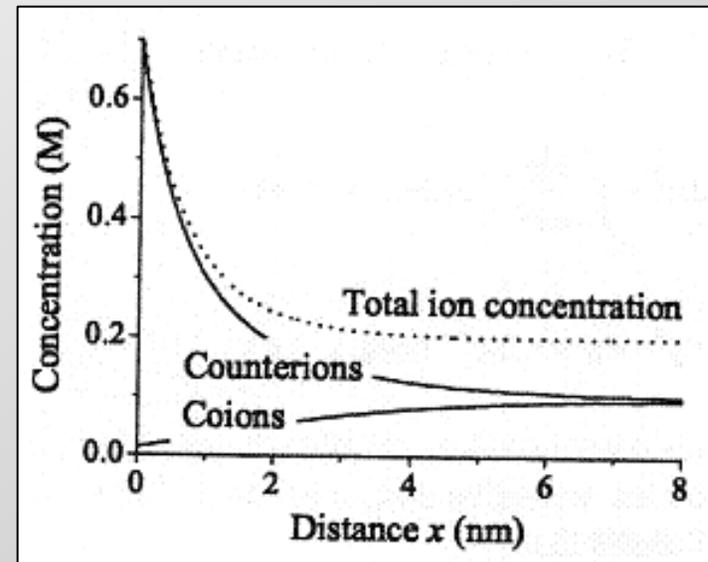
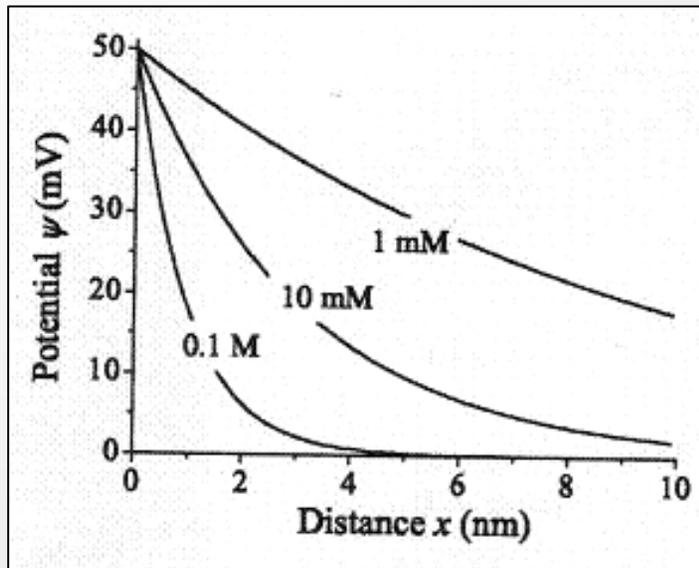
Theoretical Approach

Gouy Chapman –

planar surface II

$$\psi = \psi_0 \cdot e^{-\kappa x}$$

$\kappa^{-1} = \lambda_D$ → decay length called
Debye length



- exponential drop of potential
- increase of salt concentration
→ steeper drop, shorter λ_D

reason: better screening of surface charge with more ions

Theoretical Approach

Gouy Chapman –

linear and full solution

Comparing linear and full solution of PBE:

$$\nabla^2 \psi = \frac{c_0 e}{\epsilon \epsilon_0} \cdot \left(e^{-\frac{e\psi}{k_B T}} - e^{\frac{e\psi}{k_B T}} \right)$$

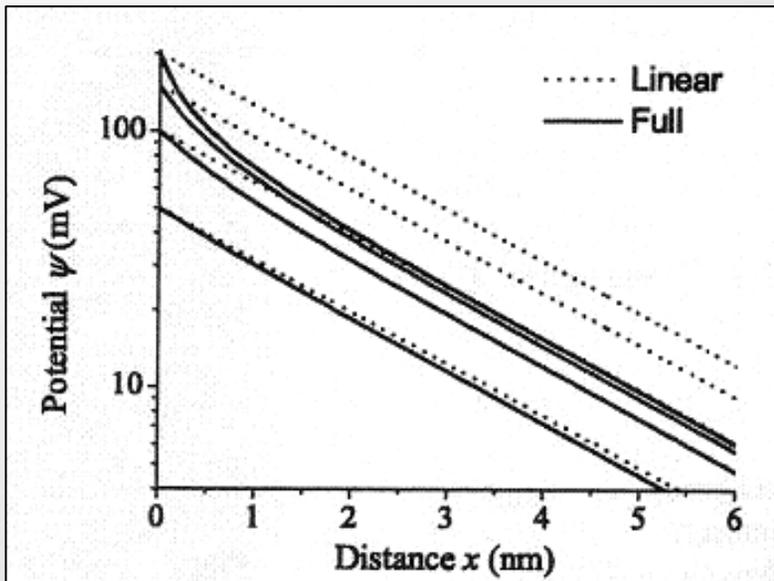
$$\psi = \psi_0 \cdot e^{-\kappa x}$$

$$\underbrace{\frac{e^{y/2} - 1}{e^{y/2} + 1}}_Y = \underbrace{\frac{e^{y_0/2} - 1}{e^{y_0/2} + 1}}_{Y_0} \cdot e^{-\kappa x}$$

$$\left(y = \frac{e\psi}{k_B T} \right)$$

- small surface potential:
good linear fit
- higher potentials:

full solution has lower potentials
+ steeper decay for $x < \lambda/2$



20 mM monovalent salt

Theoretical Approach

Gouy Chapman – capacity

Capacity of the diffuse electric double layer:

→ relation between surface charge σ and surface potential ψ_0 ?

Grahame equation:

$$\sigma = -\int_0^{\infty} \rho \cdot dx = \dots = \sqrt{8c_0 \varepsilon \varepsilon_0 k_B T} \cdot \sinh\left(\frac{e\psi_0}{2k_B T}\right) \approx \frac{\varepsilon \varepsilon_0 \psi_0}{\lambda_D}$$

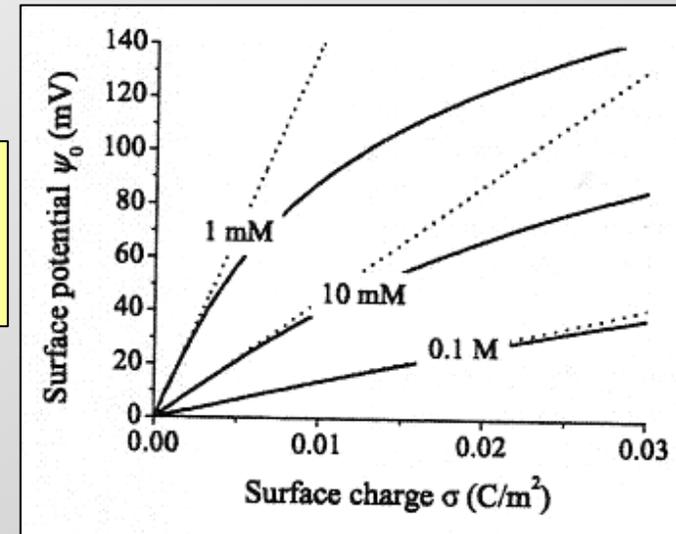


Capacitance:

$$C_{GC}^A = \frac{d\sigma}{d\psi_0} = \frac{\varepsilon \varepsilon_0}{\lambda_D} \cdot \cosh\left(\frac{e\psi_0}{2k_B T}\right) \approx \frac{\varepsilon \varepsilon_0}{\lambda_D}$$

$$\left(C = \frac{dQ}{dU} \right)$$

electric double layer like plate capacitor with $d = \lambda_D$!



- low potentials: linear behaviour
- high salt concentration:
→ more surface charge required for same potential

Discussion – limitations of GCT:

- finite size of ions neglected
- continuous charge distribution considered
- non-Coulombic interactions disregarded
- continuous solvent with constant permittivity ϵ
- flat surface assumed
- ...

BUT - good predictions for symmetric electrolytes at: salt concentrations < 0.2 M
potentials < 50 - 80 mV

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Experiment

Adsorption – mercury drop

Adsorption at the Interface:

charge density at interface?

→ experiment: **mercury drop** in electrolyte

special: **surface tension** -

$$\gamma = \frac{\partial G}{\partial A}$$

• p, T - const

• formation of surface unfavourable

Gibbs Adsorption Equation:

$$\cancel{S^\sigma} dT - \cancel{V^\sigma} dp + A_S d\gamma + \cancel{Q^\sigma} d\varepsilon + \sum_{j=1}^{j=J_0-1} \sum_{k=0}^{k=K-1} n_{j,k}^\sigma d\mu_{j,k} = 0$$

σ – surface related, ε – overall potential diff.

n – # of charge carriers on surface, μ - chem. potential

→ p, T const:

$$-d\gamma = \sum_i \frac{n_i^\sigma}{A} d\bar{\mu}_i$$

- **Gibbs Adsorption isotherm**

$$\sigma^M = -F \frac{n_e}{A}$$

- **excess charge**

$$-d\gamma = \sigma^M dE$$

- **electrocapillary equation**

Experiment

Adsorption – mercury drop II

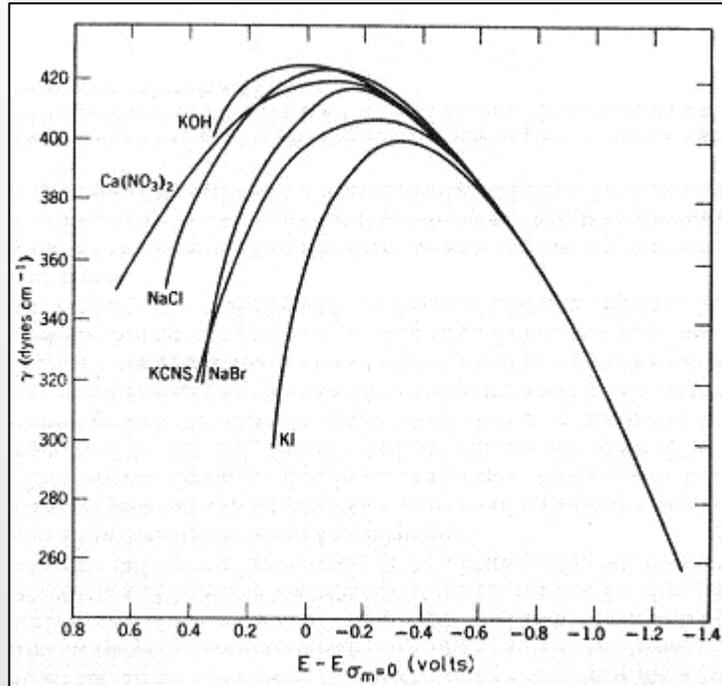
$$\sigma^M = - \left(\frac{d\gamma}{dE} \right)$$

- excess charge

repelling excess charge carriers \rightarrow lowering of γ

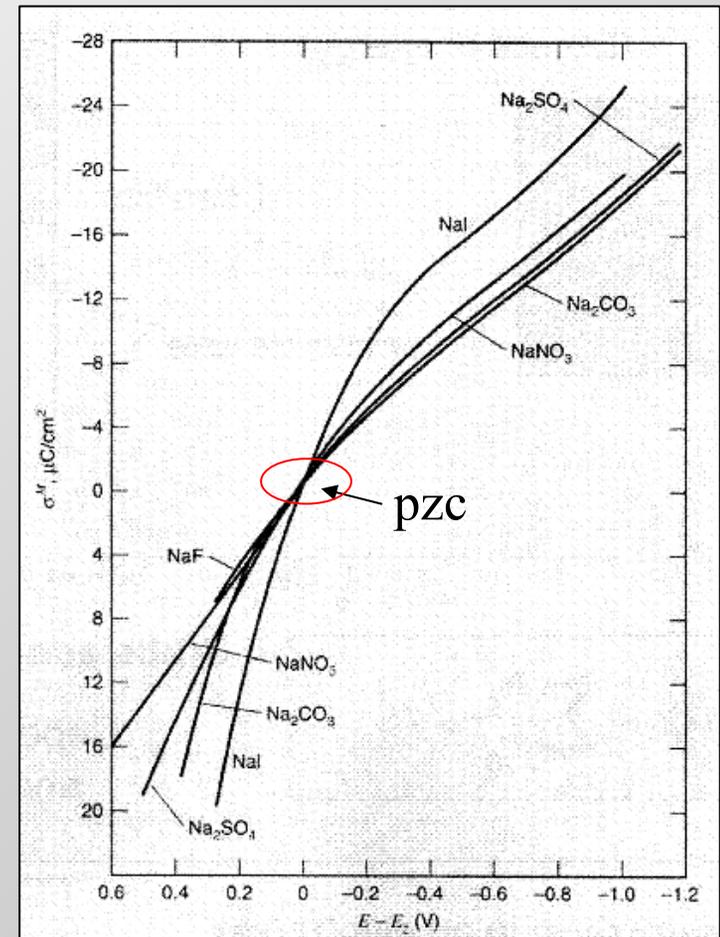
Def.: **point of zero charge (pzc)** \equiv no charge within the metal

expectation for γ over potential?



asymmetric! \rightarrow coulombic + **specific adsorption**

here anions specifically adsorb, cations not



Experiment

Specific Adsorption – parameters

Parameters influencing specific adsorption:

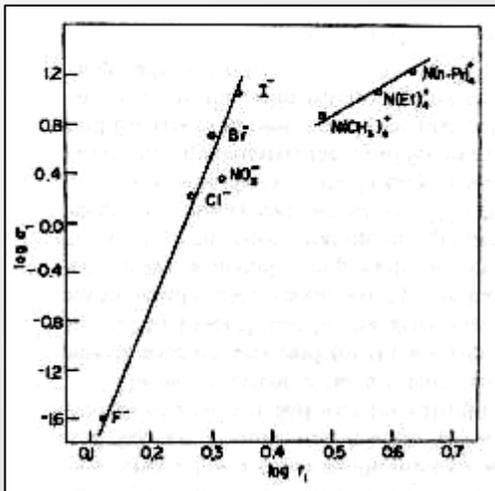
- **Charge density on solid surface**

specific adsorption of ion \uparrow

\leftrightarrow opposite charge within solid \uparrow

note:

anions can be adsorbed at negative charge (see graph)

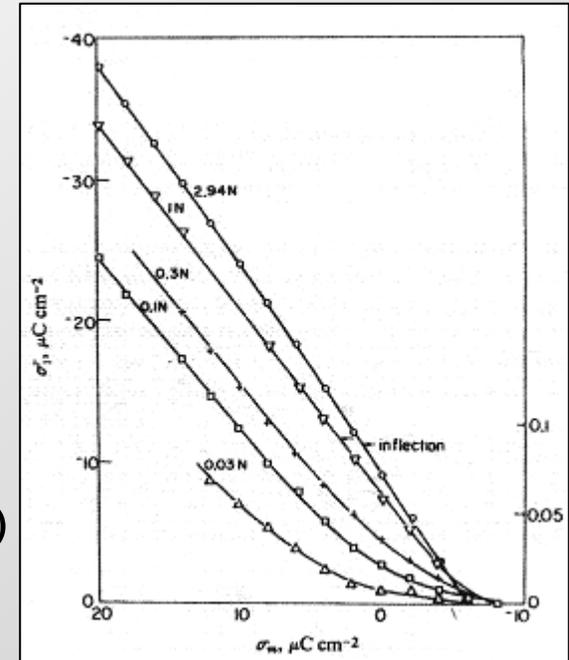


- **Ion Size Effect**

size of ion \uparrow

\rightarrow specific adsorption \uparrow

(hydration weaker...)



- **Ion Type**

anions have greater tendency to spec. adsorb than cations

(for metals observed...)

Experiment

Specific Adsorption – parameters II

- **Hydration**

strong primary hydration sheath → little specific adsorption

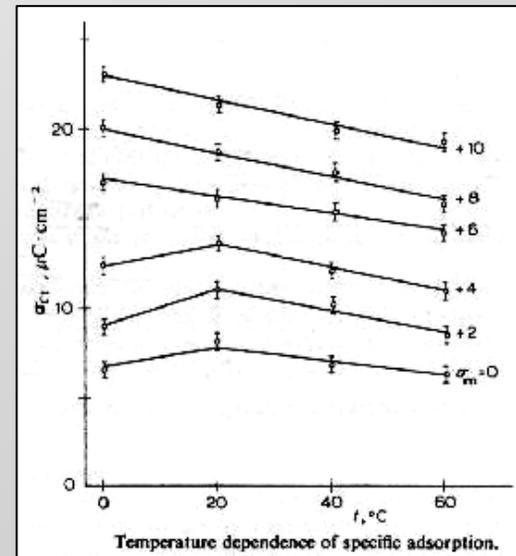
Anion	F(-)	Cl(-)	Br(-)	I(-)
Ion-Solvent Interaction [kcal/mol]	-20.6	-13.6	-12.2	-10.7

- **Concentration Change**

higher concentration → higher specific adsorption

- **Temperature**

increase of temperature
→ decrease of
specific adsorption



Experiment (Specific) Adsorption – general parameters

of general importance is:

- type of the solid
 - type of “docking stations” for adsorbates (surface texture)
- solvent-solid interaction
 - solvation of surface + desorption for creating vacancies
- solvent-adsorbate interaction
 - hydration sheath
- ...

Problem:

- many influences can be measured directly, others cannot
- there are experimental results striking the so far developed theory
- complexity of parameters to be considered is rising

→ no “all-describing”-theory found yet!

Way out:

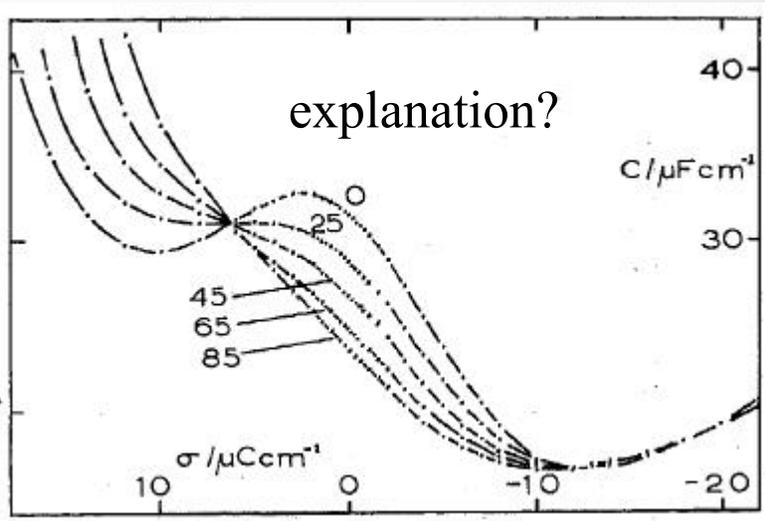
developing models for simulation +
comparing results with real experiment

Simulation

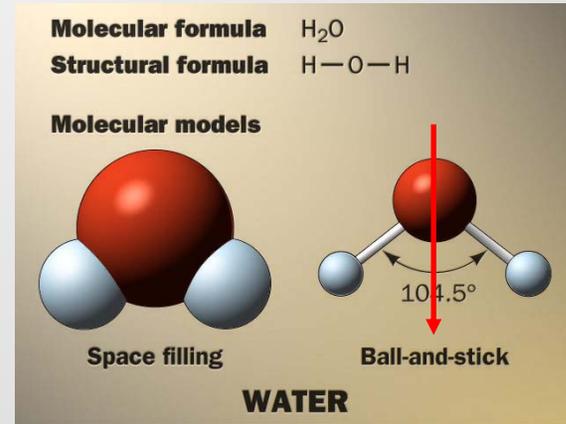
Four State Model - idea

Four state model (1975):

experimental data –
capacity over excess charge:

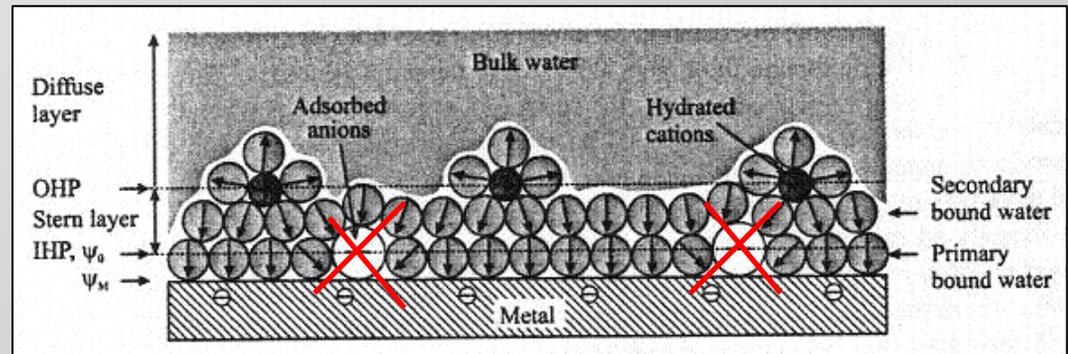


special property of water:
DIPOLE



idea: dipoles cause extra potential drop
→ influence on capacitance

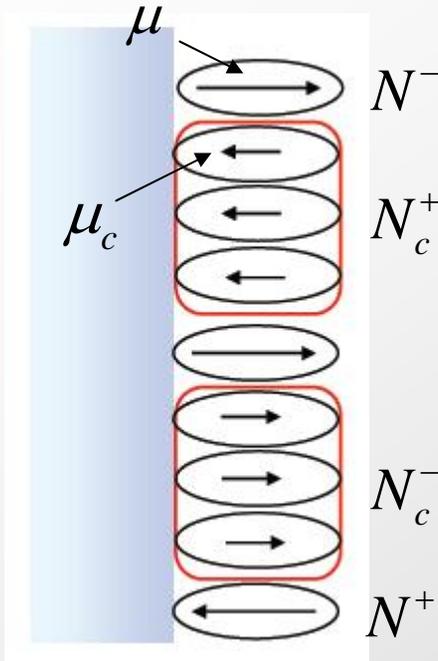
assumption: no specific adsorption
→ first adsorbed layer *only* water
→ four states to be differed



Simulation

Four State Model - model

Monolayer of water with single molecules + clusters of molecules – 2 dipole directions



→ 4 states

N – # molecules of certain state in monolayer
 μ – dipole moment

Energies:

solvent molecule in cluster -

$$\begin{aligned} U_c^+ &= -\mu_c \overbrace{\sigma}^{\text{charge on metal}} / \epsilon \\ U_c^- &= \mu_c \overbrace{\sigma} / \epsilon \end{aligned}$$

monolayer permittivity

free solvent molecule -

$$\begin{aligned} U^+ &= -\mu\sigma / \epsilon + U_b^+ \\ U^- &= \mu\sigma / \epsilon + \underbrace{U_b^-}_{\text{due to different bonding}} \end{aligned}$$

Potential drop across inner layer:

due to different bonding

$$\Delta\phi = \overbrace{\psi}^{\text{free charge}} + \underbrace{\chi}_{\text{dipoles}} = \frac{\sigma}{C_0} + \chi$$

$$\chi = -\mu_c N_c^+ / \epsilon + \mu_c N_c^- / \epsilon - \mu N^+ / \epsilon + \mu N^- / \epsilon$$

idea: Boltzmann for N + varying parameters

Simulation

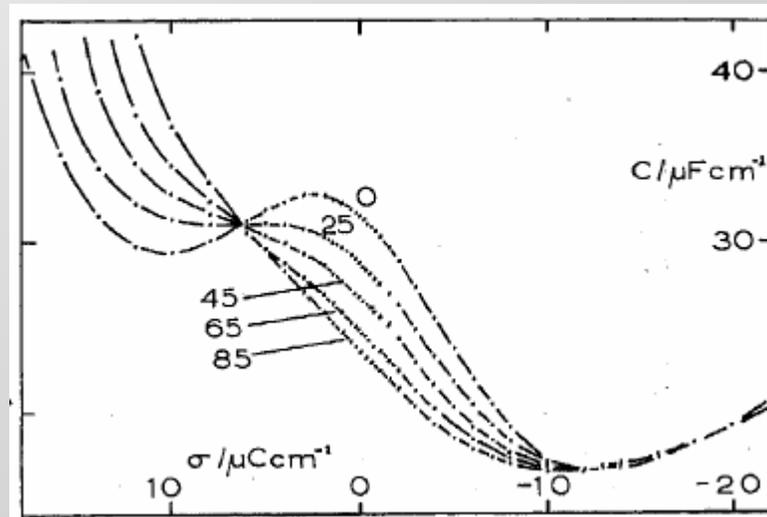
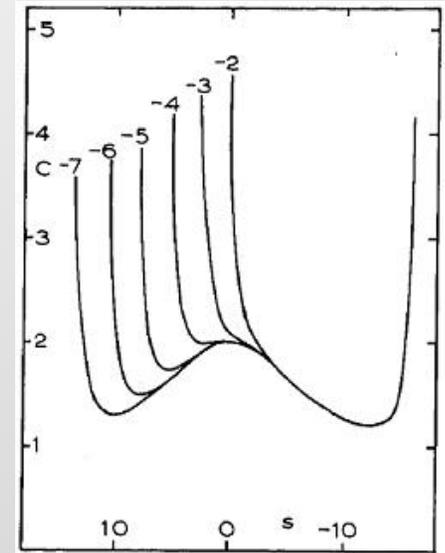
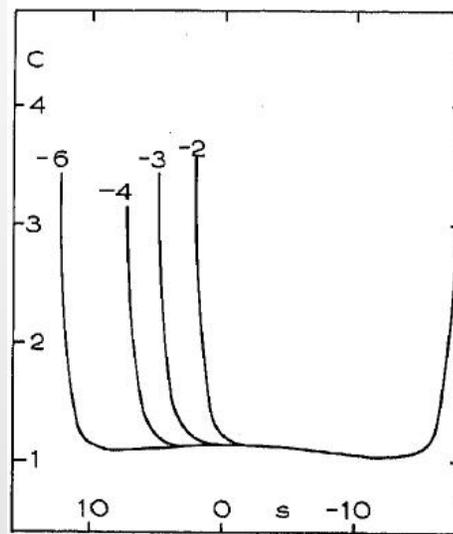
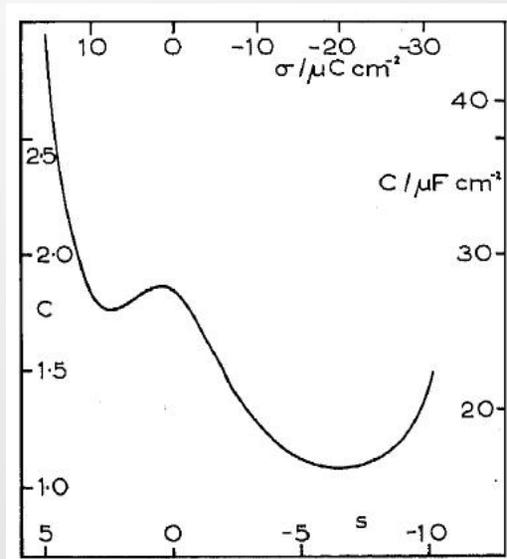
Four State Model - results

Total capacitance:

$$\frac{1}{C_i} = \frac{d\Delta\phi}{d\sigma} = \frac{1}{C_0} + \frac{d\chi}{d\sigma}$$

achieved plots:

simulation



experiment

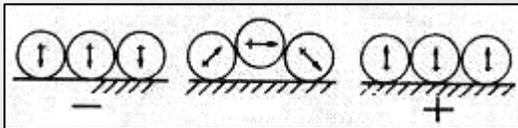
Simulation

Four State Model - results II

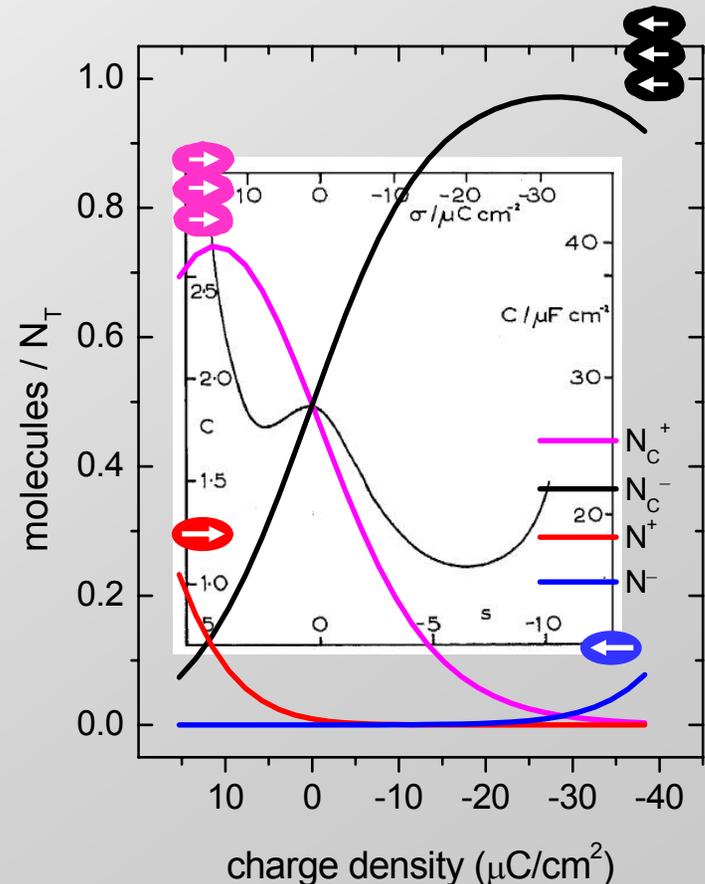
results from adapting the parameters:

$$\varepsilon, \mu_c, U_b^+, U_b^-, C_0$$

- asymmetry, because of different stability of 2 orientations of free molecules
- 3 water molecules per cluster
- total dipole moment of cluster approx same as dipole moment of free molecule
→ ring groupings of water possible:



- maxima + minima are deduced as high or low switching-possibilities of the dipole orientation:

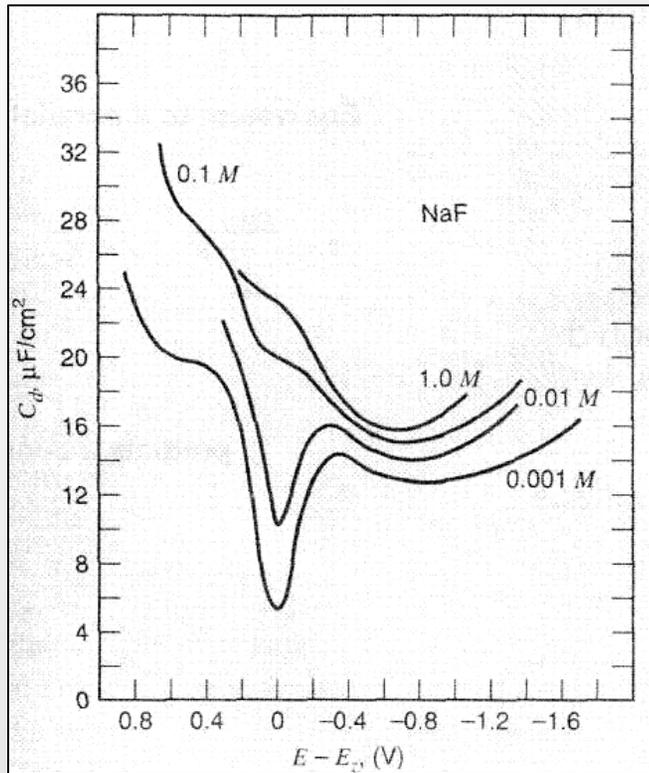


Simulation

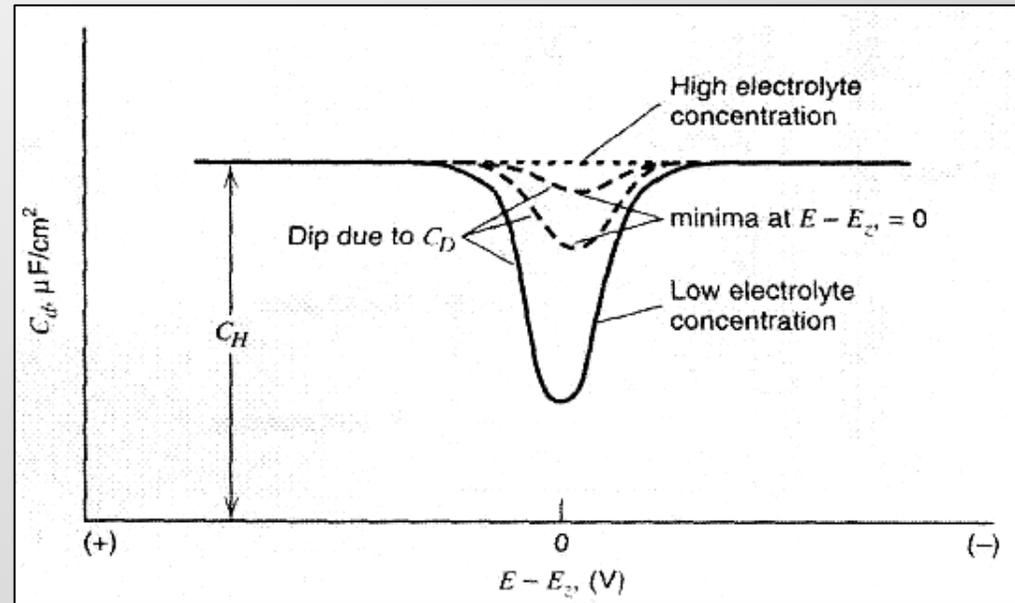
Diffuse Layer Capacitance

Diffuse Layer Capacitance:

More experimental capacitance-data:



Influence of diffuse layer around pzc strong for low concentrations:



$$C_{GC}^A = \frac{d\sigma}{d\psi_0} = \frac{\epsilon\epsilon_0}{\lambda_D} \cdot \cosh\left(\frac{e\psi_0}{2k_B T}\right) \approx \frac{\epsilon\epsilon_0}{\lambda_D}$$

Huge minimum at very low concentrations

Simulation

Adsorption Capacitance

Adsorption Capacitance:

- Assume absorbed charged molecules

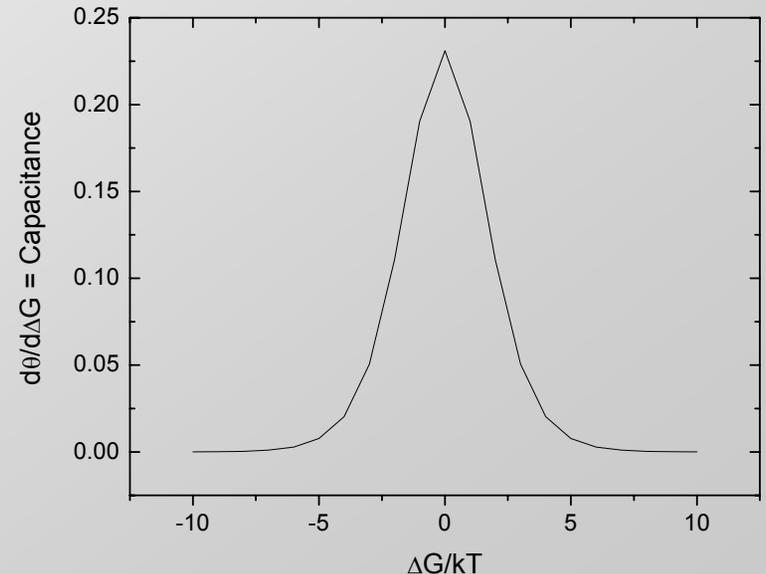
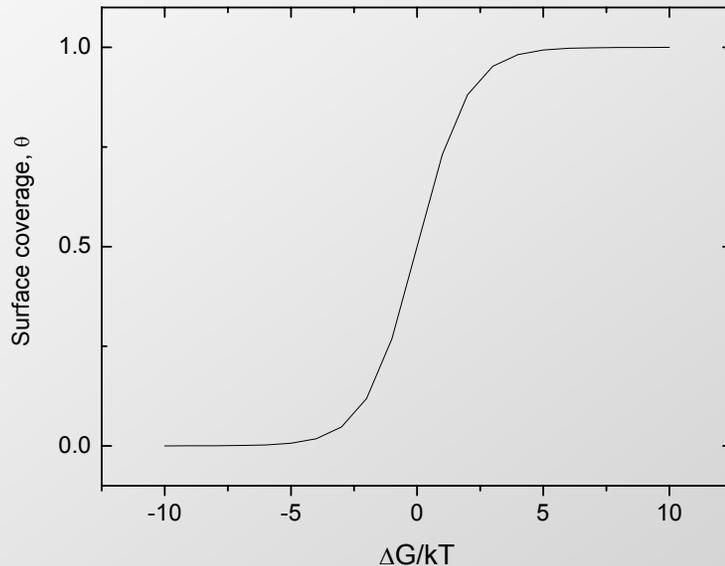
→ Adsorption isotherm – here: Langmuir isotherm:

- Surface charge: $Q_{Sadsp} = q_i \cdot \theta$

→ Capacitance due to adsorbed molecules = $\frac{dQ_{Sadsp}}{d\phi} = q_i \frac{d\theta}{d\phi} = q_i (z_i F / RT) \theta(1 - \theta)$

$$\frac{\theta}{1 - \theta} = a_i^b e^{-\Delta G_i^0 / RT} e^{-z_i F \phi / RT}$$

(θ – surface coverage)

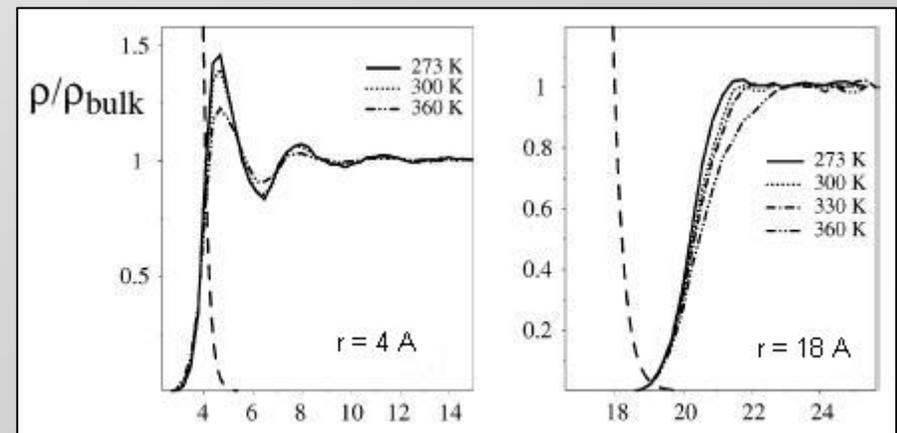


Molecular Dynamics Simulations (MDS) of water at hydrophobic substrates: (2004)

- Aim: water density depending on
 - curvature (spherical, planar)
 - temperature
 - pressure
- Model: for interactions used models
 - Lennard-Jones + Coulomb potential
 - Buckingham potential

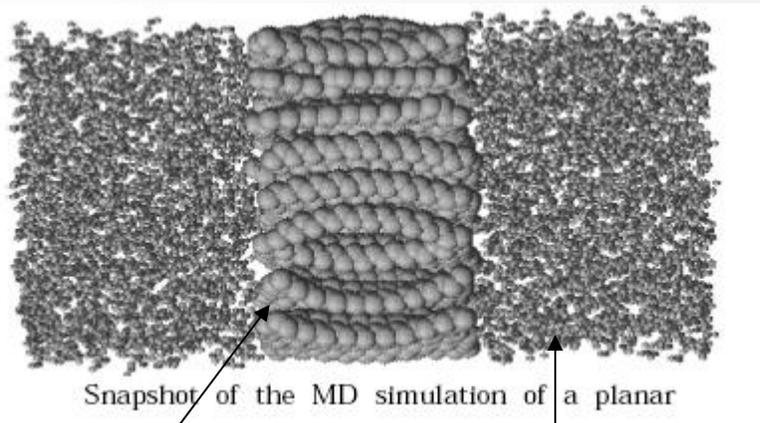
simulation cell: cubic box filled with $\sim 1000 - 3000$ water molecules
periodic boundary conditions

- Results I: *spherical* solute in box
 - increased density for small solute
 - water depletion for large solute
 - Temperature increase causes decrease of density
 - Same pressure dependence as at Results II



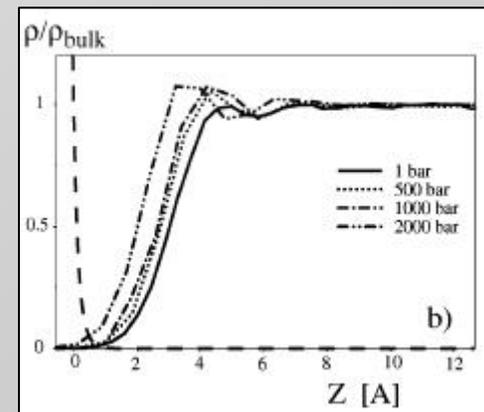
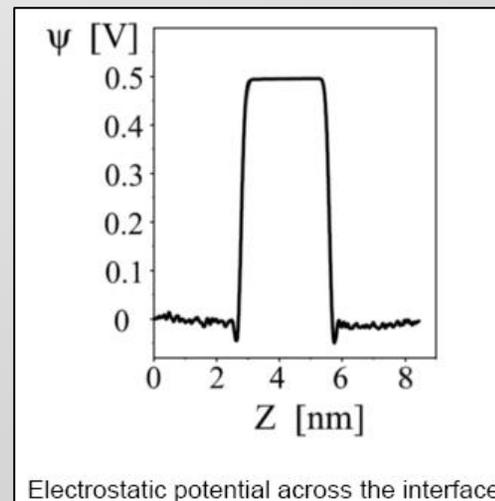
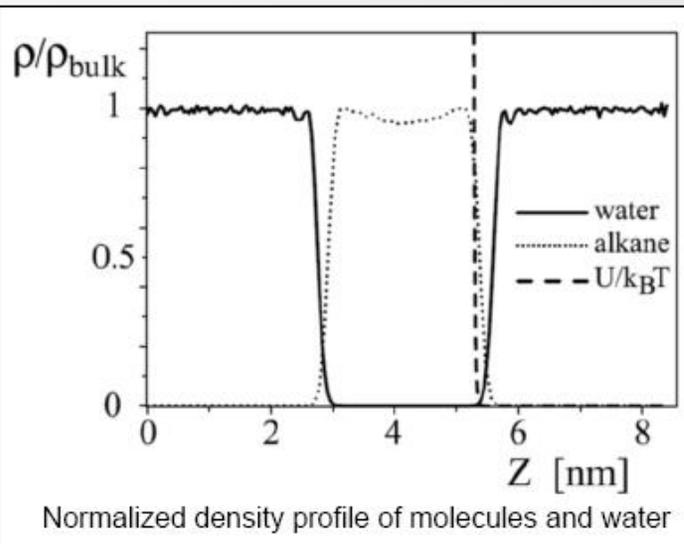
Simulation Molecular Dynamics Simulations – results II

- Results II: *planar* surface in box



Snapshot of the MD simulation of a planar surface in a box
64 alkane molecules + 2781 water molecules

- water depletion at interface
→ layer thickness ~ 2.5 Å
- *high* pressure reduces depletion layer
- layer thickness rises with Temperature
- potential drop at interface
→ caused by dipoles
→ top water layer oriented



Experiments on depletion (2003):

Experimental data also gives reason to a depletion layer of water on hydrophobic substrates:

- Observed interface:

D_2O on a hydrophobic plane

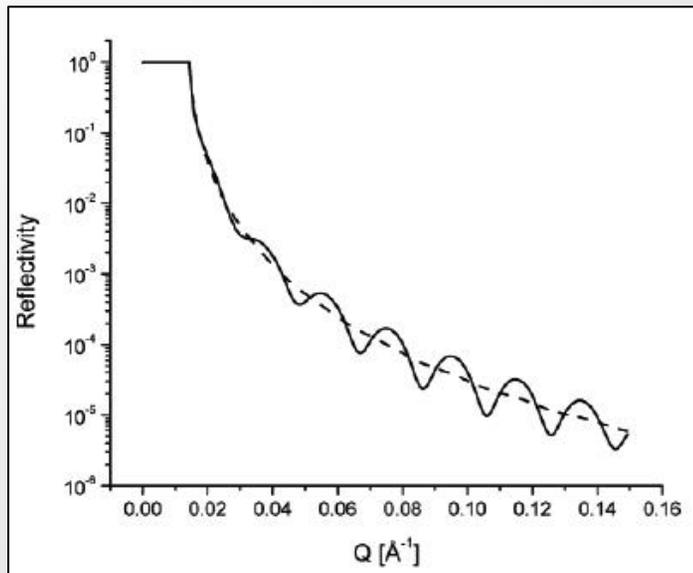
Neutron Reflectivity Measurements & Atomic Force Microscopy

- Layer thickness:

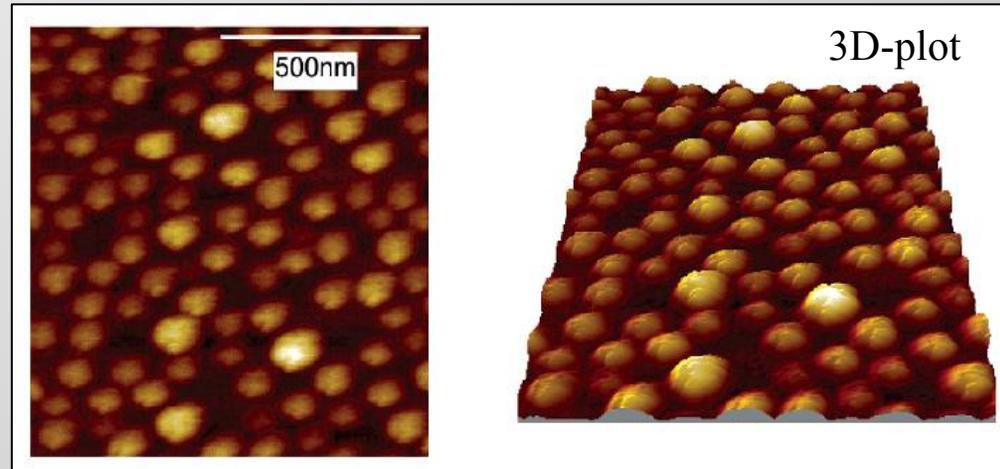
2-5nm

20nm

- memory-effect observed



NRM: Kiessig oscillations due to gas layer



AFM: tapping mode topology image of „nanobubbles“

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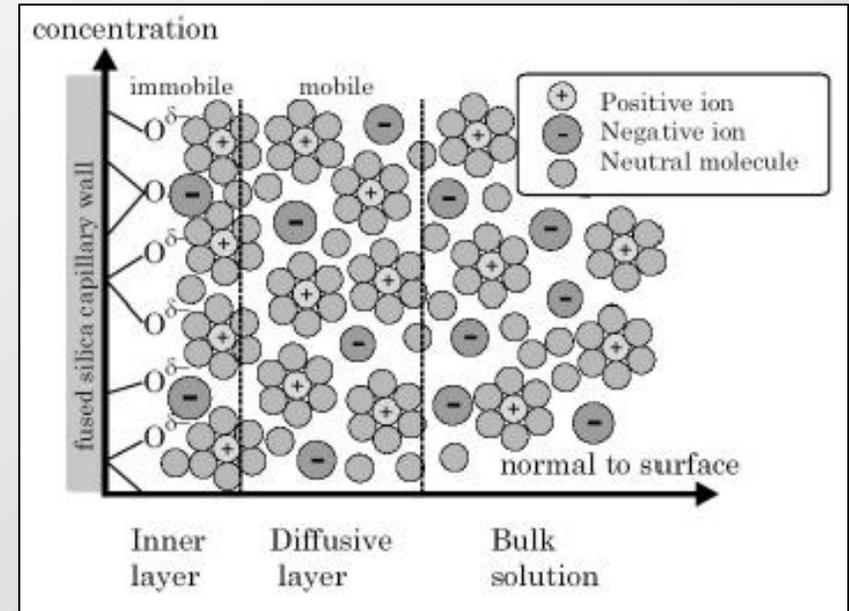
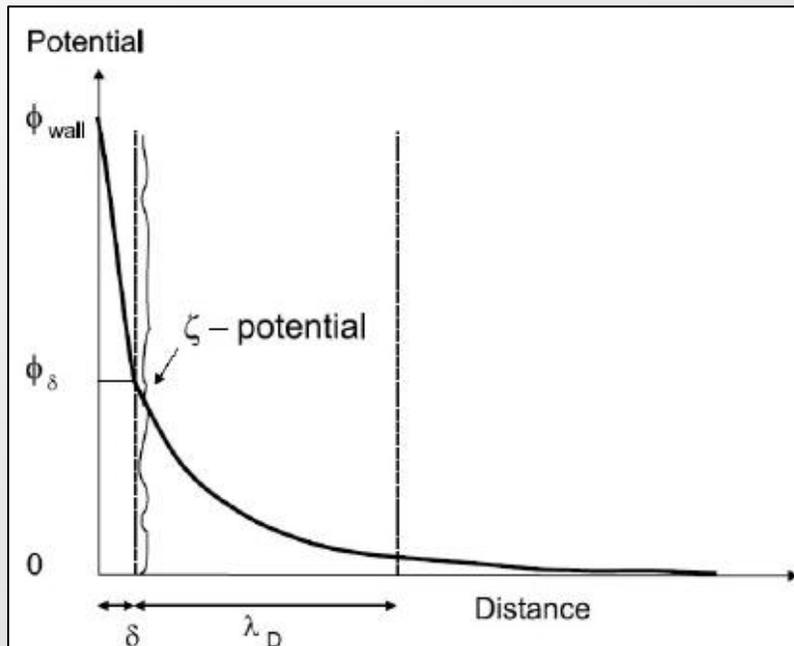
VII. Review

Application

Electrokinetics – zeta potential

Electrokinetics:

- due to strong electrostatic forces ions in the inner layer are *immobile*
- under pressure driven flow (pdf) ions of the diffuse layer are able to *move* → shear plane is formed



zeta-potential:

$$\zeta = \psi(x_{shear}) - \psi(x_{bulk})$$

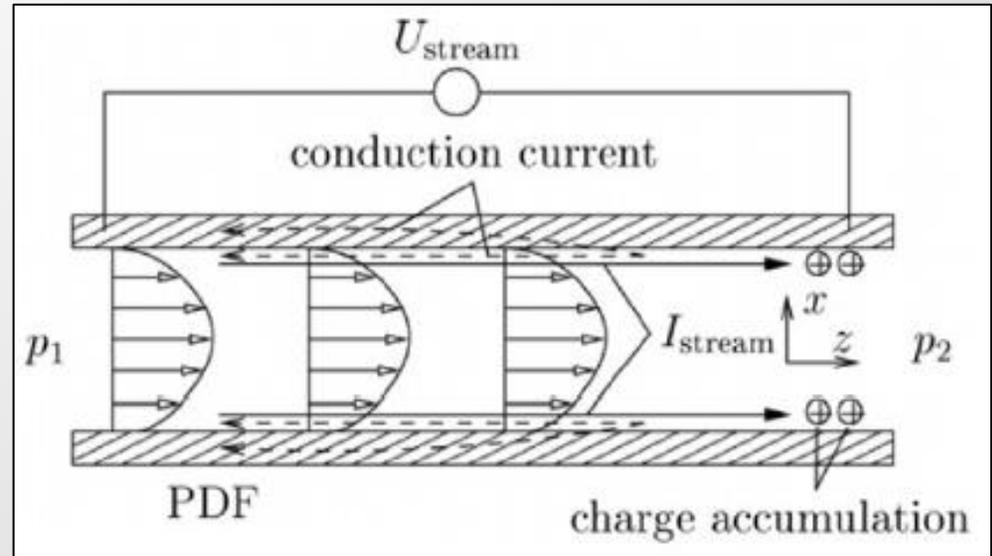
Application

Electrokinetics –

stream current & potential

fluid in a (micro)tube:

- zeta-potential $\neq 0$ grants movable net charges in diffuse layer
- pdf induces a stream of charges in a capillary:



$$I_{stream} = \int_A v_D(r) \rho(r) dA = 2\pi r \underbrace{\rho_D}_{\text{capillary radius}} v_D$$

σ_D - charge density in diffuse layer

v_D - drift velocity in diffuse layer

- depletion and accumulation of charges at ends of capillary respectively:

$$C = \frac{\pi r^2 k}{l} \text{ - conductance} \quad \longrightarrow \quad \text{Ohm's law}$$

$$U_{stream} = \frac{i}{C} = \frac{2\sigma_D v_D l}{r \cdot k}$$

(k = specific conductivity of solution)

Application Electrokinetic Measurements on Adsorption - idea

Analysing charge density of the inner layer using electrokinetic measurements:
(2001)

ζ -potential separates *immobile* and *mobile* layer

basic idea:

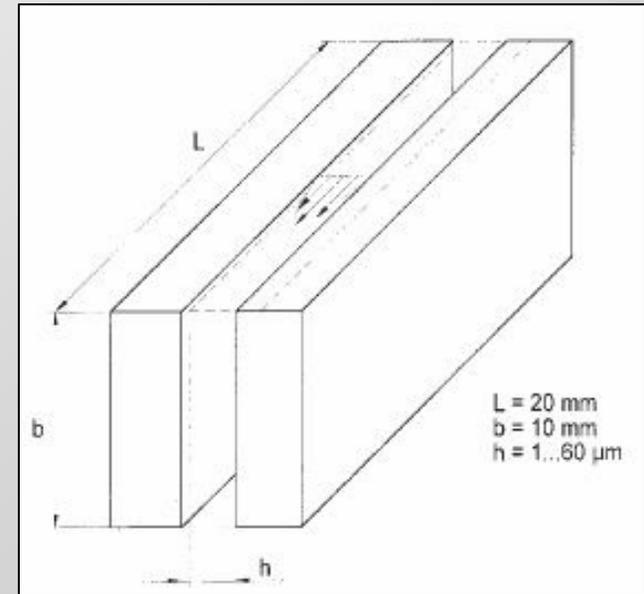
sign of ζ -potential reveals sign of total charge within the inner layer

electrokinetic values measured:
streaming potential & current

correlation with ζ -potential:

$$\zeta(U_S) = \frac{\eta K_B}{\varepsilon_0 \varepsilon_r} \frac{dU_S}{dp}$$

$$\zeta(I_S) = \frac{\eta L}{\varepsilon_0 \varepsilon_r b h} \frac{dI_S}{dp}$$



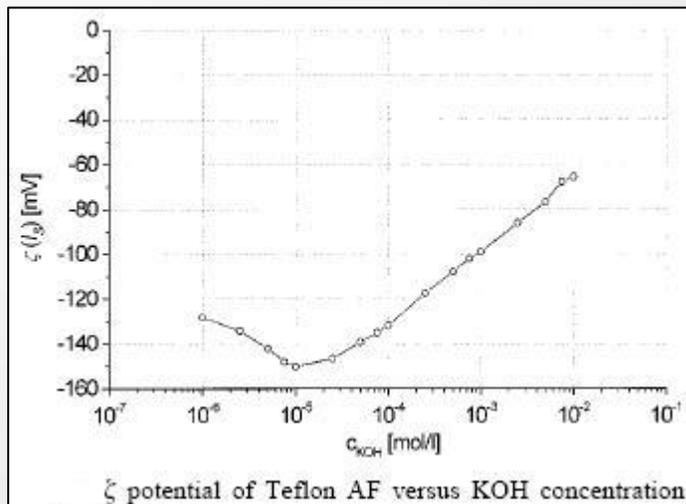
experimental setup

Application Electrokinetic Measurements on Adsorption - plots

Obtained data:

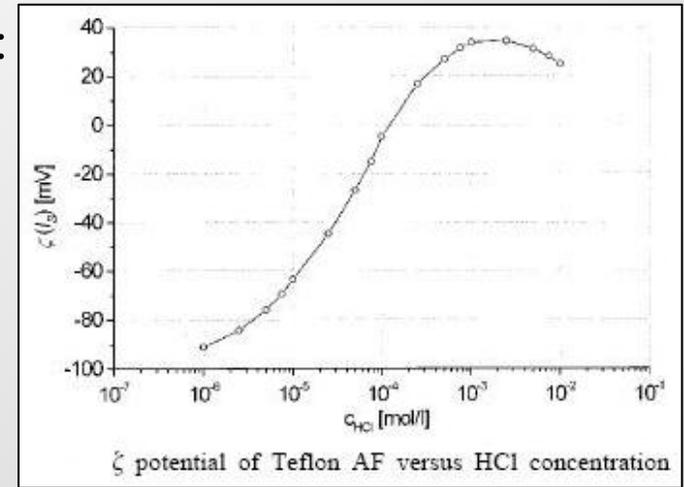
- pure water: $2H_2O \leftrightarrow OH^- + H_3O^+$
→ negative ζ -potential

- KOH:



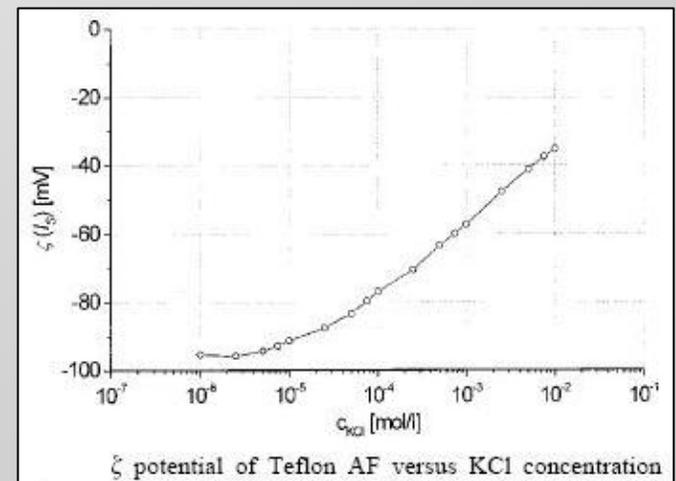
- first OH-ions preferred, afterwards:
- compression of the double layer
→ increasing surface charge compensation already within inner layer (screening...)

- HCl:



- first H-ions preferred → sign reversal
- then: double layer compression

- KCl:



- only double layer compression

Application Electrokinetic Measurements on Adsorption - results

Conclusions:

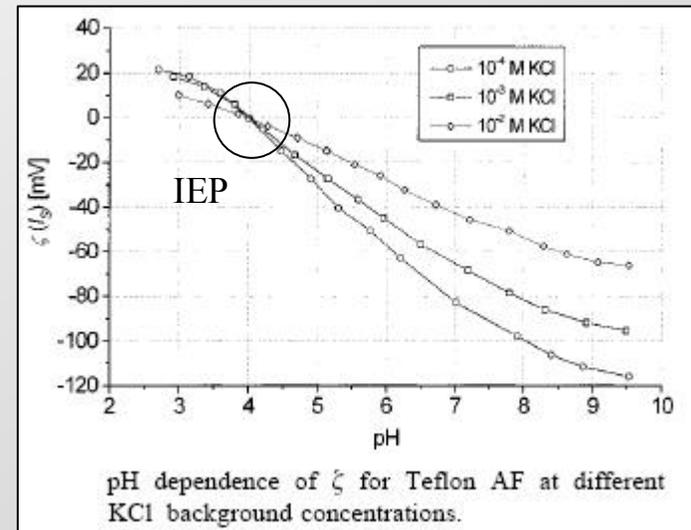
preferential adsorption: $OH^- > H_3O^+ \gg Cl^- = K^+$

- pH-dependence:

→ low IEP proves result above

important factors for adsorption:

- structure of hydration shell important (OH-ion known to have less stable hydration structures → escapes more easily and builds up hydrogen bonds with interfacial water)
- capability to bind interfacial water via hydrogen bonds
- another experiment using **pH-Dependant Force Spectroscopy** leads to conclusion:
 - immobilized interfacial *water acting as template* for hydroxyl adsorption
 - density of molecular units of water building networks on the surface crucial

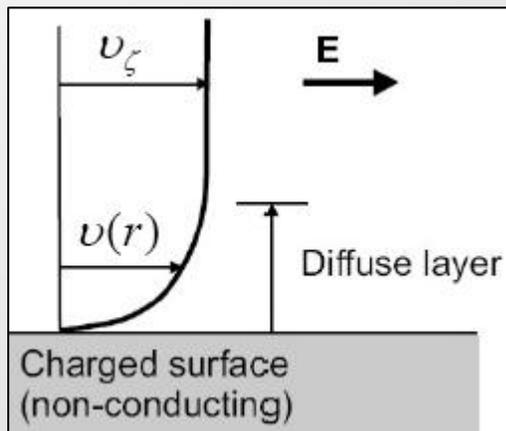
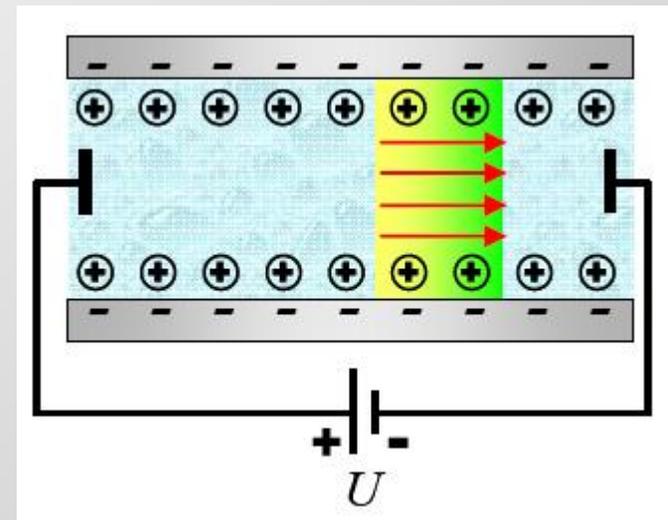


Application

Electroosmosis – what it is

Electroosmosis:

- Applying *electric field* along capillary
→ movement of liquid relative to stationary charged surface
- electric field induces *force* on net charge in diffuse layer
- diffuse layer displacement leads to *dragging* of bulk fluid



drift velocity of fluid:

$$v_{\zeta} = \frac{\epsilon \zeta}{\eta} E_x$$

- Helmholtz-Smoluchowski

μ_c - osmotic mobility

Application

Electroosmosis – properties

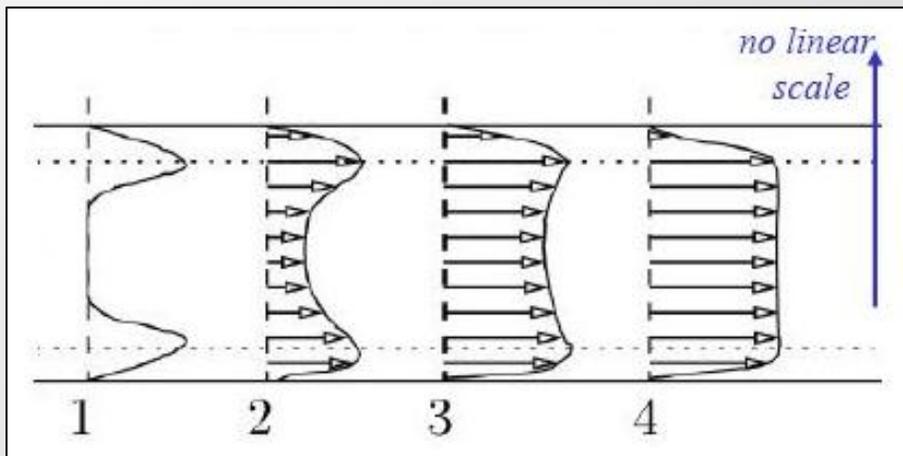
- advantage of electroosmosis:

*the way to have **laminar flow** in microfluidics at low Reynold's numbers*

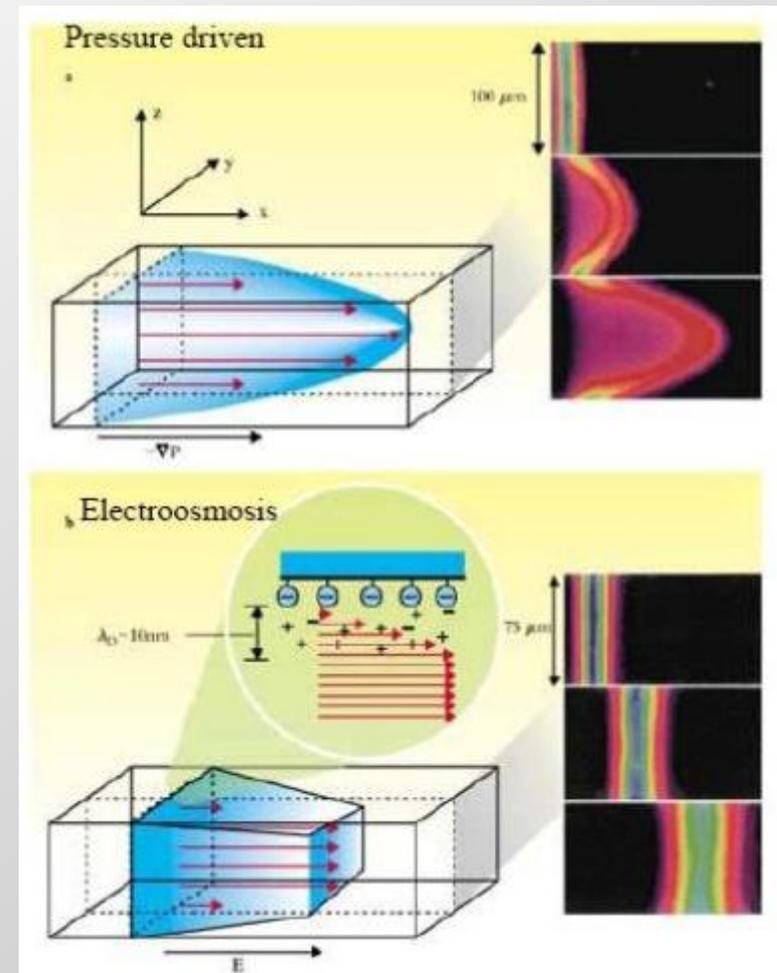
- example:

- ζ -potential = -100mV
- electric field = $2.5 \times 10^3 \text{V/m}$

$$v_{\zeta} = 200 \mu\text{m} / \text{s}$$



time development after switching on the e-field → dragging → laminar flow



Review

Helmholtz
Gouy-Chapman
Stern

Theory

4.



1.



2.

Experiment

3.

Simulation

4 state model, MDS...

Adsorption &
its parameters,
AFM, NRM...



Application

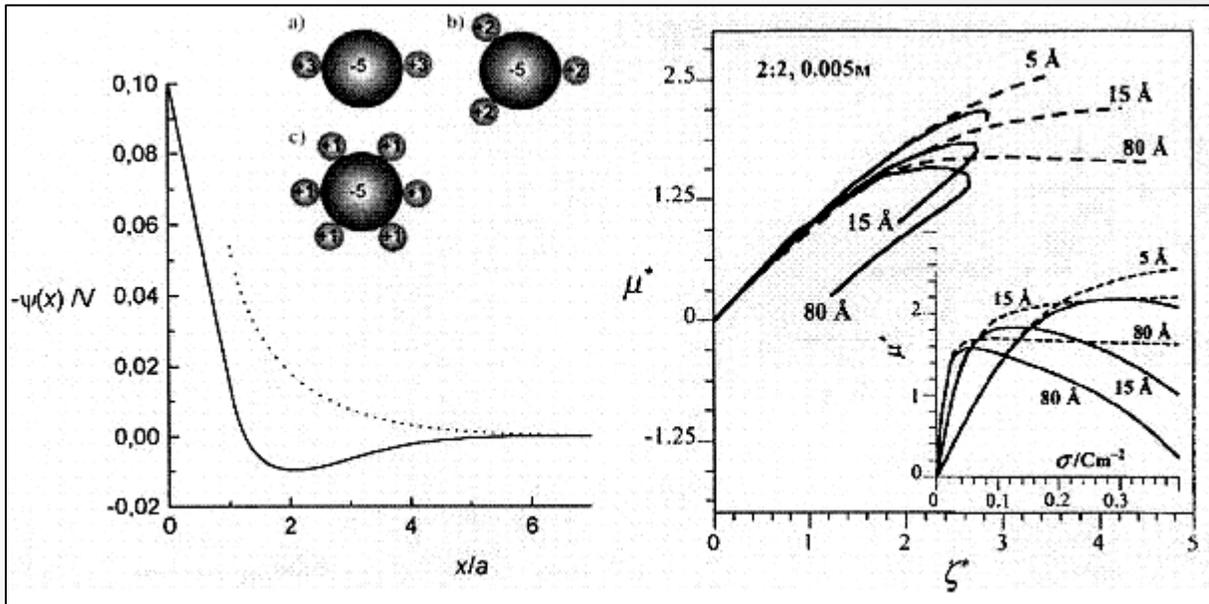
Electrokinetics, microfluidics...

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Qualitative:

$$\left. \begin{array}{l} \varepsilon = 5.3 \cdot \varepsilon_0 \\ d = 0.31 \text{ nm} \end{array} \right\} C_0 = \frac{\varepsilon}{d} \approx 15 \mu\text{F} / \text{cm}^2$$

$$\mu_c = 0.28 \cdot \mu = 1.4 \cdot 10^{-30} \text{ Cm}$$

$$N_{tot} = 7 \cdot 10^{14} \text{ cm}^{-2}$$

