Light, Liquids & Interfaces
Micro-390

Lecture 10

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Material to study:
Lecture notes
Atkins 19.15(b): Gibbs isotherm

Exercises: 22-23

Key concepts Lecture 9

IR spectroscopy probes vibrational modes

- IR transitions arise from a change in dipole moment at the equilibrium position
- IR spectra can be used to identify molecular structures and interactions in liquids

Raman spectroscopy probes vibrational modes and is complementary to IR (can be done with visible light)

- Raman transitions arise from a change in the polarizability at the equilibrium position

Second Harmonic scattering is a probe for nanoscale orientational correlations in liquids

Topic 5: Interfaces in 2D and 3D

Surface tension
Surface excess and the Gibbs adsorption equation
Interfaces 2D: The electrical double layer
How to measure zeta potentials
Poisson-Boltzmann’s equation
Interfacial models
How to measure surface potentials
Interfaces 3D:
How to measure zeta potentials
How to measure surface potentials

Surface tension

Surface tension

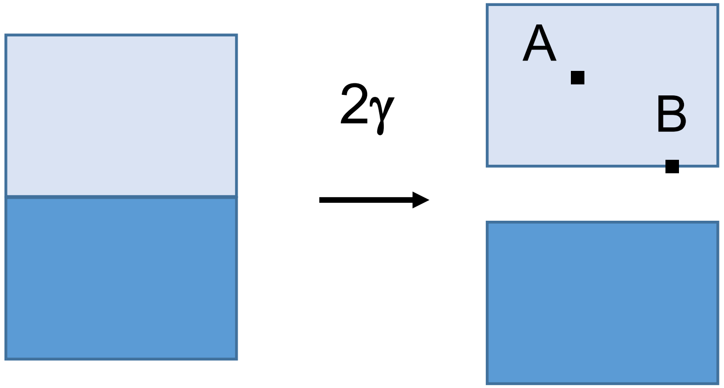
- Boundary between two bulk substances = interface
- Forming an interface costs energy
- This is described by the surface tension (or interfacial energy)
- Result of an imbalance of intermolecular forces

Surface tension:

$$\gamma = \frac{dw}{dA}$$

$$[\gamma] = \frac{J}{m^2} = \frac{N}{m}$$

(compare to pressure: $P = -\frac{dw}{dV}$)



Surface → Imperfect "bulk"
Restricted in configuration (ΔS ↘)
Less bonds/molecule (water: 3.6/molecule)

Surface tension

- Two primary forces: Tangential and inward

- Tangential force is usually referred to as the surface tension γ

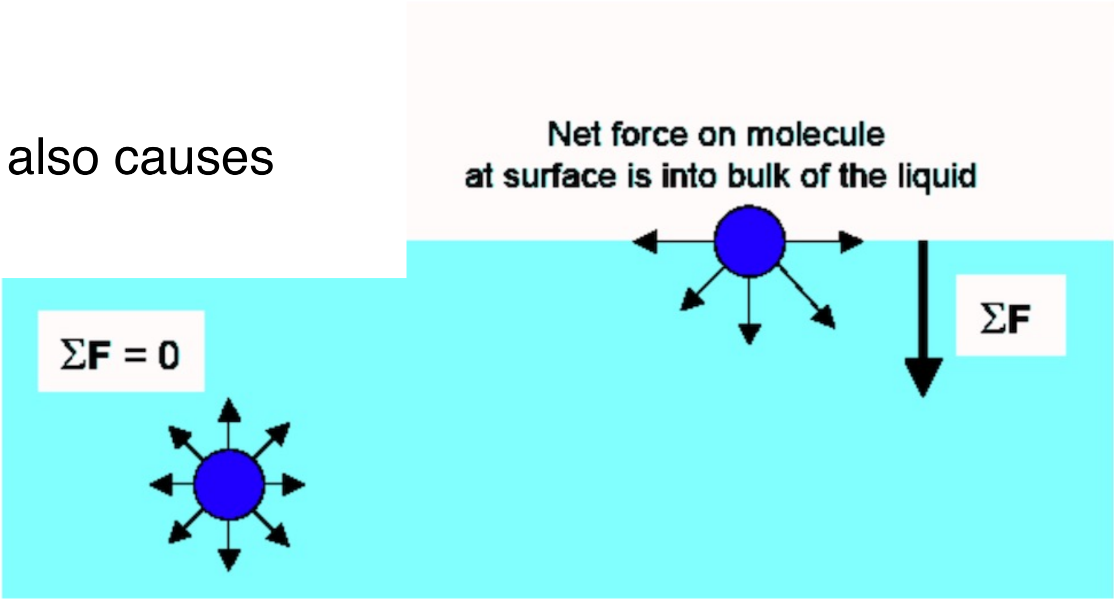
Expand:

Tangential force

Direction of γ

Surfaces tend to contract
(dA: Need to supply energy to expand)

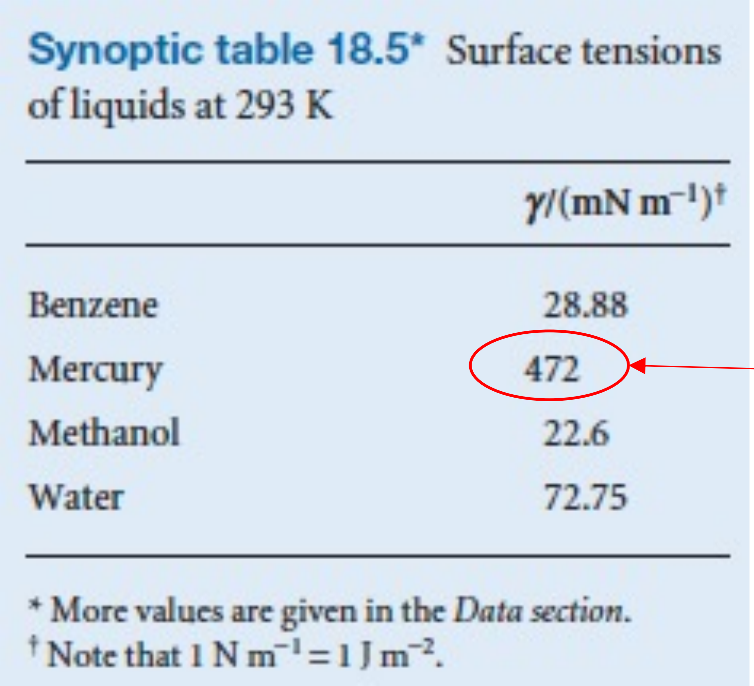
- Inward force also causes contraction:



http://labman.phys.utk.edu/phys221core/modules/m7/surface_tension.html

Surface tension

- Liquids tend to adopt shapes that minimize their surface area:
- The maximum number of molecules are in the bulk, where they are surrounded by and interacting with neighbors
- Droplets and spheres have the smallest surface/volume ratio and $\Delta w = \gamma \cdot 4\pi R^2$



Synoptic table 18.5* Surface tensions of liquids at 293 K

	$\gamma/(\mathrm{mN\ m^{-1}})^{\dagger}$
Benzene	28.88
Mercury	472
Methanol	22.6
Water	72.75

* More values are given in the *Data section*.

† Note that $1\ \mathrm{N\ m^{-1}} = 1\ \mathrm{J\ m^{-2}}$.

Mercury droplets!

Atkins, Physical Chemistry

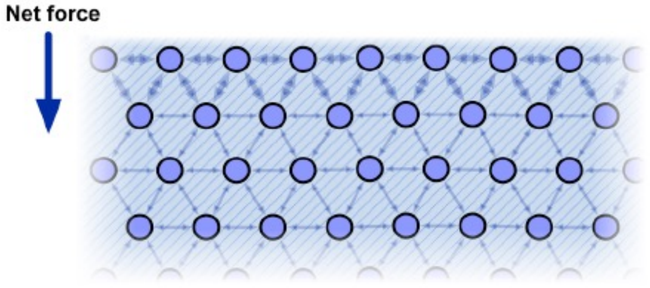
Modify the surface tension

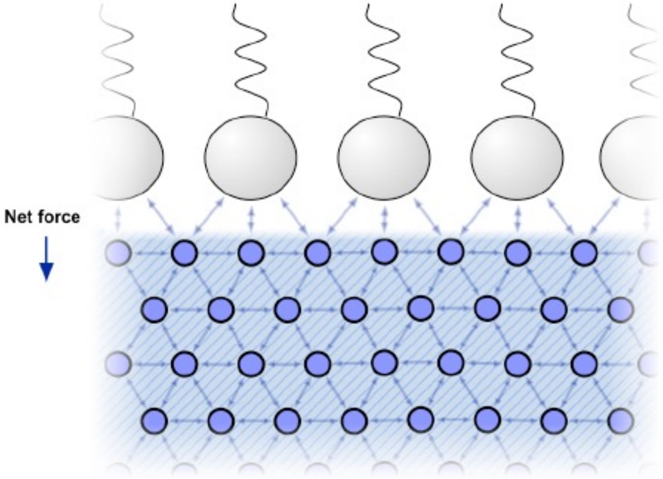
- Lowering the surface tension of a solvent is a prerequisite for wetting, spreading, foaming and emulsification
- Oil molecules can spread at the surface of water

Pictures: Esther Amstad

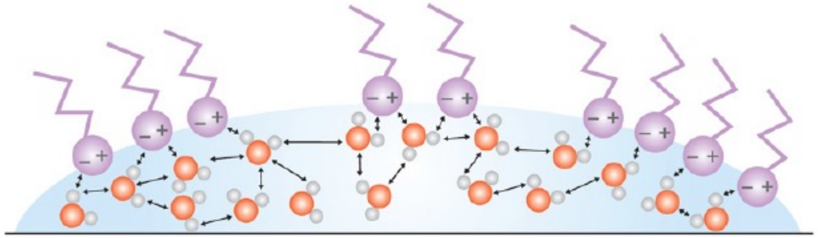
$$\gamma_{oil} < \gamma_{water}$$

More favorable to have an oil surface in contact with air!

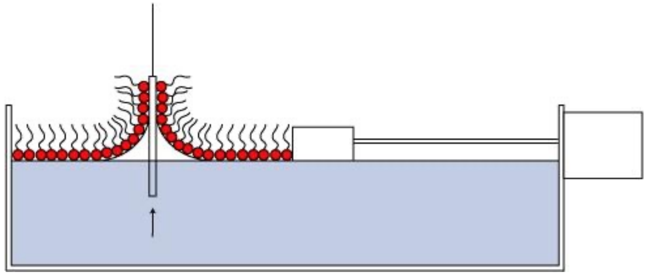




- Charged groups of surfactants (ex: phospolipids) interact with water (↘ γ)



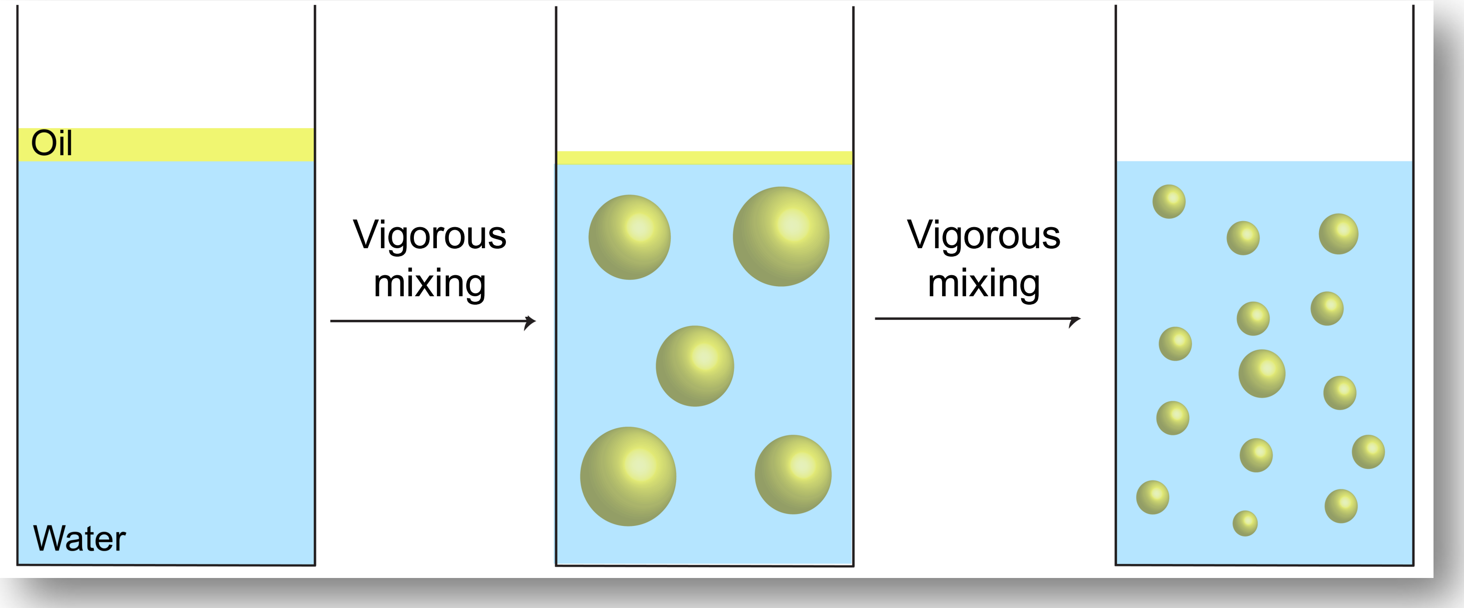
- Study the properties of monolayers of amphiphilic molecules: Langmuir trough



https://commons.wikimedia.org/w/index.php?curid=46512977

Emulsions

- Emulsions are drops of a liquid dispersed in a second, immiscible liquid
- Oil in water emulsions: milk (3.5 % fat)
- Water in oil emulsions: butter (80 % fat)



- The presence of a surfactant provides a decrease in surface tension, which permits stability of small droplets of oil in the bulk of water (or vice versa).
- Ex.: lecithin (phospholipid from egg) in mayonnaise (oil-in-water)

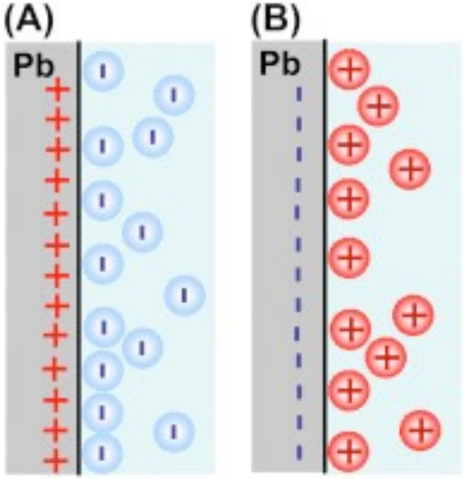
Surface excess and the Gibbs adsorption equation

The electrical double layer

EDLs in everyday life (2D and 3D)

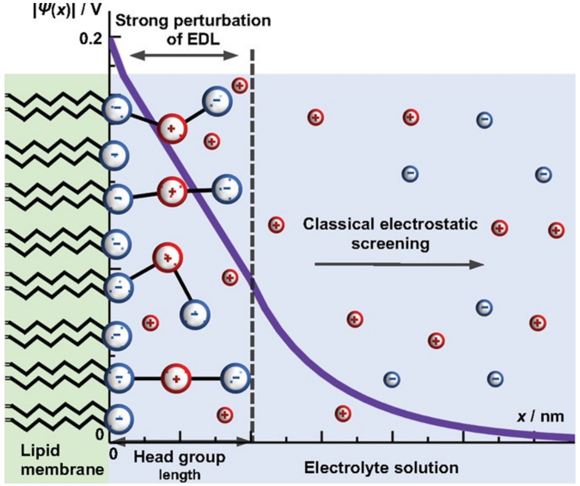
- Electrical double layer (EDL) , sometimes called double layer (DL) only
- Charged structure that appears on surfaces exposed to a liquid (electrodes, solid particles, gas bubbles, liquid droplets, porous bodies, cell membranes...)

Electrochemistry:
Metal electrodes



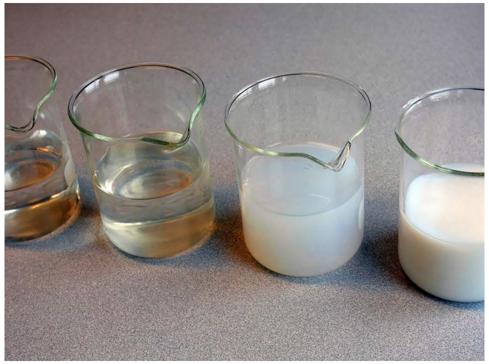
https://www.sciencedirect.com/topics/engineering/electric-double-layer

Biology:
Cell membrane



J. Chem. Theory Comput. 2022, 18, 1, 448-460

Colloidal science:
Colloidal particles
(see *Interfaces 3D*)

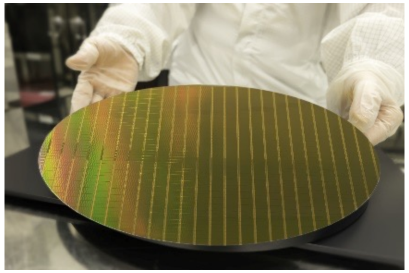


https://www.nouryon.com/products/colloidal-silica/what-is-silica/

Example: SiO_2 surface

Sedimentary rocks

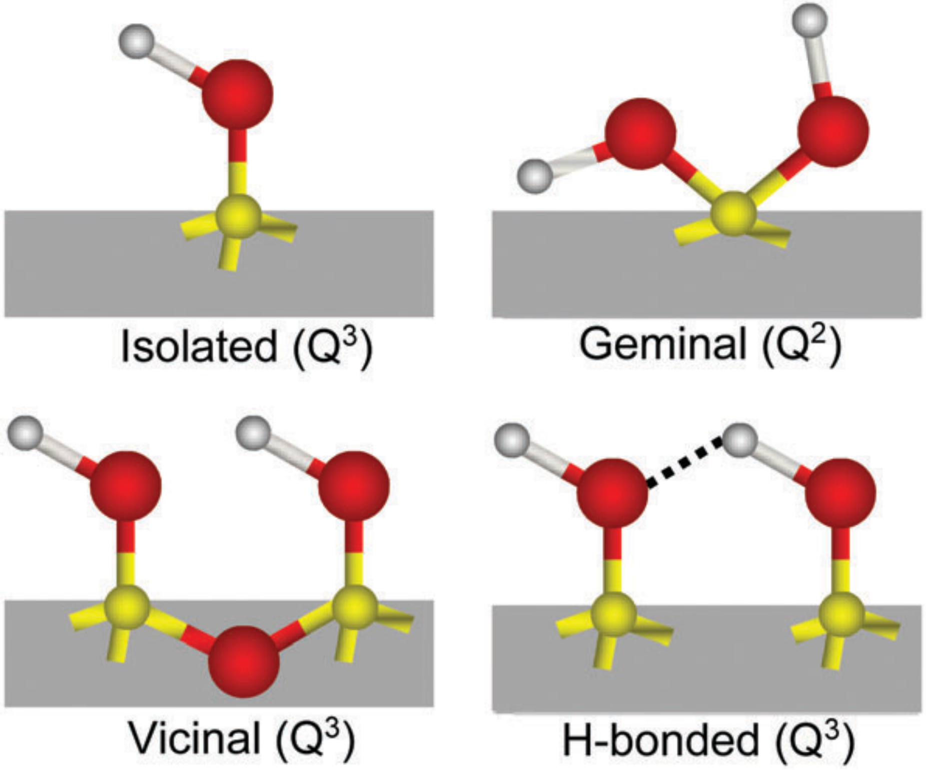
https://commons.wikimedia.org/w/index.php?curid=350499



SiO_2 protective layer on silicon

How does the surface look like when in contact with water?

- Siloxane (Si–O–Si)
- Silanol (Si–OH)
- Silanolate (Si–O^-) resulting from the partial deprotonation of silanols
- Different groups have different deprotonation constants (different pk_A)

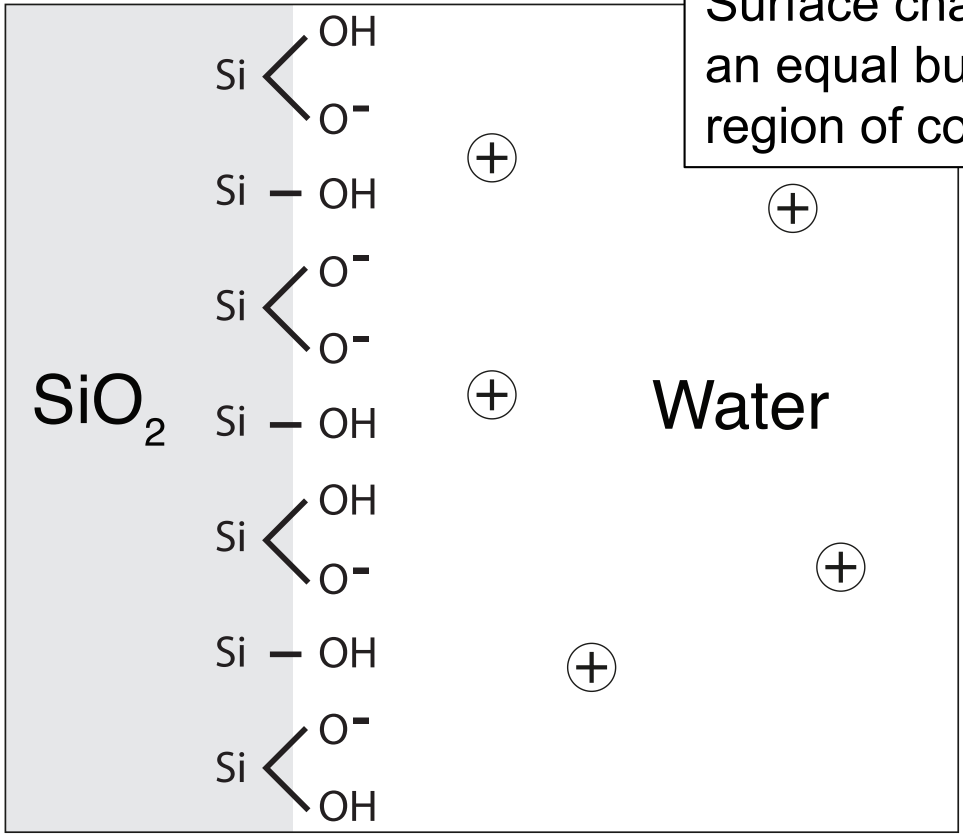


Dalstein, Popatova, Tyrode,
Phys. Chem. Chem. Phys., **2017**, *19*, 10343

Surface charge

Charging mechanism: Ionization or dissociation of surface groups

Surface silanol groups Si–OH → $Si–O^- + H^+$



Surface charge is balanced by an equal but oppositely charged region of counterions

Other charging mechanisms: Adsorption of ions on uncharged surface

Ex.: binding of Ca^{2+} onto zwitterionic headgroups of lipid bilayer surfaces

Earliest model for the EDL

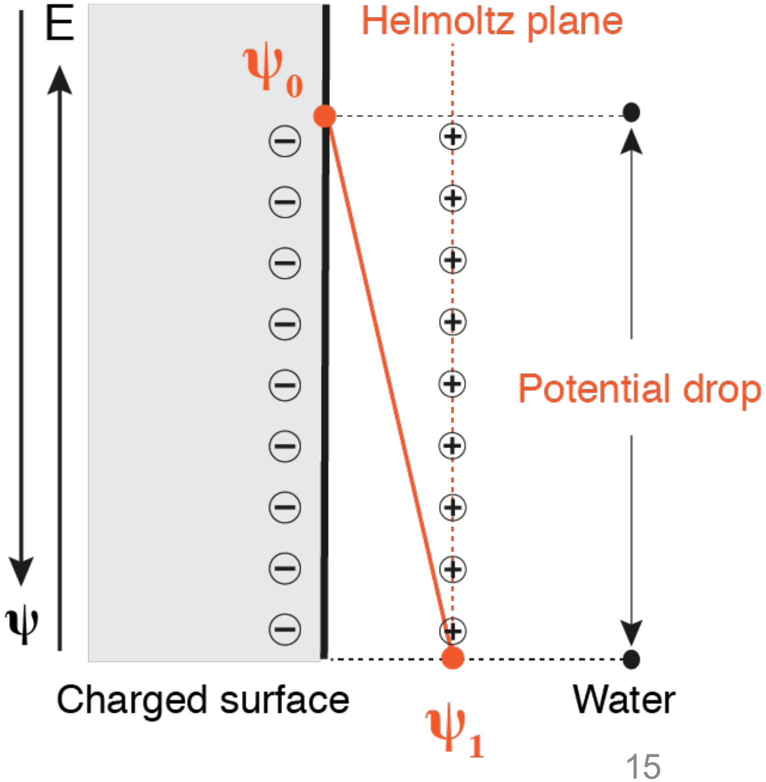
- Helmoltz put forward the concept of EDL in 1853
- Capacitor is formed between charged surface and counterions in solution
- The formation of any kind of EDL implies the development of strong electrostatic fields at the interface

➢ Distance between the two sides of an EDL is generally < 1 nm

➢ Potential differences can reach several volts

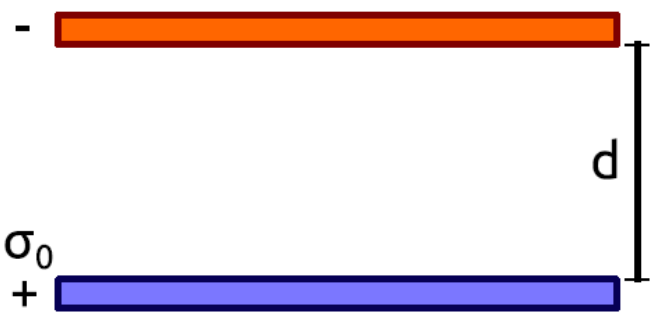
➢ E field strength within EDLs can be > 10^7 V/cm

Hermann von Helmholtz (1821–1894).



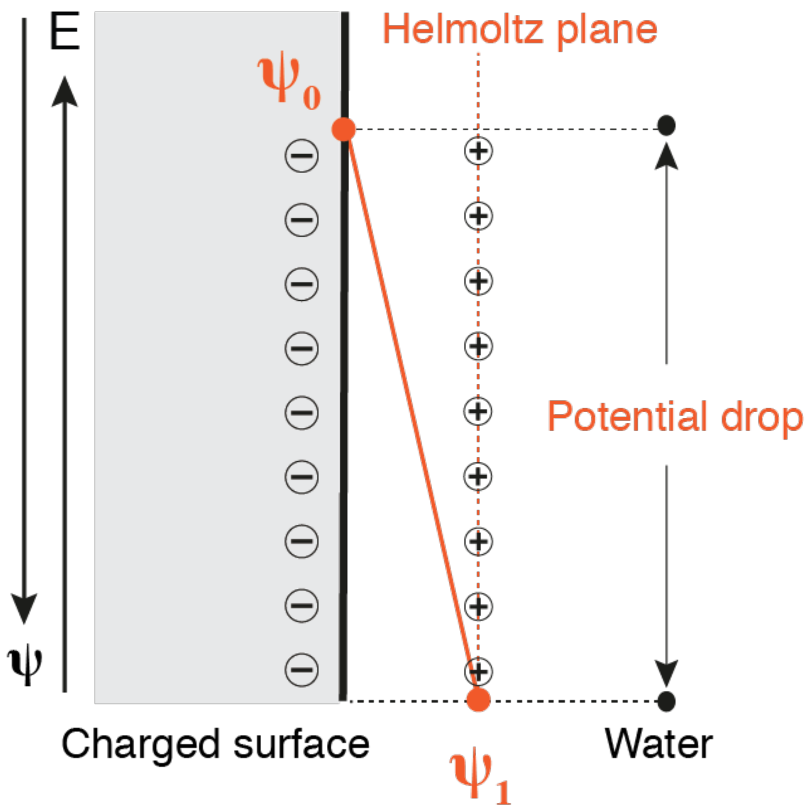
Earliest model for the EDL

Planar capacitor:



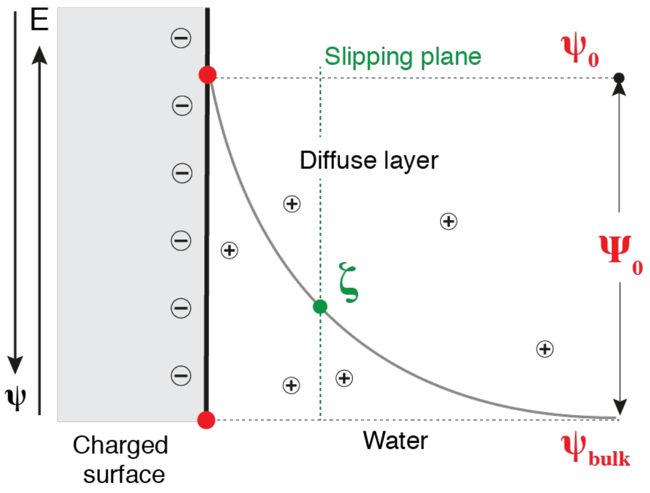
$$C = \frac{Q}{\Delta V} \qquad [C] = F$$

σ_0 = surface charge density

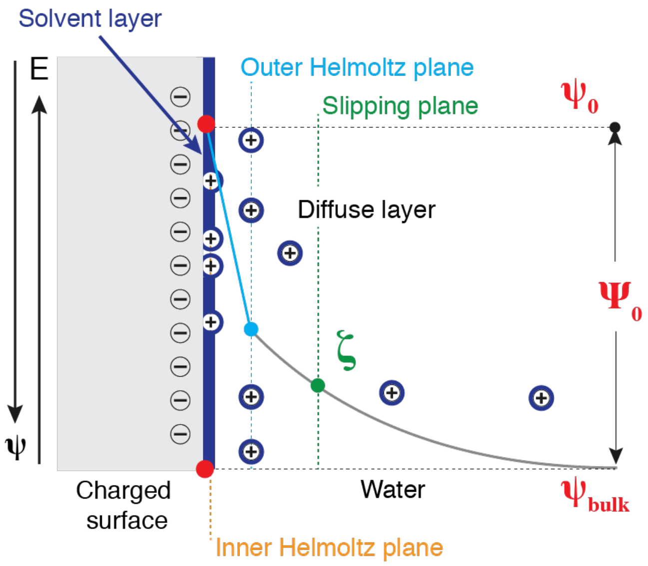


$$Q = \sigma_0 A \Rightarrow C = \frac{\sigma_0 A}{\psi_0 - \psi_1}$$

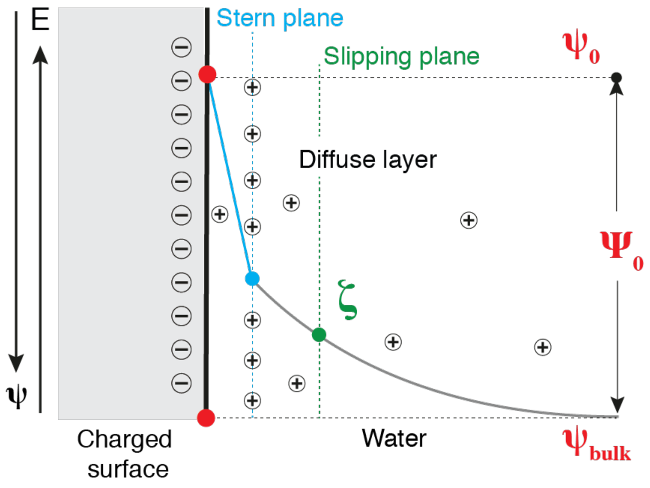
EDL: more models



Gouy-Chapman



Grahame



Gouy-Chapman-Stern

Characterize charged interfaces:

1. Point of zero charge
2. Zeta potential (or surface zeta potential)
3. Surface potential

Point of zero charge

- For planar surfaces, corresponds to the neutral surface
- Point where the **average** surface charge density is zero
- The way it is obtained depends on the material, usually electroanalytical techniques are used.
- Not the easiest characterization technique!

Metals: cyclic voltammetry on electrodes

→ The pzc is indicated by the minimum of the capacitance in dilute solutions

→ Difficulty in preparing single crystal electrodes and excluding specific adsorption of electrolyte ions

Oxides (pH-dependent surface charging):

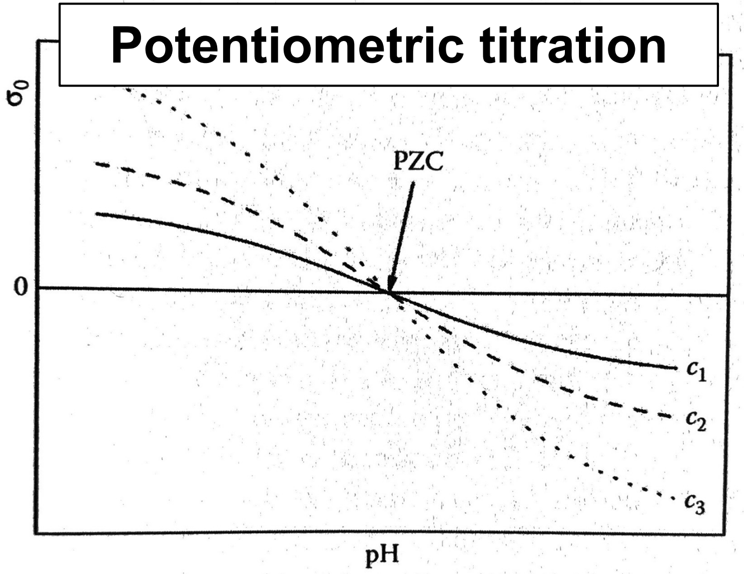
Potentiometric titrations

→ Measures potential difference between the reference electrode at a constant potential and the working electrode whose potential changes with the sample's composition as fct of pH

→ Common intersection point of potentiometric curves obtained at various ionic strengths (c_i)

→ Problem: ion-specific adsorption

Potentiometric titration



Point of zero charge

Can be quite tedious….

Is there any other characterization parameter that we can use instead?

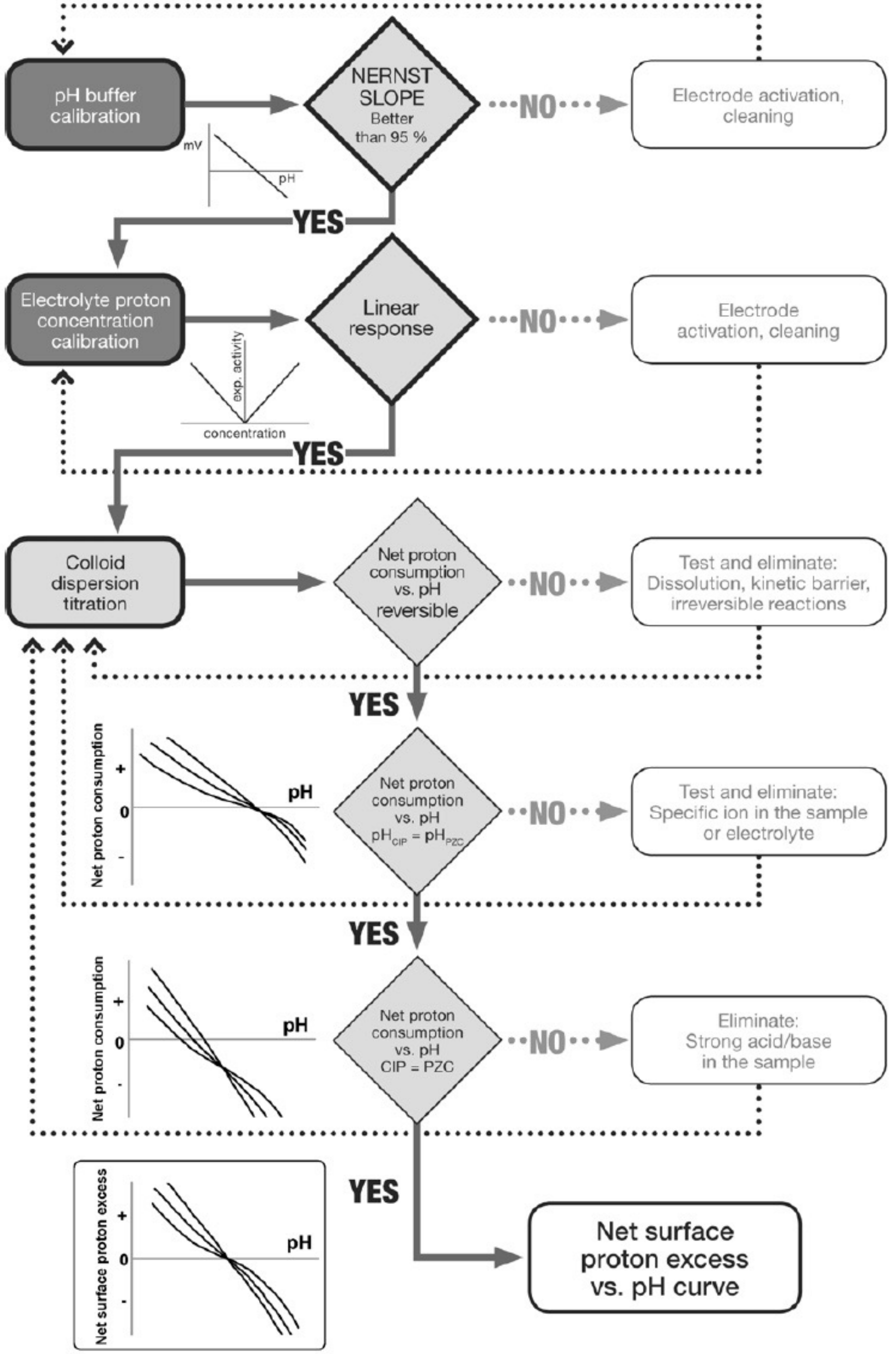
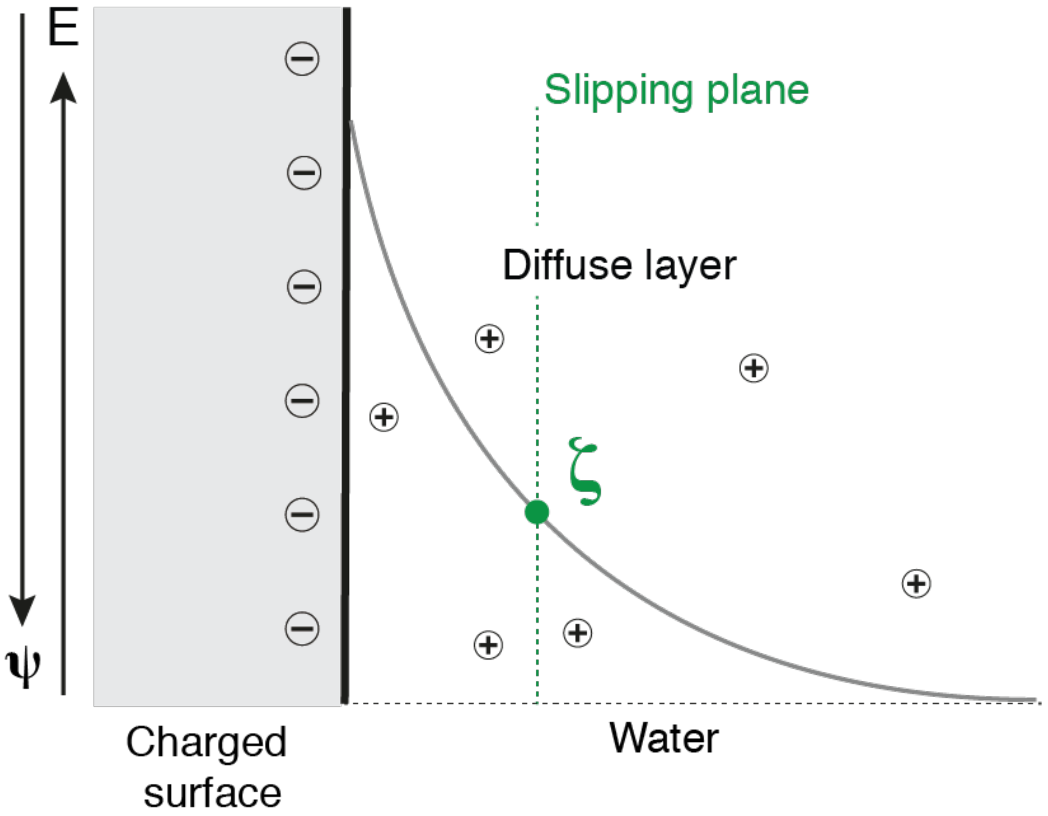


Fig. 8. The flow chart of the procedure of potentiometric acid–base titrations of oxides.

Colloids and Surfaces A: Physicochem. Eng. Aspects 414 (2012) 302– 313

Zeta potential (ζ) – most common!



- Potential at an arbitrary boundary in the solution: **Slipping plane**
- Within this boundary: ions and solvent molecules that remain firmly associated with the surface when exposed to **E** (but not necessarily adsorbed)
- For colloidal suspensions, gives an indication of stability (cf. next week)
- Often the isolectric point (IEP, $\zeta = 0$) is given instead of the PZC (easier to measure than the PZC)

Zeta potential (ζ)

Applications:

- Microfluidics: moving liquids in an electrical potential

- Biology and health care:
  - Bones
  - Tooth enamel (interactions of saliva and enamel)
  - Protein binding at surfaces
  - Implants

- Geological samples
- Thin films/coatings
- Membranes used for water cleaning

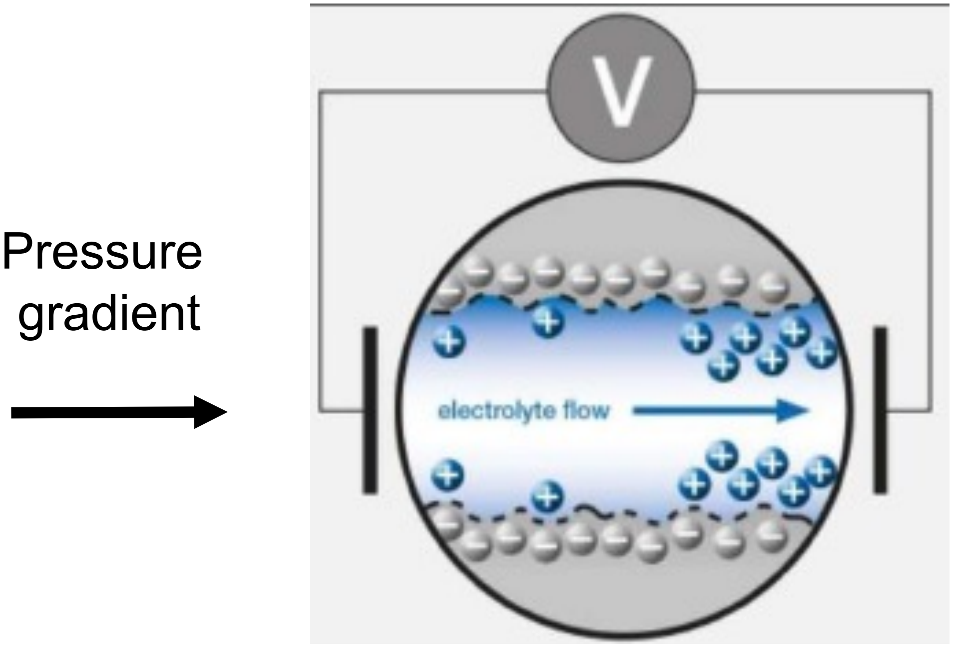
Zeta potential for planar surfaces can be determined in several ways:

- Measuring the ***streaming potential***: The electric field generated when a liquid is forced to flow past a stationary charged surface
- Measuring the ***electro-osmotic effect***: The movement of a liquid relative to a stationary charged surface under the influence of an electric field

How to measure zeta potentials for flat surfaces?

Streaming potential:

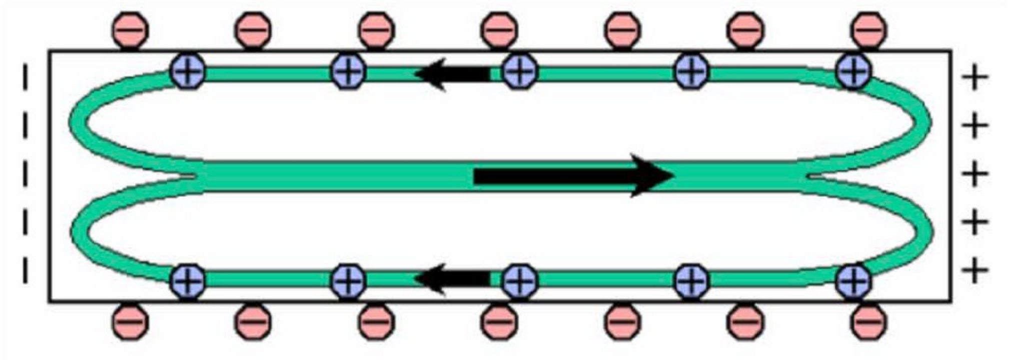
- A pressure gradient is applied between both ends of a capillary flow channel, which generates a liquid flow
- Two electrodes held at the same potential measure the streaming current flowing though the electrodes
- Zeta potential is related to the streaming current



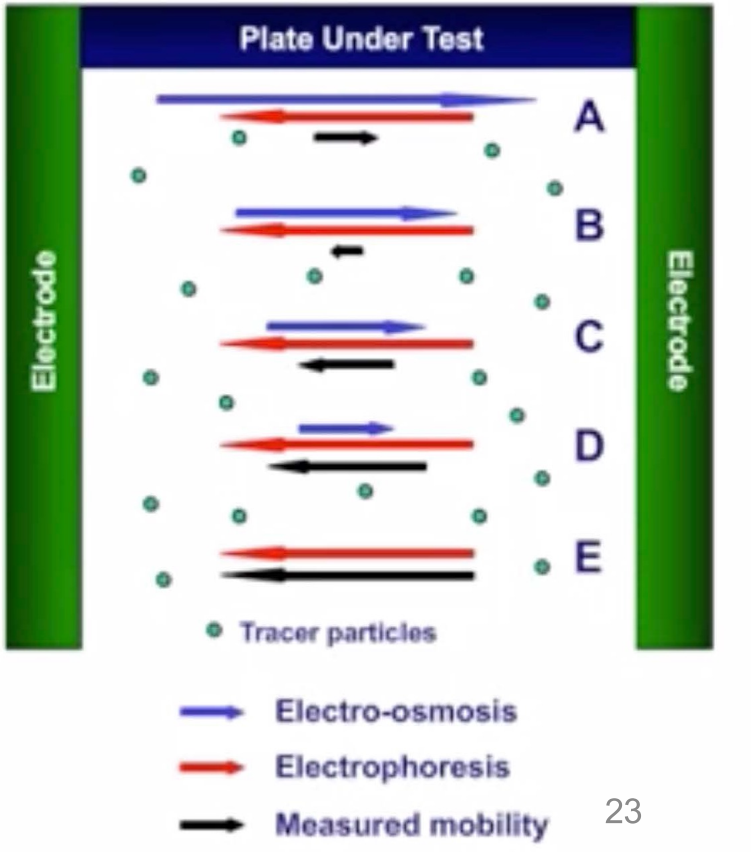
https://wiki.anton-paar.com/ch-de/zetapotenzial/

How to measure zeta potentials for flat surfaces?

Electro-osmosis:

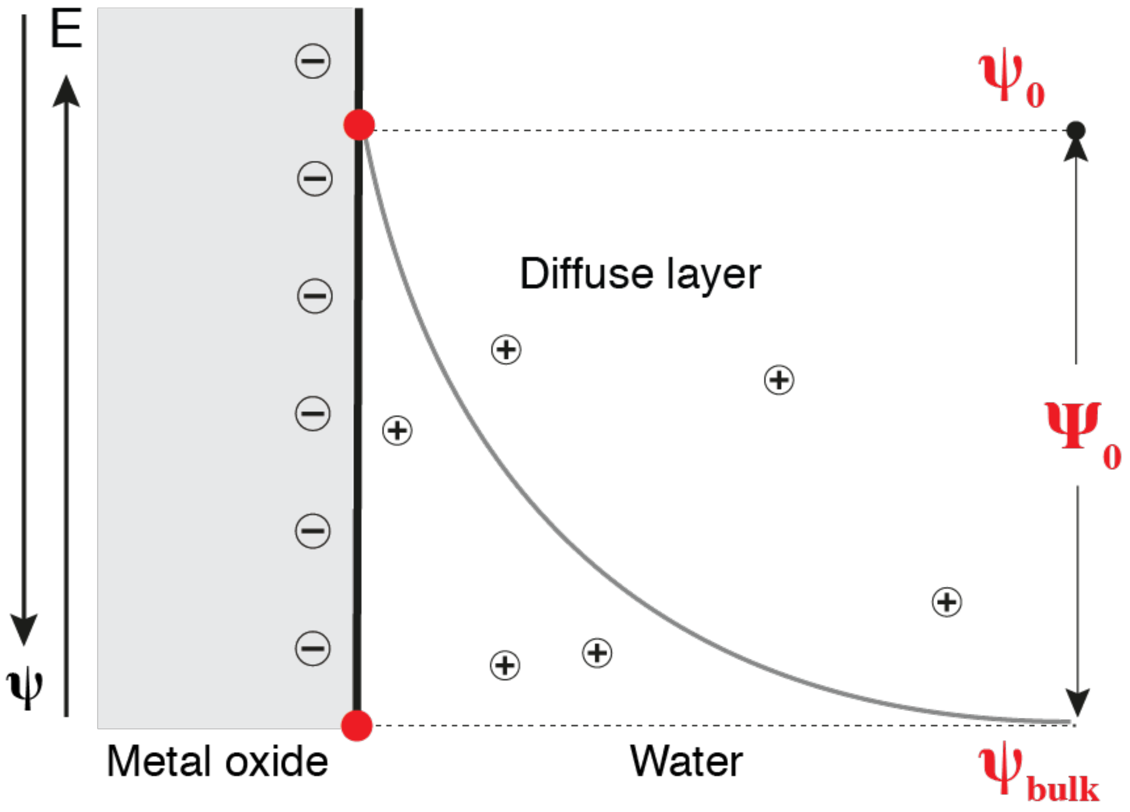


- Counter-ions near the capillary surface at the “same sign” pole are depleted with **E**
- Replenished by counter-ions from the center of the cell (concentration gradient)
- **Solvent flow from – to +**



- Detect movement of tracer particles at various distances from the plate under test
- Under external **E**: Tracer particles move under the effect of the electro-osmosis and electrophoresis
- Mobility is the sum of these 2 phenomena
- Position (E): pure electrophoresis, can be subtracted

Surface potential (ψ_0)



- Surface characterization
- ”Real” potential at the surface, not an arbitrary plane
- Important for electrochemistry, catalysis
- Most often determined by theory
- Often $\psi_{\text{bulk}} = 0$ so $\psi_0 = \mathbf{\Psi}_0$ (you will also find $\mathbf{\Phi}_0$ in the literature)

Key concepts Lecture 10

- Surface excess and the Gibbs adsorption equation
- Relationship between surface tension, entropy and surface excess
- The electrical double layer
- Zeta potential is the potential at the slipping plane, measured by electrokinetic methods