

# DLVO - Theorie

Derjaguin

Landow

Verwey

Overbeek

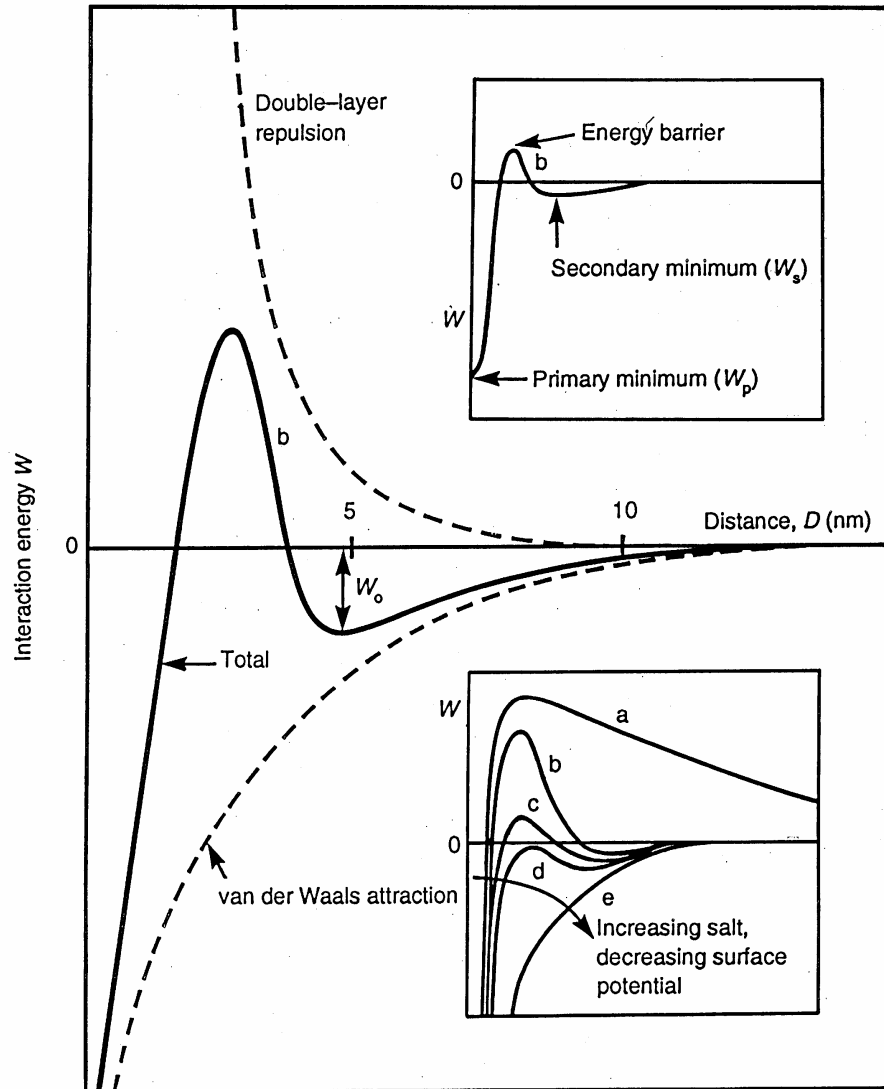
Combination

- van der Waals – attraction
- electrostatic repulsion

$$W(D) = \left( 64 kT R \rho_0 \gamma^2 / \kappa^2 \right) e^{-\kappa D} - AR/6D$$

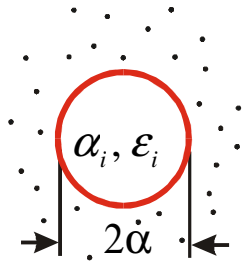
Mean – Field Approach

# DLVO - Theory



**Interaction energy** of two surfaces at various salt concentrations as function of surface separation  
- qualitative o.k.

## Dispersion Interaction in Medium



$$\alpha = 4\pi \epsilon_0 \left( \frac{\epsilon - 1}{\epsilon + 2} \right) a^3$$

### Electronic Polarizability

$$\epsilon(r) = n^2 \qquad \alpha = 4\pi \epsilon_0 \left( \frac{n^2 - 1}{n^2 + 2} \right) a^3$$

$$\Rightarrow w(r) = -\frac{\sqrt{3}}{4} \frac{h\nu_e a^6 (n^2 - 1)^2}{4r^6 (n^2 + 1)^2}$$

### 2 particles in medium 3

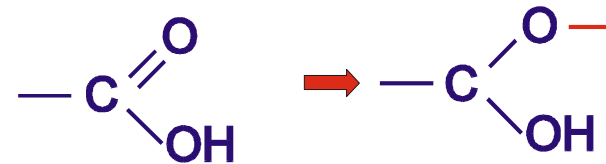
$$w(r) = -\frac{\sqrt{3}}{2r^3} h\nu_e a_1^3 a_2^3 \frac{h\nu_e a^6 (n_1^2 - n_3^2)^2 (n_2^2 - n_3^2)}{(n_1^2 + n_3^2)^{1/2} (n_2^2 - 2n_3^2)^{1/2} \sqrt{.+.+.+.}}$$

- $h\nu_e \gg kT$ : large dispersion interaction
- force in vacuum ( $n_3 = 1$ ) much larger than in medium
- identical particles attract each other
- in principle, the interaction can have each sign

## Electrostatic Interactions

Surface charge caused by

- dissociation of surface groups
- adsorption of ions



### Poisson – Boltzmann - Equation

$$\mu = z \cdot e \cdot \psi + kT \ln \rho$$

↓                      ↓  
Potential            Ion Density

$$\rho = \rho_0 e^{-ze\psi/kT}$$

↓  
Ion density in the bulk phase

Ion next to a charged wall

$$ze\rho = -\varepsilon \varepsilon_0 \frac{d^2\psi}{dx^2} = ze\rho_0 \exp(-ze\psi/kT)$$

2. order differential equation  $\Rightarrow$  2 additional constraints necessary:
- electro neutrality
  - dependent on sample geometry

## Surface Charge $\sigma$

$$\sigma = - \int_0^{D/2} z e \rho \, dx = \varepsilon \varepsilon_0 \int_0^{D/2} \left( \frac{d^2 \psi}{dx^2} \right) dx = \varepsilon \varepsilon_0 (d\psi/dx)_s = \varepsilon \varepsilon_0 E_s \quad \text{independent of } D$$

## Relationship between surface charge $\sigma$ and surface potential $\psi_s$

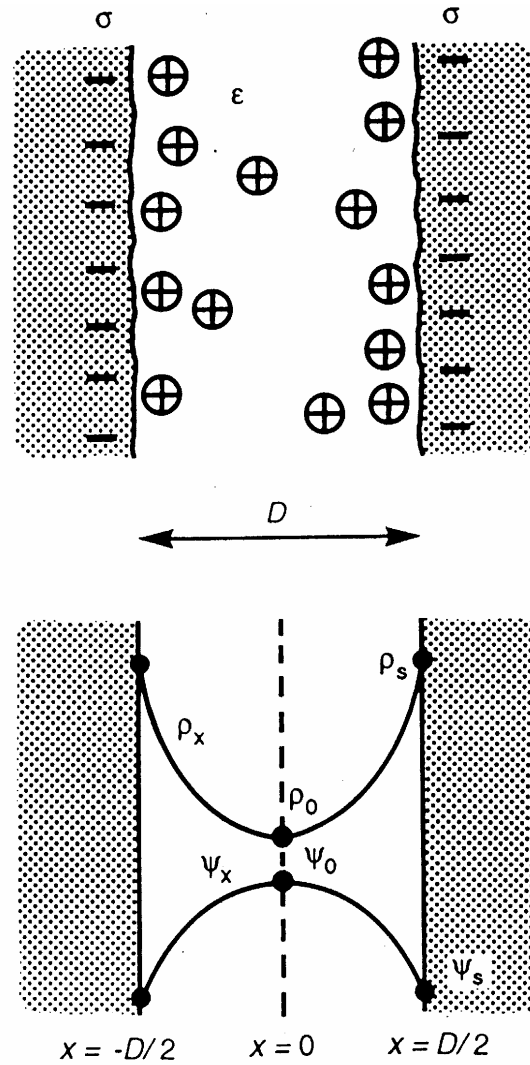
$$\frac{d\rho}{dx} = - \left( \frac{z e \rho_0}{kT} \right) e^{-ze\psi/kT} \left( \frac{d\psi}{dx} \right) = \frac{\varepsilon \varepsilon_0}{kT} \left( \frac{d\psi}{dx} \right) \left( \frac{d^2 \psi}{dx^2} \right) = \frac{\varepsilon \varepsilon_0}{kT} \left( \frac{d}{dx} \right) \left( \frac{d\psi}{dx} \right)^2$$

$$\Rightarrow \rho_x - \rho_0 = \int_0^x d\rho = \frac{\varepsilon \varepsilon_0}{kT} \int_0^x \frac{d}{dx} \left( \frac{d\psi}{dx} \right) \left( \frac{d^2 \psi}{dx^2} \right)^2 dx = \frac{\varepsilon \varepsilon_0}{kT} \left( \frac{d\psi}{dx} \right)^2 \Big|_x$$

$$\mathbf{x = 0} \quad \rho_s = \rho_0 + \frac{\sigma^2}{2\varepsilon \varepsilon_0 kT}$$

$\rho_0$ : bulk salt concentration

## 2 Flat Surfaces



$$2.) \left. \frac{\partial \psi}{\partial x} \right|_{x=0} = 0$$

Two negatively charged surfaces of surface charge density  $\sigma$  separated a distance  $D$  in water. The only ions in the space between them are the counterions that have dissociated from the surfaces. The counterion density profile  $\rho_x$  and electrostatic potential  $\psi_x$  are shown schematically in the lower part of the figure. The 'contact' values are  $\rho_s$  and  $\psi_s$ .

## Ions of different valency

$$\rho_{xi} = \rho_{oi} \exp(-ze\psi_x/kT)$$

$$\Rightarrow \sum_i \rho_{si} = \sum_i \rho_{oi} + \frac{\sigma^2}{2\epsilon\epsilon_0 kT}$$

$\rho_{si}$ : surface concentration of ion i

$$\sigma^2 = 2\epsilon\epsilon_0 kT \left( \sum_i \rho_{si} - \sum_i \rho_{oi} \right)$$

**i.e.**  $= 2\epsilon\epsilon_0 kT \left( [Na^+]_0 e^{-e\psi_s/kT} + [Ca^{2+}]_0 e^{-2e\psi_s/kT} + [Cl^-]_0 e^{e\psi_s/kT} - [Na^+]_0 - [Ca^{2+}]_0 - [Cl^-]_0 \right)$

only monovalent ions

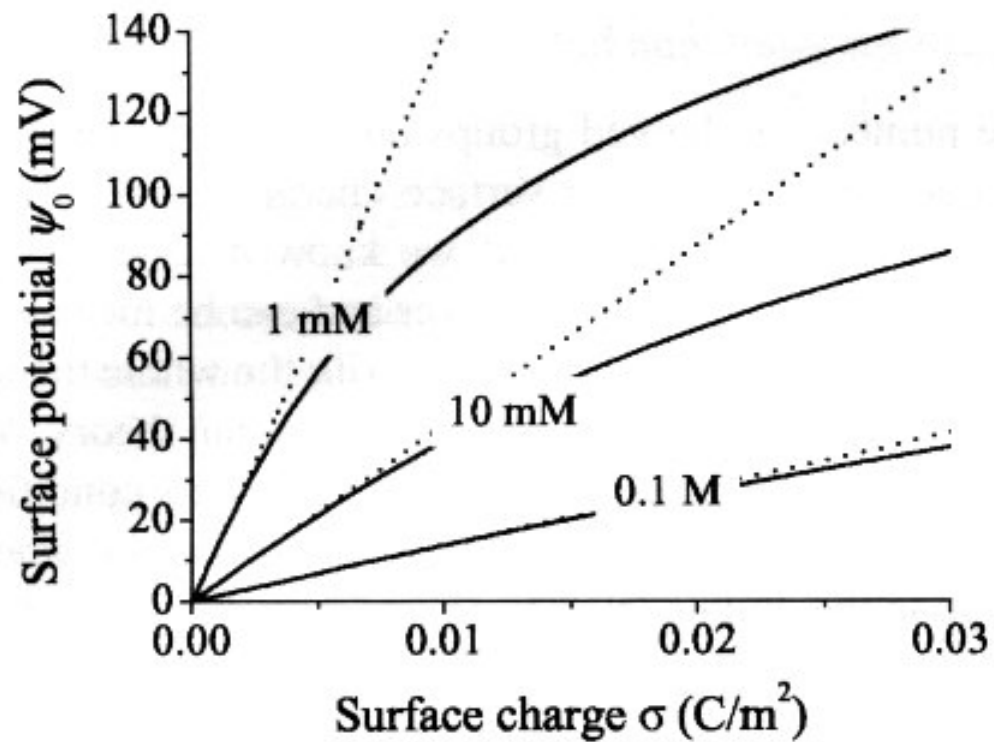
$$[Na^+]_0 = [Cl^-]_0$$

$$\sigma^2 = 2\epsilon\epsilon_0 kT [NaCl] \left( e^{e\psi_s/kT} + e^{-e\psi_s/kT} - 2 \right) = 2\epsilon\epsilon_0 kT \sinh^2(e\psi_s/2kT) [NaCl]$$

$$\Rightarrow \sigma = 0.117 \sinh(\psi_o/51.4) \sqrt{[NaCl]} \quad (\psi_o \text{ in [mV]})$$

$$[NaCl] \uparrow \Rightarrow \psi \downarrow \quad \text{for } \sigma = \text{const.} \quad \text{if } \psi_s < kT/e$$

$$\sigma = \epsilon\epsilon_0 \kappa \psi_s \quad \text{and always} \quad \kappa = \sqrt{\frac{e^2}{\epsilon\epsilon_0 kT} \sum \rho_{oi} z_i^2}$$



**Figure 4.4:** Surface potential-versus-surface charge calculated with the full Grahame equation (4.26, continuous line) and with the linearized version Eq. (4.27, dotted).



### 1/κ : Debye length

0.304 nm / √[NaCl]	1:1	[Mol/l]
0.176 nm / √[CaCl <sub>2</sub> ]	1:2 or 2:1	[Mol/l]
0.152 nm / √[MgSO <sub>4</sub> ]	2:2	[Mol/l]

$$\sum_i \rho_{xi} = \sum_i \rho_{oi} + \frac{\epsilon \epsilon_0}{2kT} \left( \frac{d\psi}{dx} \right)_x^2$$

### 1:1 Electrolyte

$$\frac{d\psi}{dx} = \sqrt{8kT \sum \rho_{oi} / \epsilon \epsilon_0} \sinh(e\psi_x / 2kT)$$

$$\psi_x = \frac{2kT}{e} \ln \frac{1 + \gamma e^{-\lambda x}}{1 - \gamma e^{-\lambda x}} \sim \frac{4kT}{e} \gamma e^{-\kappa x}$$

$$\psi_x = \psi_s e^{-\kappa x}$$

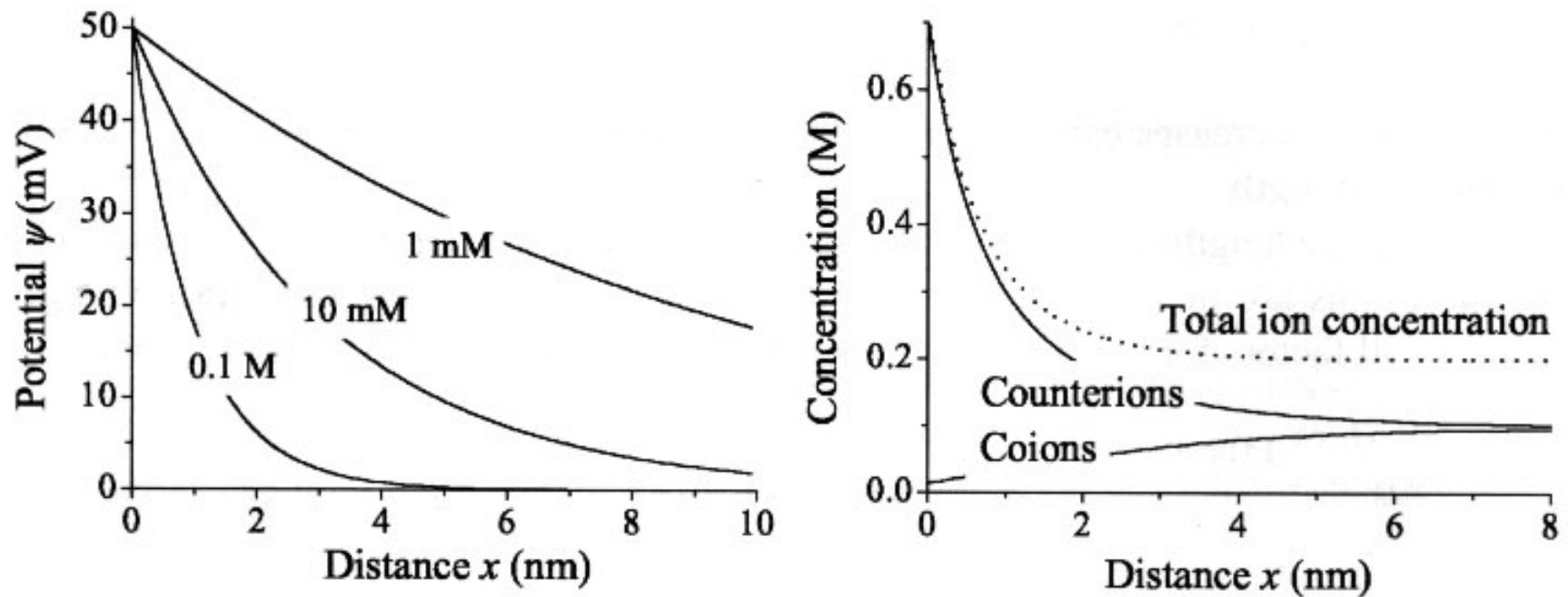
with  $\gamma = \tanh \frac{e\psi_s}{4kT}$

**Debye – Hückel – Approximation**  $\psi = kT / e$

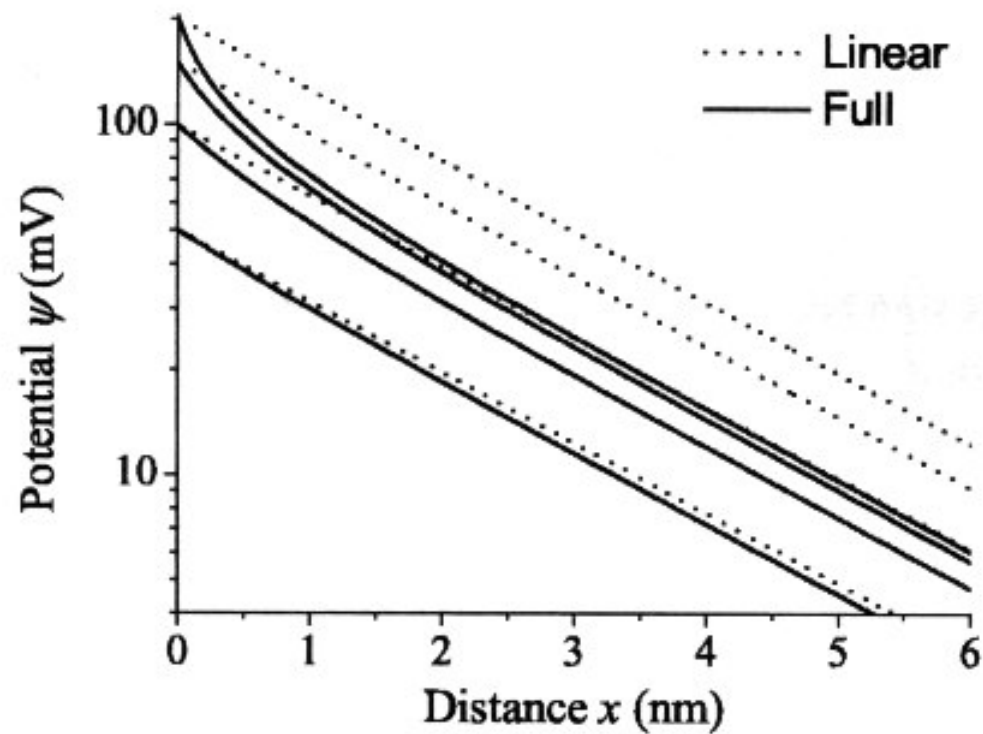
$$\psi_x = \psi_s e^{-\kappa x}$$

$$W_{||} = (64kT \rho_0 \gamma^2 / \kappa) e^{-\kappa D} \quad \text{1:1 Elektrolyt}$$

$$W_{\bullet\bullet} = (64kT R \rho_0 \gamma^2 / \kappa^2) e^{-\kappa D}$$



**Figure 4.2:** Left: Potential-versus-distance for a surface potential of  $\psi_0 = 50$  mV and different concentrations of a monovalent salt in water. Right: Local co- and counterion concentrations are shown for a monovalent salt at a bulk concentration of 0.1 M and a surface potential of 50 mV. In addition, the total concentration of ions, that is the sum of the co- and counterion concentrations, is plotted.

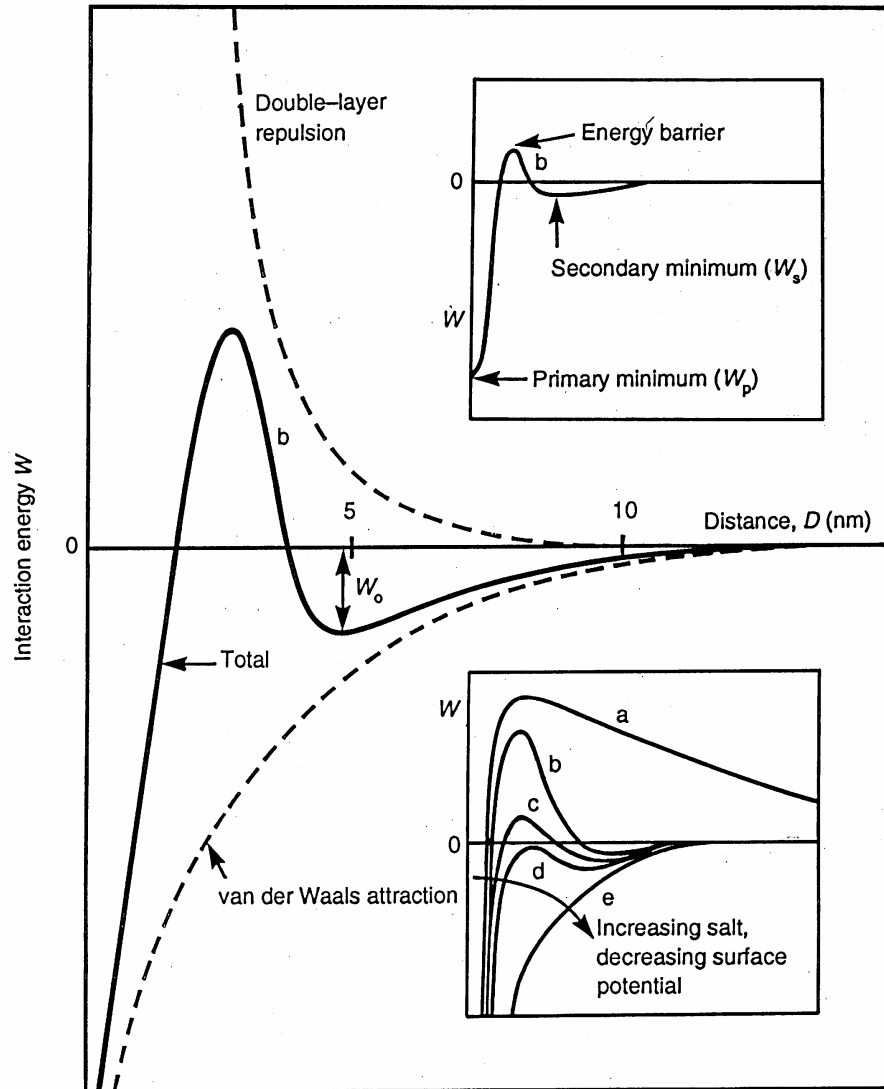


**Figure 4.3:** Potential-versus-distance for different surface potentials (50, 100, 150, and 200 mV) with 20 mM monovalent salt. The full solution Eq. (4.21) and the solution of the linearized Poisson–Boltzmann Eq. (4.9) are shown.

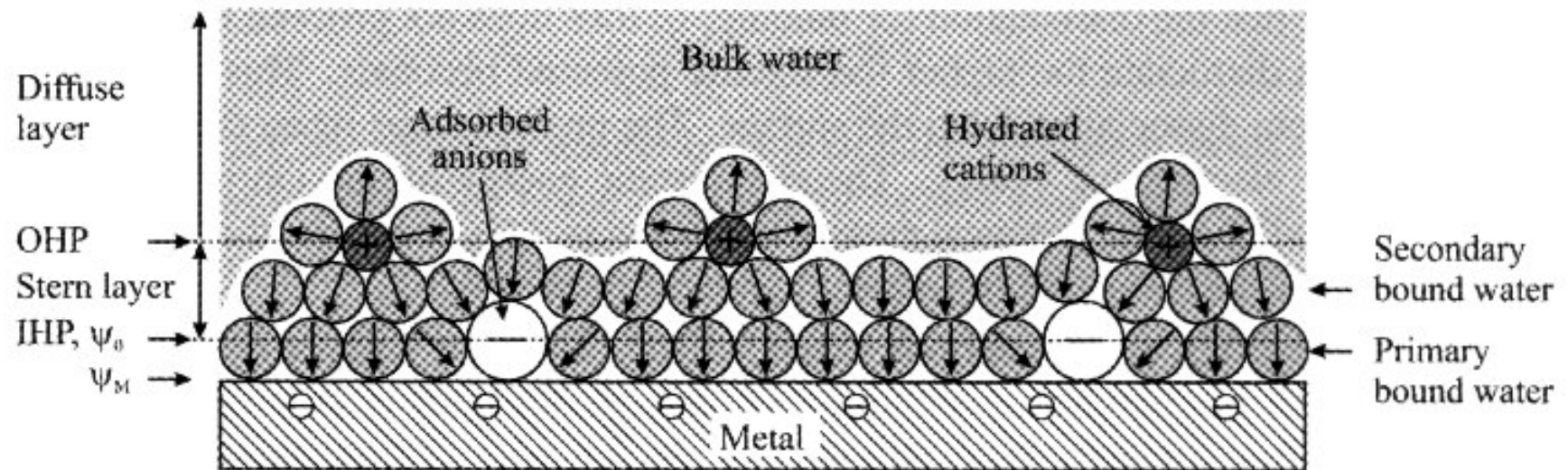
**In an aqueous medium, the electrostatic double-layer force is present. For distances  $z$  larger than the Debye length  $1/\kappa$  it decays roughly exponentially.**

**The stability of dispersions in aqueous media can often be described by The DLVO theory, which contains the double layer repulsion and the van der Waals attraction. At short range, and for hydrophilic particles the hydration repulsion prevents aggregation. Hydrophobic particles, in contrast, tend to aggregate due to hydrophobic forces.**

# DLVO - Theory



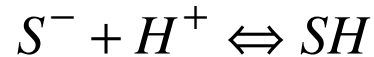
**Interaction energy** of two surfaces at various salt concentrations as function of surface separation  
- qualitative o.k.



**Figure 4.6:** Stern layer at a metal surface. Due to the high electrical conductivity, the potential in the metal  $\psi_M$  is constant up to the surface. The inner (IHP) and outer (OHP) Helmholtz planes are indicated. In the first layer of primary bound water the permittivity is typically  $\epsilon = 6$ . In the secondary layer of water it is of the order of  $\epsilon \approx 30$ .

## Surface Charge due to Ion Binding

For example, if only protons can bind to a negatively charged surface, the equilibrium condition at the surface is determined by the mass action equation



The surface charge is  $\sigma = -e[S^-]_o$  (index  $_o$  for surface concentration)

The dissociation constant is

$$K_d = \frac{[S^-]_o[H^+]_o}{[SH]_o} = \frac{\sigma_o \alpha}{\sigma_o(1-\alpha)} [H^+]_o \exp(-e\psi/kT)$$

with  $\sigma_o = e \times ([S^-]_o + [SH]_o)$  and  $\alpha = [S^-]_o / ([S^-]_o + [SH]_o)$

In equilibrium, we have for a mixed electrolyte of NaCl and HCl

$$\begin{aligned} \sigma &= \sigma_o \alpha = \sigma_o K_d / (K_d + [HCl] \exp(-e\psi_o/kT)) \\ &= 0.117 \sinh(\psi_o/51.4) \sqrt{[NaCl] + [HCl]} \end{aligned}$$

**For example, if  $K_d=10^{-4}\text{M}$ , and  $\sigma_o=-0.2\text{C/m}^2$ ,  $[\text{NaCl}]=0.1\text{ Mol/L}$ , then**

For  $\text{pH} = 7$ , we have  $\psi_o = -118\text{mV}$  and  $\alpha = 0.91$

For  $\text{pH} = 5$ ,  $\psi_o = -73\text{mV}$  and  $\alpha = 0.36$

**Proton concentration much less than NaCl-concentration, yet potential determining.**



## Interaction Energy

### Contact – Value - Theorem

$$\left(\frac{\partial P}{\partial x}\right)_{x_1 T} = p \left(\frac{\partial P}{\partial x}\right)_{x_1 T}$$

**P** ← repulsive  
pressure

**x** ← beliebiger Punkt

$$P_x = \int_{x^1=D/2}^{x^1=\infty} \left[ z e p \left( \frac{\partial \psi}{\partial x} \right)_x dx^1 + kT dp_x \right]$$

$$P_x(D) \cdot P_x(\infty) = \frac{1}{2} \varepsilon \varepsilon_0 \left[ - \left( \frac{d\psi}{dx} \right)_{x(D)}^2 + \left( \frac{d\psi}{dx} \right)_{x(\infty)}^2 \right] + kT [p_x(D) - p_x(\infty)]$$

- independent of **x**
- **x = D/2**, middle plane

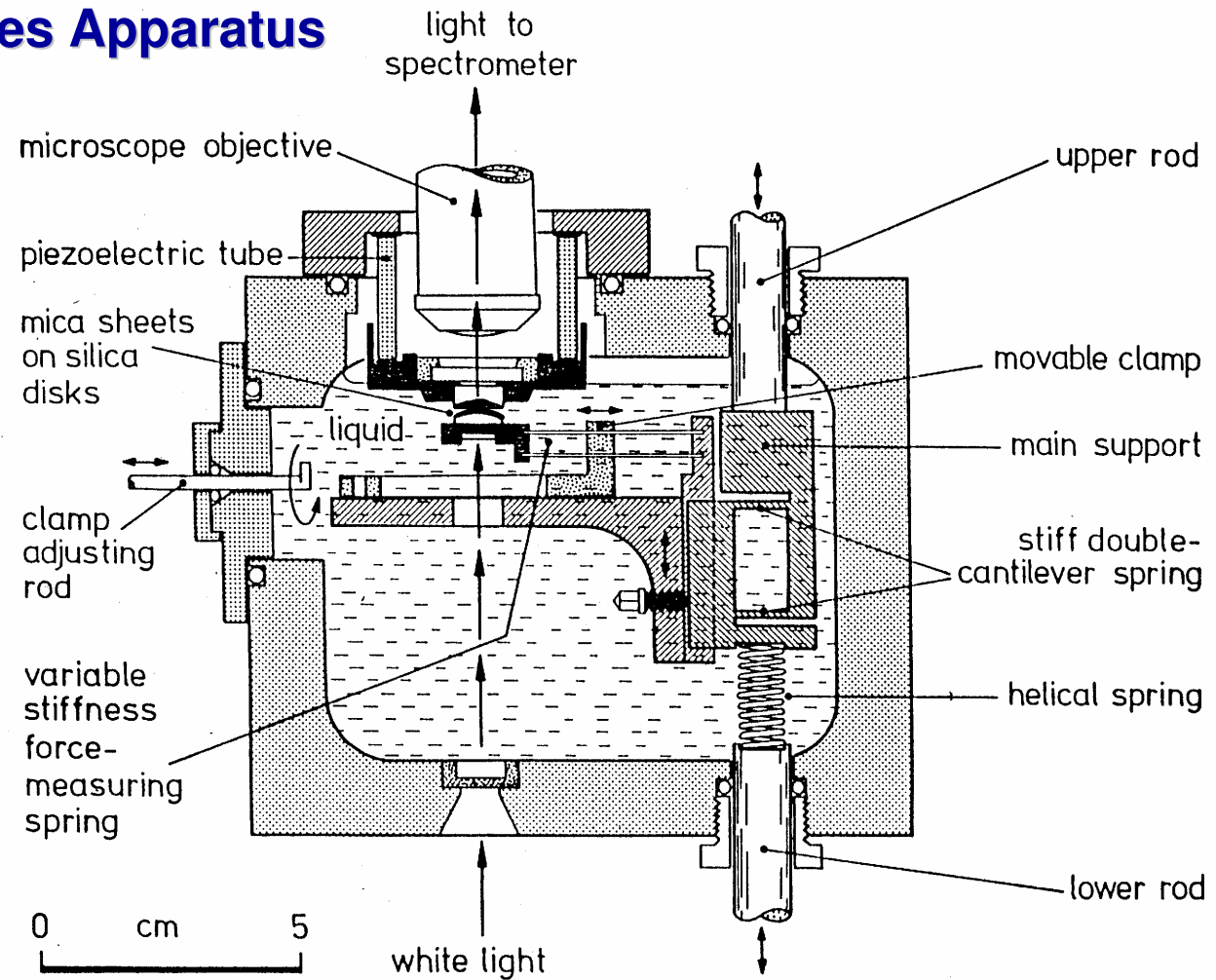
$$P(D) - P(\infty) = kT [\rho_{mi}(D) - \rho_{mi}(\infty)]$$

### Monovalent ions

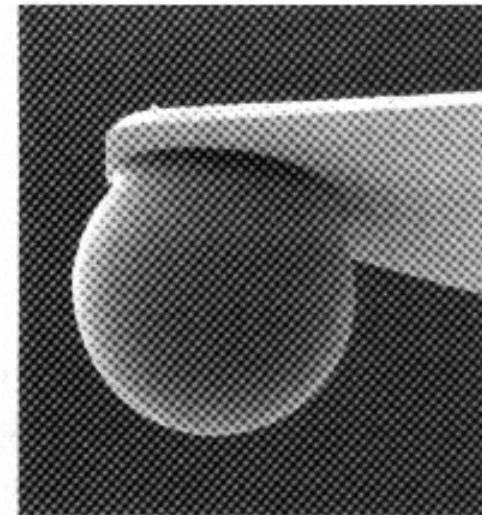
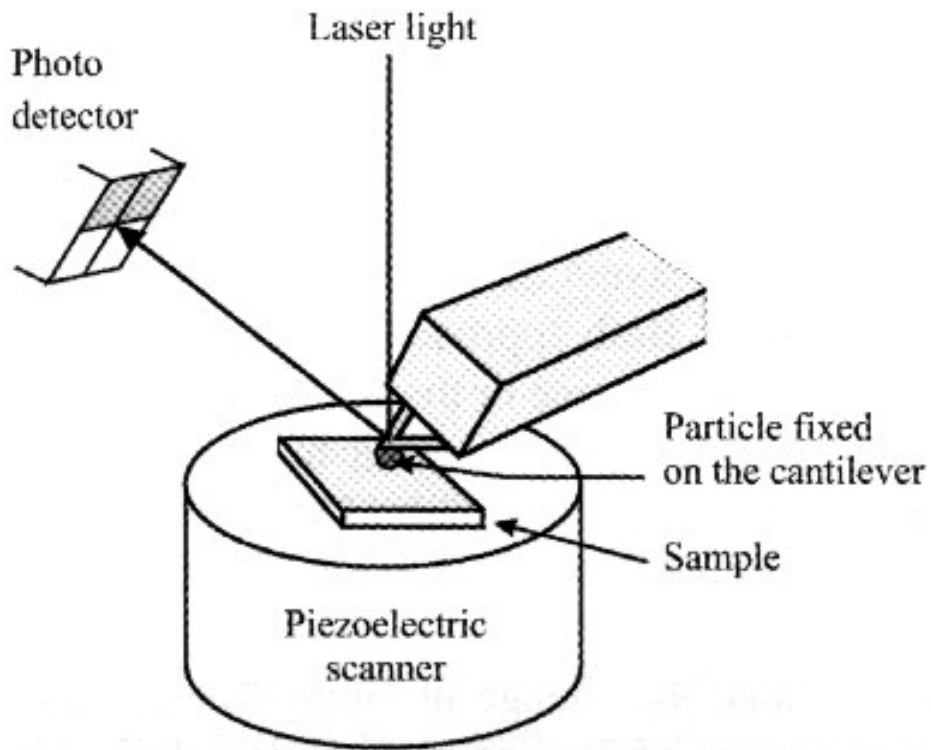
$$P(D) - P(\infty) = kT p_\infty \left[ \underbrace{\left( e^{e\psi_{mi}/kT} - 1 \right)}_{\text{Na}^+} + \underbrace{\left( e^{e\psi_{mi}/kT} - 1 \right)}_{\text{Cl}^-} \right] \approx e^2 \psi_{mi}^2 p_\infty / kT$$

$$W_{\parallel\parallel\parallel} = (64kT p_\infty \gamma^2 / \kappa) e^{-\kappa D}$$

# Surface Forces Apparatus

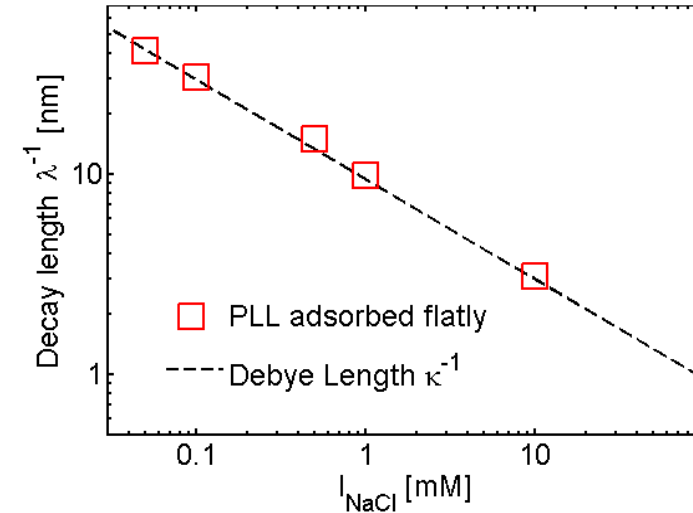
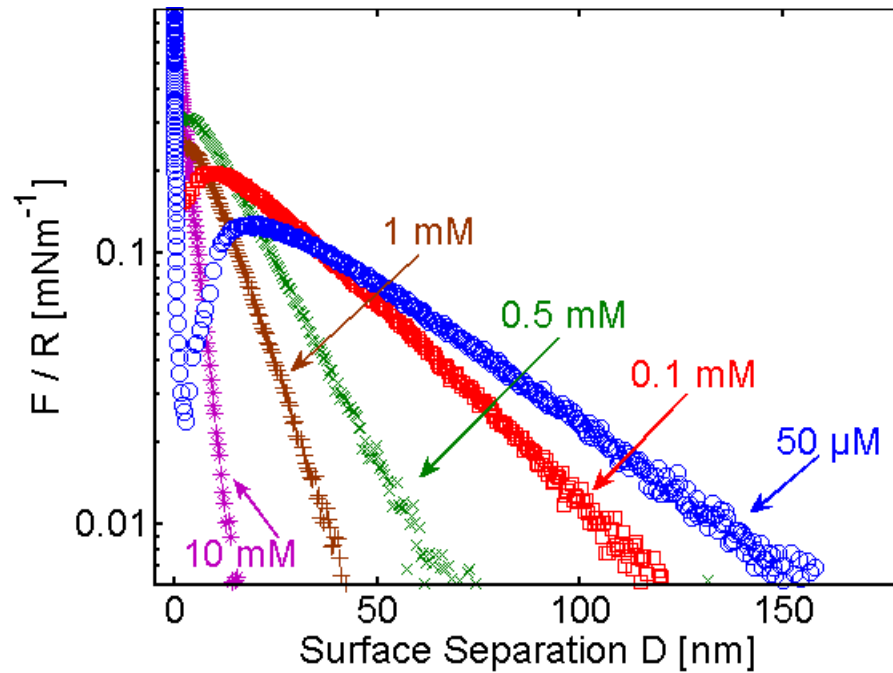


**Surfaces: Crossed Cylinder Geometry – Bilayer on Mica Aqueous Solution with Monomers**



**Figure 6.8:** Schematic of an atomic force microscope (left) and an example of a colloidal probe. The glass sphere is sintered to the end of an AFM cantilever has a diameter of  $\approx 10 \mu\text{m}$ .

# Forces between Polycation Monolayers



$$\kappa^{-1} = 3\text{\AA} / \sqrt{I[\text{M}]}$$

Poly-l-lysine (PLL), adsorbed from pure water  
 - adsorbed **flat**

- Flat adsorption
- Long-ranged electrostatic repulsion  $F = F_o \exp(-D\kappa)$
- Low salt: short ranged van der Waals attraction