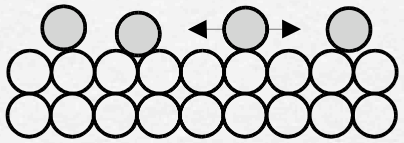
Adsorption & Monolayers

Adsorption at Surfaces

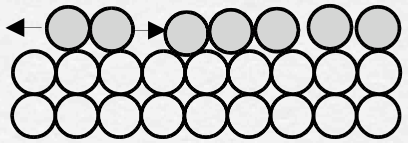
Adsorption is the accumulation of particles (**adsorbate**) at a surface (**adsorbent** or **substrate**). The reverse process is called **desorption**.

fractional surface **coverage**: $\theta = \frac{\text{Number of adsorption sites occupied}}{\text{Number of adsorption sites available}}$

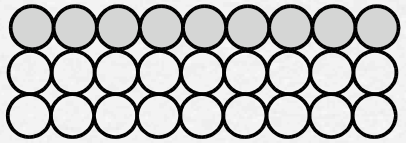
low coverage: **2D gas** (no attraction between adsorbate atoms / molecules, high mobility, disordered)



medium coverage: **2D liquid** (attraction between adsorbate atoms / molecules -> condensation, reduced mobility, disordered)



high coverage: **2D solid** (strong attraction between adsorbate atoms / molecules -> crystallization, no mobility, highly ordered)



adsorption sites: on top of atoms, between atoms (2-,3-,4-fold), edges, steps, kinks...

→ adsorbate superlattice is described by Wood notation

→ sometimes adsorbate-induced surface reconstruction of substrate [Ni(100) c(2x2)-CO]

Physisorption and Chemisorption

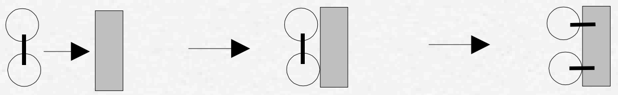
physisorption (physical adsorption): long range and weak van der Waals attraction between adsorbate and substrate ($\Delta H_{\text{physisorption}} \sim 20$ kJ mol^{-1})

- no activation barrier, fast, reversible, surface symmetry insensitive, multilayer formation possible, $T_{\text{surface}} < T_{\text{condensation}}$

chemisorption: short range and strong bonding between adsorbate and substrate ($\Delta H_{\text{chemisorption}} \sim 200$ kJ mol^{-1})

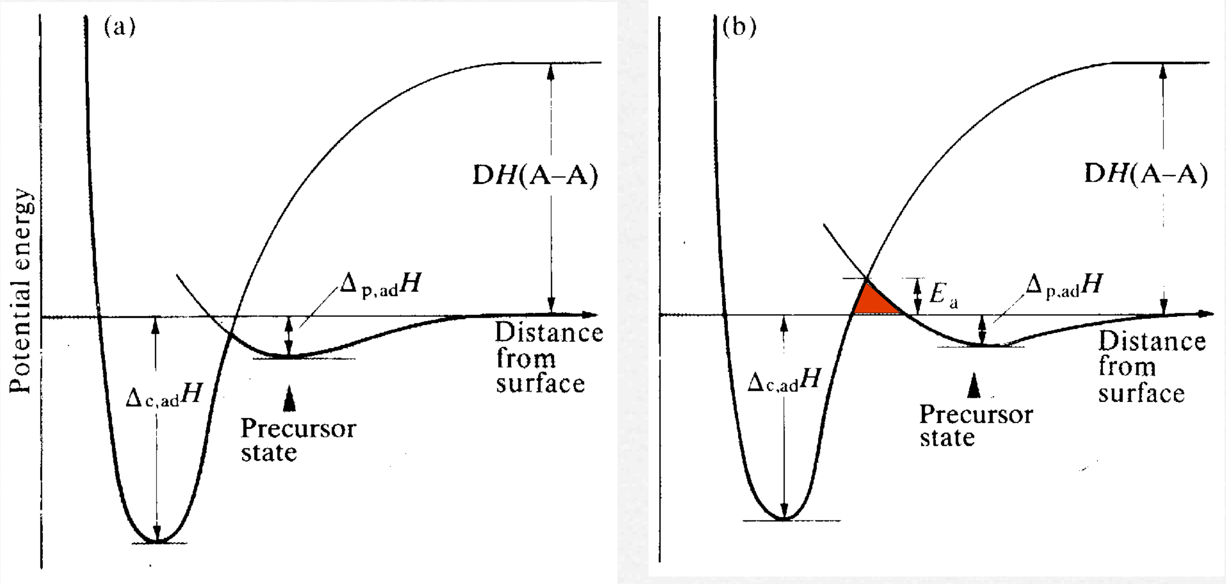
- activation barrier possible (b), variable uptake kinetics, covalent / ionic / metallic bonding, often irreversible, surface symmetry specific, limited to monolayer, wide range of T_{surface}

dissociative adsorption:
upon chemisorption the molecules can dissociate into individual atoms / fragments



physisorption

dissociative chemisorption



Langmuir Adsorption Isotherm

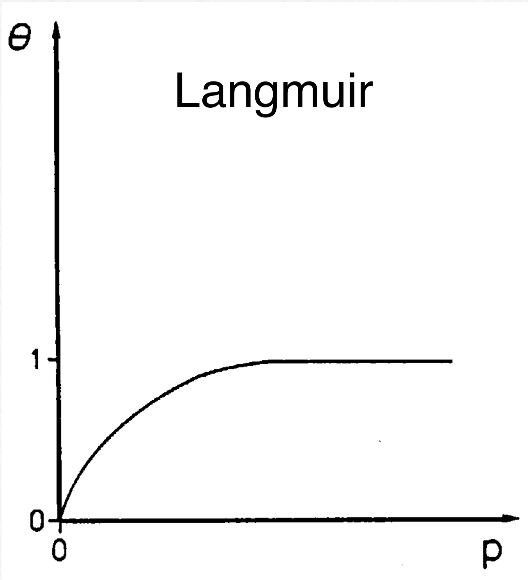
Henry isotherm: surface coverage θ depends linearly on pressure p (special case of Langmuir for $\theta \to 0$)

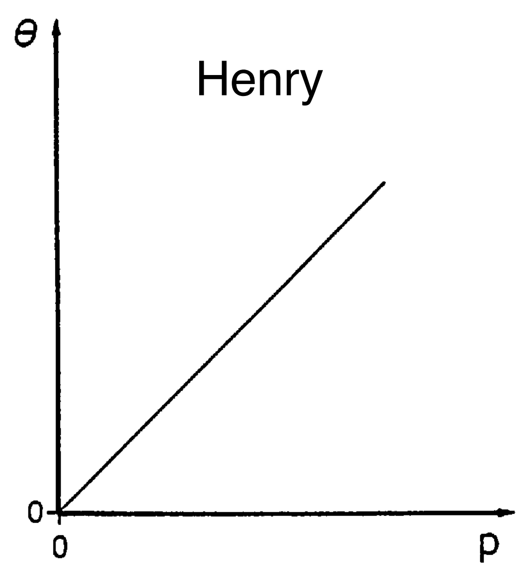
Langmuir isotherm: assumption of a) maximum monolayer coverage ($\theta = 1$); b) no interaction between adsorbate atoms / molecules; c) coverage-independent binding energy; e) thermodynamic equilibrium of adsorption (k_a) and desorption (k_d) rate, ($d\theta / dt$) being equal

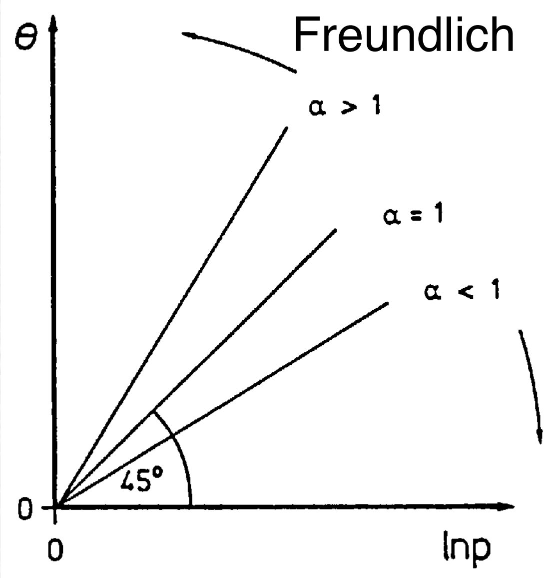
adsorption: $\frac{d\Theta}{dt} = k_a p N (1-\Theta)$ desorption: $\frac{d\Theta}{dt} = k_d N \Theta$ $\longrightarrow$ $\Theta = \frac{K p}{(1+K p)}$ $K = k_a / k_d$

Freundlich isotherm: adsorption enthalpy changes logarithmically $\theta = K p^{\alpha}$

Tempkin isotherm: adsorption enthalpy changes linearly $\theta = c_1 \ln (c_2 p)$







BET and Other Adsorption Isotherms

BET (Stepen Brunauer, Paul Emmett, Edward Teller): assumption that on first layer further physisorbed adsorbate layers can form

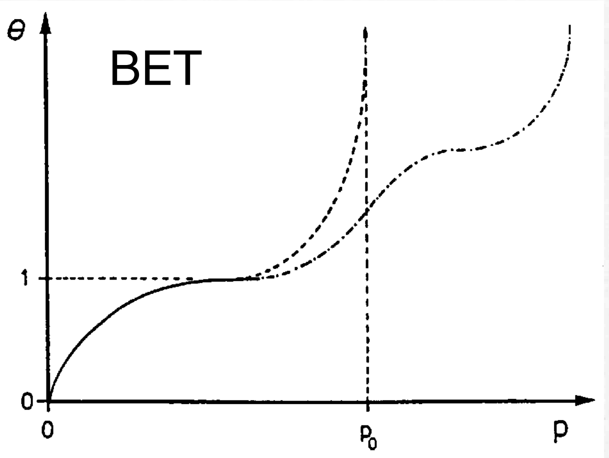
- different rate constants of adsorption and desorption for first layer (k_a, k_d) and subsequent physisorbed layers (k_a', k_d')
- condensation at p_0 (bulk vapor pressure), at high coverage $\theta >> 1$ system similar to bulk / vapor interface
- applicable to unreactive gases on polar surfaces

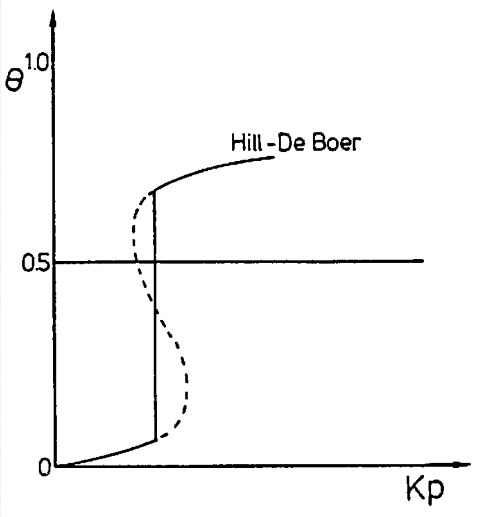
$$\Theta = \frac{c_1 p}{(p_0 - p)\left[1 + \frac{p}{p_0}(c_2 - 1)\right]}$$

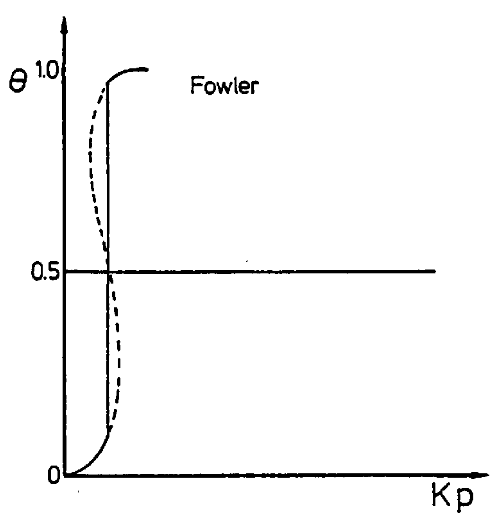
with $\theta = n / n_0$ (number of all adsorbate particles divided by particles in first layer), often $c_1 = c_2$

Hill-de Boer: mobile 2D gas, molecular dimensions and vdW interactions between adsorbed particles considered

Fowler: localized adsorption with interaction of the adsorbed particles

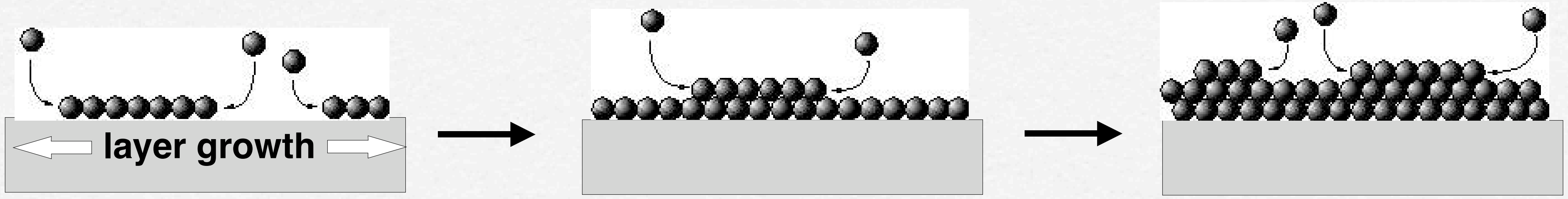




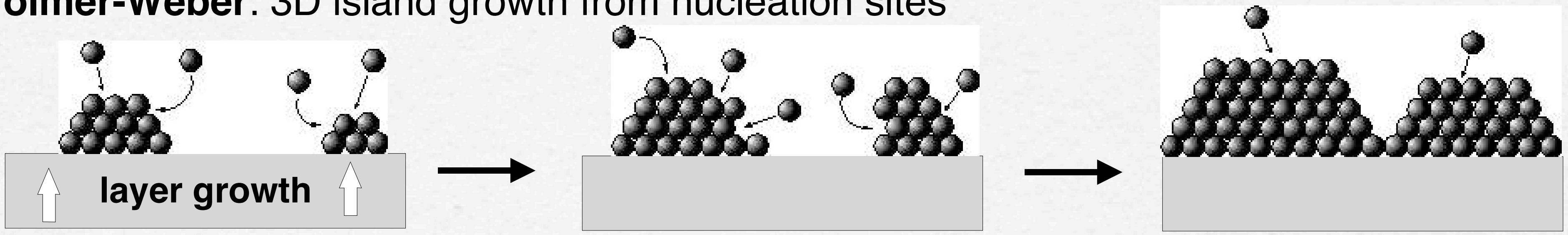


Surface Layer Growth Models

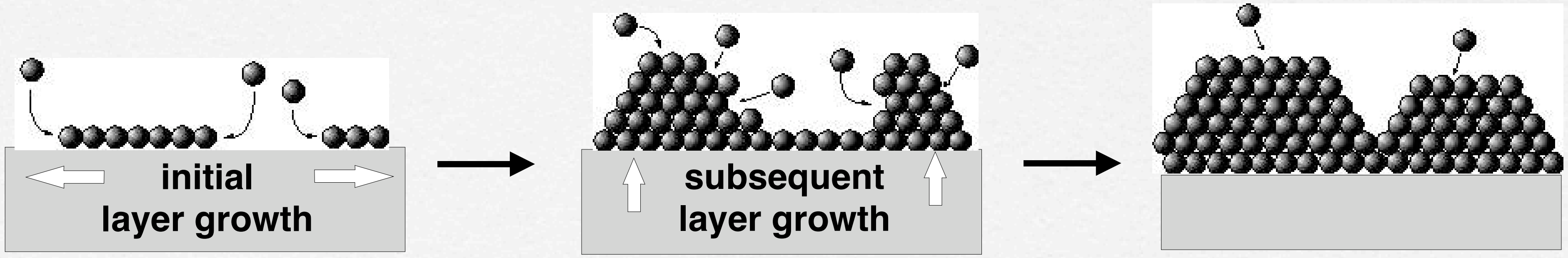
- **Frank-van der Merwe**: 2D layer growth, completion of layer before next layer growth



- **Volmer-Weber**: 3D island growth from nucleation sites



- **Stranski-Krastanov**: initial 2D layer growth, subsequent 3D island formation

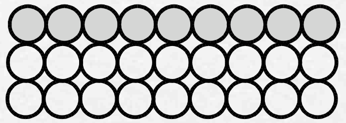


- **columnar growth**: at very low atom / molecule mobility highly defective 3D columnar structures will grow (amorphous, porous)

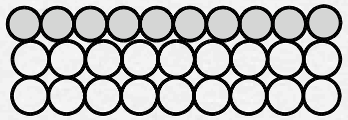
Epitaxy, Commensurability, Lattice Strain, Incoherence

epitaxy: crystal structure (lattice parameters) of the underlying substrate is transferred into the growing crystalline adsorbate layer ("induced crystallinity by substrate")

commensurability:



- if an adsorbate layer follows the same lattice spacing (or multiple integers) as the substrate the layer is commensurable



- if the lattice spacing of the adsorbate layer is not correlated (by a multiple integer) to the substrate periodicity the layer is incommensurable

lattice strain: when a material with minor lattice mismatch growth epitaxially on a substrate the mismatch will induce strain in the growing crystal layer (often involved in Stranski-Krastanov growth mode)

incoherence: if a surface layer structure is completely independent of the substrate lattice structure the layer is incoherent

Preparation of Defined Surfaces: UHV

UHV conditions: (UHV = **u**ltra-**h**igh **v**acuum, 10^{-8} Pa, 10^{-10} torr)

a) cleaving of large single crystals along specific crystal plane (mica, graphite, alkali halides)

b) heat desorption / annealing of surfaces to desorp impurities and heal defects

c) ion sputtering to clean / remove surface layers by bombardment with high energetic ions

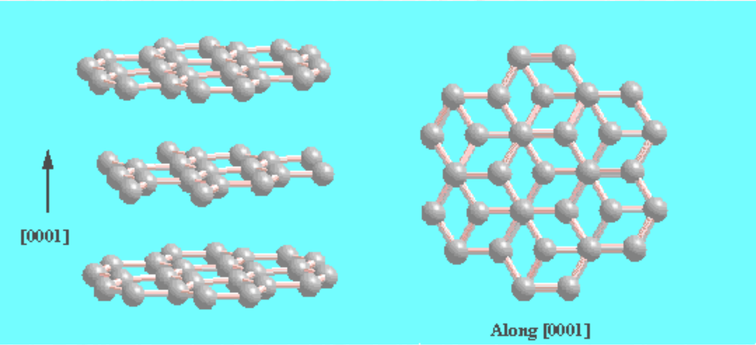
d) chemical treatment with O_2 (oxidation of hydrocarbons) or H_2 (oxygen removal)

e) epitaxial evaporation of new surface material

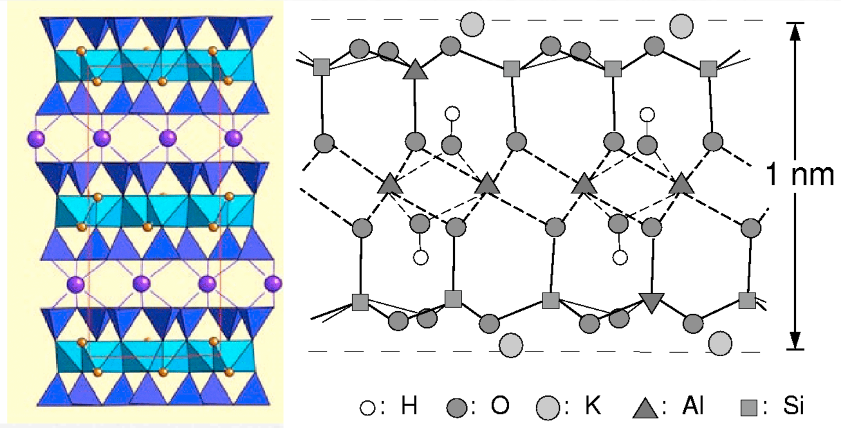
advantage: highly defined surface structure, full control over environment, many characterization methods are compatible with UHV conditions

disadvantage: labor and money intense equipment, very sensitive to contamination

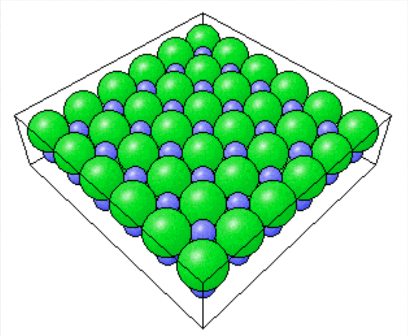
graphite (HOPG)



mica (muscovit)



NaCl(100)



Preparation of Defined Surfaces: Ambient

ambient conditions:

a) cleavage of crystalline material (e.g. mica, alkali metals, HOPG)

b) evaporation of metals (e.g. gold on mica or quartz)

c) chemical cleaning of surfaces (e.g. SiO_2 in "Piranha" = H_2SO_4 / H_2O_2 5:1 or "NoCromix")

d) plasma cleaning (high energetic ions bombarding the surface)

e) deposition of layer material from solution or gas phase (electroless plating, sputtering...)

advantage: relative simple equipment and handling, can be more easily implemented in industrial processes

disadvantage: very complex situation / chemistry / dynamics at the surface due to adsorption of different and varying contaminants from surrounding air, chemical surface reactions (oxidation O_2, hydrolysis and wetting H_2O, electrochemical and light induced reactions)

Metal Surface in Contact with Ions in Liquid

metal surfaces in contact with an ionic solution are important for electrochemistry (→ fuel cells) and corrosion processes (→ cars and ships)

simple model of the **electric double-layer**: Insertion of a metal into an ionic solution leads to a surface charge (positive or negative) at the metal surface. This surface charge attracts oppositely charged ions from solution to form the electric double-layer.

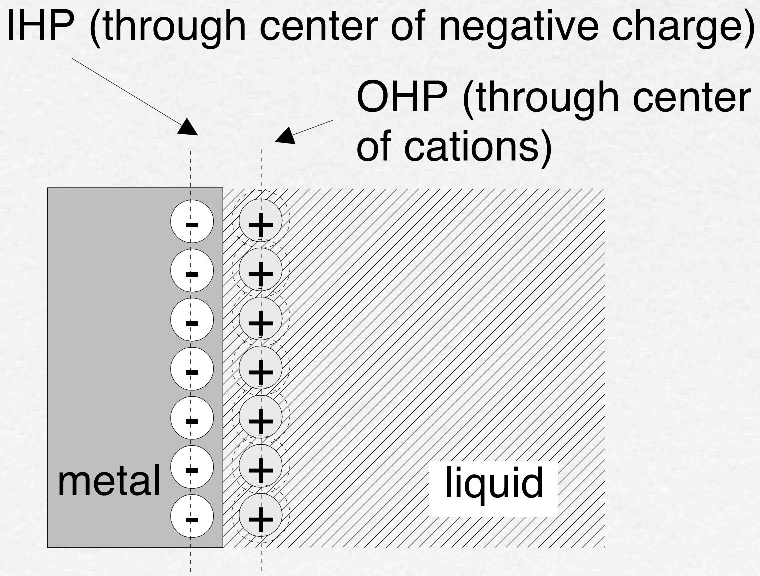
mechanisms of surface charging:

a) dissociation of surface groups / ions (e.g. solid-COOH → solid-COO$^-$ + H$^+_{aq}$)

b) adsorption of one ion species onto the uncharged surface (e.g. Ca^{2+} onto lipid bilayer)

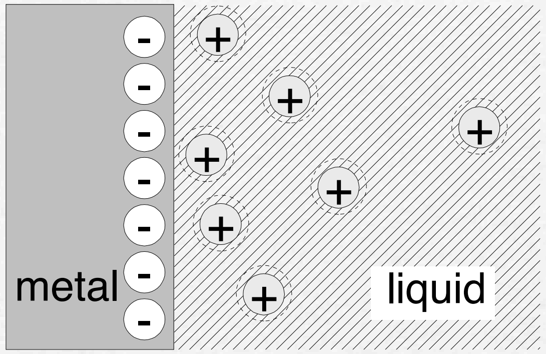
→ fully ionized surface: ~ 0.5 nm^2 per charge

Helmholtz model: negative charge in the metal surface (inner Helmholtz plane, IHP) is compensated by positive charge of the solvated cation layer condensed onto the surface (outer Helmholtz plane, OHP) → two rigid charge layers



Metal Surface in Contact with Ions in Liquid 2

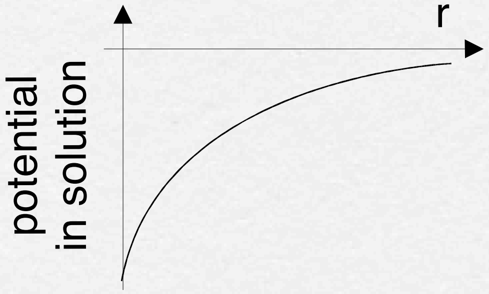
diffuse double-layer (Gouy-Chapman model): thermal motion in solution causes the ions in the outer Helmholtz layer to diffuse away from the surface (balance between Coulomb attraction and Brownian motion)



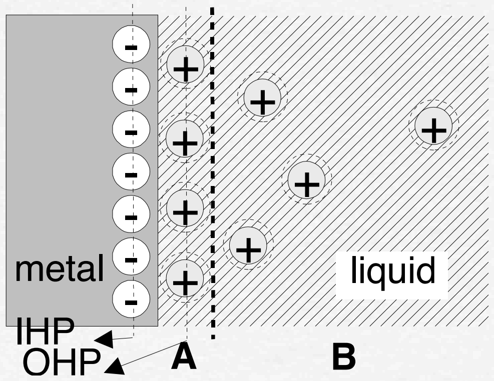
→ calculation of potential change with respect to charge distribution along the surface normal by **Poisson-Boltzmann** equation assuming appropriate boundary conditions

$$\nabla^2\Psi = \frac{n_0 e}{\varepsilon \varepsilon_0}\left(e^{\frac{e\Psi(x)}{kT}} - e^{-\frac{e\Psi(x)}{kT}}\right)$$

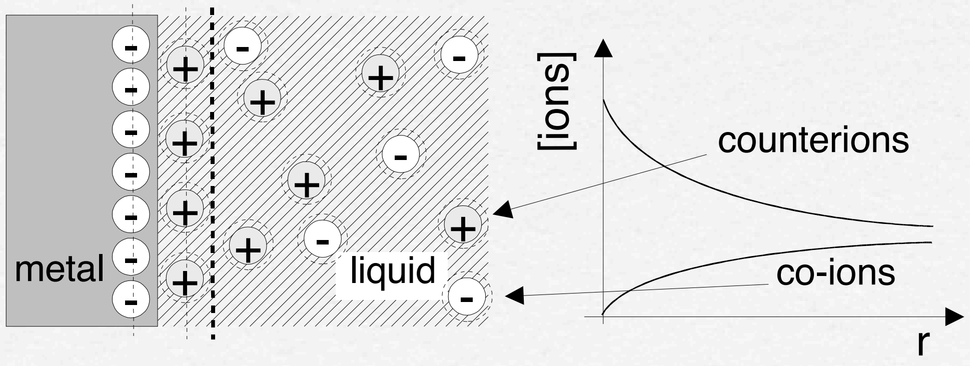
in the presence of 1:1-electrolyte



Stern model: (combination of Helmholtz and Gouy-Chapman) layer of tightly bound hydrated counterions (Helmholtz) at the surface (Stern layer, **A**) followed by a diffuse solvated ion layer **B** (Gouy-Chapman)



→ distribution of ions in the presence of salt (1:1-electrolyte)



SiO_2 Surfaces in H_2O (pH Dependence)

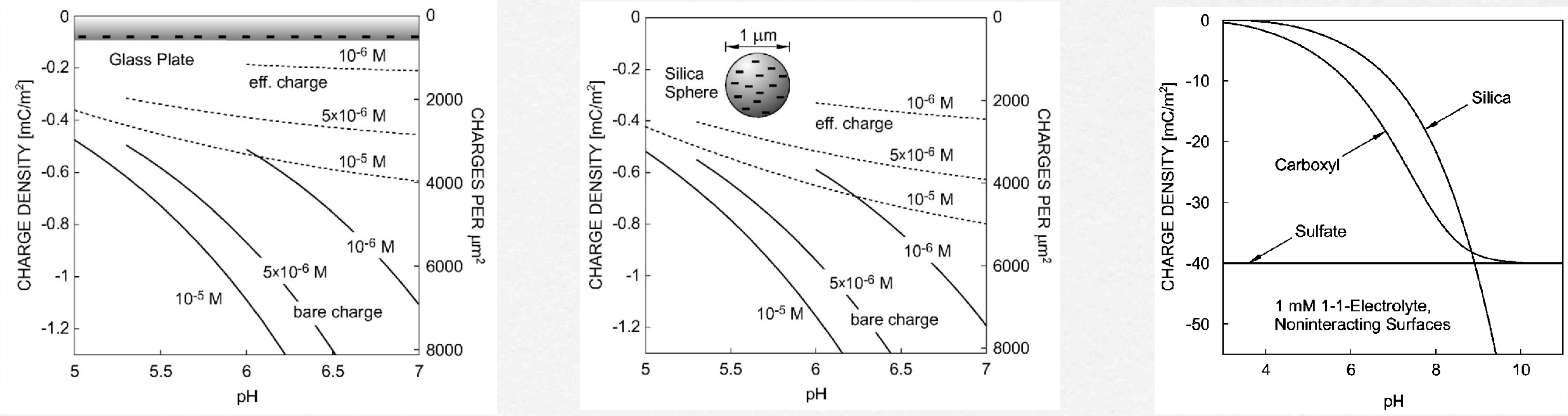
Silica surfaces (SiO_2) are **technologically** important since they are found on oxidized silicon, quartz, and many types of glass. The structure is mainly composed of Si-O-Si and Si-OH bonds, the latter can be deprotonated or chemically modified by reactive silanes.

$$SiOH \rightleftharpoons SiO^- + H^+$$

The charge of a silica surface in aqueous medium can be positively charged at very low pH < 1 and negatively charged at higher pH due to deprotonation, besides charging by ion adsorption.

"bare" charge: equilibrium of bound and mobile charges in the interfacial region (experimentally not necessarily accessible

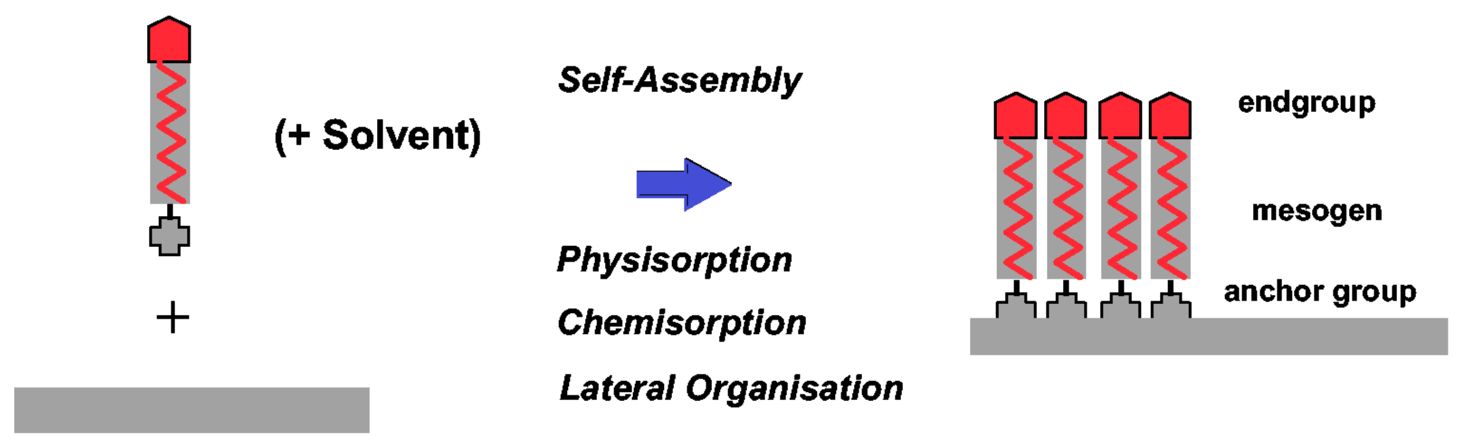
"effective" charge: implicitly accounts for overexponential decay of electrostatic potential near the surface



S. H. Behrens and D. G. Grier; "The charge of glass and silica surfaces", *J. Chem. Phys.*, Vol. **115**, No. 14, 8 October 2001

Molecular Surface Layers (SAM and LB)

SAM (self-assembled monolayers): adsorption of molecules from solution onto solid substrates to form ordered molecular monolayers (e.g. alkylthiols on gold)



LB (Langmuir-Blodgett mono- and multilayers): transfer of molecules from the air-water interface onto solid substrates to form ordered molecular mono- and multilayers (e.g. phospholipids)