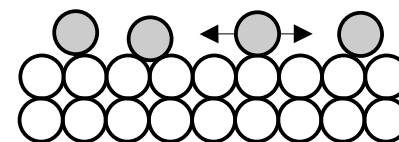# Adsorption at Surfaces

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

fractional surface **coverage**: $\quad \theta = \dfrac{\text{Number of adsorption sites occupied}}{\text{Number of adsorption sites available}}$
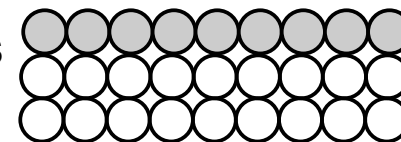
low coverage: **2D gas** (no attraction between adsorbate atoms / molecules, high mobility, disordered)

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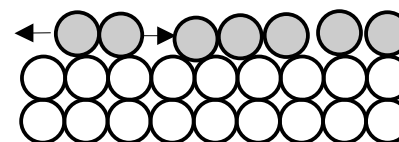
high coverage: **2D solid** (strong attraction between adsorbate atoms / molecules -> crystallization, no mobility, highly ordered)

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 ($\Delta H_{physisorption} \sim 20$ kJ mol^{-1})

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

chemisorption: short range and strong bonding between adsorbate and substrate ($\Delta H_{chemisorption} \sim 200$ 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
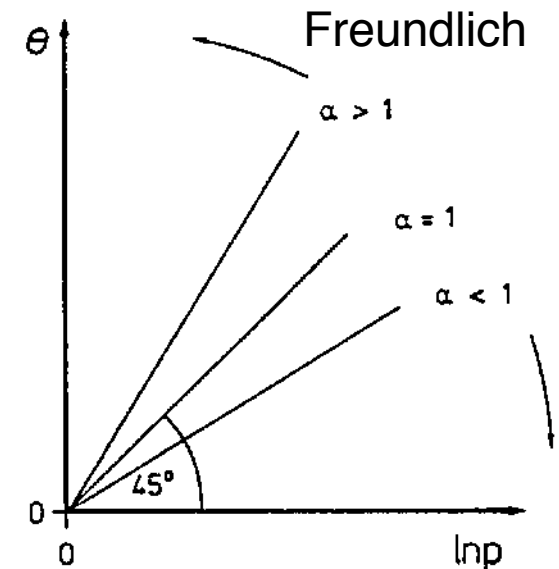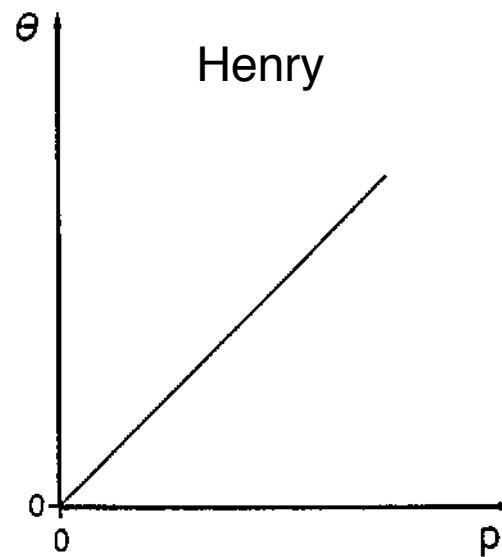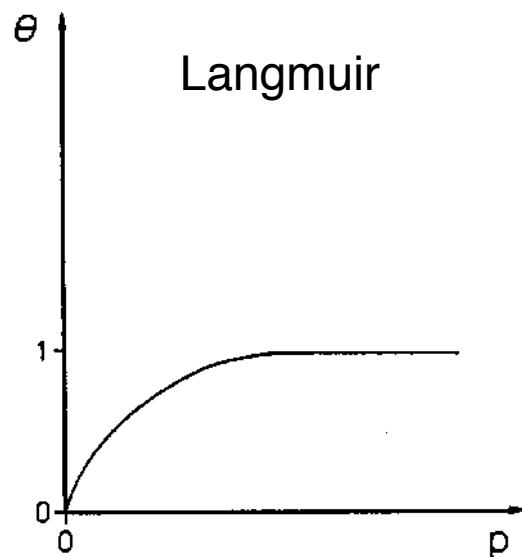
physisorption

dissociative chemisorption
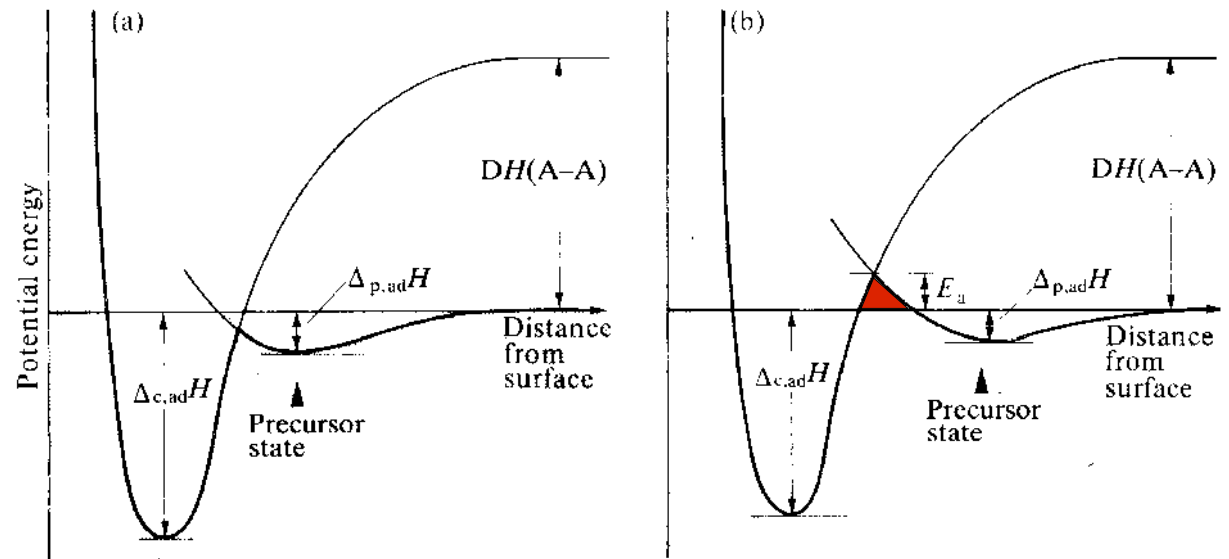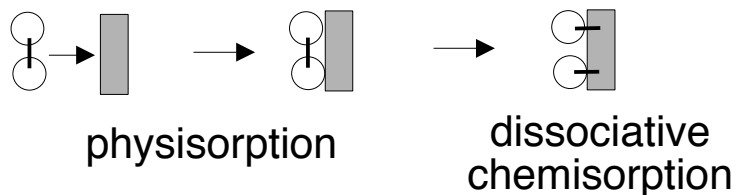
Langmuir Adsorption Isotherm

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

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 $\theta \gg 1$
  system similar to bulk / vapor interface

- applicable to unreactive gases on polar surfaces

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

with $\theta = n / n_0$ (number of all adsorbate particles divided by particles in first layer), often $c_1 = c_2$
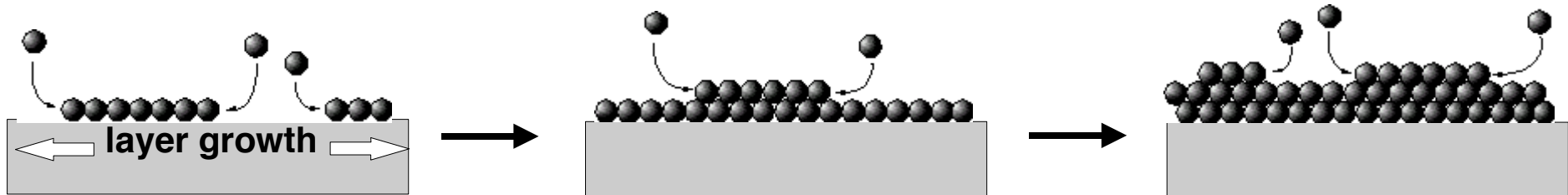
Hill-de Boer: mobile 2D gas, molecular dimensions and vdW interactions between adsorbed particles considered

Fowler: localized adsorption with interaction of the adsorbed particles
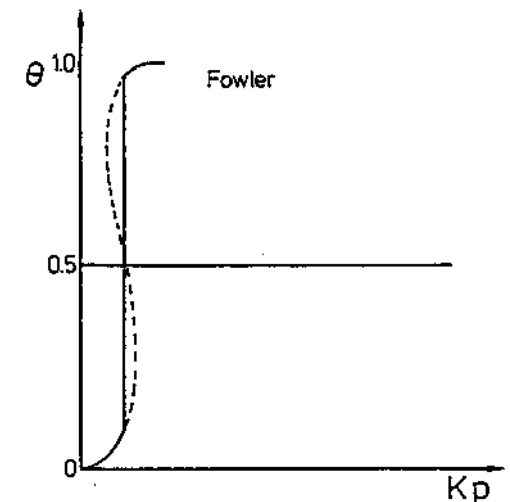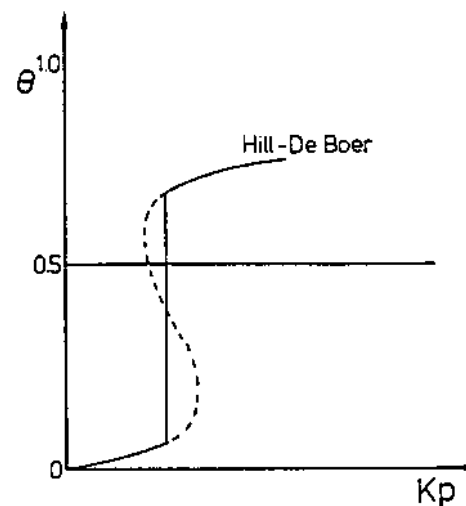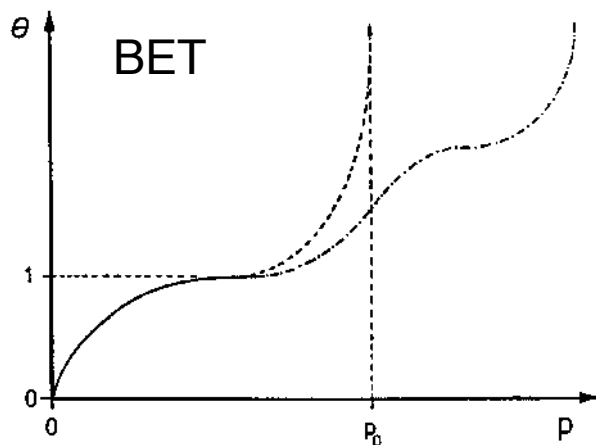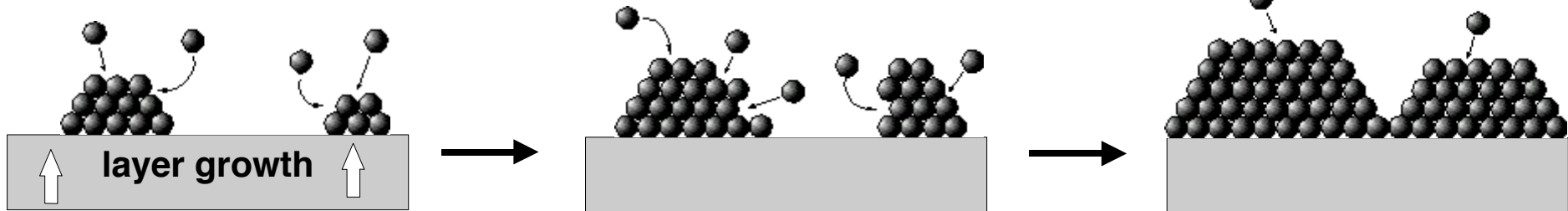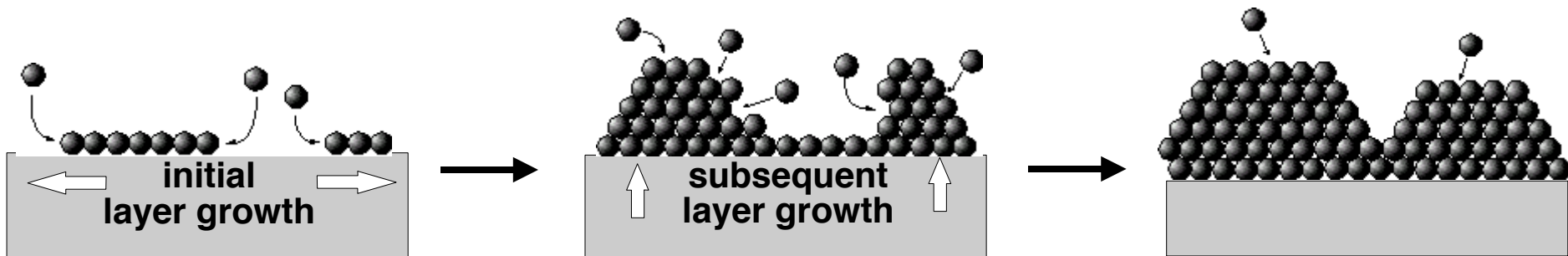
Surface Layer Growth Models

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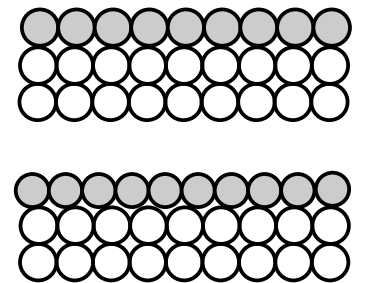
lattice strain: when a material with minor lattice mismatch growth epitaxially on a substrate the mismatch will induce strain in the growing crystal layer (often involved in Stranski-Krastanov growth mode)

incoherence: if a surface layer structure is completely independent of the substrate lattice structure the layer is incoherent
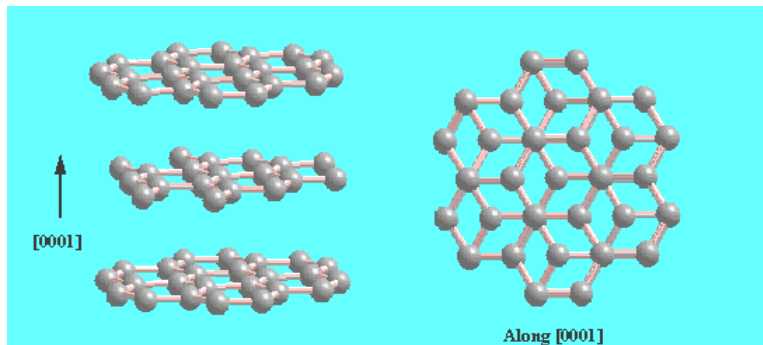
Preparation of Defined Surfaces: UHV

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)
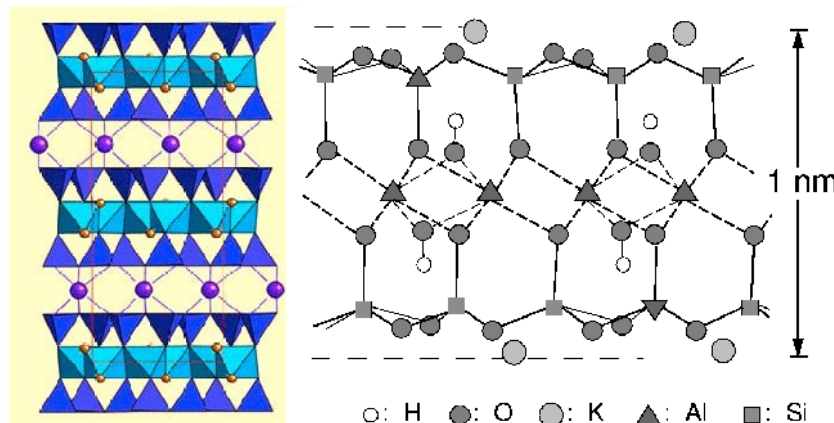e) epitaxial evaporation of new surface material

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

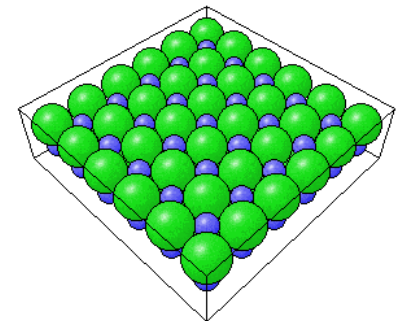disadvantage: labor and money intense equipment, very sensitive to contamination

mica (muscovit)

graphite (HOPG)

NaCl(100)

o: H ●: O ◐: K ▲: Al ■: Si

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 ($\rightarrow$ fuel cells) and corrosion processes ($\rightarrow$ 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 $\rightarrow$ solid-COO$^-$ + H$^+_{aq}$)

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

$\rightarrow$ fully ionized surface: ~ 0.5 nm^2 per charge

IHP (through center of bound ions)

OHP (through center of cations)

Helmholtz model: negative charge in the metal surface and chemisorbed dehydrated ions (inner Helmholtz plane, IHP) is compensated by positive charge of the solvated cation layer condensed onto the surface (outer Helmholtz plane, OHP) $\rightarrow$ two rigid charge layers
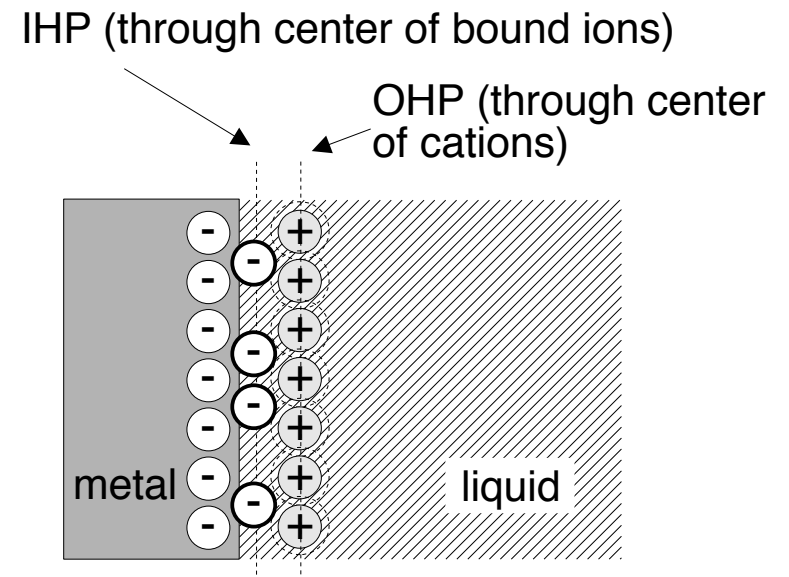
Metal Surface in Contact with Ions in Liquid 2

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

$$\nabla^2 \Psi = \frac{n_0 e}{\varepsilon \, \varepsilon_0}\left(e^{\frac{e \Psi(x)}{kT}} - e^{-\frac{e \Psi(x)}{kT}} \right)$$
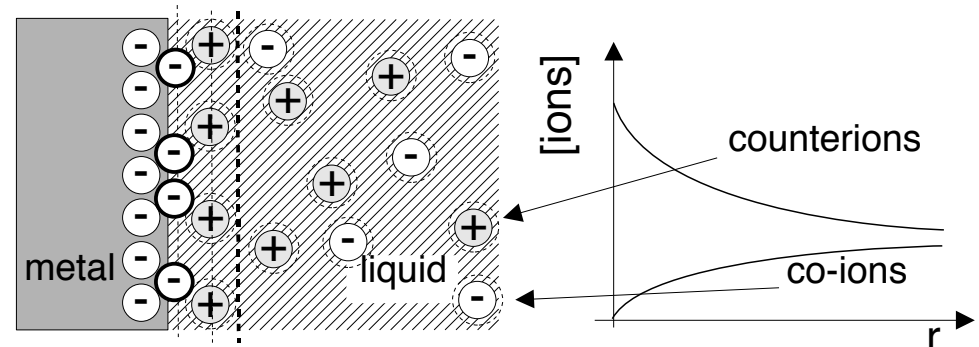
in the presence of 1:1-electrolyte
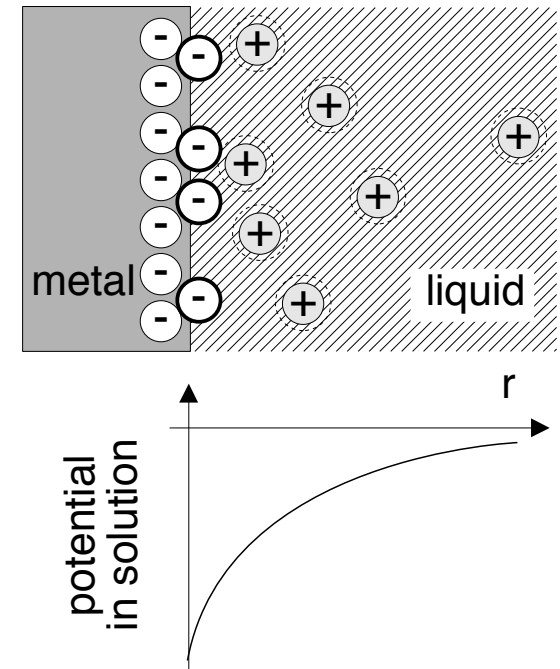
Stern model: (combination of Helmholtz and Gouy-Chapman) layer of tightly bound hydrated counterions (Helmholtz) at the surface (Stern layer, **A**) followed by a diffuse solvated ion layer **B** (Gouy-Chapman)
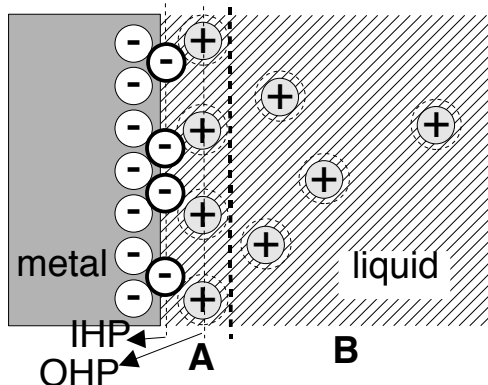
→ distribution of ions in the presence of salt (1:1-electrolyte)
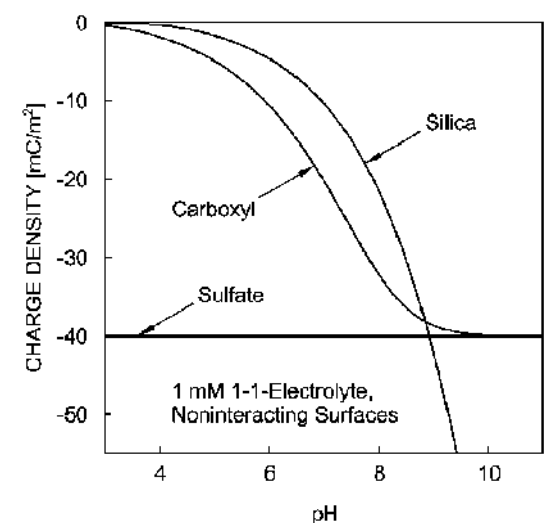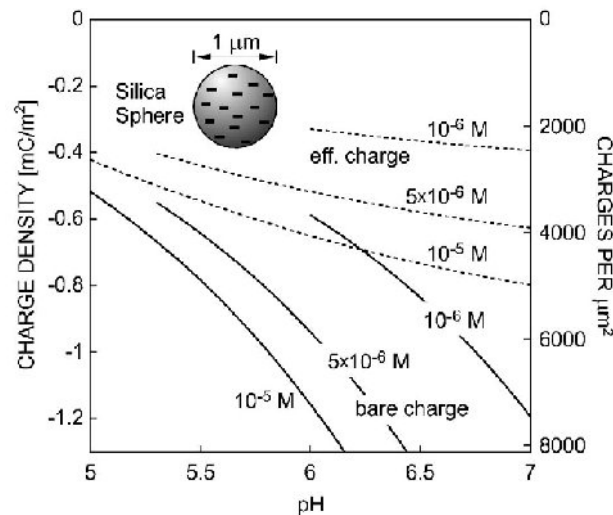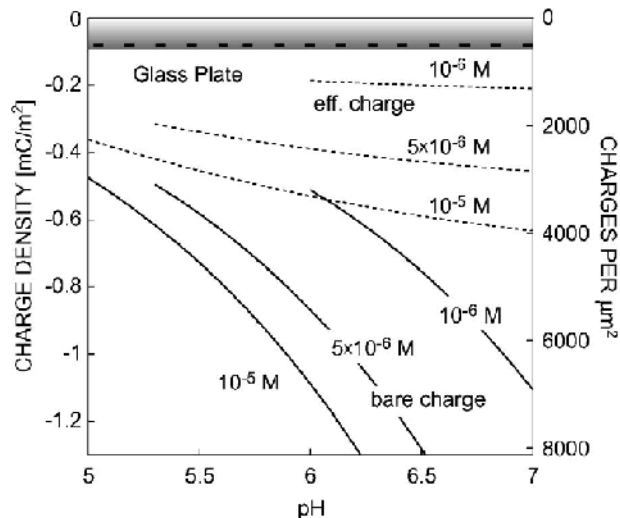
SiO₂ Surfaces in H₂O (pH Dependence)

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.

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

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
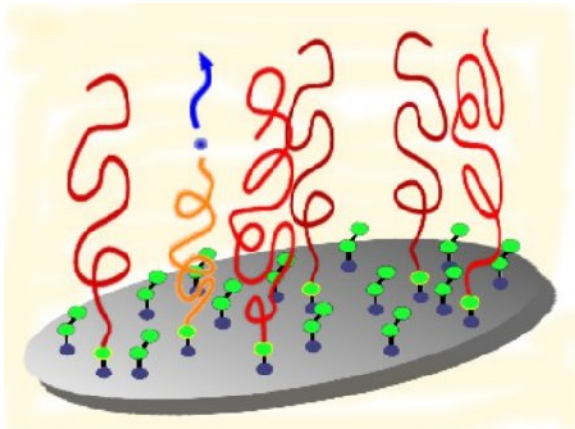
Surface-Grafted Polymer Layers

polymer brushes: polymer chains terminally tethered to a solid surface at high anchoring density → controls surface properties like tribological behavior, corrosion resistance or biocompatibility, e.g.

methods to generate polymers brushes:
a) "grafting from": the polymer is **grown from** initiator sites attached to the surface
b) "grafting onto": the polymer chains are **attached to** reactive groups on the surface

depending on the solvent the modified surface is exposed to the polymer brushes swell (good solvent) or collapse into their coil state (bad solvent), limit between good and bad solvent is theta-solvent (interaction between solvent molecules,solvent / polymer, and polymer / polymer is balanced for a given temperature)
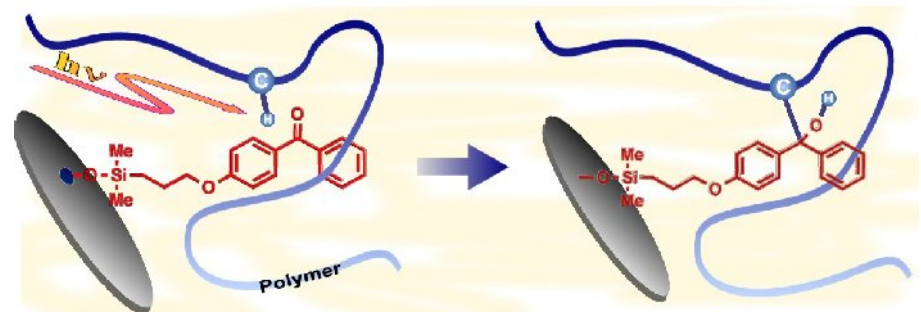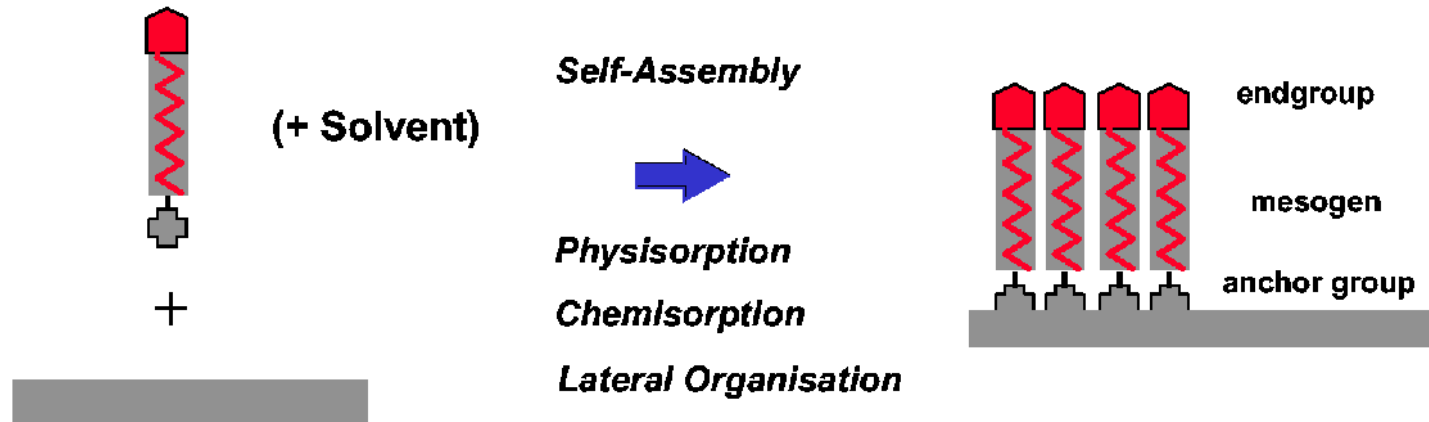
"grafting from"   silane initiators / anchors

"grafting onto"

J. Rühe; http://www.imtek.uni-freiburg.de/cpi/science/brushes/Brushes.htm
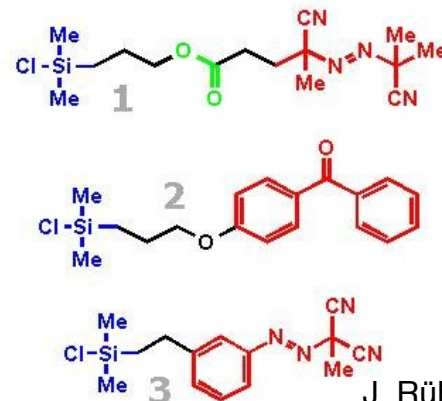
Molecular Surface Layers (SAM and LB)

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)