Molecular assembly at surfaces and interfaces

CHEM-E5120 INTERFACES AND NANOMATERIALS

MASTER PROGRAMME OF FUNCTIONAL MATERIALS

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Outline

- Interactions between molecules direct self-assembly

- Adsorption at interfaces
  - Langmuir adsorption
  - Cooperative binding/adsorption

- Self-assembly
  - Self-assembled monolayers
  - Self-assembly of amphiphilic molecules

- Inorganic thin films
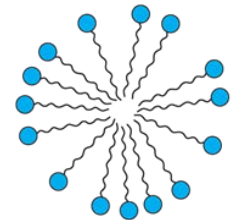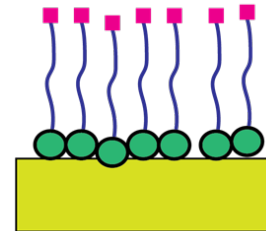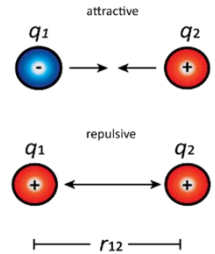
Forces acting between molecules and surfaces – general remarks

- Short range interactions

- Long range interactions

- Attractive and repulsive forces

- Useful unit for interaction potential between molecules is $k_\mathrm{B}T$, which describes the thermal fluctuations

    At room temperature

    $$k_\mathrm{B}T = 1.38 \cdot 10^{-23}\, \mathrm{J}/\mathrm{K} \cdot 300\mathrm{K} = 4.1 \cdot 10^{-21}\mathrm{J}$$

    $$[k_\mathrm{B}T] = \mathrm{pN} \cdot \mathrm{nm} = 1 \cdot 10^{-12}N \cdot 1 \cdot 10^{-9}m$$

- In order to form a stable bond, the magnitude of the attractive potential needs to be larger than $k_\mathrm{B}T$ (but negative)

Intermolecular forces

- Total interaction is a sum of variety of different forces acting between the molecules

- Depending on the molecules, one force may predominate

- Typically force (F) between molecules is given in terms of potential energy (V):
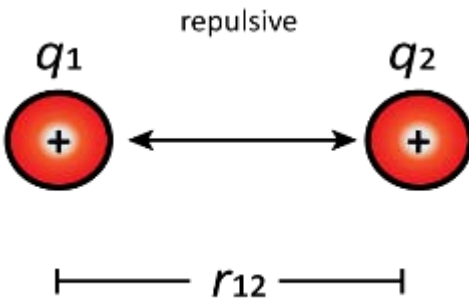
$$F(r) = -\frac{dV(r)}{dr}$$

where r is the distance between the molecules

Electrostatic forces (ion-ion)

- Two ions interact with each other mainly through Coulombic forces due to their charge

- Coulombic force between two charged molecules is:

attractive

q_1 q_2

$$F(r) = \frac{q_1 q_2}{4\pi\varepsilon_0 r_{12}^2}$$

repulsive
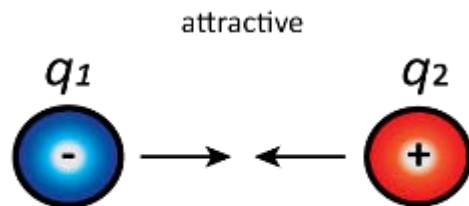
q_1 q_2

$\longmapsto r_{12} \longmapsto$

q_1 = charge of ion 1
q_2 = charge of ion 2
ε_0 = permittivity of vacuum
$8.854 \cdot 10^{-12} m^{-3} kg^{-1} s^4 A^2$
r_{12} = distance between the ions
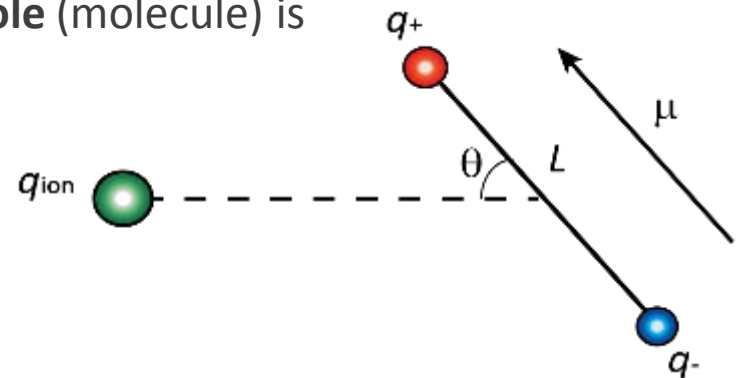
Electrostatic forces (ion-dipole)

- Some molecules don not have a permanent charge, but their electron density is unequally distributed due to different electronegativity of the atoms
  - Water molecule
  - Partial charges δ+ and δ-

- Polarity causes a permanent dipole moment μ:

$$\mu = qL$$
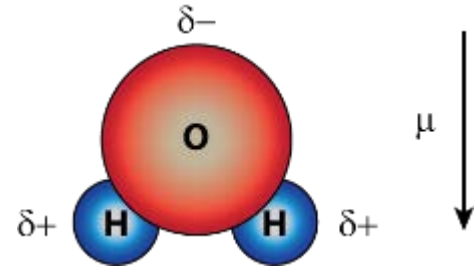
- The Coulomb force between an **ion and a dipole** (molecule) is

$$V(r,\theta) = \frac{q_{ion}\mu cos\theta}{4\pi\varepsilon_0 r_{12}^2}$$
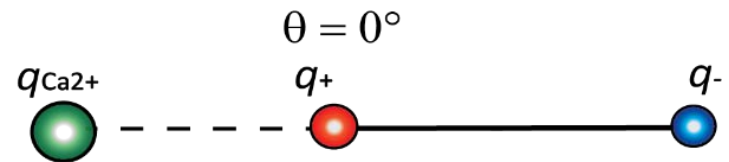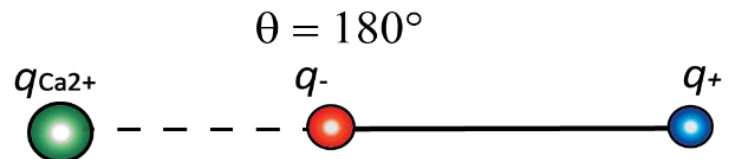
Ion-dipole forces

$$\cos 0 = 1 \Rightarrow V(r, 0) = \frac{q_{ion}\mu}{4\pi\varepsilon_0 r_{12}^2}$$

Maximal potential

$$\cos 180° = 0 \Rightarrow V(r, 180°) = -\frac{q_{ion}\mu}{4\pi\varepsilon_0 r_{12}^2}$$

Minimal potential

Van der Waals interaction (vdW)

- Collective term to describe attractive or repulsive forces, or non-covalent interactions between molecules (excluding electrostatic and covalent interactions)

- These have a key role in biology, polymer science and nanoscience

- Many natural phenomena are due to van der Waals forces, for instance the sticky gecko feet:

Hierarchical structure of the feet: features on meso- micro- and nano levels
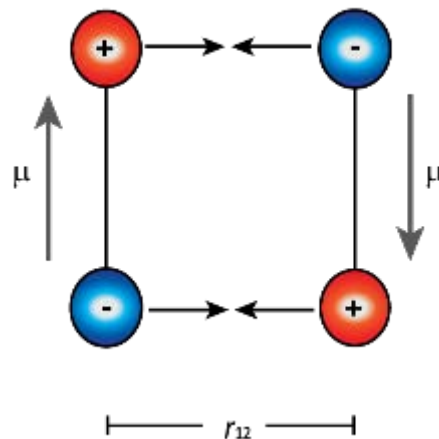➔ Huge surface area
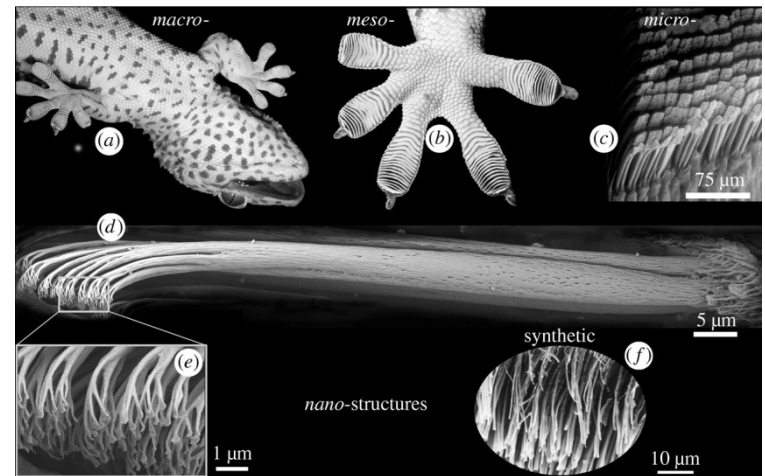
K. Autumn, N. Gravish *Phil. Transact. A* 2008
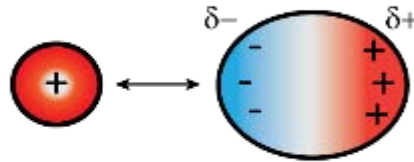
Dipole-dipole interactions (vdW)

- Molecules with permanent dipoles interact with each other in angle dependent way

- Often the largest interaction occurs in antiparallel position
  - Analogous to attraction between two bar magnets

Induced dipole interactions (vdW)

- An ion or polar molecule may cause polarisation of the electrons of a non-polar molecule on close proximity ➜ induction of a dipole

- The electron cloud of the non-polar molecule becomes distorted and effective charge separation occurs

- Polarizability describes how much the electron cloud of a certain molecule can be distorted and can be expressed in terms of the induced dipole moment and the strength of the electric field

$$\mu_{induced} = \alpha E$$

- Interaction between ion and induced dipole is always attractive

| Molecule	Polarizability (10^{-24} cm^3/$4\pi\varepsilon_0$)
H_2O	1.45
H_2	0.8
Benzene	10.2

Dispersion (London) forces (vdW)

- Quantum mechanical correlation between the electrons of two neighbouring molecules

- Think about two neutral non-polar molecules, at any given moment, the distribution of electrons may be asymmetrical ➔ momentary dipole moment, which induces dipole moment to the neighbour

- The earliest theory to describe the interactions is by London in the 1930s

- For two identical molecules:

$$V(r) = \frac{-3}{4(4\pi\varepsilon_0)^2}\frac{\alpha^2 I}{r_{12}^6} = \frac{-C_{dispersion}}{r_{12}^6}$$

- The interaction decays fast as a function of separation and is always attractive

- Important role in cohesion of liquids and solids

Hydrogen bonds

- Form of dipole interaction between species where a hydrogen is bound to an electronegative atom such as N, O or F

- The electrons are strongly with drawn by the electronegative atom leaving a positive partial charge to the hydrogen, which then interacts with another molecule possessing a dipole moment

- The neighbouring molecule can now be drawn much closer than normally, meaning a much higher interaction between the two molecules

- For instance, the length of the O-H bonds in water is 0.96 Å, whereas the hydrogen bond formed between two different molecules may be 1.5 Å
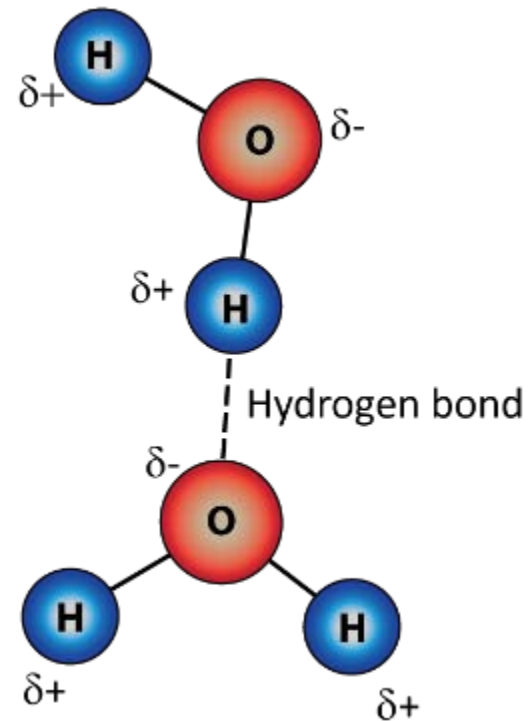
"Hydrophobic effect"

- The tendency of non-polar molecules to form aggregates in water

- For instance hydrocarbon molecules interact with other hydrocarbons rather than water ➔ phase separation (**enthalpy driven** minimisation of the contacting interface)

- At hydrophobic surface, water has to reorganize ➔ **entropy gain** due to release of water molecules into bulk

http://www.treehugger.com/clean-technology/nasa-uses-lotus-leaf-as-inspiration-for-space-gear-dust-repellent.html

Summary - Forces between molecules

Increasing strenght

- **Covalent interactions**, strength 100-200 $k_\mathrm{B}T$

- **Hydrophobic interactions** are strong and act at varying distances

- **Electrostatic forces** have a key role in phase separation of condensed phases and self-assembly, they act at short and long distances, strength varies

- **Hydrogen bonds** are rather strong and act at short distance (0.3 nm), strength ~ 10 $k_\mathrm{B}T$

- **van der Waals forces** of individual atoms are weak and act at very short distances (0.3-0.6 nm), a fraction of $k_\mathrm{B}T$

http://chemwiki.ucdavis.edu/Physical_Chemistry/Physical_Properties_of_Matter/Intermolecular_Forces/Van_Der_Waals_Interactions

Assembly at surfaces and interfaces - Adsorption

Adsorption at surfaces and interfaces

- Surface active molecules have a tendency to adsorb to surfaces
  - May be based on chemical or physical interactions

- The curve describing the *surface coverage* as a function of the concentration at certain temperature is called **adsorption isotherm**

- Stoichiometry and mechanism of adsorption depends on the system
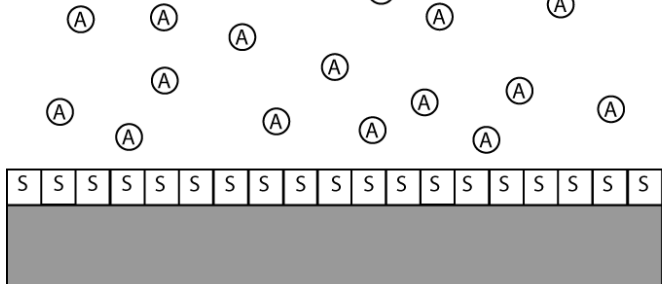 - Planar surfaces, curved surface, binding to other molecules
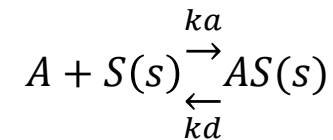
Adsorption - Langmuir model

- The adsorbing species do not interact with each other
  - The adjacent adsorbed species do not affect the adsorption

- The surface sites are equally distributed and identical

- One species adsorbs to one surface site ➔ The probability of adsorption scales with the vacant surface sites
  - Describes a monolayer
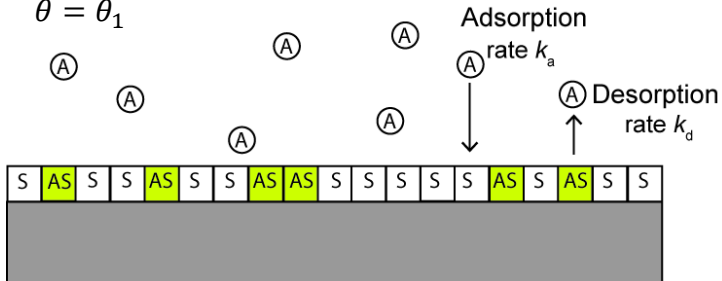
Langmuir isotherm 1/2

$t = 0$
$\theta = 0$

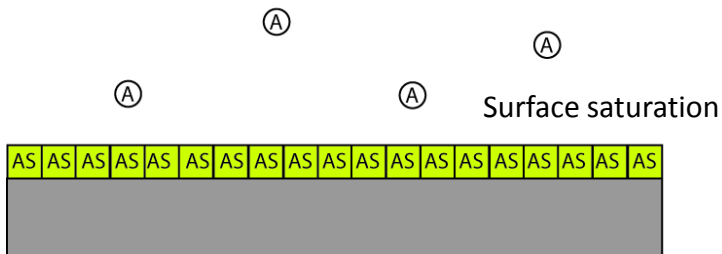Species *A* adsorbs to a surface site *S*:

$$A + S(s) \overset{ka}{\underset{kd}{\rightleftarrows}} AS(s)$$

$t = t_1$
$\theta = \theta_1$

Adsorption rate k_a

Desorption rate k_d

The rate of the adsorption reaction follows 1st order kinetics:

$$\frac{d[AS]}{dt} = k_a[A][S] - k_d[AS]$$

$t = \infty$
$\theta = 1$

Surface saturation

The equilibrium constant *K* is obtained from:

$$K = \frac{k_a}{k_d}$$

Langmuir isotherm 2/2

At equilibrium the net rate of adsorption is zero:

$$\frac{d[AS]}{dt} = 0 \Rightarrow k_a[A][S] - k_d[AS] = 0$$

Substituting the equilibrium constant gives:

$$[AS] = K[A][S]$$
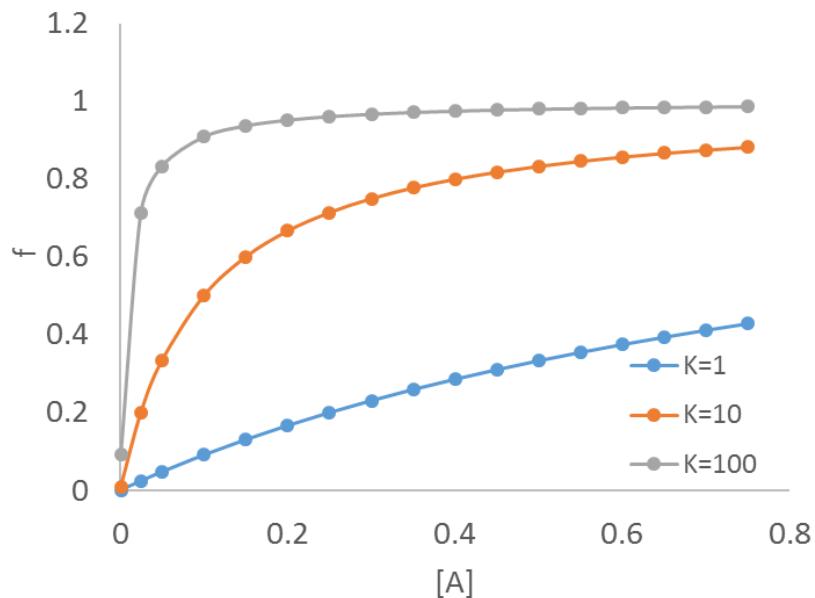
The surface coverage depends on the adsorbed species and the total surface sites:

$$f = \frac{[AS]}{[S]_{tot}} \qquad \text{where} \quad [S]_{tot} = [AS] + [S]$$

Combining these, we get the *Langmuir isotherm*:

$$f = \frac{K[A]}{1 + K[A]}$$

Langmuir adsorption isotherm

- Surface coverage *f* as a function of concentration [*A*]

- The equilibrium constant *K* of adsorption determines the shape of the curve

- The higher the *K* is, the lower concentration is needed for saturation (full) coverage of the surface

Cooperativity – Hill model

- Binding to the surface site is affected by consecutive binding species ➡ isotherm has sigmoidal shape

- Empirical model to describe cooperativity

- Example: allostery of oxygen binding to hemoglobin

- Cooperativity is described by Hill coefficient n
  - $n > 1$ ➡ positive cooperativity
  - $n < 1$ ➡ negative cooperativity

Cooperativity – Hill model

$$nA + S(s) \overset{ka}{\underset{kd}{\rightleftarrows}} A_nS(s)$$
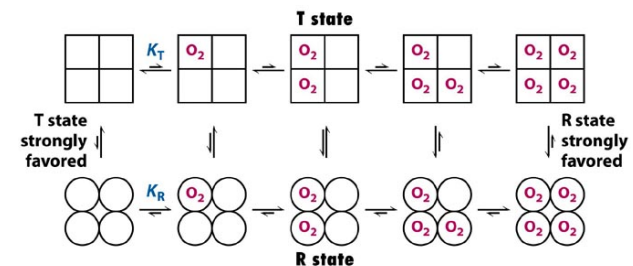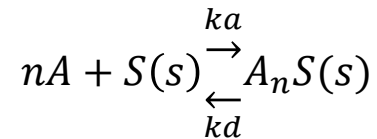
The rate of the adsorption reaction:

$$\frac{d[A_nS]}{dt} = k_a[A]^n[S] - k_d[A_nS]$$

The equilibrium constant K is obtained from:

$$K = \frac{k_a}{k_d}$$

Hill isotherm 2/2

At equilibrium the net rate of adsorption is zero:

$$\frac{d[A_nS]}{dt} = 0 \Rightarrow k_a[A]^n[S] - k_d[A_nS] = 0$$
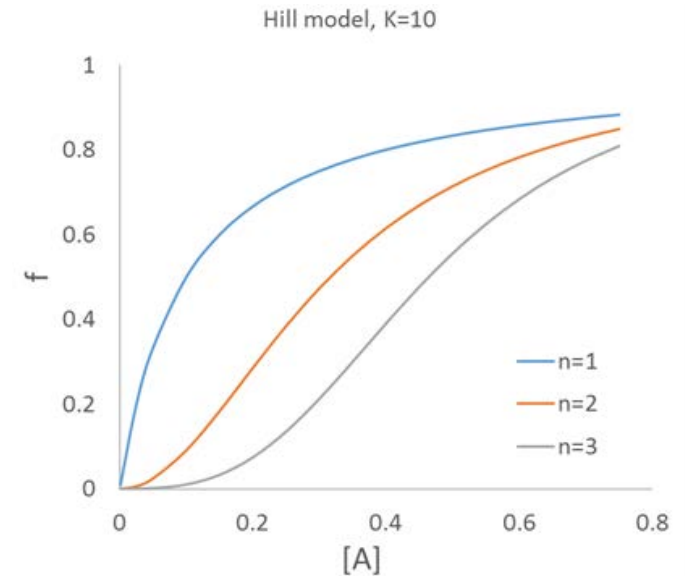
Substituting the equilibrium constant gives:

$$[A_nS] = K[A]^n[S]$$

The surface coverage depends on the adsorbed species and the total surface sites:

$$f = \frac{[A_nS]}{[S]_{tot}} \quad \text{where} \quad [S]_{tot} = [A_nS] + [S]$$

Combining these, we get the *Hill isotherm*:

$$f = \frac{K[A]^n}{1 + K[A]^n}$$

Hill model, K=10

Determining the *n*

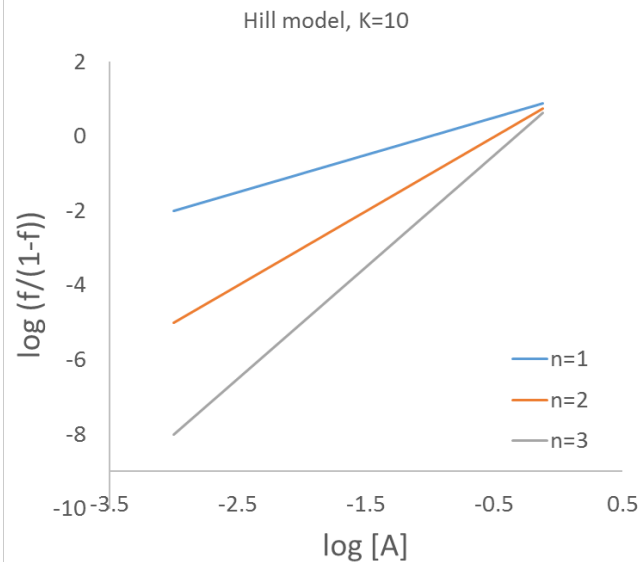Linearizing the Hill isotherm enables finding the Hill coefficient *n*

$$f = \frac{K[A]^n}{1 + K[A]^n}$$

Form ratio of bound and unbound fraction:

$$\frac{f}{1-f} = \frac{\dfrac{K[A]^n}{1+K[A]^n}}{1-\dfrac{K[A]^n}{1+K[A]^n}} = K[A]^n$$

Taking logarithm linearizes the equation:

$$\log\frac{f}{1-f} = \log K + n\log[A]$$

Hill model, K=10

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Which one is the weakest force?

A) Hydrogen bond

B) van der Waals interaction

C) Electrostatic force

True or false?

A) Surface coverage is independent of the equilibrium constant of adsorption

B) Langmuir isotherm equals Hill isotherm with $n = 1$

C) Adsorption isotherm describes the binding at equilibrium

Self-assembled monolayers

What is self-assembly?

- "Process during which molecular fragments spontaneously and often reversibly organize themselves into nanomaterials"

- Combination of thermodynamic factors, kinetic factors and intermolecular interactions

- Has many names: aggregation, agglomeration, flocculation, self-organization
  - These may have different time scales
  - Favorable vs. unfavorable
  - Reversible vs. irreversible

- May result in 3D, 2D, 1D and 0D structures

Formation of SAMs

• Self-assembled monolayer (SAM) is formed on a surface due to strong interaction between the surface and surface active organic molecules

• Often follows the Langmuir adsorption

• The head group adsorbs and binds strongly to the surface
  • Example: thiol bond on gold surface has interaction energy ~ 75 $k_B T$

• The tail interacts much less with the surface and more with other tails

Terminal functionality

Alkyl chain

Surface active head

Self-assembled monolayer
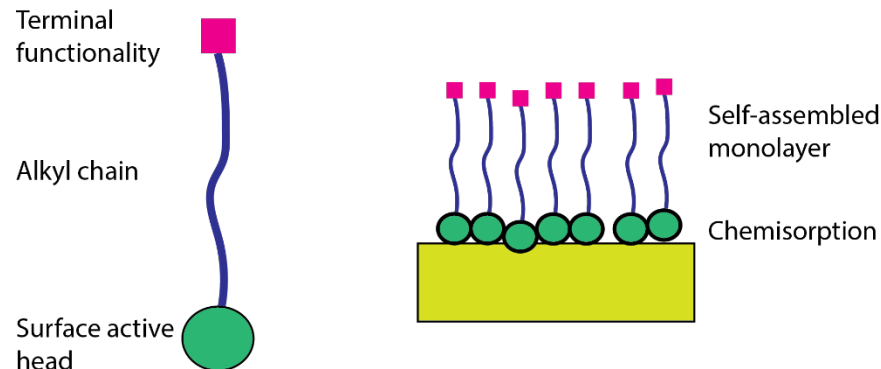
Chemisorption

Types of SAMs

- May be categorized by the main driving interaction:
  - Electrostatic forces, hydrophobicity/hydrophilicity, capillary force, **chemisorption**

- Organosilicon on hydroxylated surfaces, alkanethiols and sulfides on noble metal surfaces, carboxylic acids, amines and alcohols on metals

- Irreversible vs. reversible

http://syntheticremarks.com/?p=3711
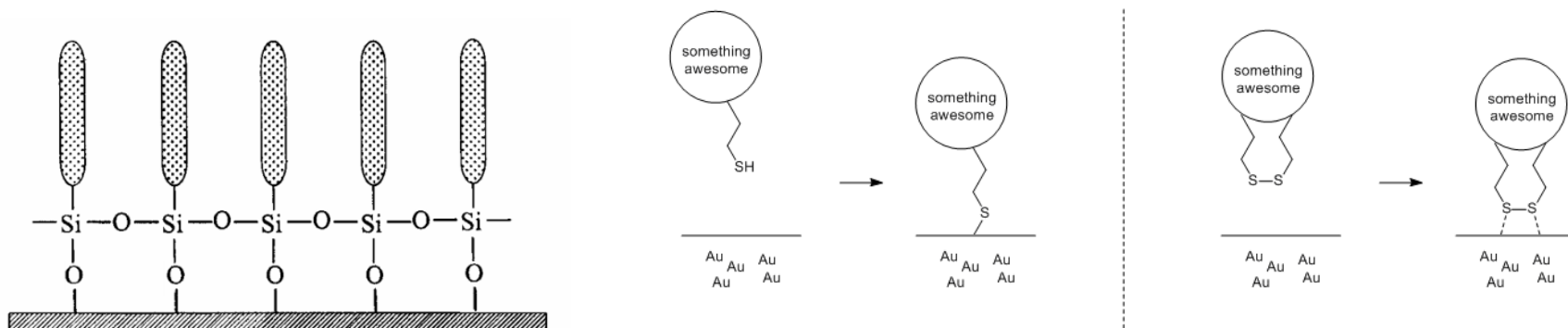
SAMs on curved surfaces

- Stabilisation of nanoparticles
  - Formation of SAM on the surface of growing nanoparticle
  - Steric and electrostatic hindrance against aggregation

- Functionalization of nanoparticles
  - So called thiol-exchange reactions
  - Determines the particle solubility
  - Attachment of numerous chemical groups including large biomolecules

Excess of functionalised free thiols

Equilibrium between bulk and surface
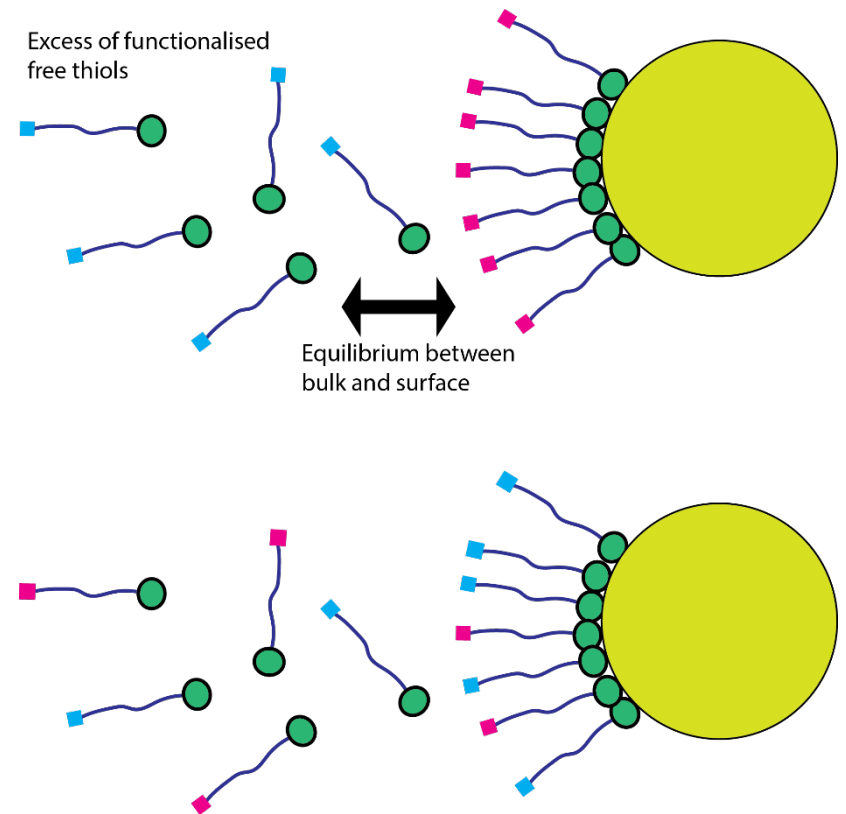
Properties of SAMs

- Properties depend on the monolayer functionalities, composition and surface coverage

- Barrier properties: SAM may form an electrically insulating layer

- Surface energy: SAM may modify the wetting of the surface

- Specific adsorption: SAM may bind specific target molecules

Self-assemblies of amphiphilic molecules
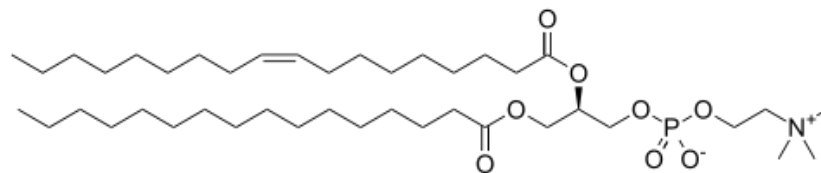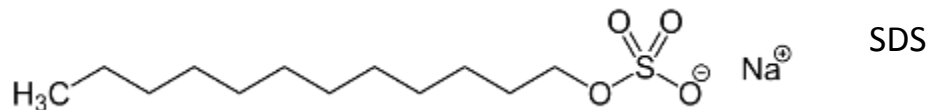
Amphiphilic molecules (surfactants)

- Typically organic molecules, two parts with different polarity

- One part is a non-polar (hydrophobic) hydrocarbon chain, other a polar (hydrophilic) head

- They have tendency to assemble and enrich at the interface between hydrophilic and hydrophobic phases (water/oil, water/air, water/solid hydrophobic) ➔ reduction of the interfacial energy

- Interfacial assembly is spontaneous and thermodynamically favorable (stable)
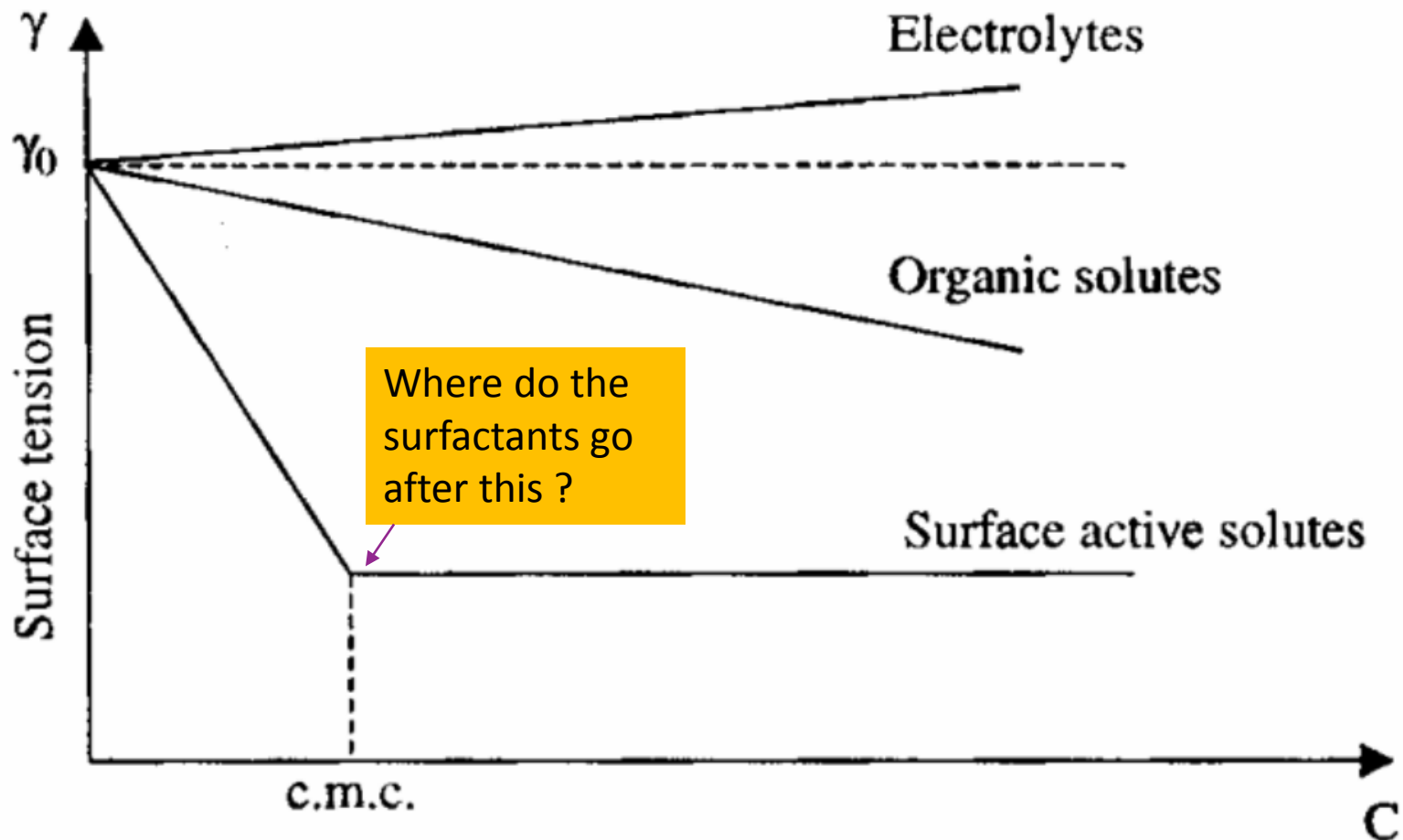
Adsorption at interfaces

- Amphiphilic molecules (surfactant) lower the surface tension of water
  - Orientation at the interface, the surface molecules of water interact more strongly with the hydrophilic end of the molecule (become more like bulk molecules)

- Surface tension depends on the density of the molecules at the interface, which depends on the bulk concentration

SDS

Phosphatidylcholine derivative

The graph shows Surface tension (γ) versus concentration (C) for three types of solutes:
- Electrolytes (increasing γ)
- Organic solutes (decreasing γ)
- Surface active solutes (sharp decrease to c.m.c., then flat)

Where do the surfactants go after this ?

Cao *et al.* Nanostructures and Nanomaterials - Synthesis, Properties and Applications

Micelle and microemulsion formation

- When concentration of a surfactant is increased further after the surface saturation is reached
  - → Self-assembly of micelles at the critical micelle concentration (CMC)
    - ◦ Thermodynamically stable, soluble in water

- Also more complex configurations of the assemblies possible

- Reverse micelles and microemulsions in oil/water systems

- Synthetic vesicles are called liposomes
  - Encapsulation of drugs, reactants etc.

AQUEOUS

Micelle

Vesicle

OIL/AQUEOUS

Microemulsion

water

Oil

Reverse micelle

oil

water
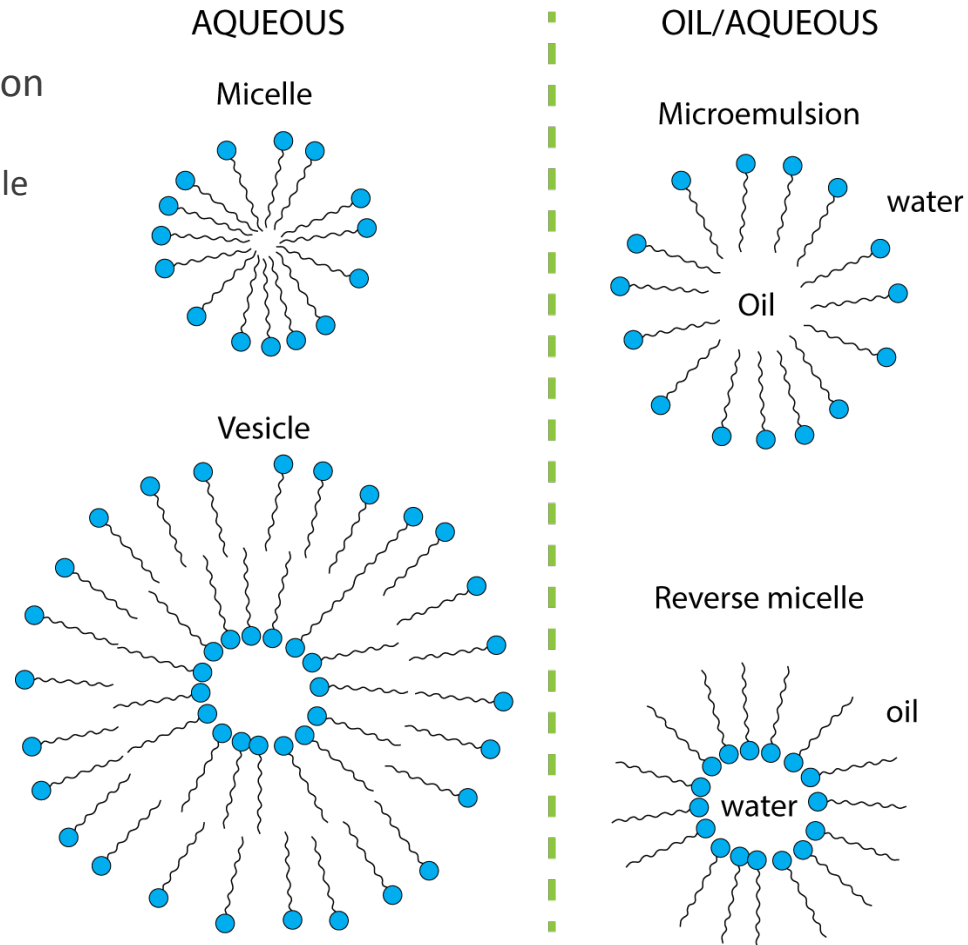
Micellar structures

• Increasing the surfactant concentration above the CMC leads into cylindrical rods

• Further increase of concentration leads to ordered hexagonal packing of the cylinders ➜ lamellar structure
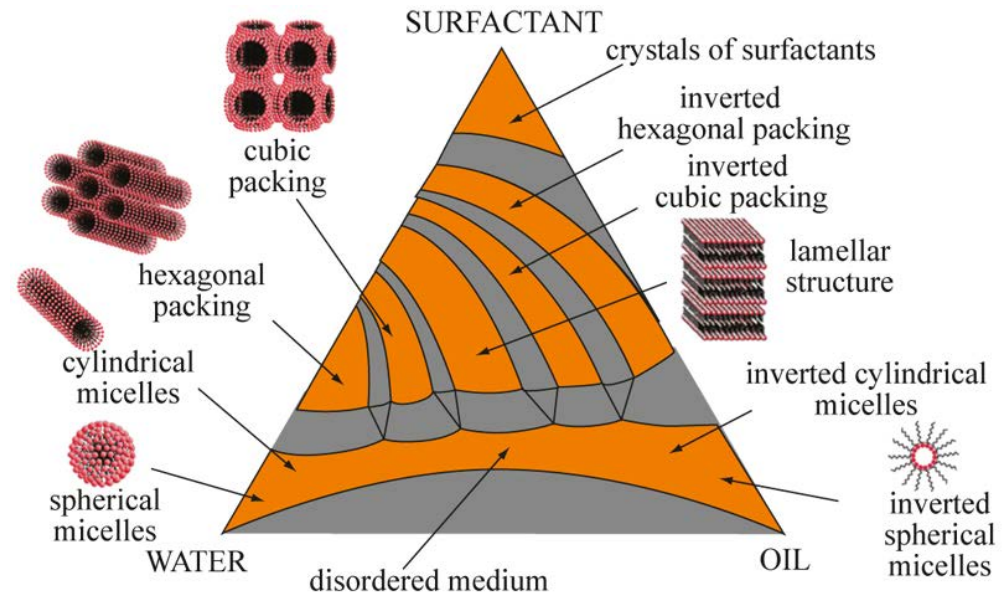
# Deposition of inorganic thin films by ALD

Atomic layer deposition (ALD)

• Method for growing atomically precise conformal films on nanometer and subnanometer scale (inorganic materials)

• A key feature is the self-limiting nature of growth ➔ only one molecular layer can grow at a time

• Also called atomic layer epitaxy (ALE), atomic layer growth (ALG), atomic layer chemical vapor deposition (ALCVD), molecular layer epitaxy (MLE)

ALD (Atomic Layer Deposition) — Heaters, Wafer, Vapor Pulse 1, Vapor Pulse 2, Vacuum Pump Out
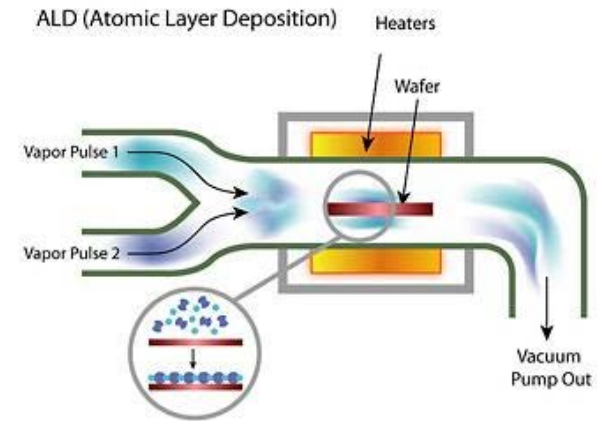
The principle of ALD

1) Surface is activated

2) Chemical precursor in vapor phase is introduced

3) Condensation reaction to the surface

4) Surface is activated again

5) New precursor introduced…

Deposition of various oxides, nitrides, fluorides, elements…
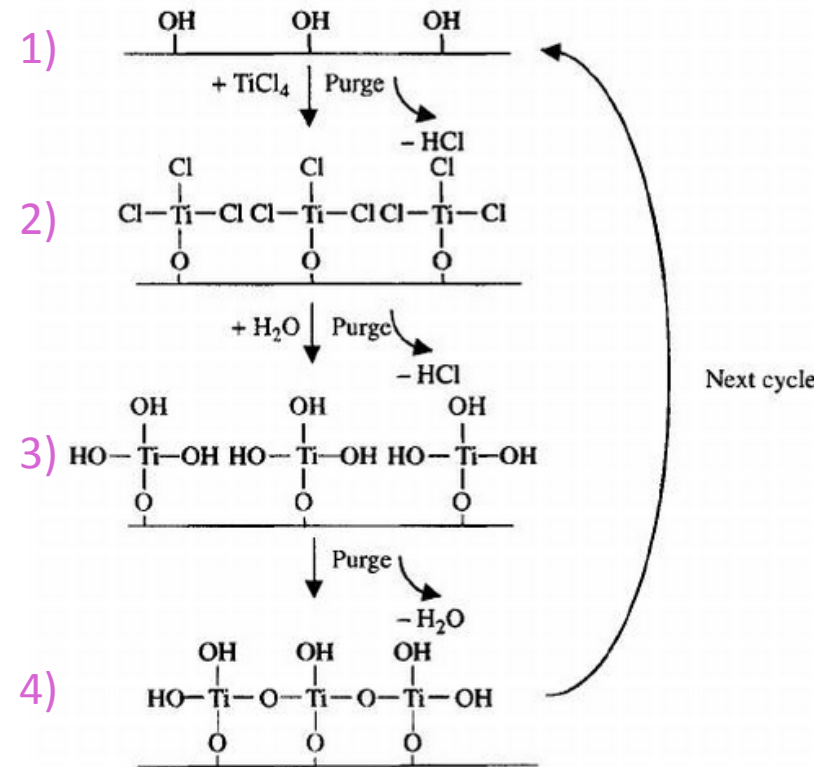
ALD precursors

•Metal chlorides, metallorganic compounds, hydrides

•Requirements for ALD precursors

- Volatility
- No self-decomposition
- High reactivity, complete reactions
- No etching of the film or substrate material
- No dissolution to the film
- Unreactive byproduct
- Sufficient purity

Activated surface   Non-active surface
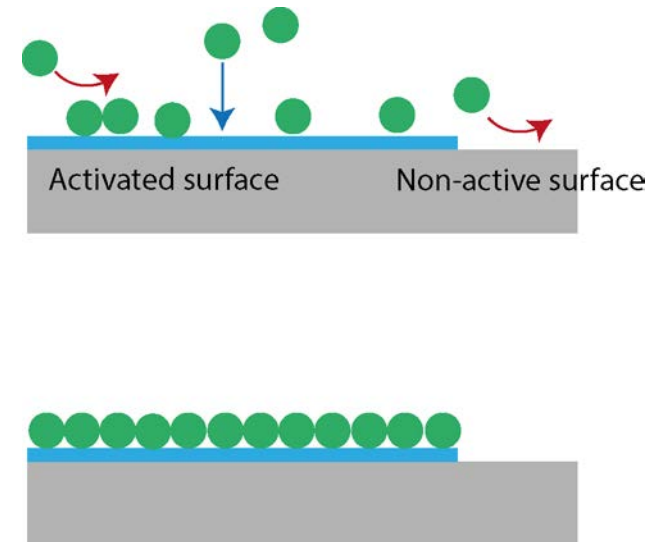
ALD multilayers
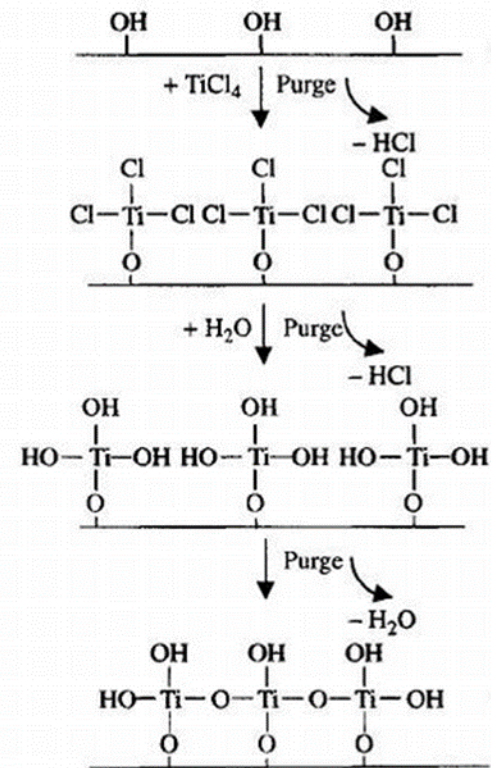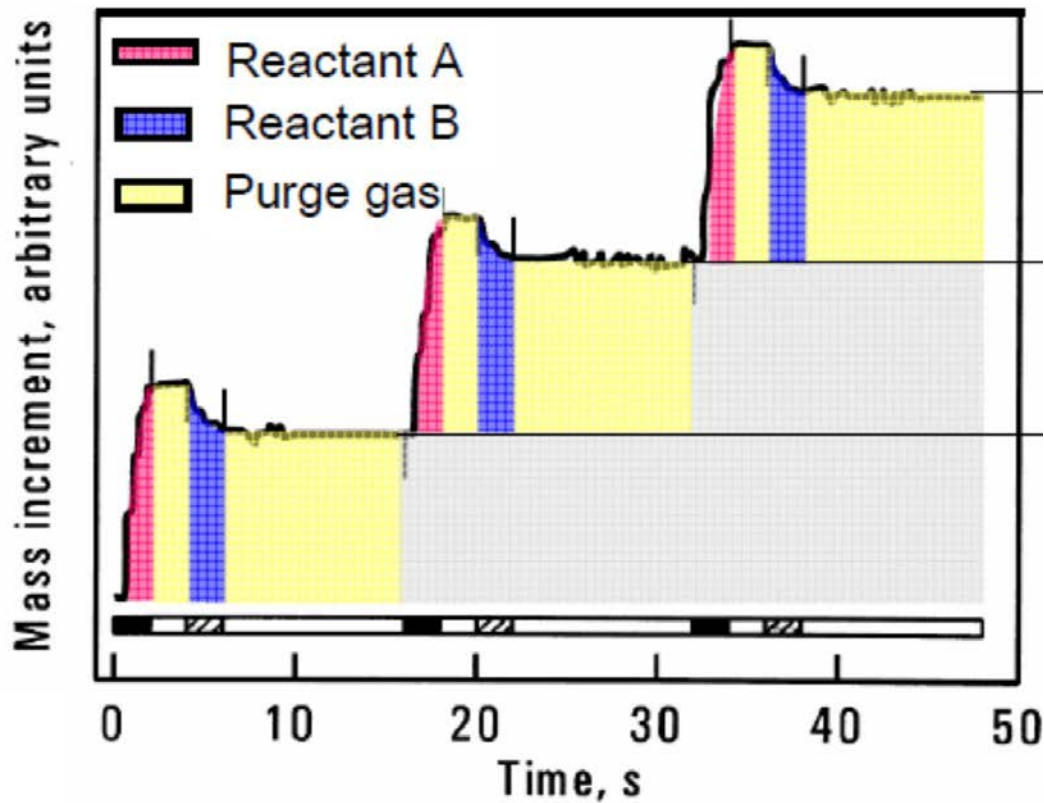
Aarik et al., Thin Solid Films 340 (1999) 110, for $HfCl_4/H_2O$ ALD

Features of ALD (compared to other deposition methods)

- Only heterogeneos reaction at the solid surface happens

- Precise control on the thickness
  - Even surface coverage when surface saturation is achieved
  - very thin layers, but multiple cycles may be applied
  - High step coverage

- Low deposition rate

- Difficult to scale up

Related literature

Molecular interactions:

- Any physical chemistry book, or
- Malkiat S. Johal: Understanding nanomaterials, CRC Press.

SAMs and surfactants, ALD:

- Guozhong Cao:Nanostructures and Nanomaterials - Synthesis, Properties and Applications, World Scientific (available as e-book at Aalto)
- Section 5.6 ALD, 5.8 Self-assembly

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Self-assembly

True or false?

A) Self-assembly is spontaneous

B) Self-assembled monolayers do not affect the surface properties on macroscopic level

C) ALD can be used for growing layers with any thickness

D) Surfactants only form lamellar assemblies