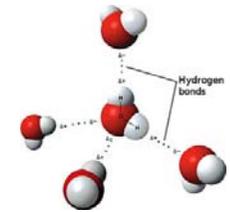


Physical bases of dental material science

Irén Bárdos-Nagy

Secondary (weak) chemical bonds (binding energy less than 50 kJ/mol few 0.1 eV/bond)

a./ **the H – bond** (~20 kJ/mol, 0.3 eV/bond) (water, HF)



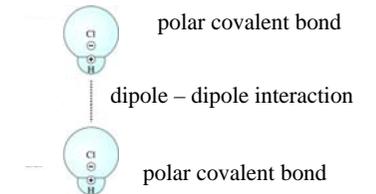
b./ **electrostatic interaction**

ion – dipole (few kJ/mol, 0.05 eV/bond)

dipole – dipole (~ 2 kJ/mol, 0.02 eV/bond)

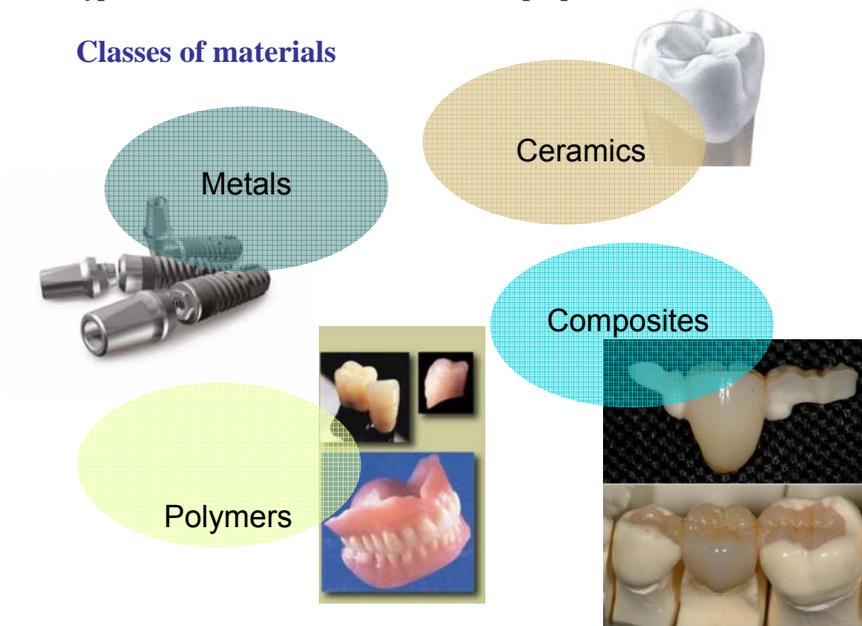
hydrophobic (~2 kJ/mol, 0,02 eV/bond)

van der Waals (dispersion) (~ 0.1 kJ/mol, 0. 001 eV/bond)
(Noble gases, F₂, H₂, Cl₂ molecules)



type of bonds → structure → properties

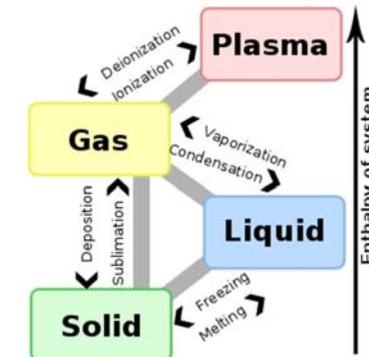
Classes of materials



The broad states of matter: gas
liquid
(liquid – crystal)
solid

General phase transitions

phase: physically and chemically homogeneous part of the material



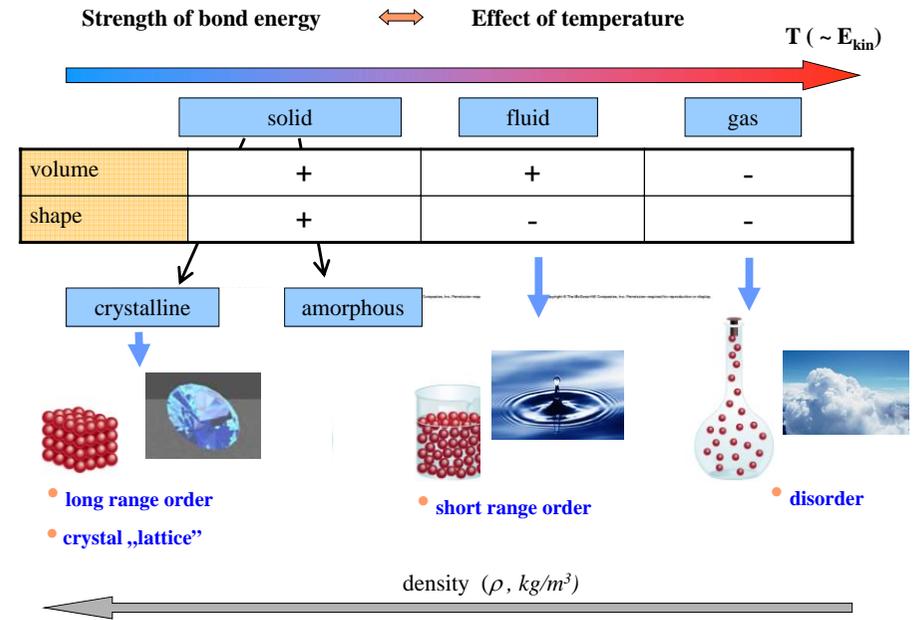
General properties of different phases:

gas: no definite volume and shape (there is no (or very weak) interaction between the particles), isotropic

liquid: the volume is definite, the shape is changing, short range order (secondary interactions between the molecules), isotropic

liquid – crystal: special shape of individual molecules, relatively long range of order, anisotropy (intermediate phase between liquids and crystals)

solid: definite shape and volume (strong (primer) bonds between the particles)
macroscopic range order (crystals)
periodic crystal structure, symmetry, frequent anisotropy
low degree of translational motion



Density of materials used in Dentistry

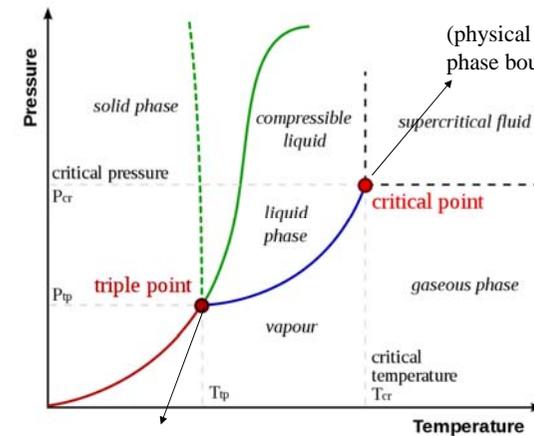
$$1 \frac{kg}{m^3} = \frac{10^3 g}{(10^2)^3 cm^3} = \frac{10^3 g}{10^6 cm^3} = 10^{-3} \frac{g}{cm^3}$$

Broad scale of materials – broad scale of structures and properties

material	ρ (g/cm ³)
dental enamel	2,2
dentine	1,9
water	1
amalgam	≈ 12
gold	19,3
gold-alloys	12-17
Pd-Ag alloys	10-12
Co-Cr alloys	8-9
Ni-Cr alloys	≈ 8
glass	2,2-2,7
ceramic	1,6-3,9
porcelain	2,2-2,4
gypsum (CaSO ₄ ·x2H ₂ O)	2,31-2,76
PMMA poly(methylmethacrylate)	≈ 1,2
silicon poly(dimethylsiloxane)	≈ 1,4

A typical phase diagram

phase diagram: graphical presentation of stable phases as a function of different parameters



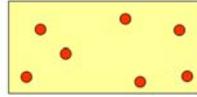
simultaneous transition of Ar from solid to liquid and to gas

Classes of materials

Gas phase (ideal gas)

characteristics

- filling the container – no volume in itself
- disorder
- composed of independent particles
- isotropy



Macroscopic properties/parameters

p, V, ν, T

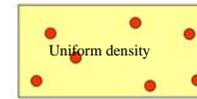
R – universal gas constant
 $R = 8.314 \text{ J/mol}\cdot\text{K}$

$$pV = \nu RT$$

Equation of state

↑
mole number

Gas phase (ideal gas) without force field



Macroscopic properties/parameters

$$pV = \nu RT$$

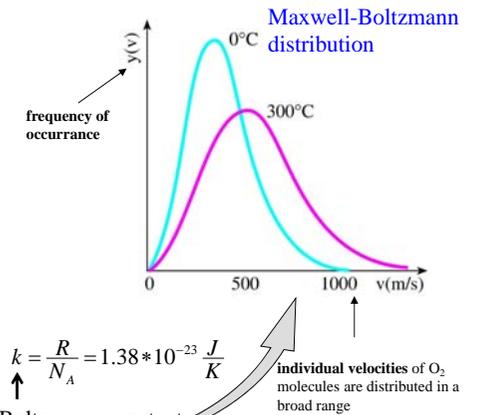
$$\frac{1}{2} m \bar{v}^2 = \frac{3}{2} kT$$

average kinetic energy

$$k = \frac{R}{N_A} = 1.38 \cdot 10^{-23} \frac{\text{J}}{\text{K}}$$

Boltzmann constant

Microscopic description



The ionization energy of the sodium atom is 496 kJ/mol. How large energy is necessary in eV to ionize one atom?

The ionization energy of a single atom:

$$\varepsilon_i = \frac{E_i}{NA} = \frac{496000}{6 \cdot 10^{23}} = 8,27 \cdot 10^{-19} (\text{J} / \text{atom}) = \frac{8,27 \cdot 10^{-19}}{1,6 \cdot 10^{-19}} = 5,15 \text{ eV} / \text{atom}$$

where E_i is the molar ionization energy, NA is the Avogadro number.

There is CO_2 gas in a 20 l tank. At 25 C° temperature the pressure in the tank is $2 \cdot 10^5$ Pa. How many moles of CO_2 gas are in the tank. How large is the total mass and the density of the gas?

$$pV = \nu RT$$

$$\nu = \frac{p \cdot V}{R \cdot T}$$

$$\nu = \frac{2 \cdot 10^5 \cdot 20 \cdot 10^{-3}}{8,31 \cdot 298} = 1,62 (\text{mol})$$

$$m = \nu \cdot M = 1,62 \cdot 44 = 71,07 (\text{g})$$

$$\rho = \frac{m}{V} = \frac{71,07}{20000} = 0,0035 (\text{g} / \text{cm}^3)$$

$$\text{specific volume} = \frac{V}{m} = \frac{20000}{71,07} = 281,4 (\text{cm}^3 / \text{g})$$

Calculate the velocity of the molecules in the nitrogen gas at room temperature (20 C°)!
 Suppose the same velocities! The molar mass of the nitrogen (considering that the particles are N₂ molecules) is 28 g/mol (0.028 kg/mol). How large is the kinetic energy of one molecule?

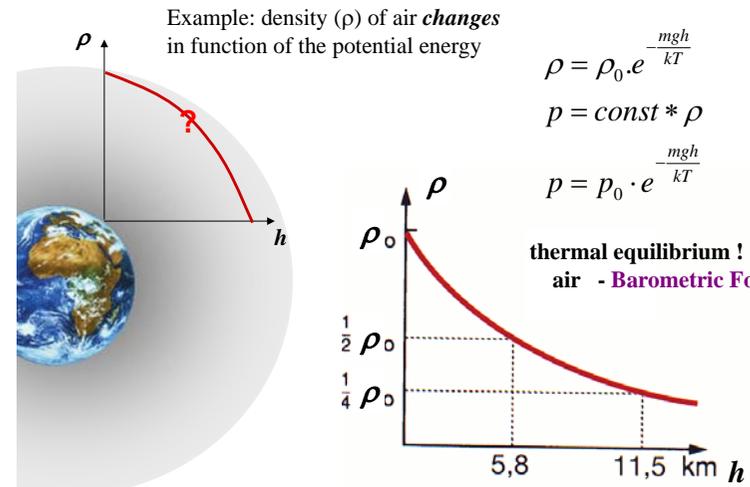
$$\frac{1}{2} m \bar{v}^2 = \frac{3}{2} kT$$

$$\bar{v} = \sqrt{\frac{3 \cdot k \cdot T}{m}}$$

$$\bar{v} = \sqrt{\frac{3 \cdot 1,38 \cdot 10^{-23} \cdot 293}{0,028 / 6 \cdot 10^{23}}} = 509,8 (m/s)$$

$$\varepsilon_{kin} = \frac{3 \cdot k \cdot T}{2} = \frac{1}{2} m \cdot v^2 = \frac{3 \cdot 1,38 \cdot 10^{-23} \cdot 293}{2} = \frac{1}{2} \cdot 0,028 \cdot 509,8^2 = 6,04 \cdot 10^{-21} (J / molecule) = 0,038 (eV)$$

Gas phase (ideal gas) in a force field – gravitation



less and less particles are found (in the same volume) at the levels of higher potential energy (at higher altitudes)

The Barometric formula is a special case of a general law

Boltzmann distribution

Distribution of particles on the levels of potential energy ε_i

$$\left. \begin{array}{l} n_i \\ n_0 \end{array} \right\} \Delta\varepsilon \quad n_i = n_0 \cdot e^{-\frac{\varepsilon_i - \varepsilon_0}{kT}}$$

$$n_i = n_0 \cdot e^{-\frac{\varepsilon_i}{kT}} = n_0 \cdot e^{-\frac{\Delta\varepsilon}{kT}} = n_0 \cdot e^{-\frac{\Delta E}{RT}} \quad \left(\begin{array}{l} \Delta E = \Delta\varepsilon \cdot N_A \\ R = k \cdot N_A \end{array} \right)$$

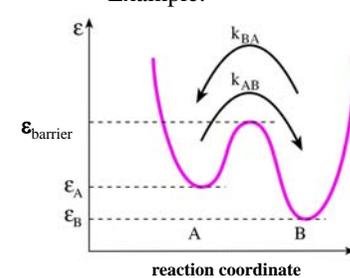
- the number of particles is smaller at the levels of higher energy
- on the same level, the number is smaller at higher temperatures
- the lowest energy level has the highest number of population

Wide range of applications

- barometric formula
- thermal emission of metals
- Nernst equation
- ~~equilibrium and rate of chemical reactions~~
- concentration of thermal defects in ordered, structured systems
- conductivity of semiconductors...

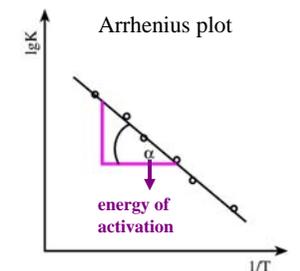


Example:



$$k_{AB} = const. \cdot e^{-\frac{\varepsilon_{barrier} - \varepsilon_A}{kT}}$$

$$K = \frac{n_A}{n_B} = e^{-\frac{\varepsilon_A - \varepsilon_B}{kT}}$$



At which altitude decreases the oxygen concentration by half of the sea level if the temperature is 0°C? Suppose that the atmosphere is in rest!

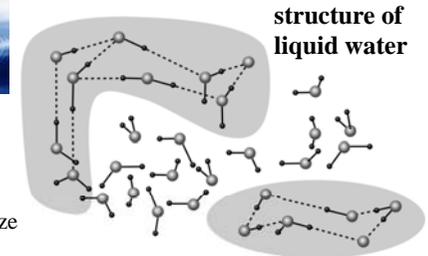
$$p = p_0 \cdot e^{-\frac{mgh}{kT}}$$

$$n = n_0 \cdot e^{-\frac{mgh}{kT}} = n_0 \cdot e^{-\frac{Mgh}{RT}}$$

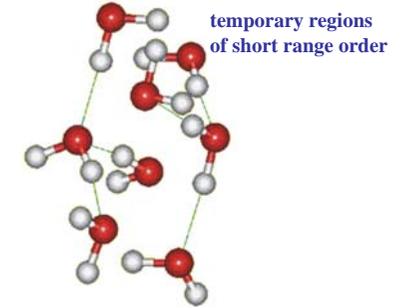
$$n = n_0 / 2$$

$$h = -\frac{RT \cdot \ln \frac{1}{2}}{M \cdot g} = -\frac{8,31 \cdot 273 \cdot (-0,693)}{0,032 \cdot 9,81} = 5010(m)$$

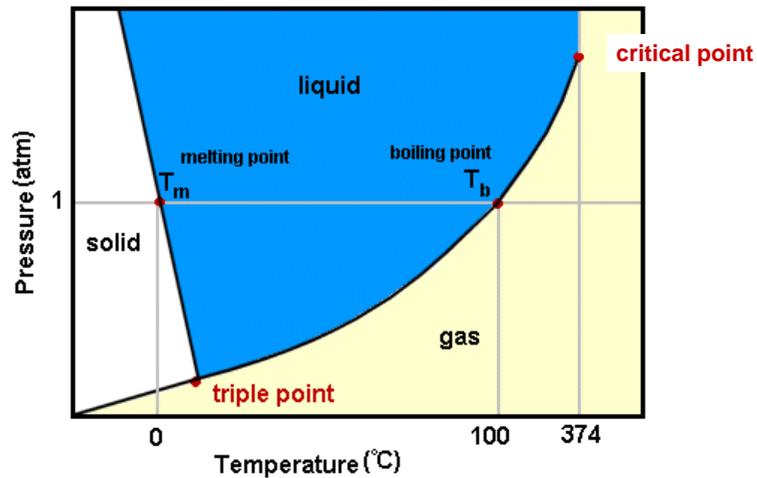
Fluids



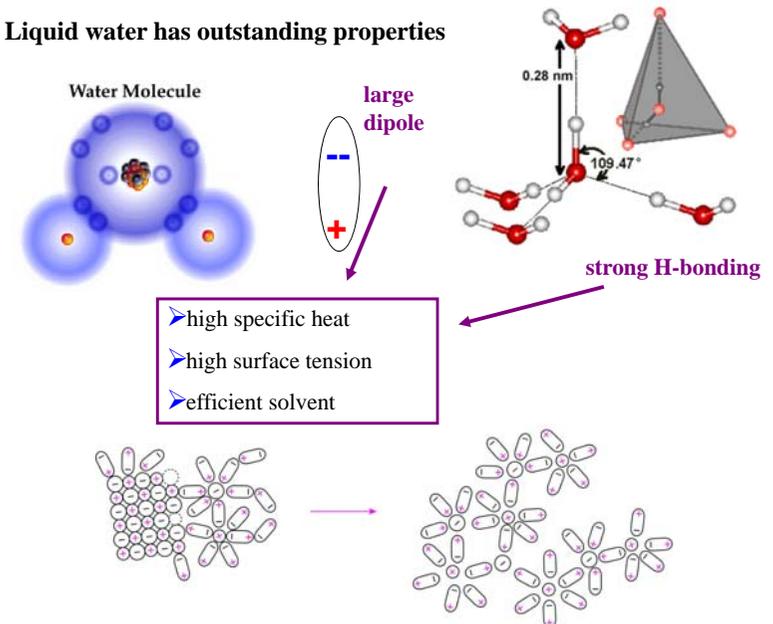
- Temporary regions of short range order within a few molecules ~10 nm domain size
- High concentration of structural defects
- Constant volume
- No firm shape - liquid
- High motional freedom of particles
- Isotropy



Phase diagram of water



Liquid water has outstanding properties

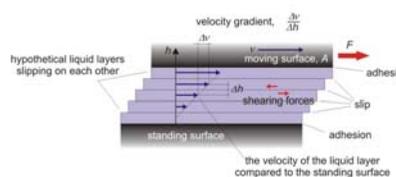


Important properties of fluids

1. Viscosity (η)

– an intrinsic mechanical property

Resistance to shearing motion: frictional force between adjacent layers as they slide past one another



$$F = \eta * A * \frac{\Delta v}{\Delta h}$$

$$[\eta] = Pa * s$$

$$\sigma_s = \frac{F}{A} = \eta * \frac{\Delta v}{\Delta h} = \eta * g_v \quad [Pa]$$

$\left(\frac{F}{A}\right)$ Shear stress

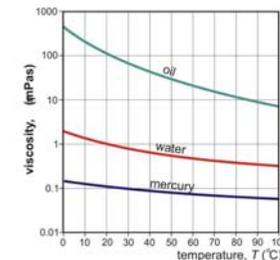
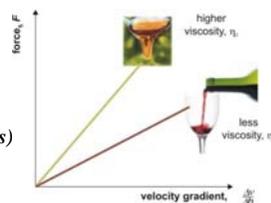
laminar flow

Newton's law – viscosity is a constant

η depends on - the temperature
- the magnitude of F/A

(η is a constant only up to a certain magnitude of the shear stress)

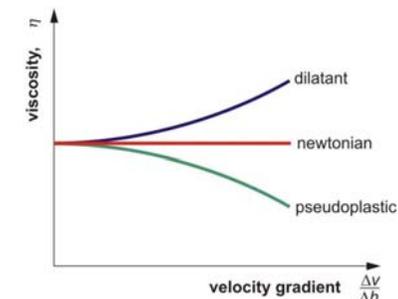
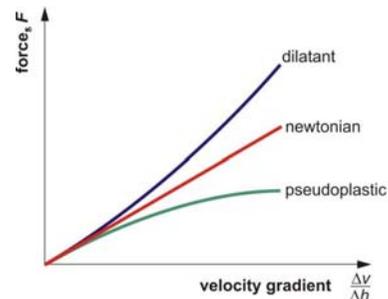
fluidity $\sim 1/\eta$



viscosity of some material as the function of temperature

exponential decrease (Boltzmann distribution)

Non-Newtonian fluids: the viscosity depends on the velocity gradient (not constant)



Time dependence of viscosity (chemical and/or physical change in the structure)

thixotropic (η decreases in time)

rheopectic (η increases in time)

Viscosity of fluids/materials of dental applications

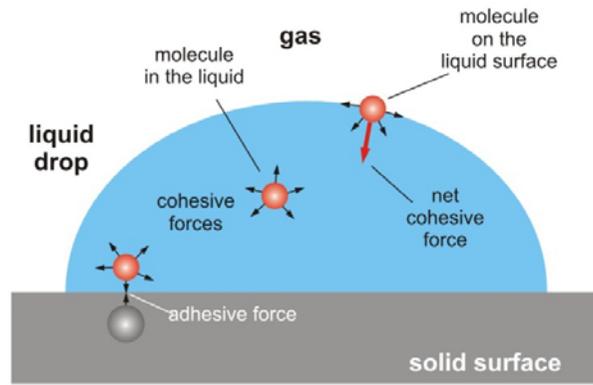
material	η (mPas)
liquid water	1 (20°C)
glycerol	60 (20°C)
methylmethacrylate monomer	0,5 (25°C)
ethylene glycol dimethacrylate monomer	3,4 (25°C)
Zn-phosphate	95 000 (25°C)
Zinc oxide eugenol dental cement	100 000 (37°C)
silicon	60 000-1 200 000 (37°C)

To move a 20 cm² glass plate in a fluid with 100 1/s velocity gradient 1 mN force is required. How large is the viscosity of the fluid?

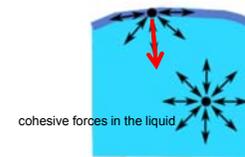
$$F = \eta * A * \frac{\Delta v}{\Delta h}$$

$$\eta = \frac{F}{A \cdot g_v} = \frac{0,001}{20 \cdot 10^{-4} \cdot 100} = 5 \cdot 10^{-3} (Pas)$$

2. Properties of fluid interfaces



2.1. Fluid-air (gas) interfaces – surface tension (surface energy)



energy ΔE is required to increase the surface by an area ΔA

$$\sigma = \frac{\Delta E}{\Delta A} \quad \left(\frac{\text{J}}{\text{m}^2} = \frac{\text{N}}{\text{m}} \right)$$

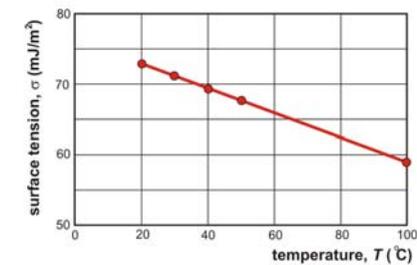
surface tension

Surface tension of materials in air

$$\sigma = \frac{\Delta E}{\Delta A} \quad \left(\frac{\text{J}}{\text{m}^2} = \frac{\text{N}}{\text{m}} \right)$$

material	σ (J/m ²)
liquid water	0,073
blood	0,06
saliva	0,05
paraffin	0,025
alcohol	0,023
dentine	0,092
enamel	0,087
Hg	0,484
PMMA	0,037

Temperature dependence of water surface tension



The spherical shape of a liquid drop is due to the surface tension

2.2. Liquid-solid interfaces

Adhesion



Interfacial energy of the boundary between two materials
the energy changes when the area of the boundary changes

interfacial energy < surface energy of the two material

↓
attraction between the two materials

↓
aggregation
adhesion

Classification of adhesion forces:

mechanical
chemical
electrostatic
dispersive
diffusive

} adhesion forces ~ area



velcro

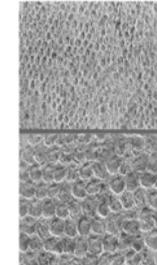
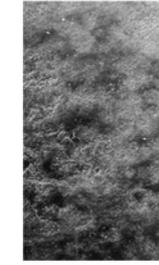
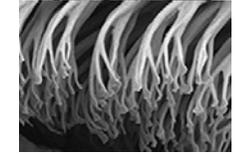


Figure 1. Morphological aspect of the surface of enamel conditioned with 30% phosphoric acid for 20s. The formation of micropores with typical pattern of conditioning can be observed. (Digital magnification: x40,000, between 1982).

chemically purified surface of enamel



wetted surface of enamel



gecko's foot

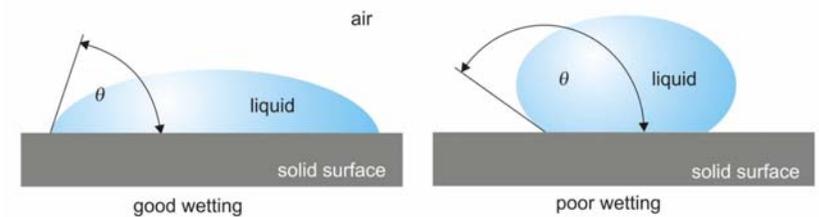
Wetting



Water drops on different materials (metal, glass, wax)

What the shape of the drop depends on?

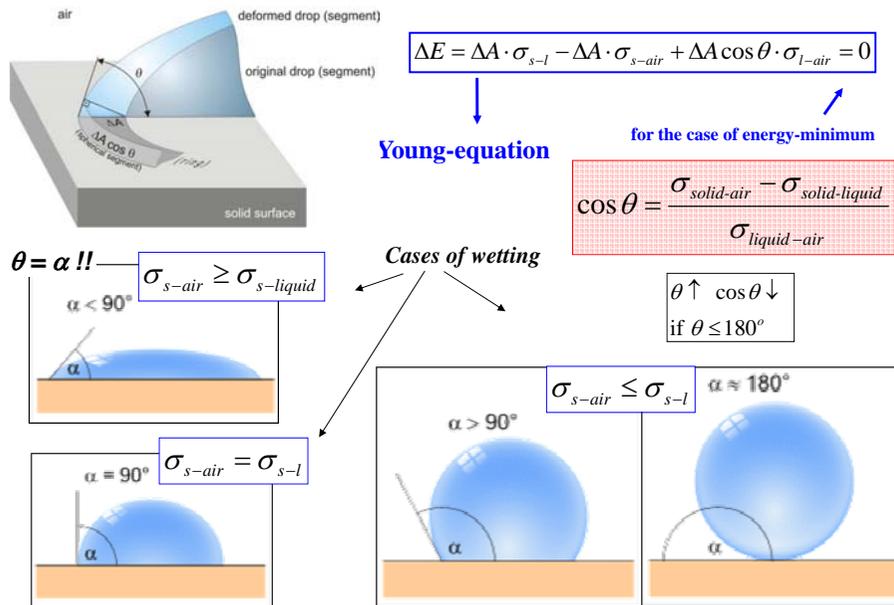
How can we characterise the shape of the drop?



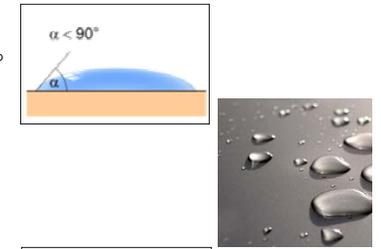
θ : Contact angle (wetting angle)

Basic issue: what is energetically more favorable?

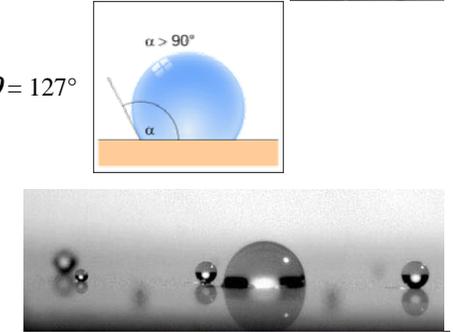
To form a solid-liquid or a solid-air interface?



e.g. liquid = water : 73 mJ/m²
 solid = glass: 130 mJ/m²
 glass - water: 60 mJ/m² } $\theta = 16,5^\circ$



e.g. Liquid = Hg: 500 mJ/m²
 solid = glass: 130 mJ/m²
 glass - Hg: 430 mJ/m² } $\theta = 127^\circ$



Contact angle of a mercury drop is 140° on glass. How large is the interfacial tension of the glass-mercury boundary? Other surface tension values: mercury-air 480 mJ/m², glass-air 90 mJ/m².

$$\cos \theta = \frac{\sigma_{solid-air} - \sigma_{solid-liquid}}{\sigma_{liquid-air}}$$

$$\sigma_{solid-air} - \sigma_{liquid-air} \cdot \cos \theta = \sigma_{solid-liquid}$$

$$90 - 480 \cdot \cos 140 = \sigma_{solid-liquid}$$

$$458 (mJ / m^2) = \sigma_{solid-liquid}$$