Physical bases of dental material science

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

The ionization energy of a single atom:

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

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 $2*10^5$ Pa.
How many moles of CO_2 gas are in the tank.
How large is the total mass and the density of the gas?

$$pV = \nu RT$$

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

$$\nu = \frac{8{,}31 \cdot 298}{2 \cdot 10^5 \cdot 0{,}02} = 0{,}62 (mol)$$

$$m = \nu \cdot M = 0{,}62 \cdot 44 = 27{,}28 (g)$$

$$\rho = \frac{m}{V} = \frac{27{,}28}{20000} = 0{,}00136 (g / cm^3)$$

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 N_2 molecules) is 28 g/mol (0.028 kg/mol). How large is the kinetic energy of one molecule?

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

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

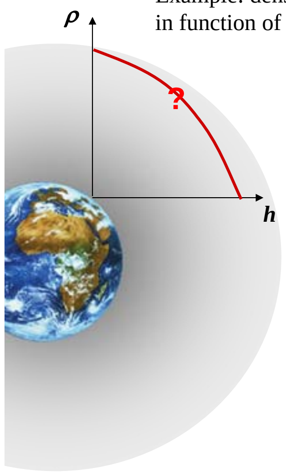
$$\overline{v} = \sqrt{\frac{3 \cdot 1{,}38 \cdot 10^{-23} \cdot 293}{0{,}028 / 6 \cdot 10^{23}}} = 509{,}8 (m/s)$$

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

Gas phase (ideal gas)

in a force field – gravitation

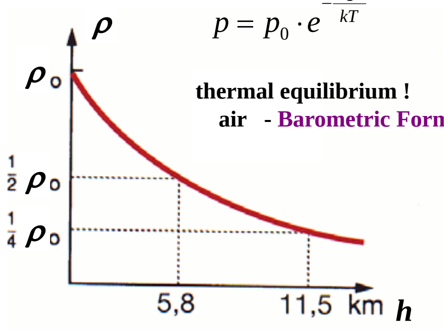
Example: density (ρ) of air ***changes*** in function of the potential energy



$$\rho = \rho_0 . e^{-\frac{mgh}{kT}}$$

$$p = const * \rho$$

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



thermal equilibrium !
air - Barometric Formula

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

n_i ———— ε_i
n_0 ———— ε_0 $\Big\}\,\Delta\varepsilon$

$$n_i = n_0 \cdot e^{-\frac{\varepsilon_i - \varepsilon_0}{kT}}$$

$$n_i = n_0 \cdot e^{-\frac{\varepsilon_i}{kT}} = n_0 \cdot e^{-\frac{\Delta\varepsilon}{kT}} = n_0 \cdot e^{-\frac{\Delta E}{RT}}$$

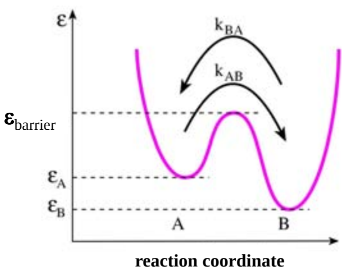
$$\Delta E = \Delta\varepsilon \cdot N_A \qquad R = k \cdot N_A$$

- **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…**

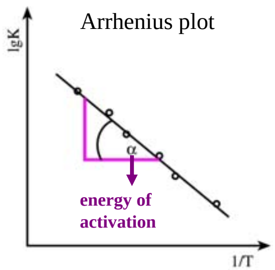
Example:



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

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

Arrhenius plot



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!

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

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

$$n = n_0 / 2$$

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

Strength of bond energy ⟺ Effect of temperature

T (~ E_{kin})

	solid	fluid	gas
volume	+	+	-
shape	+	-	-

solid: crystalline, amorphous

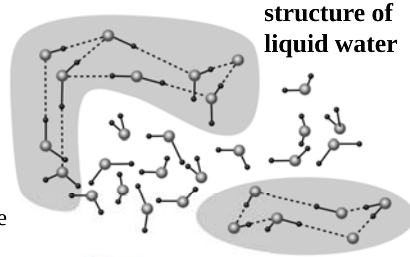
- long range order
- crystal „lattice”

- short range order

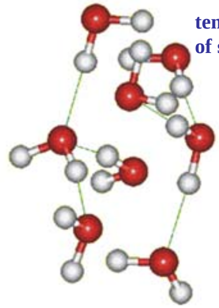
- disorder

density (ρ, kg/m^3)

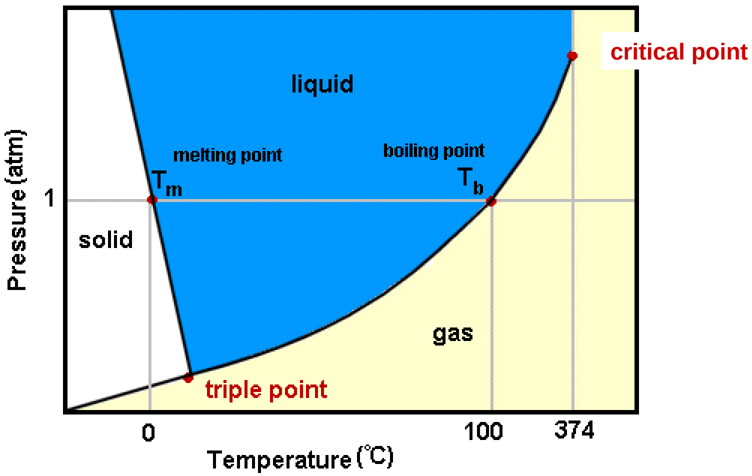
Fluids



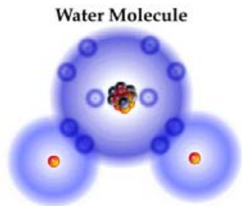
- Temporary regions of short range order within a few molecules ~10 nm domain size
- High concentration of structural defects
- No firm volume or shape - liquid
- High motional freedom of particles
- Isotropy

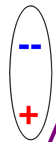


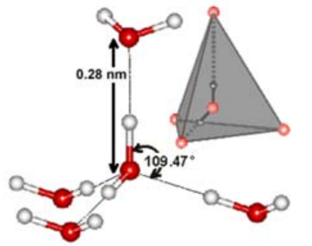
Phase diagram of water



Liquid water has outstanding properties

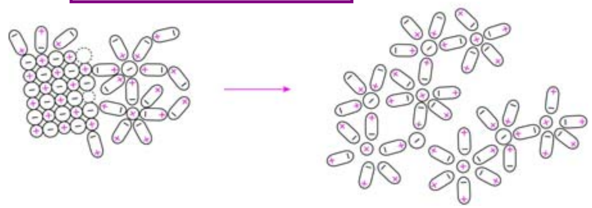






strong H-bonding

- high specific heat
- high surface tension
- efficient solvent

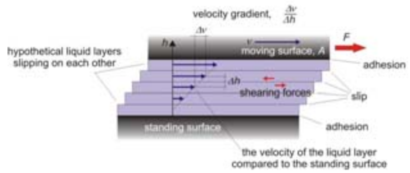


Important properties of fluids

1. Viscosity (η)

– an intrinsic mechanical property

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



laminar flow

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

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

$\frac{F}{A}$ **Shear stress**

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

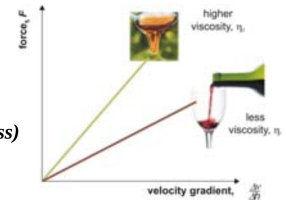
Newton's law – viscosity is a constant

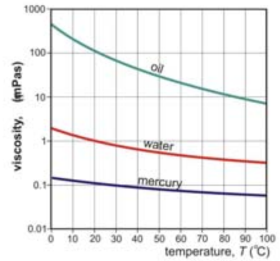
***η* depends on** - **the temperature**

- **the magnitude of F/A**

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

fluidity ~ 1/*η*

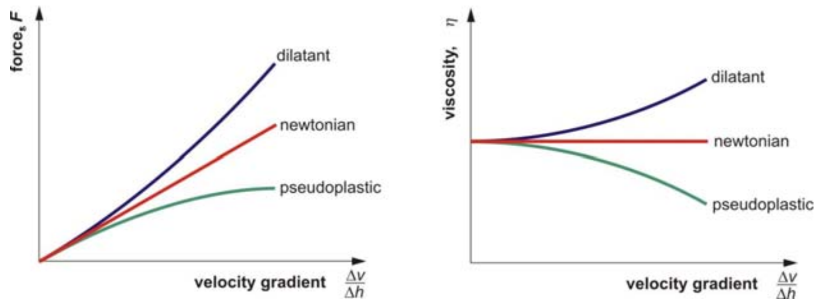




viscosity of some material as the function of temperature

exponentional 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

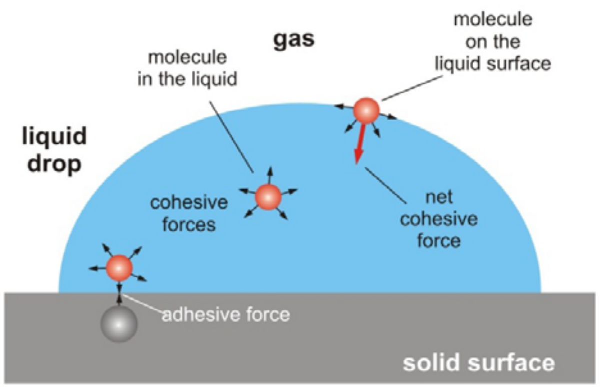
material	*η* (mPas)
liquid water	1 (20°C)
glycerol	60 (20°C)
methylmethacrylate monomer	0,5 (25°C)
ethylene glycol dimethacrylate monomer	3,4 (25°C)
Zn-phosphate	95 000 (25°C)
Zinc oxide eugenol dental cement	100 000 (37°C)
silicon	60 000-1 200 000 (37°C)

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?

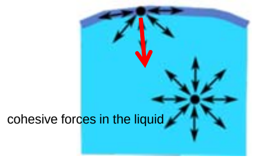
$$F = \eta * A * \frac{\Delta v}{\Delta h}$$

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

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

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

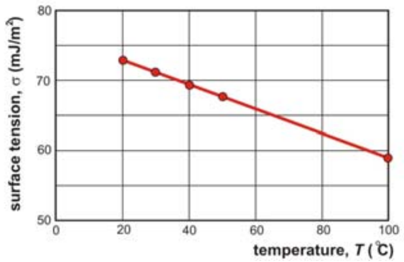
surface tension

Surface tension of materials in air

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

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

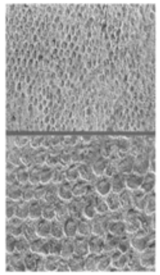
adhesion

Classification of adhesion forces:

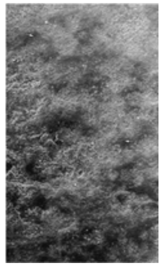
- mechanical
- chemical
- electrostatic
- dispersive
- diffusive

} **adhesion forces ~ area**

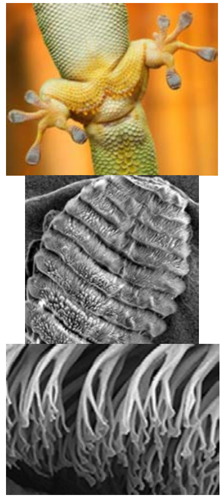
velcro



chemically purified surface of enamel



wetted surface of enamel



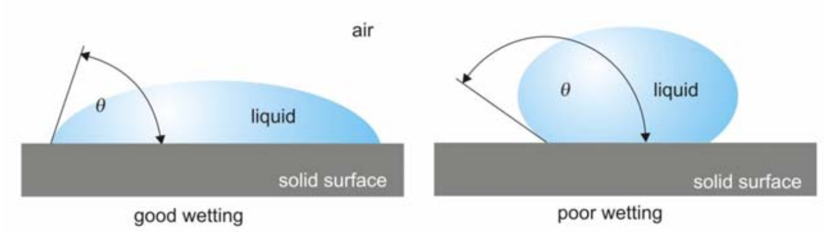
gecko’s foot

Wetting

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

What the shape of the drop depends on?

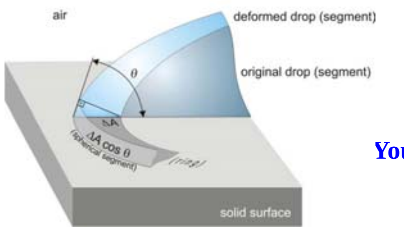
How can we characterise the shape of the drop?



θ : Contact angle (wetting angle)

Basic issue: what is energetically more favorable?

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



$$\Delta E = \Delta A \cdot \sigma_{s-l} - \Delta A \cdot \sigma_{s-air} + \Delta A \cos\theta \cdot \sigma_{l-air} = 0$$

Young-equation

for the case of energy-minimum

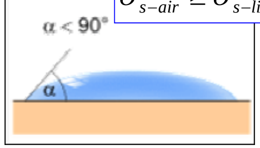
$$\cos\theta = \frac{\sigma_{solid\text{-}air} - \sigma_{solid\text{-}liquid}}{\sigma_{liquid-air}}$$

$\theta \uparrow \quad \cos\theta \downarrow$

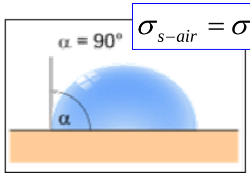
if $\theta \leq 180^o$

Cases of wetting

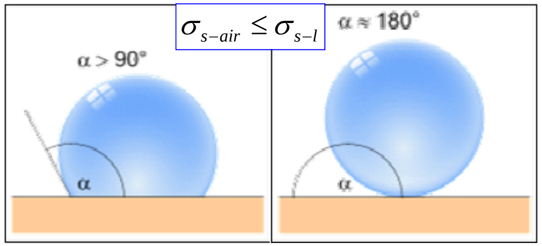
θ = α !! — $\sigma_{s-air} \geq \sigma_{s-liquid}$



$\sigma_{s-air} = \sigma_{s-l}$



$\sigma_{s-air} \leq \sigma_{s-l}$



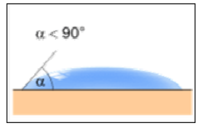
e.g.

liquid = water : 73 mJ/m^2

solid = glass: 130 mJ/m^2

glass - water: 60 mJ/m^2

θ = 16,5°



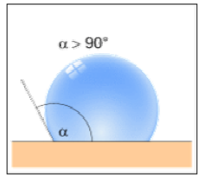
e.g.

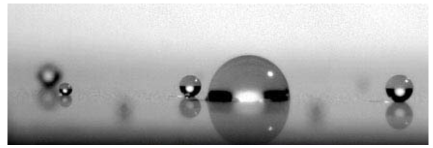
Liquid = Hg: 500 mJ/m^2

solid = glass: 130 mJ/m^2

glass – Hg: 430 mJ/m^2

θ = 127°





Contact angle of a mercury drop is 140° on glass. How much is the interfacial tension of the glass-mercury boundary? Other surface tension values: mercury–air 480 mJ/m^2, glass–air 90 mJ/m^2.

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

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

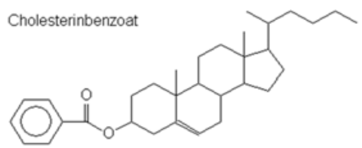
$$90 - 480 \cdot \cos 140 = \sigma_{solid-liquid}$$

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

Liquid crystals: a mesomorphous state of matter

Thermotropic - liotropic

General properties
- elongated shape of molecules
- relativly long range order stabilized by secondary bonds
- fluidity, deformability
- anisotropy in fluid state



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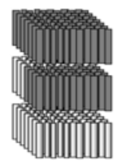

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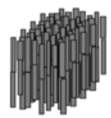

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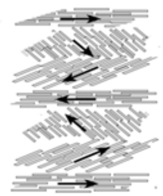
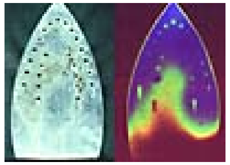
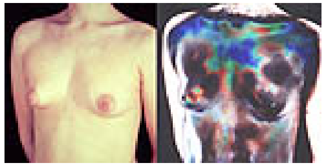


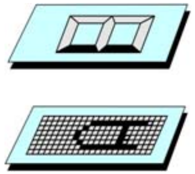
cholesteric

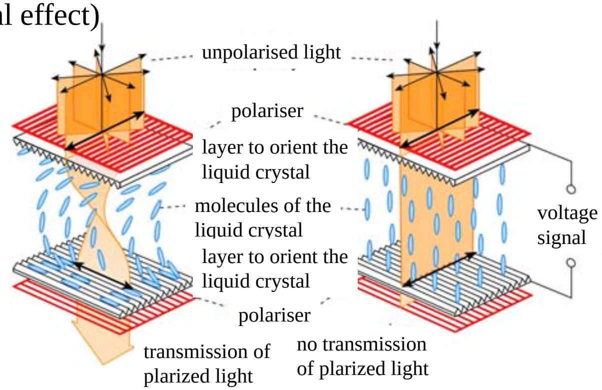
Use of thermotropic liquid crystals



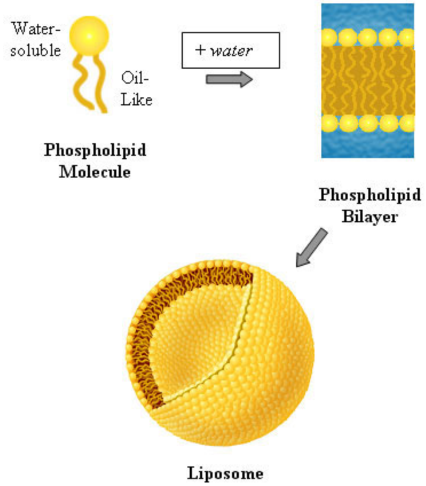


LCD (electro optical effect)





Liotropic liquid crystals



Cellular bi-layer membranes