Physical bases of dental material science

Irén Bárdos-Nagy

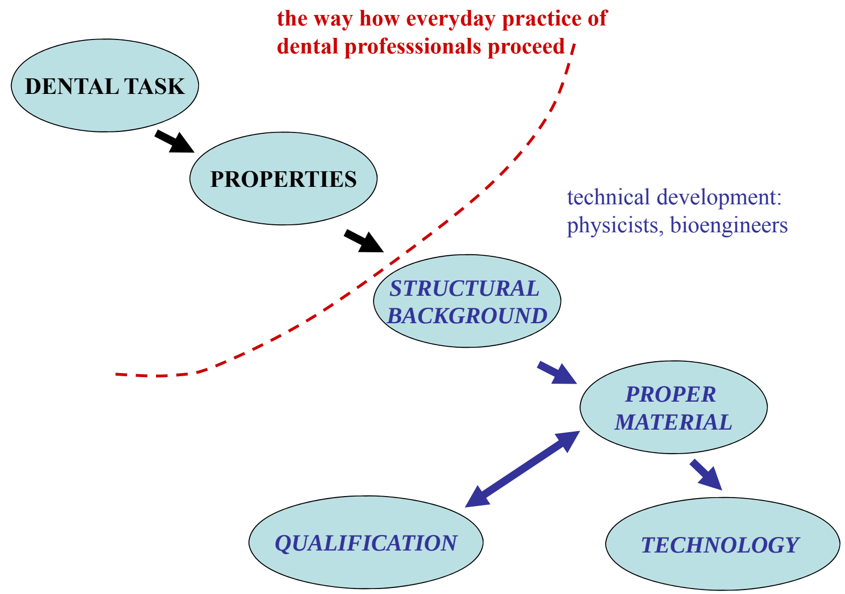
Materials Science – Dentistry

Physics ↔ Biophysics

Important informations

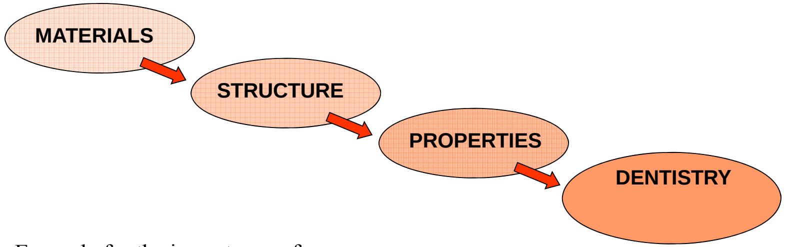
- **Tutor:** Károly Módos, PhD, Assistant Professor (karoly.modos@eok.sote.hu)
- Biofizikai és Sugárbiológiai Intézet – Department of Biophysics and Radiation Biology, EOK left, 2nd floor, Director: Prof. Miklós Kellermayer
- max 3 absencies
- http://biofiz.sote.hu
- www.tankonyvtar.hu
- W.D. Callister: *Materials Science and Engineering*. An Introduction (7th ed.), Wiley&Sons, 2007
- K.J. Anusavice: Phillips' *Science of Dental Materials* (11th ed.), Saunders, 2003
- Damjanovich, Fidy, Szöllősi: *Medical Biophysics*, Medicina, Budapest, 2009
- Exam: written test, completed by an oral exam for results higher then the passing mark

Good luck!



How to start? – How to proceed?

The way how the lectures proceed



Example for the importance of structure

All are Al_2O_3 !

Classes of materials - structural basis

The structure of atoms

Demokritos (**5th century BC**): materials are constructed of an infinite number of indivisable units, **atoms**

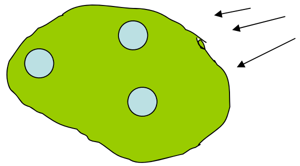
Dalton (**~ 1800**): materials are constructed of **elements** characterized by **specific atoms**

J.J.Thomson (**1897**): discovery of the **electron**
identical constituents in the specific atoms of each elements

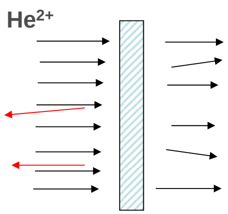
electron is a particle of
mass << lightest atom, H m_e=9.11*10^{-31} kg
~ 2x10^3-times smaller
charge: ***negative,*** q_e***= -1.6*10***$^{-19}$ ***Coulomb*** (C)

plum/raisin ~e$^-$

atom = plummy pudding
structure of the atom was not known



Ernest Rutherford (**1909-11**) : scattering of He-ions (α particles) on a thin metal foil



Only a few particles were influenced in their path, some slightly deviated, and very few got reflected/repelled

- the mass of the atoms is concentrated in very small regions
- these small regions carry positive charges
- Rutherford's model: atom is like Sun and its orbiting planets
- most part of the volume of materials is „empty"

Structure of atoms: **atomic nucleus** (small, carries the mass, positive charge)
electron, with negative charge

Results and models concerning the electronic structure of atoms

Niels Bohr (1913) ⟶ model

James Franck, Gustav L. Hertz (1914) ⟶ verification by experiment

$$(hf = h\frac{c}{\lambda}$$
$$h = 6.62 * 10^{-34}\, Js$$
$$c = 2.998 * 10^{8}\, m/s)$$

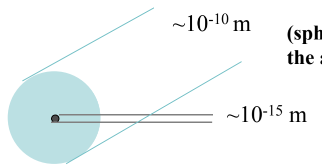
Atomic electrons are bound on atomic orbitals of discrete energies

Results of quantum physics and supposting experimental results

Albert Einstein, Max Planck, Johannes de Haas, Otto Stern, Walther Gerlach

Present understanding of the atomic structure

Dimensions of the atomic structure



(spherical model about the region where the atomic electrons are present)

„diameter" of a H-atom ~ 10^{-10}m

10^{-3}	10^{-6}	10^{-9}	10^{-12}	10^{-15}
milli-	micro-	nano-	pico-	femto-

The atoms interact with each other by their electronic „clouds"/orbitals. The physical/chemical properties of materials derive from the properties of electronic orbitals.

The atomic mass

It is based on the atomic nucleus composed of protons (p) and neutrons (n)

Proton (+)

Electric charge = (-1)* charge of the electron = $1.6 \cdot 10^{-19}$ C
Mass m_p~ $1.66 \cdot 10^{-27}$ kg, (~1840*m_e)
Number of protons in a nucleus: Z

Neutron

Electrically neutral
Mass m_n~$1.67 \cdot 10^{-27}$ kg, slightly larger than m_p
Number of neutrons in a nucleus: N

nucleons (protons and neutrons)

The atoms are electrically neutral

Number of protons = number of bound electrons = Z — **Atomic number**

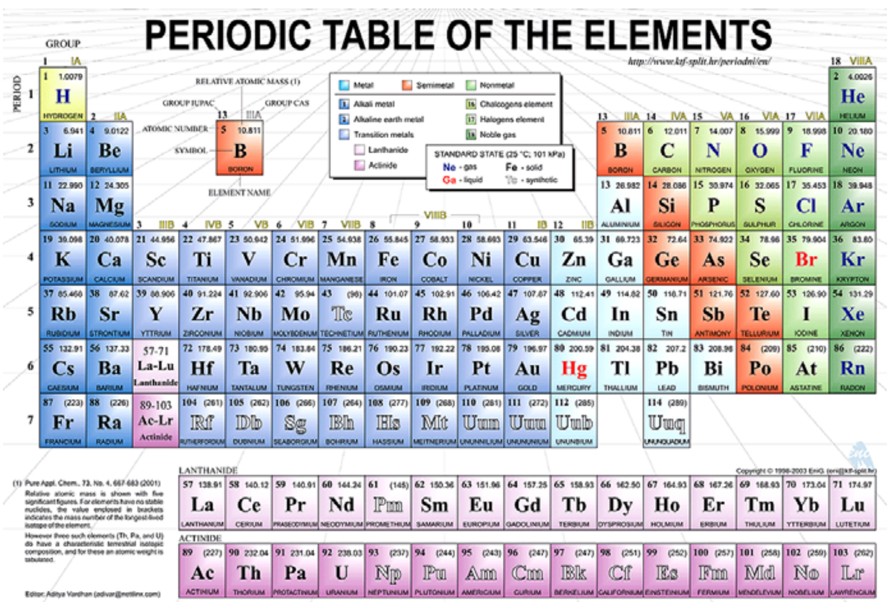
Mass number $A = N+Z$ (the total number of nucleons)

$^{A}_{Z}X$ — **Symbol of an element X „nuclide"**

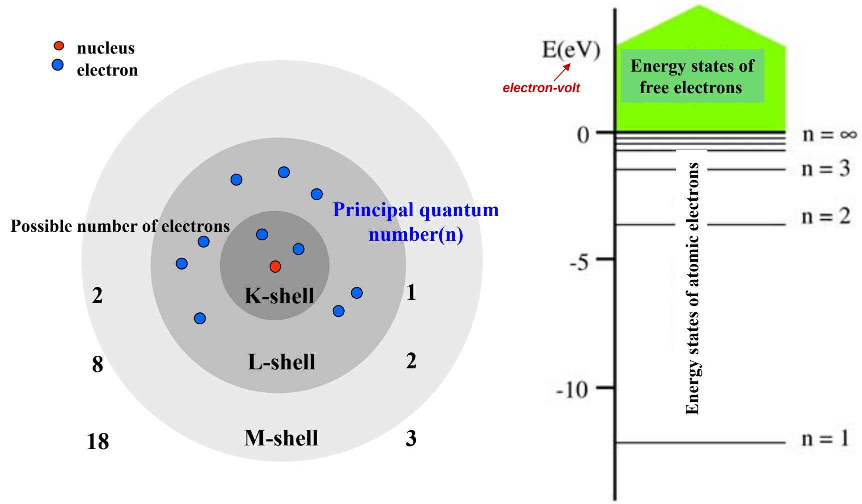
The absolute value of the atomic mass is based on the „unified atomic mass unit" (u)

u = 1.660 538 782 × 10^{-27} kg (one-twelfth of the mass of the nucleus of a ^{12}C atom)

1 u ~ m_p ~ m_n



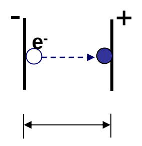
The structure and energetics of atomic electrons



Electronic energy and momenta are quantized properties in the bound state.
Quantum numbers: principal-, angular momentum-, magnetic-, spin-

Pauli's principle: the bound electrons can not have identical quantum numbers

The „electron-volt” as an energy unit



1 eV energy = the kinetic energy of one electron after it got accelerated by a voltage of 1 V

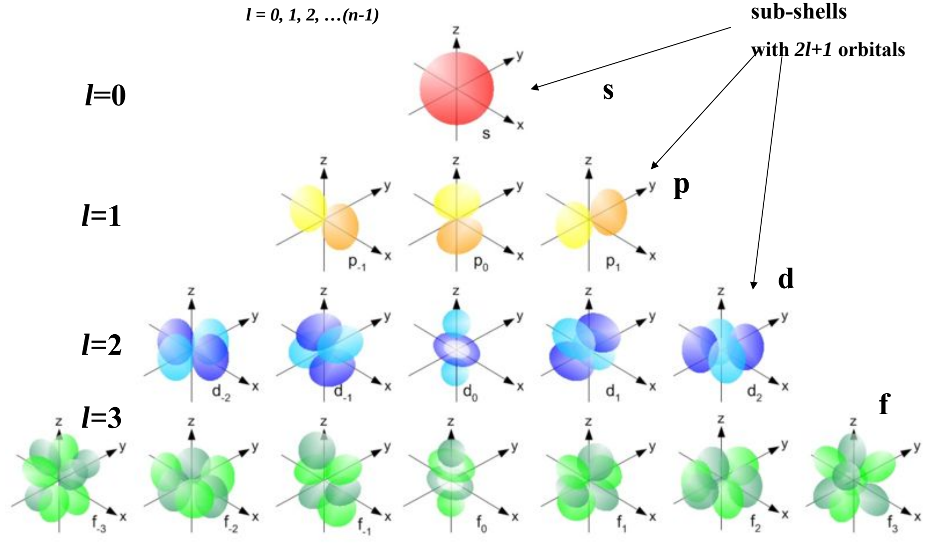
$$1eV = q * U = 1.6*10^{-19} C * 1V = 1.6*10^{-19}\ Joule$$

charge (q), voltage (U)

The electron-volt unit is widely used in the field of spectroscopy, and radiations like light and ionizing radiations (X-rays, **γ, β, α,** etc.)

Role of the orbital angular momentum quantum number (*l*)

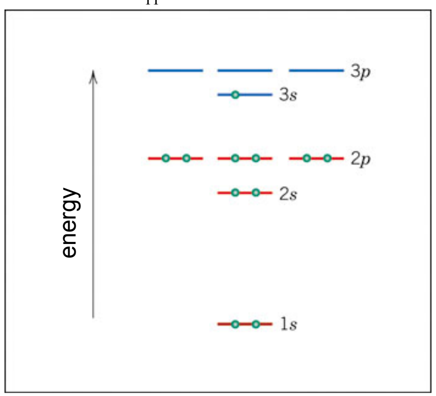
l = 0, 1, 2, …(n-1)



Examples for the population of electronic orbitals

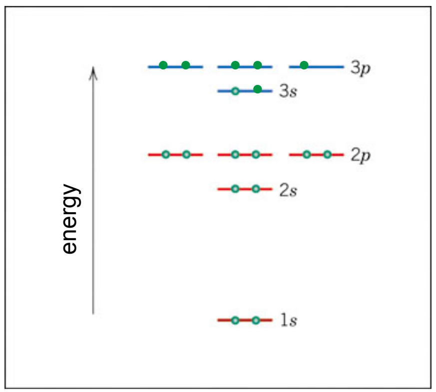
subshells may lead to a fine structure of the energy levels

$_{11}$Na atom



$1s^2 2s^2 2p^6 3s^1$

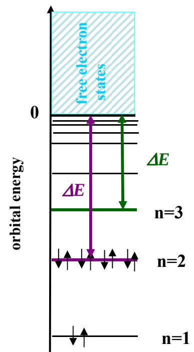
$_{17}$Cl atom



$1s^2 2s^2 2p^6 3s^2 3p^5$

Population of electronic orbitals – relation to the state of free electrons

Symplified sketch of the electronic energy levels in an atom (subshells are not shown separately)



$_{10}$Ne

$1s^2 2s^2 2p^6$

the energy states affected the most in chemical reactions, atomic bond formation, etc.

LUMO Lowest Unoccupied Molecular Orbital

HOMO Highest Occupied Molecular Orbital

ΔE ~ Ionization energy – I (eV/atom or kJ/mol)

ΔE ~ Electron affinity - E_{ea} (eV/atom or kJ/mol)

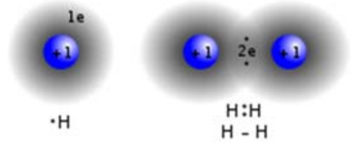
Interaction between the atoms → chemical binding

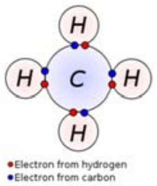
General concept of the formation of atomic bonds: minimizing the potential energy

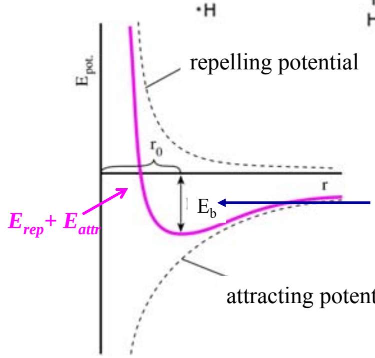
Primer (strong) chemical bonds (binding energy 100 – 500 kJ/mol few eV/bond)

(1eV/bond ~ 100 kJ/mol)

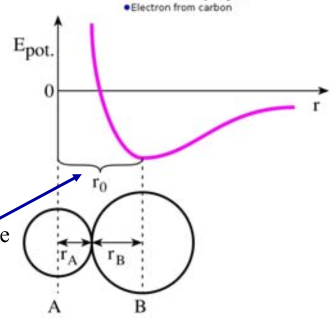
a./ **the covalent bond** formation of unified electronic orbitals





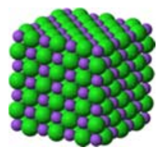


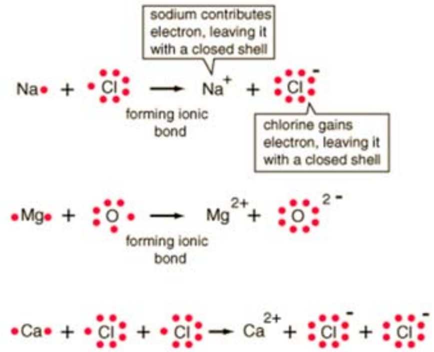
binding distance



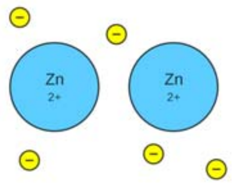
$r_0 \sim 0{,}1$ nm

b./ **the ionic bond**



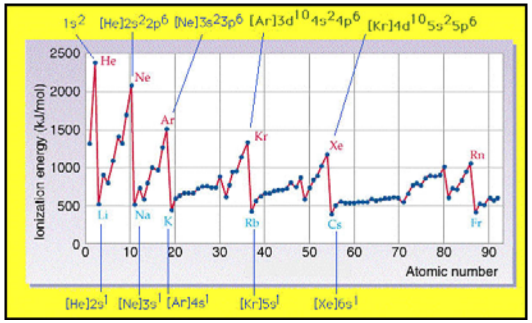


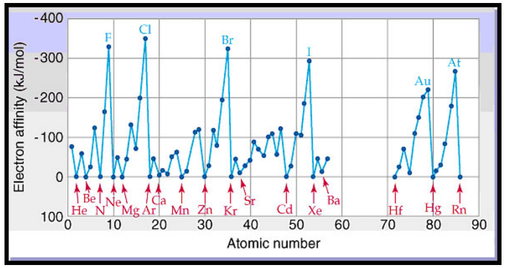
c./ **the metallic bond**



Ionization energy (I):

The minimum energy required to remove an electron bound in an atom in the gas phase (eV/atom; kJ/mol)





Electronaffinity (E_{ea}):

The energy released when an electron attaches to an atom in the gas phase (eV/atom; kJ/mol)

Exothermic electron attachment: $E_{ea}>0$
-- incoming electron interacts strongly with the nucleus on its orbital
Endothermic electron attachment: $E_{ea}<0$
-- A^- has higher energy than A and e-

Electronegativity χ

is the measure of the power of an atom of an element to attract electrons when it is part of a compound

Mulliken's absolute definition: $\chi_M = \frac{1}{2}(I + E_{ea})$

arithmetical average of the ionization energy and electron affinity

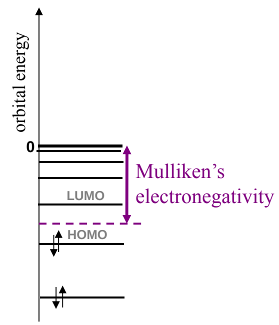
Pauling's relative scale:
characterizes the polar character of bonds

$$\Delta = E_{bond,AB}(\exp.) - E_{bond,AB}(theor., non-polar)$$

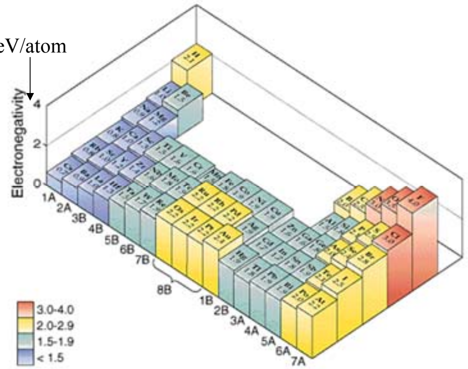
$$E_{bond,AB}^{non-polar} = \frac{E_{bond}^{A-A} + E_{bond}^{B-B}}{2}$$ ← if the bonds were purely covalent

$$0.104 * \sqrt{\Delta} = |\chi_A - \chi_B|$$

one of the electronegativities is empirically fixed – relative scale



Pauling-scale (relative):



Practical use of electronegativity
(e.g. for molecule AB)

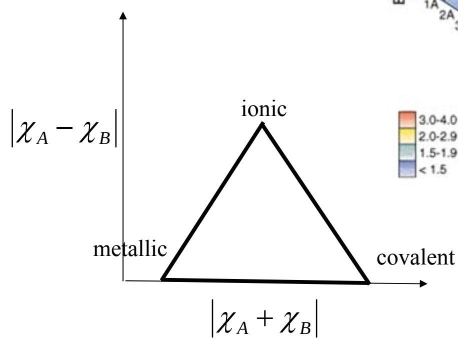
$$|\chi_A - \chi_B|$$

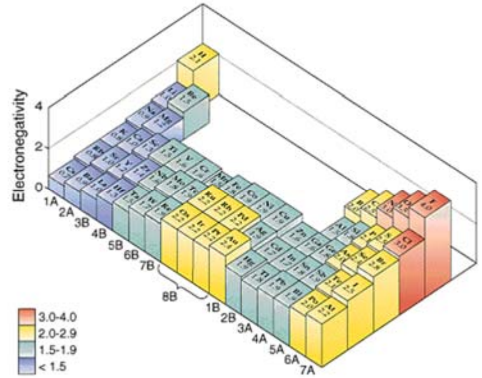
is related to the - electric dipole moment
- ionic character of the bond, given in %
- ionic-covalent resonance energy

When a molecule is formed, the electrons flow towards the atoms of high electronegativity, the electronegativities of the atoms tend to equalize and acquire the same, uniform value

$$|\chi_A + \chi_B|$$

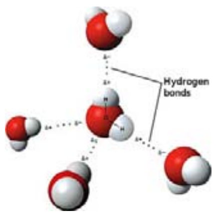
is related to the type of primary bond formed between A and B





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

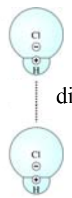
a./ **the H – bond** (~20 kJ/mol, 0.3 eV/bond) (water, HF)



b./ **electrostatic interaction**

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

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

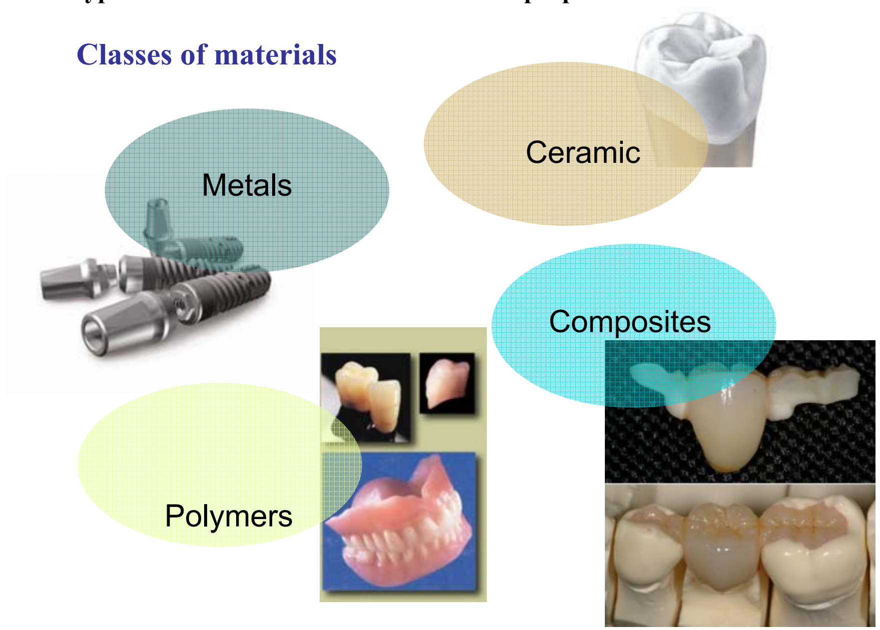


hydrophobic (~2 kJ/mol, 0,02 eV/bond)

van der Waals (dispersion) (~ 0.1 kJ/mol, 0. 001 eV/bond)
(Noble gases, F_2, H_2, Cl_2 molecules)

type of bonds → structure → properties

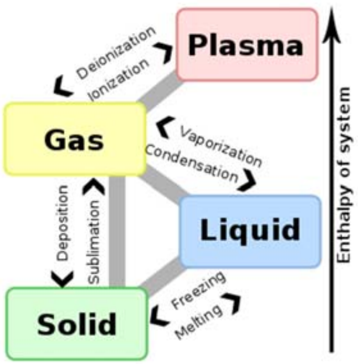
Classes of materials



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

General phase transitions

<u>phase:</u> physically and chemically homogeneuos part of the material



General properties of different phases:

gas: no definite volume and shape (there is no (or very week) 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

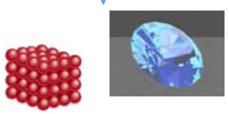
Strength of bond energy ⟺ **Effect of temperature**

T (~ E_{kin})

	solid	fluid	gas
volume	+	+	-
shape	+	-	-

solid → crystalline, amorphous

crystalline



- **long range order**
- **crystal „lattice”**

amorphous

- **short range order**

- **disorder**

density (ρ , kg/m^3)

Density of materials used in Dentistry

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

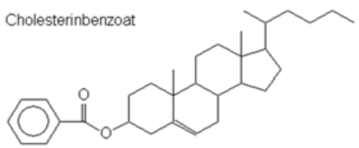
Broad scale of materials – broad scale of structures and properties

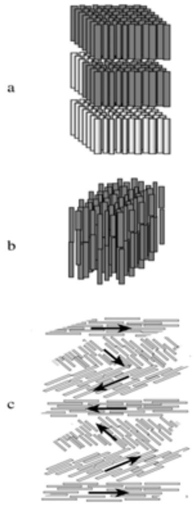
material	ρ (g/cm^3)
dental enamel	2,2
dentine	1,9
water	1
amalgam	≈ 12
gold	19,3
gold-alloys	12-17
Pd-Ag alloys	10-12
Co-Cr alloys	8-9
Ni-Cr alloys	≈ 8
glass	2,2-2,7
ceramic	1,6-3,9
porcelain	2,2-2,4
gypsum ($CaSO_4 x 2H_2O$)	2,31-2,76
PMMA poly(methylmethacrylate)	≈ 1,2
silicon poly(dimethylsiloxane)	≈ 1,4

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



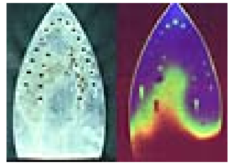


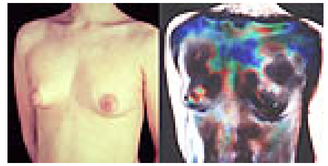
smectic

nematic

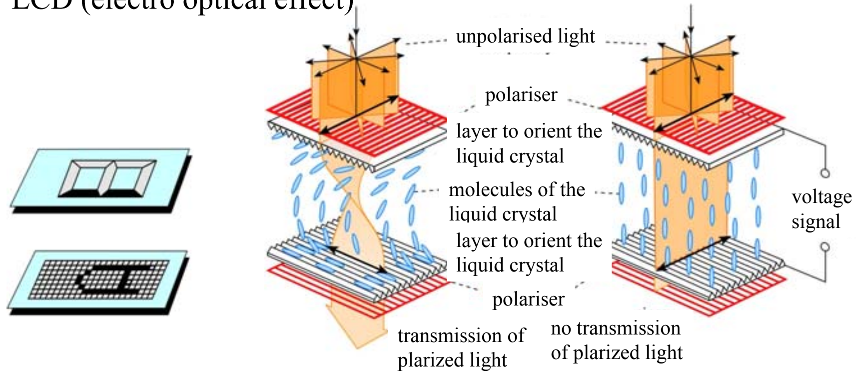
cholesteric

Use of thermotropic liquid crystals

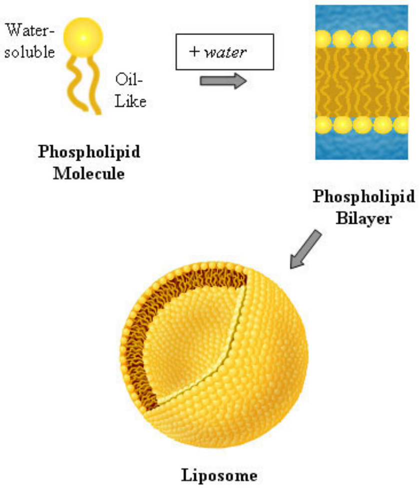




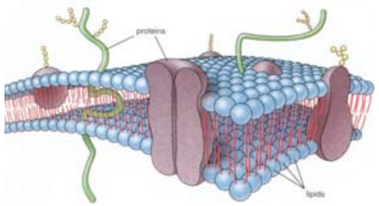
LCD (electro optical effect)

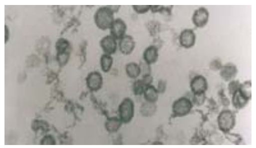


Liotropic liquid crystals



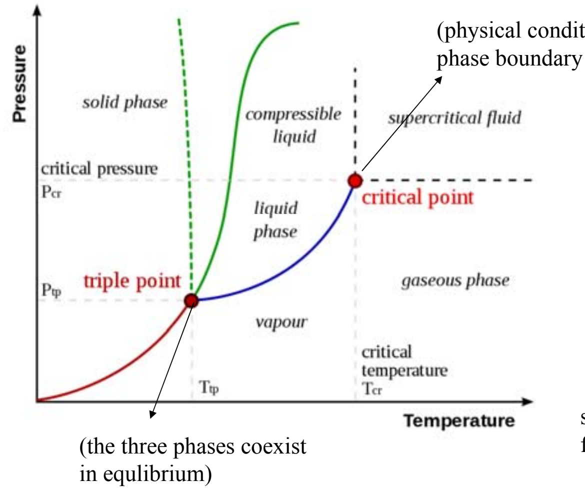
Cellular bi-layer membranes





A typical phase diagram

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



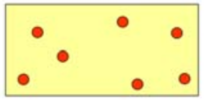
simultaneous transition of Ar from solid to liquid and to gas

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

$$pV = \nu RT$$

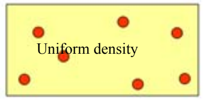
Equation of state

↑ mole number

R – universal gas constant
R= 8.314 J/mol*K

Gas phase (ideal gas)

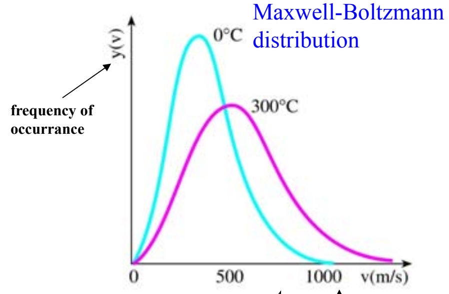
without force field



Macroscopic
properties/parameters

$$pV = \nu RT$$

Microscopic description



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

average kinetic energy

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

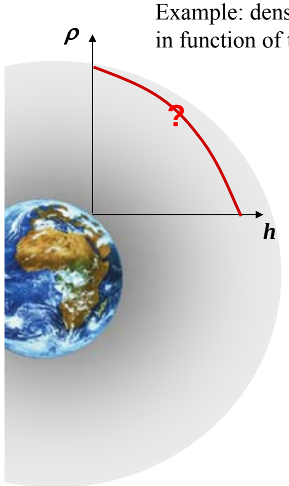
↑ Boltzmann constant

↑ **individual velocities** of O_2 molecules are distributed in a broad range

Gas phase (ideal gas)

in a force field – gravitation

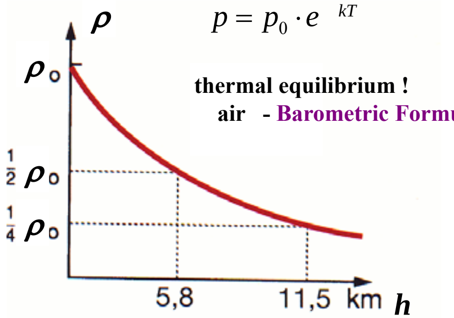
Example: density (ρ) of air ***changes*** in function of the potential energy



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

$$p = const * \rho$$

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



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 } $\Delta\varepsilon$
n_0 ———— ε_0

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

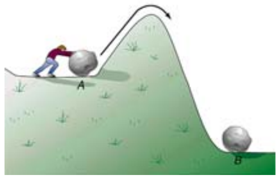
$$n_i = n_0 \cdot e^{-\frac{\varepsilon_i}{kT}} = n_0 \cdot e^{-\frac{\Delta\varepsilon}{kT}} = n_0 \cdot e^{-\frac{\Delta E}{RT}}$$

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

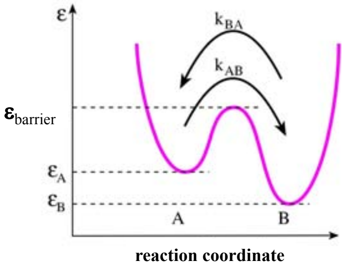
- **the number of particles is smaller at the levels of higher energy**
- **on the same level, the number is smaller at higher temperatures**
- **the lowest energy level has the highest number of population**

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:



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

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