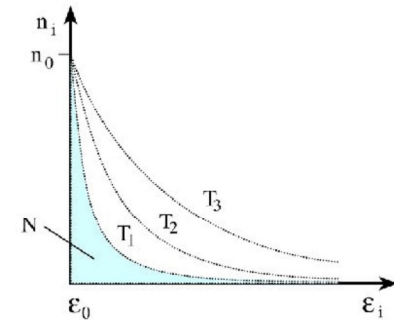# Applications of the Boltzmann distribution;

Gases, solids, liquids, liquid crystals

Miklós Kellermayer

Boltzmann's distribution is a universal organizing principle

- In a thermally equilibrated system the energy levels are populated according to an exponential distribution.
- Relative population is regulated by the ratio of the energy difference between the levels and the thermal energy.
- At higher temperatures higher energy levels are more populated.

$$\frac{n_i}{n_0} = e^{-\frac{\varepsilon_i - \varepsilon_0}{k_B T}}$$

Boltzmann-distribution applications

1. Barometric height formula

Partial oxygen pressure progressively drops with the distance from the sea level: concentration (number of molecules in unit volume, n) becomes progressively reduced

$$\frac{n_h}{n_0} = e^{-\frac{mgh}{k_B T}}$$

n_h : concentration at height h
n_0 : concentration at the reference height
mgh : potential energy

2. Thermal emission of metals

Upon thermal excitation, electrons leave the metal surface (e.g., x-ray tube, photoelectron multiplier tube)

$$\frac{N_l}{N} = e^{-\frac{W_a}{k_B T}}$$

N_l : number of emitted electrons
W_a : work fuction (work needed by the e^- to leave the atom)

Boltzmann-distribution applications

3. Nernst equation

If, between two places (A, B), the concentration of charged particles (n_A, n_B) is different, then electrical voltage (U) arises between these two places:

$$\frac{n_A}{n_B} = e^{-\frac{qU}{k_B T}} \qquad \boxed{U = \frac{k_B T}{q} \ln \frac{n_A}{n_B}}$$

q : elementary charge
U : voltage between A and B

Fundamental equation describing the behavior of concentration cells and the resting potential.
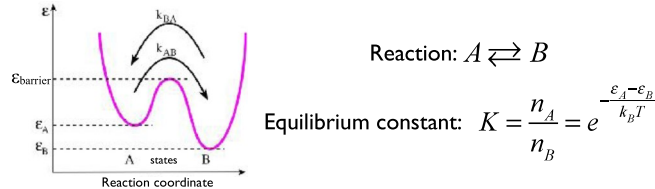
Walther Nernst (1864-1941)
Nobel-prize (1920)

Boltzmann-distribution applications

4. Reaction equilibrium, rate

The equilibrium (distribution among energy states) and rate (speed of transition between states) of a reaction are determined by relative differences between energy levels.
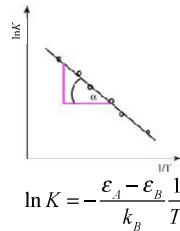

Reaction: $A \rightleftarrows B$

Equilibrium constant: $K = \dfrac{n_A}{n_B} = e^{-\frac{\varepsilon_A - \varepsilon_B}{k_B T}}$

Svante Arrhenius (1859-1927)
Nobel-prize (1903)

Rate constants:

$$k_{AB} = \omega e^{-\frac{\varepsilon_{barrier} - \varepsilon_A}{k_B T}} \qquad k_{BA} = \omega e^{-\frac{\varepsilon_{barrier} - \varepsilon_B}{k_B T}} \qquad \omega : \text{constant (s}^{-1})$$

Ratio of rate constants = equilibrium constant:

$$k_{BA}/k_{AB} = e^{-\frac{\varepsilon_{barrier} - \varepsilon_B}{k_B T} + \frac{\varepsilon_{barrier} - \varepsilon_A}{k_B T}} = e^{-\frac{\varepsilon_A - \varepsilon_B}{k_B T}} = K$$

$$\ln K = -\frac{\varepsilon_A - \varepsilon_B}{k_B} \frac{1}{T}$$

Ideal gas relationships

Average energy of a particle (equipartition theorem):
$$\frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T$$

Internal energy of a system containing N particles:
$$E_b = \frac{3}{2} N k_B T$$

Universal gas law (from the Clausius-Clapeyron, Boyle-Mariotte, Charles laws): relationship between the pressure, volume, temperature and matter content of the ideal gas (state equation).


Pressure-volume isotherms
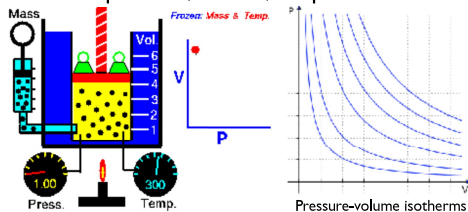
$$PV = nRT$$
$$PV = N k_B T$$

P = pressure (Pa)
V = volume (m³)
n = amount of material (mol)
R = gas constant (8.314 JK⁻¹mol⁻¹)
T = absolute temperature (K)
N = number of particles
k_B = Boltzmann's constant

Speed distribution - Maxwell distribution

Upon increasing temperature:
- the average of the absolute value of molecular speeds increases (see equipartition)
- the width of the distribution increases

speed distribution of O_2 molecules
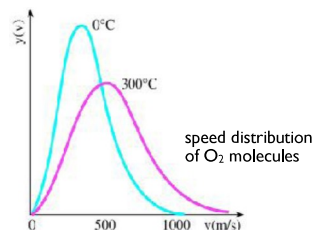
The ideal (perfect) gas

- Composed of a large number of identical particles (Avogadro number)
- Particles are spherical, their volume is negligible
- There is no interaction between the particles
- Collisions are elastic (sum of energies is constant)
- In the limiting case (point particles) collisions occur only with the wall of the container
- Particle motion follows the laws of classical (Newtonian) mechanics.
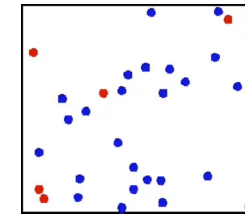
The real gas

- Particles are not point-like, their volume (b) is not negligible.
  Consequence: the volume available for motion =
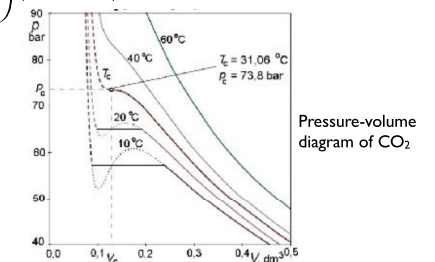 $$V - Nb$$
  N = particle number

- Interactions (a) arise between the particles.
  Consequence: pressure becomes reduced
  $$p = \frac{N k_B T}{V - Nb} - an^2$$
  n = number of particles in unit volume (N/V)

- Van der Waals state function: $\left(p + a\dfrac{N^2}{V^2} \right)(V - Nb) = N k_B T$

- Van der Waals isotherms:

Below a critical temperature (T_c), at low pressures phase transition occurs (e.g., condensation)

Pressure-volume diagram of CO_2

Phase, phase transition

- Phases: regions of the material with identical chemical, but different physical properties
- Phase diagram: plot displaying the nature of phases as a function of thermodynamic variables (pressure, temperature)
- Phase curve: two phases are in equilibrium
- Area between phase curves: a single phase is present
- Intersection of phase curves: triple point

CO_2

H_2O
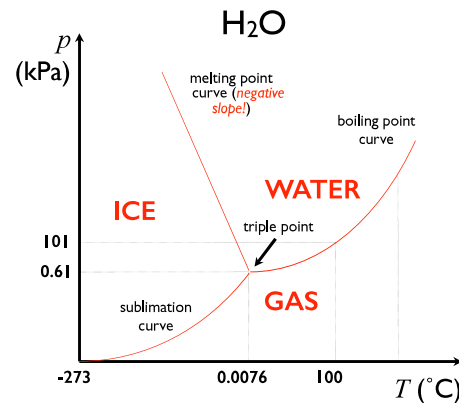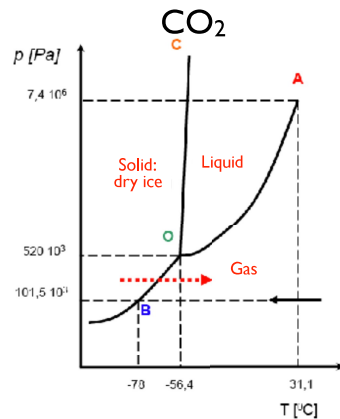


Solids

A. Crystalline materials

- Periodic long-range order
- Lattice - elementary cell (in nature 14 different, "Bravais-lattices")
- According to the nature of interactions (bonds)
  - covalent bond: atomic lattice
  - ionic bond: ionic lattice
  - metallic bond: metal lattice
  - secondary bonds: molecular lattice
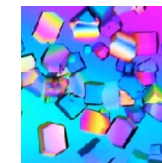
Lysozyme protein crystals in polarized light (anisotropy)
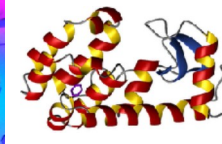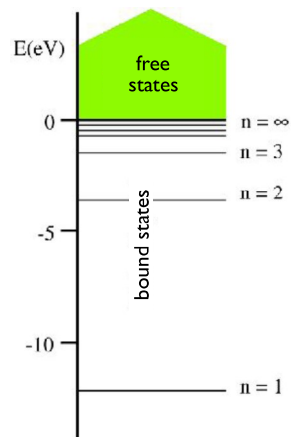
Lysozyme protein molecule
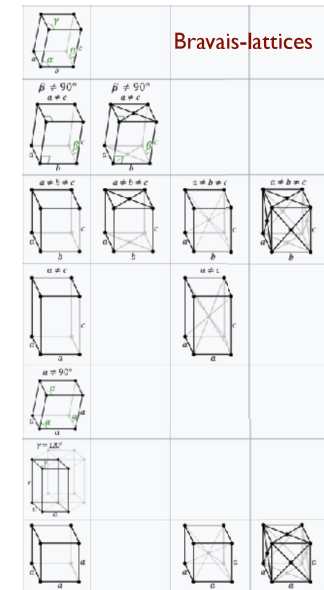
B. Amorphous materials

glass-like, viscous "fluids"

Bravais-lattices

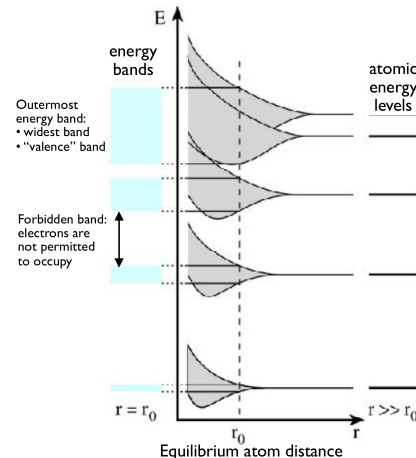# Energy levels in crystals (*vs* an atom)

Isolated hydrogen atom

- No interaction with other atoms
- Discrete (quantized) energy levels
- Pauli's principle
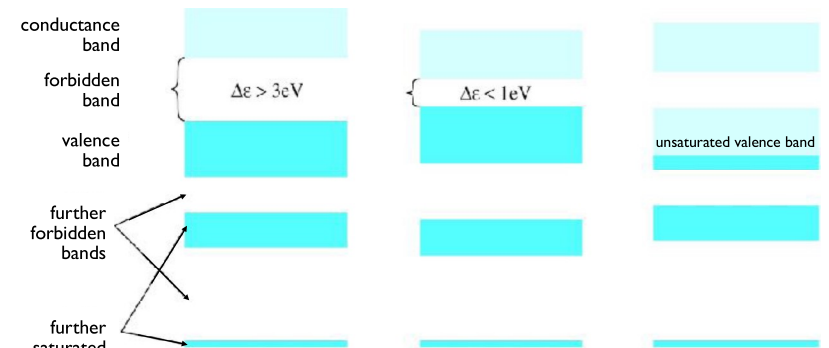

Crystal

- Atoms interact
- Pauli's principle: electron energy levels of interacting atoms split
- Nearby levels merge into energy bands

Equilibrium atom distance

Solids with different band structure

The probability of electrons entering the conductance band from the valence band is determined by the width of the forbidden band ("band gap", $\Delta\varepsilon$) relative to thermal energy ($k_B T$), based on the Boltzmann distribution:

$$\frac{n_{conduct}}{n_{valence}} = e^{-\frac{\Delta\varepsilon}{k_B T}}$$

@T=300 K, $k_B T \sim 0.023$ eV

conductance band
forbidden band
valence band
further forbidden bands
further saturated bands

$\Delta\varepsilon > 3eV$

$\Delta\varepsilon < 1eV$

unsaturated valence band

Insulator
- No electrical conduction
- Energy of visible photons insufficient to transfer electrons across band gap; hence, optically transparent (e.g., diamond)

Semiconductor
- Band gap may be crossed by thermal activation
- Electron-hole pair forms
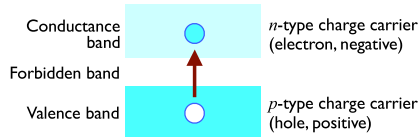- Visible photons are absorbed: not transparent

Conductor
- No forbidden band: good electrical conductor
- Not transparent
- Conductance: $\sigma \approx \dfrac{1}{T}$

Semiconductors

A. Pure semiconductors

- Forbidden band ($\Delta\varepsilon$) may be crossed by thermal activation
- Width of forbidden band <1 eV
- Two types of charge carriers (n, p):

Conductance band — n-type charge carrier (electron, negative)

Forbidden band

Valence band — p-type charge carrier (hole, positive)

- Electrical conductance is temperature-dependent:

$$\sigma = const \cdot e^{-\frac{\Delta\varepsilon}{2k_BT}}$$

- Crossing of forbidden band may be evoked by the absorption of visible light (1.5-3 eV):
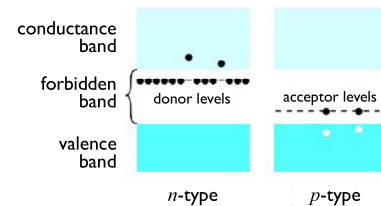
$$hf_{vis} > \Delta\varepsilon$$

- Optically not transparent

B. Doped semiconductors

- Dopant: small number of foreign atoms in between the host atoms of the lattice:

$$\frac{N_{host}}{N_{dopant}} \approx 10^6$$

- 5-valence dopant (P, As, Bi) in a 4-valence host (Si, Ge): e-donor, n-type conductor
- 3-valence dopant (Al, Ga, In) in a 4-valence host (Si, Ge): e-acceptor, p-type conductor
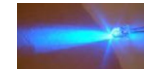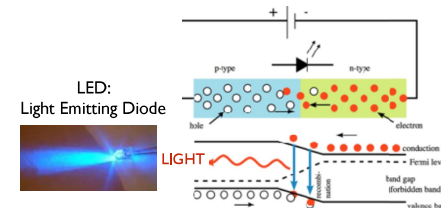
conductance band

forbidden band { donor levels   acceptor levels

valence band

n-type p-type

Semiconductor diode and transistor

Microelectronic devices constructed by adjoining doped, p- and n-type semiconductors

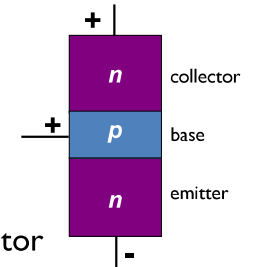+ | p | n | -

Diode

- asymmetric conductance
- electrical voltage → light emission, LED
- illumination → voltage → CCD pixel

LED: Light Emitting Diode

LIGHT

Isamu Akasaki, Shuji Nakamura, Hiroshi Amano, Nobel-prize 2014

n collector
p base
n emitter

Transistor

- amplifier
- elements of digital memory
- counters, multivibrators
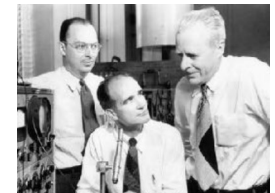
John Bardeen, William Shockley, Walter Brattain, Nobel-prize 1956

Liquids

- One of the four states of matter (besides solids, gases and plasma)
- Incompressible: retains nearly constant volume independent of pressure.
- Density similar to that of the solid ("consensed matter").
- Flows: displays fluid behavior (as gases and plasma); conforms to the shape of the container; internal friction ("viscosity", η) decreases with temperature:

$$\eta \sim e^{E/k_BT}$$

Viscosity decreases with increase in the relative concentration of vacancies.

Monoatomic liquid

cohesive forces at the surface
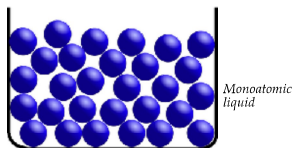
cohesive forces in the bulk
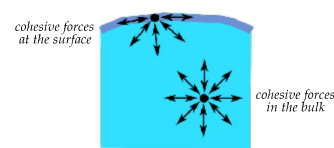
- Microscopically: composed of particles (atoms, molecules) held together by short-range cohesive forces (no long-range order)
- Imbalance of cohesive forces (between bulk *versus* surface) results in surface tension (tendency to contract into spherical shape)
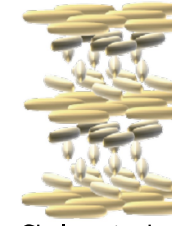
Liquid crystals

- Display both liquidlike and solidlike behavior: flow (weak intermolecular interactions), long-range order.
- Molecules are not spherically symmetric: calamitic (rod-like), discotic (disc-like)
- Order type: translational, rotational
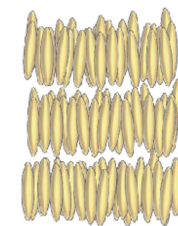
Smectic phase (orientational and translational order)
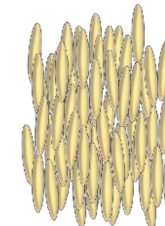
Nematic phase (only orientational order, but no translational order)

Cholesteric phase (nematic order in different planes; special case: twisted nematic phase - pitch affects color)

Discotic phase (disc-shaped molecules, translational order)

Liquid crystals

Thermotropic
(order depends on temperature)

- Color changes with temperature (thermo-optical properties); application: contact thermography

- If molecules are electrical dipoles, polarization, transmittance changes with electrical field (electro-optical properties); application: LCD displays, etc.

Contact thermography

LCD display

Lyotropic
(order depends on concentration)

Amphiphilic molecule (phospholipid)

Hydrophilic head

Hydrophobic tails

Bilayer sheet

Liposome

Micelle

Cochleate

Calcium

PS Bilayer

Drug

Phosphatidylserine (PS)

50-500 nm