

BOLTZMANN-DISTRIBUTION APPLICATIONS; GASES, SOLIDS

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Boltzmann-distribution applications

- 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**.

$$\frac{n_i}{n_0} = e^{-\frac{\epsilon_i - \epsilon_0}{k_B T}}$$

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)

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

N_I : number of emitted electrons
 W_a : work function (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:

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

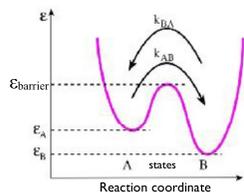
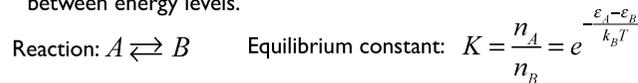
q : elementary charge
 U : voltage between A and B



Walther Nernst (1864-1941)
Nobel-prize (1920)

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.



Rate constants:

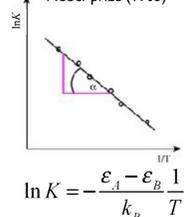
$$k_{AB} = \omega e^{-\frac{\epsilon_{barrier} - \epsilon_A}{k_B T}} \quad k_{BA} = \omega e^{-\frac{\epsilon_{barrier} - \epsilon_B}{k_B T}} \quad \omega : \text{constant (s}^{-1}\text{)}$$

Ratio of rate constants = equilibrium constant:

$$k_{BA} / k_{AB} = e^{-\frac{\epsilon_{barrier} - \epsilon_B}{k_B T} + \frac{\epsilon_{barrier} - \epsilon_A}{k_B T}} = e^{-\frac{\epsilon_A - \epsilon_B}{k_B T}} = K$$

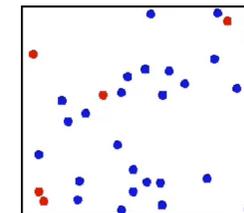


Svante Arrhenius (1859-1927)
Nobel-prize (1903)



The ideal (perfect) gas

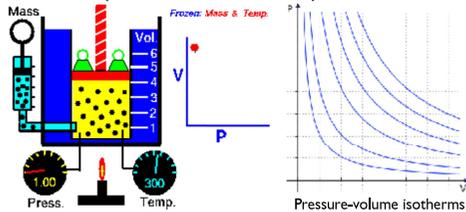
- Composed of a **large** number of identical particles (Avogadro number)
- Particles are **spherical**, their volume is **negligible**
- There is **no interaction** between the particles
- Collisions are **elastic** (sum of energies is constant)
- In the limiting case (point particles) collisions occur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



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).



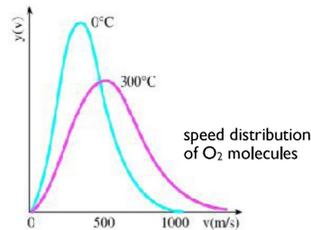
$$PV = nRT$$

$$PV = Nk_B T$$

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

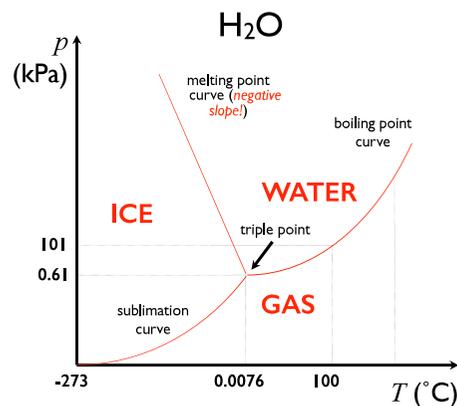
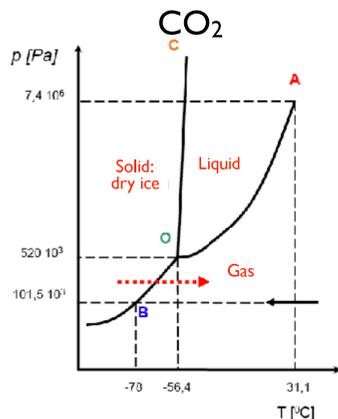
Speed distribution - Maxwell distribution

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



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



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

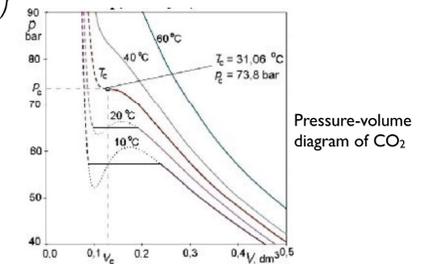
$$p = \frac{Nk_B T}{V - Nb} - an^2$$

n = number of particles in unit volume (N/V)

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

- Van der Waals isotherms:

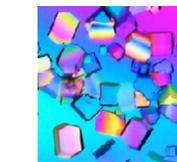
Below a critical temperature (T_c), at low pressures phase transition occurs (e.g., condensation)



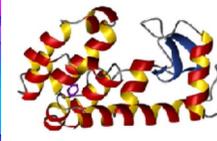
Solids

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

		Bravais-lattices	
$\beta \neq 90^\circ$ $a \neq c$	$\beta \neq 90^\circ$ $a \neq c$		
$a \neq b \neq c$	$a \neq b \neq c$	$a \neq b \neq c$	$a \neq b \neq c$
$a \neq c$	$a \neq c$	$a \neq c$	$a \neq c$
$a \neq 90^\circ$	$a \neq 90^\circ$		
$\gamma \neq 120^\circ$	$\gamma \neq 120^\circ$		

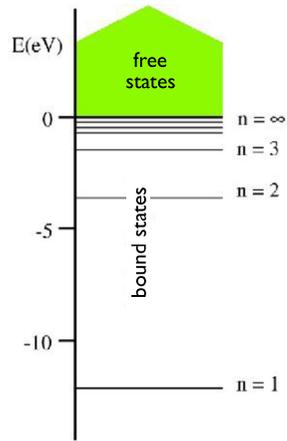
B. Amorphous materials

glass-like, viscous "fluids"

Energy levels in crystals

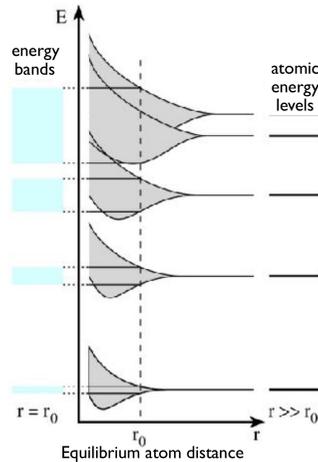
Isolated hydrogen atom

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



Crystal

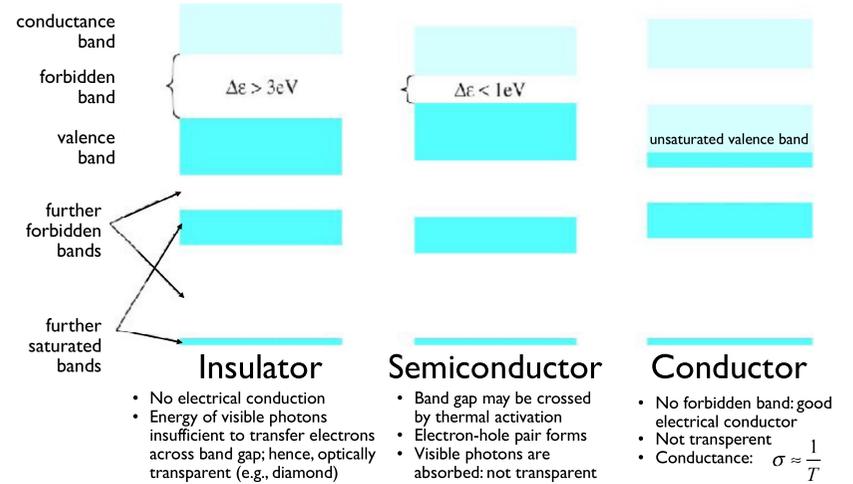
- Atoms interact
- Pauli's principle: electron energy levels of interacting atoms split
- Nearby levels merge into **energy bands**



Solids with different band structure

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

$$\frac{n_{conduction}}{n_{valence}} = e^{-\frac{\Delta\epsilon}{k_B T}} \quad @T=300 \text{ K}, k_B T \sim 0.023 \text{ eV}$$

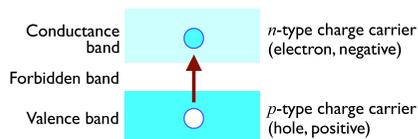


- Insulator**
 - No electrical conduction
 - Energy of visible photons insufficient to transfer electrons across band gap; hence, optically transparent (e.g., diamond)
- Semiconductor**
 - Band gap may be crossed by thermal activation
 - Electron-hole pair forms
 - Visible photons are absorbed: not transparent
- Conductor**
 - No forbidden band: good electrical conductor
 - Not transparent
 - Conductance: $\sigma \approx \frac{1}{T}$

Semiconductors

A. Pure semiconductors

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



- Electrical conductance is temperature-dependent:

$$\sigma = const \cdot e^{-\frac{\Delta\epsilon}{2k_B T}}$$

- Crossing of forbidden band may be evoked by the absorption of visible light (1.5-3 eV):

$$hf_{vis} > \Delta\epsilon$$

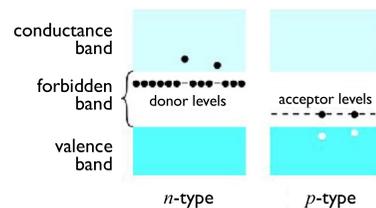
- Optically not transparent

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



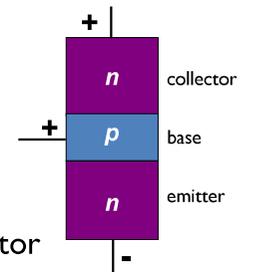
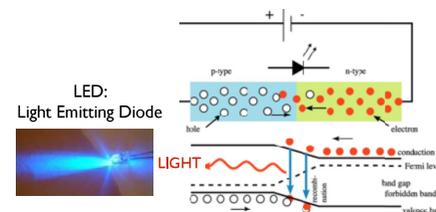
Semiconductor diode and transistor

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



Diode

- asymmetric conduction
- electrical voltage \rightarrow light emission, LED
- illumination \rightarrow voltage \rightarrow CCD pixel



Transistor

- amplifier
- elements of digital memory
- counters, multivibrators



John Bardeen, William Shockley, Walter Brattain, Nobel-prize 1956



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