GASES, SOLIDS, LIQUIDS AND LIQUID CRYSTALS

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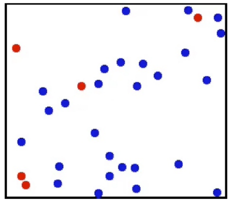
The ideal (perfect) gas

- 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.

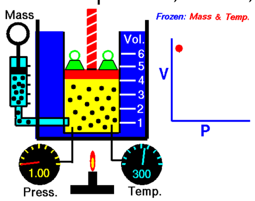


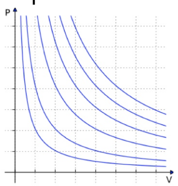
Ideal gas relationships

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

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

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).





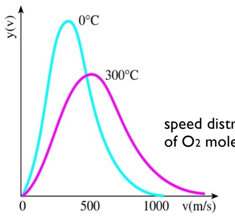
Pressure-volume isotherms

$$PV = nRT$$
$$PV = Nk_BT$$

P = pressure (Pa)
V = volume (m^3)
n = amount of material (mol)
R = gas constant (8.314 JK^{-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



speed distribution of O_2 molecules

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

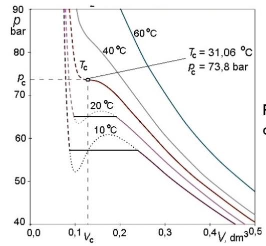
$$p = \frac{Nk_BT}{V - Nb} - an^2$$

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

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

- Van der Waals isotherms:

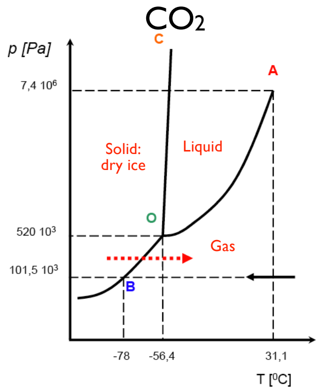
Below a critical temperature (T_c), at low pressures phase transition occurs (e.g., condensation)

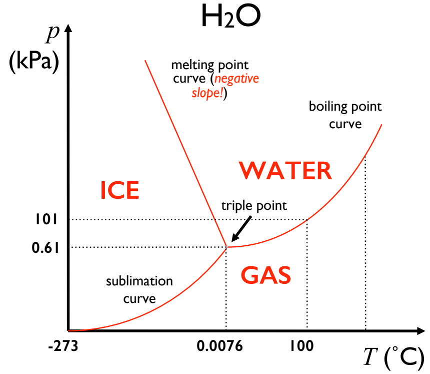


Pressure-volume diagram of CO_2

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

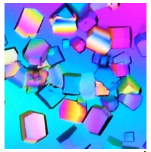




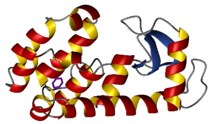
Solids

A. Crystalline materials

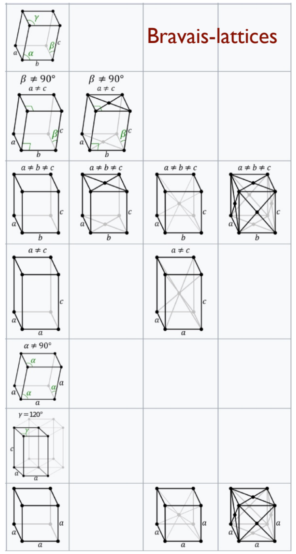
- Periodic long-range order
- Lattice - elementary cell (in nature 14 different, "Bravais-lattices")
- According to the nature of interactions (bonds)
  - -covalent bond: atomic lattice
  - -ionic bond: ionic lattice
  - -metallic bond: metal lattice
  - -secondary bonds: molecular lattice



Lysozyme protein crystals in polarized light (anisotropy)



Lysozyme protein molecule



B. Amorphous materials

glass-like, viscous "fluids"

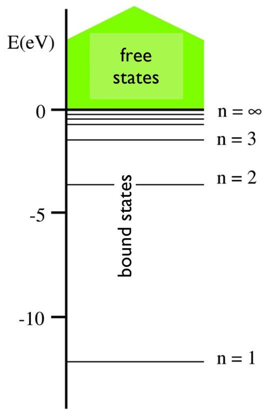
Amorphous materials

University of Queensland pitch drop experiment: 9 drops since 1927

Energy levels in crystals

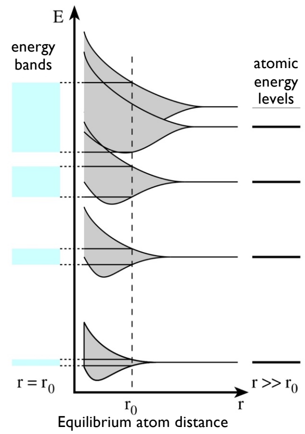
Isolated hydrogen atom

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



Crystal

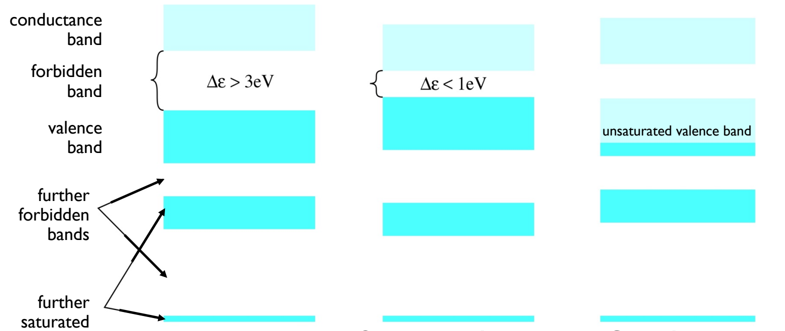
- Atoms interact
- Pauli's principle: electron energy levels of interacting atoms split
- Nearby levels merge into energy bands



Solids with different band structure

The probability od 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_BT), based on the Boltzmann distribution:

$$\frac{n_{conduct}}{n_{valence}} = e^{-\frac{\Delta\varepsilon}{k_B T}} \qquad \text{@T=300 K, } k_BT\text{~0.023 eV}$$



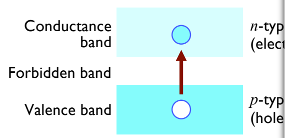
Insulator
- No electrical conduction
- Energy of visible photons insufficient to transfer electrons across band gap; hence, optically transparent (e.g., diamond)

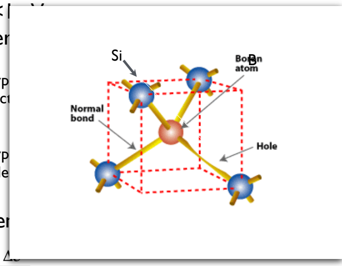
Semiconductor
- Band gap may be crossed by thermal activation
- Electron-hole pair forms
- Visible photons are absorbed: not transparent

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

Semiconductors

A. Pure semiconductors
- Forbidden band ($\Delta\varepsilon$) may be crossed by thermal activation
- Width of forbidden band <
- Two types of charge carrier





- Electrical conductance is te 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):

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

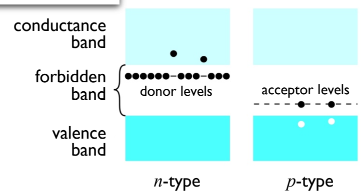
- Optically not transparent

B. Doped semiconductors
- Dopant: small number of foreign atoms in between the host atoms of the lattice:

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

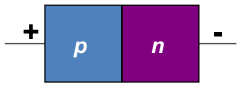
dopant (P, As, Bi) in a 4- st (Si, Ge): e-donor, n-type

dopant (Al, Ga, In, B) in a 4- st (Si, Ge): e-acceptor, p-type



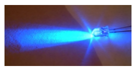
Semiconductor diode and transistor

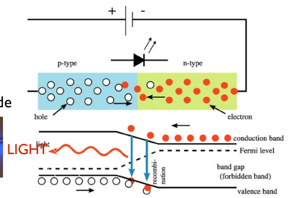
Microelectronic devices constructed by adjoining doped, p- and n-type semiconductors



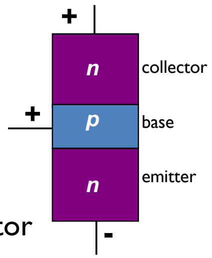
Diode
- asymmetric conductance
- electrical voltage → light emission, LED
- illumination → voltage → CCD pixel

LED: Light Emitting Diode





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



Transistor
- amplifier
- elements of digital memory
- counters, multivibrators

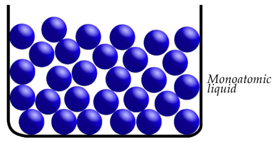
John Bardeen, William Shockley, Walter Brattain, Nobel-prize 1956

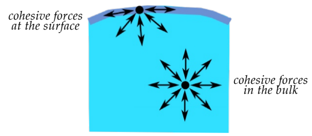
Liquids

- 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.

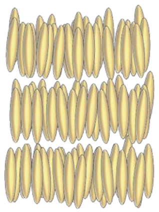




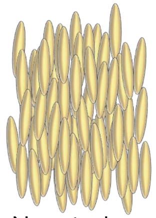
- Microscopically: composed of particles (atoms, molecules) held together by short-range cohesive forces (no long-range order)
- Imbalance of cohesive forces (between bulk *versus* surface) results in surface tension (tendency to contract into spherical shape)

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

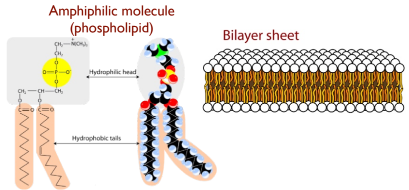
Thermotropic
(order depends on temperature)

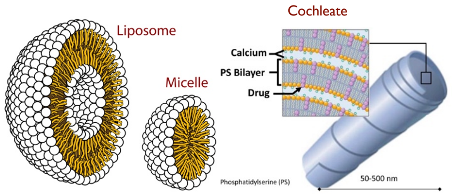
- Color changes with temperature
  (thermo-optical properties);
  application: contact thermography
- If molecules are electrical dipoles,
  polarization, transmittance changes with
  electrical field (electro-optical
  properties);
  application: LCD displays, etc.

Contact thermography

LCD display

Lyotropic
(order depends on concentration)





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