First part

Practical application of liquid crystalline materials:
electro-optical phenomena
Gaseous state of matter.

Phase transitions.

Examples for the variety of consequences
of the Boltzmann distribution

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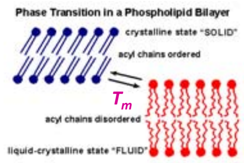
Biological –medical aspects

Lipid membranes: ***combination of liotropic and thermotropic properties***

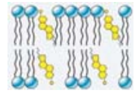
$T<T_m$



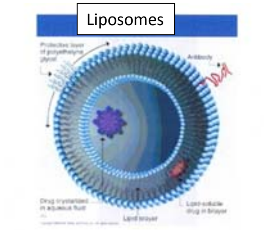
$T>T_m$

Crystalline/solid/ordered state below Tm
biologically non-functional
e.g. ends of nerve cells in frozen limbs- numbness
Liq.Cryst. state above Tm – capable of biological functioning

Role of cholesterol
-T> T_m rigidity
-T<T_m flexibility



Artificial membranes – liposomes – tools in therapy



Targeting of medications

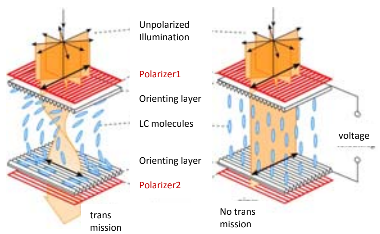
Practical aspects

Electro-optical properties: electric field→structural order change in liq.crys.s of polar or polarizable molecules → optical properties change

light transmission change → liq.crys. displays based on reflection

LCD monitors: pixels operate in transmission mode
based on ***polarization effects regulated by electric field***

Few μm thick cholesteric layer of polarizable molecules



p. 467

2. Gasous systems
2.1. Ideal gas

Thermodynamics:
kinetic gas theory

$$E_{total} = N\frac{1}{2}m(v^2)_{average} \qquad \varepsilon_i = \tfrac{1}{2}mv_i^2$$

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

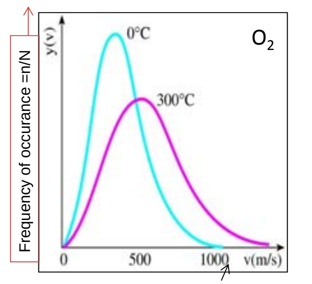
Only translational motion

$$pV = NkT = nRT$$

Derived from elastic collision with the wall of complete rigidity
(n is the number of moles)

Characteristics:
- composed of uniform, point-like particles
- **no interaction energy – no bond formation – no „structure"**
- **isotropy**
- deformability
- fills the volume of the container
- only kinetic energy

Boltzmann distribution applied for the kinetic energy → **Maxwell – Boltzmann distribution function**



The average kinetic energy (and the total internal energy) is fully determined by the temperature, and also the population of the individual velocities.

2.2. Real gas

Corrections: - the ***volume*** of the particles (b) is not negligible

- the ***pressure*** is decreased due to the non negligible attractive interaction between the particles

Maintained: the kinetic energy is related to the temperature

Internal energy ***E*** → $E_{total} = E_{kin} + E_{interaction}$

Volume V → V – Nb → gas Law → p(V – Nb)=NkT → p=NkT/(V-Nb)?

But pressure is also decreased p → NkT/(V-Nb)- a(N/V)² = p

characterizes the strength of interaction

Van der Waals – equation:
one possible approach

$$\left(p + a\frac{N^2}{V^2}\right)(V - Nb) = NkT$$

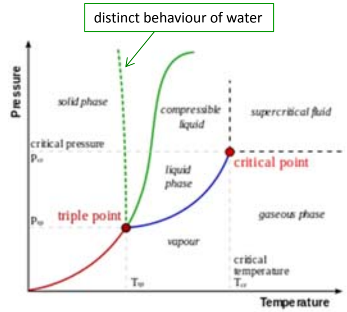
The ideal gas description is usually valid at higher temperatures

Textbook p. 59 - 60

Phase transition :

transitions between solid, liquid and gaseous states of matter

First order phase transitions: at the transition state the density of the material has a step-like, discontinuous change, the transition involves latent heat.

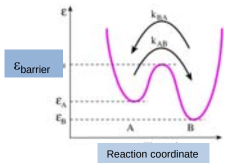


Phase: the physical and chemical properties of the volume elements are identical

Boltzmann distribution - more examples (see textbook)

Thermal emission of electrons from metals
Nernst equation p. 54-57

Equilibrium rate of chemical reactions



Reaction : A⟷B

The k_{AB} and k_{BA} rates are proportional to the number of reactants which are higher in energy, reaching the top of the barrier

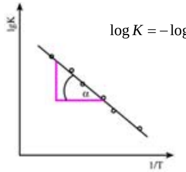
$$k_{AB} = const \times e^{-\frac{\varepsilon_{barrier} - \varepsilon_A}{kT}}$$

$$k_{BA} = const \times e^{-\frac{\varepsilon_{barrier} - \varepsilon_B}{kT}}$$

$$K = \frac{k_{BA}}{k_{AB}} = e^{-\frac{\varepsilon_A - \varepsilon_B}{kT}}$$

Experimental determination of the energy of activation

Arrhenius plot



$$\log K = -\log e \frac{\varepsilon_A - \varepsilon_B}{k}\frac{1}{T}$$

Barometric formula

Density of air in the atmosphere decreases with the altitude (h) by the formula:

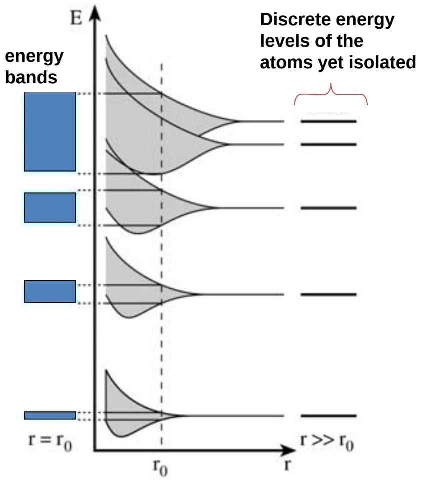
$$\frac{\rho(h)}{\rho(0)} = e^{-\frac{mgh}{kT}}$$

m average mass of particles in the air
g gravitational acceleration

Second part

Electronic energy levels in ordered systems.
Electric and optical properties.

Crystalline materials

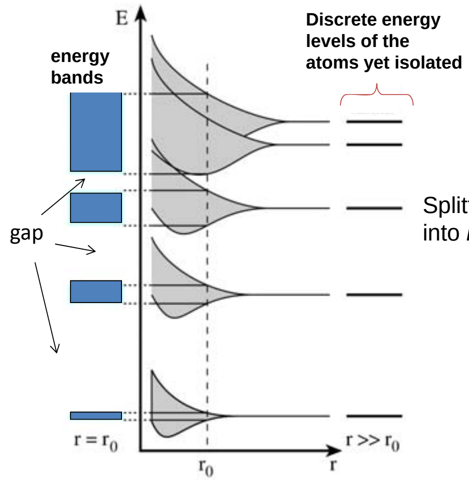


$N \sim 10^{23}$

N no.of isolated atoms with discrete energy levels change their electronic states when they interact to form a crystalline state with bond distance r_0.

Splitting of discrete levels into ***N*** new levels results in continuous ranges : ***energy bands***

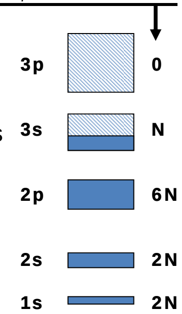
Interaction of ordered atoms changes the electronic energy levels
discrete energy levels → continuous ranges of energies (bands) separated by forbidden states (energy gaps)



Splitting of discrete levels into ***N*** new levels

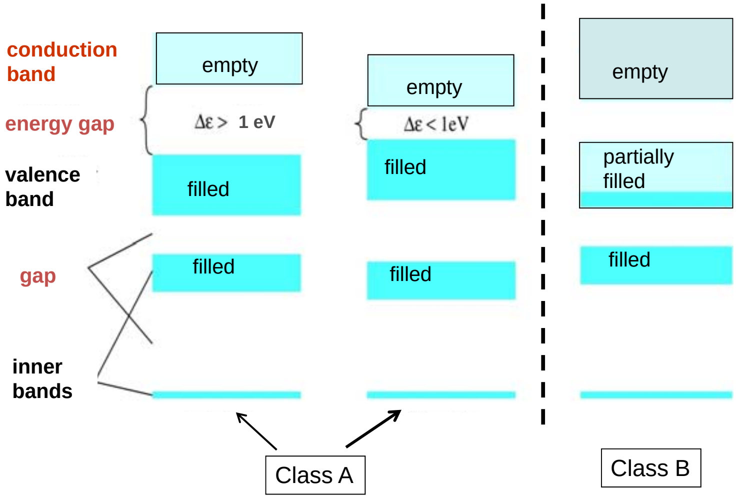
Example: solid state Na
$1s^2 2s^2 2p^6 3s^1$

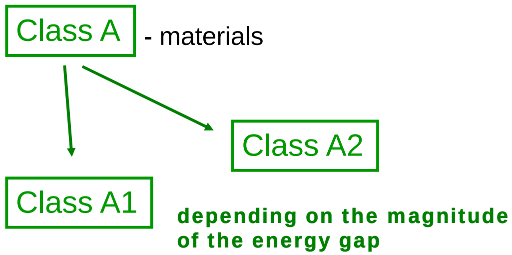
$2(2l+1)N = number\ \ of\ \ electrons\ \ in\ one\ band$

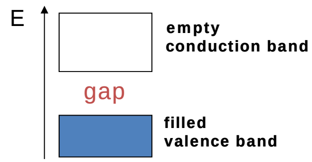


The 3s level is only half-filled

The physical (chemical) properties depend on the energetic relations of highest filled and lowest empty electronic states → ***three important classes of materials***







Why?

$$\frac{n_{cond.}}{n_{valence}} = e^{-\frac{\Delta\varepsilon}{kT}}$$

the relation of $\Delta\varepsilon = E_{gap}$ and kT **determines** if the gap energy can be overcome by Boltzmann distribution

$kT \sim 0.023$ eV T=300 K,
k=1.38x10^{-23}JK^{-1} *Boltzmann constant*

Class A1

$$E_{gap} >> 1eV$$

Insulators: E_{gap} is large

e.g diamond E_{gap} = 5.4 eV

$$\frac{n_{cond}}{n_{val}} = e^{-\frac{5.4}{0.023}} = e^{-235} = 0$$

- *-No electric conductivity (dielectric break-down: ~V/bond → 10^{10}V/m)*
- *-No photon absorption in the **VIS range -> transparency***
- *- UV photons may be absorbed, IR: excitation of lattice vibrations*

Class A2

$$E_{gap} \leq 1eV$$

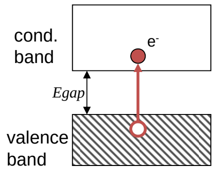
E_{gap} is small - intrinsic semiconductors

Non-transparent crystalline materials
Reasonable number of thermally excited electrons in the conduction band

		$E_g(eV)$
0 K	*Si*	**1.1**
	Ge	**0.75**

$$\frac{n_{cond}}{n_{val}} = e^{-\frac{0.75}{0.023}} = e^{-33} = 7*10^{-15}$$

$$n_{val} \approx 6*10^{23}! \Rightarrow n_{cond} \approx 4*10^{8}$$ **/cm³**



n* - type conductivity** (electron*** conduction)

$$\sigma \approx e^{-\frac{E_{gap}}{2kT}}$$

p* - type conductivity** (electron-hole***: + charge conduction)

Two kinds of charge carriers

Class A2

intrinsic semiconductors

$$\sigma = const * e^{-\frac{E_{gap}}{2kT}}$$

Slightly depends on T

Equilibrium: generation and recombination of charge carriers is of equal probability

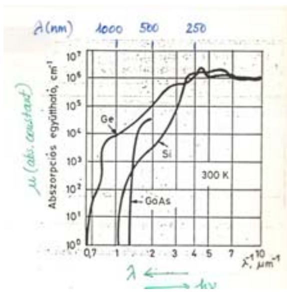
p(recombination)~n^2, p(generation)~ Boltzmann factor

Specific conductivity is increased by temperature increase
*→ **thermoresistors***

Optical properties: non-transparency in the VIS range

$$hf_{VIS} > E_{gap}$$

Photon absorption induces conductivity
→ ***photodetectors***



Class B

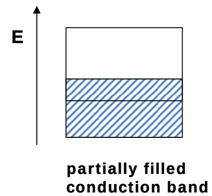
Metals :no gap

e.g. 1-valence and 2-valence metals Na, Mg, Cu..

	Cu	Si
n(charge)/m³	**9x10²⁸**	**1x10¹⁶**
specific resistance (Ohmxm)	**2x10⁻⁸**	**3x10³**

T=293 K

high electric conductivity



Energy absorption is possible within the partially filled highest energy band

-Electrons conduct electricity

-Optical non-transparency

$$\sigma \approx \frac{1}{T}$$

Specific conductivity decreases with T-increase
↔ *semiconductors*

Class A2**

doped semiconductors

Doping: incorporation of a second component (dopant) into the crystal lattice of an intrinsic semiconductor (host) in a small amount

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

⟶ ***Dopant atoms are isolated in the crystal matrix***

Idea: properly selected ***dopant may reduce E_{gap}***, thus increasing the number of thermally excited charge carriers : electrons or electron-holes

Two combinations:

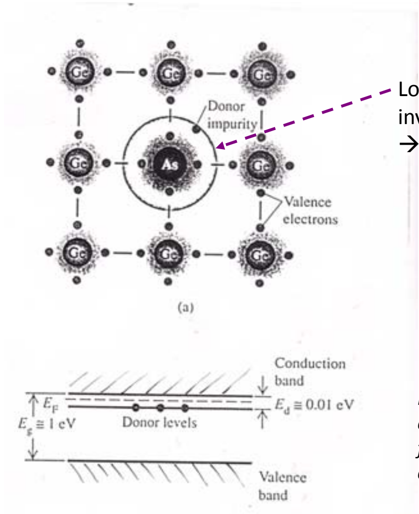
-4-valent host combined with 5-valent dopant ⟶ *n-type* doped semiconductor

-4-valent host combined with 3-valent dopant ⟶ *p-type* doped semiconductor

Hosts: Ge, Si

Dopants: 5-valent : P, As, Bi
3-valent : B, Al, Ga, In

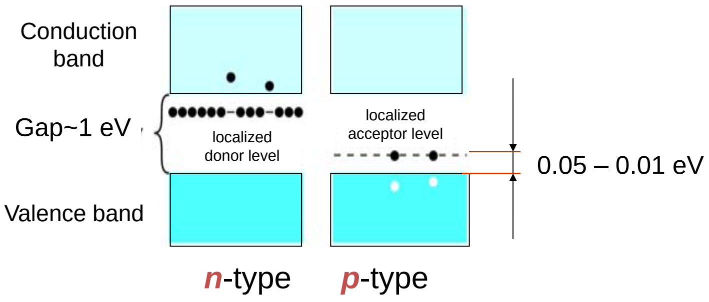
4-valence Ge crystal lattice doped with 5-valence As atoms



Loosely bound fifth electron can be easily involved in conduction
→ *n-type conduction*

Donor level exists only at impurities. These electrons can not be moved by electric field. But, these can be raised into the conduction band by a low energy-surplus.

Summary: n-type and p-type conduction



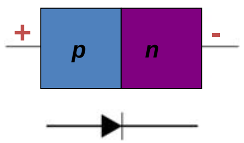
electrons **thermally excited from the donor level of impurity conduct electricity**

electrons thermally excited to the acceptor level of impurity are localized, but *electron-holes* conduct electricity

diode and transistor:

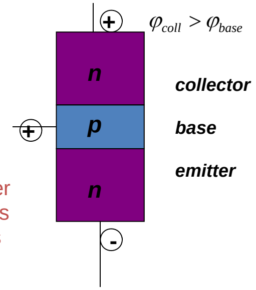
constructed from n- and p– type doped semiconductors

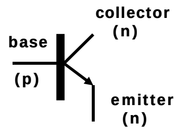
forward biased



diode:
- rectifier
- light source
  if voltage is switched on : LED
- transducer of light
  into voltage – pixels of CCD camera

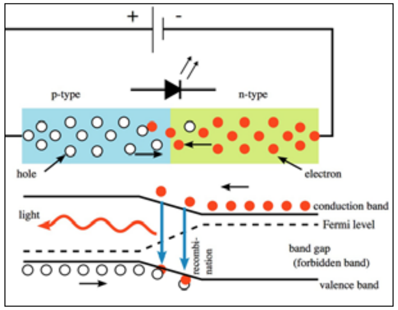
transistor:
- electric current amplifier
- digital unit of computers
  : bistable multivibrators





Doping makes possible miniature sizes ⟶ *microelectronics*

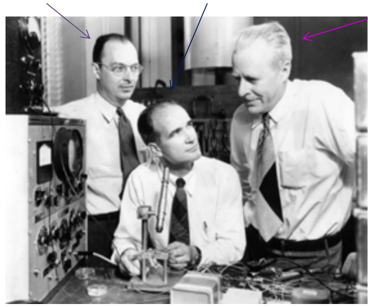
Most modern light source: LED



Recombination of electrons and holes produces light

1956 - Nobel price in physics for the realzation of the transistor

John **Bardeen**, William **Shockley** and Walter **Brattain** at Bell Labs, 1948.



John Bardeen
II.Nobel 1972
Theory of superconductivity

Walter Brattain
Extremely talented experimental physicist

2014 – Nobel price in physics for the realization of the blue LED

Isamu Akasaki , Shuji Nakamura, Hiroshi Amano ,

LED: Light Emitting Diode

Thank you for your attention!