Structure of materials: gas – liquids - solids
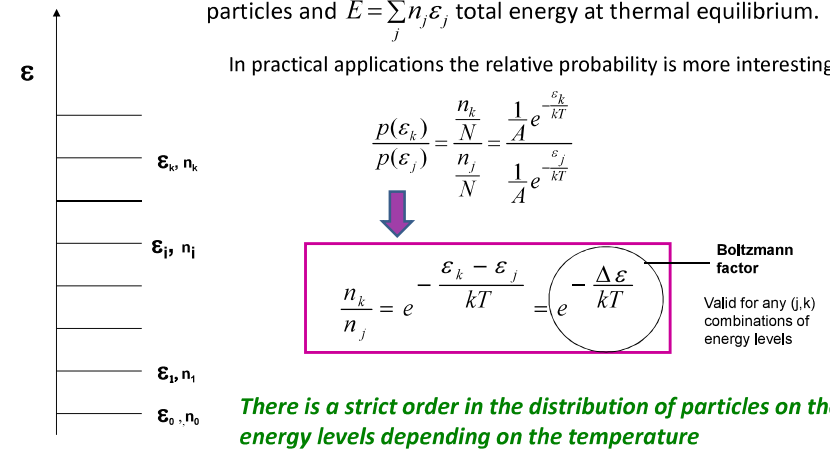
Electronic energy states in ordered materials

Prof. Judit Fidy
2018 október 24

Boltzmann distribution function – *remember the previous lecture*

yields the number of particles (n_j) with ε_j **energy** in a system of $N = \sum_j n_j$ particles and $E = \sum_j n_j \varepsilon_j$ total energy at thermal equilibrium.

In practical applications the relative probability is more interesting

$$\frac{p(\varepsilon_k)}{p(\varepsilon_j)} = \frac{\dfrac{n_k}{N}}{\dfrac{n_j}{N}} = \frac{\dfrac{1}{A}e^{\frac{\varepsilon_k}{kT}}}{\dfrac{1}{A}e^{\frac{\varepsilon_j}{kT}}}$$

$$\frac{n_k}{n_j} = e^{-\frac{\varepsilon_k - \varepsilon_j}{kT}} = e^{-\frac{\Delta\varepsilon}{kT}}$$

Boltzmann factor

Valid for any (j,k) combinations of energy levels

ε

εk, nk

εi, ni

ε1, n1

ε0, n0

There is a strict order in the distribution of particles on the energy levels depending on the temperature

Textbook p. 52 - 57

Validity of Boltzmann distribution in various fields of nature - examples

1.Thermal emission of electrons from metals

2. Nernst equation

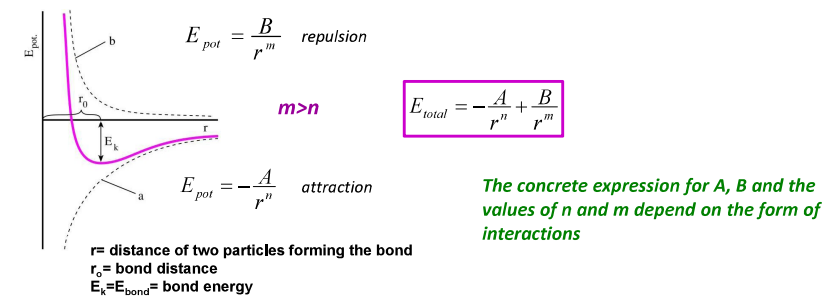3. Temperature dependence of the rate of chemical reactions

4. Barometric formula

5. Role of Boltzmann distribution in the structure of materials

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5. Structural consequences of B. distribution in the classes of materials : gas – liquids – solids (crystals)
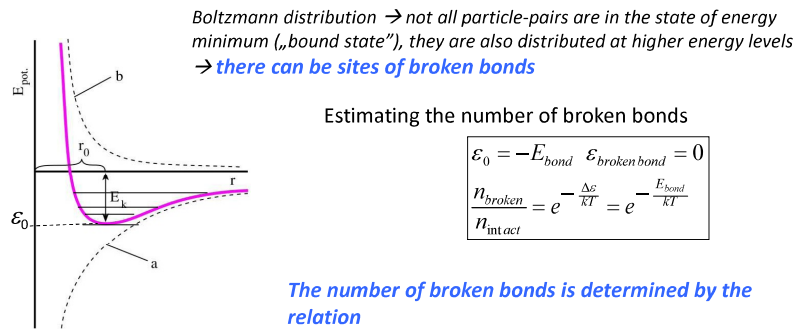
Concept of „structural order": the interaction of particles within the system determines the spacial coordinates (relative position and orientation) of the particles.

- Lack of interaction → *disordered structure*: ideal gas
- Only a small fraction of particles are bound by interaction → *short range order*
- A large proportion of particles are in well defined position → *long range order*

Interactions lead to ordering→ *bond* formation

$$E_{pot} = \frac{B}{r^m} \quad \text{repulsion}$$

$$E_{pot} = -\frac{A}{r^n} \quad \text{attraction}$$

m>n

$$E_{total} = -\frac{A}{r^n} + \frac{B}{r^m}$$

r= distance of two particles forming the bond
r₀= bond distance
Ek=Ebond= bond energy

The concrete expression for A, B and the values of n and m depend on the form of interactions

Boltzmann distribution and bond formation

Boltzmann distribution → not all particle-pairs are in the state of energy minimum („bound state"), they are also distributed at higher energy levels
→ *there can be sites of broken bonds*

r= distance between two particles forming the bond
r_o= equilibrium bond distance
$E_k=E_b$= binding energy

Estimating the number of broken bonds

$$\varepsilon_0 = -E_{bond} \quad \varepsilon_{broken\,bond} = 0$$

$$\frac{n_{broken}}{n_{int\,act}} = e^{-\frac{\Delta\varepsilon}{kT}} = e^{-\frac{E_{bond}}{kT}}$$

The number of broken bonds is determined by the relation

$$\Delta\varepsilon = E_{bond} \quad \Longleftrightarrow \quad kT$$

kT ~ 0.027 eV
Example: *T=310 K, body temperature*
k=1.38x10⁻²³JK⁻¹ Boltzmann constant

elektronvolt
1 eV= 23 kcal/mole ~
~ 100 kJ/mól

Magnitude of bond energies

elektronvolt
1 eV= 23 kcal/mole ~
~ 100 kJ/mól

E_b ~ **primary bonds**: covalent
  ionic   **2 − 10 eV/bond ~ 150- 1000 kJ/mól**
  (metallic)

E_b ~ **secondary bonds**

H-bond	**0.1 − 1** (water: 0.2 eV)
Hydrophobic interactions	**~ 0.1**
dipole − point charge	**~ 0.1-0.2**
van der Waals dipole− dipole	**~ 0.02**
dipole− induced diole	**~ 0.01**
temporary dipole-induced dipole	**~ 0.02 eV/bond**
(dispersion interaction)	

A 100 times difference depending on the type of interaction!

What is the probability that the primary bonds stabilizing the structure of molecular building elements would be broken at body temperature?

$$\frac{n_{broken}}{n_{int\,act}} = e^{-\frac{\Delta\varepsilon}{kT}}$$

$$\Delta\varepsilon = E_{bond}$$

if $\;n_{broken} << n_{int\,act} \;\Rightarrow\; \frac{n_b}{n_i} \cong \frac{n_b}{N}$

$$\frac{n_b}{N} \cong e^{-\frac{\Delta\varepsilon}{kT}} = e^{-\frac{E_{bond}}{kT}}$$

kT ~ 0.027 eV   T=310 K,
k=1.38x10⁻²³JK⁻¹ Boltzmann constant

e.g. E_{bond}= 2.7 eV →

$$\frac{n_b}{N} \cong e^{-\frac{E_{bond}}{kT}} = e^{-100} = 3.72*10^{-44}$$

Probability   **very well zero!**

No danger that molecules would be degraded by thermal fluctuations

---

What is the probability that the secondary bonds stabilizing the structure of macromolecular structures would be broken at body temperature?

Are the H-bonds always intact in a dsDNA?

Example: DNA of T7 bacteriophage

DNA with about 40000 base pairs → about 100 000 H-bonds → N= 100 000

$$\frac{n_{broken}}{n_{int\,act}} = e^{-\frac{\Delta\varepsilon}{kT}} = e^{-\frac{0.2}{0.026}} = 0.00046 \cong \frac{n_{broken}}{N}$$

$$\Delta\varepsilon = E_{bond} = 0.2\;eV$$

$$n_b \cong N \times 0.00046 = 46$$

n_{broken} ~ 46/DNA

↑
time-average!

The probability is still low, but the absolut number of broken bonds in one macromolecule is significant number → flexibility of macromolecular complexes →
Possibility for ligand binding and chemical reactions

Structural dynamics in living materials

Structure of crystalline materials - ideal and real crystals

Particles: **atoms** - *bonds:* **primary** bonds -> **ordered structure**

Single crystal (ideal) **microcrystalline state (real crystals)**

grain

long range order in ideal crystals
large number of atoms in periodic array

grain boundary: accumulation of crystal defects

NaCl

Si

unit cells – periodic repetition → crystal lattice
14 kinds of units cells in nature: Bravais lattices

long range order: distance of periodic repetition >> 100 times r_0(=0.15nm)

Characteristics of „crystalline" state
-**anisotropy**: properties depends on the direction
-mechanical stability
-defined volume
-defined shape
-structure: **long range order**

44–12 Types of crystal lattices. (a) Simple cubic (sc); (b) face-centered cubic (fcc); (c) body-centered cubic (bcc); (d) hexagonal close-packed (hcp).

The 14 kinds of unit cells found in nature

---

crystal defects in **real** crystals ?

Considering two states of bonds – intact
- broken

$$\frac{n_b}{n_i} = e^{-\frac{E_b}{kT}} \approx \frac{n}{N} = e^{-\frac{6.31}{0.023}} = e^{-270} = 0$$

$$n_i + n_b = N \qquad n_b << n_i$$

e.g. NaCl, E_b=6.31eV, *kT(room tempr.)=0.023eV*

But:
imperfections in crystal growth

Primary bonds can not be broken by thermal fluctuations at room temperature
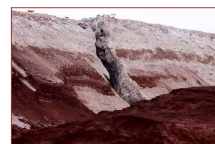
$E_{local} < E_b$

$$\boxed{n \approx e^{-\frac{E_{local}}{kT}}}$$

physical/chemical **point defects**

vacancy

interstitium

Frenkel pair

point defects →diffusion to grain boundaries →
→line defects→surface defects→**fracture**
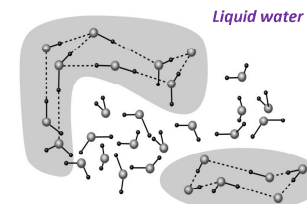
diffusion takes time!
„fatigue"

Liquid state – case of partial (short range) and temporary order

Particles: molecules
Interaction energy: E_b~ secondary bonds
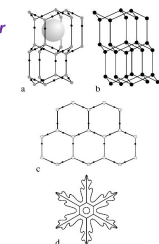ordered and disordered regions → average E_b is small →**many broken bonds**

$$\frac{n_{broken}}{n_0} \cong 1\% - 0.05\% \quad (T = 300 \ K)$$

Liquid water

Properties of liquid state
-**isotropy**
-deformability
-it has a volume
-the shape of its volume is defined by the container
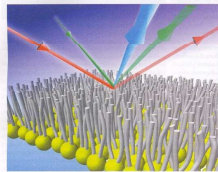-**short range order** in temporary regions

Crystalline water

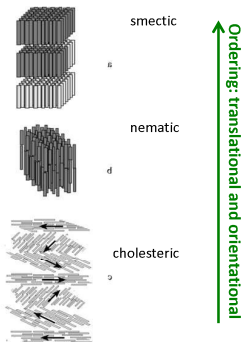**Short range order**: clusters of 5-10 molecules in continuous rearrangement

Mesomorphous materials – liquid crystals

Average interaction energy between molecules is small *like in liquids*
Long range order (but not so strict) ~ *like in crystals*
Deformability *like in liquids*
Constituting molecules are of special shape ~ string-like, disc-like
                                                        polarizable
Anisotropy

Forms of order of string-like molecules

smectic

nematic

cholesteric

Ordering: translational and orientational

Weak bond energy → order can be easily perturbed by

-temperature (by Boltzmann distr.)
-concentration , pH, polarity of solvents
-electric field

thermotropic   **liotropic**

classes

Practical aspects

1. Thermotropy
  Cholesteric order → the distance of the ordered layers is sensitive to temperature → interference of diffracted light →
    →destructive interference for given λ-component of white light → compensating color is observed in reflection
    Contact thermography

**Color ~ T
thermometers**

.2. Lyotropic liq.crys.: membranes formed by amphiphilic molecules   (like phopholipids)
                    in proper solvents– *lipid membranes: bi-layers or multi-layers*

Lipid content

0%   100%

micelles   crystalline

p. 467

Biological significance: structure of the cell membrane, vesicules enclosing subcellular compartments, endoplasmic reticullum
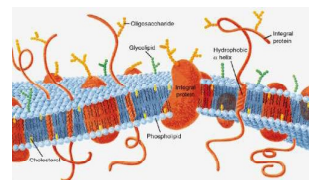
Cell-membrane: lipid bilayer

Schematic figures !

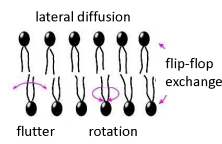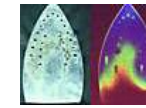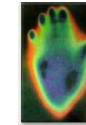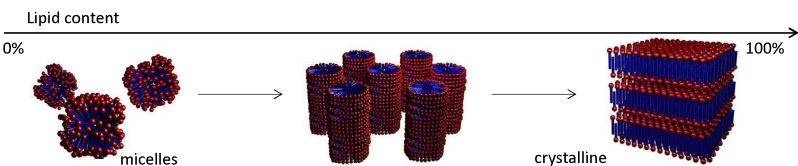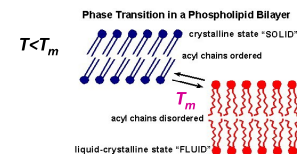Real structure of „parallel" lipid
(cell membrane)
***Boltzmann distribution allows
flexibility of lipid chains!***

(blue: transmembrane protein)

Result of computational modeling of bond breaking by Boltzmann distribution

40 – 60 % lipid
50 – 30 % protein

lateral diffusion

flip-flop
exchange

flutter   rotation

Biological –medical aspects

Lipid membranes: *combination of liotropic and thermotropic properties*

Phase Transition in a Phospholipid Bilayer

$T<T_m$ crystalline state "SOLID"
                   acyl chains ordered

                   T_m
                   acyl chains disordered $T>T_m$

liquid-crystalline state "FLUID"

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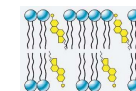   biologically non-functional
   e.g. ends of nerve cells in frozen limbs- numbness
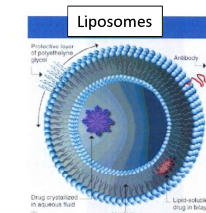**Liq.Cryst. state above Tm** – capable of biological functioning

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

Artificial membranes – liposomes – tools in therapy
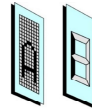
Liposomes

Targeting of medications
    - antibodies attached to the surface
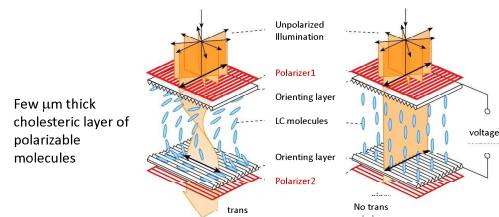   - stealth liposomes: protection against macrophages

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
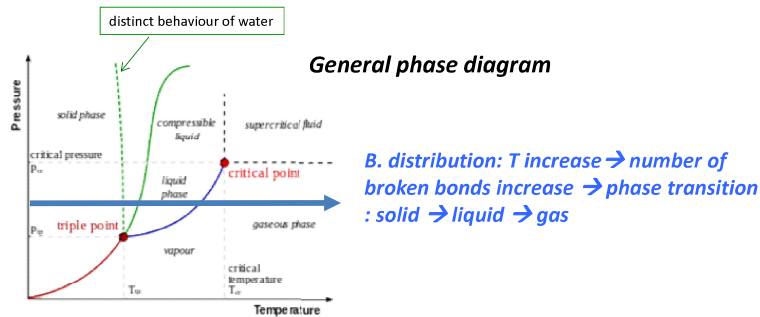based on **polarization effects regulated by electric field**

Unpolarized
Illumination
Polarizer1
Orienting layer
LC molecules
Few μm thick
cholesteric layer of
polarizable
molecules
Orienting layer
Polarizer2
voltage
trans
mission
No trans
mission

p. 467

Gasous systems – *summary of previous lecture*

kinetic gas theory elaborated for ideal gas

> **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

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

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

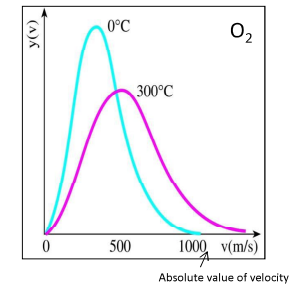Only translational motion

$$pV = NkT = nRT$$

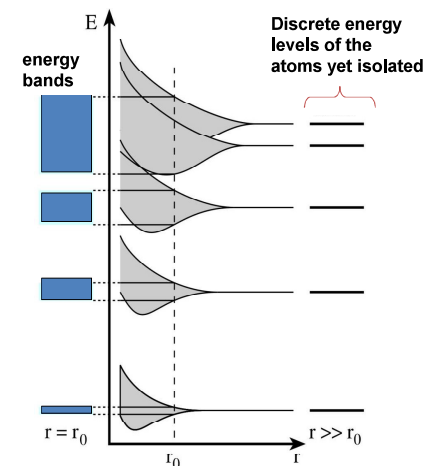Derived from elastic collision with the rigid wall of the container
(n is the number of moles)

Maxwell's velocity distribution (probability density function – depends on the particle mass and the temperature)

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

p.58 - 61

Phase transition :
transitions between <u>solid</u>, <u>liquid</u> and <u>gaseous</u> <u>states of matter</u>

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

distinct behaviour of water

General phase diagram

B. distribution: T increase→ number of broken bonds increase → phase transition : solid → liquid → gas

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

Electronic energy states in ordered systems
Crystalline materials

E
energy bands
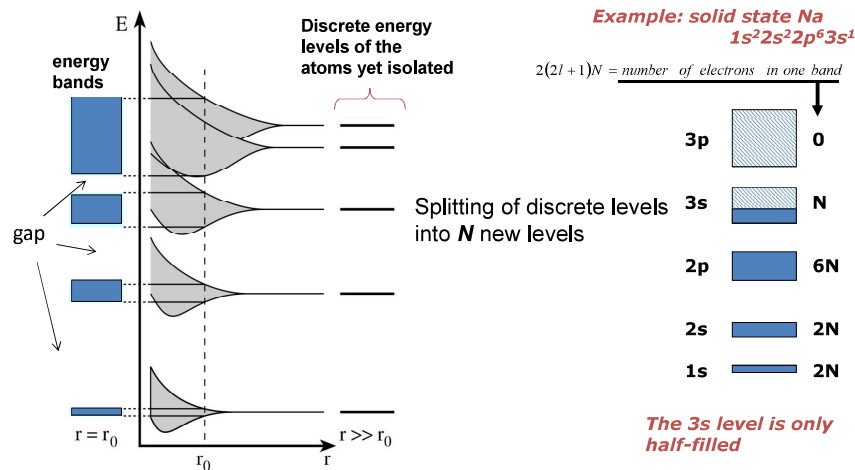Discrete energy levels of the atoms yet isolated
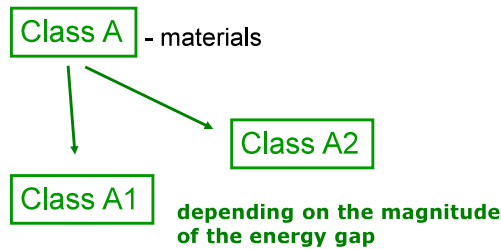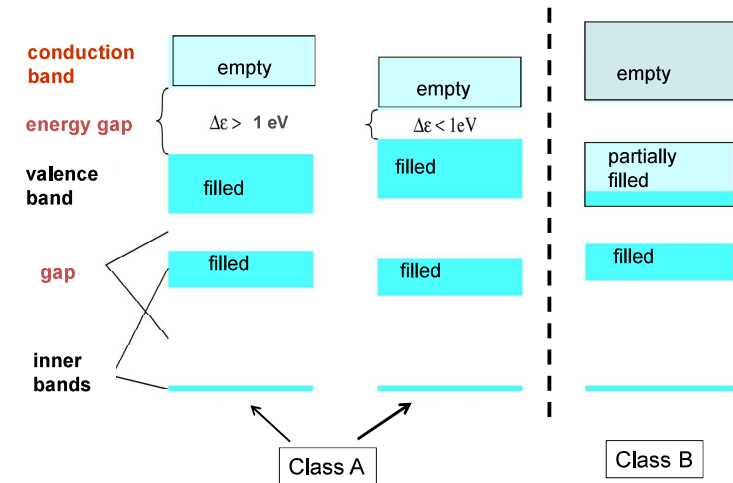r = r₀
r >> r₀
r₀
r

N~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 dicrete energy levels → continuous ranges of energies (bands) separated by forbidden states (energy gaps)

E

energy bands

gap

Discrete energy levels of the atoms yet isolated

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

$r = r_0$

r_0

r

$r \gg r_0$

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

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

3p	0
3s	N
2p	6N
2s	2N
1s	2N

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**

conduction band

empty

empty

empty

energy gap

$\Delta\varepsilon > 1\ eV$

$\Delta\varepsilon < 1eV$

valence band

filled

filled

partially filled

gap

filled

filled

filled

inner bands

Class A

Class B

Class A - materials

Class A1

Class A2

depending on the magnitude of the energy gap

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

E

empty conduction band

gap

filled valence band

kT ~ 0.023 eV   T=300 K,
k=1.38x10⁻²³JK⁻¹ *Boltzmann constant*

Class A1

Insulators: E_{gap} is large

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

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 (electric break-down: ~V/bond → 10^{10}V/m)*

- *No photon absorption in the **VIS range -> VIS transparency***

- *UV photons may be absorbed → **no transparency in UV***

- *IR: excitation of lattice vibrations*

Class A2 — E_{gap} is small - intrinsic semiconductors

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

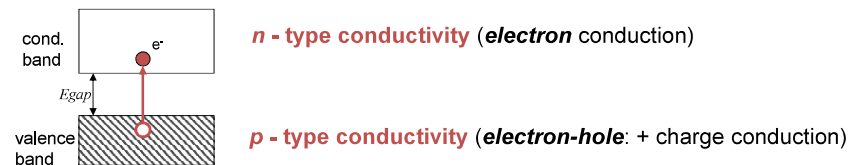| 0 K		E_g (eV)
	Si	1.1
	Ge	0.75

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

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

Not too many, but reasonable

1 M→ 32g (ρ=5.5 g/cm³) → 4*10⁸ e⁻/6 cm³

Electrons populating the conduction band originate from the valence band → two kinds of conducting charge carriers

cond. band

e⁻

E_{gap}

valence band

n - type conductivity (*electron* conduction)

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

Class A2 — intrinsic semiconductors

Electric properties

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

Slightly depends on T

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

p(recombination)~n², p(generation)~ Boltzmann factor

U=I*R

Specific conductivity increases with the temperature
→ **thermoresistors**
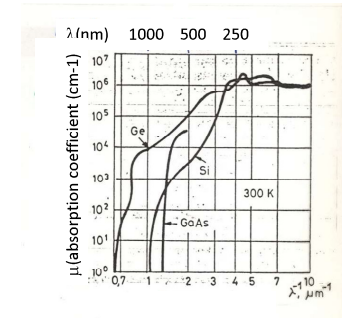
Optical properties

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

- non-transparency in the VIS range
- 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	T=293 K
specific resistance (Ohmxm)	2x10⁻⁸	3x10³	

high electric conductivity

E

partially filled conduction band

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:

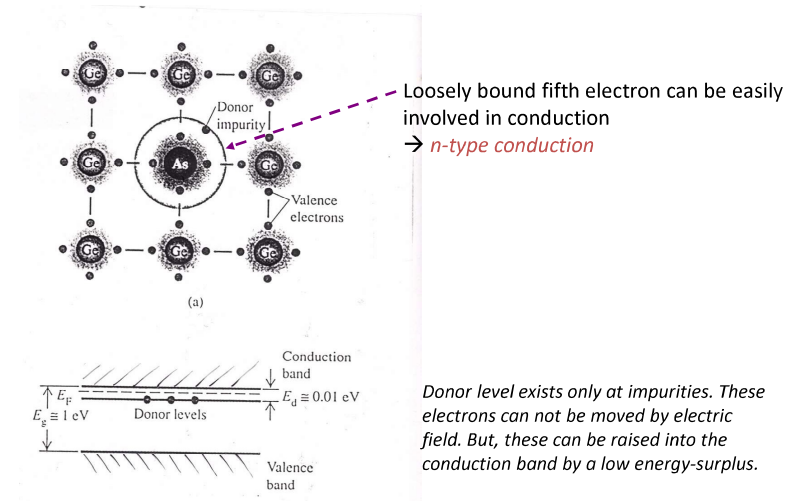-4-valent host combined with 5-valent dopant   ⟶ *n-type* doped semiconductor

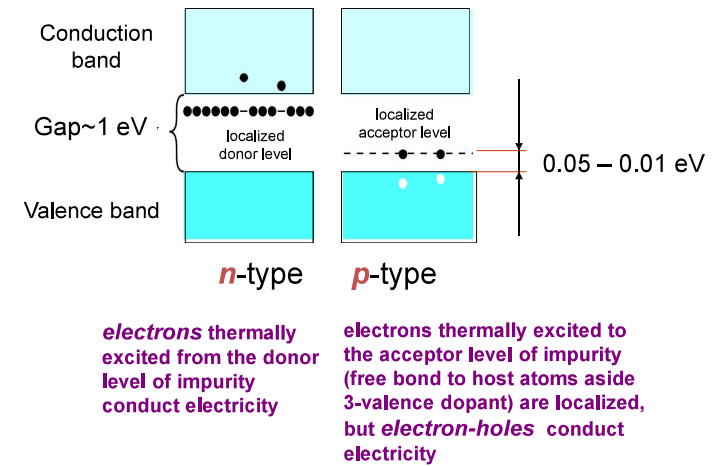-4-valent host combined with 3-valent dopant   ⟶ *p-type* doped semiconductor

Hosts: Ge, Si   **Dopants: 5-valent : P, As, Bi**
                              3-valent : B, Al, Ga, In
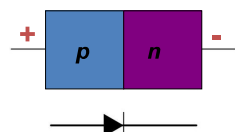
4-valence Ge crystal lattice doped with 5-valence As atoms

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

Conduction band

Gap~1 eV

Valence band

localized donor level

localized acceptor level

$0.05 - 0.01$ eV

n-type   *p*-type

electrons thermally excited from the donor level of impurity conduct electricity

electrons thermally excited to the acceptor level of impurity (free bond to host atoms aside 3-valence dopant) are localized, but **electron-holes** conduct electricity

diode and transistor:

constructed from n- and p— type doped semiconductors

forward biased

+   **p**   **n**   -

$\varphi_{coll} > \varphi_{base}$

n   *collector*

p   *base*

n   *emitter*

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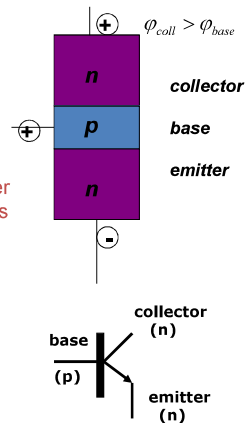- digital unit of computers
  : bistable multivibrators

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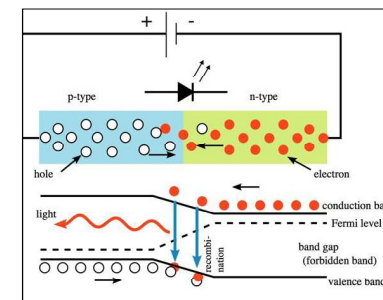- rectifier
- light source
  if voltage is switched on : LED
- transducer of light
  into voltage – pixels of CCD camera

collector (n)

base (p)

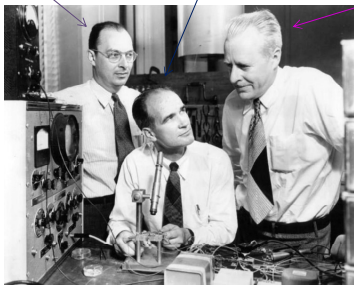emitter (n)

Most modern light source: LED

Recombination of electrons and holes produces light

Doping makes possible miniature sizes ⟶ *microelectronics*

1956 - Nobel price in physics for the realization of the semiconductor transistor → microelectronic circuit

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!