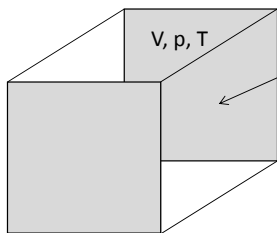


Describing many-particle systems

Prof. Judit Fidy
2014, October 16

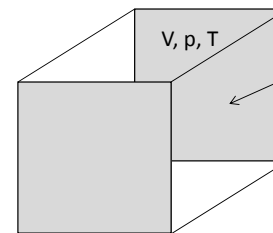
particle: - atom, atomic group
- molecule
- macromolecule
many: 6×10^{23}

Simple example



*Air molecules in the room...
What do the particles „do“, when the
macroscopic parameters are constant:
 V, p, T ?*

Simple example



*Air molecules in the room...
What do the particles „do“, when the
macroscopic parameters are constant:
 V, p, T ?*

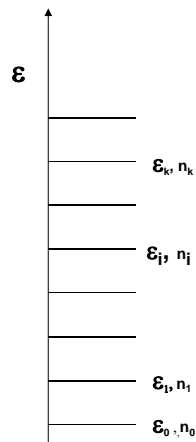
They are moving around.....? How?
What is the rule?

Another thought

*Air molecules in the room...
They are in the gravitational force field of the Earth!*

Why don't they observe the rule of „energy minimum“?
They all should sit on the ground!

Boltzmann distribution



N distinguishable independent particles at thermal equilibrium, $T \neq 0$ in a closed system, exposed to a force field

ε_i possible energy status for one particle
 n_i number of particles having ε_i energies

$$E = \sum_j n_j \varepsilon_j \quad N = \sum_j n_j$$

Boltzmann distribution function

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

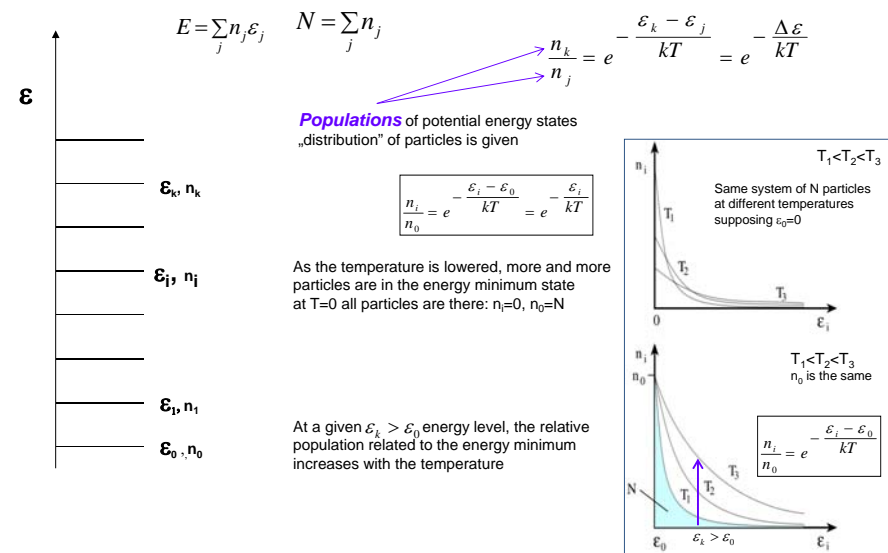
Boltzmann factor

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



Ludwig Eduard Boltzmann
1844-1906, Austrian physicist

Boltzmann distribution - conclusions



Boltzmann distribution – a general rule in nature

Considering the classes of materials

1. Gasous systems (ideal gas) -> lack of order in the structure

Rules based on Thermodynamics and Boltzmann distribution

1. average of kinetic energy is determined by the temperature

$$E_{total} = N \cdot \frac{1}{2} m \bar{v}^2 \quad \varepsilon_i = \frac{1}{2} m v_i^2$$

$$\frac{1}{2} m \bar{v}^2 = \frac{f}{2} kT$$

$$f = 3$$

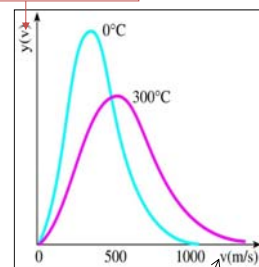
$$pV = NkT$$

degree of freedom of motion for point-like particles

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

$$\text{Frequency of occurrence} = n/N$$



Absolute value of velocity

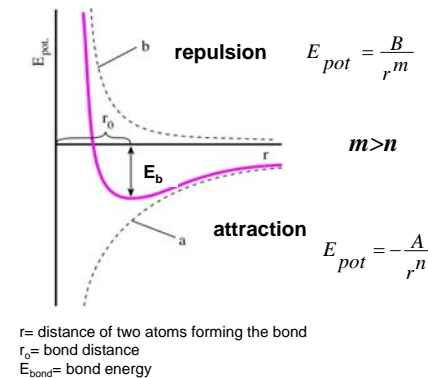
2. deviations from the average velocity are determined by the

Maxwell – Boltzmann distribution function

2. Classes of materials with structural order.

Order is based on interactions (bonds) between the constituting atoms or molecules

General concept of bond formation



Is it true that all constituting atoms are at bond distances from each other all the time?

Boltzmann distribution allows for having broken bonds!

$$\frac{n_{brokenbonds}}{n_{intactbonds}} = \frac{n_b}{n_i} = e^{-\frac{\Delta \varepsilon}{kT}}$$

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

The probability of breaking bonds by thermal fluctuations depends on the relation:

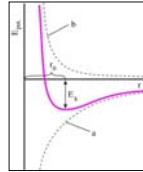
$$\Delta \varepsilon \longleftrightarrow kT$$

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

$kT \sim 0.027 \text{ eV}$ $T=310 \text{ K}$,
 $k=1.38 \times 10^{-23} \text{ J/K}$ Boltzmann constant

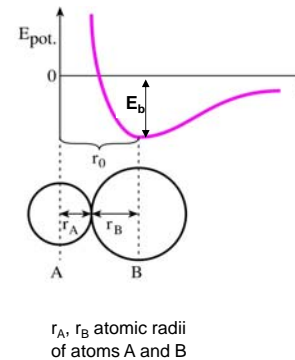
Examples for the functional form of attractive interactions

The distance dependence in the energy formulae of electrostatic interactions



Interaction	Distance in the energy function	Magnitude of the Energy of interaction (kJ/mól)
ion-ion	r^{-1}	200 - 300
ion – static dipole	r^{-2}	10 - 20
static dipole – static dipole	r^{-3}	1 - 2
dipole – dipole with Brown motion	r^{-6}	0.3
dispersion	r^{-6}	2

Atomic/molecular bond distances ($r_0 = r_A + r_B$) and binding energies E_b depend on the **type of interactions** (functions **a** and **b**)



Atom	Z	van der Waals radius (nm)	Covalent radius (nm)	Ionic radius (nm)	Ion
H	1	0,120	0,037	–	H ⁺
C	6	0,170	0,077	0,029	C ⁺
N	7	0,155	0,075	0,025	N ⁺
O	8	0,152	0,073	0,140	O ²⁻
F	9	0,147	0,071	0,117	F ⁻
P	15	0,180	0,106	0,058	P ³⁺
S	16	0,180	0,102	0,184	S ²⁻

Bond energies in materials with structural order

Great variety!

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

$E_b \sim$ **primary bonds**: covalent
ionic
metallic

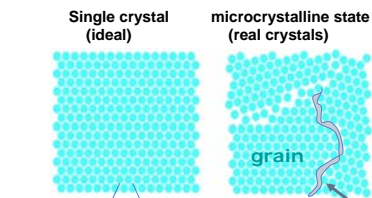
2 – 10 eV/bond

$E_b \sim$ **secondary bonds**

	E_b (eV)
H-bond	several x 0.1 (water: 0.2 eV)
hydrophobic	~ 0.1
van der Waals dipole – point charge	~ 0.1-0.2
dipole – dipole	~ 0.02
dipole – induced dipole	~ 0.01
dispersion (temporary dipoles)	~ 0.02

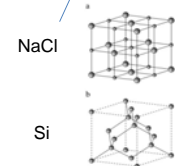
2.1. Structure of crystalline materials = ideal state of order

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



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

grain boundary:
accumulation of
crystal defects

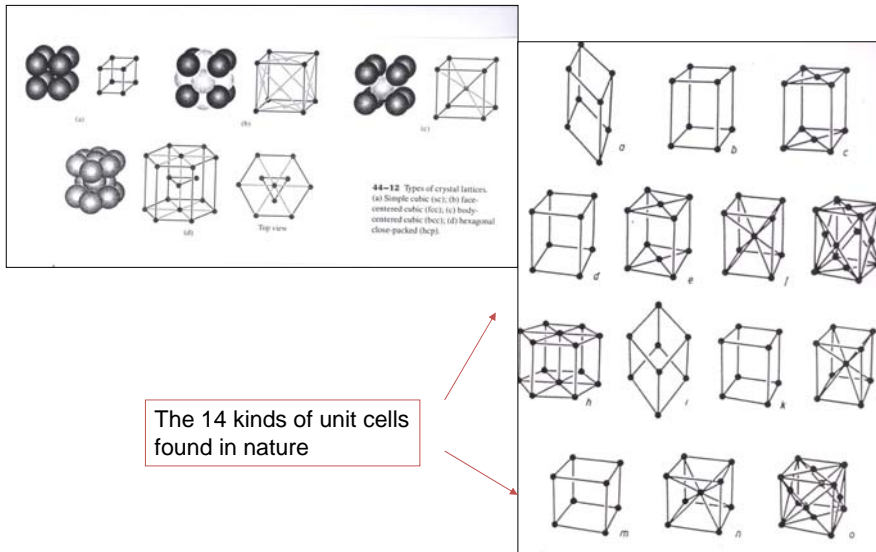


unit cells – periodic repetition -> crystal lattice
14 kinds of units cells in nature: Bravais lattices

long range order: distance of periodic repetition \gg 100 times r_0 ($=0.15\text{nm}$)

Characteristics of „crystalline” state

- anisotropy: properties depends on the direction
- mechanical stability
- defined volume
- defined shape
- structure: long range order



crystal defects in *real* crystals ?

Considering two states of bonds – intact – broken

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

$$n_i + n_b = N \quad n_b \ll n_i$$

e.g. NaCl, $E_b = 6.31 \text{ eV}$, $kT(\text{room tempr.}) = 0.023 \text{ eV}$

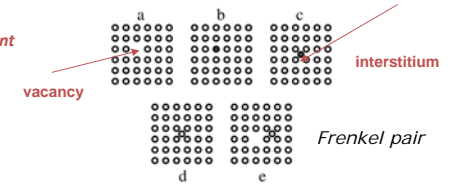
But:
imperfections in crystal growth

Primary bonds can not be broken by thermal fluctuations at room temperature

$$E_{\text{local}} < E_b$$

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

physical/chemical **point defects**



point defects → diffusion to grain boundaries →
→ line defects → surface defects → **fracture**

diffusion takes time!
„fatigue”



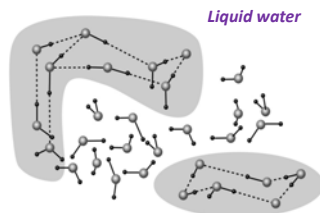
2.2. Liquid state – case of partial and temporary order

Particles: molecules

Interaction energy: $E_b \sim$ secondary bonds

ordered and disordered regions → average E_b is small → **many broken bonds**

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

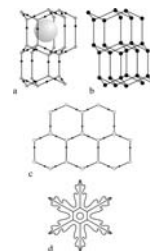


Short range order: clusters of 5-10 molecules in continuous rearrangement

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



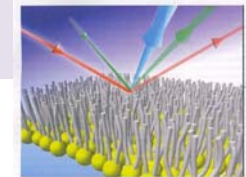
2.1.-2.2. Mesomorphous materials – liquid crystals

Average interaction energy between molecules \sim small like in liquids

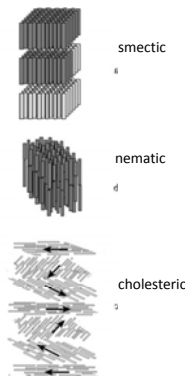
Long range order (but not so strict) \sim like in crystals

Deformability

Constituting molecules are of special shape \sim string-like



Forms of order of string-like molecules



Weak bonding energy → order can be easily perturbed by

- temperature
- concentration and polarity of solvents
- electric field

Practical aspects

1. Cholesteric order → sensitivity to temperature → color change → **Contact thermography**

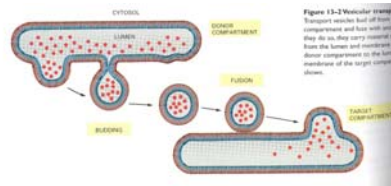


2. **Electro-optical properties:** electric field → structural order change → light transmission change → liq.crys. displays

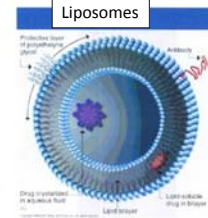


3. **Lyotropic liq.crys.:** membranes formed by amphiphilic molecules (like phospholipids) in proper solvents– **lipid membranes**

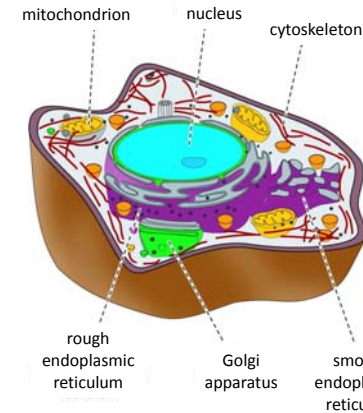
Cell-membrane: lipid bilayer



Liposomes



2.3. Macromolecular systems: order is stabilized by a wide range of interactions

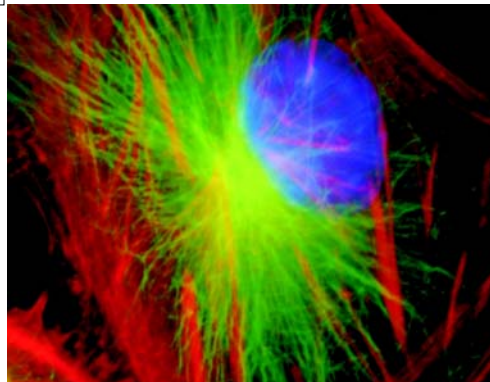


Hierarchy in

- bond strengths
- bond distances
- distance dependence of interaction energies
- binding water molecules and ions
- structural constraint of prosthetic groups

Blue: nucleus

Red: actin filament



Green: microtubular system

Wide range of interaction energies → „structural dynamics“

How is this observed in the functioning of a dsDNA? Are the H-bonds always intact?

$$\frac{n_{broken}}{n_{bound}} = e^{-\frac{\Delta\epsilon}{kT}}$$

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

$$\text{if } n_{broken} \ll n_{bound} \Rightarrow \frac{n_{broken}}{n_{bound}} \cong \frac{n_{broken}}{N}$$

Example: The T7 DNA with about 40000 base pairs → about 100 000 H-bonds → N= 100 000

$$\frac{n_{broken}}{n_{bound}} = e^{-\frac{\Delta\epsilon}{kT}} = e^{-\frac{0.2}{0.026}} = 0.00046 \cong \frac{n_{broken}}{N}$$

$$\Delta\epsilon = E_{bond} = 0.2 \text{ eV}$$

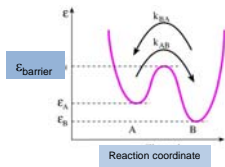
$$n_{broken} \sim 46/\text{DNA}$$

↑
time-average!

Significant number of secondary bonds are broken at body temperature → flexibility of macromolecular complexes → Possibility for ligand binding and chemical reactions

Boltzmann distribution - more examples

3. Equilibrium rate of chemical reactions



Reaction : $A \rightleftharpoons B$

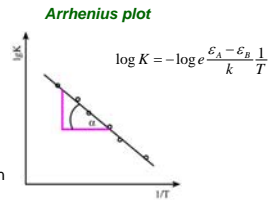
The k_{AB} and k_{BA} rates are proportional to the number of reactants which are higher in energy, reaching the top of the barrier

$$k_{AB} = \text{const} \times e^{-\frac{E_{\text{barrier}} - E_A}{kT}}$$

$$k_{BA} = \text{const} \times e^{-\frac{E_{\text{barrier}} - E_B}{kT}}$$

$$K = \frac{k_{BA}}{k_{AB}} = e^{-\frac{E_A - E_B}{kT}}$$

Experimental determination of the energy of activation



4. Barometric formula

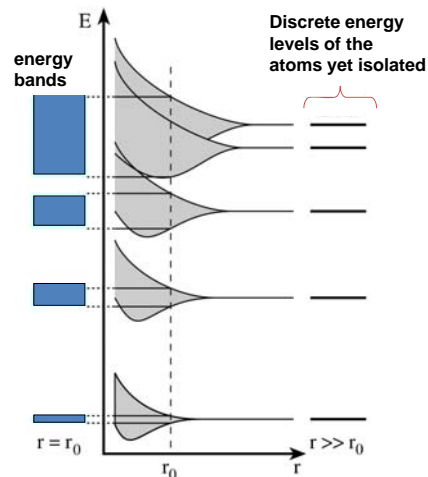
Density of air in the atmosphere decreases with the altitude (h) by the formula:

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

m : average mass of particles in the air
 g : gravitational acceleration

The interaction of particles in ordered systems changes the electronic energy levels

Crystalline materials

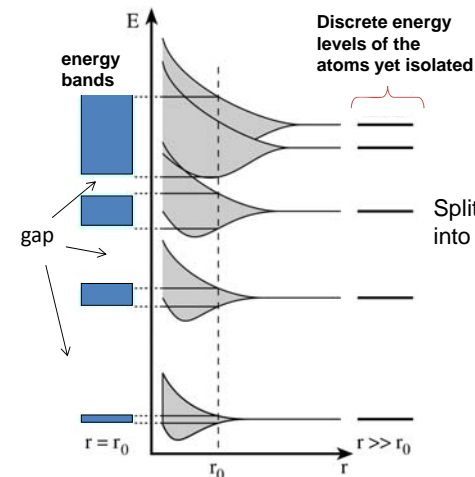


$N \sim 10^{23}$

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 \rightarrow continuous ranges of energies (bands) separated by forbidden states (energy gaps)



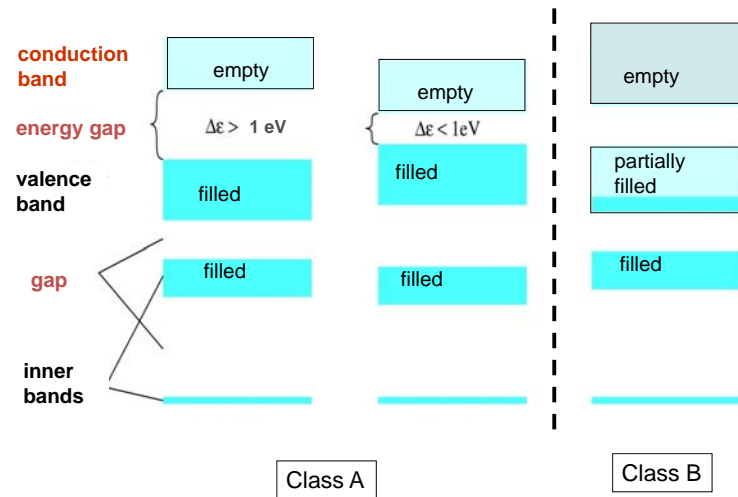
Example: solid state Na
 $1s^2 2s^2 2p^6 3s^1$

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

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

The fourth 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**



Class A - materials

depending on the magnitude of the energy gap

Class A1

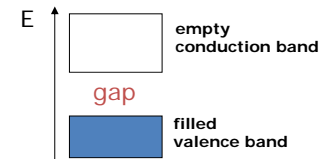
Class A2

Why?

$$\frac{n_{\text{cond}}}{n_{\text{valence}}} = e^{-\frac{\Delta\epsilon}{kT}}$$

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

$kT \sim 0.023 \text{ eV}$ $T=300 \text{ K}$,
 $k=1.38 \times 10^{-23} \text{ J K}^{-1}$ Boltzmann constant



Class A1

$E_{\text{gap}} \gg 1 \text{ eV}$ **insulators**

e.g. diamond $E_{\text{gap}} = 5.4 \text{ eV}$

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

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

Class A2

$E_{\text{gap}} \leq 1 \text{ eV}$ **intrinsic semiconductors**

Non-transparent crystalline materials

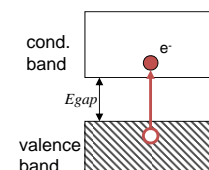
Reasonable number of thermally excited electrons in the conduction band

	$E_g \text{ (eV)}$
Si	1.1
Ge	0.75

At 0 K:

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

Result: $n_{\text{val}} \approx 6 \times 10^{23} \text{ cm}^{-3} \Rightarrow n_{\text{cond}} \approx 4 \times 10^8 \text{ cm}^{-3}$



n - type conductivity (**electron** conduction) $\sigma \approx e^{-\frac{E_{\text{gap}}}{2kT}}$

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

Two kinds of charge carriers

Class A2

intrinsic semiconductors

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

Slightly depends on T

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

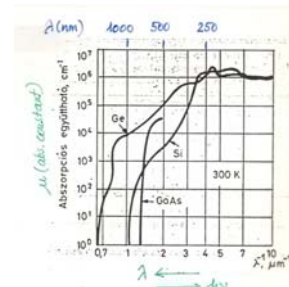
$p(\text{recombination}) \sim n^2$, $p(\text{generation}) \sim \text{Boltzmann factor}$

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

Optical properties: non-transparency in the VIS range

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

Photon absorption induces conductivity
→ **photodetectors**



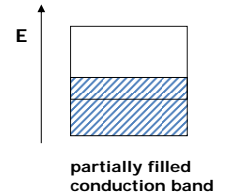
Class B

metals

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

	Cu	Si	T=293 K
n(charge)/m ³	9x10 ²⁸	1x10 ¹⁶	
specific resistance (Ohmxm)	2x10 ⁻⁸	3x10 ³	

↑
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**

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

Isamu Akasaki, Shuji Nakamura, Hiroshi Amano,



LED: Light Emitting Diode
Application of doped semiconductors:
energy saving in light production!



Thank you for your attention!



Additional information....

Class A2**

doped semiconductors

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

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

→ 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:

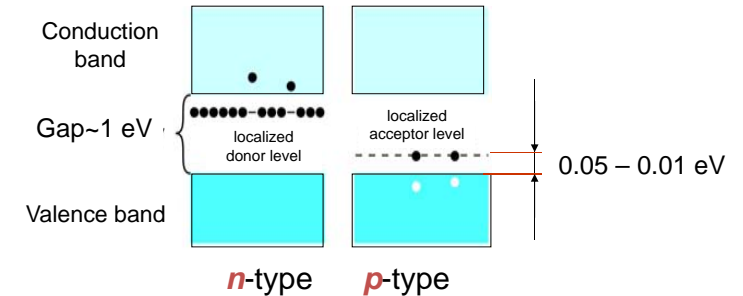
-4-valent host combined with 5-valent dopant → **n-type** doped semiconductor

-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

Summary: n-type and p-type conduction

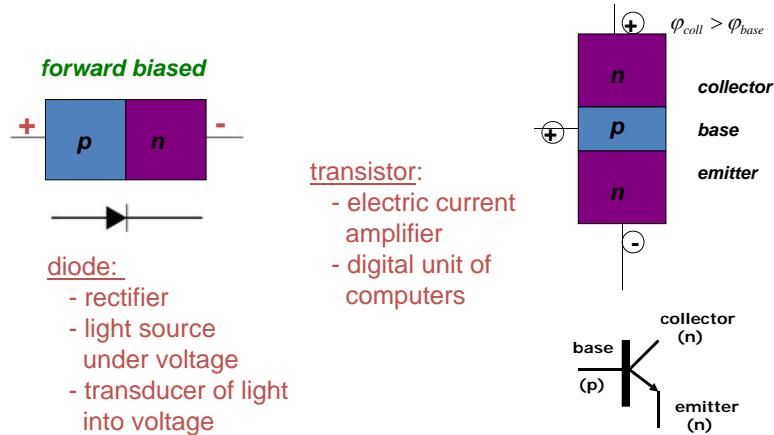


electrons thermally excited from the donor level of impurity conduct electricity

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

diode and transistor:

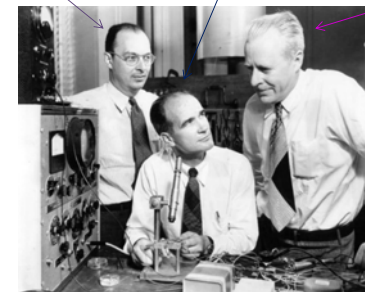
constructed from n- and p- type doped semiconductors



Doping makes possible miniature sizes → microelectronics

1956 - Nobel price in physics for the realization 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