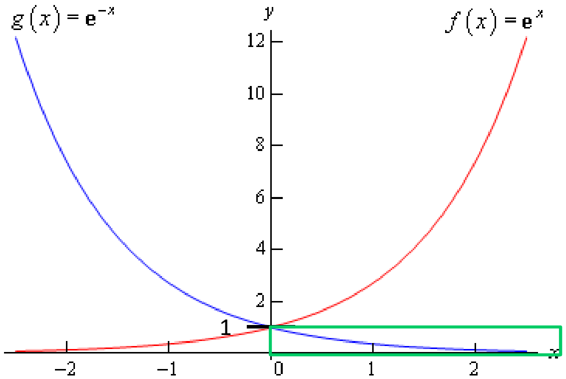
Boltzmann-distribution

Ludwig Boltzmann (1844-1906)

$$\frac{n_i}{n_0} = e^{-\frac{\varepsilon_i - \varepsilon_0}{k_B T}}$$

- thermally equilibrated system: T = const

n_0 – occupation number of energy level ε_0
n_i – occupation number of energy level ε_i
k_B – Boltzmann constant



$\varepsilon_i > \varepsilon_0$

$k_B, T > 0$

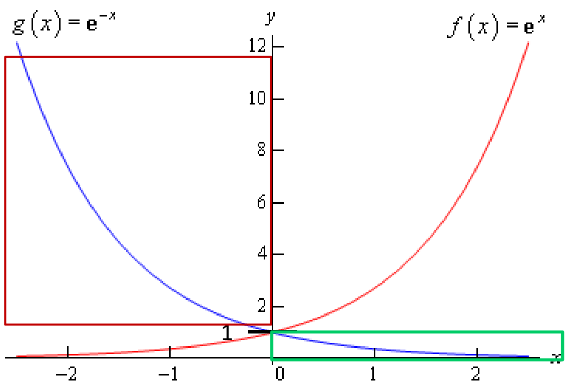
$\frac{\varepsilon_i - \varepsilon_0}{k_B T} > 0$

- at higher temperatures higher energy levels are more populated

$T \nearrow$ $\quad \frac{\varepsilon_i - \varepsilon_0}{k_B T} \searrow$ $\quad \frac{n_i}{n_0} \nearrow$ $\quad n_i \nearrow$

Boltzmann-distribution

$$\frac{n_i}{n_0} = e^{-\frac{\varepsilon_i - \varepsilon_0}{k_B T}}$$



- thermally equilibrated system: T = const

n_0 – occupation number of energy level ε_0
n_i – occupation number of energy level ε_i
k_B – Boltzmann constant

$\varepsilon_i > \varepsilon_0$

$k_B, T > 0$

$\frac{\varepsilon_i - \varepsilon_0}{k_B T} > 0$

- at higher temperatures higher energy levels are more populated

Could we increase the temperature such, that $n_i > n_0$?

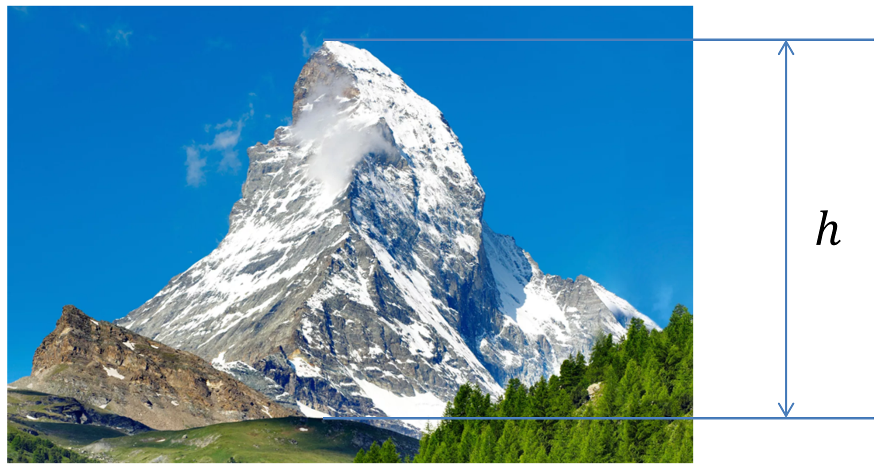
NO! T[K] can not be < 0!

It is not possible have population inversion in a two level system!

Boltzmann-distribution
examples

1. Barometric height formula – eg. the concentration of oxygen (number of molecules in unit volume) decreases in function of height

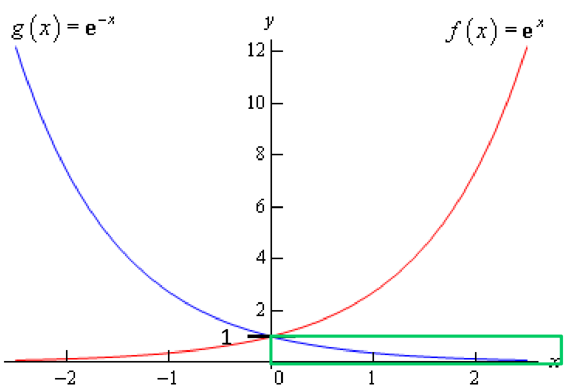
$$\frac{n_h}{n_0} = e^{-\frac{mgh}{k_B T}}$$



n_h - concentration at height h

h

n_0 - concentration at the reference height

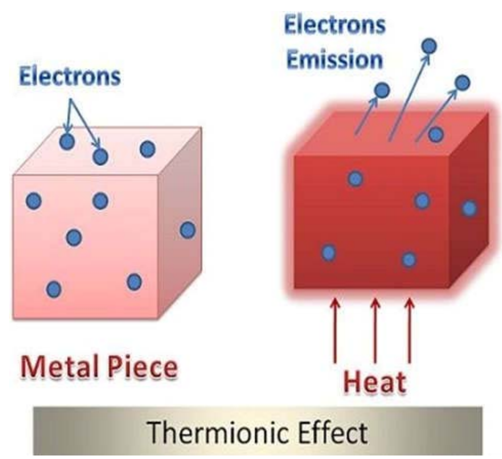


$h \nearrow \qquad n_h \searrow$

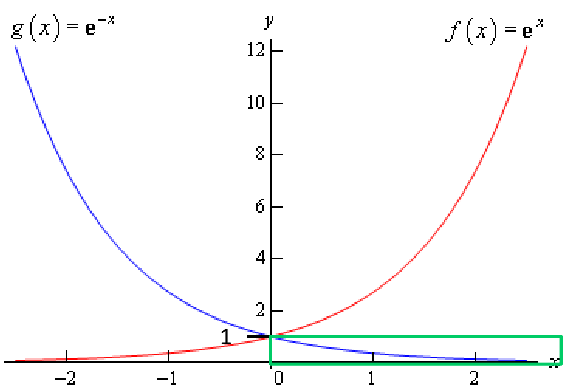
Boltzmann-distribution
examples

2. Thermal emission of metals – upon heating the electrons leave the metal (eg. cathode of the X-ray tube, cathode of the photomultiplier tube).

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



N_i - number of emitted electrons
W_a – work needed by the e⁻ to leave the metal lattice



$T \nearrow \qquad n_i \nearrow$

Boltzmann-distribution
examples

3. Nerst equation

If there is a voltage between point A and B (e.g. in a cell), then the concentration of charged particles (n_A, n_B) at these points are given by:

$$\frac{n_A}{n_B} = e^{-\frac{qU}{k_B T}}$$

q- elementary charge
U− voltage between A and B

OR

If the concentration of charged particles is different at two points (n_A, n_B), then an electrical voltage (U) arises between these two points with a value of:

$$U = \frac{k_B T}{q}\, ln \frac{n_A}{n_B}$$

The formula describes the distribution of concentrations in cells, the resting potential.

Walther Nerst (1864-1941)

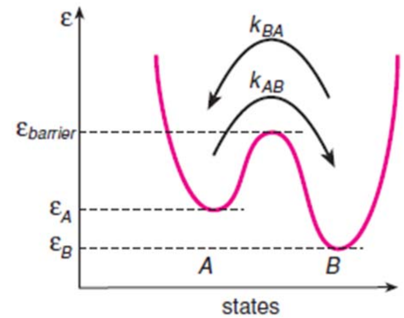
Nobel-prize (1920)

Boltzmann-distribution
examples

4. Equilibrium, rate of chemical reactions

The *equilibrium* (distribution among the states) and
rate (speed of transition between the states) of a reaction follow Boltzmann distribution.

reaction: $A \rightleftarrows B$



equilibrium constant: $\mathrm{K} = \frac{n_A}{n_B} = e^{-\frac{\varepsilon_A - \varepsilon_B}{k_B T}}$

rate constants: $k_{AB} = \omega \cdot e^{-\frac{\varepsilon_{barrier} - \varepsilon_A}{k_B T}}$ $\quad k_{BA} = \omega \cdot e^{-\frac{\varepsilon_{barrier} - \varepsilon_B}{k_B T}}$

ratio of the rate constants = equilibrium constant:

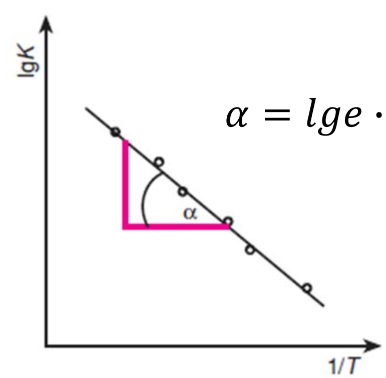
$$\frac{k_{BA}}{k_{AB}} = \frac{\omega \cdot e^{-\frac{\varepsilon_{barrier} - \varepsilon_B}{k_B T}}}{\omega \cdot e^{-\frac{\varepsilon_{barrier} - \varepsilon_A}{k_B T}}} = e^{-\frac{\varepsilon_{barrier} - \varepsilon_B}{k_B T} + \frac{\varepsilon_{barrier} - \varepsilon_A}{k_B T}} = e^{-\frac{\varepsilon_A - \varepsilon_B}{k_B T}} = K$$

Savante Arrhenius (1859-1927)

Nobel-prize (1903)

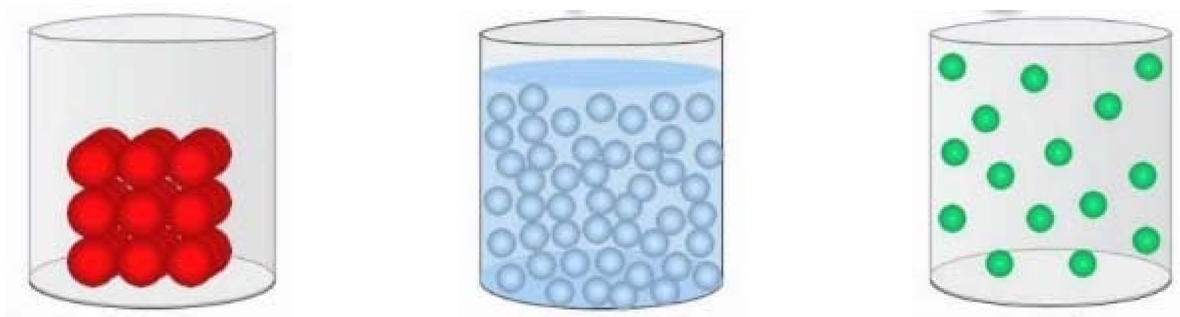
$$K = e^{-\frac{\varepsilon_A - \varepsilon_B}{k_B T}}$$

$$lgK = -lge \cdot \frac{\varepsilon_A - \varepsilon_B}{k_B} \frac{1}{T}$$



$$\alpha = lge \cdot \frac{\varepsilon_A - \varepsilon_B}{k_B}$$

Gases, liquids, liquid crystals and solids

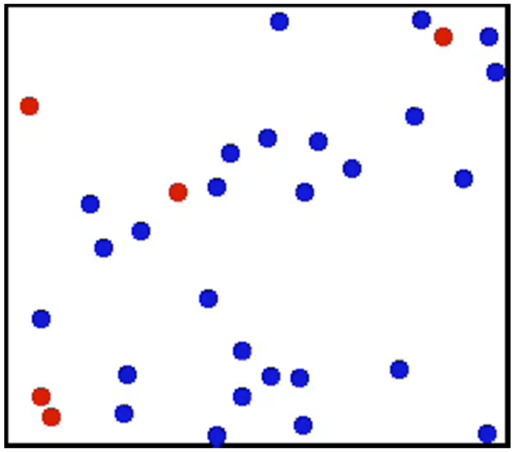


Solid (crystals)	Liquid	Gas
long-range order	short-range order	no order
rigid	not rigid	not rigid
fixed shape	no fixed shape	no fixed shape
fixed volume	fixed volume	no fixed volume

Gases

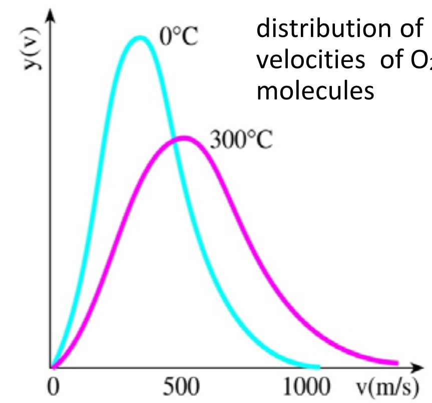
The ideal gas

- Composed of a large number (Avogadro number) of particles with identical masses.
- Particles are point-like, their volume is negligible.
- There is no interaction between the particles.
- They collide elastically with each other and with the wall of the container (sum of energies is constant).
- Particle motion follows the laws of classical (Newtonian) mechanics.



The ideal gas

Maxwell velocity distribution



distribution of velocities of O_2 molecules

Average energy of a particle:

Equipartition theorem: in a system of thermal equilibrium (T=const) the total energy is distributed in such a way that an average of ½ k_BT energy corresponds to each degree of freedom.
- translational motion: 3 degrees of freedom:

$$\frac{1}{2}m\langle v^2\rangle = \frac{3}{2}k_BT$$

Upon increasing temperature:
- the average of the absolute value of molecular velocities increases
- the width of the distribution increases

Internal energy of a system containing *N* particles:

$$E_{internal} = \frac{3}{2}Nk_BT$$

Universal gas law (state equation) - relationship between the parameters characterizing the state of the gas (pressure, volume, temperature and number of particles):

$$pV = Nk_BT$$

P = pressure (Pa)
V = volume (m^3)
R = gas constant (8.314 $JK^{-1}mol^{-1}$)
T = absolute temperature (K)
N = number of particles
k_B = Boltzmann's constant

Gases

The ideal gas

- Particles no point-like, their volume is negligible.
- There is no interaction between the particles.
- State equation:

$$pV = Nk_BT$$

The real gas

- Particles are not point-like, their volume (b) is not negligible.

$$V - Nb$$

- Interactions (a) arise between the particles.

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

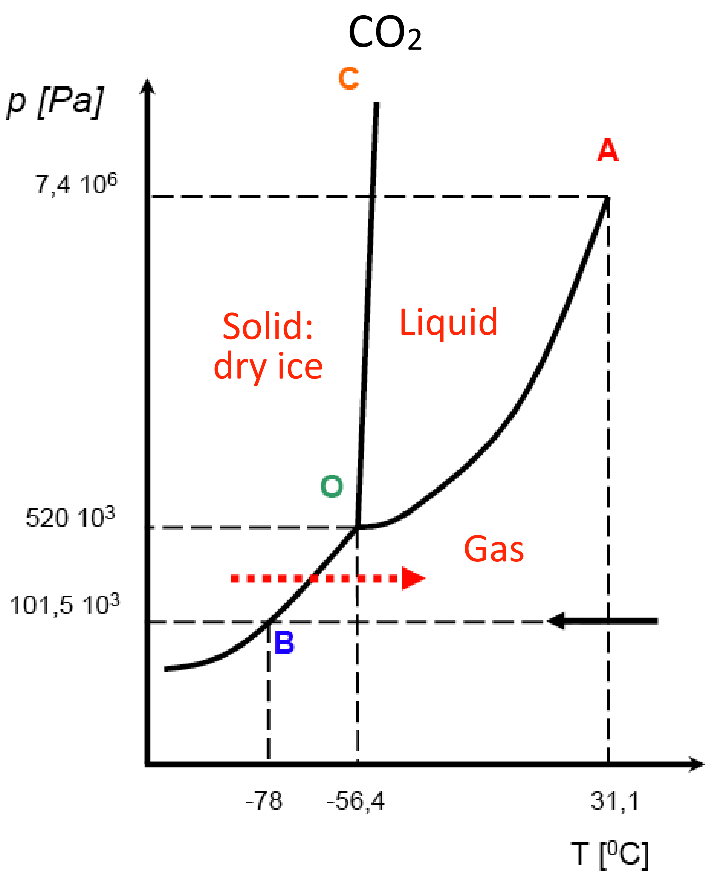
- Van der Waals state equation:

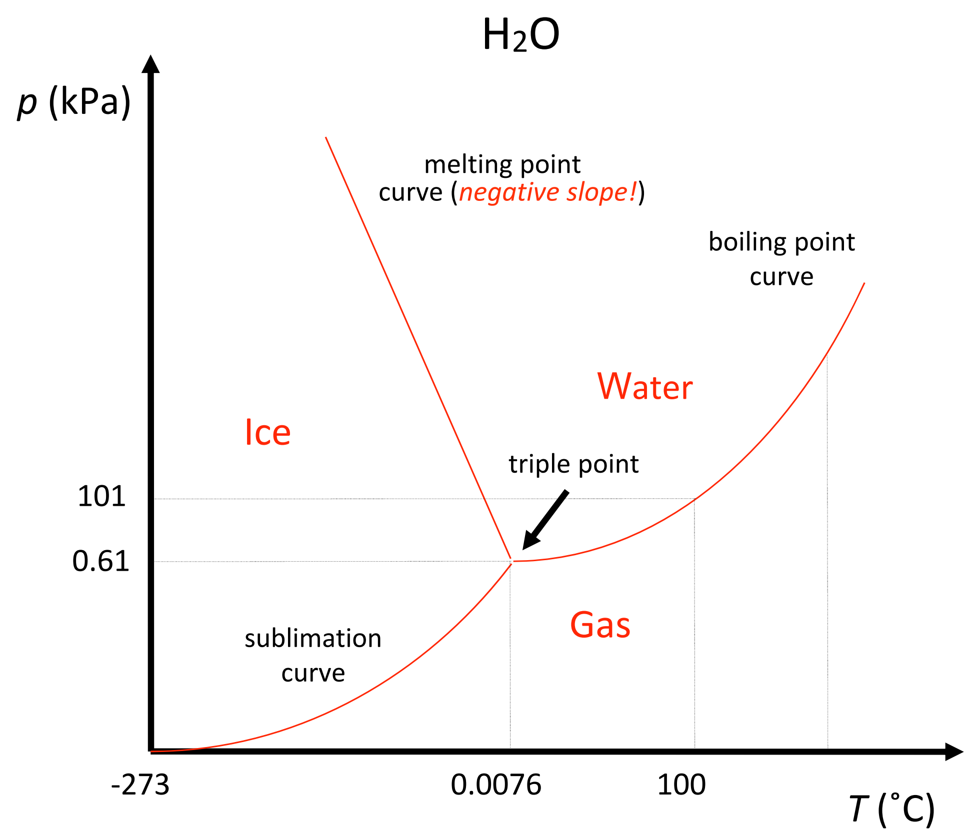
$$\left(p + a\frac{N^2}{V^2}\right)(V - Nb) = Nk_BT$$

P = pressure (Pa)
V = volume (m^3)
T = absolute temperature (K)
N = number of particles
k_B = Boltzmann's constant

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

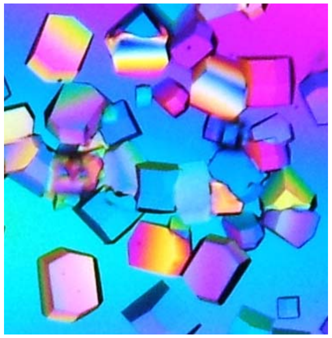




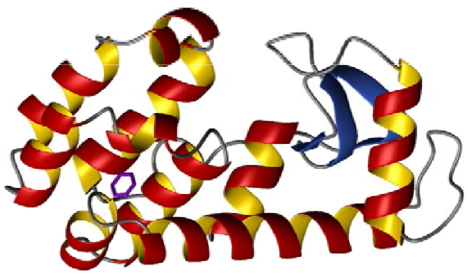
Solids

A. Crystalline materials

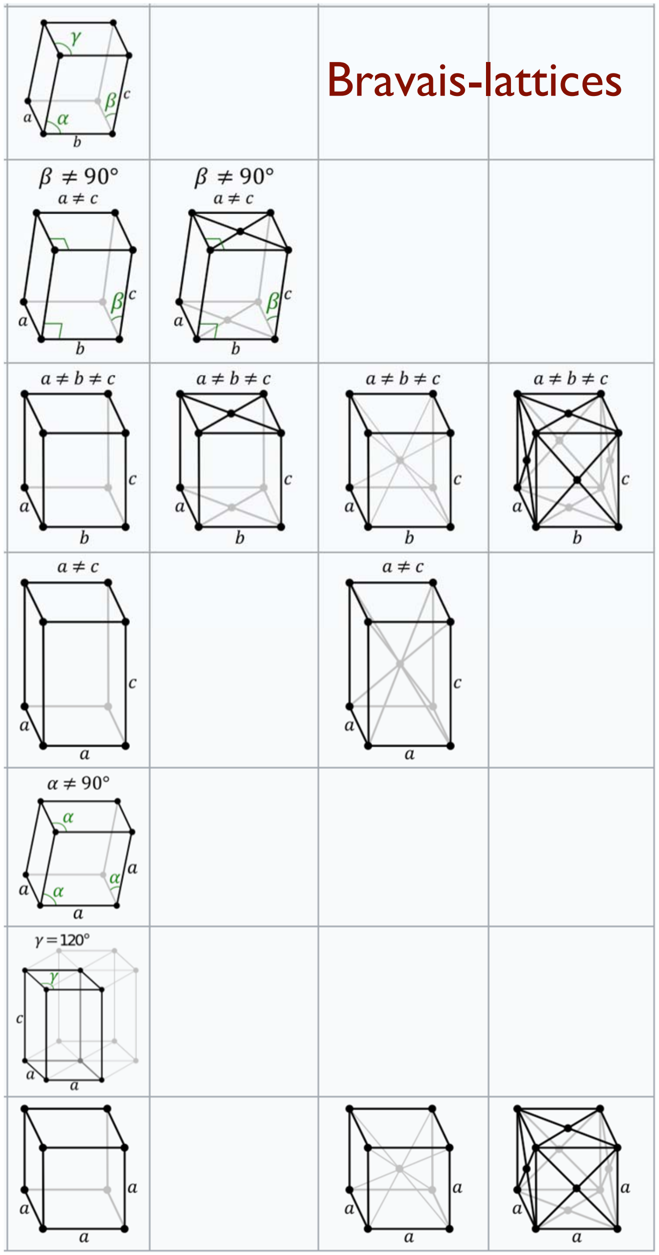
- Periodic long-range order
- Lattice - elementary cell (in nature 14 different, "Bravais-lattices")
- According to the nature of interactions (bonds) of the structural elements:
  -covalent bond: atomic lattice (Si)
  -ionic bond: ionic lattice (NaCl)
  -metallic bond: metal lattice (positive ions)
  -secondary bonds: molecular lattice (molecules eg. lysozyme)



Lysozyme protein crystals in polarized light (anisotropy)



Lysozyme protein molecule



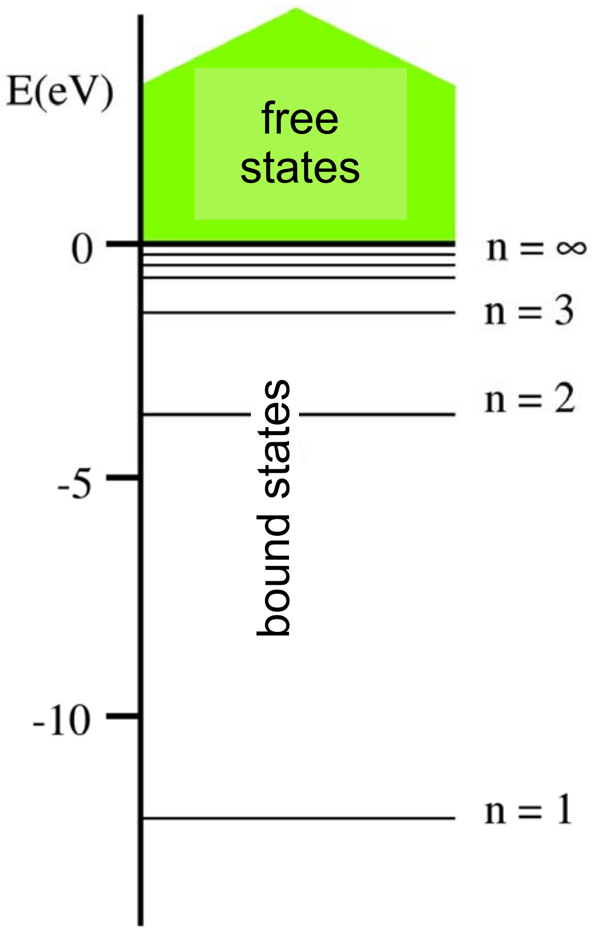
B. Amorphous materials

glass-like, viscous "fluids"

Energy levels in crystals

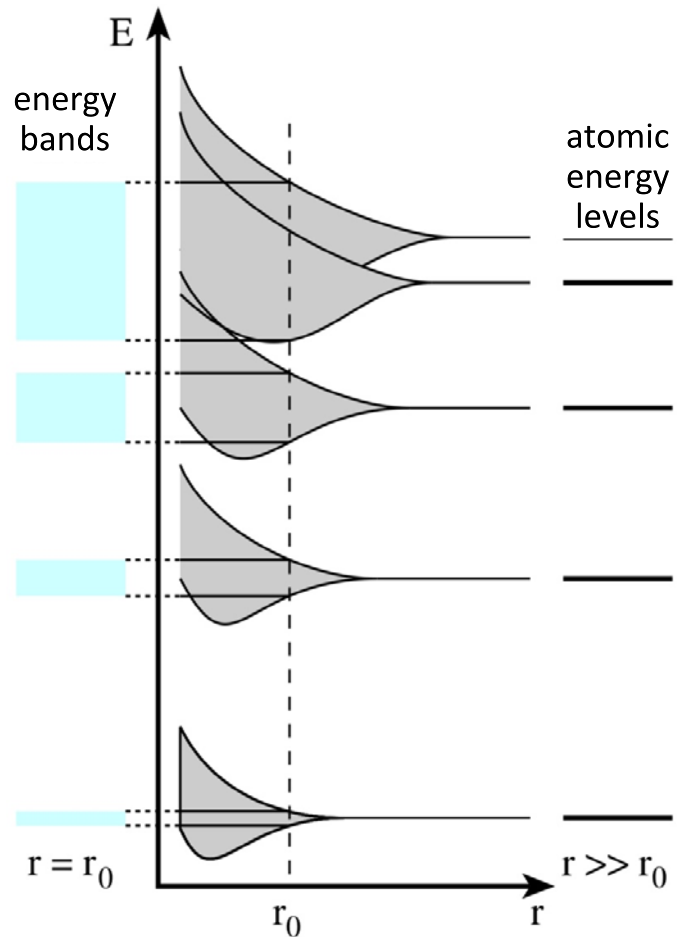
Isolated hydrogen atom

- No interaction with other atoms
- Discrete (quantized) energy levels
- Pauli's principle: there can not be two electrons bound to the same atom with all 4 quantum numbers being identical



Crystal

- Atoms interact
- consequence of Pauli's principle: in order to avoid identical quantum states, the discrete atomic energy levels of interacting atoms split, forming: energy bands
- Nearby levels merge into energy bands



Solids with different band structure

Completely saturated | Unsaturated

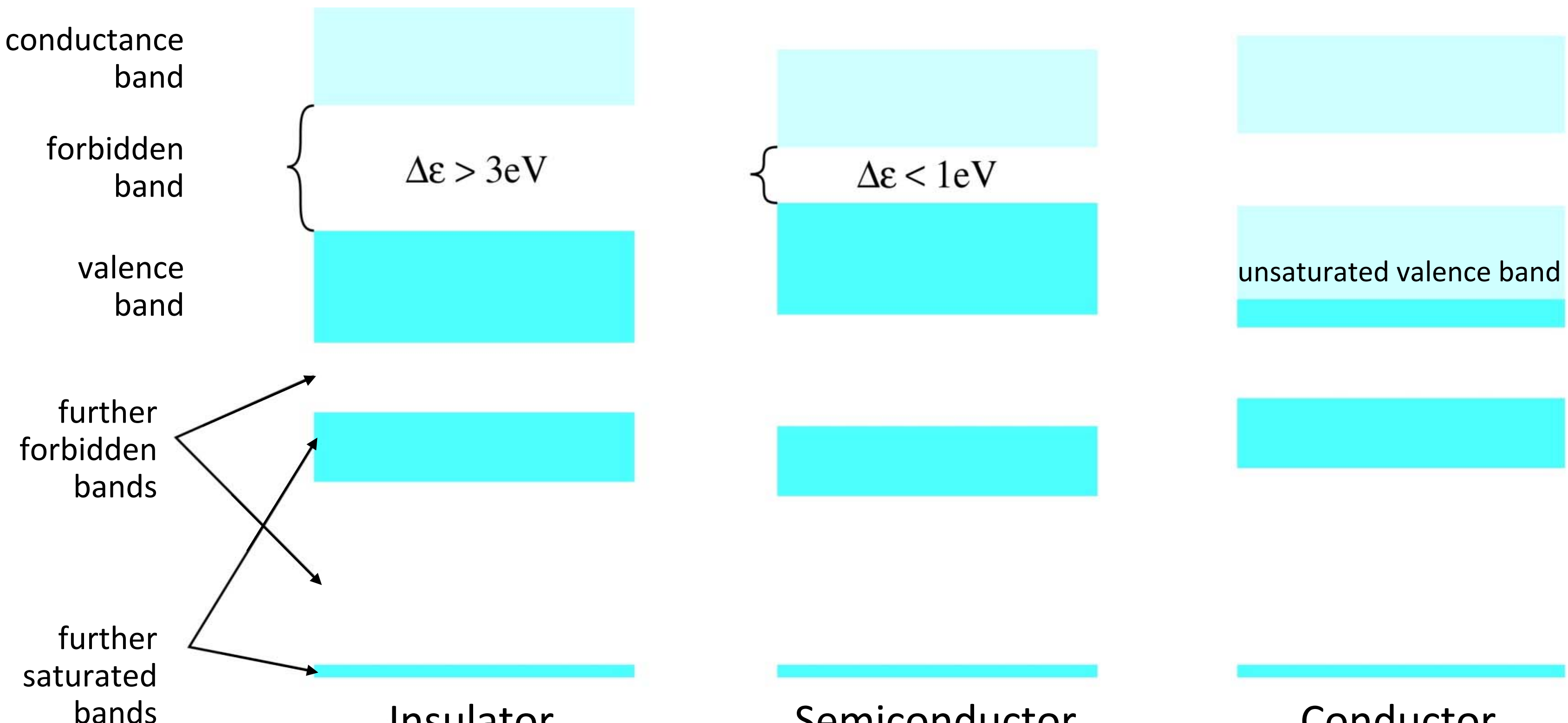
@T=300 K, $k_B T$~0.023 eV

$\Delta\varepsilon \gg kT$

$\Delta\varepsilon > kT$
by 1-2 order

$$\frac{n_{conduct}}{n_{valence}} = e^{-\frac{\Delta\varepsilon}{k_B T}}$$

Conductance:
$$\sigma \sim \frac{1}{T}$$



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

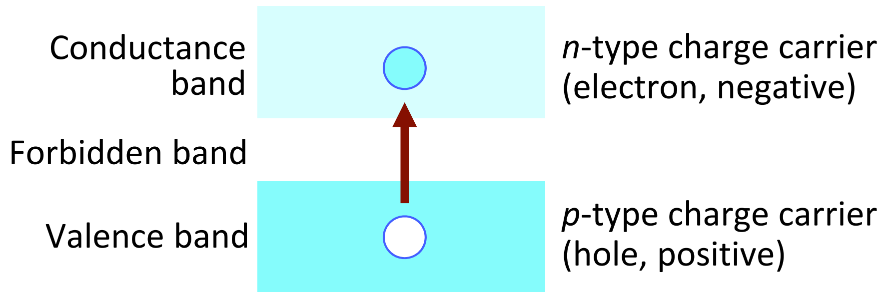
Conductor

- No forbidden band: good electrical conductor
- Not transperent

Semiconductors

A. Pure semiconductors

- Two types of charge carriers (*n, p*):



- Electrical conductance is temperature-dependent: $\sigma = konst \cdot e^{-\frac{\Delta\varepsilon}{2k_B T}}$

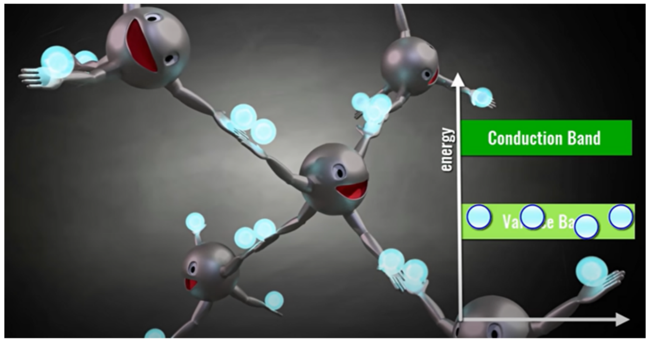
- Width of forbidden band ($\Delta\varepsilon$) <1 eV

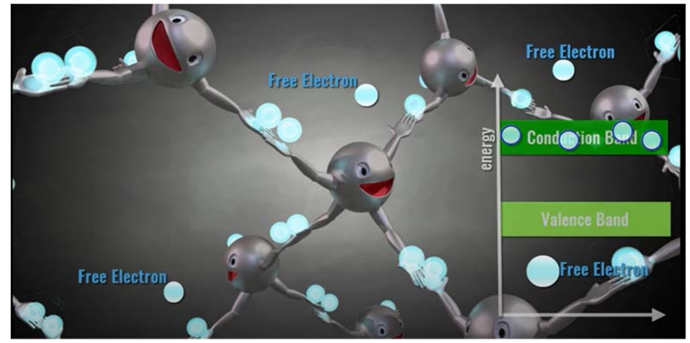
- Crossing of forbidden band may be evoked by the absorption of visible light (1.5-3 eV):

- Forbidden band may be crossed by thermal activation $hf_{vis} > \Delta\varepsilon$

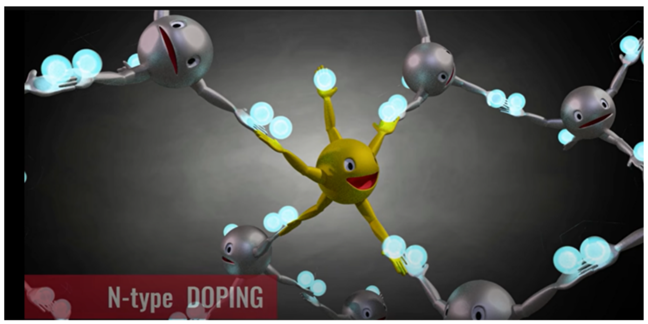
- Optically not transparent

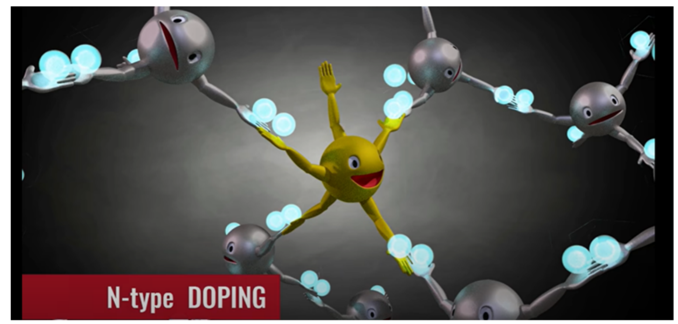
Si


energy
Conduction Band


Free Electron
Free Electron
energy
Valence Band
Free Electron

Si


N-type DOPING


N-type DOPING

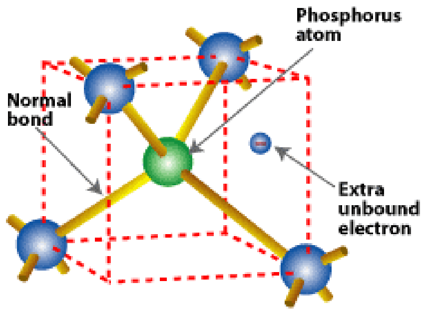
Si - P

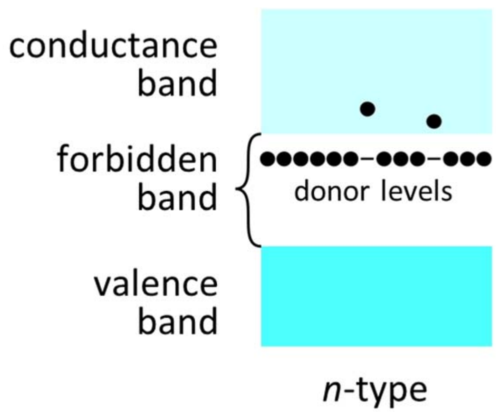
Semiconductors

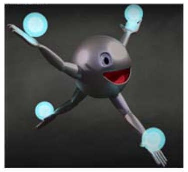
B. Doped semiconductors

Dopant: - small number of foreign atoms in between the host atoms of the lattice: $\frac{N_{host}}{N_{dopant}} \approx 10^6$
- provides a new electron state that narrows the forbidden band

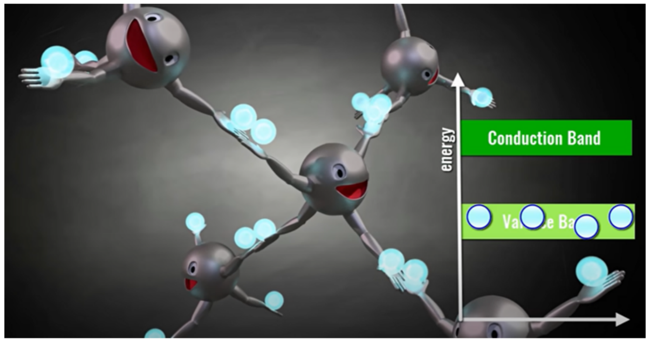
n-type semiconductor (*e*-donor): 5-valence dopant (P, As, Bi) in a 4-valence host (Si, Ge)

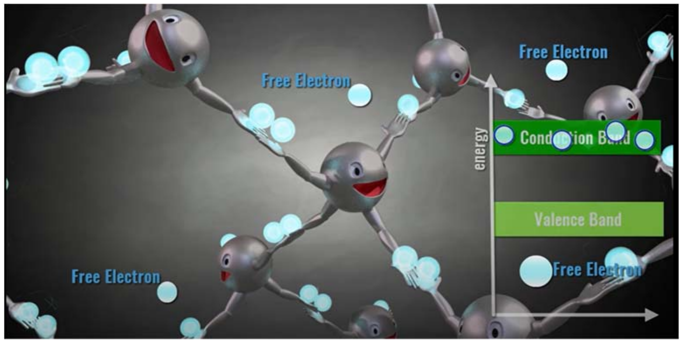




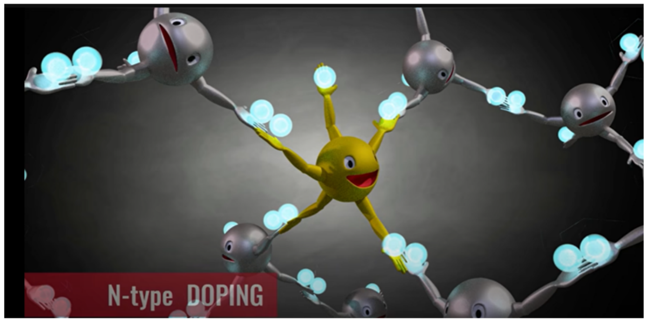


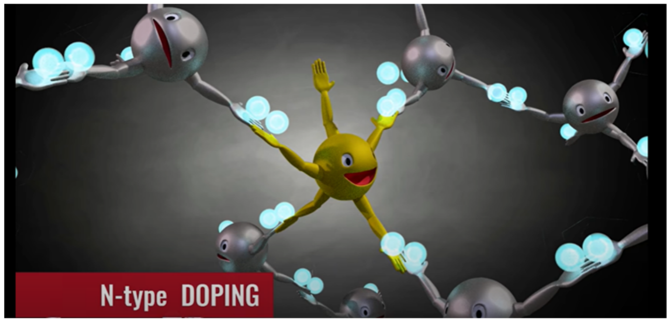
Si



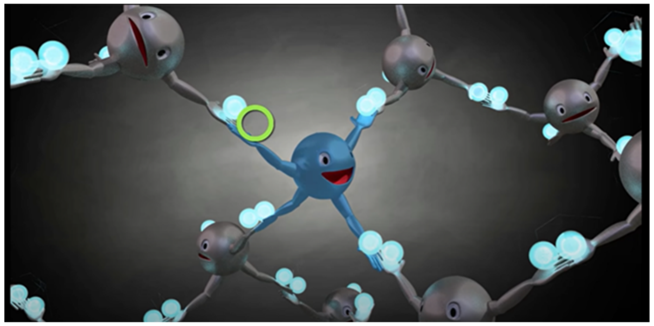


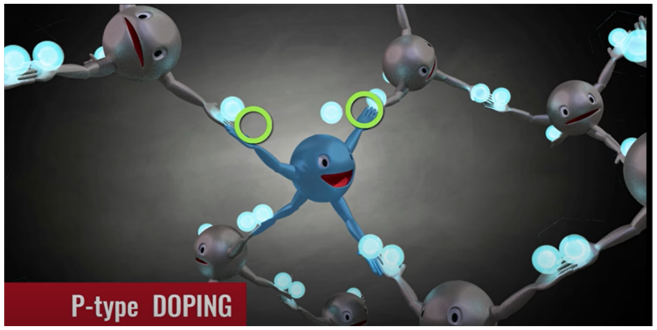
Si





Si - P





Si - B

https://www.youtube.com/watch?v=7ukDKVHnac4

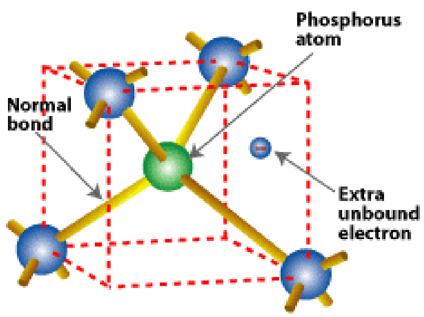
Semiconductors

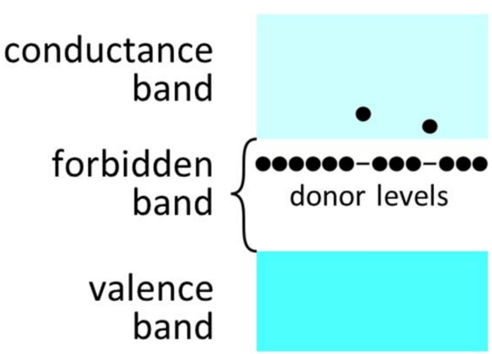
B. Doped semiconductors

Dopant: - small number of foreign atoms in between the host atoms of the lattice:
- provides a new e^- state that narrows the forbidden band

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

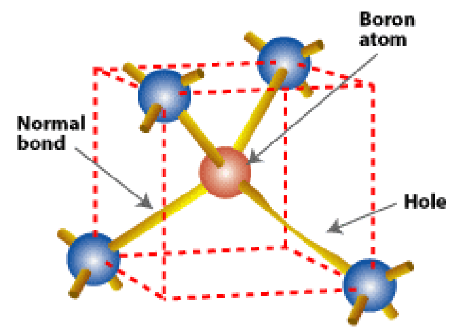
n-type semiconductor (*e*-donor): 5-valence dopant (P, As, Bi) in a 4-valence host (Si, Ge)

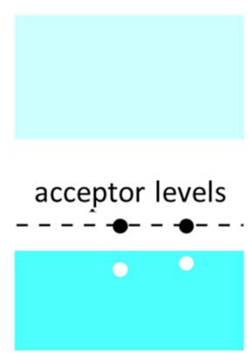




n-type

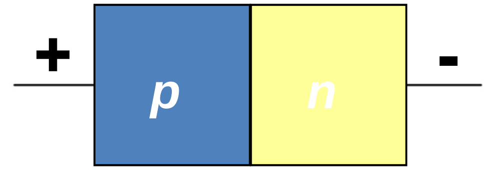
p-type semiconductor (*e*-acceptor): 3-valence dopant (Al, Ga, In, B) in a 4-valence host (Si, Ge)

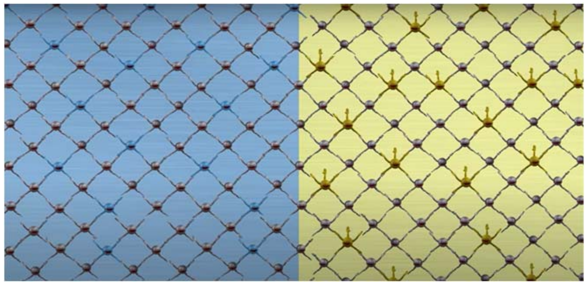


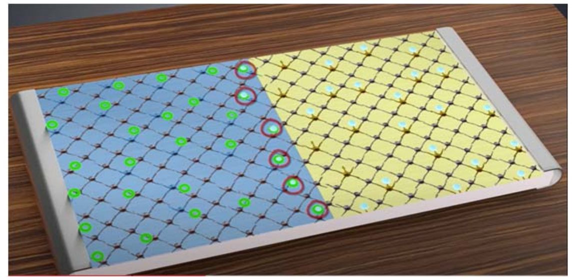


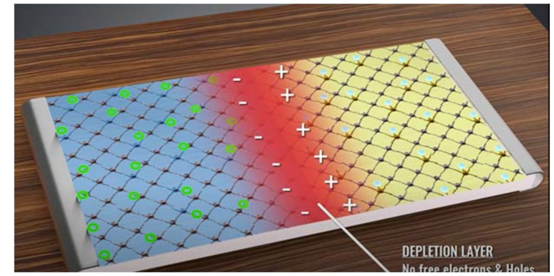
p-type

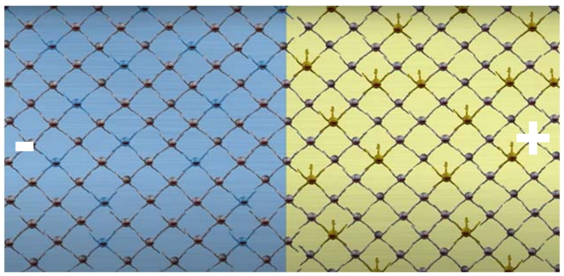
Diode - microelectronic devices constructed by adjoining doped, *p*- and *n*-type semiconductors

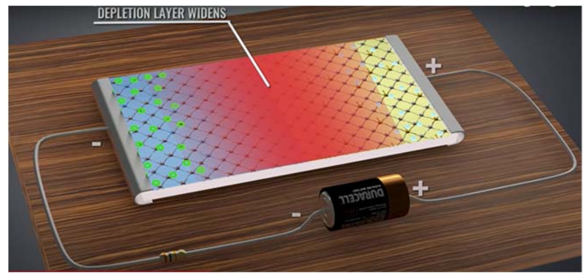






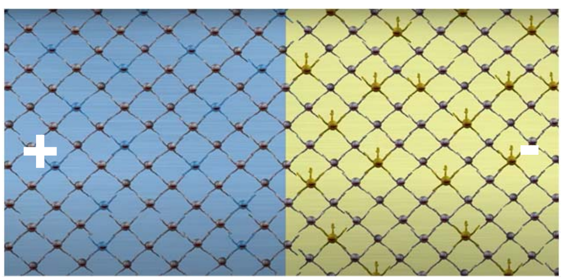


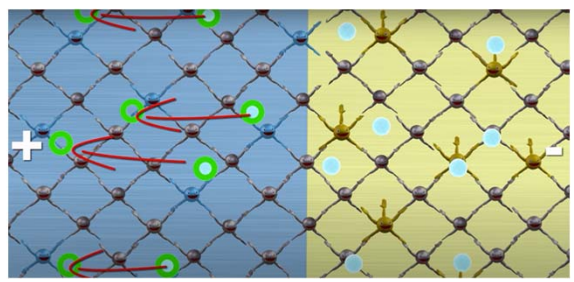




- reverse biasing

- asymmetric conductance

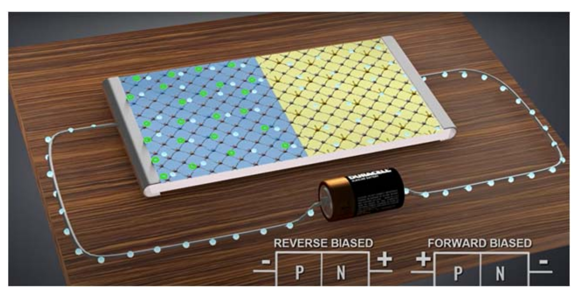




- forward biasing

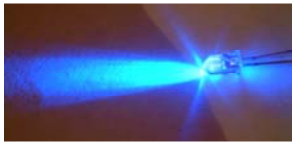
Usage:

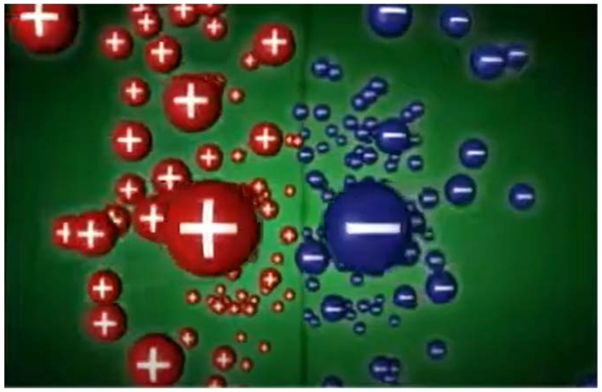
- electrical voltage → light emission, LED
- illumination → voltage → CCD pixel

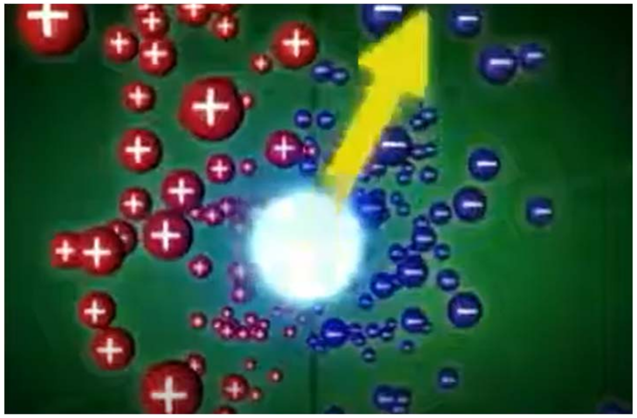


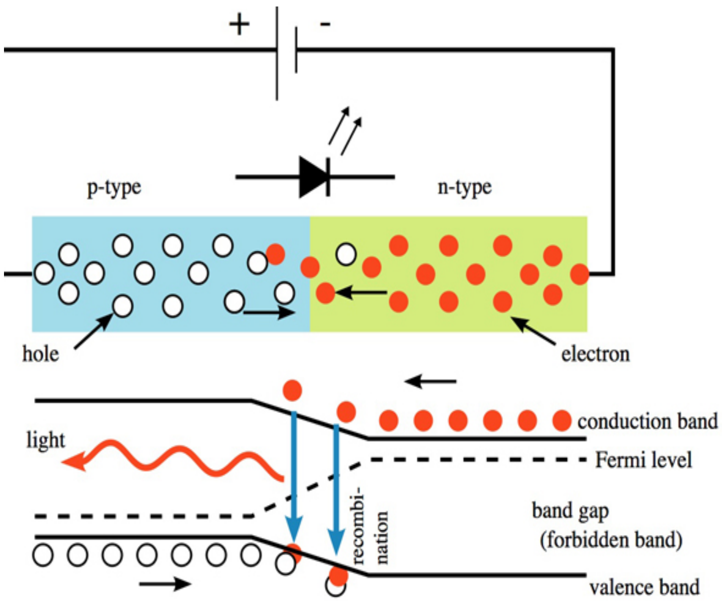
https://www.youtube.com/watch?v=7ukDKVHnac4

Light Emitting Diode (LED)





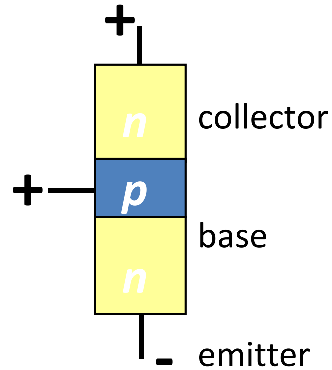


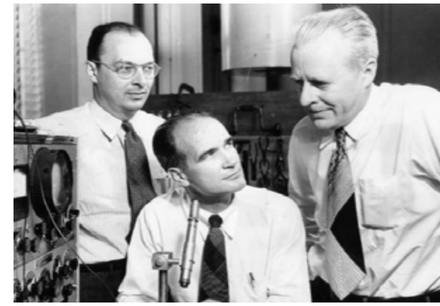


Isamu Akasaki, Shuji Nakamura, Hiroshi Amano, Nobel-prize 2014

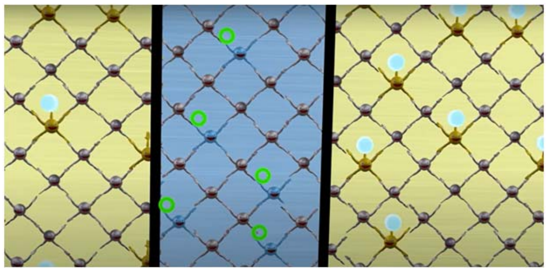
Transistor

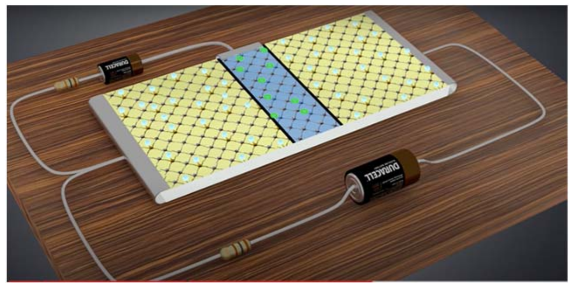
Smart phone processor:

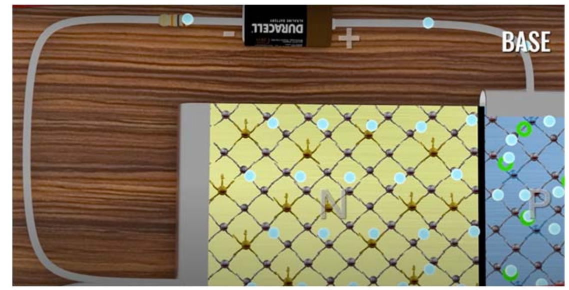


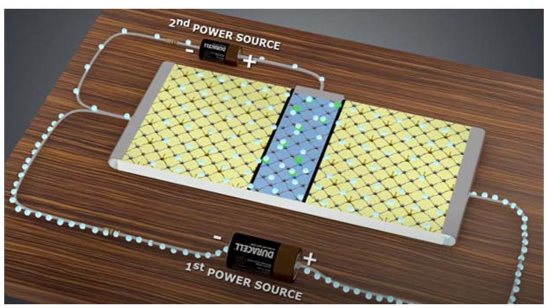


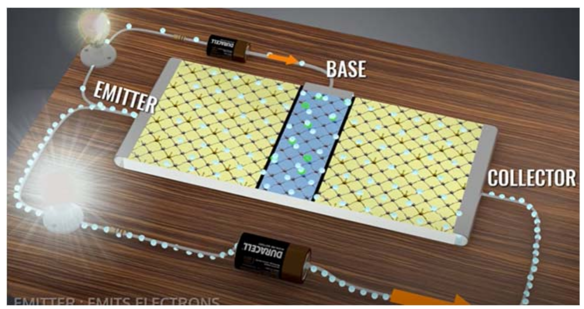
John Bardeen, William Shockley, Walter Brattain, Nobel-prize 1956

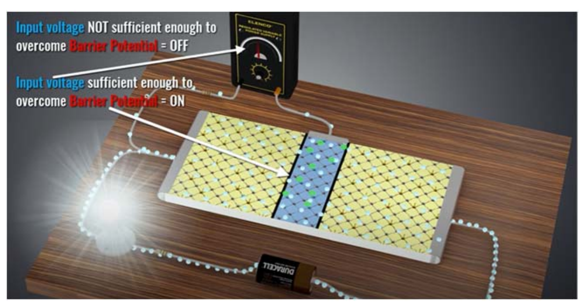










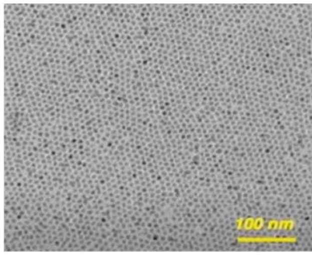


Usage

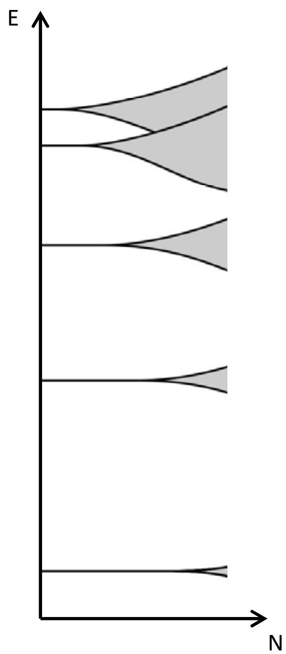
- amplifier
- elements of digital memory
- counters, multivibrators

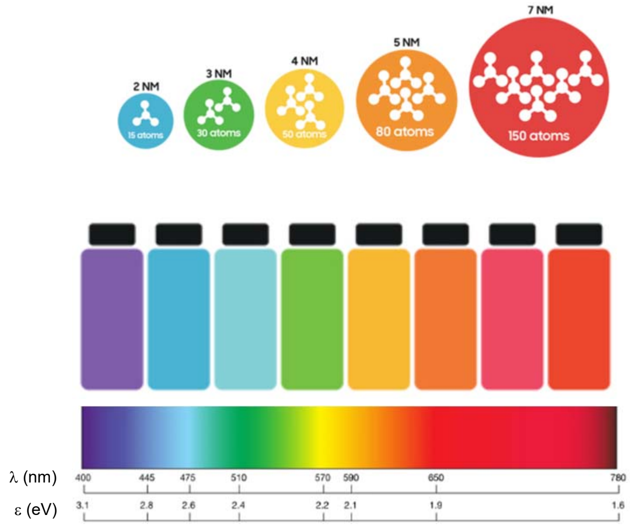
https://www.youtube.com/watch?v=7ukDKVHnac4

Quantum dots:



- very small (nm size) semiconductors, made of 100-1000 of atoms.
- their size determines their properties: the energy of the emitted light depends on the size of the quantum dot.
- the with of the forbidden band determines the energy (colour) of the fluorescent light.
- the energy is inversely proportional to the size of the quantum dot.





Usage:
- imaging in cells (they are the same size as proteins),
- lasers, microscopes
- medical imaging, TV-QLED

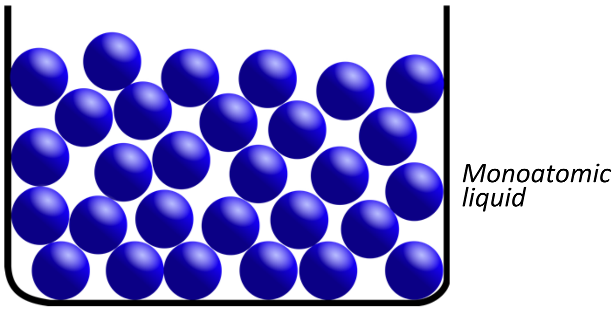
Moungi G. Bawendi, Louis E. Brus, Alexei I. Ekimov
Nobel-prize in chemistry 2023

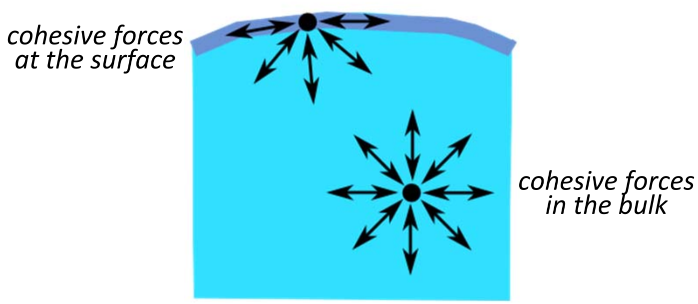
Liquids

- 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:

$$\eta \sim e^{\frac{E}{k_B T}}$$

Viscosity decreases with increase in the relative concentration of vacancies.

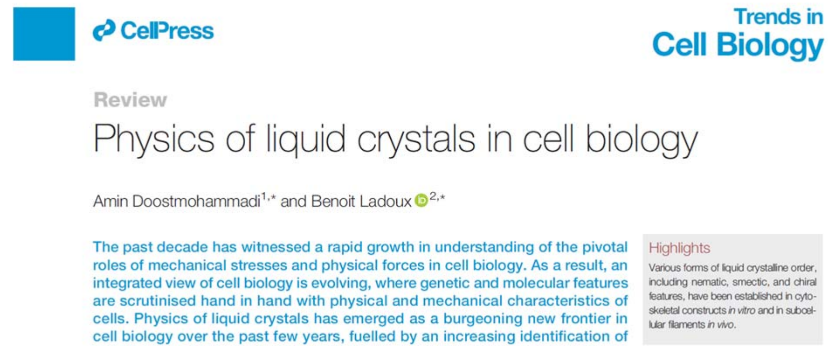




- Microscopically: composed of particles (atoms, molecules) held together by short-range cohesive forces (no long-range order)
- Imbalance of cohesive forces (between bulk *versus* surface) results in surface tension (tendency to contract into spherical shape)

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


CellPress
Trends in Cell Biology
Review

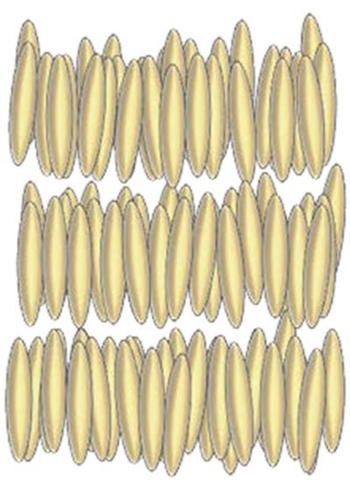
Physics of liquid crystals in cell biology

Amin Doostmohammadi[1,*] and Benoit Ladoux[2,*]

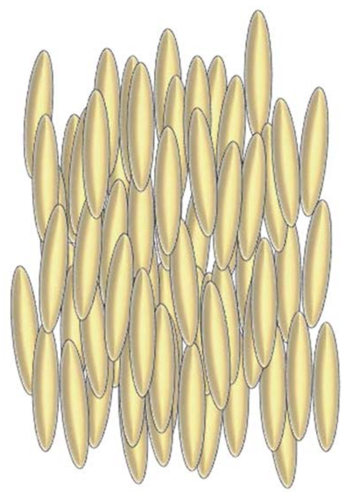
The past decade has witnessed a rapid growth in understanding of the pivotal roles of mechanical stresses and physical forces in cell biology. As a result, an integrated view of cell biology is evolving, where genetic and molecular features are scrutinised hand in hand with physical and mechanical characteristics of cells. Physics of liquid crystals has emerged as a burgeoning new frontier in cell biology over the past few years, fuelled by an increasing identification of

Highlights

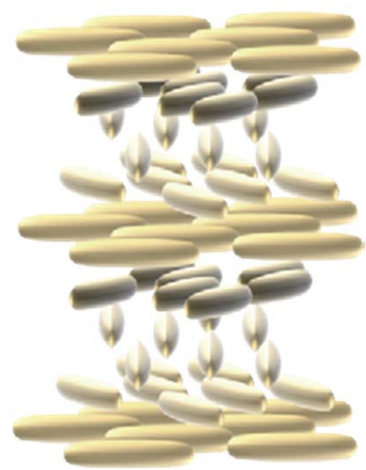
Various forms of liquid crystalline order, including nematic, smectic, and chiral features, have been established in cyto-skeletal constructs *in vitro* and in subcel-lular filaments *in vivo*.



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)

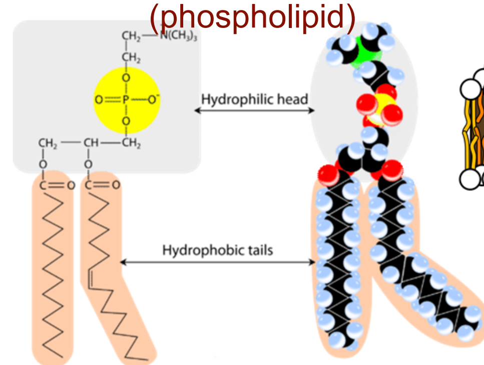
- Color changes with temperature (thermo-optical properties) – cholesteric liq. cryst; application: contact thermography
- If molecules are electrical dipoles, polarization, transmittance changes with electrical field (electro-optical properties) – nematic liq. cryst; application: LCD displays, etc.

Contact thermography

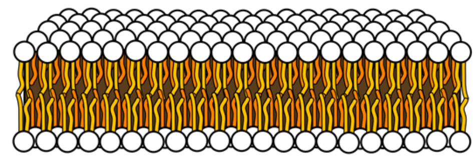
LCD display

Lyotropic
(order depends on concentration of the components)

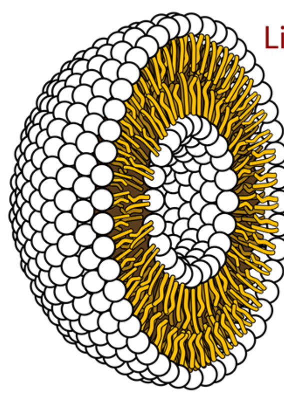
Amphiphilic molecule (phospholipid)



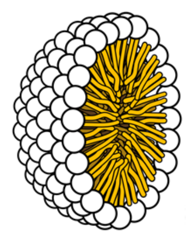
Bilayer sheet



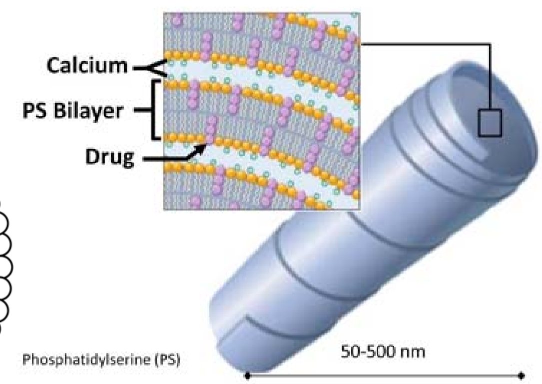
Liposome



Micelle

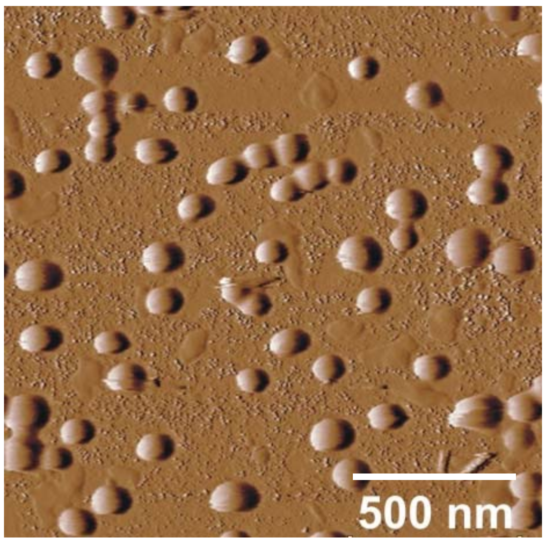


Cochleate

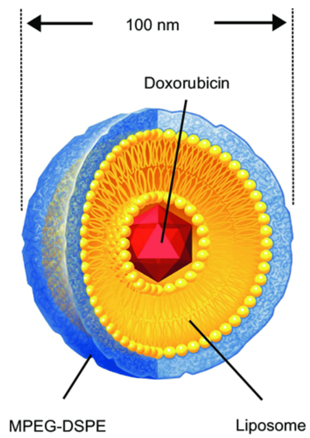


Liposome applications

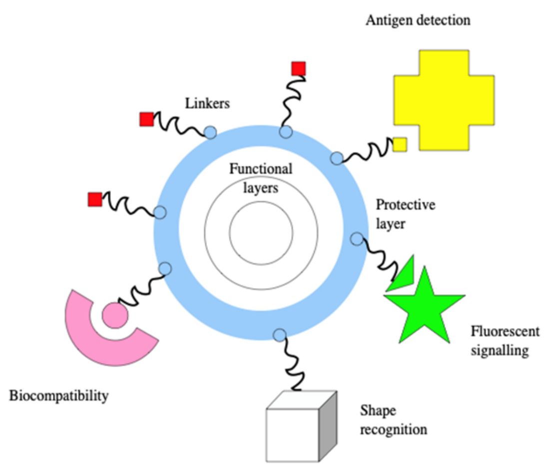
AFM image of liposomes on substrate surface



Liposome as carrier of toxic drug



“Intelligent” liposome



Teranostics
(therapy + diagnostics)