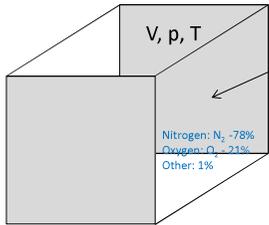


Describing many-particle systems

Prof. Judit Fidy
2017, October 16

- particle: - atom, atomic group
- molecule
- molecular complexes, macromolecules
- etc.
- 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 ?

Macrostate:

Described by parameters that characterize the whole system (p, V, T, N)

Microstate:

Given by a set of the parameters of all individual distinguishable particles in the system (position, velocity etc. for each)

One given macrostate can be realized by numerous varieties of microstates.



Ludwig Eduard Boltzmann
1844-1906, Austrian physicist



$\Omega \Leftrightarrow W$

II. Law of Thermodynamics: in isolated systems, spontaneous processes driving toward equilibrium are of **- increasing Entropy**

No heat exchange
No particle exchange of **- increasing „probability“ ?**

„Equilibrium“ state: of highest **Entropy** or highest **„probability“**

L.E. Boltzmann defines the absolute value of Entropy „S“

Definition of „thermodynamic“ probability of a macrostate = number of ways how microstates can produce the same macrostate: Ω

$$S = k \ln \Omega$$

$k = 1.38 \times 10^{-23} \text{ J K}^{-1}$
Boltzmann constant

„ln“ logarithmus naturalis – e-based logarithm
 $e^{\ln \Omega} = \Omega$ $\ln x = \frac{\log x}{\log e}$
„e“ natural base number: Euler-number / Napier constant
 $(1 + \frac{1}{n})^n \xrightarrow{n \rightarrow \infty} e$
 $e = 2,718\ 281\ 828\ 459\ 045\ 235\ 360\ 287\ 471\ 35\dots$

Statistical definition of the absolute value of Entropy!

III. Law of Thermodynamics

The **Entropy** of a chemically pure (of one component) crystalline (totally ordered) system is **zero at T=0 K**.

Direct consequence of Boltzmann's statistical definition of the Entropy:

$$S = k \ln \Omega$$

There is only **one** kind of microstate that results in a totally ordered, chemically pure system, and total order exists only at T=0 →

$$\text{if } \Omega = 1 \rightarrow S = 0 \quad (e^{\ln \Omega} = \Omega \quad \Omega = 1 \quad \ln \Omega = 0)$$

The many-particle system of kinetic gas theory: **ideal gas**

- composed of point-like particles
- no interaction between the particles – no bond formation
- only kinetic energy, that is distributed according to the distribution of the velocities
- the average kinetic energy is determined by the temperature
- only straight, translational motion
- elastic collisions with the wall and with each other

Description of the particle distribution on the possible „v“ microstates in ideal gas which is in thermal equilibrium at T temperature

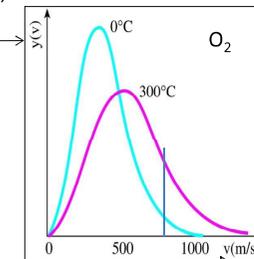
Maxwell-Boltzmann distribution:

Maxwell 1859
Generalized by Boltzmann :1877
Derived by statistical physics and kinetic gas theory: Gibbs 1902

$f(v)$ – probability of finding particles with a velocity „v“ in the system (probability density function):

$$f(v) = \sqrt{\frac{2}{\pi}} \left(\frac{m}{kT}\right)^{3/2} v^2 e^{-\frac{mv^2}{2kT}}$$

Graphical representation



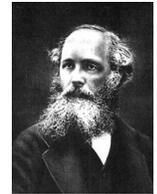
Mathematical description of the kinetic gas theory – interpretation of pressure, temperature

$$E_{total} = N \frac{1}{2} m \langle v^2 \rangle_{average} \quad \epsilon_i = \frac{1}{2} m v_i^2$$

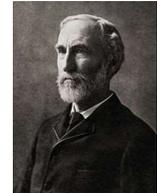
$$\frac{1}{2} m \overline{v^2} = \frac{3}{2} kT$$

$$pV = NkT = nRT$$

ϵ_i – energy of one particle
 m – mass of one particle
 n – mole number
 N – total number of particles



James Clerk Maxwell
1831 –1879



Josiah Willard Gibbs
1839 –1903

Boltzmann distribution function (or Gibbs-distribution)

Describes the probability of finding particles with ϵ_j energy in the system

ϵ_j energy is now generalized

(If ϵ_i is the kinetic energy of one particle, one obtains the M-B distribution.)

The system:

N distinguishable independent particles at thermal equilibrium at non-zero temperature, with E total energy and N total number of particles

$$N = \sum_j N(\epsilon_j) = \sum_j n_j \quad E = \sum_j n_j \epsilon_j$$

Macrostate: given by the **number of particles at each energy level:**

{ $n_1, n_2, n_3, \dots, n_k, \dots$ }

Microstate: **which** of the particles are at the individual levels

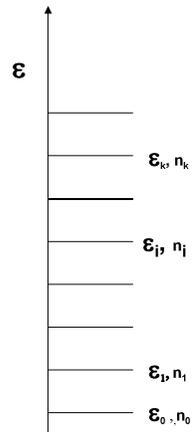
$$p(\epsilon_j) = \frac{N(\epsilon_j)}{N} = \frac{n_j}{N} = \frac{1}{A} e^{-\frac{\epsilon_j}{kT}}$$

constant

ϵ_j possible energy status of one particle:
potential or kinetic energy
 n_j number of particles having ϵ_j energies,
Population number

Boltzmann distribution function (or Gibbs-distribution)

yields the number of particles (n_j) with ϵ_j energy in a system of $E = \sum_j n_j \epsilon_j$ total energy.



In practice applications the relative probability is more interesting

$$\frac{p(\epsilon_k)}{p(\epsilon_j)} = \frac{\frac{n_k}{N}}{\frac{n_j}{N}} = \frac{\frac{1}{A} e^{-\frac{\epsilon_k}{kT}}}{\frac{1}{A} e^{-\frac{\epsilon_j}{kT}}}$$

$$\frac{n_k}{n_j} = e^{-\frac{\epsilon_k - \epsilon_j}{kT}} = e^{-\frac{\Delta \epsilon}{kT}}$$

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

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

M.-B. distribution is a special case with $\epsilon = 1/2mv^2$

Textbook p. 52 - 57

Understanding the Boltzmann distribution function

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

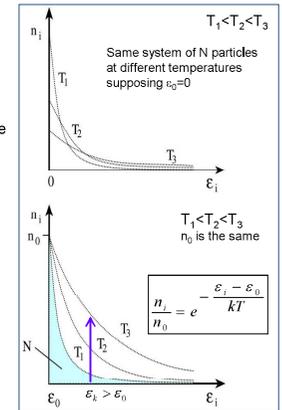
$$\frac{n_k}{n_j} = e^{-\frac{\epsilon_k - \epsilon_j}{kT}} = e^{-\frac{\Delta \epsilon}{kT}}$$

Populations of energy states – n_k : number of particles in ϵ_k energy state „distribution“ of particles is supposed

$$\frac{n_i}{n_0} = e^{-\frac{\epsilon_i - \epsilon_0}{kT}} = e^{-\frac{\epsilon_i}{kT}}$$

As the temperature is lowered, more and more particles are in the energy minimum state at $T=0$ all particles are there: $n_1=0, n_0=N$

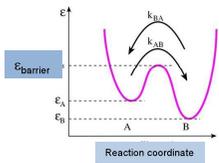
At a given $\epsilon_k > \epsilon_0$ energy level, the relative population related to the energy minimum increases with the temperature



Boltzmann distribution - practical examples

Equilibrium rate of chemical reactions

More examples in textbook:
Thermal emission of electrons from metals
Nernst equation p. 54-57



Reaction: $A \rightleftharpoons B$

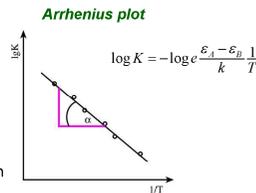
The k_{AB} and k_{BA} rates are proportional to the number of reactants which are higher in energy, reaching the top of the barrier

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

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

$$K = \frac{k_{BA}}{k_{AB}} = e^{-\frac{\epsilon_A - \epsilon_B}{kT}}$$

Experimental determination of the energy of activation



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 concept of Boltzmann distribution helps to understand the structure and properties of the classes of materials – a general rule in nature

1. Classes of materials with structural order.

Order is based on primary bonds

- solid crystalline materials
- ideal crystals → perfect, long range order
- real crystals

Order is based on secondary bonds

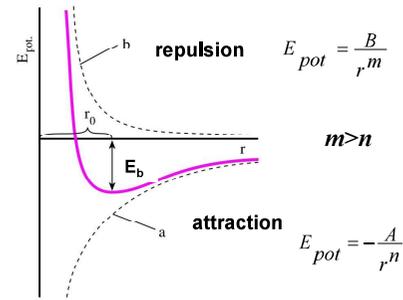
- liquid crystals → case of imperfect, long range order
- liquids → case of short range order

2. Gasous systems

- ideal gas → lack of order (no binding energy) in the structure
- real gases

1. Classes of materials with structural order.

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



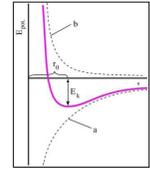
General concept of bond formation (applicable for all kinds of interactions)

r = distance of two atoms forming the bond
 r_0 = bond distance
 E_{bond} = bond energy

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

Examples for the functional form of attractive interactions

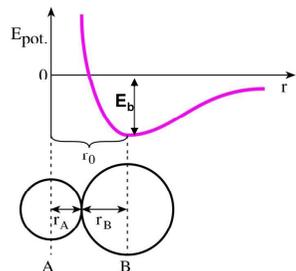
The distance dependence in the energy formulae of **electrostatic** interactions



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

↑ great variety ↓

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**)



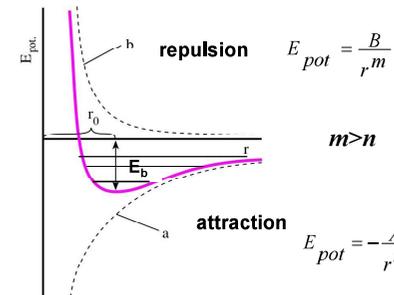
r_A, r_B atomic radii of atoms A and B

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⁻

„atomic radius“

1.2. Stabilizing binding energy ↔ statistical nature, Boltzmann distribution

General concept of bond formation ↔ some percentage of bonds may not be intact



r = distance of two atoms forming the bond
 r_0 = bond distance
 E_{bond} = bond energy

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

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

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

$$\Delta\epsilon \leftrightarrow kT$$

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

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

Bond energies in materials with structural order
Great variety!

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

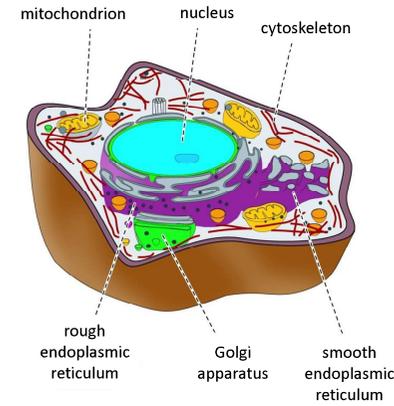
$E_b \sim$ **primary bonds**: covalent
 ionic
 metallic **2 – 10 eV/bond**

$E_b \sim$ **secondary bonds**

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

Great variety! Even 100-times differences!

Typical example for the variety of stabilizing energies:
structure of living „material“ : cells, tissues, organs,.....



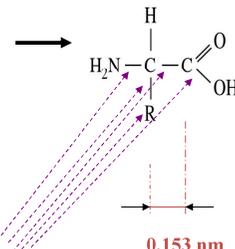
Hierarchy in

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

Atoms

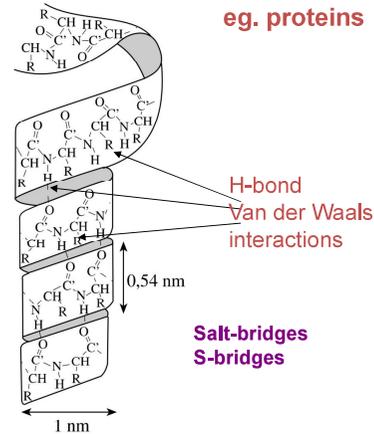
H
O
C
N
S
.
.
.

Molecules



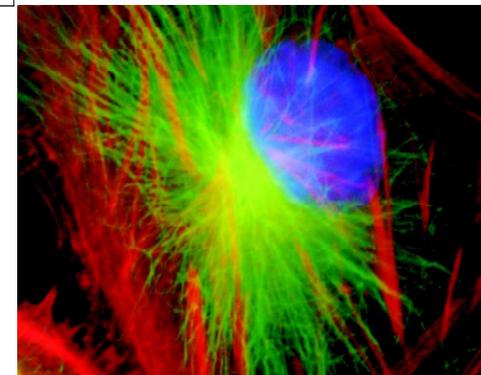
Macromolecules

eg. proteins



Red: actin filament

Blue: nucleus



Green: microtubular system



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

$$\frac{n_{broken}}{n_{intact}} = e^{-\frac{\Delta\varepsilon}{kT}}$$

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

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

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

$$kT \sim 0.027 \text{ eV} \quad T=310 \text{ K,}$$

$$k=1.38 \times 10^{-23} \text{ JK}^{-1} \text{ Boltzmann constant}$$

$$\text{e.g. } E_{bond} = 2.7 \text{ eV} \Rightarrow \frac{n_b}{N} \cong e^{-\frac{E_{bond}}{kT}} = e^{-100} = 3.72 \times 10^{-44}$$

↓ **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

$$\frac{n_{broken}}{n_{intact}} = e^{-\frac{\Delta\varepsilon}{kT}} = e^{-\frac{0.2}{0.027}} = 0.00046 \cong \frac{n_{broken}}{N}$$

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

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

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

↑
time-average!

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

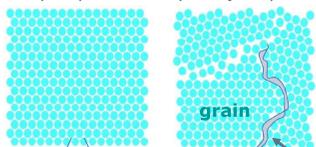
Structural dynamics in live material

1.3. Structure of crystalline materials = ideal state of order

Particles: **atoms/ions** - bonds: **primary** bonds → **ordered structure**

Single crystal (ideal)

microcrystalline state (real crystals)

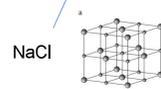


Characteristics of „crystalline“ state

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

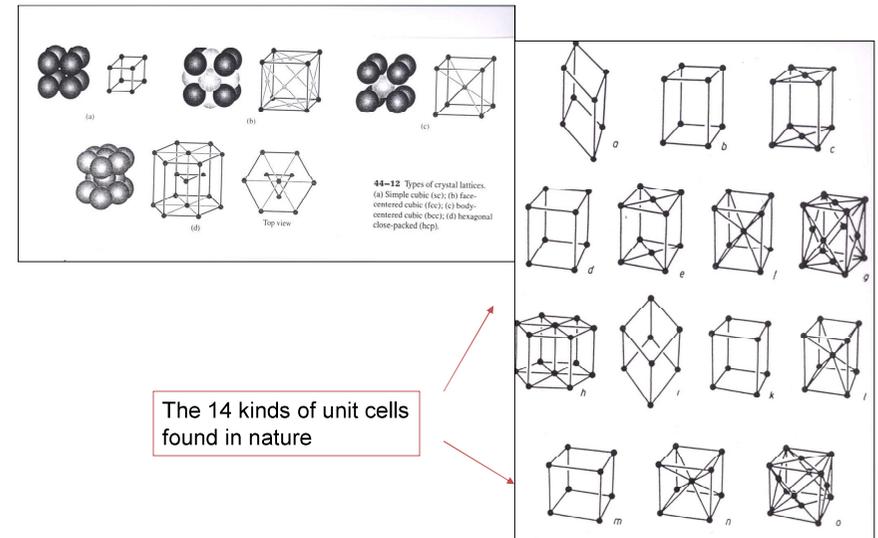
grain boundary: accumulation of crystal defects

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



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 $r_0 (=0.15\text{nm})$



crystal defects in real crystals ?

Considering two states of bonds – intact
– broken



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

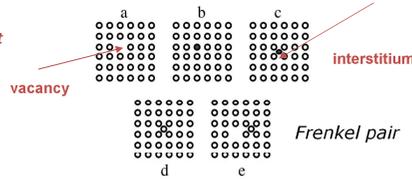
But:
imperfections in crystal growth

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

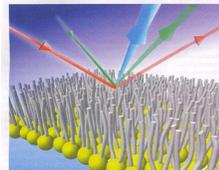
diffusion takes time!
„fatigue“



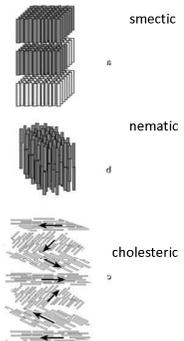
1.1.-1.2. Mesomorphous materials – liquid crystals

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



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

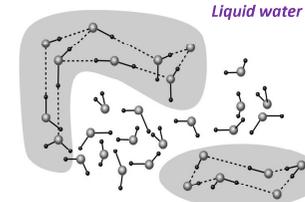
1.4. Liquid state – case of partial (short range) and temporary order

Particles: molecules

Interaction energy: $E_b \sim$ secondary bonds

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

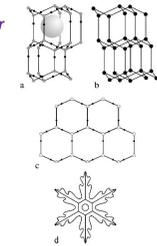
$$\frac{n_{\text{broken}}}{n_0} \approx 1\% - 0.05\% \quad (T = 300 \text{ K})$$



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



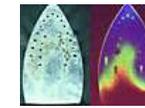
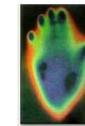
Short range order: clusters of 5-10 molecules in continuous rearrangement

Practical aspects

1. Thermotropy

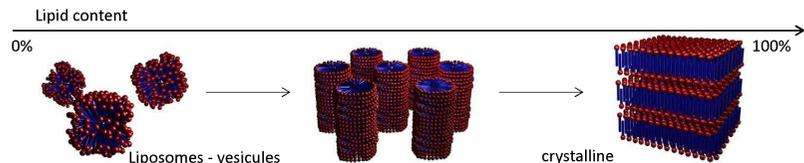
Cholesteric order → the distance of the ordered layers is sensitive to temperature → interference of diffracted light →
→ destructive interference for given λ -component of white light → compensating color is observed in reflection

Contact thermography



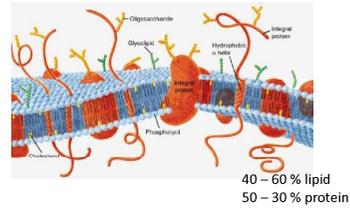
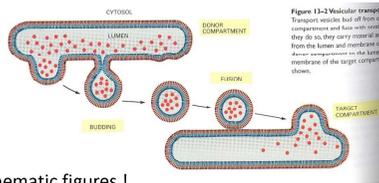
Color ~ T
thermometers

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



Biological significance: structure of the cell membrane, vesicles, enclosing subcellular compartments

Cell-membrane: lipid bilayer



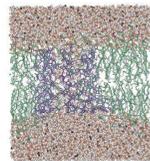
Schematic figures !

Real structure of „parallel“ lipids (cell membrane)

Boltzmann distribution allows for flexibility of lipid chains!

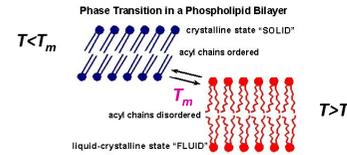
(blue: transmembrane protein)

Result of computational modeling of bond breaking by Boltzmann distribution



Biological – medical aspects

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



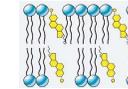
Crystalline/solid/ordered state below T_m

biologically non-functional
e.g. ends of nerve cells in frozen limbs- numbness

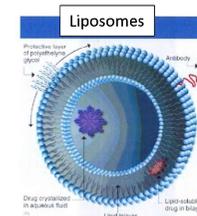
Liq.Cryst. state above T_m – capable of biological functioning

Role of cholesterol

- $T > T_m$ rigidity
- $T < T_m$ flexibility



Artificial membranes – liposomes – tools in therapy

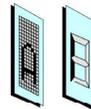


Targeting of medications by attached antibodies
Stealth liposomes to avoid degradation by macrophages

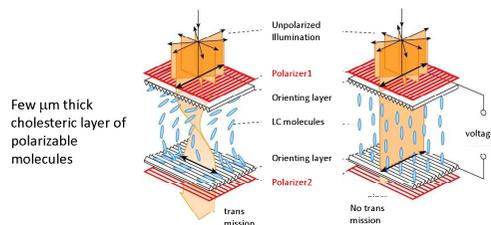
Practical aspects

Electro-optical properties: electric field → structural order change in liq.crys. 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**



2. Gasous systems

2.1. Ideal gas (already discussed)

Thermodynamics:

kinetic gas theory

$$E_{total} = N \frac{1}{2} m \langle v^2 \rangle_{average} \quad \epsilon_i = \frac{1}{2} m v_i^2$$

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

Only translational motion

$$pV = NkT = nRT$$

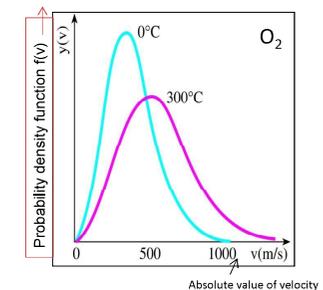
Derived from elastic collision with the wall of complete rigidity (n is the number of moles)

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 $E \rightarrow E_{\text{total}} = E_{\text{kin}} + E_{\text{interaction}}$

Volume $V \rightarrow V - Nb \rightarrow$ gas Law $\rightarrow p(V - Nb) = NkT \rightarrow p = NkT / (V - Nb)?$

But pressure is also decreased $p \rightarrow NkT / (V - Nb) - a(N/V)^2 = p$
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

Continuation in the next lecture:

Change of the electronic orbitals of particles due to interactions in many-particle systems
Properties of conductors, semiconductors and insulators.

Thank you for your attention!

