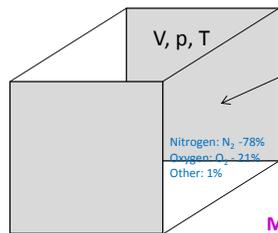


Describing many-particle systems

Prof. Judit Fidy
2016, October 11

- 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 particles in the system (position, velocity etc. for each)



Ludwig Eduard Boltzmann
1844-1906, Austrian physicist



$\Omega \leftrightarrow W$

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

An isolated system will spontaneously drive itself into the macrostate that can be realized by the highest variety of microstates \rightarrow which is of highest „probability“

Ω : thermodynamic probability of a macrostate (= number of microstates that result in this macrostate)

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

$$S = k \ln \Omega$$

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

Boltzmann constant

logarithmus naturalis – e-based logarithm
 $e^{\ln \Omega} = \Omega$ $\ln x = \frac{\log x}{\log e}$

„e“ natural base number: Euler-number / Napier constant

$$\left(1 + \frac{1}{n}\right)^n \xrightarrow{n \rightarrow \infty} e$$

$e = 2,718\ 281\ 828\ 459\ 045\ 235\ 360\ 287\ 471\ 35\dots$

III. Law of Thermodynamics

The **Entropy** of a chemically pure (of one component) crystalline system is **zero at $T=0\text{ K}$** . $\Omega = 1 \rightarrow S = 0$

Statistical definition of the Absolute value of Entropy!

Boltzmann distribution function

Connecting the energetic macrostate and microstates of a system of a large number of particles.

Consider N distinguishable independent particles at thermal equilibrium – total energy is constant - , $T \leq 0$, in a closed system,

ϵ

Model: the individual particles may have different energetic states

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

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

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

Boltzmann's statement: there is a strict order in the distribution of particles on the energy levels depending on the temperature

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

Boltzmann factor

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

Textbook p. 52 - 57

Understanding the Boltzmann distribution function

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

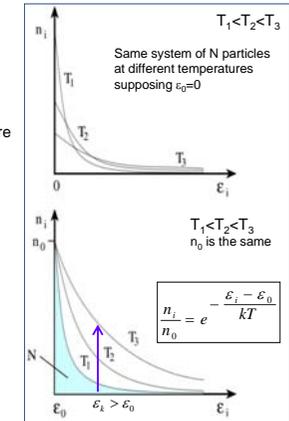
$$\frac{n_k}{n_j} = e^{-\frac{\epsilon_k - \epsilon_j}{kT}} = e^{-\frac{\Delta \epsilon}{kT}}$$

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 – a general rule in nature

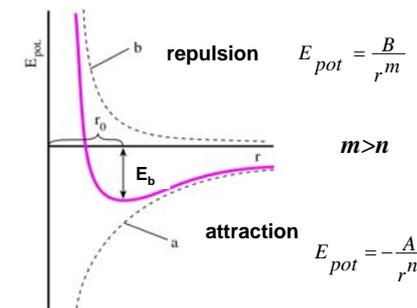
Considering the classes of materials – structural consequences

1. Classes of materials with structural order.

- | | | | |
|-----------------------------------|---|-------------------------------|---------------------------------------|
| Order is based on primary bonds | - | - solid crystalline materials | |
| | | - ideal crystals | → perfect, long range order |
| Order is based on secondary bonds | - | - real crystals | |
| | | - 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



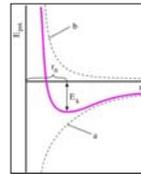
General concept of bond formation (applicable for all kinds of interactions)

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

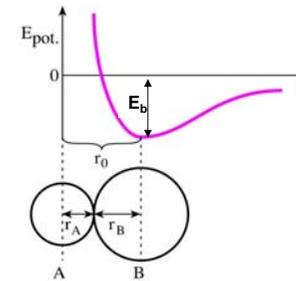
The distance dependence in the energy formulae of **electrostatic** interactions



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**)



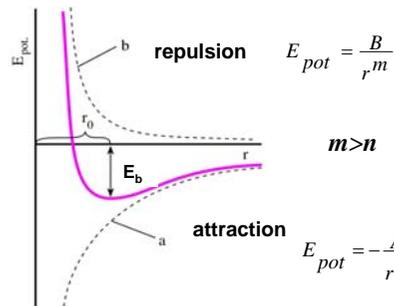
r_A, r_B atomic radii of atoms A and B

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 ↔ and Boltzmann distribution

General concept of bond formation



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

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

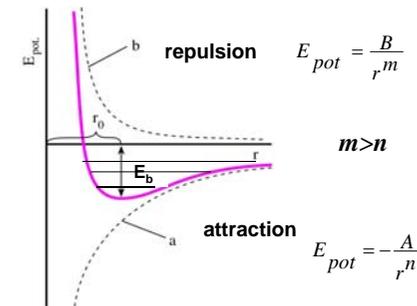
$$m > n$$

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

Is it true that all constituting atoms are at bond distances (r_0) from each other all the time?

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

General concept of bond formation ↔ Boltzmann distribution allows for having **broken bonds!**



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

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

$$m > n$$

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

$$\frac{n_{\text{broken bonds}}}{n_{\text{intact bonds}}} = \frac{n_b}{n_i} = e^{-\frac{\Delta \epsilon}{kT}}$$

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

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

$$\Delta \epsilon \leftrightarrow kT$$

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

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

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/mol

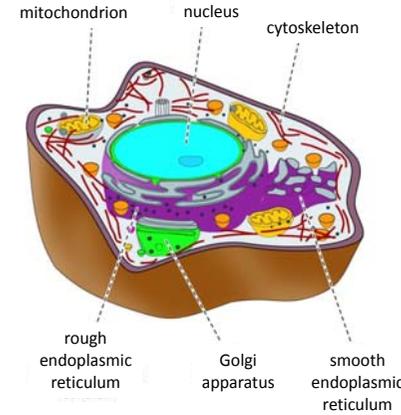
E_b ~ **primary bonds**: covalent
 ionic
 metallic **2 – 10 eV/bond**

E_b ~ **secondary bonds**

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

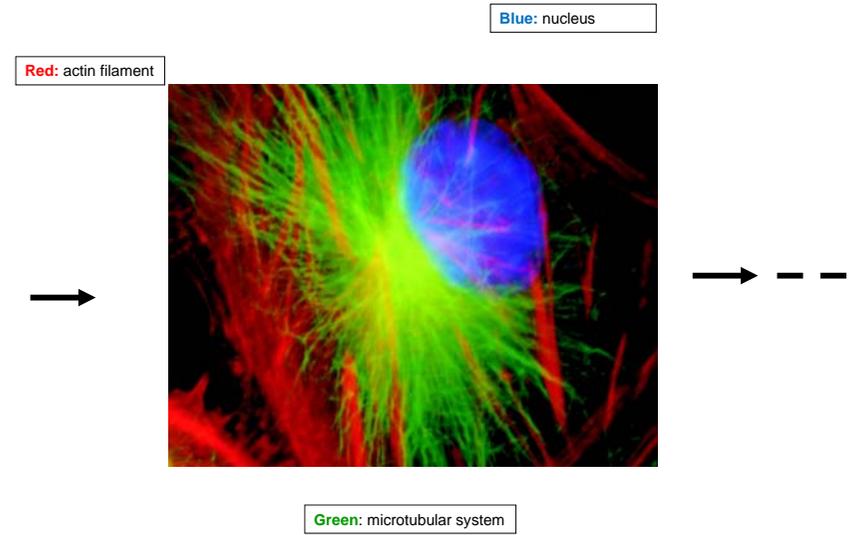
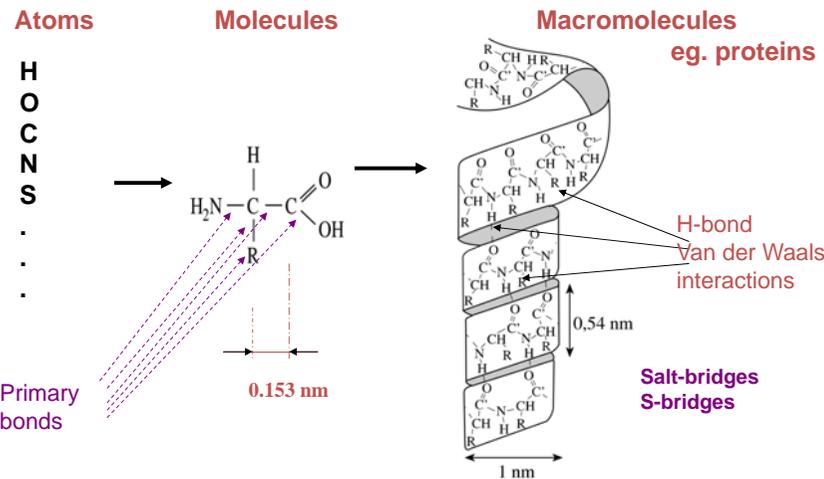
Great variety! Even 100-times differences!

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



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

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

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

$$ha \quad n_{broken} \ll n_{intact} \Rightarrow \frac{n_b}{n_i} \cong \frac{n_b}{N}$$

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

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

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

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 \rightarrow about 100 000 H-bonds $\rightarrow N = 100\ 000$

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

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

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

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

↑
time-average!

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

Structural dynamics in live material

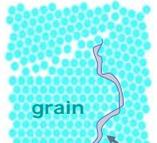
1.3. Structure of crystalline materials = ideal state of order

Particles: **atoms/ions** - bonds: **primary** bonds \rightarrow **ordered structure**

Single crystal (ideal)



microcrystalline state (real crystals)



grain

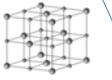
Characteristics of „crystalline” state

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

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

grain boundary: accumulation of crystal defects

NaCl

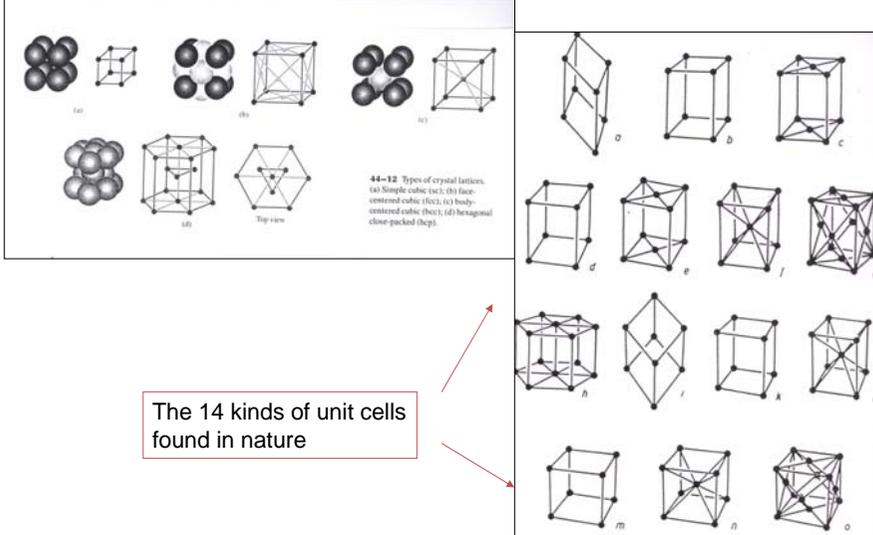


Si



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

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



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

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

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

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

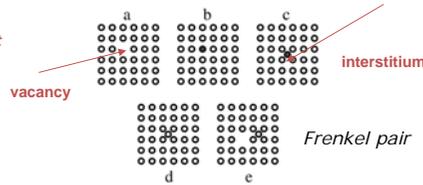
But:
imperfections in crystal growth

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“



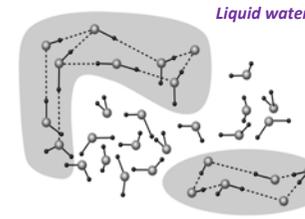
1.4. Liquid state – case of partial (short range) and temporary order

Particles: molecules

Interaction energy: $E_b \sim$ secondary bonds

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

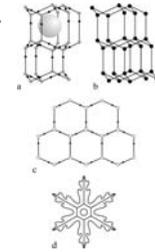
$$\frac{n_{\text{broken}}}{n_0} \cong 1\% - 0.05\% \quad (T = 300 \text{ K})$$



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

1.1.-1.2. Mesomorphous materials – liquid crystals

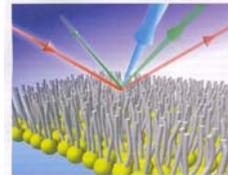
Average interaction energy between molecules is small *like in liquids*

Long range order (but not so strict) *~ like in crystals*

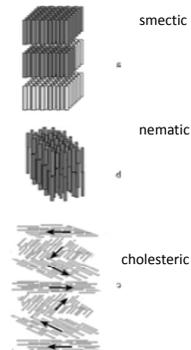
Deformability *like in liquids*

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

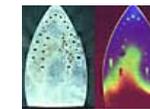
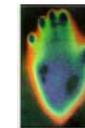
Practical aspects

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

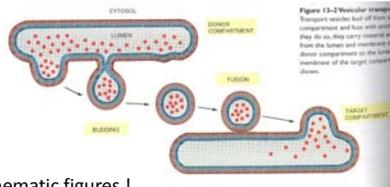
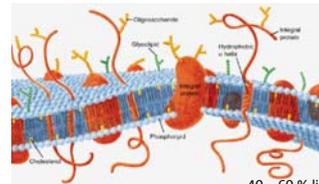


Figure 13-2 Molecular transport vesicles bud off from a compartment and fuse with another. They do so, they carry material out from the former and material in from the latter and material in from the latter appears in the membrane of the target compartment.



40 – 60 % lipid
50 – 30 % protein

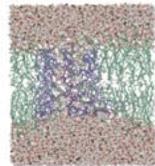
Schematic figures !

Real structure of „parallel“ lipids (cell membrane)

Boltzmann distribution allows for flexibility of lipid chains!

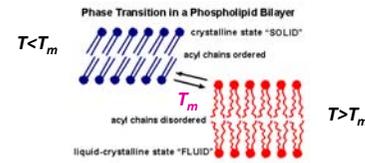
(blue: transmembrane protein)

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 Tm

biologically non-functional

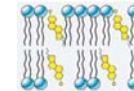
e.g. ends of nerve cells in frozen limbs- numbness

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

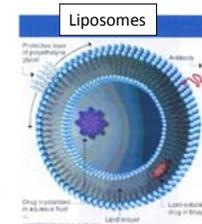
Role of cholesterol

-T > Tm rigidity

-T < Tm flexibility



Artificial membranes – liposomes – tools in therapy



Targeting of medications by attached antibodies

Stealth liposomes to avoid degradation by macrophages

Continuation in the next lecture:

electrooptical properties of liquid crystals

gaseous systems: ideal gas

real gas

Thank you for your attention!

