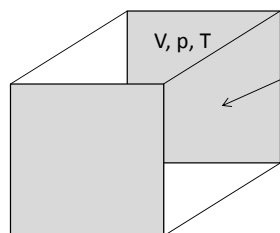


## Describing many-particle systems

Prof. Judit Fidy  
2015, October 14

**particle:** - atom, atomic group  
- molecule  
- molecular complexes, macromolecules  
- etc.  
**many:**  $6 \times 10^{23}$

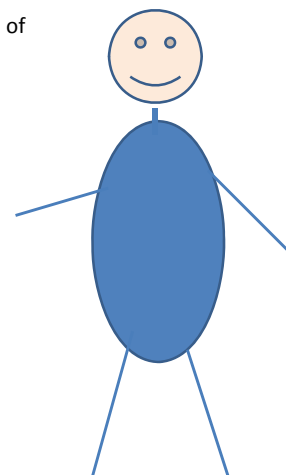
### Simple example



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

### Complicated example

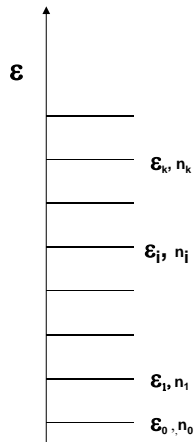
Complex system of  
large number of  
atoms and  
molecules in  
interaction with  
each other



**Energetic** states  
*In the field of interactions?*

**Electronic** states  
*In the field of interactions?*

## Boltzmann distribution



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

$\epsilon_i$  possible energy status for one particle  
 $n_i$  number of particles having  $\epsilon_i$  energies

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

### Boltzmann distribution function

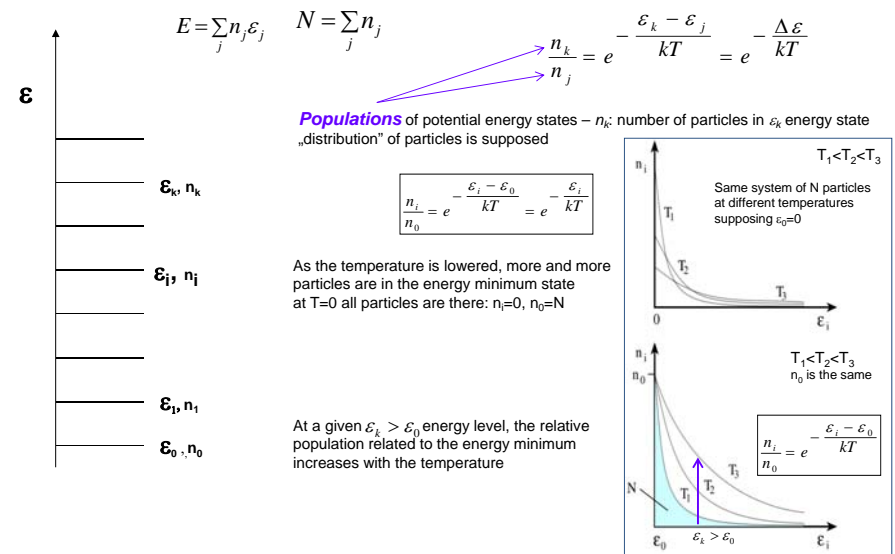
$$\frac{n_k}{n_j} = e^{-\frac{\epsilon_k - \epsilon_j}{kT}} = e^{-\frac{\Delta \epsilon}{kT}}$$

Boltzmann factor

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



## Boltzmann distribution - conclusions



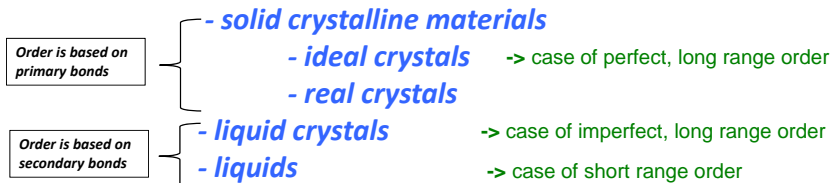
## Boltzmann distribution – a general rule in nature

Considering the classes of materials – structural consequences

### 1. Gasous systems (ideal gas)

-> lack of order in the structure

### 2. Classes of materials with structural order.



↑  
 Absolute value of velocity

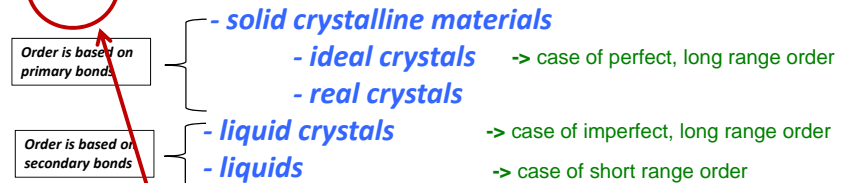
## Boltzmann distribution – a general rule in nature

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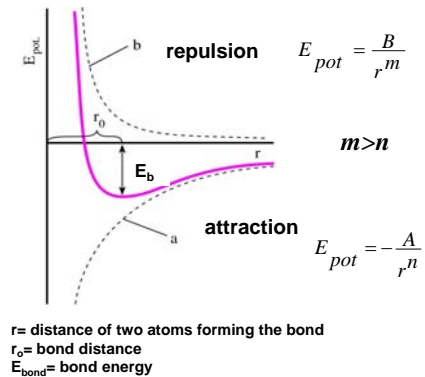


↑  
 Absolute value of velocity

## 2. Classes of materials with structural order.

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

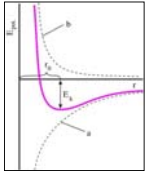
**General concept of bond formation (applicable for all kinds of interactions)**



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

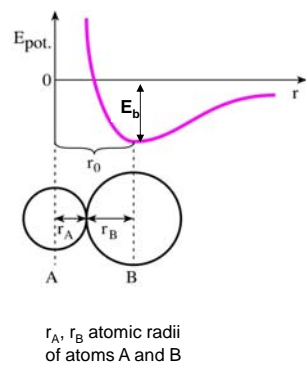
## Examples for the functional form of attractive interactions

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

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**)



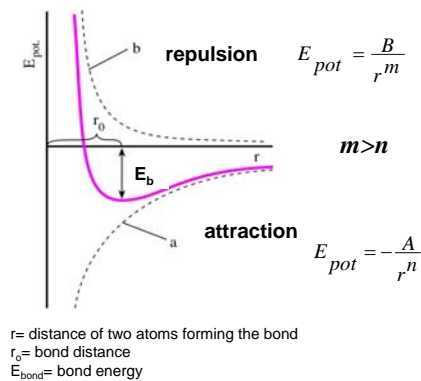
Atom	Z	van der Waals radius (nm)	Covalent radius (nm)	Ionic radius (nm)	Ion
H	1	0,120	0,037	–	H <sup>+</sup>
C	6	0,170	0,077	0,029	C <sup>+</sup>
N	7	0,155	0,075	0,025	N <sup>+</sup>
O	8	0,152	0,073	0,140	O <sup>2-</sup>
F	9	0,147	0,071	0,117	F <sup>-</sup>
P	15	0,180	0,106	0,058	P <sup>3+</sup>
S	16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

„atomic radius”

## 2. Classes of materials with structural order.

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

**General concept of bond formation**



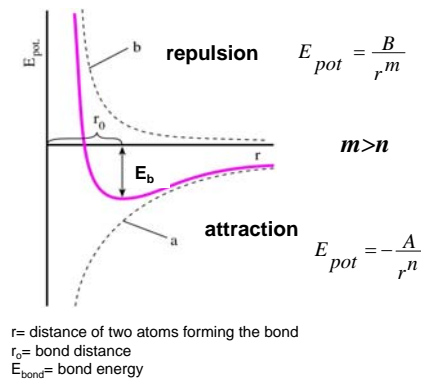
Is it true that all constituting atoms are at bond distances from each other all the time?!

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

## 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!

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

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

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

$$\Delta\epsilon \longleftrightarrow kT$$

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

$kT \sim 0.027 \text{ eV}$   $T=310 \text{ K,}$   
 $k=1.38 \times 10^{-23} \text{ JK}^{-1}$  Boltzmann constant

## 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

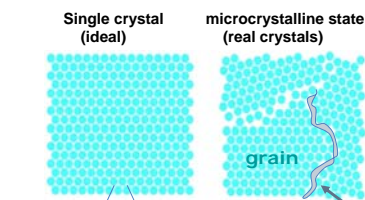
2 – 10 eV/bond

$E_b \sim$  secondary bonds

	$E_b(\text{eV})$
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

## 2.1. Structure of crystalline materials = ideal state of order

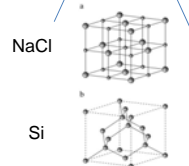
Particles: **atoms** - bonds: **primary** bonds -> **ordered structure**



### Characteristics of „crystalline” state

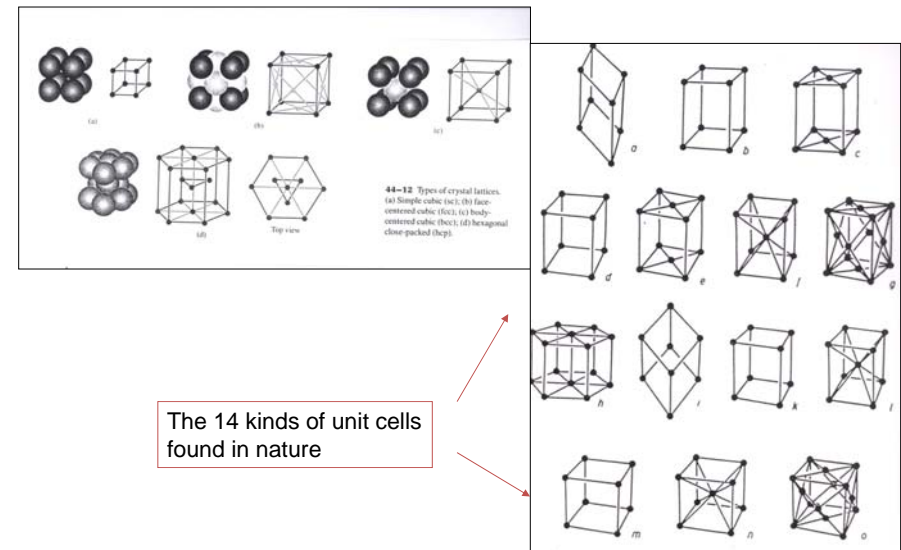
- anisotropy: properties depends on the direction
- mechanical stability
- defined volume
- defined shape
- structure: long range order

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



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

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

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

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

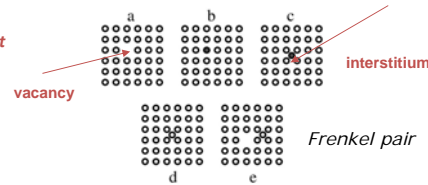
But:  
imperfections in crystal growth

**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 (short range) and temporary order

Particles: molecules

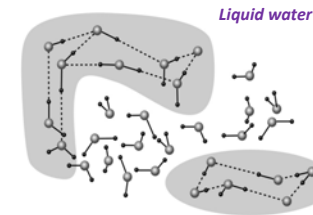
Interaction energy:  $E_b \sim$  secondary bonds

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

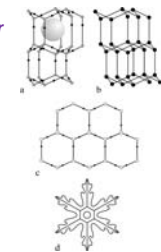
$$\frac{n_{\text{broken}}}{n_0} \cong 1\% - 0.05\% \quad (T = 300 \text{ K})$$

### 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

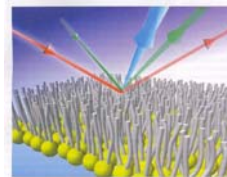
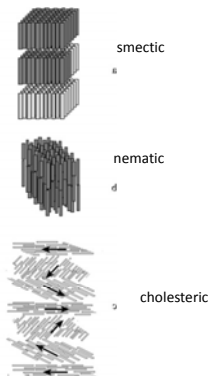


**Short range order:** clusters of 5-10 molecules in continuous rearrangement

## 2.1.-2.2. 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

### Forms of order of string-like molecules



Weak bonding energy → order can be easily perturbed by

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

### Practical aspects

1. Cholesteric order → sensitivity to temperature of the distance of ordered layers → diffraction change in reflection → color change

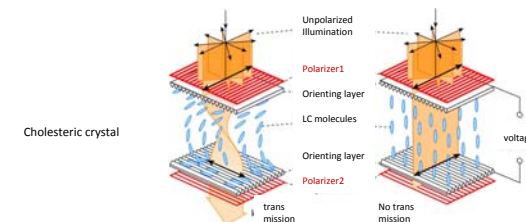
### Contact thermography



Color ~ T thermometers

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

→ pixels of LCD monitors in transmission mode



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

Cell-membrane: lipid bilayer

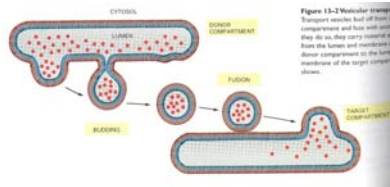
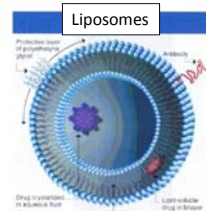


Figure 13-3 Molecular transport. Transport vesicles bud off from a compartment and fuse with another. They do so, they carry material from the lumen and insert it in the membrane of the target compartment.



Liposomes

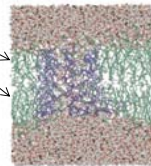
Targeting of medications

Real structure of „parallel“ lipids (cell membrane)

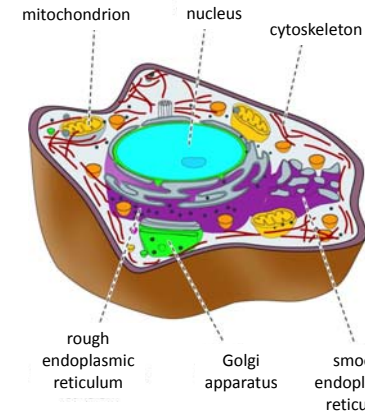
**Boltzmann distribution!**



Schematics of Figures



## 2.3. Macromolecular systems (e.g. cells): order is stabilized by a wide range of interactions

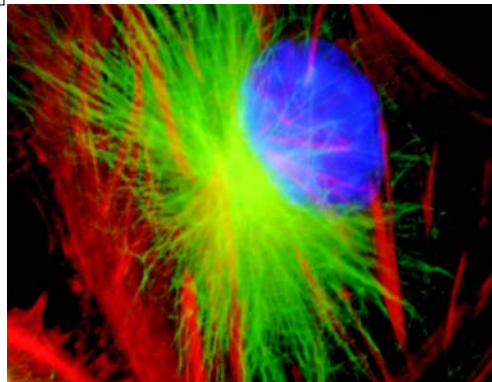


**Hierarchy in**

- 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**

## Get back to gases

### 1. Gaseous 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

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

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

$$f = 3$$

$$pV = NkT$$

degree of freedom of motion for point-like particles

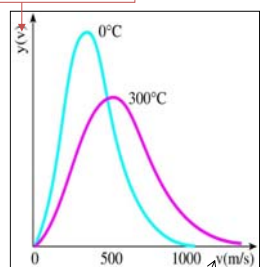
#### 2. deviations from the average velocity are determined by the

**Maxwell – Boltzmann distribution** function

#### 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

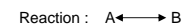
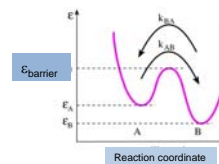
Frequency of occurrence =  $n/N$



Absolute value of velocity

## Boltzmann distribution - more examples (see textbook)

### 3. Equilibrium rate of chemical reactions



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

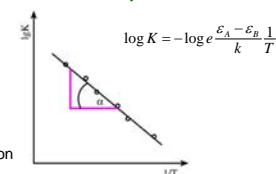
$$k_{AB} = \text{const} \times e^{-\frac{E_{\text{barrier}} - E_A}{kT}}$$

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

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

Experimental determination of the energy of activation

#### Arrhenius plot



### 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

Thank you for your attention!

