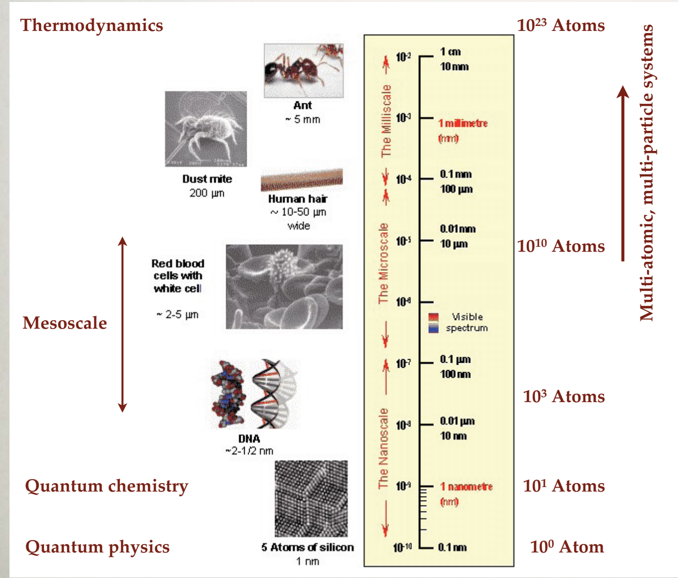
MULTI-ATOMIC SYSTEMS, WATER, MACROMOLECULES

MIKLÓS KELLERMAYER

DIMENSIONS OF LIVING SYSTEMS



Particles may be:
- atoms
- molecules
- macromolecules

"Multi" refers to:
- number on the molar scale (10^{23})

Interaction between particles determines:
- state (solid, liquid, gas)
- structure
- properties (physical, chemical, biological)

DISTRIBUTION OF STATES

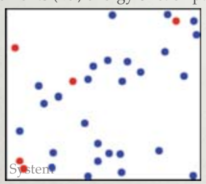
BOLTZMANN DISTRIBUTION

Average energy of a system in thermal equilibrium (T = constant)

Equipartition theorem:
Energy per degree of freedom $= \frac{1}{2}k_B T$

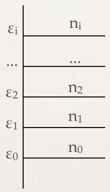
k_B = Botzmann's constant, T = absolute temperature

Average doesn't reveal microscopic arrangements (i.e., energy of each particle).



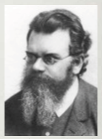
- ***Microscopic state ("microstate")*** describes: momentary energy of each particle.
- ***Macroscopic state ("macrostate")*** describes: distribution across energy states; i.e., how many particles (n_0, n_1, n_2,...) occupy each energy level (ε_0, ε_1, ε_2,...).
  Note: a macrostate can be realized by several different microstates.

Distribution across energy states
Boltzmann distribution

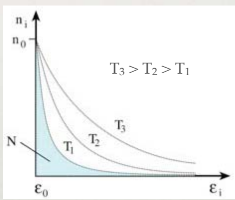


$$\frac{n_i}{n_0} = n_0 e^{-\frac{\varepsilon_i - \varepsilon_0}{k_B T}}$$

Relative occupancy of states (n_i/n_0) depends on energy difference (ε_i-ε_0) and temperature (T).

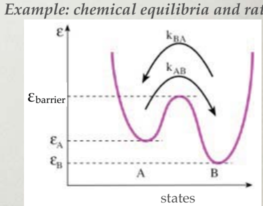


Ludwig Eduard **Boltzmann** (1844-1906)



- Increasing temperature increases occupancy of higher energy states.
- N = total number of particles.
- Probability (p) of occupying a given (i^{th}) state: $p_i = n_i/N$.

Example: chemical equilibria and rates



- Equilibrium constant (K=n_A/n_B) depends on difference between energy states (ε_A-ε_B) and temperature (T).
- Reaction rates (k_{BA}, k_{AB}) depend on respective barrier heights ($\varepsilon_{barrier}$-ε_A, $\varepsilon_{barrier}$-ε_B) and temperature (T).

News Headlines

The first prize of the Idaho Falls High School Science Fair was awarded on April 26 to a student of Eagle Rock High School. The student wanted to demonstrate the extent to which the public is manipulated by vague references to science in generating environmental concern. He prepared a proposal for banning the use of the chemical *dihydrogen monoxide* and investigated whether he can convince supporters to sign it. He argued for the toxicity of the chemical based on the following:

1. the chemical induces strong perspiration and vomiting,
2. it is one of the main components of acid rain,
3. its gaseous form may cause serious burns,
4. its excessive inhalation may lead to suffocation,
5. it contributes to erosion,
6. it significantly reduces the efficiency of car brakes,
7. it has been shown to be present in cancer.

The student surveyed 50 people for support of the proposal:

Forty three (43) signed immediately.
Six (6) asked for time to think.

Only one (1) person knew that the chemical is water. . .

Biophysics of water

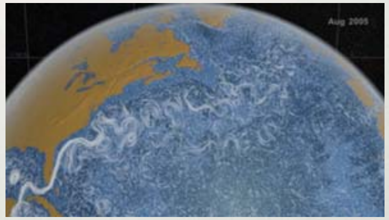
Water

- Source of *inspiration* (music, paintings).
- Thales (580, B.C.): "...water is *source of all things*..."
- Henry Cavendish (1783): water is H_2O.
- Only chemical that naturally exists in *all three states* (solid, liquid, gas).
- 71% of the Earth's surface is covered with water ("blue planet").
- Water is of utmost importance for *life*:
  98% of jellyfish
  94% of three-month human fetus
  72% of newborn
  60% of adult
- Average daily water intake: 2.4 liters.

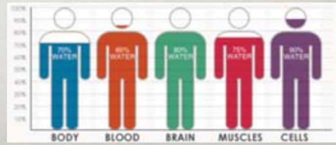
Georg Friedrich **Händel** (1685-1759): ***"Water music"***.

Georg Friedrich Händel (*center*) and King George I (*right*) on the Thames River, 17 July 1717.

Hokusai (1760-1849): Great wave off Kanagawa



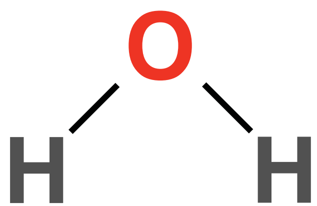
Perpetual motion of oceans on Earth's surface.



Structure of the water molecule I.

One of the smallest molecules:
barely larger than a single atom

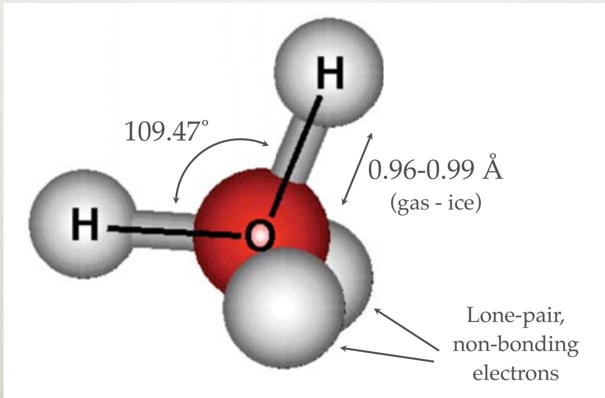
Oxygen: $2s^2p^4$



Molecular diameter:
2.75 Å

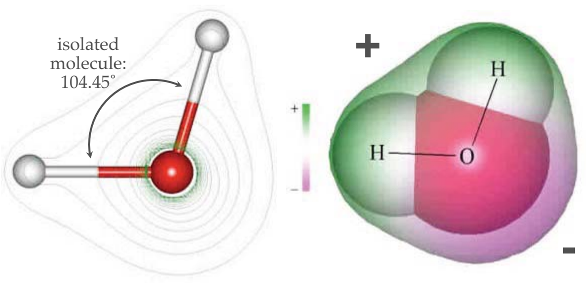
Structure of the water molecule II.

- Tetrahedral structure
- sp^3 hybridization (Hybridization: combination of states with identical principal quantum number but different symmetry)



Structure of the water molecule III.

Large constant dipole moment

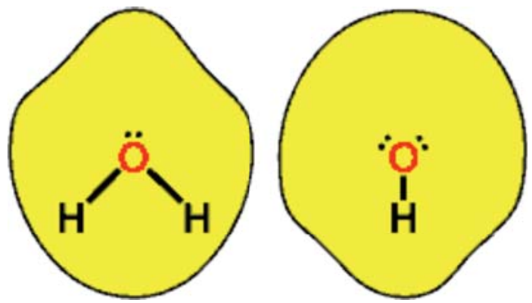


Chemical	Dipole moment
Polyethylene	2.25
Methanol	30
Ethylene glycol	37
Glycerol	47
Water	80
Titanium dioxide	86-173

Dipole moment: amount of electrical energy stored in the material by an applied voltage, relative to vacuum. It shows how good an electrical insulator the material is. Consequence: water is good solvent.

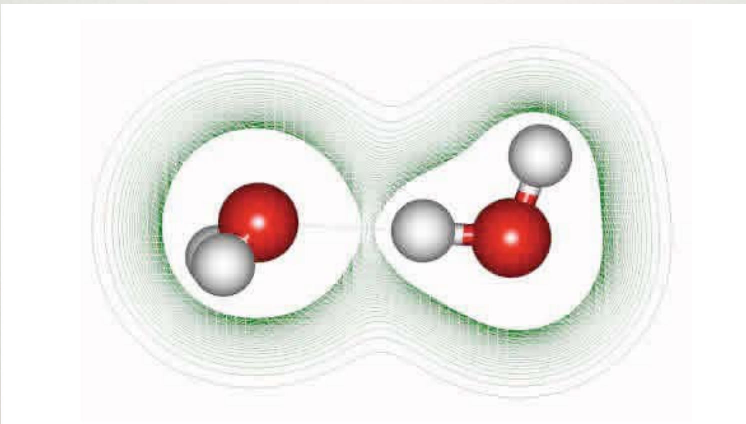
Structure of the water molecule IV.

van der Waals radius: ~ 3.2 Å
non-spherical shape

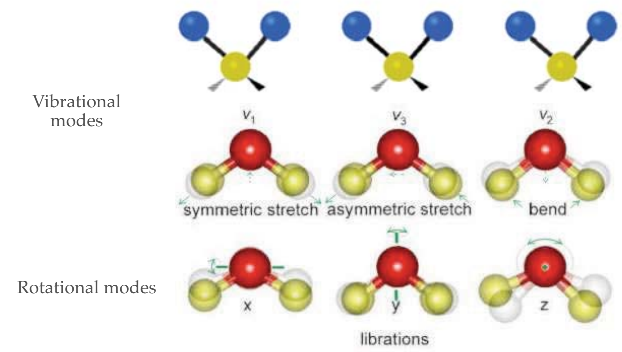


Structure of the water molecule V.

Water dimer:
H-bond between the proton and lone-pair electrons



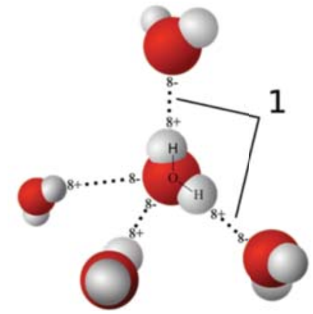
Rotational and vibrational motion of the water molecule



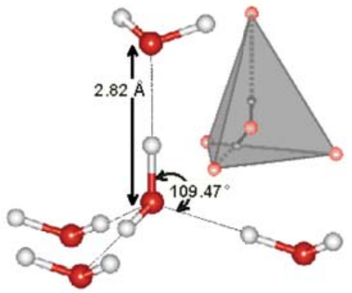
Absorption in the infrared and red spectral region -> "blue" color of natural waters: *blue planet*

Hydrogen bonding in water

Hydrogen bonds in the vicinity of a water molecule

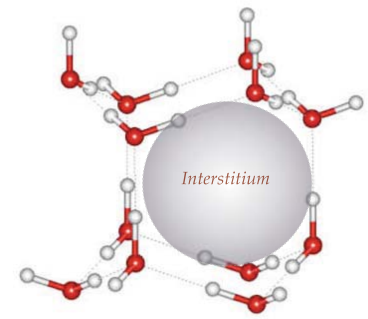


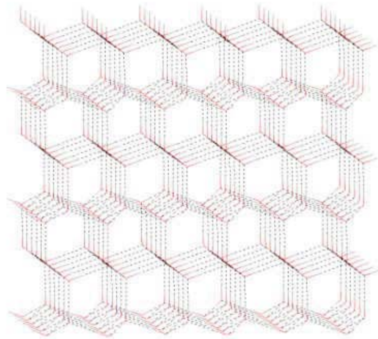
Formation of pentameric water



Structure of ice

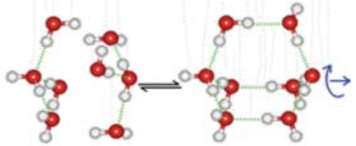
- 9 different forms
- Conventional ice: hexagonal structure
- Coordination number: 4 (each molecule coordinates another four)
  Interstitium: could incorporate a water molecule - important in the diffusion of gases

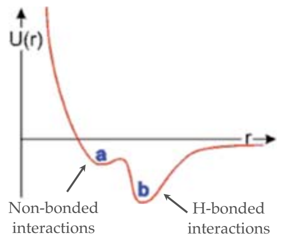




Structure of liquid water

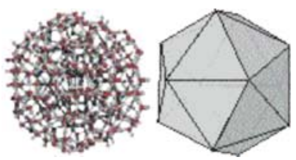
H-bridge: cohesion + repulsion
Cluster formation: bicyclo-octamer





From clusters to networks: 280 molecules form icosahedral structure

(*icosahedron*: regular polyhedron with 20 identical equilateral triangular faces)

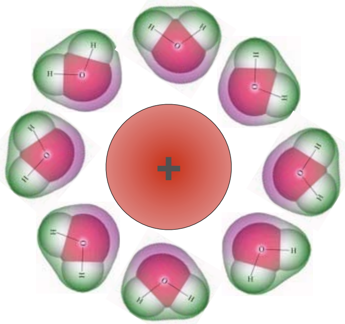


Spatial networks:
May explain anomalous properties of water

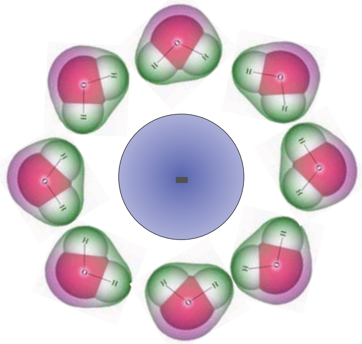
Physical properties of water I.

Because of large dipole moment: very good solvent

Solvation of a cation



Solvation of an anion



In the ***microwave oven***: dipoles rotate with oscillating electromagnetic field.
Water molecules acquire kinetic energy, which dissipates into the surroundings.

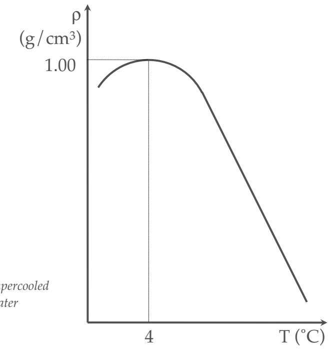
Physical properties of water II.

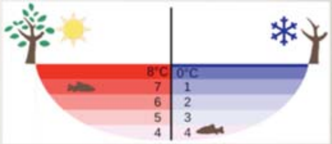
Anomalous density-temperature function

Temp (°C)	Density (kg/m³)[17][18]
+100	958.4
+80	971.8
+60	983.2
+40	992.2
+30	995.6502
+25	997.0479
+22	997.7735
+20	998.2071
+15	999.1026
+10	999.7026
+4	**999.9720**
0	999.8395
−10	998.117
−20	993.547
−30	983.854

Density of liquid water

supercooled water (−10 to −30 °C)



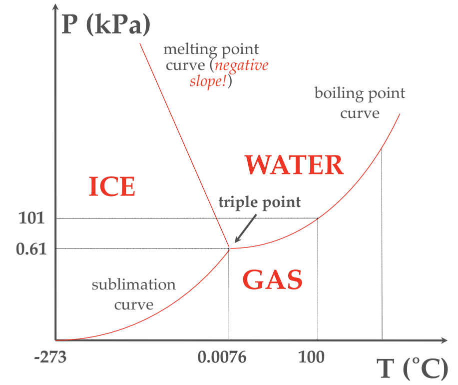


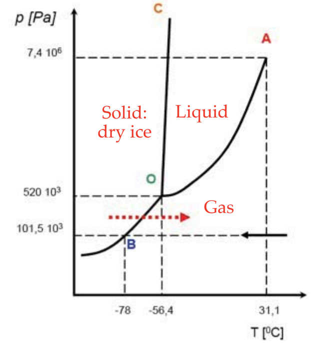
Consequences:
Life persists under the frozen lake
Creek runs under ice

Physical properties of water III.

Anomalous phase diagram

- Phase curve: two phases are in equilibrium
- Area between phase curves: a single phase is present
- Intersection of phase curves: triple point



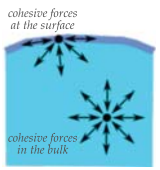


Physical properties of water IV.

Large surface tension

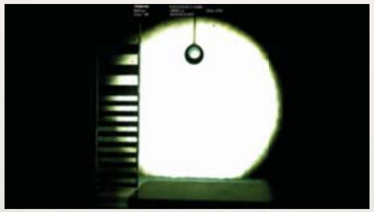
Surface tension: contractive tendency of the liquid that resists external force.

Imbalance of cohesive forces in the *bulk* versus the *surface* of the liquid.



Chemical	Surface tension (mN/m)
Ethanol	24.4
Methanol	22.7
Acetone	23.7
Chloroform	27.1
Benzene	28.5
Water	72.9

Consequences on ***hydrophobic*** surface



Persisting droplet on a superhydrophobic surface

Consequences on ***hydrophilic*** surface

Capillary action (model)

Capillary action aiding plant root function

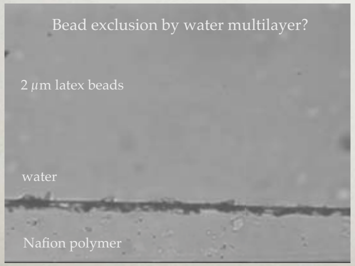
Consequences in macrosopic living systems

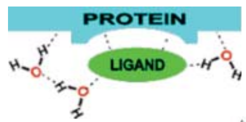
Water striders

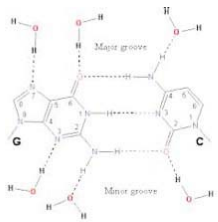
"Jesus Christ lizard" (basilisk)

Water hydration

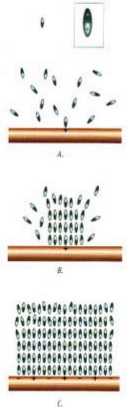
1. **Electrolyte solutions**
2. **Non-electrolyte solutions, apolar molecules**
   hydrophobic hydration
3. **Protein hydration**
   Maintenance of 3D structure
   Polarized "multilayers"
4. **Nucleic acids**
   Base pairing







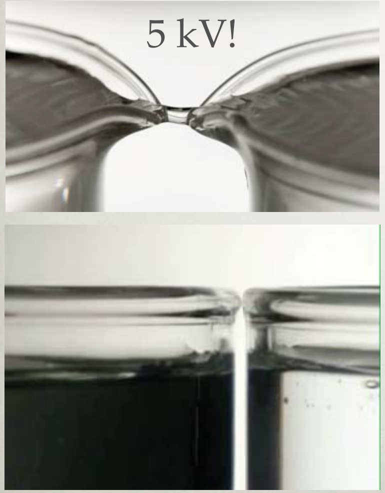
Base pairing



Multilayer formation

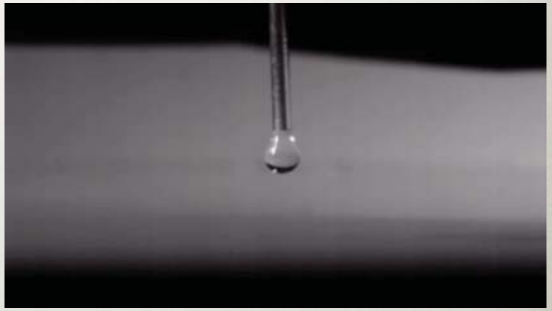
Further anomalies

Floatig water bridge



Elmar Fuchs, Wetsus

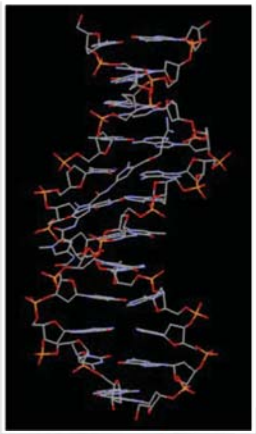
Persisting water droplets on vibrating water surface



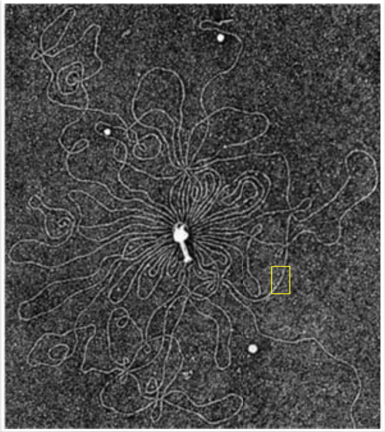
Pablo Cabrera et al, Mexico

Macromolecules

Biological macromolecules are GIANT molecules

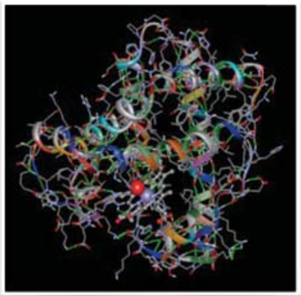


DNS double helix

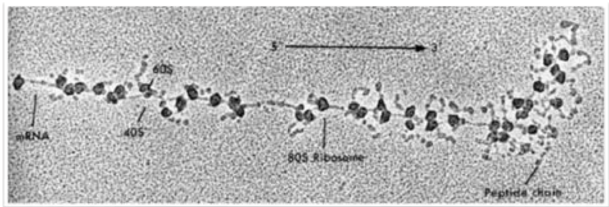


DNA released from bacteriophage head

Biological macromolecules are EXCITING molecules

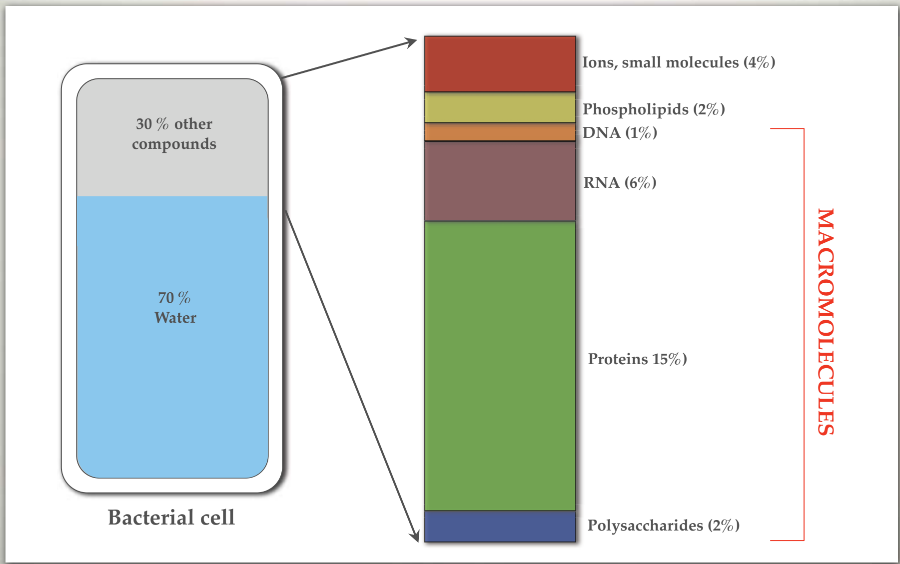


Structure of hemoglobin subunit



Newly synthesized protein (silk fibroin)

Proportion of macromolecules in the cell by mass is LARGE



Biological macromolecules: biopolyers

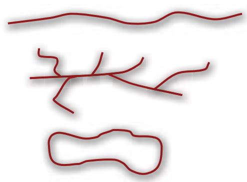
Polymers:
chains built up from monomers

Number of monomers: N>>1;
Typically, N~10^2-10^4,
but, in DNA, e.g.: N~10^9-10^{10}

Biopolymer	Monomer	Bond
Protein	Amino acid	Covalent (peptide bond)
Nucleic acid (RNA, DNA)	Nucleotide (CTUGA)	Covalent (phosphodiester)
Polysaccharide (e.g., glycogen)	Sugar (e.g., glucose)	Covalent (e.g., α-glycosidic)
Protein polymer (e.g., microtubule)	Protein (e.g., tubulin)	Secondary

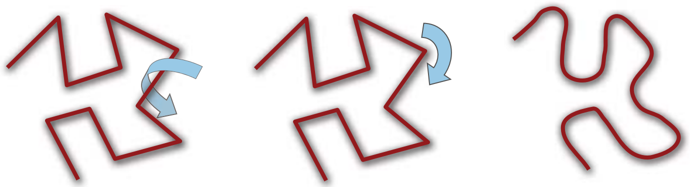
Shape of polymers

1. Linear
2. Branched
3. Circular



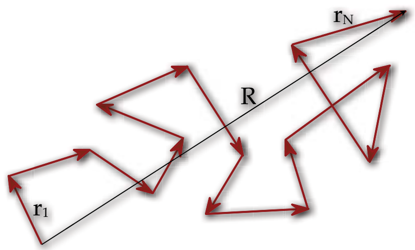
Shape of polymer chain changes dynamically. Possible mechanisms:

1. Rotation around CC-bonds
2. Freely jointed chain (FJC)
3. Bending, wormlike chain (WLC)



Shape of the polymer chain resembles random walk

Brown-movement - "random walk"



"Square-root law":

$$\langle R^2 \rangle = Nl^2 = Ll$$

R = end-to-end distance
N = number of elementary vectors
$l = |\vec{r}_i|$ = correlation length
r_i = elementary vector
$Nl = L$ = contour length
l is related to **bending rigidity**.

In case of Brown-movement R=displacement, N=number of elementary steps, L=total path length, és l=mean free path length.

Mechanics of polymers

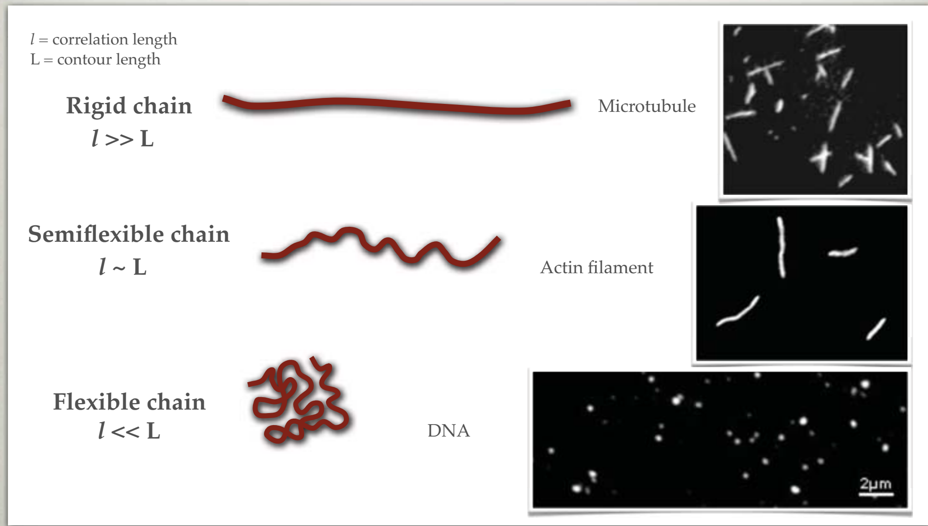
Entropic elasticity

Thermal fluctuations of the polymer chain

Configurational entropy (orientational disorder of elementary vectors) increases.

The chain shortens.

Biopolymer elasticity



Visualization of biopolymer elasticity

Tying a knot on a single DNA molecule