Macromolecular colloids. Size and shape of linear macromolecules. Osmosis and osmotic pressure.

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What are macromolecules

- Macromolecules (macro = large, big) are large molecules
  - larger in solution than 1 nm (colloidal size range)
  - having a molecular weight of more than 1000 g/mol
  - The term refers mainly to individual molecules.
- Polymers (poly = many, meros = parts)
  - Polymers are composed of many repeating units (monomers)
  - If removal or addition of one unit significantly change the properties of the molecule, it is an oligomer (oligos = few)
  - Otherwise they are called polymers.
Making polymers

• The process of making polymers from monomers is called polymerization.

• Different types of polymerization:
  • **Addition polymerization** → addition of monomers without elimination of small molecules.
  • **Condensation polymerization** → formation of small molecules during polymerization beside the polymers.

• Main polymerization techniques:
  • Bulk polymerization.
  • Solution polymerization.
  • Emulsion polymerization.
Homopolymers and heteropolymers

- **Homopolymers**: made from one monomer, they consist of the repetition of the same building block
- **Heteropolymers** or **copolymers**: synthesized from two or more monomers
  - statistical → e.g. poly(vinyl alcohol-co-vinyl acetate)
  - alternating → e.g. poly(styrene-\textit{alt}-maleic anhydride)
  - block → e.g. poly(ethylene-\textit{b}-ethylene oxide)
  - graft → e.g. poly(styrene-\textit{g}-butadiene)
Monomers:

Polymers:

Homopolymer:

Random copolymer:

Alternating copolymer:

Block-copolymer:

HERMANN STAUDINGER (1881-1965) NOBEL PRIZE 1953

Branched

Cross-linked
„Industrial” Nobel prizes

Karl Ziegler   Giulio Natta

The Nobel Prize in Chemistry 1963 was awarded jointly "for their discoveries in the field of the chemistry and technology of high polymers".

Paul J. Flory

The Nobel Prize in Chemistry 1974 was awarded to Paul J. Flory „for his fundamental achievements, both theoretical and experimental, in the physical chemistry of the macromolecules".
„Industrial” Nobel prizes

Alan J. Heeger     Alan G. MacDiarmid     Hideki Shirakawa

The Nobel Prize in Chemistry 2000 was awarded jointly to Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa "for the discovery and development of conductive polymers".
Main polymer types

- Polyolefins (polyethylene=PE, polypropylene=PP)
- Polyfluoroolefins (polytetrafluoroethylene=PTFE or Teflon)
- Polyaromatic polymers (polystyrene=PS)
- Polyvinyls (polyvinyl acetate=PVAc, polyvinyl alcohol=PVA, polyvinyl chloride=PVC)
- Polyacrylates (polyacrylic acid=PAA, polymethyl methacrylate=PMMA or plexiglass)
- Polyesters (polyethylene terephthalate=PET)
- Polyamides (Nylons, Kevlar, peptides, proteins)
- Polyethers (epoxies, polyethylene glycol, polysaccharides)
- etc.
50% POLYMER OR POLYMER COMPOSITES
20% ALUMINUM
15% TITANIUM
10% STEEL
5% OTHER

BOEING 787 (DREAMLINER)

20% LESS FUEL CONSUMPTION

787 Flight Test Milestones
Shape of the polymers

- Polymers consist of one or multiple chains (sequence of repeating monomer units)
  - Straight chain polymers
  - Branched chain polymers
  - Comb-like polymers
  - Circular polymers
  - Star-shaped polymers
  - Dendritic (fractal-like) polymers
  - Cross-linked polymers (solubility sharply decreases with increasing crosslink density, heavily crosslinked=one giant molecule)
Size and size distribution

- Small molecules have a well-determined molar weight (and chain length)
- Polymers consist of a population of macromolecules of different molar weight and chain length
- If all molecules are of the same molecular weight, the sample is monodisperse
- If the sample contains both smaller and larger molecules, it is polydisperse
  - When the weight distribution has one maximum, the sample is monomodal otherwise polymodal
Monomodality and polymodality

Polymodal distribution

Monomodal distribution

(c) Zhu & Szostak, 2009
Molecular weight averages

- **Number-average** molecular weight
  \[ M_n = \left[ \sum n_i M_i \right] / \sum n_i \]

- **Weight-average** molecular weight
  \[ M_W = \sum n_i M_i^2 / \sum n_i M_i \]

- **Weight-square average** molecular weight
  \[ M_z = \sum n_i M_i^3 / \sum n_i M_i^2 \]

- **Viscosity-average** molecular weight
  \[ M_v = \left[ \sum n_i M_i^{1+a} / \sum n_i M_i \right]^{1/a} \]

- **Polydispersity index**
  \[ PDI = M_W / M_n \]
Molecular weight averages

- The degree of polymerization shows from how many monomer units a polymer is composed
  \[ DP = \frac{M}{M_0} \]
A practical example

- Let's have a polymer solution consisting of
  - \( n_{3000} = 100 \) molecules of \( M_{3000} = 3000 \)
  - \( n_{4000} = 200 \) molecules of \( M_{4000} = 4000 \)
  - \( n_{5000} = 150 \) molecules of \( M_{5000} = 5000 \)
- Which makes a total of \( \Sigma n = 100 + 200 + 150 = 450 \) molecules

What is the number-average molecular weight?

\[
M_n = \frac{\sum n_i M_i}{\sum n_i} = \frac{(100 \times 3000 + 200 \times 4000 + 150 \times 5000)}{(100 + 200 + 150)} = 4111
\]

The weight-average molecular weight is

\[
M_w = \frac{\sum n_i M_i^2}{\sum n_i M_i} = \frac{(100 \times 3000^2 + 200 \times 4000^2 + 150 \times 5000^2)}{(100 \times 3000 + 200 \times 4000 + 150 \times 5000)} = 4243
\]
A practical example

- Generally $M_Z > M_W > M_n$ (except for a monodisperse sample, where $M_n = M_w = M_z$)

- The polydispersity index of this sample is

  \[
  PDI = \frac{M_W}{M_n} = \frac{4125}{4000} \approx 1.032
  \]

This is still considered a quite monodisperse sample! (it is under PDI=1.1)
Polymers in solution

• Polymers interact with the solution
  • **Lyophilic** polymers (=*hydrophilic* when the solvent is water) → solvated
  • **Lyophobic** polymers (=*hydrophobic* when in water) → non-solvated, these behave as *liquid* or *solid particles*
  • **Amphiphilic** polymers → partly solvated, partly non-solvated
    - non-associating: “unimolecular micelles”
    - associating: *association colloids*
• Interaction with the solution determine the polymers' shape, conformation, size in solution, etc.
$r_M$ is the hypothetical rigid sphere radius (radius of the sphere which has the same mass and density as lysozyme). There is no simple relation between $r_M$ and $r_H$. $r_H$ is the hydrodynamic radius, equivalent to the radius of a rigid sphere having the same diffusion coefficient than the molecule.
Size of macromolecules in solution

- Stokes radius (hydrodynamic radius)

\[ r_H = \frac{k_B T}{6\pi \eta D} \]

- Radius of gyration

\[ r_g = \sqrt{\left(\frac{\sum m_i r_i^2}{\sum m_i^2}\right)} \]

For a random coil polymer:

\[ r_g = \sqrt{\frac{h^2}{6}} \]

- \( k_B \) : Boltzmann constant (J/K)
- \( T \) : temperature (K)
- \( \eta \) : viscosity of the solvent (Pa×s)
- \( D \) : diffusion coefficient (m²/s)
- \( m_i \) : mass of a segment (kg)
- \( r_i \) : distance of the unit from the mass center (m)
- \( h \) : end-to-end distance (m)
Thermal (kinetic) energy provides the continuous spontaneous motion of the molecules or particles.  

\[ \langle E_{\text{kin}} \rangle = \frac{1}{2} m \left( \frac{\langle x \rangle}{t} \right)^2 = \frac{3}{2} k_B T \]

\[ x^2 = 2 D t \]

Mathematics of the Brownian motion

\[ D = \frac{k_B T}{f} = \frac{k_B T}{6\pi \eta r_H} = \frac{R T}{6\pi \eta r_H N_A} \]

\[ <E_{\text{kin}}>: \text{average kinetic energy an atom (J)} \]
\[ m : \text{mass (kg)} \]
\[ x : \text{distance of the random walk (m)} \]
\[ t : \text{time (s)} \]
\[ k_B : \text{Boltzmann constant (m}^2\cdot\text{kg} \cdot \text{s}^{-2} \cdot \text{K}^{-1}) \]
\[ T : \text{absolute temperature (K)} \]

\[ x : \text{distance (m)} \]
\[ t : \text{time (s)} \]
\[ D : \text{diffusion coefficient (m}^2\cdot\text{s}^{-1}) \]
\[ f : \text{friction factor (kg} \cdot \text{s}^{-1}) \]
\[ k_B : \text{Boltzmann constant (m}^2\cdot\text{kg} \cdot \text{s}^{-2} \cdot \text{K}^{-1}) \]
\[ \eta : \text{viscosity of the solvent (Pa} \cdot \text{s}) \]
\[ r_H : \text{hydrodynamic radius (m)} \]
\[ R : \text{gas constant (J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \]
\[ T : \text{absolute temperature (K)} \]
Ideal chain model for polymers

Consider a linear polymer to be a freely-jointed chain with $n$ subunits (segments), each of length $l$, that occupy zero volume, so that no part of the chain excludes another from any location. One can regard the segments of each such chain in an ensemble as performing a random walk (or "random flight") in three dimensions, limited only by the constraint that each segment must be joined to its neighbors. This is the ideal random chain chain mathematic model.

Segments are considered being rigid rods of a fixed length $l$, and their orientation is completely independent of the orientations and positions of neighboring monomers, to the extent that two monomers can co-exist at the same place.
Random walk

http://physchem.ox.ac.uk/~rkt/lectures/liqsolns/polymer_solutions.html

The square root of the end-to-end distance of the configuration shown and the accumulated root mean square end-to-end distance.
Each segment may take up any orientation with respect to its nearest neighbour, i.e. $l$ is the length of segment then the determination of the average end to end distance, $<h>$, is the same as for random walk. After a large number of steps the walker will on average end up exactly where he started, i.e. $<h>=0$, because backward (negative) steps are as likely as forward ones. However, the mean squares distance is not zero and this can be used to characterize the chain length. Which, gives the average square end-to-end distance of the ideal chain:

$$\langle h^2 \rangle = n l^2 = \frac{M}{m} l^2$$

Where $h$ is the end-to-end distance, $n$ is the number of segments, and $M$ and $m$ respectively the polymer and monomer molecular weights. The random walk model should apply when each unit in the chain consists of enough chemical segments.

The maximum, fully extended length $L$ of the chain composed of $n$ segments is $n \times l$
Shape of polymers in solution

- The macromolecules and the solvent interact with each other. Depending on these interactions and the structure of the molecule, polymer chains assume different shapes in solution:
  - When the solvent interacts strongly with the macromolecules, these are solvated and tend to be in extended form (good solvent).
  - When the solvent is a bad solvent (=weak interaction with the polymer), polymer chains are strongly coiled.
  - In a theta solvent the polymer acts as an ideal chain and behaves like in bulk phase (solvent-polymer interaction strength = polymer-polymer interaction strength).
  - Adding a nonsolvent to a polymer solution makes the polymer precipitate (reduction of attractive forces between the polymer and the solvent mixture → the solvent becomes bad solvent).
Shape of polymers in solution

The effect of polymerisation

- Ideal mixture
- Polymerization colloid
- Good solvent → extended
- Theta solvent ↓
- Random coil
- Poor solvent → Highly coiled
Excluded volume

The mean square dimensions of a polymer in dilute solution depend on its interaction with the solvent. The size of the solvent effect on the mean square dimensions versus the dimension in bulk state is represented by an expansion factor ($\alpha$):

$$\langle h \rangle = \langle h_0 \rangle \alpha$$

The average chain length depends on the mean molecular weight:

$$\langle h \rangle = \text{const} \cdot M^\alpha$$

The chain will expand in a good solvent, in order to increase its favorable interaction with that medium. $\alpha^2 > 1$. The size of the effect increases with $M$; alpha$^2$ is proportional to $M^{0.2}$.

The chain will contract in a poor solvent, in order to reduce the unfavorable interaction. $\alpha^2 < 1$. These systems are not easily studied in experiments, because the polymer molecules tend to aggregate or precipitate in such poor solvents.

Flory’s Theta solvent marks the boundary between the good and bad solvents. In the Theta solvent, the medium provides an exact compensation for the excluded volume effect. The mean square dimensions are controlled entirely by the short-range intramolecular interactions, and they are unaffected by the solvent. $\alpha^2 = 1$. The Theta state is achieved in carefully selected solvents, at specified temperature, where the excluded volume vanishes. It is also obtained (Flory hypothesis) in the amorphous bulk state of the pure polymer.

This hypothesis tells us that the conformations of a polymer in the bulk can be inferred from the study of the polymer in dilute solution, so long as the dilute solution is at the Theta condition.
Folded and unfolded configurations

(Folded)
T = 1.0

(Unfolded)
T = 5.0

FIG. 2: Above we see a folded configuration at a low temperature and an unfolded configuration at a high temperature, each with a chain length of \( N = 40 \). In these models, spheres represent monomers, and cylinders represent bonds between monomers.
Semipermeable membranes or selectively permeable membranes are porous membranes which allow certain molecules to pass through but exclude other molecules.

- Permeating molecules pass the membrane by diffusion or facilitated diffusion.
- Macromolecules are retained by semipermeable membranes if they exceed the pore size.
- The molecular weight cut-off (MWCO) value defines the molecular weight above which macromolecules can not pass through the membrane (more exactly less than 10% can pass under 24 hours).
Osmosis and dialysis

- The passage of the solvent molecules through a membrane is called **osmosis**
- Movement of solute ions across the membrane is termed **dialysis**
- All these molecules move by **diffusion along their chemical potential (concentration) gradient**
Osmotic pressure

\[ \Pi = \rho gh \]

\[ \Pi V = nRT \]

\[ \Pi = cRT \]

\(\Pi\): osmotic pressure
\(\rho\): density of the solution
\(g\): gravitational acceleration
\(h\): height of the solution
\(n\): number of moles
\(c\): concentration
\(R\): gas constant

\(\Pi\) is a \textbf{colligative} property

If two solutions of different concentration are separated only by means of a semipermeable membrane, the solutions try to attain the same concentration by \textit{diffusion}. \textit{Osmosis} is the tendency of the system to reach the same concentration in both solutions. It is possible to reverse the process and cause the solvent to pass to the less concentrated solution (\textit{reverse osmosis} or \textit{ultrafiltration}). It is used also to purify water, to concentrate solutions, etc.
Osmotic pressure

- Hypertonic
- Isotonic
- Hypotonic
Osmotic pressure

\[ \Pi = cRT \]  

Ideal case

At higher solute concentrations, there are deviations from the ideal linear relation, thus a virial series is needed to describe the relationship:

\[ \Pi = cRT \left(1 + B_1 c + B_2 c^2 + \ldots\right) \]  

Real case

\[ \Pi \] : osmotic pressure (Pa)
\[ c \] : molar concentration (mol/dm\(^3\))
\[ B \] : virial constant (empiric constant without unit)
\[ M_n \] : number-average molar mass (g/mol)
Determination of molar mass

\[
\frac{h}{c} = \frac{RT}{\rho g M_n} \left(1 + \frac{B_1 c}{M_n}\right)
\]

\[
M = \frac{RT}{\rho g} \times \frac{1}{0.21} = 120 \text{ kg mol}^{-1} = 120,000 \text{ Da}
\]

\(h\): height of column (m)

\(\rho\): density of the solution (kg m\(^{-3}\))

\(g\): gravitational acceleration (m s\(^{-2}\))

\(M_n\): number-average molar mass (mol kg\(^{-1}\))

\(R\): gas constant (J K\(^{-1}\) mol\(^{-1}\))

\(T\): temperature (K)
The Donnan membrane equilibrium

Pr\(^-\): large macromolecular anion

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<td>(Cl^-)</td>
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Initial concentrations

\[(a+y)\ K^+ + y\ Cl^- \iff (b-y)\ K^+ + (b-y)\ Cl^-\]

\[K_d = \frac{(b-y) \cdot (b-y)}{(a+y) \cdot y}\]

In equilibrium, \(K_d = 1\)

\[(a+y) \cdot y = (b-y) \cdot (b-y)\]

Equilibrium concentrations

\[K^+ = a+y\]
\[Pr^- = a\]
\[Cl^- = y\]

Electroneutrality must be fulfilled for both compartments

\[y = \frac{(b-y)^2}{(a+y)}\]

Large ions “hinder” the diffusion of small ions.

Animation: [http://entochem.tamu.edu/Gibbs-Donnan/index.html](http://entochem.tamu.edu/Gibbs-Donnan/index.html)
Donnan membrane equilibrium and sedimentation potential

http://butler.cc.tut.fi/~malmivuo/bem/bembook/03/03.htm
Instrumental techniques

• Size exclusion chromatography (SEC)
  – molecules penetrate though a porous column matrix according to their hydrodynamic radii (bigger elute first)

• Light scattering
  – Molecules scatter light
    • $M_w$, the scattering radius $a$, the radius of gyration $r_g$, and $B^*$ can be calculated from static scattering
    • The diffusion coefficient $D$ and the hydrodynamic radius $r_H$ can be determined from dynamic scattering

• NMR
  – nuclear magnetic resonance: PGSE-NMR, DOSY
  – the diffusion coefficient ($D$) can be determined
Size exclusion chromatography
Size exclusion chromatography

Large particles cannot enter gel and are excluded. They have less volume to traverse and elute sooner.

Small particles can enter gel and have more volume to traverse. They elute later.
Molecular causes of light scattering

The electric field of the light ray illuminating the sample induces a synchronous polarization of the electron cloud around the molecules. The oscillating electric dipole – which is a moving charge – emits secondary (=scattered) light.
Applications of light scattering

- **Tyndall effect**
  - colloidal dispersions scatter light → colored

- **Rayleigh scattering**
  - for small \((r<\lambda/20)\) spherical particles which do not absorb light
  - if they are ordered or their distribution is homogeneous the extinction is complete
  - if not, then positive and negative interferences are equally probable

- **Debye (Rayleigh-Gans-Debye) scattering**
  - For larger particles than the wavelength of light \((r>\lambda)\)
  - Intensity of scattered light is proportional to the number of scattering centers

- **Mie scattering**
  - for particles \(\approx \lambda\) (depends on the angle of view).
    Doppler broadening is proportional to the diffusion coefficient

\[
\frac{I}{I_0} = \frac{8\pi^4}{\lambda^4 H^2} \left( \frac{n^2 - 1}{n^2 + 2} \right)^2 r^6 \left(1 + \cos^2 \Theta\right)
\]

\[
\frac{I}{I_0} = \frac{8\pi^4 \alpha^2}{\lambda^4 H^2} \left(1 + \cos^2 \Theta\right)
\]
Why is the sky blue?

Atmospheric gas molecules scatter light
• shorter wavelengths are more scattered → blue color of the sky
• longer wavelengths are less scattered → red-orange colored sun at sunset
Light scattering photometer