Macromolecular colloids. Size and shape of linear macromolecules. Osmosis and osmotic pressure.
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
  - The term refer 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

- 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 $\rightarrow$ poly(vinyl alcohol-co-vinyl acetate)
  - alternating $\rightarrow$ poly(styrene-alt-maleic anhydride)
  - block $\rightarrow$ poly(ethylene-$b$-ethylene oxide)
  - graft $\rightarrow$ poly(styrene-$g$-butadiene)
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, peptides, proteins)
- Polyethers (epoxies, polyethylene glycol, polysaccharides)
- etc.
Shape of the polymers

- Polymers consist of one or multiple chains (sequence of repeating monomer units)
  - Straight chain polymers
  - Branched chain polymers
  - Circular polymers
  - Dendritic (fractal-like) polymers
  - Cross-linked polymers (solubility decreases with increasing crosslink density)
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
  \[ M_n = \left[ \sum n_i M_i \right] / \sum n_i \]

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

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

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

- 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?
  \[
  M_n = \frac{\Sigma n_i M_i}{\Sigma n_i} = \frac{(100 \times 3000 + 200 \times 4000 + 150 \times 5000)}{450} = 4111
  \]

• The weight-average molecular weight is
  \[
  M_w = \frac{\Sigma n_i M_i^2}{\Sigma n_i M_i} = \frac{(100 \times 3000^2 + 200 \times 4000^2 + 150 \times 5000^2)}{(100 \times 3000 + 200 \times 4000 + 150 \times 5000)} = 4243
  \]
A practical example

- Generally $M_Z > M_W > M_n$

- The polydispersity index of this sample is

$$PDI = \frac{M_w}{M_n} = \frac{4125}{4000} \approx 1.032$$
Polymers in solution

- Polymers interact with the solution
  - Lyophilic polymers (hydrophilic when in water) $\rightarrow$ solvated
  - Lyophobic polymers (hydrophobic when in water) $\rightarrow$ non-solvated, these behave as solid particles
  - Amphiphilic polymers $\rightarrow$ partly solvated, partly non-solvated
- Interaction with the solution determine the polymers' shape, conformation, size in solution, etc.
Molecules in solution: the Brownian motion

- Particles or molecules in solution are constantly colliding with solvent molecules
- The random collisions cause the molecule to have a “random walk” motion
- The effect was first observed for pollen grains in water

Brownian motion (movie)

Robert Brown (1773-1858)
First observed in 1827 by the botanist Robert Brown. He only observed pollen grains under a microscope

Albert Einstein (1879-1955)
1905: the mathematical theory of Brownian motion was developed by Einstein.
Mathematics of the Brownian motion

\[ \langle E_{\text{kin}} \rangle = \frac{1}{2} m \left\langle \frac{dx}{dt} \right\rangle^2 = k_B T \]

Thermal (kinetic) energy provides the continuous spontaneous motion

\[ \sqrt{\langle x^2 \rangle} = \sqrt{2D t} \]

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

\( E_{\text{kin}} \): kinetic energy (J)
\( x \): distance of the random walk (m)
\( t \): time (s)
\( D \): diffusion coefficient (m\(^2\)·s\(^{-1}\))
\( k_B \): Boltzmann constant
\( T \): absolute temperature (K)

\( E_{\text{kin}} \): kinetic energy (J)
\( x \): average distance (m)
\( t \): time (s)
\( D \): diffusion coefficient (m\(^2\)·s\(^{-1}\))
\( k_B \): Boltzmann constant
\( \eta \): viscosity of the solvent (Pa·s)
\( r_H \): hydrodynamic radius (m)
\( R \): gas constant (J·mol\(^{-1}\)·K\(^{-1}\))
\( T \): absolute temperature (K)
A comparison of the radius of gyration to other types of radii can be shown using lysozyme (N-acetylmuramide glycanhydrolase enzyme) from egg white as an example.

From the crystallographic structure, lysozyme can be described as a 26 x 45 Å ellipsoid with an axial ratio of 1.73. The molecular weight of the protein is 14.7 kDa,

The radius of gyration ($R_g$) is defined by the expression given before.

$R_M$ is the equivalent radius of a sphere with the same mass and particle specific volume as lysozyme,

$R_R$ is the radius established by rotating the protein about the geometric center.

$R_H$ or the hydro-dynamic radius is the radius of a hypothetical hard sphere that diffuses with the same speed as the particle under examination, which includes both solvent (hydro) and shape (dynamic) effects.

The hydrodynamic radius ($R_H$) is then calculated from the diffusion coefficient using the Stokes-Einstein equation.
Size of macromolecules in solution

• Stokes radius (hydrodynamic radius)

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

- \( k_B \): Boltzmann constant
- \( T \): temperature
- \( \eta \): viscosity of the solvent
- \( D \): diffusion coefficient

• Radius of gyration

\[ R_g = \left( \frac{\sum m_i r_i^2}{\sum m_i} \right)^{0.5} \]

- \( m_i \): mass of an unit
- \( r_i \): distance of the unit from the mass center
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 molecules, these are solvated and tend to be in extended form (*good solvent*).

- When the solvent is a *bad solvent*, polymer chains are strongly coiled.

- In a *theta solvent* the polymer acts as an ideal chain and behaves like in bulk phase.

- Adding a *nonsolvent* to a polymer solution makes the polymer to precipitate.
Shape of polymers in solution

The effect of polymerisation

mixture of red and blue

good solvent → extended

theta solvent ← random coil

ideal mixture → polymerization (colloid)

poor solvent → Highly coiled
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.
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 model.

Segments are rigid rods of a fixed length \( l \), and their orientation is completely independent of the orientations and positions of neighbouring monomers, to the extent that two monomers can co-exist at the same place.
Random coils

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 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:

\[
\langle h_0^2 \rangle = nl^2 = \frac{M}{m} l^2
\]

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

The maximum, fully extended length \( L \) of the chain is clearly \( n \times l \).
Random walk

The square root of the end-to-end distance of the configuration shown and the accumulated root mean square end-to-end distance.

http://physchem.ox.ac.uk/~rkt/lectures/liqsolns/polymer_solutions.html
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 is represented by an expansion factor, alpha:

\[ \langle h \rangle = \langle h \rangle_0 \alpha \]

\[ \langle h \rangle = \text{const} \, M^\alpha \]

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 tends 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.
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.
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 gradient.
Osmosis is the spontaneous net movement of water across a semipermeable membrane from a region of high solvent potential to an area of low solvent potential, up a solute concentration gradient. In general, these membranes are impermeable to organic solutes with large molecules, such as polysaccharides, while permeable to water and small, uncharged solutes.
Osmotic pressure: \( \Pi \)

\( \Pi = \rho gh \)
\( \Pi V = nRT \)
\( \Pi = cRT \)

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

\( \Pi \) is a colligative property

If you place two solutions of different concentration side by side, keeping them separated only by means of a membrane, you will see the level of the more concentrated solution increase, because the two solutions try to attain the same concentration by diffusion. It is possible to reverse the process and cause the solvent to pass to the less concentrated solution. This is the process of the reverse osmosis or ultra filtration. It is used also to purify water, to concentrate solutions, etc. Osmosis is the tendency of the system to reach the same concentration in both solutions.
Osmotic pressure
**Determination of molar mass**

\[ \Pi = cRT \quad \text{Ideal case} \]

\[ \Pi = cRT(1 + Bc + Cc^2 + Dc^3 + \ldots) \quad \text{Real case} \]

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<th>(c/(g/l))</th>
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<th>2</th>
<th>4</th>
<th>7</th>
<th>9</th>
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<td>(h/cm)</td>
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<td>0,71</td>
<td>2,01</td>
<td>5,1</td>
<td>8,0</td>
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<tr>
<td>(h/c)</td>
<td>0,28</td>
<td>0,36</td>
<td>0,503</td>
<td>0,73</td>
<td>0,889</td>
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</table>

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

\[
M = \frac{RT}{\rho g} \times \frac{1}{0,21} \left[\text{kg mol}^{-1}\right]
\]

\[= 120 \text{ kg mol}^{-1} = 120 \text{ kDa}\]

\(h\): height of column
\(\rho\): density of the soln.
\(g\): gravitational acceleration
\(M\): molar weight
\(R\): gas constant
\(T\): temperature
The Donnan membrane equilibrium

Pr⁻: large macromolecular anion

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<tbody>
<tr>
<td>K⁺ = a</td>
<td>K⁺ = b</td>
</tr>
<tr>
<td>Pr⁻ = a</td>
<td>Cl⁻ = b</td>
</tr>
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Initial concentrations

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<tbody>
<tr>
<td>K⁺ = a + y</td>
<td>K⁺ = b - y</td>
</tr>
<tr>
<td>Pr⁻ = a</td>
<td>Cl⁻ = b - y</td>
</tr>
<tr>
<td>Cl⁻ = y</td>
<td></td>
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</tbody>
</table>

Equilibrium concentrations

At equilibrium, the rates of diffusion are equal

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

Electroneutrality must be fulfilled for both compartments

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

Large ions “hinder” the diffusion of small ions.

Animation:  http://entochem.tamu.edu/Gibbs-Donnan/index.html
Donnan membrane equilibrium and sedimentation

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