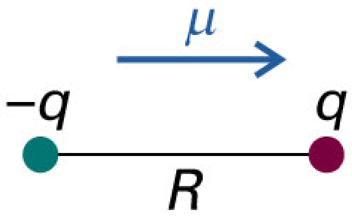
Lecture 6

Molecular interaction.
Macromolecules and aggregates

Lecture plan

1. Interaction of molecules with each other and external field:
    - Dipole moment
    - Polarizability
    - Dipole-dipole interactions
    - Hydrogen bonding
    - Hydrophobic interaction
2. Macromolecules
    - Measurements on macromolecules:
        - Light scattering
        - Sedimentation
        - Electrophoresis
    - Random coil model of a polymer
    - DNA as an example of a polymer
    - Micelles, colloids and SAM

Electric dipole moment



1 Electric dipole

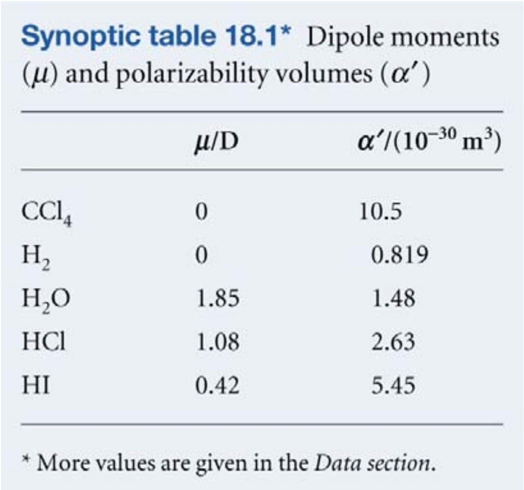
Dipole moment measured in **C·m** or in debye:

$$1D = 3.33564\times 10^{-30}\ Cm$$

dipole moment of 2 electrons separated by 1Å:

$$4.8\mathrm{D}=1.6\times 10^{-29}\ Cm$$

- Dipole moment of a molecule can be calculated by taking into account the locations and magnitudes of the partial charges on all the atoms



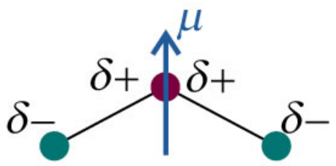
Synoptic table 18.1* Dipole moments (μ) and polarizability volumes (α')

	μ/D	$\alpha'/(10^{-30}\ \mathrm{m}^3)$
CCl_4	0	10.5
H_2	0	0.819
H_2O	1.85	1.48
HCl	1.08	2.63
HI	0.42	5.45

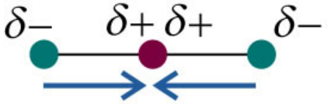
* More values are given in the *Data section*.

$$\mu_x = \sum_j q_j x_j$$

$$\mu = \mu_x{}^2 + \mu_y{}^2 + \mu_z{}^2$$



Ozone, O_3



Carbon dioxide, CO_2

Electric dipole moment

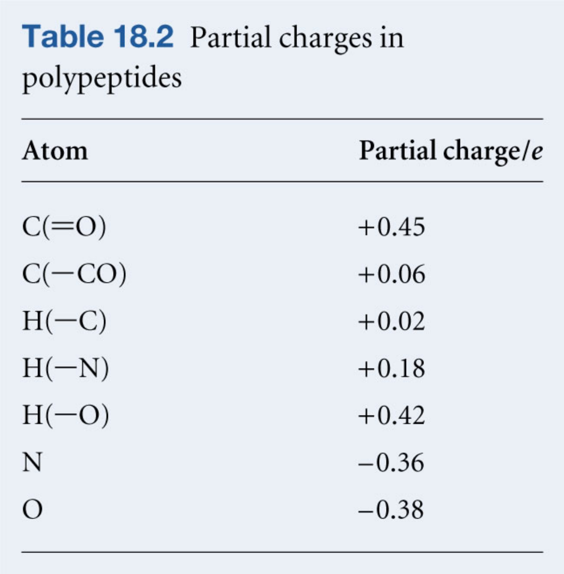
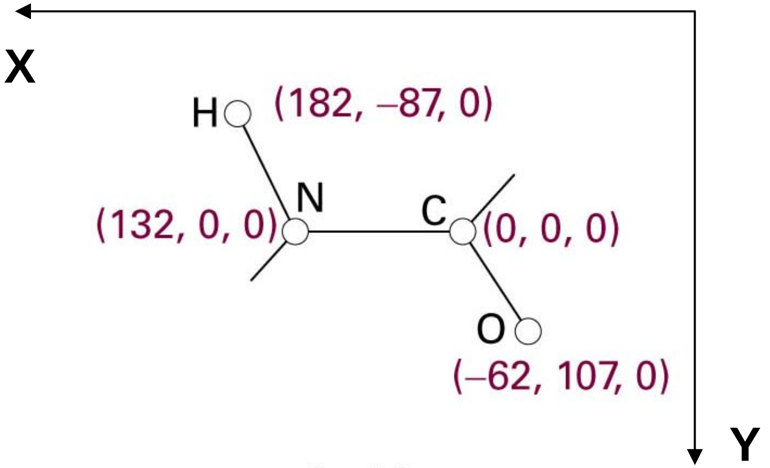


Table 18.2 Partial charges in polypeptides

Atom	Partial charge/*e*
C(=O)	+0.45
C(−CO)	+0.06
H(−C)	+0.02
H(−N)	+0.18
H(−O)	+0.42
N	−0.36
O	−0.38

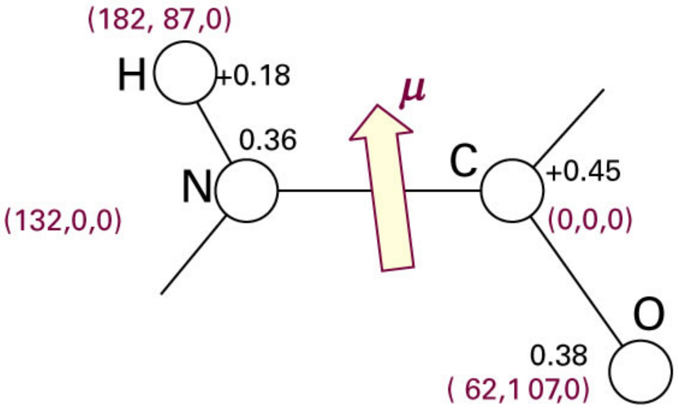


Amide group

$$\mu_x = -0.36e \times 132\,pm + 0.45e \times 0\,pm + 0.18e \times 182\,pm + (-0.38e) \times (-62\,pm) = 8.8e\ pm$$

$$\mu_y = -0.36e \times 0\,pm + 0.45e \times 0\,pm + 0.18e \times (-87\,pm) + (-0.38e) \times (107\,pm) = -56e\ pm$$

$$\mu_z = 0$$



Polarization

- The polarization, P, of the sample is the dielectric dipole moment density: mean electric dipole moment of a the molecules multiplied by the number density

$$P = \langle \mu \rangle N$$

$\langle \mu \rangle = 0$ Ìn an isotropic fluid sample in the absence of an applied electric field

$\langle \mu_z \rangle = \dfrac{\mu^2 E}{3kT}$ In an electrical field E applied along z direction

This equation can be obtained using Boltzmann distribution:

$$\langle \mu_z \rangle = \int \mu \cos\theta dp$$

$$dp = \frac{e^{-E(\theta)/kT} \sin\theta d\theta}{\int_0^\pi e^{-E(\theta)/kT} \sin\theta d\theta}, \qquad \text{where: } E(\theta) = -\mu E\cos\theta,\ 0 \le \theta \le \pi$$

Polarizabilities

- An applied electric field can distort a molecule as well as align its permanent electric dipole moment.
  The induced dipole moment

$$\mu^* = \alpha E$$

where α – polarizability of the molecule

- Polarizability is usually expressed as polarizability volume:

$$\alpha' = \frac{\alpha}{4\pi\varepsilon_0}$$

that has dimension of volume and similar in magnitude to molecular volumes

- Polarizability volume usually correlates with HOMO-LUMO gap, large polarizability correspondes to small gaps
- At high frequencies polarizability drops:
  - **orientation polarization**: it takes 1ps for a molecule in liquid to rotate by 1 rad in fluid, so it's lost above 10^{11} Hz
  - **distortion polarization** (due to distortion of nuclear position): lost at frequencies above the particular bond vibration frequency
  - electronic polarization (due to distortion of electron distribution), the only polarization that survives in the visual region.

Relative permittivities

- Coulomb interaction of two charges in media

$$V = \frac{q_1 q_2}{4\pi\varepsilon_r\varepsilon_0 r}$$

relative permettivity of the medium

- Permettivity of a substance is large if its molecules are polar or highly polarizable

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{\rho P_m}{M}$$

Debye equation

- Molar polarization, P_m is defined as:

$$P_m = \frac{N_A}{3\varepsilon_0}\left(\alpha + \frac{\mu^2}{3kT}\right)$$

  - in case of no permanent dipole moment: Clausius-Mossotti equation

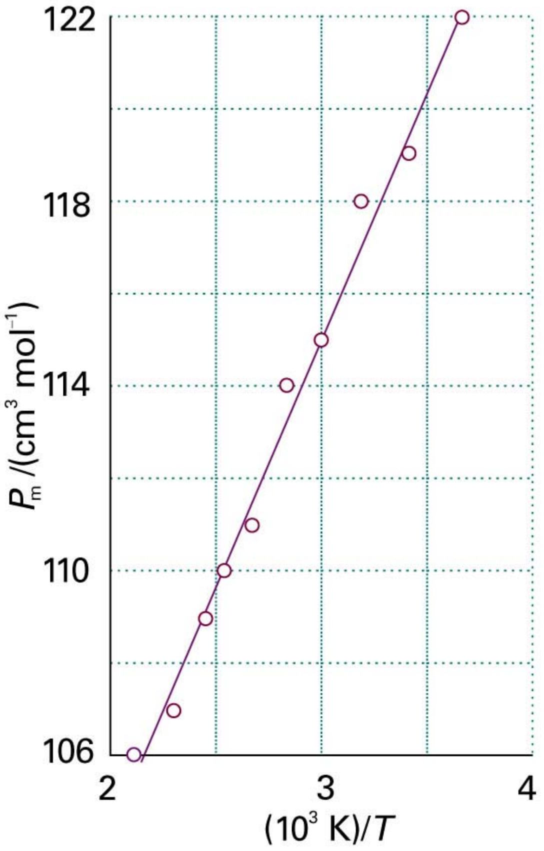
$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{\rho N_A \alpha}{3M\varepsilon_0}$$

Experimental determination of dipole moment and polarizabilitiy

- the sample is placed inside a capacitor and capacitance is measured with the sample and without vs temperature

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{\rho}{M}\frac{N_A}{3\varepsilon_0}\left(\alpha + \frac{\mu^2}{3kT}\right)$$

- the slope gives molecular dipole moment and the intercept at 1/T=0 gives polarizability



- at the frequencies of visible light Clausius-Mossotti equation can be used to determine molecular polarizability from refractive index

$$n_r = \varepsilon_r^{\frac{1}{2}}$$

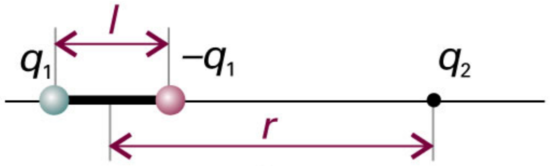
Interaction between molecules

- van der Waals interaction: the attractive interaction between closed-shell molecules that depends on distance as $1/r^6$.
- interaction between charges of polar molecules
- strong repulsive interaction at low distances

Interaction between dipoles

- interaction of a dipole and a point charge

$$V = -\frac{\mu_1 q_2}{4\pi\varepsilon_0 r^2}$$



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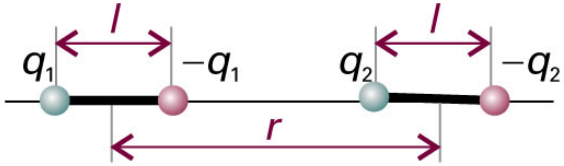
- dipole-dipole interaction

$$V = -\frac{\mu_1 \mu_2}{2\pi\varepsilon_0 r^3}$$



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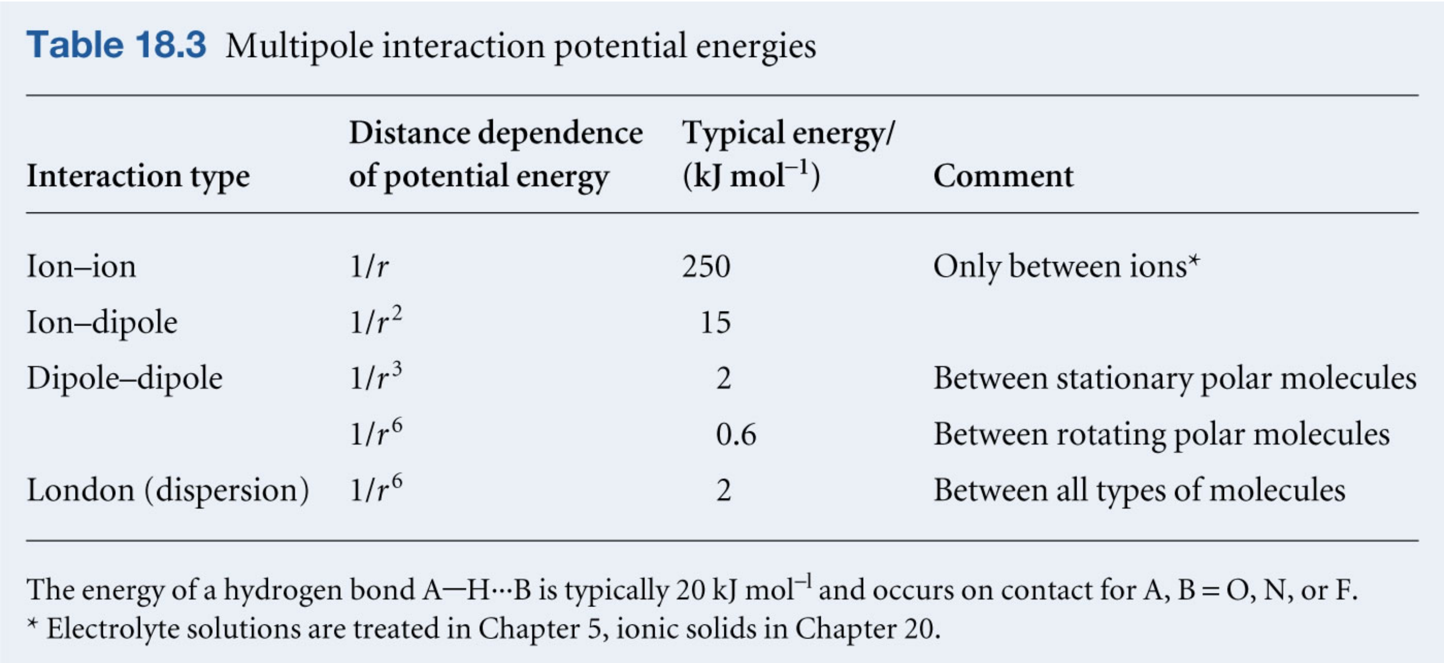
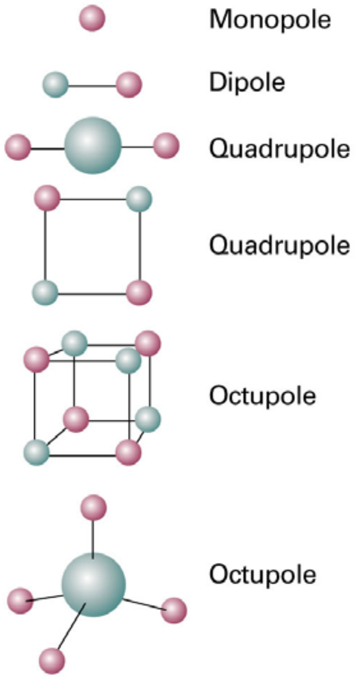


Table 18.3 Multipole interaction potential energies

Interaction type	Distance dependence of potential energy	Typical energy/ (kJ mol^{-1})	Comment
Ion–ion	$1/r$	250	Only between ions*
Ion–dipole	$1/r^2$	15	
Dipole–dipole	$1/r^3$	2	Between stationary polar molecules
	$1/r^6$	0.6	Between rotating polar molecules
London (dispersion)	$1/r^6$	2	Between all types of molecules

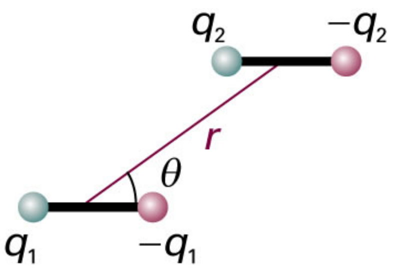
The energy of a hydrogen bond A—H···B is typically 20 kJ mol^{-1} and occurs on contact for A, B = O, N, or F.

* Electrolyte solutions are treated in Chapter 5, ionic solids in Chapter 20.



Interaction between dipoles

- dipole-dipole interaction



$$V = \frac{\mu_1 \mu_2 f(\theta)}{4\pi\varepsilon_0 r^3} \qquad f(\theta) = 1 - 3\cos^2\theta$$

in case of free rotation the interaction would be zero, but as the dipoles interact the rotation is not free even in a gas phase!

$$\langle V \rangle = -\frac{C}{r^6} \qquad C = \frac{2\mu_1^{\ 2}\mu_2^{\ 2}}{3 \cdot (4\pi\varepsilon_0)^2 kT}$$

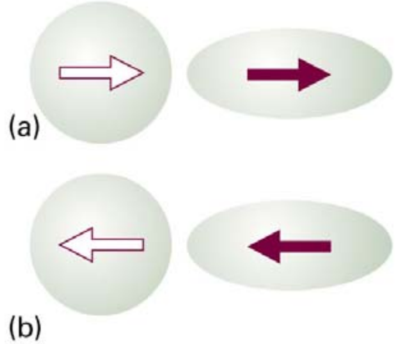
Keesom interaction

attractive interaction

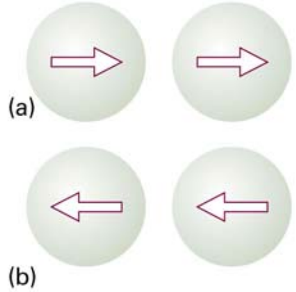
Interaction between dipoles

- dipole-induced dipole interaction

$$V = -\frac{C}{r^6} \qquad C = \frac{\mu_1^{\,2}\alpha'}{4\pi\varepsilon_0}$$



- induced dipole-induced dipole interaction
  - interaction due to transient dipoles resulting from fluctuations of electron distribution.
  - called **dispersion attraction** or **London interaction**

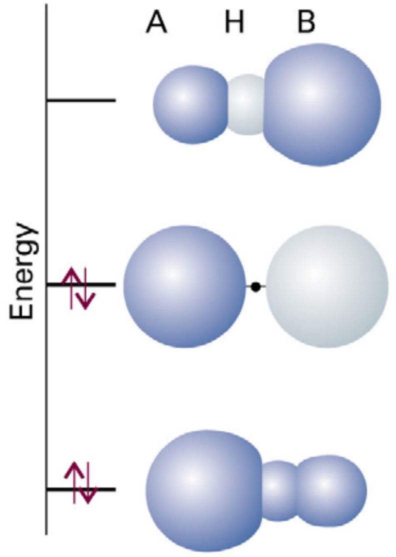


$$V = -\frac{C}{r^6} \qquad C = \frac{1}{2}\alpha_1'\alpha_2'\frac{I_1 I_2}{I_1 + I_2}$$

I_1, I_2 – ionization energies of the two molecules

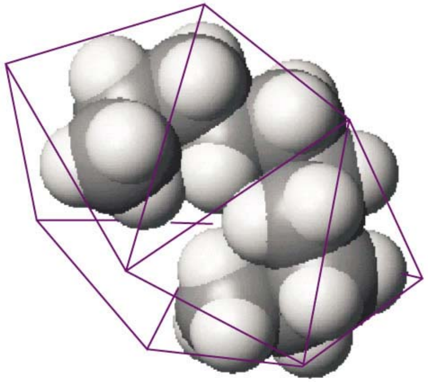
Hydrogen bonding

- **Hydrogen bonding** is an attractive interaction between two species that arises from a link of the form A-H …B where A and B are highly electronegative elements and B possesses a lonely pair of electrons. Typical for N, O and F
  Typical strength: 20kJ/mol (0.2eV)



Hydrophobic interaction

- individual non-polar molecules when dissolved in water cause formation of clathrate cage around each molecule. As a result this process causes decrease in the entropy



$$CH_4(\text{in } \mathrm{CCl}_4) \rightarrow CH_4(aq)$$

$$\Delta_{\text{transfer}}\mathrm{G}{=}{+}12\text{kJ/mol}, \ \Delta_{\text{transfer}}\mathrm{H}{=}{-}10\text{kJ/mol},$$

$$\Delta_{\text{transfer}}\mathrm{G}{=}{-}75\text{kJ/mol at } 298\text{K}$$

- hydrophobicity of a molecular group R can be quantified using a hydrophobicity constant:

$$\pi = \log \frac{S}{S_0}$$

where S is the ratio of the molar solubility of the compound R-A in octanol to that in water and S0 is the ratio of the molar solubility of the compound H-A in octanol to that in water.

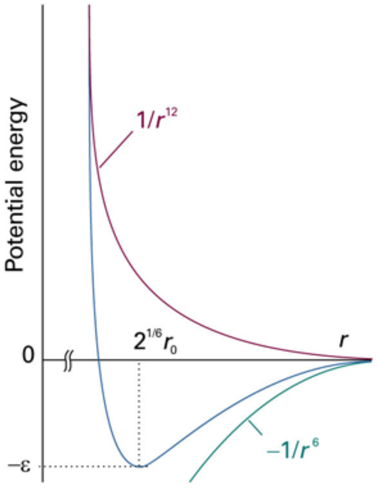
measurements suggest group additivity:

$$\begin{array}{llll} R = CH_3, & CH_2CH_3 & (CH_2)_2CH_3 & (CH_2)_3CH_3 \\ \pi = 0.5 & 1.0 & 1.5 & 2.0 \end{array}$$

Total attractive interaction

- If hydrogen bonds are not formed than total attractive interaction between rotating molecules is sum of dipole-dipole, dipole-induced-dipole and induced-dipole-induced-dipole interactions. Overall:

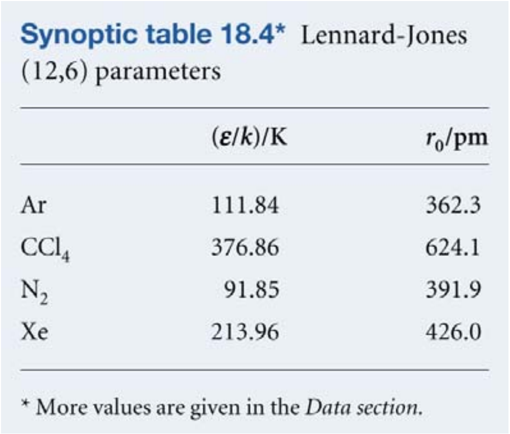
$$V = -\frac{C}{r^6}$$



- Repulsive interaction:
  - hard sphere approximation: $\begin{Bmatrix} V = \infty & r \le d \\ V = 0 & r > d \end{Bmatrix}$
  - Mie potential $$V = \frac{C_n}{r^n} - \frac{C_m}{r^m}$$
  - Lennard-Jones potential

$$V = 4\varepsilon\left\{\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^{6}\right\}$$

$$F = -\frac{dV}{dr} = \frac{24\varepsilon}{r_0}\left\{2\left(\frac{r_0}{r}\right)^{13} - \left(\frac{r_0}{r}\right)^{7}\right\}$$



Synoptic table 18.4* Lennard-Jones (12,6) parameters

	(ε/k)/K	r_0/pm
Ar	111.84	362.3
CCl_4	376.86	624.1
N_2	91.85	391.9
Xe	213.96	426.0

* More values are given in the *Data section.*

Macromolecules

- Macromolecules:
  - – Natural: DNA, polysaccharides, polypeptides etc
  - – Synthetic: polymers
- Macromolecule is **monodispersed** if it has single definite molar mass.
  Otherwise, if it is a mixture of molecules of different length, it is **polydispersed**

- **weight-averaged molar mass:**

$$\tilde{M}_w = \frac{1}{m}\sum_i m_i M_i = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$$

Mean molecular mass of Macromolecules

- Various experimental technique used to measure molar masses will result in different types of mean values:
  - Osmometry: number-average molar mass

$$\tilde{M}_n = \frac{1}{N}\sum_i N_i M_i$$

  - Viscosity: viscosity-average molar mass
  - Light-scattering: weight-average molar mass

$$\tilde{M}_w = \frac{1}{m}\sum_i m_i M_i = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$$

  - Sedimentation: Z-average molar mass

$$\tilde{M}_z = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i^2}$$

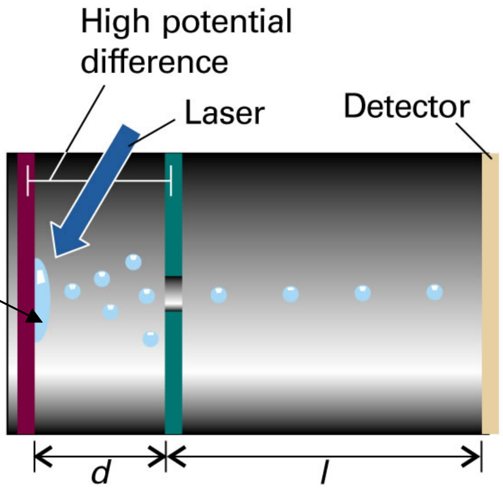
Mass spectroscopy of macromolecules

- Mass spectroscopy is one of the most accurate techniques for determination of molar masses
- Challenge with macromolecules:
  difficult to produce gaseous ions without fragmentation
- Most useful techniques:
  - Electrospray ionization
  - MALDI-TOF (matrix-assisted laser desorbtion/ionization)

MALDI-TOF spectroscopy

- MALDI-TOF – matrix-assisted laser desorption/ionization – time-of-flight spectroscopy

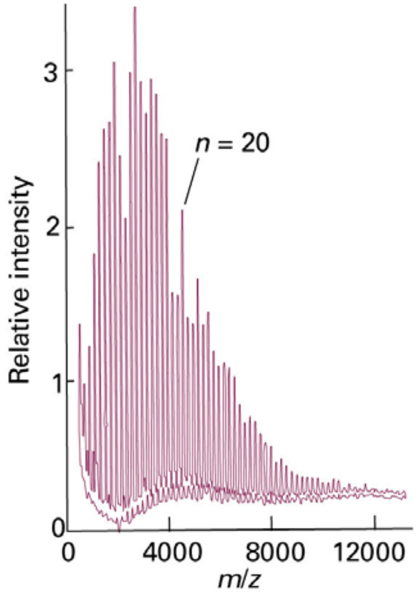
macromolecules embedded in a matrix of organic material and inorganic salts



$$\frac{mv^2}{2} = zeEd$$

$$t = l\left(\frac{m}{2zeEd}\right)^{\frac{1}{2}}$$

$$\frac{m}{z} = 2eEd\left(\frac{t}{l}\right)^2$$

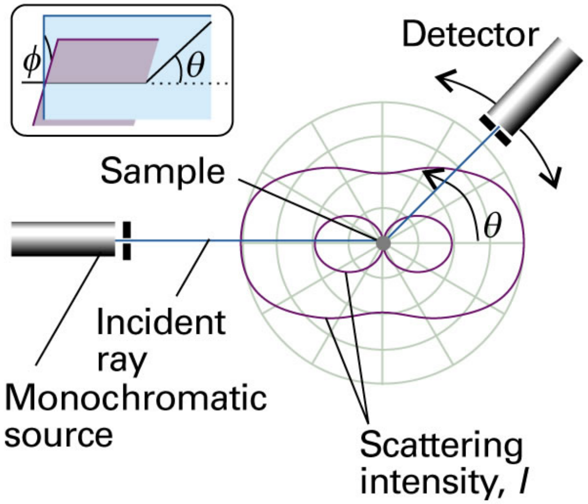


Laser-light scattering

- as light shines on a particle it creates an oscillating dipole proportional to polarizability and light intensity
- **Elastic** light scattering: oscillating dipoles in the particle radiate at the incident frequency
- In perfectly homogeneous media all scattered waves interfere destructively and disappear; in an inhomogeneous media radiation is scattered

Laser-light scattering

- **Rayleigh scattering:** scattering of light by the particles much smaller than the wavelength of light
- **Properties:**
  - intensity of scattered light proportional to λ^{-4}.
  - intensity of scattered light proportional to the molar mass of the particle
  - intensity of scattered light depends on the scattering angle θ;
  - for a very dilute solution excited by plane-polarized light, the Rayleigh ratio:



$$R_\theta = \frac{I}{I_0} \times \frac{r^2}{\sin^2 \phi}$$

for a polymer: $R_\theta = K P_\theta c_p \tilde{M}_w$, where $K = \dfrac{4\pi^2 n_{r,0}{}^2 V (dn_r / dc_p)^2}{\lambda^4 N_A}$

structure factor, takes into account interference of light scattered from different of the same molecule

small → $P_\theta \approx 1$

macro → $P_\theta \approx 1 - \dfrac{16\pi^2 R_g{}^2 \sin^2\left(\frac{1}{2}\theta\right)}{3\lambda^2}$

Scattering by non-ideal solutions of polymer

- Large molecules displace and reorganize large quantities of solvant i.e. introduce extra entropy changes
- Large molecules exclude other solute molecules from occupied regions
- Enthalpy contribution as solvent-solvent interaction is different from solvent-macromolecule interaction

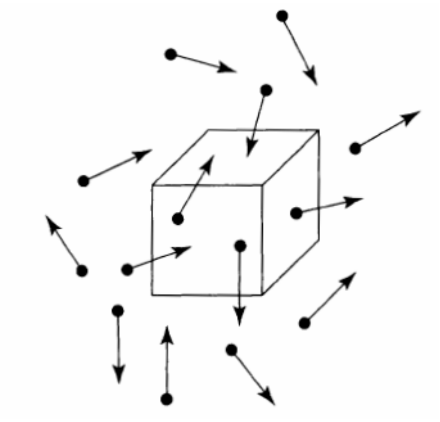
$$\frac{Kc_p}{R_\theta} = \frac{1}{P_\theta \tilde{M}_w} + Bc_p$$

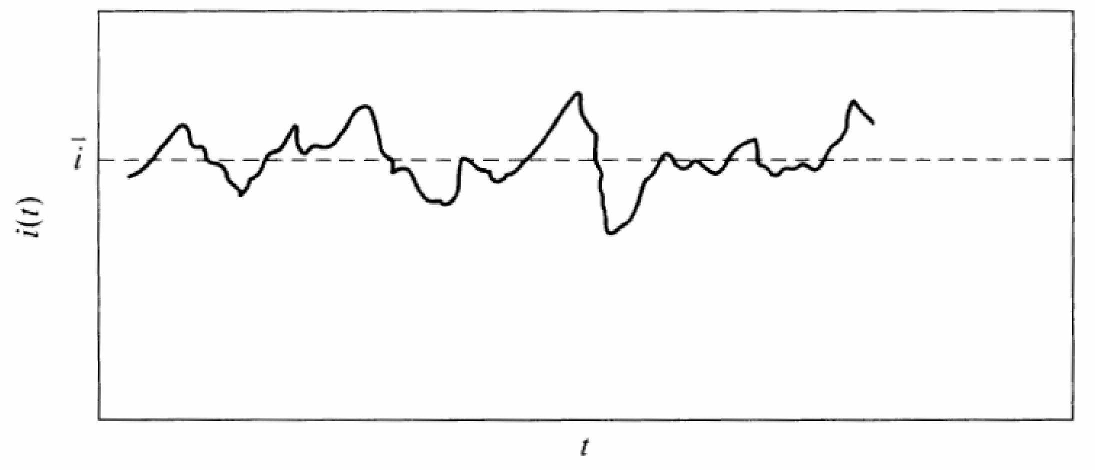
empirical constant

- Θ**-temperature** – temperature at which B=0, the solution at this temperature behaves nearly ideal

Dynamic light scattering

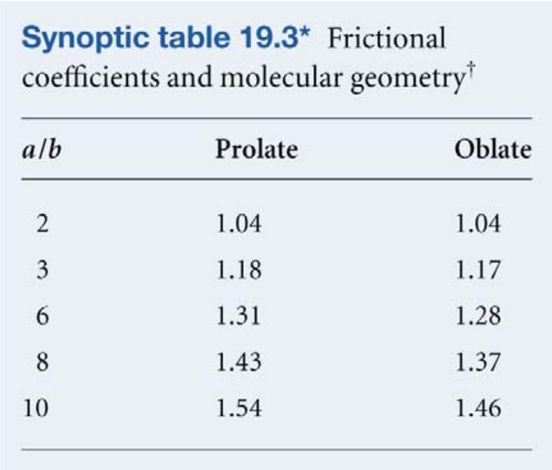
- **Dynamic light scattering**: as two molecules moves in the solution the light scattered from them will change from interfering constructively to destructively and back. For large number of particles it results in intensity fluctuations that depend on diffusion coefficient.





$$D = \frac{kT}{f}, \text{ where frictional coefficient } f = 6\pi a\eta$$

The size obtained from DLS assumes spherical object, otherwise corrections should be made:



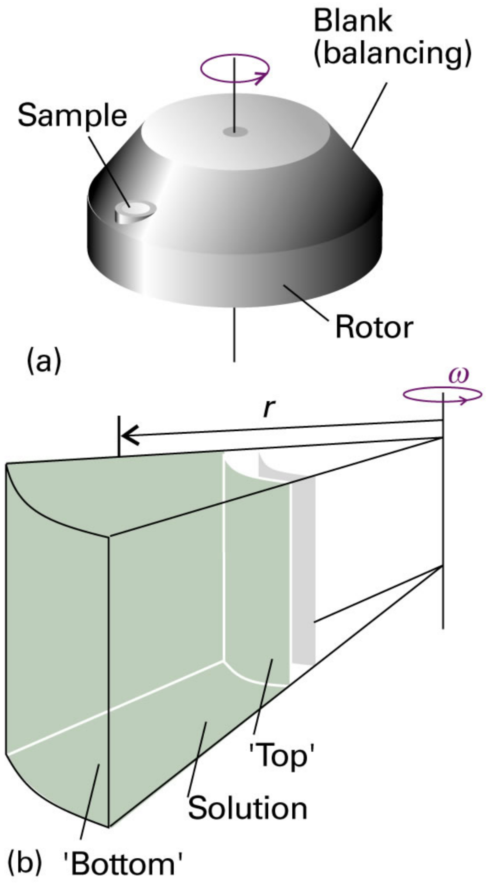
Synoptic table 19.3* Frictional coefficients and molecular geometry†

a/b	Prolate	Oblate
2	1.04	1.04
3	1.18	1.17
6	1.31	1.28
8	1.43	1.37
10	1.54	1.46

For dilute monodispersed polymer, consisting of random coils: $D = \beta_D M^{-0.6}$

Ultracentrifugation

- **sedimentation:** process where heavy particles settle towards the foot of column, can be greatly accelerated by **ultracentrifugation**



$$m_{eff} = bm = (1 - \rho v_s)m$$

drift speed: $$s = \frac{m_{eff} r\omega^2}{f} = \frac{bmr\omega^2}{f}$$

Sedimentation constant $$S = \frac{s}{r\omega^2} = \frac{b\tilde{M}_n}{fN_A}$$

$$S = \frac{b\tilde{M}_n}{6\pi a\eta N_A}$$

if we combine DLS and ultracentrifugation we can find molar mass without assuming a particular shape of a molecule

$$\tilde{M}_n = \frac{SRT}{bD}$$

Sedimentation equilibrium

- during prolonged centrifugation (several days!) an equilibrium concentration profile can be reached

Chemical potential at a point r in the solution $\tilde{\mu}(r) = \mu(r) - \frac{1}{2} m\omega^2 r^2$

at equilibrium: $\left(\frac{\partial \tilde{\mu}}{\partial r}\right)_T = \left(\frac{\partial \mu}{\partial r}\right)_T - M\omega^2 r = 0$

$$\left(\frac{\partial \mu}{\partial r}\right)_T = \left(\frac{\partial \mu}{\partial p}\right)_{T,c}\left(\frac{\partial p}{\partial r}\right)_{T,c} + \left(\frac{\partial \mu}{\partial c}\right)_{T,p}\left(\frac{\partial c}{\partial r}\right)_{T,p}$$

$$\boxed{V_m = Mv}$$

$$\boxed{p(r) = p(r_0) + \tfrac{1}{2}\rho\omega^2(r^2 - r_0^2)}$$

$$\boxed{\mu = \mu^{\theta} + RT\ln c}$$

$$\tilde{M}_w = \frac{2RT}{(r_2{}^2 - r_1{}^2)b\omega^2}\ln\frac{c_2}{c_1}$$

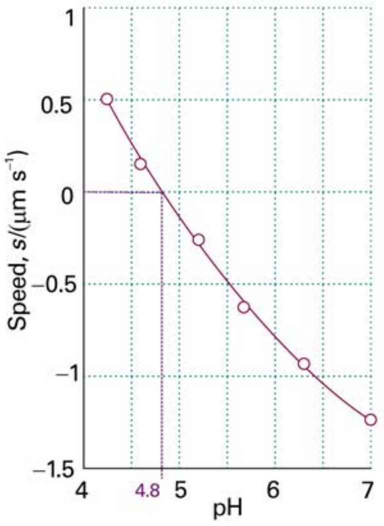
Electrophoresis

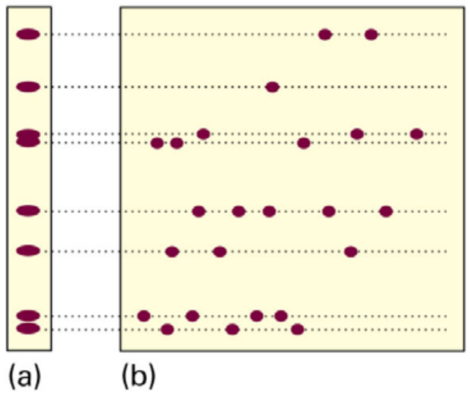
- Charged macromolecules (like DNA) move in response to electric field

drift speed in electrical field E: $$s = \frac{zeE}{f}$$

challenge: large molecules might require high voltage applied to reach reasonable drift speed, that leads to heating. Solved by **capillary electrophoresis**

- Common materials: agarose (large pores, good for large macromolecules like DNA) and polyacrylamide (PAGE)
- Proteins have different charge and shape that affect results of electrophoresis. SDS (sodium dodecyl sulfate) denatures proteins and forms a rod-shaped complex with constant charge: SDS-PAGE
- Isoelectric focusing: in a gradient of pH, the protein will stop moving when isoelectric point is reached.
- 2D-electrophoresis: result of isoelectric focusing is further separated by SDS-PAGE





Viscosity

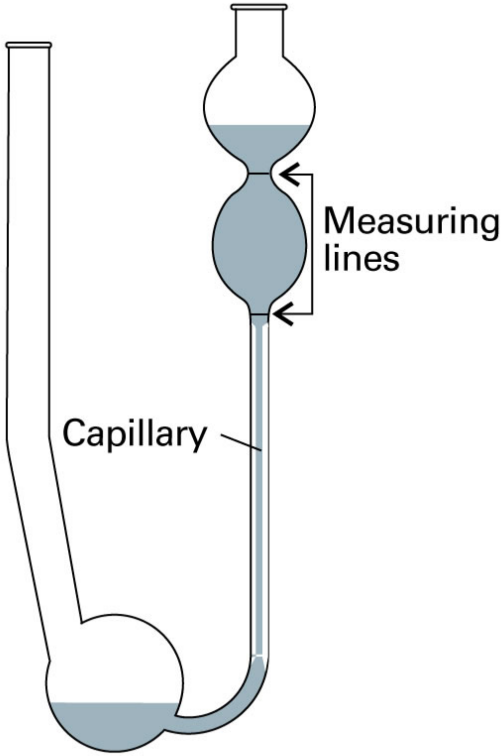
- presence of macromolecules increases viscosity of the solution

$$\eta = \eta_0 (1 + [\eta] c + \ldots) \quad [\eta] = \lim_{c \to 0} \left(\frac{\eta - \eta_0}{c \eta_0} \right)$$

$$\frac{\eta}{\eta_0} = \frac{t}{t_0} \times \frac{\rho}{\rho_0}$$

- Solution of macromolecules often fits Mark-Kuhn-Houwink-Sakurada equation

$$[\eta] = K \tilde{M}_v^{\,a}$$



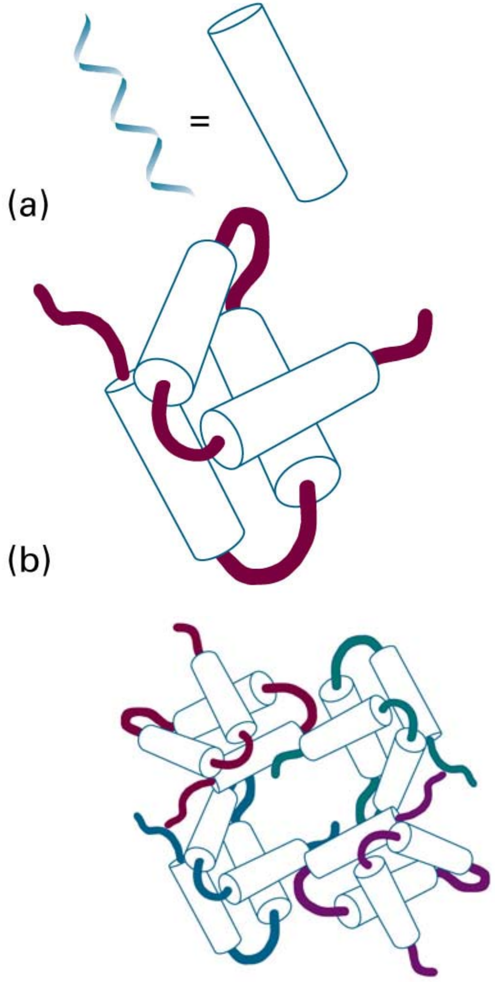
Ostwald viscometer

Structure and dynamics

- **configuration** – structural features of a molecule that can be only changed by breaking chemical bonds
- **conformation** – spatial arrangement of different parts of a chain

Structure and dynamics

- **levels of structure:**
  - primary: the sequence of molecular residues
  - secondary: spatial arrangement of a chain (coils, helicies etc.). Loss of secondary structure is called denaturation
  - tertiary: overall three-dimensional structure of the molecule
  - quaternary structure: the manner in which large molecules are formed by aggregation of others, e.g. 4 sub-units of haemoglobin

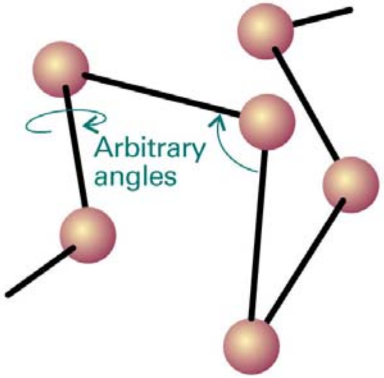


Structure and dynamics

- **Random coils** – most likely configuration for identical units not forming hydrogen bonds

Simplest model of random coils:

Freely joint chain, zero residues volume



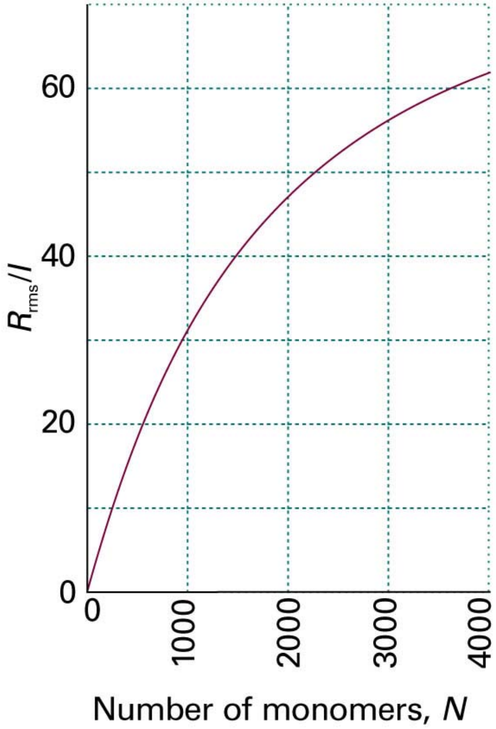
Probablity that ends of a one-dimensional freely jointed chain of **N** units of length **l** are distance **nl** apart:

$$P = \left(\frac{2}{\pi N}\right)^{\frac{1}{2}} e^{-n^2/2N}$$

$$f(r) = 4\pi \left(\frac{a}{\pi^{1/2}}\right)^3 r^2 e^{-a^2 r^2} \qquad a = \left(\frac{3}{2Nl^2}\right)^{\frac{1}{2}}$$

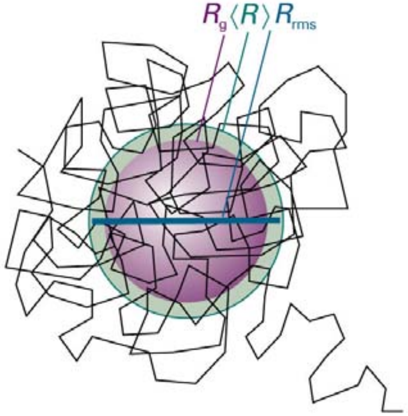
Structure and dynamics

- **Measures of the geometrical size of a random coil**



Contour length: $R_c = Nl$

Root mean square separation (average separation of the ends fo a coil): $R_{rms} = N^{\frac{1}{2}}l$

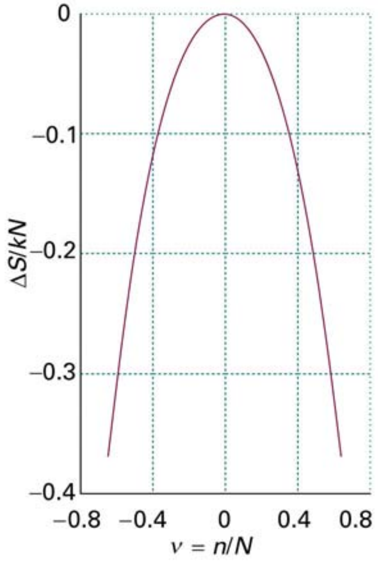


Radius of gyration (radius of a shell with equivalent moment of inertia):

$$R_g = \frac{1}{N}\left(\tfrac{1}{2}\sum_{i,j} R_{i,j}^2\right)^{\frac{1}{2}} = \left(\frac{N}{6}\right)^{\frac{1}{2}} l$$

Conformational entropy and Entropic force

- Random coil is a state with highest entropy stretching reduces the entropy



Change in entropy of random coil due to stretching by ***nl***:

$$\Delta S = -\tfrac{1}{2} kN \ln\left\{(1+v)^{1+v}(1-v)^{1-v}\right\}, \text{ where } v = n/N$$

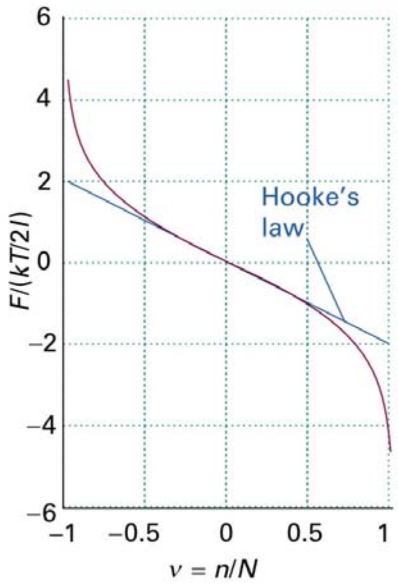
$$dU = TdS - PdV + Fdx$$

$$\left(\frac{\partial U}{\partial x}\right)_{T,V} = T\left(\frac{\partial S}{\partial x}\right)_{T,V} + F$$

$$F = -T\left(\frac{\partial S}{\partial x}\right)_{T,V}$$

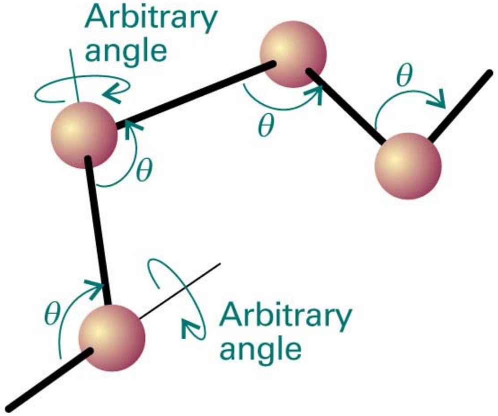
$$\Rightarrow \quad \boxed{F = -\frac{T}{l}\left(\frac{\partial S}{\partial n}\right)_{T,V} = -\frac{kT}{2l}\ln\left(\frac{1+\nu}{1-\nu}\right)}$$

Small extension: $F \approx \dfrac{vkT}{l} = \dfrac{nkT}{Nl}$



Constrained chain model

- Freely joined chain model can be improved by restricting the bond angles



correction factor for R_{rms} and R_g:

$$F = \left(\frac{1 - \cos\theta}{1 + \cos\theta} \right)^{1/2}$$

for example for tetrahedral bonds:

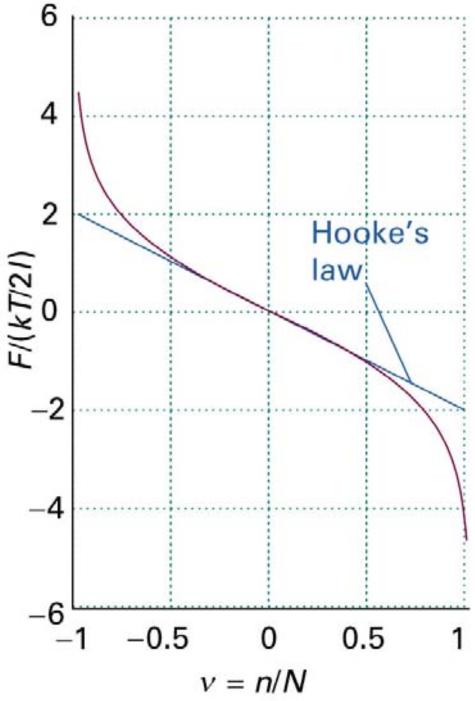
$$\theta = 109.5^0 \Rightarrow F = \sqrt{2}$$

$$R_{rms} = (2N)^{1/2} l \qquad R_g = \left(\frac{N}{3} \right)^{1/2} l$$

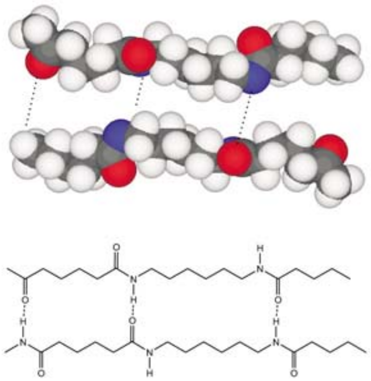
Structure and stability of polymers

- Synthetic polymers:
  - **elastomers:** can expand and contract easily.

    perfect elastomer: internal energy independent on the extension, can be modeled as random coil



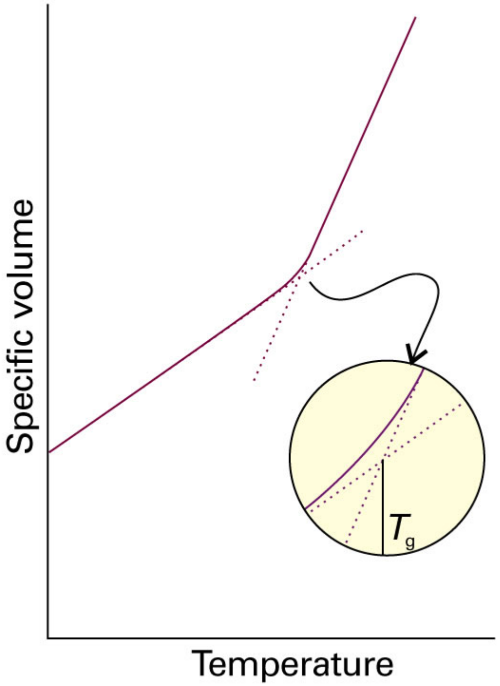
  - **fibre:** strong polymer due to interaction between chains, example: Nylon-66
  - **plastic**: situation intermediate between elastomer and fibre



Phase transitions in synthetic polymers

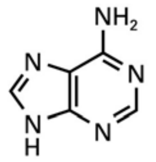
- **melting temperature**

- **glass transition** temperature:
  at temperatures lower than Tg writhing motion of bonds is frozen

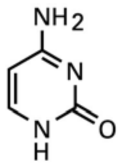


Nucleic acids: primary structure

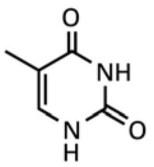
- Nucleotide monomers



3 Adenine, A

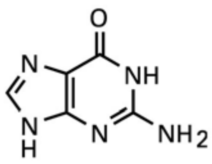


4 Cytosine, C

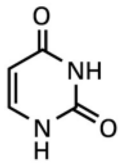


6 Thymine, T

DNA only



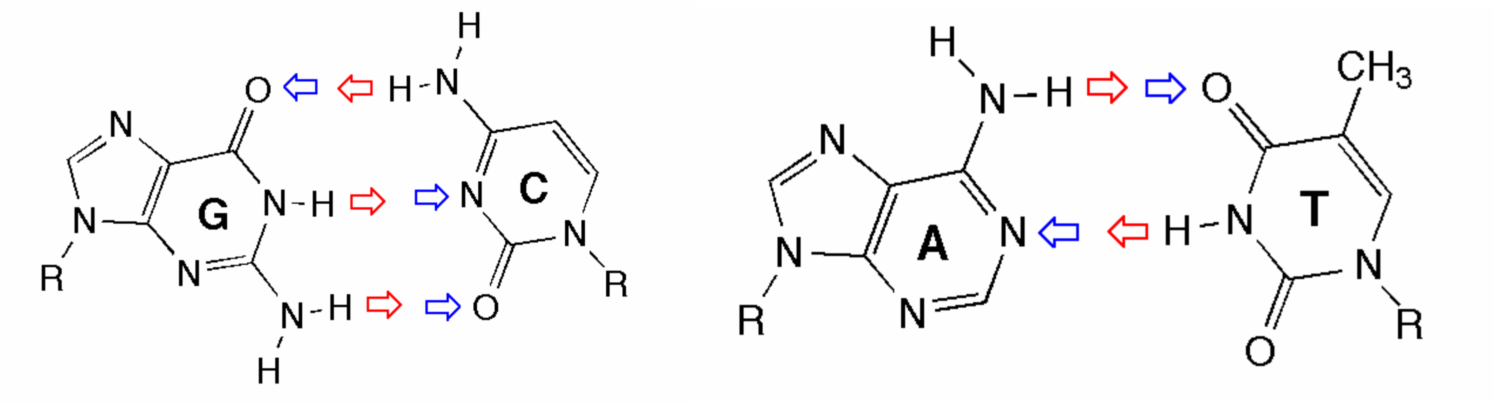
5 Guanine, G

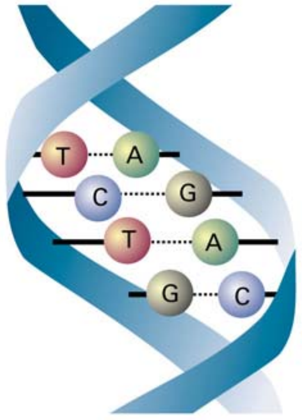


7 Uracil, U

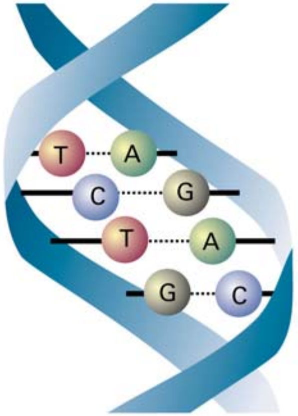
RNA only

- Watson-Crick base pairs

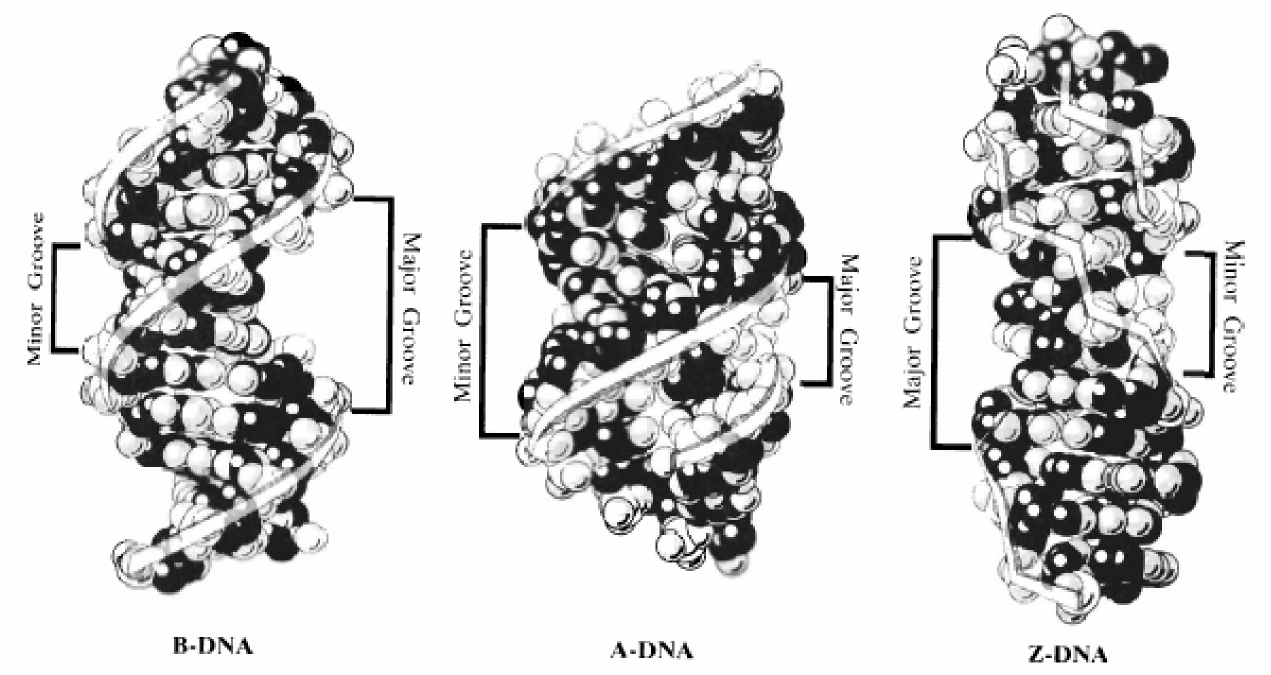




Nucleic acids: secondary structure



- DNA secondary structures: All helical !



Standard for DNA;
In solution or high humidity;
0.34 nm/bp, 10-10.5 bp/turn

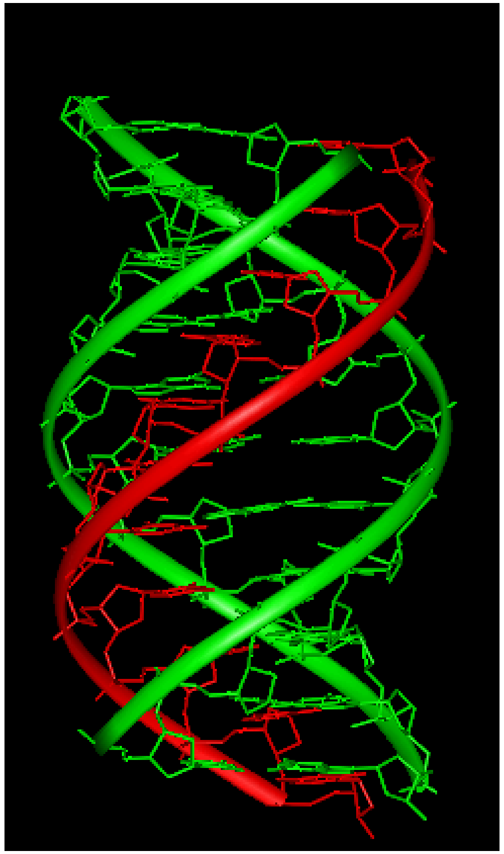
0.26 nm/bp

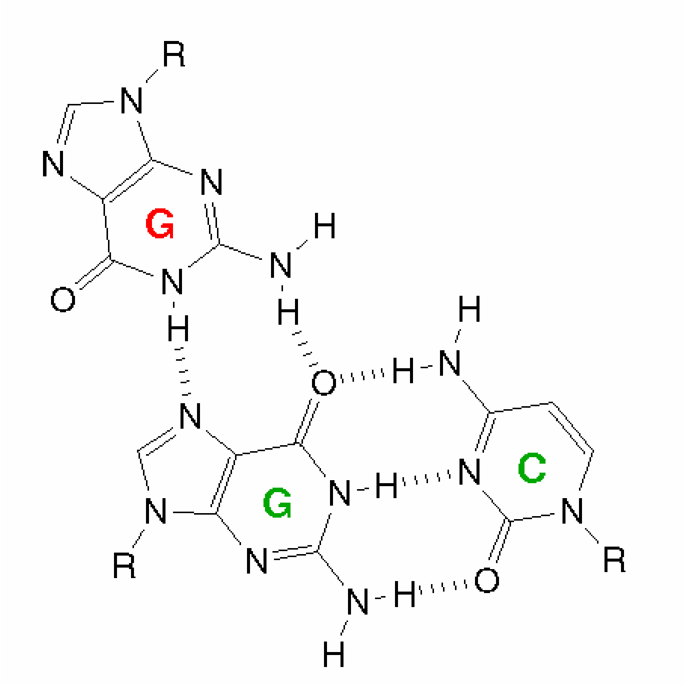
-12 bp/turn (left handed)

Low humidity, high salt, ethanol environment

Nucleic acids

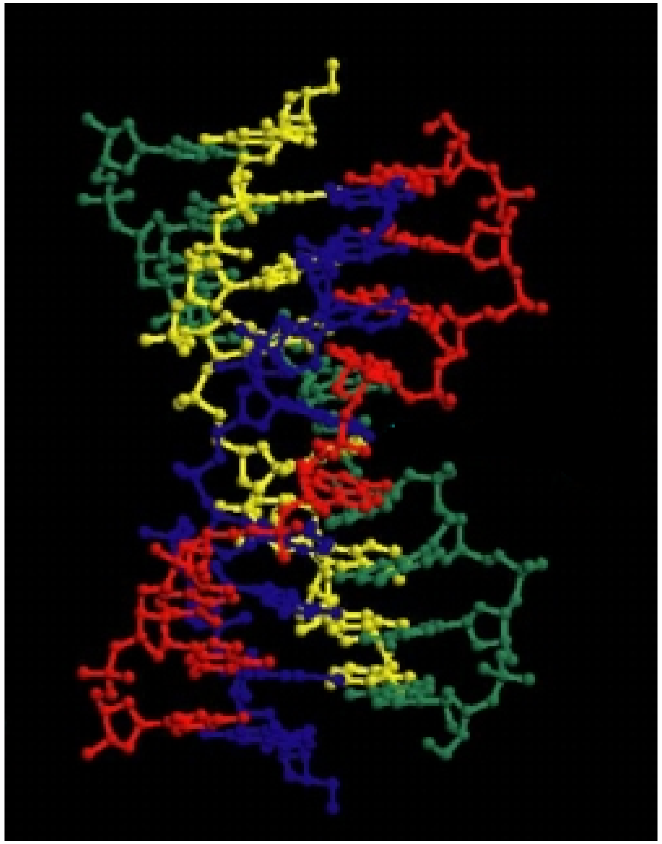
- Hoogsteen pairing: triplex DNA

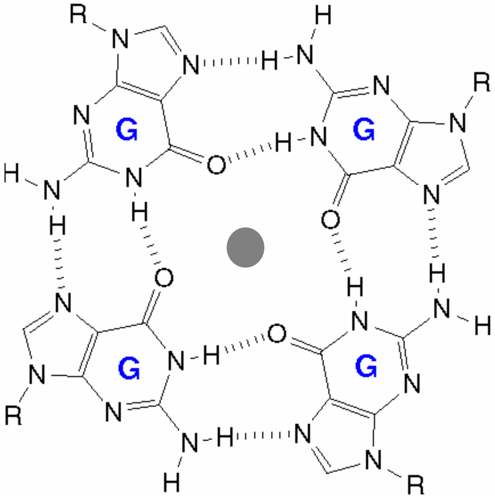




Nucleic acids

- Hoogsteen pairing: quadruplex G4 (found at the telomere ends)

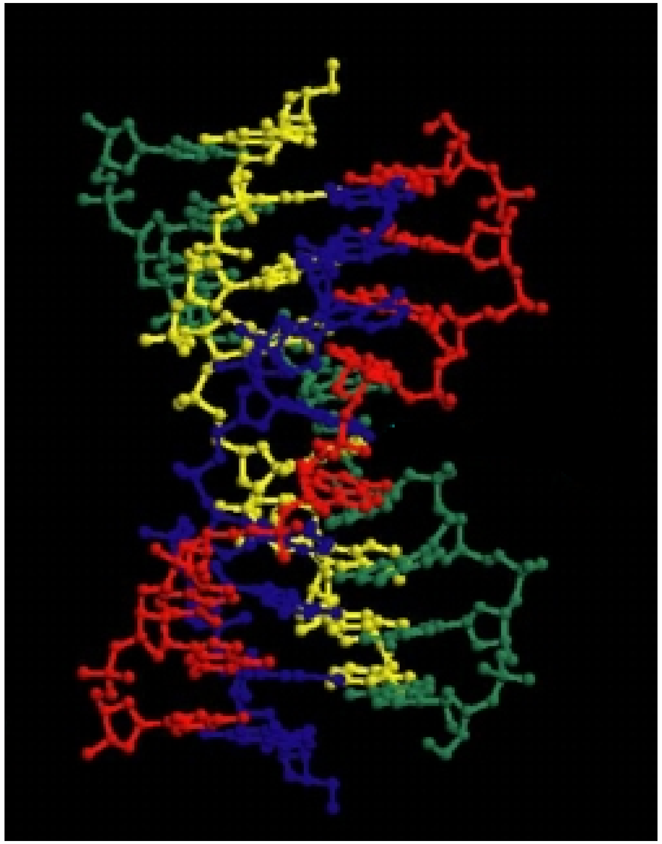


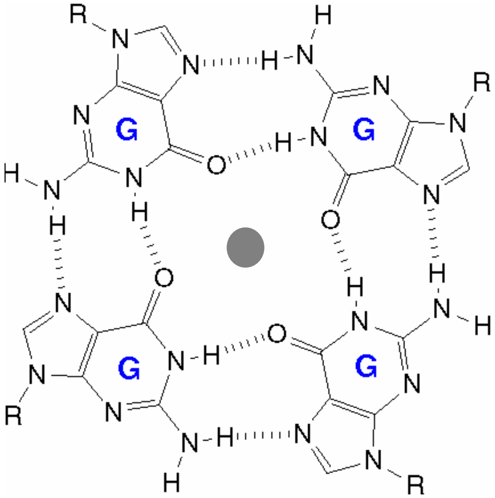


● K^+ or Na^+

Nucleic acids

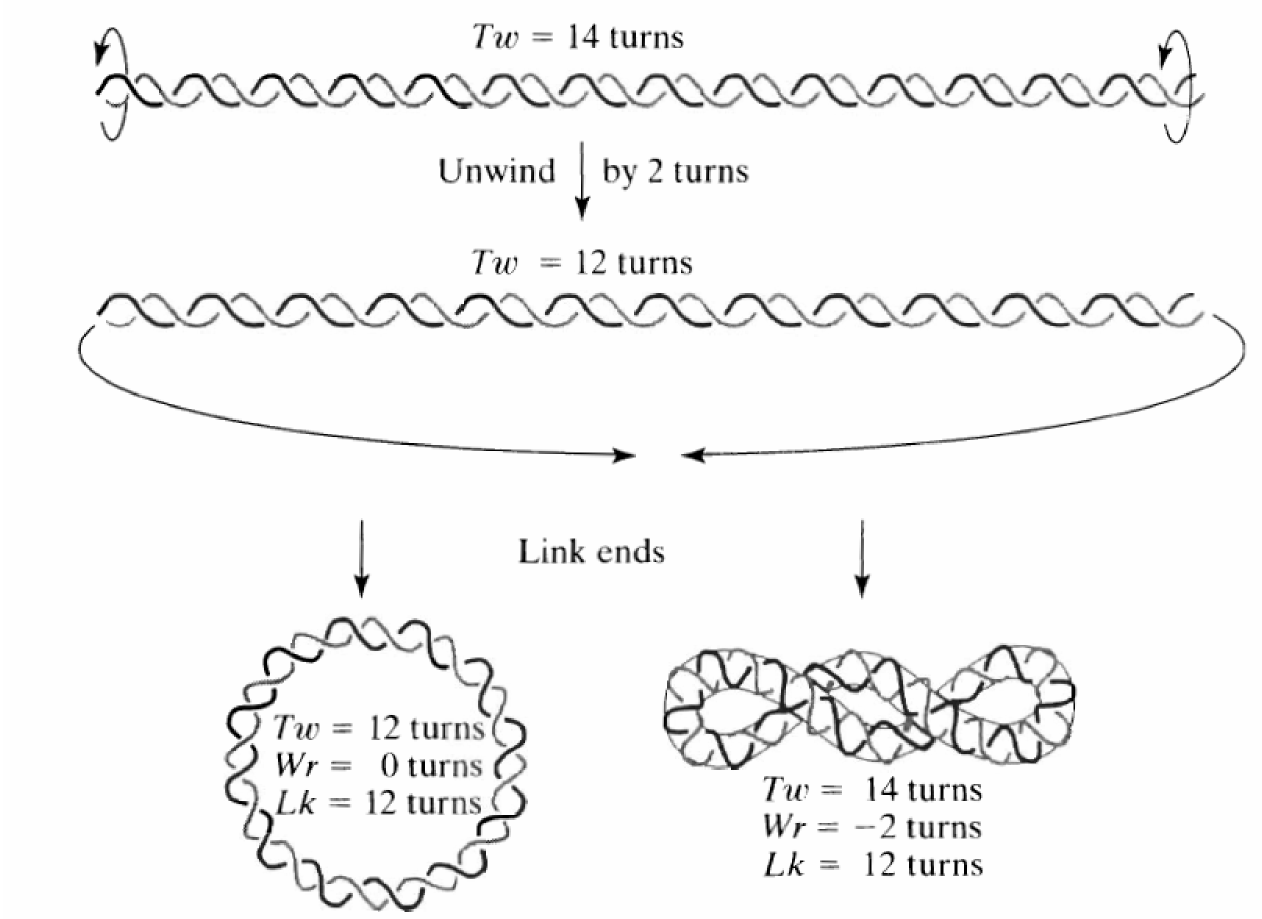
- Hoogsteen pairing: quadruplex G4 (found at the telomere ends)

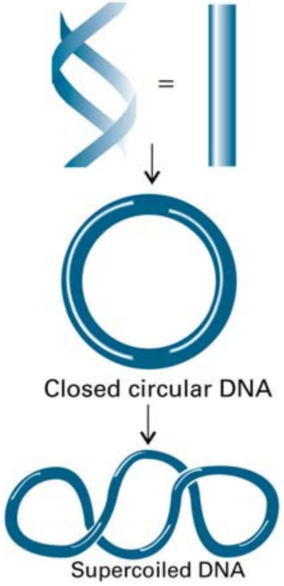




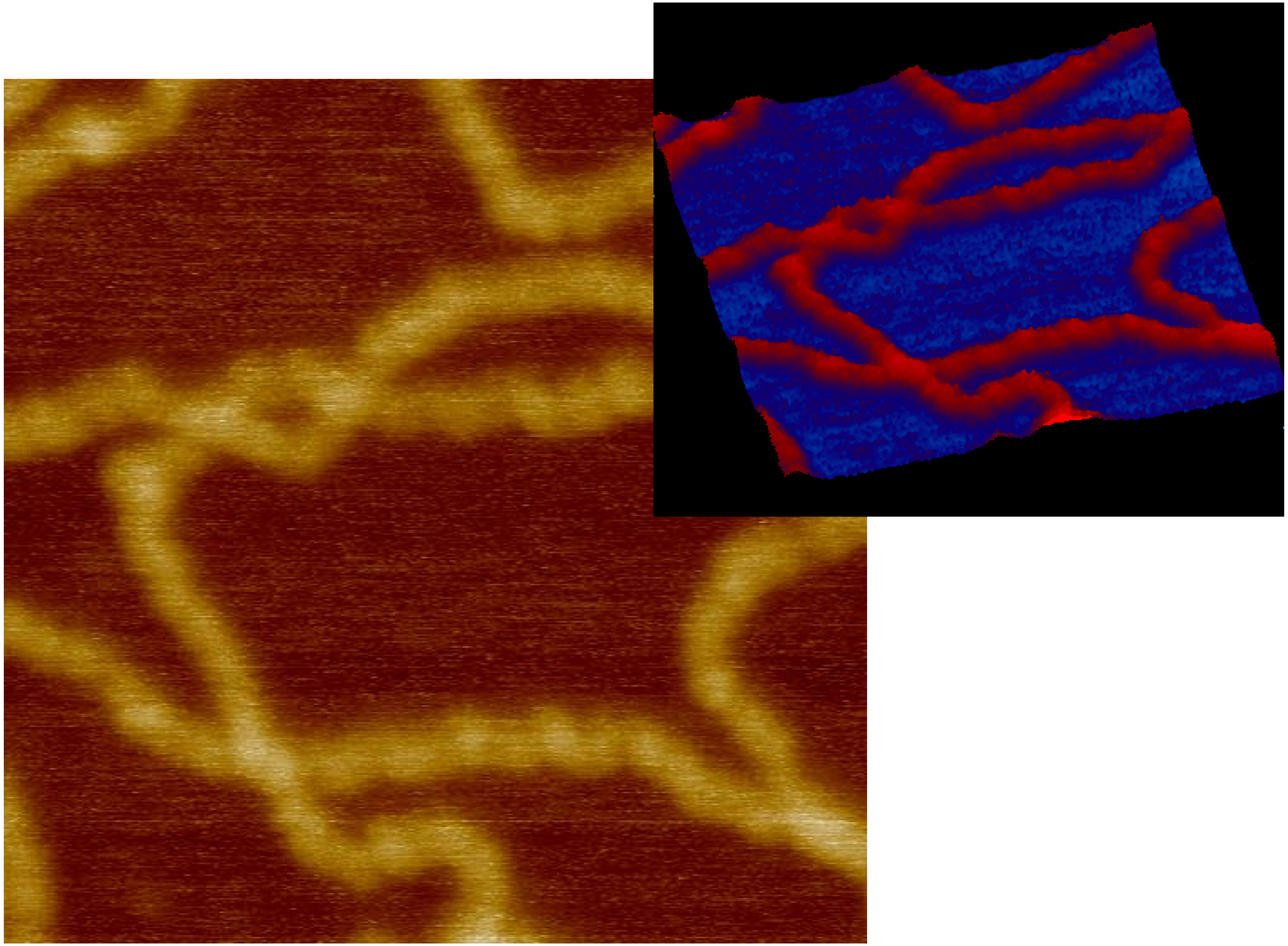
● K^+ or Na^+

DNA: tertiary structure

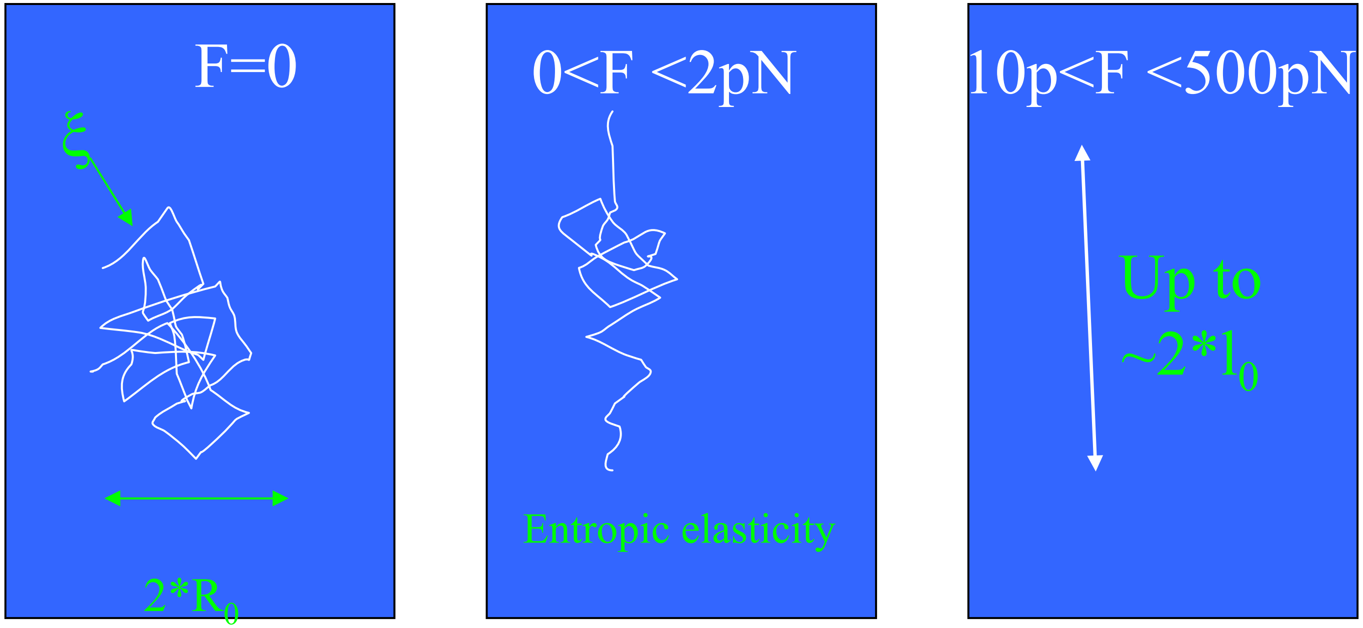




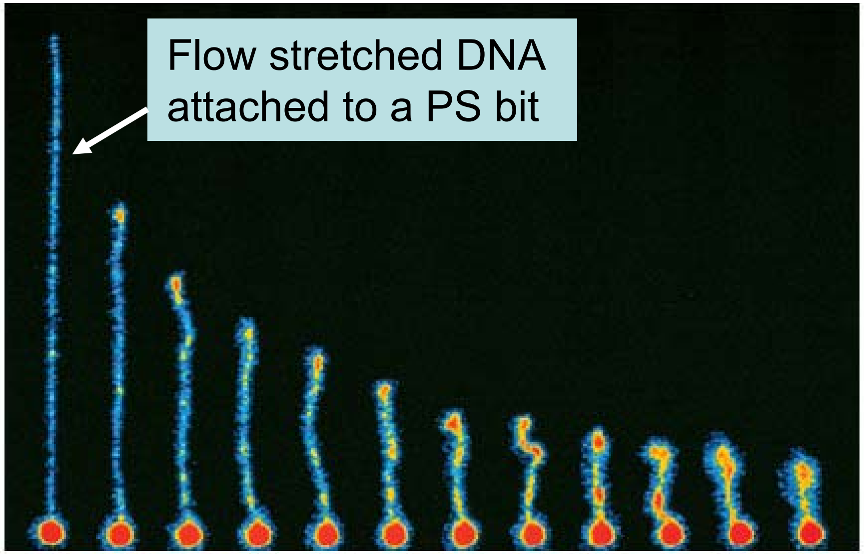
AFM on DNA



DNA stretching

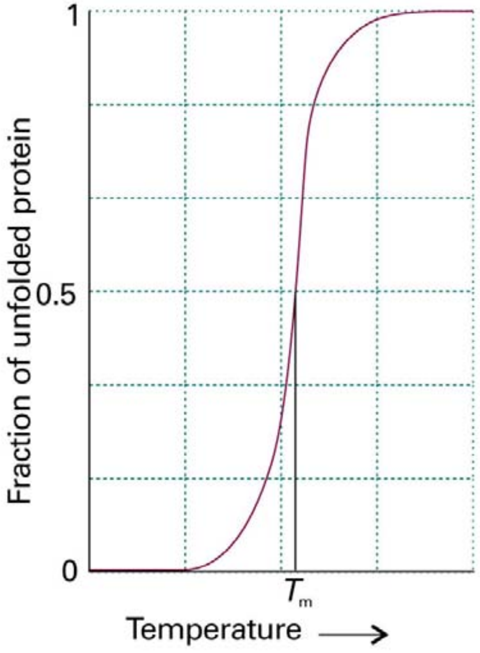


The relaxation of a single, 39 μm–long DNA molecule stained with YOYO-1 iodide imaged at 4.5 second intervals. *Perkins TT, Quake SR, Smith DE, Chu S. Science 264, 822-826 (1994)*


Flow stretched DNA attached to a PS bit

Denaturation of proteins and nucleic acids

- Denaturation: loss of the natural conformation, can be achieved by temperature of chemical agents
- Thermal denaturation - melting



Colloids

- colloids:
  - sol – dispersion of solid in liquid
  - aerosol – dispersion of liquid or solid in gas
  - emulsion – dispersion of liquid in liquid
- colloids are thermodynamically unstable due to large surface energy involved
- factors stabilizing colloids: electric charge, protective layer, surfactants etc.

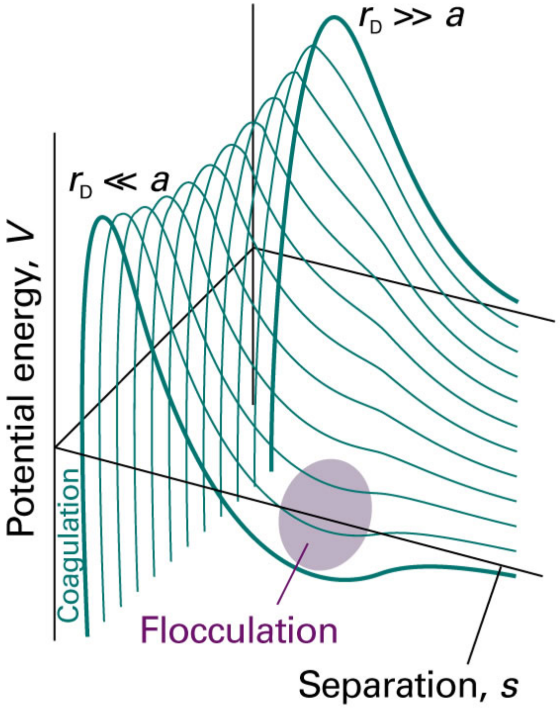
Colloids

- **Electrical double layer**
  - fairly immobile layer of ions and solvent molecules tightly adhered to the surface: **radius of shear.** electric potential at this layer relative to the bulk of medium is called ζ zeta potential.
  - outer ionic atmosphere

$$V_{repulsion} = +\frac{Aa^2\zeta}{R} e^{-s/r_D}$$

$$r_D = \frac{\varepsilon RT}{2\rho F^2 l b^{\ominus}}$$

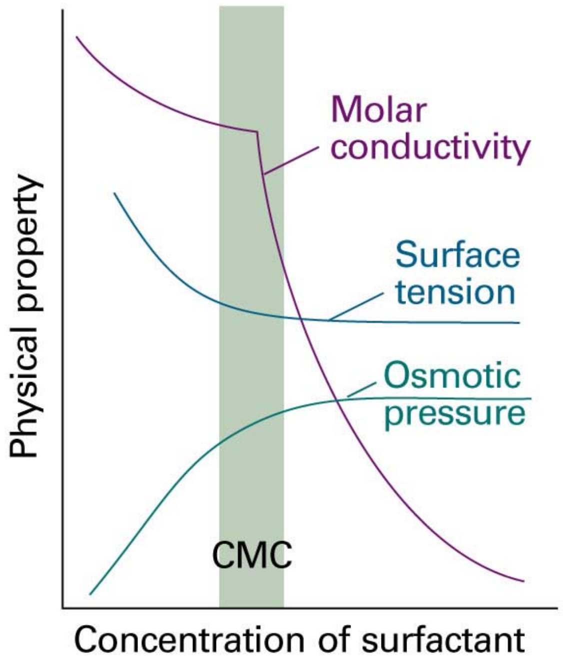
$$V_{attractive} = -\frac{B}{s}$$

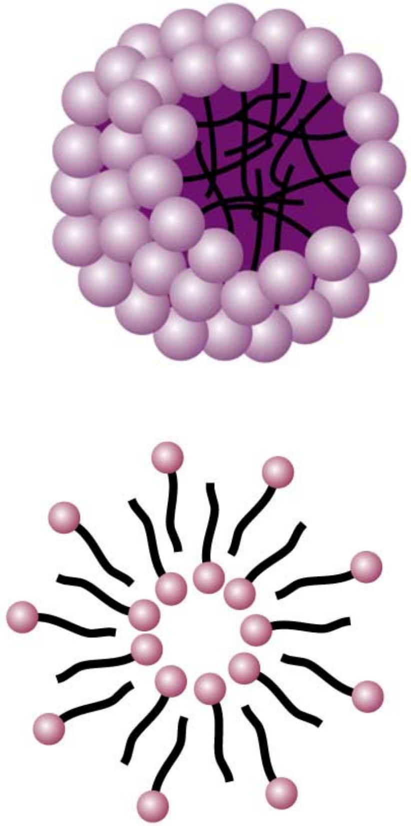


- **Schulze-Hardy rule**: hydrophobic colloids are flocculated more effectively by ions of opposite charge with high charge number

Micelles and membranes

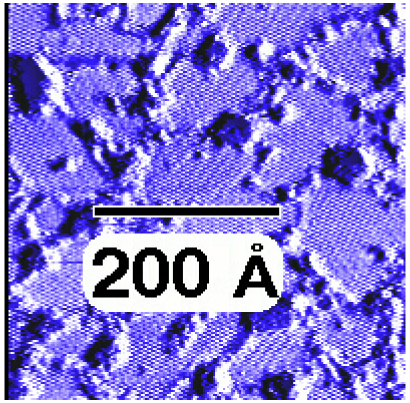
- Surfactant or ions can cluster together forming micelles

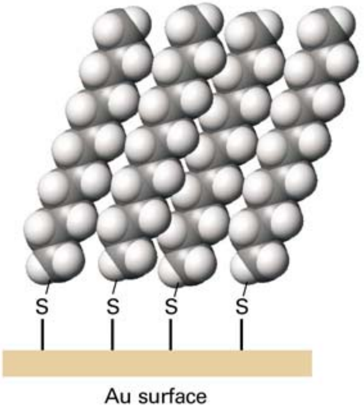




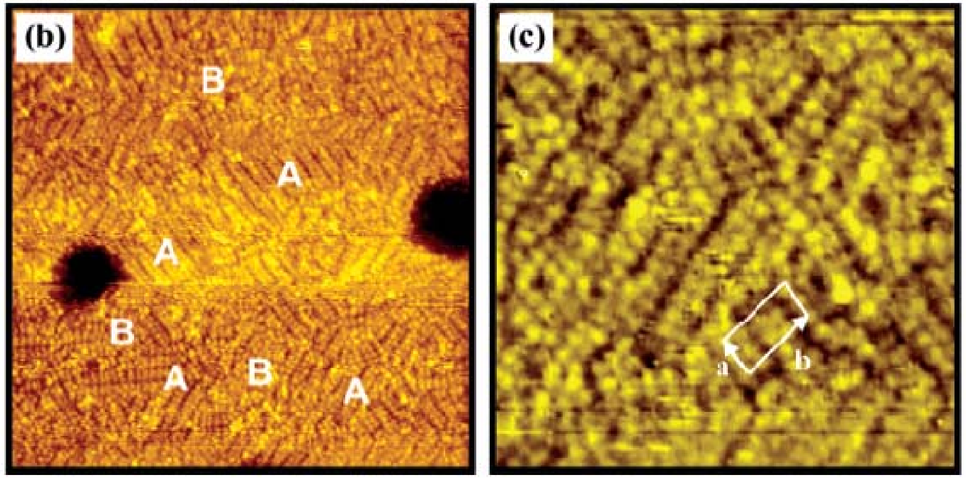
Self-Assembled Monolayers

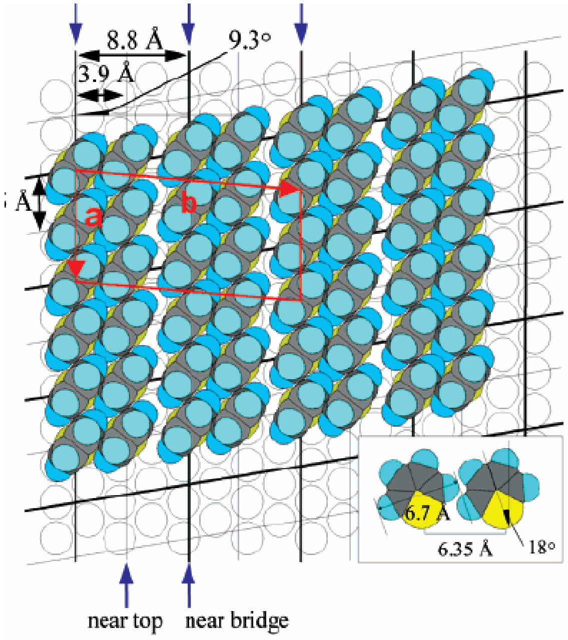
- Alkylthiols monolayers on gold





- Thiophene monolayers on gold





Problems

- **19.2a** The radius of gyration of a long chain molecule is found to be 7.3 nm. The chain consists of C–C links. Assume the chain is randomly coiled and estimate the number of links in the chain.
- **19.6a** Human haemoglobin has a specific volume of 0.749×10^{-3} m^3 kg^{-1}, a sedimentation constant of 4.48 Sv, and a diffusion coefficient of 6.9×10^{-11} m^2 s^{-1}. Determine its molar mass from this information.
- **19.12a** Calculate the contour length (the length of the extended chain) and the root mean square separation (the end-to-end distance) for polyethylene with a molar mass of 280 kg mol^{-1}.

- **19.2a** The radius of gyration of a long chain molecule is found to be 7.3 nm. The chain consists of C–C links. Assume the chain is randomly coiled and estimate the number of links in the chain.
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