- Macromolecules are everywhere (inside and outside us).
- Some are natural (polysaccharides, polypeptides, etc.) and others are synthetic (polyethylene, nylon, polystyrene, etc.).
- Prepared by addition/stringed together and in some cases cross-linked by smaller units called monomers by a process called **polymerization**.
- Large and small molecules may gather together in a process called ***self-assembly***, and to form ***aggregates***, ***e.g.***, assembly of protein actin and solution of polymers known as ***colloids***.

- Macromolecules and aggregates give rise to **problems** that need some investigation and description of ***their shapes***, **size determination** and so on.

Structure and dynamics

- Configuration, the structural features that can be changed **only** by breaking chemical bonds and form new ones. e.g., - A – B – C and - A - C - B
- Conformation, the spatial arrangement of the different parts of a chain, and one conformation can be changed into another by **rotating one part of a chain around a bond**.

- They are useful in synthesis of copolymers and biological macromolecules (e.g. polypeptides).
- Polymers can be degraded, i.e. chain breaking into shorter components.
- Determination of a primary structure is quite challenging of chemical analysis called **sequencing**

- Though *Eq.* 18.2, gives nonzero propability for $r > Nl \rightarrow$ value is small, that errors in pretending that r can range up to infinity $\rightarrow$ ***negligible***.

- By using *Eq.* 18.2, we can also regard each coil in a sample as ceaselessly writhing from one conformation to another, then $f(r)\mathbf{d}r$ is the probability that at any instant chain will be found with separation ends between r and $r + \mathbf{d}r$.

- e.g., solid uniform sphere of radius R has;

$$R_g = \sqrt{\frac{3}{5}}R$$

- Long thin uniform rod of length l has $R_g = \frac{l}{\sqrt{12}}$ for rotation about an axis perpendicular to the long axis.
- Solid sphere (with same radius and mass) has greater radius of gyration than random coil.
- N.B.: RC model ignores the role of a solvent, i.e. a poor solvent causes the coil to tighten and vise-versa.

(b) Conformational entropy (CE)

- Random coil is the least structured conformation of a polymer chain and corresponds to the state of greater entropy, i.e. **degree of disorder**.
- Stretching of a coil reduce an entropy and introduces the ordering.
- Statistical entropy arising from bond arrangement (1-dimensional chain N bonds of length ***l*** stretched or compressed by **n*l***) called CE.

$$\Delta S = -\tfrac{1}{2} kN \ln\left\{(1+v)^{1+v}(1-v)^{1-v}\right\} \qquad v = \frac{n}{N} \qquad (18.7)$$

From ***Further information 18.1*** that

$$R_{rms} = N^{1/2} lF \quad \text{where} \quad F = \left(\frac{2l_p}{l} - 1 \right)^{1/2} \qquad \textbf{(18.11)}$$

- For random coil, $l_p = l$, so $R_{rms} = N^{1/2} l$, as we already found. For $l_p > l$, $F > 1$ coil has swollen as anticipated.

18.5 The structures of biological macromolecules.

- A protein is a polypeptide composed of linked α-amino acids, $NH_2CHRCOOH$, where R is one of about 20 groups.
- For as protein to function correctly, its needs to have a well defined conformation

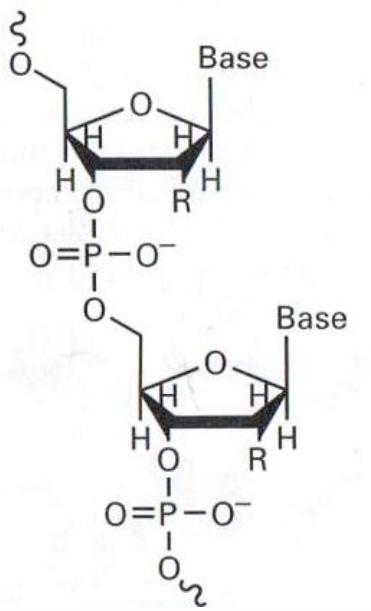
(a) Proteins

- Secondary structures of protein originated from rules formulated by **Corey-Pauling** in 1951, identify the principal contributions to the lowering of energy of molecules by focusing on the role of hydrogen bonds and peptide link, -CONH-.

(b) Nucleic acid

- Both DNA and RNA are polynucleotide → base sugar phosphate units linked by phosphodiester bond.

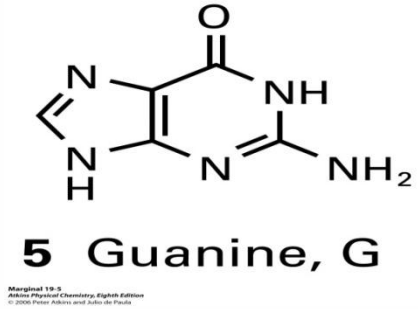
- RNA sugar is B-D-ribose.
- DNA sugar is B-D-Z-deoxyribose .



- The most common base; adenine (A, 3), cytosine (C, 4), guanine (G, 5), thymine (T, found in DNA only, 6) and uracil (U, found in RNA only, 7).

3 Adenine, A

4 Cytosine, C



5 Guanine, G

6 Thymine, T

- DNA double helix polynucleotide chains are linked together by hydrogen bonds between A-T and C-G base pair.

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- It is stabilized further by interaction between the planar **π** systems of bases.
- In biological cell right-handed helix with diameter of 2.0 nm and pitch of 3.4 nm are formed.

Aggregation and self-assembly

- The aggregation of particles form by self-assembly → spontaneous formation of molecules or macromolecules held together by molecular interactions such as coulombic, dispersion, hydrogen bonding.

  Examples: liquid crystals, DNA.

- We will look at additional self-assembly systems that include small aggregate that are at the heart of detergent action and extended sheet like those forming biological cell membranes.

- Emulsifying agent such as soap or surfactant or lyophilic sol has to be added to stabilize the product.

Example: in milk, which is an emulsion of fats in water, has emulsifying agent casein (contain phosphate group).

- Formation of cream (droplets) on the surface of the milk shows that casein not good emulsifier.
- Make sure that emulsion is dispersed very finely initially followed by intense agitation with ultrasonicator to homogenized milk.
- Colloids are purified by dialysis to remove the charge materials.

- At certain experimental conditions **liposome** may form,

- Liposomes may be used to carry nonpolar drug molecules in blood.
- The **increase in ionic strength** of the aq. soln reduces repulsions surface heads which results to formation of **cylindrical micelles (CM)**.
- **CM** can stack together in a closed-packed (hexagonal) arrays to form **lyotropic mesomorphs and liquid crystalline phases.**

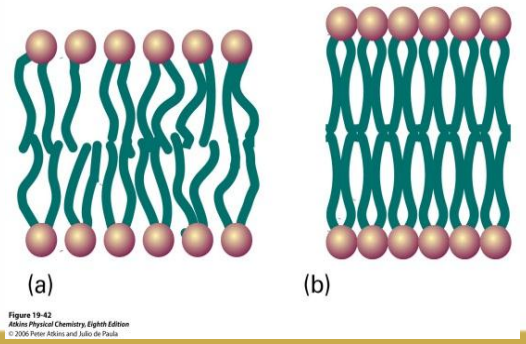
- The micelles form above the CMC shows that the entropy accompanying their formation is + and the energy of 14 $JK^{-1}mol^{-1}$.
- The +S even though molecules are clustering together shows that hydrophobic interaction are important in the formation of micelles.

(b) Bilayers, vesicles and membranes

- Micelle at concentrations well above CMC form extended parallel sheets two molecules thick called **planar bilayer.**
- The individual molecules lie perpendicular to the sheet with hydrophilic heads on the outside in aqueous solution and inside in nonpolar media.

- When segments of planar bilayers fold back on themselves,→ **unilamellar vesicles**.
- Bilayer shows resemblance of biological membranes.
- The basic structural element of a membrane is phospholipid, such as phosphotidyl choline contains long hydrocarbon chains (C_{14}-C_{24}), and variety of polar group $-CH_2CH_2N(CH_3)^+_3$.
- Lipids molecules forms layers instead of micelles because of long structure.

- Has viscosity higher than that of water and always move over the surface.
- The average distance the lipids travel in time *t* is equal to $(4Dt)^{1/2}$.
- Typically a phospholipid migrate 1μm in about 1 min.
- All lipids bilayer undergo transition from a state of high to low chain mobility at a temperature that depends on the structure of the lipids.



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- The mean obtained from the determination of molar mass by **osmometry** (5.5e), is the **number average molar mass**, M_n, which is the value obtained by weighting each molar mass by the number of molecules of the mass present in the sample.

$$\bar{M}_n = \frac{1}{N}\sum_i N_i M_i = \langle M \rangle \qquad \textbf{(18.19)}$$

where N_i is number of molecules with molar mass M_i and there are N molecules in all. <X> denotes the usual (number) average of property X.

- For reasons related to the way macromolecules contribute to the physical properties, **(1) viscosity measurement** gives viscosity average molar mass, M_v, **(2) light scattering experiments** give the weight average molar mass, M_w, **(3) and sedimentation experiments** give the ***Z***-average molar mass, M_z.

- Weight average molar mass is the average calculated by weight of molar mass of the molecules by the mass of each one present in the sample:

$$\bar{M}_w = \frac{1}{m}\sum_i m_i M_i \qquad \textbf{(18.20a)}$$

where m_i is the total mass of molecules of molar mass M_i and m is the total mass of sample.

18.9 The techniques

(a) Mass Spectroscopy

- Mass spectroscopy is among the most accurate techniques for the determination of molar masses.
- The procedure consists of ionizing the sample in the gas phase and then measuring the mass to charge ratio (m/z) of all ions.
- Macromolecules present a challenge because it is difficult to produce gaseous ions of large fragmentations.
- **Matrix assisted laser desorption/ionization** (MALDI) and **electrospray ionization** are used to overcome that.

- On substituting this expression into *eqn* 18.30;

$$S = \frac{b\bar{M}_n}{6\pi a \eta N_A} \qquad (18.32)$$

- ***S*** may be used to determine M_n or ***a***, and for **non-spherical molecules** we use values given in Table 18.3.

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

* More values and analytical expressions are given in the *Data section*.
† Entries are the ratio f/f_0, where $f_0 = 6\pi\eta c$, where $c = (ab^2)^{1/3}$ for prolate ellipsoids and $c = (a^2b)^{1/3}$ for oblate ellipsoids; $2a$ is the major axis and $2b$ is the minor axis.

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- Extrapolated intercept at c = 0 is 0.0504,

  so $[\eta]$ = 0.0504 $dm^3 g^{-1}$

- Therefore,

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

$$M_v = \left(\frac{[\eta]}{K}\right)^{1/a} = 9.0 \times 10^4 \, g.mol^{-1}$$

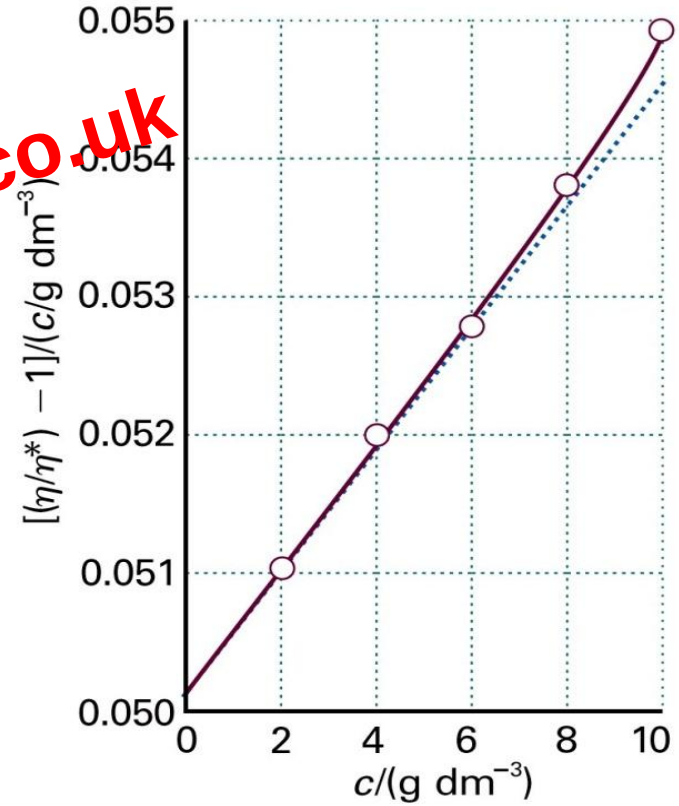

Figure 19-12
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