081010 Quiz 2 Morphology of Complex Materials

1) On Wednesday we considered circular dichroism as a method to monitor protein folding.
   a) What is the difference between linearly-polarized and unpolarized light?
   b) Explain how plane-polarized light can be produced from two circularly polarized beams.
   c) For linearly polarized light explain the difference between absorption and refraction. (Absorption coefficient and the index of refraction).
   d) For plane polarized light that is passed through a protein solution explain the state of polarization of the exiting light and explain why the exiting light has this state of polarization.
   e) Explain what the ellipticity, θ, is.

2) Proteins spontaneously form certain local secondary structures due to simple associations between residues
   a) List two types of secondary structure that form in proteins.
   b) Describe the local associations that lead to the formation of these structures.
   c), d) e) Sketch the structures you mentioned in a and b showing how the local structures are arranged. Show both parallel and antiparallel structures as well as a helical structure.

3) A helical structure for a protein can form when every 4 residues associate. Considering that there are two dihedral angles in the residue and that they can be arranged in 3 main categories of bond rotations in the Ramachandran plot,
   a) How many permutations of these 3 main categories of bond rotation are possible for a 12 residue polypeptide? (That is how many states can a 12 residue polypeptide take?) Remember that probabilities multiply so that if there are 3 states for one residue there are 3^2 states for two residues.
   b) What is the probability of forming this helical structure in a 12 residue polypeptide if there were no associations?
   c) The conformational entropy of a polypeptide molecule is related to the log of the number of states, Ω,so $S = k\ln(\Omega)$. How does the conformational entropy change when this helical secondary structure forms?
   d) The enthalpy of a molecule decreases when a bond forms. How does the enthalpy change when this secondary structure forms? Why?
   e) In class we observed several computer simulations of protein folding and secondary structure formation. How do you think the overall free energy of this polypeptide changes when this secondary structure forms? Is this a positive or negative change in free energy for this spontaneous process?

1) a) The electric field vector for linearly polarized light is normal to the direction of propagation and restricted to a plane that includes the direction of propagation. For unpolarized light the electric field vector is normal to the direction of propagation but is not restricted otherwise.

b) If two circularly polarized light contain one component (y for instance) that is out of phase by +90° while the other circularly polarized light contains the same (y) component that is out of phase by -90° then summing the two circularly polarized beams will lead to a plane polarized beam in the x-direction.

c) Absorption leads to a reduction in the amplitude (and intensity) of the light. Refraction changes the speed and leads to a phase shift when compared with a non-refracted beam.

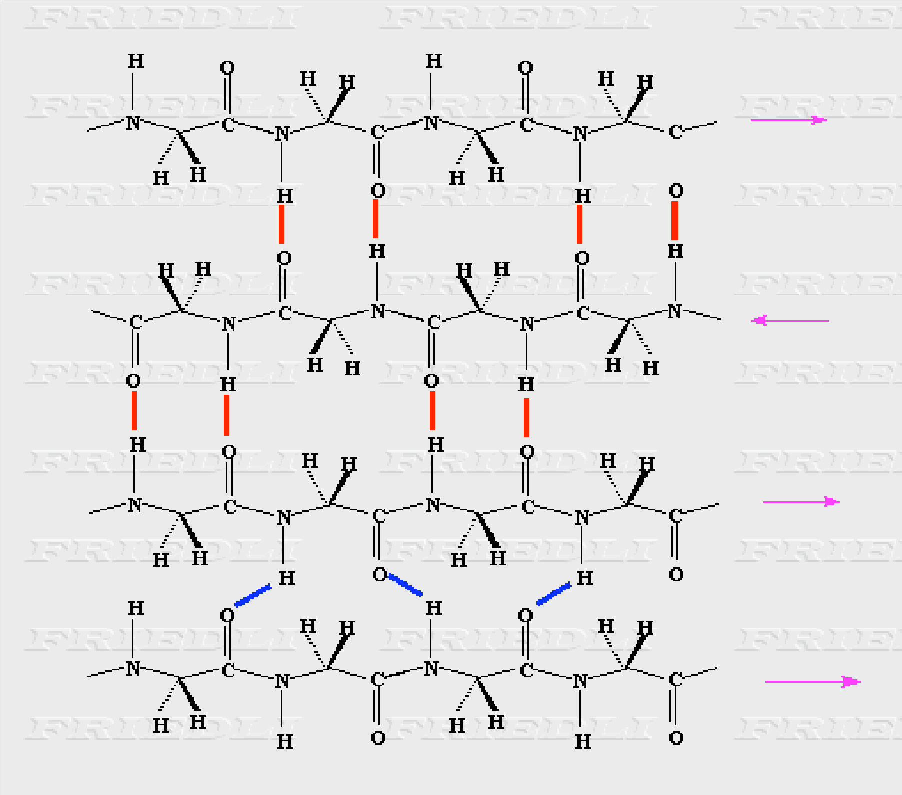
d) The protein solution displays circular dichroism so plane polarized light becomes elliptically polarized after passing though the solution. This is understood by considering that the plane polarized light can be decomposed into two circularly polarized beams of opposite phase (180 degrees for the y component for instance). The circularly dichroic solution preferentially absorbs one of the two circular polarized components leading to a phase shifted elliptically polarized beam. The major axis of polarization is offset from that of the plane polarized incident beam due to circular birefringence.

e) Ellipticity is proportional to the difference between the absorption of right and left hand circularly polarized light.

2) a) Alpha-Helix and Beta sheet structures.

b) These two structures are primarily held together by hydrogen bonds. Alpha helicies have hydrogen bonds within the chain between residues separated by 4 chain index values, i.e. 1 and 4 will hydrogen bond. The alpha carbon subsitutent groups pont outward from the helix allowing for steric, ionic and hydrophilic stabilization of the structure. Beta sheets are held together by hydrogen bonds between the same chain at some distance in anti-parallel sheets and in hydrogen bonds between distant chains segments in parallel Beta-sheets. Describe the local associations that lead to the formation of these structures.

c), d) e) Sketch the structures you mentioned in a and b showing how the local structures are arranged. Show both parallel and antiparallel structures as well as a helical structure.



Anti-parallel and parallel beta-sheets.

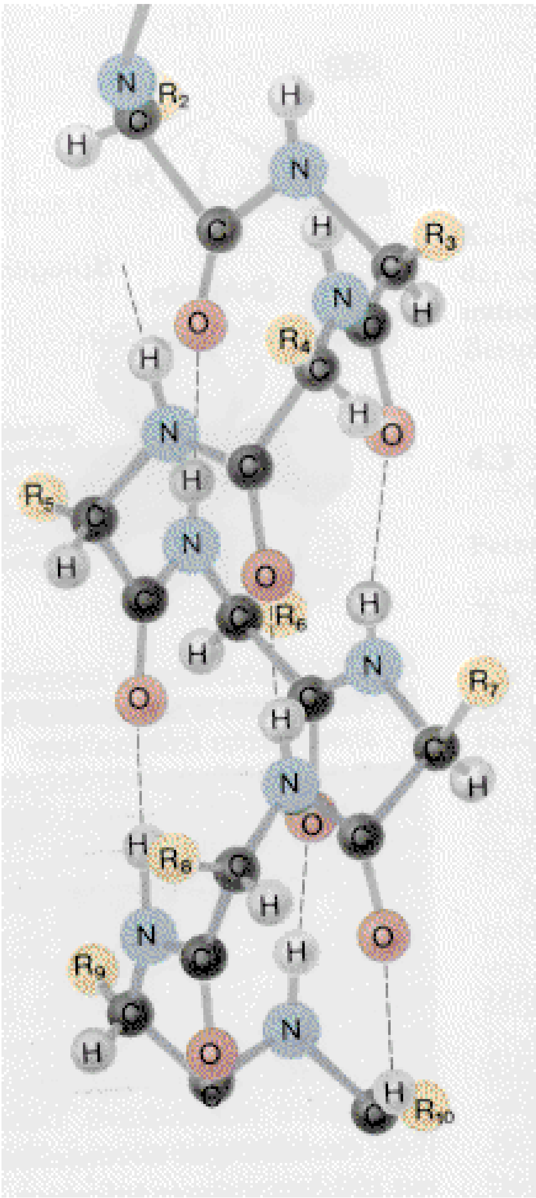


Figure 3: An alpha helix:
The backbone is formed as a helix.
An ideal alpha helix consists
of 3.6 residues per complete turn.
The side chains stick out.
There are hydrogen bonds
between the carboxy group of amino acid n
and the amino group of another amino acid n+4 [1][2].
The mean phi angle is -62 degrees
and the mean psi angle is -41 degrees [3].

3) a) 3^{12} = 531,000 states
b) 1 in about half a million
c) ΔS = -k ln(531,000) = -13.2 k
d) Enthalpy drops because stable hydrogen bonds and ionic interactions form. Hydrophobic and hydrophilic interactions may also contribute to the drop in enthalpy.
e) The free energy must drop for a spontaneous process to occur.