070926 Quiz 1 Morphology of Complex Materials

1) We discussed in class that many materials can be described as displaying a hierarchy similar to the hierarchy displayed by globular proteins. Consider the polyurea shown in Figure 1.

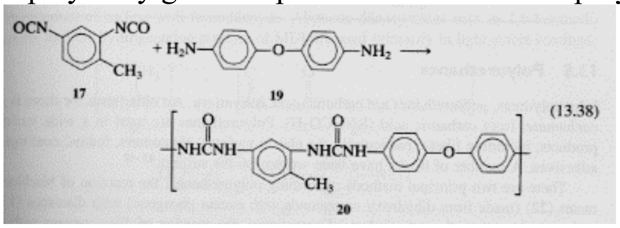


Figure 1 Polyurea (from MP Stevens Polymer Chemistry An Introduction p. 377). The O-C bond is extremely flexible.

a) What parts of this molecule will display rigid planar sheet structure?

b) Sketch the molecule in terms of these sheets indicating where hydrogen bonding is possible.

c) Could this molecule form β-sheet like structures? Sketch how this could look.

d) Could this molecule form helical structures? Explain how this might be possible.

e) Comment on the type of tertiary structure that you might see in a polyurea. Is micro-phase separation possible?

2) Proteins are the seminal model for molecular hierarchy. The primary structure is a sequence of amino acids.

a) Give the generic chemical structure for an amino acid and a protein molecule.

b) Label the α-carbon, the β-carbon and the N and C termini of the protein.

c) Show what parts of the structure are coplanar (sheet-like).

d) Indicate the two bond angles used to make a Ramachandran plot.

e) What values of these angles are forbidden? Why?

3) A folded protein displays 0 conformational entropy since it exists in a single state. The unfolded protein has a high conformational entropy.

a) What causes a protein to spontaneously lose its entropy during folding?

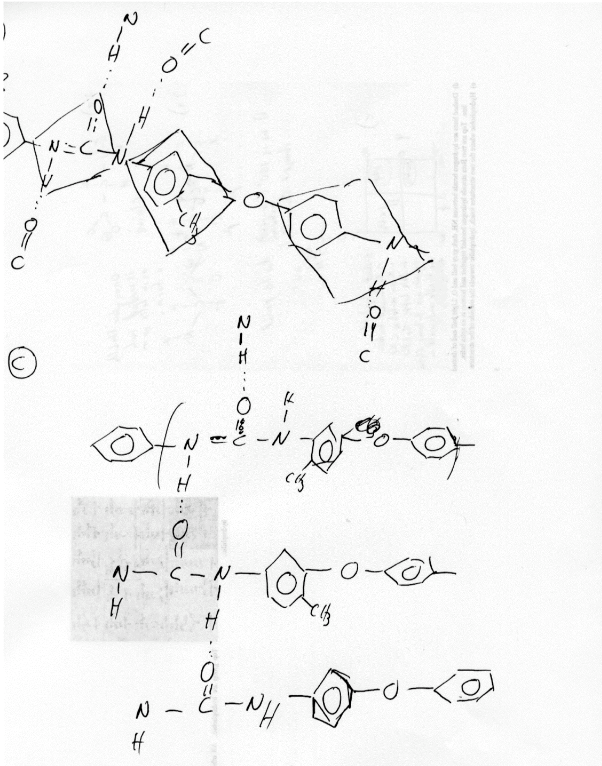
b) Sketch two protein chains showing an anti-parallel β-configuration indicating hydrogen bonding by dashed lines. Indicate the coplanar parts of the two chains. Why is this called a pleated sheet?

c) What is a disulfide bond and which amino acids are involved in this bond?

d) Sketch the structure of the amino acid proline and indicate the importance of proline to β-sheet structure.

e) Sketch a cell membrane (amphiphilic bilayer) and indicate how a membrane protein can spontaneously embed itself in such a bilayer.

1) a) The aromatic ring and the urea group will display planar structures due to conjugation.



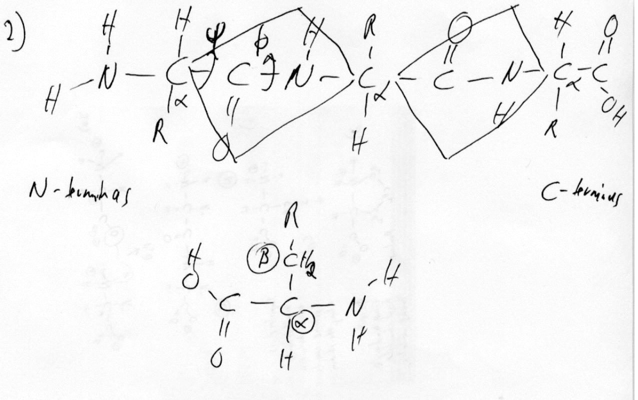
φ–O–φ can be a hydrogen bond acceptor (like NH)
Molecule has too many acceptors so sheet structure is weak.

②

d) This polyurea is probably too rigid to form helical structures.

e) Micro phase separation is well known in polyureas, it is related to ionic strength h-bonding. You might expect strands between them to associate ⓦ water & perhaps phase separate

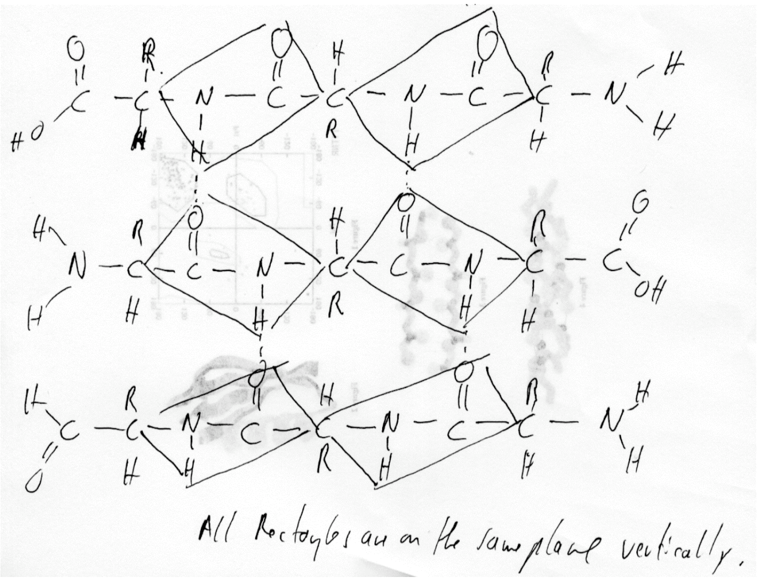
2)



φ = ψ = 0° is forbidden
& also φ = 0 or ψ = 0 due to steric constraints

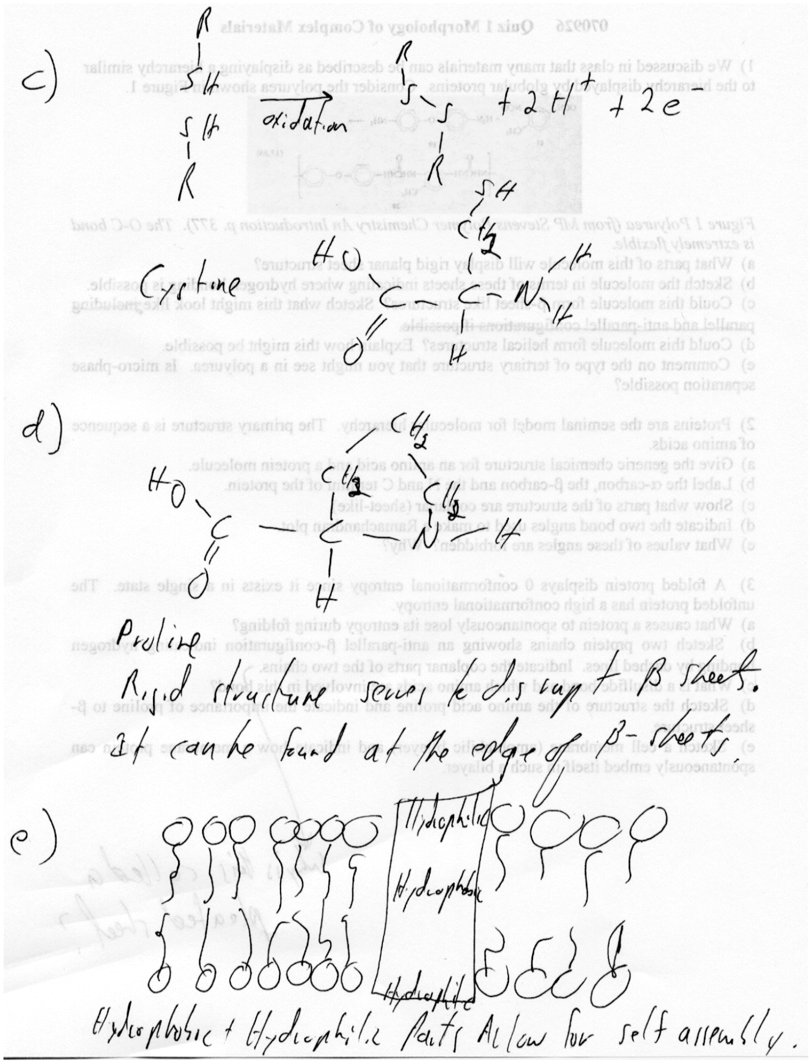
3) a) The protein lowers its overall energy through the formation of hydrogen bonds, disulfide bonds and by reducing the exposure of hydrophobic groups to water and by increasing the exposure of ionic groups to the aqueous environment.

b)



All Rectangles are on the same plane vertically.

c) A disulfide bond is a bond between two sulfur atoms that is stronger than any other secondary bond in a protein.



Rigid structure serves to disrupt β sheet. It can be found at the edge of β-sheets.

Hydrophobic + Hydrophilic Parts Allow for self assembly.

071003 Quiz 2 Morphology of Complex Materials

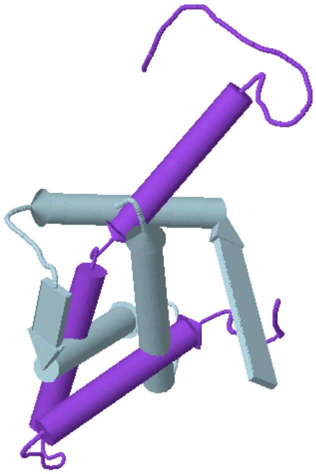
1) Explain the following terms: (for states comment on biological activity and relative size of the structure)

   a) Native State
   b) Unfolded State
   c) Denatured State
   d) Free Energy Landscape
   e) Levinthal Paradox
   f) Directed Process
   g) Stop Flow Kinetics
   h) Molten Globule

2) Give the structure of the following compounds and explain their effect on proteins.

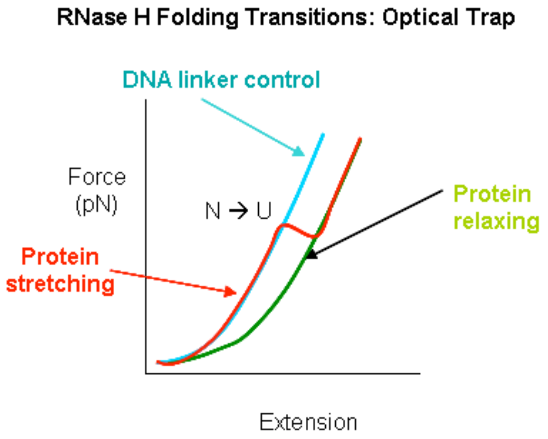
   a) Iodoacetate
   b) β-mercaptoethanol (catalytic and concentrated)
   c) urea
   d) guanidine
   e) How else can protein structure be manipulated?

3) The figure below, left, shows the native (lighter) and denatured (darker) state superimposed for the protein engrailed homeodomain (http://employees.csbsju.edu/hjakubowski/classes/ch331/protstructure/olprotfold.html Religa, T. L., Markson, J. S., Mayor, U., Freund, S. M. V., Fersht, A. R. *Nature* **437**, 1053-1056 (13 October 2005).)



enHD (2 superimposed states)

RNase



Extension with DNA "Handle"

   a) Is the definition of the denatured state you gave in question 1 consistent with this picture (left)?

   b) The middle figure is the native state of RNase studied by Anfinsen. The oblong dark cylinders are 4 disulfide linkages while the bold dotted lines are hydrogen bonds. Explain the process that Afinsen took to produce 1) a denatured state then 2) an intermediate state with no biological activity; followed by 3) an intermediate state with 1% activity and finally 4) recreation of the native state.

   c) Sketch a free energy diagram along this sequence of conformational changes.

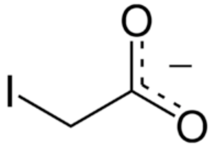
d) Explain the conformational changes that may occur between steps 3 and 4.

e) The plot to the right shows force versus extension for RNase held in an atomic force microscope cantilever by two DNA chains. The DNA extension is shown as the highest curve (light shade) while the Protein stretching crosses from this curve to the protein relaxing curve about half way on the force axis. Is this result consistent with your free energy diagram of part c? If it differs resketch the free energy diagram including features from this plot.

ANSWERS 071003 Quiz 2 Morphology of Complex Materials

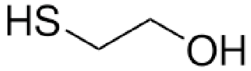
1) a) Native state is the biologically active state, generally the most compact structure observed in a folding sequence. The native state has essentially 0 conformational entropy.
b) Unfolded state is a state with no significant secondary structure, generally the least compact structure possible with the highest conformational entropy, that is, many different conformations are explored in the unfolded state due to thermal fluctuations
c) Denatured state is a state that results from chemical, thermal, physical or mechanical disruption of secondary and tertiary structure and leads to a molecule that is not biologically active. The denatured state can be related to a wide range of structures.
d) We can consider the free energy of a range of conformations that are possible across different physical, thermal and chemical conditions as constructing a free energy topology or landscape that the molecule "explores" to find the global minimum. The general shape of the free energy landscape is of a funnel with the native state at the lowest free energy.
e) Levinthal Paradox refers to a calculation of the number of possible states a protein can take and the time that would be associated with exploring all of these conformations to find the global minimum. It is a paradox that exploring all states even for a simple protein would preclude formation of native state structures in a reasonable time.
f) "Directed process" indicates that protein folding occurs loosely along a given pathway that is preprogrammed in the amino acid sequence.
g) Stop flow kinetics is an experimental method to observe protein folding involving rapidly changing the protein conditions in a flow cell to favor folding and observing the folding after flow has been frozen.
h) Molten Gobule is an intermediate state with some secondary structure but little or no tertiary structure. Molten globule is close in size to the native state but lacks most biological function.

2) a)



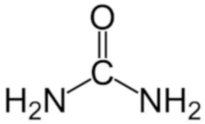
Bonds perminantly with cisteine residues to prevent disulfide bonds

b)



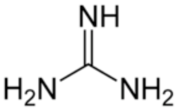
reduce disulfide bonds. At low concentrations it acts to catalyze reformation (mix and matching) of disulfide linkages, at high concentrations it disrupts disulfide bonds (reversibly).

c)



hydrogen bond donor and acceptor can disrupt secondary structure held together by hydrogen bonds such as helices and sheets.

d)

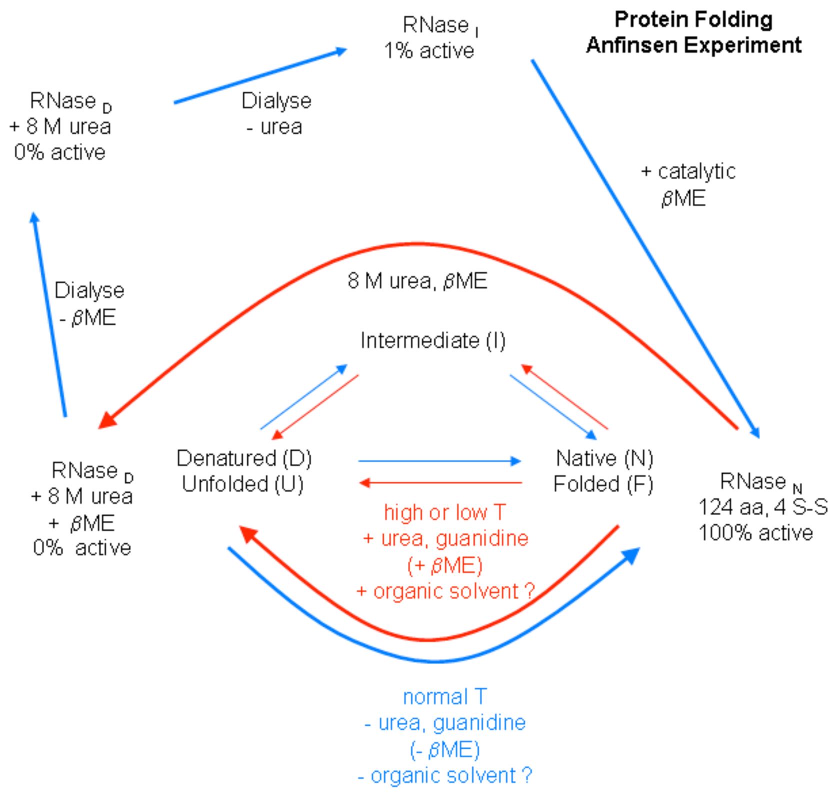


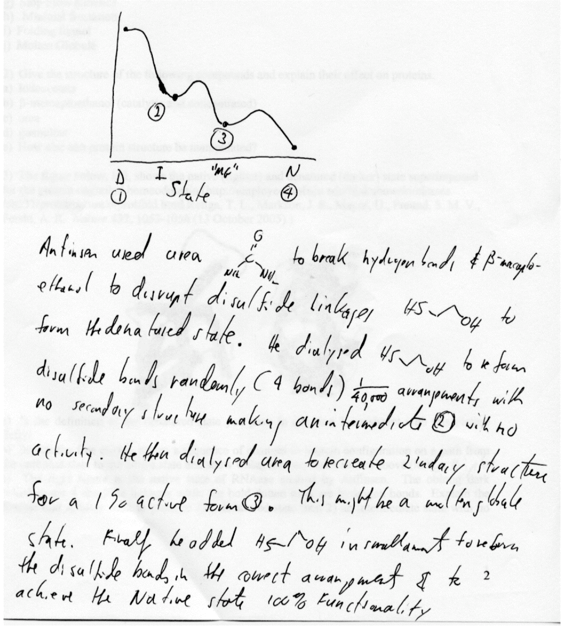
Hydrogen bonding donor. Disrupts secondary structure held together by hydrogen bonds.

e) Protein structure can be manipulated by temperature, pressure, pH, ionic conditions, and recently by mechanical manipulation applied in an AFM using optical tweezers.

3) a) The state shown as denatured is an intermediate state that may have some biological function since it is very close to the native state in size and secondary structure so it is probably not consistent with a fully denatured protein description above.
b) c)

Figure: Anfinsen Experiment: Folding of RNase

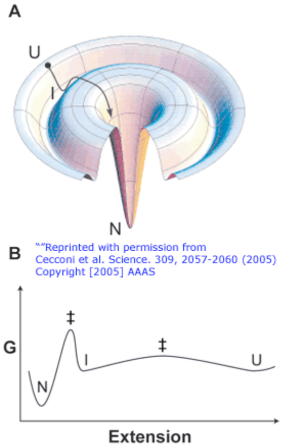




Anfinsen used urea $H_2N-\overset{\overset{O}{\|}}{C}-NH_2$ to break hydrogen bonds & β-mercapto-ethanol to disrupt disulfide linkages $HS\sim OH$ to form the denatured state. He dialysed $HS\sim OH$ to re form disulfide bonds randomly (4 bonds) $\frac{1}{40,000}$ arrangements with no secondary structure making an intermediate ② with no activity. He then dialysed urea to recreate 2'ndary structure for a 1% active form ③. This might be a molten globule state. Finally he added $HS\sim OH$ in small amounts to reform the disulfide bonds in the correct arrangement & to achieve the Native state 100% functionality

d) Between steps 3 and 4 the disulfide linkages are shuffled and reach the lowest energy conformation of the native state. This is achieved with catalytic amounts of β-mercaptoethanol.

e) The plot is somewhat different since this does not involve chemical denaturing but a physical process where the chain is strained from the two ends. The published free energy diagram is shown below. The large double cross peak corresponds to the major shift from the DNA mechanical propert curve. A smaller shift between I and U is not visible in the force plot without magnification of the scales.



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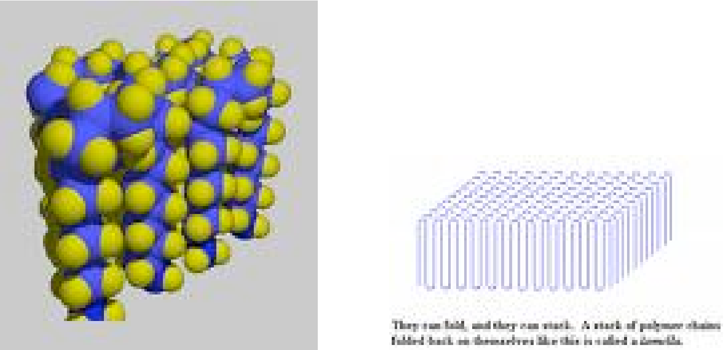
071010 Quiz 3 Morphology of Complex Materials

1) Circular dichroism as a tool to quantify protein secondary structure.
   - a) Explain how a right-handed circularly polarized light beam can be obtained from two linearly polarized light beams.
   - b) Explain how a linearly polarized light beam is composed of two circularly polarized light beams.
   - c) When a linearly polarized light beam passes through a material displaying circular dichroism what is the state of polarization for the exiting beam?
   - d) When a linearly polarized light beam passes through a material displaying circular birefringence what is the state of polarization for the exiting beam?
   - e) Explain the terms ellipticity and optical rotation. Which is usually plotted in a UV circular dichroism measurement?

2) Tacticity and chirality.
   - a) Explain why an amino acid is a chiral molecule.
   - b) How does this chirality affect the properties of proteins?
   - c) If a polymer sample displays 50% syndiotactic traids and 50% isotactic triads from an NMR measurement can it be described as an atactic polymer in terms of diads?
   - d) Can it be atactic in terms of pentads? Explain why and give the arrangement of diads in the polymer of part c.
   - e) Why does tacticity affect the melting point of monosubstituted vinyl polymers but not the glass transition?

3) Synthetic polymer chain helicity and conformations.
   - a) Explain the relationship between the β-sheet and planar zig-zag conformations in proteins and polyethylene respectively.
   - b) Sketch the unit cell for polyethylene on the (100) plane (normal to the c-axis).
   - c) Sketch an anti-parallel β-sheet structure.
   - d) Explain why the two polymers in b and c form different higher level structures despite the similarities between the chain conformations.
   - e) Would it be possible to crystallize a protein as a folded chain crystal similar to the polyethylene crystal shown below?



They can fold, and they can stack. A stack of polymer chains folded back on themselves like this is called a lamella.

Folded Chain Crystals.

ANSWERS: ***071010 Quiz 3 Morphology of Complex Materials***

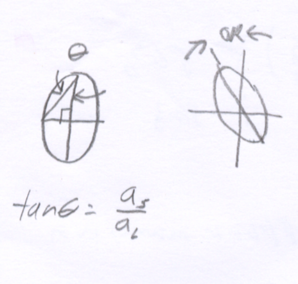
1) a) If the planes of polarization for the two beams are orthogonal and if the phase of the clockwise beam is delayed by 90° then a circularly polarized beam results.

b) A right-handed circularly polarized beam can be decomposed into two plane polarized beams, a vertically polarized beam and a horizontally polarized beam that is out of phase by 90°. A left-handed circularly polarized beam is composed of a vertically polarized beam and a horizontally polarized beam that is out of phase by -90°. If a left- and right-handed beam are added the vertical amplitude doubles but the horizontal amplitudes are out of phase by 180° so they cancel each other resulting in a vertically polarized beam. This can be done in reverse so a linear polarized beam can be decomposed into right- and a left-handed circular polarized beams.

c) Circular dichroism will lead to excess absorption of one of the two circular polarized beams that compose the linearly polarized beam leading to an elliptically polarized beam with no optical rotation (that is with the major axis of the ellipse on the vertical or horizontal axies).

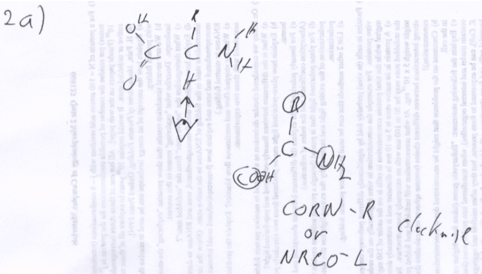
d) Circular birefringence will lead to a phase shift in the left or right handed circularly polarized beams and cause a net optical rotation for the plane polarized beam but it will remain plane polarized.

e) Optical rotation (OR) is the angle of rotation in question d. The ellipicity is shown below as θ.



Ellipicity (or molar ellipicity) is usually plotted since optical rotation does not change with wavelength.

2) a)



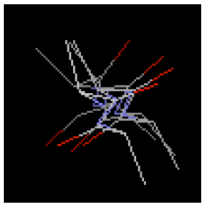
b) The chirality of naturally occurring residues is L allowing for regular secondary structure formation.

c) Isotactic triads are meso-meso units and syndiotactic are racemic-racemic. In order for a polymer to be 50% isotactic and 50% sydiotactic it would have to be a block copolymer of half isotactic and half syndiotactic or a mixture of chains that were pure isotactic and pure syndiotactic. In either case the polymer is atactic in terms of diads since it is 50% m and 50% r.

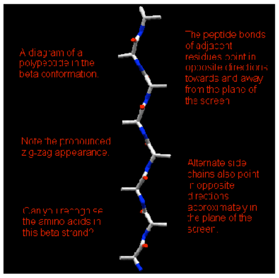
d) It can not be atactic in terms of pentads since this would require some significant population of mmrr groups for instance that can't exist in the block copolymer described above.

e) Tacticity affects the melting point because different helical forms are created with different tacticities. It doesn't affect the glass transition because the chain motion over 7 to 10 mer units is not affected.

3) a) The figure below shows that the β-sheet conformation is close to a planar zig-zag conformation. The β-sheet has a slight kink.



Beta Strand



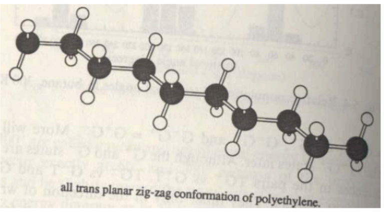
A diagram of a polypeptide in the beta conformation.

The peptide bonds of adjacent residues point in opposite directions towards and away from the plane of the screen

Note the pronounced zig-zag appearance.

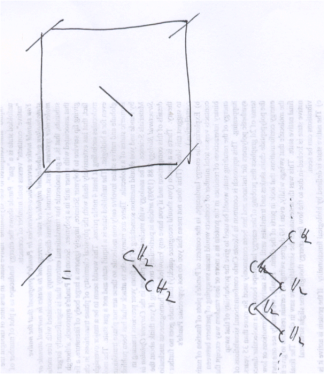
Alternate side chains also point in opposite directions approximately in the plane of the screen.

Can you recognise the amino acids in this beta strand?

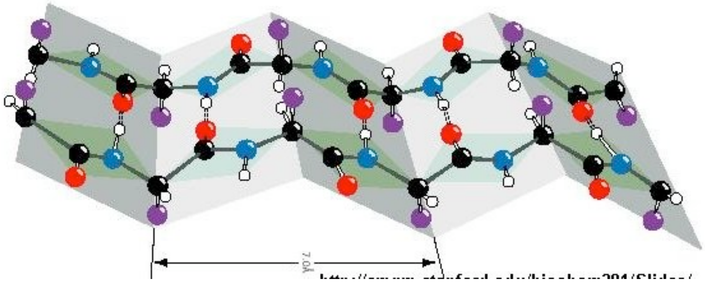


all trans planar zig-zag conformation of polyethylene.

b)



c)



d) Hydrogen bonding in the β-sheet ensures a planar structure, the weak interchain bonding in PE allows for a 3-d structure. The different side groups in the protein chain do not allow for 3-d organization in a crystal similar to polyethylene. The difference is governed by the interchain bonding differences in the two systems and the variable side groups on the protein chain.

e) It would not be possible to crystallize a protein in a folded chain crystal since the structure isn't sufficiently regular.j

071019 Quiz 4 Morpholgoy of Complex Materials

Polymers in dilute solution display a stochastic hierarchy described by statistics. This is in contrast to the deterministic hierarchy of proteins characterized by discrete structures.

1) a) From a stochastic (governed by the statistics of random disorder) view what is the primary structure for a polymer in dilute solution?

b) Give an equation that defines this primary structure and explain how this equation is related to a statistical view of a random structure.

c) This equation is of similar form to the linear absorption equation (Beer's Law). Explain the relationship.

d) Explain the error in the following equation (does it describe a linear decay?),

$$d\left(\langle t(s) \bullet t(0)\rangle\right) = \langle t(s) \bullet t(0)\rangle \left(\frac{1}{l_p}\right) ds$$

e) For a sample displaying linear absorption (following Beer's Law) we can obtain the optimum thickness for a diffraction experiment by realizing that the diffracted intensity is proportional to the sample thickness, t, and proportional to the transmitted intensity ($I_{diff} = t \exp(-\mu t)$). The maximum intensity is found from the derivative to be at a thickness $t = 1/\mu$. In view of this what does the value l_p correspond to?

2) The stochastic secondary structure for a polymer coil in dilute solution is described by the Gaussian probability function, $P(R) = k \exp(-R^2/(nl^2))$

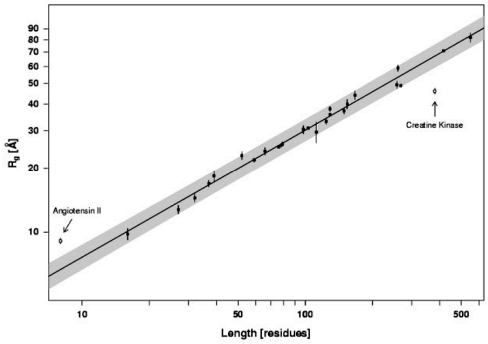
a) The integral of $R^2P(R)$ yields $R^2 = nl^2$. Show that the derivative of this function yields the same scaling behavior (i.e. find the most probable, maximum probability).

b) What is the relationship between this analysis and the mathematical description of diffusion.

c) Write a similar probability function for a self-avoiding walk (SAW).

d) What is the resulting scaling function for end-to-end distance?

e) Kohn et al. (2004 PNAS) published the following graph for a wide range of "unfolded proteins". From this plot do proteins obey stochastic hierarchies in the "unfolded" state? What are the problems with this proposition?



Kohn graph shows a slope of ~0.6.

3) Dilute polymer coils do not display super-secondary structure but display a kind of sub-secondary structure associated with thermal equilibration of stochastic hierarchies.

   a) Give an expression for the free energy of a Brownian coil based on the Gaussian Function and comparison with the Boltzman function.

   b) Calculate the spring constant for an isolated coil, k_{spr}, using this expression ($dE/dR = F = k_{spr} R$).

   c) If $R \sim n^{1/2} l \sim \xi_F$, where ξ_F is the tensile blob size, explain how you can obtain $\xi_F = kT/F$ and explain the behavior of the tensile blob sub-secondary structure with applied force.

   d) Give an expression for the free energy of an isolated self-avoiding walk (SAW).

   e) Give an expression for the thermal blob size, ξ_T, based on this free energy expression and explain the sub-secondary structural behavior in temperature.

ANSWERS: 071019 Quiz 4 Morpholgoy of Complex Materials

1) a) The primary structure is the persistence length.

b) $\langle t(s) \bullet t(0) \rangle = e^{-s/l_p}$

The coil follows a random walk similar to the walk of the red ball shown in class. In that case depending on the density of gas atoms hitting the ball the persistence length changed though the ball moved in a random manner for distances larger than a cutoff size. Below this size the motion is ballistic on average, that is it moves in a straight line or for the case of a polymer coil, it can be represented by a rod. The rods length is $2l_p$ if we consider freely jointed, Kuhn rods.

c) Beer's Law $(I/I_0) = e^{(-\mu t)}$ describes the decay in intensity with sample thickness due to linear absorption. Beer's Law depends on linear absorption $dI = -I \mu\, dt$. For the persistence length we consider a linear decay the correlation of the chain tangent.

d) This equation describes a linear increase. We need a "-" sign to describe a decay similar to the linear absorption function given in question c.

e) It is the length most likely to be observed as a ballistic step in a random walk.

2) a) Set the derivative of $R^2P(R)$ to 0 and solve for R^* yields $2/3\ nl^2$.

b) In diffusion the moving molecule follows a path whose end-to-end distance follows a Gaussian function in time so the RMS path length is proportional to $t^{1/2}$. Time, t, is analogous to n for the polymer coil.

c) $P_{SAW}(R) = \exp\left(-\frac{3R^2}{2nl^2} - \frac{n^2V_c(1-2\chi)}{2R^3}\right)$

d) $R \sim n^{3/5}\ l_p$

e) The plot shows the dependence $R_g \sim n^{3/5}$ consistent with SAW scaling. Problems are that "unfolded proteins display residual secondary structure and are polyelectrolyes so are unlikely to display good solvent scaling.

3) a) $E_a = (3kTR^2)/(2nl^2)$

b) $k_{spr} = 3kT/(nl^2)$

c) $F = k_{spr}\ \xi_F = 3\xi_F kT/(nl^2) \sim 3\xi_F kT/(\xi_F^2) \sim kT/\xi_F$ so $\xi_F \sim kT/F$

As the force applied to the ends of the coil increase the chain extends by forming a rod at large scales composed of random walks at a small scale.

d) $E_{a,SAW} = \frac{3R^2}{2nl^2} + \frac{n^2V_c(1-2\chi)}{2R^3}$

e) $\xi_T = l_p/(1-2\chi)$ where $\chi \sim 1/T$. As the temperature drops the coil collapses from a small scale first and to larger scales as the temperature approaches the critical point for phase separation where the entire coil becomes Gaussian.

071026 Quiz 5 Morphology of Complex Materials

1) The Rouse model involves a hierarchical view of the dynamics of a chain that looks very familiar to someone who has just considered the sub-secondary structures associated with thermodynamic equilibrium (i.e. blobs).
   a) Is the Rouse model an equilibrium model?
   b) How is the spring constant, used in the Rouse model, related to the tensile blob?
   c) Could the Rouse unit be observed through rheology?
   d) What is the difference between the friction factor and the viscosity as well as the spring constant and the modulus?

2) a) Write an expression for a force balance between kinetic and potential forces in the Rouse chain.
   b) When we consider a force balance for a pendulum we write an expression for a force balance that includes momentum (ma) as well a viscous dissipation and storage of potential energy (like a spring). Why is there no acceleration term in the force balance of part a? How would the response change with a momentum term.
   c) Explain why discrete values are needed for the phase lag term δ in order to develop the Rouse model.
   d) Why is a cyclic chain model used in polymer physics and in simulations to simplify macromolecular problems?
   e) Explain the difference in relaxation time between the Rouse theory for a cyclic and for a linear chain.
   f) We usually only consider the lowest order Rouse mode ($m = 1$) because this relaxation can be shown to account for 87% of the energy dispersed across the polymer chain spectrum. Is this mode the longest or shortest Rouse relaxation time.
   g) Would you expect the shortest relaxation time to depend on the Rouse unit more than the longest relaxation time?
   h) Give the molecular weight dependence of viscosity predicted by the Rouse theory and explain how this relationship relates to the theory.

3) Many researchers including 2 new professors in Chemistry and several in Environmental Health at UC are interested in simulating the dynamics of protein folding involve the transition from an unfolded chain to the native state. To date no one has been successful in simulating folding for a moderately complicated protein.
   a) Comment on the appropriateness of using the Rouse model to approximate early stages of protein folding by listing the assumptions inherent in the Rouse approach.
   b) List the special conditions that distinguish a folding protein from a synthetic polymer in solution.
   c) Judge if the assumptions are appropriate for the conditions of protein folding at an early stage.

ANSWERS: 071026 Quiz 5 Morphology of Complex Materials

1) a) No, the Rouse model describes dynamics.

b)

$$F = \left(\frac{3kT}{n\ell^2}\right)R = K_{spr} R$$

we say $n\ell^2 \sim \xi_R \sim R$ $\quad \xi_F \sim \frac{kT}{F}$

c) No, the Rouse unit is a mathematical tool used to calculate the dynamic response of the chain. The Rouse unit does not exist.

d) We use friction factor for molecules and objects that do not have a cross sectional area. The friction factor relates drag force to velocity while the viscosity relates stress (force/area) to strain rate (velocity gradient). Similarly the spring constant relates force to distance while the modulus relates stress (force/area) to strain (change in distance by initial distance).

2)

2 a)

$$\xi_R \frac{dz_\ell}{dt} = b_R\left(z_{\ell+1} + z_{\ell-1} - 2z_\ell\right)$$

$$F_{vis} = F_{spr}$$

b) The mass of a rouse unit is extremely small and the momentum term is ignored. If the momentum term were included the rouse units would oscillate rather than just showing a decay towards the equilibrium position. This oscillation would complicate the behavior of the chain.

c) Discrete values of the phase lag allow the consideration of modes of vibration for the Rouse chain. With modes we can consider the distribution of energy among modes and find that most energy is stored in the lowest order mode. This allows a discrete value for the Rouse relaxation time as well as allowing us to ignore the Rouse unit that becomes important for high order modes.

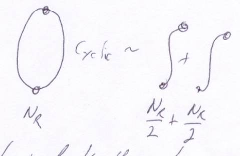
d) Cyclics are used because all chain units are identical for a cyclic. There is no end effect for cyclics.

e)

e)

$$\delta_{m,\,cyclic} = \frac{2\pi m}{N_R}$$

$$\delta_{m,\,Linear} = \frac{\pi m}{(N_R \cancel{-N_R})}$$

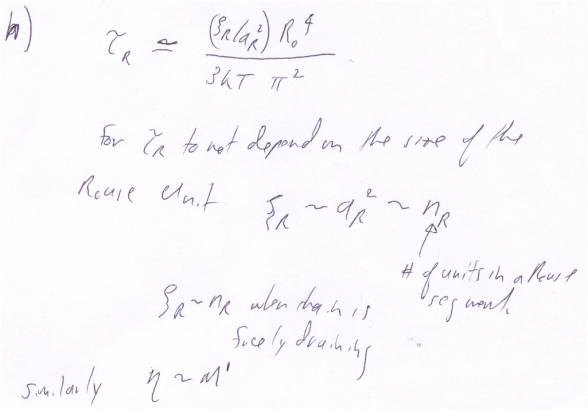


Cyclic behaves like a chain of ½ the molar mass.

f) m = 1 is the longest Rouse relaxation time.

g) The shortest relaxation time depends strongly on local structure.

h)



b)

$$\tau_R \simeq \frac{(\zeta_R / a_R^2)\, R_0^4}{3kT\,\pi^2}$$

for τ_R to not depend on the size of the Rouse unit $\zeta_R \sim a_R^2 \sim n_R$

# of units in a Rouse segment

$\zeta_R \sim n_R$ when chain is freely draining

similarly $\eta \sim M^1$

3) a) Assumptions of Rouse Model:
i) Gaussian chain
ii) Free draining chain
iii) Friction factor follows Stokes law, this assumes domains are spheres and velocity is slow.
iv) We ignore momentum, that is we assume the mass is small.

Gaussian chain is a bad assumption for a polyelectrolyte in a good solvent (water).
Free draining is a poor assumption for a protein where some residual folding exists and water is probably trapped sterically and by ionic association with the chain.
The Rouse units are probably not spherical especially if they are free draining.
The momentum assumption is probably pretty good. That is, the mass of a subunit of a chain is small.
b) Mainly the protein chain displays hydrophobic regions that initiate chain folding as well as ionic and disulfide interactions that drive folding enthalpically. These effects are not seen in the Rouse model.
c) As a crude approximation the Rouse model might add some information that could be useful in studies of protein folding. The disparity between the actual situation and the assumptions needs to be carefully considered.

071107 Quiz 6 Morphology of Complex Materials

1) The dynamics of a high molecular weight polymer chain in dilute solution, $c << c^*$, is similar to the dynamics of a low molecular weight polymer chain, $M < M_c$, in the melt.
    a) What is c^*?
    b) What is M_c?
    c) Why would polymer chains in these two conditions behave in a similar manner?
    d) The plateau modulus can be obtained from a dynamic mechanical measurement of log of the elastic modulus versus log of the frequency. Sketch this plot and show how the plateau modulus is measured.
    e) Give an equation that relates the plateau modulus to the entanglement molecular weight and explain the origin of this equation briefly.

2) The tube model is used to describe chains above M_c in molecular weight or above c^* in concentration.
    a) Explain the source of the "tube".
    b) How is the Rouse model incorporated in the tube model?
    c) Show how the scaling of relaxation time with molecular weight is obtained in the tube model.
    d) How is the scaling of the diffusion coefficient obtained?
    e) If the tube obeyed good solvent scaling (while within the tube Gaussian scaling was retained) such as in a thermal blob how would the scaling of the diffusion coefficient change?

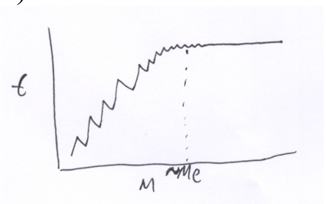
3) Polymers crystallize forming a hierarchical structure.
    a) Describe the levels of structural hierarchy in polymer crystals.
    b) Sketch the crystallite thickness versus molecular weight for low molecular weight linear alkanes (waxes) to polyethylene of high molecular weight.
    c) Why do linear alkanes crystallize into asymmetric crystallites?
    d) From a kinetic/topological perspective, why doesn't polyethylene crystallize as an extended chain crystal? Give several reasons and draw a few cartoons showing possible kinetic barriers to an extended chain structure.
    e) From a thermodynamic perspective give some reasons why an extended chain crystal might be unlikely.

ANSWERS: 071107 Quiz 6 Morphology of Complex Materials

1) a) M/R_0^3 M is the polymer molar mass and R_0 is the coil end-to-end distance.
b) M_c is the transition molecular weight between Rouse scaling of viscosity and the scaling associated with entanglements.
c) In both cases the chains are not entangled.
d) At low frequency a power 2, moderate frequency a plateau and high frequency a power ½. The plateau modulus is the value of the modulus in the plateau region.
e) $G_0 \sim 3kT/M_e l_K^2$ arising from rubber elasticity using the entanglement molecular weight as the molecular weight between crosslinks.

2) a) The tube is created from the other chains in the melt or concentrated solution. These chains serve to confine the chain within a primitive path which is Gaussian.
b) The chain, at sizes smaller than the tube diameter or Rouse size, behaves as a Rouse chain.
c) The diffusion coefficient for diffusion within the tube is given by the Einstein Fluctuation Dissipation Theroem $D \sim kT/\xi$. Where ξ is the Rouse friction factor for the chain $\xi_R N_R$. The distance of the tube is $L_{pr} = N_R a_R$. The relaxation time is the square of the distance diffused divided by the diffusion coefficient so the relaxation time scales with N_R^3.
d) The distance diffused in the sample space is the end to end distance of the tube, $N_R^{1/2} a_R$. The relaxation time for this distance of motion scales with N_R^3 and we can write $L^2 = D\,\tau$, so $D \sim N_R^{-2}$.
e) The distance diffused would scale with $N_R^{3/5} a_R$, so $D \sim N_R^{6/5-3} = N_R^{-9/5}$

3) a) For a melt crystal: Chemical structure => Helix structure => Lamallae => Stacked Lamellae => Fibers => Spherulites.
b)



c) Linear alkanes crystallize with extended chains. The ends of the chains do not fit in the crystals so the ends are clustered at the surface making thin lamellar crystals that give rise to a waxy feel to the material.
d) Long chain polymers would have to diffuses long distances to form an extended chain crystal. The chains cluster locally during crystallization which further hinders translation to from extended chain crystals. Chain entanglements also prevent formation of extended chain crystals. Since chains are not of the same length it would be impossible to fit all chains into a single, extended chain crystal. Significant motion of the chains in the crystal would be required to align all chain ends.
e) At a low temperatures (deep quenches) it is possible to overcome the energy penalty in creating large surface areas. With chain folding the conformational entropy loss associated with crystallization is minimized since the chain, crystallized from a melt, retains the same overall radius of gyration. Local chain conformational entropy is lost but globally entropy is retained.

071116 Quiz 7 Morphology of Complex Materials

1) Polymers crystallize into thin lamellar sheets.
    a) What are typical dimensions of these lamellar sheets?
    b) How does the thickness of these sheets vary when crystals are grown from dilute solution, semi-dilute solution and from the melt?
    c) Write an expression for the free energy of a sheet crystallized at a temperature T.
    d) Apply an assumption of pseudo-equilibrium to obtain an expression for the lamellar thickness.
    e) Explain the meaning of pseudo-equilibrium.

2) a) & b) Briefly describe several models for the lamellar interface
    c) How would you expect these different models to effect the value of lamellar thickness.
    d) Explain several problems involved in a polymer lamellar interface composed of extended chains.
    e) Explain the term epitaxial crystallization and why it might be important to polymer lamellar crystals.

3) The equilibrium melting point is simple to determine in a metal or ceramic crystal.
    a) Why is it more difficult to determine the equilibrium melting point for a polymer crystal.
    b) Explain what occurs when a glass half full of ice and half full of water is brought to 0 °C.
    c) How can measurements of the lamellar thickness be used to determine the equilibrium melting point in polymers.
    d) Explain the difficult with this measurement.
    e) Explain the Hoffman-Weeks approach to the determination of the melting point for polymer crystals.

ANSWERS: 071116 Quiz 7 Morphology of Complex Materials

1) a) Thickness is typically 10 nm and lateral dimensions can be between 100 nm and 10 micron. This is similar to the aspect ratio for a sheet of paper.
b) The thickness depends only on the temperature and is identical for crystals grown under different conditions but at the same temperature.
c) $\Delta G = V\left(\Delta H - T\Delta S\right) + 2\gamma S = V\Delta H\left(1 - \frac{T}{T_\infty}\right) + 2\gamma S$
d) We assume that the free energy in (c) can be set to 0 and we solve for t using V = St. This yields,

$$t = \frac{2\gamma T_\infty}{\Delta H\left(T_\infty - T\right)}$$

e) Pseudo-equilibrium is not equilibrium since at equilibrium the crystal would be of infinite thickness. In application of pseudo-equilibrium we consider a free energy expression that includes terms that go to 0 at equilibrium such as the surface area. Then we calculate parameters associated with this pseudo (meaning false) equilibrium. This allows the calculation of parameters that are seen in kinetic processes associated with thermodynamic features.

2) a) b) Adjacent reentry is a model with the chains tightly knit in to the crystal; Switchboard model is with the chains more or less randomly reentering the crystal in what looks like an old time telephone switchboard; synoptic model involves interconnection between neighboring lamellae in what looks like nerve synapses. There are other models.
c) The nature of the interface could effect the surface energy term. Larger surface energy (associated with tighter chain reentry such as in adjacent reentry) is associated with larger lamellar thicknesses.
d) One problem with extended chains with no reentry is that the density difference between the crystal and amorphous can not be accommodated at the crystal interface. Also, if the chains extend directly from the crystal surface there isn't a real interface between crystalline and amorphous regions.
e) Epitaxial crystallization is the growth of a crystal on a seed. This can be homoepitaxy (on the same crystal) or heteroepitaxy on a seed crytal such as a low molecular weight orgainic crystal with similar crystallographic planes to a polymer crystal. We saw examples of homepitaxy in class where polypropylene seeded on its own lamellar crystals in solution growth. Epitaxy is also used to grow a silicon boule in semiconductor manufacturing.

3) a) There are three main reasons that it is difficult to determine the equilibrium melting point. 1) defects in the crystals; 2) kinetics of crystallization are very slow and 3) polymers form lamellar crystals with shifts in the melting point. Additionally, cold crystallization is a major problem in measuring thermal transitions in semi-crystalline polymers (crystallization while you heat from room temperature to the melting point).
b) At the equilibrium melting point the water will remain 50% crystalline but the water in ice will strive to reduce surface area by fusing crystals until you have one very large chunk of ice floating in water.

c) Using the Hoffman-Lauritzen equation we have $\frac{1}{t} = \left(\frac{\Delta H}{2\gamma T_\infty} \right) \left(T_\infty - T \right)$ so a plot of 1/t versus T will yield T_{inf}.

d) The problem with this measurement is the determination of t from TEM or SAXS. In SAXS you determine L and DOC and get t from L*DOC/100 assuming a two phase model (too many assumptions) and using TEM it is difficult to distinguish projections to get a thickness.

e) Polymers crystallize with defects incorporated in the crystal so that the melting point is always higher than the crystallization temperature. A plot of T_m versus T_c yields T_{inf} at the high temperature extrapolation where $T_m = T_c$. This can be easily done in a DSC.

071126 Quiz 8 Morphology of Complex Materials

The rate of crystallization is governed by the slower of two processes. Crystallization relies on transport of crystallizable species to the growth front. Crystallization also relies on supersaturation.

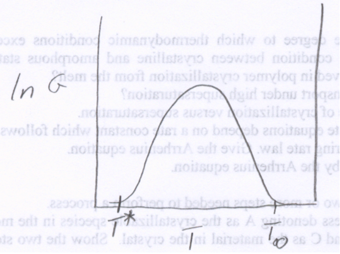
1) a) Supersaturation represents the degree to which thermodynamic conditions exceed those present at the equilibrium condition between crystalline and amorphous states. How can supersaturation be achieved in polymer crystallization from the melt?
b) What happens to the rate of transport under high supersaturation for a polymer melt?
c) Sketch a plot of the overall rate of crystallization versus supersaturation.
d) In the most general sense all rate equations depend on a rate constant which follows an Arrhenius behavior such as an Eyring rate law. Give the Arrhenius equation.
e) Explain what plot is suggested by the Arrhenius equation.

2) A rate limiting process involves two or more steps needed to perform a process.
a) Sketch a cartoon of the crystallization process denoting A as the crystallizable species in the melt; B as A near the crystal surface and C as the material in the crystal. Show the two steps needed to perform crystallization.
b) Write an equation that equates the overall rate, the rate of crystallization and the rate of transport.
c) If the final amount of crystal, C_f, is given by the sum of the initial amounts of A_i and B_i, write an expression for the final amount of crystal, C_f, in terms of A_i only using the expression of part b.
d) Use part c to obtain an expression for A_i and use this expression to describe the initial rate of crystallization, R_i.
e) The equation for part d is valid only during the initial states of crystallization. Under what conditions would this expression be valid throughout crystallization?

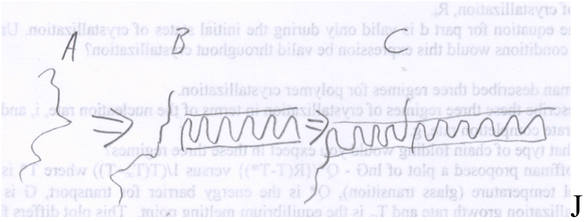
3) Hoffman described three regimes for polymer crystallization.
a) Describe these three regimes of crystallization in terms of the nucleation rate, i, and the substrate completion rate, g.
b) What type of chain folding would you expect in these three regimes?
c) Hoffman proposed a plot of $\ln G - Q^*/\{R(T-T^*)\}$ versus $1/(T(T_\infty - T))$ where T^* is the Vogel temperature (glass transition), Q^* is the energy barrier for transport, G is the crystallization growth rate and T_∞ is the equilibrium melting point. This plot differs from the plot you proposed in question 1e. Explain the x-axis by first writing an expression for the Hoffman lamellar thickness, l^*, at temperature T and an expression for the free energy difference, ΔG, between a melt and crystal for a lamellar crystal of thickness l.
d) Use the Hoffman thickness, l^*, in the ΔG expression to obtain the barrier energy for crystallization, ΔG^*.
e) Use this barrier energy, ΔG^*, in the Arrhenius function to explain the x-axis in the Hoffman plot.

ANSWERS: 071126 Quiz 8 Morphology of Complex Materials

1) a) Supersaturation is achieved in the melt by a thermal quench below the equilibrium melting point. In solution it can be achieved by a rapid increase in concentration or partial pressure in the vapor phase.
b) High supersaturation occurs at low temperatures. Transport slows at low temperatures due to Arrhenius behavior, Rate of Transport ~ $\exp(-Q^*/(T - T^*))$ where Q^* is the activation energy for transport and T^* is the Vogel temperature.

c) 

d) Rate = k A, A is the concentration of the species involved in the process and the rate constant, k, is given by $k = k_0 \exp(-\Delta E^*/kT)$, where ΔE^* is the energy barrier for the process.
e) The Arrhenius function suggest ln(Rate) versus 1/T as a linear plot to obtain k_0 and ΔE^*.

2) a)  J

b) Rate = $Ak_D = Bk_G$
c) $C_f = A_i + B_i = A_i (1 + k_D/k_G)$
d) $A_i = k_G C_f/(k_G + k_D))$
Rate = $A_i k_D = k_D k_G C_f/(k_G + k_D))$
e) This rate can be generalized if there is an infinite source of melt, A, that is not depleted during crystallization.

3) a) Regime I, i << g; Regime II, i ~ g; Regime III, i >> g.
b) Regime I, regular adjacent reentry; Regime II, Synoptic, dangling chains, well stacked lamellae due to interconnection of lamellae; Regime III, Defective crystals with few adjacent folds. Generally disorganized crystals are expected in Regime III.
c) $l^* = 2 \sigma_e T_\infty/(\Delta H(T_\infty - T)) = 2 \sigma_e/\Delta F$
$\Delta G = 2\nu a^2\sigma_e + 2al\sigma - \nu a^2 l\Delta F$
where $\Delta F = (\Delta H(T_\infty - T))/T_\infty$, ν is the number of stems, σ_e is the fold surface energy, σ is the side surface energy, a is the stem size and l is the stem length.
d) $\Delta G^* = 2\nu a^2\sigma_e + 2a\sigma (2 \sigma_e/\Delta F) - \nu a^2\Delta F (2 \sigma_e/\Delta F) = 4a\sigma\sigma_e/\Delta F = 4a\sigma\sigma_e T_\infty/(\Delta H(T_\infty - T))$
e) $k_G = k_0 \exp(-\Delta G^*/kT) = k_0 \exp(-4a\sigma\sigma_e T_\infty/(k\Delta HT(T_\infty - T)))$
so $\ln k_G = \ln k_0 - 4a\sigma\sigma_e T_\infty/(k\Delta HT(T_\infty - T))$
so the plot is linear using an x-axis of $1/(T(T_\infty - T))$