081001 Quiz 1 Morpholgy of Complex Materials

1) 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 (a tripeptide).
   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 giving the Greek letter for the angles and an English spelling of the letter, e.g. π and pi.
   e) What values of these angles are forbidden? Why?

2) Nylon displays some similarity and some differences with proteins. The following is the structure of Nylon 6,6:
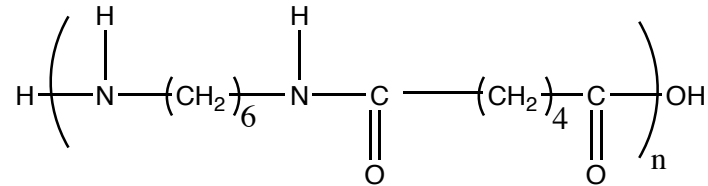
   a) Show what part of nylon is a rigid structure and compare this with a protein.
   b) Compare the flexibility of a protein to the flexibility of nylon.
   c) Show what part of nylon is a hydrogen bond acceptor and what part is a hydrogen bond donor. How does this compare with polypeptides?
   d) Does nylon have an N and a C terminus like a protein?
   e) Would you expect nylon to form a globular tertiary structure? Explain why (and describe the structure) or why not (and how nylon differs from a globular protein).

3) Amino acids are the mer units of a protein.
   a) Cystine (Cys C) is an important amino acid. Sketch the structure of cystine and explain the importance of cystine in protein structure.
   b) Proline (Pro P) is an important amino acid. Sketch the structure of proline and explain the importance of proline to protein structure.
   c) Give the structure of glycine (Gly G) and explain where glycine units might occur in the secondary structure of a protein.
   d) Give the structure of alanine (Ala A) and explain where alanine residues might occur in the secondary structure of a protein.
   e) Give the structure of methionine (Met M) and explain the special place it holds in the structure of proteins.

1)
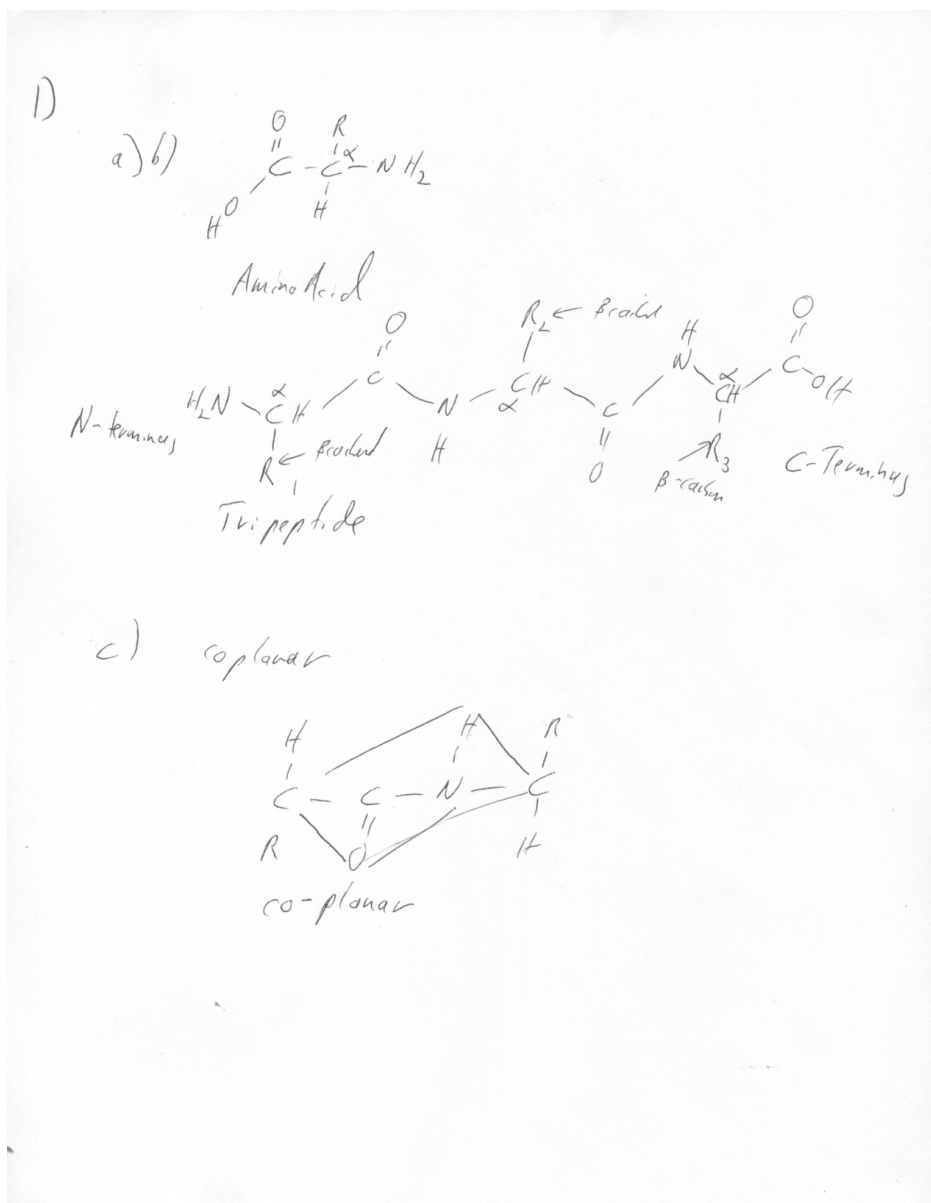
2)
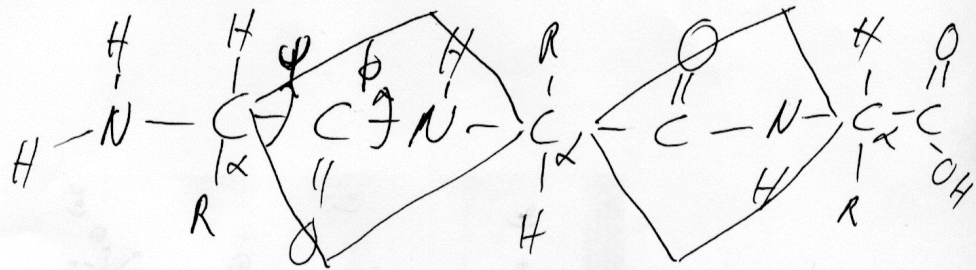
N-terminus

C-terminus
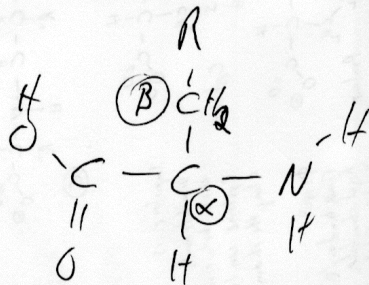
$\phi = \psi = 0°$ is forbidden

& ϕ_{10} $\phi = 0$ or $\psi = 0$ due to steric constraints

2)

a)

$$CH_2 - \underset{\underset{O}{\|}}{C} - \underset{\underset{H}{|}}{N} - CH_2$$
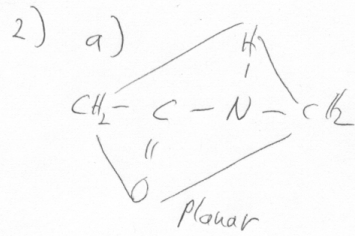
Planar

this is the same planar unit as in proteins

b) Nylon is more flexible because the extended alkane chains have free rotation about the C-C bonds.

c) $-\underset{\underset{O}{\|}}{C}-$ acceptor $-\underset{\underset{H}{|}}{N}-$ donor
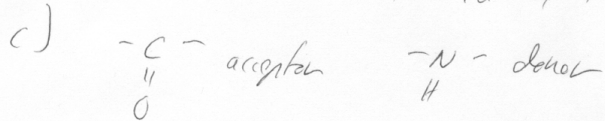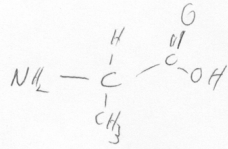
d) Yes, Nylon has an N & C - terminus.

e) No, Nylon does not form a tertiary structure because it does not have functional side groups that can have specific interactions with other side groups in the chain.

3)

d) alanine

$$NH_2 - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - \overset{\overset{\displaystyle O}{\|}}{C} - OH$$
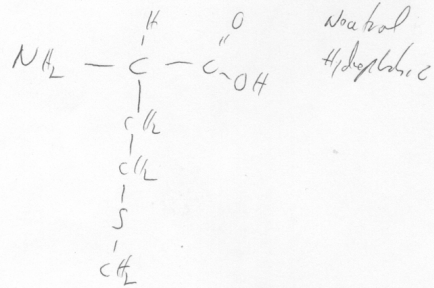
Flexible residue like glycine (folds & turns)
Hydrophobic

e) methionine

$$NH_2 - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\underset{\underset{\displaystyle CH_2}{|}}{\underset{\displaystyle S}{|}}}{\underset{\displaystyle CH_2}{|}}}{C}} - \overset{\overset{\displaystyle O}{\|}}{C} - OH \qquad Neutral \\ Hydrophobic$$

Cysteine

Proline
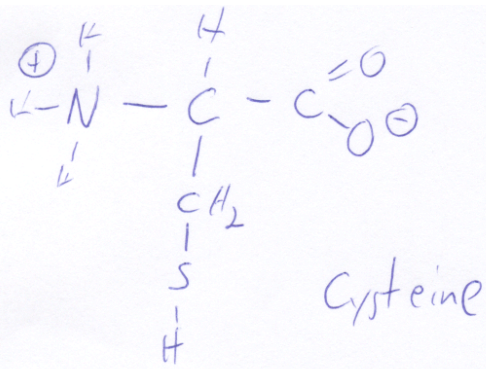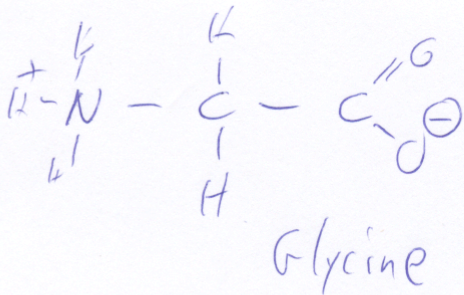
Importance is
Disulfide bonds
occur between
Cysteine units
along the chain
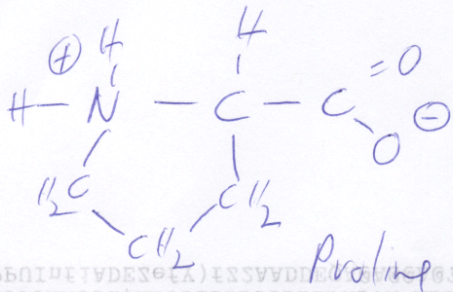
$\phi = 180°$
Fixed bond angle
Rigid structure
Breaks α-helix

Glycine

Occurs where flexibility
is needed such
as in helix or in
a turn.

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.
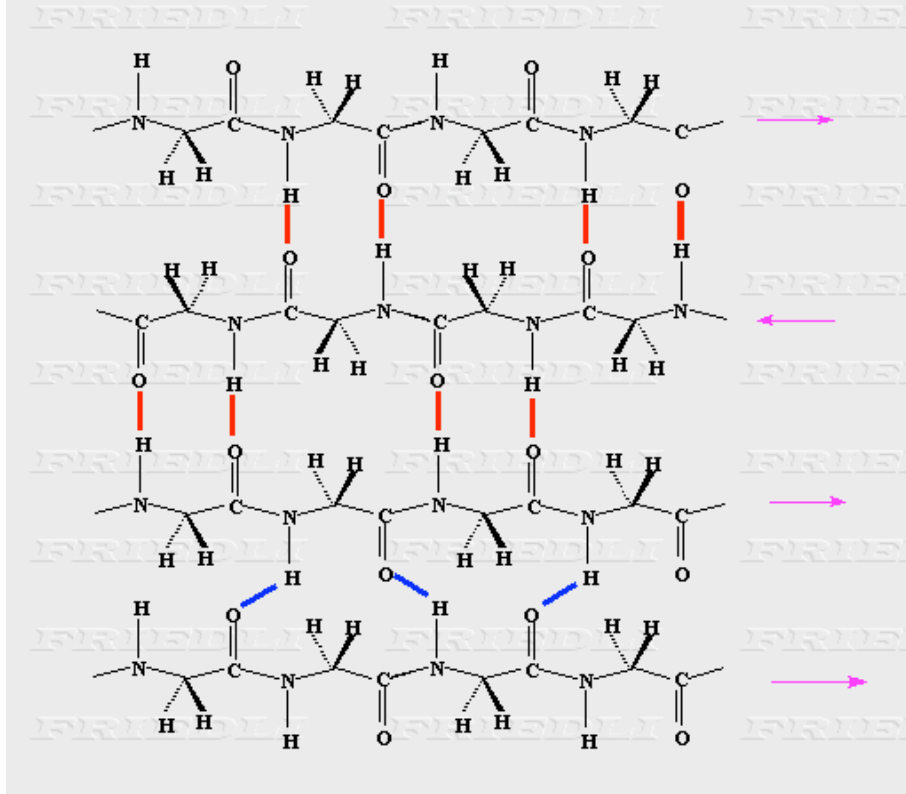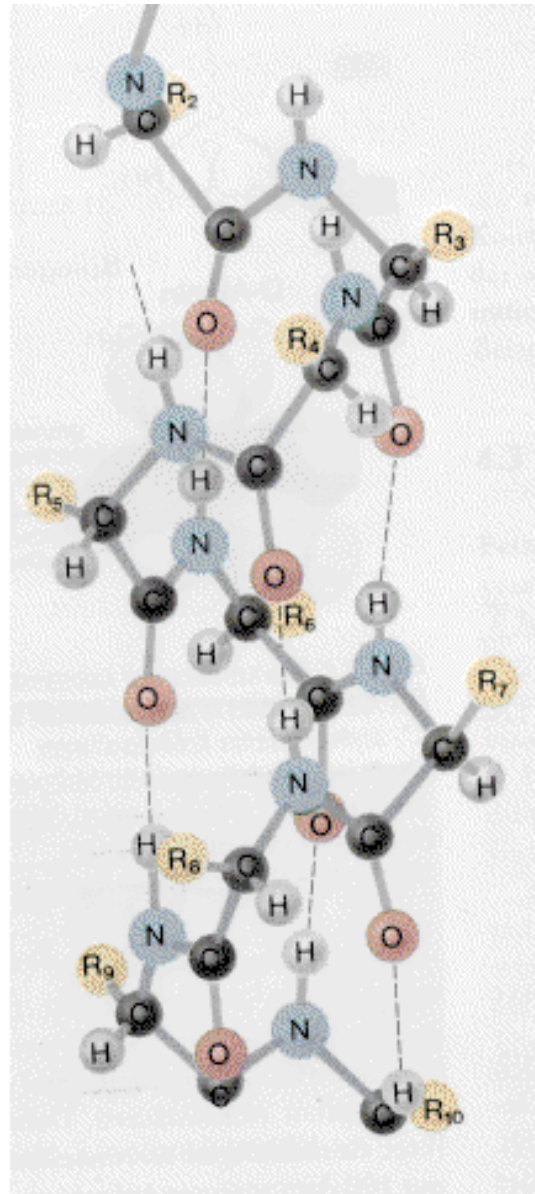
Anti-parallel and parallel beta-sheets.

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.

081017   Quiz 3 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) Explain how Anfinsen used these compounds with RNase 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.

3) Proteins in cells (in vivo) probably fold by significantly different pathways compared to in vitro proteins. For example the concentration in vitro is generally on the order of 1 mg/ml while the total protein concentration in cells is on the order of 350 mg/ml.
   a) A protein in its native state is 5 to 10 nm in diameter and is extremely dense, while in the unfolded state may be 50 to 100 nm with an extremely loose structure. Such a protein might weigh 5×10^{-19} mg. At what concentration will unfolded and folded proteins have strong interactions between different chains (assume spheres and calculate the overlap concentration)?
   b) Comment on the problems that might be encountered due to concentration of proteins in the cell.
   c) Explain the following statement: "Eukaryotic genes (taken from higher cells which contain nuclei and internal organelles), when transferred into prokaryotes (bacteria, like *E. Coli*), can be expressed to form protein, but they often misfold and aggregate in the bacterial cells and form structures called **inclusion bodies**." (from St. Johns Web page)
   d) Explain what a "chaperone" is and how it might assist in protein folding.
   e) What type of protein interaction do chaperones generally enable during folding?

ANSWERS 081017   Quiz 3 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 Globule 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.
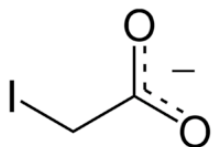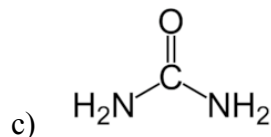
2) a)

Bonds permanently with cysteine residues to prevent disulfide bonds
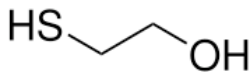
b)

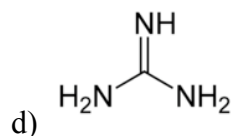reduce disulfide bonds. At low concentrations it acts to catalyze reformation (mix and matching) of disulfide linkages, at high concentrations it disrupts disulfide bonds (reversibly).
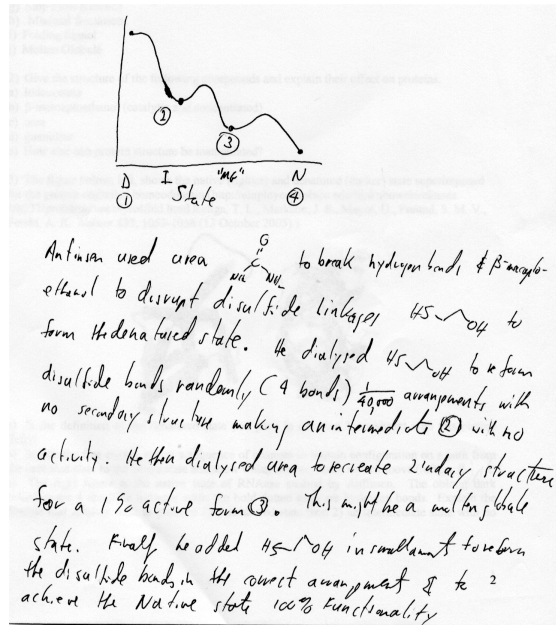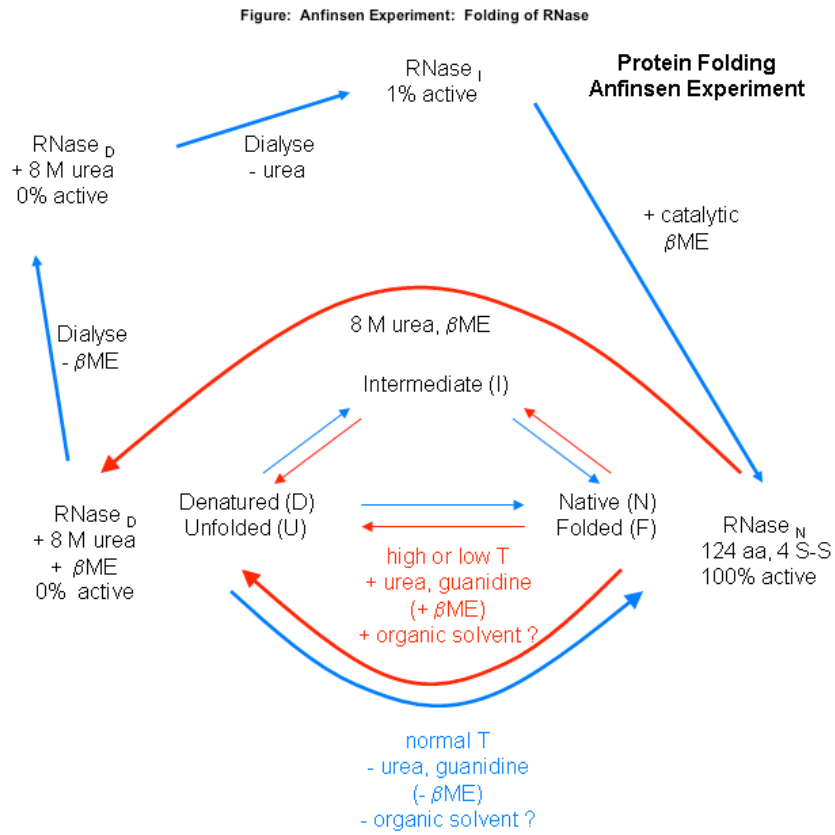
c)

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.

Figure: Anfinsen Experiment: Folding of RNase

Protein Folding
Anfinsen Experiment

RNase $_I$
1% active

RNase $_D$
+ 8 M urea
0% active

Dialyse
- urea

+ catalytic
βME

Dialyse
- βME

8 M urea, βME

Intermediate (I)

Denatured (D)
Unfolded (U)

Native (N)
Folded (F)

RNase $_D$
+ 8 M urea
+ βME
0% active

high or low T
+ urea, guanidine
(+ βME)
+ organic solvent ?

RNase $_N$
124 aa, 4 S-S
100% active

normal T
- urea, guanidine
(- βME)
- organic solvent ?

D
①   I   "MG"   N
   State   ④
②   ③

Anfinsen used urea $\underset{\text{un MG}}{\overset{G}{\rlap{—}}}$ to break hydrogen bonds & β-mercapto-ethanol to disrupt disulfide linkages HS∼OH to form the denatured state. He dialysed HS∼OH to reform 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'dary structure for a 1% active form ③. This might be a molten globule state. Finally he added HS∼OH in small amounts to reform the disulfide bonds in the correct arrangement & to achieve the Native state 100% functionality

3) a) The overlap concentration is the concentration within a protein molecule. To calculate ϕ^* we need the mass divided by the occupied volume of the protein. Here we have been given the mass and size. Assuming that the size is the diameter the 5 nm native state has an overlap concentration of 7.6 mg/ml while the 100 nm unfolded state 0.001 mg/ml. Above the overlap concentration significant overlap between different molecules are expected (aggregation is likely).

b) The hydrophobic segments of proteins will aggregate or agglomerate non-reversibly. Inclusion bodies may form that can not be broken apart.

c) While the prokaryotic cells can apparently produce the peptide sequence, the polypeptides can not fold properly in the absence of other features, perhaps including molecular chaperones that provide an *aggregation-free-zone* where proteins can fold into their native states.

d) There are two main types of molecular chaperones. Heat shock proteins (70 kg/mole) Hsp-70, and chaperonins. Heat shock proteins act as the polypeptide chain emerges from the ribosome site binding to hydrophobic sections of the polypeptide. Heat shock proteins act as single protein chains not as quartenary structures. They bind with peptides when ATP is also bound and release proteins after cleaving ATP, using energy. Chaperonins are smaller Chaperonin-60 and chaperonin-10 for instance, but act in large quartenary structures, for instance GroEL and GroES discussed in class. Chaperonins act away from the ribosome, for example in the mitochondria or other cellular structures. Chaperonins also bind ATP and cleave ATP on releasing the native state proteins.

e) Chaperonins enable hydrophobic interactions that couldn't occur in the cytoplasm since folding that leads to hydrophobic interactions often involves revealing hydrophobic segments of the polypeptide to the cellular environment where these sites would likely bond with other hydrophobic groups on other proteins and lead to aggregation.

081024 Quiz 4 Morphology of Complex Materials

The physical primary unit of synthetic polymers (and any chain molecule in a random conformation) is the persistence length, l_p, or the Kuhn length, l_K ($l_K = 2\, l_p$). Chain persistence is controlled by what are termed "*short range interactions*" (SRI) referring to interactions that occur along a polymer chain with small differences in chain index (or residue number for a protein).

1) One type of SRI is the restriction in chain conformation associated with changes in energy on rotation of the carbon-carbon bond along the main chain of a vinyl polymer.
   a) Sketch a plot of energy versus bond rotation angle (0 to 360 degrees) for the central carbon-carbon bond of butane. Indicate the trans and gauche states using a Neumann projection.
   b) How would this plot differ for isopentane?

Isopentane
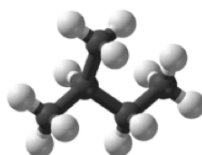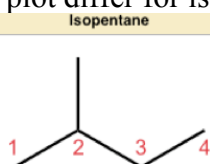
   c) Use the plot of part a to explain how temperature might effect the flexibility of a polymer chain.
   d) For a polyethylene chain sketch the trans configuration. Why is the trans configuration seen in crystals?
   e) Explain how the different energies associated with different rotational isomeric states could lead to a larger or smaller persistence length.

2) Another type of SRI involves the effect of tacticity and stereochemistry on the helicity of a vinyl polymer chain (a carbon main chain polymer).
   a) Define meso and racemic diads using polypropylene.
   b) Define the three types of triad tacticity.
   c) Define an atactic polymer.
   d) Why are polymers described in terms of triad tacticity? (You will need to briefly describe an NMR measurement in your answer.)
   e) Explain how tacticity could effect chain persistence.

3) Persistence can be described using two models.
   a,b) Describe these two models with the acronyms FJC and WLC.
   c) Derive an expression for the mean-square end-to-end size of a chain $<R^2>$ in terms of the number of Kuhn units, n, and the Kuhn length, l_K, for a random walk chain.
   d) How is the Kuhn length related to the length of a chemical unit?
   e) In the kinetic theory a gas atom (or other particle) displays a mean free path, l, which is the average distance a gas atom travels ballistically (in a straight line) before it collides with another gas atom. For a particle beam the mean free path is the inverse of the linear absorption coefficient, μ, (http://en.wikipedia.org/wiki/Mean_free_path). The linear absorption coefficient is defined by Beer's law ($I = I_0 \exp(-\mu x)$). Describe any similarity between the mean free path of a gas atom and the persistence length.
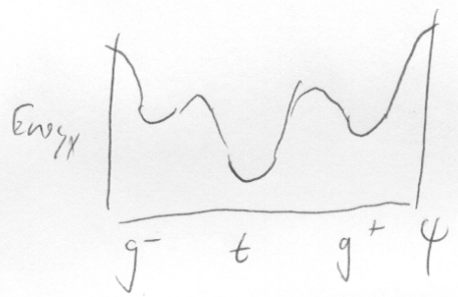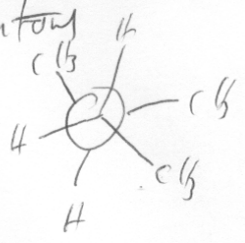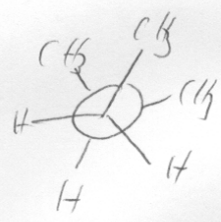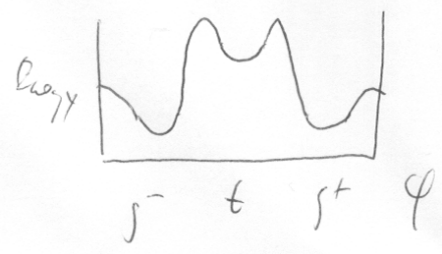
1) a) Butane

gauche "g"   trans "t"

Energy

g^- t g^+ ϕ

b) isopentane

g   H-CH₃

t   H-CH₃

Energy

g^- t g^+ ϕ
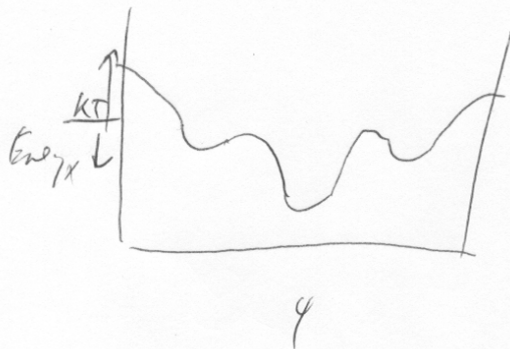
c)
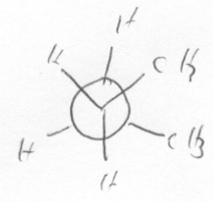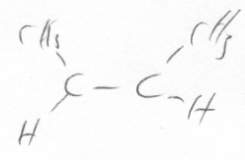
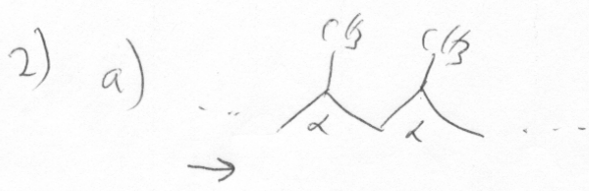As T increase, kT will overcome barriers to bond rotation making the chain more flexible.

d)

$S = 0$

this is the most regular structure so it is seen in crystals + has the lowest entropy.

e) The rotational energy barriers decide the local conformation of the chain. This combined with the interactions such as Hydrogen bonding lead to larger or smaller chain persistence.

2) a)

as you progress from left to right each α-carbon can have 2 stereochemical arrangements A or B
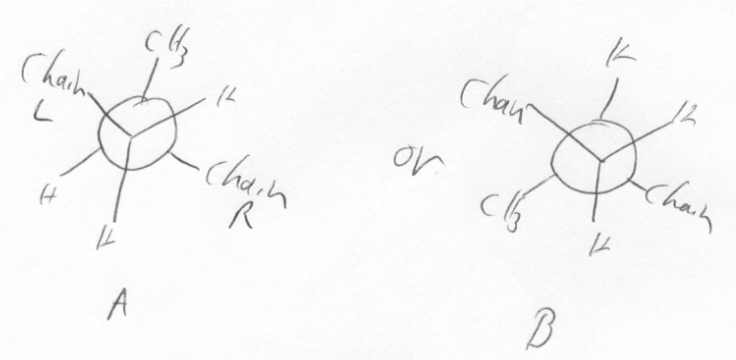
A   or   B

if the two neighbouring monomers show the same arrangement i.e. AA or BB then the diad is <u>meso</u> if they are different i.e. AB or BA then they are a <u>racemic</u> diad.

An Atactic Polymer would have 50% meso & 50% racemic diads.

b)   For triads, we can have 4 types

mm   rr

mr   rm

mm = isotactic

rr = syndiotactic

rm & mr = heterotactic

atactic would have 25% iso 25% synd.
& 50% heterotactic.

c)   atactic = No preferred tacticity so
a random statistical distribution.
For the most part atactic = Non Crystalline

d)   We can only measure triads because NMR senses
the neighborhood of the α Carbon in both directions
so it can only sense 3 mer units at a time
not 2.

(5)

c) Tacticity $\Rightarrow$ helicity $\Rightarrow$ increased chain persistence

3) a) FJC

b) Freely Jointed chain

Chain is composed of steps of length l that have free joints
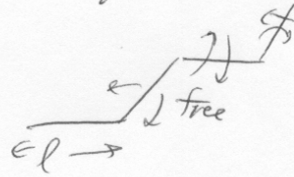
overall there is an average length of persistence to these steps such that

$$\langle R^2 \rangle = n_k l_k^2$$

# of steps — Kuhn length k

$$l_k = 2 l_p \leftarrow \text{persistence length}$$

WLC

Worm-like Chain

Chain is a free path that has a tangent at any point $\vec{t}(s)$

The correlation function for the decay in direction for the chain is given by
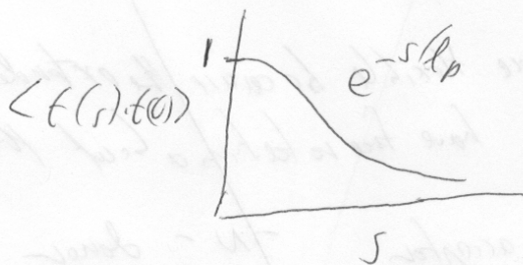
$$\langle t(s) \cdot t(0) \rangle = e^{-s/l_p}$$

where l_p is the persistence length

(similar to the mean free path of a gas atoms)

b) $\langle R^2 \rangle = \sum_i \sum_j (\underline{l_i} \cdot \underline{l_j})$

for $i = j$ $\underline{l_i} \cdot \underline{l_j} = l^2$

for $i \neq j$ $\underline{l_i} \cdot \underline{l_j} = 0$

there are n cases where $i = j$

so

$\langle R^2 \rangle = n_k \, l_k^2$

d) l_k isn't related to the length of a chemical unit.

e) The definition of persistence length

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

is identical to the kinetic theory function

$$\frac{I}{I_0} \sim \exp(-\mu x) = \exp\left(-\frac{x}{\ell}\right)$$

081031 Quiz 5 Morphology of Complex Materials

1)   a)   Polymers display short range and long range interactions.   Explain what distinguishes short- and long-range interactions.

b) A random walk can be constructed on a lattice by randomly selecting the direction along lattice coordinates or in free space by randomly selecting the angles for a step vector. For long walks (large n) and identical step length, l, would you expect R to results in the same value for the two simulations?

c) For a vector $\mathbf{r}_i$ at chain index i on a lattice with coordination number z, the next step, $\mathbf{r}_{i+1}$, can occur in any direction if the choice is random including a backtrack step on the path of the chain.   On average $<\mathbf{r}_{i+1}> = 0$.   If the backtrack step is forbidden the average value $<\mathbf{r}_{i+1}> \neq 0$. Calculate this value.

d) What effect does the a short-range interaction of question c) have on the Kuhn step length and the chain scaling?

e)   SJ Clark of the University of Durham says "Non-bonded interactions can be divided into two classes; short and long range interactions. Formally a force is defined to be short ranged if it decreases with distance quicker than r^{-d} where d is the dimensionality of the system (usually 3). Short ranged interactions are commonly dealt with by imposing a cut-off to the potential V(r), r_c, beyond which V(r) is set to 0." (the latter being a hard core potential) Explain how these "long" and "short" range interactions relate to the "long" and "short" range interactions used in polymers. (http://cmt.dur.ac.uk/sjc/thesis_dlc/node61.html)

2) High molecular weight polymers are non-linear viscoelastics.

a)   Sketch a log-log plot of viscosity versus rate of strain showing the behavior for a linearly viscous material such as water and a viscoelastic such as a high molecular weight polymer.

b) How does the zero shear rate viscosity of a polymer change with molecular weight?

c) What is the entanglement molecular weight (use your answer to b) in your answer).

d)   What is the plateau modulus? (Is a plateau modulus displayed by a linearly viscous material such as water.)

e) How can the plateau modulus be used to determine the Kuhn length?

3)   The following figure (*"Intrinsic" and "Topological" Stiffness in Branched Polymers* Connolly R, Bellesia G, Timoshenko EG, Kuznetsov YA Elli S, Ganazzoli F *Macromolecules* **38** 5288-5299 (2005).) shows the variation in chain persistence with chain index (from one end of the chain to the other) for simulated chains of variable local stiffness (stiffest chain is at the top with the highest persistence).
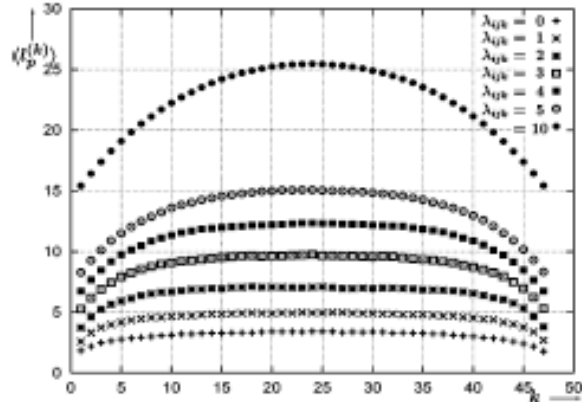
Figure 7. The persistence length plots, $\langle \ell_p^{(k)} \rangle$, obtained via eq 10, versus segment number, k, for various semiflexible, linear polymers, each of length 48. The strength of the intrinsic stiffness is varied between polymers by increasing the strength of the bending penalty, λ_{ijk} from 0 (bottom)...5, 10 (top).

a) Why would the chain persistence diminish at the ends of the chain?

b) Why does the stiffest chain display the most variability in persistence along the chain?

c) Persistence length is often used to describe biological molecules such as DNA which have extremely high rigidity and large persistence lengths. Based on this plot do you see any problem with the use of persistence to describe these biomolecules compared to more flexible synthetic polymers?

d) How is persistence length determined by scattering?

e) What result would you expect if the chain from the top curve in the plot were measured using scattering?

1) a) Short range interactions occur between chain units of similar chain index. Long range interactions occur between chain units separated by a large number of chain units; well beyond the persistence lengths.

b) R would be different but it would still scale with $\langle R^2 \rangle \sim n$. The Kuhn length would vary $l_K^2 = \dfrac{\langle R^2 \rangle}{n}$.

c) $\langle \underline{r}_{i+1} \rangle = 0 = \langle \underline{r}_{i+1} \rangle_{SRI} (z-1) - \underline{r}_i$

so $\langle \underline{r}_{i+1} \rangle_{SRI} = \dfrac{\underline{r}_i}{(z-1)}$

d) It increases $l_{K_{SRI}} = l_K \sqrt{\dfrac{z}{z-2}}$

chain scaling is not affected

$\langle R^2 \rangle \sim n$

e) Long & short range interactions for Benders are not the same as long & short range interactions for polymers. Almost all polymer interactions decay over short spatial distances so they can generally be modeled with a hard core potential.

2)

a) $\log \eta$

water

Polymer

$\log \dot{\gamma}$

b) $\log \eta_0$

2.9

M_e

$\log M_w$
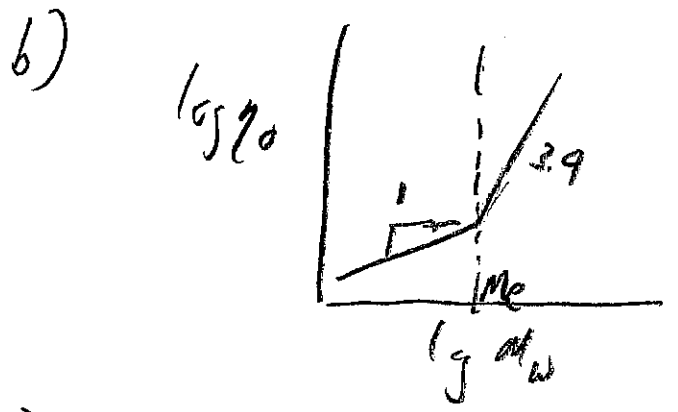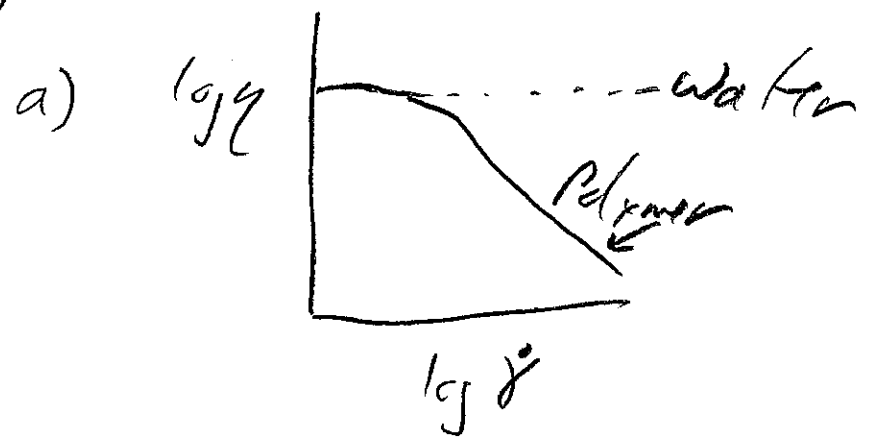
c) M_e is the transition point between Rouse scaling

$$\eta_0 \sim M_w^1$$

& reptation scaling

$$\eta_0 \sim M_w^3 \text{ or } M_w^{2.9}$$

M_e reflects the average distance between entanglements in a polymer melt.

d)

$\log G'$ G^0 ...

[graph with axes $\log G'$ (vertical) and $\log \omega$ (horizontal), with arrow labeled "Flow" and "MW"]

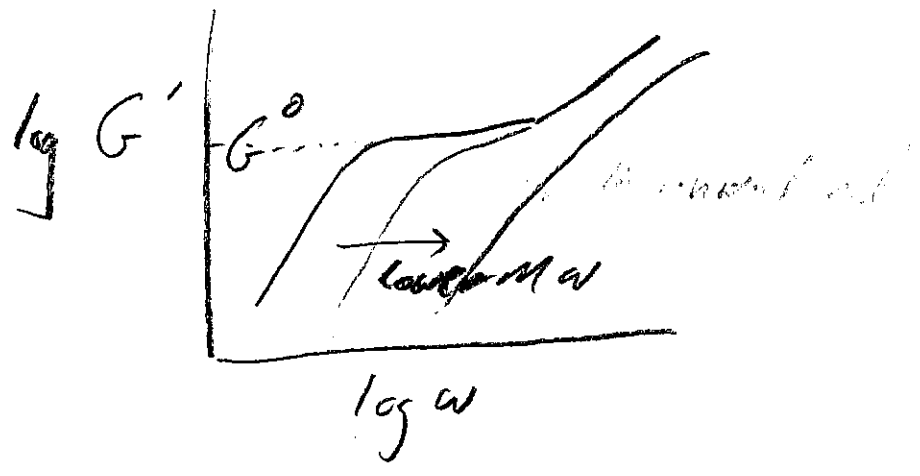G^0 is the plateau Modulus which occurs at frequencies $\omega > \frac{1}{\tau_{flow}}$, say the entanglement network dominates the storage modulus.

As the molecular weight drops the curve shifts to the right & the plateau vanishes. Water does not display G' at all since the flow is entirely viscous.

e) For single Gaussian chain (from Boltzmann analogy)

$$E = \frac{3KT}{2n\ell^2} R^2$$

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

Spring constant
$$k_{spr} = \frac{3kT}{n\ell^2}$$

For Modulus $G^0 \sim n \Rightarrow Me$

$$G^0 \sim \frac{Force}{Area}$$

$$G^0 = \frac{3RT\rho}{Me \, (\ell_k)}$$

if we have ρ (density), T (temp), Me ent. MW & G^0 we can get ℓ_k

3) a) Chains are more flexible at the ends

b) The chain end effects are greater for a stiffer chain. There are fewer Kuhn-steps for a stiffer chain, so it effectively has a lower n.

c) Chain end effects will be large for biomolecules, this means that the measured persistence will reflect an average value that may have limited relevance, it may reflect more the chain length rather than a universal feature of the molecule.

d)
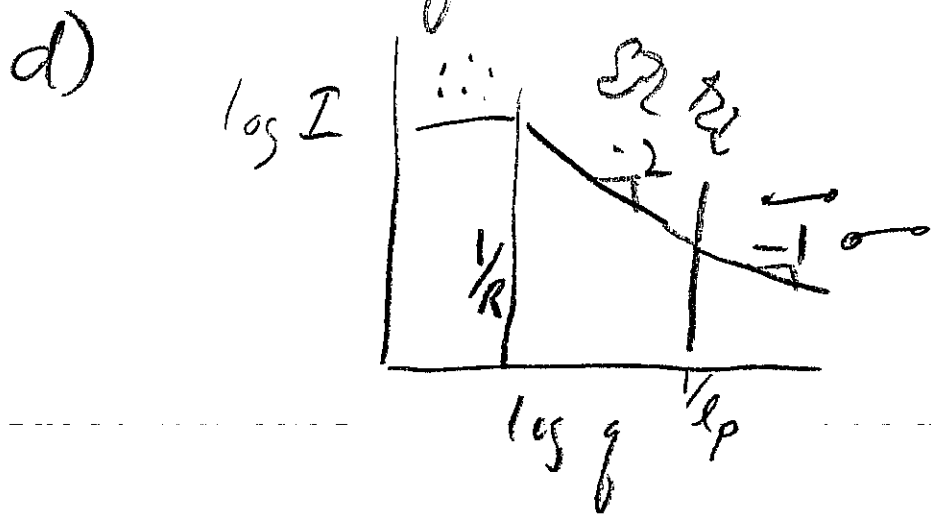
c) Would expect a smeared out than
region + you get a molecular weight
dependent persistence length.

1)   a) The term "Gaussian Chain" is often used to describe a polymer. Give the Gaussian
        function and explain what it has to do with a polymer chain. (We used a simulation to
        connect these in class.)
   b) A polymer chain is at times described as a Brownian Chain. Explain what Brownian
        diffusion has to do with a polymer chain.
        c) When a polymer is put in a good solvent it is called an expanded coil or a self-avoiding
        walk (SAW). Explain why a polymer chain expands from the Gaussian state when it is
        placed in solvent. (That is, what is a self-avoiding walk.)
        d) How can the energy of an isolated Gaussian chain be obtained from the Gaussian
        Function of part a)?
        e) How could this energy be used to calculate the spring constant k_{spr} for an isolated
        Gaussian chain, $F = k_{spr} R$.

2) The stochastic (random) tertiary structure for a polymer coil in dilute solution is described by
        the probability function, $P(R) = k \exp(-R^2/(n\, l^2))$
        a) The integral of $R^2 P(R)$ yields $<R^2> = nl^2$. Show that the derivative of this probability
        function yields the same scaling behavior (i.e. find the most probable size R*, maximum
        probability).
        b) Write a similar probability function for a self-avoiding walk (SAW).
        c) What is the resulting scaling function for end-to-end distance for a SAW?
        d) 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?
        e) What are the problems with this proposition?
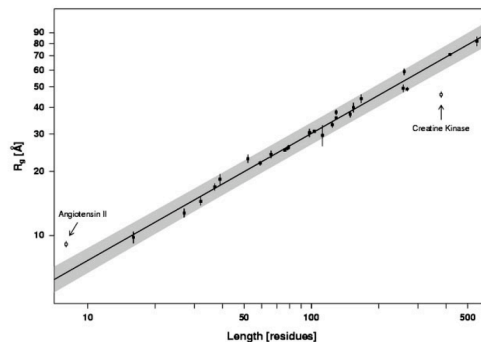

Kohn graph shows a slope of ~0.6.

3) If a thermally equilibrated polymer chain in the Gaussian state is drawn from the ends (see picture below from *Atomic Force Microscopic Study of Stretching a Single Polymer Chain in a Polymer* Brush Yamamoto S, Tsujii Y, Fukuda T *Macromolecules* **33** 5995 - 5998 (2000)) The coil responds by modification of the structure.

(a)   (b)
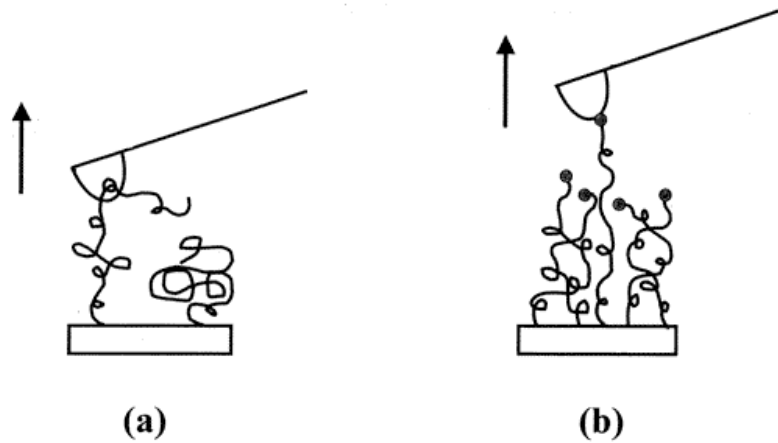
a) Explain how the coil (right in "a") can be described in terms of a scaling transition when it is stretched using a tensile blob model.

b) How can you mathematically describe the size scale introduced by a pseudo-equilibrium state between the applied force F and the thermal force resulting from kT?

c) Sketch a log Intensity-log scattering vector (q) plot that shows how the structure responds to increasing applied force.

d) How do you expect the applied force to change if the temperature is increased?

e) Write the ideal gas law and compare the change in pressure with the change in force from part "d" with increasing temperature. Explain this comparison.

1) a) $P(R,n) = \left(\frac{2\pi}{3}n\ell^2\right)^{-3/2} \exp\left[-\frac{3}{2}\frac{R^2}{n\ell^2}\right]$

A polymer chain can take many conformations in time due to thermal fluctuations in bond rotation. The most probable is at end-to-end distance $R=0$. There is a decaying probability following a Gaussian function

$P(R)$
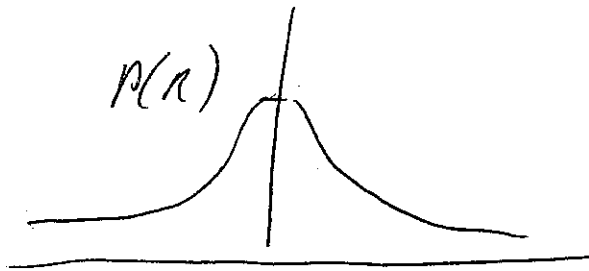
b) Brownian diffusion involves the random motion of a particle due to thermal diffusion driven by kT. If the diffusion path is frozen in space & we correlate time with number of steps (assuming a constant velocity) a direct analogy between the diffusion path and a random walk can be made.

c) A polymer expands, due to excluded volume, that is, the walk avoids itself for large chain index differences. This restriction causes the overall chain to occupy a larger volume compared to the Gaussian state.

d) Energy of an isolated chain is obtained by comparison with the Boltzmann Function,

$$P(R) = \exp\left(-\frac{E_a(R)}{kT}\right)$$

where $E_a(R)$ is the energy associated with an end-to-end distance R. This is similar to the "energy landscape" of a protein! we compare with

$$P(R) \sim \exp\left(\frac{-3R^2}{2n\ell^2}\right)$$

Yielding

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

e)

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

$$\boxed{k_{spr} = \frac{3kT}{n\ell^2}}$$

2) a)

$$\frac{d\ KR^2\exp\left(\frac{3R^2}{2n\ell^2}\right)}{dR} = \cancel{K}\left[2R\exp\left(\frac{-3R^2}{2n\ell^2}\right) - \frac{3R^2}{n\ell^2} R\ \exp\left(\frac{-3R^2}{2n\ell^2}\right)\right] \equiv 0$$

for max

$$2 = \frac{3R^2}{n\ell^2} \quad \text{or} \quad \boxed{\langle R^2\rangle = \frac{2}{3}n\ell^2}$$

b)

$$P_{snw}(R) = k \exp\left[\frac{-3R^2}{2 n \ell^2} - \frac{n^2}{2}\frac{V_c}{R^3}\right]$$

c) $\langle R^2 \rangle^{1/2} \sim n^{3/5} \ell$

d) Log log plot with slope of $0.6 \sim 3/5$

means

$$\langle R_g \rangle \sim n^{3/5} \ell$$

same as "c)" so chains are SAW's

e) He looks at a series of chains not a single chain. We know from previous discussion that the secondary structure varies for different proteins & it is likely that there is significant secondary structure in these chains, the comparision is probably fortuitous.

3) a)

$\xi_p = R_0$ Blobs $\xi_p = \ell_k$
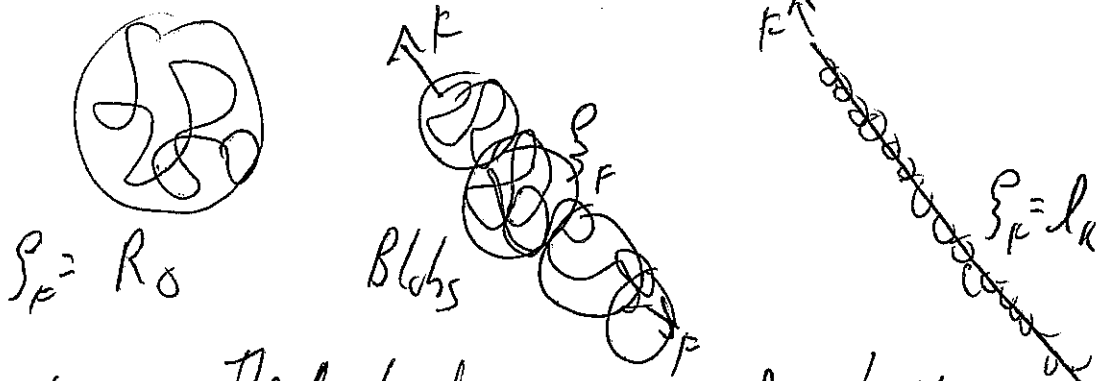
$F = 0$ The Application of force leads to the formation of a 2° structure called a "Blob"

b)
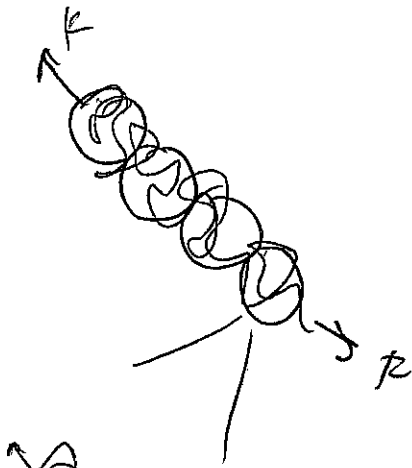
For a given force f there is a size ξ_f
where $n\ell^2 \sim R^2 = \xi_f^2$ such that

$$F = \frac{3KTR}{n\ell^2} = \frac{3kT}{\xi_F} \quad \& \quad \boxed{\xi_F = \frac{3kT}{F}}$$

single coil
springs
eqn.

c)
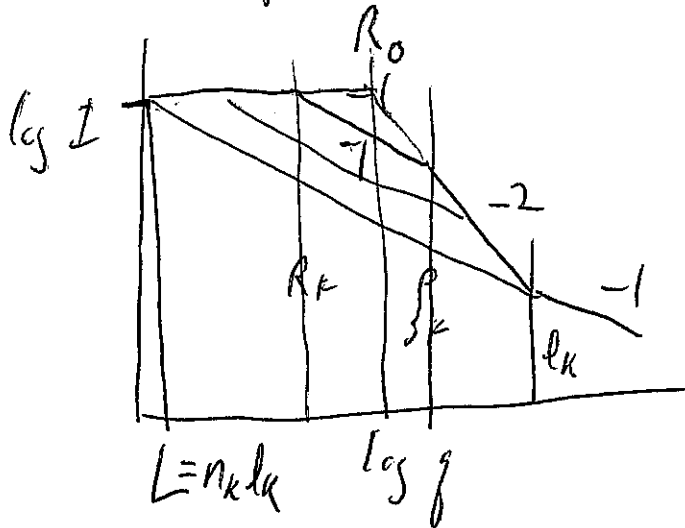
d) $F = \frac{3kT}{\xi_F} = \frac{3kTR}{n\ell^2}$ $F \sim T$ for ideal chain

e) $P = \frac{nkT}{V}$ Both depend linearly on T because both represent random Gaussian states, one for kuhn units & one for gas atoms.

081117 Quiz 7 Morphology of Complex Materials

1) The concentration blob requires calculation of the overlap concentration, c*.
    a) What is the overlap concentration for a solution of rods as a function of the rod mass n?
    b) How would you expect the concentration blob size, ξ_c, to vary with concentration for rods? (Do the same calculation we did in class but for $d_f = 1$ rather than 5/3.)
    c) Is the dependence of blob size, ξ_c, on concentration stronger or weaker for rods compared to SAW coils? Explain why this is the case from a physical perspective.
    d) Is c* a smaller or a larger number for rods compared to SAW coils of the same n? Explain.
    e) Sketch a plot of log I (log of scattered intensity) versus log q (log of the scattering vector) for a collection of rods at $c \geq c^*$ in the semi-dilute regime and compare this with the plot for SAW coils.

2) Kuhn proposed that the dynamics of a polymer coil could be explained with the dumbbell model composed of a spring and balls with a friction factor ζ.
    a) What is the spring constant for a Gaussian polymer coil in terms of n?
    b) What is the friction factor for a polymer coil using Stokes Law in terms of n for a Gaussian coil?
    c) Write an expression for the time constant for the dumbbell model in terms of n based on your answers to a and b.
    d) If the friction factor obeys Stokes law can the viscosity scaling in n seen in polymers be obtained?
    e) If the friction factor, ζ, scales with n, $\zeta \sim n$, how does the dumbbell model differ from the lowest order Rouse relaxation mode?

3) Rouse theory was derived to describe polymer dynamics. Rouse divided the polymer chain into subunits.
    a) How does a Rouse unit differ from a tensile blob?
    b) Write a force balance for a Rouse unit ℓ.
    c) What assumption does your equation in question b make concerning the distance over which dynamic units are coupled along the chain?
    d) The Rouse approach leads to an expression for the relaxation time spectrum for a polymer,

$$\tau = \frac{\zeta_R}{4 b_R \sin^2(\delta/2)} \qquad\qquad (1)$$

How can a cyclic assumption yield discrete values for δ and τ?

    e) Show that $\left(\dfrac{\zeta_R}{a_R^2} \right)$ must be a constant for Rouse theory where a_R is the size of a Rouse unit. Use the m = 1 mode; $\delta_m = 2\pi m \Big/ (N_R - 1)$; Solve (1) above for τ.

1) a)

$$c^* = \frac{n}{R^3} = k\, n^{-2}$$

$\quad R \sim n$ for a rod

b)

$$\xi_c = R_0 \left(\frac{c}{c^*}\right)^p \sim n^0$$

$$n\, n^{2p} \sim n^0 \qquad so \qquad 2p+1 = 0$$
$$p = -\frac{1}{2}$$

$$\xi_c \sim R_0 \left(\frac{c}{c^*}\right)^{-1/2} \text{ for rods}$$

c) $\quad$ SAW $\quad \xi_c \sim R_0 \left(\frac{c}{c^*}\right)^{-3/4}$

so SAW has a stronger dependence on concentration.

Concentration blob size has to do with the ability of chains to screen or block interactions between chain units. SAW coils are more effective at screening interactions because they are denser than rods.

d) c^* is a much smaller number $c^* \sim n^{-2}$ vs. $c^* \sim n^{-4/5}$ since rods are less dense & occupy more space.

e)

R_0 $R_{Gaussian}$

$lg\ I$

-2

$-2\ \ -2$

C
$(mean)$

-1

ℓ_k

ℓ_c

$lg\ q$

Rod's

R_0

$lg\ I$

$-1/3$

-2

-1

$lg\ /\ \ \xi \ \ \ell_k$

SAW's
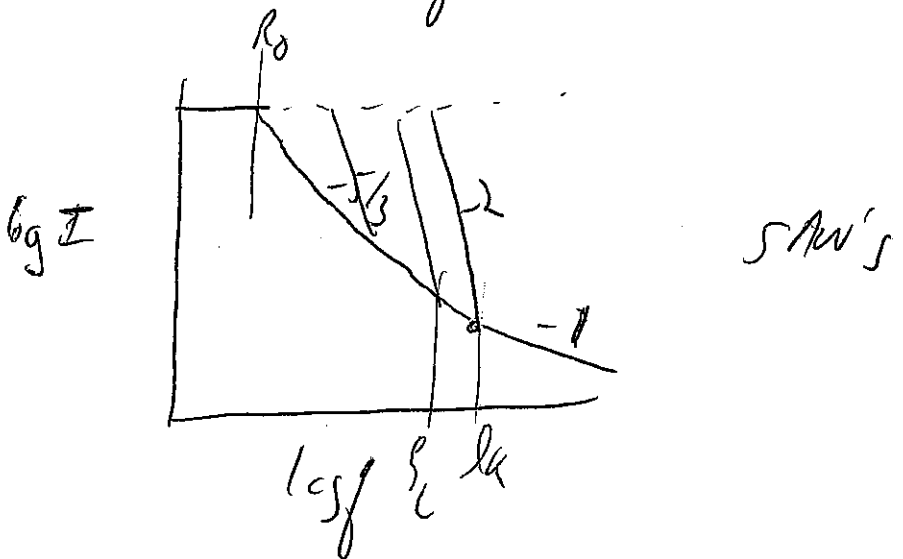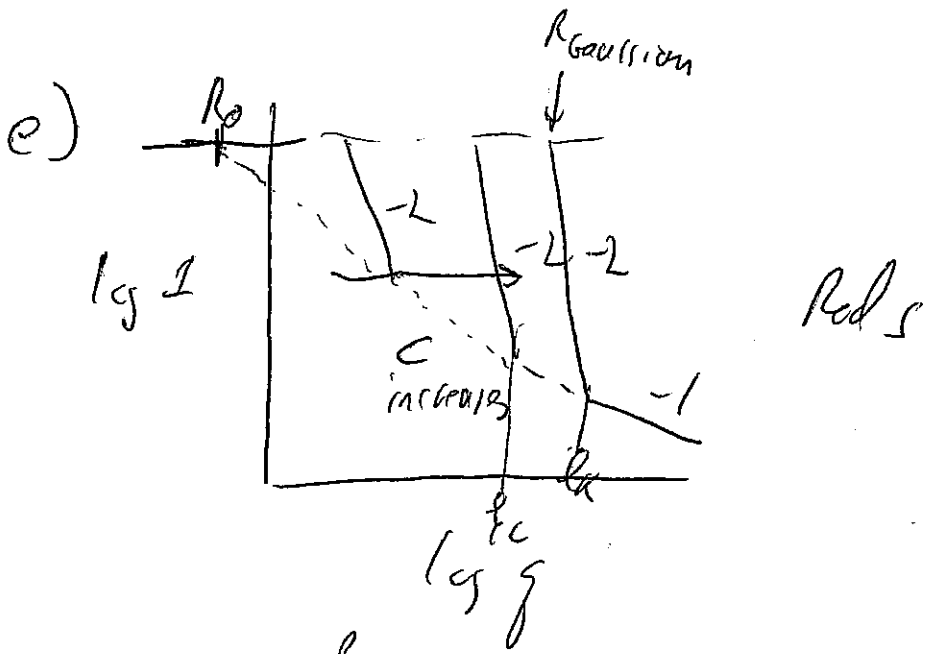
2) a)

$$K_{spr} = \frac{3kT}{R_0^2} = \frac{3kT}{n_k \ell_k^2}$$

b)

$$\zeta_F = 6\pi\eta_0 R_0 = 6\pi\eta_0 \left(n^{1/2}\ell\right)$$

c)

$$\tilde{\zeta} = \frac{\zeta}{K_{sp}} = \frac{n\ell^2}{3kT} 6\pi\eta_0 \left(n^{1/2}\ell\right)$$

$$\tilde{\zeta} = \frac{n^{3/2}\ell^3 2\pi\eta_0}{kT}$$

d) If $\xi \sim 6\pi \eta_0 (n^{1/2} l)$

then $\eta_0 \sim n^{1/2}$

this doesn't follow n' or $n^{3.4}$
seen for polymers

e) For $\xi \sim n$ the dumbbell model is
identical to the Rouse chain Rouse mode
behavior.

3) a) A Rouse unit is an arbitrary unit while
a tensile blob unit is of fixed size
$$\xi_F = \frac{3kT}{F}$$
Tensile unit doesn't have a drag coefficient
so it is a static structure.

b)
$$\xi_F \frac{dz_\ell}{dt} = b_R (z_{\ell+1} - z_\ell) + b_R (z_{\ell-1} - z_\ell)$$

$$= b_R (z_{\ell+1} + z_{\ell-1} - 2 z_\ell)$$

c) we only consider nearest neighbor interactions

(3)

(3) The Rouse theory was derived to describe polymer dynamics. ~~but had to~~ Rouse divided the chain into subunits.

a) how does a Rouse unit differ from a Tensile blob?

b) Write a force balance for a Rouse chain "i"

c) what assumption does your gen "b" make concerning the distance over which dynamic units are coupled along the chain?

d) The Rouse approach leads to an expression for the relaxation spectrum for a polymer

$$\zeta = \frac{\zeta_R}{4 b_K \sin^2(\theta/2)}$$

How can a cyclic assumption yield discrete values for ζ?

e) Show that $\left(\frac{\zeta_R}{a_R^2}\right)$ must be a constant for Rouse they.

d) For a cyclic

$$z_\ell = z_{\ell + N_R}$$

where there are N_R units in the coil

$$N \delta_m = 2\pi m \qquad \text{where } m \text{ is the mode of vibration}$$

So $\quad N_R \delta_m = \pi m$

$$\boxed{\delta_m = \frac{2\pi m}{N_R} \qquad \text{for cyclic}}$$

$$m = 0, 1, 2, 3, \dots$$

e)

$$z_R = \frac{\zeta_R}{4 b_R \sin^2 \delta/2} \qquad \text{use} \quad \delta_m = \frac{2\pi}{(N_R - 1)} \lll 1$$

$$\text{so } \sin^2 \frac{\delta}{2} = \left(\frac{\delta}{2}\right)^2$$

$$z_R = \frac{\zeta_R \, 4 (N_R - 1)^2}{4 b_R (2\pi)^2} \qquad\qquad b_R = \frac{3kT}{a_R^2}$$

$$= \frac{\zeta_R \, a_R^2 \, N_R^2}{12 kT \, \pi^2} \qquad\qquad R_0^2 = N_R \, a_R^2$$

$$z_R = \frac{(\zeta_R / a_R^2) \, R_0^2}{12 kT \, \pi^2}$$

For z_R to not depend on the Rouse Unit (ζ_R / a_R^2) must be a constant

Morphology of complex materials: Quiz 8 081124

1. The Rouse model describes the relationship between the zero shear viscosity and the molecular weight of a polymer.
    a. How does the dependence of viscosity on molecular weight change with increasing M? Does the Rouse model account for this change?
    b. Draw a plot showing the behavior in (a). Mark the region of Rouse model and Reptation model.
    c. What is the reason for this change in behavior? Explain
    d. Draw a plot of log(shear storage modulus) vs. log (frequency) for a polymer say, polyethylene, with Mwts of 10^3, 10^4 and 10^5 g/mole. Explain the change in behavior as seen from this plot.
    e. Do entanglements affect the glass transition temperature of polyethylene? Explain.

2. The tube model is used to describe a monodisperse linear polymer melt beyond its critical molecular weight of entanglement (M_c).
    a. What are the 3 major mechanisms for relaxation in the tube model?
    b. What is primitive path, as described in the Reptation model?
    c. What dependence of viscosity on M is obtained from the Reptation model? What power law dependence is actually seen in real polymers (beyond M_c)?
    d. Can you give a few reasons for the change from the predicted theoretical dependence in question (c)?
    e. Compare the dependence of viscosity, relaxation time and diffusion coefficient on M for Rouse model and the Reptation model. (Just a table is sufficient)

3. Packing model is a widely used model to relate the structural properties of a polymer with its physical properties.
    a. Write the equation for the volume occupied by one polymer chain (V_c) used in this model.
    b. What does the pervaded volume refer to? Write an equation for V_{sp}.
    c. Write the equation describing the packing length. What is the dependence of entanglement molecular weight M_e on packing length p?
    d. How is M_e related to the plateau modulus of a polymer? Derive the relationship from rubber elasticity.
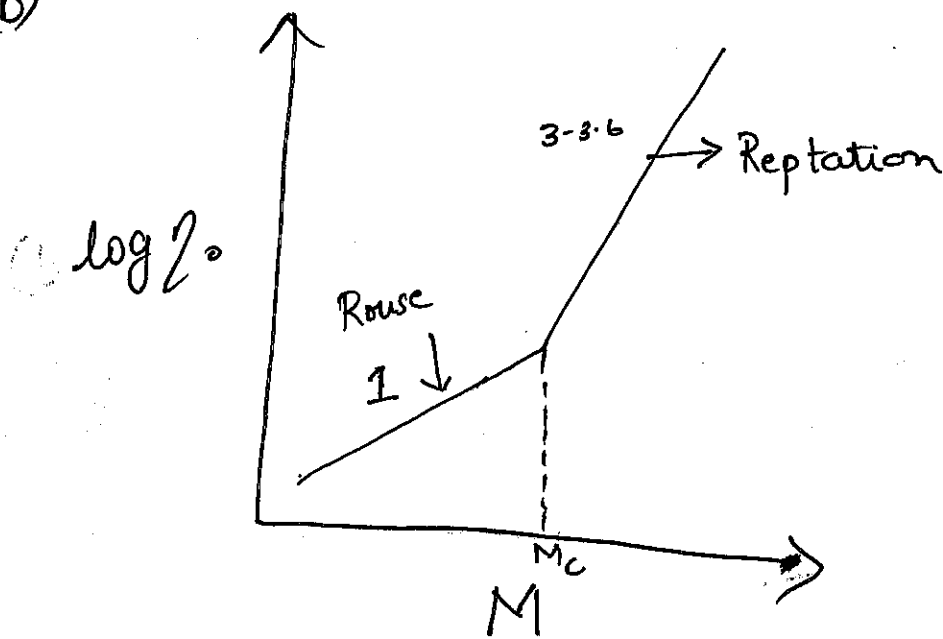   e. Can you list the dynamic hierarchy in polymer melts as understood from the discussions in class?

1) a) Below a certain molecular weight, referred to as the critical molecular weight for entanglement (M_c), $z_0 \propto M$

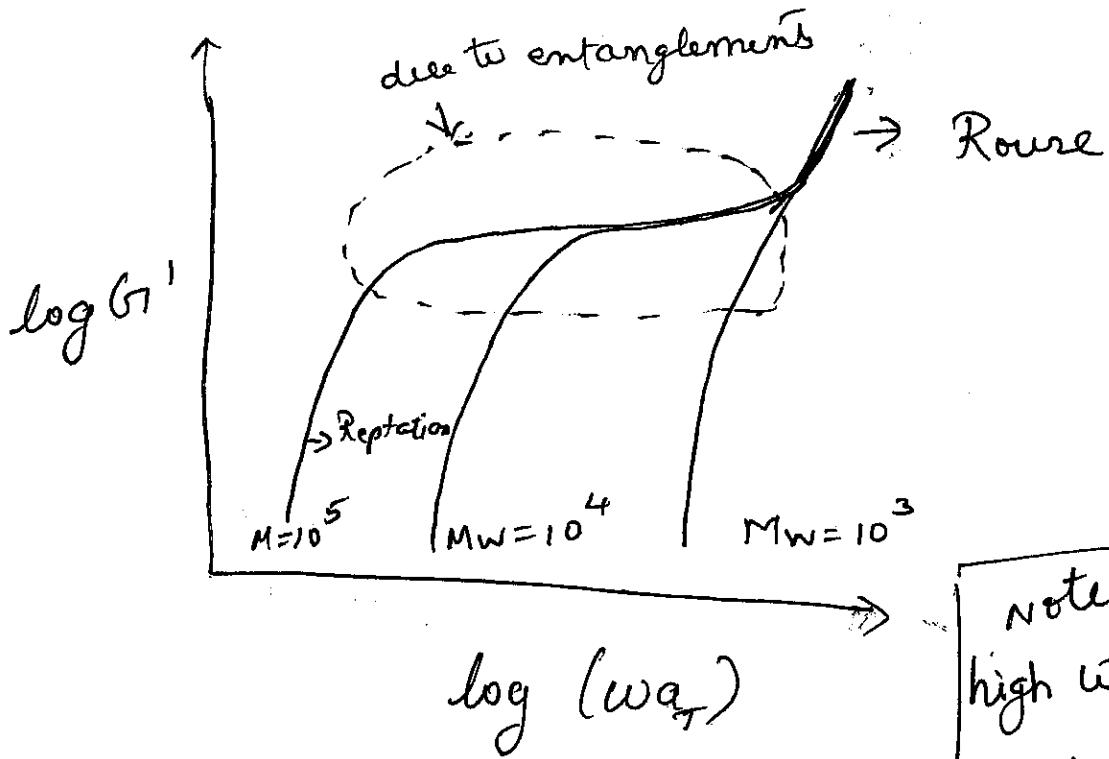Beyond M_c $z_0 \propto M^x$ ($3 \leq x \leq 3.4$

The Rouse model only describes the dependance below M_c.

2) (b)

(c) As molecular weight increases, polymer chains interpenetrate each other forming entanglements. This constrains the motion of the chains. Hence an increased dependance of z on M-wt.

(d)

As M·wt increases beyond M_c, entanglements come into the picture. This causes a plateau-like region to appear for the higher M·wt polymers. Higher the Mwt, wider is the plateau region.

(e) NO. Since glass transition temp is based on local chain motion. Entanglement affect properties that related to the entire chain.

(2) (a) (i) Reptation

(ii) Primitive path fluctuation

(iii) Constrain release - (Multiple reptation)

(b) The path of the reptation test tube is termed as the primitive path

(c) $\eta \propto M^3$

In real polymer, the exponent varies from 3 to 3.6.

The deviation could occur due to various reasons

(i) Non linear chains

(ii) Polydispersity

(iii) Reptation model is assuming a single test chain reptating among stationery chains, which is not the real case

(d)

	Rouse $\propto M^x$ $x =$	Reptation $\propto M^x$ $x =$
Z	1	3
η	2	3
D	-1	-2

(3)

(a)

$$V_c = \frac{M}{\rho N_A}$$

(b) Pervaded volume refers to the smallest sphere that can completely contain a molecule /chain

$$V_{sp} \propto \langle R_g^2 \rangle_o^{3/2}$$

(C)
$$p = \frac{M}{\langle R^2 \rangle_0 \, \rho N_A} = \frac{V_c}{\langle R^2 \rangle_0}$$

$$\langle R^2 \rangle_0 = 6 \langle R_g^2 \rangle_0$$

Then from V_c, V_{sp}, we get

$$M_e \propto p^3$$

(d) The equilibrium shear modulus in rubber elasticity theory is described by

$$G_e = \nu RT$$

where G_e is equilibrium shear modulus

ν is molar density of network strands

Replace G_e with plateau modulus G_N^0

and ν with ν_e molar density of entangled networks

$$G_N^0 = \nu_e RT = \frac{\rho}{M_e} RT$$

(e) Heirarchy

(i) Rouse Unit

(ii) Packing length

(iii) Persistence / Kuhn length

(iv) Tube dia

(v) Primitive path length of a single tube

size / Mass

(vi) Contour (α) length of ~~entire~~ polymer chains

(vii) Me / Mc

(viii) Rg / M·wt of polymer

081205   Quiz 9 Morphology of Complex Materials

1) Polymers crystallize into structures that have an aspect ratio similar to a sheet of paper.
    a) Describe how low molecular weight alkanes (waxes crystallize). Do these materials form sheet-like crystals? What is the degree of crystallization (final fraction of crystal versus amorphous).
    b) Describe how proteins crystallize. Do these materials form sheet-like crystals? What is the degree of crystallization?
    c) Explain the differences between crystals in a synthetic polymer and the materials of question a and b in terms of the ability to form chain-folded, sheet-like crystals. Why is the degree of crystallinity not 100% for polymers?
    d) Monodisperse, linear polyethylene can be produced by hydrogenation of anionically polymerized polybutadiene. This polymer has no stereochemical defects and could completely form a planar zig-zag conformation. Do you expect such polyethylene's to form chain folded lamellar crystals or extended chain crystals from the quiescent melt? Explain your answer.
    e) Metallocene-polymerized copolymers of polybutene and polyethylene have short branches of two carbon units that are regularly spaced at any interval that is desired. What effect do you think these *controlled* short-chain branches would have on the lamellar crystalline structure and on the degree of crystallinity for polyethylene copolymers?

2) Polymer crystal thickness, t, varies with the temperature of crystallization, T_c, following the functionality $1/t \sim (T_\infty - T_c)$.
    a) Why do you think deeper quenches would lead to smaller crystals (in your answer consider that small crystals are non-equilibrium structures, that is, an infinite crystal is the equilibrium structure).
    b) Write a pseudo-equilibrium expression for the free energy of a nano-crystal that displays lamellar structure.
    c) From this free energy expression write an expression for $1/t$ as a function of T_c.
    d) What parameters are needed to calculate the lamellar thickness t as a function of T_c. Which of these parameters is most difficult to obtain? Why?
    e) Explain how these parameters could be measured using SAXS or TEM.

3) The Avrami equation is used to describe the growth of crystals in terms of the geometry of crystal growth.
    a) Sketch a plot of the fraction crystallinity versus time for a typical isothermal crystallization of a polymer.
    b) Give the Avrami equation and sketch a plot associated with this equation.
    c) Describe the two parameters needed for the Avrami Equation and give their values for 2d growth with spontaneous nucleation.
    d) Could the Avrami equation be used to describe dendritic growth of ice on a car windshield? Explain.
    e) How would you expect the Avrami exponent n to vary if 2-d crystal growth with spontaneous nucleation were augmented with secondary crystalline growth (crystalline growth within a crystallite nucleated on the initial crystallographic skeleton?

Answers: 081205   Quiz 9   Morphology of Complex Materials

1) a) Low molecular weight alkanes crystallize as extended chain crystals. The degree of crystallinity is 100%. They form sheet-like crystals which gives rise to their "waxy" feel as sheets slide against each other.
b) Proteins crystallize in their native state with a collapsed native state protein at each unit cell site perfectly oriented in registry with other identical native state collapsed structures. Proteins do not form lamellar crystals. The degree of crystallinity is 100%.
c) Synthetic polymers form chain-folded sheet-like crystals. The degree of crystallinity is less than 100% since the fold surface is amorphous and there is a region between lamellae with material that can not crystallize due to defects and chain folding itself. Polymers are polydisperse and form disordered collapsed structures so a collapsed chain, protein-like crystal is not possible. The chain can not easily form extended-chain crystals like low-molecular weight alkanes due to the loss in conformational entropy as well as entanglements in the melt among other reasons.
d) Such polyethylene's form chain folded crystals. This is due to the entropy difference between an extended chain crystal and a chain folded crystal.
e) Short branches can not be included in polymer crystals so the lamellar thickness can be controlled to some extent by inclusion of regularly spaced short chain branches. This lowers the melting point of the crystals following the Hoffman-Lauritzen function. Short chain branches also dramatically decrease the degree of crystallinty leading to thermoplastic elastomer materials. These are elastomers that can be melted and processed in injection molding and extrusion equipment.

2) a) Small crystals are non-equilibrium structures and are formed far form the equilibrium point (equilibrium melting point), that is, at deep quenches.
b) For a lamellar crystal with dimensions a x b x t and where t<<<a~b we have,

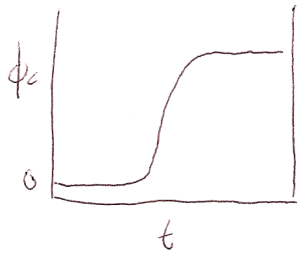-2ab γ + abt Δf_m = 0 at pseudo equilibrium. Also, $\Delta f_m = \Delta H(1-T/T_\infty)$ so,

t = 2 γ T_∞/($\Delta H(T_\infty$ - T))
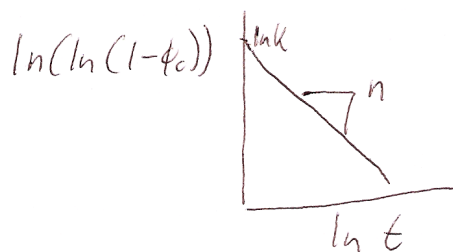c) 1/t = $(\Delta H/(2 \gamma T_\infty))(T_\infty$ - T)
d) You need γ, T_∞, and ΔH. γ is the most difficult to obtain because the exact nature of the chain fold surface is not known.
e) If t can be measured a plot of T versus 1/t yields T_∞ as the intercept and the other parameters from the slope.

3) a) b)

$$\phi_c = 1 - \exp(k\, t^n)$$

$\ln(\ln(1-\phi_c))$

$\ln(\ln(1-\phi_c)) = n\ln t + \ln k$

c) n is the Avrami exponent and it reflects the dimension of growth and the type of nucleation (spontaneous or sporatic). k is the Avrami prefactor and it reflects the details of growth. For 2d growth and spontaneous nucleation n is 2 and k is $\pi N(dr/dt)^2$.

d) Yes it could be used to describe 2d spontaneous nucleation of ice dendrites.

e) If crystallization were augmented by secondary crystallization the Avrami exponent would be slightly larger than 2.