120314 Final Morphology of Complex Materials

1) Proteins are the prototypical model for hierarchy.

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) Proteins have the ability to self-assemble into the native state. Explain why self-assembly can occur in a protein but not in a synthetic polyamide like nylon.

e) The size of a protein is often used to observe folding. Explain the difference between the radius of gyration, R_g, and the hydrodynamic radius, R_h, for a protein. Give methods used to measure R_g and R_h, a description of what they quantify and, their relative values (which is larger) for a native state protein, a rod and an expanded polymer coil.

2) a) Amphiphilic molecules display a critical micelle concentration (CMC); while chain molecules display an overlap concentration, c*. Explain the similarity and the difference between the CMC and c*.

b) In addition to structural hierarchies seen in proteins and polymer crystals we considered statistical hierarchies such as for a polymer coil in solution. One example of a statistical hierarchy occurs when a polymer coil is stretched. Explain the levels of structure observed in this type of hierarchy and explain how each level of structure (sizes) is determined.

c) In the tensile-blob hierarchy, symmetry exists between the smallest scale structural level and the largest scale structural level. That is, there are similarities between these two structural levels. Explain why the large-scale level forms at large sizes while the small-scale level forms at small sizes.

d) Flory described a polymer coil as displaying a Gaussian chain conformation in the melt state. Explain the origin of the Flory expression $\langle R^2 \rangle = nl^2$. (derive this)

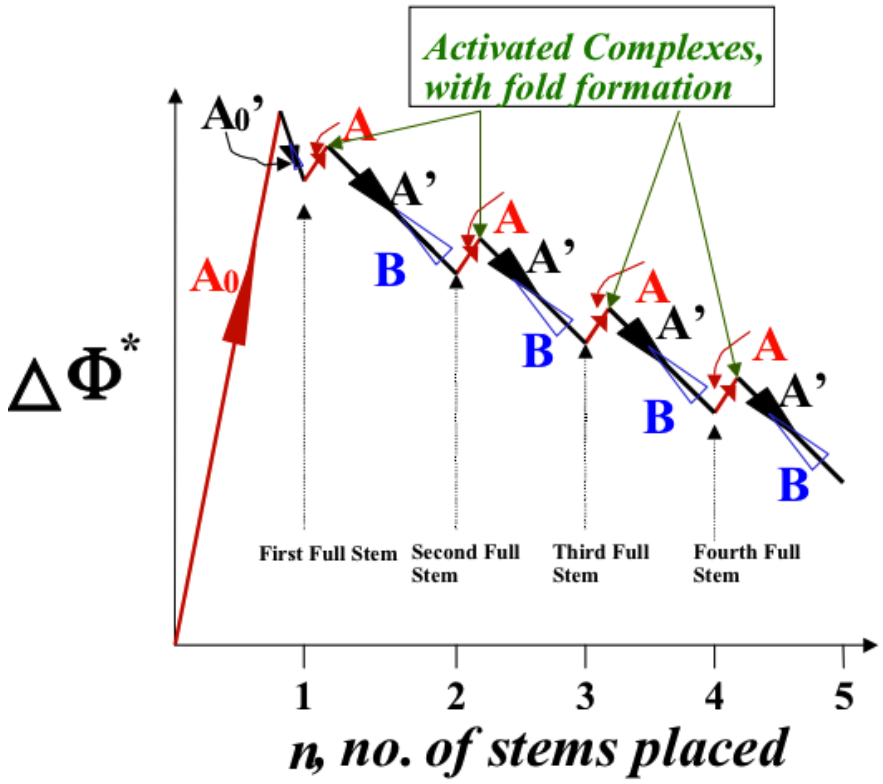
e) Explain how the Gaussian coil of question 2d) can have the same fractal dimension as a disk. Give a scaling method to distinguish between these structures.

3) a) The Rouse model and the tube model describe polymer dynamics in dilute and concentrated conditions, respectively. Explain the effect of concentration on the dynamics of polymers using these two models. (Consider a transition from dilute, to semidilute, to concentrated and the variation in the chain relaxation behavior.)

b) Polymers display different crystalline structure depending on the concentration in which they are crystallized. Describe the morphology for dilute and concentrated/melt crystals and relate the difference in morphology to your discussion in question 3a).

c) Surfactants can be used to lower the surface energy of nano-particles. Use a Gibbs-Thompson model to show that the use of surfactants could lead to smaller nano-crystals. How else can smaller nanocrystals be produced using this model?

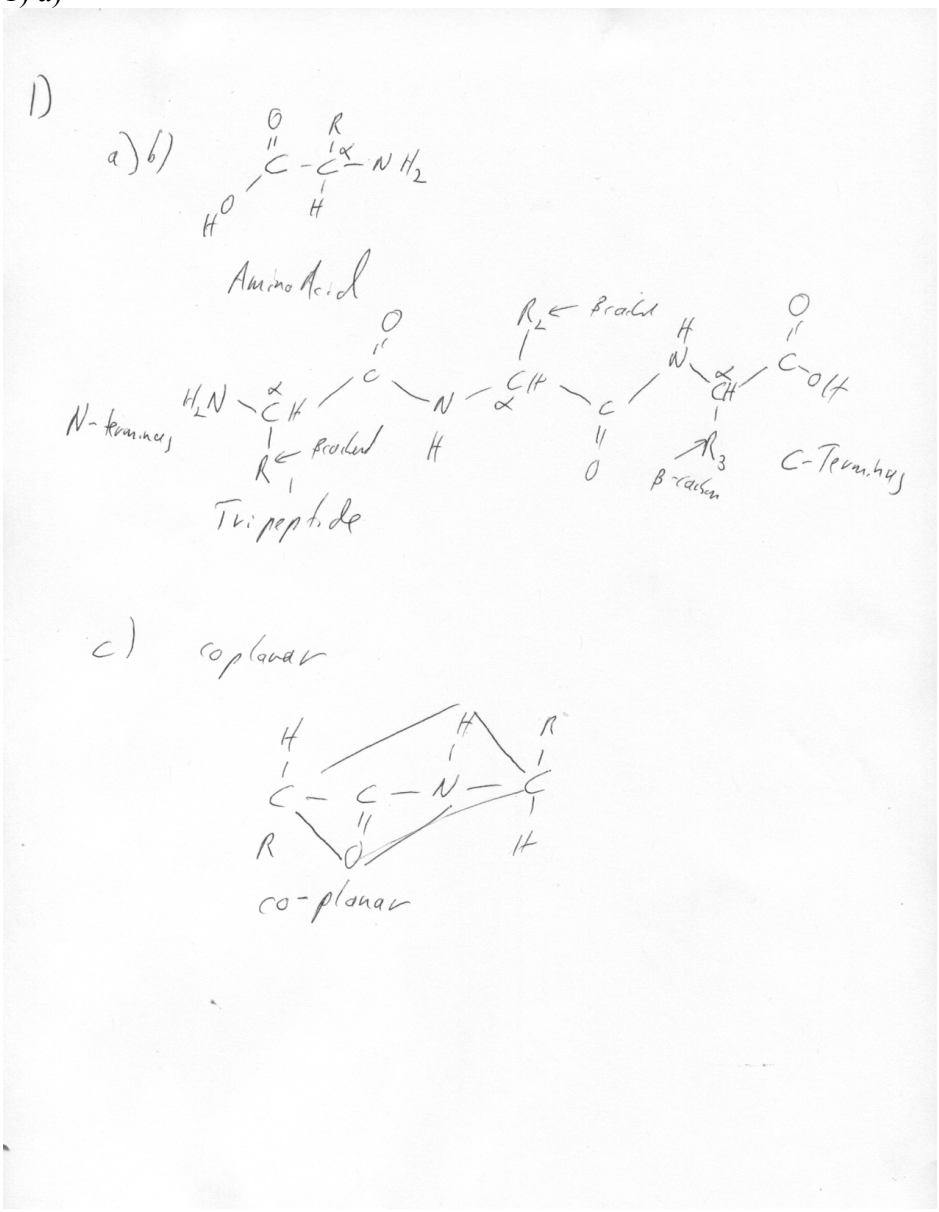
d) The following sketch shows the change in free energy for completion of a layer of secondary nucleation on a polymer crystal. Draw a cartoon of this process and explain this plot using the cartoon. Describe what occurs when the curve passes through 0 on the y-axis.



e) Polymers display polydispersity in all of their features. For example, we would expect a distribution in the crystalline lamellar thickness. Pick a suitable distribution function for this polydispersity in lamellar thickness and explain why you expect lamellar thickness to follow this distribution function.

ANSWERS: 120314 Final Morphology of Complex Materials

1) a)



d) Proteins have evolved by a more or less trial and error process over billions of years to have a specific sequence of amino acids that can facilitate folding. Further, there are complicated biochemical environmental factors such as chaparone molecules that enable folding. The details of folding have to do with local hydrophobic/hydrophilic interactions, ionic interactions, strategically placed disulfide linkages and hydrogen bonding that serve to drive folding using enthalpic interactions. Opposed to folding is the entropic thermal randomization of the protein structure. Nylon does not have an organized sequence of functional groups and does not exist in an environment that would facilitate folding.

e) The radius of gyration is the moment of inertia for a structure using the density or electron density (if x-ray scattering is used) or index of refraction (if light scattering is used) as a weighting factor. For a Gaussian chain it is directly related to the root mean square size and for a sphere it is directly related to the sphere diameter (D/2.6). The hydrodynamic radius is the radius of an equivalent sphere with the same drag coefficient. For a native state protein R_g is probably smaller than the hydrodynamic radius since for a sphere $R_g = D/2.6$ while $R_h = D/2$. For a rod R_h will be nearly the rod diameter while R_g will be closer to the rod length, so R_g should be larger. For an expanded polymer coil the relationship between R_g and R_h will vary depending on the extent of "draining" of the coil, that is the degree of association of the solvent with the polymer chain.

2) a) CMC is the concentration where micelles just begin to form for an amphiphilic molecule (soap). Below this concentration the surfactant is dispersed in the solution. c* is the concentration where polymer chains just begin to touch one another, it is also the concentration of a single coil $c^* = M/R^3$.
The similarity between CMC and c* can be categorized in terms of dynamics and statics.

Dynamically they are both concentrations where interactions between molecules become coordinated, that is, c* is the concentration where entanglements begin to occur and CMC is the concentration where we expect a dramatic shift in surfactant solution dynamics to occur, going from a dilute solution to a colloidal suspension of spherical structures with trapped solvent. We expect a jump in the viscosity at CMC and a change in the slope of the log of viscosity versus the log of concentration at c*.

Statically, c* is where we begin to see "screening" of interactions, so the chains become Gaussian at large scales. For surfactants, the CMC is where we see a dramatic change in static structure associated with new coordinated interactions. So structural changes occur associated with interactions at both concentrations.

b) Stretching of a polymer coil leads to the formation of a tensile-blob scaling transition as described by Pincus. At large sizes the coil deforms readily since there is a large lever arm acting on the chain. At small scales the lever arm is smaller so the thermal randomization of the coil is not perturbed. This leads to a transition from a 1-d extended coil to a 5/3-d expanded coil scaling. At smaller scales the local energetic interactions, steric interactions and chain connectivity lead to another transition at the persistence length or Kuhn length. This is a transition from a 5/3-d expanded coil to a 1-d persistence structure. The tensile blob transition occurs at the tensile blob size of 3kT/F.

c) The large scale and small scale structure are both 1-dimensional. For the large scale structure this is the result of the application of a directional force and the inability of the coil to resist this deformation at large size scales, up to the blob size. At small scales the 1-d structure is the result of the directionality of the chemical bond and the reinforcement of this directionality by steric interactions and other

local enthalpic interactions. The large scale occurs at large scales since it is an externally applied force that acts at large scales, while the small scale is small scale because it is the result of internal forces and bond directionality that act from a small scale up.

d)

Consider chain scaling with no long-range interactions.

The chain is composed of a series of steps with no orientational relationship to each other.

So $\langle R \rangle = 0$

$\langle R^2 \rangle$ has a value:

$$\langle R^2 \rangle = \sum_i \sum_j r_i \cdot r_j = \sum_i r_i \cdot r_i + \sum_i \sum_{j \neq i} r_i \cdot r_j$$

We assume no long range interactions so that the second term can be 0.

$$\langle R^2 \rangle = Nr^2$$

e) The scaling relationship between size and mass for a Gaussian chain and for a disk is $N \sim R^2$. This means that both objects are 2-dimensional. The difference between the two structures lies in their topological layout. For example, a short circuit path through the disk is a straight line ($d_{min} = 1$), while that "through" a Gaussian chain is a random walk of dimension 2, $d_{min} = 2$. Similarly, we can consider that a straightened out Gaussian chain has a dimension of 1 ($c = 1$) while a straightened out disk has a dimension of 2 ($c = 2$). We find that $d_f = c\, d_{min}$.

3) a) At low concentrations (below c*) the Rouse model is appropriate since there are no or limited entanglements. The viscosity is proportional to the molecular weight and the chain displays a single dominant relaxation time, the first order Rouse mode. As concentration increases the polymer chain feels the constraint of entanglements. Entanglements serve to restrict the motion of the chain by confining the chain to the space in which it already exists more or less. As concentration increases this constraint becomes more confining, that is the tube in which the chain is entrapped becomes narrower. The tube diameter reaches a minimum in the melt state. In the tube model two relaxation times are observed, one at size scales smaller than the tube diameter, that follow Rouse dynamics, and one at larger size scales that follow random motion confined to a Gaussian tube path.

b) In dilute conditions polymers form thin lamellar crystals. The chains are free to diffuse to the crystallization front and there are few constraints to regular adjacent reentry folding. As concentration increases both the transport of chains and the transport of impurities away from the crystallization front is hindered. This leads to a competition between crystalline growth and diffusion which results in the introduction of a size scale, the Keith-Padden δ-parameter, G/D, where G is the crystalline growth rate and D is the diffusion coefficient. This parameter decides the coarseness of the melt crystallized structure and the lateral extent of the lamellae. Lamellae grow from the frequent

nucleation sites that occur in a melt or high concentration polymer, they are limited in growth by impurities so form fibrillar crystals that serve as epitaxial nucleation sites for further fibrillar growth. Entanglements also play a role in the complex structure, particularly in serving to reel-in lamellae into a stacked lamellar fibrillar structure.

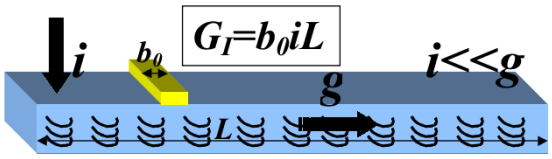
c) The Gibbs-Thompson equation we used in class is,

$$r = \frac{k\sigma T_\infty}{\Delta H \Delta T}$$

where r is the preferred crystalline growth size, k is a geometric factor for the number of crystalline growth faces, σ is the surface energy, T_∞ is the equilibrium melting point for an infinite crystal, ΔH is the enthalpy of fusion and ΔT is the quench depth. If surfactants lower the surface energy then the crystalline size would drop.

The other parameters in the Gibbs-Thompson equation can also lead to smaller nano-crystals, lower equilibrium melting point, fewer crystalline faces, larger enthalpy of fusion, and most commonly a deeper quench depth.

d)



A nucleus is deposited on the crystal surface in the "0"'th step. This requires a large amount of energy since it creates two new surfaces. The drop in free energy is associated with the enthalpy of crystallization. The addition of another stem to this surface next to the nucleation site does not create new surface area (except at the fold edge). So there is only a small energy penalty and a larger drop in free energy associated with the enthalpy of crystallization. So we see an initial jump in free energy followed by a stair like drop with further stems adding to the crystal. When the curve passes through 0 the process is spontaneous since there is a net decrease in free energy. So globally the process is spontaneous but locally there is an energy barrier to crystallization associated with the area under the curve from 0 stems to the point where the free energy chain goes negative. This is the barrier energy for crystallization.

e) The choices for distribution functions from class are rather limited, either Gaussian or log-normal. Luckily these two distribution functions can describe may if not most situations. The Gaussian function is for a random process that has equal probability of a positive and a negative deviation from the mean or from 0 if the mean is 0. In the case of polymer crystalline thickness this is not viable since it is not possible to produce a crystal of negative thickness so we are always biased towards positive end of thickness. There is no upper limit to the thickness, the lower limit is near 0. There is an optimum thickness that occurs at the prediction of the Gibbs-Thompson/Hoffman-Lauritzen function. So we are inclined to expect that the thickness will follow a function like the log-normal function.

Log-Normal Distribution

$$f(R) = \frac{1}{R\sigma(2\pi)^{1/2}} \exp\left\{-\frac{[\log(R/m)]^2}{2\sigma^2}\right\},$$

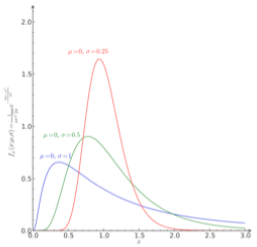
$$\langle R^r \rangle = m^r \exp\left(r^2\sigma^2/2\right) = \exp\left(r\mu + r^2\sigma^2/2\right)$$

$$\langle R \rangle = m \exp\left(\sigma^2/2\right)$$

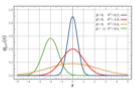
Mean

$$\sigma_g = \exp(\sigma) \quad x_g = \exp(m)$$

Geometric standard deviation and geometric mean (median)



Gaussian is centered at the Mean and is symmetric. For values that are positive (size) we need an asymmetric distribution function that has only values for greater than 1. In random processes we have a minimum size with high probability and diminishing probability for larger values.



http://www.eng.uc.edu/~gbeaucag/PDFPapers/ls5024%20japplcryst%20Beaucage%20PSD.pdf

http://en.wikipedia.org/wiki/Log-normal_distribution