071207 Final Morphology of Complex Materials

Ceramic and carbon aggregated materials display a hierarchical structure.

1) a) Describe three levels of structure for a ceramic aggregate such as fumed silica.
b) Primary particles are described by a distribution of sizes and perhaps shapes. What is the best distribution function to use to describe the distribution in sizes commonly seen in nanoparticles.
c) Give a function that describes this distribution.
d) Explain why particles tend to display this size distribution in the self-preserving limit of time.
e) Give an expression for the fifth moment of size from this distribution.

2) The average size of nanoparticles is often described by the Sauter mean diameter, d_p.
a) What moments of size does the Sauter mean diameter reflect?
b) How is the Sauter mean diameter obtained from the specific surface area measured in a gas absorption measurement?
c) How would the Sauter mean diameter be obtained from the geometric standard deviation and the geometric mean (from the distribution of question 1).
d) Why is the Sauter mean diameter a better description of the size of primary particles than the radius of gyration?
e) Describe 3 regimes of growth in nanoparticles in terms of the concentration, number and size of nanoparticles.

3) Aggregates provide access to most of the surface area of nanoparticles while allowing for dispersion.
a) Sketch the structure of an aggregate in three views: 1) the overall appearance; 2) the connectivity; and 3) the tortuosity.
b) Describe the parameters s, p and z in the context of question 3a.
c) Explain how the dimensions d_f, c and d_{min} relate to the aggregate structure.
d) Consider a 4 arm symmetric star aggregate and a cyclic aggregate. Give a values for p and s in terms of z for these two structures.
e) Explain how you would calculate the strength and drag coefficient for an aggregate using this model.

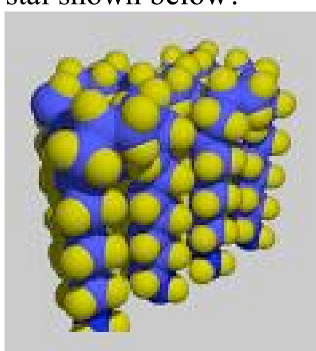
Final Quiz 2

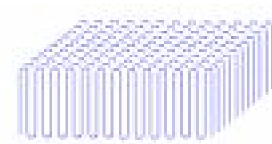
Quiz 1-2) Proteins are the seminal model for molecular hierarchy. The primary structure is a sequence of amino acids.

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?

Quiz 3-3) 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.

Quiz 4-3) 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.

Final Quiz 3

Quiz 5-1) 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?

Quiz 6-1) 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.

Quiz 6-3) 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 Quiz 1 071207 Final Morphology of Complex Materials

1) a) Primary particles: Aggregates: Agglomerates. Primary particles can not be easily broken apart and are typically 3d spherical or weakly asymmetric particles that can be individually identified. Aggregates are strongly bonded and usually open structures that display a mass fractal morphology. Aggregates typically form by diffusion limited growth. Agglomerates are weakly bound dense structures. Agglomerates typically grow by reaction limited growth. Agglomerates are typically composed of clusters of aggregates that are densely packed. Agglomerates are typically 3d objects.

b) Log-normal distribution

c)

Probability density function

The log-normal distribution has the probability density function

$$f(x;\mu,\sigma) = \frac{e^{-(\ln x-\mu)^2/(2\sigma^2)}}{x\sigma\sqrt{2\pi}}$$

for $x > 0$, where μ and σ are the mean and standard deviation of the variable's logarithm (by definition, the variable's logarithm is normally distributed).

d) Large particles move slowly, small particles move quickly and over long distances. Large particles provide a large surface area for impact. It is likely that small particles will impact large particles. The result is a large particle almost identical to the original and a dramatic loss in the number of small particles. The distribution narrows due to this process until a sharp cutoff at low size exists and a broad tail at high mass. This is the self-preserving limit and is close to a log-normal distribution in size.

e)

Moments

All moments exist and are given by:

$$\mu_k = e^{k\mu + k^2\sigma^2/2}.$$

k is the moment

2) a) The 3'rd divided by the 2'nd moments.

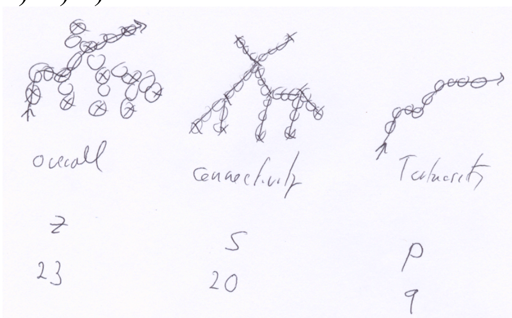
b) $6000/(S_v\rho)$

c) $\exp(\mu+5\sigma^2/2)$

d) R_g^2 reflects the 8'th by 6'th moment while the Sauter diameter reflects a lower order. R_g reflects only the largest particles for this reason.

e) Concentration increases creating supersaturation and homogeneous nucleation occurs. This is followed by a dropping concentration do to depletion and surface nucleation and finally by aggregation where the concentration is depeleted too low for surface nucleation.

3) a) b)



c) $p^c = z$; $z = (R/d_p)^{df}$; $s^{dmin} = z$

c = 1 for a linear object, dmin = 1 for a regular object

d) $p = z/2$ for both, $s = (z/2)^{1/dmin}$ for the cyclic and $s = 2\ (z/4)^{1/dmin}$ for the star.

e)

$$Modulus \sim \frac{kT}{M^{1/d_{min}}} \qquad \text{For large N} \qquad \frac{f_{agg}}{f_1} = cN^{1/c} \qquad \frac{D_{agg}}{D_1} = \frac{1}{c}N^{-1/c}$$