120302 Quiz 5 Morphology of Complex Materials

1) a) The density of a mass-fractal decreases with the size of the mass fractal. Calculate the mass density of a mass-fractal and show that it decreases with size. How does the mass density relate to c*? Explain how this makes sense for rods (d_f=1).

b) A crumpled aluminum foil and a titania aggregate can both have a mass fractal dimension of 2.3. Explain how this could be the case.

c) Heterogeneous catalyst supports are often composed of zirconia or titania mass-fractal aggregates. List the three levels of hierarchy for a mass-fractal aggregate and indicate how a structural description of each level of hierarchy would be important to a heterogeneous catalyst such as platinum quantum dots deposited on zirconia for oxidation of polyaromatic hydrocarbons and CO in engine exhaust.

d) The log-normal distribution is found to describe a wide range of nanomaterials including the primary particle, aggregate and agglomerate size for mass-fractals. Sketch the log-normal and Gaussian distributions (number versus size) and give a function for both of these distributions.

e) Explain why a log normal distribution is seen in flame growth nano-powders and in beach sand.

2) In addition to structural hierarchies seen in proteins and statistical hierarchies seen in synthetic polymer chains we described dynamic hierarchies seen in models for polymer relaxation in solution and in the melt. The dynamic and static hierarchies have some similarities and some differences.

a) Describe the Rouse hierarchy in terms of breaking down the dynamic response of a polymer chain into a hierarchical structure.

b) Describe the tube model and how the Rouse model is incorporated in this hierarchical model for dynamics in a polymer melt.

c) Describe hierarchical relaxations as envisioned by McLeish, Read and Larsen in their hierarchical dynamic model for branched polymer relaxations.

d) The viscosity of a polymer melt depends on the molecular weight of the polymer and on the rate of strain. Typically, polymers are power-law fluids showing shear thinning that follows a power-law decay of viscosity with shear rate (*a line in a log-log plot*) over a certain range determined by the molecular weight. At low shear rates we observe a plateau for Newtonian behavior where viscosity doesn't depend on shear rate. The Rouse model and the tube model predict different molecular weight dependencies for the relaxation time, τ. Explain how these molecular weight dependencies could explain the changes in viscosity versus rate of strain (hertz or inverse time) for different molecular weights shown in the plot.

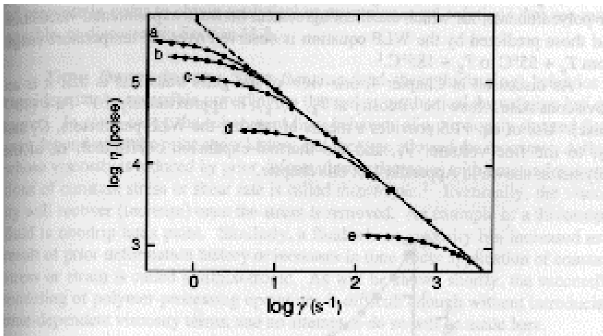


Figure 11.14. Effect of increasing molecular weight on the dependence of polymer viscosity on $\dot{\gamma}$ for polystyrene (M_c = 31,200) at 183°C. Molecular weights are (a) 242,000; (b) 217,000; (c) 179,000; (d) 117,000; and (e) 48,500. [Adapted from R. A. Stratton, *J. Colloid Interface Sci.*, 22, 517 (1966), with permission of the publisher.]

e) Explain four assumptions of the Rouse model and critique the validity of these assumptions for a polymer in solution and for a polymer in a melt.

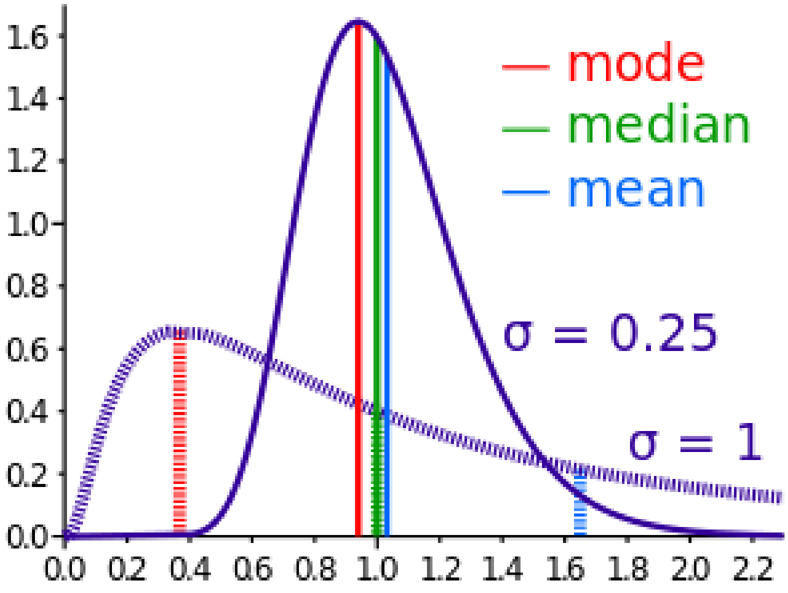
Answers: 120302 Quiz 5 Morphology of Complex Materials

1) a) $\rho = \frac{N}{V} = \frac{N}{R^3} = \frac{N}{N^{3/d_f}} = N^{1-3/d_f}$ This Is proportional to c*. For a rod the size, R is the length L which is proportional to N. As L increases the volume, L^3, increases much more rapidly than the mass so the density drops. This is a result of considering the rod in all possible orientations.

b) This can be the case since the two objects differ in their topology, which is not measured directly with the fractal dimension. The connectivity dimension for the crumpled sheet is c = 2 so the minimum dimension that measures the convolution of the structure is d_{min} = 1.15. For the titania aggregate the connectivity dimension is closer to 1 and the minimum dimension is larger since $d_f = c\, d_{min}$.

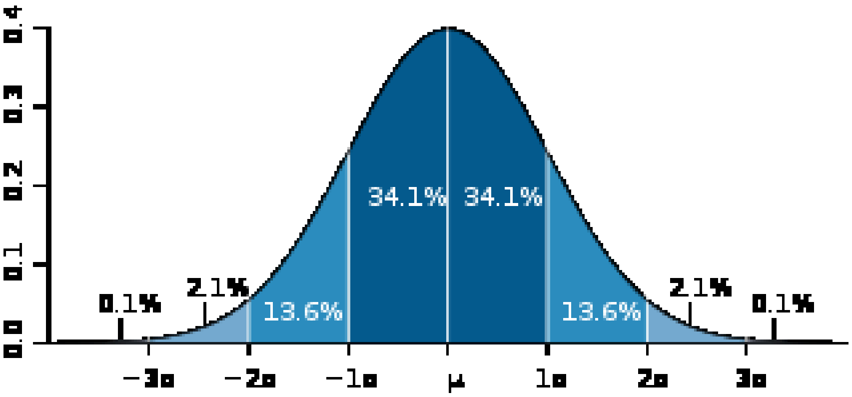
c) The three levels of structure are the primary particles, the aggregates and the agglomerates of aggregates. The primary particle determines the surface area and the S/V ratio for the catalyst. Generally activity is proportional to the surface to volume ratio. The aggregate structure ensures that there is access to the reactive surface in the catalytic converter and the agglomerate structure should be removed prior to use to ensure macroscopic access to the aggregates. This is done by making a slurry of the aggregates and coating a ceramic grid with the catalytic slurry containing the aggregates.

d)



Log normal distribution

$$p(R) = \frac{1}{R\sigma(2\pi)^{1/2}} \exp\left(\frac{-(\log R - \log m)^2}{2(\log \sigma_g)^2}\right)$$



Gaussian distribution

$$p(R) = \frac{1}{\sigma(2\pi)^{1/2}} \exp\left(\frac{-(R-\mu)^2}{2\sigma^2} \right)$$

e) In flame growth nano-powders there is a minimum size droplet that forms as a combustion product and through a nucleation process. This size grows by coalescence of droplets. A maximum in particle size occurs above the minimum size, it becomes less likely that very large particles form due to limitations on the amount of material and due to slow transport of large particles. So we see a sharp rise to the maximum and a gradual decay in the probability with size following the log normal distribution. It is a skewed distribution because the mechanisms for small and large particle formation differ about the most probable size.

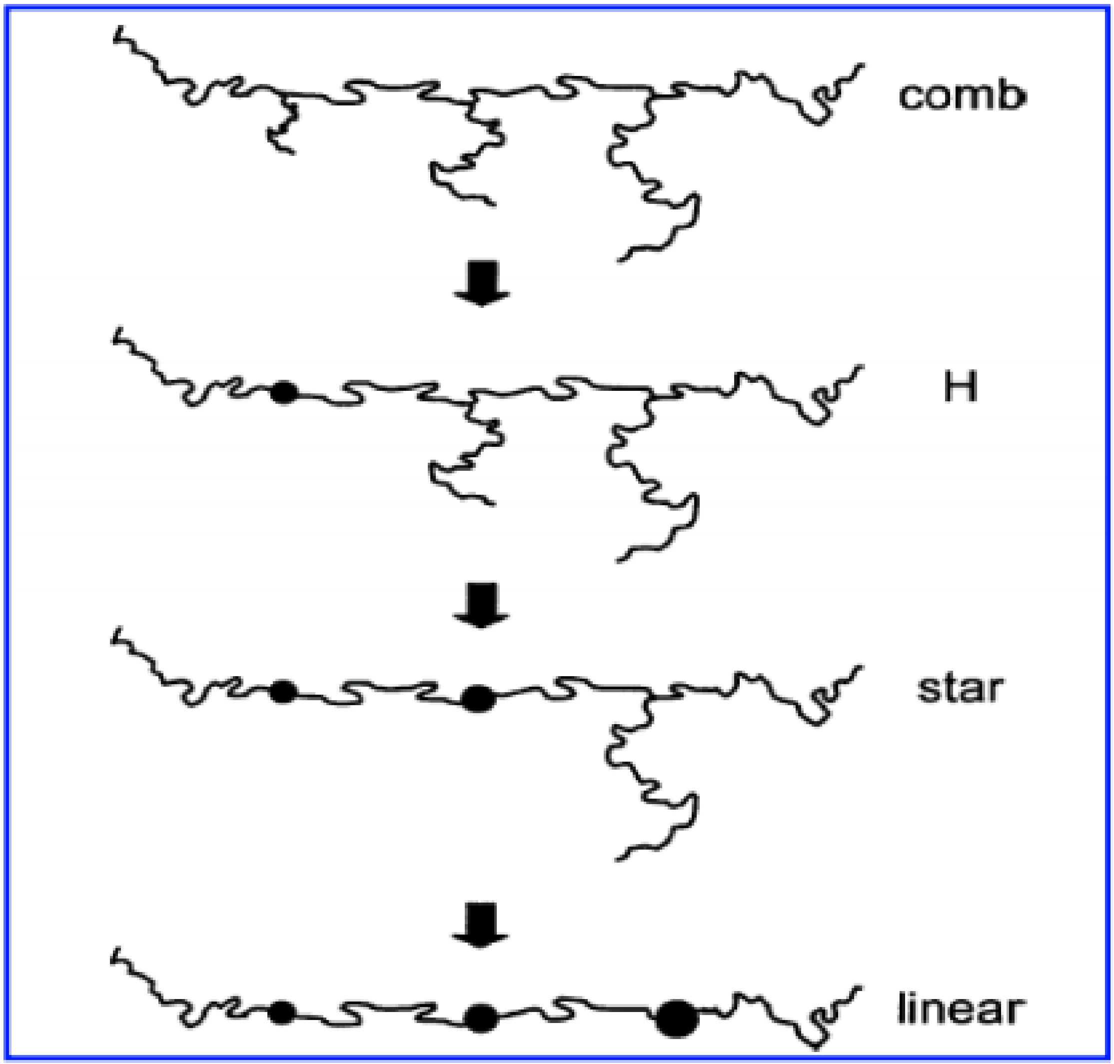
For beach sand we are looking at an attrition process. The largest particles are most easily broken since the lever arm for force applied to the particle is longer for larger particles. The required force to break very small particles is very large. For a given applied force there is a lower cutoff to the particle size. As particles are broken up they tend to accumulate a large population just above this minimum size. Some very large particles will exist even after an extended period of mastication. So the particle size distribution is skewed with a rapid rise at small sizes and a gradual decay to the largest particles which are few in number.

2) a) The chain is renormalized based on substructural Rouse units composed of n steps of length l_K. n must be large enough so that the spring constant for the subunit follows the idea chain model $k_{spr} = 3kT/(nl_K^2)$. Each subunit has a friction factor that follows Stokes Law, $\xi = 6\pi\eta_0 a$, where $a = \langle R^2 \rangle^{1/2} = n^{1/2} l_K$. These Rouse units are connected in a linear fashion to reflect the dynamic response of the chain. In order to solve the functions that result from this model the Rouse unit is allowed to become a differential element and a modal analysis is use that results in a series of modes of vibration for the chain. The 0'th order mode describes translation of the chain as a whole and can be used to calculate the diffusion coefficient. The first order mode dominates the internal vibrations of the chain.

b) The tube model assumes that there are two regimes of chain dynamics delineated by the packing distance or the tube diameter. The tube is constructed of other chains that are entangled with a target chain. The target chain follows a primitive path through a tube created by these other chains. For sizes larger than the tube the chain relaxes by Brownian motion along the length of the tube. For sizes smaller than the tube diameter the chain relaxes following the

Rouse model. The relaxation time for the chain is related to the time for the chain to reptate (move like a snake) through the tube to escape to a new tube.

c) The following graphic depicts the McLeish/Read/Larsen Hierarchical model. Short segments in a branched structure relax first (following the tube model). These become large beads with a corresponding friction factor on a linear chain. Gradually longer and longer branches relax in this way until finally the entire chain reptates out of the hierarchical tube.



d) The intersection point between a plateau viscosity at low shear rate and the power-law behavior at high shear rates has a characteristic rate of strain that changes with molecular weight. The inverse of this rate of strain is a type of relaxation time that could be modeled with the Rouse or tube models. For the Rouse model this relaxation time would increase with N so the intersection point in the plot would follow a 1/N dependence. For the tube model it would follow N^3 so the intersection point would follow a $1/N^3$ dependence.

e) The first assumption is that the Rouse subunits are Gaussian and have a spring constant associated with the ideal chain law (rubber elasticity). This is a poor assumption for chains in solution, for branched chains and for short Rouse units. At very short lengths the chains are linear due to chain persistence for example. At moderately low molecular weights there are not sufficient chain units to fully reflect a Gaussian distribution in distances.

The second assumption is that the Rouse subunits follow Stokes law for spheres with diameters that follow the Gaussian distribution. This is a poor assumption since the chains in solution have some degree of draining and in the melt a spherical assumption for drag coefficient is naïve, considering the complexities involved.

The third assumption is that the Rouse units can be represented as differential units (infinitesimally small) In order to solve the equations that result from the Rouse model it is necessary to assume that the Rouse units are differential elements. This is a poor assumption since once the Rouse units become small the first two assumptions fall apart. Also, the chain actually has a local structure that cannot be totally ignored.

The fourth assumption is that the organization of the Rouse units in space (that is that they follow a random walk) is not important to the dynamics so that the Rouse units can be connected in a straight line. This would seem to be a poor assumption. For example, a straight bar does not vibrate in the same way that a bent bar does. The bent bar has a number of vibrations, *such as a scissor vibration for an L shape*, that do not exist in a straight bar. A convoluted polymer chain should have many different vibrations that do not exist in the Rouse model structure. These vibrations may contribute such a small amount to the total vibrational energy of the chain that they do not matter.

There may be other assumptions that you can come up with.

For the most part the Rouse model seems crude.