Final Exam Polymer Properties, 6/5/2012

 The following scattering function has been proposed by Benoit [H. Benoit, *J. Polym. Sci.*, 1953, XI, 507] for scattering from Gaussian star polymers (f is the number of arms, b is the segment length, n is the number of segments per arm). (Star polymers are polymers with arms emanating from a center point.)

$$S_{Star}(q,b,n,f) = \frac{P_{11}}{f} + \frac{f-1}{f}P_{12}$$

$$P_{11}(q,b,n,f) = \frac{2}{(xn)^2} (e^{-xn} - 1 + xn)$$

$$P_{12}(q,b,n,f) = \frac{(1 - e^{-xn})^2}{(xn)^2}$$

$$x = \frac{(qb)^2}{6}$$

a) Show that the first term (P₁₁) displays Gaussian scaling at high-q.

b) Obtain the radius of gyration for the first term by extrapolating the first term to low-q and comparing with Guinier's law.

c) Explain what part of the star structure you think the first term describes.

d) Show that the second term is non-fractal in nature (fractal structures display a power-law decay between -1 and -3).

e) Do you think that this function could describe a star polymer with Gaussian arms? Explain your answer.

2) The Einstein equation for the viscosity of a dilute suspension of spherical particles is given by where η is the solution viscosity, η_0 is the solvent viscosity and ϕ is the concentration of spherical particles.

a) What is the intrinsic viscosity for this suspension of spherical particles? (Include the units for the intrinsic viscosity.)

b) Give an expression for the molecular weight dependence of intrinsic viscosity and show that the molecular weight dependence you showed in part "a" agrees with your expression. (Remember that volume $\sim R^3$ and $R \sim M^{1/df}$.)

c) DNA can form a helical conformation where the DNA particles are rod-like. DNA can also exist as a flexible chain in a good solvent (expanded coil). For a series of DNA of different molar mass how could you distinguish rods from coils using the intrinsic viscosity? (Use your answer to part "b".)

d) Polymer chains have a size of from 0.01 micron to 0.1 micron. In some cases dirt, or catalyst residue have a similar size so that it is impossible to filter these impurities from the polymer. How could you distinguish the presence of dirt in an intrinsic viscosity measurement?

e) What are the units for intrinsic viscosity?

3) In class we considered long range interactions by first discussing excluded volume. a) Consider the interaction of two hard core spheres. What is the volume excluded from one sphere by the other sphere?

b) If the two spheres were confined to a space of radius R what is the probability that the two spheres do not overlap?

c) If there were N spheres in the same volume, what is the probability that no two spheres overlap considering only binary interactions?

d) Use $exp(-x) \sim (1-x)$ (and ln(1-x) = -x) for small x to write an exponential probability for exclusion of spheres from each other.

e) Explain how this calculation might be complicated by considering elliptical particles rather than spheres. For elliptical particles do you expect a larger or smaller excluded volume compared to spheres for the same particle volume?

- 4) In class it was mentioned that polymers are the only class of materials that are defined by their dynamic behavior. For example, polymeric fluids display normal stresses (stress at a right angle to the applied shear stress) in shear flow that cause asymmetry of bubbles.
 - a) Sketch the shape of a bubble in a Newtonian fluid (like cooling oil) and a bubble in a polymeric fluid (like shampoo).
 - b) In general terms, explain why the polymeric bubble is asymmetric.
 - c) The following plot of log viscosity versus log rate of strain shows a transition from Newtonian behavior to a power-law decay. Explain how a time constant for the polymer melt can be obtained from this plot.



- d) How could the time constant obtained in part c) pertain to the shape of droplets described in part a). What parts of the plot pertain to each of the two droplets you drew in part a).
- e) Do you think that the polymer chains at the high strain rate end of the plot in question c) are Gaussian? Explain your answer.

- 5) A Gaussian chain is two dimensional, as is a disk.
 - a) Derive a function that shows that a Gaussian chain is 2-dimensional.
 - b) How can a scaling dimension be used to distinguish between a disk and a Gaussian chain?
 - c) Give an expression for the density of a polymer chain as a function of the mass of the chain, N.
 - d) The radius of gyration is one measure of the size of a polymer chain. R_g is

$$R_g^2 = \frac{\left\langle R^8 \right\rangle}{\left\langle R^6 \right\rangle}$$

given by $(\Lambda / . How can the Gaussian distribution be used to calculate the moments in this equation?$

- e) Sketch a plot of P_G(R), RP_G(R), R²P_G(R), R⁴P_G(R). What happens to the peak in the plot as n increases in the term RⁿP_G(R). (P_G(R) is the Gaussian Distribution Function.)
- 6) The Zimm equation (B. H. Zimm, *J. Chem. Phys.*, **16**, 1099 (1948)) is an approximation to describe the scattering from a polymer in solution and results in the following plot, called a Zimm Plot,



scattering intensity.

a) Give the Zimm equation.

b) Explain the origin of the two terms involved in the Zimm Equation.

c) Why is the Zimm equation an approximation?

d) Give the RPA equation for a polymer blend and explain how a Zimm-like equation can be obtained from the RPA equation.

e) Explain what a composition fluctuation is and how it can be described by a susceptibility and a field.