Final Polymer Properties 100315

1) The Gaussian function describes the distribution of chain end-to-end distances for random walks.
   a) Sketch a plot of the 1d Gaussian function.
   b) Give the Gaussian function.
   c) Indicate what part of the Gaussian function indicates that it is symmetric and what part indicates that it is a monotonically decaying function.
   d) How can the Gaussian function be used to obtain the free energy for an isolated polymer chain with no enthalpic interactions? How is this free energy changed when excluded volume (enthalpy of interaction) is included?
   e) An average projection of 3-d random walks in 1d results in the same value for σ^2 as the full 3d analysis, that is $\sigma^2 = zl^2$. In a 3-d random walk on a Cartesian lattice only 1/3 of the random walk steps occur in any one direction. Use the proposition that random placement of the no-step option does not alter a random walk to explain this.

2) Paul Flory made a distinction between non-ideality of polymer chains associated with chain stiffness and non-ideality associated with exclude volume. He used the characteristic ratio and the coil expansion factor to distinguish between these two features.
   a) Define the characteristic ratio and explain how it can describe short-range interactions.
   b) Does your expression for the characteristic ratio depend on the molecular weight?
   c) Define the persistence length and explain how it is related to short-range interactions.
   d) Define the coil expansion factor and explain how it is related to long-range interactions.
   e) Does the coil expansion factor change with molecular weight? Do you expect long-range interactions to have a larger effect at higher molecular weights? (You may want to use results from your computer programs if you wrote a program for self-avoiding walks, or to calculate the molecular weight dependence of the coil expansion factor.)

3) Rheologists are interested in a length parameter called the packing length that is close to the persistence length in size.
   a) Describe what the plateau modulus is and how it relates to the packing length.
   b) Explain how the packing length can be obtained from the occupied volume and the radius of gyration for a coil.
   c) Does the packing length depend on the molecular weight? Demonstrate the molecular weight dependence through a calculation.
   d) If a polymer is dissolved in a solvent would you expect the packing length to change? Does the persistence length change with dilution?
   e) Why are two independent primary size-scales, persistence and packing length, needed to describe a polymer coil?

4) The Einstein equation for viscosity reflects the volumetric displacement of a fluid by colloidal particles.
   a) Give the Einstein relationship and explain the conditions under which it should apply.
   b) How would the intrinsic viscosity, $[\eta]$, scale with molar mass for a polymer coil?

c) How would the intrinsic viscosity, [η], scale with molar mass of platelets for blood (a colloidal suspension of disk particles)?
d) Write the governing equation for a Newtonian fluid.
e) Sketch log(viscosity) versus log(rate of strain) for a polymer melt and for the equation given in d). Why do these two functions differ?

5) Macromolecules at thermal equilibrium can accommodate changes in temperature, concentration and applied force through the development of an internal scaling transition. This scaling transition can be modeled in terms of blobs.
a) Explain how a Gaussian chain responds to the application of a tensile force at the chain ends. Give an expression for the blob size. How does temperature affect the tensile blob size?
b) Below the theta temperature a polymer chain in dilute solution displays coil collapse. Explain how a blob model can be used to describe this collapse. Give an equation for the blob size. Explain the terms in this equation.
c) Above the theta temperature a polymer coil expands. Explain how a blob model can be used to describe this expansion. Given an equation for the blob size. How does this description improve on the Fory-Krigbaum expression for the coil size?
d) A polymer in a good solvent and under dilute conditions contracts to the theta state as concentration is increased. Explain how a blob model can be used to describe this contraction. Given an equation for the blob size including the concentration dependence. What chain scaling occurs in a polymer melt?
e) Explain the terms screening and mean field.

Extra Credit)
a) Give an expression for the spring constant for a chain that has developed tensile blobs.
b) Describe the Rouse chain for polymer dynamics. How does this compare to the blob models?
c) The interaction parameter is defined as having a functionality of B/kT. Experimentally the interaction parameter is often observed to display the behavior A + B/T. What is a possible source for the term A? (If A is positive and larger than the entropy term in the chain free energy and B is negative would coil collapse occur on cooling?)