Final Exam Polymer Properties 2005

Question 1

1) The Rouse model is based on a Gaussian assumption and on the free-draining assumption both for the Rouse unit; and also for the total chain (the collection of Rouse units).

a) How are these assumptions evidenced in the expression for the size of a Rouse unit, a_R? The number of Rouse units, N_R is given by $(R/a_R)^2$. Is this consistent with these assumptions? Explain.

b) How are these assumptions reflected in the necessary requirement that (ξ_R/a_R^2) be a constant ratio.

c) Write the Langevin equation for a structure with a viscous element and a Hookean spring that is subject to a random thermal velocity with no inertial term. Write an integral expression for the response in terms of the friction factor and spring constant.

d) Explain what a *memory function* is and how a memory function is involved in the expression for question "c".

e) Sketch the position x(t) as a function of time from part "c" and explain how the time autocorrelation function can be calculated from this sketch and sketch the expected behavior of the time correlation function for the equation of part "c".

Question 2 (Quiz 3)

Polymer chains are well described on a local scale by the rotational isomeric state model and through computer simulations and calculations based on this model. For our purposes, this results in a base size of physical significance with an associated number of base units (Kuhn units). The polymer chain develops an overall shape and size through dynamic thermal equilibration with its environment. A fundamental tenet of modern polymer science is that the size (relative to the size of the Kuhn unit) and shape of such a polymer "coil" is independent of the details of the Kuhn unit. Coils can be classified as random (Brownian), self-avoiding (good solvent), or collapsed. Determination of the size and shape of dynamic polymer coils is a statistical problem since the "coil" is a disordered structure that fluctuates in time and space.

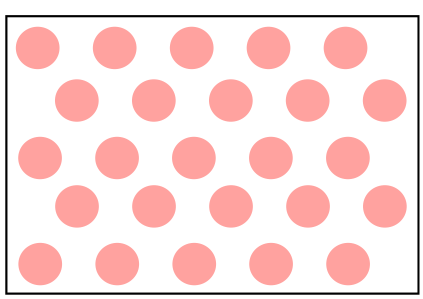
a) The coil size can be measured in a dynamic measurement through the hydrodynamic radius, R_H. Define R_H in terms of the friction factor, ξ, and solvent viscosity, η_0. Explain how the friction factor is generally related to the diffusion coefficient, D.

b) Give Fick's first and second laws. Design a hypothetical experiment using one of these laws to measure R_H from a polymer solution.

c) Static scattering measurements and computer simulations generally yield the radius of gyration, R_g, as a measure of the coil size. Give the two expressions for R_g described in class and show that the two expressions are identical.

d) For a rod with an aspect ratio (L/D) of 100 and a radius of 1 nm the measured hydrodynamic radius is about 1 nm. Calculate the radius of gyration for this rod by deriving an expression for R_g of a rod. Use your answer to judge the relative usefulness of R_g and R_H in describing chain aggregates that display large aspect ratios. (The derived expression should be $R_g^2 = \frac{R^2}{2} + \frac{(L/2)^2}{3}$. This can be obtained by integration over a differential volume element dV ~ rdrdl where the distance form R_G is given by $R^2 = (r^2 + l^2)$. You will need to integrate form r = 0 to R and from l = 0 to L/2 since R_G is at the center of the rod.)

e) The shape of a polymer coil is often described in scattering and in simulations by the pairwise correlation function g(r) or p(r). Using the rod throwing approach, sketch g(r) versus r for the following 2d structure and explain how g(r) was obtained. How does this correlation function differ from what you would expect for a disordered material such as a polymer coil?



Question 3

The concept of a blob is fundamental to modern polymer science.

a) Explain the difference between a concentration, thermal, tensile blob and a persistence length.
(Include a sketch of log I versus log q for neutron scattering)

b) Explain the similarities between these 4 types of scaling transition.

c) How do blobs compare with Rouse units?
(Include a sketch of log I versus log q from neutron scattering)

d) Derive an expression for the tensile blob size using the Flory-Krigbaum expression for the free energy of an isolated polymer coil.

e) Compare this with the Langevin equation for the Rouse unit given in question "1". Explain how the dynamic model differs from the static blob model.