## Quiz 9 Take Home Polymer Properties October 25, 2013

1) In class the Debye scattering function for a Gaussian polymer was discussed.

$$g(q)_{Gaussian} = \frac{2}{Q^2} [Q - 1 + \exp(-Q)]$$

where  $Q = q^2 N b^2 / 6 = q^2 R_g^2$ 

This function is **not** calculated by the Fourier transform of a correlation function. Rather, Debye considered that the only conditions for scattering occurred when the scattering vector followed the Gaussian scaling law  $r = nl^2$ . This greatly simplified a direct calculation of the scattered intensity.

- a) What is a Fourier transform? Give a mathematical expression involving an integral and explain in words.
- b) Normally we consider that g(q) is the Fourier transform of p(r). How did Debye calculate g(q) for the discrete steps of a polymer chain?
- c) Is it possible to perform a reverse Fourier transform of the Debye scattering function for a polymer?
- d) The Ornstein-Zernike function is often used as a substitute for the Debye function. Criticize this use. (There are at least two problems.)
- e) The correlation functions for the OZ function, Debeye-Bueche function, Teubner-Strey Function and the Sinha Function involve a "cutoff function",  $exp(-r/\xi)$ . This function terminates the correlation function at large sizes. Explain why this might be necessary for fractal objects (Sinha Function) and criticize this term. Why isn't  $exp((-r^2/\xi^2))$  used for this cutoff function?
- 2) The hydrodynamic radius can be measured using viscosity and using dynamic light scattering.

a) Stokes law is used to define the hydrodynamic radius as the radius of an equivalent sphere with the same drag coefficient as the object. Give Stokes Law and explain why the drag coefficient depends on R rather than  $R^2$ . (Why might you expect an  $R^2$  dependence?)

b) The intrinsic viscosity is another measure of the hydrodynamic radius. Show how you can obtain the hydrodynamic radius from the intrinsic viscosity. Knowing the intrinsic viscosity what would you need to know to calculate the friction factor?

c) Kirkwood proposed a method to calculate the average hydrodynamic radius for a polymer coil when he calculated an average diffusion constant in <u>J. G. Kirkwood J.</u> <u>Polym. Sci. 12(1) 1 (1954)</u>. Give an equation to calculate the hydrodynamic radius, explain its origin and compare it with the calculation for the radius of gyration. From these calculations should  $R_g$  or  $R_h$  be larger?

d) Explain what is the Martin equation and why it might be better than the standard definition of intrinsic viscosity. (Show a sketch of reduced viscosity versus concentration.)

e) How is intrinsic viscosity effected by molecular weight, solvent quality and fractal dimension?

## ANSWERS: Quiz 9 Polymer Properties October 25, 2013

1) a)  $I(q) = \int_{-\infty}^{\infty} p(r) \exp(-iq \cdot r) dr$  the exponential term is a representation of a sine wave with

wavelength  $q \cdot r$ . The integral sums a series of these sine waves of amplitude p(r). For a single value of q, this sum results in a value of I at q.

b) Debye substituted the exponential in answer "a" with

$$g(q) = \int drg(r) \exp(iq \cdot r) = \frac{1}{2N^2} \sum_{n=1}^{N} \sum_{m=1}^{N} \left\langle \exp(iq \cdot (R_m - R_n)) \right\rangle$$

since p(r) only has a value where r equals  $(R_m - R_n)$  and the integral is made up of discrete steps on the chain so that the integral can be replaced with a double sum.

c) The Debye scattering function for a Gaussian polymer does not have a discrete Fourier transform.

d) The Fourier transform of the OZ function is not symmetric so it is not an appropriate function for randomly arranged structures such as a polymer coil. Also, the limits of the OZ function do not match the high and low-q limits of the Debye polymer scattering function.

e) For a mass-fractal the scattering law,  $I(q) \sim q^{-df}$  is appropriate for sizes smaller than the overall structural size. The Fourier transform of this power law function leads to  $p(r) \sim r^{(3-df)}$ . This function must end at the overall size of the fractal object. We can describe this overall size by an arbitrary size called a "correlation length". The correlation length has something to do with the size of the fractal object. At this length scale fractal scaling ends. Then one might expect the correlation function to end. One function that can make the correlation function go to 0 at a certain size is an exponential decay  $exp(-r/\xi)$ .  $p(r) = r^{(3-df)} exp(-r/\xi)$  has an exact Fourier transform that is rather complex, the Sinha function. The exponential cutoff function is asymettric so it is not a valid correlation function  $p(r) = r^{(3-df)} exp(-r^2/\xi^2)$  does not have a Fourier transform so it does not lead to a simple scattering function.

2) a) The friction factor is given by  $\zeta = 6\pi\eta_0 R_H$ . One might expect the friction factor to depend on  $R_H^2$  since you would expect the drag coefficient to depend on the cross sectional profile of the object. However, a unit analysis shows that the power of  $R_H$  must be 1. The friction factor has units of F/velocity = F time/L. The viscosity has units of Stress/strain rate = Force time/L<sup>2</sup>. So  $R_H$  must be to the first power.

b) The intrinsic viscosity is the inverse of the overlap concentration or the specific volume for the polymer coil,  $[\eta] \sim 1/c^* = 4/3 \pi R_H^3/N$ . The friction factor could be obtained from  $\zeta = 9 \eta_0 [\eta] N/2$ .

$$\frac{1}{R_{H}} = \frac{1}{2N^{2}} \sum_{i=1}^{N} \sum_{j=1}^{N} \left\langle \frac{1}{\left| r_{i} - r_{j} \right|} \right\rangle$$
  
c)  
$$R_{g}^{2} = \frac{1}{N} \sum_{n=1}^{N} \left\langle \left( R_{n} - \frac{1}{N} \sum_{m=1}^{N} R_{m} \right)^{2} \right\rangle = \frac{1}{N} \sum_{n=1}^{N} \left\langle \frac{1}{2N} \sum_{m=1}^{N} \left( R_{n} - R_{m} \right)^{2} \right\rangle = \frac{1}{2N^{2}} \sum_{n=1}^{N} \sum_{m=1}^{N} \left\langle \left( R_{n} - R_{m} \right)^{2} \right\rangle$$

The origin of the  $R_H$  equation is ad hoc, Krigbaum just proposes it in his paper with no real justification.  $R_H$  is a first moment and is a harmonic average (inverse sum). The lower the order of the moment the lower the value and harmonic averages are always much smaller than the

arithmetic mean (normal average you are use to). The radius of gyration reflects the second order moment of sizes so it is larger than the first moment.

This is true for fractal objects. If the coil collapses to a dense spherical structure then the hydrodynamic radius is the actual radius of the sphere while the radius of gyration is  $R\sqrt{(3/5)}$ , so for the collapsed coil  $R_g$  is smaller than  $R_H$ . d)

$$\eta_r = \frac{\eta}{\eta_0} = 1 + c[\eta] \exp(K_M c[\eta])$$

This arises from the power series

 $\eta = \eta_0 \left( 1 + c[\eta] + k_1 c^2 [\eta]^2 + k_2 c^3 [\eta]^3 + \dots + k_{n-1} c^n [\eta]^n \right)$ 

and assuming  $k_1 = k_2 = k_3 = ... = K_M$  Then using the expansion of the exponential.



Martin equation is dashed line, Huggins equation is straight line. e)  $[\eta] \sim 1/c^* = 4/3 \pi R_H^3/N \sim N^{3/df-1} = N^a$ .

for good solvent a should equal 0.8 for theta solvent a should equal 0.5 for a collapsed coil a = 0 it doesn't depend on molecular weight and for an extended rod (polyelectrolyte) a could equal a maximum of 2.