040416 Quiz 3 Polymer Properties

An isolated polymer coil is a physical object and should display a size. However, since polymer coils display a mass dimension lower than 3, it is difficult to quantify this size. We mentioned two approaches in class to describe the size of an isolated coil, the radius of gyration and the hydrodynamic radius. The radius of gyration can be calculated for a simple object by a normalized integration of the distribution of mass in 3d space.

a) A sphere has a uniform distribution of mass about the center of the sphere so the squared radius of gyration is given by the normalized integral of r^2. Show that for a sphere $R_g^2 = 3/5\ R^2$. (Hint, for polydisperse spheres R_g^2 reflects the ratio of the 5'th to the third moment of radius.)

b) What is the hydrodynamic radius for a sphere. (Hint, Consider the assumptions used for Stokes law.) Explain your answer.

c) From a) and b) the relationship between R_g and R_H for a sphere can be obtained. For a Gaussian coil $6R_g^2 = nl^2$. Would you expect the hydrodynamic radius to be larger or smaller than R_g, why? How does this compare with solid spheres?

d) Hydrodynamic radius can be measured using dynamic light scattering. Explain how this measurement could give the size of suspended particles undergoing Brownian motion.

e) Why might a plot of $1/\tau$ be proportional to q^2 in a DLS measurement? (Define q in terms of size and use the relationship between distance traveled (size) and time for Brownian motion.)

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a) $$R_g^2 = \frac{\int_0^R r^2 dV}{\int_0^R dV} = \frac{\int_0^R r^2 4\pi r^2 dr}{\int_0^R 4\pi r^2 dr} = \frac{3R^5}{5R^3} = \frac{3}{5}R^2$$

b) For a sphere $R_H = R$. Stokes law states that the friction facctor is given by $\xi = 6\pi R_H \eta_0$, where R_H is an equivalent radius for a sphere and η_0 is the solvent viscosity. The equivalent spherical radius for a sphere is R.

c) For a sphere $R_g = R_H/1.3$ so the radius of gyration is smaller than the hydrodynamic radius. For a polymer coil R_H is smaller than R_g since the coil is not a solid sphere and the equivalent spherical diameter, in terms of hydrodynamics, involves some penetration of the coil by the solvent. This is related to the scaling of coil density with size, $\rho \sim R^{df-3}$, where the coil appears less dense at larger sizes so that solvent can penetrate the lower density size-scales (large size).

d) Light scattered from a polymer solution or a colloidal suspension flickers since the particles under go Brownian motion. The flickering of light is directly related to the diffusion coefficient through the pairwise time correlation function which is a measure of the correlation of the flickers in time. The correlation function exponentially decays in time following,

$$\frac{\langle I(t) I(t+\Delta t)\rangle}{\langle I(t) I(t)\rangle} = \exp\left(-Dq^2 \Delta t\right)$$

Following the fluctuation dissipation thereom of Einstein,

$$D = \frac{kT}{4\pi R_H \eta_0}$$

so R_H can be measured from the decay of correlations in flickering of light in a DLS measurement.

e) Bragg's law can be written, $d = 2\pi/q$, so q is inversely related to size or distance. For Brownian motion the average distance traveled is proportional to the square root of time. For Brownian motion we then expect that,

$$q \sim \frac{1}{R} \sim \frac{1}{t^{1/2}} \sim \frac{1}{\tau^{1/2}}$$