Polymer Properties Quiz 3 080130

The characteristic ratio, C_n, is the ratio of observed end-to-end distance, and the end-to-end distance of a freely jointed chain composed of n bonds of step length l_{chem},

$$C_n = \frac{\langle r^2 \rangle_0}{n_{chem} l_{chem}^2} = \frac{l_{\text{stat. seg. length}}^2}{l_{chem}^2}$$

The extrapolation of this value to infinite molecular weight is called C_∞.

The coil expansion factor, α, is defined as the square root of the ratio of the coil end-to-end distance to that of the coil in a Gaussian state (in the melt),

$$\alpha^2 = \frac{\langle r^2 \rangle_{Experimental}}{\langle r^2 \rangle_{GaussianState}}$$

α varies with the temperature for a polymer in solution.

1) a) In class we considered the simplest case for short range interactions (SRI) where the chain is prevented from back-tracking. Explain how this SRI might effect C_n as well as α.

b) The derivation for back-tracking relied on conversion of an infinite power series, $\sum_{\alpha=0}^{\infty} x^\alpha = \frac{1}{1-x}$ for -1<x<1. Show that this equality is true by using a recursive relationship (that is by defining the function in terms of itself, $\sum_{\alpha=0}^{\infty} x^\alpha = 1 + x\sum_{\alpha=0}^{\infty} x^\alpha$).

c) The derivation in class resulted in a simple function for the dependence of Kuhn length on coordination number, z. Give this relationship, sketch the dependence on z by drawing a graph of Kuhn length versus z and explain why this dependence makes sense.

2) One technique to measure the hydrodynamic size of a polymer or colloid involves determination of the intrinsic viscosity, [η].

a) Describe how the shear viscosity can be obtained from the force applied to and the velocity of a fluid. (A sketch is OK to describe this.)

b) Explain why the intrinsic viscosity represents a first order approximation (associated with dilute conditions).

c) Explain the dependence of intrinsic viscosity on molecular weight and hydrodynamic radius for a sphere, rod and Gaussian coil.

3) The hydrodynamic size can also be determined by dynamic light scattering (DLS) or photon correlation spectroscopy.

a) Describe the DLS instrument in simple terms, that is, what is the raw signal from the instrument, from what does it arise and how is it interpreted.

b) The Stokes-Einstein equation (SE) is used to relate thermal fluctuations associated with diffusion to molecular mobility through the friction factor. Give the SE relationship for the diffusion coefficient, used in DLS, and explain in your own terms what this expression means using the words: *Fluctuation, Dissipation and Brownian*.

c) Would you expect the Stokes-Einstein expression to yield an accurate value for the hydrodynamic radius of red blood cells? Explain your answer including the assumptions involved in the Stokes-Einstein equation.

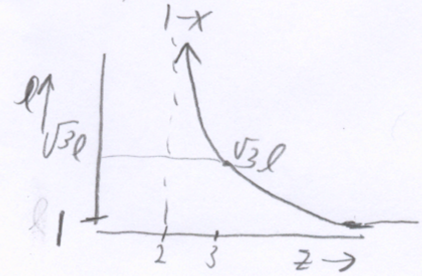
1) "C_n" is intended to reflect SRI while "α" is intended to reflect LRI. Both were developed by Flory in the late 1950's to early 1960's. Then we expect that SRI will change C_n & C_∞ but will have no affect on α. This is because changes in l_K (Kuhn length) already affect $\langle r^2 \rangle_{Gaussian}$. There is little temperature dependence to l_K. On the other hand, C_n is a direct measure of the consequences of SRI and changes in l_K due to RISM & bond angle restrictions and the like.

b) $$\sum_0^\infty x \equiv A$$

$$A = 1 + xA \quad \text{so} \quad 1 = \frac{1}{A} + x \quad \text{or} \quad \frac{1}{A} = 1 - x$$

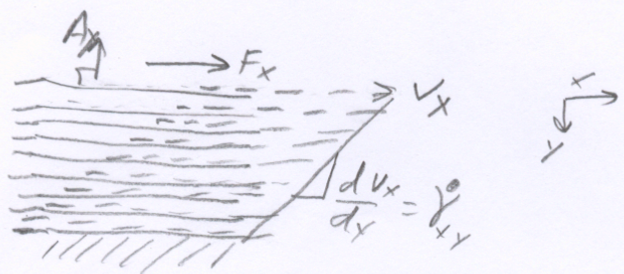
$$\therefore A = \frac{1}{1-x}$$

c) $$\left(\frac{z}{z-2}\right)^{1/2} l = l_{eff}$$



As z becomes larger the fraction of choices that are excluded become smaller so the attrition left is smaller. With only 2 choices the walk is a ballistic walk (like a bullet) and the persistence is infinite (straight line).

2) a)



$$\tau_{xy} = \frac{dF_x}{dA_y} = \eta\, \dot{\gamma}_{xy}$$

b)

for dilute

$$\eta_{solution} = \underbrace{\eta_0}_{\text{solvent}}\left(\overset{A_1}{1} + \overset{A_2}{[\eta]}\underbrace{c}_{\text{first power of } c} + A_3 \overset{0}{\cancel{c^2}} + A_4 \overset{0}{\cancel{c^3}} \ldots\right)$$

For dilute conditions higher orders in c go to 0. It is first order because c is to the power "1".

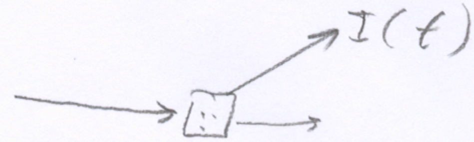
c)

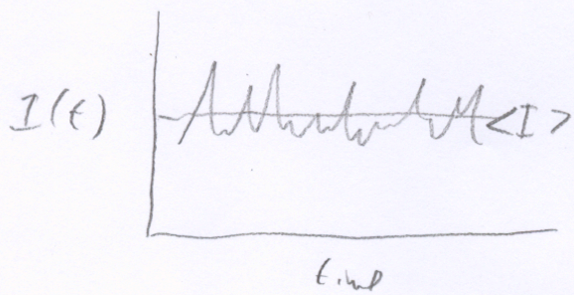
$$[\eta] = \frac{R_H^3}{\underset{\nwarrow \text{Mass}}{Z}}$$ using a fractal law $R^{d_f} \sim Z$

$$[\eta] = R_H^{3-d_f} = Z^{3/d_f - 1}$$

Object	d_f	$[\eta]$ $R_H^{3-d_f}$	$z^{3/d_f - 1}$
sphere	3	$R^0 = 1$	$z^0 = 1$
rod	1	R_H^2	z^2
coil	2	R_H^1	$z^{0.5}$

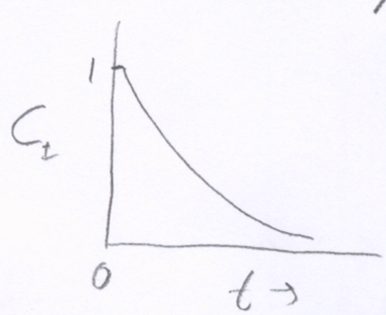
3) a)





Fluctuations due to Brownian motion of chains

$$C_t = \langle I(t)\, I(t+\tau) \rangle = \exp\left(-2 D q^2 t\right)$$



$$D = \frac{kT}{6\pi R_H \eta_s}$$

b) $D = \dfrac{kT}{6\pi R_H \eta_s}$

Brownian motion of polymer chains governed by kT & D; is the mechanism for dissipation of fluctuations associated with the friction factor $f = 6\pi \eta_0 R_H = (F/v)$.

c) Stokes-Einstein assumes spherical particles
& RBC's are disk shaped, however,
an "equivalent spherical radius" is possible
for a disk so it is possible to measure
R_H.