081117 Quiz 7 Morphology of Complex Materials

1) The concentration blob requires calculation of the overlap concentration, c*.
   a) What is the overlap concentration for a solution of rods as a function of the rod mass n?
   b) How would you expect the concentration blob size, ξ_c, to vary with concentration for rods? (Do the same calculation we did in class but for $d_f = 1$ rather than 5/3.)
   c) Is the dependence of blob size, ξ_c, on concentration stronger or weaker for rods compared to SAW coils? Explain why this is the case from a physical perspective.
   d) Is c* a smaller or a larger number for rods compared to SAW coils of the same n? Explain.
   e) Sketch a plot of log I (log of scattered intensity) versus log q (log of the scattering vector) for a collection of rods at $c \geq c^*$ in the semi-dilute regime and compare this with the plot for SAW coils.

2) Kuhn proposed that the dynamics of a polymer coil could be explained with the dumbbell model composed of a spring and balls with a friction factor ζ.
   a) What is the spring constant for a Gaussian polymer coil in terms of n?
   b) What is the friction factor for a polymer coil using Stokes Law in terms of n for a Gaussian coil?
   c) Write an expression for the time constant for the dumbbell model in terms of n based on your answers to a and b.
   d) If the friction factor obeys Stokes law can the viscosity scaling in n seen in polymers be obtained?
   e) If the friction factor, ζ, scales with n, $\zeta \sim n$, how does the dumbbell model differ from the lowest order Rouse relaxation mode?

3) Rouse theory was derived to describe polymer dynamics. Rouse divided the polymer chain into subunits.
   a) How does a Rouse unit differ from a tensile blob?
   b) Write a force balance for a Rouse unit ℓ.
   c) What assumption does your equation in question b make concerning the distance over which dynamic units are coupled along the chain?
   d) The Rouse approach leads to an expression for the relaxation time spectrum for a polymer,

$$\tau = \frac{\varsigma_R}{4b_R \sin^2(\delta/2)} \qquad (1)$$

   How can a cyclic assumption yield discrete values for δ and τ?

   e) Show that $\left(\frac{\varsigma_R}{a_R^2}\right)$ must be a constant for Rouse theory where a_R is the size of a Rouse unit. Use the m = 1 mode; $\delta_m = \frac{2\pi m}{(N_R - 1)}$; Solve (1) above for τ.

1) a) $c^* = \frac{n}{R^3} = k n^{-2}$

$R \sim n$ for a rod

b)

$$\xi_c = R_0 \left(\frac{c}{c^*}\right)^p \sim n^0$$

$$n \, n^{2p} \sim n^0 \quad \text{so} \quad 2p+1 = 0$$

$$p = -\frac{1}{2}$$

$$\xi_c \sim R_0 \left(\frac{c}{c^*}\right)^{-1/2} \text{ for rods}$$

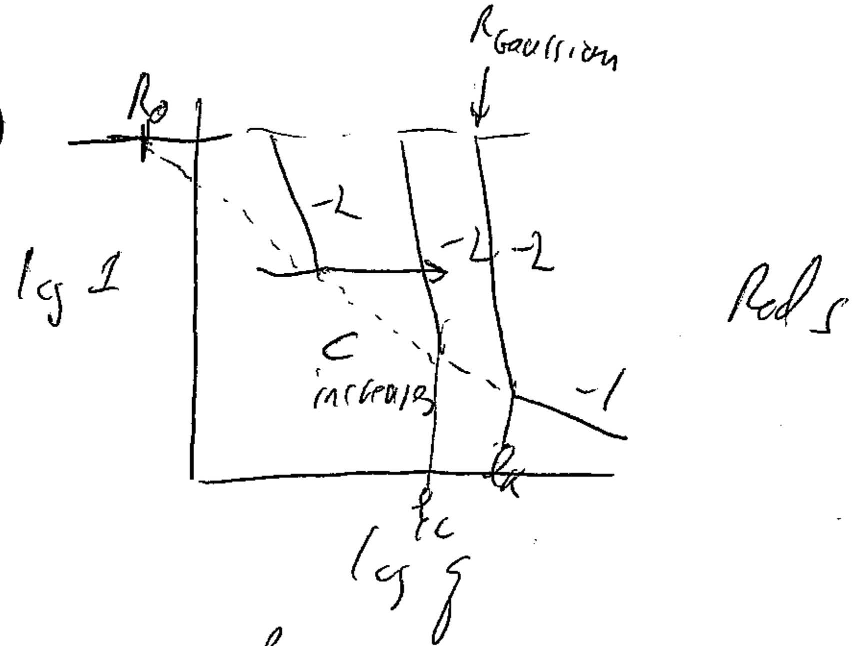
c) SAW $\xi_c \sim R_0 \left(\frac{c}{c^*}\right)^{-3/4}$

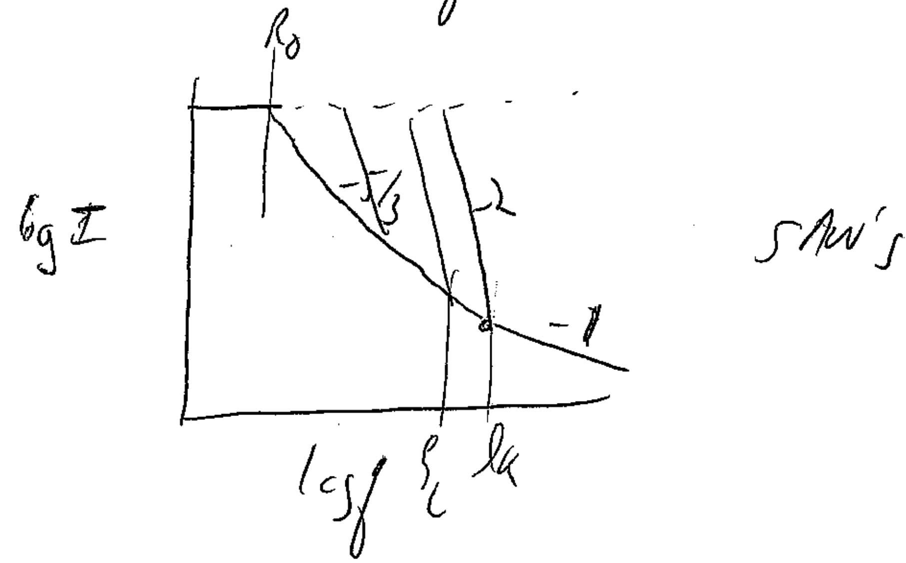
so SAW has a stronger dependence on concentration.

Concentration blob size has to do with the ability of chains to screen or block interactions between chain units. SAW coils are more effective at screening interactions because they are denser than rods.

d) c^* is a much smaller number $c^* \sim n^{-2}$ vs. $c^* \sim n^{-4/5}$ since rods are less dense & occupy more space.

e)





2) a)

$$K_{spr} = \frac{3kT}{R_0^2} = \frac{3kT}{n_k l_k^2}$$

b)

$$\zeta_F = 6\pi\eta_0 R_0 = 6\pi\eta_0 (n^{1/2} l)$$

c)

$$\tau = \frac{\zeta}{K_{sp}} = \frac{n l^2}{3kT} 6\pi\eta_0 (n^{1/2} l)$$

$$\tau = \frac{n^{3/2} l^3 2\pi\eta_0}{kT}$$

d) If $\zeta \sim 6\pi\eta_0 (n^{1/2} l)$

then $\eta_0 \sim n^{1/2}$

this doesn't follow n^1 or $n^{3.4}$ seen for polymers

e) For $\zeta \sim n$ the dumbbell model is identical to the lowest order Rouse mode behavior.

3) a) A Rouse unit is an arbitrary unit while a tensile blob unit is of fixed size

$$\zeta_F = \frac{3kT}{F}$$

Tensile unit doesn't have a drag coefficient so it is a stable structure.

b)

$$\zeta_R \frac{dz_e}{dt} = b_R (z_{e+1} - z_e) + b_R (z_{e-1} - z_e)$$

$$= b_R (z_{e+1} + z_{e-1} - 2z_e)$$

c) we only consider nearest neighbor interactions

(3) The Rouse Theory was derived to describe polymer dynamics. ~~but that is~~ Rouse divided the chain into subunits.

a) How does a Rouse unit differ from a Tangle blob?

b) Write a force balance for a Rouse unit "l"

c) What assumption does your eqn "b" make concerning the distance over which dynamic units are coupled along the chain?

d) The Rouse approach leads to an equation for the relaxation time spectrum for a polymer

$$\tau = \frac{\zeta_R}{4 b_R \sin^2(\delta/2)}$$

How can a cyclic assumption yield discrete values for δ?

e) Show that $\left(\frac{\zeta_R}{a_R^2}\right)$ must be a constant for Rouse theory.

d) For a cyclic

$$z_\ell = z_{\ell + N_R}$$

where there are N_R units in the coil

$N \delta_m = 2\pi m$ where m is the mode of vibration

$$\boxed{\delta_m = \frac{2\pi m}{N_R} \quad \text{for cyclic}}$$

$m = 0, 1, 2, 3, \ldots$

e)

$$\tau_R = \frac{\zeta_R}{4 b_R \sin^2 \delta/2} \quad \text{use } \delta_m = \frac{2\pi}{(N_R - 1)} \lll 1$$

so $\sin^2 \frac{\delta}{2} = \left(\frac{\delta}{2}\right)^2$

$$\tau_R = \frac{\zeta_R\, 4 (N_R - 1)^2}{4 b_R (2\pi)^2} \qquad b_R = \frac{3kT}{a_R^2}$$

$$= \frac{\zeta_R a_R^2 N_R^2}{12 kT \pi^2} \qquad R_0^2 = N_R a_R^2$$

$$\tau_R = \frac{(\zeta_R / a_R^2) R_0^2}{12 kT \pi^2}$$

For τ_R to not depend on the Rouse Unit (ζ_R / a_R^2) must be a constant