Quiz 11
Polymer Properties
April 8, 2016

a) Show how the Zimm equation,

$$\frac{\phi}{S(qR_g << 1)} = \left(\frac{1}{N} + (1-2\chi)\phi\right)\left(1 + \frac{q^2R_g^2}{3}\right),$$

can be obtained from the Flory expression for osmotic pressure,

$$\Pi = \frac{kT}{V_c}\left(\frac{\phi}{N} + \left(\frac{1}{2} - \chi\right)\phi^2 + \ldots\right),$$

and the expression for change in Gibbs free energy,

$$dG = \Psi_k d\phi_k = \frac{\phi_k d\phi_k}{\alpha_k}.$$

b) Obtain the athermal RPA equation using linear response theory.

c) Show how the full RPA equation,

$$\frac{1}{S(q)} = \frac{1}{\phi_1 N_1 S_U(q, R_{g1})} + \frac{1}{\phi_2 N_2 S_U(q, R_{g2})} - 2\chi,$$

can be obtained. *N* is the molecular weight, ϕ is the volume fraction and *S(q)* is the structure factor which could be Guinier's Law at low-*q*.

d) Compare the Zimm equation and the RPA equation by sketching the dependence of log I/ϕ versus log q as concentration increases for the two equations.

e) Consider a polydisperse polymer sample in dilute solution. Imagine that it is composed of two components with a 50:50 volume fraction split with 10,000 g/mole, and 100,000 g/mole. If the final scattering curve from this mixture can be fit with a single radius of gyration, R_g, and contrast factor G. **Calculate this radius of gyration and contrast factor G using the athermal RPA approach** and the low-q expansion of Guinier's Law, $1/I(q) = (1/G)(1+q^2R_g^2/3)$. Assume a Gaussian chain structure. l_k = 20Å and one Kuhn unit weights 100 g/mole. $G = \phi$
$N\Delta\rho^2$, and $\Delta\rho^2$ is the same for the two polymer fractions.

f) How will a negative interaction parameter impact the scattering curve of part d) as temperature is dropped? (Sketch log I versus log q to show the effect.)

g) DeGennes won the Nobel Prize for three branches of physics, superconductors and magnetism, liquid crystals, and polymers. In all three of these branches of physics he used the RPA approach. Explain what a field, susceptibility and response might mean in magnetic materials and in liquid crystalline materials (such as an LC display).

h) For magnetic materials and liquid crystalline materials explain how a field could affect some domains and not others as is assumed in the derivation of the RPA scattering equation.

ANSWERS: Quiz 11
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a)

$$dG = \Psi_k d\phi_k = \frac{\phi_k d\phi_k}{\alpha_k}$$

$$\alpha_k = \phi_k / \left(dG_k / d\phi_k\right) \approx \phi\left(d\pi / d\phi\right)^{-1}$$

$$S(q \Rightarrow 0) = 2kT\phi\left\langle\frac{d\phi}{d\pi}\right\rangle$$

$$\frac{\pi}{kT} = \frac{\phi}{N} + \frac{(1-2\chi)}{2}\phi^2$$

$$\frac{\phi}{S(q \Rightarrow 0)} = \left(\frac{1}{N} + (1-2\chi)\phi\right)$$

b)

$$\phi_{k,A} = \alpha_k^0 \Psi_k$$

$$\phi_{k,A} = -\phi_{k,B} = \phi_k$$

$$\phi_{k,B} = -\phi_k = \alpha_k^{BB} \underline{\Psi_k}$$

$$\phi_{k,A} = \phi_k = \alpha_k^{AA}\left(\Psi_k + \underline{\Psi_k}\right)$$

$$\phi_k = \alpha_k^{AA}\left(\Psi_k + \underline{\Psi_k}\right) = -\alpha_k^{BB}\left(\underline{\Psi_k}\right)$$

$$\underline{\Psi_k} = -\Psi \frac{\alpha_k^{AA}}{\alpha_k^{AA} + \alpha_k^{BB}}$$

$$\phi_k = -\alpha_k^{BB} \underline{\Psi_k} = \Psi_k \frac{\alpha_k^{AA} \alpha_k^{BB}}{\alpha_k^{AA} + \alpha_k^{BB}}$$

$$\phi_k = \Psi_k \frac{\alpha_k^{AA} \alpha_k^{BB}}{\alpha_k^{AA} + \alpha_k^{BB}} = \alpha_k^0 \Psi_k$$

$$\alpha_k^0 = \frac{\alpha_k^{AA} \alpha_k^{BB}}{\alpha_k^{AA} + \alpha_k^{BB}}$$

or

$$\frac{1}{\alpha_k^0} = \frac{1}{\alpha_k^{AA}} + \frac{1}{\alpha_k^{BB}}$$

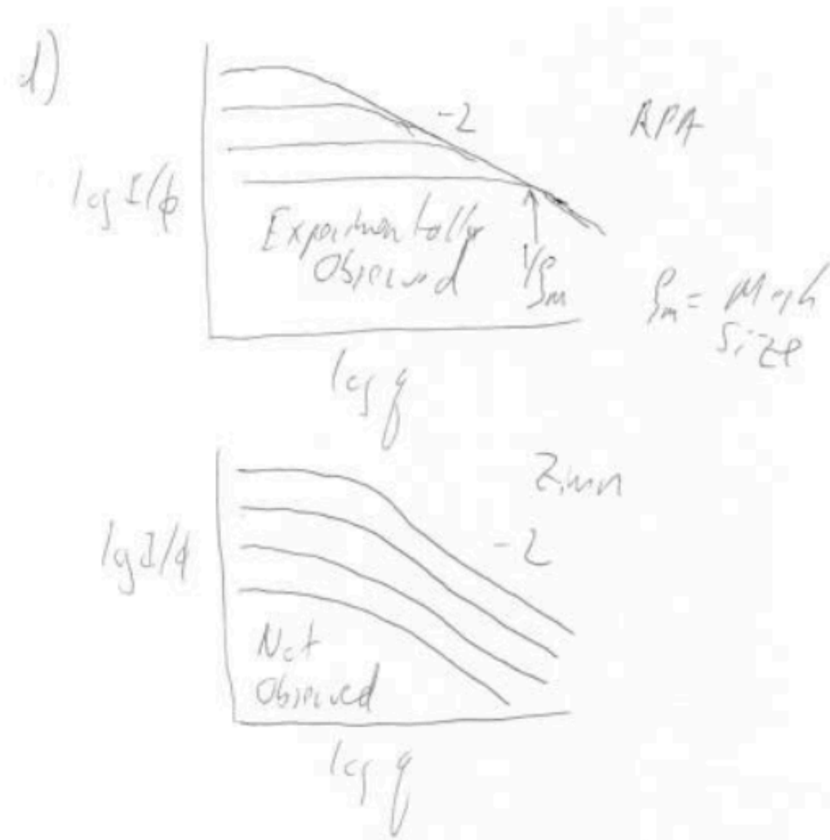
c) $\chi' = \quad 2\chi kT/V_{c'}$

$$\phi_{k,A} = \alpha_k^0\left(\Psi_k + \phi_k \chi'\right)$$

$$\phi_k = \frac{\alpha_k^0 \psi_k}{1 - \alpha_k^0 \chi'}$$

$$\frac{1}{\alpha_k} = \frac{1}{\alpha_k^0} - \chi' = \frac{1}{\alpha_k^{AA}} + \frac{1}{\alpha^{BB}} - \frac{2kT\chi}{V_c}$$

d)



e)

$$\frac{1}{S(q)} = \frac{1}{\phi_1 N_1 S_U(q,R_{g1})} + \frac{1}{\phi_2 N_2 S_U(q,R_{g2})} - 2\chi$$

Here $N_1 = 100$ and $N_2 = 1{,}000$. $\phi_1 = \phi_2 = 0.5$. $1/S(q) = 1 + q^2R_g^2/3$. $R_g^2 = R_{eted}^2/\sqrt{6} = Nl_k^2/\sqrt{6}$.

$1/S(q) = (1 + q^2 R_{g1}^2)/(\phi_1 N_1) + (1 + q^2 R_{g2}^2)/(\phi_2 N_2)$
$= 1/(\phi_1 N_1) + 1/(\phi_2 N_2) + q^2 (R_{g1}^2/(\phi_1 N_1) + R_{g2}^2/(\phi_2 N_2))$

$1/S(q) = (1 + q^2\, 100(20Å)^2)/(0.5\ 100\ 3\sqrt{6})) + (1 + q^2\, 1000(20Å)^2)/(0.5\ 1000\ 3\sqrt{6}))$

f) Same as the RPA part in "d".

g) Magnetic materials: The field is the magnetic field, the response is orientation of the magnetic field for a magnetic domain, the susceptibility is the magnetic susceptibility.

For liquid crystalline materials, the field could be an electrical field such as in an LCD display, the response is orientation of the LC domains, the susceptibility is the response of the LC domains to the applied electrical field.

h) For magnetic or LC materials there are non-magnetic domains or domains that do not orient to the field. This is much easier to visualize in these materials than in polymers.