080213 Quiz 5 Polymer Properties

1) The Debye-Bueche function has been proposed as a generic scattering function for disordered 3d objects such as dust particles. $I(q,R_g) = \frac{G}{\left(1+\xi^2 q^2\right)^2}$. For a sphere the low-q extrapolation is Guinier's law, $I(q,R_g) = G\exp\left(-\frac{q^2 R_g^2}{3}\right)$ and the high-q extrapolation is Porod's Law for a sphere, $I(q,R_g) = \frac{1.62G}{R_g^4} q^{-4}$.

   a) Find the low-q extrapolation for the Debye-Bueche function.
   b) Equate this function with Guinier's law to describe ξ in terms of R_g.
   c) Find the high-q extrapolation an compare with this with Porod's law for a sphere. Does the Debye-Bueche function seem reasonable in this light?

2) In class we discussed the excluded volume.
   a) Calculate the excluded volume for a sphere as was done in class.
   b) Calculate the excluded volume for a rod of length L and diameter D by
      i) considering only lateral approach (laterally aligned rods like spaghetti),
      ii) considering end-on-end approach and
      iii) by considering an anti-parallel approach (end-on-side).
   c) How does the excluded volume of a rod depend on the aspect ratio A = L/D?

3) The second virial coefficient depends on the excluded volume.
   a) Explain why this is the case for a gas composed of spheres.
   b) Write an expression for the conformational free energy, E, of an isolated chain in terms of the excluded volume, V_c, chain end-to-end distance, R, and temperature, T, by comparing an exponential expression for the probability of a chain of end-to-end distance R with the Boltzman probability for a chain of end-to-end distance R, $P_{Boltzman}(R) = \exp(-E/kT)$
   c) Sketch a plot of the isolated chain energy, E, versus excluded volume, V_c, and explain the behavior and limits to this plot. Is there a minimum excluded volume? Why can't a maximum excluded volume be reached?

1) a) $$I(q) = \frac{G}{(1+q^2\xi^2)^2}$$

$$1+q^2\xi^2 \underset{\substack{\text{at}\\ \text{low}\\ q}}{\Rightarrow} \exp(q^2\xi^2)$$

$$I(q) \underset{\substack{\text{at}\\ \text{low}\\ q}}{\Rightarrow} G\exp(-2q^2\xi^2)$$

b) Guinier's Law

$$I(q) = G\exp\left(-\frac{q^2R_g^2}{3}\right)$$

so by comparison

$$2\xi^2 = \frac{R_g^2}{3}$$

or

$$\xi^2 = \frac{2R_g^2}{3}$$

c) $$I(q) = \frac{G}{\left(1+\frac{2}{3}q^2R_g^2\right)^2}$$

at high q

$$I(q) = \left(\frac{9G}{4R_g^4}\right)q^{-4}$$

Porod's Law yields (for a sphere)

$$I(q) = \frac{1.62\,G}{R_g^2}\,q^{-4}$$

D-B has 1.4 times the power-law prefactor compared to a sphere. This seems reasonable. (offhand)

2 a) 

$$V_{ex} = \frac{\frac{4}{3}\pi(2r)^3 L}{2 \text{ spheres}} = 4V_0$$

b) i) 

$$V_{ex} = \frac{\pi(2r)^2 L}{2} = 2V_0$$

$V_0 = L\pi r^2$

ii)

$$V_{ex} = \frac{\frac{4}{3}\pi(L)^3}{2} = \frac{2}{3}\pi L^3$$

$A = \frac{L}{(2r)}$

$$= \frac{8}{3}V_0 A^2$$

iii)

$$V_{ex} = \frac{\frac{\cancel{4}^{2}}{3}\cancel{\pi}\left(\frac{L}{2}+r\right)^3}{\cancel{2} L\cancel{\pi}r^2} V_0 = \frac{2}{3}\left(\frac{\frac{L^3}{8}+\frac{5L^2r}{4}+\frac{3Lr^2}{2}+r^3}{Lr^2}\right)V_0$$

$$= \frac{2}{3}V_0\left(\frac{1}{8}\frac{L^2}{r^2}+\frac{5}{4}\frac{L}{r}+\frac{3}{2}+\frac{r}{L}\right)$$

$$= \frac{2}{3}V_0\left(\frac{1}{2}A^2+\frac{5}{2}A+\frac{3}{2}+\frac{2}{A}\right)$$

$$= V_0\left(\frac{1}{3}A^2+\frac{5}{3}A+1+\frac{4}{3A}\right)$$

c) See Above

3) a) $\frac{P}{KT} = C + B_2 C^2 + \cdots$

Virial expansion

B_2 is the excluded volume per gas atom since this accounts for hard core interactions

$B_2 = 4V_0$ for spheres

b)

$$E = KT\left(\frac{3}{2}\frac{R^2}{Nb^2} + \frac{V_c}{R^3}\frac{N^2}{2}\right)$$

c)

$E = KT\left(\frac{3}{2}\frac{R^2}{Nb^2} + \frac{N^2}{2}\right)$

Function fails at large V_c since it assumes $\frac{V_c}{R^3}$ is small in the derivation.

V_c is a measure of energy (enthalpy)

When $V_c = 0$ the chain is wholly entropic; Enthalpy $= 0$