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. \( I(q,R_g) = \frac{G}{(1 + \frac{q^2}{\xi^2} q^2)^{\frac{3}{2}}} \). 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, \( I(q,R_g) = \frac{1.62 G}{R_g^4} q^{-4} \).

   a) Find the low-q extrapolation for the Debye-Bueche function.
   b) Equate this function with Guinier’s law to describe \( \xi \) in terms of \( R_g \).
   c) Find the high-q extrapolation and 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 Boltzmann probability for a chain of end-to-end distance \( R \), \( P_{\text{Boltzmann}}(R) = \exp(-E/kT) \)
   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) \[ I(q) = \frac{G}{(1 + q^2 R_s^2)^2} \]

\[ 1 + q^2 R_s^2 \xrightarrow{a \text{ to low } q} \exp(q^2 R_s^2) \]

\[ I(q) \xrightarrow{a \text{ to low } q} G \exp(-2q^2 R_s^2) \]

b) Gainer's Law

\[ I(q) = G \exp(-\frac{q^2 R_s^2}{3}) \]

So by comparison

\[ 2q^2 = R_s^2 \]

or

\[ q^2 = \frac{2R_s^2}{3} \]

c) \[ I(q) = \frac{G}{(1 + \frac{2}{3} q^2 R_s^2)^2} \]

\[ a \text{ to high } q \]

\[ I(q) = \left( \frac{9G}{4 R_s^4} \right) -4 \]

Porod's Law yields (for sphere)

\[ I(q) = \frac{1.62 G}{R_s^2} -q \]

D-B has 1.4 times the power-law prefactor compared to a sphere.

This seems reasonable, (off-hand)
2a) \[ V_{px} = \frac{4}{3} \pi (2r)^2 \frac{L}{2} = 4V_0 \]

b) i) \[ V_{px} = \frac{\pi (2r)^2 L}{2} = 2V_0 \quad V_0 = \frac{L}{2\pi r^2} \]

ii) \[ V_{px} = \frac{\frac{4}{3} \pi (L)^3}{2} = \frac{2}{3} \pi L^3 \quad A = \frac{L}{(2r)} \]

\[ \frac{V_0}{3} \]

iii) \[ V_{px} = \frac{\frac{1}{2} \pi \left( \frac{L}{r} + r \right)^3}{2}\frac{L}{\pi r^2} V_0 = \frac{2}{3} \left( \frac{\frac{L}{8r^2} + \frac{5}{4} \frac{L}{r} + \frac{3}{2} + \frac{1}{L} }{3 \pi L} \right) V_0 \]

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

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

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

c) \underline{See Above}
3a) \[ \frac{P}{KT} = C + B_2 C^2 + \ldots \]

Vital expansion

\( B_2 \) is the excluded volume per gas atom

Since \( B_2 \) accounts for hard core interactions

\( B_2 = 4V_0 \) for spheres

b) \[ E = KT \left( \frac{3}{2} \frac{R^2}{N_0} + \frac{V_c N^2}{R^3} \frac{N^2}{2} \right) \]

e) \[ E = kT \left( \frac{3}{2} \frac{R^2}{N_0} + \frac{N^2}{2} \right) \text{ Fermi-Dirac at large } V_c \text{ since if assumes } V_c \text{ is small in the derivation.} \]

\( V_c \) is a measure of energy (enthalpy)

When \( V_c = 0 \) the chain is entropic; Enthalpy = 0