030423 Quiz 4 Properties

1) a &b) Give two scattering functions that are used in the literature to describe scattering from a polymer coil.
c & d) Show that these two functions yield the same power-law equation at the high-q limit.
e) Which of these functions could be used for a dilute polymer solution" in a good solvent? Explain.

2) Derive a relationship between the end to end distance of a linear Gaussian chain and the radius of gyration. Given that,

$$R_g^2 = \frac{1}{2N^2}\sum_{n=1}^{N}\sum_{m=1}^{N}\left\langle \left(R_n - R_m\right)^2 \right\rangle$$

and

$$\sum_{\mathbf{u=1}}^{\mathbf{n}} \mathbf{u}^{\mathbf{p}} = \frac{n^{p+1}}{p+1} + \frac{n^p}{2} + \frac{pn^{p-1}}{12} \quad \textbf{for p < 3}$$

(Explain each step in the derivation)

3) a) Find an expression for the end-to-end distance of maximum probability, R*, for a self-avoiding walk if the probability for a walk of length R is given by,

$$W(R) = kR^2 \exp\left(-\frac{3R^2}{2Nb^2} - \frac{N^2V_c}{2R^3}\right)$$

where k is a constant.
b) The free energy of a self-avoiding chain as a function of extension, R, is sometimes written,

$$F(R) = kT\left(\frac{R^2}{R_0^2} + \frac{N^2V_c}{2R^3}\right)$$

How can this be obtained using the Boltzmann probability and the function given above?

ANSWERS: 030423 Quiz 4 Properties

1) a) Debye Scattering Function for a Gaussian Polymer Coil,

$$g(q) = \frac{2N}{Q^2}\left[Q - 1 + \exp(-Q)\right] \quad \textbf{where } Q = q^2 R_g^2$$

b) Ornstein-Zernike Function (Lorentzian Function)

$$g(q) = \frac{N}{1 + \frac{Q}{2}}$$

c) For the Debye function at high q the exp(-Q) term goes to 0 and Q>>1 so g(q) =>2N/Q

d) For the Lorentzian function at high q, Q/2 >>1 so g(q) =>2N/Q

e) The high q power of -2 slope in q indicates a 2 dimensional mass-fractal structure. A good solvent coil shows self-avoiding statistics so the slope is -5/3 in this region. Neither of these functions is appropriate for a good solvent coil.

2) Following the web notes,
step 1: Realize that the difference between two segments in a Gaussian walk is given by nb^2 so

$$R_g^2 = \frac{1}{2N^2}\sum_{n=1}^{N}\sum_{m=1}^{N}\left\langle \left(R_n - R_m\right)^2\right\rangle = \frac{b^2}{2N^2}\sum_{n=1}^{N}\sum_{m=1}^{N}\left|n-m\right| = \frac{b^2}{N^2}\sum_{n=m}^{N}\sum_{m=1}^{N}\left(n-m\right)$$

where the second summation realizes the symmetry of the double summation.

step 2: The double summation can be written as a series in Z = N-1, this is evident after writing the first few terms of the double summation

$$R_g^2 = \frac{b^2}{N^2}\sum_{n=m}^{N}\sum_{m=1}^{N}\left(n-m\right) = \frac{b^2}{N^2}\left[Z + 2(Z-1) + 3(Z-2)\ldots(Z-1)2 + Z\right]$$

$$= \frac{b^2}{N^2}\sum_{p=1}^{Z}\left(Z+1-p\right)p = \frac{b^2}{N^2}\left\{(Z+1)\sum_{p=1}^{Z}p - \sum_{p=1}^{Z}p^2\right\}$$

step 3: using the summation of a power rule given above for the two summations the expression becomes:

$$R_g^2 = \frac{b^2}{N^2}\left\{(Z+1)\sum_{p=1}^{Z}p - \sum_{p=1}^{Z}p^2\right\} = \frac{b^2}{N^2}\frac{Z(Z+1)(Z+2)}{6} \approx \frac{Nb^2}{6} = \frac{R_0^2}{6}$$

3) a) To find the maximum probability we take the derivative of W(R) with respect to R and set this equal to 0,

$$\frac{d[W(R)]}{dR} = k\left\{2R\exp\left(-\frac{3R^2}{2Nb^2} - \frac{N^2V_c}{2R^3}\right) + R^2\left[-\frac{3R}{Nb^2} + \frac{3N^2V_c}{2R^4}\right]\exp\left(-\frac{3R^2}{2Nb^2} - \frac{N^2V_c}{2R^3}\right)\right\} = 0$$

so

$$\frac{2}{3} + \left[-\frac{R^2}{Nb^2} + \frac{N^2 V_c}{2R^3}\right] = 0$$

substituting $R^2_0 = 2Nb^2/3$

$$\frac{R^3}{R_0^3} + \left[-\frac{R^5}{R_0^3} + \frac{3N^2 V_c}{4R_0^3}\right] = 0$$

Rearranging,

$$\left[\frac{R}{R_0}\right]^5 - \left[\frac{R}{R_0}\right]^3 = \frac{3N^2 V_c}{4R_0^3} = \frac{9\sqrt{6}}{16}\frac{V_c}{b^3}\sqrt{N}$$

b) By comparison of the function for the probability of an end to end distance R given in the problem and by comparison with the Boltzman probability, exp(-F(R)/kT) we can directly write an expression for the free energy as a function of R for a self-avoiding chain.