050422 Quiz 4 Polymer Properties

Debye calculated the scattering function g(q) for a random walk coil using matrix math similar to that used in class to consider the radius of gyration of a polymer coil.

a) Give Debye's function for scattering from a random walk structure and explain the two scattering regimes it describes in a sketch of I(q) versus q. (Also, give an expression for q in terms of scattering angle)

b) Show that the low-q limit of the Debye function is Guinier's law and that the high-q limit follows a fractal scaling law with $B = 2/R_g^2$.

c) Show the major steps involved in the calculation of R_g^2 for a random walk coil. First choose an expression for R_g^2 from the two used in last week's quiz; then show how this expression can be reduced to b^2 times a double summation;

use a matrix to obtain a series expression;

reduce the series expression into a single summation over "p" and; write the final expression for R_g^2 . (just indicate the name of the math identity needed for this step).

d) Does your calculation of R_g^2 require that the units of a polymer chain be connected (bonded) into a chain or just that they follow a certain statistical scaling law that describes their distribution in space? Explain your answer by showing the step of the derivation that requires a connected (bonded) chain structure or by postulating on the meaning of not requiring the chain to be a chain.

e) Write the expression for the Gaussian probability for a chain of N steps having a length R. By comparison with the Boltzmann thermodynamic probability, $exp(-\Delta E/kT)$, write an expression for ΔE , the free energy of an isolated random walk coil of end to end distance R, contour length Nb and RMS size R_0 (equate the arguments of the exponential terms in the two expressions). Write a similar expression for the free energy of a self-avoiding walk chain (with long range interactions) and for a chain with short range interactions.





$$g(q)_{Gaussian} = \frac{2}{Q^2} \left[Q - 1 + \exp(-Q) \right]$$

where
$$Q = q^2 N b^2 / 6 = q^2 R_g^2$$

 $\mathbf{q} = |\mathbf{q}| = 4\pi/\lambda \sin(\theta/2)$

At high-q, Q is much larger than 1 so $\exp(-Q) \sim 0$ and Q >>1 so g(q) => 2/Q or $2/(R_g^2 q^2) = B q^{-2}$. At low-q, Q is much smaller than 1 and Sterling's approximation can be used to expand the exponential term to $1 - Q + Q^2/2 - Q^3/6 + ...$ so the first two terms of the expansion remove the first two terms in the brackets above and dividing by $Q^2/2$ we obtain, 1 - Q/3 + ... Using Sterling's approximation again we obtain, $g(q) = \exp(-Q/3)$ or $\exp(-R_g^2 q^2/3)$.

c) Page 5-7 of the notes.

d) Neither the Debye equation or the R_g calculation require that the chain be bonded. Any distribution of units that leads to $R^2 \sim n b^2$ will suffice. This is a manifestation of the "loss of phase information" in scattering data, that is the structure can not be reconstructed from SAXS data alone.

e) Both the short range interaction and the Gaussian coil chains show Gaussian scaling with variability in b.

$$P_{Gaussian}(R) \sim \exp\left(\frac{-3}{2}\left(\frac{R}{R_0}\right)^2\right)$$
 $P_{Boltzmann}(T) \sim \exp\left(\frac{-\Delta E}{kT}\right)$

by comparison,

$$\Delta E_{Gaussian} = \frac{3kT}{2} \left(\frac{R}{R_0}\right)^2 \qquad \mathbf{R}_0 = N^{\frac{1}{2}} b$$

For long range interactions (excluded volume),

$$P_{Gaussian}(R) \sim \exp\left(\frac{-3}{2}\left(\frac{R}{R_0}\right)^2 - \frac{N^2 V_c}{2R^3}\right) \qquad \qquad P_{\text{Boltzmann}}(T) \sim \exp\left(\frac{-\Delta E}{kT}\right)$$

by comparison,

$$\Delta E_{SAW} = kT \left[\frac{3}{2} \left(\frac{R}{R_0} \right)^2 + \frac{N^2 V_c}{2R^3} \right] \qquad \mathbf{R}_0 = N^{\frac{1}{2}} b$$

These expressions are used t calculate the force needed to stretch a chain to a length R for instance, $F_{Gaussian} = \frac{d\Delta E}{dR} = \frac{3kTR}{R_0^2} = \left(\frac{3kT}{Nb^2}\right)R$, where the spring constant for a Gaussian chain is proportional to temperature and inversely proportional to N.