090220 Polymer Properties Quiz 6

In class we considered the thermal blob, the concentration blob and the ideal gas analogy for osmotic pressure this week.

 A macromolecule differs from low molecular weight molecules in that they display structural scaling behavior manifested in the mass-fractal dimension, d_f. The thermodynamic stability of such a macromolecule can vary on different length scales leading to scaling transitions that are described using "blob" models.

a) A blob is often shown as a series of beads connected in a chain structure, within each bead being a segment of the chain coil. Explain how this discrete cartoon of "blobs" is misleading.

b) Explain how the Kuhn length could be considered a "blob".

c) The following picture is from

<u>http://nobelprize.org/nobel_prizes/physics/laureates/1991/illpres/polymers.html</u>. What kind of blob model does this picture refer to? Explain why.



d) The presence of blobs depends on variation in the thermodynamic conditions as a function of size. Explain why this is an issue for macromolecules but not for low molecular weight materials.

2) a) Give the functional dependence of R_F on N, V_0 and on χ from the Flory-Krigbaum approach.

b) Explain the scaling transition observed for a thermal blob. What scaling regimes are observed and why are they observed.

c) Write an expression for R_F in terms of the blob size and the number of blobs for a thermal blob.

d) Write an expression for the blob size in terms of the Kuhn length and the number of Kuhn units in a blob.

- e) Obtain an expression for the blob size in terms of temperature and the Kuhn length.
- f) Do the limits of this expression make sense?
- 3) As concentration increases we observe screening for a polymer solution in a good solvent.
 - a) Explain the effect of screening on chain scaling.

b) Explain why the pair wise correlation function for a semi-dilute polymer solution is a constant value (it shows no structure) for sizes larger than the screening length.

c) At what concentration does screening begin?

d) Derive an expression for the scaling of concentration blob size with concentration ($\xi \sim c^{-3/4}$).

e) Derive an expression for the coil size, R_F , with concentration ($R_F \sim c^{-1/8}$).

ANSWERS: 090220 Polymer Properties Quiz 6

1) a) The blob reflects a size scale for a scaling transition. There are no real substructural elements that can be seen. The blob is not a visible feature.

b) The Kuhn length represents a scaling transition between coil scaling and persistence unit scaling. In this sense the persistence unit (or Kuhn unit) is a blob.

c) The blob scaling is $N \sim R^{5/3}$ while the global scaling is 2 dimensional so this represents a concentration blob. Also, more than one chain is shown so this must be in the semi-dilute regime.

d) Polymers and other disordered macromolecules have the flexibility to display thermal equilibrium on size scales smaller than that of the entire molecule. So we can consider the scaling behavior of a blob independent of the scaling behavior of the entire molecule or the thermodynamic balance that leads to a persistence unit. This is directly related to the structural connection of the subunits in macromolecules. Low molecular weight materials do not display this kind of structural connection so there is no large-scale structure to consider thermodynamically.

2) a)
$$R_F \sim N^{3/5} l_p^{2/5} V_0^{1/5} (1 - 2\chi)^{1/5} = l_p N^{3/5} (1 - 2\chi)^{1/5}$$

b) At large scale the coil behaves as a self-avoiding walk so $N \sim R^{5/3}$. At small scales the coil displays less entropy of mixing so miscibility is poor. The coil collapses but only to the theta-state since complete collapse and phase separation would require the large scale (high entropy) miscible chain to also collapse. The chain accommodates worsening solvent conditions by local coil collapse to the theta state which leads to a reduction in the overall coil size but not to total phase separation.

- c) $R_F \sim N_T^{-3/5} \xi_T$ d) $\xi_T \sim n_T^{1/2} l_z$
- e) We have $N_T = N/n_T = Nl_p^2 / \xi_T^2$ so $R_F \sim N^{3/5} l_p^{6/5} \xi_T^{-1/5} \sim l_p N^{3/5} (1 2\chi)^{1/5}$ and solving for ξ_T we obtain, $\xi_T = \frac{l_p}{(1 2\chi)}$

f) This makes sense because at $\chi = 1/2$ (theta temperature) the blob size is the largest possible, i.e. the coil size so the chain is Gaussian; and at $\chi = 0$ (athemal) the blob size is the persistence length so the coil is entirely SAW.

3) a) For large N between chain units other chains interfere with the interaction of one unit with another. For small N this effect diminishes. For large N this screening of interactions makes two chain units independent of each other so that the chain at large N values behaves like a Gaussian chain.

b) For sizes larger than the screening length the chain units are randomly distributed and there is no correlation between units so the correlation function becomes the constant value of the square of the volume fraction of chain units.

c) Screening begins at the overlap concentration, $c^* = N/R_F^3$.

d) $\xi_r = R_{F0} \left(\frac{c}{c} \right)^{\rho}$ and $c^* \sim N^{-4/5}$ while $R_{F0} \sim N^{3/5}$. Since xc is smaller than the coil it can not depend on c so 3/5 + P(-4/5) = 0 and P = -3/4.

e)
$$R_F \sim N_c^{1/2} \xi_c$$
 and $N_c = N/n_c = N l_p^{5/3} / \xi_T^{5/3}$ so $R_F \sim l_p^{5/6} N^{1/2} \xi_c^{1/6} = R_{F0}^{1/6} l_p^{5/6} N^{1/2} (c/c^*)^{-1/8}$