Quiz 13 Polymer Properties November 21, 2014

a) The concept of osmotic pressure is based on an analogy between an ideal gas and a colloid in solution. Show how osmotic pressure depends on molecular weight of a colloid by writing the ideal gas law; sketching an analogy between a colloid in solution and an ideal gas; and giving an expression for $M_n$ of a colloid in dilute solution based on this analogy.

b) The Flory-Huggins equation is also based on an analogy between a polymer and an ideal gas, or a real gas with a simple binary enthalpic interaction term if $\chi \neq 0$.
- Write the Boltzmann equation for the energy of a gas atom subject to thermal motion;
- from this obtain an expression for the entropy of such a gas;
- use this entropy to calculate the energy of an athermal binary mixture of gas-like dissolved monomers in a gas-like solvent;
- add a term for binary interactions between monomer and solvent molecules;
- polymerize the monomers and modify your equation for polymer chains in a solvent.
How does the F-H model differ from the colloid model of part “a”?

c) Sketch $\chi N$ versus composition for a symmetric polymer blend (matched molecular weights) for conditions below the critical $\chi N$; at the critical $\chi N$; and above the critical $\chi N$. Show the spinodal and binodal points.

Witten wrote the following in a review article, [Witten, TA Rev. Mod. Phys. 70 1531 1996.]
“... a polymer, like any other molecule, moves via diffusion: the motion is a random walk, whose mean squared distance $<x^2>$ is the diffusion coefficient times the elapsed time, $D_t$... As the concentration approaches $\phi^*$ this ceases to be true... To characterize the motion we must specify two diffusion coefficients: the self-diffusion coefficient, $D_s$ is defined by the motion of an individual chain, $D_s = <x^2>/t$, as introduced above...$D_s$ decreases as the concentration increases. The other important aspect of diffusion is the spreading of extra local concentration in the solution. The extra material spreads over a distance $x$ whose square is proportional to time. The “cooperative diffusion coefficient" $D_c$ gives the constant of proportionality: $D_c = x^2/t$. A small region of extra concentration is under extra osmotic pressure. This extra osmotic pressure...tends to spread apart the chains in the concentrated region faster than they would otherwise spread... Thus, as the concentration increases from zero, $D_c$ increases from its limiting value of $D_s$ as $D_s$ decreases... The diffusion coefficient is inversely proportional to the radius, $\xi$: $D_c = kT/(6\pi \eta_s \xi)$... the blob size decreases with concentration: $\xi = a\phi^{3/4}$. Combining these equation we infer that $D_c = \phi^{3/4} kT/(a\eta_s)$. The cooperative diffusion becomes faster as the concentration increases. But joining the chains to make them longer has no effect on the cooperative diffusion.

d) Calculate the scaling relationship of osmotic pressure with concentration in the semi-dilute regime using Witten’s expression for $D_c$ and the fact that $PV \sim kT$, the volume being given by $a^3$, and $P$ being $\pi$ in this case.

e) If osmotic pressure can drive random thermal motion, how does it differ from our normal concept of pressure? Does this impact your analogy from question “a”?
b) a) \( PV = nkT \)
\[
\pi = \left( \frac{n}{V} \right) kT
\]
c = \( M/V \) and \( n/V = c/M_n \), so \( M_n = c \, kT/\pi \)

b) Probability = \( \exp(-E/kT) \) => \( S = -kT \ln(\phi) \) (temperature dependent part of energy, \( E = H - TS \)). Where the probability is proportional to the volume fraction.
\[
F/kT = \phi \ln(\phi) + (1-\phi) \ln(1-\phi)
\]
Helmholtz free energy per \( kT \) per monomer of mixing.
Add binary interactions: \( F/kT = \phi \ln(\phi) + (1-\phi) \ln(1-\phi) + \phi (1-\phi) \chi \)
For a polymer the number fraction of polymers is \( \phi/N \) so:
\[
F/kT = \phi/N \ln(\phi) + (1-\phi) \ln(1-\phi) + \phi (1-\phi) \chi
\]

c) 

\[
\text{F/kT} = \phi \ln(\phi) + (1-\phi) \ln(1-\phi) + \phi (1-\phi) \chi
\]

\[ d) \] In the semi-dilute regime \( \pi \sim (c/c^*)^{9/4} \). This drives the cooperative diffusion of the chains. Witten proposes that \( D_c \sim (c/c^*)^{3/4} \).

Energy = \( kT = PV \), for the semidilute regime \( P \) is \( \pi \), and \( V \sim \xi_c^{-3} \).
So, \( \pi \sim kT/\xi_c^{-3} \sim D_c (6\pi \eta \xi_c)/\xi_c^3 \). For the concentration blob, \( \xi_c \sim (c/c^*)^{-3/4} \).
Using the scaling expression for \( D_c \) from Witten,
\[
\pi \sim (c/c^*)^{3/4} / (c/c^*)^{-6/4} \sim (c/c^*)^{9/4} \]

\[ e) \] When chains cluster in the semi-dilute regime due to random thermal motion, osmotic
pressure drives these chains apart. This is identical to the role of pressure in a gas serving to flatten out density fluctuations. So the analogy is strengthened between these two types of pressure.