# 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.

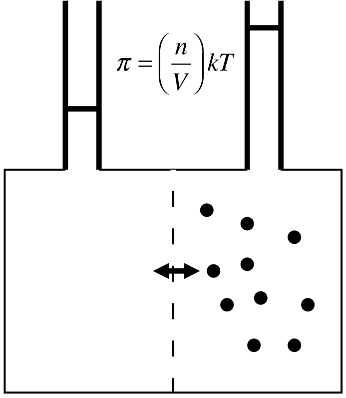
Witten wrote the following in a review article, [Witten, TA *Rev. Mod. Phys.* **70** 1531 1996.]
*"... a polymer, like any other molecule, moves via diffusion: the motion is a random walk, whose mean squared distance* $\langle x^2 \rangle$ *is the diffusion coefficient times the elapsed time, Dt... As 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,* $D_s = \langle x^2 \rangle / t$*, 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, just as* $D_s$ *decreases...The diffusion coefficient is inversely proportional to the radius,* $\xi$*:* $\boldsymbol{D_c = kT/(6\pi\eta_s\xi)}$*...the blob size decreases with concentration:* $\boldsymbol{\xi = a\phi^{-3/4}}$*. Combining these equation we infer that* $\boldsymbol{D_c = \phi^{3/4}kT/(a\eta_s)}$*. 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 $\xi_c^3$, 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"?

## ANSWERS: **Quiz 13 Polymer Properties November 21, 2014**

b) a) PV = nkT

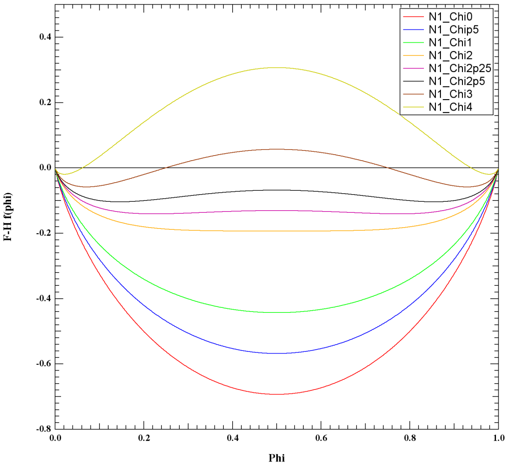


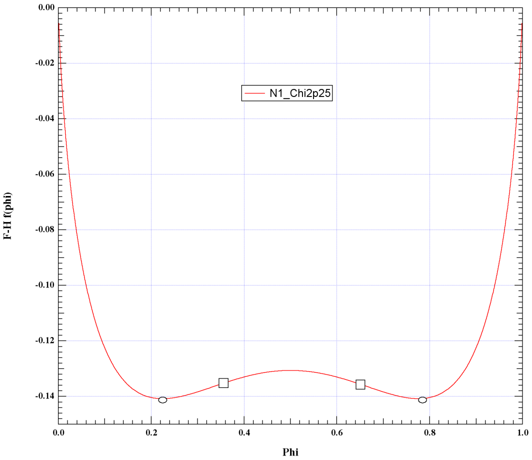
$$\pi = \left(\frac{n}{V}\right)kT$$

c = M/V and n/V = c/$M_n$, so $M_n$ = c kT/π

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

c)





d) In the semi-dilute regime π ~ $(c/c^*)^{9/4}$. 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 π, and V ~ $\xi_c^3$.
So, π ~ $kT/\xi_c^3 \sim D_c(6\pi\eta_s\xi_c)/\xi_c^3$. 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.