060505 Quiz 6 Polymer Properties

1) Polymer chains in a melt display ideal behavior. In dilute solution they display non-ideal
    behavior, for instance in terms of the second virial coefficient, A_2.

    a) Does this observation agree with the behavior of a gas? Explain.

    b) Give the virial expansion for pressure in a gas in terms of concentration (n/V) and
    explain how the deviation from ideality is effected by concentration.

    c) For a polymer in solution how would the first virial coefficient need to be modified
    compared with a gas?

    d) Explain (as best you can) what is the fundamental difference between a polymer and a
    gas that gives rise to different ideal limits in concentration.

    e) Give the Flory-Huggins expression for the second virial coefficient.

2) The size of a polymer coil decreases in concentration through the semi-dilute regime

    a) What are the limits in size scaling with molar mass, N for this decrease?

    b) At what concentration does the semi-dilute regime begin? How does this
    concentration change with the mass-fractal dimension of the chain?

    c) How does the overlap concentration differ from the percolation threshold?

    d) In the semi-dilute regime how does the concentration blob scale with concentration?

    e) In the semi-dilute regime how does the coil size, R_F, scale with concentration?

3)   a) Make a rough sketch of an osmotic pressure instrument.

    b) How can this instrument be compared with a container of gas?

    c) How is the osmotic pressure, π, determined in this instrument?

    d) In calculating the osmotic pressure what thermodynamic parameter is made equal
    between the parts of the instrument?

    e) How is the Gibbs free energy calculated from the Flory-Huggins expression for the
    free energy of mixing of a polymer in solution?

ANSWERS: 060505 Quiz 6 Polymer Properties

1) a) For a gas ideal behavior is seen in dilute conditions. Higher concentrations lead to non-ideal behavior so this is in direct contrast to the behavior of a polymer.

b) $P = (n/V) kT + A_2 (n/V)^2 + A_3 (n/V)^3 + \dots$

At higher concentration, (n/V), the non-ideal behavior, A_2 and A_3 terms, are enhanced.

c) For a polymer each chain is composed of N units so the first term becomes $(n/V) * (1/N)$.

d) The polymer chain has essentially a fixed internal concentration because it is connected together. For this reason, the dilute condition is already quite high in local concentration compared to a gas and we observed non-ideal behavior with an expanded coil structure. At high concentration these effects are screened due to interpenetration of the coils above $(n/V)*$.

e) $A_2 = (1/2 - \chi)$

2) a) In dilute conditions $R_F \sim N^{3/5}$ while in concentrated conditions $R_F \sim N^{1/2}$.

b) At the overlap concentration, $c* = N/R_F^3 \sim N/N^{3/df} = N^{1-3/df}$.

c) The percolation threshold and overlap concentration have some similarities in that both are related to a system change on increasing concentration that involve interaction of units. The percolation threshold is the concentration where a path across the system is first formed. Usually the percolation threshold is a statistically average value. Values for percolation threshold are shown below for various lattices that are randomly filled.
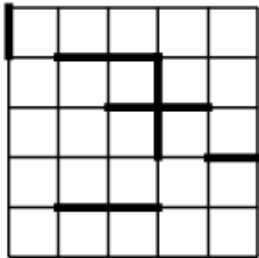
bond percolation   *site percolation*

From (http://mathworld.wolfram.com/BondPercolation.html)
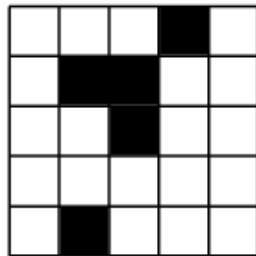
The critical fraction of lattice points that must be filled to create a continuous path of nearest neighbors from one side to another. The following table is taken from Stauffer and Aharony (1992, p. 17). Entries indicated with an asterisk (*) have known exact solutions.

lattice	p_c (site percolation)	p_c (bond percolation)
cubic (body-centered)	0.246	0.1803
cubic (face-centered)	0.198	0.119
cubic (simple)	0.3116	0.2488
diamond	0.43	0.388
honeycomb	0.6962	0.65271*
4-hypercubic	0.197	0.1601
5-hypercubic	0.141	0.1182
6-hypercubic	0.107	0.0942
7-hypercubic	0.089	0.0787
square	0.592746	0.50000*
triangular	0.50000*	0.34729*

Exactly known values include

$$p_c \text{ (square bond)} = \frac{1}{2} \tag{1}$$

$$p_c \text{ (triangular site)} = \frac{1}{2} \tag{2}$$

$$p_c \text{ (triangular bond)} = 2 \sin\left(\frac{\pi}{18}\right) \tag{3}$$

$$p_c \text{ (honeycomb bond)} = 1 - 2 \sin\left(\frac{\pi}{18}\right). \tag{4}$$

Determining an exact expression for other percolation thresholds, including of the square site percolation, remains an open problem.

From (http://mathworld.wolfram.com/PercolationThreshold.html)

The overlap concentration is for objects that have an "internal" concentration so specifically mass fractal objects like polymers. The overlap concentration is the concentration where the system has the same concentration as the object and at this is seen as the concentration where significant interpenetration of the objects can occur. For our purposes the object is a polymer coil. Such objects can also percolate at a **much lower** concentration. For instance, for a Gaussian coil percolation can occur when $c \sim 1/N$ while overlap occurs when $c \sim 1/N^{1/2}$.

d) $\xi_c \sim R_{F0}(c/c^*)^{-3/4}$

e) $R_F \sim R_{F0}(c/c^*)^{-1/8}$

3) a)
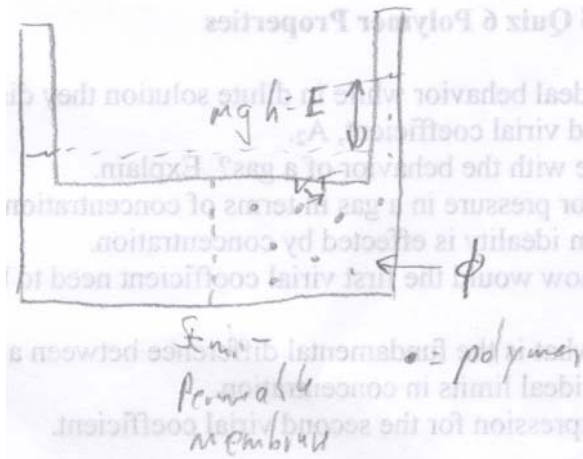
b) In the right hand chamber in part "a" the polymer chains move thermally with kT energy so they act like gas molecules in terms of the pressure generated in the system.

c) It is the pressure difference between the two cells.

d) The chemical potential of the solvent is made equal and the osmotic pressure is solved for using the Flory-Huggins expression for the Helmholtz free energy per lattice site per kT. The chemical potential of the solvent is the derivative of the Gibbs free energy with respect to the number of moles of solvent holding all other parameters constant.

e) The Flory expression,

$$f(\phi) = \phi \ln(\phi)/N + (1-\phi) \ln(1-\phi) + \phi(1-\phi)\chi$$

is per lattice site and is per kT so the Helmholtz free energy for the system of size Ω, is,

$$F(\phi) = kT\, \Omega\, f(\phi).$$

The Gibbs free energy, G, can be obtained from F using $G = F + PV$, where P is $P + \pi$ for the right side of the Pfeffer Cell shown in part "a" and P is P for the left side.