

### Quiz 5 5/1/01 Properties

- a) The osmotic pressure relates a polymer solution to the pure solvent.

**Explain** how the osmotic pressure is measured.

In this measurement, **What thermodynamic feature** is identical in the solution and the solvent at equilibrium?

- b) The Flory-Huggins expression for free energy is used to calculate and equate the thermodynamic feature of question b.

**Give the Flory Huggins** expression and

**explain** the major assumptions associated with it.

**Explain all terms** in the expression including the type of free energy to which it is associated and the structural unit to which it corresponds.

**How** can the Gibbs free energy be obtained from this expression?

- c) **Give** (do not derive) an expression for the osmotic pressure based on questions a, b and c.

- d) des Cloiseaux developed a scaling expression based on scaling limits to osmotic pressure in the semidilute regime,

$$\pi = (kT / N) (\phi / \phi^*)^{1/(3 - \chi)}$$

**Use** this expression and the Flory expression (question d) to obtain a molecular weight and composition dependence to the interaction parameter,  $\chi_{12}$ , and the second virial coefficient,  $A_2$ .

**Are such** molecular weight and composition dependences compatible with your answer to question c?

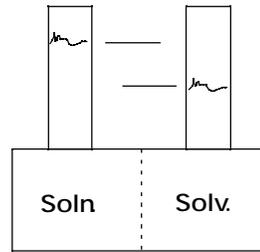
- e) The following are reported interaction parameters for PDMS in benzene at several volume fractions at 25°C (Physical Properties of Polymers Handbook, ed. J. E. Mark 1996).  $\chi_{12}$  is independent of molecular weight.

$$\chi_{12}(\phi_p=0) = 0.5; \chi_{12}(\phi_p=0.2) = 0.56; \chi_{12}(\phi_p=0.5) = 0.66; \chi_{12}(\phi_p=0.8) = 0.75; \chi_{12}(\phi_p=1) = 0.82$$

**What** are the problems with this data compared to your assumptions in question b and your answer to question c?

**Answers: Quiz 5 5/1/01 Properties**

a)



Semi-permeable  
Membrane

The chemical potential of the solvent is equal in the two chambers at equilibrium

$$b) f_m = \frac{1}{N} \ln \dots + (1 - \dots) \ln(1 - \dots) + \dots (1 - \dots)$$

Gaussian chains, random mixing, no structural changes in the polymer such as blobs.  $f$  is the volume fraction,  $N$  is the chain length,  $\dots$  is the site-site interaction parameter.

Helmholtz (volumetric) free energy per lattice site (persistence unit).

To convert to  $F_m$  you need to multiply by the number of lattice sites in the system,  $\dots$ .

To convert  $F_m$  to the Gibbs Free energy add  $PV$ .

$$c) \dots = kT / V_c (1/N + A_2 \dots), A_2 = (1/2 - \dots)$$

d) At high concentrations the Flory expression gives  $\dots = A_2 kT \dots^2 / V_c$ . The des Cloiseaux expression is  $\dots = (kT \dots^{9/4} / N) (\dots)^{-5/4}$  and  $\dots$  has a  $N^{-4/5}$  dependence.

Then  $A_2$  has no molecular weight dependence consistent with its definition.

$A_2$  depends on  $\dots^{1/4}$ . This is not predicted by the Flory definition of an interaction parameter.

e) The interaction parameter should not depend on composition at all by the classic definition.

Values of the interaction parameter larger than 0.5 lead to problems with expressions of the type  $(1/2 - \dots)$ .