050513 Quiz 7 Polymer Properties

Colligative properties pertain to the number of units (items or molecules) in a system such as molecules in a gas rather than the properties or composition of the units. For this reason, colligative properties are usually associated with an ideal, non-interacting state (since interactions are related to the details of composition of units). The Flory-Huggins equation for a non-interacting system,

$$\Delta G/kT = (n_A/z_A)\ln\phi_A + (n_B/z_B)\ln\phi_B = N\{(\phi_A/z_A)\ln\phi_A + (\phi_B/z_B)\ln\phi_B\} \quad (1)$$

where n_A/z_A pertains to the number of polymer chains of type "A", while $N\phi_A$ pertains to the number of mer units of type "A". (The log terms are obtained from the log of a pressure ratio for ideal gasses.)

a) Compare equation (1) with a similar equation for an ideal gas and explain the differences by pointing out which terms pertains to colligative properties (counting molecules) and which terms pertain to the random positioning of units that lead to a type of pressure (osmotic pressure), i.e. an interaction.

b) Explain how the combination of these two terms in this way can only be true for a Gaussian (Brownian) chain. (Remember that the ideal gas law assumes random or Brownian motion of the gas molecules.)

c) Write equation (1) for a polymer/polymer blend with interactions described by the enthalpic interaction parameter, χ. Sketch this equation (ΔG vs ϕ_A) for $\chi = 0$ and for two lower temperatures ($\chi \sim 1/T$) where the critical point is observed and where phase separation occurs.

d) Equation 1 can be used to obtain an expression for the osmotic pressure by considering the pressure dependence of the chemical potential difference between solvent in the pure state and in a solution of polymer. Define the chemical potential of the solvent (A) in a solution. Write the Flory-Huggins expression for the osmotic pressure with a non-zero χ. Does this equation assume Gaussian chains?

e) It has been observed that the osmotic pressure follows a non-integral power-law dependence in composition above the overlap concentration. Write an expression for this dependence and show how it can be obtained using the concentration blob model.

ANSWERS Quiz 7

Quiz 7

a) $\frac{\Delta G}{kT} = n_A \ln\phi_A + n_B \ln\phi_B$ for ideal gas mixture

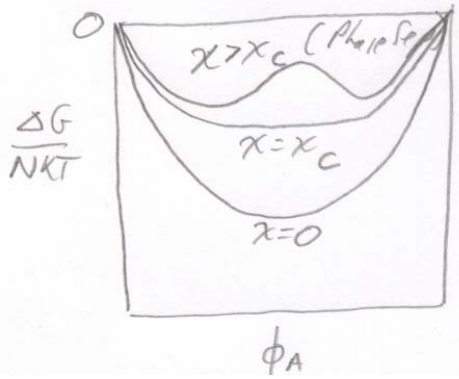
Pressure Ratio Terms

colligative properties

The colligative properties differ since there are fewer molecules for polymers

b) The interaction (pressure) terms indicate random placement of the mer units while the colligative terms indicate connected mer units. Connected mer units that are randomly placed are by definition a random walk.

c) $\frac{\Delta G}{NkT} = \frac{\phi_A}{z_A}\ln\phi_A + \frac{\phi_B}{z_B}\ln\phi_B + \phi_A\phi_B\chi$



d) $$\mu_A = \left(\frac{\partial \Delta G}{\partial n_A}\right)_{n_B, T, \ldots}$$

$$\frac{\pi}{\phi RT} = \frac{1}{M_n} + \left(\frac{1}{2} - \chi\right)\phi \quad (K)$$

Yes, the second term assumes Gaussian Coils

e) $$\pi = \left(\frac{KT\phi}{M_n}\right)\left(\frac{\phi}{\phi^*}\right)^{5/4} \sim \phi^{9/4}$$

Assume the Form

$$\pi = \left(\frac{KT\phi}{M_n}\right)\left(\frac{\phi}{\phi^*}\right)^{P}$$

Dilute Limit — Must depend on ϕ/ϕ^* for $\phi > \phi^*$ by definition

Above ϕ^*

$\pi \neq f(M_n)$ & $\phi^* \sim M_n^{1-3\nu_f} \sim M_n^{-4/5}$

So $P\left(\frac{4}{5}\right) - 1 = 0$

$\therefore \quad P = 5/4$