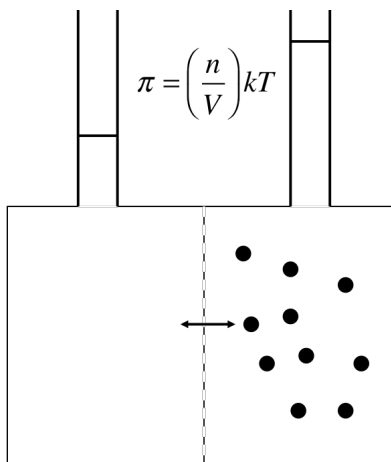


121130 Quiz 10 Polymer Properties

- 1) a) Write the Flory-Huggins expression and explain what it describes, i.e. “the ... free energy of mixing for ... per ... and per ...”.
- b) Explain how the chemical potential for the solvent in a polymer solvent mixture can be obtained from this expression.
- c) For a mixture of two polymers of the same molecular weight, N , what is the value of the critical interaction parameter? Why does this differ from the critical interaction parameter for a high molecular weight polymer in a solvent (1/2)?
- d) Sketch a plot of the Flory Huggins equation as a function of concentration for χ below the critical χ , χ at the critical χ and χ above the critical χ .
- e) For the plot with χ above the critical χ show where the meta-stable region is and explain why it is meta-stable.



- 2) The Figure above shows a model for an osmotic pressure measurement.
- a) What assumptions are necessary for the black dots in order for the equation that is shown in the figure to hold? (These are the same assumptions that are needed for an ideal gas.)
- b) Under what conditions would these assumptions be appropriate to describe a polymer in solution?
- c) How could this expression be modified if we wanted to consider binary interactions for a polymer?

Based on Flory's work, Stockmayer and Fixman² developed an intrinsic viscosity relationship for high molecular weight flexible-chain polymers, neglecting solvent draining effects:

$$[\eta] = K_\theta \sqrt{M} + \frac{0.51 \Phi_o M}{N_A V_s \rho_p^2} (1 - 2\chi) \quad (1)$$

In eq. (1), K_θ is the Mark-Houwink-Sakurada K value at the theta temperature; M , the weight-average polymer molecular weight; χ , the polymer-solvent interaction parameter; V_s , the solvent molar volume; ρ_p , the polymer density; Φ_o , the Flory constant (2.8×10^{23}); and N_A , Avogadro's number.

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- d) Equation (1), above, indicates that the second virial coefficient could be obtained from the intrinsic viscosity. Use this equation to write an expression for the second virial coefficient using the intrinsic viscosity.
- e) Do you agree with the hypothesis that it is possible to calculate the second virial coefficient from the intrinsic viscosity. (You will need to define the second virial coefficient, specifying the interacting entities and other features, and the intrinsic viscosity in order to answer this question.)

ANSWERS: 121130 Quiz 10 Polymer Properties

1) a) The Flory Huggins equation

describes the Helmholtz mixing free energy per lattice site, $kTf_m(\phi)$ for a Polymer/Solvent system in terms of the volume fraction polymer, ϕ , the degree of polymerization, N , and the Flory-

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Huggins interaction parameter, $\chi = (z/2kT) [\epsilon_{pp} + \epsilon_{ss} - 2\epsilon_{ps}]$, where z is the coordination number for the lattice,

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

The features of this equation should be familiar to you. The Helmholtz (Volumetric) free energy change on mixing for a given system is given by the above expression times the number of lattice sites in the system, Ω , $F_m(\Omega, \phi) = \Omega kT f_m(\phi)$.

b)

The chemical potential, here μ_p or μ_s , for one component of a mixture is the derivative of the Gibbs free energy for the system with respect to the number of moles of that component. The Gibbs free energy is related to the Helmholtz free energy by, $G = F + PV$. For the Flory lattice system the volume equals the number of lattice sites time the volume of one site, $V = \Omega V_c$, where $\Omega = n_s + n_p N$ and N is the degree of polymerization. Changing the number of moles of one component in the Flory lattice model, while retaining the number of moles of the other component will result in a change in the lattice size, Ω and the volume fraction ϕ , and system volume, V . This means,

$$\mu_{s: np, T, P \text{ constant}}(\phi, P, T) - \mu_s^0(T) = (\delta F / \delta \Omega)_{\phi, T} (\delta \Omega / \delta n_s)_{np} + (\delta F / \delta \phi)_{\Omega, T} (\delta \phi / \delta n_s)_{np} + PV_c$$

Where $\mu_s^0(T)$ is the chemical potential of the pure solvent.

From the definition of Ω , $(\delta \Omega / \delta n_s)_{np} = 1$; and given that $\phi = n_p N / (n_p N + n_s) = n_p N / \Omega$, so $(\delta \phi / \delta \Omega)_{np} = -n_p N / \Omega^2$. $(\delta \phi / \delta n_s)_{np} = (\delta \phi / \delta \Omega)_{np} (\delta \Omega / \delta n_s)_{np} = -n_p N / \Omega^2 = -\phi / \Omega$. $(\delta F / \delta \Omega)_{\phi, T} = kT f_m(\phi)$, and $(\delta F / \delta \phi)_{\Omega, T} = \Omega kT (\delta f_m / \delta \phi)_{\Omega, T}$, so,

$$\mu_{s: np, T, P \text{ constant}}(\phi, P, T) = \mu_s^0(T) + kT (f_m(\phi) - \phi (\delta f_m / \delta \phi)_{\Omega, T}) + PV_c$$

c) In general, the critical interaction parameter is given by,

$$\chi_{Critical} = \frac{\left(N_A^{1/2} + N_B^{1/2}\right)^2}{2N_A N_B}$$

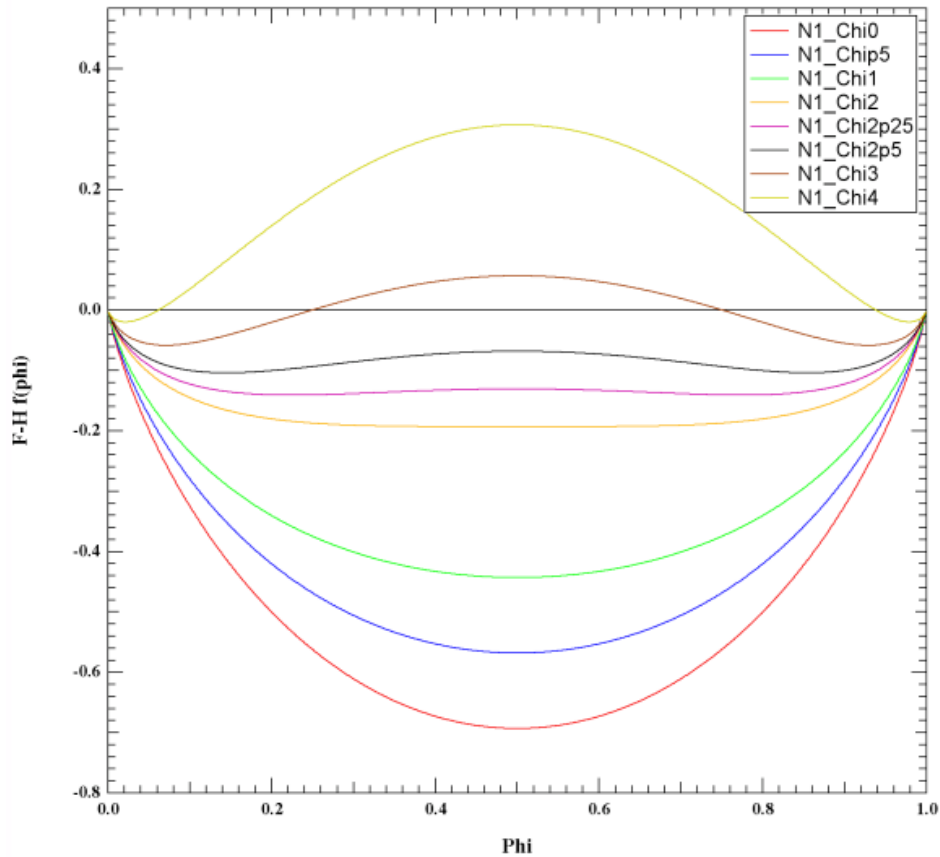
If $N_A = N_B = N$, for a symmetric blend,

$$\chi_{Critical} = \frac{4N}{2N^2} = \frac{2}{N}$$

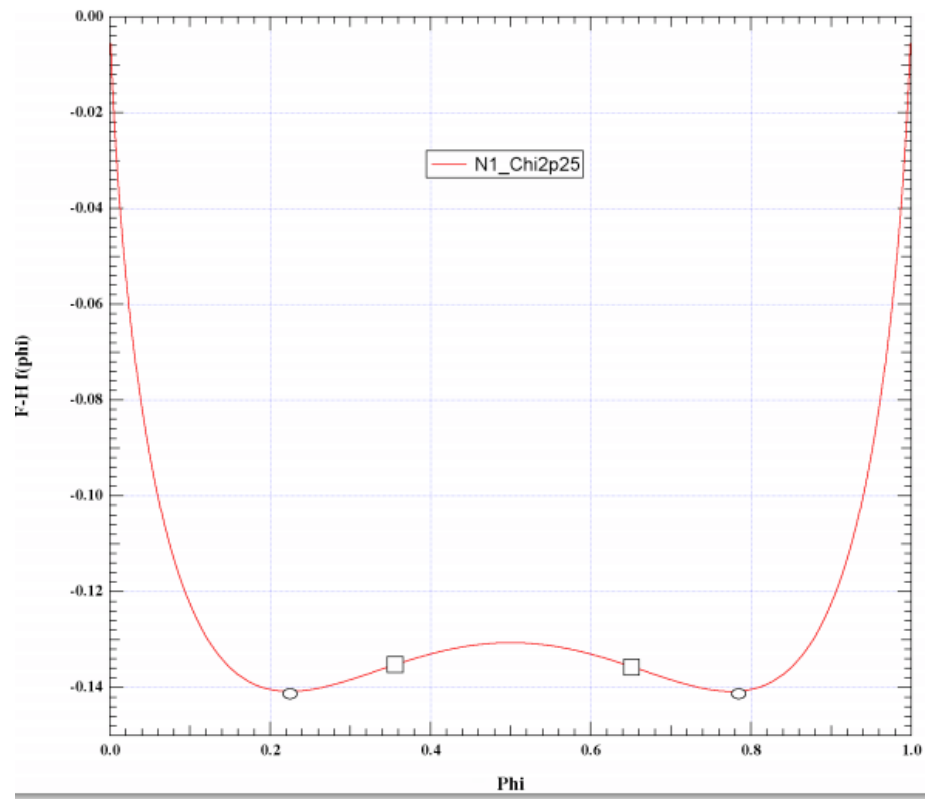
If $N_A = 1$ for a solvent and N_B is large then,

$$\chi_{Critical} = \frac{N_B}{2N_B} = \frac{1}{2}$$

d) Critical chi is 2 in plot below.



e) In the plot below, the meta-stable region is between the circle and square. In this region for small fluctuations in composition the system is stable since the curve is a smile (positive curvature) and the upward fluctuation always contributes more positive free energy than the downward fluctuation. For large fluctuations that over come the central peak all fluctuations decompose. So if a large enough nucleation site is present the system will phase separate but for small fluctuations the system is stable.



2) a) Black dots pass through each other
Phantom dots
Each dot has kT energy

b) dilute conditions Low η_0 (solvent viscosity)

c)
$$\frac{\eta}{\phi kT} = \frac{1}{N} + \left(\frac{1}{2} - \chi \right) \phi \left(\frac{A_2}{A_2} \right)$$

d)
$$A_2 = ([\eta] - [\eta]_0) \frac{N_A V_s \rho_p^2}{2(0.5) \Phi_0 M}$$

e) Second virial coefficient describes the interaction energy for binary interactions of ~~polymer chains~~ monomers & solvents in solution.

Intrinsic viscosity reflects the effect of adding a chain on the viscosity of a solution. $[\eta]$ reflects dynamics of whole chain interactions.

There is no direct link between A_2 & $[\eta]$

A_2 statics; site-site

$[\eta]$ dynamics; chain-chain