

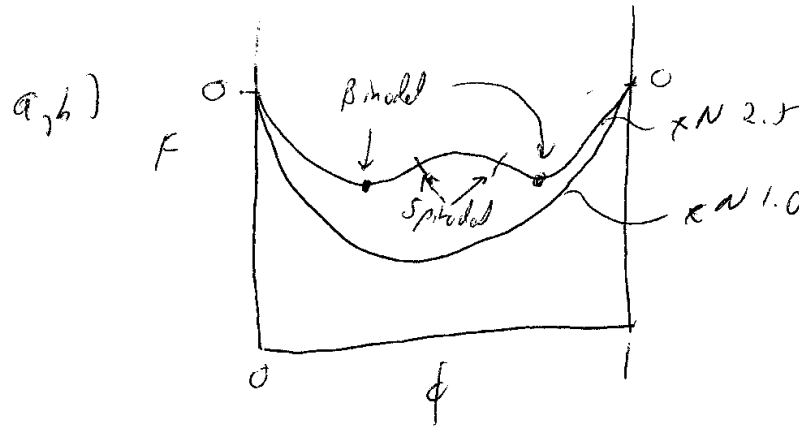
090306 Polymer Properties (Physics) Quiz 8

This week we discussed phase diagrams resulting from the Flory-Huggins equation, spinodal decomposition, nucleation and growth and the Zimm plot.

- 1)
 - a) Sketch the Helmholtz free energy versus composition for a symmetric polymer blend where $\chi N = 2.5$ and where $\chi N = 1.5$.
 - b) In the plot of part a, show from which curve and at what points the binodal and spinodal points are determined.
 - c) Explain how polydispersity might effect this free energy curve and the determination of binodal and spinodal points.
 - d) Explain why one might find phase separation on heating and phase separation on cooling.
 - e) Could both an LCST and a UCST be observed in the same polymer blend? (Explain this)
- 2)
 - a) Sketch an LCST binary phase diagram (T vs ϕ) for a polymer/polymer blend and indicate where spinodal decomposition and nucleation and growth would occur.
 - b) For the nucleation and growth regime, write an expression for the free energy that includes the surface energy.
 - c) In the nucleation and growth regime we consider a size associated with the barrier energy for nucleation and a critical size associated with phase growth. Show how these two sizes could be obtained from the expression in part b.
 - d) For spinodal decomposition we expect two sizes associated with maximum growth and a critical size for phase growth. Explain these two sizes and sketch a plot of growth rate versus q that shows these two size scales.
 - e) Why is spinodal decomposition easily observed in polymers but difficult to observe in metals?
- 3)
 - a) The Zimm equation relies on a relationship between the osmotic pressure and the scattered intensity. Explain this relationship beginning with $I \sim c^2$.
 - b) Obtain an expression for the scattered intensity as a function of concentration using the Flory-Huggins expression for Osmotic pressure.
 - c) Show how the q -dependence of scattered intensity in the Zimm equation is arrived at.
 - d) What is the main flaw of the Zimm approach?
 - e) How can a double extrapolation overcome this flaw in approximation?

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1) a)b)

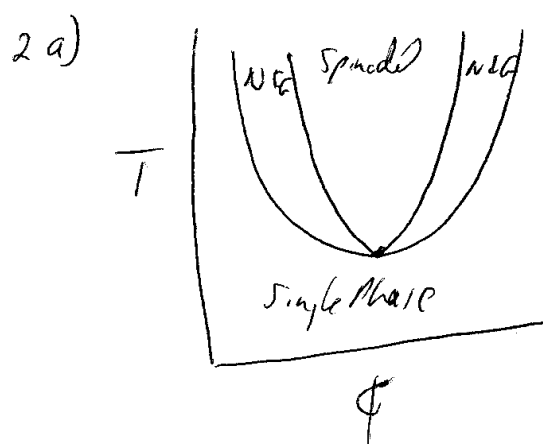


c) Polydispersity leads to a smearing of the phase separation points. We can consider a free energy curve for the highest molecular weight which would correlate with the onset of phase separation. The lowest molecular weight would phase separate at a higher temperature and have a wider miscibility gap. The binodal and spinodal will have a range for a polydisperse sample at a give temperature.

d) Phase separation on cooling occurs with a positive interaction parameter of the form $\chi = B/T$. As temperature rises this positive term in the free energy diminishes in magnitude and eventually the negative entropy of mixing dominates at a high temperature and the system becomes miscible. For phase separation on heating a more complicated interaction parameter is needed of the form $\chi = A - B/T$. At low temperature the negative term dominates over the positive term and the blend is miscible. As the temperature rises the negative term diminishes and phase separation happens. This could occur if there were a specific interaction that broke up with heating.

e) Both an LSCT and USCT can occur in the same phase diagram with a more complicated interaction parameter such as $\chi = -A + B/(T-T_0)^2$. A miscibility gap is also possible. Both of these have been observed in the literature in polymer systems.

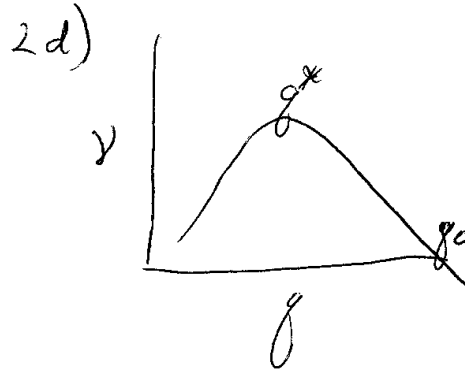
2) a)



b) $r^3 \Delta G = r^3(\Delta H - T\Delta S) + 4r^2\gamma$

c) Set ΔG to 0 for the critical size and set $d\Delta G/dr$ to 0 for the barrier energy size. For the critical size $r_c = 4\gamma/(\Delta H - T\Delta S)$ and for the barrier size $r^* = 8\gamma/(3(\Delta H - T\Delta S))$

d) For the smallest size thermodynamics predicts a negative growth rate (unstable phase) a peak is observed with a maximum growth rate because transport is poor for large size growth.



e) Spinodal decomposition is observed in polymers easily because transport is slow and the molecules are large. In metals transport is very fast and the molecules are very small.

3) a) For low angle scattering ($qR_g \ll 1$) we observe constant scattering intensity related to the contrast between the polymer and the solvent since the Debye function for polymer coils reaches a constant value at very low scattering vector q . Scattering occurs due to binary interference so we consider the concentration at two points. The scattering media has an average concentration $\langle\phi\rangle$ and we consider only deviations from this average concentration. We call this deviation ϕ , and the scattered intensity is then proportional to ϕ^2 in order to account for binary interference, i.e. the probability of contrast at two random points in the solution.

2) a) Consider scattering from a dilute solution of polymer in solvent. For a one phase system such as a polymer in solution the deviation in concentration is caused by thermal fluctuations of the concentration that are dampened by the increase in reduced osmotic pressure π with increasing concentration. The fluctuations are constantly changing in space and time. Then we consider the scattered intensity as proportional to the integral of the derivative or the average change in ϕ^2 , $2\phi\langle d\phi/d(\pi/kT)\rangle$

$$S(q \Rightarrow 0) = 2kT\phi\left\langle\frac{d\phi}{d\pi}\right\rangle \quad (1)$$

b) We have a simple expression for $d\pi/d\phi$ from the Flory-Huggins equation,

$$\frac{\pi}{kT} = \frac{\phi}{N} + \frac{(1-2\chi)}{2}\phi^2 \quad (2)$$

so,

$$\frac{\phi}{S(q \Rightarrow 0)} = \left(\frac{1}{N} + (1-2\chi)\phi\right) \quad (3)$$

c) Zimm used the approximation that equation (1) could be generalized to all q by simply multiplying the contrast factor of equation (1) by the Debye scattering function,

$$S_D(Q) = \frac{2}{Q^2} (Q - 1 + \exp(-Q)) \quad \text{where } Q = q^2 R_g^2 \quad (4)$$

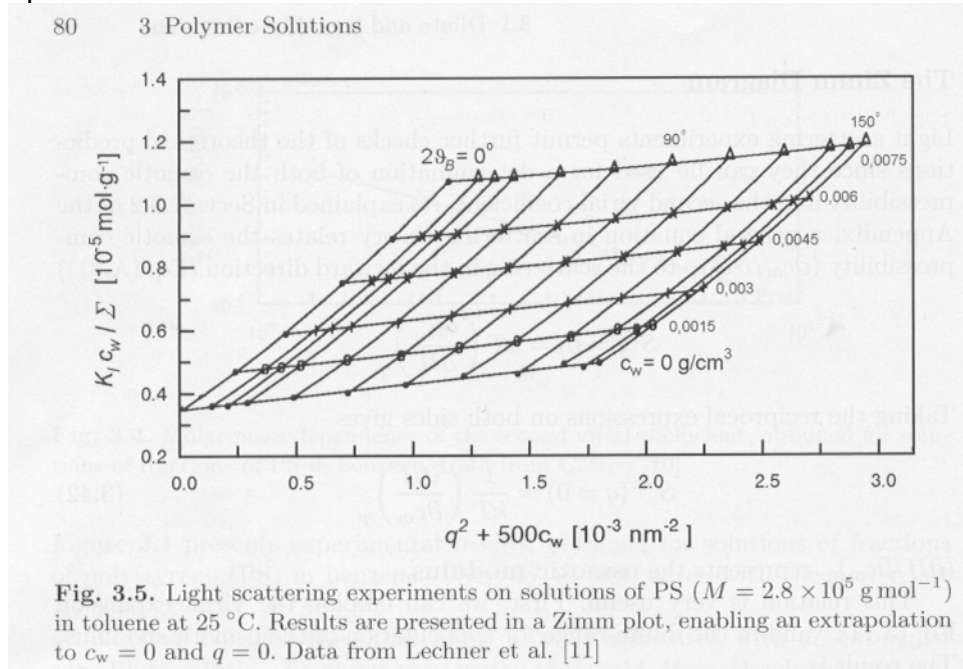
We previously found that equation (4) can be reduced to Guinier's law at low- q ,

$$S_D(q \Rightarrow 0) = \exp\left(\frac{-q^2 R_g^2}{3}\right) \quad \text{and} \quad \frac{1}{S_D(q \Rightarrow 0)} = \exp\left(\frac{q^2 R_g^2}{3}\right) \cong \left(1 + \frac{q^2 R_g^2}{3}\right) \quad (5)$$

Zimm arrived at the following equation,

$$\frac{\phi}{S(q R_g \ll 1)} = \left(\frac{1}{N} + (1 - 2\chi)\phi \right) \left(1 + \frac{q^2 R_g^2}{3} \right) \quad (6).$$

d) e) Equation (6) is based on the assumption that the chain scattering function (equation (5)) is independent of the thermodynamics causing concentration fluctuations (equation(3)) so that the two components contribute to the scattering intensity independently. This is, of course, absurd since the chain structure is determined by thermodynamics. However, the assumption becomes plausible in the limit of $\phi \Rightarrow 0$ and $q \Rightarrow 0$. For this reason Zimm suggested a plot involving a double extrapolation as shown below.



From Gert Strobl, *The Physics of Polymers 3'rd Edition*. $K_I = \frac{4\pi^2 n^2 \left(\frac{dn}{dc} \right)^2}{N_0 \lambda^4}$ and Σ is the scattering intensity.

At $c \Rightarrow 0$ (bottom line) the slope is proportional to $\frac{R_g^2}{3N}$, while at $q \Rightarrow 0$ (left curve) the slope is proportional to $(1 - 2\chi)$ or A_2 . The intercept on the y-axis is proportional to $1/N$, the weight average molecular weight for the polymer.

The Zimm plot is widely used to determine the weight average molecular weight, the coil radius of gyration and the second virial coefficient despite the approximation involved because it is only used in extrapolation.