Quiz 6 Properties, 5/8/01

The Gibbs free energy for mixing for a polymer-polymer blend is given by,

$\Delta G_{mix} = RTn_c ((\varphi_a \ln\varphi_a)/N_a + (\varphi_b \ln\varphi_b)/N_b + \varphi_a \varphi_b \chi)$

a) For a symmetric blend **show that** this expression depends on χN as the governing thermodynamic feature for a fixed composition blend.

b) What is the value of χN for a symmetric blend at the critical point?
Explain how is this value obtained. (explain, **do not** derive)
For a symmetric blend what is the composition at the critical point?

c) **Show a sketch** of ΔG_{mix} versus composition, φ, for a symmetric blend with $\chi N=2$; $\chi N>>2$ and $\chi N<<2$.
Mark the critical point binodal points and spinodal points.
How are the binodal and spinodal defined?

d) From your graph in question c, create a phase diagram for a binary polymer blend.
Indicate the meta-stable region on your phase diagram.
Explain, using blow-ups of your graph in question c, the meta-stable region of the phase diagram.

e) A ice chips in a glass of water at exactly 0°C ($\mu_{ice} = \mu_{water}$) will, over time, fuse in to a solid chunk of ice.
Explain this in terms of composition fluctuations in time.
What happens to the fraction ice in the water if the temperature remains exactly at 0°C?

Answers: Quiz 6 Properties, 5/8/01

a) $\Delta G_{mix} = RTn_c ((\varphi_a \ln\varphi_a)/N_a + (\varphi_b \ln\varphi_b)/N_b + \varphi_a \varphi_b \chi)$

where the number of moles of polymer a is given by $n_a = V\varphi_a/v_a$ and v_a is the molar volume of polymer a, V is the system volume. The degree of polymerization of polymer a is given by $N_a = v_a/v_c$ where v_c is the molar volume of a reference unit. For a symmetric system where $N_a = N_b$ this can be written,

$\Delta G_{mix} = RT(n_a + n_b)(\varphi_a \ln\varphi_a + \varphi_b \ln\varphi_b + \varphi_a \varphi_b (\chi N))$

the term (χN) is the governing term for miscibility.

b) The critical point is where $(\chi N) = 2$ for a binary blend of polymers. This is obtained by setting the second derivative with respect to molar fraction to 0 (spinodal equation) and then setting the composition to 0.5 (the critical point). It can also be obtained by setting the third derivative to 0.

c)

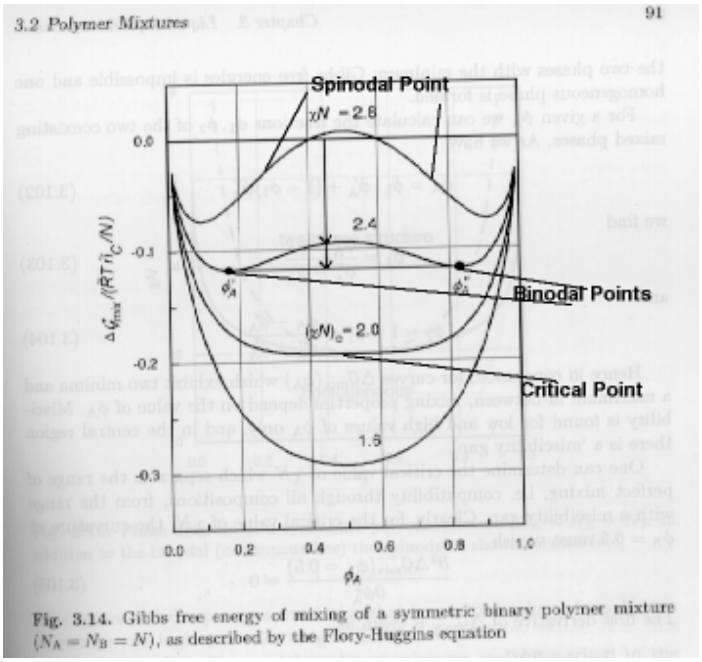


Fig. 3.14. Gibbs free energy of mixing of a symmetric binary polymer mixture ($N_A = N_B = N$), as described by the Flory-Huggins equation

Binodal is the first derivative of the Gibbs FE wrt mole fraction of one of the components = 0. Spinodal is the Second derivative of teh Gibbs FE wrt mfa =0.

d)

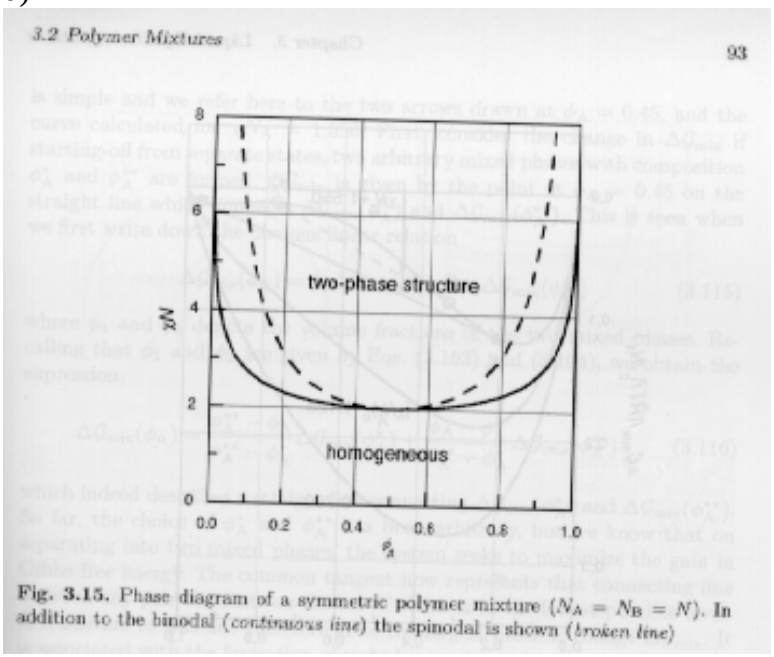
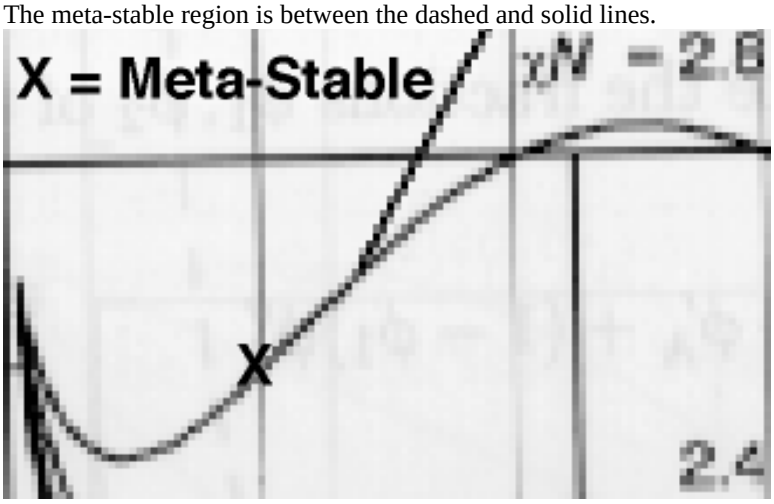


Fig. 3.15. Phase diagram of a symmetric polymer mixture ($N_A = N_B = N$). In addition to the binodal (*continuous line*) the spinodal is shown (*broken line*)

Dashed line are spinodal points, solid line are binodal points, bottom center is the critical point.
The meta-stable region is between the dashed and solid lines.



At "X" a small shift in composition leads to a net increase in free energy but a large shift leads to a net decrease in free energy.

e) The fraction of ice remains constant since the ice and water are at equilibrium. At equlibrium fluctuations between the ice phase and water phase occur leading to an equal conversion from ice to water and from water to ice. This causes the ice to fuse into a solid chunk.