040521   Quiz 8   Polymer Properties

The idea of composition fluctuations is central to understanding the formation and growth of phase structures in a variety of materials including polymers.

a) Explain what a composition fluctuation is. (Include how fluctuations are related to temperature including the behavior at absolute 0, as well as the modulation of fluctuations by transport properties such as the diffusion coefficient or mobility. Also mention the importance of an assumption of incompressibility and the importance of the free energy curve.)

b) For a symmetric polymer/polymer blend write an expression for the Flory-Huggins description of the free energy change on mixing and sketch this free energy change as a function of composition for several values of the interaction parameter below, at and above the critical value. (Explain the symmetry in composition of the curves.)

c) Explain the special condition that exists at the critical point. (Give the value of the critical interaction parameter and explain how the time-dependencies and magnitude of fluctuations depend on the change in free energy curve of question "b".)

d) Sketch the change in free energy curve for $\chi >> \chi_c$ and show how this curve relates to the phase diagram (show the binodal and spinodal curves). Sketch the phase structure you expect in the spinodal and binodal regions of this phase diagram.

e) For the nucleation and growth regime how large must a heterogeneous nucleation site be to nucleate phase growth? Why.

a) A bulk sample has a mean composition, ϕ_0. Locally, and on a certain time-scale, the composition is observed to vary from this mean value. The variation is proportional to the thermal energy in the material, kT. So such fluctuations are expected to disappear as one approaches absolute 0. Fluctuations are governed by incompressibility since, for a binary mixture of A and B, the fluctuations of the two components are linked, $\phi_A = -\phi_B$.

The average magnitude of fluctuations, root mean square, driven by kT is governed by the free energy curve and thermodynamic laws indicating a minimization of free energy for a system at equilibrium. This is because deviations from the mean composition lead to an increase in the free energy for systems in a one phase region of the phase diagram.

Kinetics are also important to the observed magnitude, size and time-scale of fluctuations since dissipation of fluctuations, through transport of material must involve diffusion. The size-scale and time-scale of the observed fluctuations, then, represents a balance between transport laws and thermal energy.

$G = F$ (**Const. T,P and incompressible assumptio**

b)
$$= kT \left[\frac{\phi \ln \phi}{N} + \frac{(1-\phi)\ln(1-\phi)}{N} + \chi \phi(1-\phi) \right]$$

The equation is symmetric about $\phi = .5$ for a symmetric blend since the two entropy terms display symmetric behavior and the enthalpy term is also symmetric.
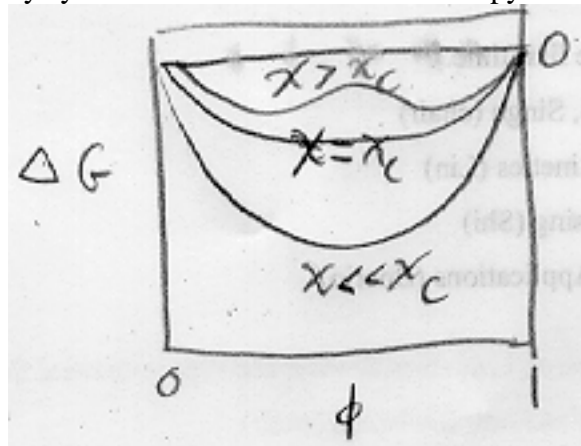
c) At the critical point the change in free energy curve is flat. This means that fluctuations can extend to very large sizes with little change in the free energy. Since the driving force that opposes fluctuations is small, the kinetics of the fluctuations become very slow. Fluctuations at the critical size are thought to be of infinite size and to exist for infinite time in extrapolation from the miscible regime. This is termed critical slowing-down.

d)

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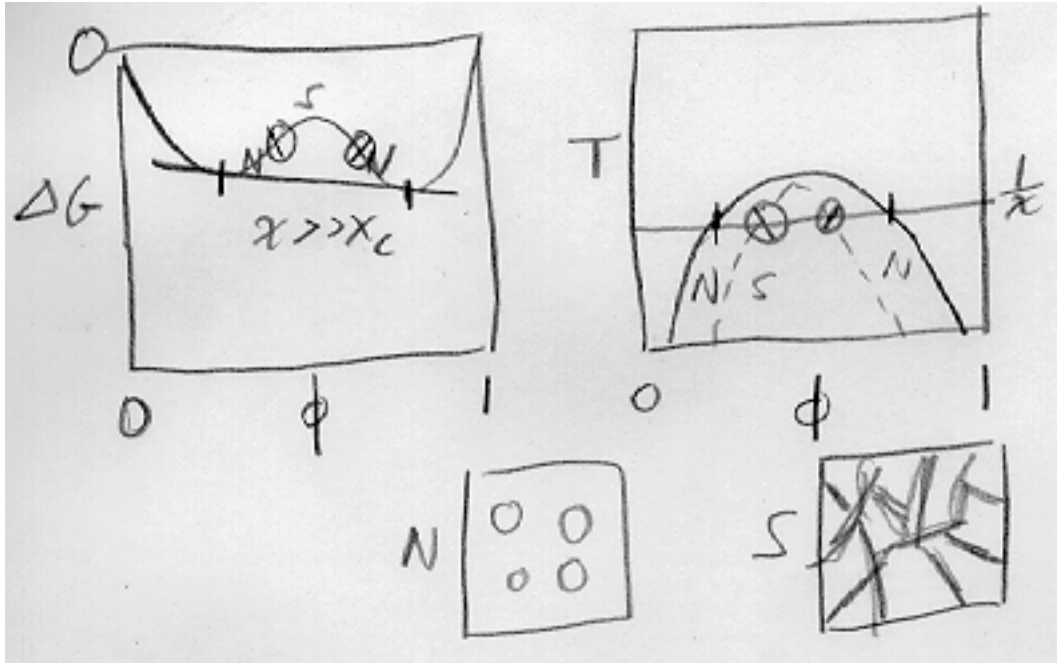
e) We can estimate the critical size for a nucleus using the Gibbs-Thompson approach, considering the free energy of a nucleus as displaying a bulk, , and a surface, , component. This free energy can be either set to 0 to obtain the critical free energy or a derivative with respect to composition can yield the minimum free energy,

$$G = V + A = k_b r^3 + k_s r^2$$

$$\text{for} \quad G = 0, \quad r^* = \frac{k_s}{k_b}$$

$$\text{for} \quad \frac{d\,G}{d} = 0, \quad r^* = \frac{2k_s}{3k_b}$$