030516 Quiz 7 Properties

1) The following figure is from Doi's text, *Introduction to Polymer Physics*,

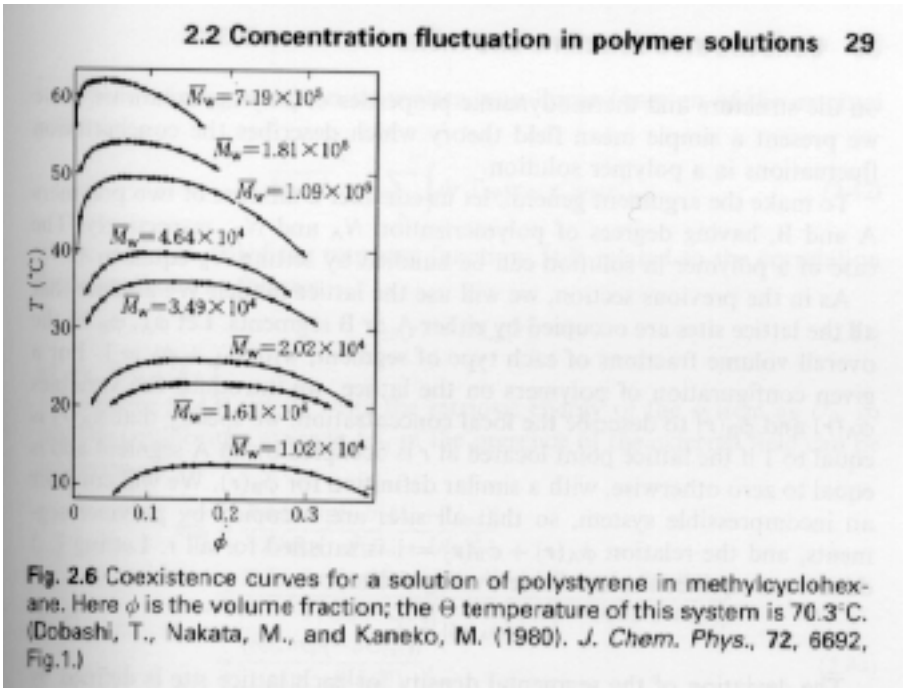

Fig. 2.6 Coexistence curves for a solution of polystyrene in methylcyclohexane. Here ϕ is the volume fraction; the Θ temperature of this system is 70.3°C. (Dobashi, T., Nakata, M., and Kaneko, M. (1980). *J. Chem. Phys.*, **72**, 6692, Fig.1.)

a) What equation would you use to describe the phase behavior seen?
b) Where are the bimodal and spinodal curves in this plot?
c) Explain the behavior of the critical point in **composition** using the equation you gave in the first part of this question.
d) Explain the behavior of the critical point in **temperature** using the equation you gave in the first part of this question.
e) Is this a UCST system? Explain giving the temperature dependence of the interaction parameter.

2) For any system whose "phase behavior" can be defined by a free energy as a function of an "order parameter" (for a polymer blend the order parameter is the mole fraction) we can calculate equilibrium states and critical behavior. Consider a soap foam whose free energy is given by the plot below where the x-axis, Ψ, is the ratio of gas to liquid volume in the foam and the curves are for different ambient pressures. A smaller bubble "phase" displays a lower Ψ.

a) Re-sketch one of the free energy curves and show how you would determine the amount of two "phases" which could coexist at equilibrium.
b) Show how you would determine Ψ for these two "phases".
c) Sketch a curve that shows the critical point for this system.
d) Would you expect to see "critical slowing down" for this system? Explain.
e) Which sketch of the foams (right) corresponds with which free energy curve (left)?

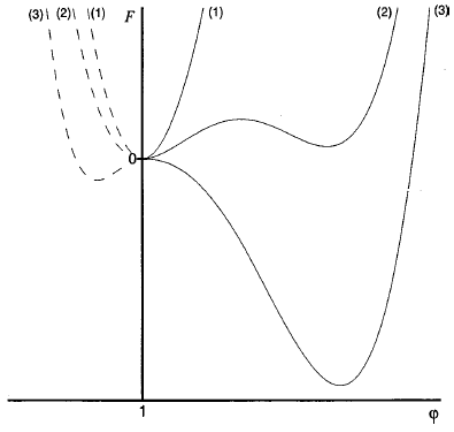

FIG. 6. Schematic plot of $F(\varphi)$ for different values of the volume V (see the text for further details). (1) $V<V_*$; (2) $V_*<V<V_{**}$; (3) $V_{***}<V$.

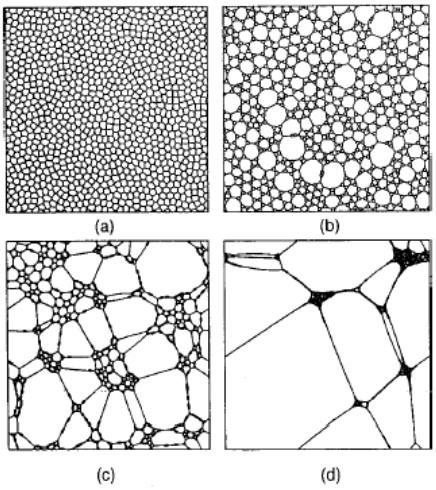

FIG. 4. Configurations of a foam consisting of 1000 bubbles with periodic boundary conditions as the volume is increased. V increases from (a) to (d): (a) $V \ll V_{cr}$; (b) $V \geq V_{cr}$; (c) $V > V_{cr}$; (d) $V \gg V_{cr}$.

Vainchtein, DL, Haef, H *Physics of Fluids* **13** 2152 (2001).

ANSWERS: **030516 Quiz 7 Properties**

1) a) $kTf_m(\varphi) = kT\left[\frac{(\varphi\ln\varphi)}{N} + (1-\varphi)\ln(1-\varphi) + \varphi(1-\varphi)\chi\right]$

setting the first derivative with respect to φ to 0 yields the binodal curve:

$$\chi = \frac{N(1+\ln(1-\varphi)) - (1+\ln\varphi)}{N(1-2\varphi)} = \frac{z\Delta E}{kT_{Binodal}}$$

b) The curves shown are binodal curves. The spinodal curves are within the bimodal curves but are not shown.

c and d) The critical point in composition follows the first and third derivatives set equal to 0. This yields:

$$\varphi_c = \frac{1}{1+\sqrt{N}} \quad ; \quad \chi_c = \frac{K}{T_c} = \frac{1}{2}\left(1+\frac{1}{\sqrt{N}}\right)^2$$

so as N decreases, the critical volume fraction increases and the critical temperature decreases. This is seen by the upper point in the U shaped phase diagrams which decays in T with N and increases in composition with decreasing N.

e) This is a UCST system since the critical point is at the highest temperature of the miscibility limit. The temperature dependence of the interaction parameter follows K/T with K being a positive constant.

2) a) See below. The amount of phase "A" is CB/AB and the amount of phase B is AC/AB following the level rule.

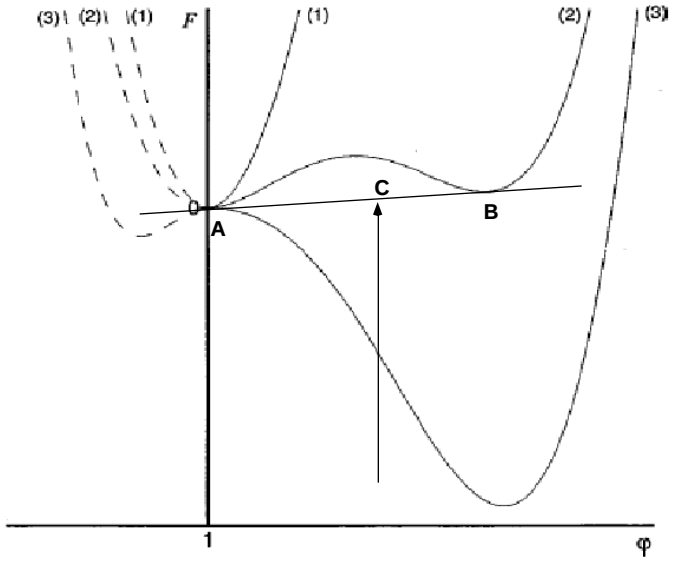

FIG. 6. Schematic plot of $F(\varphi)$ for different values of the volume V (see the text for further details). (1) $V<V_*$; (2) $V_*<V<V_{**}$; (3) $V_{***}<V$.

b) The gas to liquid volume fraction for A and B are given by their values on the plot, i.e. the value at A and the value at B.

c) Curve 1 shows the critical point at $\Psi = 1$.
d) If curve 1 is for the critical point then you wouldn't expect to see critical slowing down since the free energy curve is quite steep and doesn't display a plateau.
e) (a) is curve 1, (b) and (c) are curve 2 and (d) is curve 3.