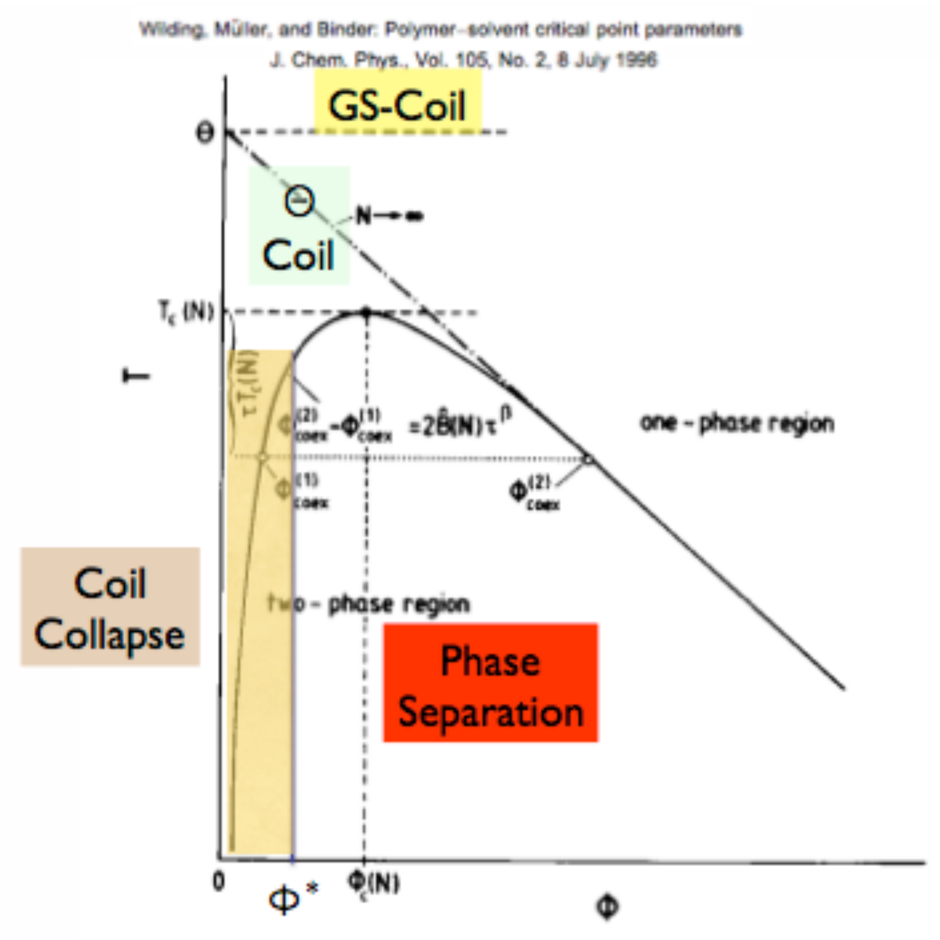
Quiz 7 Take Home Polymer Properties October 11, 2013

1) The following is a plot of the phase behavior for a polymer in solution displaying UCST behavior:



a) What is UCST behavior?

b) The solid black curve represents the miscibility limit or the cloud point curve. Why is this called the cloud point curve?

c) What equation defines the miscibility limit?

d) What does the dashed line represent? Give an equation that describes a linear relationship between critical temperature and composition.

e) Why does the shaded region to the left labeled ‘Coil Collapse’ occur in the region of T and composition that is shown? (What is the lowest effective composition possible for a polymer coil?)

2). Coil collapse can be described using a virial expansion of the energy associated with enthalpic interactions for the isolated chain:

The virial expansion of the enthalpic interactions is given by,

$$U(\alpha) = V_{Coil} kT\left[n^2 B + n^3 C + \ldots\right]$$

a) Explain the origin of the first term. What is B?
b) Explain the origin of the second term. Are C and B positive or negative?
c) The blob model for coil collapse assumes that the chain collapses locally first as temperature is dropped as shown in the following cartoon:

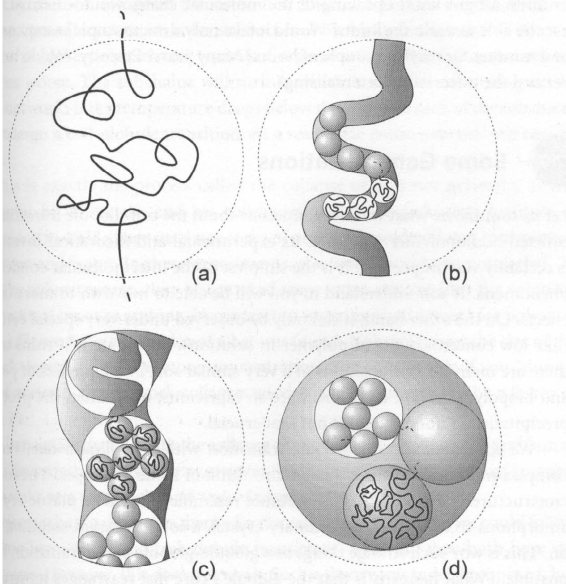


FIGURE 8.6 **A few initial stages of the coil-globule transition. This looks self-similar! (Compare with what we write about self-similarity in Chapter 10).** *Source:* Courtesy of S. Nechaev.

Why does the chain collapse on a small scale first? What is the scaling law of size to mass for the blobs, and what is the scaling law for the entire coil?

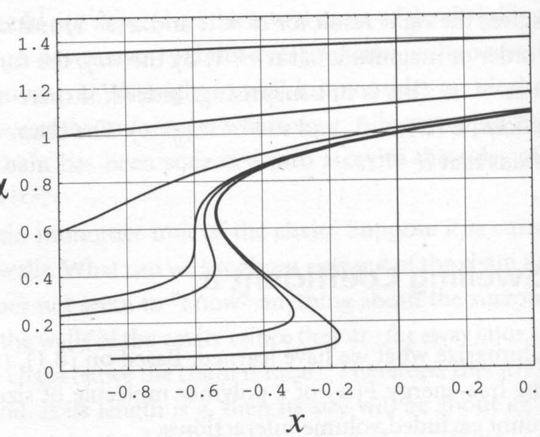
d) The free energy in the blob model for coil collapse is given by:

$$F(\alpha) \sim kT\left(\alpha^2 + \alpha^{-2}\right) + \frac{kTBz^{1/2}}{2\alpha^3 l^3} + \frac{kTC}{\alpha^6 l^6} \qquad (10).$$

Explain each of the four terms in this expression.

e) Use the following three graphs to describe both first order and second order coil collapse transitions. (Define first and second order transitions in the process.)

FIGURE 8.3
The dependence $\alpha(x)$ given by equation (8.7) for different values of y; from top to bottom, the curves correspond to the following values of y: 10, 1, 0.1, 1/60, 0.01, 0.001, 0.0001.



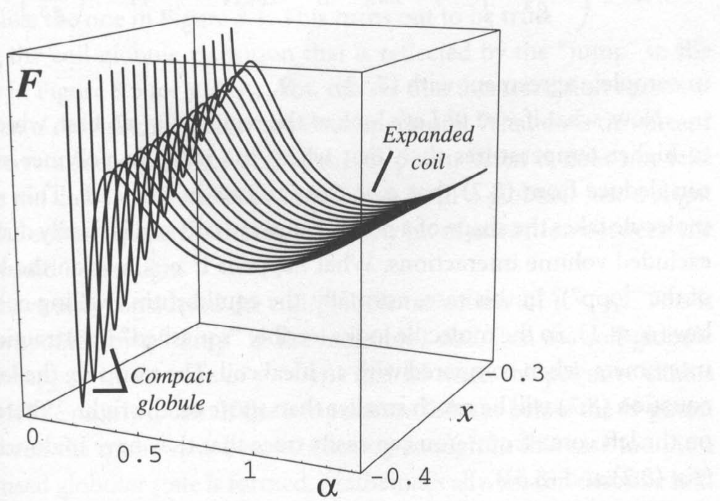
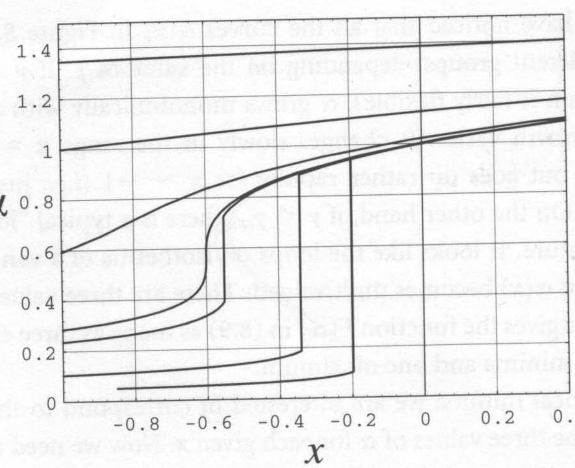


FIGURE 8.4
The dependence $F(\alpha)$ in the case where $\alpha(x)$ is multivalued. As x changes (which can be controlled by, say, temperature change), the shape of the $F(\alpha)$ dependence changes such that one minimum gets deeper at the expense of the other. Deeper minimum corresponds to the more stable state. For this figure, we choose the value $y = 0.001$.

FIGURE 8.5
The curves $\alpha(x)$ in Figure 8.3 are multivalued at some x; in this figure, one solution is selected for each x such that the values of $\alpha(x)$ correspond to the absolute minimum free energy for every x. The values of y are the same as in Figure 8.3.



ANSWERS: **Quiz 7 Polymer Properties October 11, 2013**

1) a) UCST is phase separation on cooling, the critical temperature is at the top of the two phase regime.
b) This is the point where the solution turns cloudy when it is cooled.
c) The first derivative of the free energy change on mixing set to 0 defines the temperature for a given composition at the miscibility limit.
d) The dashed line is the behavior of the critical point as a function of molecular weight.

$$T_c(N) = \Theta/(1+1/\sqrt{N})^2 \approx \Theta - 2\Theta/\sqrt{N}, \quad N \rightarrow \infty, \qquad (1)$$

$$\phi_c(N) = 1/(1+\sqrt{N}) \approx 1/\sqrt{N}, \quad N \rightarrow \infty. \qquad (2)$$

so $$T_c = \theta(1-2\Phi_c)$$

e) Below the overlap concentration the composition of the coil determines the phase behavior since this cannot be diluted with out breaking up the chain. So the phase behavior is locked at the overlap concentration behavior. In this region the chains are dilute so bulk phase separation is not possible. Individual coil collapse occurs.

2) a) The first term is the original enthalpy of an isolated chain in solution. B is $V_c(1/2 - \chi)$.
b) C is the third virial coefficient, it becomes important at high concentration. Goldberg indicates that B is usually negative and C positive.
c) The coil scaling is Gaussian and the blob is 3d. $R \sim z^{1/2}$ and $R \sim z^{1/3}$.
The chain has originally z units and a free energy

$$F(\alpha) \sim kT\left(\alpha^2 + \alpha^{-2}\right) + \frac{kTBz^{1/2}}{2\alpha^3 l^3} + \frac{kTC}{\alpha^6 l^6}$$

were $\alpha \sim 1/n^{1/2}$ and n is z for the chain with no blobs but becomes z/g* as the blobs form. z/g* << z so the free energy of a blob chain is lower than that of the original chain. When the chain reaches the collapse transition temperature and it begins to collapse it can find solubility if it forms blobs since it reduces the effective n, lower-molecular weight chains are more soluble. As the temperature if further dropped it is chains with lower effective n, larger blobs, that remain soluble. Finally the game of reducing the effective molecular weight by growing blobs reaches a limit when the entire coil is a blob and the coil has collapsed. (there may be other explainations for this)
d) The first term is the Gaussian chain free energy, the second term relates to the kT energy of each blob, the third term is the Flory Krigbaum excluded volume expression and the fourth term is the third viral coefficient that becomes important at large concentration.
e) First order transition is one in which the coil size (α) shows a discrete transition in temperature (x). A second order transition is where a continuous transition is observed (second derivative of free energy or slope changes discretely but the first derivative is continuous). In the first plot at large y the curve is continuous but at low y the curve takes on an odd shape where there are three possible values for a given temperature (x).

These three values can be resolved in the second plot has being related to different minima in the free energy. There is only one global minima for a given x y combination, this global minima shows a first order transition at the point where the two minima have the same value. Above that temperature the coil is in theta condition, below that it is collapsed and there is a sudden change in size reminiscent of crystalline melting. The final plot uses the minima in free energy to select one of the three possible α values and shows the values of y where there is a first order transition by the step change in α. The second order transition y values do not show this discrete transition.