Quiz 6
Polymer Properties
February 26, 2016

1) This week we discussed the coil to globule transition. For the case of proteins folding to a native state we considered that the transition should be "first order" while for polymers at the theta state the coil to globule transition is expected to be a "second order" transition.

a) Define first and second order transitions, give examples from other more common transitions.

b) Describe how you would propose to experimentally determine the order for the coil to globule transition for a polymer/solvent pair.

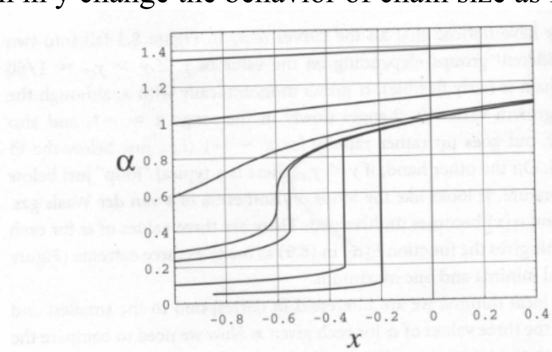
c) The following expressions were proposed for the coil to globule transition:

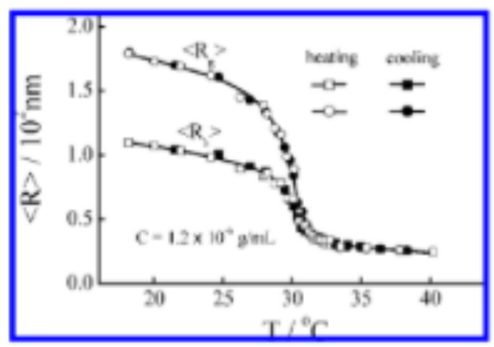
$$F(\alpha) \sim kT\left(\alpha^2 + \alpha^{-2}\right) + \frac{kTBz^{1/2}}{2\alpha^3 l^3} + \frac{kTC}{\alpha^6 l^6} \qquad\qquad R \sim \alpha z^{1/2} l \sim \left(\frac{-C}{B}\right)^{1/3} z^{1/3}$$

What are B and C in this expression and why would they govern the coil size as a ratio in this way? Why is the power 1/3 in the final expression? What is the expected sign for B and for C?

d) In the plot to the left below x is proportional to B and y (the different curves are different y) is proportional to C. Explain the behaviors shown in this plot. Why would variation in y change the behavior of chain size as function of x?

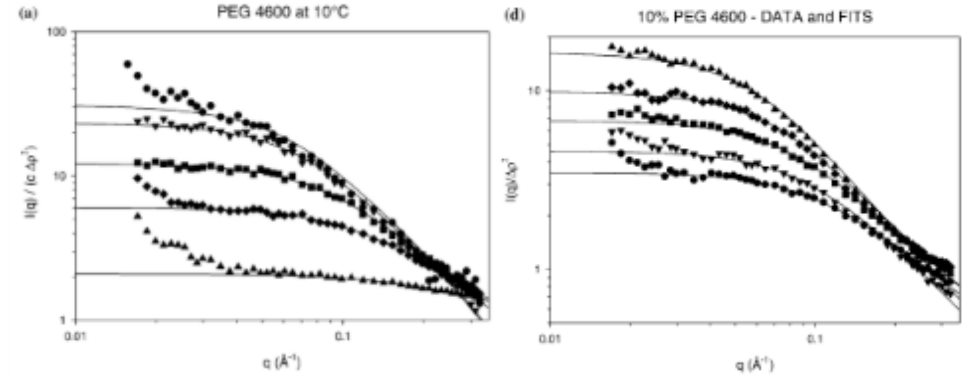
FIGURE 8.5 The curves $\alpha(x)$ in Figure 8.3 are multivalued at some x; in this figure, one solution is selected for each x such that the values of $\alpha(x)$ correspond to the absolute minimum free energy for every x. The values of y are the same as in Figure 8.3.





e) How is the plot to the right related to the plot to the left?

2) Pedersen measured the neutron scattering for polyethylene glycol (PEG) in water as a function of concentration (left) and temperature (right).



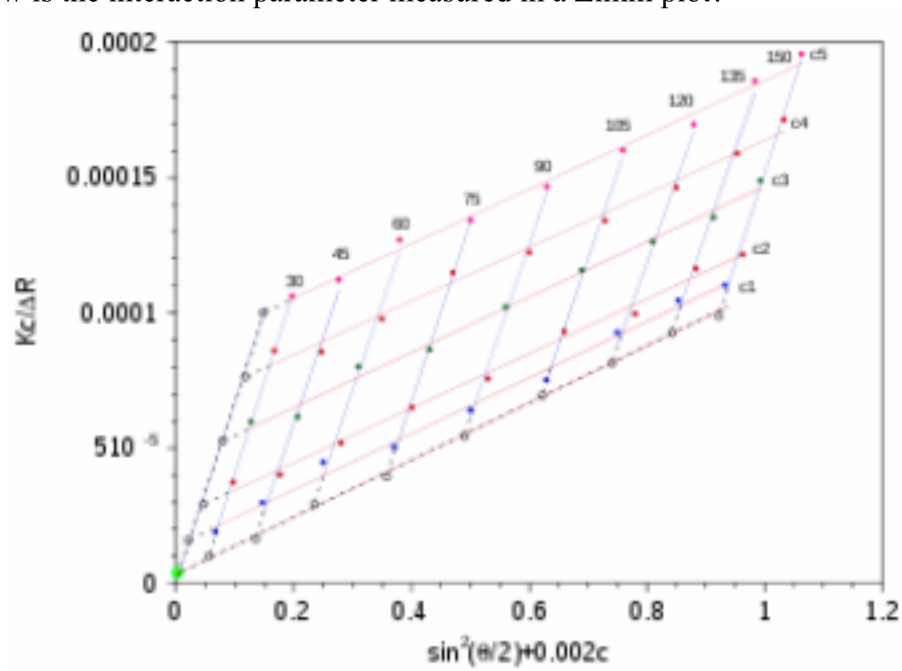
a) Explain why the left plot has intensity/concentration on the y-axis, the right just intensity.

b) Why does the intensity in the left plot at low-q, diminish with concentration?

c) Why does the intensity in the right plot at low-q diminish with temperature?

d) How would you propose to measure the interaction parameter from these plots?

e) How is the interaction parameter measured in a Zimm plot?



ANSWERS:
Quiz 6
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1)

a) Define first and second order transitions, give examples from other more common transitions.
First derivative of the free energy is discontinuous. There is a heat of transition. Melting point.
Second derivative of the free energy is discontinuous. There is no heat of transition. Glass transition.

b) Describe how you would propose to experimentally determine the order for the coil to globule transition for a polymer/solvent pair.
Measure coil size using light scattering and plot as a function of temperature. If the size shows an abrupt change it is a first order transition.

c)
What are B and C in this expression and why would they govern the coil size as a ratio in this way? Why is the power 1/3 in the final expression? What is the expected sign for B and for C?
B is the second virial coefficient, C is the third virial coefficient. $B = V_c\,(1/2 - \chi)$. For coil collapse we expect that B is negative indicating phase separation. C should be positive indicating repulsive interactions as the coil segments approach each other. The power 1/3 reflects $1/d_f$ so the globule is a 3-d object.

d) Explain the behaviors shown in this plot. Why would variation in y change the behavior of chain size as function of x?
x is proportional to B, the second virial coefficient. When this is positive the coil expands, when it is negative the coil collapses. There are two types of collapse that are observed as a function of y. The top curves show a second order transition where there is a gradual change in alpha. The bottom curves show a first order transition where there is an abrupt change in alpha. Variation in y controls the repulsive interaction of chain segments. B is negative so the binary interactions favor phase separation of the chain and the balancing energy of repulsion determines the phase behavior for a given value of x.

e) How is the plot to the right related to the plot to the left?
Alpha is proportional to <R> so the y axis is similar. x is related to temperature through the second virial coefficient. $B = V_c(1/2 - K/T)$. T and x are inverse since K is positive in this system where an LCST is observed.

2)

a) Explain why the left plot has intensity/concentration on the y-axis, the right just intensity.

In the left plot different concentration curves are compared. The curves are made comparable by removing the concentration dependence. The right plot is for a single concentration at different temperatures so it does not need a similar normalization in concentration.

b) Why does the intensity in the left plot at low-q, diminish with concentration?

The curve follows the RPA equation, $1/I(q) = 1/I(q, c \Rightarrow 0) + \nu$. ν is proportional to concentration. This reflects the screening of scattering at high concentrations due to chain overlap.

c) Why does the intensity in the right plot at low-q diminish with temperature?

$\nu = cB = cV_c(1/2\text{-}K/T)$ where K. As temperature changes ν increases leading to a reduction in the intensity at low-q.

d) How would you propose to measure the interaction parameter from these plots?

Fit any of the curves to the RPA equation, $1/I(q) = 1/I(q, c \Rightarrow 0) + \nu$, the fit will give a value for the interaction parameter.

e) How is the interaction parameter measured in a Zimm plot?

It is related to the slope of the concentration curves to the left of the plot. (Steep lines) following the Zimm equation.

$$\frac{\phi}{S(qR_g << 1)} = \left(\frac{1}{N} + (1-2\chi)\phi\right)\left(1 + \frac{q^2R_g^2}{3}\right)$$