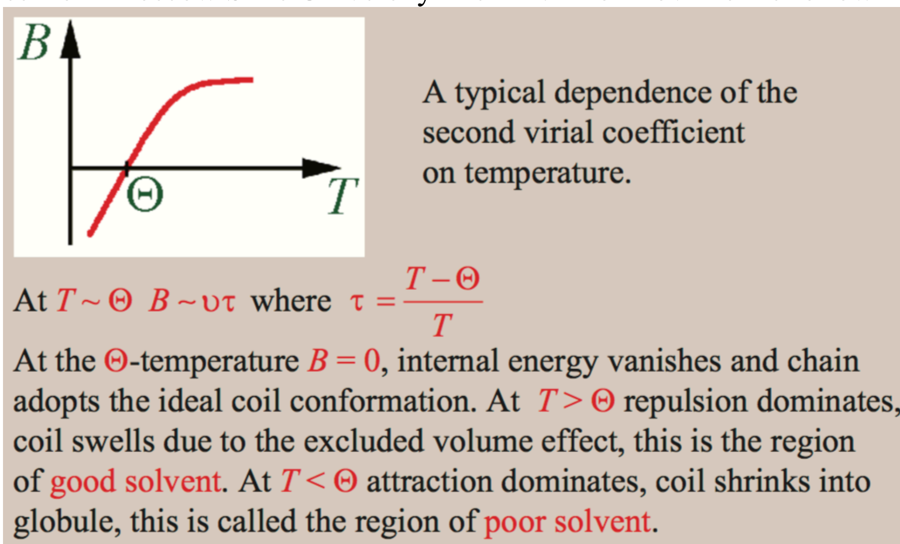
Quiz 6
Polymer Properties
February 22, 2017

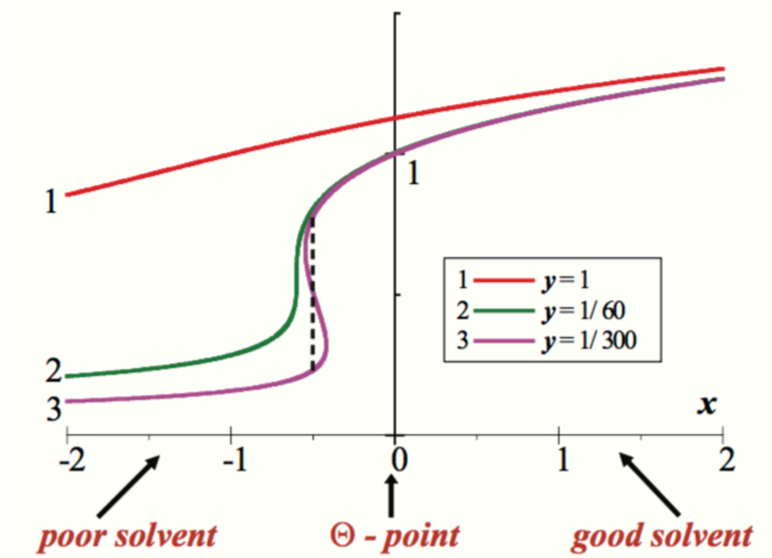
In lecture notes from Moscow State University Alexi R. Khokhlov has the following slide:



a) How does the molecular weight dependence resulting from the Flory-Huggins equation impact the behavior described by Khokhlov?
b) How is this behavior impacted by the overlap concentration, c*? (Sketch a polymer phase diagram.
c) Baysal and Karsaz [*Macromol. Theory Simul.* **12** 627–646 (2003)] state:
    The kinetics of collapse were first considered by de Gennes in 1985.[9] The collapsing chain was viewed as a ''sausage'' of collapsed blobs. With further collapse, the diameter of the ''sausage'' increases and its length decreases.
    Give an expression for the entropy of the collapsed chain based on this statement.

d) Khokhlov has the following slide concerning the parameter $y = K_2 C/l^6$, he uses ν for the hard core excluded volume of a Kuhn unit, a is the Kuhn step length, d is the diameter of the chain:

For $y \ll 1$ the chain collapse is discrete, while for $y \sim 1$ it is continuous. The value of y depends on υ/a ($y \sim \upsilon^2/a^6$). $\upsilon \ll a^3$ corresponds to $y \ll 1$, while $\upsilon \sim a^3$ corresponds to $y \sim 1$. For realistic chain models $y \ll 1$ corresponds to stiff chains, and $y \sim 1$ to flexible chains. Indeed, it can be shown that $C \sim d^3 l^3$, $a \sim l$ and therefore $y = C/a^6 \sim d^3/l^3$. Thus, for stiff polymer chains the collapse is discrete, while for flexible chains it is continuous.



DNA and proteins are considered stiff chains since the Kuhn length is much larger than the chain diameter. Synthetic polymers like polystyrene are considered flexible chains since they have short Kuhn lengths compared to their diameter. Explain why biopolymers display a first order transition in coil collapse while synthetic polymers display a second order transition.

e) What is the mass fractal dimension, d_f, for a globule based on the following slide:

In the limit of small α, $B < 0$ (i.e., in the globular region) the size of the globule is defined by the balance of the following two terms:

$$-\frac{CN^3}{R^3} = BN^2$$

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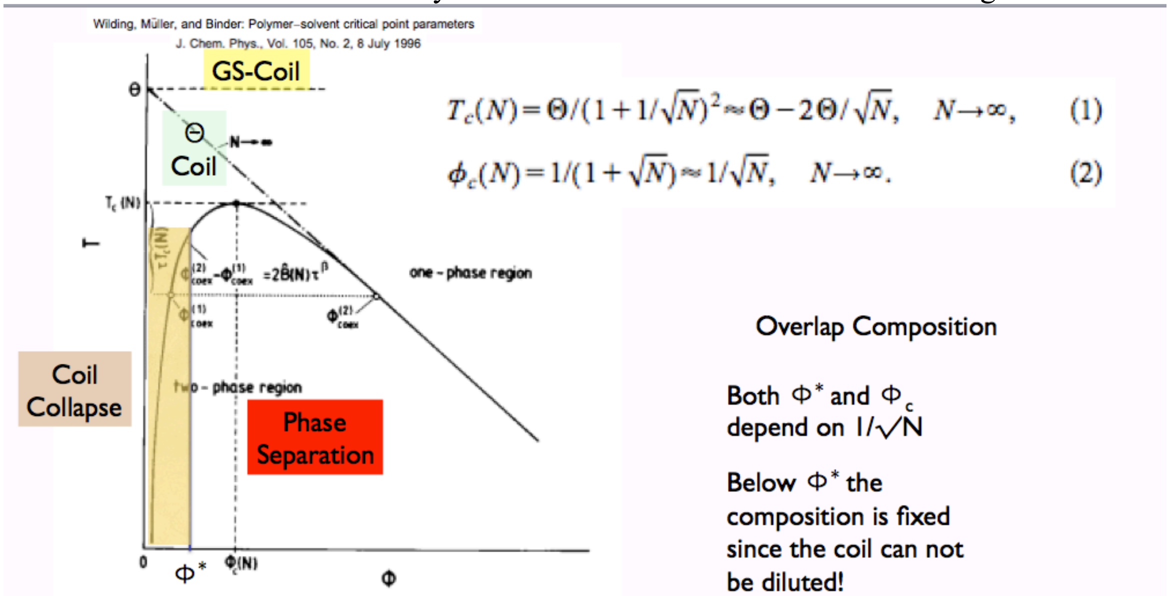
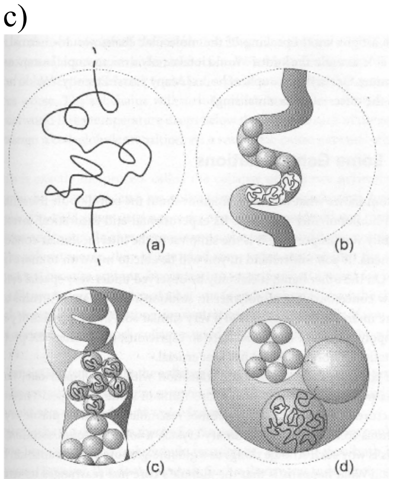
a) The critical temperature and composition are dependent on the molecular weight. So the discussion of Khokhlov is only true in the limit of infinite molecular weight.



b) The overlap concentration is shown in the plot above. The yellow part is essentially of fixed composition since the phase behavior is fixed at the phase separation point in the upper right corner of the yellow rectangle. Below this concentration the coil concentration is fixed so the phase behavior is constant. Above the yellow rectangle the solution is miscible despite being below the theta temperature for the fixed molecular weight N.

c)



$$R^2 \sim g^*$$

$$\left[-TS(\alpha)\right]_{Confinement} \sim kT\frac{z}{g^*} = kT\frac{zl^2}{R^2} = \frac{kT}{\alpha^2}$$

In the absence of confinement (coil collapse) the expression was,

$$\left[-TS(\alpha)\right]_{Expansion} \sim kT\alpha^2$$

and a sum of these terms (approximation),

$$-TS(\alpha) = \left[-TS(\alpha)\right]_{Confinement} + \left[-TS(\alpha)\right]_{Expansion} \sim kT\left(\alpha^2+\alpha^{-2}\right)$$

d) As can be seen in the plot small y leads to a discrete transition along the dotted line. This is for stiff chains such as DNA. For large y near 1 a continuous transition occurs. This is the case of flexible chains since y ~ $(d/l)^3$.

e) The expression can be rearranged to $R^3 = (-C/B)\, N$. This is a mass/size scaling law of the form R^{df} = Mass, so $d_f = 3$.