Quiz 7 Polymer Properties October 9, 2013 (Take Home)

a) Calculate the free energy of an isolated chain exhibiting $\chi = 0$, a chain exhibiting $\chi = ½$ and the free energy difference between these two free volumes (the energy of repulsion). Use V_c = 10 x 10^6, n = 10,000. Plot these three free energies from R = 0 to 15,000 on the same plot using a log-scale for energy and a linear-scale for R.

b) Explain why one of these curves displays a minimum while the others do not. Calculate the relationship between the equilibrium value for R as a function of n for the curve that displays a minimum using the free energy expression. Does this agree with the Flory-Krigbaum result? Does this result rely on the same assumptions as the F-K approach?

c) Grosberg and Khokhlov give an expression for the enthalpic component of free energy that can explain coil collapse and that includes the third virial coefficient, C, (page 24 of the class slides),

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

n is the segmental density in the coil, z/V_{coil}, and $V_{coil} = R^3$. Calculate the energy expression for the third virial term and plot this term as well as E versus R including this term as a function of R for $C = 10^{12}$ and C = 0 and χ = 0, 0.5, 0.6. Plot these six free energies from R = 0 to 15,000 on the same plot along with just the third virial term.

d) Explain the behavior of the third virial term. What does the new minimum in the $\chi = 0$ curve correspond to? What happens when χ becomes larger than ½?

e) On slide 28 the following equation is given:

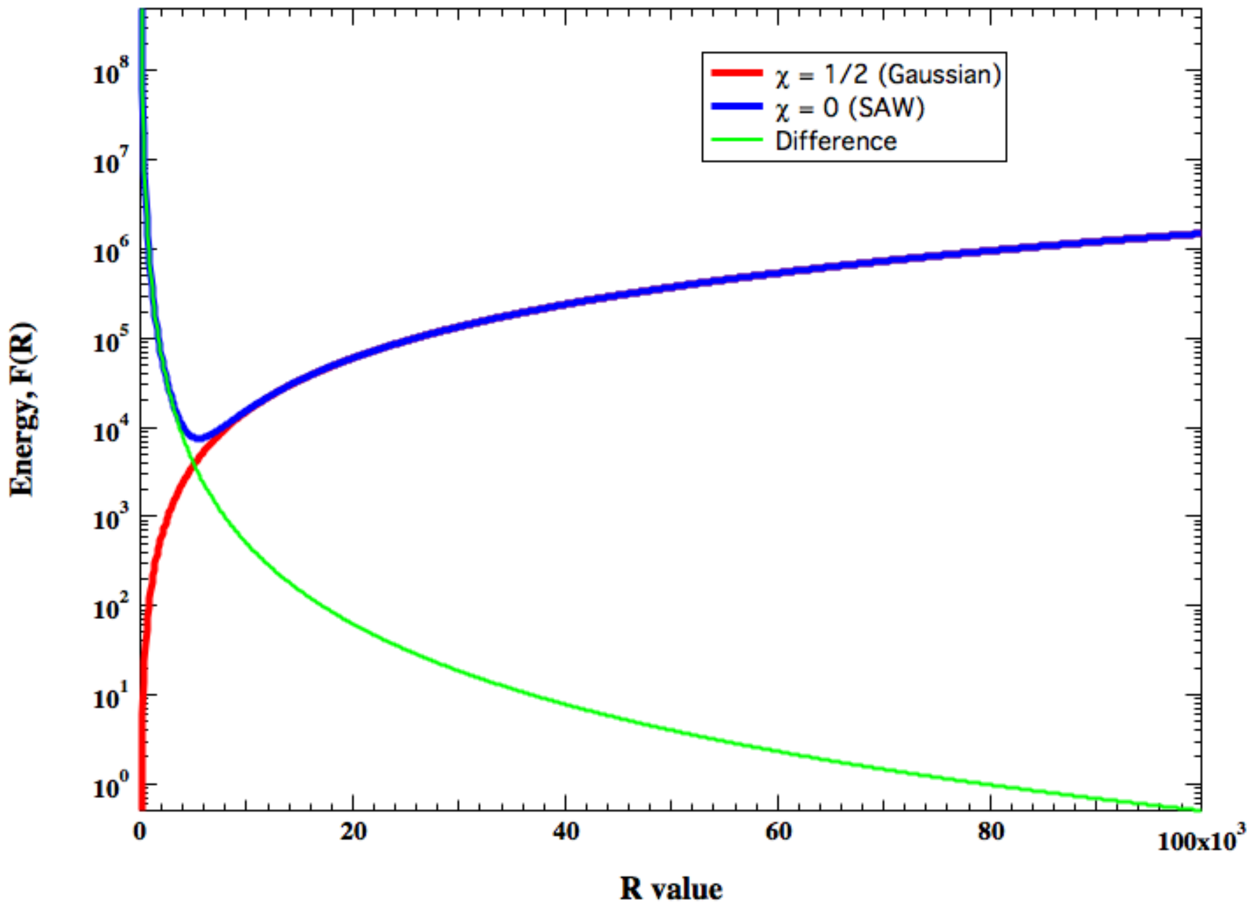
$$F(\alpha) \sim kT\left(\alpha^2 + \alpha^{-2}\right) + \frac{kTBz^{1/2}}{2\alpha^3 l^3} + \frac{kTC}{\alpha^6 l^6}$$

Explain the origin of the α^{-2} term. Why is it necessary for a complete description of coil collapse? What happens to this term when the coil expands? Include this term in a new plot of the conditions for coil collapse in question c to see the effect (Use a prefactor of ~10^7 for this α^{-2} term in your equation).

ANSWERS: **Quiz 7 Polymer Properties October 9, 2013**

1) a) From slide 23

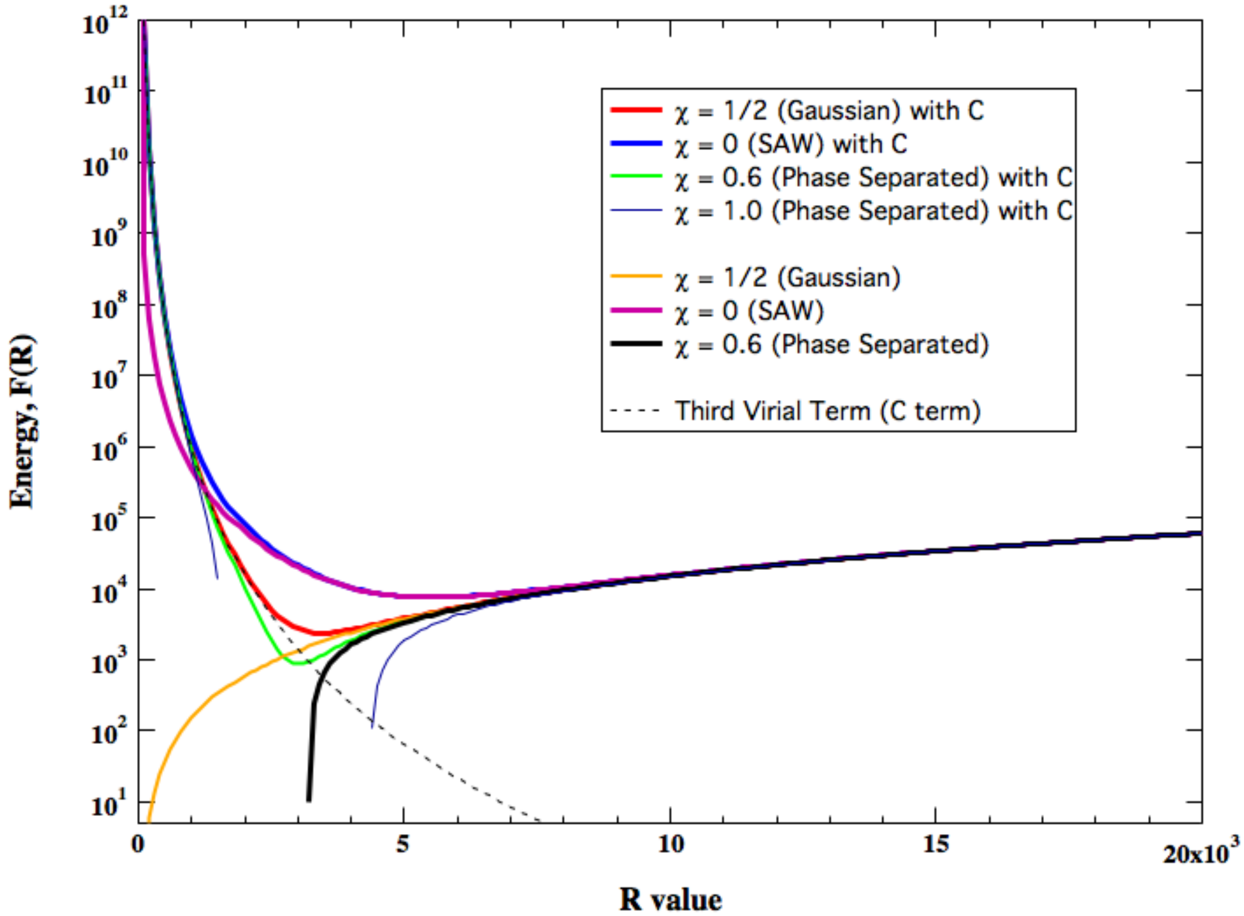
$$F(R)=\frac{z^2V_0(1-2\chi)kT}{2R^3}+\frac{3R^2kT}{2zl^2}=U(R)-TS(R) \qquad (1)$$



b) The SAW χ = 0 curve displays a minimum because the enthalpic (excluded volume) term decays with R while the entropic (Gaussian) term increases with R, having a minimum at R= 0. The balance between entropy that favors a random distribution with the average at R = 0, and the enthalpy that favors expansion with a minimum at the fully extended chain leads to a minimum.

Setting the first derivative of equation (1) to zero and solving for R* (R with the lowest free energy) yields $R^*/l = n^{3/5} (1-2\chi)^{1/5}$. This has the same scaling as the F-K result. It does not rely on the assumption that R^*/R^*_0 is large.

c) To incorporate the third virial coefficient we add to equation (1), $z^3\ C\ kT/R^6$.



d) The third virial term decays with R. It is a repulsive interaction energy that follows the inverse of R^6.
Both χ = 0 and χ = ½ display a minimum due to the repulsion at small R caused by the third virial term. The curve increases at large R due to the entropic term. It is the balance between repulsion at small R and entropic contraction towards the random state with a minimum at R = 0 that leads to a minimum in both of these curves.
When χ becomes larger than ½ phase separation occurs. The energy curve shows a gap in this case (see the χ = 1 curve above).

e) Since the critical point depends on the molecular weight with lower molecular weight chains being more miscible, just below the critical temperature for a chain it can be expected that subunits of the chain are still miscible, that is displaying SAW scaling. At large sizes the chain displays Gaussian Scaling since it is below the critical temperature. So, at temperature drops the regions displaying SAW behavior diminish in size with temperature. We consider the size scale of transition from SAW to Gaussian scaling as the blob size, ξ, and g of such blobs make up the chain. The chain can be considered as being composed of blobs that scale with a Gaussian scaling factor, $R^2 \sim g\xi^2$. Each blob has z/g units each of which has kT energy. So there is an entropy contribution of $kTz/g = kTz\xi^2/R^2 \sim kT\alpha^{-2}$.

The α^{-2} term is necessary because it accounts for a gradual collapse of the coil rather than an abrupt shift. It prevents a discontinuity in free energy from appearing.

When the coil expands the α^{-2} term quickly becomes very small.