Polymer Course – Homework #4 Due **Wednesday, March 27, 2019**

(Most problems from Chapter 7 of Lodge.)

1. Estimate the configurational entropy change ΔS_m (in J/K) that occurs when
   a) 25 g of toluene (T) (M_T = 92 g/mol) are mixed with 25 g of styrene (S) monomer (M_S = 104 g/mol).
   b) 25 g of toluene are mixed with 25 g of polystyrene (PS), M_n = 100,000 g/mol.
   c) 25 g of polystyrene (PS), M_n = 100,000 g/mol are mixed with 25 g of polyphenylene oxide (PPO), M_n = 150,000. (This is one of the rare cases where two high molecular weight polymers are soluble with each other.)

   Note that I'm looking for the entropy change of the *whole mixture* (i.e., for 25 g worth of each component).

2. Problem 7.5 (Remember Flory-Huggins counts pair wise interactions.)

3. Problem 7.4
   - Note that there are three different fractions of PS, meaning there are three different samples with different molecular weights. The original polymer with a broad MW distribution was fractionated into three amounts. Historically fractionation was used to get somewhat narrow MW polymer before controlled polymerization was invented. Each fraction (i.e., sample) will need its own graph of Π/cRT versus c to identify M_n for that fraction from the toluene and MEK data.
   - Be careful of your units. 1 dyn = 1 g cm/s^2 = 10^{-5} N
   - To get reasonable intercepts you may want to consider "a more sophisticated analysis" by including another term in your virial expansion.

4. Problem 7.8
   - Start by considering the impact of changing the temperature on the free energy of mixing and make generalizations about UCST or LCST for when $\alpha > 0$ and $\alpha < 0$.
   - To consider the impact of β, keep in mind that $\chi_c \approx 1/2$ for high MW polymer solutions, meaning that you need $\chi > 1/2$ for phase separation to occur.
   - Answer qualitatively, no calculations or derivatives required.

5. Problem 7.18
   - For a high MW polymer blend, the Gibbs free energy of mixing is

     $$\Delta G_m/kT = \varphi_A/N_A \ln \varphi_A + \varphi_B/N_B \ln \varphi_B + \chi\, \varphi_A\, \varphi_B$$

   - The second and third derivatives of ΔG_m with respect to φ set to zero can be solved to obtain the critical point $\chi_c = (N_A^{1/2} + N_B^{1/2})^2 / (2N_AN_B)$, which for high MW polymer is simply $\chi_c \approx 0$. (For $N_A = N_B = N$, $\chi_c = 2/N \rightarrow 0$ for large N.)
   - Note that for polymer blends the entropy of mixing ΔS_m is so tiny as to be basically zero, so miscibility is entirely determined by the sign of χ.

6. Problem 7.2