Homework 4 Advanced Thermodynamics
Due Tuesday September 20, 2021

In class we discussed the activity coefficient as a measure of the thermodynamics of mixtures.

a) Zhao X, Cheng S, Koh YP, Kelly BD, McKenna GB, Simon SL *Prediction of the Synergistic Glass Transition Temperature of Coamorphous Molecular Glasses Using Activity Coefficient Models* Mol. Pharm.**18** 3439-3451 (2021) used activity coefficients to describe the increase in glass transition for mixtures of two glass forming compounds by associating the increase with the enthalpy of interaction. This topic is important to the efficacy of blends of drugs and to other fields. (Elliot and Lira discuss the two parameter Margules equation and the Redlich-Kister Models in section 11.6 and the Wilson and NRTL models in sections 13.2 and 13.3 among other activity coefficient models (https://www.eng.uc.edu/~beaucag/Classes/ChEThermoBeaucage/Elliot%20Lira%20Introductory_Chemical_Engineering_Thermo.pdf). A summary of the various solution models for glass transition are given by Brostow W, Chiu R, Kalogeras IM, Vasilikou-Dova A *Predition of glass transition temperatures: Binary blends and copolymers* Mat. Letts. **62** 3152-3155 (2008). The Gordon-Taylor model uses the magnitude of the change in the heat capacity to quantify the contribution to the glass transition of various components (https://polymerdatabase.com/polymer%20physics/Gordon-Taylor.html). How is heat capacity related to the enthalpy change through the glass transition (Kirchoff's Law)? How is the enthalpy change related to the Margules parameter A_{12} and to the activity coefficients?

b) Equations 8 and 9 are the Margules one- and two-parameter models. Derive the relationship between the Margules one-parameter coefficient and the acitivty coefficients and give the relationship for the two-parameter model (from Elliot and Lira section 11.6).

c) Wilson suggested that the distribution of binary components might not be uniform since attractive or repulsive interactions could lead to clustering. Compare equation 11 to equation 9 and explain how equation 11 accounts for clustering that is not accounted for in equation 9.

d) What feature of figure 1 indicates the enthalpic contribution to the glass transition for the pure components? From Figure 2 which equation would you use to model this data and why?

e) Luo, Chen, Wu, Cao, Luo and Shi, *Molecular Dynamics Simulation Study on Two-Component Solubility Parameters of Carbon Nanotubes and Precisely Tailoring the Thermodynamic Compatibility between Carbon Nanotubes and Polymers* Langmuir **36** 9291−9305 (2020) used the Hildebrand and Hansen solubility parameters to quantify the compatibility between polymers and carbon nanotubes. They used molecular dynamics simulations and the COMPASS force field. The solubility parameter is obtained from $\delta = \sqrt{CED} = \sqrt{(E_{coh}/V)}$ and E_{coh} for various interactions are calculated and averaged using a quadratic mean, $x_m^2 = x_a^2 + x_b^2$ from the simulation results. The solubility parameters are compared with those obtained from the Flory-Huggins equation as described in reference 46. The smaller the R value the better the dispersion of SWNT in the polymer. Explain how the solubility parameter is related to the enthalpy of interaction. Interactions can be attractive or repulsive, how is this accounted for in the solubility parameter approach?

f) Explain the relationship between the Hildebrand, Hansen and the potentials available from the COMPASS simulations. How do these parameters relate to the Flory-Huggins

interaction parameter, χ? Explain the relationship between the Flory-Huggins interaction parameter as defined in equation 2 and the van der Waals expression for the second virial coefficient.