# Homework 4
# Polymer Physics
# Due Monday September 19, 2022

Venetsanos F, Anogiannakis SD, Theodorou DN *Mixing Thermodyanmics and Flory-Huggins Interaction Parameter of Polyethylene Oxide/Polyethylene Oligomeric Blends from Kirkwood-Buff Theory and Molecular Simulations* Macromolecules **55** 4852-4862 (2022) study the mixing of dodecane and an ether analogue by performing a molecular dynamics simulation, calculation of the three pairwise correlation functions, determination of the Kirkwood-Bluff integrals (*KBI*) of these correlation functions, $G_{ij}$, and use of the *KBI*'s and KB theory to determine the activity coefficients, excess Gibbs free energy, enthalpy and entropy of blends and the Flory-Huggins interaction parameter. These are compared with a Monte-Carlo simulation by Chen (2018) and an experimental measurement by Treszczanowicz (1986) with good agreement. Venetsanos also calculates the first Legendre polynomial for orientation (Hermans Orientation function) for the chain orientation with interesting results.

a) The webpage gives a link to a Wikipedia page on the KB theory and to a book by Ben-Naim *Molecular Theory of Solutions* (same author as the entropy book). Explain what a binary correlation function is and describe briefly how KB theory can obtain the reported thermodynamic parameters from binary correlation functions. How does this approach differ from the Monte-Carlo approach of Chen (2018) on the same system?

b) Equation 2 is the Flory-Huggins equation. How does it differ from the Hildebrandt equation for mixtures of low molecular weight materials? What is the reason for this difference. For this system where $N_1 = N_2 = 12$ is there any difference? Here $\chi/v^*$ has a value of about 0.003 $Å^{-3}$ which is positive indicating enthalpic demixing. Why is this a miscible system?

c) Derive equation 9. Show how equation 14 is the same as the Gibbs-Duhem equation from the first week.

d) Explain the three parts of the following statement in the first column of 4857: "*For infinite dilution,* ***the excess component's activity coefficient converges to unity*** *(xi → 1, γi → 1), while for all other compositions, both γ1 and γ2 have a value greater than unity (γi > 1),* ***denoting positive deviations from ideal solution*** *behavior for the oligomeric blends studied, an indication of unfavorable interactions between chains of different species in relation to same species interactions. The above mentioned* ***will consequently result in a positive excess Gibbs energy***"

e) Explain equation 22. What values can "S" have, and what do they indicate about the chain orientation?