Homework 4
Polymer Physics 2023
Due Tuesday February 7 at noon
(Please send one email with a **pdf** attachment to beaucag@uc.edu)

Chremos A, Douglas JF, Basser PJ and Horkay F *Molecular dynamics study of the swelling and osmotic properties of compact nanogel particles* Soft Matter **18** 6278-6290 (2022) study the swelling and osmotic pressure of "nanogel" particles which are highly crosslinked regular network molecules with $N_b = 10$ branch points in each direction $f = 4$ arms per branch point and $M = 25$ Kuhn units (beads) per arm for a total molar mass of $M_w = N_b^3 M_{w,star} = N_b^3 (f M +1) = 101{,}000$. The branched molecules have an attractive strength between beads of $\lambda\,\varepsilon$, where λ varies from 0 to 1.

a) Chremos uses the following equation to calculate the osmotic pressure: $\Pi = \rho kT + W/V$. Explain the origin of this equation (top of first column page 6281) and equations (6) and (7) page 6284. Explain what a pair virial function is, $w(r_{ij})$, how it is related to the pairwise potential, U_{ij}, and how it can be used to calculate the internal virial coefficient, W. How is W related to the second virial coefficient B_2?

b) Determination of the θ-point in λ and T is important to finding universal behavior in this system (see x-axis in Figure 3, 4, and 5). Cremos uses two methods to determine the θ-point. Briefly explain these two methods and how they differ. Why is $\lambda_{\theta gel} > \lambda_{\theta linear}$ and $\theta_{gel} < \theta_{linear}$? Describe the temperature and λ dependence for of the x-axis in Figures 3 and 4. (Flory-Krigbaum indicates $(\frac{1}{2} - \chi)$ as the parameter of interest ($\chi = B/T$) which equals 0 at $T = \theta$. On page 6280 second column Chremos relates T and λ.

c) The Flory-Krigbaum equation predicts $R_g/R_{g,\theta} = (n^{1/2} V_0(1/2-\chi)/b^3)^{1/5}$, while equation (4) for the gel bears no resemblance to this function. Figure 4 shows a plot similar to what was shown in class for FK. Show how the FK equation is obtained and critique the use of equation (4) versus use of the FK equation or a modified FK equation. At what point of the derivation of the FK equation is it inappropriate for a gel nanoparticle?

d) In Figure 6, the reduced radius of gyration, $R_g/R_{g,\rho=0}$, is plotted as a function of ρ/ρ^*. Define R_g, how does it compare with the end-to-end distance? What is the end-to-end distance for the nano gel? Why would R_g depend on concentration or monomer density? What is the meaning of $\rho/\rho^* = 1$? Why does the plateau not occur at $\rho/\rho^* = 1$? Explain the meaning of the -1/3 power law slope.

e) In Figure 8, $\hat{\rho} = \rho M_w B_2$ from equation (8) is used as the x-axis. The y-axis is also from equation (8). Explain the origin of the two axis (use the Flory expression for osmotic pressure as a starting point). What is the meaning of $\rho M_w B_2 = 1$? What would this plot look like if only the second virial term, B_2, were sufficient? At high concentrations, above $\rho M_w B_2 = 1$ the gel particles look the same as star molecules. Why is this the case?