Homework 9
Polymer Physics 2023
Due Tuesday March 21 (two weeks) at noon

(Please send one email with a **pdf** attachment to beaucag@uc.edu
The file should be called: **HW 8 Group x Last Name_Name_Name_Name.pdf**)

Indei T, Narita T *Microrheolgical study of single chain dynamics in semidilute entangled flexible polymer solutions: Crossover from Rouse to Zimm modes.* J. Rheol. **66** 1165-1179 (2022) give a fairly comprehensive description of the scaling regimes for dynamic rheology in semi-dilute solutions highlighting measurements using macro and micro-rheological tools. Indei uses a Couette viscometer (Figure 2), and a cone and plate rheometer (Figures 3, and 5) for macro-rheology and a diffusing-wave spectroscope (Figures 4-7 and 9) for micro-rheology measurements which extends the frequency range by three orders to 10^5 rad/s allowing observation of the transition from Rouse to Zimm modes as concentration is increased, Figure 1 and the description on page 1169. For concentrations below the overlap concentration, and at times longer or frequencies less than τ_Z or $1/\tau_Z$ the Newtonian flow is observed. Above this time or below this frequency, Zimm behavior is observed following the Mark-Houwink equation (constant viscosity with frequency, the Newtonian plateau), region I in Figure 1. Above this frequency at concentrations below the overlap concentration shear thinning occurs (power-law fluid), region II in Figure 1. These are the blue curves in Figure 1. At about $\eta_{sp} = 1$ the overlap concentration is reached and at higher specific viscosity concentration blobs form, the chains become smaller, and the Newtonian plateau occurs at a lower frequency. The power-law decay has two regions in the green curves, one for relaxation of the chain of concentration blobs (region III) and at higher frequencies internal power-law fluid behavior within blobs similar to that of the dilute solution coils (region II). This transition occurs at $\eta_{sp} = 1$. At higher viscosities (concentrations) the entanglement viscosity/concentration is reached and a third power law-regime is introduced for relaxation of the entangled network at low frequencies, region IV in Figure 1. Indei uses a time-concentration shift which is similar to the time-temperature shift to construct master curves at a fixed concentration in order to access a wide frequency/time range to observe these power-law transitions, Figures 3, and 5-7 (Daga VK, Wagner NJ *Linear viscoelastic master curves of neat and laponite-filled poly(ethylene oxide)-water solutions* Rheol. Acta **45** 813-824 (2006)).

a) Figures 3 and 11 of Daga validates the Cox-Mertz rule. Explain the importance of this rule to Indei's work.
b) Derive Indei's equation 4.
c) In Figure 3, left, the inset shows the frequency and modulus at the crossover frequency as a function of concentration. What is the crossover frequency and what does it represent. Why is this a useful point for shifting the curves in modulus and in frequency for the time-concentration superposition of the curves? What is (*or is there*) an equivalent point used for the shifts in time-temperature superposition?
d) Figure 5 shows "Maxwell-like behavior". Explain what this means and how Figure 5 demonstrates this. Why is it Maxwell-like and not Maxwell behavior?
e) Explain how the inset to Figure 6 right demonstrates Rouse behavior at times below 10^{-2} s. How does Figure 9 right show a transition from Newtonian plateau, to Rouse, to Zimm behavior? Explain from a structural perspective why this sequence occurs.