

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 *Microrheological 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 spectroscopy (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.