

**Homework 1**  
**Polymer Physics 2023**  
**Due Tuesday January 17 at noon**

(Please send one email with a **pdf** attachment to beaucag@uc.edu)

Schaefer C, McLeish TCB, Theoretical rheo-physics of silk: Intermolecular associations reduce the critical specific work for flow-induced crystallization *J. Rheo.* **66** 515-534 (2022) describes molecular dynamics simulations intended to mimic the crystallization of silk polymer in the spinneret of a silk worm where pH changes control binding groups between polymer chains. Highly elongated chain crystals are used commercially to produce high strength materials such as Kevlar and gel-spun ultra-high molecular weight polyethylene. Silk is one of the strongest materials (Shao Z, Vollrath F *Surprising strength of silkworm silk* *Nature* **418** 741 (2002)) on the order of 1 GPa and 160 kJ/kg. The Schaefer paper is a fairly complicated and very long paper but is interesting from a number of perspectives so it is worth looking at even though you will not be able to understand all of this paper at this stage in the course. In particular, skip section II B.

a) Figure 1 presents the hypothesis for the paper. Give a general description of the motivation for the work and a description of how this is implemented in the simulations, Figure 2.

b) Equation 5 gives an expression for the force to extend a single Gaussian chain. Derive the first part of this expression (not the  $k_s$  part). Why is the  $k_s$  modification necessary?

c) On page 520 Schaefer uses the Weissenberg number to describe the dynamics of the silk polymer chains. What is the Weissenberg number,  $Wi$ , and why is it of importance to polymer rheology?

d) In Figure 4 why is MSD linear in time? Explain the behavior seen in Figure 5a compared to Figure 4. In figure 5b what can you say about a material where  $G'' > G'$ ? Why would there be a transition to  $G' > G''$ . What does the frequency where this occurs pertain to? What is  $\tau_R$ ?

e) Figure 7 shows the alignment of chains in extensional flow for non-sticky chains and chains with stickers. Explain how this variation could enhance flow induced crystallization with the presence of stickers.