

Homework 5
Polymer Physics 2023
Due Tuesday February 14 at noon

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

The file should be called: **HW 3 Group x Last Name_Name_Name_Name.pdf**)

We discussed polymer coil collapse from the perspective of Grossberg this week. Liu J, Gou H, Gao Q, Li H, An Z, Zhang W *Coil-Globule Transition of a Water-Soluble Polymer* *Macromolecules* **55** 8524-8532 (2022) discuss the observed structure of a water soluble polymer (poly(N-isopropylacrylamide) PNIPAM) as it undergoes the coil to globule transition (CGT) at the lower critical solution temperature and under Debye charge screening due to the addition of salt. Liu uses “magnetic tweezers” to apply strain to single chains of PNIPAM undergoing the CGT in order to quantify the transition, and uses an AFM (see the graphical abstract) to image the actual structure which seems to differ somewhat from that proposed by Grossberg in the finer details, but, overall, bears a strong resemblance to the theoretical proposition of local coil collapse into “beads”.

- a) Sarkar R, Rybenkov VV *A Guide to Magnetic Tweezers and Their Applications* *Front. Phys.* **4** 48 (2016) briefly explain the magnetic tweezer approach. Explain this technique and show comparisons between Liu and Sarkar’s results, particularly Sarkar’s Figures 6, 7, 10, and 11. Look at Liu’s supplemental materials file where he explains the nuances of the technique as well as Liu’s paper.
- b) Explain the Grossberg theory as described in class for the CGT. <https://www.eng.uc.edu/~beaucag/Classes/Properties/Slides/PolymerPropSlides2c.pdf> slides 36 – 50, and “Giant Molecules” Chapter 9. What nuance to this theory is Liu proposing?
- c) The lower-critical solution temperature was mentioned in class with respect to poly(vinyl methyl ether) in water or in blends with polystyrene. Write the Flory-Huggins equation (FHE) and explain how an LCST is possible using the FHE. What is the physical basis for modifications to the χ -parameter to obtain an LCST? In addition to a thermally driven LCST, Liu uses addition of salt to obtain a CGT. How could this be incorporated into the FHE to describe salt driven phase separation? (What term would be modified and how would it be modified?)
- d) Liu’s conclusion is that:

The transition can be divided into three steps: rapid nucleation, medium-speed adjacent mergence, and the slow bead stacking process. Interestingly, the size of the nucleus is not random but corresponds to ~ 31 repeat units.

Liu’s CGT doesn’t result in a spherical globule but in a stacked structure. Explain Liu’s three steps and give experimental evidence that Liu uses to support his proposition. Does the adjacent mergence process and fixed minimum nuclei size make sense compared to Grossberg’s gradual growth of random sized beads? Is there any real difference?
- e) The CGT in PNIPAAAM has been proposed as a tool to produce artificial muscles. Explain how the mechanical properties of PNIPAAAM can be “*tuned by external stimuli*” towards this end.