Homework 14
Polymer Physics 2024
Due Thursday April 25 at noon
500 Points for two questions

1) Wu L-F, Mao L-F, Wang Z *Effective Entanglement and Constraint Release in Deformed Polymer Melts* Macromolecules **57** 3202-3211 (2024) use molecular dynamics (MD) simulations (LAMMPS) and small angle neutron scattering (SANS) to quantify the response of entangled polymers to large, rapid deformations. Wu observes a "Rouse ramp" in the number of effective kinks, Z_{ee}, versus time, with Z_{ee} defined as "effective" contacts between primitive paths of different chains. The "Rouse ramp" is a verification of tube relaxation induced by constraint release (CR).

a) Explain the tube concept, primitive path (PP), contour length fluctuations (CLF), constraint release (CR), extensional flow, entanglements as defined in a MD simulation, effective versus ineffective entanglements (as defined in the first column on page 3204), affine deformation (page 3204), and the non-affine tube model (NTM) used by Wu.

b) Wu states that neutron spin echo (NSE) has not provided direct observation of entanglements. **Explain the NSE** measurement, as described by Jon Nickels in class including the experimental instrument and how it is used, **and how NSE can** be used to demonstrate the presence of the reptation tube. **What does Wu mean** that NSE can't provide "direct observation" of entanglements such as can be provided by MD. **Why can't equilibrated SANS** provide evidence of entanglements?

c) Explain why $R(t)$ of equation 3 might be represented by Z_{ee} (last paragraph of page 3204). Explain the three regimes for Z_{ee} in figure 2b. Why does Z_{ee} follow $t^{-1/2}$? How does this relate to the plot shown in class of storage and loss modulus versus frequency across a very broad frequency range? ("New Rouse" slides 8, 28, 40)

d) How does Wu explain the last part of the Z_{ee} curve in figure 2b where the data follows an exponential decay? (Page 3206 top of first column). Does this argument make sense to you (or does this sound like something made up to explain the unexplainable)?

e) Wu indicates that the orientation in SANS from a rapid deformation is due to affine chain segments with separation distances between Kuhn units greater than N_{aff} Kuhn units, where N_{aff} is related to Z_{ee} by equation 5, so the SANS measurement under rapid strain can determine Z_{ee}. Figure 6f shows the result of a complex interpretation of the SANS data which agrees with the simulation results rather closely. What is $S^0_2(Q)$ and why does it have negative values? A SANS measurement typically takes at a minimum 30 minutes. How does Wu account for this (supplemental file). Do you think that this method is really viable? Explain the problems you expect.

2) Gandikota MC, Das S, Cacciuto A *Spontaneous crumpling of active spherical shells* Soft Mat. Accepted published online DOI: 10.1039/d4sm00015c (2024) investigates the collapse of spherical shells using molecular dynamics simulations in LAMMPS. Gandikkota notes that this might be important for viral capsids that collapse on injection of RNA into a cell, collapse of red blood cells in sickle-cell anemia, vesicle collapse and fluctuations, and nano-structures such as Buckey balls. Gandikota proposes that thermal fluctuations can collapse structures due to a "negative internal pressure". If a path is followed on the surface of a flat sheet it has a mass fractal dimension of 1 and a Flory scaling parameter of $\nu = 1/d_f = 1$. For a "self-avoiding sheet", similar to a self-avoiding chain, a mass fractal dimension of 1.25 is expected for this path along the surface and $\nu = 1/d_f = 4/5$. Gandikota calls this the "crumpled phase" and he seeks to demonstrate its existence through MD simulations.

a) Grandikota explains that for thin sheets only "stretch-free" deformations are allowed following $E_s/E_b \sim (h/t)^2$ where the first term is the energy ratio for stretching and bending of a sheet and h is the amplitude of a lateral deformation and t is the sheet thickness. Explain the origin of this equation.

b) Explain what v_p is and how it relates to the energy of the shell and the temperature (second page first column). What is the "Gaussian white-noise" in equation 2? Why is it necessary?

c) Is the crumpling observed by Grandikota in figures 1 and 2 a first or a second order transition? Explain why. Can you come up with a simple explanation for why the spherical shells collapse? Does you explanation indicate a first or a second order transition?

d) Why does reducing v_p by the spring and tortional moduli in Figure 2 result in universal behavior?

e) Explain how Grandikota obtains the shell scaling factor $\nu = 1/d_f = 4/5$ from his simulations. Is there a simpler way to obtain this scaling factor? Why do you think Grandikta didn't use this simpler method?