

Homework 8
Polymer Physics 2023
Due Tuesday March 7 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**)

Aomura K, Yasuda Y, Yamada T, Sakai T, Mayumi K *Quasi-elastic neutron scattering study on dynamics of polymer gels with controlled inhomogeneity under uniaxial deformation* *Soft Matter* **19** 147-152 (2023) investigate the behavior of PEO gels under strain, Figure 2, using quasi-elastic neutron scattering (QENS). A homogeneous and a heterogeneous gel swollen with water are investigated as well as a homopolymer solution for comparison. The hetero gel has a small fraction of short chains that are proposed to serve as stress concentrators, Figures 1, 5d and 6d. Aomura (heavily) interprets the QENS results to support the idea that a fraction of these short chains (11%) are highly strained and somehow cause bulk failure at macroscopic sizes, Figure 3. The link between molecular-scale network constraint on a fraction of the short chains and macroscopic failure is weak. Further, it is never demonstrated that the gels are homogenous or that perfect networks are formed as shown in the cartoons. Finally, gels and elastomers under fixed strain are known to relax with time. This is a characteristic feature of these materials. The QENS measurements take many hours over which time the gels are held at 300% strain and the stress relaxation is never measured or even considered by the authors. There are many other problems with this work. However, the paper gives a good introduction to a number of areas of polymer dynamics and networks.

- a) Figure 3 shows a non-linear plot of stress versus extension ratio $(1+\varepsilon)$. The modulus can't be determined in this curve since there is no linear regime. The normal way to plot the tensile properties of an incompressible material like a gel or elastomer is with a Mooney-Rivlin plot. Digitize Figure 3 using *Igor Pro*[®] and the *Igor Thief* procedure. Replot the data as a Mooney-Rivlin plot following Sombatsompop *N Practical use of the Mooney-Rivlin Equation for Determination of Degree of Crosslinking of Swollen NR Vulcanisates* *J. Sci. Soc. Thailand* **24** 199-204 (1998) and determine the tensile modulus from this plot with a linear fit using *Igor Pro*. Comment on the advantage of shear measurements versus tensile measurements for soft matter.
- b) The QENS measurements were performed on a "time-of-flight" near-backscatter spectrometer. Explain the difference between a reactor source and a spallation neutron source. How is "time-of-flight" advantageous to this measurement?
- c) A stretched exponential is used to fit the data, equations 1 and 2. The use of stretched exponentials is a way to deal with polydispersity or broadening of exponential decays. For instance, a material with a broad glass transition has a low fragility, β , while a material with a sharp glass transition has a fragility near 1. In this paper, β is plotted in figures 4c, 5c, and 6c. Figure 4a is for $q = 0.35 \text{ \AA}^{-1}$ while 5a and 6a are for $q = 0.8 \text{ \AA}^{-1}$. The curves in 4a, 5a, and 6a are quite different and are fit with the stretched exponential equation 1 or equation 3 with A_1 in equation 3 being about 1/100 of A_2 . Look at the values of β and $\langle \tau \rangle$ from these figures at these q values. Are they significantly different? The curves in 4a, 5a, and 6a are quite different and are fit with the stretched exponential equation 1 or 3. Is there some way to explain this? Discuss your opinion of this.

- d) Figures 4b, 5b and 6b show the behavior of $\langle \tau \rangle$ versus q . Explain the -2 power-law decay. For ballistic motion this power-law is -1, at low- q a “sub-diffusive” motion is observed with a power-law -3. For the Zimm model the polymer chain is treated as a non-draining sphere. Give a handwaving explanation for the observed sub-diffusive motion using a non-draining sphere model. You can glance at the deGennes paper linked on the webpage and referenced by Aomura but it might not help much.
- e) In figure 4b, homo, hetero gels and linear chains have about the same relaxation time as a function of time for unstrained materials. In figure 5b, the homo gel with no strain has the fastest relaxation time and the slowest at high strain, also the sub-diffusive motion at low- q is hindered much less at high strain. That is the structures become diffusive at large sizes under high strain for homogels. In figure 6b, the heterogel’s relaxation times are independent of strain. Aomura explains these observations. Paraphrase Aomura’s explanation. Comment on your opinion of what he has proposed. For instance, if short chains phase-separated out, or if stress relaxation occurred, or if unreacted species were present in the gel (and other factors) how would Aomura’s conclusions be undermined?