Homework 10

March 31, 2025

Polymer Physics

X-ray photon correlation spectroscopy (XPCS) is a technique to study the motion over distances of the beam footprint (~100 µm) of high X-ray contrast (high electron density) materials on the nano to colloidal scales (0.5 to 200 nm) on the time scale of seconds. For this reason, it is an ideal technique for nanofillers, curing epoxy composites, and possibly rheo-X-ray studies. Kamani KM, Shim YH, Griebler J, Narayanan S, Zhang Q, Leheny RL, Harden JL, Deptula A, Espinosa-Marzal RM, Rogers SA *Linking structural and rheological memory in disordered soft materials* Soft Matter **21** 750-759 (2025) recently studied the rheology and XPCS from fumed silica suspended in a stress yielding fluid (Bingham fluid, the classic example being Ketchup) which displays solid-gel like behavior at low strain amplitude (Ketchup doesn’t come out of bottle) and liquid viscoelastic behavior at high strain amplitude (it comes out when you whack the bottle) (Figure 1b) in oscillatory measurements (Figure 2a). The fumed silica observed by XPCS in this study is shown in the TEM micrograph below.



1. How is the response function related to the memory function? Explain the Boltzmann superposition principle? Show the response function and the memory function for a Hookean elastic, a Newtonian fluid, a Debye relaxor (Maxwell model), a harmonic oscillator and a damped harmonic oscillator. Which of these models relates best to polymers in the context of Boltzmann superposition? Why. What is the difference between the absolute and the relative memory function that Kamani discusses. To what use are the two functions used in Kamani’s study and why?
2. Explain the two-time correlation function 2D plot as shown in Figure 2 of Tsapatsaris L, Wiegart L, Petrash S, BaumeisterT, Engels T, Endoh M, Koga T *Real-time tracking of curing process of an epoxy adhesive by X-ray photon correlation spectroscop*y Front. Soft Mat. 1345791 (2024). How does Kamani’s work differ from that of Tsapatsari?
3. Compare equation 5 to the equation for a Hookean elastic, Newtonian fluid, and a Maxwell model viscoelastic. Explain the mechanical behavior seen in Figure 1. Explain Figure 3. The two plots in Figure 3 look almost identical, what is the difference between Hookean and Maxwell in the plot? What causes this difference?
4. Figure 4 compares the mechanical, model, and XPCS measures of correlation for strain amplitudes that are 1) mostly solid (Ketchup stuck in the bottle), 2) at the yielding transition, and 3) mostly liquid (Ketchup after you whack it). The colored regions in all the plots correspond to total correlation at the times t1 and t2. Explain why this colored region gets smaller with this sequence of conditions (consider the limits of Hookean, Maxwell, and Newtonian for these plots). Why are the plots star shaped? Why does the star center move from 0.25 to 0.22 and finally to 0.11? How does this indicate a greater acquisition of non-recoverable strain at higher strain amplitude?
5. Figure 5 shows the agreement between the structural measurement (XPCS) and the mechanical measurement (LAOS). For this comparison Kamani develops normalized averages of the XPCS and of the rheological data in terms of the recoverable strain and the strain amplitude and the measured correlation and the quiescent correlation from the bottom left corner of Figure 2a. (Figure 5 is like Figure 1b but in a reduced and normalized form.) Figure 5b shows that at higher strain amplitudes the memory is lost both in XPCS and in LAOS. Explain the text at the bottom of the first column on page 757 with reference to Figure 6: “*The reversible dynamics are therefore spatially confined to long-lived portions of the sample, and the recoverable strain in the non-linear regime is a manifestation of constrained positional fluctuations of the fumed silica particles.*” How does the data support this statement?
6. Explain why the Wissenberg number might be defined as the amount of recoverable strain. (you will need to define the Wissenberg number, give its value when the system relaxation and perturbation are at the same rate and then equate values above 1 with recoverable strain.) What is the Deborah number and what does a value of 1 mean (Figure 3)?

Stress= viscosity times strain rate, stress = modulus times strain, stress = modulus times e-t/tau tau = viscosity/modulus. Stress at yield over strain rate is viscosity at yield



First term is the plastic viscosity as defined in 72, second term is a modified strain rate, the stress on the left has a memory through the relaxation time lambda which is rate dependent. The function is ok for Carbopol, a strain yielding fluid. It matches pretty well Figure 1.