

**Homework 11**  
**Polymer Physics 2024**  
**Due Tuesday April 2 at noon**  
**(Please list the contributors to the HW at the top of the document)**

This week's paper is an analytic study of a new type of model colloid, Maier JD, Wagner J *Structure and short-time diffusion of concentrated suspensions consisting of silicone-stablized PMMA particles: a quantitative analysis taking polydispersity effects into account* Soft Matter **20** 1309-1319 (2024). Most latex polymerizations, polymerization in an incompatible solvent using a surfactant to make colloidal polymerization micelles, are conducted in water such as in making latex paint. For model colloids a non-polar, organic solvent is more useful to study particle-particle interactions in the absence of hydrogen bonding and ionic interactions. In this paper, a substitute is introduced for existing polyhydroxyteric acid coated PMMA model particles using a new siloxane (silicone or PDMS) coated PMMA. This is a fairly insignificant advancement except that it facilitates synthesis so that basically anyone could make these model sterically stabilized colloids for fundamental studies. Maier conducts light scattering and dynamic light scattering on colloidal suspensions of variable concentration. The solvent is decalin blended with tetralin to achieve index matching with the particles (this is required for most light scattering since without index matching the suspension would be opaque). The importance of this paper is its rather impressive use of scattering theory and dynamic scattering theory to analyze polydisperse colloidal systems. Polydispersity in particle size is necessary for this system since monodisperse spheres will crystallize preventing the intended study of disordered aggregation/association as concentration increases.

- a) Maier uses the Flory-Schultz distribution to describe the polydisperse PMMA core and shell spheres, equation 6. Plot the Schultz distribution, the log-normal distribution and the Gaussian distribution on the same plot (use log-x scale) to compare these size distributions. What, if any, is the advantage of the Schultz distribution over the log-normal distribution for this study? How many parameters do each of these normalized distributions require?
- b) Equation 1 involves the structure factor  $S(q)$  and the form factor which is a double sum in  $\alpha$  and  $\beta$ , rather than just  $P(q)$  which was used last week. Explain why the more complicated expression is necessary.
- c) In Figure 4, three structure factors are plotted. Explain how the experimental values are obtained and what each of these three structure factors represent. Why do they differ and why does only the red curve match the measured values?
- d) With limited data (essentially one point in figure 2), Maier concludes that the PDMS shell contracts at higher colloidal concentrations up to 60% volume fraction (which forms a glassy gel). Maier notes that the extended PDMS chain has a contour length of 46 nm, the plateau value for the shell thickness at low concentration is about 37 nm which Maier indicates supports the validity of the polydisperse core and shell model used to fit the data. (Note: tetralin and decalin are solvents for PMMA but are not solvents for PDMS) **Estimate the size** (end to end distance) of an **expanded coil** and **Gaussian** PDMS chain of 10 kg/mole ( $L = 46$  nm) with a persistence length of 5.3 Å. Maier doesn't indicate the

surface graft density but it could be assumed to be fairly low given the synthetic process of polymerizing in a latex of free PDMS chains with one MMA unit on one end surrounding droplets of MMA monomer and a heat activated free radical initiator (AIBN). **Does the thickness of 37 nm for the PDMS surface layer make sense? Can you make any logical explanation** for the reduction in surface thickness at very high volume fractions?

- e) The colloidal particles have a measured diffusion coefficient  $D_{\text{eff}}(q)$ , equation 9. This observed value can be decomposed into the dilute diffusion coefficient,  $D_0(q)$ , and the impact of hydrodynamic interactions between particles,  $H_M(q)$ , and the arrangement of particles as reflected in the static structure factor,  $S_M(q)$ , equation 10,  $D_{\text{eff}}(q) = D_0(q) H_M(q)/S_M(q)$ . This leads to the y-axis in figure 5, which shows roughly an inverse dependence on  $q$ , compared with the structure factor as reflected in equation 10. Maier calculates the hydrodynamic interaction term,  $H_M(q)$ , using only the static structure,  $S_M(q)$ , and a complicated integral relationship, equations 14 and 15 which is a solution to equation 13, figures 6 and 8. The fits in figure 8 are adjusted by two parameters, an amplitude factor and a factor that shifts the second order peak which are both linear in concentration reaching a value of 1 (no shifting necessary) at a volume fraction of about 0.45, figure 7. **What is special about a volume fraction of 0.45 that would lead to the agreement of the position of the second order peak and the amplitude with the theoretical prediction for the hydrodynamic interactions,  $H_M(q)$ ? (consider the percolation threshold for spheres, the packing factor for simple cubic lattice, the packing factor for FCC/HCP lattice and how these might be influenced by a surface layer of PDMS).**