Homework 11
**Polymer Physics 2023**
Due Tuesday April 4 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**)

Ken Schweizer and John Curro developed the Curro and Schweizer PRISM theory at Sandia National Labs in the late 1980s (see Tyler Martin reference Martin TB, Gartner TE, Jones RL, Snyder CR, Jayaraman A *pyPRISM: A Computational Tool for Liquid-State Theory Calculations of Macromolecular Materials* Macromolecules **51** 2906-2922 (2018).) to calculate the correlation function for polymer chains based on integral equation theories for low-molecular weight fluids developed by Chandler in the 1960s (https://en.wikipedia.org/wiki/Radial_distribution_function). Schweitzer later moved to the University of Illinois (UIUC). PRISM has been widely used for molecular dynamics simulations of polymers.

Last year Schweizer published a theory for the mechanical properties of polymer nanocomposites (NC) (Zhou Y, Schweizer KS *Theory for the Elementary Time Scale of Stress Relaxation in Polymer Nanocomposites* ACS Macro Lett. **11** 199-204 (2022).). Zhou's paper deals with the interaction between nanoparticles, ε_{nn} in a polymer NC that was mentioned by MacKay in Mackay ME, Tuteja A, Duxbury PM, Hawker CJ, Van Horn B, Guan Z, Chen G, Krishnan RS *General Strategies for Nanoparticle Dispersion* Science **311** 1740-1743 (2006) as shown in Mackay's Figure 3, specifically the brown disks which reflected van der Waals interactions for Mackay. Zhou considers that, under the conditions of strong polymer/NP interaction, large ε_{pn}, this brown disk is composed of polymer chain units/beads of size σ, shown as green dots in Zhou's Figure 1. Large ε_{pn} also leads to clusters of NPs rather than a uniform distribution. The system colloidal silica−P2VP (poly2vinylpyridine) displays such large ε_{pn}. Experimental scattering data can be used to determine the parameters needed for the PRISM simulation.
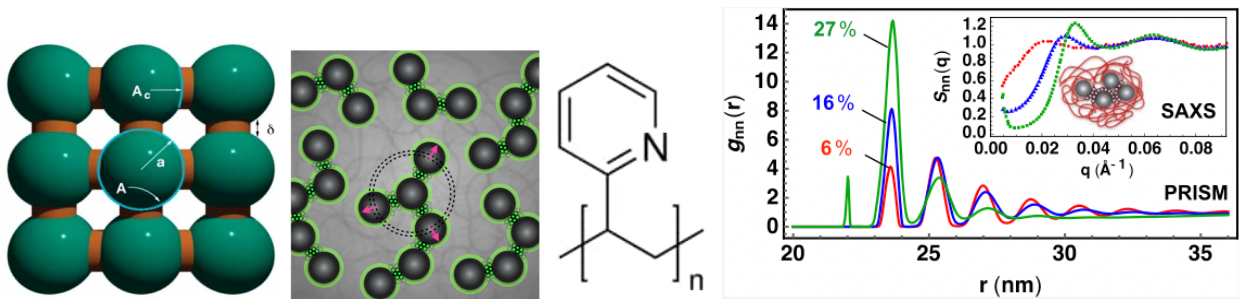
MacKay's Figure 3.   Zhou's Figure 1.   P2VP.   Graphical Abstract Zhou, Yavitt et al.(2020)

a) Zhou's Equation 1 indicates that the relaxation time associated with nanoparticle binding has two components, one associated with the polymer matrix (grey in Zhou's Figure 1) and one that has an Arrhenius thermal dependence that is associated with the energy ΔE of binding for the green dots in Zhou's Figure 1. $$\tau_{\text{rheo}}(T) \approx \tau_{\text{poly}}(T)e^{\beta\Delta E}$$ ΔE is the "…*activation energy for bridging complex relaxation based on viscoelastic data, the microscopic origin of which is not known.*". Zhou seeks to define the origin of and calculate

the value for this activation energy in his proposed model. Zhou proposes that $\Delta E \approx n_{\mathrm{B}} \Delta w$ where n_{B} is the number of green dots in his Figure 1 and Δw is the NP "*potential-of-mean force (PMF) barrier*". Explain the origin of the Arrhenius function and what type of systems it is intended to model. Is this function appropriate for Zhou's model?

b) Figure 2a shows a plot of the nanoparticle-nanoparticle correlation function obtained from PRISM using experimental parameters versus the separation distance of nanoparticles normalized by the polymer bead size. D is the nanoparticle size, $D = 10\ \sigma$. Explain why two prominent peaks are seen, why the first peak only occurs at high NP concentration. What is r_{m}? Why/how is it used to determine n_{B} from the equation in question "a". How is Δw from that equation determined?

c) n_{B}, Δw, and ΔE show interesting non-linear behavior in concentration, Figure 3. Why does the number of beads in Figure 1 increase with concentration? Why does the potential of mean force decrease? Why does the activation energy increase? The curves are normalized in the insets to Figure 3. Explain the reasoning behind each of the three insets to Figure 3.

d) Figure 4 compares the experimentally determined activation energy with that determined from the PRISM simulation based on the Zhou/Schweizer model. $\varepsilon_{\mathrm{pn}}$ is varied by variation in the matrix polymer. How is ΔE measured experimentally? Why is there no molecular weight dependence to the results? The inset to Figure 4 shows the data scaled with a parameter λ which has a value of 1 for PVAc, 2.1 for PMMA, and 5 for P2VP. Speculate on what this parameter reflects.

e) Zhou Y, Yavitt BM, Zhou Z, Bocharova V, Salatto D, Endoh MK, Ribbe AE, Sokolov AP, Koga T, Schweizer KS *Bridging-Controlled Network Microstructure and Long-Wavelength Fluctuations in Silica−Poly(2-vinylpyridine) Nanocomposites: Experimental Results and Theoretical Analysis* Macromolecules **53** 6984-6994 (2020) study the same P2VP-silica system with SAXS. Their graphical abstract (shown above) shows a discrepancy between the PRISM results for the correlation function and the measured structure factor. Can you explain this difference? How is this discrepancy resolved in Figure 4? What is the packing fraction, η_{t}? (*Ben Yavitt is a new faculty member in the Materials Program at UC.*)