

Homework 10
Polymer Physics 2024
Due Tuesday March 19 at noon
(Please list the contributors to the HW at the top of the document)

Most studies of polymer phase and chain collapse behavior take place in dilute solution. Chain collapse is intended to model the first step in biological processes such as protein folding, DNA helix formation, RNA folding and to some extent vesicle/micelle formation and coacervate formation. Alfano C, Fichou Y, Huber K, Weiss M, Spruijt E, Ebbinghaus S, De Luca G, Morando MA, Vetri V, Temussi PA, Pastore *A Molecular Crowding: The History and Development of a Scientific Paradigm* Chem. Rev. in press (2024)

<https://pubs.acs.org/action/showCitFormats?doi=10.1021/acs.chemrev.3c00615&ref=pdf> give one of about 4 reviews published this year on this subject. Robles-Hernández B, Conzález-Burgos M, de Molina PM, Asenjo-Sanz I, Radulescu A, Pomposo JA, Arbe A, Colmenero J *Structure of Single-Chain Nanoparticles under Crowding Conditions: A Random Phase Approximation Approach* Macromolecules **56** 8971-8979 (2023) published a recent study of chain collapse in concentrated solutions to model the in vivo environment.

- a) Take a glance at Alfano's review and the first two pages of Robles-Hernández's article and summarize the importance of Robles-Hernández's (RH) work. **Comment** on the validity of using single molecule nanoparticles to study protein folding. **Why** is it a good approach, **why** is it inappropriate? **Compare** Scheme 1 of RH with figures 1,3,4,6 of Alfano.
- b) The most general scattering function contains a term for the structure of a chain, the form factor $P(Q)$ (where Q is our q) and a term for the organization of the chains, the structure factor $S(Q)$ as shown in RH's equation 1 for specific interactions. When the chains are isolated the structure factor has no Q dependence and a value of 1. Equation 2 gives $P(Q)$ for a polymer chain of arbitrary mass-fractal dimension $d_f = 1/\nu$. **Show that** this expression reverts to the Debye scattering function for a Gaussian polymer chain when $d_f = 2$.
- c) As $Q \Rightarrow 0$ **does** equation 2 revert to Guinier's law? As $Q \Rightarrow \infty$ **does** equation 2 revert to Q^{-d_f} ? (for small x , $\exp(-x) \Rightarrow 1 - x + x^2/2! - x^3/3! + \dots$ and for large x , $\exp(-x) \Rightarrow 0$.)
- d) For mean field interactions $S(Q)$ takes a special form in the RPA equation and is not a multiplicative parameter as in equation 1. In the second to the last paragraph on page 8975 RH states that the RPA equation that they present in equations 6-9 has only five free parameters, R_{g1} , R_{g2} and d_{f1} , d_{f2} and χ , under the assumption that $\chi_{12} = 0$ and $\chi_{13} = \chi_{23} = \chi$. **Look at the plots in the graphical abstract and figures 1-5 and make an assessment of how many free parameters could be obtained from these curves. Show how** equations 6-9 reduce to the inverse intensity equals the sum of the inverse of the two component intensities minus two times the interaction parameter under these conditions, like equation 4. (You might need to say $(1/S_{33}^0 - 2\chi/\nu_0) = 0$ to get this answer.)
- e) The conclusion of RH's paper is that crowding reduces the solubility of polymers which could lead to chain collapse in crowded conditions. **Explain why** this might be the case.

Compare RH's result to the observations for biological systems mentioned in your answer to part "a" above especially considering the work reviewed by Alfano.