

Homework 2
Advanced Materials Thermodynamics
Due September 6, 2021 midnight

Singh MK, Hu M, Cang Y, Hsu H-P, Therien-Aubin H, Koynov K, Fytas G, Landfester K, Kremer K *Glass Transition of Disentangled and Entangled Polymer Melts: Single-Chain-Nanoparticles Approach* *Macromolecules* **53** 7312-7321 (2020) explore the dependence of glass transition on topological features that could hinder mobility. Polymer chains are linear covalently bonded molecules. At high molecular weights these chains can entangle with each other which could be envisioned as loops which form a 3d topological network. This has a dramatic impact on the viscosity of a polymer melt. T_g can be viewed from the perspective of free volume or from the perspective of molecular mobility. From the perspective of free volume topology has no relationship to the glass transition. From the perspective of mobility entanglements and topology should have a strong impact on the glass transition. Singh et al. seek to resolve this discrepancy between these two models using calorimetry, rheology, Brillion light scattering (inelastic energy absorption), and molecular dynamics simulations.

- 1) The Flory Fox equation is given by Wikipedia as $T_g = T_{g,\infty} - K/M_n$. Equation 1 differs from this equation. Explain the origin of these two equations using the free volume theory and based on molecular mobility. Compare these equations with the Fox equation for mixtures of two glass forming materials $1/T_g = x_1/T_{g,1} + x_2/T_{g,2}$
- 2) Explain what Brillion light scattering is and how it can be used to describe the glass transition and the heat capacity. This can be a superficial description based on a Wikipedia level search.
- 3) Explain how the glass transition can be measured using rheology. Does it seem reasonable to measure an equilibrium thermodynamic transition using a dynamic measurement like rheology?
- 4) Give a sketch of how a molecular dynamics simulation works. This can be at the level of a Wikipedia level search.
- 5) Could a single chain that is longer than the entanglement molecular weight make “entanglements” or knots with itself? How would this impact the molecular mobility? Has Singh considered this?
- 6) May-Mann J, Hughes TL, *Twisted Kitaev Bilayers and the Moiré Ising Model* *Physical Review B* **101** 245126 (2020) use the Ising model to consider bilayer materials like graphene that can be slightly twisted in stacking to produce a Moiré fringe lattice which can be a super conductor. Explain the origin of equation 1.