

Polymer Physics
HW 11
April 1, 2022 (Due April 5)

Luo D, Wu H, Li H, Zhang W, Zhang L, Gao Y, *Effect of shape and size of nanofillers on the viscoelasticity of polymer nanocomposites* *The Rouse model is composed of beads and springs*. Polymer **246** (2022) present coarse grain molecular-dynamics (MD) simulations of nanoparticles in low-molecular weight polymers that follow the Rouse model.

- a) The Rouse model is based on describing a polymer as a series of beads and springs called Rouse units. The Rouse unit is large enough so that Gaussian statistics describes the size $a^2 = nl^2$ but smaller than the chain. The drag coefficient is given by Stokes law using this size. The spring displays entropic spring constants $k_{spr} = 3kT/nl^2$. Compare this structure with the coarse grain model used by Luo in equations (2-4) using the spring equation $F = k_{spr} x$. Remember that $dE/dx = F$. In a molecular-dynamics simulation the temperature is related to the average kinetic energy, $\frac{1}{2} mv^2$, of the particles, a force balance based on $F = ma$ and the potential using equation (1) is made for each time step.
- b) For the Rouse model the motion of Rouse units that make up a polymer chain are broken into modes of vibration, p , as in equation (7). Luo indicates that the relaxation time in the Rouse model depends on p^2 . Strobl G *Physics of Polymers Concepts for Understanding Their Structures and Behavior* Springer Verlag Freiburg im Breisgau, Germany (2007), p. 317-330 derives the Rouse model using “m” for the mode of vibration rather than “p”, equation (8.77) p. 328 for instance. This can be obtained from equation (8.28) p. 319 using the cyclic closure relationship equation (8.37) and realizing that m/N_R is a very small number and that $\sin(x) \sim x$ for a very small value of x . Copy Strobl’s derivation in your own words and equations to obtain equation (8.44) that the Rouse relaxation time for the polymer chain is proportional to N^2 . This expression leads to the Rouse viscosity dependence of equation (8.84) $\eta_0 \sim N$, $\zeta \sim \eta_0 \sim N$, $D \sim kT/\zeta \sim kT N^{-1}$.
- c) Luo finds that the autocorrelation function for different modes of vibration for the polymer chains change significantly with the addition of nanoparticles and with the shape of the nanoparticles (clusters, rods, sheets), Figure 5. The relaxations are slowest for rods and fastest for pure polymer. Luo indicates that this reflects interaction between particles and the polymer. The interaction in the MD simulation arises from equation (1). Does this make sense? With the different energies of interaction used by Luo ($\epsilon_{pp} = 1$; $\epsilon_{nn} = 1$; $\epsilon_{pn} = 3$) do you expect interaction between filler and polymer to slow down the polymer vibrations? What other issues could be important? (A similar effect is seen in Figure 6a and Tables 1 and 3.)
- d) The Payne effect is what happens when you stretch a balloon before you blow it up. You are breaking up a filler network which lowers the modulus for a short period of time. This network reforms. Figure 3 shows that the simulated nanocomposites display a Payne effect in that at large amplitude deformations the filled systems decrease in modulus, the unfilled system is unchanged with strain amplitude. Figure 2 shows that the Payne effect only impacts the storage modulus and not the loss modulus. The effect is largest for rods and sheets, smallest for clusters. How would the Payne effect impact the dynamics of the polymer chains? Luo explains the behavior in Figures 7 and 8 for R_g to the Payne effect. Does this make sense?

- e) The simulation is subject to oscillatory shear and the average interaction energy between polymer, and filler can be calculated as a function of time, Figure 9. The difference between the peaks and valleys for pp, nm, pn interactions under this shear are plotted as a function of shear amplitude in Figure 10. It is seen that all three types of interaction are impacted. Explain how the pp interactions can be impacted in this way given the energies used in equation (1).