Homework 11
April 7, 2025
Polymer Physics

Slides 57 to 73 of the dynamics slides (https://www.eng.uc.edu/~beaucag/Classes/Properties/Slides/PolymerPropSlides4%20Dynamics.pdf) discuss the Rouse model for polymer dynamics which is based on a string of beads, with friction factor $\xi = 6\pi\eta R$, and springs with spring constant $k_{spr} = 3kT/nl^2$. A force balance (Langevin equation) $F_{drag} = dx/dt\ \xi$ and $F_{spring} = x\ k_{spr}$ for each set of three beads yields a modal response like a guitar string with a lowest order dominant mode (Rouse mode), the length of the guitar string and higher frequency overtones reflecting many integer numbers of sine waves in the string, e.g. the 10'th mode has 5 sine waves. The predictions of the Rouse model match the dynamics of low molecular weight chains since the model doesn't include entanglements. (The Rouse model is based on the Debye model for heat capacity which preceded it by 41 years (1912 and 1953) so Rouse studied the Debye model as a fundamental feature of materials. (Slides 33-77 in the advanced thermodynamics notes https://www.eng.uc.edu/~beaucag/Classes/AdvancedMaterialsThermodynamics/Heat%20Capacity/Heat%20Capacity.pdf) Polymer chain dynamics under the Rouse model have two dynamic regimes. For times shorter than the Rouse relaxation time, the time dependence of the mean square displacement follows $\langle R^2(q,t)\rangle \sim t^{1/2}$ which is slower than diffusive, $\langle R^2(q,t)\rangle \sim Dt$. This is called sub-diffusive motion. For times longer than the Rouse relaxation time, the chain moves as a whole and follows Brownian diffusion. For chains with "stickers", such as ionically-linked chains, you expect dynamics even slower than Rouse, $\langle R^2(q,t)\rangle \sim t^{1/4}$. The characteristic Rouse parameter is $\langle R^2(q,t)\rangle/t^{1/2}$ which should be constant in time for a window in timebelow the Rouse relaxation time (and above the sticker relaxation time).

Shah NJ, Fang C, Osti NC, Mamontov E, Yu X, Lee J, Watanabe H, Wang R, Balsara NP *Nanosecond solvation dynamics in a polymer electrolyte for lithium batteries* Nat. Mat. **23** 664-669n (2024) investigate lithium ions that form temporary crosslinks with a PEO like polymer with two carboxyl groups that form temporary cages around the ions but must involve multiple chains since there are only two carboxyls per mer unit. These crosslinks interfere with the dynamics with sufficient concentration of polymer so that two polymer chains can meet to ionically link, Figure 1. The application for these materials is soild-state Li^+ battery electrolytes and the work is funded by the Department of Energy.

a) List the time scales involved in this system in order of least to greatest. Show a sketch of what structure for each of these time scales. Compare this polymer with polyethylene oxide which is expected to form "crown ether" like complexes with Li^+ from a single chain (no cross-linking) due to the large number of ether groups on one chain.

b) Shah choses to inverse Fourier transform the scattering data $S(q,\omega)$ to $S(q,t)$ and then fit with equation (1) at low-q to obtain $\langle r^2(t)\rangle$ rather than converting the $S(q,\omega)$ data to the susceptibility $\chi(q,\omega)$ as was done by Niebuur B-J, Lohstroh W, Appavou M-S, Schulte A, Papadakis CM Water *Dynamics in a Concentrated Poly(N-isopropylacrylamide) Solution at Variable Pressure* Macromolecules **52** 1942-1954 (2019). Explain what the susceptibility is, how it is obtained, and what advantage the susceptibility has over the $<r^2(t)>$ approach of Shah. What is the origin of equation (2) of Niebuur? What is the origin of equation (1) of Shah? Why is equation (1) only useful at low-q (which Shah defines as 0.5$Å^{-1}$ (~ 13 Å))? Does the q-range chosen seem correct for equation (1)?

c) Explain the four behaviors seen in Figure 3 of Shah. Sketch a log $<r^2(t)>$ versus log t plot that displays these four regimes. Would this be a better way to display the data? What is the Rouse parameter from Figure 3?

d) Figure 4 compares the time scales you listed in question a. Explain Figure 4 in this context.

e) Make a guess as to the origin of the initial upward slope in Figure 3a at low ion concentration that is absent from Figure 3b. What is the difference between experiment and simulation that might generate this difference?