Homework 14 Polymer Physics
Due Friday May 2, 2025 (at the latest).

Question 1.

Moussavi A, Marshal W, Kumar SK, Ketan S Two Channel Description of Gas Permeability in Polymer-Grafted Nanoparticle Membranes Macromolecules **58** 827-835 (2025) propose a two-channel model for gas transport through membranes made from densely grafted nanoparticles (PGN) that display a transition from tensile blob structure (concentrated polymer brush, CPB) to random coil structure (semi-dilute polymer brush, SDPB) in radial distance from the nanoparticle surface. Gas transport in these two regimes and a model is proposed of two distinct "channels", a high-barrier channel (HBC) for SDPB and a low-barrier channel for CPB. Figure 6 summarizes the model with a diffusing green gas molecule that transports through the two structural regimes, the HBC having a higher solubility for the gas, while the LBC having a faster transport. The model has both structural as well as kinetic aspects that are summarized in equation (7) which is a series resistance model based on empirically determined "contributions" to the permeability of the membrane, i.e. these are kinetically determined fractions not structurally determined fractions, though the model is a structural model in Figure 6. So there is some natural conflict in the model between a structural understanding and a kinetic prediction, similar to predicting rheology from morphology (*"is theology"... RS Stein*).

a) Equations 1 and 2 are Arrhenius functions if the energy terms have fixed values. What is the model that the Arrhenius function is based on? Equation 4 has a typo, see equation 16 of Ref 10, Sanders. Moussavi calls equation 4 "an enthalpy-entropy compensation effect". Explain what Sanders means by this and what structural basis might be involved in such an expression.
b) Generally, permeability drops as selectivity increases for polymer membranes, see Ref 10 Sanders Figures 5, 7, 8, 17, 18 etc. Why is this the case? Can Moussavi's PGN membranes resolve this issue? How or why not?
c) Equation 7 is a parallel resistivity model for membrane transport, that is, both mechanisms for transport occur simultaneously. How would a series model for transport differ from equation 7, write a new equation. Explain how you could justify a series model form Figure 6. Does figure 6 as explained justify equation (7)?
d) On page 830 column 2 Moussavi states that "small (gas) molecules preferentially transport through the low-barrier channel, regions of high polymer extension". What data or results supports this statement in this paper. Why would tensile blob chains have higher transport compared to random chains?
e) Why do Figures 5 and 7 show plateaus at high d^2 and low ϕ_H?

Question 2.

Shampoo and body wash have viscoelastic properties and act as almost perfect Maxwell Model materials, though they contain no polymers. These consumer products are solutions of detergents like sodium dodecyl sulfate, SDS (a.k.a. sodium lauryl sulfate, SLS) and salt as the active ingredients. In the absence of added salt and at low concentrations, SDS forms spherical micelles. The addition of salt leads to screening of the head group charge, changing the geometric constraints on self-assembly that results in first ellipsoidal micelles and, at higher surfactant and or salt concentrations, entangled filamentary, thread-like, or worm-like micelles (WLMs) with a diameter of 1 nm and a length of microns that display viscoelastic behavior. At a fixed salt concentration, with increasing surfactant concentration the chains are known to grow in length, increasing the viscosity, and at some concentration begin to form rather unique branches. The branches differ from branches in polymers in that they have high mobility along the chain which leads to a reduction in the viscosity (a proposition of Cates). So, the surfactant (or salt) concentration dependence of the zero-shear rate viscosity shows a peak. This is shown by Degaki H, Koga T, Narita, T *Characterizing semiflexible network structures of wormlike micelles by dynamic techniques* Soft Mat. DOI: 10.1039/d5sm00116a *in press* (2025) in Figure 3b. Degaki uses "macro" oscillatory rheology, two micro-rheology techniques (DLS and DWS), dynamic light scattering (DLS), static light scattering (SLS) and several other techniques to explore the structure of SDS WLMs.

a) Degaki first determines the overlap surfactant concentration in Figure S1 of the supplemental information as determined form a Zimm plot, Figure S8. He uses the Zimm equation (first equation in the supplemenal file).
Explain how this equation relates to Guinier's law and how the mesh size is determined and why the mesh size first increases and then decreases in Figure S1. Is there any problem with using this analytic approach for this system? (Explain if there is a problem.)

b) Degaki obtains $<r^2(t)>$, the mean square displacement of a tracer bead, in DLS and DWS micro-rheology from the autocorrelation function $g^{(1)}(t)$ using equation (1) for DWS (at a high tracer bead concentration) or equation (3) for DLS micro-rheology (at a very low tracer bead concentration). He then uses a Laplace transform to convert the real valued $<r^2(t)>$ to the complex (real and imaginary) $<r^2(\omega)>$. Explain what a Laplace transform is and how it can convert a real value function to a complex value function with real and imaginary components (that is, eventually, storage and loss moduli). (You might use ChatGPT to start the answer to this question.)

c) Degaki uses the Maxwell model to obtain the terminal relaxation time, the zero-shear rate viscosity, and the plateau modulus. Explain how these are obtained from the "macro" rheology measurements.

d) Figure 5 shows how Degaki determined the transition between the Zimm Mode and the bending mode at high frequency. Explain what this transition involves. How does this high-frequency transition relate to the second crossover frequency in the inset of Figure 4a.

e) Figure 6a compares the "screening length" and the Kuhn length and finds that they are identical, while the mesh size determined form the plateau modulus in Figure 7 is about 10 times larger. This is the basis of the model shown in Figure 11. Does this make sense? That is, are chain overlap and chain entanglements different and how is the screening length the same as the Kuhn length?