Homework 6 Advanced Thermodynamics
Due Monday October 3, 2022

Qiu X, Mao S, Yin J, Yang Y *An anisotropic immerse precipitation process for the preparation of polymer membranes* Soft Matter **18** 1525-1531 (2022) numerically solve the Cahn-Hilliard equation for spinodal decomposition using anisotropic mobility and perform molecular dynamics simulations. For semi-permeable membranes it is desirable to create oriented pores. Qiu demonstrates that pores could be oriented normal to a membrane surface or in the membrane plane if the mobility of the phases could be controlled in an anisotropic fashion.

a) Explain the ternary phase diagram in Figure 1. Is the polymer concentration constant along the grey line? What process is this phase diagram showing?
b) Equation 2 describes the flux of the three components as a function of the chemical potential. How does this equation differ from Fick's law? Sketch concentration versus position for this equation and for Fick's law in nucleation and growth.
c) Qiu doesn't describe how his simulation proceeds in much detail. Shou B, Powell AC *Phase field simulations of early stage structure formation during immersion precipitation of polymeric membranes in 2D and 3D* J. Mem. Sci. **268** 150-164 (2006) gives a bit more detail. Consider starting with a random ternary mixture. How would a simulation of the formation of the spinodal structure proceed? List numbered steps.
d) Comment on Figure 5. What is being plotted. Why do the curves reach a plateau and why is there no difference between the different curves?
e) Cahn-Hilliard theory results in an "apparent" or "effective" diffusion coefficient that depends on the diffusion coefficient (that might be given by the Stokes Einstein equation $D = kT/(\zeta)$ where ζ is the drag coefficient) and the distance from the spinodal condition. The apparent diffusion coefficient is an experimentally observed parameter as shown by Hashimoto T, Kumaki J, Kawai H, *Time-Resolved Light Scattering Studies on Kinetics of Phase Separation and Phase Dissolution of Polymer Blends. 1. Kinetics of Phase Separation of a Binary Mixture of Polystyrene and Poly(viny1methyl ether)* Macromolecules **16** 641-648 (1983). The mobility is just the diffusion coefficient, so the apparent diffusion coefficient divided by the distance from the spinodal. **In the spinodal regime what is the sign of the apparent diffusion coefficient?** How does this make sense? You need to give the classical definition of the diffusion coefficient and a sketch of the concentration profile for spinodal decomposition.