Homework 7
Advanced Materials Thermodynamics
Due Monday October 9, 2023

Freeman CL, Harding JH *The transformation of amorphous calcium carbonate to calcite and classical nucleation theory* J. Cryst. Growth **603** 126978 (2023) discuss a molecular dynamics simulation of crystallization of calcite from solution. Calcite has many polymorphs and may form an amorphous hydrated layer at the crystal interface under supersaturated conditions. The concentration of this layer may impact the interfacial energy of the growing crystal and impact the growth rate.

a) In the first paragraph Freeman poses the question: "*These all suggest that the ACC phase may also interconvert without dissolution. This raises the question - under what conditions is a dissolution re-precipitation process preferred to a solid-state transition*?". Summarize his assessment of this issue.
b) Explain the origin of equation 3. (You may need to expand the logarithm term, $\ln(ab/c) = \ln(a) + \ln(b) - \ln(c)$.)
c) Derive equation 4.
d) Figure 2 shows an increase in the interfacial energy as a function of the concentration of $CaCO_3$ in the amorphous $CaCO_3$ layer. Explain why this surface energy increases and then plateaus (use Figure 3 in your explanation). Do you think it is reasonable to ignore the organization of water molecules at the surface? How would this change the surface energy?
e) Explain how the critical nucleation barrier is calculated in Figure 4. Why does the curve have the shape in surface amorphous $CaCO_3$ concentration and the trend seen for two different supersaturations? What is the difference between Figures 4a and 4b?