## Homework 14 Advanced Thermodynamics
## Due Wednesday December 4, 2024

Nanocrystalline materials can have exceptional mechanical properties compared to conventional crystals. The yield strength can increase following the Hall-Petch relationship $\sigma_y = \sigma_0 + Kd^{-1/2}$. Nanocrystalline materials do not strain harden so they display perfect or super-plasticity. The modulus decreases by 30 to 50%. Grain growth or coarsening of nanocrystalline metals during processing has hindered their application. Saber M; Kotan H; Koch CC; Scattergood RO *Thermodynamic stabilization of nanocrystalline binary alloys* J. Appl. Phys. **113** 063515 (2013) developed a predictive thermodynamic model for stabilization of nanocrystalline binary alloys using a regular solution model.

a) Explain the general features of an ideal solution and a regular solution model. Derive the entropy and enthalpy expressions for these models using a statistical thermodynamics approach.
b) Nanograin size can be explained by kinetic stabilization or by thermodynamic stabilization. Explain the logic behind these two models. What is the advantage of a metastable state model?
c) Weissmuller J *Alloy Effects in Nanostructures* Struc. Mat. B 261-272 (1993) in Figure 1 shows three possible scenarios for solid solutions involving grain boundaries. How does Saber et al. account for these three possibilities in their model?
d) Introduction of a solute atom in a lattice leads to lattice strain. This strain could be relieved if the solute were located at a grain boundary. In addition to this elastic component, there is a chemical advantage to locating the solute at a grain boundary. Explain the origin of the chemical advantage and how it is incorporated in Saber's model.
e) Derive Saber's equation 12. (Carefully define the parameters $d$, $t$ and $f_{ig}$.)
f) The coordination number, $z$, doesn't seem to be constant between the interface and the grains in Figure 1 of Saber. Explain how this is accounted for in Saber's model.
g) Weissmuller (1993) shows a plot of $G$ versus $D$ (Figure 3) explain why minimization of Saber's equations 29 a to c are necessary to find an "*equilibrium*" state, rather than just minimization with respect to the intergranular volume fraction, $f_{ig}$, as shown by Weissmuller. Is this really an equilibrium state?
h) In Figure 5 of Saber, why does grain size increase with temperature, and why does it decrease with increasing $\alpha$?