Homework 7 Advanced Thermodynamics
Due Monday October 18, 2021

We discussed in class the Wulff construction that decides the shape of growing crystals based on the surface energy. Seif MN, Beck MJ *Surface excess free energies and equilibrium Wulff shapes in variable chemical environments at finite temperatures* Appl. Surf. Sci. **540** 148383 (2021) present the results of density functional theory (DFT) and density functional perturbation theory (DFPT) calculations for the surface energy used to perform Wulff constructions for tungsten thermionic dispenser cathodes composed of faceted nanoparticles.

a) Give a paragraph describing the basic concept of DFT and DFPT based on the description by Seif on DFPT and the description on Wikipedia for DFT (https://en.wikipedia.org/wiki/Density_functional_theory). Be sure to answer "*density of what?*", and "*what is a functional?*". You might also look at the book *A Chemist's Guide to Density Functional Theory* if you are interested in DFT in more detail (https://www.eng.uc.edu/~beaucag/Classes/AdvancedMaterialsThermodynamics/Books/Holtje,%20Hans-Dieter%20-%20A%20Chemists%20Guide%20to%20Density%20Functional%20Theory-VCH%20(1997).pdf). Also, briefly explain what is a tungsten thermionic dispenser cathode (https://en.wikipedia.org/wiki/Hot_cathode or http://ebeaminc.com/thermionic-cathodes.htm) in one sentence.

b) Seif gives the following statement: *As-fabricated nanoparticle shapes are the product of kinetic and thermodynamic factors governing surface configuration and behavior, with kinetics playing a particularly important role in solution processing [22]. For nanoparticles in high-temperature or gas-phase applications, thermodynamic factors increasingly control surface configurations, and therefore the stability and evolution of particle shape.* Explain this statement giving the reason that kinetics might be more important in solution processing.

c) On page 2 Seif mentions that "phonons", the "density of states", and "vibrational entropy" can be used to calculate surface free energies. Seif introduces a "configurational entropy" associated with oxygen and barium atoms at the surface. Explain the terms in equation (4) in order to describe how Sief achieves the inclusion of these other factors. Be sure to explain "*What is a phonon?*", "*What is the density of states and states of what?*", "*What is vibrational entropy?*". Explain what is show in Figure 9.

d) Explain how the shape of a crystal can be determined from the surface energy and the logic behind this approach as well as the physical limitations to the approach. When does this approach fail and for what reason?

e) Figure 5 shows the tungsten configuration in a barium and oxygen environment while Figure 6 shows the configuration in an oxygen environment only. Explain the difference between these two figures.