Homework 2

Davit Potoyan
Statistical Mechanics, Chem 563

January 24, 2019

The goal of this problem set is to refresh our memory about the laws of thermodynamics and the powerful mathematical tools and relationships that thermodynamics provides for solving practical problems.

Problem 1.1: Conceptual questions of Thermodynamics. (i) Explain how the statement of 2nd law of thermodynamics ($\Delta S_{adiabatic} \geq 0$) is consistent with the Kelvin's statement: "it is impossible to devise a cyclically operating thermal engine, the sole effect of which is to absorb energy in the form of heat from a single thermal reservoir and to deliver an equivalent amount of work".

(ii) Decide which of the following states is in an equilibrium state, a time dependent non-equilibrium state, or time independent but still non-equilibrium state (e.g steady stae). Explain your reasoning. In some cases, the state is not a true steady or equilibrium state but close to one. Discuss under what conditions it can be treated as a steady or equilibrium state. a) a cup of hot tea, sitting on the table while cooling down b) the wine in a bottle that is stored in a wine cellar c) the sun d) the atmosphere of the earth e) electrons in the wiring of a flashlight switched off f) electrons in the wiring of a flashlight switched on

(iii) What is meant by a constraint in thermodynamics and why its removal must always lead to increase of entropy?

(iv) What is meant by a quasi-static process in thermodynamics and how this idealization is used for computing changes in thermodynamic variables?

(v) What is the meaning of Legendre transform in thermodynamics and what does it say about relationship between the Legendre transformed functions. Can you provide example(s) of well known Legendre transform in another field of physics?

Problem 1.2: Maxwell relations warm up. For a dielectric material characterized by polarization P, electric field E, and temperature T (PET system), derive the so-called Maxwell relations between various derivatives of thermodynamic quantities. The Maxwell relations follow from the fact that the differentials of the thermodynamic potentials U, H, A and G are exact, if they are expressed in terms of their natural variables.

Problem 1.3: Some short but sweet exercises from Chandler's book. Solve the problems 1.2, 1.6, 1.7, 1.8, 1.14 1.15 found in Chapter 1 in Chandler's book