Homework 3

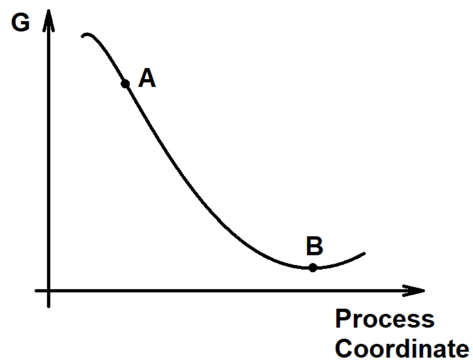
Short questions

1. Practice obtaining Maxwell's relations, show:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

2. An ideal gas system undergoes isothermal expansion from an initial volume V_i to a final volume V_f. What is the change in enthalpy of the system?

3. For an arbitrary process in a closed system, a plot of the Gibbs free energy looks like this:



   If the process is at the state **A**, is it possible for the system to spontaneously go to state **B**? Why or why not?

4. The heat capacity at constant volume C_V of many solids at low temperature has the proportionality: $C_V = \alpha T^3$. What function describes the internal energy of such a material?

5. In many thermodynamics' exercises a thermal bath is mentioned. Essentially, a thermal bath is an object or vessel, which can receive or give heat. We also consider it to be large enough so that it does not change its temperature. Usually water is used for such applications due to its large heat capacity. A copper piece (m = 10 g, C_{Cu} = 0.385 J/g·K) that has initial temperature T_{Cu} = 100 °C is dropped in a tank of water (C_{H2O} = 4.184 J/g·K) with temperature T_{H2O} = 25 °C. How much water is needed in the tank so the final equilibrium temperature of water and copper piece would be 25.1 °C? Note that in this exercise, we assume a constant heat capacity.

Exercise 1

The thermodynamics of a rubber band. Rubber bands are narrow bands of an elastic polymeric material used to hold things together. Suppose you apply a quasi-static stretching force that increases the length L of a rubber band. The force of retraction f exerted by the rubber band is equal and opposite to the applied stretching force.

a) Find the expressions of the differential of the internal and Gibbs free energy equations when elastic forces are involved. You have U= U (S, V, L) and n is fixed.

b) The retractive force f of polymeric elastomers as a function of temperature T and expansion L is approximately given by $f(T,L) = aT(L\text{-}L_0)$ where a and L_0 are constants, and doesn't depend on the pressure p. Use Maxwell relations to determine the entropy $S(L)$ at constant T and p.

c) Based on your results for the entropy $S(L)$ you obtained in b), determine the enthalpy $H(L)$ at constant T and p.

d) If you adiabatically stretch a rubber band by a small amount its temperature increases, but its volume does not change. Derive an expression for its temperature T as a function of L, L_0, a, and its heat capacity at constant volume. Assume that the heat capacity is constant.

e) Is the retraction of a rubber band driven by a change in enthalpy or in entropy? The answer to this question helps us to construct a model for the microscopic behaviour of polymeric materials. (Polymeric material refers to a molecule whose structure is composed of multiple repeating units, from which originates a characteristic of high relative molecular mass and attendant properties, e.g. plastics, etc.)