Homework 4

1.Practice obtaining Maxwell's relations

Derive the following relationship using Euler's reciprocal relation:

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

2. 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 $f(T,L) = aT(L-L_0)$ 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.