

1 Problems from Schroeder

1.1 Schroeder 6.2

1.2 Schroeder 6.34

1.3 Schroeder 6.40

1.4 Schroeder 6.44

1.5 Schroeder 6.45

2 Thermodynamic potentials

In this assignment we will have a closer look at the thermodynamic potentials, and how they are related.

(a) Write down the expressions for U , H , F and G as functions of S, T, P , V , N and μ . What are these quantities called? Give a physical interpretation of each quantity.

(b) Write down the thermodynamic identity for U (dU).

(c) Derive the Gibbs-Duhem equation:

$$SdT - VdP + Nd\mu = 0. \quad (1)$$

(d) Find the thermodynamic identities dH , dF and dG . List the independent variables of U, H, F and G , and explain how the relations between the thermodynamical identities changes the independent variables. What is this transformation between different independent variables called?

(e) Show that

$$S = - \left(\frac{\partial G}{\partial T} \right)_{P, N}, \quad (2)$$

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T, V}, \quad (3)$$

$$P = - \left(\frac{\partial U}{\partial V} \right)_{S, N}, \quad (4)$$

$$T = \left(\frac{\partial H}{\partial S} \right)_{P, N} \quad (5)$$

and

$$V = \left(\frac{\partial G}{\partial P} \right)_{T, N}. \quad (6)$$

- (f) (This was given on a recent exam) Use the thermodynamic identities to derive the following relation

$$\left(\frac{\partial\mu}{\partial T}\right)_{V,N} = -\left(\frac{\partial S}{\partial N}\right)_{T,V} \quad (7)$$

What is this type of relation called?

- (g) Assume $U = U(T)$. Use the thermodynamic identity to derive

$$S(T) = \int_0^T \frac{C_V}{T'} dT' \quad (8)$$

- (h) We will now look at the relation between the canonical partition function and the thermodynamic potentials. Use that $U = \langle \epsilon \rangle$ and show that

$$U = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} \quad (9)$$

- (i) The probability for a state n , P_n , is related to the canonical partition function through $P_n = \frac{e^{-\beta\epsilon_n}}{Z}$. Starting with the Gibbs formula for entropy (which you do not have to prove)

$$S = k \ln \Omega = -k \left(\sum_n P_n \ln P_n \right), \quad (10)$$

show that

$$F = U - TS = -kT \ln Z \quad (11)$$