Fys2160 – 2013 – Oblig 10

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 ($\mathrm{d}U$).

(c) Derive the Gibbs-Duhem equation:

$$S\mathrm{d}T - V\mathrm{d}P + N\mathrm{d}\mu = 0. \tag{1}$$

(d) Find the thermodynamic identities $\mathrm{d}H$, $\mathrm{d}F$ and $\mathrm{d}G$. 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

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

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

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

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

and

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

(f) (This was given on last years exam) Use the thermodynamic identities to derive the following relation

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

What is this type of relation called?

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

$$S(T) = \int_0^T \frac{C_V}{T'}\mathrm{d}T' \tag{8}$$

(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

$$U = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} \tag{9}$$

(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)

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

show that

$$F = U - TS = -kT \ln Z \tag{11}$$

Fluctuations

We consider a system in contact with a large reservoir, ensuring that the system has constant T, V, and N.

(a) Write down the partition function for the system and introduce all quantities in the formula.

(b) Show that the average energy is

$$U = \langle \epsilon \rangle = kT^2 \frac{\partial}{\partial T} \ln Z \ . \tag{12}$$

(c) Show that

$$\frac{\partial}{\partial T} (U \cdot Z) = \frac{\langle \epsilon^2 \rangle Z}{kT^2} \ , \tag{13}$$

(d) Use this to show that

$$\langle \epsilon^2 \rangle - \langle \epsilon \rangle^2 = kT^2 \frac{\partial U}{\partial T} \tag{14}$$

(e) Can you think of a case where this formula is useful?

(f) Show that for an ideal gas the relative size of the fluctuation in U is $(2/3N)^{1/2}$.

(g) How large are the fluctuations in energy in a gas with $N = N_A$?

End of Oblig 10