Thermal Physics II – Solutions for Problem Sheet 4

1. Partition Function and Internal Energy

- We start from $F = -k_B T \ln Z$. Re-arranging for $\ln Z$ and inserting the definition of Helmholtz free energy, $F = U - TS$, yields

$$\ln Z = -\beta F = -\beta\Big[U - TS\Big] = -\beta U - k_B^{-1} S\,,$$

- As only the first term depends explicitly on β, we have

$$\frac{\partial \ln Z}{\partial \beta} = -U \qquad \text{or} \qquad U = -\frac{\partial \ln Z}{\partial \beta}\,.$$

2. Maxwell Relation — first Example

- Start from enthalpy/Gibbs energy: $H = U + pV$.
- This function has exact differential (using $dU = TdS - pdV$)

$$dH = dU + pdV + Vdp + \mu dN = TdS + Vdp + \mu dN \, .$$

- Then the first derivatives are

$$\left(\frac{\partial H}{\partial S}\right)_{p,N} = T \, , \qquad \left(\frac{\partial H}{\partial p}\right)_{S,N} = V \, , \qquad \left(\frac{\partial H}{\partial N}\right)_{S,p} = \mu$$

- The mixed derivatives of H must be equal as the internal energy is a total differential. Hence, we have

$$\left(\frac{\partial}{\partial p}\left(\frac{\partial H}{\partial S}\right)_{p,N}\right)_{S,N} = \left(\frac{\partial}{\partial S}\left(\frac{\partial H}{\partial p}\right)_{S,N}\right)_{p,N}$$

- Now we insert the first derivatives from above (the first on the left side, the second on the right side) and obtain as required

$$\left(\frac{\partial T}{\partial p}\right)_{S,N} = \left(\frac{\partial V}{\partial S}\right)_{p,N} \, .$$

2. Maxwell Relation — second Example

- Start from Gibbs free energy: $G = U - TS + pV$.
- This function has exact differential

$$\begin{aligned} dG &= dU - TdS - SdT + pdV + Vdp + \mu dN \\ &= -SdT + Vdp + \mu dN \, . \end{aligned}$$

- Then the first derivatives are

$$\left(\frac{\partial G}{\partial T}\right)_{p,N} = -S \, , \qquad \left(\frac{\partial G}{\partial p}\right)_{T,N} = V \, , \qquad \left(\frac{\partial G}{\partial N}\right)_{T,p} = \mu$$

- The mixed derivatives of G must be equal as the internal energy is a total differential. Hence, we have

$$\left(\frac{\partial}{\partial p}\left(\frac{\partial G}{\partial T}\right)_{p,N}\right)_{T,N} = \left(\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial p}\right)_{T,N}\right)_{p,N}$$

- Now we insert the first derivatives from above (the first on the left side, the second on the right side) and obtain as required

$$-\left(\frac{\partial S}{\partial p}\right)_{T,N} = \left(\frac{\partial V}{\partial T}\right)_{p,N} \, .$$

3. Probability to Find a Given State

- Start with the definition of the probability to find the system in energy E and re-arrange it to a form that contains '$\ln Z$' (this is needed for the introduction of the Helmholtz free energy)

$$\begin{aligned} p(E) &= \frac{1}{Z}\exp(-\beta E) \\ &= \exp\Big[\ln(Z^{-1})\Big]\exp(-\beta E) \\ &= \exp[-\ln(Z)]\exp(-\beta E)\,. \end{aligned}$$

- Now we use the connection between thermodynamics and statistics

$$F = -k_B T \ln Z \qquad \text{or in the form} \qquad -\ln Z = \beta F\,.$$

- The probability to find the system in energy E is thus given by

$$p(E) = \exp(\beta F)\exp(-\beta E) = \exp[-\beta(E - F)]$$

as requested.