5.5 Calculation of the grand canonical ensemble

Maximize

$$S' = -k \sum_i p_i \ln(p_i) \tag{5.40}$$

with the restrictions

$$0 = \sum_i p_i - 1 \text{ , and } \quad 0 = \sum_i p_i U_i - U \text{ , and } \quad 0 = \sum_i p_i N_i - N \quad . \tag{5.41}$$

Introducing the Lagrange parameters α, β, and γ the variation of the function

$$\delta \left[S' - k\alpha \left(\sum_i p_i - 1 \right) - k\beta \left(\sum_i p_i U_i - U \right) - k\gamma \left(\sum_i p_i N_i - N \right) \right] = 0 \tag{5.42}$$

without restrictions leads to

$$-\ln(p_i) - 1 - \alpha - \beta U_i - \gamma N_i = 0 \quad . \tag{5.43}$$

Defining

$$\frac{1}{Z} = \exp(-1 - \alpha) \tag{5.44}$$

we find

$$p_i = \frac{1}{Z} \exp(-\beta U_i - \gamma N_i) \quad . \tag{5.45}$$

Taking into account the first restriction one gets

$$Z(\beta, V, \gamma) = \sum_i \exp(-\beta U_i - \gamma N_i) \quad . \tag{5.46}$$

Finally we get

$$S = k \ln(Z) + \beta k U + \gamma k N \quad . \tag{5.47}$$

Just by comparison we see

$$U = \sum_i p_i U_i = \frac{\sum_i \exp(-\beta U_i - \gamma N_i) U_i}{\sum_i \exp(-\beta U_i - \gamma N_i)} = -\left(\frac{\partial \ln(Z)}{\partial \beta} \right) := U(\beta, V, \gamma) \tag{5.48}$$

and

$$N = \sum_i p_i N_i = \frac{\sum_i \exp(-\beta U_i - \gamma N_i) N_i}{\sum_i \exp(-\beta U_i - \gamma N_i)} = -\left(\frac{\partial \ln(Z)}{\partial \gamma} \right) := N(\beta, V, \gamma) \quad . \tag{5.49}$$

Thus the total derivative is:

$$\begin{aligned} \frac{dS}{k} &= \left(\frac{\partial \ln(Z)}{\partial \beta} \right) d\beta + \left(\frac{\partial \ln(Z)}{\partial \gamma} \right) d\gamma + \left(\frac{\partial \ln(Z)}{\partial V} \right) dV \\ &\quad + U d\beta + \beta dU + N d\gamma + \gamma dN \\ &= \left(\frac{\partial \ln(Z)}{\partial V} \right) dV + \beta dU + \gamma dN \end{aligned} \tag{5.50}$$

So

$$S = S(V, N, U) \tag{5.51}$$

and S is the Legendre transformed of $k \ln(Z)$.
From classical thermodynamics it is well known that

$$dU = TdS - pdV + \mu dN \quad \text{, i.e.} \quad \left(\frac{\partial S}{\partial U} \right) = \frac{1}{T} \quad \text{, and} \quad \left(\frac{\partial S}{\partial N} \right) = -\frac{\mu}{T} \quad . \tag{5.52}$$

So by comparison with Eq. (5.50) we see

$$\beta = \frac{1}{kT} \quad \text{, and} \quad \gamma = -\frac{\mu}{kT} \quad . \tag{5.53}$$

Multiplying Eq. (5.47) with T we find

$$\Omega = U - \mu N - TS \tag{5.54}$$

and

$$\Omega(T, V, \mu) = -kT \ln(Z(T, V, \mu)) \quad . \tag{5.55}$$