2.3 Calculation of the canonical ensemble

Maximize

$$S' = -k \sum_i p_i \ln(p_i) \tag{2.10}$$

with the restrictions

$$U = \sum_i p_i U_i \quad \text{and} \quad 1 = \sum_i p_i \quad . \tag{2.11}$$

The restrictions are handled by Lagrange parameters α and β:
Variation of the function

$$\delta \left[S' - k\alpha \left(\sum_i p_i - 1 \right) - k\beta \left(\sum_i p_i U_i - U \right) \right] = 0 \tag{2.12}$$

without restrictions leads to

$$-\ln(p_i) - 1 - \alpha - \beta U_i = 0 \quad . \tag{2.13}$$

With

$$\frac{1}{Z} := \exp(-1 - \alpha) \tag{2.14}$$

follows

$$Z(\beta, V, N) = \sum_i \exp(-\beta U_i) \quad \text{and} \quad p_i = \frac{1}{Z} \exp(-\beta U_i) \quad . \tag{2.15}$$

Z is called the **canonical partition function (sum of states)**.
We get

$$U = \sum_i p_i U_i = \frac{\sum_i \exp(-\beta U_i) U_i}{\sum_i \exp(-\beta U_i)} = -\left(\frac{\partial \ln(Z)}{\partial \beta} \right) := U(\beta, V, N) \tag{2.16}$$

and

$$S = -k \sum_i \left[\frac{1}{Z} \exp(-\beta U_i) \left(-\ln(Z) - \beta U_i \right) \right] = k \ln(Z) + \beta k U \tag{2.17}$$

leading to:

$$\begin{aligned} \frac{dS}{k} &= \left(\frac{\partial \ln(Z)}{\partial \beta} \right) d\beta + \left(\frac{\partial \ln(Z)}{\partial N} \right) dN + \left(\frac{\partial \ln(Z)}{\partial V} \right) dV + U d\beta + \beta dU \\ &= \left(\frac{\partial \ln(Z)}{\partial N} \right) dN + \left(\frac{\partial \ln(Z)}{\partial V} \right) dV + \beta dU \end{aligned} \tag{2.18}$$

This means

$$S = S(V, N, U) \tag{2.19}$$

and S is the Legendre transformed of $k \ln(Z)$.
We define

$$\left(\frac{\partial S}{\partial U} \right) := \frac{1}{T} \quad \text{and get} \quad \beta = \frac{1}{kT} \quad . \tag{2.20}$$

Comparison of

$$TS = kT \ln(Z) + \beta k T U \quad \text{and} \quad F(V, N, T) = U - TS \tag{2.21}$$

gives

$$F = -kT \ln(Z(V, N, T)) \quad . \tag{2.22}$$

In statistical mechanics the calculation of the thermodynamic potentials is transformed into the calculation of partition functions.