Partition function [pln16]

$$Z = \sum_{\{N_m\}} W(\{N_m\}) e^{-\beta E(\{N_m\})} = W(\{\hat{N}_m\}) e^{-\beta E(\{\hat{N}_m\})} \Big[1 + \ldots \Big].$$

Ingredients: energy $E(\{N_m\})$ and multiplicity $W(\{N_m\})$ from [pln14]. Term with most probable populations $\{\hat{N}_m\}$ dominant in macroscopic systems.

Statistical mechanical analysis [Wu1994] uses Sterling asymptotics without terms of $\mathrm{O}(\ln \hat{N}_m)$:

$$\ln Z = \sum_m \bigg[\Big(A_m + \sum_{m'} (\delta_{mm'} - g_{mm'}) \hat{N}_{m'} \Big) \ln \Big(A_m + \sum_{m'} (\delta_{mm'} - g_{mm'}) \hat{N}_{m'} \Big) \\ - \Big(A_m - \sum_{m'} g_{mm'} \hat{N}_{m'} \Big) \ln \Big(A_m - \sum_{m'} g_{mm'} \hat{N}_{m'} \Big) - \hat{N}_m \ln \hat{N}_m - \beta \hat{N}_m \epsilon_m \bigg].$$

Extremum condition $\partial \ln Z / \partial \hat{N}_m = 0$ yields

$$\ln \hat{N}_m + \beta \epsilon_m = \ln \Big(A_m + \sum_{m''} (\delta_{mm''} - g_{mm''}) \hat{N}_{m''} \Big) \\ + \sum_{m'} g_{m'm} \Big[\ln \Big(A_{m'} - \sum_{m''} g_{m'm''} \hat{N}_{m''} \Big) - \ln \Big(A_{m'} + \sum_{m''} (\delta_{m'm''} - g_{m'm''}) \hat{N}_{m''} \Big) \Big]$$

Solution of these coupled equations for the $\{\hat{N}_m\}$ proceeds in two steps.

First step: the auxiliary quantities,

$$w_m \doteq \frac{A_m}{\hat{N}_m} - \sum_{m'} g_{mm'} \frac{\hat{N}_{m'}}{\hat{N}_m},$$

are the solutions of a more compact set of coupled algebraic equations and the partition function has a more compact form:

$$e^{\beta \epsilon_m} = (1 + w_m) \prod_{m'=1}^{M} \left(1 + w_{m'}^{-1} \right)^{-g_{m'm}}, \quad Z = \prod_{m=1}^{M} \left(1 + w_m^{-1} \right)^{A_m}.$$

Second step: the $\{\hat{N}_m\}$, which represent average populations $\langle N_m \rangle$ in macroscopic systems, are the solutions of the linear equations,

$$w_m \langle N_m \rangle + \sum_{m'=1}^{M} g_{mm'} \langle N_{m'} \rangle = \bar{A}_m.$$

The configurational entropy of [pln15] follows from $S = k_B \ln W(\{N_m\})$ using the same intermediate steps and can be rendered most compactly as follows:

$$S = k_B \sum_m \langle N_m \rangle \Big[(1 + w_m) \ln(1 + w_m) - w_m \ln w_m \Big].$$

Remarks:

1. In applications where average populations are controlled by chemical potentials, all occurrences of ϵ_m must be replaced by $\epsilon_m - \mu_m$.
2. The auxiliary quantities w_m represent the number of open slots into which particles from species m can be placed, scaled by the number $\hat{N}_m$ of such particles already in the macrostate. When a population $\hat{N}_m$ is depleted or frozen out by a particular choice of control variables or parameters, the associated w_m diverges.
3. Particle species with vanishing capacity constants A_m contribute no factor $(1 + w_m^{-1})$ to the partition function. They contribute only indirectly. The factor $(1 + w_m^{-1})$ of a particle species with $A_m > 0$ is (effectively) removed from the partition function if $w_m \to \infty$, which is the case if $\hat{N}_m \to 0$.