Statistical Mechanics: Reminder of central ideas

$$S = k_{\mathrm{B}} \ln W \tag{1}$$

where W = number of **available microstates**.

Available microstates = mutually orthogonal quantum states available to the system in that they are consistent with the macroscopic constraints (such as total energy, number of particles, etc.)

We can also write

$$S = -k_{\mathrm{B}} \sum_i p_i \ln p_i \tag{2}$$

which is often more useful.

The distribution which maximises S subject to constraints of fixed total energy U and number of particles N is

$$p_i \propto e^{-\beta\epsilon_i} \qquad \textbf{Boltzmann factor} \tag{3}$$

Therefore

$$p_i = \frac{e^{-\beta\epsilon_i}}{Z} \tag{4}$$

where

$$Z = \sum_{i \in \text{ states}} e^{-\beta\epsilon_i} \tag{5}$$

$$= \sum_{r \in \text{ energy levels}} g_r e^{-\beta\epsilon_r} \tag{6}$$

For a system of N small things (let's call them particles) which are only **weakly interacting** (they don't influence each other's energy levels or eigenstates, but they can exchange energy):

$$Z = \begin{cases} Z_1^N & \text{distinguishable particles} \\ \dfrac{Z_1^N}{N!} & \text{identical particles in classical (high temperature) limit} \\ \text{no simple formula} & \text{identical particles in quantum (low temperature) limit} \end{cases}$$

Also:

$$\begin{aligned} U &= -\frac{\partial \ln Z}{\partial \beta}, \qquad C_\epsilon = \left.\frac{\partial U}{\partial T}\right|_\epsilon \\ F &= -k_\mathrm{B} T \ln Z \\ S &= \frac{U-F}{T}, \qquad \text{or use } S = -\left.\frac{\partial F}{\partial T}\right|_\epsilon \end{aligned}$$

Eqn of state is usually obtained from F, using

$$\mathrm{dF} = -\mathrm{SdT} + \mathrm{XdY}$$

for some X, Y (e.g. $\{-p,\, V\}$ or $\{-m,\, B\}$) so

$$X = \left.\frac{\partial F}{\partial Y}\right|_T$$