Statistical Mechanics: Reminder of central ideas

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

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

$$S = -k_{\rm B} \sum_{i} p_i \ln p_i \tag{2}$$

which is often more useful.

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

$$p_i \propto e^{-\beta \epsilon_i}$$
 Boltzmann factor (3)

Therefore

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

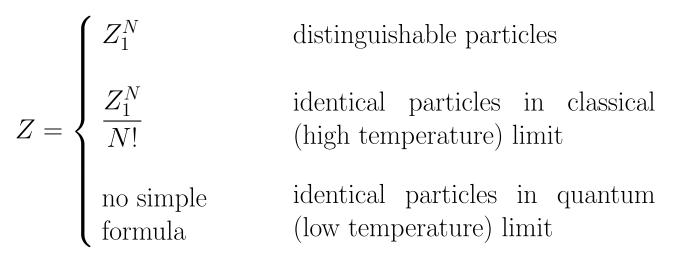
where

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

$$= \sum_{\epsilon \text{ operaturbused}} g_r e^{-\beta \epsilon_r} \tag{6}$$

$$r \in \text{energy levels}$$

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):



Also:

$$U = -\frac{\partial \ln Z}{\partial \beta}, \qquad C_{\epsilon} = \frac{\partial U}{\partial T}\Big|_{\epsilon}$$

$$F = -k_{\rm B}T \ln Z$$

$$S = \frac{U - F}{T}, \qquad \text{or use } S = -\frac{\partial F}{\partial T}\Big|_{\epsilon}$$

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

$$X = \frac{\partial F}{\partial Y} \bigg|_T$$