

Entropy in the canonical ensemble

$$S = -\frac{\partial F}{\partial T} = +\frac{\partial[k_B T \ln Z]}{\partial T} = k_B \left[\ln Z + T \frac{1}{Z} \frac{\partial Z}{\partial T} \right]$$

but

$$Z = \sum_n e^{-E_n/k_B T}$$

so

$$\frac{\partial Z}{\partial T} = \frac{1}{k_B T^2} \sum_n E_n e^{-E_n/k_B T}$$

and

$$S = k_B \left[\ln Z + \frac{1}{k_B T} \frac{1}{Z} \sum_n E_n e^{-E_n/k_B T} \right] = k_B \left[\ln Z + \frac{1}{k_B T} \sum_n p_n E_n \right].$$

Compare this to

$$\begin{aligned} -k_B \sum_n p_n \ln p_n &= -k_B \sum_n p_n \ln \left(\frac{e^{-E_n/k_B T}}{Z} \right) \\ &= -k_B \left[\sum_n p_n \ln e^{-E_n/k_B T} - \sum_n p_n \ln Z \right] \\ &= -k_B \left[\sum_n p_n (-E_n/k_B T) - \ln Z \right] \\ &= k_B \left[\ln Z + \frac{1}{k_B T} \sum_n p_n E_n \right]. \end{aligned}$$

They match up!

This is a significant result. The equation $S = k_B \ln \Omega$ applies *only* to the microcanonical ensemble. It turns out that the equation $S = -k_B \sum_n p_n \ln p_n$ applies to *all* ensembles: microcanonical, canonical, grand canonical, isobaric, etc.