20.8: Entropy Can Be Expressed in Terms of a Partition Function

We have seen that the partition function of a system gives us the key to calculate thermodynamic functions like energy or pressure as a moment of the energy distribution. We can extend this formulism to calculate the entropy of a system once its Q is known. We can start with Boltzmann's (statistical) definition of entropy:

$$S = k \ln(W) \tag{20.8.1}$$

with

$$W = \frac{A!}{\prod_j a_j!}$$

Combining these equations, we obtain:

$$S_{ensemble} = k \ln \frac{A!}{\prod_j a_j!}$$

Rearranging:

$$S_{ensemble} = k \ln A! - k \sum_j \ln a_j!$$

Using Sterling's approximation:

$$\begin{aligned} S_{ensemble} &= kA \ln A - kA - k \sum_j a_j \ln a_j + k \sum_j a_j \\ &= kA \ln A - k \sum_j a_j \ln a_j \end{aligned}$$

Since:

$$\sum_j a_j = A$$

The probability of finding the system in state a_j is:

$$p_j = \frac{a_j}{A}$$

Rearranging:

$$a_j = p_j A$$

Plugging in:

$$S_{ensemble} = kA \ln A - k \sum_j p_j A \ln p_j A$$

Rearranging:

$$S_{ensemble} = kA \ln A - k \sum_j p_j A \ln p_j - k \sum_j p_j A \ln A$$

If A is constant, then:

$$k \sum_j p_j A \ln A = kA \ln A \sum_j p_j$$

Since:

$$\sum_j p_j = 1$$

We get:

$$S_{ensemble} = kA\ln A - k\sum_j p_j A\ln p_j - kA\ln A$$

The first and last term cancel out:

$$S_{ensemble} = -k\sum_j p_j A\ln p_j$$

We can divide by A to get the entropy of the system:

$$S_{system} = -k\sum_j p_j \ln p_j \tag{20.8.2}$$

If all the p_j are zero except for the for one, then the system is perfectly ordered and the entropy of the system is zero. The probability of being in state j is

$$p_j = \frac{e^{-\beta E_j}}{Q} \tag{20.8.3}$$

Plugging Equation 20.8.3 into Equation 20.8.2 results in

$$\begin{aligned} S &= -k\sum_j \frac{e^{-\beta E_j}}{Q}\ln\frac{e^{-\beta E_j}}{Q} \\ &= -k\sum_j \frac{e^{-\beta E_j}}{Q}(-\beta E_j - \ln Q) \\ &= -\beta k\sum_j \frac{E_j e^{-\beta E_j}}{Q} + \frac{k\ln Q}{Q}\sum_j e^{-\beta E_j} \end{aligned}$$

Making use of:

$$\beta k = \frac{1}{T}$$

And:

$$\sum \frac{e^{-\beta E_j}}{Q} = \sum p_j = 1$$

We obtain:

$$S = \frac{U}{T} + k\ln Q \tag{20.8.4}$$