Calculation of Entropy from the Partition Function

We suppose the partition function $Z = Z(E,V,N) = Z(T,V,N)$; then

$$d\ln Z = \frac{\partial \ln Z}{\partial T}dT + \frac{\partial \ln Z}{\partial V}dV\,.$$

Using our earlier results,

$$d\ln Z = \frac{E}{kT^2}dT + \frac{p}{kT}dV\,.$$

Now, consider the identity

$$d\left(\frac{E}{kT}\right) = \frac{1}{kT}dE - \frac{E}{kT^2}dT\,.$$

Next, add the last two equations:

$$\begin{aligned} d\left(\ln Z + \frac{E}{kT}\right) &= \frac{1}{kT}dE + \frac{p}{kT}dV \\ &= \frac{1}{kT}(dE + p\,dV) \end{aligned}$$

But from the fundamental equation of thermodynamics, we have

$$dE = TdS - pdV \quad \Rightarrow \quad TdS = dE + pdV$$

Whence

$$d\left(\ln Z + \frac{E}{kT}\right) = \frac{1}{kT}(TdS) = \frac{1}{k}dS$$

or

$$dS = k\,d\left(\ln Z + \frac{E}{kT}\right)$$

And finally

$$S = k\ln Z + \frac{E}{T} + S_0$$

where S_0 is a constant of integration. Compare with Baierlein Eq. 5.25.

Exercise: Recall the third law of thermodynamics: $S \to 0$ as $T \to 0$. Show that the third law suggests that $S_0 = 0$. Hint: Suppose the ground state of our system has energy ε_0. All other energy levels are higher, so that at low temperatures, the system should be found in this state. Use this assumption to show $S \to S_0$ as $T \to 0$.

Moreover, apart from the third law, we measure only entropy differences. Hence we can always choose $S_0 = 0$, just as we can always choose an arbitrary zero for an energy scale.