Unit 2-5: Entropy of the Ideal Gas in the Microcanonical Ensemble

From the last section we had for the number of states for the ideal gas,

$$\Omega(E, V, N) = \frac{V^N}{h^{3N}} \frac{(2\pi m E)^{3N/2}}{(\frac{3N}{2} - 1)!} \frac{\Delta E}{E} \tag{2.5.1}$$

Using $S = k_B \ln \Omega$, we then get for the entropy,

$$S(E, V, N) = k_B \left\{ N \ln \left[\frac{V(2\pi m E)^{3/2}}{h^3} \right] - \ln \left[\left(\frac{3N}{2} - 1 \right)! \right] + \ln \left[\frac{\Delta E}{E} \right] \right\} \tag{2.5.2}$$

For large N we can use Stirling's approximation for the factorial, $\ln N! \approx N \ln N - N$ (we will derive this later). We then get,

$$S(E, V, N) = k_B \left\{ N \ln \left[\frac{V(2\pi m E)^{3/2}}{h^3} \right] - \left(\frac{3N}{2} - 1 \right) \ln \left(\frac{3N}{2} - 1 \right) + \left(\frac{3N}{2} - 1 \right) + \ln \left[\frac{\Delta E}{E} \right] \right\} \tag{2.5.3}$$

Now we use

$$\ln \left(\frac{3N}{2} - 1 \right) = \ln \left[\frac{3N}{2} \left(1 - \frac{2}{3N} \right) \right] = \ln \frac{3N}{2} + \ln \left(1 - \frac{2}{3N} \right) \approx \ln \frac{3N}{2} - \frac{2}{3N} \tag{2.5.4}$$

where we used the Taylor series to expand $\ln(1 + \epsilon) \approx \epsilon$ in the last step. We now have,

$$S(E, V, N) = k_B \left\{ N \ln \left[\frac{V(2\pi m E)^{3/2}}{h^3} \right] - \frac{3N}{2} \ln \frac{3N}{2} + \frac{3N}{2} \left(\frac{2}{3N} \right) + \ln \frac{3N}{2} - \frac{2}{3N} + \frac{3N}{2} - 1 + \ln \left[\frac{\Delta E}{E} \right] \right\} \tag{2.5.5}$$

$$= k_B \left\{ N \ln \left[\frac{V}{h^3} \left(\frac{2\pi m E}{3N/2} \right)^{3/2} \right] + \frac{3N}{2} + \ln \frac{3N}{2} + O \left(\frac{1}{N} \right) + \ln \left[\frac{\Delta E}{E} \right] \right\} \tag{2.5.6}$$

Recall, we took $\Delta E \sim E/N$, so $\ln \left[\frac{\Delta E}{E} \right] \sim -\ln N$. Since we are interested in the thermodynamic limit of $N \to \infty$, we can drop all but the leading terms that scale proportional to N, and we then get,

$$\boxed{S(E, V, N) = N k_B \left\{ \frac{3}{2} + \ln \left[\frac{V}{h^3} \left(\frac{4mE}{3N} \right)^{3/2} \right] \right\}} \tag{2.5.7}$$

since as $N \to \infty$ the terms $\ln(3N/2)$ and $\ln(\Delta E/E)$ become negligible.

Note, our result does not depend on ΔE, just as we desired.

With the above expression for the entropy, we can recover some familiar results,

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{V,N} = \frac{\partial}{\partial E} \left(N k_B \frac{3}{2} \ln E \right) = \frac{3}{2} N k_B \frac{1}{E} \qquad \Rightarrow \qquad E = \frac{3}{2} N k_B T \tag{2.5.8}$$

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V} \right)_{E,N} = \frac{\partial}{\partial V} \left(N k_B \ln V \right) = N k_B \frac{1}{V} \qquad \Rightarrow \qquad pV = N k_B T \tag{2.5.9}$$

So far, so good!

But there is a problem. S, as given by Eq. (2.5.7) above, is *not* extensive. If we take $E \to 2E$, $V \to 2V$, and $N \to 2N$, we do *not* get $S \to 2S$. It is the $\ln V$ term in Eq. (2.5.7) that spoils the desired extensivity. When we double E, V, and N, the argument of the logarithm doubles, whereas we would need it to stay constant if S is to double.

We can compare Eq. (2.5.7) to the entropy for the ideal gas that we found in Notes 1-3, where we used the experimental $pV = Nk_BT$ and $E = \frac{3}{2}Nk_BT$ together with the Gibbs-Duhem relation to get,

$$S(E, V, N) = \frac{N}{N_0}S_0 + k_B N \ln\left[\left(\frac{V}{V_0}\right)\left(\frac{E}{E_0}\right)^{3/2}\left(\frac{N}{N_0}\right)^{-5/2}\right] \tag{2.5.10}$$

where N_0, S_0, V_0 and E_0 are all constants. The result above in Eq. (2.5.10) is properly extensive. Compared to Eq. (2.5.7), the entropy of Eq. (2.5.10) has an extra factor of N^{-1} inside the logarithm, which makes the argument of the logarithm stay constant as E, V, and N are all doubled, as is needed if S is to double and so be extensive.

Note: The Gibbs-Duhem relation was derived *assuming* the entropy S was extensive. Hence it should not be surprising the entropy of Eq. (2.5.10), derived using the Gibbs-Duhem relation, is indeed extensive.

What is the physical reason that the entropy of Eq. (2.5.7), as obtained in the microcanonical ensemble, fails to be extensive?

Note, the entropy of Eq. (2.5.7) is not properly additive over subsystems, as is the entropy of Eq. (2.5.10). That is, the entropy of Eq. (2.5.7) does not obey the desired condition,

$$\lambda S(E, V, N) = S(\lambda E, \lambda V, \lambda N) \tag{2.5.11}$$

that it must. Rather Eq. (2.5.7) obeys the relation $\lambda S(E, V, N) = S(\lambda E, V, \lambda N)$.

What is the origin of this problem?