Appendix E: Entropy of an Ideal Gas – Entirely based on thermodynamics (Optional)

Question: How far we can go in getting at expression for S in an ideal gas based on what we know about the thermodynamics of an ideal gas?

Answer: Quite far!

Known (ideal gas): $\left\{ \begin{array}{l} pV = NkT \\ E = \frac{3}{2}NkT \end{array} \right\} pV = \frac{2}{3}E$

$\therefore E = \frac{3}{2}pV$

- From definition of S in thermodynamics, we look at $\left(\frac{dQ}{T}\right)_{rev}$
- $dQ = dE + pdV$
- $$\left(\frac{dQ}{T}\right)_{rev} = \frac{dE}{T} + \frac{pdV}{T} = \frac{3}{2}\frac{d(pV)}{T} + \frac{pdV}{T}$$
$$= \frac{5}{2}\frac{p}{T}dV + \frac{3}{2}\frac{V}{T}dp$$
$$= \frac{5}{2}Nk\frac{dV}{V} + \frac{3}{2}Nk\frac{dp}{p}$$

- For a reversible process from equilibrium state a to equilibrium state b,

$$\int_a^b \left(\frac{dQ}{T}\right)_{rev} = \left[\frac{5}{2}Nk\ln V + \frac{3}{2}Nk\ln p\right]_a^b$$
$$= \left[Nk\ln\left(p^{\frac{3}{2}}V^{\frac{5}{2}}\right)\right]_a^b$$
$$= Nk\ln\left(p_b^{\frac{3}{2}}V_b^{\frac{5}{2}}\right) - Nk\ln\left(p_a^{\frac{3}{2}}V_a^{\frac{5}{2}}\right)$$
$$= S_b - S_a$$

Clausius (1865) introduced the term "entropy"

$\therefore$ For an ideal gas, the entropy is of the form

$$S = Nk\ln\left(\frac{p^{3/2}V^{5/2}}{C}\right) \quad (1)$$

where C is a constant (meaning not dependent on p and V) that can depend on N

- So far so good!

Eq.(1) can be expressed as:

$$S = Nk\ln\left(\frac{p^{3/2}V^{3/2}\,V}{C}\right) = Nk\ln\left(\frac{\left(\frac{2}{3}\right)^{3/2}E^{3/2}V}{C}\right)$$
$$= Nk\ln\left(\frac{E^{3/2}V}{C'}\right) \quad (2)$$

- We start to see $S(E,V,N)$ from thermodynamics!
- But S is an extensive property.

$$S(\lambda E, \lambda V, \lambda N) = \lambda S(E,V,N)$$

Scale up the system by a factor λ

Q: What does it say about the constant C', which can depend on N?

$$\lambda N k \ln\left(\frac{E^{3/2}V}{C'(N)}\right) = \lambda N k \ln\left(\frac{\lambda^{3/2}E^{3/2}\lambda V}{C'(\lambda N)}\right)$$

- S is extensive
- True if $C'(N) = c\,N^{5/2}$

another constant that does not depend on p, V, N

Check:

$$LHS = \lambda N k \ln\left(\frac{E^{3/2}V}{cN^{5/2}}\right)$$

$$RHS = \lambda N k \ln\left(\frac{\lambda^{3/2}E^{3/2}\lambda V}{c\,\lambda^{5/2}N^{5/2}}\right) = \lambda N k \ln\left(\frac{E^{3/2}V}{cN^{5/2}}\right) = LHS$$

$\therefore$ From Eq.(2),

$$S = Nk\ln\left(\frac{E^{3/2}V}{cN^{3/2}}\right)$$ from thermodynamics

Summary:

- Entirely based on thermodynamics, we have

$$S(E,V,N) = Nk\ln\left(\frac{E^{3/2}V}{cN^{5/2}}\right) = Nk\ln\left(\frac{1}{c}\left(\frac{E}{N}\right)^{3/2}\left(\frac{V}{N}\right)\right)$$

form that makes sure S is extensive

- Compare with stat. mech. result

$$S(E,V,N) = Nk\ln\left(\left(\frac{V}{N}\right)\left(\frac{m}{3\pi\hbar^2}\frac{E}{N}\right)^{3/2}\right) + \frac{5}{2}Nk$$

(Quite close!)

- Remark: Replacing $\left(\frac{E}{N}\right)^{3/2}$ by $\left(\frac{3}{2}kT\right)^{3/2}$ in S, we get an expression that can be compared with the Sackur-Tetrode Equation (1911).