Temperature and Entropy for the Ideal Gas

We now have a quantity called entropy:

$$S(E) = k_B \ln[\Omega(E)]$$

We have found $\Omega(E)$ for the ideal gas, so now let's use entropy to understand temperature and pressure in the ideal gas.

Recall, in momentum space,

$$\Omega(E) = \frac{(3Nm)\pi^{3N/2}}{(3N/2)!} R^{3N-2} \qquad R = \sqrt{2mE}$$

We also need the number of states in configuration space. We can ask, what is the probability density that particles will be in a particular configuration Q inside the box of volume V?

- We know ρ is a constant
- We know the particles are in some configuration,

$$\int \rho(Q)\, dQ = 1$$

- For one particle,

$$\int dQ = \int_V dx_1 dy_1 dz_1 = V$$

- Hence, each particle will contribute a factor of V.

$$\therefore \rho(Q) = \frac{1}{V^N}$$

So now we can write down the complete phase space volume:

$$\Omega(E) = \Omega_{\mathbb{P}}(E)\,\Omega_{\mathbb{Q}}(E)$$

$$= V^N (3Nm)\, \pi^{3N/2} \frac{(2mE)^{3N/2}}{2mE} \Big/ (3N/2)!$$

$$= V^N \pi^{3N/2} (2mE)^{3N/2} \Big/ (3N/2)!$$

We drop the term $\left(\frac{3N}{2E}\right)$ as it effectively just adds a negligible constant to the energy

Now,

$$S(E) = k_B \ln\left[V^N \pi^{3N/2} (2mE)^{3N/2} \Big/ (3N/2)!\right]$$

$$= N k_B \ln(V) + \frac{3N k_B}{2} \ln\left(2\pi m E\right) - k_B \ln\left[(3N/2)!\right]$$

And we can take derivatives to get

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{3Nk_B}{2} \cdot \frac{1}{2\pi m E} \cdot 2\pi m$$

$$= \frac{3N k_B}{2E}$$

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{N k_B}{V}$$

$$\Rightarrow k_B T = \frac{2E}{3N} \quad \text{or} \quad E = \frac{3}{2} N k_B T$$

Each dimension has $\langle E \rangle_{D} = \frac{1}{2} k_B T$!

$$\Rightarrow PV = N k_B T$$

Equation of state!

Refinements to the Microcanonical Energy Shell

① Notice

$$\Omega(E) \simeq \frac{V^N \pi^{3N/2} (2mE)^{3N/2}}{(3N/2)!}$$

has units

$$\left([\text{length}][\text{momentum}]\right)^{3N}$$

So the volume of the shell depends upon the units chosen for length, mass, and time. Changing these units requires a constant (3N times)

$$\sim C^{3N}(\text{length} \cdot \text{momentum})^{3N}$$

$$S \sim \ln \Omega \sim \ln C^{3N} + \ln\left[(\text{length} \cdot \text{momentum})^{3N}\right]$$

However, T and P only care about derivatives of entropy, so the constant doesn't matter ⇒ in classical stat mech, the zero of entropy is undefined.

In QM, zero entropy <u>is</u> set. Note that Ω has units of $h = [\text{length}][\text{momentum}]$

We'll show later that the factor to set $S=0$ is h^{3N}

② The Gibbs Factor

Classical mechanics deals with "undistinguished" particles ⇒ particles are <u>not</u> identical, but the Hamiltonian and measurements treat equivalent configurations identically. i.e.

is a different configuration, but both should not contribute to the Hamiltonian.

Hence, the phase space volume $\Omega(E)$ should be divided by 2 as compared to calculations w/ distinguished particles.

For N undistinguished particles, Ω should be divided by $N!$, the number of ways of permuting N labels.

Hence,

$$\Omega(E) = \int_{E < \mathcal{H}(P,Q) < E+\delta E} \frac{dP\,dQ}{N!\,h^{3N}}$$

Note we dropped $\frac{1}{\delta E}$ ... again, this adds a negligible constant to the entropy.