Partition Function of Ideal Gas

- The energy of an ideal gas is

$$E_{TOT} = \frac{p_1^2}{2m} + \cdots + \frac{p_N^2}{2m}$$

$$= \varepsilon_1 + \cdots + \varepsilon_N$$

this is a sum of N terms
Z_{TOT} will be a product

- The partition function is a sum over classical configurations

$$Z_{TOT} = \frac{1}{N!}\int \frac{d^3r_1\, d^3p_1}{h^3} \cdots \frac{d^3r_N\, d^3p_N}{h^3} \; e^{-E_{TOT}/kT}$$

weighted by $e^{-E/kT}$

- Now the integrals factorize:

$$Z_{TOT} = \frac{1}{N!}\left[\int \frac{d^3r_1 d^3p_1}{h^3}\, e^{-\varepsilon_1/kT}\right]^N = \frac{1}{N!}\, Z_1^N$$

- We need to discuss two things more carefully

① Why the N! : It's because interchanging two particles does not give a new state. (see below).

this means they are indistinguishable

② Why the sum over states becomes $\frac{d^3r\, d^3p}{h}$.

- We will turn to ① & ②, after calculating Z_1, and discussing the result.

- Then To find Z_1 we note.

$$Z_1 = \int \frac{d^3r\, d^3p}{h^3}\, e^{-p^2/2mk_BT} \leftarrow Z_1 \text{ is dimensionless}$$

$$d\mathcal{P} = \frac{1}{Z}\, e^{-p^2/2mk_BT}\, \frac{d^3p\, d^3r}{h^3} = C\, e^{-p^2/2mkT}\, \frac{d^3r\, d^3p}{h^3}$$

$1/Z$ is just the normalization const C multiplying the phase-space volume element $d^3r\, d^3p / h^3$.

Doing the integral:

$$Z_1 = \frac{V}{h^3} \int d^3p\, e^{-p^2/2mk_BT} = \frac{V}{h^3} \int_0^\infty 4\pi p^2\, dp\, e^{-p^2/2mk_BT}$$

recognize that $\sqrt{mk_BT}$ is the typical momentum scale

$$= \frac{V(\sqrt{mk_BT})^3}{h^3} \times \int \frac{p^2\, dp}{(\sqrt{mk_BT})^3}\, e^{-p^2/2mkT} \cdot 4\pi$$

$$= \frac{V}{h^3}(mk_BT)^{3/2} \underbrace{\int_0^\infty u^2\, du\, e^{-u^2/2}\, 4\pi}_{I = (2\pi)^{3/2}}$$

So:

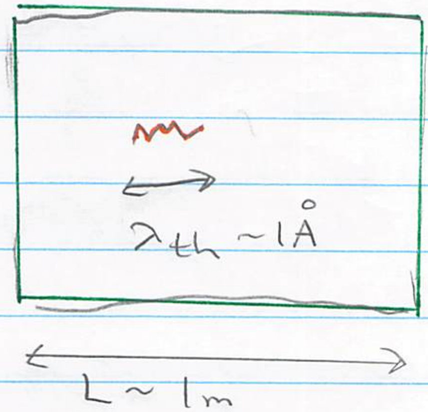
$$Z = V\left(\frac{2\pi m k_BT}{h}\right)^{3/2}$$

$$\boxed{Z_1 = \frac{V}{\lambda_{th}^3} \quad \text{with} \quad \lambda_{th} \equiv \frac{h}{(2\pi m k_BT)^{1/2}}}$$

Comments:

- λ_{th} is the typical thermal de Broglie wavelength:

$p_{th} \sim (m k_B T)^{1/2}$ so $\boxed{\lambda_{th} \sim \frac{h}{p_{th}} \sim \frac{h}{(m k_B T)^{1/2}}}$



- Typically $\lambda_{th} \sim$ angstrom or less, while the box size is meters.

Z_1 is the Volume in units of λ_{th}^3. Z_1 is a big number $\sim 10^{30}$

- So

$$Z_{tot} = \frac{Z_1^N}{N!}$$ using the stirling approximation $N! \simeq \left(\frac{N}{e}\right)^N$

- We have

$$\boxed{Z_{TOT} = \left(\frac{eV}{N\lambda_{th}^3}\right)^N}$$

So

$$F = -k_B T \ln Z_{TOT}$$

$$\boxed{F = -k_B T N \ln\left(\frac{eV}{N\lambda_{th}^3}\right)}$$

number per volume used a lot below

Or defining the density $\boxed{n = N/V}$ we have

$$\boxed{F_{TOT} = N k_B T \left(\ln(n \lambda_{th}^3) - 1 \right)}$$

and also

$$\ln Z_{TOT} = -N \left(\ln(n \lambda_{th}^3) - 1 \right)$$

- Now we can use the free energy and Z to derive quantites of interest. For istance

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z_{TOT} \qquad \left(\text{note } \lambda_{th}^3 = h^3 \left(\frac{\beta}{2\pi m} \right)^{3/2} \right)$$

$$\langle E \rangle = N \frac{\partial}{\partial \beta} \left(\ln \beta^{3/2} + \text{stuff indep of } \beta \right)$$

note $\ln \lambda_{th}^3 = \ln \beta^{3/2} \frac{h^3}{(2\pi m)^{3/2}}$

$$\langle E \rangle = \frac{3}{2} \frac{N}{\beta} = \frac{3}{2} N k_B T$$

- Similarly

$$S = -\left(\frac{\partial F}{\partial T} \right)_V = -N k_B \left(\ln(n \lambda_{th}^3) - 1 \right) - N k_B T \frac{\partial}{\partial T} \left(\ln T^{-3/2} + \text{indep of } T \right)$$

$$S = N k_B \left(-\ln(n \lambda_{th}^3) + \frac{5}{2} \right)$$

this is the sackur tetrode equation again!

- So

$$\frac{S}{Nk_B} = -\ln(n\lambda_{th}^3) + 5/2$$

☆☆ as we discuss now, the classical dynamics is valid when the volume per particle is much longer than the debroglie wavelength

☆ draw a picture

$$\boxed{\frac{V}{N} \gg \lambda_{th}^3} \quad \text{or} \quad \boxed{n\lambda_{th}^3 \ll 1}$$

draw a picture!

(recall $n = N/V$) thus, $-\ln(n\lambda_{th}^3) \sim 8$, is positive, and somewhat large number. If Eq. ☆ didn't hold the wave-fcns would begin to overlap and quantum mechanics would be necessary.

- Finally lets derive the pressure:

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = -\frac{\partial}{\partial V}\left[Nk_BT(\ln(n\lambda_{th}^3) - 1\right]$$

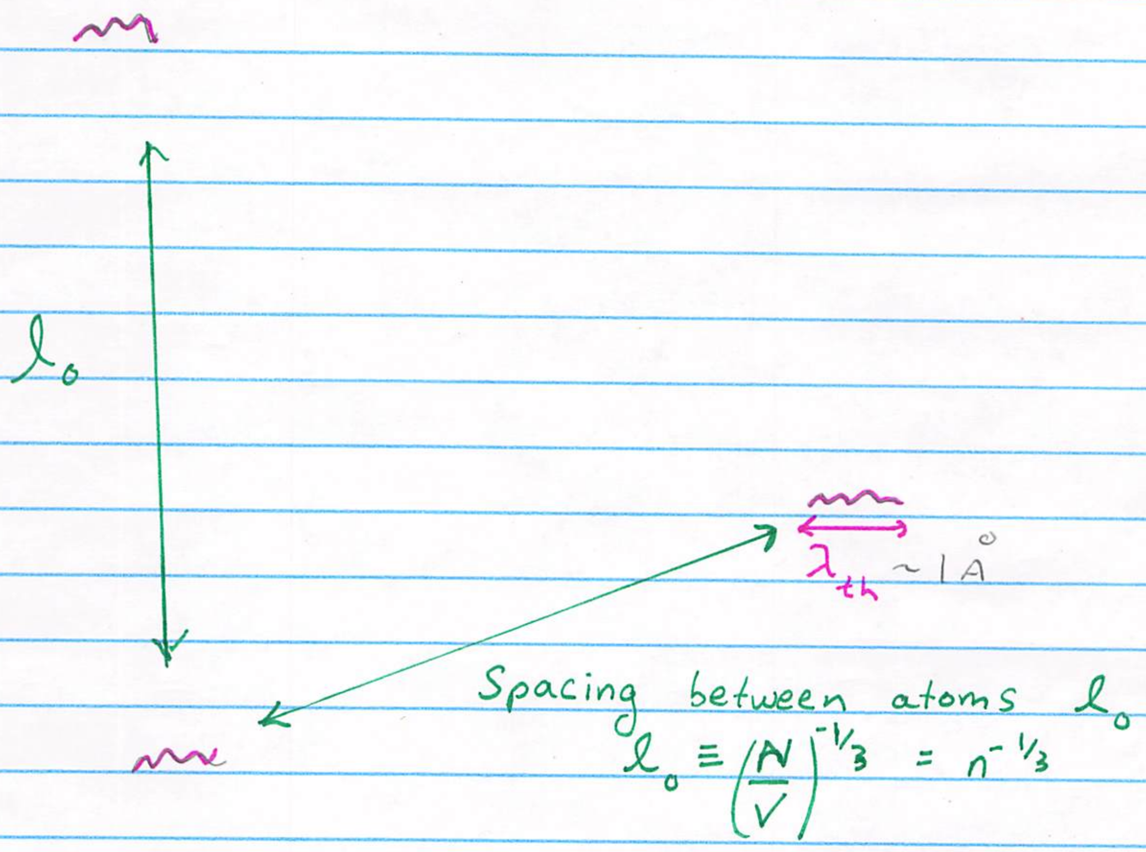
The volume is in $n \equiv N/V$ so

$$p = -\frac{\partial}{\partial V} Nk_BT(\ln V^{-1} + \text{stuff indep of } V)$$

$$\boxed{p = \frac{Nk_BT}{V}} \quad \checkmark$$

rederiving the ideal gas law.

Picture:



- The typical atomic debroglie wavelength is $\lambda_{th} \sim 1 \text{Å}$. The typical spacing between atoms is $l_0 \equiv n^{-1/3} \sim 3.3 \text{ nm}$. So

$$n \lambda_{th}^3 \sim \frac{1}{(33)^3} \sim \frac{1}{27000}$$

$$-\ln n \lambda_{th}^3 \sim 10$$