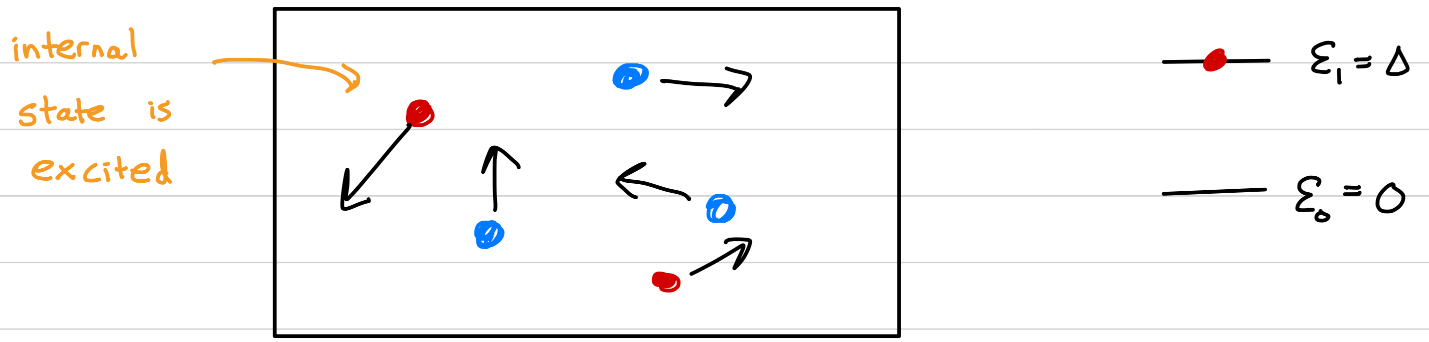
The two state Gas

Consider the gas shown below



Each atom is labelled by its internal state as well as its momentum

$$\varepsilon(\vec{p}, s) = \frac{p^2}{2m} + \varepsilon_s$$

labells the internal state either ground or excited

Then we have the energy

$$E = \varepsilon(\vec{p}_1, s_1) + \varepsilon(\vec{p}_2, s_2) + \ldots + \varepsilon(\vec{p}_N, s_N)$$

Then

$$Z_N = \frac{1}{N!} \sum_{s_1 \ldots s_N} \int \frac{d^3 r_1 \, d^3 p_1}{h^3} \cdots \frac{d^3 \vec{r}_N \, d^3 p_N}{h^3} \, e^{-\beta E}$$

It factorizes

$$Z_N = \frac{Z_1^N}{N!} \simeq \left(\frac{e Z_1}{N} \right)^N$$

Sterling Approx

Where

$$Z_1 = \sum_s \int \frac{d^3\vec{r}\, d^3\vec{p}}{h^3} e^{-\beta p^2/2m} e^{-\beta \varepsilon_s}$$

$$= Z_{1trans} \cdot Z_{1int}$$

Where

$$\underbrace{Z_{1trans} = \int \frac{d^3\vec{r}\, d^3\vec{p}}{h^3} e^{-\beta p^2/2m}}$$

This is the partition fcn of the mono-atomic gas we studied alread

$$\underbrace{Z_{int} = \sum_{s=0} e^{-\beta \varepsilon_s}}$$

Internal Partition Fcn e.g $Z_{int} = 1 + e^{-\beta\Delta}$

Since the partition function factorizes, the free energy (and then everything else $S, U,$ etc) is just a sum

$$F = -kT \ln Z_N = N\left[-kT \ln\left(\frac{e Z_{1trans}}{N}\right) + -kT \ln Z_{int}\right].$$

$$= N F_{1trans} + N F_{1int}$$

where

(1) $$F_{1trans} = -kT \ln\left(\frac{e Z_{1trans}}{N}\right) = -kT \ln\left(\frac{e V_N}{\lambda^3}\right)$$ ⇐ See ideal gas

(2) $$F_{1int} = -kT \ln Z_{int} = -kT \ln(1 + e^{-\beta\Delta})$$ ⇐ See two state system

Now everything else is a derivate of the free energy

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = \underbrace{N S_{1trans}}_{\text{entropy of MAIG see preivous}} + \underbrace{N S_{1int}}_{\text{entropy of N two state system see previous}}$$

entropy $S_{int} = -\partial F_{int}/\partial T$ of N two state system

$$U = -\left(\frac{\partial \ln Z}{\partial \beta}\right)_V = \left(\frac{\partial(\beta F)}{\partial \beta}\right)_V = \underbrace{N U_{1trans}}_{\text{energy of MAIG}} + \underbrace{N U_{1int}}_{\text{internal energy}}$$

$U = \frac{3}{2} NkT$

where for example

$$U_{Int} = \left(\frac{\partial(\beta F_{1int})}{\partial \beta}\right)_V = -\frac{\partial \ln Z_{int}}{\partial \beta} = \frac{\Delta e^{-\beta\Delta}}{1 + e^{-\beta\Delta}}$$