Average of some quantity Q in terms of v is

$$\langle Q \rangle = \frac{\int_0^\infty v^2 e^{-\beta(\frac{1}{2}mv^2)} Q(v)\, dv}{\int_0^\infty v^2 e^{-\beta(\frac{1}{2}mv^2)}\, dv}$$

Mean speed. We can use $Q(v) = v$ then we get

$$\langle v \rangle = \bar{v} = \frac{\int_0^\infty v^2 e^{-\beta(\frac{1}{2}mv^2)} v \, dv}{\int_0^\infty v^2 e^{-\beta(\frac{1}{2}mv^2)}\, dv}$$

Note on integrals: $\int_0^\infty x^n e^{-x^2} dx = \frac{1}{2}\left(\frac{n-1}{2}\right)!$

e.g. if $n=3$ we have $\int_0^\infty x^3 e^{-x^2} dx = \frac{1}{2}(1)! = \frac{1}{2}.$

If $n = 2$ then $\int_0^\infty x^2 e^{-x^2} dx = \frac{1}{2}\left(\frac{2-1}{2}\right)! = \frac{1}{2}\cdot\left(\frac{1}{2}!\right) = \frac{1}{2}\frac{\sqrt{\pi}}{2}$

$= \sqrt{\pi}/4$

Return to the question: using the above integrals, with all the constants

we get $\bar{v} = \dfrac{\sqrt{8}}{\sqrt{\pi\,\beta M}} \simeq 1.60\ 1/\sqrt{\beta M}$

$n = 4$

$\int_0^\infty x^4 e^{-x^2} dx$

$= \frac{1}{2}\left(\frac{4-1}{2}\right)!$

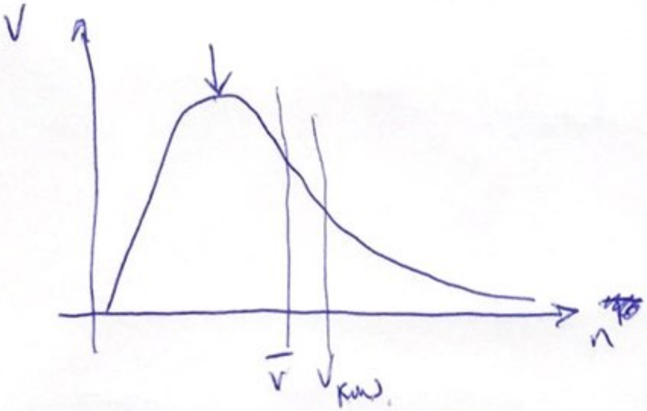
$= \frac{1}{2}\left(\frac{3}{2}\right)!$

$= \frac{3}{8}\sqrt{\pi}$

RMS speed: this is

$$v_{RMS}^2 = \frac{\int_0^\infty v^2 e^{-\beta(\frac{1}{2}mv^2)} v^2 dv}{\int_0^\infty v^2 e^{-\beta(\frac{1}{2}mv^2)} dv}$$

$= 3/\beta M \Rightarrow v_{RMS} \simeq \sqrt{3/\beta M} \simeq 1.73 \cdot 1/\sqrt{\beta M}$



The average kinetic energy per particle is

$$\bar{\mathcal{E}}_{KE} = \tfrac{1}{2} m v_{RMS}^2 = \frac{3}{2\beta} = \underline{\underline{\tfrac{3}{2} k_B T}}.$$

Equipartition of energy: each degree of freedom contributes $\tfrac{1}{2} k_B T$ to the internal energy of the system.

The partition function. We found that for 3D ∞-square well we had

$$Z_1 = V\left(\frac{2\pi M}{\beta h^2}\right)^{3/2} = V/\lambda_D^3$$

We get for the internal energy:

$$U = -N \frac{\partial \ln Z_1}{\partial \beta} = \frac{\partial \ln Z_1^N}{\partial \beta} = \frac{3 N k_B T}{2}$$

$$\frac{\partial}{\partial x}\left(a f(x)\right) = a \frac{\partial}{\partial x}\left(f(x)\right)$$

Free energy: $F = -N k_B T \ln Z_1 = -k_B T \ln Z_1^N$

$$= -N k_B T \left(\ln V - 3 \ln \lambda_D \right)$$

If we have the single-particle partition function Z_1 then the many particle partition function is

$$Z_N = Z_1^N.$$

Ly we define Z_N as $Z_N = \sum_{\substack{i \\ \{\text{states}\}}} e^{-\beta \varepsilon(i_1, i_2, i_3, \ldots)}$

where $\varepsilon(i_1, i_2, \ldots)$ is the energy of the particles in states $i_1, i_2 \ldots$

This means, e.g. the first particle is in state i_1 with energy $\varepsilon(i_1)$.

Properties of exponentials means that the N particle energy is

$$\underline{\varepsilon(i_1, i_2, i_3, \ldots) = \varepsilon(i_1) + \varepsilon(i_2) + \varepsilon(i_3) + \ldots} \quad \text{(additive)}$$

$$Z_N = \sum_{i_1} e^{-\beta\varepsilon(i_1)} \cdot \sum_{i_2} e^{-\beta\varepsilon(i_2)} \sum_{i_3} e^{-\beta\varepsilon(i_3)} \ldots = Z_1^{\,N}$$

Notice that since the energy is additive it means that the particle's individual energies don't depend on the interaction with other particles, i.e. they are non-interacting and hence distinguishable or classical. (i.e. Maxwell-Boltzmann statistics).

<u>Summarise</u> For the M-B distribution of mono atomic gas the single particle partition function is $Z_1 = V\left(\frac{2\pi m}{\beta h^2}\right)^{3/2} = V/\lambda_B^3$ defining $\lambda_B(\beta) \equiv \lambda_B(T)$

We get internal energy $U = -\partial/\partial\beta \ln Z_N = \frac{3N}{2\beta} = 3/2\, k_B T \cdot N$

Free energy: $\overset{(N,V)}{F} = -k_B T \ln (Z_1)^N$

$$= -N k_B T \left[\ln V - 3 \ln \lambda_D \right]$$

Let's double volume and particle number, i.e.

$$F(2N, 2V) = -(2N) k_B T \left[\ln (2V) - 3 \ln \lambda_D \right]$$

$$\neq 2 F(N, V). \quad :($$

For N distinguishable particles we can arrange them proportional to $N!$

Let's look at $Z_N = Z_1^N / N!$ - what's the consequences?

$$\ln\left(Z_1^N/N!\right) = \ln Z_1^N - \ln N!$$

$$= N \ln Z_1 - N \ln N + N$$

$$= N(\ln Z_1 - \ln N + 1) = N\left(\ln Z_1/N + 1\right)$$

Therefore we get $\ln Z_N = N\left(\ln V/N - 3\ln \lambda_D + 1\right)$

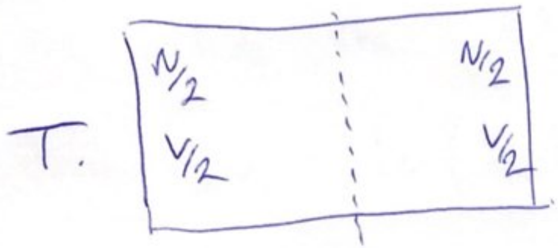
Hence $F(N, V) = -N k_B T \left[\ln(V/N) - 3\ln \lambda_D + 1\right]$

So $F(2N, 2V) = -(2N) k_B T \left[\ln\left(2V/2N\right) - 3\ln \lambda_0 + 1\right]$

$$= 2F(N, V).$$

This is known as Gibb's Paradox.

Let's have a container with a partition dividing it in two, i.e.



Density N/V.

For entropy:

$$S\left(\tfrac{N}{2}, \tfrac{V}{2}\right) + S\left(\tfrac{N}{2}, \tfrac{V}{2}\right)$$

$$= 2\left(\tfrac{3}{2} k_B \tfrac{N}{2}\right) + 2 \cdot \tfrac{N}{2} k_B \left[\ln\left(\tfrac{V}{2}\right) - 3 \ln \lambda_0\right]$$

$$= \tfrac{3}{2} N k_B + N k_B \left[\ln\left(\tfrac{V}{2}\right) - 3 \ln \lambda_0\right]$$

Calculate the difference $S(N, V) - 2S\left(\tfrac{N}{2}, \tfrac{V}{2}\right) = N k_B \ln 2 > 0$

The removal of this partition is reversible so the change in entropy should be zero.

We can do the same argument but, similar to free energy, we include the $N!$ term. When we do that the entropy has a term in $\ln(V/N)$ rather than $\ln(V)$ and so we get

$$2\, S\left(N/2, V/2\right) = S(N, V). \quad \checkmark$$

Hence we require the $N!$ term - this makes entropy and free energy do as required, i.e. double when system size doubles, etc.

This is telling us about the distinguishability of particles.

When they are indistinguishable we have $N!$ less arrangements.