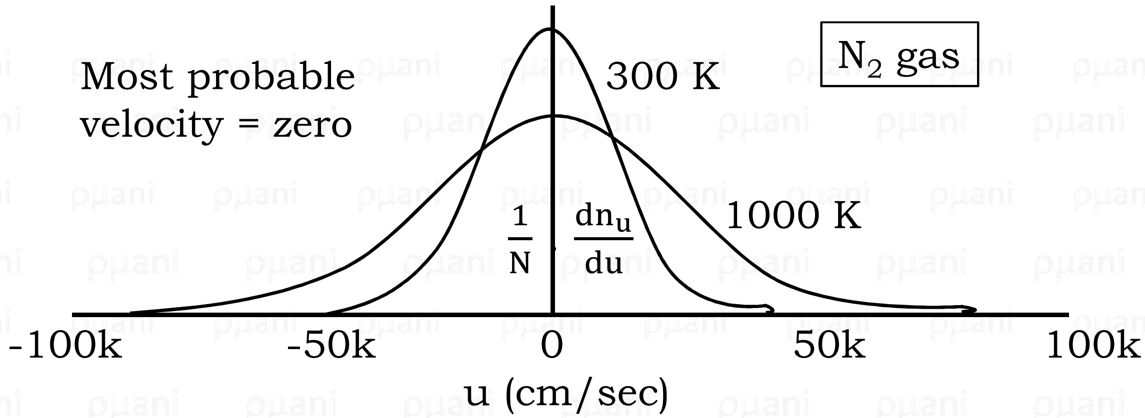
Lectures 7-8

Maxwell distribution plots at different temperatures

We know, $dn_u = N \cdot A \cdot e^{-\beta u^2} \cdot du$ where $A = (\frac{m}{2\pi k T})^{\frac{1}{2}}$ and $\beta = \frac{m}{2kT}$

$$\frac{dn_u}{N} = (\frac{m}{2\pi k T})^{\frac{1}{2}} \cdot e^{-\frac{m u^2}{2kT}} \cdot du$$

When a equation/function takes the form of $A \cdot e^{-\beta u^2}$, then it is typically known as Gaussian distribution function.



$\Rightarrow$ Velocity distribution

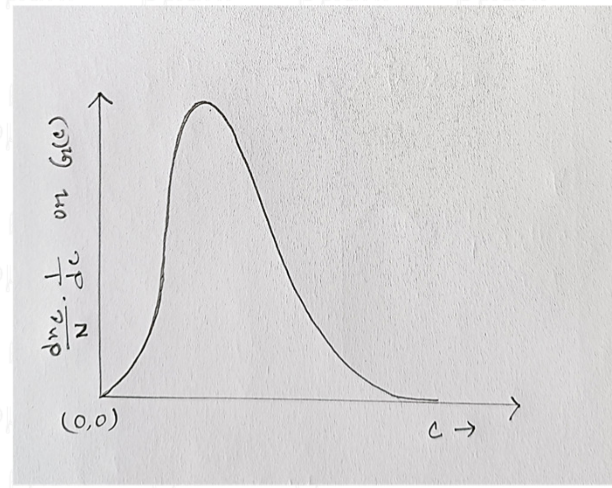
Question: Does the most probable velocity change because of change in temperature?

Question: Why does the curve become broader?

For 3D, Maxwell distribution of speed takes the functional form: $dn_c = N \,.\, \underbrace{4\pi \,.\, \left(\frac{m}{2\,\pi\, k\, T}\right)^{\frac{3}{2}} .\, e^{-\frac{m\,c^2}{2\,k\,T}} .\, c^2}_{G(c)} \,.\, dc$

$\Rightarrow \quad \frac{dn_c}{N} = G(c) \,.\, dc$

Thus, the final shapes takes the following:



For very small value of ‘c’ , $(e^{-\frac{m\,c^2}{2\,k\,T}})$ is close to 1.

At this extreme end, with the increase in ‘c’, c^2 term dominates,

and takes the parabolic shape of the curve.

Thus, the value of dn_c or G(c) increases with the increase in ‘c’.

At very high value of ‘c’, $(e^{-\frac{m\,c^2}{2\,k\,T}})$ dictates the shape of the curve

and at this extreme end, as ‘c’ increases $(e^{-\frac{m\,c^2}{2\,k\,T}})$ decreases, thus, the value of dn_c or G(c) decreases.

Because of this, initially the value of dn_c or G(c) increases (parabolic), then reaches a maximum and finally decays exponentially.

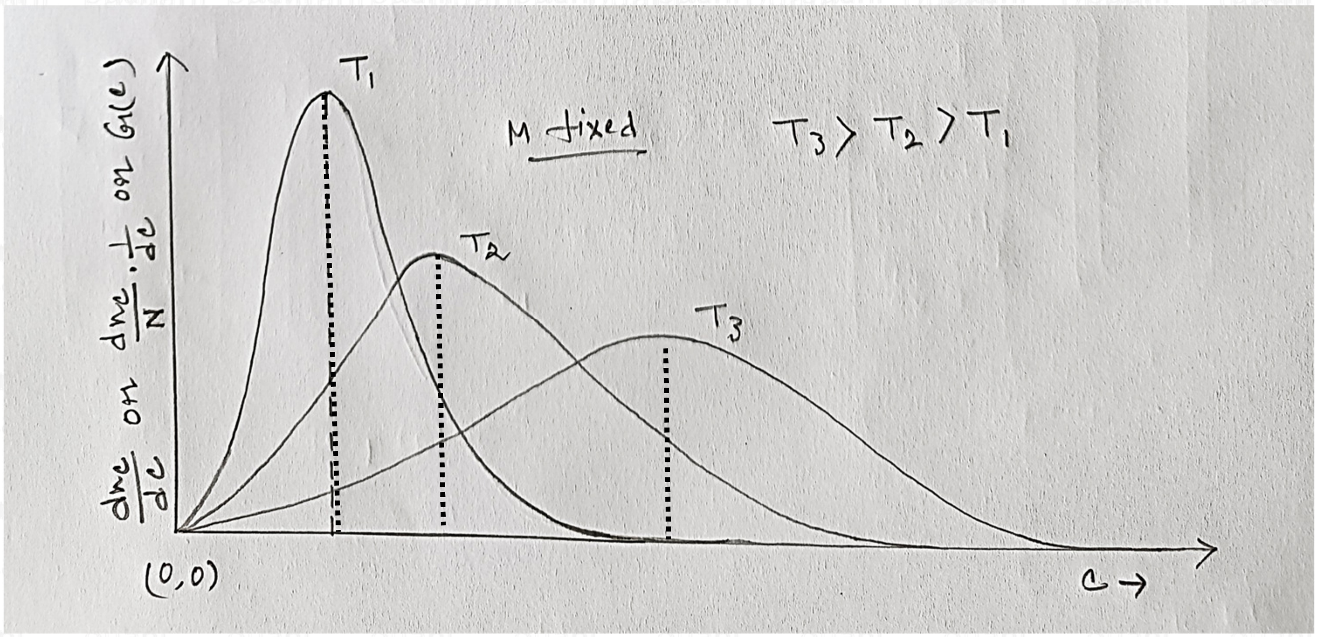
So, the shape is not Gaussian.

Question:

(a) What is the total area under the curve?

(b) What will be the shape if $\frac{dn_c}{dc}$ is plotted against 'c' ? What would be the total area under the curve in this case?

Now let us see, how the Maxwell 3D speed distribution curve will change as temperature is changed.



(A) Two domains , at low ‘c’ and at high ‘c’

(B) Two cases, at very low and at very high T

(C) Does the total area under the curve change?

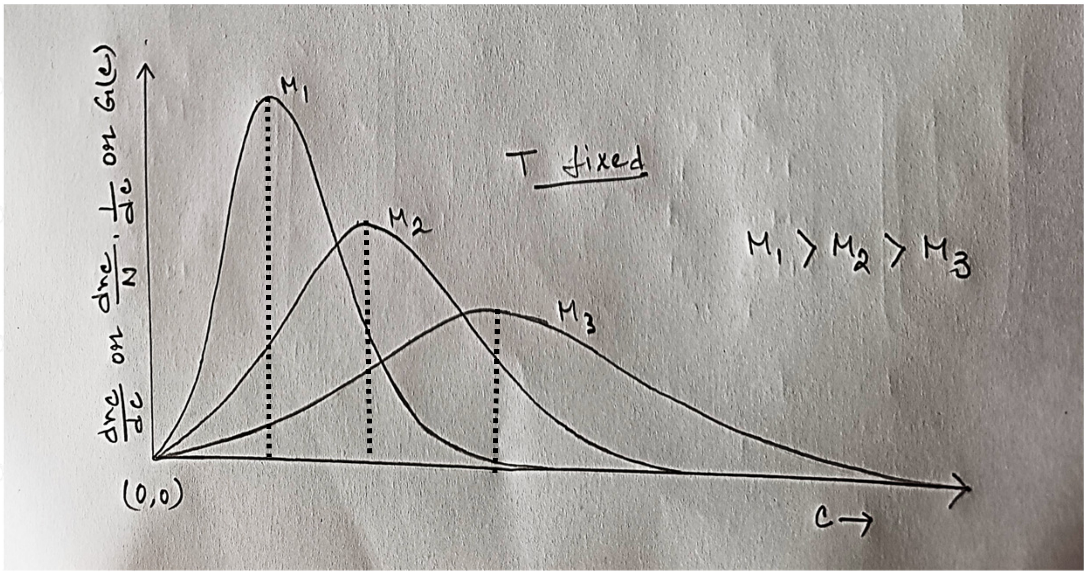
$$dn_c = N \cdot \left(\frac{m}{2\pi k T}\right)^{\frac{3}{2}} \cdot e^{-\frac{m c^2}{2 k T}} \cdot 4\pi c^2 \cdot dc$$

As T increases, distribution gets broader and shifts towards higher speed.   Explanation ?

<u>Question:</u> Why does the chemical reaction become faster at high temperature?

Now, let us see how the shape of the curve will change as molar mass of the of the gas changes

$dn_c = N \cdot \left(\frac{M}{2\pi RT}\right)^{\frac{3}{2}} \cdot e^{-\frac{Mc^2}{2RT}} \cdot 4\pi c^2 \cdot dc$



How do you explain ?

At a particular low values of c, $4\pi c^2$ is fixed, contribution of $e^{-\frac{Mc^2}{2RT}}$ is small, hence $\left(\frac{M}{2\pi RT}\right)^{\frac{3}{2}}$ term dominates, the plot with higher M value has higher dn_c value.

At a particular high values of c, $4\pi c^2$ is fixed, contribution of $e^{-\frac{Mc^2}{2RT}}$ is high, hence the plot with higher M value has lower dn_c value.

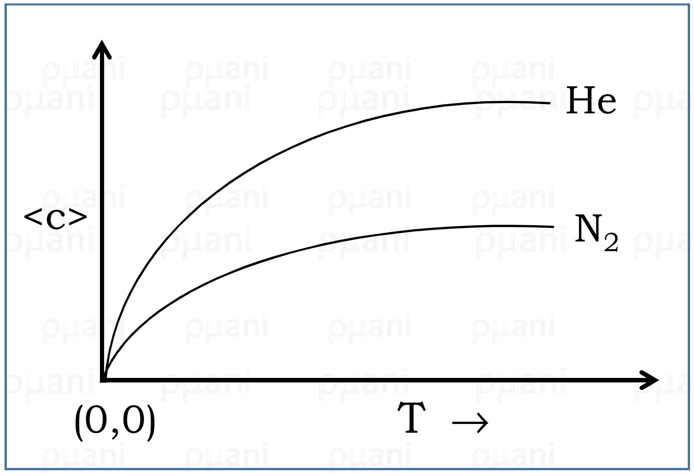
Application of Maxwell distribution

Average speed of gas molecules can be calculated using Maxwell distribution curve

$$<c> = \frac{1}{N}\int_0^{\infty} c\,.\,dn_c \quad \Rightarrow \quad <c> = \frac{1}{N}\int_0^{\infty} c\,.\,G(c)\,dc$$

$$= \int_0^{\infty} 4\pi\, c^2 .\ \left(\frac{m}{2\,\pi\,k\,T}\right)^{\frac{3}{2}} .\ e^{-\frac{m\,c^2}{2\,k\,T}} .\ c\ .\ dc$$

$$= 4\pi\ .\ \left(\frac{m}{2\,\pi\,k\,T}\right)^{\frac{3}{2}} \int_0^{\infty} e^{-\frac{m\,c^2}{2\,k\,T}} .\ c^3 .\ dc$$



Now, mathematically, $\int_0^{\infty} e^{-\,a\,x^2} .\ x^3 .\ dx = \frac{1}{2}\ .\ \frac{1}{a^2}$

$$\Rightarrow \quad <c> = 4\pi\ .\ \left(\frac{m}{2\,\pi\,k\,T}\right)^{\frac{3}{2}} .\ \frac{1}{2}\ .\ \frac{1}{\left(\frac{m}{2\,k\,T}\right)^2}$$

$$\Rightarrow \quad \boxed{<c> = \left(\frac{8\,k\,T}{\pi\,m}\right)^{\frac{1}{2}} = \left(\frac{8\,R\,T}{\pi\,M}\right)^{\frac{1}{2}}}$$

Thus <c> is directly proportional to $T^{\frac{1}{2}}$ and inversely proportional to $M^{\frac{1}{2}}$.

Question: How will be the plot of

(a) <c> vs. $\sqrt{T}$ (at constant M) ? and

(b) <c> vs. $\frac{1}{\sqrt{M}}$ (at constant T) ?

Calculation of most probable speed ($c_{m.p.s.}$)

For the calculation of c_{mps}, $\frac{d}{dc}\left(\frac{dn_c}{N\,.\,dc}\right) = 0$ or $\frac{d}{dc}(G(c)) = 0$

Now, $$\frac{d}{dc}\left[\frac{1}{dc}\,.\,\frac{dn_c}{N}\right] = \frac{d}{dc}\left[\underbrace{4\pi\,.\,\left(\frac{m}{2\,\pi\,k\,T}\right)^{\frac{3}{2}}}_{\text{Non-zero}}\,.\,e^{-\frac{m\,c^2}{2\,k\,T}}\,.\,c^2\right] = 0$$

$$\Rightarrow \frac{d}{dc}\left[c^2\,.\,e^{-\frac{m\,c^2}{2\,k\,T}}\right] = 0$$

$$\Rightarrow 2c\,.\,e^{-\frac{m\,c^2}{2\,k\,T}} + c^2\,.\,\frac{-2\,m\,c}{2\,k\,T}\,.\,e^{-\frac{m\,c^2}{2\,k\,T}} = 0$$

$$\Rightarrow e^{-\frac{m\,c^2}{2\,k\,T}}\left(2c - \frac{2\,m\,c^3}{2\,k\,T}\right) = 0$$

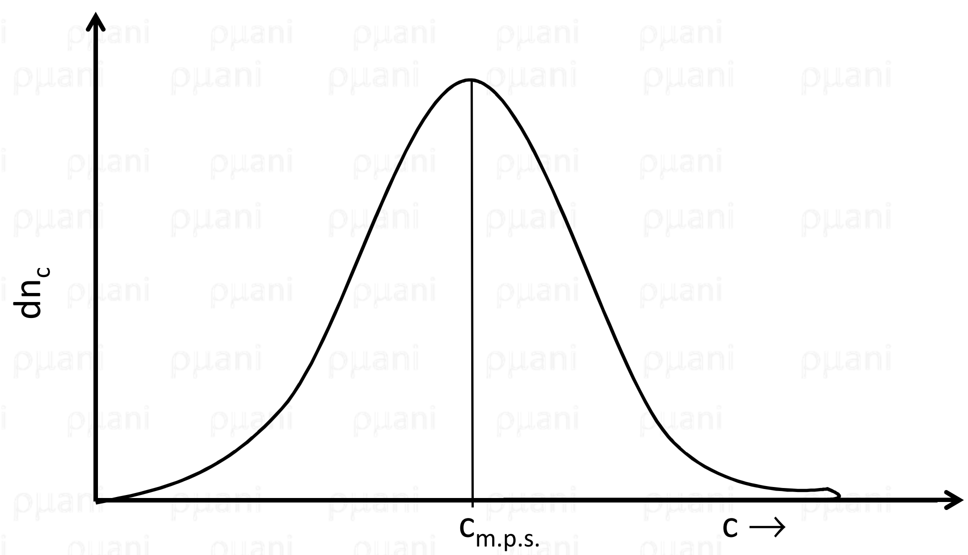
$$\Rightarrow 2c - \frac{2\,m\,c^3}{2\,k\,T} = 0$$

$$\Rightarrow 2c = \frac{2\,m\,c^3}{2\,k\,T}$$

$$\Rightarrow c^2 = \frac{2\,k\,T}{m}$$

$$\Rightarrow \boxed{c_{mps} = \sqrt{\frac{2\,k\,T}{m}} = \sqrt{\frac{2\,R\,T}{M}}}$$

Most probable speed is the speed for which dn_c is maximum



Question: How c_{mps} value change with the change in T?
How c_{mps} value change with the change in M?

<u>Comparison between different kinds of speed</u>

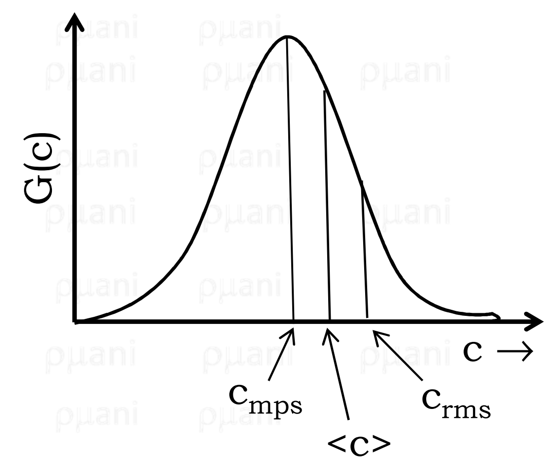
$$c_{rms} = \sqrt{\frac{3\,k\,T}{m}} = \sqrt{\frac{3\,R\,T}{M}}$$

$$<c> = \sqrt{\frac{8\,k\,T}{\pi\,m}} = \sqrt{\frac{8\,R\,T}{\pi\,M}}$$

$$c_{mps} = \sqrt{\frac{2\,k\,T}{m}} = \sqrt{\frac{2\,R\,T}{M}}$$

$$<c^2> = \frac{1}{N}\int_0^\infty c^2 \,.\, dn_c = \frac{3\,k\,T}{m} = \frac{3\,R\,T}{M}$$

$$\Rightarrow \sqrt{<c^2>} = \sqrt{\frac{3\,k\,T}{m}} = \sqrt{\frac{3\,R\,T}{M}}$$



$$\Rightarrow \quad c_{mps} : <c> : c_{rms} = \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$$

$$= (1.414) : (1.596) : (1.732)$$

$$= 1 : 1.128 : 1.225$$

Question: Calculate c_{rms} (speed) from Maxwell distribution of speed.

Question: Calculate c_{rms} , <c> , c_{mps} for O_2 at 25 °C, 1 bar.

Question: Show the position of c_{rms} , <c> , c_{mps} in the plot of Maxwell distribution of speed.

Question: Calculate the expression for c_{rms} , <c> , c_{mps} in 1D & 2D.

Question: Most probable velocity = 0 but most probable speed ≠ 0. Why?

Let us calculate the number of molecules moving with a translational kinetic energy of ε_{tr} to $(\varepsilon_{tr} + d\varepsilon_{tr})$

We know, $\varepsilon_{tr} = \frac{1}{2} mc^2 \Rightarrow c^2 = \frac{2\,\varepsilon_{tr}}{m}$

$\Rightarrow c = \sqrt{\frac{2\,\varepsilon_{tr}}{m}}$

$\Rightarrow dc = \sqrt{\frac{1}{2m}} \cdot \frac{1}{\sqrt{\varepsilon_{tr}}} \cdot d\varepsilon_{tr}$

If a molecule has a speed of c to (c+dc) then it will have a translational kinetic energy between $\frac{1}{2} mc^2$ to $\frac{1}{2} m\,(c+dc)^2$

Now, $\frac{1}{2} m\,(c+dc)^2 = \frac{1}{2} m\,[c^2 + 2c \cdot dc + (dc)^2] \simeq \frac{1}{2} mc^2 + mc \cdot dc$ $\quad [(dc)^2$ is neglected]

This means, it's translational kinetic energy is between ε_{tr} to $(\varepsilon_{tr} + d\varepsilon_{tr})$

So, $d\varepsilon_{tr} = mc \cdot dc$

We know, $\frac{dn_c}{N} = 4\pi \cdot (\frac{m}{2\pi kT})^{\frac{3}{2}} \cdot e^{-\frac{mc^2}{2kT}} \cdot c^2 \cdot dc$

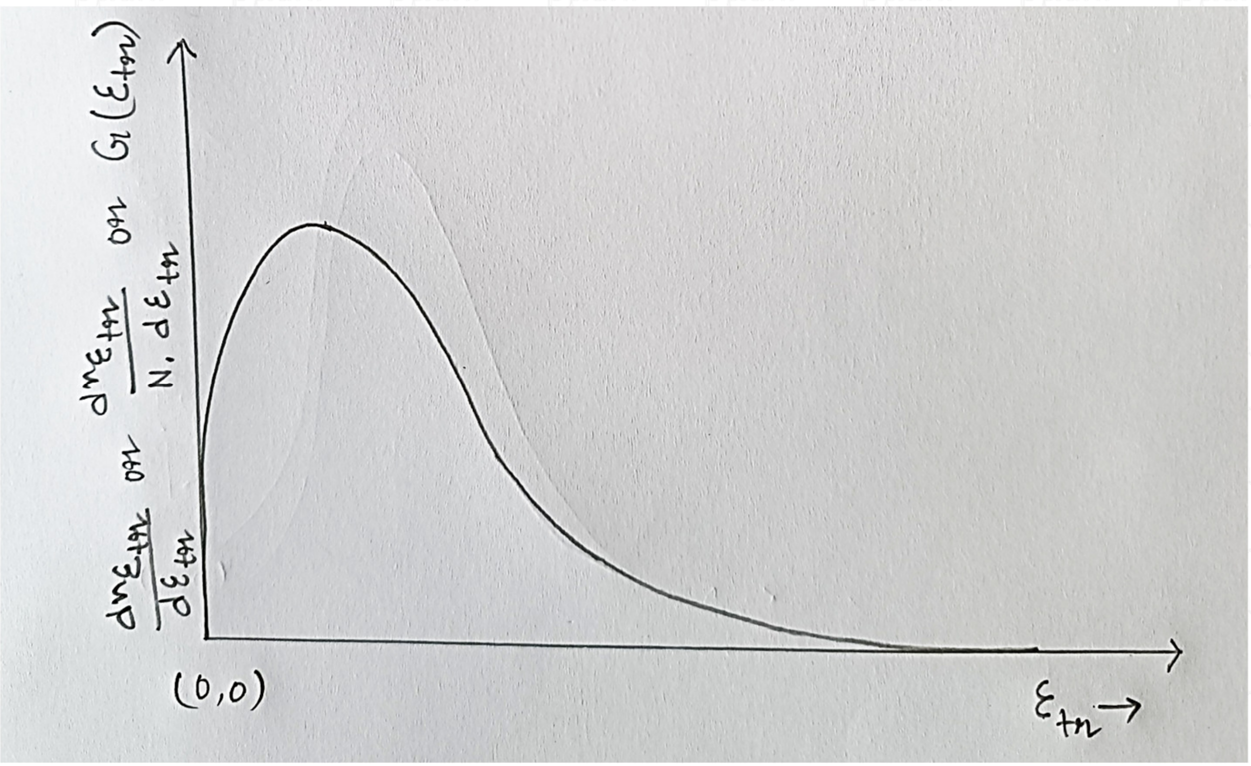
Thus, $\frac{dn_\varepsilon}{N} = 4\pi \cdot (\frac{\cancel{m}}{2\pi kT})^{\frac{3}{2}} \cdot e^{-\frac{\varepsilon_{tr}}{kT}} \cdot \frac{2\,\varepsilon_{tr}}{\cancel{m}} \cdot \sqrt{\frac{1}{2\cancel{m}}} \cdot \frac{1}{\sqrt{\varepsilon_{tr}}} \cdot d\varepsilon_{tr}$

$\Rightarrow \frac{dn_{\varepsilon_{tr}}}{N} = 4\pi \cdot (\frac{1}{2\pi kT})^{\frac{3}{2}} \cdot \sqrt{\varepsilon_{tr}} \cdot \sqrt{2} \cdot e^{-\frac{\varepsilon_{tr}}{kT}} \cdot d\varepsilon_{tr} = \frac{1}{\cancel{\sqrt{2}}} \cdot \frac{1}{\cancel{\sqrt{2}}} \cdot \frac{1}{\cancel{\sqrt{2}}} \cdot (\frac{1}{\pi kT})^{\frac{3}{2}} \cdot \cancel{2} \cdot 2\pi \cdot \sqrt{\varepsilon_{tr}} \cdot \cancel{\sqrt{2}} \cdot e^{-\frac{\varepsilon_{tr}}{kT}} \cdot d\varepsilon_{tr}$

$$\Rightarrow \boxed{\frac{dn_{\varepsilon_{tr}}}{N} = 2\pi \, . \, \left(\frac{1}{\pi\, k\, T}\right)^{\frac{3}{2}} . \, \sqrt{\varepsilon_{tr}} \, . \, e^{-\frac{\varepsilon_{tr}}{k\,T}} . \, d\varepsilon_{tr}} \quad \Rightarrow \frac{1}{N} \, . \, dn_{\varepsilon_{tr}} = G(\varepsilon_{tr}) \, . \, d\varepsilon_{tr}$$

This is the Maxwell distribution of translational kinetic energy.

From the above expression we know that there is no 'm' parameter. So, the plot will be independent of 'm' or 'M'.



$\Rightarrow$ Rapid rise, slow fall

Question: How will the Maxwell distribution plot of translational kinetic energy will vary with (i) M and (ii) T?

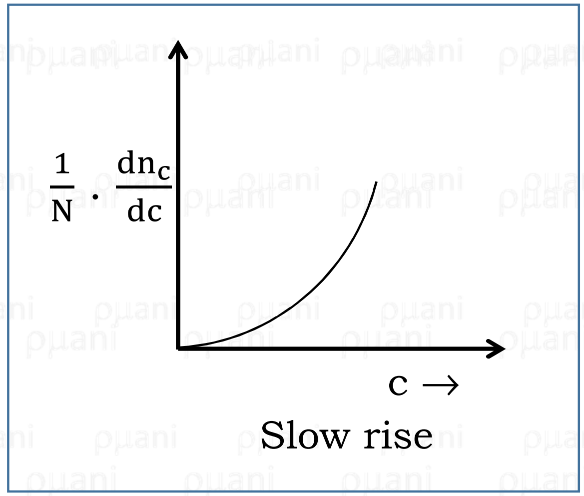
Question: What is the difference between the shape of Maxwell distribution plot of speed and translational K.E.?

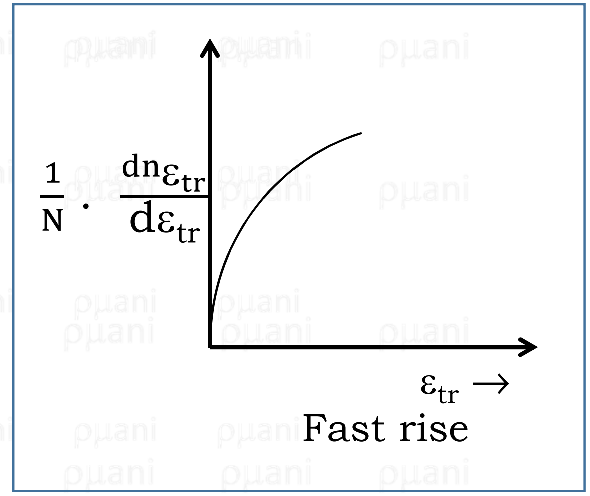
Question: Derive an expression of average translational K.E. , most probable translational K.E. starting from Maxwell distribution of translational K.E.

Question: Obtain an expression for r.m.s. velocity.

At low speed $\frac{1}{N}\cdot\frac{dn_c}{dc} \propto c^2 \quad \Rightarrow y = x^2$

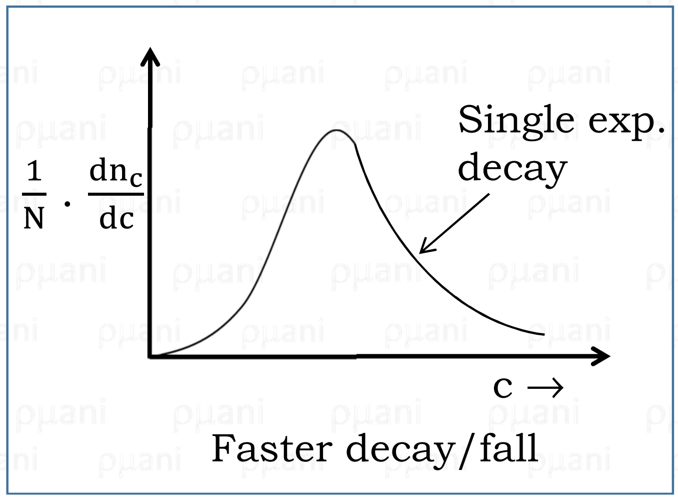
At low $<\varepsilon_{tr}>$ $\frac{1}{N}\cdot\frac{dn_{\varepsilon_{tr}}}{d\varepsilon_{tr}} \propto \sqrt{\varepsilon_{tr}} \quad \Rightarrow y^2 = x$

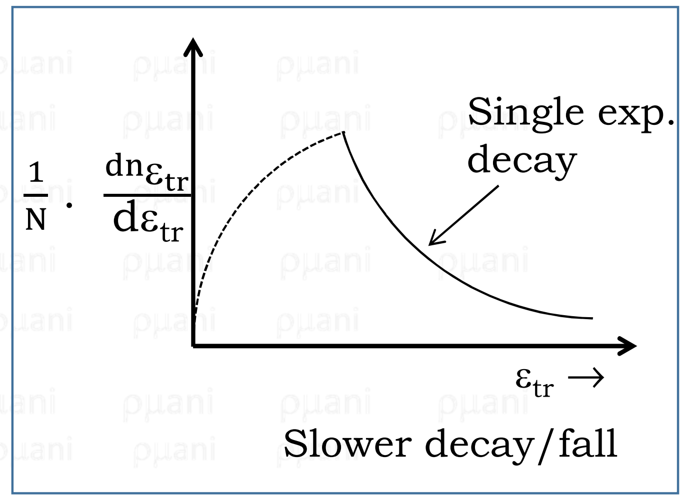




At high speed $\frac{1}{N}\cdot\frac{dn_c}{dc} \propto e^{-\frac{mc^2}{2kT}}$

At high $<\varepsilon_{tr}>$ $\frac{1}{N}\cdot\frac{dn_{\varepsilon_{tr}}}{d\varepsilon_{tr}} \propto e^{-\frac{\varepsilon_{tr}}{kT}}$





Plot 1

Plot 2