PHY HC 3026: Thermal Physics: Kinetic Theory of Gases

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0.1 Maxwell's Velocity Distribution or the Maxwellian

We have already talked about the *probability density function* $f(\vec{v})$: the probability of finding a gas particle with a velocity in the range $[\vec{v}, \vec{v} + d\vec{v}]$ is given by $f(\vec{v})d\vec{v}$, we used it in deriving the expression for *thermodynamic pressure* from a microscopic description of the gas using classical mechanics, but we did not need explicit functional form for that. Therefore, it's time we did that.

Derivation of Maxwellian using symmetries: we will try to derive $f(v)$ using some general symmetry principles:

- space is assumed to be isotropic, meaning: space looks the same in all directions (x, y, z), therefore, the function $f(\vec{v}$ should not be direction-dependent, which means it should be a function of just $|\vec{v}| = v$ or equivalently of v^2. Therefore, we can write down our $f(\vec{v})$ is some function of the magnitude of the velocity, therefore, we can write down:

$$f(\vec{v}) = f(v) = g(v^2) \tag{1}$$

- Maxwell also assumed that the three components of the random velocity of any gas particle v_x, v_x, and v_x were also independent random variables. That means, simultaneously, those three components can take any possible values, and in such a situation we know what the combined probability should look like from the *probability theory.* It should be a product of the three individual independent probabilities, therefore, we can write down the $g(v^2)$ of Eq. 1 in terms of some other function h as:

$$f(\vec{v}) = f(v) = g(v^2) = h(v_x^2) \times h(v_y^2) \times h(v_z^2) \tag{2}$$
$$\implies g(v^2) = g(v_x^2 + v_y^2 + v_z^2) = h(v_x^2) \times h(v_y^2) \times h(v_z^2) \tag{3}$$

Taking natural log on both sides:

$$\ln g(v_x^2 + v_y^2 + v_z^2) = \ln h(v_x^2) + \ln h(v_y^2) + \ln h(v_z^2) \tag{4}$$

Let us rename the above *logged* functions:

$$\begin{aligned} \ln g &= \Psi \\ \ln h &= \Phi \end{aligned} \tag{5}$$

Using these in Eq. 4, we get:

$$\Psi(v^2) = \Psi(v_x^2 + v_y^2 + v_z^2) = \Phi(v_x^2) + \Phi(v_y^2) + \Phi(v_z^2) \tag{6}$$

Eq. 6 is only possible when the functions $\Psi(X)$ and $\Phi(X)$ are both linear in X, that is, when they have the forms:

$$\begin{aligned} \Psi(X) &= \quad aX + b \\ \Phi(X) &= - \quad \alpha X + \beta \end{aligned}$$

We intentionally chose a negative sign in the unknown α, but we are free to do so. Let us now re-write down the Φ functions:

$$\begin{aligned}\Phi(v_x^2) &= -\alpha v_x^2 + \beta \\ \Phi(v_y^2) &= -\alpha v_y^2 + \beta \\ \Phi(v_z^2) &= -\alpha v_z^2 + \beta \end{aligned} \tag{7}$$

Using Eq. 7, we can re-write Eq. 6 as:

$$\begin{aligned} \Psi(v^2) &= (-\alpha v_x^2 + \beta) + (-\alpha v_y^2 + \beta) + (-\alpha v_z^2 + \beta) \\ &= -\alpha(v_x^2 + v_y^2 + v_z^2) + 3\beta \\ \implies \quad \Psi(v^2) &= -\alpha v^2 + 3\beta \end{aligned} \tag{8}$$

Let us now revert to our original functions, that is h, g, and finally to $f(\vec{v})$, therefore, we use Eq. 8 in Eq. 5:

$$\begin{aligned} \Psi(v^2) &= \ln g(v^2) \\ &= e^{\Psi(v^2)} \\ &= e^{-\alpha v^2 + 3\beta} \\ &= e^{-\alpha v^2} e^{3\beta} \\ \implies g(v^2) &= Ce^{-\alpha v^2} = f(v) \end{aligned} \tag{9}$$

Where $C = e^{3\beta}$. We have done it, we got the velocity distribution function, all we need is to find the values of the two unknown constants α and C, the latter is easy, it can be evaluated using the normalization condition that the total probability, that is the probability of a gas particle to have any possible value is one, mathematically speaking:

$$\int_{-\infty}^{\infty} f(v)\, dv_x dv_y dv_z = 1 \tag{10}$$

In polar co-ordinates with volume element $v^2 \sin\theta d\theta d\phi$ it becomes:

$$\begin{aligned} & \int_0^{\pi} \sin\theta d\theta \int_{-\pi}^{\pi} d\phi \int_0^{\infty} f(v)\, v^2\, dv = 1 \\ \implies \quad & 4\pi \int_0^{\infty} f(v)\, v^2\, dv = 1 \\ \implies \quad & 4\pi \int_0^{\infty} Ce^{-\alpha v^2}\, v^2\, dv = 1 \\ \implies \quad & C = \left(\frac{\alpha}{\pi}\right)^{3/2} \end{aligned} \tag{11}$$

Therefore, the *Maxwellian* now takes the form:

$$\boxed{f(\vec{v}) = f(v) = \left(\frac{\pi}{\alpha}\right)^{3/2} e^{-\alpha v^2}} \tag{12}$$

The only constant left to be known is α, and we can easily find its value if we could relate it to a macroscopic quantity that we already know. Remember that we extracted the thermodynamic pressure applying classical mechanics to the microscopic description of the classical ideal gas at moderate temperatures, the value of which was:

$$P = \frac{1}{3} mN \langle v^2 \rangle \tag{13}$$

Where $\langle v^2 \rangle$ is the average of v^2 over all N number of gas particles. Let us calculate the average of velocity squared:

$$\begin{aligned}\langle v^2\rangle &= \int_0^\infty v^2 f(v)\, v^2 dv \sin\theta d\theta d\phi \\ &= 4\pi\Big(\frac{\alpha}{\pi}\Big)^{3/2}\int_0^\infty v^4 e^{-\alpha v^2} dv \\ &= 4\pi\Big(\frac{\alpha}{\pi}\Big)^{3/2}\times\frac{3}{8}\frac{\pi^{1/2}}{\alpha^{5/2}} \\ \Longrightarrow \langle v^2\rangle &= \frac{3}{2\alpha}\end{aligned} \tag{14}$$

Putting the value of $\langle v^2\rangle$ in Eq. 13 we get:

$$P = \frac{1}{3}mN\frac{3}{2\alpha} \tag{15}$$

But we know that for an *ideal gas*:

$$PV = Nk_BT \tag{16}$$

Where k_B is *Boltzmann*'s gas constant and T is the absolute temperature of our ideal gas. Combining Eq. 15 and 16, we obtain:

$$\alpha = \frac{m}{2k_BT} \tag{17}$$

Substituting the above α in Eq. 9 we obtain our desired *Maxwellia's velocity distribution function* or the velocity probability density for a classical ideal gas in moderate (quantum and relativistic effects are negligible) temperature.

$$\boxed{f(\vec{v}) = \Big(\frac{m}{2\pi k_BT}\Big)^{3/2} e^{-\frac{1}{2}mv^2/k_BT}} \tag{18}$$

Which is valid as long as our velocities obey $v \ll c$, that is $k_BT \ll mc^2$, the limiting temperature is about 10^4 K, but at this temperature even atoms will disintegrate, therefore our non-relativistic assumption is safe. But we cannot have pressure too much higher than the atmospheric pressure, otherwise quantum correlations among gas particles will start to dominate and our classical-mechanics-based result Eq. 18 won't hold.

Note: the assumption of three velocity components to be independent random variables is due to *Maxwell* himself. A more correct derivation will be through the use of ***Maxwell-Boltzmann*** statistics.

What is temperature? From the *Maxwellian* it is clear that k_BT has the dimension of the *kinetic energy*, or it the temperature is related to particle velocities. It is now very clear why temperature-equalization across the gas volume is a requirement for equilibrium. Gas volumes of different temperatures brought in contact, will proceed towards attaining the same temperature or microscopically speaking, gas particles will reach a common *Maxwellian velocity distribution* through collisions and hence re-distribution of their individual kinetic energies.

0.1.1 The speed probability density

Consider Eq. 18, let us write down the probability $d\Pi$ of finding a particle with velocity lying between $\vec{v}$ and $\vec{v} + d\vec{v}$:

$$d\Pi = f(\vec{v})dv_xdv_ydv_z = \Big(\frac{m}{2\pi k_BT}\Big)^{3/2} e^{-\frac{1}{2}mv^2/k_BT}\, v^2 \sin\theta\, d\theta\, d\phi \tag{19}$$

If we integrate out the angular co-ordinates θ and ϕ over the full solid angle 4π, we will be left with just the radial or the *speed probability* $d\Pi_{\text{speed}}$, that is the probability of finding a particle with a speed between v and $v + dv$, which is given by:

$$d\Pi_{\text{speed}} = 4\pi v^2 f(v)dv = v^2\Big(\frac{m}{2\pi k_BT}\Big)^{3/2} e^{-\frac{1}{2}mv^2/k_BT} dv \tag{20}$$

Therefore the *speed probability density* is given by:

$$\boxed{f_{\text{speed}}(v) = 4\pi v^2 f(v) = 4\pi\, v^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{1}{2}mv^2/k_BT}} \tag{21}$$

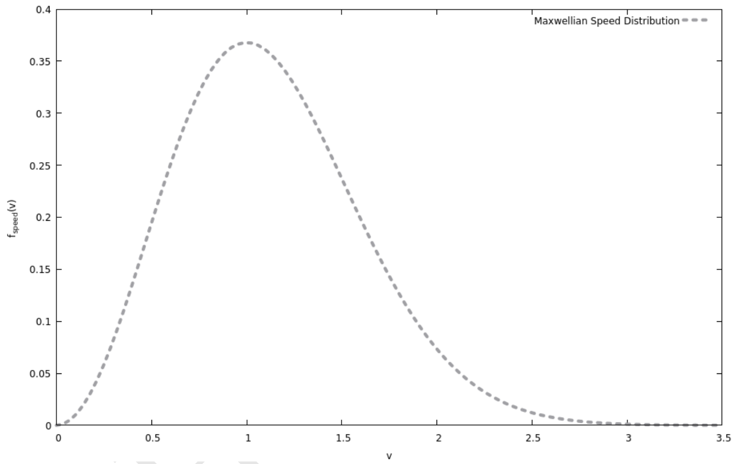

Figure 1: Graphical representation of the *Maxwellian* speed probability distribution.

Most probable speed: optimizing $f_{\text{speed}}(v)$ in Eq. 20 will give us the most probable speed (or magnitude of velocity or casually just velocity), that is the speed that most particles are likely to have. Taking derivative of $f_{\text{speed}}(v)$ w.r.t v^2 in Eq. 21 and using the form of $f(v)$ in terms of C and α instead of their actual values, and applying the optimization condition, we get:

$$\begin{aligned} \frac{df_{\text{speed}}(v)}{dv^2} &= Ce^{-\alpha v^2}[1-\alpha v^2] = 1 \\ v_{\max} &= \frac{1}{\sqrt{\alpha}} = \sqrt{\frac{2k_BT}{m}} \end{aligned} \tag{22}$$

Therefore the most probable speed is $\boxed{v_m = \sqrt{2k_BT/m}}$.

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Average or Mean Velocity (actually the magnitude of *velocity*) or the speed What we really mean is the average of ***speed*** or the average of the ***magnitude of velocity***, because the average velocity should of course be zero, to understand why so, let us look at the definition of the average. The probability of finding a gas particle with velocity lying between $\vec{v}$ and $\vec{v}+d\vec{v}$ is given by $dP(\vec{v}) = f(\vec{v})dv_x dv_y dv_z$, therefore, the average of any function of $\vec{v}$, let's say $\chi(\vec{v})$ will be given by:

$$\langle\chi(\vec{v})\rangle = \int f(\vec{v})dv_x dv_y dv_z\, \chi(\vec{v}) \tag{23}$$

In our case, we are going to calculate the average of the velocity, that is $\chi(\vec{v}) = \vec{v} = v_x\hat{i} + v_y\hat{j} + v_z\hat{k}$, therefore $< \vec{v} >$ will be:

$$\langle\vec{v}\rangle = \int f(\vec{v})dv_x dv_y dv_z\, \vec{v} \tag{24}$$

But, $f(\vec{v}) = f(v)$, which means it's direction-independent, but $\vec{v}$ is a *directional vector*, so taking its average over all directions is like looking at it from all angles and summing all those views, therefore, obviously the total will be zero! An one-dimensional analogy will be the vanishing of the integration of an odd function, e.g.

$$\textstyle\int_{-a}^{a} f(x) \quad = 0, \text{ if } f(x) = \text{odd}$$

In Eq. 24, everything is even (direction-independent or scalar function of $|\vec{v}| = v$) except $\vec{v}$, which makes the integral an ***integration of an odd function***! Now that this is clear, let us proceed to calculate the average of $|\vec{v}| = v$, which is not a vector, and we can therefore, use the *speed probability density* $f_{\text{speed}}(v)$ of Eq. 22:

$$\begin{aligned}\langle v\rangle &= \int_0^\infty f_{\text{speed}} dv v \\ &= \int_0^\infty 4\pi\Big[v^2 C\, e^{-\alpha v^2} dv\Big]\, v \\ &= 4\pi C \int_0^\infty v^3 e^{-\alpha v^2} dv\end{aligned} \tag{25}$$

Where, $C = (m/2\pi k_B T)^{3/2}$ and $\alpha = m/2k_B T$. Above integration is easy if we use *Feynman*'s trick! Let us name the integral I_F, and try to write it in a different way:

$$\begin{aligned}I_F &= \int_0^\infty v^3 e^{-\alpha v^2} dv \\ &= \int_0^\infty v\Big[-\frac{d}{d\alpha}\Big(e^{-\alpha v^2}\Big)\Big] dv\end{aligned} \tag{26}$$

So far so good, now if we could pull out the derivative w.r.t α, we would be good, then we would be left with just the integration of $vExp[-\alpha v^2]$, can we do that? Well, the v sitting just on the left of $-d/d\alpha$ is not a function of α, neither is dv so in principle, yes, we could pull out the derivative outside, but there's a catch! We can do this without making the mathematicians angry if we knew that the integral converges, meaning integration of $v^3Exp[-\alpha v^2]$ is finite and we know for sure it is, because for a positive α, which we know it is because its value is $m/2k_BT$, integration of $v^nExp[-\alpha v^2]$ for any finite n, because doesn't matter how big v^n is an exponential is always going to kill it! Therefore, yes, we can take the $-d/d\alpha$ outside the integral, therefore, Eq. 26 becomes:

$$
\begin{aligned}
I_F &= -\frac{d}{d\alpha}\int_0^\infty v e^{-\alpha v^2} dv \\
&= -\frac{d}{d\alpha}\int_0^\infty e^{-\alpha v^2}\frac{1}{2} d(v^2) \\
&= -\frac{1}{2}\frac{d}{d\alpha}\int_0^\infty e^{-\alpha v^2} d(v^2) \\
&= -\frac{1}{2}\frac{d}{d\alpha}\Big[\frac{e^{-\alpha v^2}}{-\alpha}\Big]_0^\infty \\
&= -\frac{1}{2}\frac{d}{d\alpha}\Big[\frac{1}{\alpha}\Big] \\
I_F &= \frac{1}{2\alpha^2} \qquad (27)
\end{aligned}
$$

Substituting the value of I_F (Eq. 27) in Eq. 25, we get:

$$
\begin{aligned}
\langle v\rangle &= 4\pi C\, I_F \\
&= 4\pi\frac{C}{2\alpha^2} \\
&= 4\pi\Big(\frac{m}{2\pi k_B T}\Big)^{3/2}\frac{1}{2}\Big(\frac{m}{2k_B T}\Big)^2 \\
\langle v\rangle &= \bar{v} = \sqrt{\frac{8k_B T}{\pi m}} \qquad (28)
\end{aligned}
$$

Therefore, the mean/average speed is $\sqrt{8k_BT/\pi m} \simeq 1.59\sqrt{k_BT/m}$.

Root mean square (r.m.s) speed (v_{rms}) This is defined as the *square-root of the mean/average of the square speed*, that is $\langle v^2\rangle$. So if we use our definition of average given in Eq. 23, we need to put $\chi(\vec{v}) = v^2$, then in the end take a square root of the result, that is:

$$
\begin{aligned}
v_{rms} &= \sqrt{\langle v^2\rangle} = \sqrt{\int_0^\infty f_{\text{speed}}(v)\, dv\, v^2} \\
&= \sqrt{\int_0^\infty 4\pi\Big[v^2 C\, e^{-\alpha v^2}\, dv\Big]\, v^2} \\
&= \sqrt{4\pi C}\sqrt{\int_0^\infty v^4 e^{-\alpha v^2}\, dv} \qquad (29)
\end{aligned}
$$

Here again we can use the *Feynman*'s trick by taking $-d/d\alpha$ twice:

$$\begin{aligned}
v_{rms} &= \sqrt{4\pi C}\sqrt{(-1)^2\frac{d}{d^2\alpha^2}\int_0^\infty e^{-\alpha v^2}\,dv} \\
&= \sqrt{4\pi C}\sqrt{\frac{d^2}{d\alpha^2}\frac{1}{2}\sqrt{\frac{\pi}{\alpha}}} \\
&= \sqrt{4\pi C}\sqrt{\frac{\sqrt{\pi}}{2}\frac{d^2}{d\alpha^2}\alpha^{-1/2}} \\
&= \sqrt{2}\Big(\frac{m}{2\pi k_B T}^{3/4}\pi\Big)^{3/4}\frac{\sqrt{3}}{4}\alpha^{-5/4} \\
&= \sqrt{2}\Big(\frac{m}{2\pi k_B T}^{3/4}\pi\Big)^{3/4}\frac{\sqrt{3}}{4}\Big(\frac{m}{2k_B T}\Big)^{-5/4} \\
&= \sqrt{\frac{3k_B T}{m}} \qquad (30)
\end{aligned}$$

We have used the value of an integral that is too common in physics:

$$\int_0^\infty e^{-x^2}\,dx = \frac{\sqrt{\pi}}{2} \qquad (31)$$

Evaluation of this integral is again easy though, I am giving it in an end note. Therefore, the *root mean square speed* is $v_{rms} = \sqrt{3k_B T/m}$.

End note: evaluation of the *Gaussian* integral

$$I_G = \int_0^\infty e^{-x^2}\,dx = \frac{1}{2}\int_{-\infty}^\infty e^{-x^2}\,dx \qquad (32)$$

Let us calculate the square of this integral first and then we will take a positive square root. So,

$$\begin{aligned}
I_G^2 &= \frac{1}{4}\Big[\int_{-\infty}^\infty e^{-a^2}\,da\Big]\Big[\int_{-\infty}^\infty e^{-b^2}\,db\Big] \\
&= \frac{1}{4}\int_{-\infty}^\infty\int_{-\infty}^\infty e^{-(a^2+b^2)}\,da\,db \qquad (33)
\end{aligned}$$

But this is just an integral in a *Cartesian* co-ordinates with axes a and b, we could convert it into a polar integral by $da\,db \to r\,dr\,d\theta$, where $r^2 = a^2 + b^2$, the radius. Therefore, the above integral just becomes:

$$\begin{aligned}
I_G^2 &= \frac{1}{4}\int_0^\infty\int_0^{2\pi} e^{-r^2}\,r\,dr\,d\theta \\
&= \frac{1}{4}2\pi\int_0^\infty e^{-r^2}\,d(r^2/2) \\
&= \frac{1}{4}2\pi\frac{1}{2}\Big[\frac{e^{-r^2}}{-1}\Big]_0^\infty \\
&= \frac{\pi}{4} \\
\implies I_G &= \frac{\sqrt{\pi}}{2} \qquad (34)
\end{aligned}$$

References

Schekochihin, A. A. (n.d.), 'Oxford physics paper a1 lecture notes'.