Lecture X

Kinetic theory of gas

Maxwell-Boltzman velocity distribution

James Clerk Maxwell was a physicist who is mostly famous for his four equations of electricity and magnetizm — the Maxwell's equations. However, he worked in the area of thermodynamics and made a huge impact on kinetic theory of gas. In 1859, he was inspired by a paper of Clausius on diffusion in gases to conceive of ~~the~~ his theory of speed distribution in gases. He worked out the velocity distribution totally on the mechanical and probabilistic ground. He published his findings with a title "On the motion and collision of perfectly ~~solid~~ elastic spheres" in London and Edinburgh Philosophical Magazine and Journal of Science. Later, Ludwig Boltzmann independently worked on kinetic theory of gases from a statistical mechanics perspective and found more precise results, published in around 1870. The distribution is hence known as "Maxwell-Boltzmann distribution".

Maxwell's calculations based on probability

Maxwell argued and showed that, for a large number of particles, the direction of velocity after a particle collision is arbitrary, that is, all the directions are equally probable. If there are a great many ~~number~~ number of particles, subjected to elastic collisions, then their velocity will be altered after each collision. Although the velocities are changing, one can calculate the number of particles having velocities in between a particular range.

Let, the total number of particles is $= N$. Say, V_x, V_y and V_z are components of the velocity of each particle in Cartesian coordinate. Let, the fraction ~~number~~ of particles ~~per unit volume~~ having velocity in the range V_x and $V_x + dV_x$ is $= f(V_x)dV_x$

So, total particles in that range $= N f(V_x)\, dV_x$.

Similarly, for V_y and $V_y + dV_y$ it is $= f(V_y)\, dV_y$

V_z and $V_z + dV_z$ it is $= f(V_z) dV_z$

Now, V_x, V_y and V_z are independent of each other. So, the fraction of particles that has velocity between V_x and $V_x + dV_x$, V_y and $V_y + dV_y$, V_z and $V_z + dV_z$ is given by,

$$f(V_x)\, f(V_y)\, f(V_z)\, dV_x\, dV_y\, dV_z$$

and number of particles $= N f(V_x) f(V_y) f(V_z) dV_x dV_y dV_z$

The number of particles in this range per unit volume is then $= N f(V_x) f(V_y) f(V_z)$. But the directions of the velocity coordinates are perfectly arbitrary, and so the number must depend on the magnitude of velocity (distance from the origin) only.

$$\therefore \quad f(V_x)\, f(V_y)\, f(V_z) = \phi\left(V_x^2 + V_y^2 + V_z^2\right) \quad \text{——— (1)}$$

To find $f(V_x)$, we have to solve this functional equation. We must have $f(0) = \alpha$, where α is a positive constant (fraction of particles having 0 velocity along x-axis and non zero in y and z). Plugging $V_y = 0$, $V_z = 0$ in (1),

$$f(V_x)\, f(0)\, f(0) = \phi(V_x^2)$$

$$\therefore \quad f(V_x) = \frac{1}{\alpha^2}\, \phi(V_x^2)$$

Similarly, $$f(V_y) = \frac{1}{\alpha^2}\, \phi(V_y^2)$$

$$f(V_z) = \frac{1}{\alpha^2}\, \phi(V_z^2)$$

$$\therefore (1) \Rightarrow \quad \frac{1}{\alpha^6}\,\phi(v_x^2)\,\phi(v_y^2)\,\phi(v_z^2) = \phi(v_x^2+v_y^2+v_z^2)$$

Let's write $v_x^2 = \varsigma$, $v_y^2 = \eta$ and $v_z^2 = \xi$ for simplicity.

$$\therefore \frac{1}{\alpha^6}\,\phi(\varsigma)\,\phi(\eta)\,\phi(\xi) = \phi(\varsigma+\eta+\xi) \longrightarrow (ii)$$

Let's take a derivative w.r.t. η in equation (ii).

$$\frac{1}{\alpha^6}\,\phi(\varsigma)\,\phi(\xi)\,\frac{d\phi(\eta)}{d\eta} = \frac{d}{d\eta}(\varsigma+\eta+\xi)\,\frac{d\phi(\varsigma+\eta+\xi)}{d(\varsigma+\eta+\xi)}$$

$$\Rightarrow \frac{1}{\alpha^6}\,\phi(\varsigma)\,\phi(\xi)\,\phi'(\eta) = \frac{d\phi(\varsigma+\eta+\xi)}{d(\varsigma+\eta+\xi)}$$

Plugging $\xi=\eta=0$ in the equation above.

$$\frac{1}{\alpha^6}\,\phi(\varsigma)\,\phi(0)\,\phi'(0) = \frac{d\phi(\varsigma)}{d\varsigma}$$

$$\Rightarrow A\,\phi(\varsigma) = \frac{d\phi(\varsigma)}{d\varsigma}$$

$$\boxed{\left.\frac{d\phi(x+y)}{d(x+y)}\right|_{x=0} = \frac{d\phi(y)}{dy}}$$

$$\Rightarrow \int \frac{d\phi(\varsigma)}{\phi(\varsigma)} = A\int d\varsigma$$

$A = \frac{1}{\alpha^6}\,\phi(0)\,\phi'(0)$

$$\Rightarrow \ln\phi(\varsigma) = A\varsigma + B$$

$B =$ integration constant

$$\therefore \phi(\varsigma) = e^{B+A\varsigma} = e^{B}\,e^{A\varsigma}$$

$$\boxed{\therefore \phi(\varsigma) = C\,e^{A\varsigma}}$$

$C = e^{B}$

$$\therefore \quad \phi(v_x^2) = C e^{A v_x^2}$$

$$\therefore \quad f(v_x) = \frac{1}{\alpha^2} C e^{A v_x^2}$$

$$\boxed{\therefore f(v_x) = D e^{A v_x^2}} \quad \boxed{\therefore f(v_y) = D e^{A v_y^2}} \quad \boxed{f(v_z) = D e^{A v_z^2}}$$

Now, if A is positive, the number of particles will increase with velocity, which will lead to infinite number of particles. We therefore make A negative and write $A = -\frac{1}{\beta^2}$.

$$\boxed{\therefore \quad f(v_x) = D e^{-\frac{v_x^2}{\beta^2}}}$$

So, total number of particles between v_x and $v_x + dv_x$ is,

$$N(v_x) = N f(v_x) = N D e^{-v_x^2/\beta^2} \quad \text{—— (III)}$$

If we integrate (III) from $v_x = -\infty$ to $v_x = +\infty$, we should get the total number of particles.

$$\therefore \quad \int_{-\infty}^{\infty} N(v_x)\, dx = N$$

$$\Rightarrow \quad \cancel{N} D \int_{-\infty}^{\infty} e^{-v_x^2/\beta^2} = \cancel{N}$$

$$\Rightarrow \quad D \cdot \sqrt{\frac{\pi}{1/\beta^2}} = 1$$

$\therefore$ ~~$D = 1/\sqrt{\pi}\,\beta$~~ $\therefore D = \frac{1}{\sqrt{\pi}\,\beta}$

$$\boxed{\therefore \quad f(v_x) = \frac{1}{\beta\sqrt{\pi}}\, e^{-v_x^2/\beta^2}} \quad (*)$$

Now, generalizing this for v_y and v_z, we can write, the number of particles having velocity $\vec{v}$ and $\vec{v}+d\vec{v}$ is,

$$N(\vec{v})\, dv_x\, dv_y\, dv_z = N \cdot \left(\frac{1}{\beta\sqrt{\pi}}\right)^3 e^{-\frac{v_x^2+v_y^2+v_z^2}{\beta^2}}\, dv_x\, dv_y\, dv_z$$

$$\cancel{\Rightarrow N(v)\, dv = N \frac{1}{\beta^3 \pi^{3/2}} e^{-\frac{v^2}{\beta^2}}\, 4\pi v^2\, dv}$$

$$\cancel{\boxed{\therefore N(v) = N \frac{4}{\beta^3 \sqrt{\pi}} v^2 e^{-v^2/\beta^2}}}$$

$$\boxed{\therefore N(\vec{v})\, dv_x\, dv_y\, dv_z = \frac{N}{\beta^3 \pi^{3/2}}\, e^{-\frac{v^2}{\beta^2}}\, dv_x\, dv_y\, dv_z}$$

Boltzman calculations based on Statistical mechanics

Consider some gas molecules contained in a box. The molecules can be monoatomic or polyatomic. We will assume that the molecular size is negligible compared to intermolecular spacing. So, the molecules spend most of their times whizzling around and rarely bump into each other. We will ignore any intermolecular forces. Molecules can exchange energy with each other through collision, but everything remains in equilibrium. We can then ~~thing~~ think a particular molecule as a small distinguishable system in a heat reservior, where the reservior is all other molecules in the box at temperature T. The energy of a molecule,

$$E_n = \frac{p^2}{2m} + E^{int} = \frac{1}{2}mv^2 + E^{int} = \left(\frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2\right) + E^{int}$$

So, the probability of the particle being in a microstate with position between $\vec{r}$ and $\vec{r}+d\vec{r}$ and momentum $\vec{p}$ and $\vec{p}+d\vec{p}$ and internal state s,

$$P_s(\vec{r},\vec{p})\, d^3r\, d^3p \propto e^{-\frac{\frac{1}{2}mv^2 + E_s^{int}}{k_B T}} d^3r\, d^3p$$

The internal energy arises when the gas is not monoatomic so, there can be molecular vibration and rotation about the center of mass. Since we are concerned with only the translational velocity and momentum, irrespective of the probability irrespective of internal energy will E^{int}, the probability irrespective of internal energy will be sum over the all possible internal states s. Then, sum of the factor $e^{-\frac{E_s^{int}}{k_B T}}$ will just be a constant. So, the probability of finding the moleeule between $\vec{p}$ and $\vec{p}+d\vec{p}$ and $\vec{r}$ and $\vec{r}+d\vec{r}$ is,

$$P(\vec{r},\vec{p})\, d^3r\, d^3p \propto e^{-\frac{\frac{1}{2}mv^2}{k_B T}} d^3r\, d^3p$$

If one multiplies the probability with the total number of particles, s/he gets the mean number of particles in that range. So, the mean number of molecules between $\vec{r}$ and $\vec{r}+d\vec{r}$ having velocity between $\vec{v}$ and $\vec{v}+d\vec{v}$ is,

$$f(\vec{r},\vec{v})\, d^3\vec{r}\, d^3v = CNe^{-\frac{\frac{1}{2}mv^2}{k_BT}} d^3r\, d^3v$$

If we integrate this over all possible r and velocity $\vec{v}$ from $-\infty$ to ∞, we will get the total number of molecules.

$$\therefore \int_r \int_v f(\vec{r},\vec{v})\, d^3r\, d^3v = N$$

$$\Rightarrow \int_r \int_v CNe^{-\frac{mv^2}{2k_BT}} d^3v\, d^3r = N$$

$$\Rightarrow \int_r d^3r \int_v C\cancel{N}e^{-\frac{mv^2}{2k_BT}} d^3v = \cancel{N}$$

$$\Rightarrow CV \int_v e^{-\frac{mv^2}{2k_BT}} d^3v = 1$$

V = volume of the box

Now, this is a tripple integral.

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\frac{m(v_x^2+v_y^2+v_z^2)}{2k_BT}} \, dv_x \, dv_y \, dv_z$$

$$= \int_{-\infty}^{\infty} e^{-\frac{mv_x^2}{2k_BT}} dv_x \int_{-\infty}^{\infty} e^{-\frac{mv_y^2}{2k_BT}} dv_y \int_{-\infty}^{\infty} e^{-\frac{mv_z^2}{2k_BT}} dv_z$$

$$= \sqrt{\frac{\pi}{m/2k_BT}} \cdot \sqrt{\frac{\pi}{m/2k_BT}} \sqrt{\frac{\pi}{m/2k_BT}}$$

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

$$\therefore \; C = \frac{1}{V}\left(\frac{m}{2\pi k_BT}\right)^{3/2}$$

$$\therefore \; f(\vec{v})\, d^3r\, d^3v = \frac{N}{V}\left(\frac{m}{2\pi k_BT}\right)^{3/2} e^{-\frac{mv^2}{2k_BT}} d^3r\, d^3v$$

We have omitted $\vec{r}$ since f doesn't depend on it. Also, f only depends on magnitude of velocity $v = |\vec{v}|$, rather than $\vec{v}$. This is obvious, since there is no preferred direction.

If we divide (iv) by d^3r (the infinitesimal volume element), then we get $f(\vec{v})\, d^3v$, which gives the mean number of molecules per unit volume in the range of velocity between $\vec{v}$ and $\vec{v} + d\vec{v}$.

$$\therefore\ f(\vec{v})\, d^3v = n \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{mv^2}{2k_B T}}\, d^3v$$

n → no. of molecules per unit volume

Distribution of component of velocity

The mean number of molecules per unit volume with x-component of velocity between v_x and $v_x + dv_x$

$$g(v_x)\, dv_x = \int_{v_y}\int_{v_z} f(\vec{v})\, d^3v$$

which is found by summing over all possible v_y

and v_z value of a particular v_x.

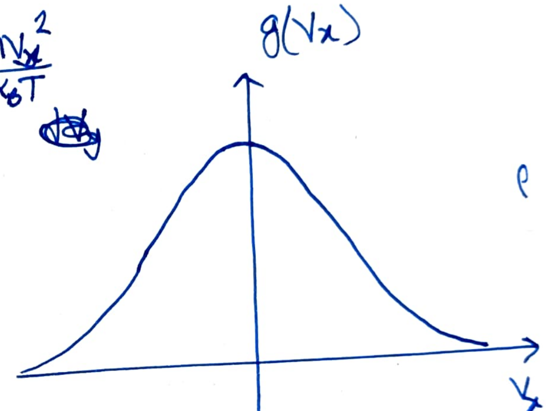
$$\therefore g(v_x)dv_x = n\left(\frac{m}{2\pi k_B T}\right)^{3/2} \int_{-\infty}^{\infty} e^{-\frac{mv_y^2}{2k_BT}} dv_y \int_{-\infty}^{\infty} e^{-\frac{mv_z^2}{2k_BT}} dv_z \; e^{-\frac{mv_x^2}{2k_BT}} dv_x$$

$$= n\left(\frac{m}{2\pi k_B T}\right)^{3/2} \cdot \sqrt{\frac{\pi}{m/2k_BT}} \cdot \sqrt{\frac{\pi}{m/2k_BT}} \; e^{-\frac{mv_x^2}{2k_BT}} dv_x.$$

$$\boxed{\therefore g(v_x)\,dv_x = n\sqrt{\frac{m}{2\pi k_B T}}\, e^{-\frac{mv_x^2}{2k_BT}} dv_x}$$

Similarly, $g(v_y) = n\sqrt{\frac{m}{2k_BT}}\, e^{-\frac{mv_y^2}{2k_BT}}$

$$g(v_z) = n\sqrt{\frac{m}{2k_BT}}\, e^{-\frac{mv_z^2}{2k_BT}}$$



Obviously, the fraction of total particles in whole volume between v_x and v_x+dv_x,

$$G(v_x) = \sqrt{\frac{m}{2k_BT}}\, e^{-\frac{mv_z^2}{2k_BT}}$$

So, $G(v_x) = \frac{V}{N_{tot}} g(v_x)$

with $\int_{-\infty}^{\infty} G(v_x)\,dv_x = 1.$

Now, mean velocity along x-axis, $\langle v_x \rangle = \int_{-\infty}^{\infty} v_x G(v_x)\,dx$

$$= \int_{-\infty}^{\infty} v_x e^{-\frac{mv_x^2}{2k_BT}} \sqrt{\frac{m}{2k_BT\pi}}\, dv_x$$

$= 0$ (~~reason~~ argue why this is true

$$\langle v_x^2 \rangle = \int_{-\infty}^{\infty} \sqrt{\frac{m}{2\pi K_B T}}\, v_x^2\, e^{-\frac{m v_x^2}{2K_BT}} = \frac{K_B T}{m}$$

$$\boxed{\therefore\ \frac{1}{2} m \langle v_x^2 \rangle = \frac{1}{2} K_B T} \rightarrow \frac{1}{2}K_BT \text{ energy is for a degree of freedom}$$

$\downarrow$

equipartition of energy

So, total mean kinetic energy $= \frac{1}{2} m v^2$

$$= \frac{3}{2} K_B T$$

Also, $\langle v_x^2 \rangle = \frac{K_B T}{m} \Rightarrow v_{x,\,rms} = \sqrt{\langle v_x^2 \rangle} = \sqrt{\frac{K_B T}{m}}$

So, lower the temerature, narrower will be the width of the distribution function and vice versa.

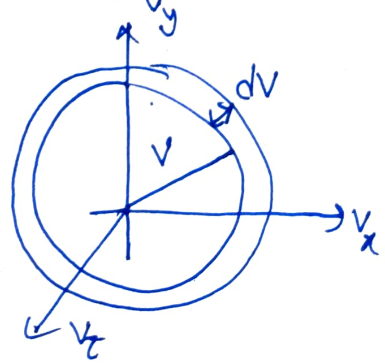
Distribution of speed

Let, $F(v)\,dv$ gives the mean number of molecules per unit volume with speed between v and $v+dv$.

So, we have to integrate $f(\vec{v})\,d^3v$ over all velocities in the range satisfying,

$$v < |\vec{v}| < v + dv.$$

So, this integration is over all velocity vectors that lie in the velocity space ~~that~~ within a shell of inner radius v and outer radius $v+dv$.



$$\therefore F(v)\,dv = \int_{v<|\vec{v}|<v+dv} f(\vec{v})\,d^3v$$

So, the integration is over all velocities satisfying $v < |\vec{v}| < v+dv$.

Since $f(\vec{v})$ depends only on the $|\vec{v}|$, $f(\vec{v}) \equiv f(v)$, the integration is just $f(v)$ times $\int_{v<|\vec{v}|<v+dv} d^3v$, that is the volume of the shell, which is $4\pi v^2 dv$.

$$\therefore F(v)\,dv = 4\pi v^2 dv \cdot n \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{mv^2}{2k_B T}}$$

$$\boxed{\therefore F(v)\,dv = \frac{4n}{\sqrt{\pi}} \left(\frac{m}{2k_B T}\right)^{3/2} v^2 e^{-\frac{mv^2}{2k_B T}}\,dv}$$

This is Maxwell-Boltzmann speed distribution.

The fraction of particles with speed between v and $v+dv$ in the whole volume,

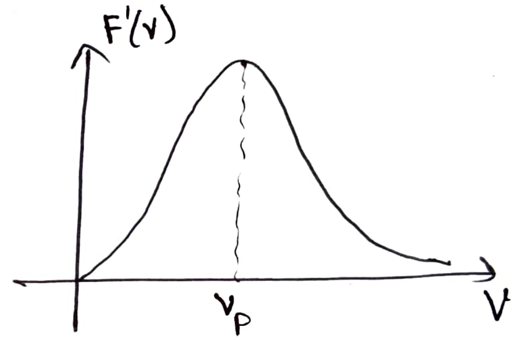
$$\boxed{F'(v)\,dv = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_B T}\right)^{3/2} v^2 e^{-\frac{mv^2}{2k_B T}}\,dv}$$

Of course, $\int_0^\infty F'(v)\,dv = 1$, since $F'(v)dv$ gives you the fraction of particles with speed v and $v+dv$. So, $F'(v)$ works like a probability density function for the random variable v.

You can then find the average speed,

$$\langle v \rangle = \int_0^\infty v F'(v)\,dv = \sqrt{\frac{8k_BT}{\pi m}}$$

Root mean squared speed, $v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3k_BT}{m}}$

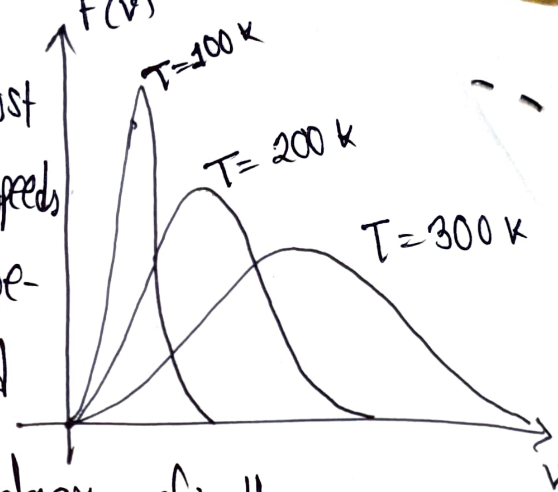


The most probable speed is defined as the speed having the maximum value of $F'(v)$. So, at $v = v_p$, the $F'(v)$ is maximum. You can show that,

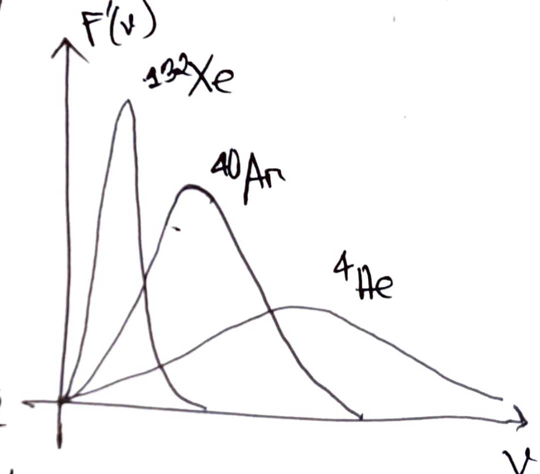
$$v_p = \sqrt{\frac{2k_BT}{m}}$$

Now, let's see the dependence of $F(v)$ with temperature. As we can see, $v_{rms} \propto \sqrt{T}$, and we know v_{rms} is a measure of full width at half maximum. So, the graph will flatten out with increasing temperature.

So, at lower temperature, most of the particles have low speeds as compared to higher temperature. Also, the peak should decrease with increasing flatness of the curves since the area under the curve must be 1.



Also, $V_{rms} \propto \frac{1}{\sqrt{m}}$. So, as the molecules gets heavier, the rms velocity decreases. A graph for few different molecules is shown here.



And, $\langle v \rangle : V_{rms} : V_p = \sqrt{\frac{8}{\pi}} : \sqrt{3} : \sqrt{2}$
$= 1.13 : 1.22 : 1$

$\therefore V_p < \langle v \rangle < V_{rms}$.