Lecture 6

Maxwell distribution of velocity/speed

Maxwell distribution : Derivation

James Clerk Maxell 1860

In a container the gas molecules move with different speed and the motion of the molecules is completely random. We want to calculate what is the probability of finding a molecule with a speed range of c to (c+dc) (regardless of the direction of motion.

Let us consider u, v, and w denote the velocity components in x, y, z directions respectively.

Let dn_u be the number of molecules which have an x-component of velocity with a range of u to (u+du)

Then the probability of finding such molecules is

$\frac{dn_u}{N}$ [Let N be the total no. of molecules in the container]

If the width of the interval du is small then it is a reasonable assumption that doubling the width double the number of molecules.

Thus, $\frac{dn_u}{N} \propto du$

Also, the probability $\frac{dn_u}{N}$ will depend on the magnitude of velocity component u.

Thus, $\frac{dn_u}{N} = f(u^2)\, du$

[We assume implicitly that $(\frac{dn_u}{N})$ is independent of the values along the y and z components (i.e. v and w)]

We have assumed that the nature of molecular motion is random. So, the probability of finding a molecule with an x component of velocity in the range of u to (u+du) must be the same as the probability of finding one with an x-component of (-)u to (-) (u+du)

This means there is same chance for a molecule to go in (+) ve as well as in (-) ve direction. If direction would have mattered, then motion can't be considered to be random and the entire mass of gas would have a net velocity in a preferred direction. The required symmetry in the function is assured if we consider $f(u^2)$ rather than $f(u)$

In the same way we can write

$$\frac{dn_v}{N} = f(v^2)\,dv \qquad \text{and} \qquad \frac{dn_w}{N} = f(w^2)\,dw$$

These functions must have exactly the same form since the randomness of distribution does not allow one direction to be different from the other.

(Assuming that the gas molecules are under no force field, for example gravity etc.)

Now, let us calculate what is the probability of finding a molecule that has simultaneously an x-component of speed of u to (u+du) and an y-component in the range of v to (v+dv). Let that number be dn_{uv}

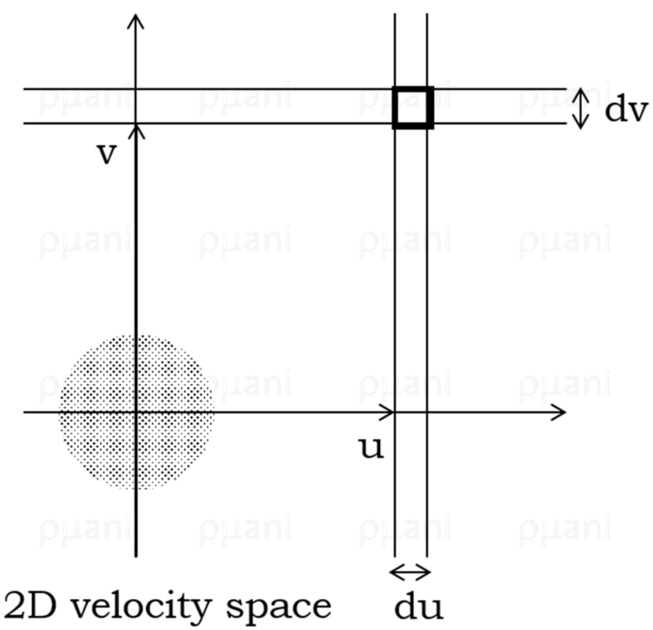
Then, $\frac{dn_{uv}}{N} = \left(\frac{dn_u}{N}\right)\left(\frac{dn_v}{N}\right)$

$$\Rightarrow \quad \frac{dn_{uv}}{N} = f(u^2)\,f(v^2)\,du\,dv$$

The values of u and v for each molecule determines a representative point marked with a dot (Representative points of two molecules might coincide but that's not critical, total no. of points = total no. of molecules = N)

The total no. of molecules with x component lying in the range of u to (u+du) is represented by the no. of points in the strip, u to (u+du).

Similarly in y direction.



2D velocity space

Thus, $dn_u/N = f(u^2)\,du$ and $dn_v/N = f(v^2)\,dv$

The number of molecules that satisfied both the conditions is the number of representative points that lie in the small rectangle (at the intersection of two strips).

This number of molecules dn_{uv} is given by

$$dn_{uv}/N = f(u^2)\,f(v^2)\,du\,dv$$

The area of the rectangle = $du \times dv$

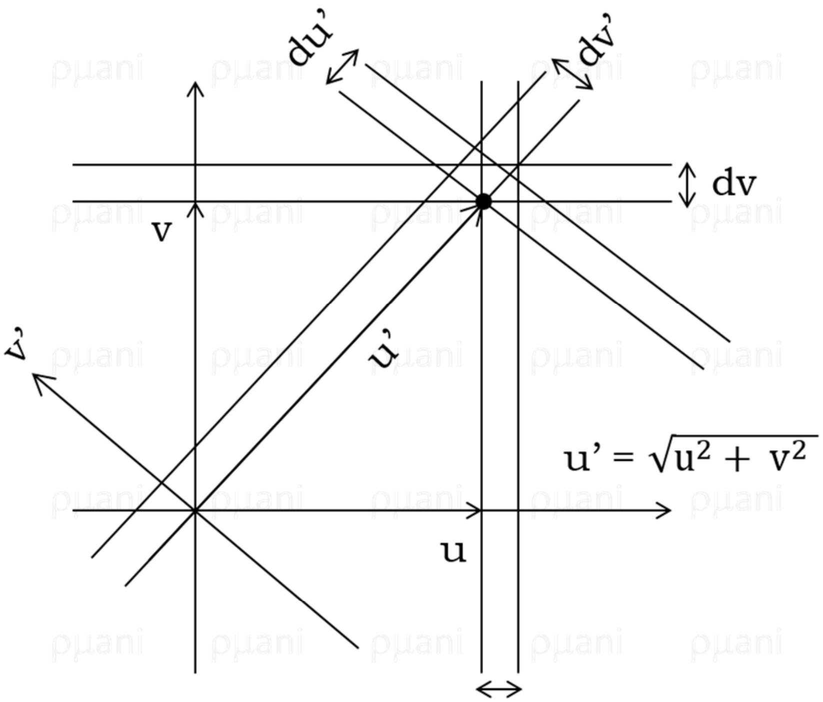
Thus, the density of representative points is given by:

Point density, which is equal to $\dfrac{dn_{uv}}{du\;dv} = N\,f(u^2)\,f(v^2)$

Now, let us set a new set of coordinate u' and v' and the velocity range be du' and dv'
In a similar way the number of representative points in the area (du' . dv') is given by

$$dn_{u'v'} / N = f(u'^2)\ f(v'^2)\ du'\ dv'$$

The 'density' of representative points $dn_{u'v'} / du'\ dv' = N\ f(u'^2)\ f(v'^2)$



2D velocity space

Now, the position (u, v) is same as (u', v'). So, the density of representative points must be same regardless of which coordinate system is chosen.

Thus, $N\ f(u^2)\ f(v^2) = N\ f(u'^2)\ f(v'^2)$

Graphically, $u' = \sqrt{u^2 + v^2}$ and $v' = 0$ is the corresponding coordinate of uv (of first coordinate) in 2nd coordinate.

Thus, $f(u^2 + v^2)\ \ f(0) = f(u^2)\ f(v^2)$

Since, f(0) is a constant, so let us write f(0) = A (constant)

Then, $A\ f(u^2 + v^2) = f(u^2)\ f(v^2)$

Now, only functions that satisfies above equation are

$f(u^2) = A\ .\ e^{\beta u^2}$ and $f(u^2) = A\ .\ e^{-\beta u^2}$

where β is a (+)ve constant

If we choose the first one then $\frac{dn_u}{N} = A\ .\ e^{+\beta u^2}\ .\ du$

This means as velocity component u becomes infinite, the probability of finding such molecules becomes infinite. This would require infinite kinetic energy for the system and thus an impossible case.

Instead if we choose the second one, then

$$\frac{dn_u}{N} = A \,.\, e^{-\beta u^2} \,.\, du \qquad (1D)$$

Then the probability of finding a molecule with infinite x-component of velocity is zero. This is physically feasible.

This is in 1D. Distribution curve is of Gaussian nature $(A \,.\, e^{-\beta u^2} \Rightarrow$ Gaussian$)$

Let us now try to understand the situation in 2D

$$\frac{dn_{uv}}{N} = A^2 \,.\, e^{-\beta(u^2+v^2)} \,.\, du \,.\, dv$$

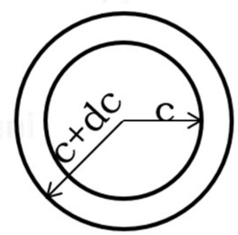
Point/Number density in 2D: $\frac{dn_{uv}}{dudv} = N.\, A^2 \,.\, e^{-\beta(u^2+v^2)}$

In 2D: $u^2 + v^2 = c^2$

Area $= \pi(c+dc)^2 - \pi c^2$

$= \pi c^2 + 2\pi c\, dc + \pi\,(dc)^2 - \pi c^2$

$= 2\pi c\, dc$ [as dc is small, so $(dc)^2$ can be neglected in comparison to other terms]



Thus, $\boxed{dn_c = N \,.\, A^2 \,.\, e^{-\beta(c^2)} \,.\, 2\pi c \,.\, dc}$

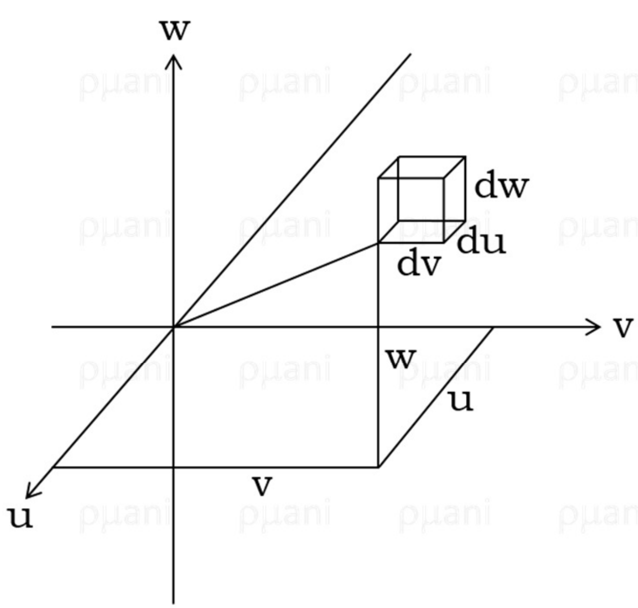
This is the Maxwell speed distribution equation for 2D. How will the speed distribution plot look like?

Let us extend the situation to 3D

$$\frac{dn_{uvw}}{N} = f(u^2)\, f(v^2)\, f(w^2)\, du\, dv\, dw$$

which can be rewritten as

$$\frac{dn_{uvw}}{N} = A^3 \,.\, e^{-\beta(u^2+v^2+w^2)} \,.\, du \,.\, dv \,.\, dw$$



3D velocity space

Now, a three dimensional velocity space is constructed. In this space a molecule is represented by a point determined by the values of the three components of velocity u, v, w. The total number of representative points in the parallelopiped at u, v, w is dn_{uvw}

The density of points in the parallelepiped

$$= \frac{dn_{uvw}}{du\, dv\, dw} = N \,.\, A^3 \,.\, e^{-\beta(u^2+v^2+w^2)}$$

$$= N \,.\, A^3 \,.\, e^{-\beta(c^2)} \quad [\text{as } c^2 = u^2 + v^2 + w^2]$$

This equation tells us that the value of point density depends on N, A and β and on c^2. Consequently it does not depend on any particular direction of velocity vector but only on the length of the vector, that is on the speed. The density of representative points has the same value everywhere on the sphere of radius 'c' in the velocity space.

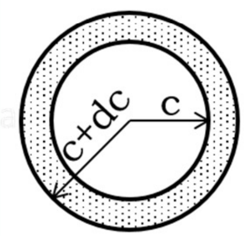
We now ask the question: How many points lie in the shell between spheres of radius c and (c+dc).

This number of points (dn_c) in the shell is the density of points on the sphere of radius 'c' multiplied by the volume of the shell, thus,

$$dn_c = \text{point density on sphere} \times \text{volume of shell}$$

Now, the volume of the shell dV_{shell} is the difference in volume between the outer and inner sphere,

$$\text{i.e. } dV_{shell} = \frac{4}{3}\pi\,(c+dc)^3 - \frac{4}{3}\pi\,c^3 = \frac{4}{3}\pi\,[c^3 + 3\,.\,c^2\,.\,dc + 3c\,.\,(dc)^2 + (dc)^3 - c^3]$$



Spherical shell (3D)

Now, since dc is small, so $(dc)^2$ and $(dc)^3$ can be neglected in comparison to other terms.

Thus, $dV_{shell} = \frac{4}{3}\pi\,.\,3\,.\,c^2\,.\,dc = 4\pi\,.\,c^2\,.\,dc$

Thus, we have $\boxed{dn_c = 4\pi\,.\,c^2\,.\,N\,.\,A^3\,.\,e^{-\beta(c^2)}\,.\,dc}$

This is the Maxwell equation for speed distribution in 3D.

The equation relates dn_c (i.e. number of molecules with speed between c and (c+dc)) to N, c, dc and the constant A & β.

We will see how the profile looks like. Will it be Gaussian?

In order to know that, the constants A & β needs to be evaluated.

Evaluation of A & β

We know that $\int_0^\infty \frac{dn_c}{N} = 1$

$$\Rightarrow \quad \int_0^\infty 4\pi \,.\, A^3 \,.\, e^{-\beta(c^2)} \,.\, c^2 \,.\, dc = 1$$

$$\Rightarrow \quad 4\pi\, A^3 \int_0^\infty e^{-\beta(c^2)} \,.\, c^2 \,.\, dc = 1$$

It can be shown that $\int_0^\infty e^{-\beta(c^2)} \,.\, c^2 \,.\, dc = \frac{\pi^{\frac{1}{2}}}{4\beta^{\frac{3}{2}}}$

Thus, $4\pi\, A^3 \,.\, \frac{\sqrt{\pi}}{4\beta^{\frac{3}{2}}} = 1$

$$\Rightarrow \quad A^3 = \left(\frac{\beta}{\pi}\right)^{\frac{3}{2}}$$

Again, $\langle\varepsilon\rangle = \frac{\int_{c=0}^{c=\infty} \frac{1}{2} m\, c^2\, dn_c}{N}$

$$= \frac{\int_{c=0}^{c=\infty} \frac{1}{2} m\, c^2 \,.\, 4\pi \,.\, N \,.\, A^3 \,.\, e^{-\beta(c^2)} \,.\, c^2 \,.\, dc}{N}$$

Using $A^3 = \left(\frac{\beta}{\pi}\right)^{\frac{3}{2}}$, the above equation becomes

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

It can be shown that $\int_0^\infty c^4 \, . \, e^{-\beta(c^2)} \, . \, dc \; = \; \frac{3\sqrt{\pi}}{8\beta^{\frac{5}{2}}}$

Thus, $<\varepsilon> = \frac{3m}{4\beta}$

$$\Rightarrow \; \beta = \frac{3m}{4 <\varepsilon>}$$

Thus, β is expressed in terms of average energy per molecule $<\varepsilon>$.

However, we know that $<\varepsilon> = \frac{3}{2}$ kT , where k is the Boltzmann constant.

Thus, $\boxed{\beta = \frac{m}{2\,k\,T}}$ and hence, $\boxed{A = \left(\frac{m}{2\,\pi\,k\,T}\right)^{\frac{1}{2}}}$

Thus we could evaluate A & β. Putting the values of A & β we get

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

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

$$\Rightarrow \; \boxed{\frac{1}{N} \, . \, \frac{dn_c}{dc} = 4\pi \, . \, \left(\frac{m}{2\,\pi\,k\,T}\right)^{\frac{3}{2}} . \, e^{-\frac{m\,c^2}{2\,k\,T}} . \, c^2}$$

$\Rightarrow \; \boxed{\frac{dn_c}{N} = \left(\frac{m}{2\,\pi\,k\,T}\right)^{\frac{3}{2}} . \, e^{-\frac{m\,c^2}{2\,k\,T}} . \, 4\pi \, . \, c^2 \, . \, dc} \; \Rightarrow$ This is the Maxwell equation for speed distribution in 3D.

Thus, in a nutshell, Maxwell equation for velocity/speed distribution in different dimensions:

$$\frac{dn_u}{N} = A \,.\, e^{-\beta u^2} \,.\, du$$

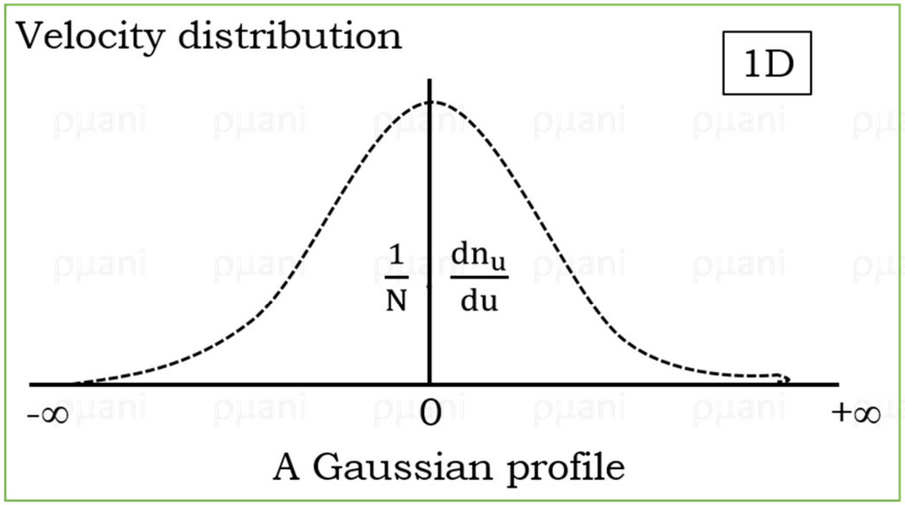
$$\frac{dn_u}{N} = \left(\frac{m}{2\,\pi\,k\,T}\right)^{\frac{1}{2}} . \; e^{-\frac{m\,u^2}{2\,k\,T}} \; du \qquad (1D)$$

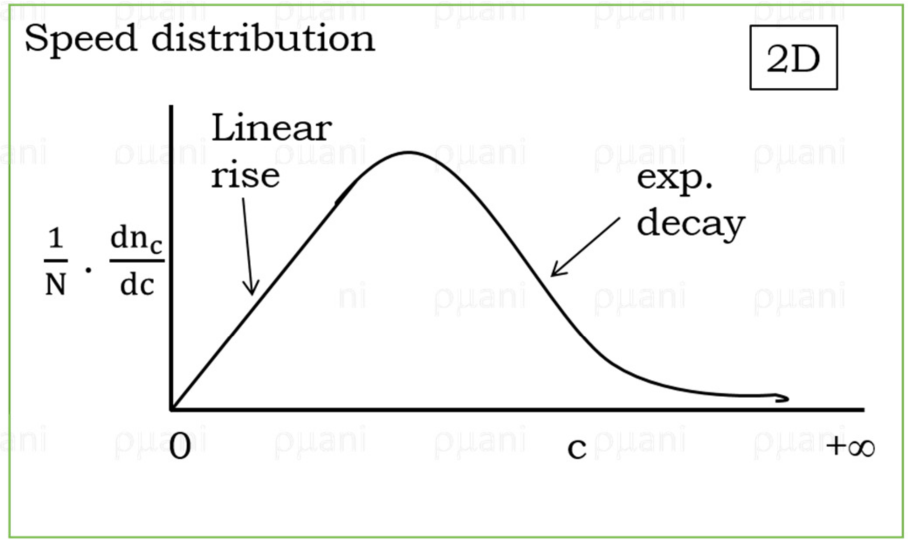
$$\frac{dn_c}{N} = \left(\frac{m}{2\,\pi\,k\,T}\right)^{\frac{2}{2}} . \; e^{-\frac{m\,c^2}{2\,k\,T}} . \; 2\pi c \; dc \qquad (2D)$$

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

A common equation: $$\frac{dn_D}{N} = \left(\frac{m}{2\,\pi\,k\,T}\right)^{\frac{D}{2}} . \; e^{-\frac{m\,c^2}{2\,k\,T}} . \; 2^{D-1} . \pi \,.\, c^{D-1} \,.\, dc \qquad (1D,\, 2D,\, 3D)$$

Let us now try to plot:





Maxwell distribution in different dimensions:

1D: $$\frac{dn_u}{N} = A \, . \, e^{-\beta u^2} \, . \, du$$

$$\frac{dn_u}{N} = \left(\frac{m}{2\pi k T}\right)^{\frac{1}{2}} . \, e^{-\frac{m u^2}{2 k T}} \, . \, du$$

2D: $$\frac{dn_c}{N} = \left(\frac{m}{2\pi k T}\right)^{\frac{2}{2}} . \, e^{-\frac{m c^2}{2 k T}} . \, 2\pi c \, . \, dc$$

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