Statistical Mechanics
Lecture 7

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Maxwell Velocity Distribution (Momentum and Energy Distribution) :

If $f(u_x), f(u_y)$ & $f(u_z)$ are distribution function of molecules in three mutually perpendicular direction , then the probability that molecules have velocity component between u_x & $u_x + du_x, u_y$ & $u_y + du_y, u_z$ & $u_z + du_z$ are $f(u_x)du_x, f(u_y)du_y$ & $f(u_z)du_z$ respectivly.

Maxwell derivation is based on two assumptions –

(a) The distribution of molecules moving from a point in any direction is isotropic otherwise molecules would drift in preferred direction. All direction in space are equivalent and hence any direction of velocity of molecules is equally probable i.e. $f(u_x)du_x = f(u_y)du_y = f(u_z)du_z$.

(b) The movement of molecules along three mutually perpendicular directions are independent i.e. u_x, u_y & u_z are independent of each other.

The second assumption is true for velocity less than c. If the molecules move with velocity c, the component of velocity are no longer independent then theory is related by the equation

$$u_x{}^2 + u_y{}^2 + u_z{}^2 = c^2 \rightarrow (i)$$

From Maxwell second assumption the number of molecules with velocities in the range of u_x & $u_x + du_x$, u_y & $u_y + du_y$, u_z & $u_z + du_z$ are

$$N = N_0 f(u_x) f(u_y) f(u_z) du_x du_y du_z \rightarrow (ii)$$

Where N_0 is the total number of molecules of gas. Here $du_x du_y du_z$ can be considered as volume element in velocity space and $f(u_x) f(u_y) f(u_z)$ as probability density of velocity. Because of property of isotropy the probability for component of u_x & $(-u_x)$ should be same. Hence probability density function $f(ux)$ must be even number of u_x .Therefore

$$f(u_x) = \phi(u_x{}^2), f(u_y) = \phi(u_y{}^2) \& f(u_z) = \phi(u_z{}^2)$$

If u is the resultant velocity the probability density of velocity is

$$\varphi(u^2) = f(u_x) f(u_y) f(u_z) \rightarrow (iii)$$

$$\varphi(u^2) = \phi(u_x{}^2)\phi(u_y{}^2)\phi(u_z{}^2) \rightarrow (iv)$$

Taking log of both sides

$$ln\varphi(u_x{}^2) = ln\phi(u_x{}^2) + ln\phi(u_y{}^2) + ln\phi(u_z{}^2) \rightarrow (v)$$

By differentiating

$$\frac{1}{\varphi(u^2)} \frac{\partial\varphi(u^2)}{\partial(u^2)} 2u = \frac{1}{\phi(u_x{}^2)} \frac{\partial\phi(u_x{}^2)}{\partial(u_x{}^2)} 2u_x$$

$$\frac{1}{\phi(u_x{}^2)} \frac{\partial\phi(u_x{}^2)}{\partial(u_x{}^2)} 2u_x = \frac{1}{\varphi(u^2)} \frac{\partial\varphi(u^2)}{\partial(u^2)} 2u \rightarrow (vi)$$

$$\frac{1}{\phi(u_y{}^2)} \frac{\partial \phi(u_y{}^2)}{\partial (u_y{}^2)} 2u_y = \frac{1}{\varphi(u^2)} \frac{\partial \varphi(u^2)}{\partial (u^2)} 2u \rightarrow (vii)$$

$$\frac{1}{\phi(u_z{}^2)} \frac{\partial \phi(u_z{}^2)}{\partial (u_z{}^2)} 2u_z = \frac{1}{\varphi(u^2)} \frac{\partial \varphi(u^2)}{\partial (u^2)} 2u \rightarrow (viii)$$

Hence we can write

$$\frac{1}{\phi(u_x{}^2)} \frac{\partial \phi(u_x{}^2)}{\partial (u_x{}^2)} = \frac{1}{\phi(u_y{}^2)} \frac{\partial \phi(u_y{}^2)}{\partial (u_y{}^2)} = \frac{1}{\phi(u_z{}^2)} \frac{\partial \phi(u_z{}^2)}{\partial (u_z{}^2)} = -\alpha \rightarrow (ix)$$

Where α is constant and negative sign introduced for convenience.

Integrating this equation we get

$$\frac{1}{\phi(u_x{}^2)} \frac{\partial \varphi(u_x{}^2)}{\partial (u_x{}^2)} = -\alpha \rightarrow (x)$$

Where

$$\phi(u_x{}^2) = C.e^{-\alpha u_x{}^2}$$

Where C is another constant. The probability that molecules has between u_x & $u_x + du_x$ is

$$f(u_x)du_x = C.e^{-\alpha u_x{}^2}.du_x \rightarrow (xi)$$

The constant C can be found from normalization is as

$$\int_{-\alpha}^{+\alpha} f(u_x)du_x = \int_{-\alpha}^{+\alpha} Ce^{-\alpha u_x^2} \ du_x = 1 \rightarrow (xi)$$

Since the integrand must convergence α must be necessarily positive. Now

$$\int_{-\alpha}^{+\alpha} Ce^{-\alpha u_x}du_x = C\sqrt{\frac{\pi}{\alpha}} = 1 \rightarrow (xii)$$

Therefore

$$C = \sqrt{\frac{\pi}{\alpha}} \text{ and } f(u_x)du_x = \sqrt{\frac{\alpha}{\pi}}\, e^{-\alpha u_x^2}\, du_x \rightarrow (xii)$$

Hence number of molecules whose velocities lies between $u \,\&\, u + du$ is

$$N(u)du = N_0 \left(\frac{\alpha}{\pi}\right)^{3/2} e^{-\alpha u^2} du_x du_y du_z \rightarrow (xiii)$$

Or using spherical polar coordinate we get

$$N(u)du = 4\pi N_0 \left(\frac{\alpha}{\pi}\right)^{3/2} e^{-\alpha u^2} u^2 du \rightarrow (xiv)$$

Now we identify the parameter α. First we calculate pressure of gas in vessel in volume V In equilibrium the molecules will be distributed over volume of vessel in such a way that their concentration is $n = \dfrac{N}{V}$. The number of molecular density with velocity between u_x & $u_x + du_x$ is

$$n(u_x) = n \left(\frac{\alpha}{\pi}\right)^{1/2} e^{-\alpha u_x^2} du_x \;\rightarrow (xv)$$

The number of molecules hitting unit area of wall perpendicular to u_x per unit time is equal to the number in parallelopiped of volume u_x is

$$n \left(\frac{\alpha}{\pi}\right)^{1/2} e^{-\alpha u_x{}^2} u_x du_x$$

Every time molecules hits the walls, their change of momentum equal to $2mu_x$. Hence momentum transferred per unit area of wall per unit time is

$$n \left(\frac{\alpha}{\pi}\right) 1/2 \, e^{-\alpha u_x{}^2} u_x 2mu_x du_x$$

Total momentum transferred is equal to force which in present case is pressure P

$$P = \int\limits_0^{\alpha} n \left(\frac{\alpha}{\pi}\right)^{1/2} e^{-\alpha u_x^2} 2mu_x 2du_x \rightarrow (xvi)$$

$$P = n \left(\frac{\alpha}{\pi}\right)^{1/2} 2m \int\limits_0^{\alpha} u_x 2e^{-\alpha u_x^2} du_x$$

$$P = n \left(\frac{\alpha}{\pi}\right)^{1/2} 2m \frac{\sqrt{\pi}}{4\alpha^{3/2}}$$

$$P = \frac{nm}{2\alpha} \rightarrow (xvii)$$

The equation of state of gas is

$$P = nKT \rightarrow (xviii)$$

Where $K = 1.38 \times 10^{-23} \frac{J}{K}$

Therefore

$$nKT = \frac{nm}{2\alpha}$$

$$\alpha = \frac{m}{2KT} \rightarrow (xix)$$

Therefore

$$N(u)du = 4\pi N_0 \left(\frac{m}{2\pi KT}\right)^{3/2} e^{-mu^2/2KT} u^2 du \rightarrow (xx)$$

This is known as Maxwell Velocity Distribution

Again we know $P = mu$, then

$$N(P)dP = 4\pi N_0 \left(\frac{1}{2\pi mKT}\right)^{3/2} e^{P^2/2mKT} P^2 dP \rightarrow (xxi)$$

Which is known as Maxwell Momentum Distribution.

The energy Distribution is $\epsilon = \frac{1}{2}mu^2$.

Therefore

$$d\epsilon = mudu = \sqrt{2\epsilon m}\, d\epsilon$$

Therefore

$$N(\epsilon)d\epsilon = 4\pi N \left(\frac{m}{2\pi KT}\right)^{3/2} e^{-\epsilon/KT} \frac{2\epsilon}{m} \frac{d\epsilon}{\sqrt{2\epsilon m}} \rightarrow (xxi)$$

$$N(\epsilon)d\epsilon = \frac{2N}{\sqrt{\pi}} \left(\frac{1}{KT}\right)^{3/2} e^{-\epsilon/KT} \epsilon^{1/2}\, d\epsilon \rightarrow (xxii)$$

This is known as Maxwell Energy Distribution