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Maxwell's distribution law of velocities

Consider an ideal gas in a vessel of volume V. If the gas is in equilibrium, then according to Maxwell-Boltzmann's canonical distribution law the number of molecules in a cell of energy ϵ_1 will be

$$n_i = Ae^{-\beta\epsilon_i}$$

Clearly the number of molecules having position co-ordinates in the range x to $x+dx$, y to $y+dy$, z to $z+dz$ and the velocity components in ranges v_x to v_x+dv_x, v_y to v_y+dv_y, v_z to v_z+dv_z, will be proportional to the element of phase of volume $dx\,dy\,dz\,dv_x\,dv_y\,dv_z$.

Therefore the number of molecules having energy ϵ_i and having position co-ordinates between x and $x+dx$, y and $y+dy$, z and $z+dz$ and velocity components 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

$$n_i\,dx\,dy\,dz\,dv_x\,dv_y\,dv_z = Ae^{-\beta\epsilon_i}\,dx\,dy\,dz\,dv_x\,dv_y\,dv_z$$

But ϵ_i=energy of a particle$=\frac{1}{2}mv^2=\frac{1}{2}m\,(v_x^2+v_y^2+v_z^2)$

Which yields

$$n_i\,dx\,dy\,dz\,dv_x\,dv_y\,dv_z=Ae^{-m\beta\,[\frac{1}{2}v_x^2+v_y^2+v_z^2)]}\,dx\,dy\,dz\,dv_x\,dv_y\,dv_z \quad ...(1)$$

The constant A can be determined by the fact that the total number of molecules is constant, equal to N, which will be obtained by integrating eqn., (1) over all available volume and all ranges of velocities, *i.e.*

$$N=\iiiiiint Ae^{-m\beta\,[\frac{1}{2}\,(v_x^2+v_y^2+v_z^2)]}\,dx\,dy\,dz\,dv_x\,dv_y\,dv_z$$

But $\iiint dx\,dy\,dz=V=$volume of the vessel containing gas.

$$\therefore \quad N=AV\iiint e^{-\frac{m\beta}{2}\,(v_x^2+v_y^2+v_z^2)]}\,dv_x\,dv_y\,dv_z$$

$$=AV\int_{-\infty}^{+\infty}e^{-\frac{\beta mv_x^2}{2}}\,dv_x\int_{-\infty}^{+\infty}e^{-\frac{\beta mv_y^2}{2}}\,dv_y\int_{-\infty}^{+\infty}e^{-\frac{\beta mv_z^2}{2}}\,dv_z \quad ..(2)$$

We have $\int_{-\infty}^{+\infty}e^{-\frac{\beta mv_x^2}{2}}\,dv_x=\sqrt{\left(\frac{2\pi}{m\beta}\right)}$

$$\int_{-\infty}^{+\infty}e^{-\frac{\beta mv_y^2}{2}}\,dv_y=\sqrt{\left(\frac{2\pi}{m\beta}\right)}$$

and
$$\int_{-\infty}^{+\infty}e^{-\frac{\beta m_z^2}{2}}\,dv_z=\sqrt{\left(\frac{2\pi}{m\beta}\right)}$$

Substituting these values in eqn. (1), we get

$$N=AV\left(\frac{2\beta}{m\beta}\right)^{3/2}$$

or
$$A=\frac{N}{V}\left(\frac{m\beta}{2\pi}\right)^{3/2}$$

But we know
$$\beta=\frac{1}{kT}$$

$$\therefore \quad A=\frac{N}{V}\left(\frac{m}{2\pi kT}\right)^{3/2}$$

Substituting values of A and β in eqn. (1), we get

$$n_i\,dx\,dy\,dz\,dv_x\,dv_y\,dv_z=\frac{N}{V}\left(\frac{m}{2\pi kT}\right)^{3/2}e^{-\frac{m\,(v_x^2+v_y^2+v_z^2)}{2kT}}\,dx\,dy\,dz\,dv_x\,dv_y\,dv_z \quad ...(3)$$

The number of molecules having velocity co-ordinates in the range v_x to v_x+dv_x, v_y to v_y+dv_y, v_z to v_z+dv_z irrespective of the position co-ordinates, can be found by integrating eqn. (3) with respect to position co-ordinates, which gives

$$n_i\, dv_x\, dv_y\, dv_z=\frac{N}{V}\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{m\,(v_x^2+v_y^2+v_z^2)}{2kT}}\, dv_x\, dv_y\, dv_z\, V.$$

$$=N\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{m\,(v_x^2+v_y^2+v_z^2)}{2kT}}\, dv_x\, dv_y\, dv_z. \quad \ldots(4)$$

Finally let us find the number of molecules having velocity components in the range v_x to v_x+dv_x irrespective of v_y, v_z, x, y, z. This will be obtained by integrating eqn. (4) with respect to v_y and v_z, *i.e.*

$$n_i\, dv_i=N\left(\frac{m}{2\pi kT}\right)^{3/2}\iint e^{-m\left(\frac{v_x^2+v_y^2+v_z^2}{2kT}\right)}\, dv_x\, dv_y\, dv_z$$

$$=N\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv_x^2/2kT}\, dv_x \int_{-\infty}^{+\infty} e^{-my_y^2/2kT}\, dv_y \int_{-\infty}^{+\infty} e^{-mv_z^2/2kT}\, dv_z$$

$$=N\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv_x^2/2kT}\, dv_x\left[\sqrt{\frac{2\pi kT}{m}}\right]\times\left[\sqrt{\left(\frac{2\pi kT}{m}\right)}\right]$$

$$=N.\left(\frac{m}{2\pi kT}\right)^{1/2} e^{-m_x^2/2kT}\, dv_x. \quad \ldots(5)$$

The probability that a molecule will have x-component of velocity in the range v_x to v_x+dv_x is given by

$$P\,(v_x)\, dv_x=\frac{n_i}{N}\, dv_x=\left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT}\, dv_x \quad ..(6)$$

Equations (5) and (6) represent **Maxwell's distribution law of velocities.**

The probability function

$$f\,(v_x) \text{ or } P\,(v_x) \text{ is given by } \frac{P\,(v_x)\, dv_x}{dv_x}$$

$$\therefore\ f\,(v_x)=P\,(v_x)=\left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT} \quad \ldots(7)$$

Equation (7) can also be expressed in terms of momentum component p_x. Substituting $mv_x=p_x$ and $m\, dv_x=dp_x$ on R.H.S. of equation (6) and dividing by dp_x we get

$$P\,(p_x)=\left(\frac{1}{2\pi mkT}\right)^{1/2} e^{-p_x^2/2mkT} \quad \ldots(8)$$

Discussion of Maxwell's velocity distribution formula. The probability that a molecule will have velocity component between v_x and v_x+dv_x is given by

$$P\,(v_x)\,dv_x=\left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT}\,dv_x \qquad \ldots(9)$$

(i) From this equation it is obvious that the function $P\,(v_x)$ is symmetrically distributed about the value $v_x=0$ since average value of v_x for Maxwellian distribution is zero, *i.e.*

$$\bar{v}_x=\int_{-\infty}^{+\infty} v_x\,P\,(v_x)\,dv_x$$

$$=\int_{-\infty}^{+\infty}\left(\frac{m}{2\pi kT}\right)^{1/2} v_x e^{-mv_x^2/2kT}\,dv_x$$

$$=0\left[\text{ since}\int_{-\infty}^{+\infty} v_x e^{-mv^{\circ x}/2kT}\,dv_x=0\right].$$

Also from equation (9) it is clear that

$$P\,(-v_x)=P\,(v_x).$$

This again indicates that $P\,(v_x)$ is symmetrical about $v_x=0$.

(ii) The probability distribution function is maximum for that value of v_x for which

$$\frac{\partial P\,(v_x)}{\partial v_x}=0$$

or
$$\frac{\partial}{\partial x}\left[\left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/\cdot T}\right]=0$$

This gives $v_x=0$ and the maximum value is

$$P_{max.}=\left(\frac{m}{2\pi kT}\right)^{1/2} \qquad \ldots(10)$$

This shows that the $P_{max.}$ increases as m increases and T decreases

(iii) P falls to $\frac{1}{e}$ times $P_{max.}$ at value of v_x, given by

$$P\,(v_x)=\frac{1}{e}\,P_{max.}=\frac{1}{e}\left(\frac{m}{2\pi kT}\right)^{1/2}$$

or
$$\left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT}=\frac{1}{e}\left(\frac{m}{2\pi kT}\right)^{1/2}.$$

or
$$e^{-mv_x^2/2kT}=1/e$$

or
$$\frac{mv_x^2}{2kT}=1$$

This gives $v_x=\sqrt{\left(\frac{2kT}{m}\right)}$ ...(11)

This probability function $P\,(v_x)$ is plotted against v_x for three different temperatures As T increases, the peak at $v_x=0$ becomes lower and the distribution spreads out. The area under the curve is always **unity.**