Applications of Maxwell Boltzmann Statistics

3.1. The classical perfect gas

By the definition of a classical perfect gas as an assembly of non-interacting molecules, each distinguishable from the other, it is clear that, for such a gas, the classical, Maxwell-Boltzmann statistics are applicable. It is not necessary to assume that the volume occupied by the individual molecule is negligible since this volume could easily be included in the theory by taking the integrals over phase space to be only over the volume which is actually available to the molecules. However, for convenience, the volume of the molecules will be ignored in the present discussion.

In considering the properties of a perfect gas it is useful to give the distributions of the properties of the molecules in more than one form. Already the distribution of the energies has been given in equation 2.59 where $n(\epsilon)d\epsilon$ was taken as the number of molecules with energies in the range ϵ to $\epsilon+d\epsilon$. If the distribution is expressed as a function of momentum or velocity then it is possible to take $n_p(p)dp$ as the number of molecules with momentum in the range p to $p+dp$ and as the number with velocity in the range v to $v+dv$.

The element of phase space corresponding to a volume V i.e. $V=\int dxdydz$ and to a total momentum in the range p to $p + dp$ is given as

$$\Delta\Gamma(p \rightarrow p+dp) = 4\pi p^2\, dp\, .\, V$$

The corresponding element for a total velocity in the range v to $v+dv$ is obtained by substituting $p = mv$ to give

$$\Delta\Gamma(v \rightarrow v+dv) = m^3\, .\, 4\pi v^2\, dv\, .\, V$$

Substituting for these values of $\Delta\Gamma$ in equation 2.57, and putting the value of e^{α} gives the momentum and velocity distributions as

$$n_p(p)\, dp = \frac{4\pi N}{(2\pi mkT)^{\frac{3}{2}}}\, e^{-p^2/2mkT} p^2\, dp \qquad \textbf{3.1}$$

and

$$n_v(v)\, dv = 4\pi N \left\{\frac{m}{2\pi kT}\right\}^{\frac{3}{2}} e^{-mv^2/2kT} v^2\, dv \qquad \textbf{3.2}$$

(The left-hand sides of the equations 3.1 and 3.2 are equivalent to the number of systems, dn, as given in equation 2.57 for the respective volumes of phase space.)

These distributions, in which the energy has been expressed as $p^2/2m$ and $\frac{1}{2}mv^2$ respectively, can be compared with the energy distribution of equation 2.59, i.e.

$$n(\epsilon)\,d\epsilon = \frac{2\pi N}{(\pi kT)^{\frac{3}{2}}}\,e^{-\epsilon/kT}\epsilon^{\frac{1}{2}}\,d\epsilon$$

The result presented in equation 3.2 is known as the Maxwell Velocity Distribution. and its form is indicated in Fig. 1 for different values of the temperature of the gas. While, strictly speaking, it is a *speed* distribution which is defined by equation 3.2 since v is taken independent of direction, the expression *velocity distribution* is in general use.

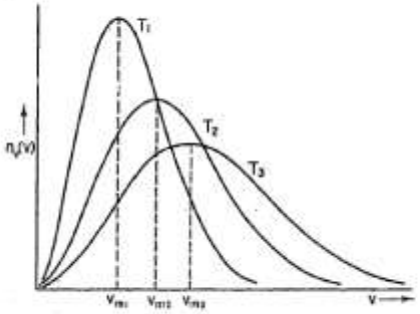

Fig. 1. The Maxwell velocity distribution for the temperatures T1 < Ti < T3

A velocity distribution for a perfect gas may also be given in terms of the three component velocities of the molecules; v_x, v_y and v_z Since $p_x = mv_x$ etc., the element of phase space for the velocity range v_x to $v_x + dv_x$ etc., is

$$\Delta\Gamma = V\,.\,m^3 dv_x dv_y dv_z \qquad \textbf{3.3}$$

for a gas of volume V. Substitution for this value of $\Delta\Gamma$ in equation 2.57 and for e^{α} from equation 2.55 gives the number of molecules in the element of velocity space $dv_x dv_y dv_z$ as

$$\begin{aligned} n_3(v_x, v_y, v_z)\,dv_x dv_y dv_z &= N\left\{\frac{m}{2\pi kT}\right\}^{\frac{3}{2}} \\ &\quad \times \exp[-m(v_x^2 + v_y^2 + v_z^2)/2kT] \qquad \textbf{3.4} \\ &\quad \times dv_x dv_y dv_z \end{aligned}$$

where the energy has been written as $\frac{1}{2}(mv_x^2 + mv_y^2 + mv_z^2)$. Again the left-hand side of the equation represents the number dn in equation 2.57 for the particular volume of phase space.

The number of molecules which have a velocity component v_x to $v_x + dv_x$ irrespective of the values of the other components, may be found by integrating the expression in equation 3.4 over all possible values of v_y and v_z . Thus

$$n_x(v_x)\,dv_x = N\left\{\frac{m}{2\pi kT}\right\}^{\frac{1}{2}} \exp(-mv_x^2/2kT)\,dv_x \qquad \textbf{3.5}$$

there being similar expressions for $n_y(v_y)dv_y$ and $n_z(v_z)dv_z$.

If the probability distribution function $f_x(v_x)$ is defined as $n_x(v_x)/N$ so that $f_x(v_x)dv_x$ is the probability that the *x*-component of the velocity is in the range v_x to v_x+dv_x then, from equation 3.5,

$$f_x(v_x) = \left\{\frac{m}{2\pi kT}\right\}^{\frac{1}{2}} \exp(-mv_x^2/2kT) \qquad \mathbf{3.6}$$

There is a corresponding probability function for the three velocities together which is obtained from equation 3.4 as

$$\begin{aligned} f_3(v_x, v_y, v_z) &= \frac{n_3(v_x, v_y, v_z)}{N} \\ &= \left\{\frac{m}{2\pi kT}\right\}^{\frac{3}{2}} \exp[-m(v_x^2+v_y^2+v_z^2)/2kT) \end{aligned} \qquad \mathbf{3.7}$$

where $f_3(v_x, v_y, v_z)dv_xdv_ydv_z$ the probability that a molecule has velocity-components v_x to v_x+dv_x, v_y to v_y+dv_y , v_z to v_z+dvz. **A** comparison between equations 3. 6 and 3.7 clearly leads to the relationship

$$f_3(v_x, v_y, v_z) = f_x(v_x)f_y(v_y)f_z(v_z) \qquad \mathbf{3.8}$$

3 .2. Mean and most probable velocities

Unless the gas as a whole is undergoing a translational movement the mean *velocity* of the molecules in the gas will strictly be zero. At the same time it is possible to determine a mean speed for the molecules. This mean speed, or mean velocity as it is most frequently termed, may be determined by defining a probability function similar to those given in the previous section. Thus, if $f(v)dv$ is the probability that a molecule has a total velocity in the range v to $v + dv$ then, by equation 3.2.

$$f_v(v)\,dv = \frac{n_v(v)\,dv}{N} = 4\pi\left\{\frac{m}{2\pi kT}\right\}^{\frac{3}{2}} \exp(-mv^2/2kT)v^2\,dv \qquad \mathbf{3.9}$$

With this probability function the mean velocity of the molecules is

$$\bar{v} = \sqrt{\left(\frac{8kT}{\pi m}\right)} \qquad \mathbf{3.10}$$

The value of the mean square velocity v^2 may be determined in a manner similar to that used for the mean velocity. Thus

$$\overline{v^2} = \frac{3kT}{m} \qquad \mathbf{3.11}$$

This is, of course, identical with the value obtained in simple kinetic theory by setting the mean energy $\frac{1}{2}mv^2$ equal to $\frac{3}{2}kT$. The most probable velocity (or speed) v_m, is that velocity for which the probability function is a maximum m. Taking $f(v)dv$ from equation 3.9 this maximum value occurs when

$$\frac{df_v(v)}{dv} = 4\pi\left\{\frac{m}{2\pi kT}\right\}^{\frac{3}{2}}\left\{2v - \frac{mv^3}{kT}\right\}\exp(-mv^2/2kT) = 0$$

or

$$2v_m - \frac{mv_m^3}{kT} = 0$$

That is, ignoring the minimum at v_m=0,

$$v_m = \sqrt{\left(\frac{2kT}{m}\right)} \qquad \textbf{3.12}$$