The molecular description of the bulk properties of a gas depends upon our knowing the mathematical form of the velocity distribution; That is, the probability, \( F(v_x, v_y, v_z) \Delta v_x \Delta v_y \Delta v_z \), of finding a molecule with velocity components in the range \( v_x \) to \( v_x + \Delta v_x \), \( v_y \) to \( v_y + \Delta v_y \), and \( v_z \) to \( v_z + \Delta v_z \) (see the last chapter). This can be found by making two very simple assumptions:

a) All directions are equivalent (space is isotropic). This implies that the probability of finding a molecule moving with a certain velocity cannot depend on the direction; it is equally probable to find a molecule with any speed \( v \) moving in any direction. Mathematically, this implies that the probability density can only depend on the magnitude of the velocity, or the molecular speed. Hence,

\[
F(v_x, v_y, v_z) = F(\sqrt{v_x^2 + v_y^2 + v_z^2})^{1/2}. \tag{1}
\]

b) The three components of the velocity are independent of each other. This implies that the velocity probability density can be written as:

\[
F(v_x, v_y, v_z) = f(v_x)f(v_y)f(v_z) \tag{2}
\]

By comparing Eqs. (1) and (2), we have

\[
f(v_x)f(v_y)f(v_z) = F(\sqrt{v_x^2 + v_y^2 + v_z^2})^{1/2}. \tag{3}
\]

Very few functions can satisfy Eq. (3); in fact, the only one is:

\[
f(v_i) = Ae^{-bv_i^2}, \quad i = x, y, z, \tag{4}
\]

where \( A \) and \( b \) are, as yet, arbitrary constants. Verify that \( f \) given by Eq. (4) satisfies Eq. (3). To show that Eq. (4) is the only possible function requires some mathematics which might be beyond the level of the course; nonetheless, the proof is contained in the appendix for those of you who are interested.

How do we determine the values of the constants \( A \) and \( b \)? The function \( f \), is a probability density and every molecule must have some velocity. From the previous section, we know that this means

\[
1 = \sum_{v_i=-\infty}^{\infty} f(v_x)\Delta v_x \rightarrow \int_{-\infty}^{\infty} f(v_x)dv_x, \tag{5}
\]

where the integral is obtained when we make \( \Delta v_x \) very small. By going to a table of integrals we find that

\[
\int_{-\infty}^{\infty} dv Ae^{-bv^2} = A\left(\frac{\pi}{b}\right)^{1/2}, \tag{6}
\]

which when used in Eq. (5) gives

\[
A = \left(\frac{b}{\pi}\right)^{1/2}. \tag{7}
\]
The parameter b is found as follows: We will compute the pressure that a dilute gas exerts on the walls of its container and then compare the result with experiment (i.e., the ideal gas equation of state). What is the pressure and how do we get it from the velocity distribution? The pressure is the force exerted by the gas per unit area. Moreover, the force is the rate of change of momentum per unit time due to collisions with the wall.

Imagine the molecules which comprise our gas as billiard balls and assume that the walls are perfectly smooth. What happens when a molecule collides with the wall? Actually relatively little; the normal component of the velocity changes sign (see Fig. 1).

If the wall is taken to be the y-z plane, the momentum change, $\Delta P$, is

$$\Delta P = -2mv_x = -F_{x,\text{molecule on wall}} \Delta t,$$

where $m$ is the mass of the molecule and where $F_{x,\text{molecule on wall}}$ is the x-component of the force exerted by the molecule on the wall when it collides. A typical velocity is $10^5$ cm/sec; what is a typical momentum change for argon? How many molecules with velocity $v_x$ will collide with the wall per unit area in time $\Delta t$? From Fig. 1, it should be clear that any molecule within a distance $v_x \Delta t$ will hit the wall in time $\Delta t$, assuming of course, that $v_x < 0$ for the way the figure was drawn (i.e., with the wall on the left). The number per unit area is therefore:

$$n(v_x)|v_x| \Delta t,$$

where $n(v)$ is the number of molecules per unit volume with x component of velocity in the range $v_x$ to $v_x + \Delta v_x$. This is related to the molecular velocity distribution by

$$n(v_x) = n_0 f(v_x) \Delta v_x,$$

where $n_0$ is the number of molecules per unit volume. By multiplying Eqs. (8) and (9), then substituting according to Eq. (10), and dividing by $\Delta t$, we finally arrive at the pressure exerted by
those molecules with x velocity component in the range \( v_x \) to \( v_x + \Delta v_x \), one has

\[
2mn_0v_x^2f(v_x)\Delta v_x = \frac{F_{v_x, v_x + \Delta v_x}}{\text{Area}} = P_{v_x, v_x + \Delta v_x},
\]

(11)

where \( F_{v_x, v_x + \Delta v_x} \) is the contribution to the force on the wall from molecules with x velocity component in the range \( v_x \) to \( v_x + \Delta v_x \). All that remains is to include the contributions from all velocities corresponding to molecules moving towards the wall. The total pressure, \( P \), thus equals:

\[
P = \sum_{v_x=-\infty}^{0} dv_x 2mn_0v_x^2f(v_x) = \int_{-\infty}^{0} dv_x 2mn_0v_x^2f(v_x) = \int_{0}^{\infty} dv_x 2mn_0v_x^3\left(\frac{b}{\pi}\right)^{1/2} e^{-bv_x^2},
\]

(12)

where the last equality comes from using the explicit form of the probability density, [see Eqs. (4) and (7)]. The value of the integral is:

\[
\int_{0}^{\infty} dv_x v_x^2 e^{-bv_x^2} = \frac{1}{4b} \left(\frac{\pi}{b}\right)^{1/2}.
\]

If we use this result in Eq. (12), we find that

\[
P = \frac{mn_0}{2b}.
\]

(13)

Next we write the ideal gas equation of state in terms of the number density:

\[
P = n_0k_B T,
\]

where \( k_B \) is Boltzmann’s constant:

\[
k_B \equiv \frac{R}{N_A} = \frac{R}{6.0225 \times 10^{23}} = 1.38 \times 10^{-23} \text{J/K}.
\]

By comparing this with Eq. (13) we see that

\[
\frac{b}{k_B} = \frac{m}{2k_B T}.
\]

The velocity probability density for the x component can now be written as

\[
f(v_x) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-\frac{mv_x^2}{2k_B T}},
\]

(14)

or for the full velocity as

\[
F(v_x, v_y, v_z) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{E}{k_B T}},
\]

(15)

where \( E = m(v_x^2 + v_y^2 + v_z^2)/2 \) is the kinetic energy of a molecule. This is referred to as the Maxwell-Boltzmann distribution function and is illustrated in the following figure:
Notice that increasing the temperature or reducing the mass makes it more probable to find molecules with higher velocities and that the probability of observing any given velocity will decrease as the energy associated with that velocity increases. This last comment is not limited to our simple billiard ball model of the molecules.

What is the average kinetic energy of the molecules; i.e., what is

$$\langle \frac{m}{2} (v_x^2 + v_y^2 + v_z^2) \rangle = \frac{3m}{2} \langle v_x^2 \rangle = \frac{3m}{2} \left( \frac{m}{2\pi k_B T} \right)^{1/2} \int_{-\infty}^{\infty} dv_x \, e^{-mv_x^2/(2k_B T)} v_x^2 = \frac{3}{2} k_B T,$$

where the first equality follows from our assumption that all directions are equivalent and where the last uses the integral given above. Notice that the average kinetic energy is independent of the mass of the molecules and predicts a constant heat capacity; specifically

$$\tilde{C}_V = \left( \frac{\partial \tilde{E}}{\partial T} \right)_{N,V} = \frac{3}{2} R.$$

This is well born out for noble gases and is an example of the so-called law of Dulong and Petit. For example, our result predicts a constant volume heat capacity of 12.471 J K\(^{-1}\) mol\(^{-1}\) the value in the CRC Handbook gives 12.472 J K\(^{-1}\) mol\(^{-1}\). It turns out that our result is more general, in that it also applies to all molecules as long as rotation, vibration and electronic effects can be ignored. In addition, in molecular dynamics computer simulations the temperature is often defined in terms of the average kinetic energy.

For many applications, the full Maxwell-Boltzmann velocity distribution gives too much detail. In particular, remember that it is a probability density for the vector velocity. Suppose we are interested in some property which depends only on the speed of the molecules and not their direction. What is the probability density which describes the distribution of molecular speeds?

---

*Note, that the CRC reports \(\tilde{C}_P\). As we shall see later, \(\tilde{C}_P = \tilde{C}_V + R\) for an ideal gas.
The speed distribution function, \( F(c) \, dc \), is the probability of observing a molecule with a speed in the interval \( c \) to \( c + dc \) irrespective of its direction. It can be obtained from the full velocity distribution, cf. Eq. (15), by integrating (summing) over the possible velocity directions, i.e.,

\[
F(c) \, dc = \sum_{c \leq |v| \leq c+dc} F(v_x, v_y, v_z) \Delta v_x \Delta v_y \Delta v_z = \left. F(v_x, v_y, v_z) \right|_{|v|=c} \sum_{c \leq |v| \leq c+dc} \Delta v_x \Delta v_y \Delta v_z, \tag{16}
\]

The sums in these last equations are over all velocities such that the speed is between \( c \) and \( c + dc \). The second equality comes from noting that \( F \) only depends on the magnitude of the velocity (see Eq. (15)). What is this last sum? \( \Delta v_x \Delta v_y \Delta v_z \) is a volume element in a coordinate system whose axes are the components of velocity. The sum represents the volume between two concentric spheres of radius \( c \) and \( c + dc \), respectively. Thus

\[
\sum_{c \leq |v| \leq c+dc} \Delta v_x \Delta v_y \Delta v_z = \frac{4\pi}{3} [(c + dc)^3 - c^3] \approx 4\pi c^2 dc, \tag{17}
\]

dropping nonlinear terms in \( dc \) (remember that we will consider infinitesimally small \( dc \)). If we use Eq. (17) in (16), we find that

\[
F(c) = 4\pi c^2 F(v_x, v_y, v_z) \bigg|_{|v|=c} = 4\pi c^2 \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-mc^2 / 2k_B T}. \tag{18}
\]

This is the speed distribution and is shown in Fig. 3 below. Notice that it vanishes when \( c = 0 \) even though the velocity distribution is a maximum at zero velocity. Why?

There are various ways to characterize the molecular speed in the gas. For example, consider the most probable speed, \( c^* \), is found by setting the \( c \) derivative of Eq. (18) to zero; i.e.,

\[
0 = 4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-mc^2 / 2k_B T} \frac{mc^2}{k_B T} c \left( \frac{2k_B T}{m} - c^2 \right),
\]

which gives physical roots at \( c = 0 \) (a minimum) and at \( c^* = (2k_B T/m)^{1/2} \), which is the maximum. This can be compared with \( \langle c \rangle = (8k_B T/\pi m)^{1/2} \) and \( c_{RMS} \equiv \sqrt{\langle c^2 \rangle} = (3k_B T/m)^{1/2} \). cf. Eq. (19). Note that \( c^* < \langle c \rangle < c_{RMS} \). All three results have the form \((k_B T/m)^{1/2}\) times some dimensionless number; the first factor has the units of speed (length / time) and must be there unless there is another quantity that has the units of speed, which is not the case here. The dimensionless number depends on the details of the question being asked.
The speed distribution is used to average quantities that don’t depend on the direction the molecules are moving. Among these, the most useful are the mean-speed and root-mean squared speed (or velocity), $\sqrt{\langle c^2 \rangle}$, where

$$\langle c^n \rangle = \left( \frac{m}{2\pi k_B T} \right)^{3/2} 4\pi \int_0^\infty dc \ c^{n+2} e^{-mc^2/2k_BT} = \begin{cases} \left( \frac{8k_BT}{\pi m} \right)^{1/2}, & n = 1 \\ \frac{3k_BT}{m} \left( \frac{2k_BT}{m} \right)^{n/2} \Gamma((n+3)/2), & n = 2 \\ \left( \frac{2k_BT}{m} \right)^{n/2} \frac{2}{\sqrt{\pi}} \Gamma((n+3)/2), & \text{in general} \end{cases}$$

(19)

where $\Gamma(x)$ is the gamma function and where a table of integrals can be used to look up these results. Notice that all the averages contain factors of $\sqrt{k_BT/m}$ which has units of velocity.

1. Appendix: Proof of Equation (4)

You are not responsible for this proof. Differentiate both sides of Eq. (3) with respect to $v_x$, using the chain rule for the right hand side, and divide by $v_x$. You get:

$$\frac{df(v_x)}{dv_x} f(v_x) f(v_z) \bigg|_{v_x} = \frac{dF(v)}{dv} \bigg|_{(v_x^2+v_y^2+v_z^2)^{1/2}}.$$  

(20)

By repeating this for $v_y$, equating the results and carrying out a little algebra, we find that:
\[
\frac{df(v_x)}{dv_x} = \frac{df(v_y)}{dv_y}
\]

The right hand side of the equation depends only on \( v_y \) and the left hand side depends only on \( v_x \). Since these two components of velocity can be chosen independently, the only way that this last equation can be satisfied is if both sides are equal to the same constant. Hence,

\[
\frac{df(v_x)}{dv_x} = -2bv_x f(v_x),
\]

where \( b \) is, as yet, some arbitrary constant. This is a first order differential equation. It has a general solution which will depend on a single multiplicative constant. This solution is given by Eq. (4).