5.2 MAXWELL DISTRIBUTION OF MOLEC-ULAR SPEEDS

The molecules of an ideal gas move independently of each other. When a molecule bounces off the wall, its speed does not change because we assume that the collision with the walls are elastic. Furthermore, since the molecules of an ideal gas do not interact with one another, there will also be no collision among the molecules of ideal gas. Therefore, the speeds of molecules of ideal gas would be constant. But, molecules of real gases do interact and collide with each other and with the walls of the container, resulting in the change of velocity and speed upon collision. Therefore even if you start out by giving the same speeds to all the molecules, the speeds will soon become different in a real gas.

James Clerk Maxwell studied this problem and found a formula for the distribution of speeds at a particular temperature, but his results apply only to ideal gases, whose molecules can be allowed to collide with one another as billiard balls. Since most real gases, when they are dilute or at high temperature, behave like an ideal gas, the distribution function worked out by Maxwell can be used also for understanding real gases at the molecular level.

Suppose there are N molecules of a gas at temperature T. Let the mass of each molecule be m. According to Maxwell, molecules have many different speeds and since the number of molecules N is very large in any finite sample, the speeds of molecules can be considered to be distributed continuously and the speed can be treated as a continuous real variable for mathematical purposes. We can speak of number of molecules whose speeds fall in a certain range, e.g. between v and $v + \Delta v$. Maxwell distribution of speeds for molecules of a gas gives the number $f(v)dv$ of molecules that have speed between v and $v + dv$.

$$f(v)dv = \alpha v^2 \exp\left(-\frac{\frac{1}{2}mv^2}{k_B T}\right)dv, \qquad (5.10)$$

where α is a normalization constant and k_B is the Boltzmann constant. The normalization constant α is determined by requiring that the integration over all possible speeds be equal to the total number N of molecules in the system.

$$N = \int_0^\infty f(v)dv \qquad (5.11)$$

By using $f(v)dv$ from Eq. 5.10 and integrating, we find the normal-

ization constant α to be

$$\alpha = 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{3/2}. \qquad (5.12)$$

The Maxwell distribution function depends on the speed as a product of the square of the speed and an exponential function with a negative exponent containing the ratio of kinetic energy of one molecule and an energy scale $k_B T$. Thus, the distribution of speeds critically depends upon the relative magnitudes of the kinetic energy of molecules and the energy scale $k_B T$ set by the temperature T.

The negative exponential factor makes it less likely that a molecule will have much higher kinetic energy than $k_B T$ while the quadratic prefactor of velocity squared makes low speeds less likely. The competition between the two factors results in a maximum for the distribution.

In Fig. 5.3 we plot the distribution function $f(v)$ for the Helium gas at 300 K. Note that the distribution is not symmetric about the peak, and the most probable speed is not the same as the average speed of molecules. The lowest speed is zero, but the distribution trails off to infinity for the highest speed.
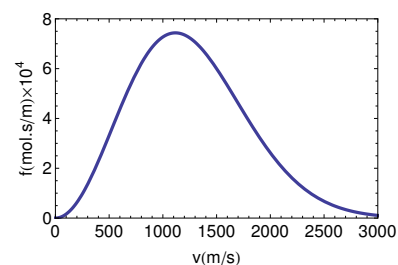

Figure 5.3: Maxwell molecular speed distribution in one mole of helium at 300 K. The distribution function was multiplied by 10^4 for plotting.

In Fig. 5.4 we plot distribution of molecular speeds in the same system but at different temperatures. The peak speed of the dis-
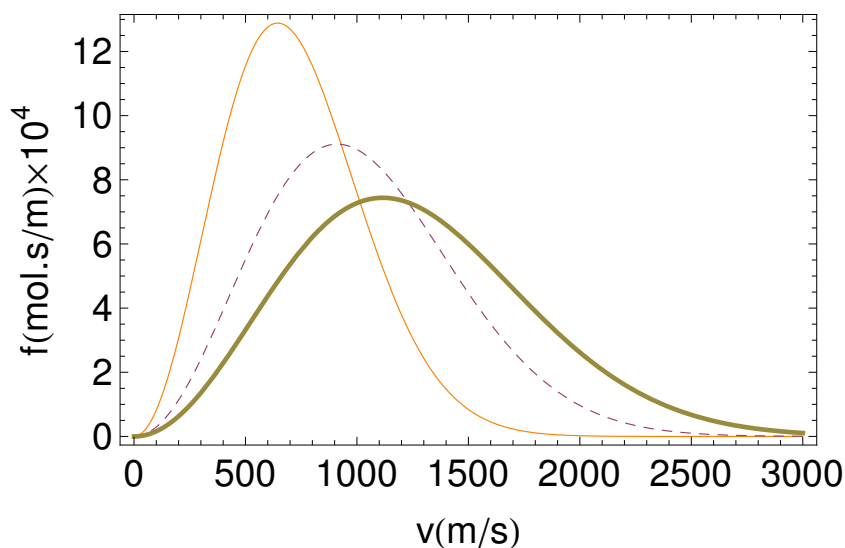

Figure 5.4: Molecular speed distributions of one mole of helium at T=100 K (thin line), T=200 K (dashed line), and T=300 K (thick line). The three distribution functions were multiplied by 10^4 for plotting purposes. With increasing temperature, the peak speed shifts to higher speeds and the distribution becomes wider.

tribution shifts to higher values for higher temperatures. Since the

number of molecules is the same in the three graphs, the areas under
the curves for different temperatures must be equal to each other.
Therefore, as the peak speed shifts to the right the distribution curve
flattens out.

5.2.1   Using Maxwell's Molecular Speed Distribution

Maxwell distribution $f(v)dv$ gives the number of molecules whose
speed is expected to be between v and $v+dv$. For a system containing
N molecules $\frac{1}{N}f(v)dv$ will give the probability that any one randomly
picked molecule will have speed between v and $v + dv$. We can use
the probability distribution to deduce a number of characteristics of
the speed of the molecules in a gas.

Example 5.2.1. Average Speed of Molecules.

Find the average speed of molecules of nitrogen gas treated as an
ideal gas at 300 K.

Solution. The average speed $< v >$ can be obtained by averaging
speed of all the molecules. We can obtain the average speed by adding
up the speed v_i of each molecule, and then dividing up the sum by
the total number N of molecules.

$$< v >= \frac{1}{N} \sum_{i=1}^{N} v_i$$

Since there are $f(v)dv$ molecules with speed v, we can multiply
$vf(v)dv$ by speed v to find the contribution of these molecules to
the average speed. The contributions of all molecules in the sum
is obtained by integrating over dv over the entire range of v values,
which is from 0 to ∞.

$$\boxed{< v >= \frac{1}{N} \int_{0}^{\infty} vf(v)dv.}$$

Substituting the distribution function and performing the integral
leads to the following result for the **average speed** of a gas whose
molecular mass is m and which is at temperature T.

$$\boxed{< v >= \sqrt{\frac{8k_BT}{\pi m}}.} \tag{5.13}$$

We can write this result also in terms of molar mass M, which is the
mass of one mole of the gas. Since there are an Avogadro number N_A

of molecules in one mole, the molar mass is $N_A m$, where m is mass of one molecule.

$$< v > = \sqrt{\frac{8RT}{\pi M}}.$$

Therefore, average speed of a molecule of nitrogen gas is

$$< v > = \sqrt{\frac{8 \times 8.31 \ (\text{J/mol.K}) \times 300 \ \text{K}}{\pi \times 28 \times 10^{-3} \ \text{kg/mol}}} = 476 \ \text{m/s}.$$

Example 5.2.2. The Root-mean Square Speed

Find a formula for the root-mean squared speed of a gas molecule obeying Maxwell's velocity distribution.

Solution. The **root mean square speed** v_{rms} is obtained by first summing over the squares of speeds v_i of molecules, dividing the sum by the total number of molecules, and then taking the square root of the result. It is easier to write the square of rms speed formula.

$$v_{rms}^2 = \frac{1}{N} \sum_{i=1}^{N} v_i^2$$

Once again, the sum can be replaced by an integral over speed v if we use the distribution function.

$$v_{rms}^2 = \frac{1}{N} \int_0^\infty v^2 f(v) dv.$$

Substituting the distribution function and integrating we find the following for the square of the root-mean square speed.

$$v_{rms}^2 = \frac{3k_B T}{m}.$$

The positive root of this equation gives the root-mean square speed as

$$v_{rms} = \sqrt{\frac{3k_B T}{m}}.$$

Example 5.2.3. The Most Probable Speed Find the most probable speed of nitrogen gas molecules at 300 K, and compare it to the average speed of molecules at the same temperature.

Solution. The most probable speed v_p will be the speed corresponding to the peak of the distribution function, which we find by setting the derivative of the distribution function $f(v)$ to zero.

$$\left. \frac{df}{dv} \right|_{v=v_p} = 0.$$

Performing the derivative and setting it to zero at $v = v_p$ we find the following expression for the most probable speed.

$$v_p = \frac{2k_B T}{m}, \quad \text{(peak speed)} \tag{5.14}$$

Putting numerical values of k_B, T and m we find the peak speed of nitrogen molecules at 300 K to be:

$$v_p = \frac{2k_B T}{m} = \frac{2RT}{M} = \sqrt{\frac{2 \times 8.31 \ (\text{J/mol.K}) \times 300 \ \text{K}}{\times 28 \times 10^{-3} \ \text{kg/mol}}} = 422 \ \text{m/s}.$$

The peak speed is less the average speed. This is due to the fact that the distribution is not symmetric, and more molecules have speeds larger than the peak speed.