Lecture 18 - Maxwell-Boltzmann distribution

What's Important:
• mean speeds
• molecular flux
Text: Reif

Mean speeds

The Maxwell-Boltzmann speed distribution that was derived in the previous lecture has the appearance

\[ F(v) \, dv \]

where \( F(v) \, dv \) is the number of particles per unit volume with a speed between \( v \) and \( v + dv \).

Now, there are three common measures of the velocity distribution

\[ \overline{v^2}^{1/2} \equiv v_{\text{rms}} \quad \text{(root mean squarespeed)} \]
\[ \overline{v} \equiv (\text{mean speed}) \]
\[ \tilde{v} \equiv (\text{most likely speed}) \]

These quantities are straightforward to calculate, and the details can be found in Reif.

Root mean square
One can work through the integral of \( F(v) \) to obtain \( v_{\text{rms}} \), or just invoke the equipartition theorem in three dimensions:

\[ \frac{3}{2} k_B T = [\text{mean kinetic energy}] = \frac{1}{2} m \overline{v^2} \]

or

\[ v_{\text{rms}} = \sqrt{\frac{3k_B T}{m}}. \] (18.1)

Mean Evaluate the integral

\[ \overline{v} = \frac{1}{n} \int_0^\infty v F(v) \, dv = \sqrt{\frac{8 k_B T}{\pi m}} \] (18.2)

Most likely Determine the derivative

\[ \frac{dF(v)}{dv} = 0 \Rightarrow \tilde{v} = \sqrt{\frac{2k_B T}{m}} \] (18.3)
From these results, one can see that all the factors outside \( (k_B T / m)^{1/2} \) have similar values:
\[
\sqrt{3} = 1.73 \\
\left( \frac{8}{\pi} \right)^{1/2} = 1.60 \\
\sqrt{2} = 1.41,
\]
so that an order-of-magnitude estimate for the mean speed is \( (k_B T / m)^{1/2} \), just as the kinetic energy is \( k_B T \).

**Example** Find the rms velocity of a gas of neon atoms at \( T = 300 \) K (near room temperature); \( m_{\text{Ne}} \approx 20 m_p = 20 \times 1.67 \times 10^{-27} \) kg.

\[
v_{\text{rms}} = \left( \frac{3 \times 1.38 \times 10^{-23} \times 300}{20 \times 1.67 \times 10^{-27}} \right)^{1/2} = 610 \text{ m/s}.
\]

**Molecular flux**

Among the quantities that we wish to measure are the pressure and effusion rate, both of which require a knowledge of the molecular flux, the number of particles passing through a unit area in unit time. We start with a simple calculation in one dimension, before treating the general problem in three dimensions.

**One dimension**

Let the system have a *linear* density of \( n \) particles per unit length (*linear*, since the system is confined to one dimension). At any given time, \( n / 2 \) of them are moving to the left, and \( n / 2 \) to the right. For a specific speed \( v \) the particles capable of striking the wall in time \( t \) lie within a distance \( vt \) of it.

Allowing for a distribution of speeds, the number of particles hitting the wall is
\[
\text{number} = \bar{v} t \cdot \frac{n}{2} = \frac{\bar{v} n}{2} t
\]

Dividing by \( t \) gives the number of particles hitting per unit time
\[
\text{number per unit time} = \frac{\bar{v} n}{2} \quad (18.4)
\]
Three dimensions

This calculation can be easily extended to include the number hitting a unit area on a wall.

\[ \text{[number hitting wall area } A \text{ in time } t \text{ with velocity } \mathbf{v}] \]
\[ = f(v) \, d^3v \cdot A \, vt \cos \theta. \] \hfill (18.5)

number per volume of unit volume capture cylinder

The volume of the capture cylinder arises from

\[ \text{[volume] } = Avt \cos \theta \]

Dividing Eq. (18.5) by the area \( A \) and time \( t \) gives

\[ \text{[number hitting wall per area } A \text{ per unit time } t \text{ with velocity } \mathbf{v}] \]
\[ = f(v) \, v \cos \theta \, d^3v. \] \hfill (18.6)

The flux \( \Phi \) is obtained by integrating Eq. (18.6) over all velocities \( v \):
\[ \Phi = \int f(v) \, v \cos \theta \, d^3v. \] \hfill (18.7)

Details:
\[ d^3v = \sin \theta \, d\theta \, d\phi \, v^2 \, dv \quad \text{so} \quad \Phi = \int f(v) \, v \cos \theta \, \sin \theta \, d\theta \, d\phi \, v^2 \, dv. \]

Because only right-moving particles will hit \( A \), the \( \theta \) integral runs only over 0 to \( \pi/2 \):
\[ \int_0^{\pi/2} \sin \theta \cos \theta \, d\theta = \int_0^1 \cos \theta \, d\cos \theta = \frac{1}{2} \cos^2 \theta \bigg|_0^1 = \frac{1}{2} \]
\[ \int d\theta = 2\pi \]
leaving
\[ \Phi = 2\pi \cdot (1/2) \int f(v) v^3 dv = \pi \int f(v) v^3 dv. \]

But the mean speed is
\[ \bar{v} = \frac{4\pi}{n} \int v^3 f(v) dv \]
so
\[ \Phi = \frac{1}{4} n\bar{v} \quad (18.8) \]

Comparing with Eq. (18.4), the flux is less in 3D than in 1D because the velocities are averaged over directions, and \( v_z \) is less than \( v \). This equation can be massaged in a variety of ways once the ideal gas law has been established.

**Effusion**

The Maxwell-Boltzmann predictions for the velocity distributions has been tested experimentally through a process known as effusion. A tiny hole is drilled in a container,

![Diagram of a container with a hole and two co-rotating disks](image)

and the velocities of the escaping molecules are measured by means of two co-rotating disks, acting as choppers to select the molecular velocities:

![Diagram showing the axis of rotation](image)

Because it is sensitive to the escape rate of molecules through the hole, this technique measures the flux \( \Phi \sim f(v)v^3 \), not \( f(v) \) itself.