Lecture 18 - Maxwell-Boltzmann distribution

*What's Important:*

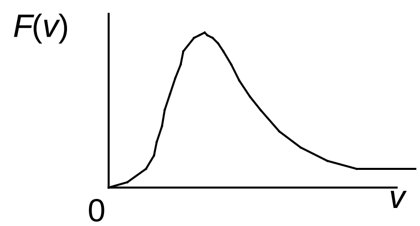
· mean speeds

· molecular flux

*Text*: Reif

## Mean speeds

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




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

$$\overline{v^2}^{1/2} \equiv v_{rms} \quad (\textit{root mean square speed})$$

$$\bar{v} \equiv (\textit{mean speed}) \quad .$$

$$\tilde{v} \equiv (\textit{most likely speed})$$

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 $v_{\rm rms}$, or just invoke the equipartition theorem in three dimensions:

$$\frac{3}{2}k_BT = [\textit{mean kinetic energy}] = \frac{1}{2}m\overline{v^2}$$

or

$$v_{rms} = \sqrt{\frac{3k_BT}{m}} \,. \qquad (18.1)$$

*Mean* Evaluate the integral

$$\bar{v} = \frac{1}{n}\int_0^\infty v\,F(v)\,dv = \sqrt{\frac{8}{\pi}\frac{k_BT}{m}} \qquad (18.2)$$

*Most likely* Determine the derivative

$$\frac{dF(v)}{dv} = 0 \qquad \tilde{v} = \sqrt{\frac{2k_BT}{m}} \qquad (18.3)$$

From these results, one can see that all the factors outside $(k_B T\ /m)^{1/2}$ have similar values

$\sqrt{3} = 1.73$
$(8/\pi)^{1/2} = 1.60$
$\sqrt{2} = 1.41$,

so that an order-of-magnitude estimate for the mean speed is $(k_B T\ /m)^{1/2}$, just as the kinetic energy is $\sim k_B T$.

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

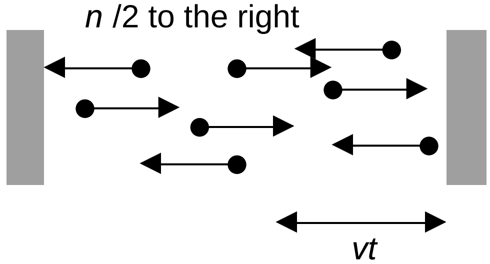
$$v_{rms} = \left( \frac{3 \bullet 1.38 \times 10^{-23} \bullet 300}{20 \bullet 1.67 \times 10^{-27}} \right)^{1/2} = 610 \text{m/s}.$$

## 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

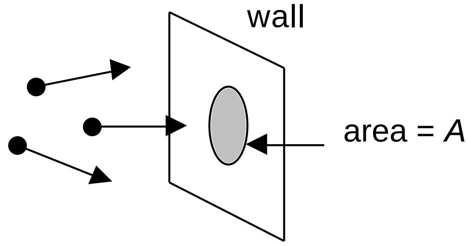
$$number = \bar{v} t \bullet \frac{n}{2} = \frac{\bar{v} n}{2} t$$

Dividing by $t$ gives the number of particles hitting per unit time

$$number\ per\ unit\ time = \frac{\bar{v} n}{2} \tag{18.4}$$

*Three dimensions*

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

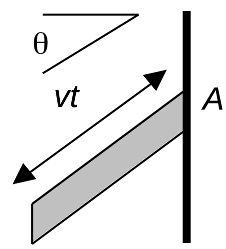



[*number hitting wall area A in time t with velocity* ***v***]

$$= f(v)\, d^3v \quad \bullet \quad A\, vt \cos\theta. \tag{18.5}$$

number per unit volume — volume of calpture cylinder

The volume of the capture cylinder arises from




$[volume] = Avt \cos\theta$

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

[*number hitting wall per area A per unit time t with velocity* ***v***]

$$= f(v)\, v \cos\theta\, d^3v. \tag{18.6}$$

The flux $\Phi$ is obtained by integrating Eq. (18.6) over all velocities **v**:

$$\Phi = \int f(v)\, v \cos\theta\, d^3v. \tag{18.7}$$

Details:

$d^3v = \sin\theta\, d\theta\, d\phi\, v^2 dv$ so $\Phi = \int f(v)\, v \cos\theta \sin\theta\, d\theta\, d\phi\, v^2 dv$.

Because only right-moving particles will hit $A$, the $\theta$ integral runs only over 0 to $\pi/2$:

$$\int_0^{\pi/2} \sin\theta \cos\theta d\theta = \int_0^1 \cos\theta\, d\cos\theta = \frac{1}{2}\cos^2\theta \Big|_0^1 = \frac{1}{2}$$

$\int d\theta = 2\pi$

leaving

$$\Phi = 2\pi \bullet (1/2) \int f(v)\, v^3 dv = \pi \int f(v)\, v^3 dv.$$

But the mean speed is

$$\bar{v} = \frac{4\pi}{n} \int v^3 f(v)\, dv$$

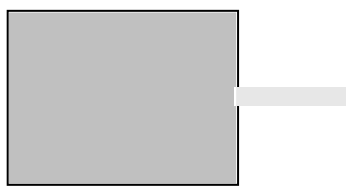
so

$$\Phi = \frac{1}{4} n \bar{v} \qquad (18.8)$$

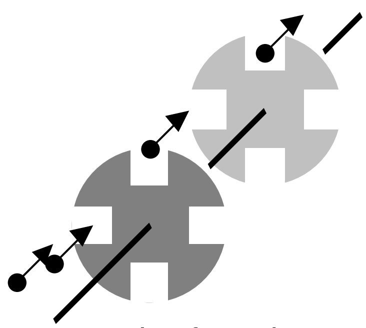
Comparing with Eq. (18.4), the flux is less in 3D than in 1D because the velocities are averaged over directions, and $v_z$ is less than $v$. This equation can be massaged in a variety of ways once the ideal gas law has been established.

*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,



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




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.