Kinetic Theory of Gases: the Maxwell-Boltzmann Distribution

Where have we been so far in 5.62?

<table>
<thead>
<tr>
<th>&quot;micro&quot; world</th>
<th>Equilibrium statistical mechanics</th>
<th>&quot;macro&quot; world</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ensemble theory</td>
<td></td>
</tr>
</tbody>
</table>

Where are we going?

- Time-dependent processes (transport, chemical kinetics)
- Non-equilibrium statistical mechanics

Since we are going to concentrate on transport and kinetics in gases, it behooves us to begin by deriving the fundamental property of bulk gases, viz:

- Distribution of Molecular Speeds [translational energies]
  - Maxwell (J.C.) - Boltzmann (L.) Distribution Function

Define \( f(c)\,dc \) = probability of finding a molecule in a gas at temperature \( T \) having speed between \( c \) and \( c + dc \)

To start, we know:

\[
f(e_x) = (\pi kT)^{-1/2} e_x^{-1/2} e^{-e_x/kT}
\]

\( e_x \) = probability of finding molecule with energy \( e_x \) in \( x \)-direction from Boltzmann distribution function (Lecture #9)

*This is a probability as a function of energy, but we want it as a function of speed.* We perform a change of variable similar to Lecture #9.

What is \( f(u) \)? Probability that the molecule has velocity \( u \) in the \( x \) direction.

\[
e_x = \frac{1}{2} mu^2
\]
\( \varepsilon_x \) is the same for \(+u\) or \(-u\), so
\[
f(\varepsilon_x) d\varepsilon_x = f(u) du + f(-u) du = 2 f(u) du
\]
\[
f(u) = \frac{1}{2} f(\varepsilon_x) \frac{d\varepsilon_x}{du}, \quad \frac{d\varepsilon_x}{du} = mu
\]
\[
f(u) = \frac{1}{2} (\pi kT)^{-1/2} \left( \frac{2}{m} \right)^{1/2} \frac{1}{u} e^{-mu^2/2kT} mu
\]
\[
f(u) = \left( \frac{m}{2\pi kT} \right)^{1/2} e^{-mu^2/2kT}
\]

Be sure this probability function is properly normalized:
\[
\int_{-\infty}^{\infty} \left( \frac{m}{2\pi kT} \right)^{1/2} e^{-mu^2/2kT} du = 2 \left( \frac{m}{2\pi kT} \right)^{1/2} \int_{0}^{\infty} e^{-mu^2/2kT} du = 1
\]

Normalized 1-D probability distribution \( f(u) = \left( \frac{m}{2\pi kT} \right)^{1/2} e^{-mu^2/2kT} \)

Extend to 3D velocity distribution: \( f(\vec{c}) \)
\( (u,v,w) = (x,y,z) \) components of \( \vec{c} \)
\( c^2 = u^2 + v^2 + w^2 \)
\[
f(u,v,w) du dv dw = f(u) f(v) f(w) du dv dw
\]
..because probability in each direction are independent and uncorrelated. (Is this an assumption or a demonstratable fact?)
\[
f(u,v,w) = \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-m(u^2+v^2+w^2)/2kT} = f(\vec{c})
\]
3D MAXWELL-BOLTZMANN VELOCITY DISTRIBUTION
in Cartesian Coordinates

Extend to 3D speed distribution: \( f(c) \)
Velocity: \( \vec{c} \neq c \)
Speed is the magnitude: \( |c \cdot c|^{1/2} \)

Change to spherical coordinates:
\[
\begin{align*}
\{ u = c \sin \theta \cos \phi \\
\{ v = c \sin \theta \sin \phi \\
\{ w = c \cos \theta 
\end{align*}
\]

The Jacobian in this case is:
\[
dudvdw = c^2 \sin \theta dcd\theta d\phi
\]

So
\[
f(c, \theta, \phi) = \left( \frac{m}{2\pi kT} \right)^{3/2} c^2 \sin \theta e^{-mc^2/2kT}
\]
Maxwell-Boltzmann Distribution (3D) in \((c, \theta, \phi)\).

To obtain the distribution in terms of speed (magnitude only - don't care about direction) integrate over angles:
\[
f(c)dc = \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta f(c, \theta, \phi)dc
\]
\[
f(c)dc = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} c^2 e^{-mc^2/2kT} dc
\]
This is the Maxwell-Boltzmann distribution of molecular speeds
For $T_2 > T_1$, $f(c)$ is broader and flatter (but $\int f(c) dc = 1$ for any $T$) $4\pi c^2$ is the "degeneracy" associated with speed $c$ ($KE = mc^2/2$). $e^{-mc^2/2kT}$ is the Boltzmann factor.

Properties of the Maxwell-Boltzmann speed distribution:

1. Most probable speed: $c_{mp} \equiv c$ for which $\frac{df(c)}{dc} = 0$ (maximum likelihood)

\[ c_{mp} = \left( \frac{2kT}{m} \right)^{1/2} = 4.07 \left( \frac{T}{m} \right)^{1/2} \text{ m/s, } m \text{ in kg/mol, } T \text{ in K} \]

2. Average speed:

\[ \bar{c} = \int_0^\infty cf(c) dc = \left( \frac{8kT}{\pi m} \right)^{1/2} = 4.59 \left( \frac{T}{m} \right)^{1/2} \text{ m/s} \]

3. Root Mean Square speed:

\[ \sqrt{\bar{c}^2} = \left[ \int_0^\infty c^2 f(c) dc \right]^{1/2} = \left( \frac{3kT}{m} \right)^{1/2} = 4.98 \left( \frac{T}{m} \right)^{1/2} \text{ m/s} \]

So for example, air at room temperature:

\[ T=300K, \ \text{m}_{\text{ave}}= \text{29 amu (28 for N}_2, \ \text{32 for O}_2) = 0.029 \text{ kg/mole} \]

So $c = 4.59 \left( \frac{300}{0.029} \right)^{1/2} = 467 \text{ m/sec} = 4.67 \times 10^4 \text{ cm/sec} = 1679 \text{ km/hr} \approx 1000 \text{ m/hr}$

(Actually the $O_2$ and $N_2$ have independent M-B distributions with slightly different average speeds)
TRANSLATIONAL ENERGY DISTRIBUTION IN 3 DIMENSIONS

\[ f(\varepsilon) = f(c) \frac{dc}{d\varepsilon} \]

\[ f(\varepsilon) = 2\pi \left( \frac{1}{\pi kT} \right)^{3/2} \varepsilon^{1/2} e^{\varepsilon/kT} \]

\[ \bar{\varepsilon} = \int_{0}^{\infty} \varepsilon f(\varepsilon) d\varepsilon = \frac{3}{2} kT \left\{ \begin{array}{l} \neq \frac{1}{2} mc^2 = \frac{1}{2} m \left( \frac{8kT}{\pi m} \right) = \frac{4}{\pi} kT \\ = \frac{1}{2} mc^2 = \frac{1}{2} m \left( \frac{3kT}{m} \right) = \frac{3}{2} kT \end{array} \right. \]

The classical Boltzmann distribution for the translational energy of an ideal gas is:

\[ \frac{dN(x, y, z, p_x, p_y, p_z)}{N} = \frac{1}{\hbar^3} e^{-(p_x^2 + p_y^2 + p_z^2)/(2mkT)} dx dy dz dp_x dp_y dp_z \]

where \( \frac{dN}{N} \) is the fraction of the molecules with center-of-mass coordinates between \( x \) and \( x+dx \), \( y \) and \( y+dy \), \( z \) and \( z+dz \) and with components of linear momentum between \( px \) and \( px+dp_x \), \( px \) and \( px+dp_x \), \( px \) and \( px+dp_x \), \( px \) and \( px+dp_x \). The translational partition function for a molecule, \( q_{\text{trans}} \), is just the integral of the numerator in the above expression and it has been shown that

\[ q_{\text{trans}} = V \left( \frac{2\pi mkT}{\hbar^2} \right)^{3/2} \]

for a molecule of mass \( m \) in a volume \( V \) at temperature \( T \).

Now let’s use the expression for \( \frac{dN}{N} \) and \( q_{\text{trans}} \) to find the fraction of the molecules with momentum components between \( px \) and \( px+dp_x \), \( px \) and
py+dpy, and p_z and p_z+dp_z, irrespective of their x, y, and z coordinates. This is obtained by integrating over all possible values of x, y, and z:

\[ \int dx dy dz \left\{ \frac{dN(x, y, z, p_x, p_y, p_z)}{N} \right\} = \frac{1}{\hbar^3} e^{-\left(p_x^2 + p_y^2 + p_z^2\right)/2mkT} dx dy dz dp_x dp_y dp_z \]

\[ \frac{dN(p_x, p_y, p_z)}{N} = e^{-\left(p_x^2 + p_y^2 + p_z^2\right)/2mkT} \frac{dp_x dp_y dp_z}{\hbar^3} \frac{V}{q_{\text{trans}}} \]

Now let's replace \( u_x, u_y, u_z \) by the polar coordinates, c, \( \theta, \phi \) where c is the scalar speed and \( \theta, \phi \) specify its direction of travel. Since

\[ c^2 = \left(u_x^2 + u_y^2 + u_z^2\right) \]
\[ du_x du_y du_z = c^2 \sin \theta d\theta d\phi dc, \]

\[ \frac{dN(c, \theta, \phi)}{N} = \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-mc^2/2kT} c^2 \sin \theta d\theta d\phi dc \]

If we integrate this over all directions of travel, we obtain

\[ \frac{dN(c)}{N} = \int_0^\pi d\theta \int_0^{2\pi} df \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-mc^2/2kT} c^2 \sin \theta d\theta d\phi dc \]

\[ = \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-mc^2/2kT} 4\pi c^2 dc = f(c)dc \]

where \( \frac{dN(c)}{N} \) is the fraction of molecules with scalar speeds in the range \( c \) to \( c+dc \) irrespective of their positions or the direction in which they may be moving. The function \( f(c) \) is called the Maxwell distribution function.

Now that the distribution function \( f(c) \) is known, we can immediately find the average value of any quantity \( X \) which depends only on the molecular speed \( c \):

\[ \bar{X} = \frac{1}{N} \int_0^\infty X(c) dN(c) = \int_0^\infty X(c) f(c) dc \]

Using these relations and common definite integrals, we find the average speed \( \bar{c} \) and the root-mean-square speed \( \sqrt{\frac{\bar{c}^2}{2}} \) to be
\[
\bar{c} = \int_0^\infty cf(c)dc = \left(\frac{8kT}{\pi m}\right)^{1/2}
\]
\[
\bar{c}^2 = \int_0^\infty c^2 f(c)dc = \frac{3kT}{m}; \sqrt{\bar{c}^2} = \left(\frac{3kT}{m}\right)^{1/2}
\]

**Translational energy of an ideal gas**

The translational energy of an ideal gas is given by:

\[
\overline{E_{\text{trans}}} = N_a \left[ \frac{1}{2} m \left( u_x^2 + u_y^2 + u_z^2 \right) \right] = N_a \left( \frac{1}{2} m \bar{c}^2 \right)
\]

where \( N_a \) is Avogadro's number. Simplifying with the expression for \( \bar{c}^2 \), we get

\[
\overline{E_{\text{trans}}} = \frac{3}{2} N_a kT = \frac{3}{2} RT
\]

If the ideal gas is a monatomic gas, we have

\[
\overline{E} = \overline{E_0} + \frac{3}{2} RT
\]

where \( \overline{E_0} \) is an unknown constant which is different for each chemical species. (\( \overline{E_0} \) will depend on the energy of an atom relative to the separate fundamental particles of which it consists.) Note that \( E \) for an ideal gas depends only on \( T \) and is independent of \( V \).

**Ideal Gas Law**

Consider an ideal gas of \( N \) molecules in a volume \( V \) at temperature \( T \). There will exist a Maxwellian distribution of velocities. Collisions between molecules are elastic and cause no change in the distribution. Elastic collisions with the wall will cause a pressure, which is the time rate of transfer of the normal component of momentum per unit area of wall. From the overall number density (\( N/V \)) and the angular dependent Maxwell
distribution, we find that the number of molecules per cm$^3$ with speeds in the range of $c$ to $c+dc$ and directions of travel within a solid angle defined by $\theta$ to $\theta+d\theta$ and $\phi$ to $\phi+d\phi$ is:

$$\left(\frac{N}{V}\right)f(c)\frac{\sin \theta d\theta d\phi dc}{4\pi}$$

The number of molecules in this class which will strike an element $dS$ of wall in the time interval $t$ to $t+dt$ is then:

$$\left(\frac{N}{V}\right)f(c)\frac{\sin \theta d\theta d\phi dc(dS \ cdt \cos \theta)}{4\pi}$$

where $(dS \ cdt \cos \theta)$ is the volume of the cylinder shown in Fig. 1.

Fig. 1. Molecules with speed $c$ and direction $\theta, \phi$ will strike $dS$ in the time interval $t$ to $t+dt$ if they lie within the cylinder shown at time $t$.

The change in the component of momentum normal to the element $dS$ per molecule striking the wall is $2p_\perp = 2mu_\perp = 2mc \cos \theta$

From the definition of pressure, $p$ will be the integral:

$$\int \int \int \left(\frac{N}{V}\right)f(c)\frac{\sin \theta d\theta d\phi dc(dS \ cdt \cos \theta)}{4\pi} \times 2mc \cos \theta$$

$$\frac{dS \ dt}{dS \ dt}$$

Thus
\[ p = \left( \frac{N}{V} \right) \frac{2m}{4\pi} \int_0^\infty c^2 f(c) dc \int_0^{\pi/2} \cos^2 \theta \sin \theta d\theta \int_0^{2\pi} d\phi \]

\[ = \left( \frac{N}{V} \right) \left( \frac{2m}{4\pi} \right) \left( \frac{c^2}{c^2} \right) \left( \frac{1}{3} \right) (2\pi) = \frac{Nm c^2}{3V} = \frac{2E_{\text{trans}}}{3V} \]

Note that the upper limit on \( \theta \) is only \( \pi/2 \) since there is no gas outside the wall.

Since we already know \( \overline{c^2} \) as an explicit function of \( T \) we can immediately rewrite the above as

\[ pV = NkT \]

Therefore we see that the Maxwell distribution law, which is a special case of the more general Boltzmann distribution law, allows us to derive an equation of state for an ideal gas.

**Effusion:**
For molecular effusion, one is concerned with the "independent" escape of molecules through a very small orifice. The rate of effusion, which is the number of molecules effusing per unit area in unit time, is given by the expression:

\[ \int_0^\infty \int_0^{2\pi} \int_0^\pi \left( \frac{N}{V} \right) f(c) \frac{c^2}{4\pi} \sin \theta d\theta d\phi dc (dS cdt \cos \theta) \]

\[ dS \ dt \]

Thus,
\[
\frac{dN}{dt} = \left( \frac{N}{V} \right) \frac{1}{4\pi} \int_{0}^{\infty} cf(c) dc \int_{0}^{\pi/2} \sin \theta \cos \theta d\theta \int_{0}^{2\pi} d\phi
\]
\[
= \left( \frac{N}{V} \right) \bar{c} \frac{1}{4\pi} 2\pi = \frac{N \bar{c}}{V} \]
\[\text{ov}\]