Kinetic Theory of Gases: Elementary Ideas

9th February 2011

1 Kinetic Theory: A Discussion Based on a Simplified View of the Motion of Gases

1.1 Pressure:

Consul Engel and Reid (Ch. 33.1) for a discussion of the derivation for the pressure of a rarefied collection of particles of mass m. In the following, we provide a connection from the one-dimensional version to the full scalar pressure. The connection is not quite direct from the discussion of Engel and Reid.

In 3-D, for a collection of many particles (on the order of Avogadro number), using **average** values of velocity and velocity components (in Cartesian coordinates); these are not generalized coordinates (as physicists would consider), the **total** kinetic energy is:

$$
\begin{aligned}
KE_{total} &= \frac{N}{2}\, m \; (\vec{v} \cdot \vec{v}) \\
&= \frac{N}{2}\, m \; \left(v_x^2 + v_y^2 + v_z^2\right) \\
&= \frac{N}{2}\, m\, v_x^2 \; + \; \frac{N}{2}\, m\, v_y^2 \; + \; \frac{N}{2}\, m\, v_z^2 \\
&= (KE)_x + (KE)_y + (KE)_z
\end{aligned}
$$

The last equality is really just a notational trick; there really **does not** exist a **thermodynamic** or kinetic property $(KE)_x$ or $(KE)_y$ or $(KE)_z$! The lowercase m is mass.
The velocity is a vector so the v^2 we treat casually is really a **dot product**.

The pressure components for the x , y , and z directions as we determined in class are:

$$p_x = \left(\frac{N}{V}\right) m\ v_x^2 = \frac{1}{V} 2\ (KE)_x$$

$$p_y = \left(\frac{N}{V}\right) m\ v_y^2 = \frac{1}{V}\ 2\ (KE)_y$$

$$p_z = \left(\frac{N}{V}\right) m\ v_z^2 = \frac{1}{V}\ 2\ (KE)_z$$

N is the number of particles. V is the volume of space we are considering. From statistical mechanics (which you will learn more about in the future) we have the relation for the special case of a fluid or state of matter with extremely weak interactions (or no interactions):

$$(KE)_x = \frac{N}{2\ N_{Avogadro}}\ RT$$

$$(KE)_y = \frac{N}{2\ N_{Avogadro}}\ RT$$

$$(KE)_z = \frac{N}{2\ N_{Avogadro}}\ RT$$

Thus,

$$2\ (KE)_x = \frac{N}{N_{Avogadro}}\ RT$$

$$2\ (KE)_y = \frac{N}{N_{Avogadro}}\ RT$$

$$2\ (KE)_z = \frac{N}{N_{Avogadro}}\ RT$$

Substituting the above relations for $2\ (KE_x)$, etc. into the pressure equations yields:

$$p_x = \left(\frac{N}{V}\right) \frac{1}{N_{Avogadro}}\ RT$$

$$p_y = \left(\frac{N}{V}\right) \frac{1}{N_{Avogadro}}\ RT$$

$$p_z = \left(\frac{N}{V}\right) \frac{1}{N_{Avogadro}}\ RT$$

Recall that $\frac{N}{N_{Avogadro}}$ is the number of moles N_{moles}. Thus, the equations for pressure become:

$$
\begin{aligned}
p_x &= \left(\frac{N_{moles}}{V}\right) RT \\
p_y &= \left(\frac{N_{moles}}{V}\right) RT \\
p_z &= \left(\frac{N_{moles}}{V}\right) RT
\end{aligned}
$$

Here, we stop and realize that we have a x-component of pressure, a y-component and a z-component. This is not an artificial result, as rigorously, pressure is a **tensorial** property (it is a 3x3 matrix). The diagonal elements (which we have computed) have special meaning in that they can be used to determine the pressure as we know it. Rigorously, the scalar pressure (that we normally measure and talk about) is determined from the **trace** of the pressure tensor (or matrix). This is:

$$
\begin{aligned}
p_{total}^{scalar} &= \frac{1}{3}\left(p_x + p_y + p_z\right) \\
&= \frac{1}{3}\left(\frac{N_{moles}}{V}\right)(RT + RT + RT) \\
&= \left(\frac{N_{moles}}{V}\right) R\,T \\
pressure &= \left(\frac{N_{moles}}{V}\right) R\,T
\end{aligned}
$$

This should be a more convincing argument for the equality of kinetic theory description of fluids to that of an ideal gas.

2 Maxwell-Boltzmann Distribution of Velocities

For a collection of particles that do not interact, we recall that the ideal gas description is sufficient to predict properties of fluids at certain limiting conditions. Within such a description, the particles, of certain masses, are considered to be moving with velocities that are distributed in a certain fashion. We now consider this distribution of velocities, starting with the distribution of velocity in one-dimension. The generalization to three dimensions follows.

We are concered with finding a **velocity distribution function**. This mathematical description provides the probability of a particle having the Cartesian components of velocity in the range $v_x + dv_x$, $v_y + dv_y$, and $v_z + dv_z$.

We let the distribution function be:

$$\Omega(v_x, v_y, v_z) \;=\; f(v_x)\; f(v_y)\; f(v_z)$$

With the definition of the probability *density* distribution above, we can determine the probability of a particle having the components of velocity $v_x \;+\; dv_x$, $v_y \;+\; dv_y$, and $v_z \;+\; dv_z$ as:

$$\Omega(v_x, v_y, v_z)\; dv_x\; dv_y\; dv_z = \;[f(v_x)\; dv_x]\;[f(v_y)\; dv_y]\;[f(v_z)\; dv_z]$$
$$\Omega(v_x, v_y, v_z)\; dv_x\; dv_y\; dv_z = \;[f(v_x)\; f(v_y)\; f(v_z)]\; dv_x\; dv_y\; dv_z$$

An assumption regarding the nature of this distribution: the gas is isotropic such that the direction of particle movement does not affect the properties of the fluid. In this sense, the velocity distribution is effectively dependent on the magnitude of the velocity. The magnitude of the velocity is:

$$|\,\nu\,| = \;\sqrt{v_x^2 \;+\; v_y^2 \;+\; v_z^2}$$

We now consider the natural logarithm of the distribution function:

$$ln\;\Omega(v_x, v_y, v_z) \;=\; ln\; f(v_x) \;+\; ln\; f(v_y) \;+\; ln\; f(v_z)$$
$$ln\;\Omega(\nu) \;=\; ln\; f(v_x) \;+\; ln\; f(v_y) \;+\; ln\; f(v_z)$$

with

$$\nu^2 \;=\; v_x^2 \;+\; v_y^2 \;+\; v_z^2$$

To determine $f(v_x)$, we consider the derivative of the probability function $\Omega(\nu)$ with respect to the variable v_x.

- *Effectively, we are interested in finding that distribution of velocities (along the x-direction) that distributes the total kinetic energy of the system among the available degrees of freedom in the collection of particles (recall that the internal energy of an ideal gas is only dependent on the temperature and amount of fluid) under the constraint that the total number of particles is constant, the volume we consider remains constant, and the temperature is constant and thus known.*

$$\left(\frac{\partial\; ln\;\Omega(\nu)}{\partial\; v_x}\right)_{v_y, v_z} \;=\; \frac{d\;\, ln\;\; f(v_x)}{d\;\; v_x}$$
$$\left(\frac{d\; ln\;\Omega(\nu)}{d\;\nu}\right)\left(\frac{\partial\;\nu}{\partial\; v_x}\right)_{v_y, v_z} \;=\; \frac{d\;\, ln\;\; f(v_x)}{d\;\; v_x}$$

One can show that $\left(\frac{\partial\ \nu}{\partial\ v_x}\right)_{v_y,v_z} = \frac{v_x}{\nu}$.

$$\begin{aligned}\left(\frac{\partial\ \nu}{\partial\ v_x}\right)_{v_y,v_z} &= \left(\frac{\partial}{\partial v_x}\left(v_x^2+v_y^2+v_z^2\right)^{1/2}\right)_{v_y,v_z} \\ &= \frac{1}{2}(2v_x)\left(v_x^2+v_y^2+v_z^2\right)^{-1/2} \\ &= \frac{v_x}{\nu}\end{aligned}$$

Using this last relation, we obtain:

$$\begin{aligned}\left(\frac{d\ ln\Omega(\nu)}{d\ \nu}\right)\left(\frac{\partial\ \nu}{\partial\ v_x}\right)_{v_y,v_z} &= \frac{d\ ln\ f(v_x)}{d\ v_x} \\ \left(\frac{d\ ln\Omega(\nu)}{d\ \nu}\right)\left(\frac{v_x}{v}\right) &= \frac{d\ ln\ f(v_x)}{d\ v_x} \\ \left(\frac{d\ ln\Omega(\nu)}{\nu\ d\ \nu}\right) &= \frac{d\ ln\ f(v_x)}{v_x\ d\ v_x}\end{aligned}$$

Since each direction is equivalent (under our assumption of isotropy of the medium), we can write for the v_y and v_z differentials (and you can show yourself independently):

$$\begin{aligned}\left(\frac{d\ ln\Omega(\nu)}{\nu\ d\ \nu}\right) &= \frac{d\ ln\ f(v_y)}{v_y\ d\ v_y} \\ \left(\frac{d\ ln\Omega(\nu)}{\nu\ d\ \nu}\right) &= \frac{d\ ln\ f(v_z)}{v_z\ d\ v_z}\end{aligned}$$

Thus, the following equality is clear:

$$\frac{d\ ln\ f(v_y)}{v_y\ d\ v_y} = \frac{d\ ln\ f(v_x)}{v_x\ d\ v_x} = \frac{d\ ln\ f(v_z)}{v_z\ d\ v_z}$$

Since the individual functions of x, y, and z are equal to one another for all space, we can justifiably argue that each is a constant (equal in all cases); in general we can write:

$$\frac{d\ ln\ f(v_j)}{v_j\ d\ v_j} = \frac{d\ f(v_j)}{v_j\ f(v_j)\ dv_j} = -\gamma \qquad for\ j\ = x,y,z$$

We use the negative of a **positive** γ in order to obtain a probability function that is well-behaved as v_j approaches ∞. The solutions for the previous equation are:

$$
\begin{aligned}
\int \frac{d\ f(v_j)}{f(v_j)} &= -\int \ \gamma\ v_j\ dv_j \\
ln\ f(v_j) &= -\frac{1}{2}\ \gamma\ v_j^2 \\
f(v_j) &= A\ e^{-\gamma\ v_j^2\ /2}
\end{aligned}
$$

This last equation is the general expression of our solution; it applies to the individual probability distributions in each direction (x,y,z) (recall we decomposed our total distribution into a product of the three individual distributions).

We still need to consider 2 missing elements:

- A
- γ

To determine an expression for A, we need to consider that the distribution is **normalized** over the domain for which it is defined. What does this mean operationally? Since this expression represents a **probability**, the sum of the individual probabilities for each infinitesimal region of space (or in this case, each window in 'velocity" space) must sum to **1**. Thus we have:

$$
\begin{aligned}
\int_{-\infty}^{\infty} f(v_j)\ dv_j \ = \ 1 &= \int_{-\infty}^{\infty} \ A\ e^{-\gamma\ v_j^2\ /2}\ dv_j \\
1 &= 2\ A \int_{0}^{\infty} \ A\ e^{-\gamma\ v_j^2\ /2}\ dv_j \\
1 &= A\ \sqrt{\frac{2\pi}{\gamma}} \\
A &= \sqrt{\frac{\gamma}{2\pi}}
\end{aligned}
$$

We used the property of even integrands to change the lower limit of integration. Thus, the distribution becomes:

$$
f(v_j) \ = \ \sqrt{\frac{\gamma}{2\pi}} e^{-\gamma\ v_j^2\ /2}
$$

To evaluate γ, we introduce from statistical mechanics (which we just state here without proof, which is left for another course or to the individual student):

$$
\left\langle v_x^2 \right\rangle \ = \ \frac{k_B\ T}{m}
$$

where m is the mass of the particles. Thus,

$$\begin{aligned}
\langle v_x^2 \rangle &= \frac{k_B\ T}{m} = \int_{-\infty}^{\infty} v_x^2\ f(v_x)\ dv_x \\
&= \sqrt{\frac{\gamma}{2\pi}} \int_{-\infty}^{\infty} v_x^2\ e^{-\gamma\ v_x^2\ /2}\ dv_x \\
&= \sqrt{\frac{\gamma}{2\pi}} \left(\frac{1}{\gamma} \sqrt{\frac{2\ \pi}{\gamma}} \right) \\
&= \frac{1}{\gamma} \\
\frac{m}{k_b\ T} &= \gamma
\end{aligned}$$

We have thus arrived at the famous **Maxwell-Boltzmann velocity distribution in one dimension**:

$$f(v_j) = \left(\frac{m}{2\ \pi\ k_B\ T} \right)^{1/2} e^{-m\ v_j^2\ /2\ k_B\ T)} = \left(\frac{M}{2\ \pi\ R\ T} \right)^{1/2} e^{-M\ v_j^2\ /2\ R\ T)}$$

where mass, m, is in units of kg and **molar mass**, M, is in units of $\frac{kg}{mol}$ (we use the relation $R = N_A\ k_B$ for the conversion between the forms using m and M.

In three dimensions (Cartesian represenatation) the total distribution becomes:

$$\begin{aligned}
\Omega(v_x, v_y, v_z) &= \prod_{j=1,3} f(v_j) \\
\Omega(v_x, v_y, v_z) &= \prod_{j=1,3} \left(\frac{m}{2\ \pi\ k_B\ T} \right)^{1/2} e^{-m\ v_j^2\ /2\ k_B\ T)} \\
\Omega(\nu) &= \prod_{j=1,3} \left(\frac{m}{2\ \pi\ k_B\ T} \right)^{1/2} e^{-m\ v_j^2\ /2\ k_B\ T)}
\end{aligned}$$

Example Problem 33.1 (Engel and Reid)

- Compute average velocity, $\langle v_x \rangle$.

$$
\begin{aligned}
\langle v_x \rangle &= \int_{-\infty}^{\infty} v_x \; f(v_x) \; dv_x \\
&= \int_{-\infty}^{\infty} v_x \; \left(\frac{m}{2 \; \pi \; k_B \; T} \right)^{1/2} \; e^{-m \; v_x^2 \; / 2 \; k_B \; T)} \; dv_x \\
&= \left(\frac{m}{2 \; \pi \; k_B \; T} \right)^{1/2} \; \int_{-\infty}^{\infty} v_x \; e^{-m \; v_x^2 \; / 2 \; k_B \; T)} \; dv_x \\
&= 0
\end{aligned}
$$

The result reflects the vectorial nature of velocity.

3 Maxwell Distribution of Speeds

We stipulated in the above discussion of the Maxwell-Boltzmann distribution that the medium defined by the particles is **isotropic**; that is, properties are not dependent on a direction (on internal or external gradients). Furthermore, though we wrote $\Omega(\nu)$ as a function of speed, ν, there was no **explicit** dependence on **speed**, a non-vectorial quantity, in the final expression. With this in mind, we next consider the distribution of speeds that emerges from the velocity distribution we derived. Again, bear in mind that speed is not vectorial, velocity is.

Based on our earlier definition of the probability distribution based on speed, ν, we can write now:

$$
\begin{aligned}
F(\nu) \; d\nu &= f(v_x) \; f(v_y) \; f(v_z) \; dv_x \; dv_y \; dv_z \\
&= \left[\left(\frac{m}{2 \; \pi \; k_B \; T} \right)^{1/2} e^{-m \; v_x^2 \; /2 \; k_B \; T)} \right] \left[\left(\frac{m}{2 \; \pi \; k_B \; T} \right)^{1/2} e^{-m \; v_y^2 \; /2 \; k_B \; T)} \right] \\
&\quad \left[\left(\frac{m}{2 \; \pi \; k_B \; T} \right)^{1/2} e^{-m \; v_z^2 \; /2 \; k_B \; T)} \right] \; dv_x \; dv_y \; dv_z \\
&= \left(\frac{m}{2 \; \pi \; k_B \; T} \right)^{3/2} e^{-m \; (v_x^2 + v_y^2 + v_z^2) \; /2 \; k_B \; T)} \; dv_x \; dv_y \; dv_z
\end{aligned}
$$

We are almost to the point of having our expression for the speed distribution, since we can see clearly that $v_x^2 + v_y^2 + v_z^2 = \nu^2$. However, the differential volume element $dv_x \; dv_y \; dv_z$ is the troubling part. Here we consider the idea of **change of variables** from Cartesian components of velocity to a spherical coordinate representation of speed.

Thus, the volume element becomes $4\ \pi\ \nu^2\ d\nu$ after integrating over the angular dimensions. The Maxwell speed distribution thus becomes:

$$F(\nu)\ d\nu\ =\ 4\ \pi\ \left(\frac{m}{2\ \pi\ k_B\ T}\right)^{3/2}\ \nu^2\ e^{-m\ \nu^2\ /2\ k_B\ T)}\ d\nu$$

$$F(\nu)\ d\nu\ =\ 4\ \pi\ \left(\frac{M}{2\ \pi\ R\ T}\right)^{3/2}\ \nu^2\ e^{-M\ \nu^2\ /2\ R\ T)}\ d\nu$$

Properties of this distribution include:

- At a particular temperature, there is a single maximum value of the speed
- Despite including a Gaussian factor, the distribution is not symmetric due to the ν^2 term which introduces contributions from tail values at higher speeds
- At higher temperatures, the distribution becomes broader (more speeds, or translational energy levels accessible)
- At lower masses, the distribution becomes broader (more speeds are accessible)
- Comparison of distribution for gases of different mass At same temperature, kinetic theory says all gases have some energy (depends on T); thus, heavier masses have distributions that are narrower and peaked at lower speeds.

4 Measures of the Maxwell Distribution of Speeds

We can consider individual distributions of different gases (or even a single gas) at different temperatures, for instance. But there are certain measures of the distribution of speeds for a particular gas that we can consider in order to make quick comparisons. We consider these next.

- Most probable speed, ν_{mp}

$$\begin{aligned}
\frac{d\ F(\nu)}{d\ \nu} &= \frac{d}{d\ \nu}\left(4\ \pi\ \left(\frac{m}{2\ \pi\ k_B\ T}\right)^{3/2}\ \nu^2\ e^{-m\ nu^2/2\ k_B\ T}\right) \\
&= 4\ \pi\ \left(\frac{m}{2\ \pi\ k_B\ T}\right)^{3/2}\frac{d}{d\ \nu}\ \left(\nu^2\ e^{-m\ nu^2/2\ k_B\ T}\right) \\
&= 4\ \pi\ \left(\frac{m}{2\ \pi\ k_B\ T}\right)^{3/2}\ e^{-m\ nu^2/2\ k_B\ T}\left[2\ \nu-\frac{m\nu^3}{k_B\ T}\right]
\end{aligned}$$

The maximum probability occurs when the derivative is identically 0; we thus obtain:

$$2\ \nu_{mp}\ -\ \frac{m\ \nu_{mp}^3}{k_B\ T}\ =\ 0$$
$$\nu_{mp}\ =\ \sqrt{\frac{2\ k_B\ T}{m}}$$

- Average Speed

$$< \nu > =\ \nu_{ave}\ =\ \int_0^\infty\ \nu\ F(\nu)\ d\nu$$
$$=\ 4\ \pi\ \left(\frac{m}{2\ \pi\ k_B\ T}\right)^{3/2}\ \int_0^\infty\ \nu^3 e^{-m\ \nu^2/2\ k_B\ T}\ d\nu$$
$$=\ \left(\frac{8\ k_B\ T}{\pi\ m}\right)^{1/2}\ =\ \left(\frac{8\ R\ T}{\pi\ M}\right)^{1/2}$$

- Root-Mean-Square Speed

$$\nu_{rms}\ =\ \left[\langle\nu^2\rangle\right]^{1/2}\ =\ \left(\frac{3k_B\ T}{m}\right)^{1/2} \tag{1}$$

- Using the previous expressions for average speed and root-mean-square speed, we obtain the following relation between the two measures of the speed distribution:

$$\left[\langle\nu^2\rangle\right]^{1/2}\ =\ \sqrt{\frac{3\ \pi}{8}}\ \langle\nu\rangle$$

- $\nu_{rms} > \nu_{ave} > \nu_{mp}$
- All measures are proportional to $T^{1/2}$ and $M^{-1/2}$.

5 Collisions and Collision Frequency

5.1 Gas of Dissimilar Particles, 1 and 2

The rudimentary concept of molecular collisions will be relevant to future discussions of reaction kinetics and mechanisms. Here we consider what insights kinetic theory (separate from the field of reaction kinetics) can provide.

First, consider a gas of dissimilar particles, 1 and 2. We want to estimate the number of collisions a single particle of 1 will make with all other 2 particles. Then, we'll consider the total number of collisions per unit of time. Since these properties are per unit of time, they are intuitively *frequencies* One of the assumptions that we will invoke is that the density is low (or the distance between is particles is "sufficiently" large; or the particles have very weak "effective" interactions). All of these assumptions can justifiably argued and leave room for further exploration. For now, we proceed with a simplistic model.

Consider Figure 33.13 in Engel and Reid. Here we have a particle moving with some effective speed (which we can determine based on our earlier discussion of measures of probability distributions of speeds; we'll see how to do this shortly). Consider the cylindrical volume swept out by a particle moving with average effective speed $< \nu_{eff} >$.

- length of the cylinder generated by particle moving for a time Δt: $length \ = < \nu_{eff} > \ \Delta t$
- surface area of base of cylinder $A \ = \ \sigma \ = \ \pi \ (r_1 \ + \ r_2)^2$ $(r_1 + r_2)$ is the effective radius of the cylinder
- The volume is then $V_{cylinder} \ = \ \pi \ (r_1 \ + \ r_2)^2 \ < \nu_{eff} > \ \Delta t \ = \ \sigma \ < \nu_{eff} > \ \Delta t$.
- The effective speed, $< \nu_{eff} >$ is determined from consideration of the apparent speed between two particles in a collision when both have a certain speed. We can approximate this effective speed as follows:

$$
\begin{aligned}
< \nu_{eff} > \ &= \ \left(< \nu_1 >^2 \ + \ < \nu_2 >^2 \right)^{1/2} \ = \ \left[\left(\frac{8 \ k_B \ T}{\pi \ m_1} \right) + \left(\frac{8 \ k_B \ T}{\pi \ m_2} \right) \right]^{1/2} \\
&= \ \left[\frac{8 \ k_B \ T}{\pi} \left(\frac{1}{m_1} \ + \ \frac{1}{m_2} \right) \right]^{1/2} \\
&= \ \left(\frac{8 \ k_B \ T}{\pi \ \mu} \right)^{1/2}
\end{aligned}
$$

where the reduced mass μ is defined as:

$$
\frac{1}{\mu} \ = \ \frac{m_1 + m_2}{m_1 \ m_2}
$$

The average effective speed, $< \nu_{eff} >$, is determined by considering the relative velocity of two particles traveling with veolcites $\vec{v}_1$ and $\vec{v}_2$.

$$\vec{v}_{eff} = \vec{v}_1 - \vec{v}_2$$

The magnitude of this effective velocity, the effective speed, is :

$$\nu_{eff} = \sqrt{\vec{v}_{eff} \cdot \vec{v}_{eff}}$$
$$\nu_{eff} = \sqrt{(\vec{v}_1 - \vec{v}_2) \cdot (\vec{v}_1 - \vec{v}_2)}$$

The square of the effective speed is:

$$\nu_{eff}^2 = \vec{v}_{eff} \cdot \vec{v}_{eff}$$
$$\nu_{eff}^2 = (\vec{v}_1 - \vec{v}_2) \cdot (\vec{v}_1 - \vec{v}_2)$$

The average of the square of the effective speed is:

$$\left\langle \nu_{eff}^2 \right\rangle = \langle \vec{v}_{eff} \cdot \vec{v}_{eff} \rangle$$
$$\left\langle \nu_{eff}^2 \right\rangle = \langle (\vec{v}_1 - \vec{v}_2) \cdot (\vec{v}_1 - \vec{v}_2) \rangle$$
$$\left\langle \nu_{eff}^2 \right\rangle = \langle \vec{v}_1 \cdot \vec{v}_1 - 2\, \vec{v}_1 \cdot \vec{v}_2 + \vec{v}_2 \cdot \vec{v}_2 \rangle$$
$$\left\langle \nu_{eff}^2 \right\rangle = \langle \vec{v}_1 \cdot \vec{v}_1 \rangle - 2 \langle \vec{v}_1 \cdot \vec{v}_2 \rangle + \langle \vec{v}_2 \cdot \vec{v}_2 \rangle$$

Because the velocities of particle 1 and particle 2 are **uncorrelated**, the average of their dot product (or projection on one another) is zero. Thus, $\langle \vec{v}_1 \cdot \vec{v}_2 \rangle = 0$.

$$\left\langle \nu_{eff}^2 \right\rangle = \langle \vec{v}_1 \cdot \vec{v}_1 \rangle + \langle \vec{v}_2 \cdot \vec{v}_2 \rangle$$

Thus,

$$\sqrt{\left\langle \nu_{eff}^2 \right\rangle} = \sqrt{\langle \vec{v}_1 \cdot \vec{v}_1 \rangle + \langle \vec{v}_2 \cdot \vec{v}_2 \rangle}$$
$$\sqrt{\left\langle \nu_{eff}^2 \right\rangle} = \sqrt{\left\langle \nu_1^2 \right\rangle + \left\langle \nu_2^2 \right\rangle}$$

From our discussion above concerning the relation between root-mean-square and average speeds, we can write the last expression (which is in terms of root-mean-square speeds really) as an expression in terms of average speeds:

$$
\begin{aligned}
\sqrt{\left\langle \nu_{eff}^2 \right\rangle} &= \sqrt{\langle \nu_1^2 \rangle \; + \; \langle \nu_2^2 \rangle} \\
\sqrt{\frac{3\,\pi}{8}} \; \langle \nu_{eff} \rangle &= \sqrt{\left(\frac{3\,\pi}{8}\right) \; \langle \nu_1 \rangle^2 + \left(\frac{3\,\pi}{8}\right) \; \langle \nu_2 \rangle^2} \\
\sqrt{\frac{3\,\pi}{8}} \; \langle \nu_{eff} \rangle &= \sqrt{\frac{3\,\pi}{8}} \sqrt{\langle \nu_1 \rangle^2 + \; \langle \nu_2 \rangle^2} \\
\langle \nu_{eff} \rangle &= \sqrt{\langle \nu_1 \rangle^2 + \; \langle \nu_2 \rangle^2}
\end{aligned}
$$

With the above definitions, we can now define the number of collisions that a *single* particle will have with other particles in the cylindrical volume in a unit of time as follows:

$$
\begin{aligned}
z_{12} &= \frac{N_2}{V} \left(\frac{V_{cyl}}{\Delta t}\right) = \frac{N_2}{V} \left(\frac{\sigma \; \langle \nu_{eff} \rangle \; \Delta t}{\Delta t}\right) \\
&= \frac{N_2}{V} \, \sigma \left(\frac{8 \; k_B \; T}{\pi \; \mu}\right)^{1/2}
\end{aligned}
$$

Are the units of this property consistent?

For the collision frequency of a particle 1 with another particle 1, z_{11}, we have:

$$
z_{11} = \frac{N_1}{V} \, \sigma \, \sqrt{2} \left(\frac{8 \; k_B \; T}{\pi \; m_1}\right)^{1/2}
$$

The total collisional frequency is thus:

$$
\begin{aligned}
Z_{12} &= \frac{N_1}{V} \, z_{12} \\
Z_{12} &= \frac{N_1}{V} \, \frac{N_2}{V} \, \sigma \left(\frac{8 \; k_B \; T}{\pi \; \mu}\right)^{1/2}
\end{aligned}
$$

$$
\begin{aligned}
Z_{11} &= \frac{1}{2} \, \frac{N_1}{V} \, z_{11} \\
Z_{11} &= \frac{1}{\sqrt{2}} (\frac{N_1}{V})^2 \, \sigma \left(\frac{8 \; k_B \; T}{\pi \; m_1}\right)^{1/2}
\end{aligned}
$$

Note the units for the total collisional frequency; it is per unit volume.

6 Mean Free Path

Knowing the distribution of velocities, we can determine the collision frequency (as shown above). Knowing the previous two kinetic properties of a gas, we can now consider the Mean free path, the average distance a particle travels in between collisions. The question we are asking is:

In a unit of time, a particle travels a certain distance, along the way participating in a number of collisions. Thus, the mean free path (the distance travelled between collision events) is:

$$Mean\ Free\ Path\ =\ \frac{\langle \nu \rangle}{(z_{12} + z_{11})}$$