

0.1 Particles of a gas

0.1.1 Probability distribution of velocities in a particular direction

The normal distribution is

$$N(\mu, \sigma) = \frac{e^{\frac{-(x-\mu)^2}{2\sigma^2}}}{\sigma\sqrt{2\pi}} = (\text{for } \mu = 0) \frac{e^{\frac{-x^2}{2\sigma^2}}}{\sigma\sqrt{2\pi}}$$

Let S be a container containing a gas, whose molecules are small spheres of possibly different masses, in equilibrium. For particles of a particular mass — say m — we shall be interested in the probability distributions of certain continuous random variables $f : S \rightarrow \mathbb{R}$ for example $f_x : S \rightarrow \mathbb{R}$ where $f_x(m)$ is the velocity of the particle m in the x direction and similarly for f_y and f_z .

Assumption 1. The velocities of the molecules of a given mass m in a given direction are normally distributed with mean 0. In particular for the x direction the probability distribution of the random variable $f_x : S \rightarrow \mathbb{R}$ is given by

$$p_{f_x} = \frac{e^{\frac{-v_x^2}{2\sigma^2}}}{\sigma\sqrt{2\pi}}$$

where σ depends on the mass m .

Assumption 1. There is no preferred direction for the velocity of the molecules. This implies that the probability distributions $p_{f_x} : \mathbb{R} \rightarrow \mathbb{R}^{\geq 0}$, $p_{f_y} : \mathbb{R} \rightarrow \mathbb{R}^{\geq 0}$, $p_{f_z} : \mathbb{R} \rightarrow \mathbb{R}^{\geq 0}$ are all equal.

Assumption 2. The random variables f_x, f_y, f_z are mutually independent.

This implies that the proportion of molecules with x direction velocities in $[v_x, v_x+dx]$ and y direction velocities in $[v_y, v_y+dy]$ and z direction velocities in $[v_z, v_z+dz]$ is

$$p_{f_x}(v_x)p_{f_y}(v_y)p_{f_z}(v_z)dx dy dz = \frac{1}{\sigma^3 2\sqrt{2\pi}^{\frac{3}{2}}} e^{\frac{-(v_x^2+v_y^2+v_z^2)}{2\sigma^2}} dx dy dz = \frac{1}{\sigma^3 2\sqrt{2\pi}^{\frac{3}{2}}} e^{\frac{-s^2}{2\sigma^2}} dx dy dz$$

where s is the speed of a molecule.

We can also infer that there is a function $\phi : \mathbb{R} \rightarrow \mathbb{R}$ such that

$$p_{f_x}(v_x)p_{f_y}(v_y)p_{f_z}(v_z) = \phi((v_x^2 + v_y^2 + v_z^2)^{\frac{1}{2}}) \equiv \phi(s)$$

where s is the speed of a molecule. for otherwise there would be a v'_x, v'_y, v'_z with $v_x^2 + v_y^2 + v_z^2 = (v'_x)^2 + (v'_y)^2 + (v'_z)^2$ (i.e. same speed but different direction) and with different numbers of molecules travelling with the same speed in each of the unprimed and primed directions.

By inspection (rather than deduction) we see that $p_{f_x}(v_x) = Ce^{Av_x^2}$ (and the analogues for y and z) satisfy this functional equation, Since, as the integrand is a probability distribution

$$\int \int \int C^3 e^{A(x^2+y^2+z^2)} dx dy dz = 1 \text{ where } x, y, z \text{ are the velocities in the } x, y, z \text{ direction}$$

the constant A must be negative so we can write $A \equiv -\alpha^{-2}$. For the particular random variable f_x we have

$$\int_{-\infty}^{+\infty} p_{f_x}(v_x) dv_x = \int_{-\infty}^{+\infty} Ce^{-\frac{x^2}{\alpha^2}} dx = 1$$

Since $\int_{-\infty}^{+\infty} e^{-x^2} dx = \sqrt{\pi}$ we obtain

$$C = \frac{1}{\alpha\pi^{\frac{1}{2}}}$$

$$\text{Hence } p_{f_x}(v_x) = Ce^{Av_x^2} = \frac{1}{\alpha\pi^{\frac{1}{2}}} e^{-\frac{v_x^2}{\alpha^2}}$$

For a gas in equilibrium (i.e. at a definite temperature) the constant α depends only on the mass m . The integral $\int xe^{-x^2} dx$ is exactly integrable and we obtain that the mean velocity of particles of mass m in some definite direction is zero as one would expect

0.1.2 Probability distribution of speeds

Our next goal is to obtain the probability distribution for the random variable $f_s : S \rightarrow \mathbb{R}^{\geq 0}$ where $f_s(m)$ is the speed of the particle m (in any direction).

This is given by

$$p_{f_s}(s) = \frac{4}{\alpha^3 \pi^{\frac{1}{2}}} s^2 e^{-\frac{s^2}{\alpha^2}}$$

From the above, since $p_{f_x}(v_x) = C e^{-\frac{v_x^2}{\alpha^2}}$ and similarly for y and z , we have

$$\phi(u) = C^3 e^{-\left(\frac{v_x^2}{\alpha^2} + \frac{v_y^2}{\alpha^2} + \frac{v_z^2}{\alpha^2}\right)} = \frac{1}{\alpha^3 \pi^{\frac{3}{2}}} e^{-\frac{u^2}{\alpha^2}}$$

. where if δV is any small volume in velocity space containing (v_x, v_y, v_z) then the proportion of molecules with velocities in δV is $\phi(u)\delta V$ where $u = \sqrt{v_x^2 + v_y^2 + v_z^2}$. We can visualise all the velocities corresponding to a certain speed s as radii of a sphere of radius s . We can further imagine a large finite set of such radii distributed all around the sphere of radius s and with each radius we associate an element of volume δV in the shell between the sphere of radius s and radius $s + \delta s$ so that the entire shell of volume $4\pi s^2 \delta s$ is covered without overlaps by the δV s. Thus the proportion of molecules with speeds between s and $s + \delta s$ is given by

$$\phi(s) \times 4\pi s^2 \delta s = \frac{1}{\alpha^3 \pi^{\frac{3}{2}}} e^{-\frac{s^2}{\alpha^2}} \times 4\pi s^2 \delta s = \frac{4}{\alpha^3 \pi^{\frac{1}{2}}} s^2 e^{-\frac{s^2}{\alpha^2}} \delta s$$

as required where α is to be determined by the requirement $\int_0^\infty p_{f_s}(s) ds = 1$.

0.1.3 Mean of speed and of speed²

By definition the mean speed $\bar{s}$ is given by

$$\bar{s} = \int_0^\infty s p_{f_s}(s) ds = \int_0^\infty \frac{4}{\alpha^3 \pi^{\frac{1}{2}}} s^3 e^{-\frac{s^2}{\alpha^2}} ds = 2\alpha \pi^{-\frac{1}{2}}$$

To carry out the integration we need to use

$$\int x^3 e^{-x^2} = -\frac{1}{2} \left(x^2 e^{-x^2} + e^{-x^2} \right)$$

which is obtained by substituting $u = x^2$ and integrating by parts.

By definition the mean square speed $\overline{s^2}$ is given by

$$\overline{s^2} = \int_0^\infty s^2 p_{f_s}(s) ds = \int_0^\infty \frac{4}{\alpha^3 \pi^{\frac{1}{2}}} s^4 e^{-\frac{s^2}{\alpha^2}} ds = \frac{3}{2} \alpha^2$$

To carry out the integration we need to evaluate

$$\int x^4 e^{-x^2}$$

but this is also exactly integrable by parts with $u = x$ and $v = x^3 e^{-x^2}$.

We have $\overline{s^2} = \frac{3}{2}\alpha^2 = \frac{3kT}{m}$ where m is the mass of a molecule and k is Boltzmann's constant, $\frac{R}{N}$, where N is Avogadro's number and $R = \frac{PV}{T}$ for an ideal gas. This gives

$$\alpha = \sqrt{\frac{2kT}{m}} \Rightarrow p_{fs}(s) = 4\pi \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} s^2 e^{-\frac{ms^2}{2kT}}$$

which is the definitive form of Maxwell's distribution.

0.1.4 Relative speeds

0.1.4.1 Distribution of relative velocity in a direction

The relative velocity of two particles, like the velocity itself, has **i**, **j**, **k** direction components. The **i** component of the relative velocity is just the difference in the **i** components of the velocities of each of the particles.

Let us fix a direction - say the **i** direction. Then if there are N_1 particles of mass m_1 the number with speeds between x and $x + \delta x$ in the **i** direction is:

$$N_1 \frac{1}{\alpha_1 \pi^{\frac{1}{2}}} e^{-\frac{x^2}{\alpha_1^2}} \delta x$$

where $\alpha_1 = \sqrt{\frac{2kT}{m_1}}$. If there are N_2 particles of mass m_2 the number with speeds between $x + y$ and $x + y + \delta y$ is:

$$N_2 \frac{1}{\alpha_2 \pi^{\frac{1}{2}}} e^{-\frac{(x+y)^2}{\alpha_2^2}} \delta y$$

where $\alpha_2 = \sqrt{\frac{2kT}{m_2}}$. Therefore the number of pairs for which the 1st member has its component of velocity along the **i** direction between x and $x + \delta x$

and for which the second member has its component of velocity along the $\mathbf{i}$ direction between $x + y$ and $x + y + \delta y$ in the $\mathbf{i}$ direction is

$$N_1 N_2 \frac{1}{\alpha_1 \pi^{\frac{1}{2}}} e^{-\frac{x^2}{\alpha_1^2}} \frac{1}{\alpha_2 \pi^{\frac{1}{2}}} e^{-\frac{(x+y)^2}{\alpha_2^2}} \delta x \delta y$$

The second particle is moving with velocity between y and $y + \delta y$ relative to the first which is moving with velocity between x and $x + \delta x$ for $-\infty < x < +\infty$. If we integrate w.r.t. x we will have an expression for the number of particles in which the second is moving with velocity along the $\mathbf{i}$ direction between y and $y + \delta y$ relative to the first. Thus we have

$$\frac{N_1 N_2}{\alpha_1 \alpha_2 \pi} \left(\int_{-\infty}^{+\infty} e^{-\frac{x^2}{\alpha_1^2}} e^{-\frac{(x+y)^2}{\alpha_2^2}} dx \right) \delta y = N_1 N_2 \left(\frac{1}{\sqrt{(\alpha_1^2 + \alpha_2^2) \pi}} e^{-\frac{y^2}{\alpha_1^2 + \alpha_2^2}} \right) \delta y$$

(The exponent of e is a quadratic expression which we can recast as a square plus number — $a(x + b)^2 + c$ — which by appropriate substitution reduces to the evaluating $\int_{-\infty}^{+\infty} e^{-u^2} du$.)

0.1.4.2 Distribution of relative speeds

If we write $\beta^2 = \alpha_1^2 + \alpha_2^2$ and change y to x , then the number of pairs of molecules, for which the magnitude of the component of their relative velocity in the $\mathbf{i}$ direction lies between x and $x + \delta x$ is:

$$N_1 N_2 \left(\frac{1}{\beta \sqrt{\pi}} e^{-\frac{x^2}{\beta^2}} \right) \delta x$$

As this is of the same form as for actual velocities we can duplicate the above argument to conclude that the number of pairs of molecules with relative speed between s and $s + \delta s$ is:

$$N_1 N_2 \frac{4}{\beta^3 \pi^{\frac{1}{2}}} s^2 e^{-\frac{s^2}{\beta^2}} \delta s$$

Thus, as before, the mean relative speed is $\frac{2\beta}{\sqrt{\pi}}$. Where the two particles have the same mass i.e $\alpha_1 = \alpha_2 \equiv \alpha$ then we have $\beta = \sqrt{2}\alpha$ and $\frac{2\beta}{\sqrt{\pi}} = \sqrt{2} \times \frac{2\alpha}{\sqrt{\pi}}$

i.e. the mean relative speed is $\sqrt{2}$ times the mean speed of the individual particles.

This conforms with what Maxwell goes on to state (p. 383) *the mean relative velocity is the square root of the sum of the squares of the mean velocities of the two systems*,. Assuming that by velocity he means speed, what this is saying is that the mean relative speed is:

$$\sqrt{(2\alpha_1\pi^{-\frac{1}{2}})^2 + (2\alpha_2\pi^{-\frac{1}{2}})^2} = \frac{2}{\sqrt{\pi}} \sqrt{\alpha_1^2 + \alpha_2^2} = \frac{2\beta}{\sqrt{\pi}}$$

0.1.5 Distribution of CoM speeds.

Any pair of particles has a centre of mass which moves with a speed determined by the size and speed of the particles. Subject to reasonable assumptions we can work out the distribution of the CoM speeds.

Let m_1, m_2 be the masses of the particles and $\mathbf{v}_1, \mathbf{v}_2$ be the velocities, The velocity of the CoM is thus $\frac{m_1\mathbf{v}_1 + m_2\mathbf{v}_2}{m_1 + m_2}$. Thus the $\mathbf{i}$ component of the CoM velocity is $\frac{m_1v_1^x + m_2v_2^x}{m_1 + m_2}$. The distribution of v_1^x is normal with mean 0 and variance σ_1^2 where $\sigma_1^2 = \frac{k}{m_1}$ where k depends on the temperature and similarly for v_2^x . Consequently the distribution of $\frac{m_1v_1^x}{m_1 + m_2}$ is also normal with mean 0 and variance $\left(\frac{m_1}{m_1 + m_2}\right)^2 \sigma_1^2$.

In general for independent normal variables X and Y with means μ_1 and μ_2 and standard deviations σ_1 and σ_2

$$aX + bY \sim N(a\mu_1 + b\mu_2, a^2\sigma_1^2 + b^2\sigma_2^2)$$

Thus, on the assumption that the x components of the velocities of the two particles are independent, the distribution of the velocity of the $\mathbf{i}$ component of the velocity of the CoM, p_{CoM}^x is given by

$$p_{CoM}^x \sim N \left[0, \left(\frac{m_1}{m_1 + m_2} \right)^2 \sigma_1^2 + \left(\frac{m_2}{m_1 + m_2} \right)^2 \sigma_2^2 \right] \sim N(0, \sigma^2)$$

where $\sigma^2 = \left(\frac{m_1}{m_1+m_2}\right)^2 \sigma_1^2 + \left(\frac{m_2}{m_1+m_2}\right)^2 \sigma_2^2$

The explicit formula for the distributon of the velocity of the CoM in the x direction ia

$$p_{CoM}^x = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{x^2}{2\sigma^2}}$$

where σ is as above. Comparing this with the formula for the distribution of the velocity of individual particles in the x direction

$$p_{f_x}(v_x) = \frac{1}{\alpha\pi^{\frac{1}{2}}} e^{-\frac{v_x^2}{\alpha^2}}$$

we see that $\alpha = \sigma\sqrt{2}$ and thus that the mean speed of the CoM is $\frac{2\alpha}{\sqrt{\pi}}$.

We need to reconcile this with the Maxwell formula for the square of the mean speed of the CoM — to wit $\frac{m_1^2\bar{s}_1^2+m_2^2\bar{s}_2^2}{(m_1+m_2)^2}$. We have

$$\frac{4\alpha^2}{\pi} = \frac{8\sigma^2}{\pi} = \frac{8}{\pi} \left(\left(\frac{m_1}{m_1+m_2}\right)^2 \sigma_1^2 + \left(\frac{m_2}{m_1+m_2}\right)^2 \sigma_2^2 \right)$$

Now we have the formulas to express the above in terms of the mean speeds

$$\sigma_1^2 = \frac{\alpha_1^2}{2} \quad \sigma_2^2 = \frac{\alpha_2^2}{2} \quad \bar{s}_1 = 2\alpha_1\pi^{-\frac{1}{2}} \quad \bar{s}_2 = 2\alpha_2\pi^{-\frac{1}{2}} \Rightarrow \alpha_1^2 = \frac{\pi\bar{s}_1^2}{4} \quad \alpha_2^2 = \frac{\pi\bar{s}_2^2}{4}$$

Thus as $\sigma_1^2 = \frac{\alpha_1^2}{2}$ and $\sigma_2^2 = \frac{\alpha_2^2}{2}$ we have

$$\left(\frac{2\alpha}{\sqrt{\pi}}\right)^2 = \frac{4\alpha^2}{\pi} = \frac{8\sigma^2}{\pi} = \frac{8}{\pi} \left(\left(\frac{m_1}{m_1+m_2}\right)^2 \frac{\pi\bar{s}_1^2}{8} + \left(\frac{m_2}{m_1+m_2}\right)^2 \frac{\pi\bar{s}_2^2}{8} \right)$$

i.e.

$$\frac{4\alpha^2}{\pi} = \frac{m_1^2\bar{s}_1^2 + m_2^2\bar{s}_2^2}{(m_1+m_2)^2}$$

in accordance with Maxwell. If we take $m_1 = m_2 \equiv m$ and thus $s_1 = s_2 \equiv s$ we obtain

$$\bar{s}_{CoM}^2 = \frac{\bar{s}^2}{2} \Rightarrow \bar{s}_{CoM} = \sqrt{2} \times \frac{\bar{s}}{2}$$

as would be expected as the distribution of $|\mathbf{u} + \mathbf{v}|$ is the same as that for the relative speed $|\mathbf{u} - \mathbf{v}|$ and the mean of the distribution of $\left|\frac{\mathbf{u}+\mathbf{v}}{2}\right|$ half that of $|\mathbf{u} + \mathbf{v}|$.

0.1.6 The mean kinetic energy

However, once we accept that for any given type of particle we have (see above)

$$\overline{s^2} = \frac{3\alpha_m^2}{2} = \frac{3kT}{m} \Rightarrow \frac{1}{2}m\overline{s^2} = \frac{3}{2}kT$$

i.e. that the mean kinetic energy of a particle of any type (i.e. mass) does not depend on the type of particle and thus is the same for particles of all types. We also have

$$m\overline{s^2} = \frac{3m\alpha_m^2}{2} = \frac{3m}{2} \times \frac{\pi\overline{s}_m^2}{4} = \frac{3\pi m\overline{s}_m^2}{8}$$

which is Maxwell's formula for the mean vis viva (twice the kinetic energy) in terms of the mean speed.

0.1.7 Mean speed relative to the CoM

The velocity of m_1 relative to the CoM is

$$\mathbf{v}_1 - \frac{m_1\mathbf{v}_1 + m_2\mathbf{v}_2}{m_1 + m_2} = \frac{m_2(\mathbf{v}_1 - \mathbf{v}_2)}{m_1 + m_2} = \frac{m_2\mathbf{v}_1}{m_1 + m_2} - \frac{m_2\mathbf{v}_2}{m_1 + m_2}$$

Thus the $\mathbf{i}$ component of the velocity of m_1 relative to the CoM is $\frac{m_2(v_1^x - v_2^x)}{m_1 + m_2}$. The distribution of v_1^x is normal with mean 0 and variance σ_1^2 where $\sigma_1^2 = \frac{k}{m_1}$ where k depends on the temperature and similarly for v_2^x . Consequently the distribution of $\frac{m_2 v_1^x}{m_1 + m_2}$ is also normal with mean 0 and variance $\left(\frac{m_2}{m_1 + m_2}\right)^2 \sigma_1^2$.

In general for independent normal variables X and Y with means μ_1 and μ_2 and standard deviations σ_1 and σ_2

$$aX + bY \sim N(a\mu_1 + b\mu_2, a^2\sigma_1^2 + b^2\sigma_2^2)$$

Thus, on the assumption that the $\mathbf{i}$ components of the velocities of the two particles are independent, the distribution of the velocity of the $\mathbf{i}$ component

of the velocity of m_1 relative to the CoM, r_{CoM}^x is given by

$$r_{CoM}^x \sim N \left[0, \left(\frac{m_2}{m_1 + m_2} \right)^2 \sigma_1^2 + \left(\frac{m_2}{m_1 + m_2} \right)^2 \sigma_2^2 \right] \sim N(0, \sigma^2)$$

where $\sigma^2 = \left(\frac{m_2}{m_1 + m_2} \right)^2 (\sigma_1^2 + \sigma_2^2)$

The explicit formula for the distributon of the velocity of m_1 relative to the CoM in the $\mathbf{i}$ direction is

$$r_{CoM}^x = \frac{1}{\sigma \sqrt{2\pi}} e^{-\frac{x^2}{2\sigma^2}}$$

where σ is as above. Comparing this with the formula for the distribution of the velocity of individual particles in the x direction

$$p_{f_x}(v_x) = \frac{1}{\alpha \pi^{\frac{1}{2}}} e^{-\frac{v_x^2}{\alpha^2}}$$

we see that $\alpha = \sigma\sqrt{2}$ and thus that the mean speed of m_1 relative to the CoM is $\frac{2\alpha}{\sqrt{\pi}}$.

We need to reconcile this with the Maxwell formula for the square of the mean speed of m_1 relative to the CoM — to wit $\left(\frac{m_2^2}{(m_1 + m_2)^2} \right) (\bar{s}_1^2 + \bar{s}_2^2)$. We have

$$\frac{4\alpha^2}{\pi} = \frac{8\sigma^2}{\pi} = \frac{8}{\pi} \left(\frac{m_2}{m_1 + m_2} \right)^2 (\sigma_1^2 + \sigma_2^2)$$

Now we have the formulas to express the above in terms of the mean speeds

$$\sigma_1^2 = \frac{\alpha_1^2}{2} \quad \sigma_2^2 = \frac{\alpha_2^2}{2} \quad \bar{s}_1 = 2\alpha_1\pi^{-\frac{1}{2}} \quad \bar{s}_2 = 2\alpha_2\pi^{-\frac{1}{2}} \Rightarrow \alpha_1^2 = \frac{\pi\bar{s}_1^2}{4} \quad \alpha_2^2 = \frac{\pi\bar{s}_2^2}{4}$$

Thus as $\sigma_1^2 = \frac{\alpha_1^2}{2}$ and $\sigma_2^2 = \frac{\alpha_2^2}{2}$ we have

$$\left(\frac{2\alpha}{\sqrt{\pi}} \right)^2 = \frac{4\alpha^2}{\pi} = \frac{8\sigma^2}{\pi} = \frac{8}{\pi} \left(\frac{m_2}{m_1 + m_2} \right)^2 \left(\frac{\pi\bar{s}_1^2}{8} + \frac{\pi\bar{s}_2^2}{8} \right)$$

i.e.

$$\frac{4\alpha^2}{\pi} = \left(\frac{m_2}{m_1 + m_2} \right)^2 (\bar{s}_1^2 + \bar{s}_2^2)$$

in accordance with Maxwell.

0.1.8 Mean speed after one collision

The pre-collision velocity of m_1 relative to the CoM is

$$\mathbf{v}_1 - \frac{m_1 \mathbf{v}_1 + m_2 \mathbf{v}_2}{m_1 + m_2} = \frac{m_2(\mathbf{v}_1 - \mathbf{v}_2)}{m_1 + m_2} = \frac{m_2 \mathbf{v}_1}{m_1 + m_2} - \frac{m_2 \mathbf{v}_2}{m_1 + m_2}$$

If $\theta \leq 90^\circ$ is the angle of incidence that m_1 makes with the planr perpendicular to the line of centres at the moment of collision then this vector is reversed and rotated through 2θ by the collision and the rebound is coplanar with the incident vector and the line of centres. So the post collision velocity of m_1 relative to the CoM is

$$R_{2\theta} \left(\frac{m_2 \mathbf{v}_2}{m_1 + m_2} - \frac{m_2 \mathbf{v}_1}{m_1 + m_2} \right)$$

where $R_{2\theta}$ is a matrix representing the reversal of direction followed by a rotation. Therefore the post-collision velocity of m_1 in the original frame is

$$\frac{m_1 \mathbf{v}_1 + m_2 \mathbf{v}_2}{m_1 + m_2} + R_{2\theta} \left(\frac{m_2 \mathbf{v}_2}{m_1 + m_2} - \frac{m_2 \mathbf{v}_1}{m_1 + m_2} \right)$$

The main point to appreciate is that from a statistical point of view the operation $R_{2\theta}$ makes no difference and the statistics of the post-collision particles of a given type will be identical to the statistics of the pre-collision particles of the same type. Therefore we can do the statistical on the pre-collision velocity

$$\frac{m_1 \mathbf{v}_1 + m_2 \mathbf{v}_2}{m_1 + m_2} + \left(\frac{m_2 \mathbf{v}_2}{m_1 + m_2} - \frac{m_2 \mathbf{v}_1}{m_1 + m_2} \right)$$

The $\mathbf{i}$ component of this is

$$\frac{m_1 v_1^x + m_2 v_2^x}{m_1 + m_2} + \frac{m_2 v_2^x}{m_1 + m_2} - \frac{m_2 v_1^x}{m_1 + m_2}$$

As before we have a linear combination of normal distributions each with mean zero. Thus the distribution of the $\mathbf{i}$ component of the velocities of

Particles of mass m_1 which we shall write as p_{Oa}^x is

$$p_{Oa}^x \sim N \left[0, \left(\frac{m_1}{m_1 + m_2} \right)^2 \sigma_1^2 + \left(\frac{m_2}{m_1 + m_2} \right)^2 \sigma_2^2 + \left(\frac{m_2}{m_1 + m_2} \right)^2 \sigma_2^2 + \left(\frac{m_2}{m_1 + m_2} \right)^2 \sigma_1^2 \right]$$

and thus

$$p_{Oa}^x \sim N(0, \sigma^2)$$

where

$$\sigma^2 = \left(\frac{m_1}{m_1 + m_2} \right)^2 \sigma_1^2 + \left(\frac{m_2}{m_1 + m_2} \right)^2 \sigma_2^2 + \left(\frac{m_2}{m_1 + m_2} \right)^2 \sigma_2^2 + \left(\frac{m_2}{m_1 + m_2} \right)^2 \sigma_1^2$$

As before we have that the square of the mean speed is $\frac{8\sigma^2}{\pi}$ Thus we have

$$\frac{8\sigma^2}{\pi} = \frac{8}{\pi} \left(\left(\frac{m_1}{m_1 + m_2} \right)^2 \frac{\pi \bar{s}_1^2}{8} + \left(\frac{m_2}{m_1 + m_2} \right)^2 \frac{\pi \bar{s}_2^2}{8} + \left(\frac{m_2}{m_1 + m_2} \right)^2 \frac{\pi \bar{s}_2^2}{8} + \left(\frac{m_2}{m_1 + m_2} \right)^2 \frac{\pi \bar{s}_1^2}{8} \right)$$

which equals

$$\frac{1}{(m_1 + m_2)^2} (m_2^2(\bar{s}_1^2 + \bar{s}_2^2) + m_1^2 \bar{s}_1^2 + m_2^2 \bar{s}_2^2)$$

in accordance with Maxwell.

0.1.9 Individual Elastic Collisions

In Dourmashkin's *LibreText Mechanics* the basic facts about elastic collisions viewed from the centre of mass frame are proved. These are in the first two points below.

1. The total momentum is zero. (See proof below) This means that the two colliding particles (viewed as hard spheres) will approach each other along parallel (which may be one and the same) lines and after the collision will continue to move similarly. The post collision lines will not in general be parallel to the pre-collision lines but may be rotated through an angle called the scattering angle.

2. The collision does not change the speed of either particle.
3. When the gas is in equilibrium and two particles of different type collide all directions are equally likely and thus the mean angle between the directions as they approach collision is 90^0 . Hence OA and OB are drawn with lengths representing the mean speeds and at an angle of 90^0 . i.e. OA and OB are velocity vectors, say, $\mathbf{v}_1$ and $\mathbf{v}_2$ of sizes v_1 and v_2 . and $AB = \mathbf{v}_2 - \mathbf{v}_1$.
4. Letting $P = m_1$ and $Q = m_2$ then the mean velocity of the centre of mass is $\frac{m_1\mathbf{v}_1+m_2\mathbf{v}_2}{m_1+m_2}$. This is represented by OG where G divides AB in the ration $AG : GB = m_2 : m_1$ i.e. $AG = \frac{m_2}{m_1+m_2}\sqrt{v_1^2 + v_2^2}$ and $GB = \frac{m_1}{m_1+m_2}\sqrt{v_1^2 + v_2^2}$. The proof is immediate — $OG = OA + AG = \mathbf{v}_1 + \frac{m_2}{m_1+m_2}(\mathbf{v}_2 - \mathbf{v}_1) = \frac{m_1\mathbf{v}_1+m_2\mathbf{v}_2}{m_1+m_2}$.
5. Thus GA is the mean of the velocities of particles of mass m_1 relative to the centre of mass of the two colliding particles and GB that of particles of mass m_2 .
6. As a result of the collision we have the velocity of m_1 relative to G, Ga, being of the same size as GA but at a different direction and similarly for Gb and GB. Oa and Ob are thus the absolute velocities of m_1 and m_2 after the collisions.
7. Maxwell then says that aGB is at 90^0 to OG. This corresponds to Feynmann's assertion(Volume 1 Ch 39) that dot product of the relative velocity and the velocity of the CoM is on average zero except that Maxwell is applying this to velocitues after an impact..

The rest follows by geometry. The formula for OG follows from the application of the Cosine formula — $OG^2 = OA^2 + AG^2 - 2OA \times AG \times \cos O\hat{A}a$.. The value for $p' = Oa$ follows by Pythagoras applied to the right angled triangle

OGa using $Ga = AG$ and similarly for $q' = Ob$. Maxwell's final formula then follows by algebraic calculation from the formulas for p' and q' . The conclusion is that the typical collision between particles of different masses reduces the difference in the kinetic energies by factor $[(m_1 - m_2)/(m_1 + m_2)]^2$.

Theorem 0.1 *In any collision the total momentum, viewed in the centre of mass frame is 0.*

Proof

Let $m_1\mathbf{v}_1 + m_2\mathbf{v}_2$ be the total momentum in the laboratory frame. In the C.o.M. frame the total momentum becomes:

$$m_1 \left(\mathbf{v}_1 - \frac{m_1\mathbf{v}_1 + m_2\mathbf{v}_2}{m_1 + m_2} \right) + m_2 \left(\mathbf{v}_2 - \frac{m_1\mathbf{v}_1 + m_2\mathbf{v}_2}{m_1 + m_2} \right)$$

which simplifies to

$$\frac{m_1 m_2}{m_1 + m_2} (\mathbf{v}_1 - \mathbf{v}_2) + \frac{m_1 m_2}{m_1 + m_2} (\mathbf{v}_2 - \mathbf{v}_1) = 0$$

□

With further reference to Point (a) above let us consider two particles of mass m_1, m_2 with initial velocities along the x axis of $u_1 = 0$ and u_2 which elastically collide and have subsequent velocities v_1, v_2 . We have the equations

$$m_2 u_2 = m_1 v_1 + m_2 v_2 \quad : \quad m_2 u_2^2 = m_1 v_1^2 + m_2 v_2^2$$

Thus

$$v_1 = \frac{m_2(u_2 - v_2)}{m_1} \quad \& \quad m_2 u_2^2 = \frac{m_2^2(u_2 - v_2)^2}{m_1} + m_2 v_2^2$$

from which

$$m_1 m_2 u_2^2 = m_2^2(u_2^2 - 2u_2 v_2 + v_2^2) + m_1 m_2 v_2^2$$

Dividing by m_2 and simplifying we obtain

$$(m_1 - m_2)u_2^2 = (m_1 + m_2)v_2^2 - 2m_2 u_2 v_2$$

Solving the quadratic for v_2 we have

$$v_2 = \frac{1}{2(m_1 + m_2)} \left(2m_2 u_2 \pm \sqrt{4m_2^2 u_2^2 - 4(m_2^2 - m_1^2)u_2^2} \right)$$

which simplifies to (taking the minus sign as the correct one)

$$v_2 = \frac{u_2}{m_1 + m_2} \left(m_2 - \sqrt{m_2^2 - (m_2^2 - m_1^2)} \right)$$

Then from the above equation for v_1 we have

$$m_1 v_1 = m_2 u_2 - m_2 v_2 = m_2 u_2 - m_2 \left(\frac{u_2}{m_1 + m_2} \left(m_2 - \sqrt{m_2^2 - (m_2^2 - m_1^2)} \right) \right)$$

We can check that in the simple Newton's cradle case where $m_1 = m_2$ we have $v_1 = u_2$ and $v_2 = 0$ as expected.

The motion of the centre of mass is unaffected by the collision and it moves with velocity

$$\frac{m_2 u_2}{m_1 + m_2} = \frac{m_1 v_1 + m_2 v_2}{m_1 + m_2}$$

along the x axis. Thus the initial velocities u_1^G relative to the centre of mass are

$$u_1^G = -\frac{m_2 u_2}{m_1 + m_2} = -\frac{m_1 v_1 + m_2 v_2}{m_1 + m_2}$$

and of u_2^G is

$$u_2^G = \frac{m_1 u_2}{m_1 + m_2} = \frac{m_1(u_2 - v_1) + m_2(u_2 - v_2)}{m_1 + m_2}$$

Similarly v_1^G is given by

$$v_1^G = v_1 - \frac{m_2 u_2}{m_1 + m_2} = \frac{1}{m_1 + m_2} (m_1 v_1 + m_2(v_1 - u_2))$$

and v_2^G is given by

$$v_2^G = v_2 - \frac{m_2 u_2}{m_1 + m_2} = \frac{1}{m_1 + m_2} (m_1 v_2 + m_2(v_2 - u_2))$$

We now want to show that in magnitude $u_1^G = v_1^G$ and $u_2^G = v_2^G$ For the first of these we show that $v_1^G = -u_1^G$ i.e. ie.

$$\frac{m_2 u_2}{m_1 + m_2} = v_1 - \frac{m_2 u_2}{m_1 + m_2}$$

which, writing $m_1 v_1 = m_2 u_2 - m_2 v_2$ simplifies to

$$m_2 u_2 = m_2 u_2 - m_2 v_2 + m_2 v_1 - m_2 u_2 \Leftrightarrow u_2 = v_1 - v_2$$

i.e. the speed of separation = speed of approach which is well known to be true of elastic collisions. Similarly we show $v_2^G = -u_2^G$ i.e.

$$-\frac{m_1 u_2}{m_1 + m_2} = v_2 - \frac{m_2 u_2}{m_1 + m_2}$$

which simplifies to

$$m_2 u_2 = m_1 u_2 + m_1 v_2 + m_2 v_2$$

which, writing $u_2 = v_1 - v_2$ becomes

$$m_2 u_2 = m_1(v_1 - v_2) + m_1 v_2 + m_2 v_2 \Leftrightarrow m_2 u_2 = m_1 v_1 + m_2 v_2$$

as required. Here is a numerical example. Let a particle of mass 2 moving at speed 3 to the right collide with a stationary particle of mass 1. The centre of mass is thus moving to the right with speed $\frac{2 \times 3 + 1 \times 0}{3 + 1} = 2$. Thus, relative to the c.o.m. particle 1 is moving to the right at speed 1 and particle 2 to the left at speed 2. The equations for the collision are

$$6 = 2u_2 + v_2 \quad : \quad 18 = 2u_2^2 + v_2^2 \quad : \quad u_2 < v_2 \quad (0.1.1)$$

which has the solution $u_2 = 1, v_2 = 4$. Thus relative to the c. of m. the first particle is moving to the left with speed 1 and particle 2 to the right with speed 2 as expected. For the more general case where particle 2 is initially moving to the right at speed v , we just work in a frame where the 2nd particle is stationary. Thus if initially particle 1 is moving to the right with speed 3 + v , the c.o.m. with speed 2 + v and particle 2 with speed v then the relative speeds are exactly as before and we reach the same conclusion.

0.1.10 Mean time between collisions - B & B Chapter 8

The initial picture is that of a gas where all the molecules are of the same type. We consider one molecule to be moving with speed s_0 in some direction while all the rest are stationary. The molecule that is moving has a *collision cross sectional area* σ so that in time δt it traces out a cylinder of volume $\sigma \times s_0 \delta t$. If another molecule is in this cylinder then this represents the occurrence of a collision.

Let $P(t)$ = probability that no collision will occur between time = 0 and time = t . Therefore $1 - P(t)$ is the probability that there will be a collision in this time interval. We have

$$P(t + \delta t) = P(t) + \frac{dP}{dt} \delta t = P(t)(1 - n\sigma s_0 \delta t) \Rightarrow \frac{1}{P} \frac{dP}{dt} = -n\sigma s_0$$

where n is the number of molecules per unit volume. The second equation follows since, making an independence assumption, the probability of there being no collision up to $t + \delta t$ is the product of the probabilities of there being no collision up to time t i.e. $P(t)$ and the probability of there being no collision between t and $t + \delta t$. As the volume of the cylinder swept out in δt is $\sigma \delta t$ and as there are n molecules (considered as point masses) per unit volume and $\frac{1}{\sigma \delta t}$ little such cylinders in a unit volume, the chances of a collision are n in $\frac{1}{\sigma \delta t}$ i.e. a probability of $n \frac{1}{\sigma \delta t}$. The third equation is just a rearrangement. As $P(0) = 1$ we have

$$P(t) = e^{-n\sigma s_0 t}$$

The probability of a collision between t and $t + \delta t$ is thus

$$P(t) \times n\sigma s_0 \delta t = e^{-n\sigma s_0 t} n\sigma s_0 \delta t$$

Hence the mean time to collision is

$$\int_0^\infty t e^{-n\sigma s_0 t} n\sigma s_0 dt = \frac{1}{n\sigma s_0}$$

as the integral can be evaluated exactly. We still need to clarify the meaning of σ , If we view our moving molecule as a sphere of radius r_1 and the stationary molecules as having radius r_2 then the collision cylinder base has radius $r_1 + r_2$ so that the centre of a stationary molecule entering the cylinder corresponds to a collision. The assumption that the molecules are stationary (probably) does not make any difference as the molecules will still be randomly distributed throughout the volume.

We also need to clarify the meaning of s_0 here which has been constructed in a fictional way by supposing many molecules to be stationary. Instead of taking s_0 as the mean speed, we need to take it as the **the mean relative speed** which, as shown above, is $\sqrt{2}s$ where s is the mean speed. Thus we have

Mean time between collisions is $\frac{1}{n\sigma\sqrt{2}s}$ where s is the mean speed

0.1.11 The mean free path

The mean free path λ is stated (as if it were intuitively obvious) to be the product of the mean time between collisions and the mean speed.i.e.

$$\lambda = \frac{1}{n\sigma\sqrt{2}s} \times s = \frac{1}{n\sigma\sqrt{2}} \Rightarrow \frac{k_B T}{\sqrt{2}p\sigma}$$

since the pressure $p = nk_B T$ where k_B is Boltzmann's constant.