Appendix C

The Maxwell-Boltzmann distribution

In this section we will derive the probability density function (pdf) that describes the distribution of speeds of the molecules in a gas of a certain temperature, the famous Maxwell-Boltzmann distribution. Suppose we look at a molecule with mass m in a gas at temperature T and consider first only the x-component of its velocity, v_x. The value of v_x taken on by a given molecule at a given time will be the end result of a tremendous number of collisions, each of which changes its v_x by some random value. According to the *Central Limit Theorem*, a random variable that is the sum of a very large number of terms will follow a Gaussian distribution. The conditions for this to hold are fairly unrestrictive and satisfied to a high degree of accuracy in our problem, so the pdf for v_x is well modeled as a Gaussian. If we work in the centre-of-momentum frame of the gas (i.e., there is no wind), then the mean value $\langle v_x \rangle$ is zero, so the pdf of v_x is

$$f_x(v_x) = \frac{1}{\sqrt{2\pi}\sigma} e^{-v_x^2/2\sigma^2} \; . \tag{C.1}$$

By symmetry, the pdfs for the y and z components should have exactly the same form, i.e., we assume that there is no preferred direction. The parameter σ in (C.1) characterizes the width of the Gaussian pdf and we will show below that it is in fact equal to the standard deviation of the distribution. We do this by finding the mean value of v_x^2,

$$\langle v_x^2 \rangle = \int_{-\infty}^{\infty} v_x^2 f_x(v_x)\, dv_x = \int_{-\infty}^{\infty} \frac{v_x^2}{\sqrt{2\pi}\sigma} e^{-v_x^2/2\sigma^2}\, dv_x = \sigma^2 \; . \tag{C.2}$$

Thus the variance of the distribution, defined as $\langle v_x^2 \rangle - \langle v_x \rangle^2$ is equal to σ^2. The standard deviation, defined as the square root of the variance, is therefore equal to σ.

The speed v of a molecule is

$$v = \sqrt{v_x^2 + v_y^2 + v_z^2} \tag{C.3}$$

and by symmetry we have

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle \; , \tag{C.4}$$

and so therefore the mean value of v^2 is

$$\langle v^2 \rangle = 3\langle v_x^2 \rangle = 3\sigma^2 \ . \tag{C.5}$$

Now the Equipartition Theorem tells us that each quadratic term in the expression for the energy of a molecule contributes on average $kT/2$, where k is Boltzmann's constant and T is the temperature. Therefore we have

$$\tfrac{1}{2}m\left(\langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle\right) = 3\sigma^2 = \frac{3}{2}kT \tag{C.6}$$

or

$$\sigma = \sqrt{\frac{kT}{m}} \ . \tag{C.7}$$

It is reasonable to assume that the components of the velocity are *statistically independent*, i.e., a molecule's value of v_x has no influence on the probability to find a certain value for v_y, etc. If this is true, then the joint distribution for all three components of the velocity is simply the product of the individual pdfs. Using equation (C.1), this is found to be

$$f(v_x, v_y, v_z) = f_x(v_x) f_y(v_y) f_z(v_z) = \frac{1}{(2\pi)^{3/2}\sigma^3} e^{-(v_x^2+v_y^2+v_z^2)/2\sigma^2} = \frac{1}{(2\pi)^{3/2}\sigma^3} e^{-v^2/2\sigma^2} \ . \tag{C.8}$$

Using this we can find the probability to have the speed in an interval between v and $v + dv$ by integrating the joint probability density (C.8) over the infinitessimal volume in velocity space (i.e., axes v_x, v_y and v_z) where the speed is in the range $[v, v + dv]$. This volume is simply a spherical shell at "radius" v and with thickness dv. Furthermore, since the joint pdf (C.8) $f(v_x, v_y, v_z)$ in fact only depends on v, its integral over the shell is found by evaluating the integrand $f(v_x, v_y, v_z)$ at the speed v and multiplying by the volume of integration, which is the area of a sphere of radius v times the thickness of the shell dv:

$$f(v)\, dv = \frac{1}{(2\pi)^{3/2}\sigma^3} e^{-v^2/2\sigma^2}\, 4\pi v^2 dv = \sqrt{\frac{2}{\pi}} \frac{v^2}{\sigma^3} e^{-v^2/2\sigma^2}\, dv \ , \tag{C.9}$$

where as before $\sigma = \sqrt{kT/m}$ refers to the standard deviation of the velocity components. Equation (C.9) is the Maxwell-Boltzmann distribution. Its mode (most probable value) is at a speed $v_{\rm mode} = \sqrt{2kT/m}$, its mean is at $\langle v \rangle = \sqrt{8kT/\pi m}$, and its rms value is $v_{\rm rms} = \sqrt{3kT/m}$.