

### The Maxwell Velocity Distribution

The beginning of chapter 14 covers some things we've already discussed. Way back in lecture 6, we calculated the pressure for an ideal gas of non-interacting point particles by integrating over the velocity distribution. In lecture 5, we discovered the Maxwell velocity distribution for non-interacting point particles. In homework 2, you worked out some of the velocity moments for the Maxwell distribution and you also worked out the distribution of velocities of gas molecules emerging from a small hole in an oven. Rather than derive the earlier results again, we'll just summarize them here for convenient reference.

First, of all, let  $f(t, \mathbf{r}, \mathbf{v}) d^3\mathbf{r} d^3\mathbf{v}$  be the number of molecules with position vector in the small volume element  $d^3\mathbf{r}$  centered at position  $\mathbf{r}$  and velocity vector in the small velocity volume  $d^3\mathbf{v}$  centered at velocity  $\mathbf{v}$  at time  $t$ . The function  $f$  is the distribution function (usually, we've assumed it to be a function of the energy, but we're working up to bigger and better things!). When we have a Maxwell distribution,

$$f_{\text{Maxwell}}(t, \mathbf{r}, \mathbf{v}) = n \left( \frac{m}{2\pi\tau} \right)^{3/2} e^{-m(v_x^2 + v_y^2 + v_z^2)/2\tau},$$

where  $m$  is the molecular mass, and  $n$  is the concentration. The Maxwell distribution does not depend on  $t$  nor  $\mathbf{r}$ . Integrating  $d^3\mathbf{v}$  over all velocities produces  $n$ , and integrating  $d^3\mathbf{r}$  multiplies by the volume of the container, and we get  $N$ , the total number of particles. If we want the probability distribution for just the velocity components, we just leave off the  $n$  (and then we also don't consider it to be a function of  $\mathbf{r}$ ).

Sometimes, we want to know the probability distribution for the magnitude of the velocity. We change variables from  $v_x, v_y, v_z$  to  $v, \theta, \phi$ , and  $dv_x dv_y dv_z = v^2 dv \sin\theta d\theta d\phi$ . We integrate over the angles, pick up a factor of  $4\pi$ , and the probability distribution for  $v$  is

$$P(v) dv = 4\pi \left( \frac{m}{2\pi\tau} \right)^{3/2} e^{-mv^2/2\tau} v^2 dv.$$

With this distribution, one finds the most probable speed (peak of the probability distribution) is

$$v_{\text{mp}} = \sqrt{\frac{2\tau}{m}} = 1.414 \sqrt{\frac{\tau}{m}}.$$

The mean speed (denoted by  $\bar{c}$  by K&K) is

$$\bar{c} = \langle v \rangle = \sqrt{\frac{8\tau}{\pi m}} = 1.596 \sqrt{\frac{\tau}{m}}.$$

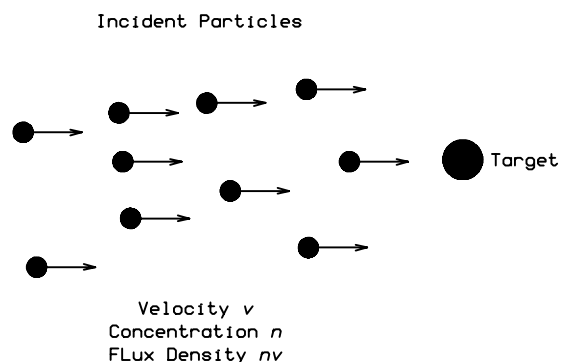
The root mean square speed (which appears in the energy) is

$$v_{\text{rms}} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3\tau}{m}} = 1.732 \sqrt{\frac{\tau}{m}}.$$

## Cross Sections

The next topic discussed in K&K is the mean free path. We're going to use this as an excuse to discuss cross sections and develop an expression for reaction rates based on cross sections and the Maxwell velocity distribution. The first thing we need to do is to see where a cross section comes from and what it means.

Consider a situation in which two particles can undergo some sort of interaction when they "collide." The interaction may be probabilistic; examples might be a nuclear or chemical reaction, an elastic scattering, or an inelastic scattering (which means one or both particles must be in an excited state after the interaction). Suppose one has a stationary target particle, and one shoots other particles at it with velocity  $v$ . The concentration of the incident particles (number per unit volume) is  $n$ . The flux density of incident particles, or the particle current, is the number crossing a unit area in a unit time and this is just  $nv$ . Note that this has the dimensions of number per unit area per unit time. Now the number of interactions per second must be proportional to  $nv$ . If we double the density, we have twice as many particles per second with a chance to interact. Similarly, if we double the velocity, particles arrive at twice the rate and we have twice as many particles per second with a chance to interact. Actually, the "strength" of the interaction may depend on the relative velocity, so it's not strictly true that the rate is proportional to  $v$ , but in a simple process, like the collision of hard spheres, it's certainly true. We take as a starting point that the interaction rate is proportional to the velocity, and effects having to do with the energy of the collision are included in the proportionality "constant."



The interaction rate is then

$$R = \sigma(v)nv,$$

where  $\sigma$  is **NOT** the entropy. Instead it's the proportionality constant and is called the *cross section*. We've explicitly shown that it might depend on  $v$ . There can be more complicated dependencies. For example, if the incident and target particles have spin, the cross section might depend on the spins of the particles as well as the relative velocity. The proportionality constant is called a cross section because it must have the dimensions of an area.  $R$  has the dimensions of a number (of interactions) per unit time, while  $nv$  has dimensions of number per unit area per unit time. The cross section can be thought of as an area that the target particle "holds up," perpendicular to the incoming beam. If an incident particle hits this area presented by the target, an interaction occurs.

Now some jargon. It's often the case that one considers a scattering, in which case the question asked is how many particles per second scatter into the solid angle  $d\Omega$  centered on

the direction  $(\theta, \phi)$ ? In this case, the number is proportional to  $d\Omega$ , and the proportionality constant is often written as a differential so the rate into  $d\Omega$  is

$$R(\rightarrow d\Omega) = \frac{d\sigma}{d\Omega} nv d\Omega,$$

where  $d\sigma/d\Omega$  is called the differential cross section. If one integrates over all solid angles to find the rate for all interactions (no matter what the scattering direction), one has

$$\sigma = \int \frac{d\sigma}{d\Omega} d\Omega,$$

and  $\sigma$  is called the total cross section in this case. Of course, a reaction (not just a scattering) may result in particles headed into a solid angle  $d\Omega$ , so reactions may also be described by differential and total cross sections.

If one knows the forces (the interaction) between the incident and target particles, one may calculate the cross sections. Cross sections may also be measured. One uses a target which has many target particles. One counts the scattered particles or the outgoing reactants using particle detectors. The total number of events is just  $Nnv\sigma(v)t$  where  $N$  is the number of target particles exposed to the incident beam and  $t$  is the duration of the experiment. This assumes that the chances of a single interaction are so small that the chances of interactions with two target particles are negligible. Of course, sometimes this isn't true and a multiple scattering correction must be deduced and applied. Sigh...

#### Example: Cross Section for Smooth Hard Sphere Elastic Scattering

As an example, we'll work out the differential cross section for smooth hard sphere scattering. You might say, what does this have to do with thermal physics? Answer: not much, but it's to motivate the use of the cross section as part of the next topic. We'll consider a stationary target and an incident particle with velocity  $v$ . Both particles are smooth hard spheres with radius  $a$  and mass  $m$ . (Think of billiard balls.) We assume the collision conserves the kinetic energy of motion. This is what's meant by an elastic collision. The momentum of the incident particle is  $\mathbf{p}_0$  before the collision and  $\mathbf{p}_1$  after the collision. The momentum of the target particle is  $\mathbf{p}_2$  after the collision. Conservation of momentum and energy tell us

$$\mathbf{p}_0 = \mathbf{p}_1 + \mathbf{p}_2, \quad \frac{1}{2m}p_0^2 = \frac{1}{2m}p_1^2 + \frac{1}{2m}p_2^2.$$

If we square the conservation of momentum equation, we have

$$p_0^2 = p_1^2 + 2\mathbf{p}_1 \cdot \mathbf{p}_2 + p_2^2.$$

If we compare with the conservation of energy equation, we conclude

$$\mathbf{p}_1 \cdot \mathbf{p}_2 = 0 ,$$

which means that either one of the particles is at rest after the collision or their momenta (and velocities) are perpendicular after the collision. I'm sure you knew this trick from Physics 103/5, right? Suppose the incident particle scatters at an angle  $\theta$  relative to its initial direction. The target particle must recoil at angle  $\theta - \pi/2$  from the initial direction of the incident particle. We have

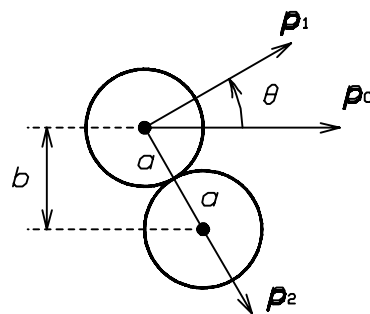
$$\begin{aligned} p_0 &= p_1 \cos \theta + p_2 \cos(\theta - \pi/2) , \\ 0 &= p_1 \sin \theta + p_2 \sin(\theta - \pi/2) , \end{aligned}$$

from which we conclude

$$p_1 = p_0 \cos \theta , \quad p_2 = p_0 \sin \theta .$$

So far, our analysis has proceeded very much as it would have in Physics 103/5. We've applied conservation of momentum and energy, but we've not completely "solved" the collision. We have expressed the final momenta in terms of the initial momentum (known) and an angle (unknown). This is typical for collision problems. Conservation of energy and momentum provides four constraints but there are six components of momentum to be determined. (In case you're wondering how come we have only one unknown,  $\theta$ , the plane in which the scattering occurs is also undetermined. That is, we don't know  $\phi$ , either!

To make further progress, we must examine the collision in more detail and specify the initial conditions more carefully. So we suppose that in the absence of a collision, the centers of the two spheres would pass within distance  $b$  of each other.  $b$  is called the *impact parameter*. The initial momentum points in the  $z$ -direction, as we've been assuming. Finally, the plane containing the initial momentum vector and the centers of the two spheres makes an angle  $\phi$  with respect to the  $x$ -axis. It's easy to see that the collision will be confined to this plane. Since we've assumed an elastic collision between smooth spheres, the incident particle can exert only a radial, not a tangential, force on the target particle. So we can calculate the angle at which the target particle recoils just from the geometry of the collision. Inspection of the diagram shows that



$$\sin(\pi/2 - \theta) = \frac{b}{2a} ,$$

which means

$$\cos \theta = \frac{b}{2a} , \quad \sin \theta = \sqrt{1 - \frac{b^2}{4a^2}} .$$

At this point, we've completely solved the collision. Given the initial momentum or velocity, the impact parameter, and the initial plane of the collision, we've determined the final plane (same as initial), the scattering and recoil angles, and all the final momentum components.

However, we still haven't figured out the cross section! We assumed specific values for  $\phi$  and  $b$ . But we usually don't have such control over the initial conditions. Instead we should assume that the impact parameter is in the range  $b \rightarrow b + db$  and the azimuthal angle is in the range  $\phi \rightarrow \phi + d\phi$ . Then the cross section is just the area that this implies,

$$d\sigma = b db d\phi.$$

However, it's customary to express the cross section in terms of  $\theta$  and  $\phi$  rather than  $b$  and  $\phi$ , since  $b$  cannot usually be measured, but  $\theta$  is relatively easy to measure (it's just the angle describing the location of the particle counter). From our previous expression relating  $b$  and  $\theta$ , we have

$$\sin^2 \theta = 1 - \frac{b^2}{4a^2}.$$

Differentiate,

$$2 \sin \theta \cos \theta d\theta = -2b db \frac{1}{4a^2},$$

so

$$b db = |4a^2 \cos \theta \sin \theta d\theta|,$$

where we don't care that increasing  $b$  means decreasing  $\theta$ , and

$$d\sigma = 4a^2 \cos \theta \sin \theta d\theta d\phi = 4a^2 \cos \theta d\Omega,$$

or

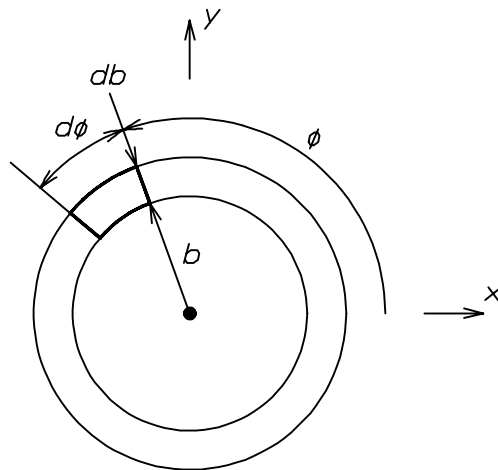
$$\frac{d\sigma}{d\Omega} = 4a^2 \cos \theta.$$

Note that  $\theta$  is confined to the range  $0 \leq \theta \leq \pi/2$ .

The total cross section is found by integrating the differential cross section over all allowed angles,

$$\sigma = \int_0^{\pi/2} \sin \theta d\theta \int_0^{2\pi} d\phi 4a^2 \cos \theta = 4\pi a^2.$$

This makes sense. If the center of the incident sphere passes within  $2a$  of the target sphere, there will be a collision. The area within  $2a$  of a point is  $4\pi a^2$ . We didn't really need to



do all this work to get the total cross section; in this case, we could have just written it down by inspection!

### Reaction Rates

Consider a gas composed of weakly interacting particles. We want the gas to be essentially an ideal gas and the distribution functions to be the Maxwell distribution functions. Suppose the gas contains two kinds of molecules with masses  $m_1$  and  $m_2$  and concentrations  $n_1$  and  $n_2$ . Suppose these two kinds of molecules, upon colliding, can undergo a reaction. The (total) cross section for this reaction is  $\sigma(v)$  where  $v$  is the relative velocity of the molecules. We want to calculate the rate at which the reaction occurs.

Consider a molecule of type 1 moving with velocity  $\mathbf{v}_1$ . The molecules of type 2 are coming from all directions with different velocities, so how do we calculate anything? We isolate a particular velocity and direction. Consider molecules with velocity  $\mathbf{v}_2$  in the range  $d^3\mathbf{v}_2$ . The concentration of such molecules is

$$f_2(\mathbf{v}_2) d^3\mathbf{v}_2 .$$

The relative velocity is  $v = |\mathbf{v}_2 - \mathbf{v}_1|$ , so the rate of interactions with our single target molecule is

$$dR = \sigma(v)v f_2(\mathbf{v}_2) d^3\mathbf{v}_2 .$$

We consider target molecules in a small volume  $d^3\mathbf{r}_1$  and with velocities in the range  $d^3\mathbf{v}_1$ . There are  $f_1(\mathbf{v}_1) d^3\mathbf{r}_1 d^3\mathbf{v}_1$  such molecules. The interaction rate for this number of target particles is

$$dR = \sigma(v)v f_1(\mathbf{v}_1) f_2(\mathbf{v}_2) d^3\mathbf{v}_1 d^3\mathbf{v}_2 d^3\mathbf{r}_1 .$$

A little thought shows that  $dR$  has the dimensions of inverse time.

To get the overall rate we need to integrate over all differentials. The integral over  $d^3\mathbf{r}_1$  just gives the volume of the container,  $V$ . The integrals over the velocity elements are a little trickier since the integrand includes a dependence on the relative velocity. We have

$$R = V n_1 n_2 \left( \frac{m_1}{2\pi\tau} \right)^{3/2} \left( \frac{m_2}{2\pi\tau} \right)^{3/2} \int d^3\mathbf{v}_1 \int d^3\mathbf{v}_2 \sigma(v) v e^{-m_1 v_1^2/2\tau} e^{-m_2 v_2^2/2\tau} .$$

We're going to change variables to the center of mass velocity and the relative velocity. The center of mass velocity is

$$\mathbf{u} = \frac{1}{M} (m_1 \mathbf{v}_1 + m_2 \mathbf{v}_2) ,$$

where  $M = m_1 + m_2$ . The relative velocity is

$$\mathbf{v} = \mathbf{v}_2 - \mathbf{v}_1 .$$

Expressing  $\mathbf{v}_2$  and  $\mathbf{v}_1$  in terms of  $\mathbf{u}$  and  $\mathbf{v}$ , we have

$$\mathbf{v}_2 = \frac{m_1}{M}\mathbf{v} + \mathbf{u} , \quad \mathbf{v}_1 = -\frac{m_2}{M}\mathbf{v} + \mathbf{u} .$$

The kinetic energy can be expressed as

$$E = \frac{1}{2}m_1v_1^2 + \frac{1}{2}m_2v_2^2 = \frac{1}{2}\frac{m_1m_2}{M}v^2 + \frac{1}{2}Mu^2 = \frac{1}{2}\mu v^2 + \frac{1}{2}Mu^2 ,$$

where

$$\mu = \frac{m_1m_2}{m_1 + m_2} ,$$

is called the reduced mass. We've already used  $\mu$  for a number of things—chemical potential, magnetic moment, mobility—oh well. The Jacobian of the transformation is unity, so

$$R = Vn_1n_2 \left[ \left( \frac{M}{2\pi\tau} \right)^{3/2} \int e^{-Mu^2/2\tau} d^3\mathbf{u} \right] \left[ \left( \frac{\mu}{2\pi\tau} \right)^{3/2} \int \sigma(v)ve^{-\mu v^2/2\tau} d^3\mathbf{v} \right] .$$

We started with an integral written for a pair of particles. We've now rewritten the integral in terms of the center of mass motion and the motion relative to the center of mass. The collision occurs in the relative motion! The integral over the center of mass motion gives unity and finally, the rate per unit volume is

$$r = \frac{R}{V} = n_1n_2 \left( \frac{\mu}{2\pi\tau} \right)^{3/2} \int \sigma(v)ve^{-\mu v^2/2\tau} d^3\mathbf{v} .$$

This expression is generally applicable whenever the gas can be described by a classical Maxwell Boltzmann distribution and the reaction rate is slow enough that the gas is always essentially in thermal equilibrium and the Maxwell Boltzmann distribution applies. For example, expressions like the above are used to calculate the nuclear reaction rates in the Sun when computing a numerical model of the Sun.

If particles of types 1 and 2 are in fact the same, then  $\mu = m/2$ ,  $n_1 = n_2 = n$ , and we need a double counting correction of  $1/2$ ,

$$r = \frac{1}{2}n^2 \left( \frac{m}{4\pi\tau} \right)^{3/2} \int \sigma(v)ve^{-mv^2/4\tau} d^3\mathbf{v} .$$

Usually,  $\sigma$  depends only on the magnitude of  $v$ , so we can integrate over the angles and

$$r = 2\pi n^2 \left( \frac{m}{4\pi\tau} \right)^{3/2} \int \sigma(v)v^3 e^{-mv^2/4\tau} dv .$$

## The Collision Rate and the Mean Free Path

We can use the expression we've just derived to calculate the collision rate among molecules in a gas. We assume the molecules are hard spheres of radius  $d/2$ . We ignore the correction to the concentration (as in the van der Waals equation of state). As we worked out earlier, the total cross section for a collision is  $\pi d^2$ , so the collision rate is

$$r = 2\pi^2 d^2 n^2 \left(\frac{m}{4\pi\tau}\right)^{3/2} \int v^3 e^{-mv^2/4\tau} dv.$$

This integral is straightforward and the result is

$$r = n^2 d^2 \sqrt{\frac{4\pi\tau}{m}}.$$

This is the number of collisions per unit time per unit volume. Now we want to convert this into the number of collisions per unit time per particle. A unit volume contains  $n$  particles, so we need to divide by  $n$ . In addition, each collision involves two molecules, so we need to multiply by 2. The rate per molecule is

$$r_1 = nd^2 \sqrt{\frac{16\pi\tau}{m}}.$$

All the factors in this expression make sense. The bigger the concentration, the higher the collision rate; the larger the cross sectional area of a molecule, the higher the collision rate; the faster the molecular speed ( $\sqrt{\tau/m}$ ), the higher the collision rate. Except for the numerical factor of  $\sqrt{16\pi}$ , we could have written down this expression just from dimensional analysis.

The mean time between collisions is  $1/r_1$ . If we assume that between collisions a particle typically moves with the average speed, we can get an estimate of the typical distance a particle moves between collisions. This is called the mean free path,

$$\ell = \frac{\bar{c}}{r_1} = \sqrt{\frac{8\tau}{\pi m}} \bigg/ nd^2 \sqrt{\frac{16\pi\tau}{m}} = \frac{1}{\sqrt{2}n\pi d^2}.$$

You will notice that this expression differs by  $\sqrt{2}$  from the expression given in K&K, and derived by a completely different method. The method used by K&K is to imagine a particle sweeping out a cylinder of base area  $\pi d^2$  as it travels. If another particle in the gas has its center within this cylinder, then the first particle will collide with it. As the height of the cylinder grows, the chance that another particle is in the cylinder grows. When the height of the cylinder is such that there's one particle (on average) within the cylinder, declare that a collision has occurred and the height of the cylinder is the mean free path. In other words,

$$n\pi d^2 \ell_{\text{K\&K}} = 1, \quad \text{or} \quad \ell_{\text{K\&K}} = \frac{1}{n\pi d^2}.$$

In actual fact, neither method is completely kosher! Our discussion of the collision rate is legitimate (within the assumptions of hard sphere molecules), but dividing the average rate into the average velocity is not strictly legal since the average of a ratio is not the same as the ratio of the averages. The K&K method ignores the relative velocities of the molecules. Why is this important? The simple argument applies to a fast moving molecule. On the average, it will run into another molecule after going a distance  $\ell_{\text{K\&K}}$ . But a slow moving molecule (consider the limit of a molecule that happens to be at rest) will more than likely be hit by another molecule in the gas before it has a chance to move  $\ell_{\text{K\&K}}$ . Averaging over both slow and fast molecules, the mean free path will be shorter than  $\ell_{\text{K\&K}}$ .

At this point, it's useful to plug in some numbers just to get a feel for the collision rate and the mean free path. We consider a neon atom which has a diameter of about 2 Å. The mass of neon is about 20.2 atomic mass units. We assume it's an ideal gas and evaluate the concentration at 0°C and one atmosphere. Under these conditions, one mole occupies 22.4 liters, and the concentration is

$$n_0 = \frac{N_0}{V} = 2.69 \times 10^{19} \text{ molecules cm}^{-3},$$

also known as *Loschmidt's number*. The mean free path is

$$\ell = \frac{1}{\sqrt{2}n\pi d^2} = 2.10 \times 10^{-5} \text{ cm},$$

about 1000 times the atomic diameter. The mean speed is

$$\bar{c} = \sqrt{\frac{8kT}{\pi m}} = 5.35 \times 10^4 \text{ cm s}^{-1}.$$

The collision rate per atom is

$$r_1 = \frac{\bar{c}}{\ell} = 2.55 \times 10^9 \text{ collisions s}^{-1}.$$

An interesting thing happens in a vacuum. Since the mean free path and the collision rate are inversely proportional to and proportional to the concentration (density), lowering the density increases the mean free path and lowers the collision rate. Just as an example, consider a "vacuum" of  $10^{-6}$  atmospheric pressure (not a particularly good vacuum). The collision rate drops to about 2550 times per second and the mean free path rises to about 21 cm. This is a macroscopic length! It's comparable to the size of laboratory equipment. In good vacuums, the residual gas interacts more with the container than with other gas molecules.