## Chapter 1

# Kinetic Theory of Gas

In your study of classical thermodynamics so far, you have been taught the *macrophysics* of thermodynamic sysytems, by which I mean the system is described by *macrostate* properties like temperature T, pressure p, entropy S etc. On the other hand, a system is made up of a lot of little things, e.g. oxygen gas is made up of many tiny di-atomic oxygen molecules. Suppose we know the physics that govern the behaviour of oxygen molecules, i.e. we know its *microphysics*, then in principle we can try to derive the *macroscopic* properties of the gas from solving all the equations of the gas molecules. Given that a mole of gas has  $6.23 \times 10^{23}$  molecules, this is obviously a dauntingly nigh impossible task.

All is not hopeless however. Even if we cannot solve all the equations to precision, in most cases, we *don't really need to*. Indeed, all we need to do is to understand the *statistical* properties of the gas, and from there, we can derive its macroscopic properties. This endeavour is known as **statistical mechanics**, and will be the subject of your 3rd year module 6CCP3212 Statistical Mechanics.

## 1.1 Billiard ball model of gas

In this last section of your Thermal Physics module, we will study a pre-cursor model of the microphysics of gas in which the gas particles are treated as tiny little billiard balls. This theory is called the **Kinetic Theory of Gas**, which was originated by **Daniel Bernoulli** in the late 18th century, but refined over the centuries. While much of its utility as microphysical description of thermal systems has been superseded by statistical mechanics, it is still an extremely useful tool in the modern context (e.g. as a way to understand non-equilibrium thermodynamics).

For the moment, we will make the following assumptions about the gas

- The particles' sizes are much smaller than the average separation. This means that the gas rarely collide into each other. Note that in real life, molecules can and do interact with each other without having to bump with each other (e.g. through Van de Waals' forces).
- When they do collide with each other, they can exchange energy, but in such a way that the whole system remain in equilibrium.
- We will ignore all other forms of energies of the particles, including rotation and vibration. So all the internal energy of the gas is held up in the kinetic energy of all the particles, such that

$$U = \sum_{i=1}^{i=N} \frac{1}{2} m \mathbf{v}_i^2 , \qquad (1.1)$$

where m is the mass of the particles and i labels each individual particle.

#### 1.1.1 The Maxwell-Boltzmann Distribution

Obviously N is a very big number of (e.g.  $\sim 10^{23}$  for a mole), so literally calculating the sum Eq. (1.1) is a fool's errand. However, when the gas is in equilibrium at some temperature T, its **distribution** can be exactly calculated as it turns out. What we mean by that is that while we do not know exactly the velocities (and hence energies) of each particle, we know the probabilities. We define the **velocity distribution**  $g(v_x)dv_x$  to be the fraction of particles with their velocity in the x direction between  $v_x$  and  $v_x + dv_x$ . This is given by the formula

$$g(v_x) = \sqrt{\frac{m}{2\pi k_b T}} e^{-mv_x^2/2k_b T} , \qquad (1.2)$$

where  $k_b$  is the Boltzmann constant as usual. The factor  $e^{-E/k_bT}$  (here *E* is simply the kinetic energy of the particle in the *x* direction) is often called the **Boltzmann Factor**, who first derived this distribution. Unfortunately, you will have to wait until your 3rd year module Statistical Mechanics to learn how this is derived.

The distribution is **normalized** to unity, i.e.

$$\int_{-\infty}^{\infty} g(v_x) dv_x = 1 , \qquad (1.3)$$

which makes sense since the sum over all the probabilities must be 1. To do the integral Eq. (1.3), we note that it has the form of a **Gaussian integral** 

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}} , \qquad (1.4)$$

for real  $a \neq 0$ . Using Eq. (1.4), Eq. (1.3) is immediately obtained.

Notice that  $g(v_x) \to 0$  when  $v_x$  approaches either  $\infty$  or  $-\infty$ : intuitively, we expect that for any gas in equilibrium, high speed particles are an exception instead of a norm. The eagle eye amongst you will protest that particles cannot travel faster than the speed of light c, and you will be right. But the argument holds as long as  $|E| \gg k_b T$ , in other words as long as the absolute value of the kinetic energy of the particle is much more than a characteristic energy determined by the temperature T of the system – the higher the temperature T, the more likely we can find a very fast particle (unsurprisingly).

In the other limit, when  $v_x \to 0$ ,  $g(v_x)$  will be maximum. This suggests that, at least in 1 dimension, the most likely velocity of a particle of a gas in equilibrium is basically 0, lazy burns them [1].

However, we don't live in a 1D world, we live in a 3D world. For each direction, there exist an identical distribution  $g(v_y)$  and  $g(v_z)$ . The probability of finding a particle between the "velocity volume"  $(v_x + dv_x, v_y + dv_y, v_z + dv_z)$  is then

$$g(v_x)dv_xg(v_y)dv_yg(v_z)dv_z = \left(\frac{m}{2\pi k_b T}\right)^{3/2} e^{-m(v_x^2 + v_y^2 + v_z^2)/2k_b T} dv_x dv_y dv_z .$$
(1.5)

But  $v_x^2 + v_y^2 + v_z^2 = \mathbf{v}^2 \equiv v^2$ , is simply the square of the **speed** of each particle, so we can define

$$F(v) \equiv \left(\frac{m}{2\pi k_b T}\right)^{3/2} e^{-mv^2/2k_b T} .$$
 (1.6)

This distribution is normalized via  $\int_{-\infty}^{\infty} F(v) dv_x dv_y dv_z = 1$ . You can chec : since the exponentials factor, i.e.  $\exp[-mv^2/(2k_bT)] = \exp[-mv^2_x/(2k_bT)] \exp[-mv^2_y/(2k_bT)] \exp[-mv^2_z/(2k_bT)]$ , this integral is actually very easy to do – it is just 3 separate Gaussian integrals. (Try it!)

<sup>&</sup>lt;sup>1</sup>While this is a joke, it is not actually farfetched – dynamics tell us that things want to be at their *lowest energy state*, all things being equal.

However, in general we are interested in the *speed* v instead of individual velocites. So, instead of doing 3 integrals, we "change coordinates" (akin to how we change Cartesian to spherical coordinates) via

$$v = \sqrt{v_x^2 + v_y^2 + v_z^2} , \ v_z = v \cos\theta , v_x = v \sin\theta \cos\phi , v_y = v \sin\theta \sin\phi ,$$
(1.7)

with the domain  $v = [0, \infty), \theta = [0, \pi)$ , and  $\phi = [0, 2\pi)$ . In these coordinates, the integral becomes

$$\int_{-\infty}^{\infty} dv_x \int_{-\infty}^{\infty} dv_y \int_{-\infty}^{\infty} dv_z \ F(v) = \int_0^{\infty} v^2 F(v) dv \int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} d\phi \quad . \tag{1.8}$$

Since F(v) does not depend on  $\phi$  and  $\theta$ , the angle integrals can be immediately completed  $\int d\phi \sin \theta d\theta = 4\pi$ , leaving us with

$$\int_{0}^{\infty} \sqrt{\frac{2}{\pi}} \left(\frac{m}{k_b T}\right)^{3/2} v^2 e^{-mv^2/2k_b T} dv = 1.$$
(1.9)

This defines a speed distribution

$$f(v)dv \equiv \sqrt{\frac{2}{\pi}} \left(\frac{m}{k_b T}\right)^{3/2} v^2 e^{-mv^2/2k_b T} dv , \qquad (1.10)$$

which is now known as the Maxwell-Boltzmann Distribution. Don't be alarmed by the presence of dv on both sides of the equation – it is simply there to remind you that f(v) is a *distribution* and to compute actual probabilities, one need to do an integration.



Figure 1.1: The Maxwell-Boltzmann distribution.



Figure 1.2: A speed selector. Gas particles are channeled into a rotating helical grooved drum. By varying the rotation speed, we can selectively extract particles of fixed speed. The particle detector count the number of particles. Figures stolen from tecscience.com

Notice that since v > 0 is now semi-positive definite (unlike e.g.  $v_x$ ), the peak of the distribution is no longer at 0. To find  $v_{max}$ , simply take derivative df/dv = 0, and we get

$$v_{max} = \frac{2k_b T}{m} . \tag{1.11}$$

This means that if you make a random drawing of a particle from the gas, the most *likely* speed is  $v_{max}$ .

Here it is worth looking at how one might do the integral Eq. (1.9) to check that it does result in unity. As you will soon see below, integrals of the kind  $\int_0^\infty x^n e^{-ax^2} dx$  for some integer  $n \ge 0$  occurs frequently in thermal physics and statistical mechanics, so let's get some practice in. Defining  $a \equiv -m/2k_bT$ , Eq. (1.9) then has the form

$$\int_0^\infty v^2 e^{-av^2} dv = \sqrt{\frac{\pi}{2}} \left(\frac{k_b T}{m}\right) . \tag{1.12}$$

We want integrate the LHS to prove that it is equal to the RHS. When confronted with integrals like these, the key goal is to integrate by parts until you get the integrand to be of the form  $ve^{-av^2}$  or  $e^{-av^2}$ . For the former,

$$\int_{0}^{\infty} v e^{-av^{2}} dv = -\frac{1}{2a} e^{-av^{2}} + \text{const} , \qquad (1.13)$$

so that's clear, which we have again used the Gaussian integral Eq. (1.4). The eagle eye amongst you will point out that the integral Eq. (1.8) has the limits  $(0, \infty)$  instead of  $(-\infty, \infty)$ . But since the argument in the integral is  $x^2$ , hence

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \int_{-\infty}^{0} e^{-ax^2} dx + \int_{0}^{\infty} e^{-ax^2} dx = 2 \int_{0}^{\infty} e^{-ax^2} dx , \qquad (1.14)$$

 $\mathbf{so}$ 

$$\int_{0}^{\infty} e^{-ax^{2}} dx = \frac{1}{2} \sqrt{\frac{\pi}{a}} .$$
 (1.15)

You should commit both Eq. (1.4) and Eq. (1.15) to memory.

Given these, then integrating by part Eq. (1.12)

$$\int_{0}^{\infty} v^{2} e^{-av^{2}} dv = \int_{v=0}^{v=\infty} d\left(-\frac{v}{2a}e^{-av^{2}}\right) + \int_{0}^{\infty} \frac{1}{2a}e^{-av^{2}} dv$$
$$= 0 + \frac{1}{4a}\sqrt{\frac{\pi}{a}}$$
$$= \sqrt{\frac{\pi}{2}} \left(\frac{k_{b}T}{m}\right)^{3/2}, \qquad (1.16)$$

as required. Note that the first ("boundary") term vanishes in the limits of the integral 0 and  $\infty$ .

The power of a distribution comes from it enabling us to compute *expectation values* of any quantity X

$$\langle X \rangle \equiv \int_0^\infty X f(v) dv \ . \tag{1.17}$$

For example, the *expectation value* of the velocity  $\langle v \rangle$  is

$$\langle v \rangle \equiv \int_0^\infty v f(v) dv = \sqrt{\frac{8k_b T}{\pi m}} ,$$
 (1.18)

which you will be asked to demonstrate in a homework problem.  $\langle v \rangle$  of course, is also known as the **mean** or **average** of the distribution – this is what you get when you make a large number of random drawings from the distribution, and then compute the average.

What is the expectation value some other quantities which are not functions of v, say  $\langle v_x^2 \rangle$ ? To do that, we need to "unpack" Eq. (1.17) where we have integrated away the angle information

$$4\pi = \int_0^\pi \int_0^{2\pi} \sin\theta \ d\theta d\phi , \qquad (1.19)$$

so restoring the angles integration

$$\langle X \rangle = \frac{1}{4\pi} \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \int_0^\infty X f(v) dv . \qquad (1.20)$$

Using Eq. (1.20), you can show that  $\langle v_x \rangle = 0$  (as you will in a homework problem). This is completely expected – the gas on its own is not moving, so one would expect its mean to be zero  $\langle v_x \rangle = \langle v_y \rangle = \langle v_z \rangle = 0$ .

#### 1.1.2 Equipartition Theorem

In another homework problem, you can also use the distribution to compute the expectation value of the energy per particle  $\langle U \rangle$ 

$$\langle U \rangle = \frac{1}{2} m \langle v^2 \rangle$$

$$= \frac{1}{2} m \int_0^\infty dv \ v^2 f(v) e^{-mv^2/2k_b T}$$

$$= \frac{3k_b T}{2} .$$

$$(1.21)$$

This calculation also gives us  $\sqrt{\langle v^2 \rangle} \equiv v_{rms} = \sqrt{3k_bT/m}$  which is the **root mean squared** of the velocity. Note that  $v_{max} < \langle v \rangle < v_{rms}$ . To "see" the distribution, we can do this using a "speed selector" (Fig. (1.2)).

Notice that the Maxwell-Boltzmann distribution is a function of speed v, not velocities – this means that the particles in the distribution has no preferred direction. In other words, if we randomly draw a particle from the distribution, its velocity is equally likely in all the directions. This suggest that the energy E is "carried equally" by the kinetic energy of the particles in the 3 spatial dimensions  $v_x$ ,  $v_y$  and  $v_z$ , i.e.

$$U \stackrel{?}{=} \frac{1}{2}m\langle v_x^2 \rangle + \frac{1}{2}m\langle v_y^2 \rangle + \frac{1}{2}m\langle v_z^2 \rangle , \qquad (1.22)$$

i.e. the kinetic energy is in **equipartition** in the 3 possible directions. Turns out that Eq. (1.22) is actually true, i.e. that each **translational degree of freedom** carry on average an energy  $k_b T/2$  per particle. This is called the **Equipartition Theorem**. To explicitly prove that  $\langle mv_x^2/2 \rangle = \langle mv_y^2/2 \rangle =$  $\langle mv_z^2/2 \rangle = \langle k_b T/2 \rangle$ , we substitute  $v_x$  (or  $v_y$  or  $v_z$ ) into the expectation value formula Eq. (1.20)

$$\langle v_x^2 \rangle = \frac{1}{4\pi} \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \int_0^\infty (v\cos\theta\sin\phi)^2 f(v)dv$$
(1.23)

and brute force compute (which you will do in a homework problem). More elegantly, one can simply argue that since there is no preferred direction in the distribution, the energy  $U = 3k_bT/2$  must be divided equally between all 3 directions.

Indeed, this is a very general theorem that goes beyond translational degrees of freedom. In a point particle, rotation and vibration degrees of freedom do not exist. However, if one consider a di-atomic particle, then it has both rotational and vibrational degrees of freedom, and it can be shown that each such degree of freedom carry an average of  $k_b T/2$  energy per particle. So a diatomic particle has 7 degrees of freedom (3 translation, 3 rotations and 1 vibration), would have  $7k_b T/2$  energy per particle<sup>2</sup>

Can this be measured? Turns out that you can! Recall that the heat capacity for fixed volume is given by  $C_V = (\partial U/\partial T)_V$ , then for a diatomic gas with particle number N, one would expect  $C_V/N = 7k_b/2$ . When we does this measurement however, we see something weird in Fig. 1.3. The reason for this is that

<sup>&</sup>lt;sup>2</sup>As it turns out, not all degrees of freedom has  $k_bT/2$  energy – and the equipartition theorem does not hold always. We will discuss this more general theorem when we derive the general formula for partitions of energy in your next module 6CCP3212 Statistical Mechanics.

quantum effects must be taken account of – you will study this, and the derivation of the Equipartition theorem when you take the next module 6CCP3212 Statistical Mechanics.



Figure 1.3: The heat capacity  $C_V$  of a diatomic gas as a function of temperature. Instead of the classically predicted  $C_V = (7/2)k_b$ ,  $C_V$  stays constant at  $(3/2)k_b$  at low temperatures, until some fixed temperature  $T_{\rm rot}$  where it jumps to  $(5/2)k_b$ . It stay at that value until  $T_{\rm vib}$  is reached, where it then jumps to the predicted value of  $(7/2)k_b$ . (Figure stolen from Wikipedia.)

## 1.2 Collisions

Particles zipping around in a box will undergo two kind of collisions : with one another and with the walls of the box. In general, collisions can be elastic (no loss of energy) or inelastic – as we discussed earlier, for now we will assume that all collisions are elastic and thus both energy and momentum are conserved in the collision.

#### 1.2.1 Pressure and the Ideal Gas Law

What is pressure? Consider a gas in equilibrium at temperature T in a box, but with door held in place by a spring. Intuitively, one can imagine the particles of the gas hitting the door, pushing it open only to be held back by the tension in the spring. If one heats up the gas, the on average according to the Maxwell-Boltzmann distribution, the mean speed of the particles would increase, and at some point the gas will be so hot as to push the door open and escape. Thus, an operational definition of "pressure" would be *momentum imparted on the container by particles colliding on it.* Let's see how we can derive a term for the pressure of a gas given its temperature T.

To compute this momentum exchange, consider a small area A of the box. We want to know the **rate** of particles collide with the area A as a function of **collision angle** – the latter is important since the *momentum* change on the wall due to the collision of a particle of mass m and velocity v at angle  $\theta$  is given by

$$\Delta p = 2mv\cos\theta \,\,, \tag{1.24}$$

where the 2 comes from the fact that collision is elastic – in the limit when  $\theta = 0$  (i.e. head on collision),

the velocity of the particle goes from  $\mathbf{v}$  to  $-\mathbf{v}$  (see Fig. 1.4.) The total pressure is then the sum over all the collisions.



Figure 1.4: A particle bounces off elastically off the wall imparts a momentum of  $2mv\cos\theta$ .

To take into account angles, let's review some basic facts about angles and solid angles. Recall that an angle  $\theta$  is defined by the ratio of the arc length s with its radius r, i.e.  $\theta \equiv s/r$ . Here,  $\theta$  is measured in **radians** as you will recall, such that if s is the entire circle, i.e.  $s = 2\pi$ , then  $\theta = 2\pi r/r = 2\pi$ , which is to say that  $\theta = [0, 2\pi)$ .

Equivalently, one can ask what if instead of arc length s, one has an "arc area" A. We can define a solid angle

$$\Omega \equiv \frac{A}{r^2} , \qquad (1.25)$$

where we have used  $r^2$  instead of r to ensure that  $\Omega$  is dimensionless. The (dimensionless) name for the "unit" of  $\Omega$  is called **steradians** (although like radians, it is simply a matter of definition). Equally, if A is the entire spherical surface, i.e.  $A = 4\pi r^2$ , then  $\Omega = 4\pi$ , and thus  $\Omega = [0, 4\pi)$ .



Figure 1.5: Angles and Solid Angles.

Consider an infinitisimal solid angle element  $d\Omega$ , we want to ask how many particles are colliding with  $d\Omega$  at any time t. Now particles in a gas in general do not have a preferred direction – there is equal likelihood for each particle to move in any of the  $4\pi$  solid angle directions. (Otherwise, the bulk of the gas will be in motion.) Hence, the *fraction* of particles that will collide with  $d\Omega$  must be

$$\frac{d\Omega}{4\pi} = \frac{r^2 d\Omega}{4\pi r^2} , \qquad (1.26)$$

where we have multiplied both the numerator and denominator by  $r^2$  to make explicit the fact that  $r^2 d\Omega$ is the infinitisimal area on the sphere of radius r subtended by a solid angle  $d\Omega$ . From your first year math class, this must be equal to (see Fig 1.6)

$$r^2 d\Omega = 2\pi r^2 \sin\theta d\theta \ , \ . \tag{1.27}$$

or

$$\frac{d\Omega}{4\pi} = \frac{1}{2}\sin\theta d\theta \ . \tag{1.28}$$

Since the particles have no preferred direction, the fraction of particles between v and v + dv moving through the solid angle  $d\Omega$  must then be the Maxwell-Boltzmann distribution multiply by  $d\Omega$ , i.e.

fraction = 
$$f(v)dv\frac{d\Omega}{4\pi} = f(v)dv\frac{1}{2}\sin\theta d\theta$$
. (1.29)

You can check that Eq. (1.29) makes sense by integrating it over  $\theta$  and v to get 1 as expected (i.e. all the particles pass through the surface at some point.)



Figure 1.6: An infinitisimal element of solid angle  $d\Omega$  defined.

Next, we want to find the *rate* of particles colliding with some area dA of the wall, at an angle  $\theta$  to it. In an infinitisimal amount of time dt, the volume swept out by particles of velocity v at angle  $\theta$  is  $v \cos \theta dA dt$ . Hence, the number of particles between v and v + dv hitting the wall area dA per unit time dt at angle  $\theta$  is given by

$$n \times v \cos \theta f(v) dv \times \text{fraction} = n \times v \cos \theta f(v) dv \times \frac{1}{2} \sin \theta d\theta dA dt , \qquad (1.30)$$

where n = N/V is the number density. The rate per unit area per unit angle between v and v + dv is then

$$\Gamma(v,\theta) = nv\cos\theta f(v)dv\frac{1}{2}\sin\theta d\theta . \qquad (1.31)$$

With this equation Eq. (1.31) in hand, the momentum exchange, which we call Pressure p, is then the sum over all the particles colliding on all the angles, i.e.

$$p = \int_{0}^{\infty} dv \int_{0}^{\pi/2} d\theta \underbrace{\Delta p}_{\text{mom exchange per coll}} \times \underbrace{\Gamma(v,\theta)}_{\text{rate}}$$
$$= n \int_{0}^{\infty} dv \int_{0}^{\pi/2} d\theta (2mv \cos \theta) \times v \cos \theta f(v) \frac{1}{2} \sin \theta$$
$$= n \underbrace{\int_{0}^{\pi/2} d\theta \, \cos^{2} \theta \sin \theta}_{1/3} \underbrace{\left(\int_{0}^{\infty} dv v^{2} f(v)\right)}_{\langle v^{2} \rangle}$$
(1.32)

which is, using n = N/V where V is the total volume and N is the total number of particles

$$P = \frac{1}{3} \frac{N}{V} m \langle v^2 \rangle .$$
(1.33)

But from Eq. (1.21), we replace  $\langle v^2 \rangle = 3k_b T/m$ , to finally get

$$PV = Nk_bT av{1.34}$$

which is the famous Ideal Gas Equation of State.

Notice that in Eq. (1.34), the mass of the particles does not appear – it doesn't matter how massive the particles is, the pressure only depends on the number density N/V and the temperature T. This might seem counter-intuitive – if the particle is more massive, surely this means for fixed v it carries more momentum mv? The key to resolving this paradox is to realize that the pressure depends not just on T, but on  $k_bT$ , i.e. it depends on the *energy* of the particle, not on the velocity nor mass. Hence a more massive particle would require more energy to bring it to a higher temperature. So for a given T, the momentum exchange is the same.

#### 1.2.2 Dalton's Law

Suppose we have a mixture, i.e. a gas containing two or more different species of particles, in the same box with volume V and at the same temperature T. Labeling the species by i, then the number of particles per species is  $N_1, N_2, \ldots, N_i$ . Supposing that the species do not interact with each other, then as far as each species is concerned, they individually behave like a gas of  $N_i$  particles in a volume V. Assuming that each of them obey the Ideal Gas Law, then the pressure for each species is

$$P_i = \frac{N_i}{V} k_b T . aga{1.35}$$

The total pressure on the box is then the sum

$$P = \sum_{i} P_i = \sum_{i} \frac{N_i}{V} k_b T . \qquad (1.36)$$

Eq. (1.36) is known as **Dalton's Law**, and each individual pressure  $P_i$  is called a **partial pressure**. This *linearity* in pressure was discovered empirically by Dalton, which you would have spend studying in your Matter module year one. As you can see now, this law is only valid for ideal gasses – it is due to the linearity of P as a function of density N/V for the ideal gas law. In general, this is not obeyed and hence Dalton's Law is only an approximation valid for ideal gasses.

#### 1.2.3 Mean Free Path and Relaxation Time

We will now consider *collisions between particles*. In general, collision rates will depend on the geometry of the particles, but for simplicity (and without losing much physics), let's assume the particles as spheres with diameter d. Suppose with have a systems of N particles occupying the volume V, we want to calculate the **mean free path** l of a particle, which is defined to be the *average distance travelled by* a particle between collisions. Now, viewed head on, each particle has an area  $\pi(d/2)^2$ . However, since every other particle also has diameter d, the "space" in which a particle can occupy before colliding with another particle is a cylinder  $\pi d^2 l$  (see Fig. 1.7). This volume must be equal to the total volume available per particle, i.e. V/N, so  $\pi d^2 l = V/N$ , or

$$l = \frac{V}{N} \frac{1}{\pi d^2} . (1.37)$$

Suppose now the mean time between collisions, or the relaxation time is  $\tau$ , then by dimensional analysis, one expect

$$l \stackrel{?}{=} v_{col} \tau , \qquad (1.38)$$

where  $v_{col}$  is a variable with the dimensions of velocity. The question is, what v should we use? A naive guess would be the mean velocity  $v_{col} \stackrel{?}{=} \langle v \rangle$ , but this would be wrong since the velocities of the *target* 



Figure 1.7: On average, a particle (red) of radius 2d has "elbow room" of  $\pi d^2 l$  before colliding with another particle (blue), where l is defined as the mean free path.

particles is as important as the velocity of the protoganist particle. What we want is the **mean relative velocity** 

$$\langle v_{rel}^2 \rangle \equiv \langle |\mathbf{v_1} - \mathbf{v_2}|^2 \rangle$$

$$= \langle v_1^2 + v_2^2 - 2\mathbf{v_1} \cdot \mathbf{v_2} \rangle$$

$$= \langle v_1^2 \rangle + \langle v_2^2 \rangle - 2 \langle v_1 v_2 \cos \theta \rangle ,$$

$$(1.39)$$

where we have defined  $v_1 = |\mathbf{v_1}|$  and  $v_2 = |\mathbf{v_2}|$  respectively.

Now the last term  $\langle v_1 v_2 \cos \theta \rangle = 0$  vanishes, which can be brute force computed by substituting the term into the expectation value formula Eq. (1.20), and noticing that the  $\theta$  integral  $\int_0^{\pi} \sin \theta \cos \theta d\theta = 0$  (regardless of what  $v_1 v_2$  integrates to). A more elegant argument is to notice that since the distribution has no perferred direction (each particle is equally likely to travel in any direction), then its mean should be zero.

Meanwhile,  $\langle v^2 \rangle = 3k_bT/m$  as we have previously computed, and since  $v_1$  and  $v_2$  are both drawn from the same distribution,  $\langle v_1^2 \rangle + \langle v_1^2 \rangle = 6k_bT/m$ . Thus the mean free path is then

$$l = \sqrt{\langle v_{rel}^2 \rangle} \tau = \sqrt{\frac{6k_b T}{m}} \tau \tag{1.40}$$

Using Eq. (1.37), we can express the relaxation time as

$$\tau = \frac{1}{n\pi d^2} \sqrt{\frac{m}{6k_b T}} , \qquad (1.41)$$

where we have defined the number density

$$n \equiv \frac{N}{V} \ . \tag{1.42}$$

The area variable in Eq. (1.41)  $\pi d^2$  is called the **effective cross-sectional area** (or just cross-sectional area) – it denotes "how big" the particle is as a target. Defining it as

$$\sigma \equiv \pi d^2 , \qquad (1.43)$$

Eq. (1.41) can the be written as

$$\tau = \frac{1}{n\sigma} \sqrt{\frac{m}{6k_b T}} , \qquad (1.44)$$

Taking stock, the relaxation time depends inversely on number density n (the more dense it is, the shorter the time), inversely on the effective cross-sectional area (the bigger the target, the shorter the time) and the square root of the temperture T (the hotter it is, the more likely it will collide since things generally move faster).

In these variables, the mean free path can also be written as

$$l = \frac{1}{n\sigma} . \tag{1.45}$$

## 1.3 Transport

Now we will turn to how things move. A gas in equilibrium clearly is not static – particles zip about and collide with each other, carrying energy, heat and itself around. This motion, which is called **transport**, leads to physical properties which can then be measured as follows:

- Viscosity : The transport of momentum.
- Conductivity : The transport of heat.
- **Diffusion** : The transport of particles.

We will study this in turn in the following.

#### 1.3.1 Viscosity

While not recommended, if you try to swim in a pool of honey, you will find that it is much more difficult than trying to swim in a pool of water. Honey is in general much more "stick" than water. You would have studied in your first year mechanics that viscosity exerts a friction force that is proportional the the velocity  $F_{vis} \propto \eta v$  where  $\eta$  is the **viscosity** of the liquid.

As it turns out, gasses also possess viscosity. The Kinetic theory of gas provides a nice way of deriving vicosity as we will now discuss.



Figure 1.8: Two parallel plates of area A are held between a gas. The bottom plate is held firm while we slide the top plate in the x direction by applying a force F. The particles in the gas reacts and "fights back", generating a viscous force against the motion. Newton's 3rd law imply that the gas' particles must also feel the force, and hence experience a mean momentum transfer  $m\langle u_x \rangle$ .

Consider the system in Fig. 1.8 We set up two parallel plates of area A between a gas (or a liquid). Holding the bottom plate fixed, we try to slide the top plate in the positive x direction. But the particles in the gas fights back, hence to slide the plate requires the application of a force F. Newton's 3rd law imply that the particles of the gas must also feel the force, hence experience a momentum transfer. We want to compute this force.

Before we beginning sliding the top plate, the gas on the whole is not moving (even if the individual particles are), so the mean velocity  $\langle u_x \rangle = 0$ . As we begin to slide the top plate, the particles feel a force in the x direction, and hence we expect a momentum change in this direction. Since the bottom plate is still not moving, we expect  $\langle u_x(z=0)\rangle = 0$ . On the other hand, the top plate is moving so must experience the maximum motion  $\langle u_x(z=z_0)\rangle = u_x^{max}$ . This sets up a **mean velocity gradient** 

$$\frac{d\langle u_x\rangle}{dz} > 0 , \qquad (1.46)$$

in the z direction. Notice that  $u_x$  is still within the expectation value brackets  $\langle \rangle$  sign – it is an *average*. Physically this is not hard to understand : near the top plate, the particles are in direct contact with the plate, so experience maximum change in momentum. These then collide with particles in the next "layer" further down in z transfering momentum, but since collisions are not guaranteed – it depends on the relaxation time – the net change in  $\langle u_x \rangle$  then would be less etc.

Turns out that deriving a formula of the viscous force from particle collisions from first principle is rather hard. However, we can rely experiments and some intuition. First, we expect that if we apply a bigger force, the velocity gradient will be bigger, so we  $|F| \propto d\langle u_x \rangle/dz$ . However, if the area of the plate A increases, more of the plate is in contact with the particles, so we expect the velocity gradient to be inversely proportional to A, so we guess that

$$\frac{F_{vis}}{A} = \eta \frac{d\langle u_x \rangle}{dz} , \qquad (1.47)$$

where  $F_{vis}$  is the viscous force.  $\eta$  is a constant of proportionality, and as you have guessed, defines the viscosity. Using the *ansatz* Eq. (1.47), all we need to is compute the velocity gradient which we can do as it is just the expectation value of a distribution which in our studies today is the Maxwell-Boltzmann distribution. Let's derive the viscosity  $\eta$  in the following.

We begin by computing the velocity gradient  $\langle u_x(z) \rangle$ , i.e.  $u_x$  as a function of z. Let's consider a thin dz layer of particles. Particles will pass through this layer in the z direction – the rate which of course depends on the velocity distribution in the z direction, which happily we know since we have the Maxwell-Boltzmann distribution. Recalling that n = N/V is the number density, then using  $v_z = v \cos \theta$ ,

rate of particles passing through layer per unit area 
$$= nv\cos\theta \times \frac{f(v)}{4\pi}\sin\theta \ d\theta d\phi dv$$
, (1.48)

Now consider a particle in a layer at position z. It gets hit from another particle passing through this layer (the rate which we have computed above in Eq. (1.48), experience a momentum transfer of *per particle* in the x direction

$$\Delta p_x = m(u_x(z + \Delta z) - u_x(z)) \approx m \frac{du_x}{dz} \Delta z .$$
(1.49)

Apologies for the reuse of  $p_x$  as momentum when we have used it for pressure p – another reason why in your next year module on stat mech we will use P for pressure instead like sensible people.

We have calculated the rate of particles passing through the layer – what is the collision rate of these particles passing through? In other words, how many of these passing through particles actually collide with a particle in the layer? On average, this occurs when a particle has travelled the mean free path l, or

$$\Delta z = l\cos\theta,\tag{1.50}$$

where the  $\cos \theta$  is the direction where the particle is traveling from. In other words, if  $\Delta z$  is set to Eq. (1.50), then all the particles passing through the layer are expected to collide with a particle in the layer.

The force imparted by this particle is then given by  $\Delta p_x/\Delta t$ . Since this is the *force per collision*, the mean force is then a product of  $\Delta p_x/\Delta t$  and the rate per particle per unit area Eq. (1.48). Plugging these in we get

$$\frac{F}{A} = \int_{0}^{2\pi} d\phi \int_{0}^{\pi} d\theta \int_{0}^{\infty} dv \, mnvl \cos^{2} \theta \sin \theta \frac{f(v)}{4\pi} \frac{du_{x}(z)}{dz} ,$$

$$\approx \frac{d\langle u_{x}(z)\rangle}{dz} \times mnl \int_{0}^{2\pi} d\phi \int_{0}^{\pi} d\theta \cos^{2} \theta \sin \theta d\theta \frac{vf(v)}{4\pi} dv .$$
(1.51)

In the 2nd line, we have cheated (hence the  $\approx$  sign) by extracting the  $du_x(z)/dz$  term from inside the integral, and putting them outside the integral, while callously slapping a  $\langle \rangle$  symbol on it. Why are we allowed to do that? Morally speaking, what we should do is to replace  $du_x(z)/dz$  with  $d(v \cos \theta \sin \phi)dz$ , and then compute, keeping the v inside the integral. Indeed, while each individual particle  $u_x$  can be

big, its mean is  $\langle u_x \rangle = 0$ , so how are we to reconcile this fact? The "word calculus" answer is that since we have applied a force F in the x direction, the *symmetry* of the gas velocity distribution is broken – in other words, the gas is no longer a Maxwell-Boltzmann distribution. However, as long as the mean change  $\langle u_x \rangle \ll \langle v \rangle$ , this is a very small deviation from the Maxwell-Boltzmann distribution, so we are allowed<sup>3</sup> For now we assume that this approximation holds (experimentally it does). The v integral gives us  $\langle v \rangle$ , leaving us with

$$\frac{F}{A} = mnl\langle v \rangle \frac{d\langle u_x(z) \rangle}{dz} \times \frac{1}{4\pi} \int_0^{\pi} d\theta \cos^2 \theta \sin \theta d\theta \int_0^{2\pi} d\phi ,$$

$$= \frac{1}{3}mnl\langle v \rangle \frac{d\langle u_x(z) \rangle}{dz}.$$
(1.52)

Comparing this result to our ansatz Eq. (1.47), we see that the viscosity is

$$\eta = \frac{mnl}{3} \langle v \rangle \ . \tag{1.53}$$

Remarkably, the viscosity is independent of number density n. Wait! There is an n right there you say. Yes, but note that the mean free path  $l \propto 1/n$  (see Eq. (1.45)), so  $\eta \sim m \langle v \rangle$ . For fixed T, the ideal gas law then imply that the viscosity also doesn't depend on pressure P. This also means that since  $\langle v \rangle \propto T^{1/2}$  via Eq. (1.18), the hotter the gas, the more viscous it is – this is opposite to what you expect from liquids.

Indeed, the fact that  $\eta$  is independent of density so startled Maxwell, who first derived the Eq. (1.53), he thought he had made a mistake at first especially when the data at the time showed otherwise. Maxwell, being Maxwell, decided that he'd build *his own experiment*. So he did, and verified that indeed, he was correct.

#### 1.3.2 Conduction

Next up, we return to something that you have studied previously, which is thermal conduction. As you have learned, the total heat flow (with Q being the total heat energy)

$$\frac{\partial \mathbf{Q}}{\partial t} = -\kappa \nabla T \times \text{Area} \tag{1.54}$$

where  $\kappa$  is called the **conductivity**. Note that **Q** is a vector as direction of heat flow depends on the (negative of) the thermal gradient  $\nabla T$ . In one dimension (say z) this equation is

$$\frac{\partial Q}{\partial t} = -\kappa A \frac{\partial T}{\partial z} , \qquad (1.55)$$

which is sometimes known as the **Newton's Law of Cooling.** As it turns out, instead of total heat flow, we define the **heat flux**, which is the heat flow *per unit area* 

$$\mathbf{J} \times \text{Area} = \frac{\partial \mathbf{Q}}{\partial t} \ . \tag{1.56}$$

In this notation, Eq. (1.54) becomes

$$\mathbf{J} = -\kappa \nabla T \ . \tag{1.57}$$

The kinetic theory of gas again provide a way to derive Eq. (1.55) – indeed the derivation follows that of viscosity in the previous section very similarly. Instead of momentum exchange Eq. (1.49), we want a *heat exchange*. How does a particle carry heat? We know from the equipartition theorem that the energy of a particle  $U = 3k_bT/2$ . Suppose set up a gas where two ends are fixed at different temperature  $T_1$  and  $T_2$  such that there is a temperature gradient  $T_1 > T_2$ , see Fig. 1.9 This means that T(z), so

<sup>&</sup>lt;sup>3</sup>A more detailed calculation will show that we need to replace the 1/3 in the final answer Eq. (1.53) by  $5\pi/32$ .

$$U(z) = \frac{3k_b T(z)}{2} . (1.58)$$

Here, you should raise an objection – since a temperature gradient imply that the gas is no longer has a fixed T, how are we to know that the equipartition theorem still holds? The answer is (again) we have cheated, but we have cheated in a small way – as long as the gradient is sufficiently small then we can assume then the difference is sufficiently small we can ignore it.



Figure 1.9: The heat flow J is opposite to the temperture gradient  $\partial T/\partial z$ .

Again consider a layer of particles at z. The rate of particles passing through it per unit area is as given by Eq. (1.48) which we have calculated before. However, instead of imparting momentum changes, we consider the heat absorbed by the layer as particles come in and out. A particle coming from a hotter place  $U(z + \Delta z/2)$  will increase its total heat, while a particle from a colder place  $U(z - \Delta z/2)$  will decrease is total energy. The change in energy is then

$$\Delta U = U(z - \Delta z/2) - U(z + \Delta z/2) = -\frac{3k_b}{2} \frac{dT}{dz} \Delta z .$$
 (1.59)

Note the negative sign – we want to calculate transfer of energy in the -z direction. Similarly to the viscosity case,  $\Delta z$  depends on the mean free path and the direction of particle travel i.e.,  $\Delta z = l \cos \theta$  as in Eq. (1.50). The rate of energy change is then  $\Delta E/\Delta t$ .

Combining Eq. (1.59) with Eq. (1.48), we get the same integral as before, with the simple replacement  $md\langle u_x\rangle/dz \rightarrow (3/2)k_b dT/dz$ , with the final answer

$$J = -\frac{3}{2}k_b n l \langle v \rangle \frac{dT}{dz} \times \frac{1}{4\pi} \int_0^{\pi} d\theta \cos^2 \theta \sin \theta d\theta \int_0^{2\pi} d\phi ,$$
  
$$= \frac{1}{2}k_b n l \langle v \rangle \frac{dT}{dz} .$$
(1.60)

Comparing Eq. (1.60) to Eq. (1.57), we see that the conductivity is

$$\kappa = \frac{1}{2} k_b n l \langle v \rangle . \tag{1.61}$$

Recalling that  $C_V = (3/2)k_b n$ ,  $\kappa$  can then (usually) be expressed as

$$\kappa = \frac{1}{3} C_V l \langle v \rangle . \tag{1.62}$$

Again, if we look at Eq. (1.61), the same argument applies that since  $l \propto n^{-1}$ ,  $\kappa$  is independent of number density and hence pressure. Similarly,  $\kappa \propto T^{1/2}$  – the hotter the gas, the better the conduction. In fact, Eq. (1.61) is so similar to Eq. (1.53), one might be tempted equate the two, to obtain

$$\frac{\kappa}{\eta} = \frac{3k_b}{2m} = c_V , \qquad (1.63)$$

where  $c_V \equiv C_V/m$  is the specific heat capacity. This seems amazing  $-\kappa$ ,  $\eta$  and  $c_V$  are experimentally measurable properties, are they equal like this in real life? Sadly, this viscosity-conductivity relationship does not hold up too well in experiments – the root cause as you might have expected is the two "cheats" we have made in deriving viscosity and conductivity. However, as we will see in section 1.4.3 such ratios can be used to compare the efficiencies of heat transfers of conduction and convection.

#### 1.3.3 Diffusion

Finally, we discuss how particles get transported – if you drop some milk into a cup of tea, the milk will spread into the tea. This process is called **diffusion**. Consider again the system of gas with two plates as before, but this time we set it up such that the top plate has a number density  $n_1$  while the bottom plate has  $n_2$ , such that  $n_1 > n_2$  (see Fig. 1.10). Intuitively, since there are more particles on average at the top, the particles will diffuse towards the -z direction.



Figure 1.10: The number densities at the top place is  $n_1$  and at the bottom plate is  $n_2$  such that  $n_1 > n_2$ . The flux  $\Phi_z$  flows towards points of lower densities.

At any layer z, the flux  $\Phi_z$  is defined to be the total number of particles flowing through it in the z direction per unit area per unit time. In a gas, there are of course some particles moving upwards and some moving downwards, but one might expect that since the density is higher at the top, there will be more particles moving downwards. This means that  $\Phi_z$  must depend on the **density** gradient  $\partial n(z)/\partial z$ , i.e.

$$\Phi_z = -D\frac{\partial n(z)}{\partial z} , \qquad (1.64)$$

where D is called the **diffusion constant**. We will now derive Eq. (1.64). Fortunately, most of the work for this derivation is already done in the previous section. Recall Eq. (1.48) defines the rate of particles passing through the layer at z per unit area

rate of particles passing through layer per unit area 
$$= nv\cos\theta \times \frac{f(v)}{4\pi}\sin\theta \ d\theta d\phi dv$$
, (1.65)

but now n in this equation depends on z. Indeed, what we want is an equation which describe rate of particles passing through layer per unit area per per unit difference in density  $\Delta n$ , i.e.

rate of particles passing through layer per unit area per unit difference in  $n = \Delta nv \cos\theta \times \frac{f(v)}{4\pi} \sin\theta \, d\theta d\phi dv$ . (1.66)

You can see that as a sanity check, if there is no difference in densities  $\Delta n = 0$  there is no diffusion.  $\Delta n$  itself is simply,

$$\Delta n = \frac{\partial n}{\partial z} \Delta z , \qquad (1.67)$$

where again  $z = l \cos \theta$ . The rate is then  $\Delta n / \Delta t$ , which we can then combine with Eq. (1.66) to obtain the equation for the flux  $\Phi_z$ 

$$\Phi_z = \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \int_0^{\infty} dv \, v l \cos^2 \theta \sin \theta \frac{f(v)}{4\pi} \frac{dn(z)}{dz} ,$$
  
$$\approx \frac{d\langle n(z) \rangle}{dz} \times l \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \cos^2 \theta \sin \theta d\theta \frac{v f(v)}{4\pi} dv .$$
(1.68)

which again we have cheated by extracting dn/dz out of the integral and slapping  $\langle \rangle$  around it. The argument is again the same as we have discussed previously in the derivation of the viscosity. The v integral gets us  $\langle v \rangle$  as usual, and the angles integral give us 1/3, giving us the final answer

$$\Phi_z = -\frac{1}{3}l\langle v \rangle \frac{\partial\langle n \rangle}{\partial z} , \qquad (1.69)$$

which when compared with Eq. (1.64) we see that the diffusion constant is

$$D = \frac{1}{3} l \langle v \rangle . \tag{1.70}$$

Unlike viscosity and conductivity, since there is no n in the diffusion constant, but there is an  $l \propto 1/n$ , diffusion depends on density. Using the ideal gas law  $P = nk_bT$ , this means that  $D \propto 1/P$  also depends on pressure. Subtituting l with T using the ideal gas law again, we get  $D \propto T^{3/2}$  as  $\langle v \rangle \propto T^{1/2}$ .

#### **1.3.4** The Diffusion and the Heat Equations

Suppose instead of wanting to know what is the flux  $\Phi_z$  at any layer, we want to know how *n* change as a function of time at layer *z*, e.g. we want to know  $\partial n(z)/\partial t$ ? We can derive this as follows.

Consider a layer with thickness  $\Delta z$ . The flux at the top is given by  $\Phi_z(z+\Delta z) = \Phi_z - (\partial \Phi_z/\partial z)\Delta z+...$ via Taylor expanding to first order. Meanwhile at the botton<sup>4</sup> it is  $\Phi(z)$ . So per unit time, the rate of particles traveling through z is the difference, which is  $-(\partial \Phi_z/\partial z)\Delta z$ . If A is the area of the layer, then the volume of a layer is  $A\Delta z$ . By considering the **conservation of particles**, the rate of particles going in/out of the layer must be equal the change in the number of particles in the layer, i.e.

$$\frac{\partial nA\Delta z}{\partial t} = -\frac{\partial \Phi_z}{\partial z} A\Delta z , \qquad (1.71)$$

and using Eq. (1.69), we get the **Diffusion equation** 

$$\frac{\partial n(t,z)}{\partial t} = D \frac{\partial^2 n(t,z)}{\partial z^2} . \qquad (1.72)$$

It is easy to generalize the derivation to 3D - Eq. (1.71) in words mean "the rate of change of density of particles in any small volume is equal to the gradient of the fluxes through all the surface area of the volume", or

$$\frac{\partial n}{\partial t} = -\nabla \Phi_z \ , \tag{1.73}$$

which is sometimes known as the **continuity equation** which enforces particle conservation.

The diffusion equation Eq. (1.72) in 3D is then

$$\frac{\partial n(t, \mathbf{x})}{\partial t} = D\nabla^2 n(t, \mathbf{x}) , \qquad (1.74)$$

with the continuity equation

$$\frac{\partial n}{\partial t} = -\nabla \cdot \mathbf{\Phi} \,\,, \tag{1.75}$$

<sup>&</sup>lt;sup>4</sup>You can do the same calculation by considering the fluxes of the top and bottome layers to be  $\Phi(z - \Delta z/2)$  and  $\Phi_z(z + \Delta z/2)$  if you like and get the same answer.

where  $\mathbf{\Phi} = (\Phi_x, \Phi_y, \Phi_z)$  is the flux vector. We will derive this exactly in a later Section 1.4.1

The diffusion equation is a 1st order (in time) linear partial differential equation. You probably have solved equations like these in your 1st year math modules (if not you should probably ask for your money back). You can check that the solution in 1D has the form

$$n(t,z) = \text{const} \times t^{-1/2} e^{-z^2/4Dt}$$
 (1.76)

Recall that the Gaussian distribution  $P(z) \propto e^{-z^2/\sigma}$  where  $\sigma$  is its variance that tells us how "spreaded" out it is. Comparing this to Eq. (1.76) and ignoring the factor  $t^{-1/2}$  for the moment, we see that the distribution n as a Gaussian form, with a time dependent variance  $\sigma = 4Dt$  which grows with time. That's it, the distribution spreads out exactly what we expect from diffusion. The  $t^{-1/2}$  factor tells us that it is also losing overall amplitude, to conserve particles.

The rate of "spreading" is determined by how fast the variance  $\sigma$  grow with time, which here depends linearly on the diffusion constant D – the bigger the diffusion the faster the growth.

As should be clear to you, the diffusion equation is simply a restatement of the conservation of particles. What about the conservation of energy? It won't surprise you that we can derive a similar equation. Consider the heat flux J, and using the transport of heat equation Eq. (1.60)

$$J = -\kappa \frac{dT}{dz} , \qquad (1.77)$$

which in 3d is

$$\mathbf{J} = -\kappa \nabla T \ , \tag{1.78}$$

where  $\mathbf{J} = (J_x, J_y, J_z)$ .

Following the exact same argument as above, but replacing the flux  $\Phi_z$  with the heat flux  $J_z$ , and the density gradient n(z) with the temperature gradient T, we obtain the **Heat equation** 

$$\frac{\partial T}{\partial t} = \frac{\kappa}{C_V} \frac{\partial^2 T}{\partial z^2} , \qquad (1.79)$$

or in 3D

$$\frac{\partial T}{\partial t} = \frac{\kappa}{C_V} \nabla^2 T. \tag{1.80}$$

The equivalent continuity equation (as you will show in a homework problem) is

$$\frac{\partial U}{\partial t} = -\nabla \cdot \mathbf{J} \ . \tag{1.81}$$

The Heat equation has exactly the same form as the diffusion equation, and hence has the same solution – concentrated heat wants to spread out. Here the "heat diffusion constant" is  $\kappa/C_V = D$ , which is actually just the diffusion constant!

Now you must be waiting with baited breath – what about viscosity? You will be right – there is a conservation law associated with it, and its the conservation of momentum as you would expect. The derivation is slightly more difficult (but not overly so), and I will leave it to the enterprising student to work it out. The final anser is

$$\frac{\partial \mathbf{p}}{\partial t} = \frac{\eta}{mn} \nabla^2 \mathbf{p} , \qquad (1.82)$$

where **p** is the 3-momentum. This equation, which sadly doesn't have a name, is exactly of the same form as the Heat and Diffusion equations, and have the same behaviour. Again the "momentum diffusion constant"  $\eta/mn = D$  is just the diffusion constant.

#### 1.3.5 Random Walk

Why is the diffusion constant D so important? As per usual in physics, when something pops up again and again, it probably tells you something very fundamental about the physics of the system. In this case, this is the physics of **random walk**. The idea of a random walk is very simple. Let's consider a 1 dimensional lattice (see Fig. 1.11) where a single particle can "hop" either forward or backward by one step at every time step  $\Delta t$ . The probability of either is 50% and uncorrelated (i.e. every hop is not related to the previous hop).



Figure 1.11: A 1D lattice with sites labeled by k, with distance  $\Delta x$  between sites.

We want to know what is the probability P(x,t) that the particle is at some site k, or distance  $x = k\Delta x$ , after time N steps or  $t = N\Delta t$ . For this to occur, the particle must hop forward (N + k)/2 times and backward (N - k)/2 times – for simplicity we have assumed that  $N \gg k$  and N is an even number. The probability is then the total number of ways we can do this, which is N!/[((N - k)/2)!((N + k)/2)!], divided by the total number of combinations,  $2^N$ , thus

$$P(x,t) = \frac{N!}{2^N((N-k)/2)!((N+k)/2)!} \approx \sqrt{\frac{2}{\pi N}} e^{-k^2/2N} = \sqrt{\frac{2\Delta t}{\pi t}} e^{-x^2 \Delta t/2\Delta x^2 t} , \qquad (1.83)$$

where we have used **Stirling's Approximation**  $N! \approx \exp[N \log N - N]$ , and then Taylor expand around the small number k/N (homework). Notice the solution Eq. (1.83) has exactly the same solution as the diffusion equation Eq. (1.76) where the "diffusion constant"

$$D \sim \frac{\Delta x^2}{\Delta t} . \tag{1.84}$$

Comparing this to  $D = (1/3)l\langle v \rangle \sim l(\Delta l/\Delta t) \sim l^2/\Delta t$ , we see that the dimensions checked out.

The main moral of the story is that transport processes in gasses (and indeed in general) are random walk processes - particles wander around like a drunk, taking each step at random. The collective motion of *microscopic* random walks leads to the *macroscopic* properties of diffusion, conduction and viscosity. This is a very general principle, and indeed is called **Fluctuation theory**, and is the starting point for many investigations into statistical physics and fluids dynamics (e.g. it describes **Brownian motion**). Sadly, we will have to postpone its study until your 4th year.

## 1.4 Heat Transfer

How does heat get from one point to another? In the previous section, we have studied transport, which is the physics of how things move. In this section, we will focus on how those transport processes translate to how *heat* itself move.

In previous lectures, you have briefly studied that there are three primary ways: Conduction, Convection and Radiation. Using our knowledge of kinetic theory of gas and heat transport, we will now make the connection on how transport leads to heat transfer in more detail.

#### 1.4.1 Heat transfer via Conduction : Heat Diffusion

You have learned the Newton's Law of Cooling,

$$\frac{\partial Q}{\partial t} = -\kappa A \frac{dT}{dx} , \qquad (1.85)$$

which the eagle-eyed amount you would have spotted that is the 1-D version of our heat flux derived in Eq. (1.57), with  $\dot{Q} = J \times A$ . We will use the more general heat flux equation, and the generalization to 3D Eq. (1.78)

$$\mathbf{J} = -\kappa \nabla T \ . \tag{1.86}$$

Instead of calculating the rate of heat exchange via the flux equation Eq. (1.78), we will instead focus on solving the Heat Equation Eq. (1.80)

$$\frac{\partial T}{\partial t} = D\nabla^2 T , \ D = \frac{\kappa}{C_V} , \tag{1.87}$$

where D is the diffusion constant as usual. Thus, sometimes conduction is called **heat diffusion**.



Figure 1.12: Positive Heat flux **J** means heat is flowing out of the volume V through the boundary  $\Sigma$ .

We will begin by rederiving the 3D Heat equation Eq. (1.80) in a slicker way. Consider a gas in a compact 3D volume V, with boundary  $\Sigma$ . The heat flux **J** flowing through the boundary is given by the surface integral (see Fig. 1.12)

$$\int_{\Sigma} \mathbf{J} \cdot d\Sigma = \int_{V} \nabla \cdot \mathbf{J} dV , \qquad (1.88)$$

where we have used the divergence theorem.

Meanwhile, suppose the heat capacity at constant volume of the gas is  $C_V$ , then the rate of change of the energy due to the heat flow is

$$\frac{\partial}{\partial t} \int_{V} C_{V} T \ dV \ . \tag{1.89}$$

Conserving of energy means that the two terms Eq. (1.88) and Eq. (1.89) must be equal

$$\nabla \cdot \mathbf{J} = -C_V \frac{\partial T}{\partial t} , \qquad (1.90)$$

which is the continuity equation. Substituting in Eq. (1.86) yields the Heat equation Eq. (1.87) as desired. Replacing the heat flux with the particle flux  $\Phi$  and considering the conservation of particles yields the diffusion equation Eq. (1.74).

Let's consider the 1D heat equation.

$$\frac{\partial T}{\partial t} = D \frac{\partial^2 T}{\partial^2 x} , \qquad (1.91)$$

The form Eq. (1.91) looks suspiciously like the Schrödinger's wave equation, except for a missing *i*. So one can write the following *ansatz* for a solution which looks like a wave

$$T(x,t) = A \exp[i(kx - \omega t)], \qquad (1.92)$$

where A is some constant which is determined by the boundary and initial conditions. As usual, one shouldn't worry about the imaginary component for T as we will take only the Real component as the final answer as usual  $T_{actual} = \text{Re}(T)$  – the exponential form is simply book keeping. If you like, you can write down  $T(x,t) = A\cos(kx - \omega t) + B\sin(kx - \omega t)$  but that is a lot more algebra.

Plugging Eq. (1.92) into the Heat equation Eq. (1.91) yields a relationship between the wave vector k and frequency  $\omega$ 

$$-i\omega = Dk^2 . (1.93)$$

Solving for k, we get two solution

$$k = \pm (1+i)\sqrt{\frac{\omega}{2D}} . \tag{1.94}$$

Recalling that the spatial part of the wave solution Eq. (1.92) looks like  $\exp(ikx)$ , so the presence of a an imaginary component in the wavevector Eq. (1.94) means that there will be either an exponentially growing  $\exp(\sqrt{\omega/2Dx})$  or exponential decaying  $\exp(-\sqrt{\omega/2Dx})$  solution for  $x \to \infty$  and vice versa for  $x \to -\infty$ . Which solution is "picked out" depends on the **boundary conditions**. For simplicity in the following, we will consider  $x \ge 0$  which of course can be made without loss of generality since it is a coordinate choice.

Now  $\omega$  (or k) labels the solutions – and since the Heat equation is a linear equation, a general solution for the Heat equation is a sum of waves

$$T(x,t) = \sum_{\omega} A(\omega) \exp\left[-i(\omega t - \sqrt{\frac{\omega}{2D}}x)\right] \exp\left[-\sqrt{\frac{\omega}{2D}}x\right] , \qquad (1.95)$$

where  $A(\omega)$  is the coefficient for each linear wave of frequency  $\omega$ . Note that the x dependence has an oscillatory term  $\exp[-i\sqrt{\omega/2D}x]$  and a decaying term  $\exp[-\sqrt{\omega/2D}x]$ . We will see this in action later.

Let's now consider several cases.

#### Steady State

Consider a stick of length L such that x = (0, L]. The simplest case is when the temperature of the system is not changing, such as

$$\frac{\partial T}{\partial t} = 0 \ . \tag{1.96}$$

This means that the system is in *equilibrium* and T is not a function of time t. What is T as a function of space x then depends on the boundary conditions at x = 0 and x = L, which must satisfies the following **Laplace equation** 

$$\frac{\partial^2 T}{\partial x^2} = 0 , \qquad (1.97)$$

or its 3D generalisation  $\nabla^2 T = 0$ , which immediately follows from the Heat equation with  $\partial T / \partial t = 0$ .

An equation like Eq. (1.97) is called a **boundary value problem** – it depends on the boundary values T(x = 0) and T(x = L). A particularly simple case is when  $T(x = 0) = T(x = L) = T_0$ , and  $\partial T/\partial x(x = 0) = \partial T/\partial x(x = L) = 0$  (remember that it's a 2nd order PDE in x so requires both zero and 1st order derivatives as boundary conditions). Intuitively, you might guess that the solution is  $T(x) = T_0$ ,

i.e. the stick is in constant temperature, and you would be right. In 1D, this equation has the simple solution

$$T = Ax + B av{1.98}$$

where A and B are integration constants. Setting  $T(x = 0) = T(x = L) = T_0$ , we find  $B = T_0$  and A = 0, and we get  $T(x) = T_0$ .

What about in 3D? I.e. suppose we immerse a ball inside a pot of hot water held at  $T_0$  – does this imply that the ball will be evenly distributed in  $T_0$  at steady state? The answer is yes, though the *proof* is quite cute though and actually uses quite an important trick in solving boundary value problem, let's show it :

Consider the following term

$$\nabla \cdot (T\nabla T) = |\nabla T|^2 + T\nabla^2 T = |\nabla T|^2 , \qquad (1.99)$$

where we have used the Laplace equation in the 2nd equality.

Integrating both sides over the volume V

$$\int_{V} \nabla \cdot (T \nabla T) dV = \int_{V} |\nabla T|^{2} dV ,$$
  
$$\int_{\Sigma} (T \nabla T) \cdot \mathbf{n} d\Sigma = \int_{V} |\nabla T|^{2} dV , \qquad (1.100)$$

where in the 2nd line above we have used Stokes' theorem on the LHS to convert the volume integral into an integral over the boundary  $\Sigma$  with **n** being the normal vector through the boundary. Applying the boundary condition  $T(\Sigma) = \nabla T(\Sigma) = 0$ , we get

$$\int_{V} |\nabla T|^2 dV = 0 . (1.101)$$

However, since  $|\nabla T|^2 > 0$  unless  $\nabla T = 0$  everywhere, this means that T must be a constant, and the boundary condition fixes  $T = T_0$  everywhere.  $\Box$ .

The case where  $T(x = 0) = T_L$  and  $T(x = L) = T_R$  with  $T_L \neq T_R$  is discussed by Stefano using the Newton's Cooling equation. In our language, from the general solution T = Ax + B, applying the boundary conditions we get  $B = T_L$  and  $A = (T_R - T_L)/L$  as he has shown.

#### Non steady-state

But wait, these solutions have no waves, so why did we start by looking for wave solutions? The general solution Eq. (1.92) comes into play when we consider *non steady state* solutions, i.e. where  $\partial T/\partial t \neq 0$ .

Consider a stick of length L again. We will fix the Temperature at the ends x = 0 and x = L at  $T_0$  (this is the boundary condition) as usual, so  $T(t,0) = T(t,L) = T_0$ . On the other hand, the *initial* temperature of the stick is at  $T_i$ , i.e.  $T(t = 0, x) = T_i$  – this is its **initial condition**. We will now solve the 1D Heat equation using these conditions. One can use the general solution Eq. (1.95), plugging in the boundary and initial conditions to find the *spectrum*  $A(\omega)$ . However, we will use a simplying trick to solve this more efficiently here. Instead of T(x, t), let's consider the function

$$F(x,t) \equiv T(x,t) - T_0 . (1.102)$$

At the boundary x = 0 and x = L, F(x,t) = 0, so this suggests that F(x,t) must be periodic in L, so this suggests the following *ansatz* 

$$F(x,t) = A(\omega)\sin(kx)e^{-i\omega t} . \qquad (1.103)$$

It's easy to see by plugging Eq. (1.103) into the heat equation, we get the following condition

$$i\omega = Dk^2 , \qquad (1.104)$$

just like we did previously.

Now, to satisfy the boundary conditions the wavevector k must satisfy

$$k_n = \frac{n\pi}{L}$$
,  $n = 0, 1, 2, 3, \dots$  (1.105)

so for every value of n, we have its equivalent frequency

$$i\omega_n = D\left(\frac{n\pi}{L}\right)^2 \ . \tag{1.106}$$

The Heat equation is a linear equation, so its general solution is a superposition of all possible solutions i.e.

$$T(x,t) = T_0 + \sum_n A_n \sin\left(\frac{n\pi x}{L}\right) \exp\left(-D\frac{n^2\pi^2}{L^2}t\right) , \qquad (1.107)$$

where  $A_n$  is the coefficient for A for each possible frequency  $\omega_n$ . Notice that the time dependence is a decaying exponential – there is no oscillation of temperature at all. Indeed, as we take  $t \to \infty$ , the exponent kills off all the  $A_n$  terms and we get the final steady state answer  $T(x,t) = T_0$  – the stick equilibriates with the boundary.

To find  $A_n$ , we have to use the initial condition  $T(0, x) = T_i$ . Setting t = 0 in Eq. (1.107), we get

$$\sum_{n} A_n \sin\left(\frac{n\pi x}{L}\right) = (T_i - T_0) . \qquad (1.108)$$

If you have done Fourier Series, you would recognize the LHS – it is simply a sum of the sine modes for all integer n. To find  $A_n$ , we use the completeness relationship of Fourier series by multiplying  $\sin(m\pi x/L)$  and integrating both sides, to get

$$\int_{0}^{L} A_{n} \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{m\pi x}{L}\right) dx = \int_{0}^{L} (T_{i} - T_{0}) \sin\left(\frac{m\pi x}{L}\right) dx,$$
$$A_{n} \frac{L}{2} \delta_{mn} = \frac{2L}{m\pi} \left[1 - \cos\left(\frac{m\pi x}{L}\right)\right]. \tag{1.109}$$

Now the LHS says that m has to be an integer like n. If m is an odd integer, the RHS has the solution  $2/m\pi$  while if m is an even integer, the RHS is zero. So we have the solution

$$A_n = \frac{4}{m\pi} (T_i - T_0) , \ m = 1, 3, 5, \dots$$
 (1.110)

Putting everything together, we have the final answer

$$T(x,t) = T_0 + (T_i - T_0) \sum_n \sin\left(\frac{n\pi x}{L}\right) \exp\left(-D\frac{n^2\pi^2}{L^2}t\right) , \ n = 1, 3, 5, \dots$$
(1.111)

As we described earlier, the time dependence of all the modes  $A_n$  is an exponential decay – indeed the higher the n, the faster the decay so there is no time oscillation. Thus when the time is large  $t > L^2/(D\pi^2)$ , the n = 1 mode dominates, so we have the approximate answer

$$T(x,t) = T_0 + (T_i - T_0) \sin\left(\frac{\pi x}{L}\right) \exp\left(-D\frac{\pi^2}{L^2}t\right) , \qquad (1.112)$$

which looks like Fig. 1.13



Figure 1.13: The approximate temperature of a stick with its ends fixed at temperature  $T_0$  and its initial temperature at  $T_i$ .

#### 1.4.2 Heat transfer via Radiation : Stefan-Boltzmann Law

In previous lectures, you have learned about the **Stefan-Boltzman Law** of radiation, which states that the radiative power P of a blackbody at temperature T per unit area is given by

$$P = \sigma T^4 \tag{1.113}$$

where  $\sigma = 5.6703 \times 10^{-8}$  W m<sup>-2</sup> K<sup>-4</sup> is the Stefan-Boltzmann constant. Here, we have set the efficiency e = 1 (compared to Stefano's lectures) for a blackbody.

The derivation of Eq. (1.113) is a subject of the next year's module on Statistical Mechanics – indeed you will find that

$$\sigma \equiv \frac{\pi^2 k_b^4}{60\hbar^3 c^2} \,. \tag{1.114}$$

which you can check gives the right value. The presence of  $\hbar$  tells you that this is a truly quantum mechanical calulation.

Nevertheless, one can use the Kinetic Theory of Gas to produce a "semi-derivation" of the Stefan-Boltzmann law, by assuming that *radiation is simply a gas of photons*. As Einstein told us, the energy of a photon is given by

$$E = \hbar\omega, \tag{1.115}$$

where  $\omega$  is its frequency. Then suppose that U is the internal energy of the gas and V its volume, the **energy density** *u* is then

$$u = \frac{U}{V} = \frac{N\hbar\omega}{V} = n\hbar\omega , \qquad (1.116)$$

where N is the total number of photons and thus n = N/V is its number density.

Previously, we have derived in section 1.2.1 that the pressure of a particle with velocity v is given by Eq. (1.33), with n = N/V, this is

$$p = \frac{1}{3}nm\langle v^2 \rangle . \tag{1.117}$$

We will now allow ourselves a cheat – we say that the pressure exerted by photons is exactly the same, so we replace  $v \to c$ , and interpret the energy of the a photon by  $m\langle v^2 \rangle \to mc^2$ , such that the **photon** pressure is given by

$$p_{\gamma} = (1/3)nmc^2 = u/3$$
. (1.118)

Why is this a cheat? It's because the Eq. (1.33) is derived assuming the gas particles are non-relativistic (since the Maxwell-Boltzmann distribution is derived assuming particles are non-relativistic). Also, the kinetic energy of photons is not  $mc^2$  – photons are massless! The reason the derivation "works" is that these two inaccuracies fortuitiously cancel each other out.

Moving ahead, recall that the rate per unit area per unit angle of particles between v and v + dv hitting a wall is given by Eq. (1.31)

$$\Gamma(v,\theta) = v\cos\theta f(v)dv\frac{1}{2}\sin\theta d\theta , \qquad (1.119)$$

which means that the *total rate* is the integral over v and  $\theta$ , i.e.

$$\Psi = \int_0^\infty dv \int_0^\pi d\theta \Gamma(v,\theta) = \frac{1}{4} n \langle v \rangle , \qquad (1.120)$$

which you will show in a homework set.

The total power incident on the wall per unit area is then simply

$$P_{\gamma} = \underbrace{\hbar\omega}_{\text{energy per photon}} \times \underbrace{\Psi}_{\text{rate}}$$
$$= \frac{1}{4}uc . \tag{1.121}$$

Now, we want to derive a relationship for u in terms of thermodynamic state variables. From the 1st law, we have  $dU = TdS - p_{\gamma}dV$ , then this means that if we take partial derivative with respect to V while keeping T fixed, we get

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - p_\gamma . \tag{1.122}$$

Using the Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p_\gamma}{\partial T}\right)_V \,, \tag{1.123}$$

and substituting in the photon pressure Eq. (1.118), and remembering that  $(\partial U/\partial_V)_T = u$  is simply the energy density, we have

$$u = \frac{1}{3}T\left(\frac{\partial u}{\partial T}\right)_V - \frac{u}{3} , \qquad (1.124)$$

or, rearranging

$$\frac{1}{4}\frac{dT}{T} = \frac{du}{u} , \qquad (1.125)$$

where we have glibly changed the partial derivatives into total derivatives – the reason is that here V is fixed, so the only two state variables are T and u, which we assume to possess a relationship u(T). We can immediately integrate this equation, to get

$$u = CT^4 av{1.126}$$

where C is an integration constant. Using the power relation Eq. (1.121), we finally get

$$P = \frac{1}{4}uc \equiv \sigma T^4 , \qquad (1.127)$$

which is the Stefan-Boltzmann law. Our "derivation", as mentioned above, is a cheat, and even so we didn't manage to calculate  $\sigma$  which actually is just a bunch of fundamental constants as we seen in Eq. (1.114). Historically, Stefan was the one who made this "fake" derivation and the obtained  $\sigma$  from experiments. Boltzmann then derived the relationship including  $\sigma$  using modern statistical mechanics (as you will see next year), and hence the equation now bears both their names.

#### 1.4.3 Heat transfer via Convection

Finally, we will briefly discuss convection, which you might have guessed is the transfer of heat via momentum transport. In general, convection is an extremely complicated process – one would need to disentangle fluid motion from heat transfer. Indeed, in practice there is no "nice" analytic expressions – one often resorts to brute force numerical simulations to make predictions.

Nevertheless, given a gas, one can ask "when is convection a more important heat transport process than conduction". Or conversely, when does conduction dominate and one can ignore convection? Recall that the viscosity  $\eta$  and the conductivity  $\kappa$  are diffusion coefficients for momentum and heat transfer respectively, then one can construct the so-called **Prandtl number** by taking its ratio, and then dividing by the specific heat capacity per unit mass for constant pressure  $c_p$ , i.e.

$$\Pr \equiv \frac{\eta}{\kappa} c_p \ . \tag{1.128}$$

When particle diffusion dominates and hence convection is the primary mode of heat transfer, then  $\Pr \gg 1$ , and *vice versa*. Water is around 7, and engine oil is around 10000. For an ideal gas, using Eq. (1.63), we can write

$$\Pr = \frac{c_p}{c_V} = \frac{5}{3} . \tag{1.129}$$