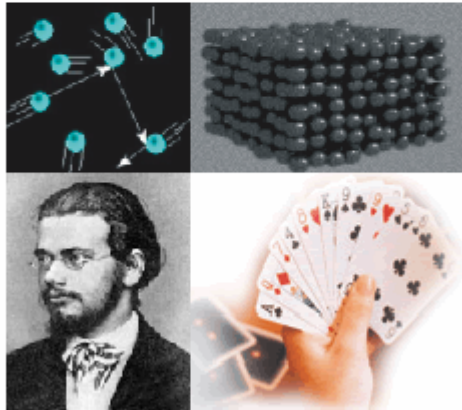


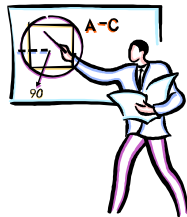
# Introduction to Thermodynamics and Kinetics

F31ST1



School of Physics & Astronomy

## *Lecture Notes* *Set 2c: Kinetic Theory III*



## Thus far.....

In Lectures 1 – 7 we've covered a broad range of topics spanning many of the key areas in classical kinetic theory including the derivation of the Maxwell-Boltzmann formula for the distribution of molecular speeds and the theorem of the equipartition of energy. We've shown how the equipartition theorem fails in circumstances where the distribution of energies is not close to the classical – i.e. continuous – limit. Two dramatic failures of classical theory – the prediction of specific heats for gases and the determination of the spectrum of blackbody radiation – were found to be due to an improper consideration of the energies of the oscillators involved in each problem. Only with quantum theory – where the system can adopt just certain *discrete* values of energy – is it possible to obtain the correct description of specific heats and the nature of blackbody radiation.

In this final component of Section 2 of the course, the motion of the individual atoms comprising a gas is explored in more detail. The key objectives of this component are:

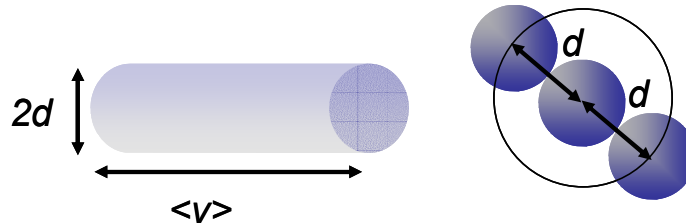
- (i) to derive an expression for the mean free path of gas molecules;
- (ii) to consider in some detail the diffusion of gas molecules and to introduce the concept of a random walk;
- (iii) to derive an equation relating the rate of change of the concentration of gas molecules to the spatial variation of the concentration (*the diffusion equation*);
- (iv) to relate the diffusion of gas molecules to the thermal conductivity,  $\kappa$ , of the gas and to derive an expression for  $\kappa$ .

What we won't cover in this component – but which will be examined in great detail in Section 3 of the module – are the fundamental physical reasons underlying both the flow of heat from hot to cold regions and the diffusion of molecules away from a region of high concentration so that, at equilibrium, they are spread out evenly over the available space. While it may seem 'obvious' that heat flows from hot to cold and that molecules will diffuse away from a region of high concentration, explaining these observations will introduce fundamental physical principles that are very much related to the Boltzmann expression described in Section 2.3.

### NOTES

## 2.11 Mean free path of gas molecules

The average distance a molecule travels between collisions is called the *mean free path* of the molecule. Referring to Fig. 2.29, in one second a molecule travels on average a distance  $\langle v \rangle$  and collides with all molecules within a cylinder of radius  $d$ .



**Fig. 2.29** If the molecules have diameter  $d$  then a collision will occur if the centres are within a distance  $d$  of each other. In 1 second, a molecule travels a distance  $\langle v \rangle$ , the mean speed.



Write down an expression for the number of molecules within the cylinder (i.e. the number of collisions the molecule undergoes in 1 second).



Write down an expression for the average distance,  $\lambda$ , between collisions.

### NOTES

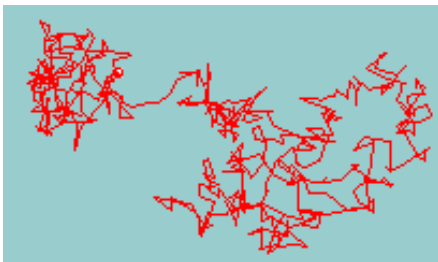
The expression for  $\lambda$ , the mean free path, which you've written down above, is over-simplified. It is based on two large assumptions: (i) the other molecules are stationary, (ii) the radius of the 'cylinder of interaction' depends only on the diameter of the molecules. You're asked in Coursework Set 4 to use the concept of reduced mass to determine an expression for the mean *relative* speed of two identical molecules – this takes into account that the molecules aren't stationary. The radius of the 'cylinder of interaction' is better described by a parameter called the *effective collision cross-section* which takes into account the interactions of the gas molecules (see Sections 1.1 and 1.2 of the lecture notes) and relaxes the assumption that they are simply

hard spheres. Taking these considerations into account we arrive at the more accurate expression for the mean free path given below:

$$\lambda = \frac{1}{n' \sigma_0 \sqrt{2}} \quad 2.57$$

where  $\lambda$  is the mean free path,  $n'$  is the number density, and  $\sigma_0$  is the effective collision cross section. Equation 2.57 is the *mean* free path – in Coursework Set 4 you will determine an expression for the distribution of path lengths.

## 2.12 Diffusion and random walks



**Fig. 2.30** A computer-generated random walk for a gas molecule

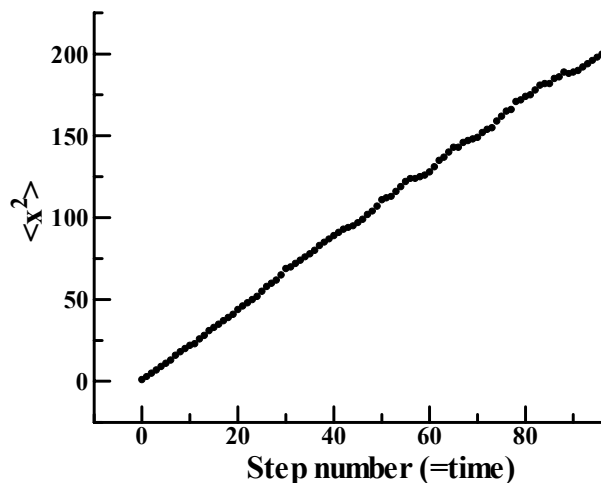
We can treat the diffusion of a molecule as a *random walk*. Imagine following the motion of an individual molecule in the air and plotting its path as it is constantly buffeted by the other gas molecules. The path the molecule will follow will resemble something like that shown in Fig. 2.30 where the motion of the molecule has been simulated by, at each step, choosing a random number (from 4 equally likely choices) and assigning the direction of motion of the molecule accordingly. Hence, if the random number is 1, the particle moves north, if the random number is 2 it moves south, etc...

Let's now determine how far the molecule travels after a certain number of steps.



*What is the average displacement of the molecule?*

Therefore, it makes much more sense to consider the *mean square displacement* of the molecule. Just as for almost everything else we've considered in this module thus far, we also need to consider the statistics associated with the problem – just considering one walk is not enough. Figure 2.31 is a graph of the mean square displacement vs the number of steps (each step represents an increment of time  $\Delta t$ ) for a random walker. Each point on the graph is the average mean square displacement measured from 1000 different random walks. Note that  $\langle x^2 \rangle$  varies linearly with time and, hence, the root-mean-square (rms) displacement varies as  $\sqrt{t}$ .



**Fig. 2.31** Mean square displacement,  $\langle x^2 \rangle$ , for a random walker as a function of the number of steps



*How does the displacement of the random walker compare with the displacement of a single free molecule traveling with a speed  $v$  that doesn't undergo collisions? Is the random walker faster or slower?*

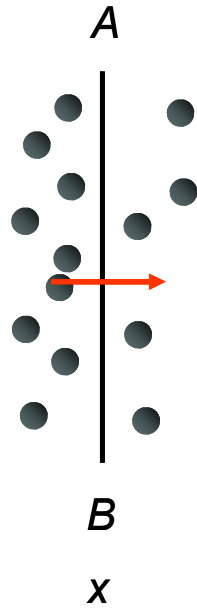
## NOTES

### *Coefficient of diffusion for a gas*

Consider a container of gas which is at thermal equilibrium. Now imagine introducing a small amount of extra gas into a small region within the container. Hence the number density, or concentration, of gas molecules within that small region is greater than that elsewhere in the container. The molecules will diffuse within the container until equilibrium is again reached – that is, the number density throughout the container is homogeneous. The rate at which equilibrium is attained depends on the *diffusion coefficient* of the molecules. In the following we'll derive an expression for the diffusion coefficient in a gas.



*NB Throughout the following we assume that there are no convective currents (i.e. there is no motion of gas molecules due to differences in density/ buoyancy differences.) We will not cover convection in any detail in this module.*



**Fig. 2.32** Molecules diffuse in the  $+x$  direction due to presence of a concentration gradient.

Referring to Fig. 2.32, let the number of molecules per unit volume at time  $t$  and position  $x$  ( $n'(x,t)$ ) vary only in the  $x$  direction with gradient:

$$\frac{\partial n'(x,t)}{\partial x} \quad 2.58$$

In addition, let the net number of molecules per second crossing unit area of the plane AB in Fig. 2.32 be  $J(x,t)$ . (Note that 2.58 is a partial derivative because  $n'$  depends on both  $x$  and  $t$ ).

The *coefficient of diffusion*,  $D$ , relates the flux of molecules to the concentration gradient as shown in the following equation:

$$J(x,t) = -D \frac{\partial n'(x,t)}{\partial x} \quad 2.59$$

Equation 2.59 is known as **Fick's law**.



*Why is there a minus sign in the equation for Fick's law?*

The presence of a concentration gradient means that the system is not at equilibrium. Equilibrium is reached by molecules moving randomly but with more moving *on average* in the  $+x$  direction<sup>†</sup>. To determine an expression for  $D$  we need to consider the fluxes of molecules in the  $+x$  and  $-x$  direction across unit area of the plane AB shown in Figs. 2.32 and 2.33. In Fig. 2.33 molecules are shown as diffusing from a distance of one mean free path,  $\lambda$ , either side of the plane AB (which is situated at  $x$ ). We now make the (rather large) assumption that all molecules move only in the positive or negative  $x$ ,  $y$ , or  $z$  direction, each with the same speed,  $\langle v \rangle$ <sup>‡</sup>.

**NOTES**

<sup>†</sup> Why?! There's no external force on the molecules driving them in one direction or the other, yet the net motion of the molecules is such that the concentration gradient is eventually removed! The physical principles underlying this important behaviour are discussed in detail in Section 3.

<sup>‡</sup> It turns out that a more detailed mathematical analysis – taking the speed and velocity distributions into consideration – yields the same result.

Making this assumption,  $1/6$  of the molecules travel in the  $+x$  direction. Thus, at time  $t$ :

$\frac{1}{6}n'(x + \lambda, t) \langle v \rangle$  molecules per second arrive at unit area of the plane  $AB$  having left the layer at  $x + \lambda$ .

Similarly,  $\frac{1}{6}n'(x - \lambda, t) \langle v \rangle$  molecules per second arrive at unit area of the plane  $AB$  having left the layer at  $x - \lambda$ .

Therefore, the net number of molecules crossing unit area of  $AB$  in the  $+x$  direction is:

$$J(x, t) = \frac{1}{6} \langle v \rangle [n'(x - \lambda, t) - n'(x + \lambda, t)] \quad 2.60$$

As  $\lambda$  is very small, by taking  $\lambda = dx$  we can approximate  $n'(x \pm \lambda, t)$  as follows:

$$n'(x \pm \lambda, t) = n'(x, t) \pm \lambda \left( \frac{\partial n'(x, t)}{\partial x} \right) \quad 2.61$$

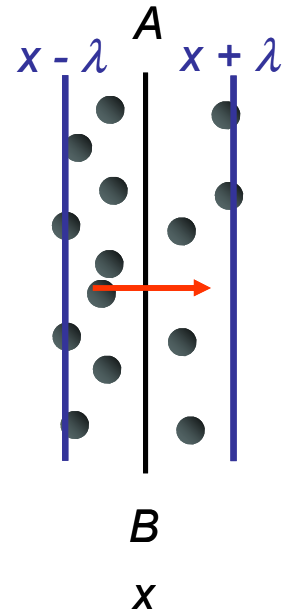
Substituting 2.61 into 2.60 we get:

$$J(x, t) = \frac{1}{6} \langle v \rangle \left[ n'(x, t) - \lambda \left( \frac{\partial n'(x, t)}{\partial x} \right) - n'(x, t) - \lambda \left( \frac{\partial n'(x, t)}{\partial x} \right) \right] \Rightarrow$$

$$J(x, t) = -\frac{\langle v \rangle \lambda}{3} \left( \frac{\partial n'(x, t)}{\partial x} \right) \quad (2.62)$$

If we now compare Equation 2.63 with Fick's law (Equation 2.59) we can get an expression for  $D$ , the diffusion coefficient for a gas:

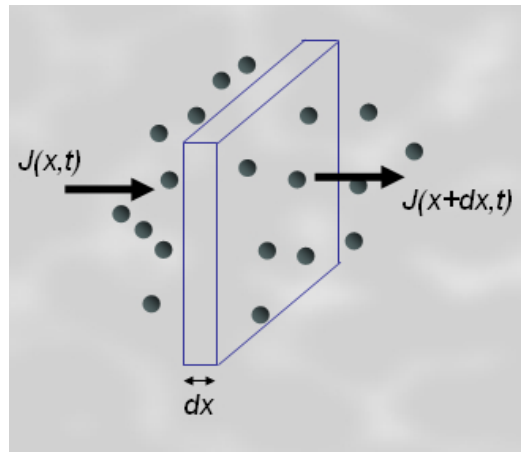
$$D = \frac{\langle v \rangle \lambda}{3} \quad (2.63)$$



**Fig. 2.33** We consider molecules diffusing from one path length either side of the plane  $AB$  which is located at  $x$ .

### *The diffusion equation*

We now wish to determine the relationship between the *rate of change* of the concentration of the molecules at a particular point in space to the *spatial variation* of the concentration at that point. This will provide us with an important equation (*the diffusion equation*), the solution to which will enable a prediction of the concentration profile at any given moment of time. As we'll see, the variation of the concentration profile as a function of time yields important insights into the molecular motion.



*Fig. 2.34 Molecules diffusing in the +x direction through unit area of a slab of thickness  $dx$ .*

As shown in Fig. 2.34, we'll consider a thin slab of cross-sectional area  $A$  that extends from  $x$  to  $x + dx$ . The concentration at  $x$  at time  $t$  is again  $n'(x,t)$ . The number of molecules that enter the slab per unit time is  $J(x,t)A$ . Thus, the rate of increase of the molecular concentration inside the slab due to the flux into the left hand side of the volume  $A dx$  is:

$$\frac{\partial n'(x,t)}{\partial t} = \frac{J(x,t)A}{A dx} = \frac{J(x,t)}{dx}$$



*What is the rate of change of concentration inside the slab due to the flux leaving the right hand side of the slab?*



*Therefore, the net rate of change of concentration inside the slab is.....?*

**NOTES**



Hence, we can write:

$$\frac{\partial n'(x,t)}{\partial t} = -\frac{\partial J(x,t)}{\partial x} \quad 2.64$$

Using Fick's law (Equation 2.59) again, we can rewrite Equation 2.64 as follows:

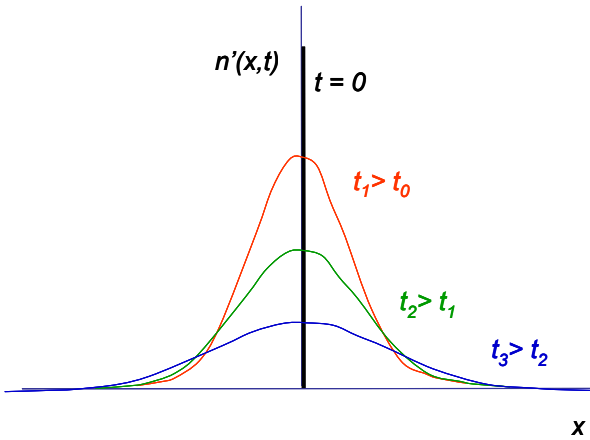
<i>The diffusion equation</i>	$D \frac{\partial^2 n'}{\partial x^2} = \frac{\partial n'}{\partial t}$	(2.65)
-------------------------------	---	--------

Equation 2.65 is a 2<sup>nd</sup> order *partial* differential equation. In the Mathematical Physics module next year you'll study the various methods used to solve partial differential equations (PDEs). In General Maths this semester you're covering the methods used to solve ordinary differential equations (ODEs). Pay particular attention to the methods used to solve differential equations – you'll see a lot (and solve a lot) of ODEs and PDEs during your degree!

Although we'll not attempt to solve Equation 2.65, to completely solve *any* differential equation we need to know the initial (or boundary) conditions. In this case, we simply write that at  $x = 0$  and  $t = 0$ , the concentration of the molecules is a value  $n'(0,0)$ . Using this initial condition, the solution of Eqn. 2.65 is:

$n'(x,t) = n'(0,0) \frac{1}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$	<i>Solution to diffusion equation</i>	2.66
--	---------------------------------------	------

**NOTES**



**Fig. 2.35** Schematic illustration of broadening of the Gaussian curve representing the concentration profile for diffusing gas molecules as a function of time.

Note that the solution to the diffusion equation involves an exponential term with a  $-x^2$  factor in the exponent. Compare Equation 2.66 with Equation 2.29 in Section 2.4. Both are *Gaussian* functions. If we plot the concentration variations given by Eqn. 2.66 as a function of time we get the profiles shown in Fig. 2.35. Hence, the molecules spread out as a function of time – the Gaussian curve *broadens*.

**What does  $D$  represent microscopically?**

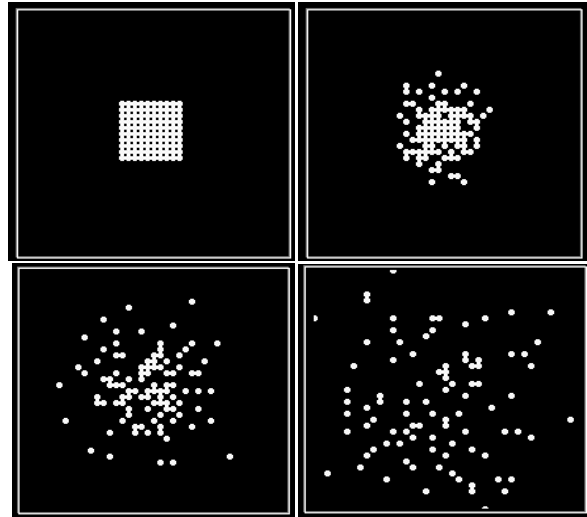
The diffusion coefficient,  $D$ , also appears - not surprisingly - in the solution to the diffusion equation. However, on a microscopic level, just what does  $D$  represent? From Fig. 2.31 we noted that  $\langle x^2 \rangle \propto t$  and that, therefore, the rms displacement varies as  $\sqrt{t}$ . The mean square displacement is related to the diffusion coefficient,  $D$ , by the following equation:

$$\langle x^2 \rangle = 2Dt \tag{2.67}$$

**NOTES**

### *Diffusion, milk drops, and the ‘arrow of time’*

A common example of diffusion is the spreading out of a droplet of cream or milk in a cup of coffee. We’ll not stir the coffee and we’ll also neglect convection (which in reality plays a big role in heat transport in this case). We’ll take our initial state as a square lattice of molecules and, as shown in Figure 2.36, as a function of time the molecules will spread out to evenly cover the available space.



? *Imagine we film the simulation. Will we observe strong differences in the evolution of the state of the drop if we run the film backwards or forwards?*

#### NOTES

**Fig. 2.36** Computer simulation of the diffusion of a cluster of molecules (eg a droplet of milk in coffee) as a function of time. Note how the molecules move from an original inhomogeneous state to an arrangement which more homogeneously covers the available space. This figure is in some regards the 2D analog of the 1D concentration profile shown in Fig. 2.35.

? *Imagine we film the motion of a single isolated molecule. How different will this motion appear if we play the film backwards?*

? *Is it possible that the molecules could ‘reorganise’ themselves into an ordered droplet?*

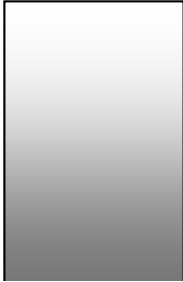
? *If there is nothing in the laws of motion forcing the molecules to spread out and become more disordered, why do they?*

#### NOTES

## 2.13 Thermal conductivity of a gas



**NB Here we consider conduction of heat through a gas via intermolecular collisions – convection is not involved.**



Consider a gas contained within a container in which there is a temperature gradient from top to bottom. Transfer of heat from the hotter to the cooler regions will occur by intermolecular collisions. To determine the flow of thermal energy we need to consider net energy flow across a given plane.

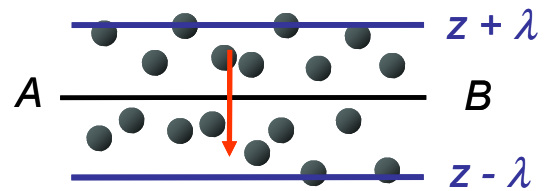
$$\frac{dQ}{dt} = -\kappa A \frac{dT}{dz}$$

2.68

Equation 2.68 allows the calculation of the *heat current* (i.e. the rate of heat flow).  $\kappa$  is the coefficient of thermal conductivity,  $A$  is the cross sectional area, and  $dT/dz$  is the temperature gradient. To evaluate the rate of heat flow we thus need to derive a formula for  $\kappa$ , the coefficient of thermal conductivity.

We'll employ a similar model to that used for the derivation of the diffusion coefficient in Section 2.12 where we consider the number of molecules which cross a unit area of a given plane.

In this case the most important effect is the different mean energy of the molecules in the layer at  $z + \lambda$  compared to the molecules in the layer at  $z - \lambda$ . We neglect the difference in  $n'$  between the two layers and also make the assumption that  $\langle v \rangle(z + \lambda) = \langle v \rangle(z - \lambda)^\dagger$ .



**Fig. 2.37** Conduction of heat in a gas. As for the derivation of Eqn. 2.63 we consider two planes in the gas a mean free path above and below the plane AB.

Hence, the number of molecules on average which cross unit area of the plane AB per second and come from a plane at position  $z + \lambda$  is:

$$\frac{1}{6} n' \langle v \rangle.$$

The average energy carried by these molecules is thus:

$$\frac{1}{6} n' \langle v \rangle \varepsilon(z + \lambda)$$

where  $\varepsilon(z + \lambda)$  is the average energy per molecule in the plane  $z + \lambda$ .

<sup>†</sup> This is a major – and, if you think about it, rather unwarranted – assumption. Grant and Phillips do not make this assumption (p. 484). However, very many textbooks DO make the assumption that the mean speed is the same for all the molecules considered in the model outlined in Fig. 2.37. We'll follow the conventional derivation of the formula for thermal conductivity in the gas. You should revise this – and not the Grant & Phillips - derivation for examination purposes.

The net flow of energy across the plane AB (in the +z direction) per unit time is thus:

$$\frac{1}{6} n' \langle v \rangle [\varepsilon(z - \lambda) - \varepsilon(z + \lambda)]$$

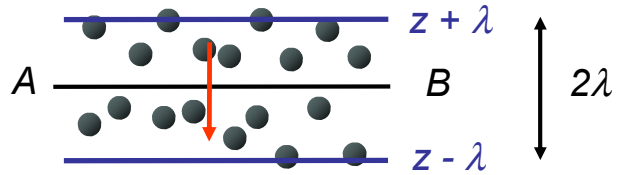
The net flow of energy is simply  $dQ/dt$  and adopting a slightly more compact notation for the mean energy per molecule we arrive at the following formula:

$$\boxed{\frac{dQ}{dt} = \frac{1}{6} n' \langle v \rangle [\varepsilon_{- \lambda} - \varepsilon_{+ \lambda}]} \quad 2.69$$

From Figure 2.38,  $\frac{d\varepsilon}{dz} = \frac{[\varepsilon_{+ \lambda} - \varepsilon_{- \lambda}]}{2\lambda}$

Therefore,

$$\varepsilon_{- \lambda} - \varepsilon_{+ \lambda} = -2\lambda \frac{d\varepsilon}{dz} \quad 2.70$$



*Fig. 2.38 The gradient of the average molecular energy wrt  $z$  is  $(\varepsilon_{+ \lambda} - \varepsilon_{- \lambda})/2\lambda$*

Substituting Eqn. 2.70 into Eqn. 2.69 we get the following:

$$\frac{dQ}{dt} = \frac{1}{6} n' \langle v \rangle -2\lambda \frac{d\varepsilon}{dz} \Rightarrow$$

$$\frac{dQ}{dt} = -\frac{1}{3} n' \langle v \rangle \lambda \frac{d\varepsilon}{dz}$$

However, we can write the gradient of average molecular energy with respect to  $z$  as follows:

$$\frac{d\varepsilon}{dz} = \frac{d\varepsilon}{dT} \frac{dT}{dz}$$

Therefore,

$$\boxed{\frac{dQ}{dt} = -\frac{1}{3} n' \langle v \rangle \lambda \frac{d\varepsilon}{dT} \frac{dT}{dz}} \quad 2.70$$

If we compare Equation 2.70 with the expression for the heat current given in Equation 2.68 we can write down the following expression for the thermal conductivity of a gas:

$$\kappa = \frac{1}{3} n' \langle v \rangle \lambda \frac{d\varepsilon}{dT} \quad 2.71$$

**NOTES**

It is important to note that  $\frac{d\epsilon}{dT}$  is  $c_v$ , the heat capacity per molecule at constant volume. (We denote the specific heat per molecule as  $c_v$  whereas the molar specific heat capacity is  $C_V$ ).



Write down  $c_v$  for a monatomic ideal gas.

Hence, the coefficient of thermal conductivity for a gas is given by the following expression:

$$\kappa = \frac{1}{3} n' \langle v \rangle \lambda \frac{C_V}{N_A} \quad 2.72$$

Note that the thermal conductivity of a gas is independent of  $n'$  (substitute Equation 2.57 into Equation 2.72). This seems a counter-intuitive result – for example, as  $n'$  approaches zero it is difficult to see how the thermal conductivity is independent of the number density. This leads to the following important disclaimer regarding Sections 2.12 and 2.13:

*All formulae in Sections 2.12 and 2.13 are derived under the assumption that the mean free path of the molecules is  $\ll$  the dimensions of the container. If the gas number density is so low that a molecule has a good chance of crossing the container without colliding with another molecule then none of the formulae in Sections 2.12 and 2.13 are valid.*

## 2.14 Convection

As mentioned previously, we won't cover convection in any detail in this module. Although it is a heat transfer mechanism which in many cases may be of at least comparable importance to conduction and radiation, a proper quantitative treatment of convection necessitates a consideration of fluid and/or hydro-dynamics – topics which are beyond the scope of this module. The key physical phenomenon underlying convection in gases is the volume increase associated with raising the temperature of a given mass of gas at constant pressure ( $PV = nRT$ ). The volume increase means that the density of the gas will decrease and hence its buoyancy increases. Thus, for example, warm air expands and rises whereas cooler air sinks.

### NOTES

**NOTES**