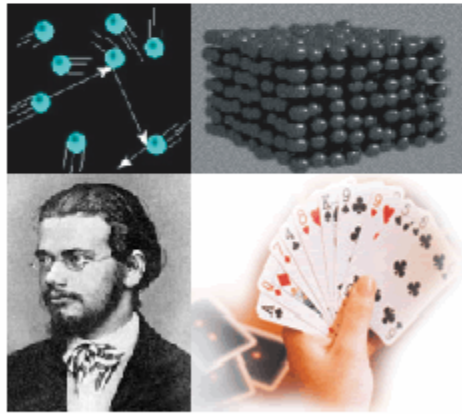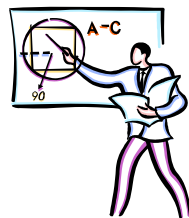# Introduction to Thermodynamics and Kinetics

F31ST1

School of Physics & Astronomy

Lecture Notes
Set 2b: Kinetic Theory II

Thus far…..

First, a brief summary of what we've done thus far in Section 2. We initially considered distribution functions and the evaluation of average quantities related to distribution functions. Building on this knowledge, the ideal gas law, $PV = NkT$ (or $PV = nRT$ for n moles of gas) was derived. The key assumptions underlying the concept of an ideal gas have also been described. An important element of our derivation of the ideal gas law was the consideration of *average* values. In Section 2.3 we introduced the exceptionally important concept of *Boltzmann factors* and outlined how these factors determined the distribution of the elements of a system amongst the available energy levels. In the remaining part of Section 2 of the module, we'll consider:

(i)   the distribution of molecular speeds in an ideal gas – the *Maxwell-Boltzmann distribution;*
(ii)   the theorem of the equipartition of energy – a fundamental law of classical thermal and kinetic physics;
(iii)   how the specific heat of a gas relates to the equipartition of energy;
(iv)   the failure of the equipartition theorem to correctly describe both specific heats *and* the spectrum of radiation emitted by certain objects known as black-bodies;

2.4 Distribution of molecular velocities in an ideal gas
[NB See the slides and your notes for Lecture 7 for a complementary discussion of this topic]

The following assumptions are particularly important throughout Section 2.4. As we're dealing with an ideal gas, there are no interactions between molecules and the molecules are *monatomic*. That is, there are no internal vibrations or rotations of the molecules to consider. (As we'll see later on, diatomic molecules (such as H_2, N_2 and O_2) have vibrational and rotational modes that may be excited and this has an important bearing on the properties of the gas.) Thus, we can say:
for an ideal gas the total energy is determined solely by the kinetic energies of the molecules.
We now want to consider the distribution of kinetic energies – i.e. the distribution of speeds – when the gas is in thermal equilibrium at a temperature T.
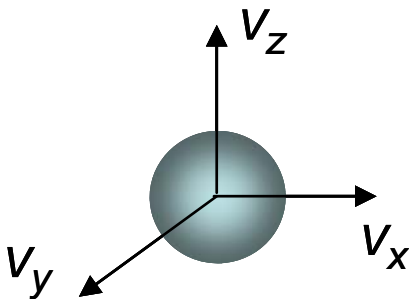

Fig. 2.13 The velocity vector for a gas molecule may be broken down into its components v_x, v_y and v_z.

The molecular speed is *continuously distributed* and is independent of the molecular position. For molecules travelling with a speed between v and $v + dv$, the components of the velocity vector lie within the following ranges: $v_x \rightarrow v_x + dv_x$, $v_y \rightarrow v_y + dv_y$, $v_z \rightarrow v_z + dv_z$.

? *What is the kinetic energy of a molecule whose velocity components lie within these ranges?*

? *…which means that the probability of a molecule occupying this state is…?*

Therefore the probability, $f(v_x, v_y, v_z) \, dv_x dv_y dv_z$, that a molecule has velocity components within the ranges $v_x \rightarrow v_x + dv_x$ etc.. obeys the following relation:

$$f(v_x, v_y, v_z) \, dv_x dv_y dv_z \propto \exp(-mv^2/2kT) \, dv_x dv_y dv_z \qquad (2.22)$$

but $v^2 = v_x^2 + v_y^2 + v_z^2 \Rightarrow$

$$f(v_x, v_y, v_z) \, dv_x dv_y dv_z = A\exp(-mv_x^2/2kT) \exp(-mv_y^2/2kT) \exp(-mv_z^2/2kT) \, dv_x dv_y dv_z \quad (2.23)$$

where A is a constant.

The question now arises as to how we evaluate the constant A.

? *What is the probability that a molecule has velocity components within the range $-\infty$ to $+\infty$?*

Therefore,

$$\frac{1}{A} = \int_{-\infty}^{+\infty} \exp\left(-\frac{mv_x^2}{2kT}\right) dv_x \int_{-\infty}^{+\infty} \exp\left(-\frac{mv_y^2}{2kT}\right) dv_y \int_{-\infty}^{+\infty} \exp\left(-\frac{mv_z^2}{2kT}\right) dv_z \qquad (2.24)$$

In addition, if we're interested in the probability distribution of only one velocity component (e.g. v_x), we integrate over v_y and v_z:

$$f(v_x)dv_x = \frac{\exp\left(-\frac{mv_x^2}{2kT}\right)dv_x \int_{-\infty}^{+\infty} \exp\left(-\frac{mv_y^2}{2kT}\right)dv_y \int_{-\infty}^{+\infty} \exp\left(-\frac{mv_z^2}{2kT}\right)dv_z}{\int_{-\infty}^{+\infty} \exp\left(-\frac{mv_x^2}{2kT}\right)dv_x \int_{-\infty}^{+\infty} \exp\left(-\frac{mv_y^2}{2kT}\right)dv_y \int_{-\infty}^{+\infty} \exp\left(-\frac{mv_z^2}{2kT}\right)dv_z} \qquad (2.25)$$

Thus, cancelling the common factors in Eqn. 2.25 we get:

$$f(v_x)dv_x = \frac{\exp(-\frac{mv_x^2}{2kT})dv_x}{\int_{-\infty}^{+\infty}\exp(-\frac{mv_x^2}{2kT})dv_x} \qquad (2.26)$$

The value of the integral may be looked up in integral tables and we find:

$$\int_{-\infty}^{+\infty}\exp(-\frac{mv_x^2}{2kT})dv_x = \sqrt{\frac{2\pi kT}{m}} \qquad (2.27)$$

(For those of you who are interested, Feynman discusses how to determine integrals of this type on p. 40-6 of the *Feynman Lectures in Physics*, Vol. I. Note however that you will not be expected to evaluate integrals such as this in the exam – the value of the integral will be provided).

Substituting the value of the integral into the denominator of Eqn. 2.26, the expression for the distribution of molecular *velocities* in an ideal gas results:

$$f(v_x)dv_x = \sqrt{\frac{m}{2\pi kT}}\exp(-\frac{mv_x^2}{2kT})dv_x \qquad (2.28)$$

NOTES

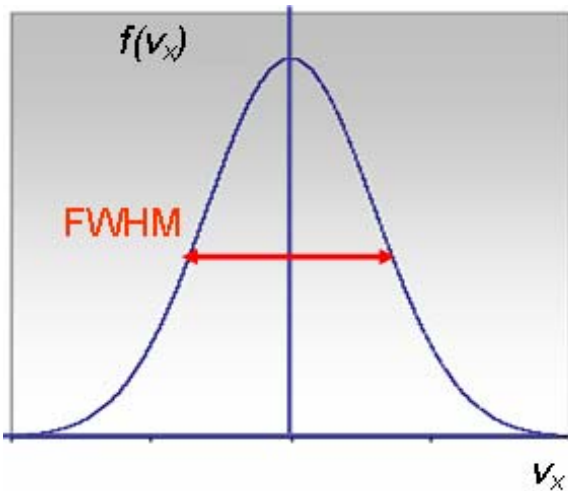Expression 2.28 is a *Gaussian distribution* (once again, see the 1st year laboratory errors manual).

Fig. 2.14 The probability distribution associated with molecular velocities in an ideal gas is a Gaussian function which is symmetric about the mean velocity (which is 0).

The mathematical expression for a Gaussian function is:

$$g(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2\right) \qquad (2.29)$$

where σ is the standard deviation and μ is the mean. The relationship between the standard deviation and the full width at half maximum (FWHM) of the distribution is:

$$\sigma = \text{FWHM}/\sqrt{(8\ln2)}$$

2.5 Distribution of molecular speeds in an ideal gas

We need to carry out a few more mathematical steps to derive an expression for the distribution of molecular *speeds*. Combining equations 2.23 and 2.28:

$$f(v_x, v_y, v_z)dv_x dv_y dv_z = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{m(v_x^2 + v_y^2 + v_z^2)}{2kT}\right)dv_x dv_y dv_z \qquad (2.30)$$

This expression is written in Cartesian coordinates (i.e. x, y, z). To derive an expression for the distribution of molecular speeds it is best to switch to spherical polar coordinates (Fig. 2.15).
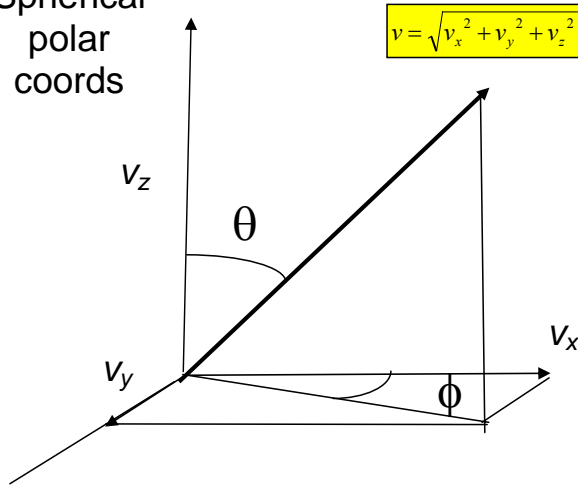
NOTES

Spherical polar coords

$$v = \sqrt{v_x^2 + v_y^2 + v_z^2}$$

v_z

θ

v_y

v_x

ϕ

Fig. 2.15 Spherical polar coordinates. The vector $\vec{v}$ is expressed in terms of the angles θ, ϕ and its length, v. θ is the angle between $\vec{v}$ and the z-axis, whereas ϕ is the angle that the projection of the vector $\vec{v}$ onto the xy plane makes with the x axis.

However, we are not only concerned with changes in the direction of the velocity vector - we also need to consider changes in the *length* of the vector. If the velocity vector changes length from v to $v + dv$ then the radius of the sphere changes by the same amount and we get an infinitesimal change of volume: $4\pi v^2 dv$.

? *Why does the volume change by $4\pi v^2 dv$ when the velocity vector changes length from v to v + dv?*

You need not at this point be concerned with the details of spherical polar coordinates (you will, however, encounter these in a number of modules next year). For now, you should realise that if we consider *all* directions of the velocity vector, the tip of the vector will trace out the surface of a hollow sphere with its centre at the origin. One octant of that sphere is shown in Fig. 2.16, as is a small surface element, dS which results from infinitesimal changes in the direction of the vector.
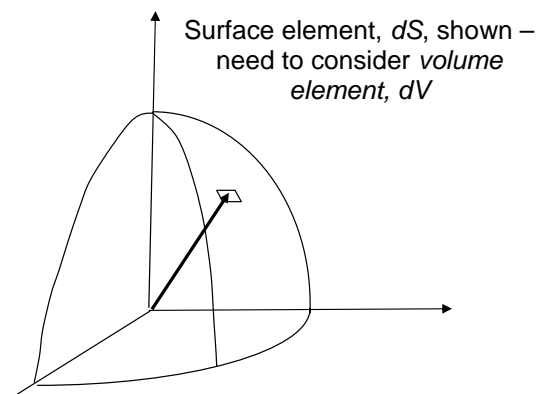
Surface element, *dS*, shown – need to consider *volume element, dV*

Fig. 2.16 *If we consider all possible directions that the velocity vector can point, the tip of the vector will trace out the surface of a hollow sphere. A small surface element, dS, resulting from infinitesimal changes in the direction of the velocity vector is shown.*

NOTES

Combining Eqn. 2.30 with the expression for the volume element, $4\pi v^2 dv$ leads to the following equation:

$$f(v)dv = 4\pi v^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp(-\frac{mv^2}{2kT})dv \qquad (2.31)$$

This is the **Maxwell-Boltzmann distribution** of molecular speeds in a gas.
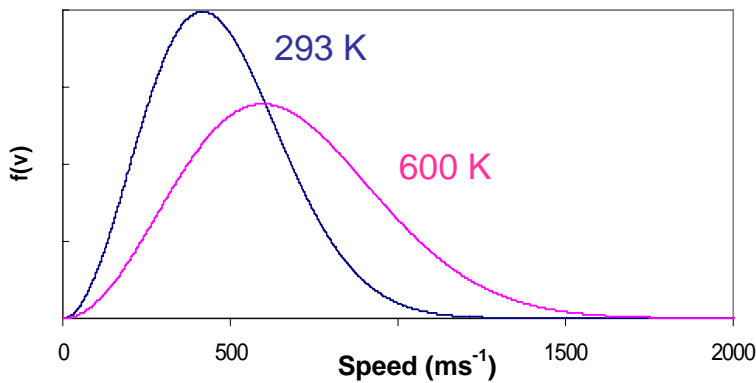

Fig. 2.17 *The Maxwell-Boltzmann distribution for ideal gas molecules at 293 K and 600 K*

Figure 2.17 shows the Maxwell-Boltzmann distribution for ideal gas molecules at two temperatures, 293 K and 600 K. In this case, the speed interval, dv, is 1 ms^{-1}. Note that the peak of the distribution moves to a larger value of speed as the temperature increases. In addition, because the distribution is asymmetric the most probable speed is a little less than the mean speed. You will derive values for the most probable speed and the mean speed in the problems for Coursework Set 3. (The integrals given in the Appendix to this set of notes will prove useful for the coursework exercises).

Note that to determine the total number of molecules with speeds between certain limits, one must integrate under the curve as shown in Fig. 2.18.
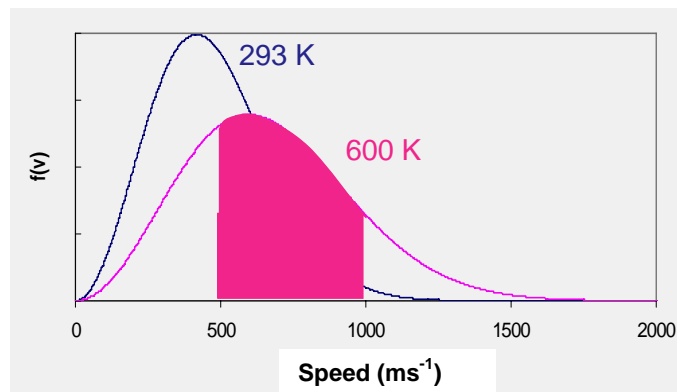

Fig. 2.18 *To determine the number of molecules with speeds between 500 and 1000 ms^{-1}, integrate under the curve within those limits*

(A useful website related to the Maxwell-Boltzmann distribution may be found at the following URL: *http://copm.uark.edu/~jgeabana/mol_dyn/KinThI.html*)

2.6 ½ *m<v²> = 3kT/2* revisited

In the derivation of the ideal gas law in Section 2.2 of the notes, the constant relating the mean kinetic energy of the gas to the absolute temperature was apparently arbitrarily chosen as *3k/2* where *k* is Planck's constant. I noted at the time that this was somewhat unsatisfactory. Having deduced the function governing the distribution of molecular speeds, we are now in a position to show that the mean energy of the gas is indeed given by 3(*½ kT*). This has very important implications for classical physics – as we shall shortly see.

$$<v^2> = \int_0^\infty v^2 4\pi v^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp(-\frac{mv^2}{2kT})dv$$

$$\Rightarrow <v^2> = \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty v^4 \exp(-\frac{mv^2}{2kT})dv \qquad (2.32)$$

Using one of the integrals given in Appendix A, we find:

$$<v^2> = 3\frac{kT}{m} \qquad (2.33)$$

$$\Rightarrow \frac{1}{2}m<v^2> = \frac{3}{2}kT$$

Therefore, we have derived 'from first principles' that the average energy of the ideal gas is given by *3kT/2*. This will be a result that we'll use repeatedly in what follows in the rest of Section 2.

2.7 Equipartition of energy and degrees of freedom

Equation 2.33 was derived by considering the translational motion of the ideal gas monatomic molecules in three directions – i.e. we were concerned with v_x, v_y, and v_z (see Fig. 2.13). We say that the molecules each have three *degrees of freedom*. If we reconsider an atom bound in a solid, as discussed in Section 1, for small displacements from equilibrium the atom behaves as a simple harmonic oscillator. The probability of finding the system in a given energy state is proportional to: $exp(-\mu x^2/2kT)$ (where μ is the spring constant of the SHO). This is analogous to the probability of finding a monatomic ideal gas molecule in a given energy state due to its translational kinetic energy, $exp(-mv_x^2/2kT)$. Using an analysis almost identical to that described in Sections 2.4 to 2.6 for kinetic energy we find that:

$$\tfrac{1}{2}\,\mu<x^2> = \tfrac{1}{2}\,kT \qquad\qquad (2.34)$$

Thus, the average potential energy of a simple harmonic oscillator is also ½ kT.

(Note that I have used μ to denote the spring constant of the SHO here in order to avoid confusion with k, Boltzmann's constant).

Theorem of equipartition of energy

"Each quadratic term in the expression for the average total energy of a particle in thermal equilibrium with its surroundings contributes on average ½ kT to the total energy"

or *"Each degree of freedom contributes an average energy of ½ kT"*

So, what is meant by a 'quadratic term?'. Consider the following:

1. Translational kinetic energy (Sections 2.4 – 2.6) comprises 3 'squared' or *quadratic* terms: $\tfrac{1}{2}\,m<v_x^2>$, $\tfrac{1}{2}\,m<v_y^2>$, $\tfrac{1}{2}\,m<v_z^2>$ $\Rightarrow$ Average energy is 3 x ½ kT = *3kT/2*

2. Rotational energy: $\tfrac{1}{2}\,I<\omega^2> = $ ½ kT per axis of rotation. Diatomic molecules (Fig. 2.19) have two axes of rotation, hence average rotational energy = kT.

Fig. 2.19 – a diatomic molecule

3. **?** *What is the average total energy of a simple harmonic oscillator?*

NOTES

2.8 Work done by a gas

For an ideal gas of *monatomic* molecules, the equipartition of energy theorem yields the following result for the total energy of 1 mole:

$$U = 3N_AkT/2 = 3RT/2 \qquad\qquad (2.35)$$

If we heat 1 mole of gas its temperature rises by a different amount depending on whether the pressure or the volume is fixed. That is, C_P *is not the same as* C_V. To consider where the differences in specific heat arise (and how these differences relate to the equipartition theorem), we need to first determine the work done by an ideal gas when it expands.
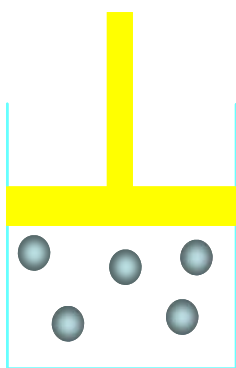
As $PV = RT$, the gas must expand if the pressure is kept fixed and the temperature is increased. (See http://intro.chem.okstate.edu/ 1314F00/Laboratory/GLP.htm for a Java applet on the relationships between *P, V* and *T* for an ideal gas).

We assume that the piston is *entirely frictionless* : all of the work done by the gas goes into pushing the piston back (work done <u>on</u> the surroundings) and not into overcoming frictional forces. That is, the force is *conservative*.

Fig. 2.20 *Expansion of an ideal gas*

Furthermore, we let the gas expand exceptionally slowly (***quasistatically***) *so that the gas is in thermal equilibrium at all times*.

The gas expands reversibly.

In Section 3 we will return to a more in-depth discussion of reversibility, quasistatic processes and thermal equilibrium.

As $P = F/A \Rightarrow F = PA$

$dW = Fdx \Rightarrow dW = PAdx \Rightarrow$

$$\boxed{dW = -PdV} \quad \textit{(reversible)} \quad (2.36)$$

Fig. 2.21 *When the gas expands quasistatically the frictionless piston moves back by an infinitesimal amount dx.*

NB The **convention** we adopt is that an expansion of the gas (ie positive dV) is associated with negative work whereas a compression of the gas leads to positive work.
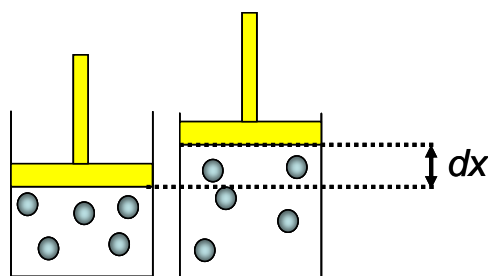
Positive work is work done **on** the *system* **by** the *surroundings*.
Negative work is work done **by** the *system* **on** the *surroundings*.

Introduction to the 1st law of thermodynamics: the conservation of energy

A mathematical statement of the 1st law of thermodynamics is:

$$dU = dW + dQ \qquad (2.37)$$

where dU is the change in energy of the gas, dW is the work done on (or work done by) the gas, and dQ is the heat energy. The 1st law simply states that the total energy of the system is increased either by doing work on the system or by supplying heat to the system – the increase in energy is equal to the sum of the work and heat, as must be the case if we are to conserve energy.

Combining equations 2.36 and 2.37, the following equation applies to a *reversible* process:

$$dQ = dU + PdV \qquad (2.38)$$

We will return to the 1st law and consider it in much more detail in Section 4 of the module.

2.9 Specific heats at constant volume and constant pressure

The specific heat capacity at constant volume, C_v, for one mole of gas is:

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V \qquad (2.39)$$

From the 1st law (Eqn. 2.38), in a constant volume process, $dQ = dU$. Furthermore, for an ideal gas (*and only for an ideal gas*), the energy of the gas is a function of temperature only. We can therefore get rid of the partial derivative in Eqn. 2.39 and write:

$$C_V = \frac{dU}{dT} \Rightarrow \qquad (2.40)$$

$$C_V = \frac{d}{dT}(\frac{3}{2}RT) \Rightarrow$$

$$\boxed{C_V = \frac{3R}{2}} \qquad (2.41)$$

The specific heat at constant pressure, C_P, for one mole is:

$$C_P = \left(\frac{\partial Q}{\partial T}\right)_P \qquad (2.42)$$

Combining Eqn. 2.40 with the first law (Eqn 2.38), for an ideal gas the following expression holds:

$$dQ = C_V dT + P dV \Rightarrow$$
$$\left(\frac{\partial Q}{\partial T}\right)_P = C_V + P\left(\frac{\partial V}{\partial T}\right)_P \qquad (2.43)$$

Using the ideal gas law:

$$PV = RT \Rightarrow$$
$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} \Rightarrow$$
$$\left(\frac{\partial Q}{\partial T}\right)_P = C_V + R \qquad (2.44)$$

Thus, for an ideal gas:

$$C_P = C_V + R \qquad\qquad (2.45)$$

However, using Eqn. 2.41:

$$C_P = \frac{5R}{2} \qquad\qquad (2.46)$$

The ratio of specific heats, γ, is thus:

$$\gamma = \frac{5}{3} \qquad\qquad (2.47)$$

C_P, C_V and problems with classical theory

At this point you might ask what all this has got to do with the equipartition of energy. It is important to remember that the formulae for C_p, C_v and γ given in equations 2.41, 2.46 and 2.47 are based on the fact that $U = 3RT/2$ for 1 mole of an ideal gas. This is a fundamental result of classical equipartition of energy theory (each degree of freedom contributes $\frac{1}{2}\,kT$ to the average energy). We should now address whether this theory does a good job of explaining experimental data.

Monatomic gases such as Ar, Xe and Ne have values of γ which are (within experimental error) 1.66. This is in excellent agreement with equation 2.47. However, diatomic gases such as H_2, O_2 and N_2 are associated with values of γ that are substantially smaller and closer to 7/5. Diatomic gases differ from the monatomic gases that comprise an ideal gas because they have *internal degrees of freedom*. A diatomic molecule has two rotational degrees of freedom and therefore there is an additional kT contribution to the average energy of the gas.

? *Write down the value of C_V for a gas comprising diatomic molecules, taking into account translational and rotational degrees of freedom.*

Taking the rotational degrees of freedom into account, we get the following result: $\gamma = \frac{7}{5}$

At this point the equipartition of energy theorem *seems* to be doing a good job – the experimentally measured values of γ for H_2 and O_2 are 1.404 and 1.399 respectively.

…..but we've forgotten something!

NOTES

C_P, C_V and problems with classical theory: Molecular vibrations

Not only can diatomic molecules rotate, they can *vibrate*. This gives another contribution of kT to the average energy (as discussed above, for a simple harmonic oscillator, there is a contribution of $\frac{1}{2}kT$ from potential energy, and $\frac{1}{2}kT$ from kinetic energy). So, classically, we expect $C_v = 7R/2$.

? *Write down the value of γ for a gas comprising diatomic molecules, taking into account translational, rotational and vibrational degrees of freedom.*

This is rather puzzling. We seem to get the correct, experimentally measured value of γ for a diatomic gas only if we *ignore* the vibrational degrees of freedom of the molecule. However, this is not the only problem. From classical equipartition of energy, the value of γ should be *temperature independent.* Yet, when γ is measured experimentally, there is a clear and strong temperature dependence as shown in Fig. 2.22 below.
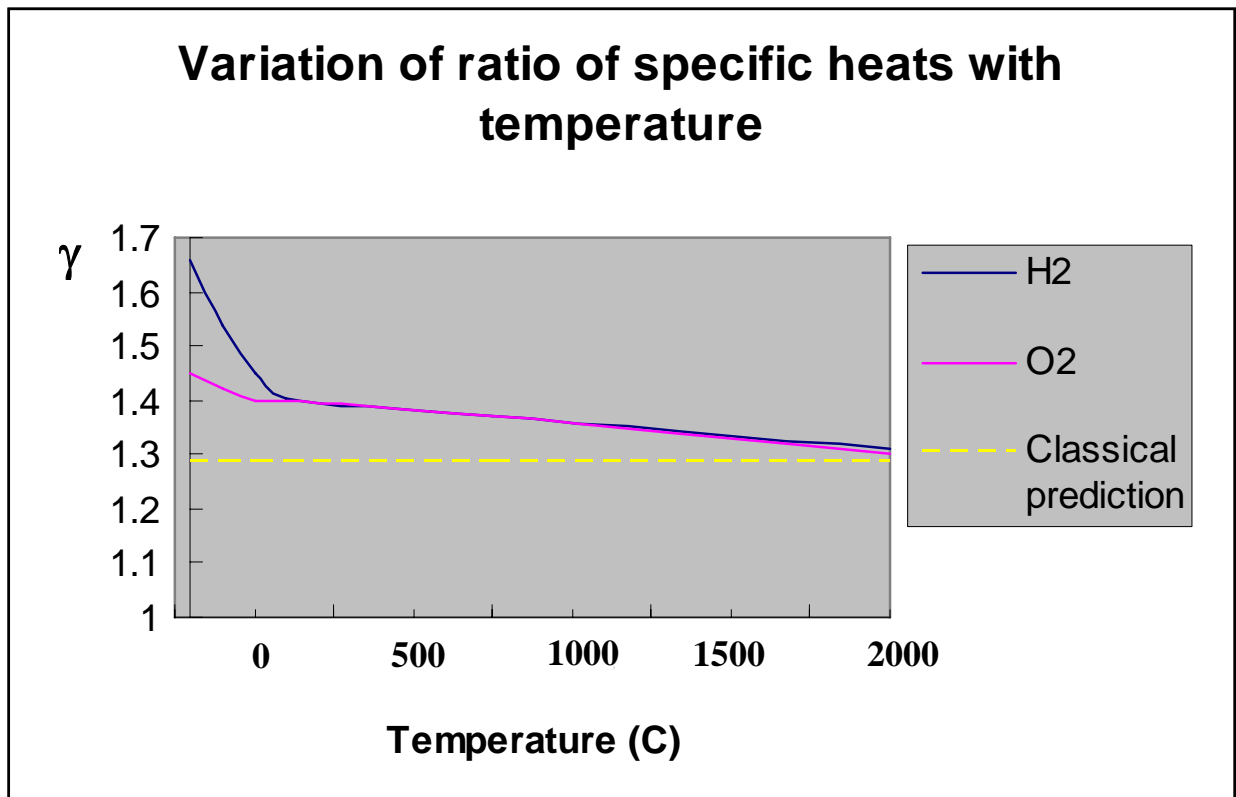

Fig. 2.22 *Schematic illustration of variation of specific heats for hydrogen and oxygen as a function of temperature. The dashed line is the classical prediction (based on the equipartition theorem).*

2.10 Towards quantum theory: 'Cracks' in the classical physics framework

"I have now put before you what I consider to be the greatest difficulty yet encountered by the molecular theory……."
James Clerk Maxwell, 1869

In order to explain the differences between classical equipartition theory, where each degree of freedom for a molecule is associated with an average energy of ½ *kT*, it is necessary to postulate that there must be a mechanism whereby some types of motion (and their associated degrees of freedom) are 'frozen out' at certain temperatures. Consider the O_2 molecule: it has a total of 7 degrees of freedom: 3 translational, 2 rotational and 2 vibrational. This means the total average energy of 1 mole of the gas at room temperature is 7R/2 and the corresponding value of γ should be 1.286. However, if we assume that – for some reason (to be explored below) – there are only 5 degrees of freedom available to the molecule at room temperature then we get the correct result, i.e. the experimentally measured value of γ, which is 7/5 = 1.4. Classically, we can't simply remove degrees of freedom like this – the rotational and vibrational energies are distributed *continuously*. The disagreement of theoretical and experimental values for γ is what led Maxwell to state that this was "*the greatest difficulty encountered by the molecular theory*".

However, the true description of the molecular nature of matter is not based on classical physics but on *quantum* physics. The energies of the vibrations and rotational motion of molecules are *not* distributed continuously. Rather, they are **quantised**. The explanation of just why the experimentally measured values of C_P and C_V did not agree with classical equipartition theory – outlined in the following - played a large role in the development of quantum theory.
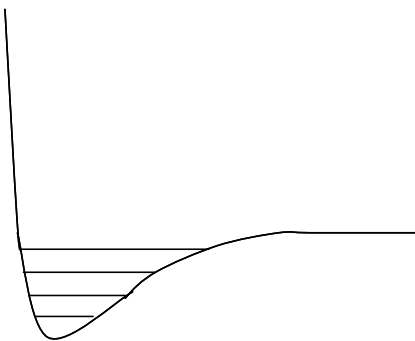
Quantum levels and specific heats

***Fig. 2.23** Quantised vibrational energy levels for interacting atoms. These energy levels are equally spaced.*

The vibrational energy of a molecule is quantised so that instead of the energy being a *continuous* function, it can only adopt certain discrete values. This is analogous to the quantisation of the electronic energy levels in an atom. As described in Section 2.1 of the lecture notes, the energy levels are given by the following formula:

$$E_n = (n + \tfrac{1}{2})\hbar\omega_0$$

(2.48)

In addition, the *rotational* energy of a molecule is also quantized. For rotational energy, the following formula applies:

$$E_l = l(l+1)\hbar^2 / 2I \tag{2.49}$$

where l is the quantum number associated with the rotation (somewhat analogous to n in Eqn. 2.48) and I is the moment of inertia of the molecule.

NOTES

For both rotational and vibrational motion of the molecule, the occupation of the associated energy levels depends on temperature and is given by a Boltzmann factor: *exp (-ΔE/kT)* where ΔE is the energy of the level above the ground state. It is important to bear in mind the following:

Rotational energy levels have spacings of a few **hundredths** of an eV.
Vibrational energy levels have spacings of a few **tenths** of an eV.

kT at room temperature (293 K) = **0.025 eV**

When the temperature is very much greater than a few hundredths of an eV (eg room temperature) then very many narrowly spaced rotational energy levels are occupied and we approach the limit of a classical distribution of energies. In the classical limit, the average rotational energy for a diatomic molecule will be *kT* (from the equipartition theorem).

However, at room temperature, the probability of occupation of vibrational energy levels above the ground state is very low. We are thus well away from the classical limit and would not expect the equipartition theorem to be applicable. This is exactly what we find for diatomic gases. Instead of having the 7 degrees of freedom expected classically they only have 5 degrees of freedom – the vibrational motion of the molecule is associated with energy levels that have a very small probability of being occupied at room temperature. We need to go much higher in temperature before vibrational effects contribute to the specific heat. Indeed, the temperature is generally so high that dissociation of the diatomic molecule (i.e. breakage of the bond between the atoms comprising the molecule) occurs before vibrational effects play a large role in determining the specific heat of the gas.
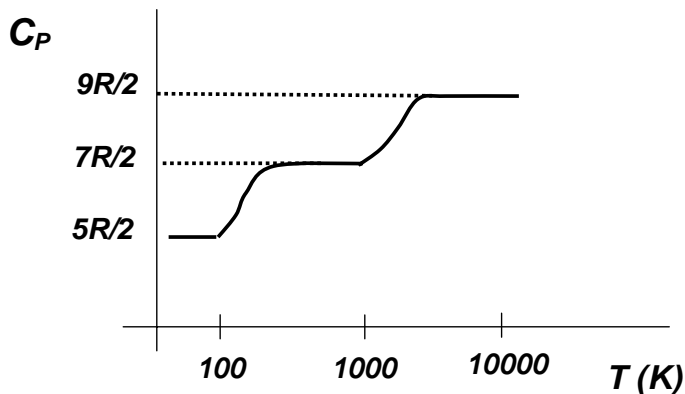

Note that of all the diatomic gases only H_2 is gaseous at temperatures sufficiently low to 'freeze out' the rotational contribution to the specific heat (the other gases solidify before this limit). Hence, only hydrogen and monatomic gases have values of specific heat corresponding to just three degrees of freedom.

Fig. 2.24 *Schematic illustration of the variation in specific heat for 1 mole of a gas of <u>hypothetical</u> diatomic molecules. The steps in the specific heat curve arise from excitation of first rotational, and then vibrational motions of the molecule.*

We can use the equipartition of energy theorem to estimate the rate at which a molecule spins due to its rotational motion. The energy associated with the rotation of the molecule is $\frac{1}{2} I \langle \omega^2 \rangle$. Equipartition tells us that the average energy is $\frac{1}{2} kT$. We can equate these two expressions to estimate the mean square angular velocity of the molecule. (**NB** See *Worked Example 12.5* on p.448 of Grant & Phillips).

NOTES

Black-body radiation and the ultraviolet catastrophe
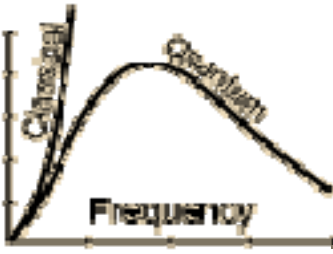
(Note that the diagram to the left – and a number of the diagrams used in this section – are taken from the "Hyperphysics" website. I strongly recommend that you visit this site (and bookmark it!).The URL is: http://hyperphysics.phy-astr.gsu.edu/hbase/hframe.html)

A solid surface at high temperature emits electromagnetic radiation spread across a wide frequency spectrum. The frequency (or wavelength) at which the peak of the radiation is found depends on the temperature of the surface. The temperature dependence of the spectrum explains why a tungsten filament, for example, changes colour from red to white hot as its temperature is increased .
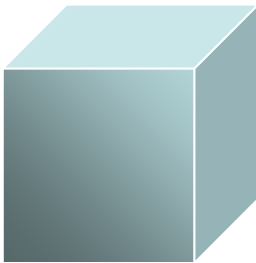

A surface is described as *ideally black* if it absorbs all the radiation that falls on it. In equilibrium an ideally black surface will emit all the energy it absorbs. However, to maintain equilibrium we must have an enclosure (otherwise the radiation will simply radiate out into space). Imagine a closed box with ideally black walls – the radiation within this box is known as **black-body radiation**.

Fig. 2.25 *Radiation enclosed within a box with ideally black walls is called black-body radiation.*

The spectrum of black-body radiation was to prove to be a particularly sharp thorn in the side of classical physics…….

The Rayleigh-Jeans expression (derived from classical physics) for the energy density associated with blackbody radiation is given in Equation 2.50. (A good discussion of the derivation of this law is given on the *Hyperphysics* website for those of you who are interested. Note that the *derivation* is beyond the level of this module and is not part of the examinable syllabus).

$$\rho(v)dv = \frac{8\pi v^2}{c^3}kTdv$$
2.50

Eqn. 2.50 is a rather strange – and, for physicists of the time (the late 19th century), exceptionally worrying - expression. Note that the density of radiation increases with the square of the frequency. Hence, *at any temperature*, we should expect to find quite an amount of high energy X-ray radiation within the cavity (or oven) shown in Fig. 2.25. Furthermore, if we consider a graph of this function (see Fig. 2.26), another very perplexing problem immediately arises.
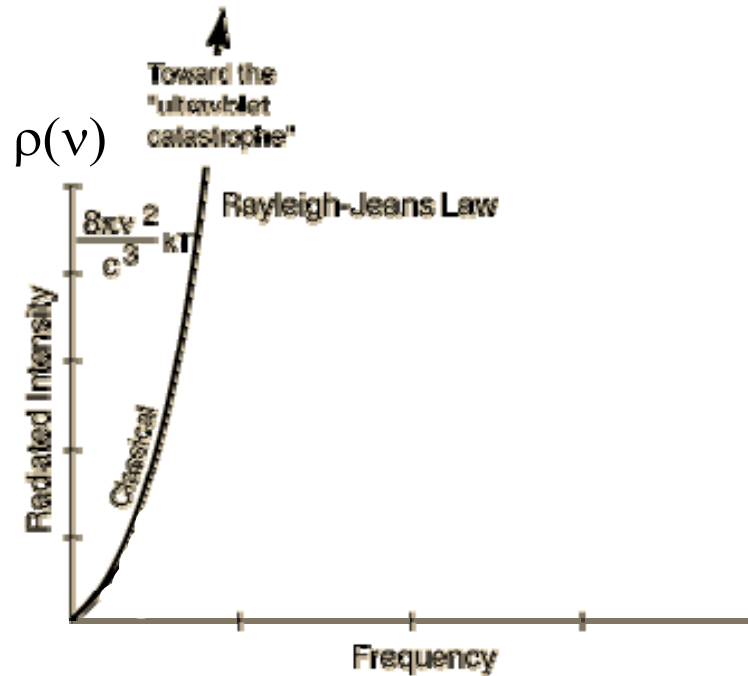
Fig. 2.26 *A plot of the radiated intensity, ρ(ν) vs frequency for the classical Rayleigh-Jeans expression for the spectrum of black-body radiation. Note that as the frequency increases, the radiated intensity increases without limit. This is the ultraviolet catastrophe. (Figure taken from the "Hyperphysics" website).*

Fig. 2.26 and Eqn. 2.50 clearly illustrate that the radiated intensity increases with no limit as a function of frequency. That means that as we approach the ultraviolet region of the spectrum and go beyond in terms of the frequency of the radiation, the amount of radiated light keeps increasing. Hence, as stated above, if we were to open an oven held at a certain temperature and look in our eyes would be burnt out from the intensity of very high energy X-ray radiation. Furthermore, because the total radiated energy is given by the integral under the curve, the total amount of energy in the box is infinite!

"This is the prediction of classical physics…it is fundamentally, powerfully, and absolutely wrong".
RP Feynman, Lectures in Physics, Vol. I

So how do we 'mend' the description of black-body radiation? How do we get rid of the ultraviolet catastrophe? These problems occupied the minds of very many scientists at the end of the 19th century.

Before we consider how to get rid of the ultraviolet catastrophe, let's discuss just what is wrong with the classical description of radiation that it yields such an absurd result. The radiation in the cavity emerges fundamentally from the oscillations of the atoms – the electrons of each atom are 'shaken' and emit radiation related to the frequency at which they're shaken. As we've seen before, the oscillators each have a classical average energy of *kT*. The classical curve for blackbody radiation 'blows up' for precisely the same reason that the classical description of specific heats fails: *the energies of the oscillators haven't been considered correctly.*

Planck's solution to the ultraviolet catastrophe.

If the average energy, *<E>* of the oscillators is not *kT*, then what is it? Planck's solution to this question was one of the first and most important achievements (although there are very many) of quantum theory.

We can work out the correct quantum mechanical formula for *<E>* by considering the appropriate Boltzmann factors for the populations of the energy levels.

Using the expression for the Boltzmann factor given in Section 2.3 we can write:

$$n_n = n_0 \exp(-\frac{n\hbar w}{kT}) \qquad (2.51)$$

where n_n is the number of oscillators with energy E_n and n_0 is the number of oscillators in the ground state (i.e. with 0 energy – we're neglecting zero point energy).
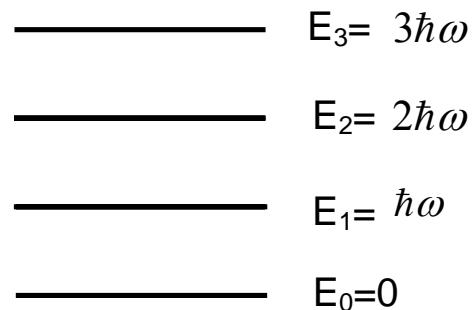
$E_3 = 3\hbar\omega$

$E_2 = 2\hbar\omega$

$E_1 = \hbar\omega$

$E_0 = 0$

Fig. 2.27 The energy levels of a simple harmonic oscillator

$$\text{Let } x = \exp(-\frac{\hbar w}{kT}) \qquad (2.52)$$

Therefore;

$$n_1 = n_0 x, \; n_2 = n_0 x^2, \ldots \ldots \; n_n = n_0 x^n \qquad (2.53)$$

Before working out the average energy, we need to work out the total energy of the oscillators. Consider the first two energy levels above the ground state...

Energy level E_1: the oscillators have energy $\hbar\omega$. The total number of oscillators in this level is n_1. Hence, the total amount of energy associated with the oscillators in level 1 is: $n_1\hbar\omega$. Therefore, from 2.53:

$$n_1\hbar\omega = n_0 x\hbar\omega$$

Energy level E_2: the oscillators have energy $2\hbar\omega$. The total number of oscillators in this level is n_2. Hence, the total amount of energy associated with the oscillators in level 1 is:

$$n_2 2\hbar\omega = n_0 x^2 2\hbar\omega$$

Add up these contributions for all energy levels to get:

$$E_{TOTAL} = n_0\hbar\omega(x + 2x^2 + 3x^3 + \ldots\ldots)$$

Similarly;

$$N_{TOTAL} = n_0(1 + x + x^2 + x^3 + \ldots\ldots)$$

The average energy, *<E>* is thus:

$$< E >= \frac{E_{TOTAL}}{N_{TOTAL}} = \frac{n_0\hbar\omega(x + 2x^2 + 3x^3 + \ldots.)}{n_0(1 + x + x^2 + x^3 + \ldots\ldots)} \qquad (2.54)$$

By evaluating the sums in the numerator and denominator and substituting in the value of x from equation 2.52 we get the following very important expression:

$$< E >= \frac{\hbar\omega}{\exp(\hbar\omega/kT) - 1} \qquad (2.55)$$

Equation 2.55 is the average quantum mechanical energy of a collection of oscillators

> *Show that Eqn. 2.55 reduces to the classical expression for the average energy of a collection of simple harmonic oscillators in the limit of either very high temperatures or very low oscillator frequency.*
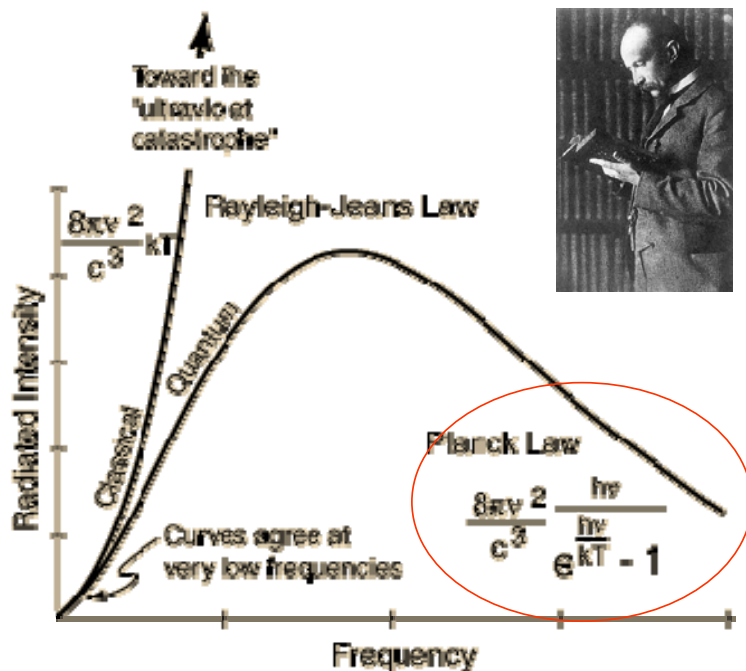
Fig. 2.28 *The Planck law expression for the intensity of a black-body plotted alongside the classical Rayleigh-Jeans law. Note that the two curves agree at very low frequencies.*
(This figure is also taken from the Hyperphysics website).

Figure 2.28 shows the Planck law solution for the radiated intensity of a black-body. The ultraviolet catastrophe has now been averted - at high frequencies the energy density in the cavity is decreasing rather than increasing without limit. Note that the expression for the Planck law:

$$\rho(v)dv = \frac{8\pi v^2}{c^3}\frac{h v}{\exp(\frac{h v}{kT}) - 1}dv \qquad (2.56)$$

differs from the classical Rayleigh-Jeans expression by the replacement of the factor kT (representing the average energy of the oscillators) by Equation 2.55 (note that $\hbar\omega = \frac{h}{2\pi}2\pi v = h v$).

NOTES

APPENDIX A: Useful integrals

$$\int_0^\infty \exp(-\alpha x^2)dx = \frac{\sqrt{\pi}}{2\sqrt{\alpha}}$$

$$\int_0^\infty x\exp(-\alpha x^2)dx = \frac{1}{2\alpha}$$

$$\int_0^\infty x^2 \exp(-\alpha x^2)dx = \frac{\sqrt{\pi}}{4\alpha^{3/2}}$$

$$\int_0^\infty x^3 \exp(-\alpha x^2)dx = \frac{1}{2\alpha^2}$$

$$\int_0^\infty x^4 \exp(-\alpha x^2)dx = \frac{3\sqrt{\pi}}{8\alpha^{5/2}}$$