

# THERMODYNAMICS & KINETIC PHYSICS

## INTRODUCTION.

It could be reasonably argued that Newton, when he identified his three laws of motion invented what is nowadays recognised as physics, at least the classical version. Interestingly, whilst he invented the concepts of force and momentum in which his three laws are grounded, and indeed the concepts of force and momentum are defined by them, Newton and his contemporaries had no use for the concept of energy. Newton's ideas as set out in the Principia described a mechanical universe running according to his laws of motion like a clockwork machine, but could the clockwork be running down? Newton's Principia (1684), and his laws ignored dissipation and worked with closed systems consisting of few bodies. Thermodynamics, a discipline making its first hesitant steps a century later would concern itself with closed and open systems and dissipation would be explicitly involved.

The term energy was first used in its modern sense by Thomas Young (Young's Slits) in 1807 although the entity had been recognised earlier by Leibnitz, a contemporary of Newton. Leibnitz identified the product of the mass of an object with its velocity squared as a quantity with significance to which attention should be paid, a property which he termed "vis viva" (living force), something we recognise today as kinetic energy. This quantity, he suggested, was conserved and the fact that this was not how things were observed to be was due to dissipation in the form of friction, the effect of the collision of the macroscopic object under investigation with many smaller particles in the air and in other bodies with which the body in question inevitably interacted. The vis viva was seen as a rival to the Newtonian notion of momentum, even though the latter was a **vector** quantity whilst the former a scalar. Eventually the two systems were seen as complementary and of equal importance and brought together within a single framework. The study of the energy of systems took on ever greater importance with the differentiation between the many different forms that energy took on, kinetic, potential, mechanical, chemical, electrostatic. An important observation was that the evolution of heat (**caloric or phlogiston**) always appeared to accompany the transformation of one kind of energy into another. This mysterious substance was believed to flow from hot to cold bodies eventually equalising their temperatures. Lack of evidence for phlogiston

never dampened the appeal of this idea for many decades until well into the nineteenth century.

With the invention of engines and their transformation of heat into mechanical work the study of how one kind of energy transformed into another became a “hot” topic. and the arrival of the industrial revolution meant that money was to be made, empires to be built and sustained and the prizes were to be taken by those who understood the limits placed on engines and how to push those limits! The subject of thermodynamics was well and truly born.

## EQUILIBRIUM, TEMPERATURE & the ZEROTH LAW of THERMODYNAMICS.

### 1.1 Heat and Internal Energy.

Heat was an elusive quality, difficult to define objectively but easy to recognise subjectively. We can all tell with a reasonable degree of accuracy which is the hotter of two bodies. For a long time heat was believed to be the substance, caloric, that flowed from hot to cold materials when they were in contact. In the 19<sup>th</sup> century, Irishman, Lord Kelvin (William Thomson) was one of the pioneers working on heat and trying to understand its properties. He famously calculated the age of the earth based on its cooling rate from an initial temperature equal to that of the sun and came up with the figure of 100 million years, an estimate he used to pour scorn on Darwinian evolution which needed far greater time scales in order to operate. Lord Kelvin had vastly underestimated the earth's age as he had no knowledge of the Earth's own internal heating effect provided by radioactivity.

Heat has finally been understood as a form of energy that is present only as a transitional energy when two systems, one at a higher temperature than the other are in contact. The heat energy is exchanged and flows to the cooler body where it is **either stored as different forms of internal energy** of that system or is used to cause the receiving system **to perform work**. *It is not stored as heat* by the receiving body! *We do not refer to any body/system as containing a given quantity of heat*. Rather the body is at some **temperature** because it has an **internal energy** due to the sum of the energies of the body's constituent parts (atoms, molecules etc). In summary heat is defined as the energy **flowing** from a hot to a cooler body by the process of conduction, convection or radiation. The internal energy of a body/system may be present as;

- (i) Kinetic energy of the constituent parts, ie. the energy of translational motion of the atoms/molecules, or their vibrational or rotational motions
- (ii) Latent energy held by the body by virtue of its phase, gas, liquid, solid etc. this, as we will see, is equivalent to potential energy of interaction among constituent parts. This is the origin of the latent heat associated with changes of phase within a system.

(iii) Chemical energy associated with the bonding of the constituent parts of the body.

(iv) Nuclear energy as the energy held by virtue of the strong nuclear interaction.

The first and second of these are the thermal energies of the body/system in which we shall be chiefly interested.

To proceed with the course now some definitions are required.

Since thermodynamics is;

(i) The study of heat transferred between systems,

(ii) Work done by those systems and

(iii) The effect on physical properties of the system under observation,

and since the results obtained on a specific system are readily generalised to any other system provided the right variables are chosen, we shall spend a lot of time studying the simple system of a box full of non-interacting atoms (or molecules). To begin with in order to ensure that the interaction between constituent parts is zero or negligible we will specify a dilute system in order that the constituent atoms or molecules are well separated. **Whether the constituents contained in the box are atoms or molecules, will make a difference when we come to look at internal energy** in some detail because **atoms cannot have internal energies of their own such as rotational or vibrational energy** whereas molecules will generally have internal motions, available to take up some energy, often in a profusion of different types. I will from now on refer to molecules the term being implicitly understood to cover atoms as well. The system will be assumed to contain a large number of molecules,  $N$ , of order of Avagadro's number,  $N_A = 6 \times 10^{23} \text{ mol}^{-1}$ , in order that we may speak of average values of macroscopic observables with confidence. Such observables include volume,  $V$ , pressure,  $P$ , temperature,  $T$ , internal energy,  $U$ , density,  $\rho$  and various fields (electric,  $E$ , magnetic induction,  $B$ , polarisation,  $P$ , magnetisation,  $\mathcal{M}$ , and others). These variables are related to one another by theories and laws in terms of closed systems of equations and coefficients, the latter being experimentally determined and including **bulk modulus,  $\kappa$ , Young's modulus,  $Y$ , thermal expansion coefficient,  $\beta$ , thermal conductivity,  $\sigma$ , specific heat,  $C$ .....**In a later course, statistical physics, these macroscopic systems, variables and coefficients will be related to microsystems such as single molecules and to quantum mechanical eigenvalues and how these values are distributed statistically. Here for now we stick with macrosystems but ultimately the

macro and the micro must be related. The properties of the macrosystem are known as **emergent properties** of a large number of microsystems and may be discovered in a **bottom up approach** by understanding how a single constituent behaves, adding more of these “entities” and trying to understand the gradual emergence of the gross behaviour which is not apparent in a collection of a small number of the constituent molecules. These emergent properties include such complicated phenomena as self organising behaviour, information, life and consciousness. Here we are less ambitious taking instead a **top down approach** that in large part depends on the observed empirical behaviour of the systems without an understanding of the underlying phenomena.

## Internal Energy

We begin a difficult subject in a simple way by asking how the internal energy,  $U$ , of this collection of molecules in a box is related to the pressure, and temperature. We are going to be interested, to begin with, only in the internal energy of the gas due to the translational kinetic energy of the molecules (ignoring vibration and rotation). All we need to say to begin with about the molecules of the gas in the container is that they are moving. Each will have a different **velocity**,  $\underline{v}$ , where I have deliberately used the vector notation to emphasise the fact that they are moving in random directions as well as at random **speeds**. We need again to specify our gas as a dilute gas such that there are no interactions between constituent molecules which are too far apart. This also means that one source of potential energy, namely the potential energy of interacting particles is negligible and may safely be ignored. It also means that the volume of actual matter is negligible compared with the volume in which our system is contained. With all of these caveats the internal energy of the gas (remember no vibration or rotation and no fields meaning no potential energy provided the atoms are separated sufficiently that there is no mutual interaction) is simply the sum of all the kinetic energies of the  $N$  molecules. With the  $n^{\text{th}}$  molecule having a velocity  $\underline{v}_n$  the internal energy is then given by;

$$U = \sum_{n=0}^N \frac{1}{2} m v_n^2 \quad (1.1)$$

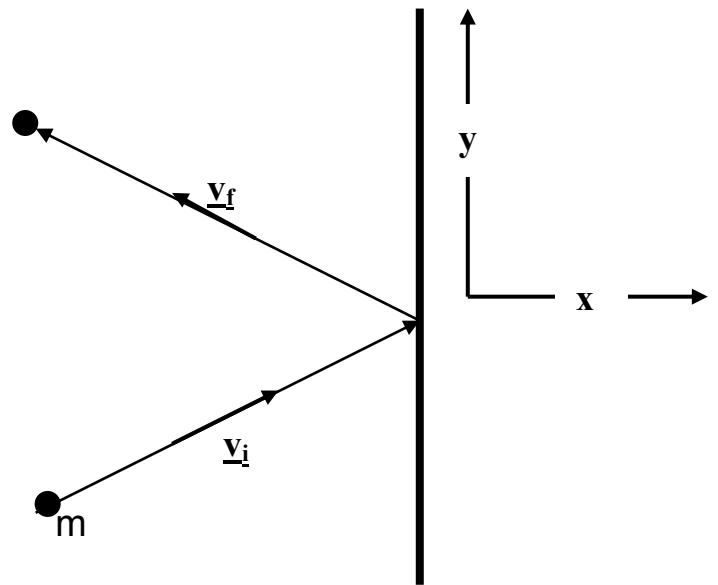
We want to relate this internal energy to the pressure,  $P$ , of the gas which in a macroscopic measurement is  $P = \frac{F}{A}$

Where  $F$  is the force exerted on the wall and  $A$  is the area.

Newton's laws tell us that the force exerted by a single particle in a collision is

$$\vec{F} = \frac{d\vec{p}}{dt} \quad (1.2)$$

Where (I drop the vector notation)  $p$  is the momentum of the particle.



The diagram shows a collision with the wall, of a single particle of mass,  $m$ , travelling with a velocity,  $\underline{v}$ . We assume all collisions to be elastic and in this elastic collision, with the co-ordinate axes as shown, only the  $x$  component of the velocity will change

$$v_{iy} = v_{fy} \quad v_{ix} = -v_{fx} \quad (1.3)$$

The  $x$  component of the momentum has changed by an ammount,

$$p_{fx} - p_{ix} = \Delta p_x = 2mv_x = 2p_x \quad (1.4)$$

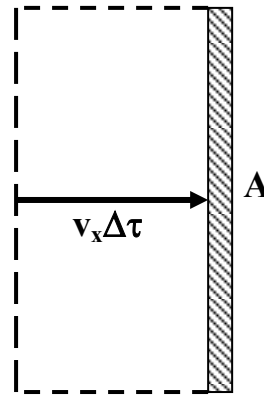
Because of the many frequent collisions of molecules in the gas each will have a different velocity and therefore contribute a different momentum change so to find the

total momentum change we need to add all of the individual changes in momenta, initially just noting in passing that there is a distribution of velocity/momenta.

$$\Delta p_{Tot} = \sum_{v_x} 2N_{v_x} m v_x \quad (1.5)$$

where  $N_{v_x}$  is the number of molecules with the x component of velocity  $v_x$ .

A collision will take place in a time  $\Delta\tau$  such that all molecules with a velocity component  $v_x$  in a volume  $v_x \Delta\tau A$  make that collision as illustrated



This a fraction  $\frac{v_x \Delta\tau A}{V}$  of the total volume,  $V$ . We can therefore identify a (sub)total momentum change due to those molecules with the x component of velocity,  $v_x$ , as

$$(\Delta p)_{v_x} = N_{v_x} \frac{v_x \Delta\tau A}{V} 2p_x \quad (1.6)$$

The total change of the  $x$  component of the momentum in time  $\Delta\tau$  is then given by the sum

$$\Delta p_x = \sum_{v_x \geq 0} \frac{N_{v_x}}{V} \Delta\tau A 2p_x v_x \quad (1.7)$$

Where we only sum the velocities of molecules travelling towards the wall, hence the stricture  $v_x \geq 0$  in the limits of the sum.

It is the force exerted on the wall that we are after (to get the pressure) and

$$F_x = \frac{\Delta p_x}{\Delta \tau} = A \frac{N}{V} \left( \left( \frac{1}{N} \right) \sum_{v_x \geq 0} N_{v_x} 2 p_x v_x \right) \quad (1.8a)$$

$$F_x = \frac{\Delta p_x}{\Delta \tau} = A \frac{N}{V} \left( \left( \frac{1}{N} \right) \sum_{all \ v_x} N_{v_x} p_x v_x \right) \quad (1.8b)$$

I have written 1.8b in this fashion, including the introduction of  $N$  in the numerator outside the bracket and in the denominator inside the bracket and summing over positive and negative values of  $v_x$  allowing removal of the 2, as **this makes the bracket simply the average value of  $p_x v_x$**  indicated by angled brackets in 1.9

$$F = A \frac{N}{V} \langle p_x v_x \rangle \quad (1.9)$$

Where I have used from statistics the identity  $\langle y \rangle = \frac{1}{N} \sum_{y=-\infty}^{y=+\infty} N_y y$

The pressure is then

$$P = \frac{F}{A} = \frac{N}{V} \langle p_x v_x \rangle = \frac{N}{V} \langle m v_x^2 \rangle \quad (1.10)$$

If the gas is isotropic then

$$\langle \vec{p} \bullet \vec{v} \rangle = \langle p_x v_x \rangle + \langle p_y v_y \rangle + \langle p_z v_z \rangle = 3 \langle p_x v_x \rangle \quad (1.11)$$

We now rewrite 1.10 as follows

$$PV = \frac{N}{3} \langle \vec{p} \bullet \vec{v} \rangle = \frac{N}{3} \langle m v^2 \rangle \quad (1.12a)$$

$$PV = \frac{2}{3} N \frac{\langle m v^2 \rangle}{2} \quad (1.12b)$$

Finally we have our relation between  $P$ ,  $V$  and  $U$

$$PV = \frac{2}{3} U$$

(1.12c)



or

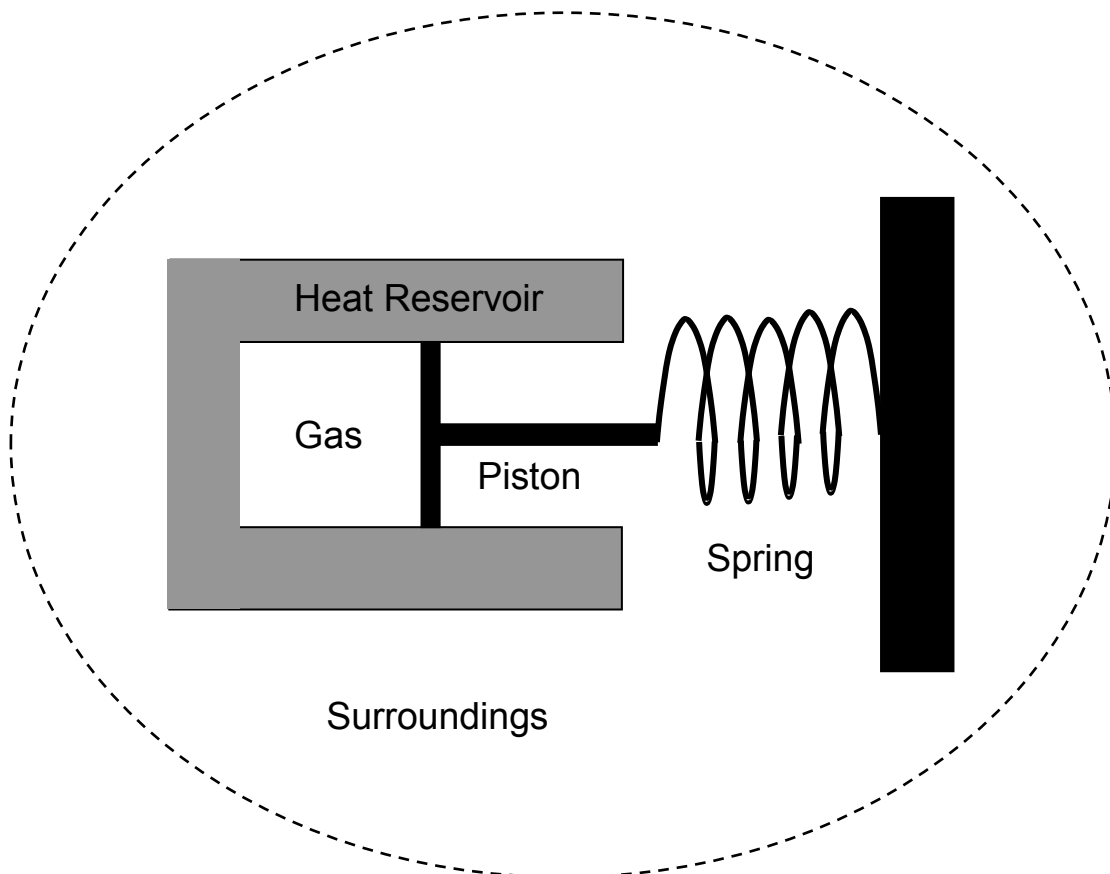
$$U = \frac{3}{2}PV \quad (1.12d)$$

Where the internal energy,  $U$ , of the gas is

$$U = N \frac{1}{2} \langle mv^2 \rangle$$

## 1.2 Equilibrium and Temperature.

We would like now to consider internal energy in terms of the temperature of the system but we as yet have no working definition of temperature and to obtain a definition we need first, to discuss equilibrium and what is meant by it. Our system is considered to be a closed system, no particles may enter or leave. We may also choose the walls of the container to be such that nothing else is exchanged with the surrounding environment, principally no energy is exchanged. This last may be dropped depending on precisely what we are studying and by the end of the course we will drop the restrictions on exchange of particles (matter). The whole, container, system and environment we term the universe and this is of course another example of a closed system. To get more specific we imagine a fluid (gas or liquid) contained within a cylinder with one end permanently closed and the other closed off by a **frictionless** piston.



It is an empirical fact that if we leave any “system” isolated for long enough, the one in the diagram above or a cup of tea, all of its macroscopic parameters,  $P$ ,  $U$  etc will cease

to change with time, in addition there are no flows of energy, momentum or particles within the system. The system is said to have reached a state of equilibrium. The pressure, volume and number of particles will **completely** and **uniquely** specify the state of the gas (internal energy is set by the other three via 1.12. Any gas of the same particles with this volume and pressure will be identical for all observational purposes. Given these properties,  $P$ ,  $V$  and  $N$ , the other macroscopic properties are automatically specified. In other words for a given quantity of gas (usually a mole) it only takes **two independent macroscopic parameters** to specify the **equilibrium state** of the fluid/gas.

These two variables (in this case  $P$  and  $V$ ) are called **State Variables**. Which are important as they have the following properties;

- (i) *Change one and the equilibrium state is a new one.*
- (ii) *Their values define the macroscopic state.*

The variables that are specified by  $P$  and  $V$ , eg,  $U$  and  $T$  (we shall see later) are called **Functions of State** and  $U = U(P,V)$ . The precise form of this function of  $P$

and  $V$  is the **Equation of State** that we met earlier,  $U = \frac{3}{2}PV$ .

We could equally have specified  $U$  and  $V$  in which case  $U$  and  $V$  would be the state variables and for example  $P = P(U,V)$  would now be the function of state.

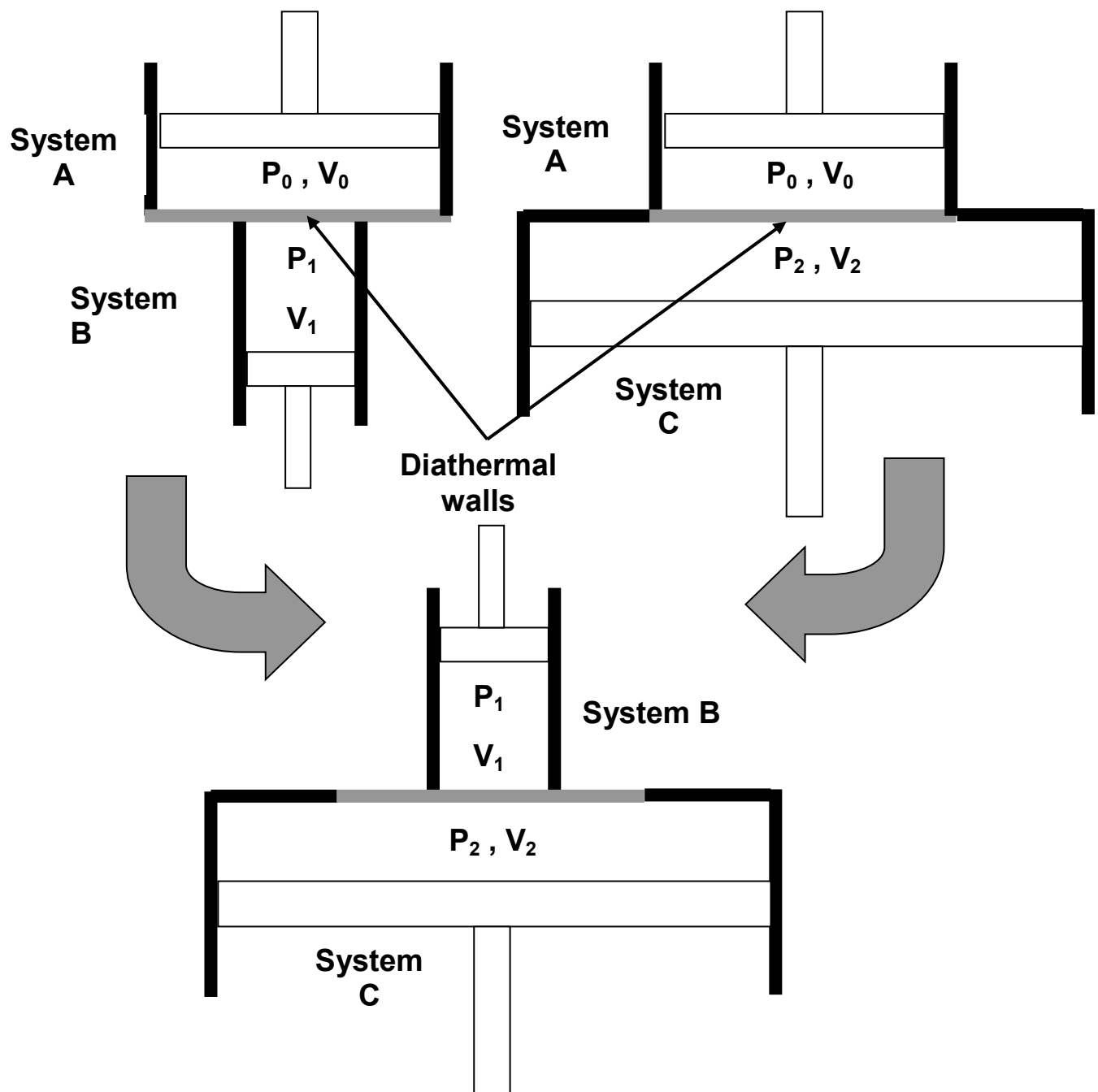
Before we can get on to temperature we need briefly to consider the interaction of a system with its surroundings. Such interactions are several and various and come under a few general headings;

- a) **Mechanical Interactions.** The gas in our example could for example push on the piston and move it thus doing work on its surroundings by compressing the spring.
- b) **Thermal Interactions.** Depending on whether the system is isolated or not; in the latter case it may change its state without doing mechanical work. If it does so then we know that its internal energy will change (**it is a state variable**). It can only do so by interaction and exchange with the environment. Walls or boundaries are never perfect but if they do not allow the passage of energy to a good approximation they are insulating and are

said to be **adiabatic** or **adiathermal** walls/boundaries, eg, fibre glass, polystyrene, whilst metal walls will readily allow conduction and are called **diathermal** walls.

### 1.3 The Zeroth Law of Thermodynamics.

Two systems can be said to be in thermal equilibrium with each other if when placed in thermal contact with one another via diathermal (eg metal) walls there is no change in in the state variables of either system.

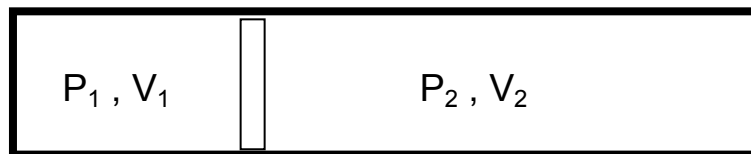


The zeroth law of thermodynamics (overlooked the first time around?), is simply stated. If system A is in equilibrium with system B and system A is in equilibrium with system C then it follows that system B is in equilibrium with system C. A, B and C can each consist of different fluids and this remains true. *We note here that  $P_0$ ,  $P_1$  and  $P_3$  can all be different as long as  $V_0$ ,  $V_1$  and  $V_2$  are also all different* but **the zeroth law implies that there must be a common property** between all three systems. It is this property that we shall call **temperature,  $T$** .

*Any systems in THERMAL equilibrium with each other are BY DEFINITION at the same temperature*

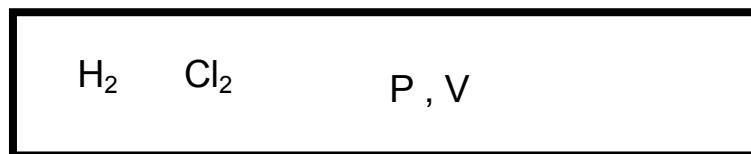
**NB.** *They do not have to be in mechanical equilibrium or chemical equilibrium in order to be at the same temperature.*

**Example 1.**



If in the above system  $P_1 \neq P_2$  then the piston would move. The two sides could still be in thermal equilibrium but not yet in mechanical equilibrium.

**Example 2.**



If there is some disturbance to the above system a chemical reaction would take place forming HCl. The temperature could nevertheless be well defined if the system is in thermal equilibrium with  $P$  and  $V$  remaining constant.

## Boyle's Ideal Gas Law

For a “box” of gas in thermal equilibrium Boyle's law, empirically arrived at (ie. it is an experimental observation that ), states that

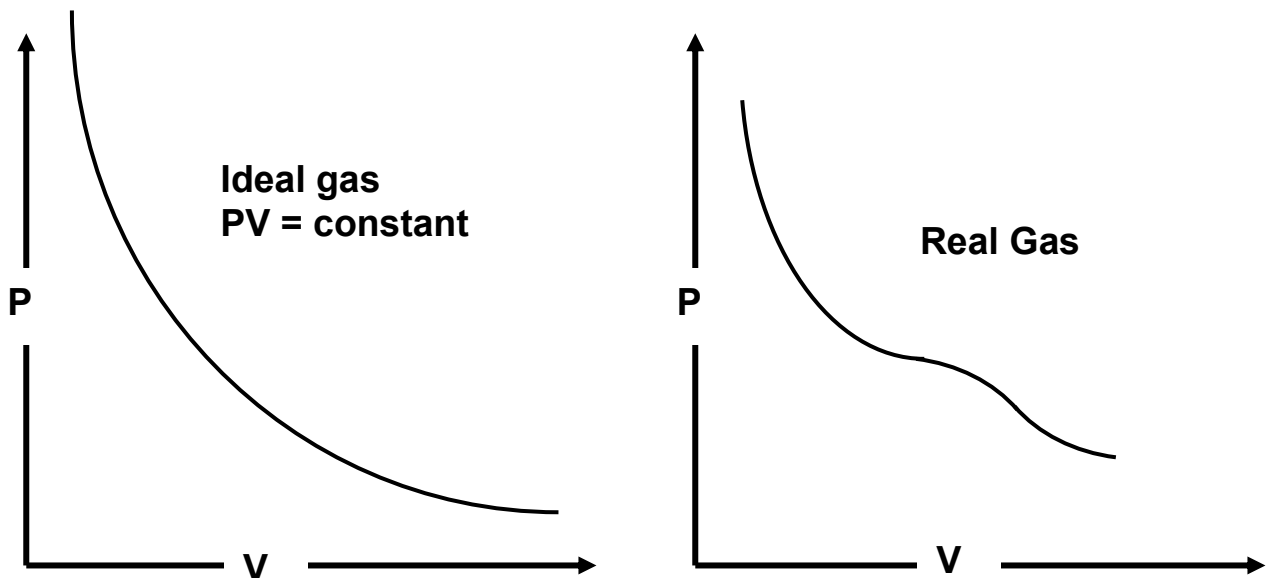
$$PV = \text{constant}$$

If several boxes with different gases but an identical particle number,  $N$ , are in thermal equilibrium with each other the constant will be the same, thus in our earlier example of three containers with pistons in thermal equilibrium, if the gas contained in each had the same mass (number of molecules for different gases) then Boyle's law states

$$P_0V_0 = P_1V_1 = P_2V_2 = \text{constant}$$

We have already derived Boyles law from a theoretical study of the kinetic behaviour of gases when we obtained the equation of state,  $U = \frac{3}{2}PV$ , as  $U$  is a constant for an isolated system in equilibrium.

This behaviour of an ideal gas can be indicated as a graph joining all the  $(P,V)$  pairs that are in thermal equilibrium (or equivalently ) at the same temperature and the curve is called an isotherm as shown below.



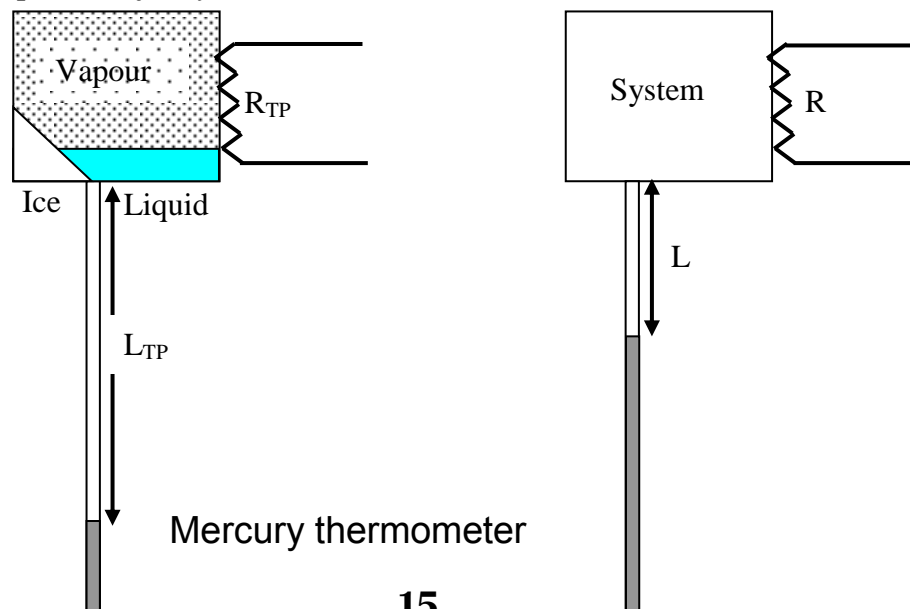
## 1.4 Temperature & Temperature Scales.

As we noted earlier, we know (most of us) when things are hot or cold, or hotter/colder as some subjective sense that we have and can agree on. Temperature was related to this subjective sense of hot and cold for a long time before ways and means of giving it an objective value that could be universally agreed upon was arrived at. This is not as straightforward as would at first appear however the new interest in thermodynamics in the eighteenth century made the establishment of agreed temperature scales an absolute requirement. Measurements of “temperature” were first made by making use of properties of materials that were empirically observed to alter as the materials became hotter/colder. We can all name a large number of these types of property such as thermal expansion which forms the basis of mercury thermometers, or electrical resistance. Boyle’s law clearly indicates that if a container of gas was held at constant pressure the volume of the gas would change if the temperature (equilibrium state) was to alter.

Such properties are known as **thermometric properties** and gave rise to

### EMPIRICAL TEMPERATURE SCALES .

The value of the thermometric property is taken when the thermometer is in equilibrium with the system being measured, let's call this **system 1** and the thermometer **system 2**. It is thanks to the zeroth law that we can define the concept of temperature for if we now take this thermometer, system 2 which is in equilibrium with system 1 and place it in thermal contact with a third system then if there is no change in the value of the thermometric property the thermometer is in thermal equilibrium with **system 3** and *therefore system 3 is in thermal equilibrium with system 1 and we can define a common temperature for system 1 and 3.*



The process of establishing a temperature is schematically indicated in the above diagram. Note that any thermometer is itself a “system” as per our definition and in order to read true it must itself come to equilibrium with the system under measurement. In this way we now know that if for example we take a block of steel (**System1**), measured to be at 50°C by some thermometer (**System 2**) and drop it in a bowl of water (**System 3**) also measured by (**system 2**) to be at 50°C then there will be no change in either as they must be in equilibrium with each other according to the zeroth law. This makes the temperature so defined a useful concept.

There are many such thermometric properties and in order that agreement was achieved whether one used the expansion of a column of mercury or the change in resistance of a conductor, there was the need for an internationally agreed system. Presently we have a system, in place by international agreement since 1954, defined as follows;

Let  $X$  be a general thermometric property. Then using a fixed point that could be established readily in any lab and that is relatively impervious to external conditions, we call the value of the property at that fixed point  $X_{TP}$ . The subscript TP stands for triple point, our chosen reproducible fixed point, and is the temperature at which the three phases (vapour, liquid, ice) of water can co-exist in equilibrium. Then the unknown temperature as measured by  $X$ ,  $T_X$ , **was defined as**

$$T_X = 273.16 \left( \frac{X}{X_{TP}} \right) \quad (2.1a)$$

eg. for the resistance thermometer,

$$T_R = 273.16 \left( \frac{R}{R_{TP}} \right) \quad (2.1b)$$

This  $T_R$  is the temperature, **by definition**, of a system for which the resistance thermometer when in thermal equilibrium has a resistance  $R$ . If we measure the temperature using an alternative thermometric property, the length of a mercury column say

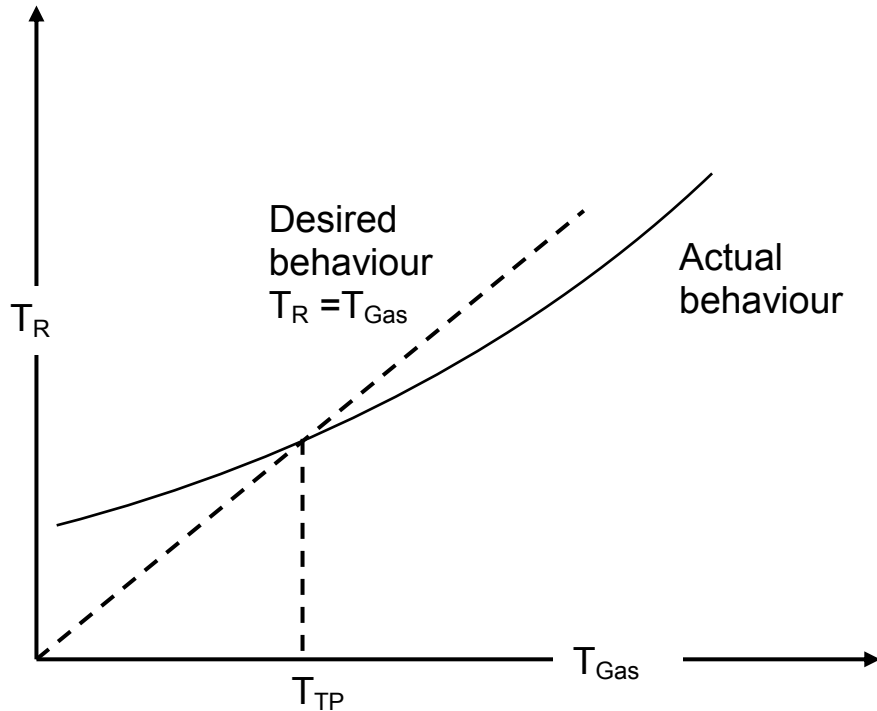
$$T_L = 273.16 \left( \frac{L}{L_{TP}} \right)$$

**there is no reason whatsoever why the two numbers  $T_L$  and  $T_R$  should agree** and it is important to understand and appreciate this. So far the temperature (number) we have is a human construct. Defining the temperature through 2.1 implies the existence of a zero of temperature ie it is of the form,



$$T = cX$$

and the thermometric property  $X$  becomes zero itself when  $T = 0$ . The equation implies that there is a linear variation between the value of the thermometric property  $X$  and  $T_X$ . ie. this is the case by definition! But this means that the temperature measured using one thermometric property will not be the same as that measured by another except at the fixed point unless  $c$  was the same for both properties.



*Thermometers using different thermometric properties will agree by definition only at one temperature, 273.16, the absolute temperature of the triple point of water. Away from this fixed point **there is no absolute meaning to the number obtained** using 2.1 with any particular thermometer. In fact **any two thermometers based on different thermometric properties will only approximately agree over a limited range of temperature and will agree exactly only at the fixed point.***

**It therefore requires that a choice of standard thermometer is made as well as a scale being set.** We need to choose one type of thermometer to hold precedence over the others. With our understanding of the behaviour of gases, they are relatively simple compared to the behaviour of electrons in a resistive material for example, the **GAS THERMOMETER** has assumed great importance in measurement of temperature. It's major benefit over other systems is that the volume (or pressure) of an ideal gas will go

to zero as the temperature is reduced to zero as required by the single fixed point definition of  $T$  (in fact there are really two fixed points with the other being the requirement that at  $T = 0$  the thermometric property,  $X = 0$ ).

There are two ways that a gas thermometer may be operated. The pressure of the gas may be used as the thermometric property whilst holding the volume constant, thus the constant volume gas thermometer where 2.1 becomes

$$T_{Gas} = 273.16 \left( \frac{P}{P_{TP}} \right) \quad (2.1c)$$

Or, the volume may be the thermometric property with the pressure held constant. This constant pressure gas thermometer holds practical difficulties and **the constant volume gas thermometer is used in the establishment of the IDEAL GAS SCALE**

This is known as the gas scale. In fact the definition given above needs to be tightened owing to the requirement that the gas used approximates a real gas by being suitably dilute,

$$T_{Gas} = 273.16 \lim_{P_{TP} \rightarrow 0} \left( \frac{P}{P_{TP}} \right)$$

The density of the gas is made as low as possible in order that the gas approximates better an ideal gas, the pressure thus drops too but not so low that measurements can't be made. We then find that all gas thermometers give the same temperature **INDEPENDENT** of the gas used!

Prior to 1954 a scale of temperature was used that was set by two fixed points. For the Celsius scale the two points chosen were the ice and steam points. The ice point was defined as the zero of temperature and there was a decision to have 100 degrees or divisions of temperature between the ice and steam points, degrees Celsius. The unknown temperature was found from a measurement of the thermometric property,  $X_{ice}$  and  $X_{steam}$ , at the two fixed points and the unknown temperature,  $T_X$ , was found from

$$T_X(^{\circ}\text{C}) = 100 \left( \frac{X - X_{ice}}{X_{steam} - X_{ice}} \right)$$

This is an equation of the form

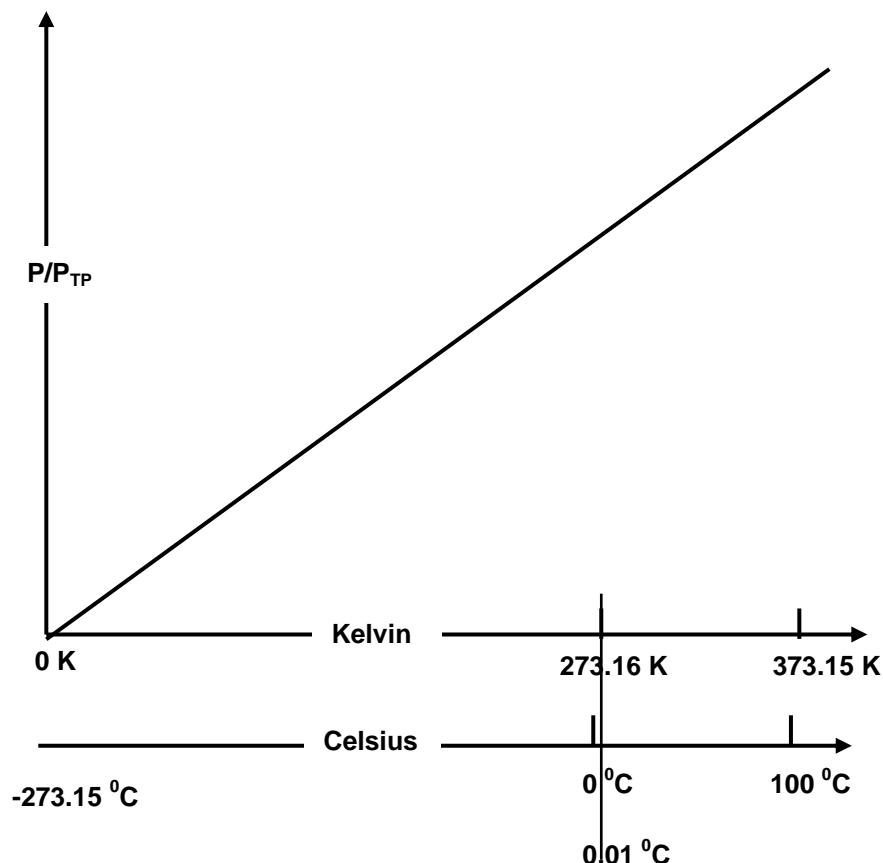
$$T = a + bX$$

The earlier equation 2.1 had a curious number associated with it, 273.16. We are now in a position to understand where this comes from. A choice was made to keep the new gas scale or Kelvin system as closely aligned with the old system as possible by defining 100K as the temperature difference between the ice and steam points as in the Celsius scale. The Celsius scale is then related to the gas scale by

$$T(^{\circ}\text{C}) = T_{\text{Gas}} - 273.15 \quad (2.3)$$

The ice point in the centigrade system is defined as  $0^{\circ}\text{C}$  and the triple point as used in the gas scale is  $0.01^{\circ}\text{C}$  hence the change from 273.16 to 273.15. The triple point on the gas scale is defined as 273.16.

The two scales are shown in the diagram below.



The earlier and scientifically meaningful definition from 2.1 is the absolute temperature scale and when it incorporates 100 degrees between ice and steam points it is called the Kelvin scale. This means that degrees Celsius and Kelvin are equal and it is the constant of the Celsius scale that allows the zero of temperature on that scale to fall at a temperature that is easily accessed in everyday situations ie. the temperature of ice, something of everyday practicality in spite of global warming!.

To convert from the centigrade temperature to the gas scale temperature requires care. The temperature on the centigrade scale may be defined using a thermometric property such as resistance but in order for there to be 100 °C between the ice and steam points an empirical relation between temperature in centigrade and resistance may need to be used.

We are now ready to use the ideal gas scale to **define** an **empirical temperature** of more universal significance. We begin by rewriting Boyle's law as follows

$$PV = nRT$$

We make this empirical statement recalling that the law refers to a particular equilibrium state, in a new equilibrium state the constant changes and it is therefore sensible to relate this constant to an empirical temperature,  $T$ . Also the amount of material,  $n$ , needs to be in the constant as twice the number of molecules requires twice the volume if the pressure is to be unchanged etc.  $R$  is the gas constant.

**This is of course an equation of state** with the state variables being  $P$  and  $V$  and the state function being  $T$ .  $n$  is the number of moles of gas and is related to  $N$ , the number of molecules, by  $\frac{N}{n} = N_A$  Avagadros number. ( $= 6.02 \times 10^{23} \text{ mol}^{-1}$ )

We may also now endow this empirical temperature in Boyle's law with further meaning by using the equation of state already established from kinetic theory of gases,

$$\frac{3}{2}PV = U = N \frac{1}{2} \langle mv^2 \rangle.$$

Boyles law can, using this alternative version of the equation of state of an ideal gas, be restated;

$$PV = \frac{2}{3}U = \frac{2}{3}N \frac{1}{2} \langle mv^2 \rangle = nRT = Nk_B T \quad (2.4)$$

$k_B$  is the Boltzmann constant ( $= 1.38 \times 10^{-23} \text{JK}^{-1}$ ) relating the kinetic energy of a molecule and the temperature and is related to  $R$  using Avagadro's number,

$$R = N_A k_B$$

Thus  $R = 8.31 \text{JK}^{-1}$ .

As noted, equation 2.4 is a further example of an **EQUATION of STATE**, where the expression, 2.4, describing the state of a fluid has only two independent state variables

$$f(P, V, T) = 0$$

And we would choose any two of  $P$ ,  $V$  and  $T$  as the independent state variables depending on the problem we are dealing with.

We can use 1.12d and 2.4 to find the relationship between temperature and internal energy whence

$$U = \frac{3}{2} PV = \frac{3}{2} N k_B T = \frac{3}{2} n R T \quad (2.5)$$

This shows us that the average translational kinetic energy of a molecule of the gas is given by

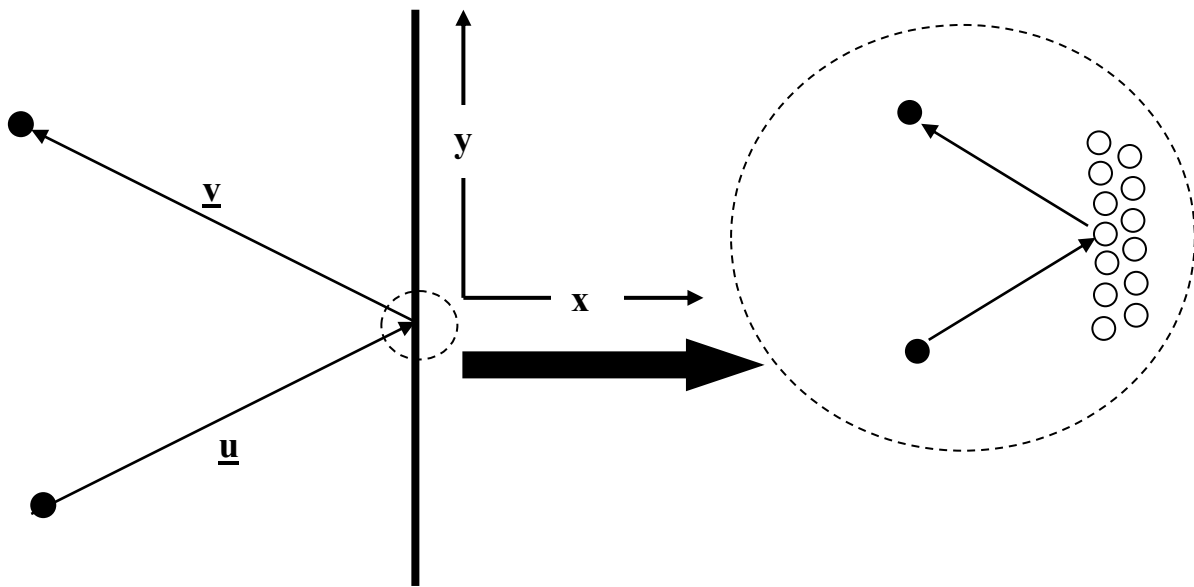
$$\frac{1}{2} \langle mv^2 \rangle = \frac{3}{2} k_B T = \frac{U}{N} \quad (2.6)$$

The kinetic energy will be equipartitioned between its three degrees of freedom ( $p_x$ ,  $p_y$  and  $p_z$ ) with  $\frac{1}{2} k_B T$  per degree of freedom. If we increase the number of degrees of freedom by allowing rotation and vibration, each new degree of freedom will have on average an additional  $\frac{1}{2} k_B T$ .

The important thing to note here is that we have shown that the ideal gas temperature is directly related to the internal energy,  $U$ , of the gas. This temperature we call the **KINETIC TEMPERATURE**.

## 1.5 Heat Transfer and equilibrium.

Earlier in this exploration we began by analysing the momentum change of a gas molecule after collision with the wall of a container to obtain a relation between pressure, volume and molecular kinetic energy. We assumed the wall to be hard and therefore ignored it, but we can now look a little closer at the molecule-wall collision and ask about the transfer of energy **BETWEEN** the gas and the wall at an atomic level. The arguments advanced were those due to Sir James Jeans in his book, Kinetic Theory of gases (Cambridge University Press, 1940)



As we saw there was a change in momentum of the gas molecule that contributed to a macroscopic pressure. Overall, momentum must be conserved so the change in momentum of the gas molecule, mass  $m_g$ , must be accounted for by a change in momentum of the wall molecules, mass  $M_w$ ,

With  $u$  and  $U$  referring to the initial gas molecule velocity and wall velocity respectively and  $v$  and  $V$  referring to the final gas molecule velocity and wall velocity respectively;

$$u_y = v_y \quad U_y = V_y \quad (3.1)$$

Momentum is conserved in the  $x$  direction (and  $y$  and  $z$ ) and so

$$m_g u_x + M_w U_x = m_g v_x + M_w V_x \quad (3.2)$$

We are considering elastic collisions and the gas molecule gains no energy thus using

$u_x = -v_x$  and  $U_x = -V_x$  we obtain;

$$(u_x - U_x) = -(v_x - V_x) \quad (3.3)$$

The wall molecule, mass  $M_w$ , gains an amount of energy,  $\Delta E_w$  as a result of the collision

$$\Delta E_w = \frac{1}{2} M_w (V^2 - U^2) = \frac{1}{2} M_w (V_x - U_x)(V_x + U_x) \quad (3.4)$$

From 3.2

$$V_x + \frac{m_g}{M_w} v_x = U_x + \frac{m_g}{M_w} u_x \quad (3.5)$$

And from 3.3

$$V_x - v_x = -U_x + u_x \quad (3.6)$$

$$3.6 \times \frac{m_g}{M_w}$$

$$\frac{m_g}{M_w} V_x - \frac{m_g}{M_w} v_x = -\frac{m_g}{M_w} U_x + \frac{m_g}{M_w} u_x \quad (3.6a)$$

Combining 3.5 and

$$\left(1 + \frac{m_g}{M_w}\right) V_x = \left(1 - \frac{m_g}{M_w}\right) U_x + 2 \frac{m_g}{M_w} u_x \quad (3.7)$$

Re-arranging

$$V_x = \left(\frac{M_w - m_g}{M_w + m_g}\right) U_x + \frac{2m_g}{M_w + m_g} u_x \quad (3.7a)$$

$$\begin{aligned}
 V_x + U_x &= \frac{2M_w}{M_w + m_g} U_x + \frac{2m_g}{M_w + m_g} u_x = \frac{2}{M_w + m_g} (M_w U_x + m_g u_x) \\
 V_x - U_x &= \frac{-2m_g}{M_w + m_g} U_x + \frac{2m_g}{M_w + m_g} u_x = \frac{2m_g}{M_w + m_g} (-U_x + u_x)
 \end{aligned}
 \tag{3.8}$$

And the change in energy of the wall molecule after 1 collision is then

$$\begin{aligned}
 \Delta E_w &= \frac{2M_w m_g}{(M_w + m_g)^2} (M_w U_x + m_g u_x) (-U_x + u_x) \\
 \Delta E_w &= \frac{2M_w m_g}{(M_w + m_g)^2} \left[ m_g U_x^2 - M_w U_x^2 + (M_w - m_g) U_x u_x \right]
 \end{aligned}
 \tag{3.9}$$

This is the energy change at the wall due to one molecular collision. We need to average over all collisions

$$\langle \Delta E_w \rangle = \frac{4M_w m_g}{(M_w + m_g)^2} \left[ \frac{\langle m_g u_x^2 \rangle}{2} - \frac{\langle M_w U_x^2 \rangle}{2} + \frac{(M_w - m_g)}{2} \langle U_x u_x \rangle \right]
 \tag{3.10}$$

We have  $\langle U_x u_x \rangle = \langle U_x \rangle \langle u_x \rangle$  and since the wall molecule is bound by the other wall molecules then  $\langle U_x \rangle = 0$  **The molecule is a wall molecule its going nowhere!!**

Also by isotropy **or equipartition from previous lecture**

$$\frac{\langle m_g u_x^2 \rangle}{2} = \frac{1}{3} \left( \frac{m_g \bar{u}^2}{2} \right) \qquad \frac{\langle M_w U_x^2 \rangle}{2} = \frac{1}{3} \left( \frac{M_w \bar{U}^2}{2} \right)
 \tag{3.11}$$



$$\langle \Delta E_w \rangle = \frac{4M_w m_g}{(M_w + m_g)^2} \frac{1}{3} \left[ \frac{\langle m_g \vec{u}^2 \rangle}{2} - \frac{\langle M_w \vec{U}^2 \rangle}{2} \right] \quad (3.12)$$

Using our relationship between kinetic temperature and internal energy we may rewrite 3.12 as;

$$\langle \Delta E_w \rangle = \frac{4M_w m_g}{(M_w + m_g)^2} \frac{1}{3} \left[ \frac{3}{2} k_B T_g - \frac{3}{2} k_B T_w \right] = \frac{4M_w m_g}{(M_w + m_g)^2} \frac{1}{2} k_B (T_g - T_w) \quad (3.13)$$

For the energy of the wall to increase it is required that  $T_g > T_w$  and to flow from the wall to the gas,  $T_w > T_g$ . This is what we would intuitively expect of course. We have shown a molecular level example of **THERMAL INTERACTION** or heat flow. The argument also demonstrates that in **thermal equilibrium** when there is **no heat flow** the **kinetic temperatures** of two systems (gas and walls) **must be equal**.

## A further example of internal energy of a gas.

### The Photon Gas.

An unusual case you may think but we can consider a system we refer to as a photon gas. This is a system of non interacting particles of light or photons. The only interaction we consider to begin with is the interaction with the reflective walls in which the gas of  $N$  photons is contained. There is no absorption at the wall (for now) only the reflection of the photons with the concomitant change in photon momentum and the accompanying radiation pressure experienced by the walls.

A photons momentum,  $p$ , and energy,  $E$ , are given by;

$$p = \frac{h}{\lambda} = \hbar k \quad E = h\nu$$

Using the relation,  $c = \nu\lambda$ , we can re-arrange to find

$$E = pc \quad \text{and we have} \quad |\vec{v}| = c$$

Therefore

$$\vec{p} \bullet \vec{v} = \left( \frac{E}{c} \right) c = E$$

We already have for an ideal gas the equation of state written in the form

$$PV = \frac{N}{3} \langle \vec{p} \bullet \vec{v} \rangle$$

Now all photons have the same momentum (if the wavelength is the same) and the average is no longer necessary. Thus for photons this equation of state, using what we have so far derived becomes

$$PV = \frac{N}{3} E = \frac{1}{3} U$$

Where  $U = NE$ , the total energy of all of the photons in the photon gas. Recalling that for a monatomic material gas we previously found

$$PV = \frac{2}{3} U$$

For a given internal energy density  $U/V$  a material gas will exert a greater pressure than a photon gas.

Unlike a material gas where the velocities of the particles are non-relativistic, in the case of the photon gas we cannot simply relate the internal energy,  $U$ , to the temperature  $T$ . It is left until later to consider how temperature and energy might be related and this must be due to interaction with the walls since the photons do not interact with each other.