

Lecture 1Introduction

The science of thermodynamics is concerned with the understanding and interpretation of the properties of matter as long as they are affected by changes in temperature. Although it might seem a very crude explanation of what thermodynamics is concerned of, what thermodynamics basically is a combination of mathematical and experimental tool to provide explanation of the observed properties of matter at all temperature in terms of the atomic constitution and the forces exerted by atoms upon one another. This statement covers perhaps a wider field of investigation than what thermodynamics is concerned of. For example, the theory of chemical forces that binds atoms together to form chemical compounds is not a branch of thermodynamics, rather a branch of quantum mechanics where ~~temp~~ the concept of temperature doesn't play any part. On the other hand, when we are interested

in the excitation or dissociation of molecules as a consequence of heating, we consider the thermodynamics. In the same way, the existence of solids and many properties of solids may be explained by mechanical consequence of the forces between atoms. Thermodynamics only enters when we want to study the temperature-dependent properties, such as heat capacity, magnetic susceptibility etc.

Thermal physics evolved in various stages and has left us with various approaches to the subject.

— The subject of classical thermodynamics deals with the macroscopic properties, such as pressure, volume and temperature, without worrying about the underlying microscopic physics. Here, the method of approach doesn't take into account the atomic constitution of matter, but seeks rather to derive from certain basic postulates,

the laws of thermodynamics, relations between the observed properties of substances. In contrast to atomic theory of thermal phenomena, classical thermodynamics makes no attempt to provide a mechanistic approach explanation of why a given substance has the properties ~~as~~ observed experimentally. The actual function of classical thermodynamics is to link together the many observable properties, so that they can be seen to be a consequence of a few. For example, if the equation of state of a gas (the relation between pressure, volume and temperature) is known, and we determine the specific heat at constant pressure over a range of temperatures, then by thermodynamic arguments we can find the specific heat at constant volume. We will be able to predict whether the gas will be heated or cooled when it is expanded through a throttle from a high to low pressure, and the magnitude of

Change in temperature can be calculated precisely.

- The "kinetic theory of gases" tries to determine the properties of gases by considering probability distributions associated with the motion of individual molecules.
- The realization that atoms and molecules exists led to the development of statistical mechanics. Rather than starting the description of macroscopic properties (as in thermodynamics), the approach of statistical mechanics begins with trying to describe each individual microscopic states. of a system and the use statistical methods to derive the macroscopic properties from them. With the development of quantum mechanics, this approach got more rigor, as QM showed explicitly how to describe the microscopic quantum states of different systems. The thermodynamic behaviour, of a system is then asymptotically approximated by the results of statistical mechanics in,

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the "thermodynamic limit".

The two approaches — classical and statistical are pretty much different, and a discussion between the relation between them is worth it. The laws of classical thermodynamics were arrived at as a consequence of experiment and observations. Continued application of the methods of classical thermodynamics to practical problem showed that these laws predict correct results in all cases. But classical thermodynamics makes no attempt to why the laws have their particular form, or how these laws come from a more fundamental set of laws. This is the one problem treated in statistical mechanics/ thermodynamics. From the consideration of the behaviour of a large number of atoms and molecules, it may be shown that the properties of matter which are observable by macroscopic measurements, are related and a consequence of the laws of statistical thermodynamics.

Our approach to study thermal physics will mostly be a statistical thermodynamics approach. We will build up everything on the basis of required mathematics. However, when we move to the heat engines etc., we will take the classical thermodynamics approach as you would require advanced mathematics to learn the statistical mechanics of those things. So, the construction is like the following —

1. Mathematical preliminaries
2. Kinetic theory of gas (in light of probability)
3. Classical thermodynamics
4. Some statistical mechanics.

Let's start our preliminary ideas by introducing few of the basic ideas and definitions in thermodynamics which we will need often now and then.

In thermal physics we deal with assemblies of a large number of atoms. We will see later, that this large number actually lets us to treat the properties of a macroscopic system in a statistical fashion. We want to study how they behave on average. To keep track of the large number, we introduce the definition of "mole".

= A mole is defined as a quantity of matter that contains as many objects (molecules, atoms, ions etc) as the number of atoms in exactly 12 g of  $^{12}\text{C}$ . A mole is also approximately equivalent to the number as of the atoms in exactly 1 g of  $^1\text{H}$ , but ~~carbon~~ carbon was chosen as solids are easier to weigh accurately.

A mole is equivalent to the Avogadro number,  $N_A$ , which is given by,

$$N_A = 6.023 \times 10^{23} \quad \left[ 6.0231417930 \times 10^{23} \text{ exactly} \right]$$

= The molar mass of a substance is the mass

of one mole of the substance. For example, the molar mass of  $^{12}\text{C}$  is 12g, of water is 18g. Now,

$$\text{molar mass} = mN_A$$

where  $m$  is the mass of a single atom or molecule.

### The thermodynamic limit

We already stated that the large number of atoms, molecules makes it easy to study the behaviour of a thermodynamic system. But why so? Because, if there is a sufficiently large number of constituents in a system, it is possible to deal with the average quantities. Consider an example.

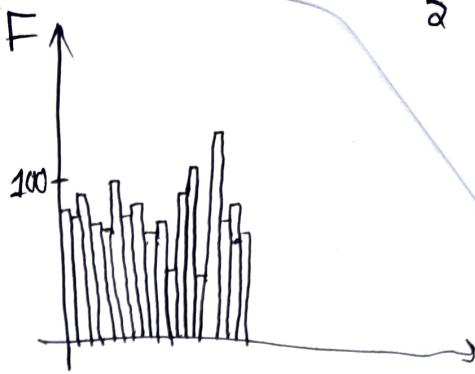
You are sitting inside a very very tiny hut with a flat roof (that makes you tiny too, haha). Say, the hut is so tiny that at ~~a~~ a particular time only one raindrop can fall on the roof. The <sup>random</sup> raindrop falling on the roof will impact

on it, and come to a stop. If you know the mass and terminal velocity of the raindrop, you would be able to calculate the force on the roof at each interval of time (by calculating the impulse on the roof). Impulse  $\vec{J}$  is defined as  $\vec{F} \times \Delta t$ , which is also equal to  $\Delta \vec{P}$ , that is change in momentum. Since the raindrops might be irregular, there might be no raindrop at some time interval, and one at some time interval. The force as a function of time will look something like shown in the following figure. Each little blip corresponds to force from one raindrop.

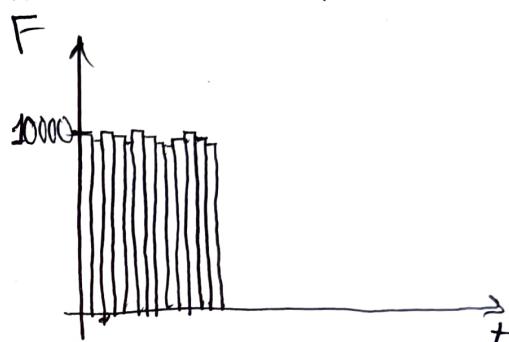


Now, assume you are inside of a much bigger hut, with a roof area much much higher than before. At a particular time interval, many raindrops will now fall on the roof and they will exert forces on the roof. If we choose the time interval large enough, we might have forces

on the roof at all time interval and the force function now will look like ~~as in~~ the shown in the following figure.



If you even make the roof area higher, maybe thousand times more than before, you are gonna get more raindrops falling within a particular time interval on the roof. The force as a function of time will now look like as shown in the figure above.



There are two key things you need to notice here:

1. The average force increases as the roof area increases. This makes sense perfectly, as more and more raindrops are falling as the area is increased.
2. The fluctuations of the forces gets smoothed out and the force looks like it pretty much stays close to the average value. The fluctuations might still be big, but they grow <sup>much</sup> more slowly than the average force does.

Also, if one is to calculate the fluctuations compared to the average, the last scenario presents the least fluctuations. What I mean, if the average is 100, then 70, 45 and 130 might seem very fluctuating from the average. But for an average of 10000, the numbers 9970, 9945 and 10130 doesn't seem to have that much fluctuation.

Although the force grow with area, it is useful to consider pressure, which is defined as -

$$\text{pressure} = \frac{\text{force}}{\text{area}}$$

The pressure will now won't increase as the roof area increases, but the fluctuation from the average pressure does decrease. In the limit where the roof area goes to infinity, the fluctuations in the pressure will be more or less negligible. This is what we will refer to the thermodynamic limit.

Now, let's consider how this idea is analogous

to the idea of ~~of~~ the thermodynamics of gas molecules in a container. The gas molecules will bounce from the container walls while they are in random motions. The net effect of these bounce backs is force, which results in pressure of the gas. If the container was very small, or the number of molecules is very small, then we would have to care about the fluctuations. But in almost all of the thermodynamic systems, the number of molecules is so gigantically high, the fluctuations smooth out and we can consider the pressure to be uniform in time. We call the description of the pressure in the system to be in the thermodynamic limit. So, the ~~number~~ number of molecules goes to infinity in the thermodynamic limit and we can consider the pressure, density etc to be constant in time and space.

## Extensive and intensive variables

Thermodynamic variables that scale with the system size are called extensive variables. The quantities that remain the same, are called intensive variables. It might not be totally clear from this definitions what they actually are, and people often get confused. So, let's think of an example.

Consider a container of gas that has a volume  $V$ , having temperature  $T$  and pressure  $P$ . The kinetic energy of all the gas molecules in  $V$ .

Now, consider an "imaginary" wall inserted at the midway of the ~~the~~ container. I emphasize on the term imaginary, because, if you really insert an actual wall, the system is now two different systems. If you now focus on the right part of the container, then the volume of this part is,

$$V^* = \frac{V}{2}$$

Kinetic energy is,

$$U^* = \frac{U}{2}$$

However, the pressure  $P$  and temperature  $T$ , of the right part is the same as the whole. Because we defined pressure of a gas as a whole. You can't say right side has this pressure and left side has this. The same is true about temperature  $T$ . The temperature doesn't get ~~half~~ halved.

$$\therefore P^* = P \quad \text{and} \quad T^* = T$$

So, quantities  $V$  and  $U$  are extensive quantities and quantities  $P$  and  $T$  are intensive quantities. Like that, density is intensive and entropy is an extensive variables.

Think about a quantity given by the square root of volume. Is it intensive or extensive?

You know that, the value of intensive properties remains the same, but the value of extensive property scales up by a factor. What would happen if a system is doubled in size just by

juxtaposing a second identical system. Now  
is square root of volume intensive or extensive?  
Its name. Argue why.

## The ideal gas

Requirements /axioms:

- (i) We assume there are no intermolecular forces.
- (ii) The molecules are point sized and have zero size.
- (iii) The collisions are fully elastic.

~~Under~~ Under these requirements, one can derive the so called ideal gas equation using the kinetic theory of gas.

However, historically, the ideal gas equation was derived not derived, rather found through series of experiments. Experiments shows that ~~the~~ with pressure  $P_a$ , <sup>(with a</sup> volume  $V$ ) ~~depends~~ depends on the

temperature  $T$ . A fixed amount of gas at constant temperature obeys,

$$P \propto \frac{1}{V}$$

a result discovered experimentally by Boyle and independently later by Edme Mariotte. At constant pressure, the gas also obeys,

$$V \propto T$$

where  $T$  is measured in kelvin. This is known as Charles' law, again found experimentally.

The Gay-Lussac's law states that,

$$P \propto T$$

found by Guillaume Amontons, and later independently by Gay-Lussac.

These three empirical laws can be combined into -

$$PV \propto T$$

It turns out that if there are  $N$  molecules in the gas, the final law, called the ideal gas law can be written as -

$$PV = Nk_B T$$

with ~~N~~  $K_B$  being the Boltzmann constant, where  $t$

$$K_B = 1.3807 \times 10^{-23} \text{ J K}^{-1}$$

Although the ideal gas equation is experimentally found, we will derive this later in this course.

## Combinatorial problem

In thermal physics, we might encounter number much greater than  $N_A$ . We consider a combinatorial problem for an example.

Consider a system with 10 atoms. Each of these atoms can exist in ~~in~~ one of the two states — one having zero unit of energy and another having one unit of energy. These units are called "quanta" of energy. The question is, how many distinct arrangement is possible for this system if you have — (a) ten quanta of energy and (b) four quanta of energy.

## Combination problem solution

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Think about a simple problem first. You have three colored balls — red, green and ~~yellow~~<sup>(distinguishable)</sup>. You have to assign them to two indistinguishable boxes, that is, you can't differentiate which box is which. How many configurations are possible here? Each box can at best carry one ball.

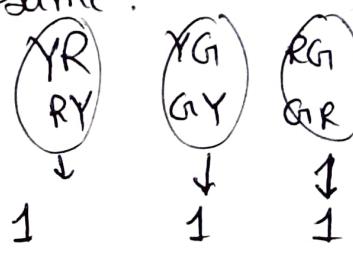
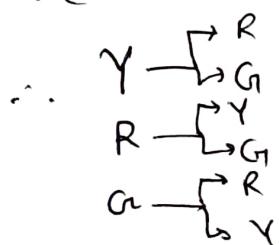
Think about distinguishable boxes first. Box A and box B you have. For putting in box A, you have three choices (R or G or Y). Given that you put any of them in box A, you have two choices to put in box B. So, in total, the number of configurations is —

$$\Omega = 3 \times 2$$

since for each of the three first choices you have two choices, in total you have six.

Now, what happens if the boxes are indistinguishable? In this case, the orders of the balls doesn't matter,

since the boxes are same.



It ultimately comes down to the fact that how many ways you could rearrange the boxes. Here it is  $2!$ . You just then divide to get the actual number of configurations.

$$\Omega = \frac{3 \times 2}{2!} = 3$$

Now, say, you have  $n$  ~~to~~ distinguishable balls and  $k$  ~~to~~ distinguishable boxes. For putting in box 1, you have  $n$  number of choices, for putting in box 2, you have  $n-1$  choices, ..., for  $k^{\text{th}}$  box, you have  $(n-k+1)$  number of choices.

$$\begin{aligned}\therefore \Omega &= n \times (n-1) \times \dots \times (n-k+1) \\ &= \frac{n \times (n-1) \times (n-2) \times \dots \times 1}{(n-k) \times (n-k-1) \times (n-k-2) \times \dots \times 1} \\ &\leftarrow \frac{n!}{(n-k)!} = \frac{n!}{(n-k)!}\end{aligned}$$

$$\boxed{\therefore \Omega = \frac{n!}{(n-k)!} = {}^n P_k}$$

However, if the boxes are indistinguishable,

then,

$$\Omega = \frac{n!}{(n-k)! k!} = nC_k$$

However, if the balls were also indistinguishable, then there is only one way really. Because, you can choose any  $k$  of the  $n$  balls to go in the  $k$  boxes, they all are the same.

$$\therefore \Omega = 1$$

Our problem

$\nwarrow$  unit energy  $\rightarrow$  distribute to  $n$  atoms.  
 $\swarrow$  indistinguishable

(i) Atoms are distinguishable!: Here, the unit energies are basically the boxes and atoms are the balls.

$$\therefore \Omega = \frac{n!}{(n-k)! k!}$$

For  $k=10$ ,  $\Omega = \frac{10!}{0! 10!} = 1$

$k=4$ ,  $\Omega = \frac{10!}{4! 6!} = 210$

(ii) Atoms are indistinguishable: Since both the atoms and the unit energies are indistinguishable, there is only one arrangement.

For  $k=10$ , all 10 gets 1 unit each.

For  $k=4$ , 6 of them gets 0 and four of them gets 1.

This could also be done in a different way. There will be  $n$  atoms with 1 unit and  $n-n$  atoms with zero unit energy. We can arrange all the atoms in  $n!$  ways. Then we can distribute  $n$  ~~units~~ units to  $n$  atoms in  $n!$  ways and  $(n-n)$  atoms zero units in  $(n-n)!$  ways.

$\therefore \Omega = \frac{n!}{n! (n-n)!}$

} since the atoms are distinguishable.

If we had 300 atoms and 40 quanta, then the number of ways  $= \frac{100!}{40! 60!} \approx 10^{28}$ . If we had 1000 atoms and 400 quanta, then the number of atoms is,

$$\Omega = \frac{1000!}{400! \times 600!} \approx 10^{290} - \text{a huge number.}$$

We already have a gigantic number for 1000 atoms. What would then happen for  $6 \times 10^{23}$  atoms? Such big numbers are difficult to handle. We can bring them down by using logarithms.

$$\Omega = \frac{n!}{(n-n)! n!} \Rightarrow \ln \Omega = \ln n! - \ln (n-n)! - \ln n!$$

There is a famous formula derived by Stirling. The Stirling's formula gives —

$$\ln n! = n \ln n - n + \frac{1}{2} \ln n n$$

For large  $n$ ,  $\ln n! \approx n \ln n - n$

## Example

Estimate the order of magnitude of  $10^{23}!$

$$\ln 10^{23}! \approx 10^{23} \ln 10^{23} - 10^{23} = 5.2 \times 10^{24}$$

$$\Rightarrow 10^{23}! = e^{5.2 \times 10^{24}}$$

If we want to see this in terms of power of 10, then we can use the following —

$$e^x = 10^y \Rightarrow x = y \ln 10$$

$$\therefore y = \frac{x}{\ln 10} = \frac{5.2 \times 10^{24}}{\ln 10} = 2.26 \times 10^{24}$$

$$\therefore 10^{23}! = 10^{2.26 \times 10^{24}}$$

How large is this?!