1   What is Thermodynamics?

It is not easy to give a definition of thermodynamics right at the beginning. Thermodynamics is usually described as the science of energy exchange through heat. But it is not limited to it, nor do we know what heat is at this stage. Rather then going into a definition let us look in colloquial terms what it is and what kind of things it deals with.

First of all, thermodynamics deals only with "*macro-systems*", systems which are at the scales much bigger than the atomic size. These systems are composed of a large number of simple microsystems such as atoms. One can apply it to discuss certain properties of a piece of chalk, a toy magnet, but not to individual magnetic molecules of the magnet. On the other hand, one can even apply it, with a limited validity, to a large nucleus if one is willing to consider ~ 100 protons and neutrons as a system composed of large number of particles. In these large systems, the goal of thermodynamics is to describe "*macro-properties*" of these systems, the properties which relate to the system as a whole, without mention to individual atoms or detailed internal working of the system. But at the same time, the phenomenon discussed in thermodynamics are really caused by some internal motion of the system. The laws of thermodynamics arise because we refuse to follow the internal motion, and rather concentrate on some general consequences of those internal motions in the macro-properties of the system. Therefore, the laws of thermodynamics are of phenomenological nature, and quite distinct from laws of mechanics.

There are basically two kinds of dynamical systems (mechanical, Electromagnetic field) of fundamental physics (at least the ones you are familiar with) with their their dynamical laws . You have your favorite dynamical equation of motion (classical, quantum mechanical, relativistic or not). For example, you may consider a particle in gravitational potential

$$V(r) = -\frac{GM}{r}, \tag{1}$$

which follows the equation of motion,

$$\frac{d^2 \overleftarrow{x}}{dt^2} = -\frac{GM}{r^2}\hat{r}. \tag{2}$$

You can solve for trajectories and know the future course of the particle. Similarly, you can have a system of fields and charges. You can apply Maxwell's equations and find future propagation of the system.

But there are other phenomenon of nature where it is not obvious how to apply the above two laws, the phenomenon which are related to some internal happenings of the system. Take a thermometer and put it close to the burner of your stove and it explodes, gas in a balloon may expand, resistance of a conductor may increase, water may solidify. Clearly these phenomena are related to some internal dynamics. As a consequence these phenomenon occur in systems composed of many particles.

How can one deal with them?

One answer could be that since the laws of nature apply to individual particles hence these phenomena must be too complex to deal with. But this is not true. There are too

approaches to deal with these phenomena.

1- One is the phenomenological approach called thermodynamics. Where one just tries to relate the external properties of systems by some general observations.

2- The other is the approach of statistical mechanics, where one tries to be bold and directly apply the fundamental laws to the individual constituents of the system, but of course, in a statistical manner. This approach is much wider in scope than thermodynamics.

Let us come back to thermodynamics. A very typical feature of changes happening around us is the exchange of energy, from one form to another, and from one system to another. However, the total energy is conserved. Thermodynamics is usually concerned with a very specific form of energy exchange, which is called heat. Heat is the energy exchanged when a hot object is brought into thermal contact of a colder object. It is a common experience that when you put a pot full of water on a stove, after some time the water is able to lift the lid. Where did that energy come from? This is what was carried by heat from hot stove to water. On the other hand when you do some good work on a squash ball (in a squash court), you have two experiences. One some of the work seems to be getting lost (the ball does not bounce back very efficiently in the beginning). And also the ball gets hot. Thermodynamics deals with these phenomena of energy exchange by heat and conversion of heat and work into each other. It does so by virtue of laws of thermodynamics, which describe how the exchanged heat and work are related and how the direction of their flow is determined.

For the most part, thermodynamics concerns with system in equilibrium. For the changes to happen, the system does need to go out of equilibrium. But thermodynamics usually describes the relations between initial and final equilibrium states of the system.

Another thing to note is that the laws of thermodynamics are based on general principles of energy exchange. They do not refer to a particular system. In this lies their usefulness and also their limitation.

Another thing worth saying about thermodynamics is that even if we use a more sophisticated theory such as statistical mechanics, we may still need to know what are the interesting ways to describe the changes in system as a whole. Thermodynamics concerns itself with "defining" appropriate quantities which are suitable to describe behavior of large scale systems.

Finally, a unifying theme in all thermodynamical discussions is temperature. It is the quantity which determines the equilibrium of a system with other systems (with respect to heat flow), and also tendency of heat to flow in a particular direction from one system to another (from hot to cold). If there is no temperature, it is not thermodynamics.

Let us now look at some basic definitions

2   Definitions

2.1   System

A part of universe which is mentally isolated from rest of the world as an object of interest/study.

2.2   Surroundings

Anything in the universe, which is not part of the system.

2.3   Boundary

Partitions separating system from surroundings.
These can be actual physical boundaries, for example, for a balloon, it is the surface of balloon, or imaginary. One can mentally think of considering the left $1m^3$ corner of one's room as a system. In this case the boundary is imaginary.

2.4   Isolated System

The system that does not exchange matter and energy with the surroundings.

2.5   Closed System

The system that does not exchange matter with the surroundings but can exchange energy.

2.6   Open System

The system that can exchange matter and energy with surroundings.

2.7   Adiabatic System

The system that is indifferent to the temperature of surroundings. Energy can not be exchanged with the surroundings as heat, though work can still be done by surroundings on the system.

For each of the above type of system, there are corresponding boundaries which restrict the system to be one of the above.

2.8   Equilibrium

A state of a system, where none of the macroscopic properties of a system changes with time. All systems, left to their own, evolve to equilibrium state. This can also be taken as a definition. The state of a system that is reached after a long time, when it is left to its own.

There are various kinds of equilibrium. Chemical equilibrium is obviously when there are no changes in the composition of the system. Mechanical equilibrium is one

there is no "net" force on system boundaries and no "net" force in the "interior" of the system, the system is said to be in mechanical equilibrium. If a system is in chemical and mechanical equilibrium, there can still be changes occurring in its properties. If a system in mechanical and chemical equilibrium and it is not in adiabatic boundaries, but still no changes occur, we say it is in thermal equilibrium with its surroundings.

2.9   State

A system in equilibrium is said to be in a particular "state". Notice somewhat circularity.

2.10   State Function

State functions or state variables are macroscopic properties of the system which only depend on the current state of the system, and not on how the system reached the state. State functions are the things which label a state. If two states have same values for all state functions, they are actually one and the same state. Example of state functions for a gas are Pressure, Volume, Temperature, refractive Index, Speed of sound etc.

Not all state functions are independent of each other. Usually we need only a few to characterize a state. The rest are related by equations which we call equations of state. For a gas, we need only two. So pressure , volume and temperature are related by an equation of state, which for an ideal gas is

$$PV = nRT. \tag{3}$$

2.11   Volume

Volume of the system

2.12   Pressure

The force exerted by the system on its boundary per unit are.

$$P = \frac{F}{A}. \tag{4}$$

2.13   Phase Diagram

A graph between independent variables of the system. A point on this graph is a particular "equilibrium state" of the system. Notice we can only show equilibrium states on phase diagram.

3   Temperature

Temperature is thought of as degree of hotness. But what is hot? Clearly we can not trust our physical senses in this regard. A mercury thermometer tells us that wood and iron, when standing in open air for a long time, are at same temperature. While our feeling of the two is quite different. Here we will develop one aspect of temperature in a precise way, using what is called the Zeroeth law of thermodynamics. To be honest, one

does not completely define temperature using zeroeth law as one may wish to use the temerature for, and we will see why. One really needs second law to define temperature. One can even defer all references to temperature until the second law is spelt out. It seems to me that one does not need Zeroeth law at all. But we are not building an axiomatic development of the subject. We want to study why physics was developed in a particular way *given the experiments and observations as they showed up to humans.* In any case it is useful to have some idea of temperature before one discusses the second law.

3.1   Zeroeth Law of Thermodynamics

Let us imagine what we do when we measure temperature. We insert the thermometer in one object. Some change occurs in the level of mercury in the thermometer. It means that mercury goes out of equilibrium. But after some time, it comes to equilibrium with the system. The level of mercury in the thermometer is just a measure of this equilibrium state of the substance. But now we put the thermometer in another material. And it reads the same number. Why is it useful to say that they are at same temperature, except for the same length of mercury column. The reason is that if we bring the two objects together now, no changes occur. After bringing them together, the thermometer still reads the same temperature. Moreover, if we bring a third object and a fourth in equilibrium with the said first object, the thermometer reads same temperature for all of them. Hence temperature is first and foremost a predictor of equilibrium. If two objects are at same temperature, no changes will occur when we bring them into thermal contact. We define temperature (rather *empirical temperature*) by this very property. The above discussion is formalized in the zeroeth law which says:

If a system A is in thermal equilibrium with system C, and system C is also in thermal equilibrium with system B, then system A and B are also in thermal equilibrium

Consider three systems A, B and C, which are in chemical and mechanical equilibrium. Which also means that there are fixed number of moles in each system (whatever that number may be). For simplicity, I will assume that they all need only two state functions to specify their state. I will write these functions as P and V to make analogy with gas, though they can be anything, such as external field and magnetization for a magnet. Suppose that the state coordinates of choice for A, B and C are $(P_1, V_1), (P_2, V_2)$ and (P_3, V_3) respectively. Now suppose that A and C are brought into thermal equilibrium with each other. It is a matter of experimental experience that once they are in thermal equilibrium, all four variables of them are not independent. Choosing a particular state of C, we have a restricted number of states of A which can be in equilibrium with this particular state of C. In fact the states of A, which can be in thermal equilibrium with a particular state of C, lie on a line in the phase diagram of system A. Since the state of C was chosen arbitrarily, we conclude that there is one and only one constraint between the four coordinates, when they are in equilibrium. Let us call this constraint F_1. Then we have

$$F_1(P_1, V_1, P_3, V_3) = 0 \tag{5}$$

Now suppose that system B is also in equilibrium with system C. Then there is also a constraint between the coordinates of B and C. let us write it as

$$F_2(P_2, V_2, P_3, V_3) = 0. \tag{6}$$

We can solve these constraints to give

$$P_3 = f_1(P_1, V_1, V_3) \tag{7}$$
$$P_3 = f_2(P_2, V_2, V_3). \tag{8}$$

7 and 8 give

$$f_1(P_1, V_1, V_3) = f_2(P_2, V_2, V_3). \tag{9}$$

Eq 9 can again be solved to give

$$P_1 = g(V_1, P_2, V_2, V_3). \tag{10}$$

But by the zeroeth law we must have A and B in equilibrium too, hence a constraint,

$$F_3(P_1, V_1, P_2, V_2) = 0 \tag{11}$$

which can be solved to give

$$P_1 = f_3(V_1, V_2, P_2). \tag{12}$$

All the state functions appearing in above equations are fairly arbitrary. Hence it is absurd that P_1 which depends only on V_1, V_2, P_2 in eq 12, depends on V_3 too in eq 10. Hence it must be that V_3 cancels out in eq 9 if zeroeth law is to hold in a meaningful way. Therefore Equation 9 reduces to

$$f_1(P_1, V_1) = f_2(P_2, V_2) \tag{13}$$
$$\theta_1(P_1, V_1) = \theta_2(P_2, V_2) = \theta. \tag{14}$$

What this means is that there are functions of state variables (θ_1, θ_2) which assume same value when two systems are in thermal equilibrium. These functions of state variables are called empirical temperature. Being function of state variable, empirical temperature is a state variable itself.

As an example, we know that gasses in equilibrium, approximately obey Boyle's law.

$$P_1 V_1 = P_2 V_2 \tag{15}$$

Hence we can take empirical temperature to be proportional to the product PV. Historically it is done with a constant of proportionality R, giving us the ideal gas law.

$$PV = nRT \tag{16}$$

where n is number of moles and R is a constant with a value

$$R = 8.31 \times 10^{-23} \frac{J}{mol K} \tag{17}$$

One may recall that one mole is $6.07 \times 10^2 3$ atoms.

From this point of view, equation of state is nothing but a definition of empirical temperature. It is useful because it describes something physical, the equilibrium of the gas.

3.2 Thermometry

One can construct empirical thermometers using the empirical temperature function. One can fix one of the parameters in the empirical temperature, and take the practical temperature scale to be proportional to the changes in other parameter. Hence, for a gas thermometer, one can fix the pressure and then construct a temperature scale depending on how much the gas has expanded in volume. The easiest way is to take a linear relationship.

$$T = aV. \tag{18}$$

The empirical temperature as defined above does tell us wether two systems are in equilibrium, by measuring their empirical temperature with a reference thermometer. However, it does not tell us which one of them is hotter. Hot being defined as the system which loses energy when brought in thermal contact with a colder substance.