Introduction

The smallest constituent of any matter that can be identified are molecules or atoms. Yet knowing the molecular or atomic details are not sufficient to describe the properties of matter as we see it. For instance, knowing that it is H_2O molecule alone would not have told us whether we are describing water, ice or steam.

A gas (liquid or solid) consists of a large numbe of molecules, typically of the order of Avogadro's number. Knowing the molecular form of the gas, we could try to describe the state of the gas in terms of the states of the individual molecules. If we treat gas molecules approximately as classical particles[1], the state of any molecule will be given in terms of the position coordinates and momentum components (x, y, z, p_x, p_y, p_z). For any classical particle given its state at some initial time, its state at any other time is completely predictable using classical equations of motion[2]. An important characteristic of a gas in a container, when held at a temperature, is the rapid motion of its constituent molecules. During this motion, they collide with each other as well as with the walls of the container. As the number of molecules is very large, every molecule undergoes millions of collisions every second and its state keep changing rapidly. The change is so rapid that, at the rate at which we are able to make observations, it is not possible for us to observe all the changes. This makes it impossible to predict their motion using classical equations of motion. All we can say is the probability of finding the particle in a certain state. Anything that we can measure to learn about the gas molecule can only be an average quantity. This indicates that the motion of gas molecules exhibit randomness. This is true, in general for all matter and many other thermodynamic systems like a ferromagnet whose constituents are not even mechanical particles. Taking into account all these we can say that, microscopically, all thermodynamic systems are random systems.

To familiarise ourself with random systems and to define the basic elements of our study, let us turn to a simple example - tossing of a coin N times. Let p be the probability for a head to occur in every one of these coins and q the probability for a tail.
When we toss a coin N times, we expect the coin to turn in a head in a certain number of tosses and tails in the remaining ones. Let us look at a possibility of n number of heads turning out in N tosses. These n heads could occur in any ordering of the N outcomes. For instance, {THHTTHHHT} is one possible ordering of $n = 5$ heads in a toss of $N = 9$ coins. How many different such orderings can be found? Answer is ${}^9C_5$. In general, the number of distinct orderings with n heads in N tosses of a coin is ${}^NC_n$. Henceforth, we will call these different orderings **microstates** of N tosses. A given value of n corresponds to ${}^NC_n$ distinct microstates. We will also term a given value of n as a **macrostate** of N tosses. Since the probability of a head is p and that of a tail is $q = 1 - p$, the probability for occurence of any one of the microstates with n heads is $p^n\, q^{N-n}$. The probability to get a macrostate with n heads in a toss of N coins is

$$P(n) = {}^N C_n\, p^n\, q^{N-n} \tag{1}$$

[1]That means, particles that obey Newton's law
[2]Such as Newton's law

One could ask what the average number of heads in N tosses. It is the expectation value of n

$$\begin{aligned} \langle n \rangle &= \sum_{n=0}^{N} n \; P(n) \qquad (2) \\ &= \sum_{n=0}^{N} n \; {}^{N}C_n \; p^n \; q^{N-n} \\ &= p \sum_{n=1}^{N} {}^{N-1}C_{n-1} p^{n-1} q^{N-n} \\ &= Np \qquad (3) \end{aligned}$$

What is interesting about the above experiment is that instead of tossing a coin N times, we could toss N identical copies of one coin. The copies are identical in the sense that probability of a head is p and that of tail is q is every copy. The collection of N identical copies is called an *ensemble*. Tossing N coins will again result in a certain number of heads and a certain number of tails. If we now look at the possibility of finding n heads in these N coins we find that there are ${}^{N}C_n$ (microstates). Hence the probability of n coins sporting a head (a macrostate) turns out to be the same as given in equation (1). Moreover the average value of n computed over the above probability is also as given in equation (2). Thus tossing an ensemble N independent copies of a coin mimics the results of tossing a single coin N times. Averages found over the ensemble gives the same results as the average found in time. This phenomenon is called ergodicity. Systems that exhibit ergodicity are called ergodic systems.
Coming back to a physical example, let us suppose we are able to observe motion of every molecule of a *thermally isolated* box of gas. Clearly the energy E of the gas remains constant. Giving the position and momentum $(\mathbf{r}, \mathbf{p})$ of any molecule will specify the state of that molecule. If we know this for all the N molecules at any instant of time, we know *a microstate of that gas* at that instant. If we observe each molecule of the gas for a long time we could notice that each one goes through all possible states it could achieve. This causes the gas to go through all possible microstates it could achieve at that energy. Probability of any one of these microstates can be found and it is equal to any other microstates. Now if we take a large number of identical copies of the box at energy E we obtain an ensemble. The probability of finding gas in a particular microstate in any one these copies happens to be identical to the probability of finding that microstate while observing a single box of gas for a long time. Thus ensemble average of any quantity will be the same as its time average and the system is ergodic.

Finally, if we remove the thermal isolation and let the box of gas reach thermal equilibrium with its surroundings the system retain ergodicity. [3] Thus ergodicity is a necessary condition for all themrodynamic systems.

This preliminary discussion shows that we need to recognize the random nature that thermodynamic systems exhibit microscopically. In the following sections of these notes we will

[3]Probability of all microstates will not be equal now. But it will depend upon the energy of that microstate

set up the basic tools to study this randomness and give a description of thermodynamics in terms of those microscopic information.