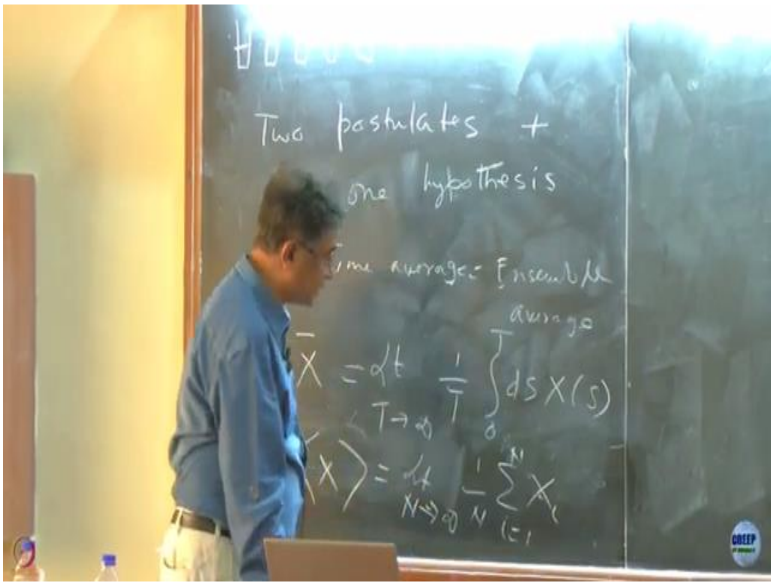
Basic Statistical Mechanics
Prof. Biman Bagchi
Department of Chemistry
Indian Institute of Technology, Bombay
Indian Institute of Science, Bangalore

Lecture - 05
Fundamental Concepts and Postulates of Statistical Mechanics Part - 1

So this is very important to know theory of probability to know the postulates of statistical mechanics. If you do not know theory of probability you do not appreciate the theory of probability. You will not be able to appreciate the beautiful postulates of statistical mechanics that go into it. Without going into details let me tell you the things on which whole statistical mechanics based on.

And I will elaborate on my comment that’s why what I made this probability theory and think many of the things I have to as I talk they will come to me and the way it happens to always a teacher.

(Refer Slide Time: 00:55)



Now, there are two postulates and one hypothesis and just like whole quantum mechanics follows from Schrodinger equation and you know it still stands as hypothesis. The two postulates and one hypothesis is the total cornerstone of statistical mechanics. Everything of statistical mechanics and by extension our understanding of thermodynamics of natural phenomena everything is from these two postulates.

And we need hypothesis and that I will explain why I need the hypothesis? What are the two postulates? The two postulates; in order to understand those two postulates you would need to know few other things. But, let me tell you the two postulates then I will go back and forth because they are very important. Then I will see to understand these two postulates we need to know some things.

The first postulate is one introduce time average equal to ensemble average. Time average is like that a quantity X, X time average the way you do you take it long trajectory as I will tell you I need to talk of trajectory and some I am observing a system for sufficiently long time, then time average is that I am just taking one random variable I am not talking correlation that has a little bit more complex and I am not going to immediately that.

So, I take snapshots I measure the values at different, may be equal time intervals. Then I say

$$\lim_{T\to\infty}\frac{1}{T}\int_0^T dsX(s)$$

This is the time average. Is this clear everybody? This is very important thing, this time average. What we are doing? We are measuring the time fluctuating as we discuss fluctuating but I have this time then I say ok I do it up to time long time T.

Then I take the limit of time T to infinity and I do that and that becomes independent of T and this is the time average. Ensemble average is the one that Gibbs introduced we have a mental replica billions of billions, so instead of time average now I construct and this was the you know, whenever it helps to be very relaxed so you have this glass of water identical many same amount of volume, same glass same water everything billions of billions of replica.

Now instantaneous configuration of water is in one of these mental replicas this is my original one. Now, the mental replica controls its volume, its density, its temperature, say in our case volume, total number of water molecules and the total energy if they are in isolation (NVE) but other than that it does not control what are the positions and orientation of the water molecules.

So in each of my mental replica position and orientation of the water molecules are different. This is very important. So, I am constructing it is a brilliant construction done by Willard Gibbs, he created a mental replica and he realized that if they are identical in macroscopic sense NVE. I have no control over this microscopy and there are huge numbers of microscopic states they are something like you can say 10^{23}.

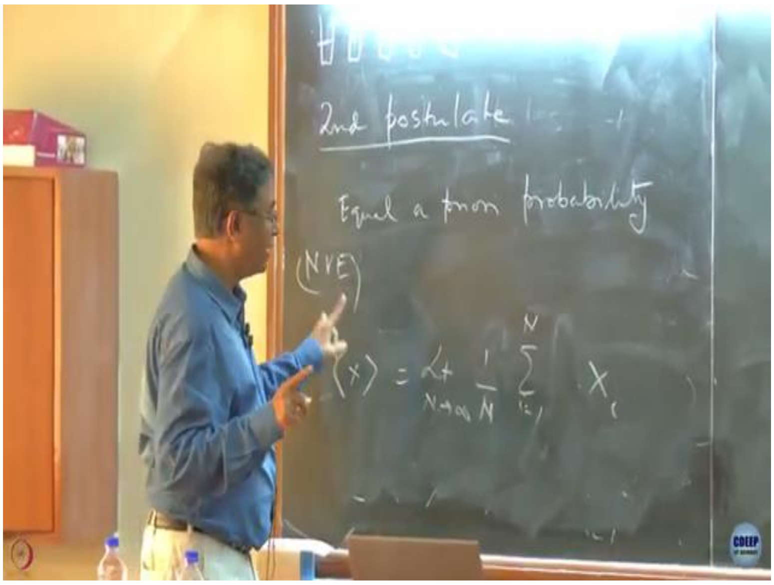
So each of them is distinct microscopically very important to understand that they are exact macroscopically but they are distinct microscopically. So, now I can go and say okay they are macroscopically identical but they are at the same time and individual of them will have a little different value of the X. But, now I can average over them and that average will be denoted by this angular brackets. The definition is

$$\lim_{N \to \infty} \frac{1}{N} \sum_{i=1}^{N} X_i$$

Here, N denotes the numbers of replica which are mentally constructed. Again, ensemble is a mental construction with the condition that macroscopically they are the same, microscopy they are distinct because a microscopic system and huge number of microscopic states. And now I go in my mind, I calculate the by the X, if for each of my system and as I said N is billions and billions.

And then the first postulate of statistical mechanics is time average equal to ensemble average that the first postulate of statistical mechanics. Now, we will do the second postulate.

(Refer Slide Time: 07:33)



Now anybody knows the second postulate? This is really beauty, exactly, equal a prior probability now tell me since you have told me what is it? Exactly, so but at the core of that all my systems are in NVE and each of the microscopic states are equally probable. Why did you need that? One thing I did not, so this number two number one I go back little when I did do this thing.

I leave it N going to infinity stick sense I have to do P_iX_i, N is the number of systems. So if they are equally probability 1 over N comes here. So that is the reason so Gibbs had no other option you know he wrote this P_iX_i but he was working in NVE he knew Boltzmann distribution that is same energy the only sensible thing is to do is to equal a prior probability.

This is really beauty, so now we have done the two postulates. I will go to little bit more detail on the trajectory and space and all these things. Now, I have done the two postulates of statistical mechanics. Now we know time average, ensemble average and equal a priori probability. So you now realize the first postulate required the second postulate without that we do not go anywhere.

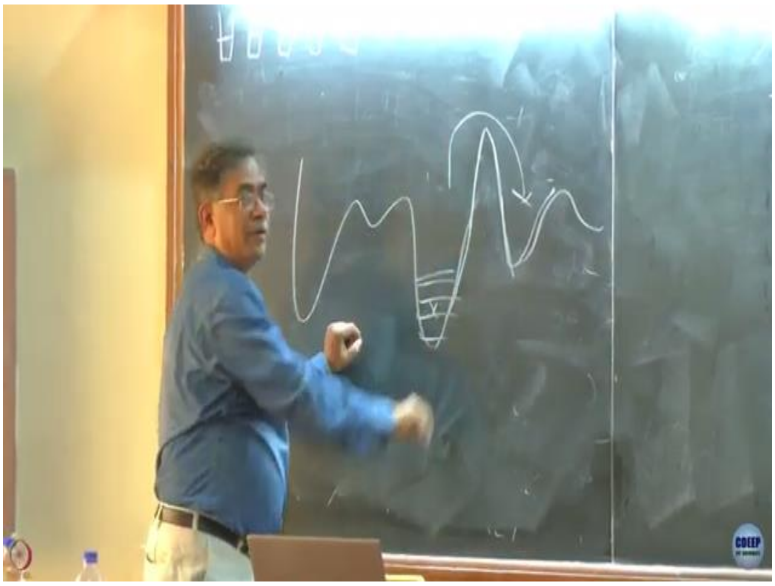
Now Gibbs needed that of course, this thing is given to Boltzmann i.e, the Ergodic hypothesis because Boltzmann used it earlier. Now anybody can tell me what is Ergodic hypothesis? And also tell me or otherwise I will tell you why we need the Ergodic hypothesis. This is really very, very impressive, really very intellectually stimulating. So we had two hypotheses, I said the whole statistical mechanics is based on two postulate and one hypothesis that is all.

Everything follows from that. The huge construction huge theoretical framework of statistical mechanics which everybody uses the biology, chemistry, science, physics that is the theory of many body systems. There is no other but this whole thing is based on two postulates and one hypothesis and the name of the hypotheses is Ergodic hypothesis. But why do we need the Ergodic hypothesis? And what is the Ergodic hypothesis?

It is not enough to have equal probability but the particle system must go from one to the other system must not remain trapped in one state so Ergodic hypothesis now tells that the system visits every state. That is why glass we have the problem breakdown of Ergodicity. So the second hypothesis guarantees forces for the system to go through all the states having equal probability.

It probably is not enough if there is a large barrier between them you do not go from one state to other.

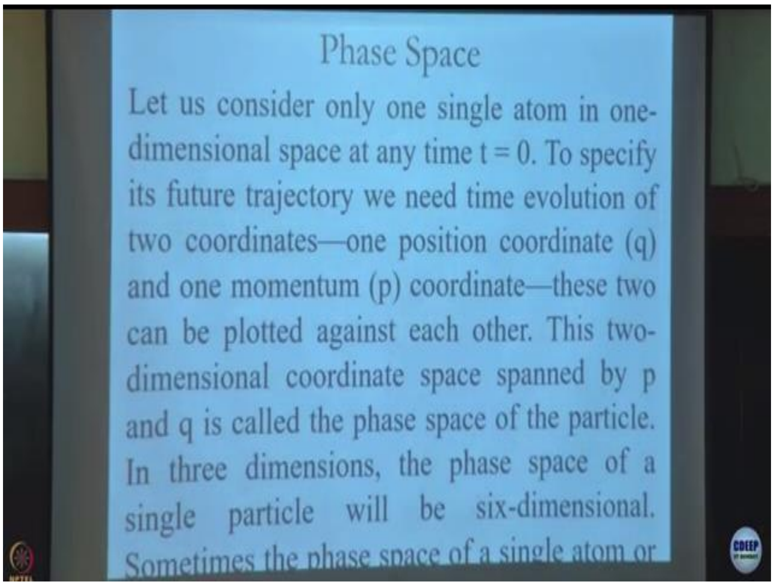
(Refer Slide Time: 11:50)



Now, I cannot put ensemble average equal to time average if I do not have equal a prior probability. Once I have equal a prior probability and if my free energy is like that it does not go from one to here it gets stuck here that is the computer simulation all the time your breakdown ergodicity. So we need it to go and that is why you need the Ergodic hypothesis. Now I go through some things so we have two postulates we have done.

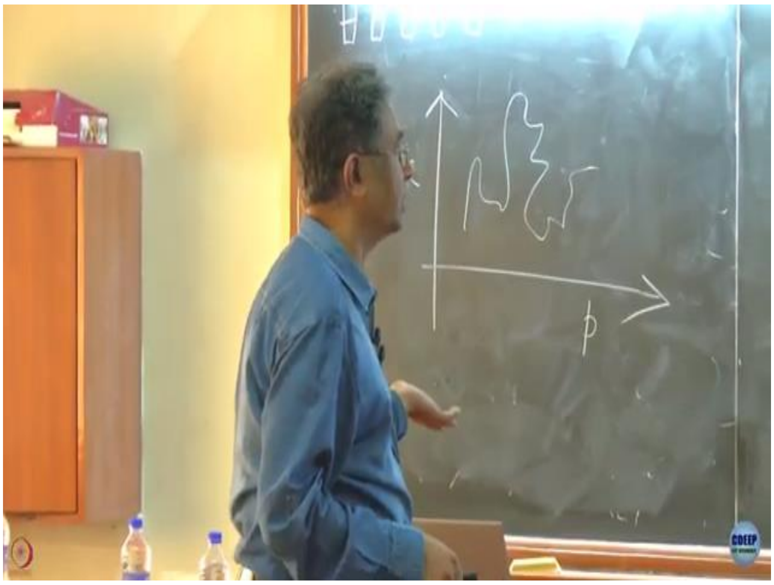
Now I would like to tell you about the concept of a phase space. I would like to tell you about the concept of trajectory because without a trajectory we do not have algorithm hypothesis or equal to probability without phase space. Phase space is a sample space we do not have the probability distribution, so these are the two things that I need to do now.

(Refer Slide Time: 13:01)



Let us consider a single atom and start following its position and velocity from time T = 0. So in order to get all its future thing in the position and momentum space we need two coordinates in one dimension we just need two coordinates. What are position and velocity? They can be plotted against each other so the way we want plots this phase space is a very initial is of the classical mechanics.

(Refer Slide Time: 13:35)

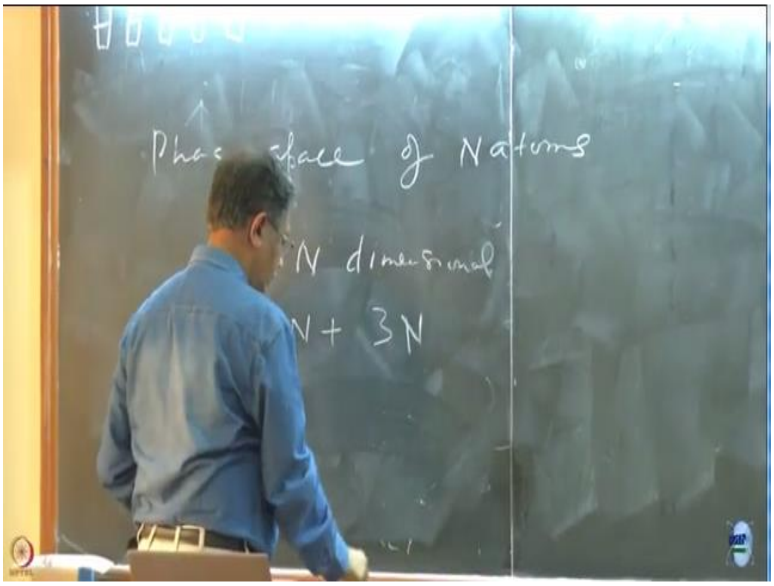


But this is the way classical mechanics is really not taught. So if its position is X and momentum P then this is the kind of thing that you get the particle moving through with the different velocity and different position and this is called the Phase Space.

Now it is very important to look. So now we are trying to understand the trajectory and quantify the trajectory and the phase space. So this phase which is defined by position and momentum of a particle gives you the movement of a system. If I have one particle only then it is sometimes called μ space and one particle in 3-dimension is 6-dimensional space.

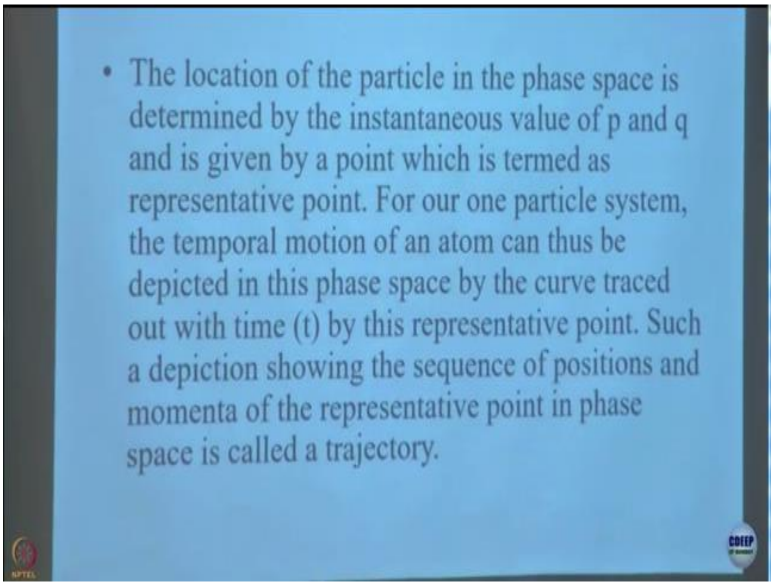
So phase space of a single particle in 3-dimension is 6-dimensional and in two dimensional the phase space is 4-dimensional. So in N particle system then we have a 6N- dimensional space this is something which puts off students but it needs not really be difficult.

(Refer Slide Time: 15:14)



So the phase space of N particle in three dimensions is 6N dimension. However you are not going to really work with it the in one of the major thing of statistical mechanics is that you have to go through the formalism to understand the formalism so this is required to derive the equations.

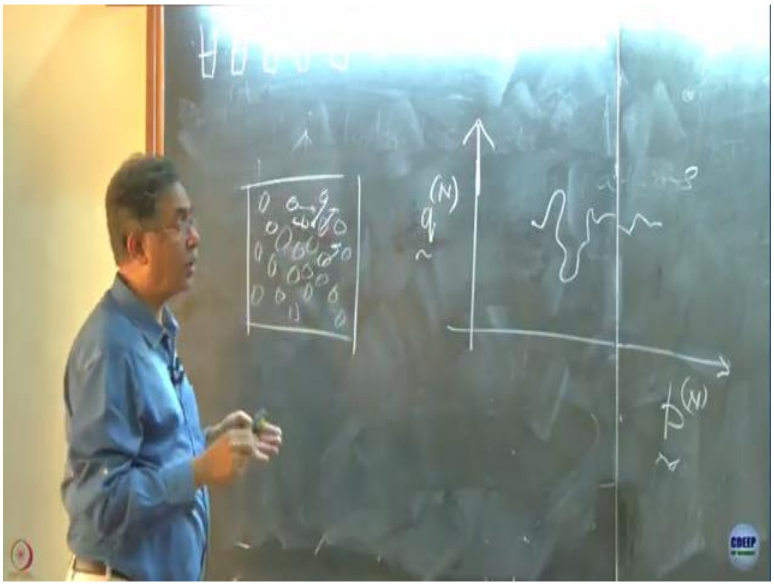
(Refer Slide Time: 15:50)



And one thing in Stat-Mech from beginning to the end it is a highly mathematical subject this is one of the reason probably in chemistry it is not taught that much. But unfortunately for all of us without Stat-Mech we cannot do anything we cannot do any of the studies theoretical understanding, so this mathematical grinding that we go through or mathematical kind of conveyor belt that you go through is not terribly difficult.

And at the end of that you have an equation which is factorable, so right now let this so the phase space is a 6N-dimensional system of 3N. This phase space of N atoms I have not gone to molecule yet in N atoms and that is 6N-dimensional 3N coordinate plus 3N velocity or momentum.

(Refer Slide Time: 16:58)



Now as I am considering a system of N number of particles here. Then I can draw a vector in the phase space which is 6N- dimensional phase space 3N position and 3N momentum. This is space this is 3N-dimensional view since I cannot draw 6N-dimensional. So drawn it two dimension but this is 3N.

Now I have N number of atoms and molecules here which are undergoing collisions are changing positions. So instantaneous state of my system is a point in this thing because a point has 6N values and then that determines position and velocity of each of the particles is a deduction in description but it is still hidden. Nothing as we solved but we are developing a formalism.

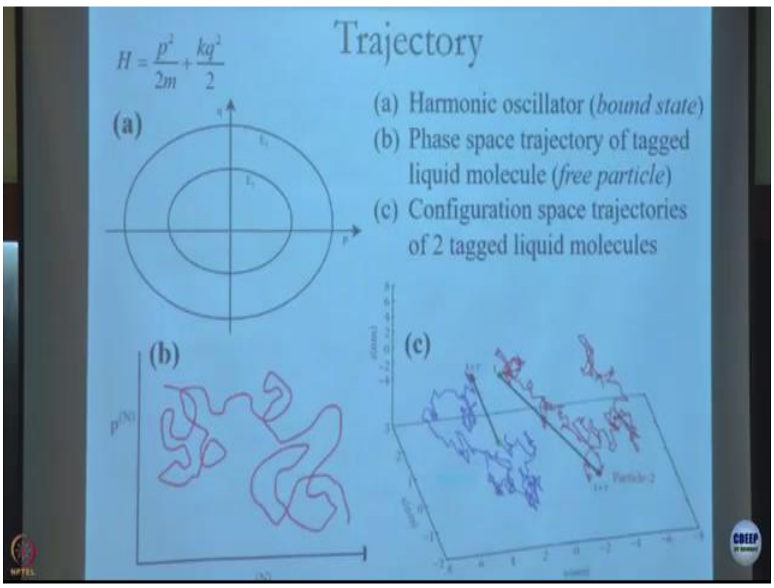
As the particle is moving and my system going from one microscopic state to another microscopic state. I am here moving in my phase space because this gives my starting position, next position in this each point is important thing each point signifies instantaneous state of the system.

This thing; so the 6N-dimensional phase space so the motion of the system in this phase space is called the trajectory. So in computer simulations when you are doing averaging over trajectory you are actually following through all the your 1,000 particles say atoms just then you have taking care of this 6,000 at any given time you are going time T to T+ΔT you are doing little bit here.

Yes, all the particles are having same momentum; they move in one direction and there will be translational movement. But all of you give the same momentum in the direction, so you will just move in that direction, that is very easy you will have a whole system moving. So this position these one will move with the same velocity. So it will parallel to momentum axis and it will move in position direction at a constant velocity.

Absolutely that is what you know the equation that gives you the motion in the Phase space is nothing but Hamilton's equation that we write as a Liouville equation. So Hamilton's equation gives exactly that quantity now a very good question because it brings to the essence of classical mechanics and movement of the particles in the phase space now. So one particle system we can do that, so now we have understood the little case a few examples.

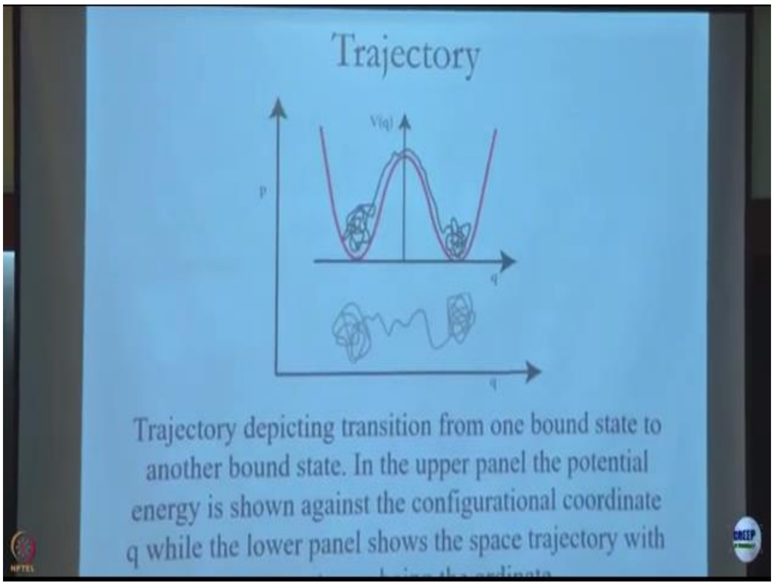
(Refer Slide Time: 21:30)



So let us take a single one particle harmonic oscillator and then depending on energy now it is a bound state. Bound state means it will be like this and it is an ellipse because the phase space is an ellipse. So phase space is now highly restrictive if you talk about of vibrational energy relaxation with the discrete energies then you will be going from one state to another state and you know some very interesting things happen.

Free particle however is not a bound state it can go all over the phase space so this is a free particle one free particle that is moving. So harmonic oscillator bound state is a free particle then two particles are tragic. Now, I want to consider trajectories of two particles and that can be generated in computer simulations.

(Refer Slide Time: 22:24)



Really interesting this trajectory, say we are doing a chemical reaction and in chemical reaction particle is going from one bound state to another bound state or one quasi bound state to another quasi bound state. Then you get this guy is going around moving here in a bound state.

Then it escapes the barrier then goes to another bound state. So character of the trajectory in the phase space tells a lot of what is going on in the system.