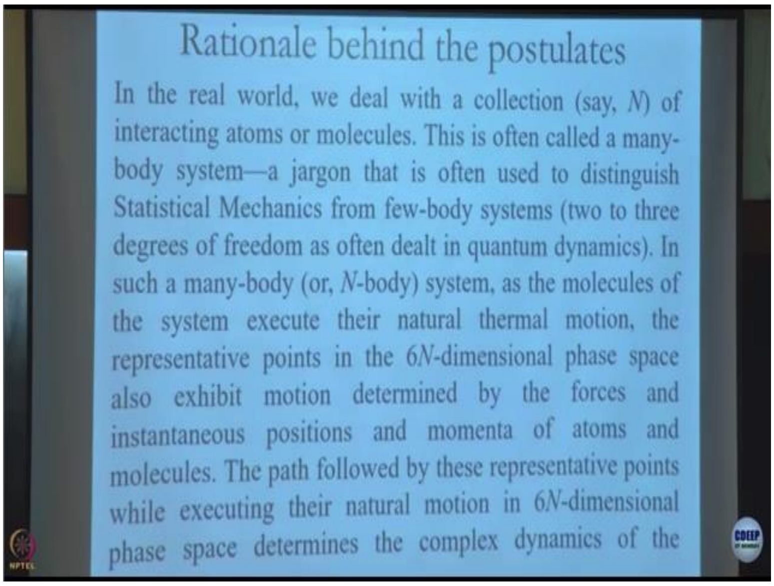
Basic Statistical Mechanics

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

Lecture - 06
Fundamental Concepts and Postulates of Statistical Mechanics Part - 2

(Refer Slide Time: 00:15)



Rationale behind the postulates

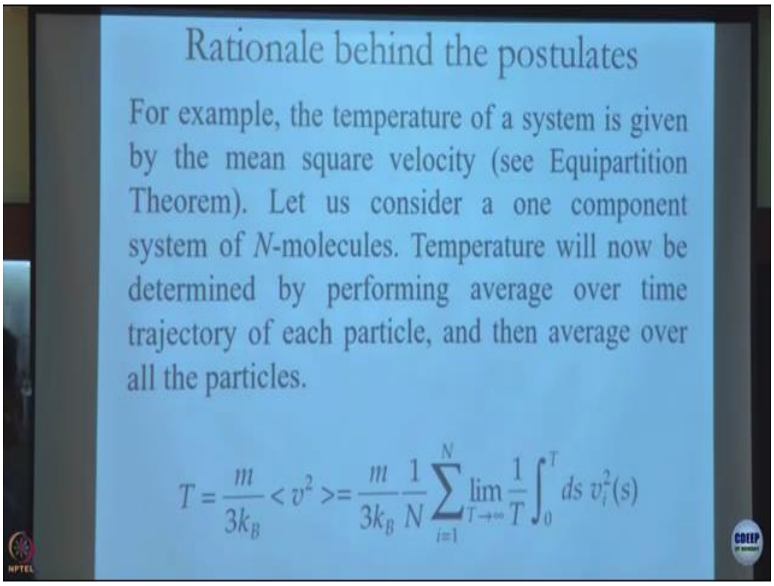
In the real world, we deal with a collection (say, *N*) of interacting atoms or molecules. This is often called a many-body system—a jargon that is often used to distinguish Statistical Mechanics from few-body systems (two to three degrees of freedom as often dealt in quantum dynamics). In such a many-body (or, *N*-body) system, as the molecules of the system execute their natural thermal motion, the representative points in the 6*N*-dimensional phase space also exhibit motion determined by the forces and instantaneous positions and momenta of atoms and molecules. The path followed by these representative points while executing their natural motion in 6*N*-dimensional phase space determines the complex dynamics of the

Now I come to the rationale behind the two postulates of statistical mechanics and I already talked about the Ergodic hypothesis. So the basic idea is that we do a huge number of interactive systems and this 6N-dimensional phase space that Boltzmann and Gibbs developed, Maxwell did not. Now, so this motion just the question you asked, motion is determined by forces and the instantaneous positions and intermolecular interactions.

That is where Hamilton's equation comes in and so the path followed by the representative executing nature. This is very important in this Kubo’s language. We had a great stat-mech guy called Ryogo-Kubo the natural motion. So what we are following is a natural motion of the system in the phase space. So trajectory is very important, no external force is there. So we want to establish now the relationship between such a microscopic trajectory.

So a trajectory is a microscopic thing and measured properties. And this is, I could calculate the pressure but if I could do Newton's equation, the whole system then all the atoms and molecules bombarding against the way Maxwell did in his ideal gas, you know calculating the pressure, **$PV = 1/3\ mNc^{2}$.** I can do that but unfortunately I cannot do that because I cannot calculate all these things.

(Refer Slide Time: 01:58)



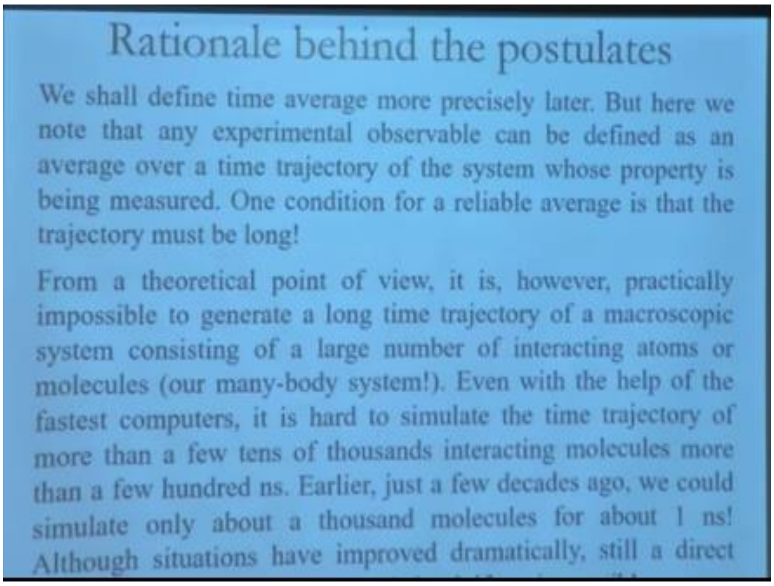
Rationale behind the postulates

For example, the temperature of a system is given by the mean square velocity (see Equipartition Theorem). Let us consider a one component system of *N*-molecules. Temperature will now be determined by performing average over time trajectory of each particle, and then average over all the particles.

$$T = \frac{m}{3k_B} < v^2 > = \frac{m}{3k_B} \frac{1}{N} \sum_{i=1}^{N} \lim_{T \to \infty} \frac{1}{T} \int_0^T ds\ v_i^2(s)$$

That is why we are now going to do first sometime averaging. This is the time averaging that I already introduced that you follow for a long time. This is the kinetic energy, mv^2 the average over a time trajectory of each particle. This is exactly what I wrote down some time ago here. I am just recapitulating the whole thing, which is a little bit of a problem.

(Refer Slide Time: 02:37)



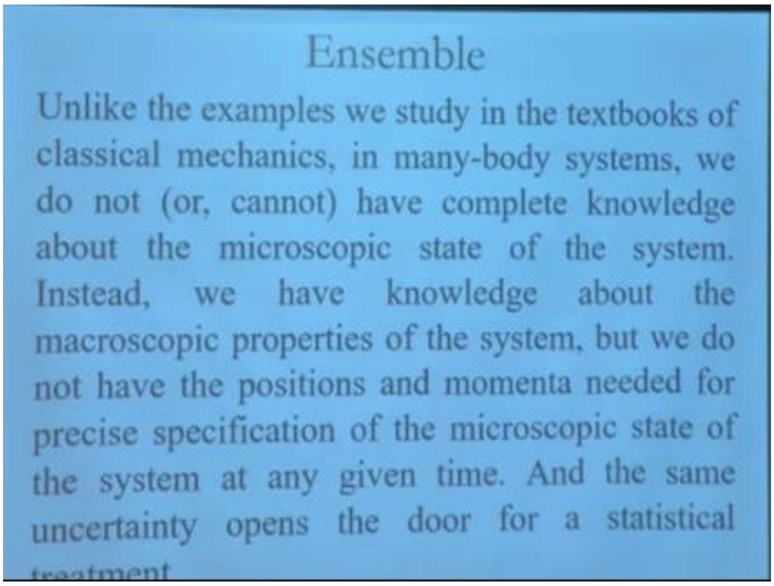
Rationale behind the postulates

We shall define time average more precisely later. But here we note that any experimental observable can be defined as an average over a time trajectory of the system whose property is being measured. One condition for a reliable average is that the trajectory must be long!

From a theoretical point of view, it is, however, practically impossible to generate a long time trajectory of a macroscopic system consisting of a large number of interacting atoms or molecules (our many-body system!). Even with the help of the fastest computers, it is hard to simulate the time trajectory of more than a few tens of thousands interacting molecules more than a few hundred ns. Earlier, just a few decades ago, we could simulate only about a thousand molecules for about 1 ns! Although situations have improved dramatically, still a direct

So time average view, so from a theoretical point of view, it is impossible to generate a long term trajectory of a microscopic system with a large number of particles that I have been telling. So we had no other option but to go to a probabilistic description, the one that I described. Fortunately, the probabilistic description can be developed with the help of only two postulates and one hypothesis.

(Refer Slide Time: 03:05)



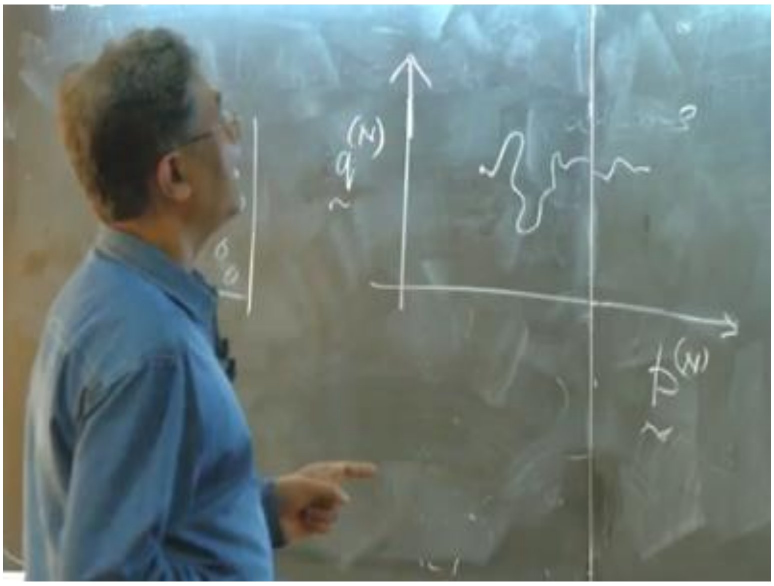
Ensemble

Unlike the examples we study in the textbooks of classical mechanics, in many-body systems, we do not (or, cannot) have complete knowledge about the microscopic state of the system. Instead, we have knowledge about the macroscopic properties of the system, but we do not have the positions and momenta needed for precise specification of the microscopic state of the system at any given time. And the same uncertainty opens the door for a statistical treatment

That is the beauty of the whole thing. So they that is in order to do that, Gibbs came out with the brilliant mental construction of the ensemble and that was really amazing though it was one should remember that he followed the same ensemble which Boltzmann followed which is NVE. So, all these two postulates and the Ergodic hypothesis are valid in the microcanonical ensemble.

Then the ensemble is called the micro canonical ensemble as we will do more later. So this is a language that the kind of uncertainty or the imprecise.

(Refer Slide Time: 03:51)

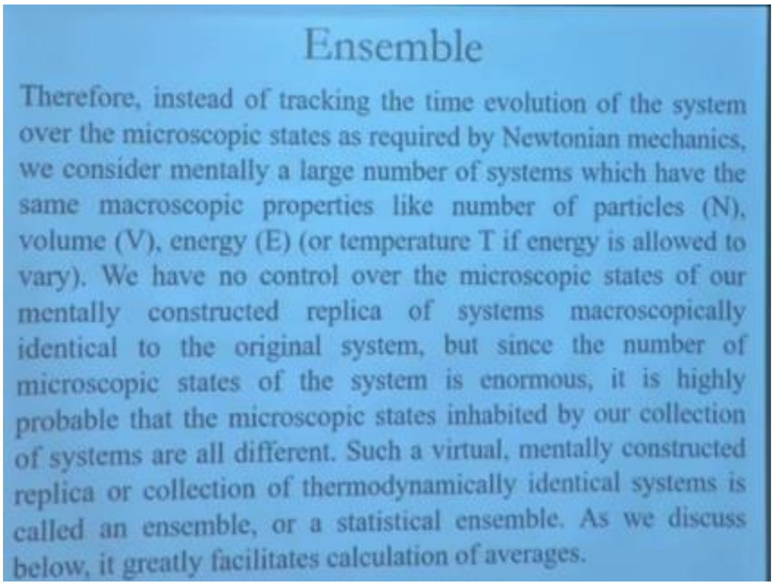


Is the same statistical description. So if this is an important interesting thing again as I am saying, recapitulating. The concept of an ensemble is based on the realization that the system at equilibrium must have a very large number of microscopic states. This is partly probably my query. The natural motion of the system at non-zero temperature takes the system through a finite fraction of these states. There is a very delicate question here which we will deal with much later in a time comparable time of measurement is very important.

Even when you are doing experimental measurement, we are going through a very tiny fraction of the total of sample space very important and there is a concept of cell similarity and these things will come in to do that measurement of the micro body. If you now consider the system remains at fixed energy at all these times, then the trajectory moves on a constant energy surface.

And according to the laws of mechanics, the classical or quantum and that generates the trajectory. But we do not need the detailed information it is extremely important we do not need the detailed information at least for the ensemble based equilibrium statistical mechanics that will gives developed. We do not need that is again and again saying but we need a certain realistic understanding of this trajectory and realistic understanding of what we are talking about ever it is.

(Refer Slide Time: 05:29)



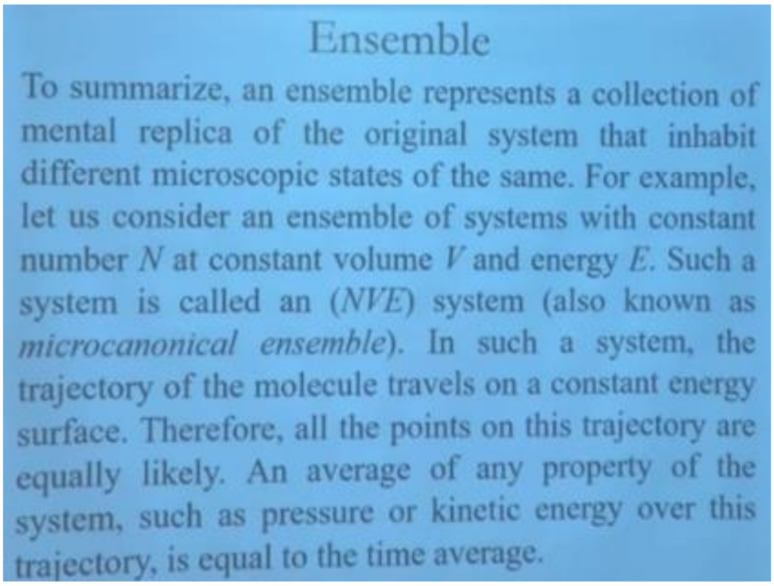
Ensemble

Therefore, instead of tracking the time evolution of the system over the microscopic states as required by Newtonian mechanics, we consider mentally a large number of systems which have the same macroscopic properties like number of particles (N), volume (V), energy (E) (or temperature T if energy is allowed to vary). We have no control over the microscopic states of our mentally constructed replica of systems macroscopically identical to the original system, but since the number of microscopic states of the system is enormous, it is highly probable that the microscopic states inhabited by our collection of systems are all different. Such a virtual, mentally constructed replica or collection of thermodynamically identical systems is called an ensemble, or a statistical ensemble. As we discuss below, it greatly facilitates calculation of averages.

Instead of tracking the time evolution of the system over the microscopic states as required by Newtonian mechanics, we consider mentally a huge number of states and as I keep saying is NVE thing was set up. But going from NVE to temperature T is a little different thing. We have no control over the microscopic states of the system and neither do we want to have any control you do not want there.

But we want them to flow over the phase space. That is why equal probability and organic hypothesis is important. The flow in the microscopic state in the phase space in the trajectory should cover a significant part of the system.

(Refer Slide Time: 06:13)



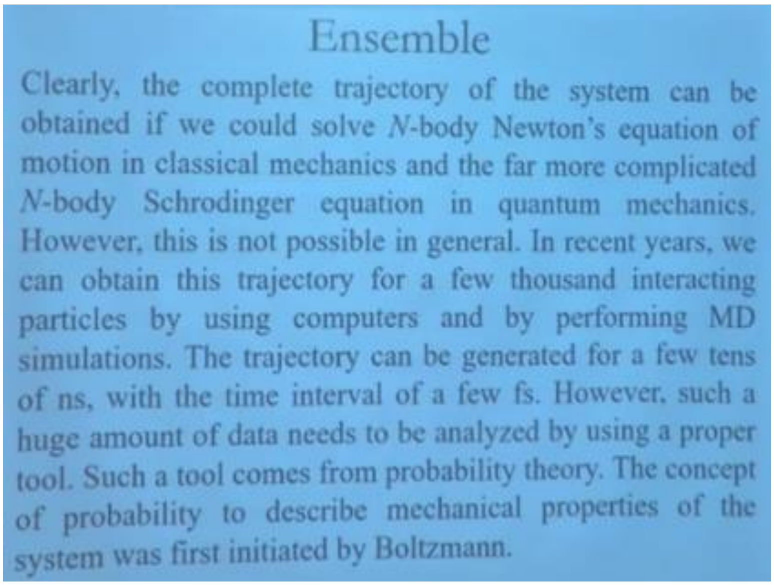
Ensemble

To summarize, an ensemble represents a collection of mental replica of the original system that inhabit different microscopic states of the same. For example, let us consider an ensemble of systems with constant number N at constant volume V and energy E. Such a system is called an (NVE) system (also known as *microcanonical ensemble*). In such a system, the trajectory of the molecule travels on a constant energy surface. Therefore, all the points on this trajectory are equally likely. An average of any property of the system, such as pressure or kinetic energy over this trajectory, is equal to the time average.

So ensembles represent a collection of mental replicas and is called micro canonical ensembles. Trajectory system travels on a constant energy surface. All the points in trajectory are equally likely. This is what I said, there is no other option and good fortune as that this works out and actually it was still very doubtful for a long time.

Even in 1950, there was a guy called, who wanted to push Shannon entropy called James, who wrote to Woolenbeck saying to making that, because of your difficulties statement you should probably consider information entropy and this kind of mainstream statement. So Woolenbeck gave the famous answer saying that, since the Lian Young proved that one can explain statistical phase transition within statistical mechanics, we do not need your Shannon entropy and that turned out to be correct. We did not need that.

(Refer Slide Time: 07:16)

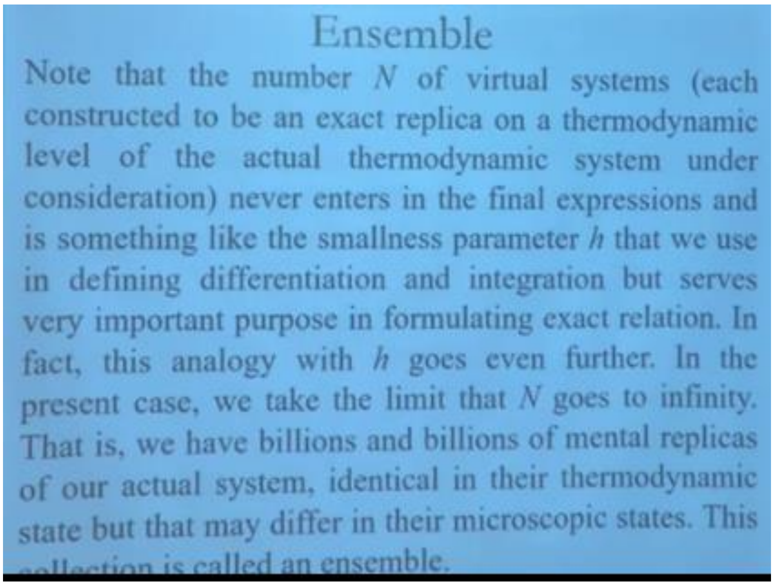


Ensemble

Clearly, the complete trajectory of the system can be obtained if we could solve N-body Newton's equation of motion in classical mechanics and the far more complicated N-body Schrodinger equation in quantum mechanics. However, this is not possible in general. In recent years, we can obtain this trajectory for a few thousand interacting particles by using computers and by performing MD simulations. The trajectory can be generated for a few tens of ns, with the time interval of a few fs. However, such a huge amount of data needs to be analyzed by using a proper tool. Such a tool comes from probability theory. The concept of probability to describe mechanical properties of the system was first initiated by Boltzmann.

So the complete trajectory of the system can be obtained if we cancel N-body Newton's equation. That is the one partly when you do time difference statistical mechanics as a part of it. The trajectory can be generated for a few tens of nanoseconds and few femtoseconds and the time interval we dumps it. Even then huge data is there which comes handy sometime.

(Refer Slide Time: 07:38)

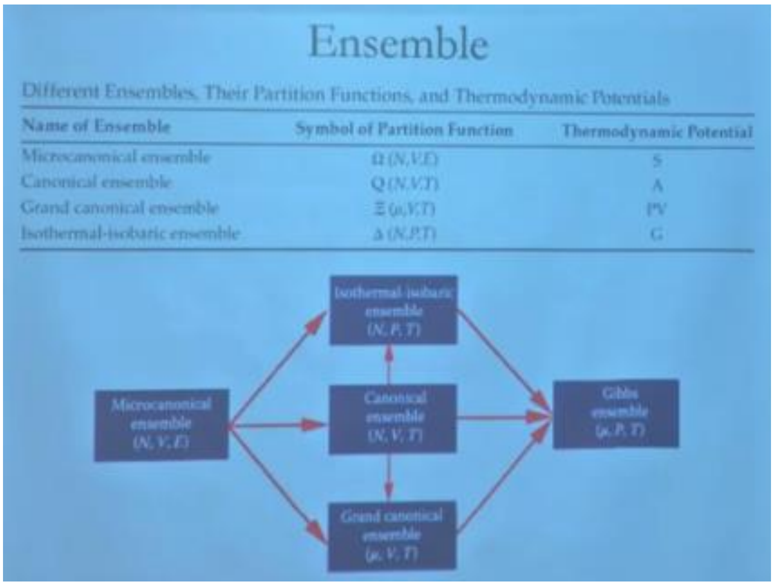


Ensemble

Note that the number N of virtual systems (each constructed to be an exact replica on a thermodynamic level of the actual thermodynamic system under consideration) never enters in the final expressions and is something like the smallness parameter h that we use in defining differentiation and integration but serves very important purpose in formulating exact relation. In fact, this analogy with h goes even further. In the present case, we take the limit that N goes to infinity. That is, we have billions and billions of mental replicas of our actual system, identical in their thermodynamic state but that may differ in their microscopic states. This collection is called an ensemble.

So this kind of all details of the understanding of how phase space can be quantified? The smallness parameter turns out to be Planck's constant and this analogy is beautiful, but I am not going into detail on that.

(Refer Slide Time: 07:59)



Ensemble

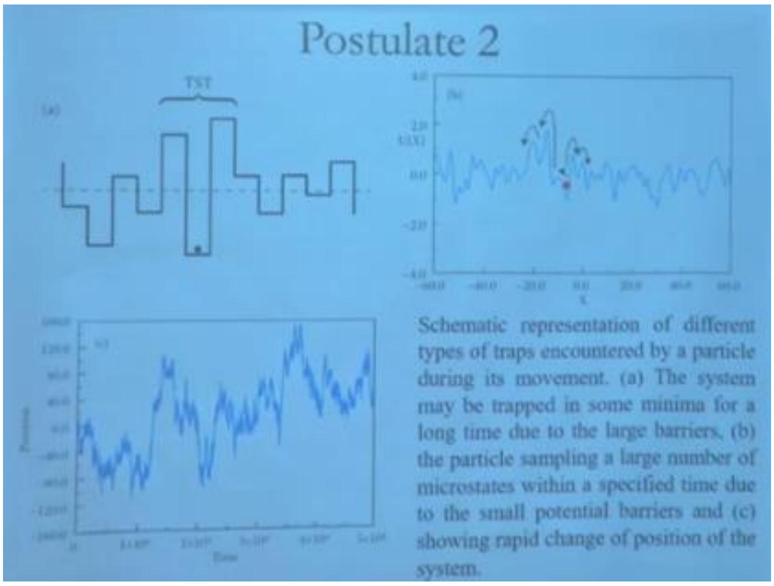
Different Ensembles, Their Partition Functions, and Thermodynamic Potentials

Name of Ensemble	Symbol of Partition Function	Thermodynamic Potential
Microcanonical ensemble	$\Omega\,(N,V,E)$	S
Canonical ensemble	$Q\,(N,V,T)$	A
Grand canonical ensemble	$\Xi\,(\mu,V,T)$	PV
Isothermal-isobaric ensemble	$\Delta\,(N,P,T)$	G

Right now, I just want to say the following are the different kinds of ensembles that I will do in the next lecture. So the main idea of this lecture is something which may be intensely found on these two postulates. Because I figured out how to extend the interrelation between the two postulates, the necessity of the postulates and the Ergodic hypothesis is only when I wrote the book.

So all these things can be connected and was done by again is a very strange person who does everything like Maxwell did everything of kinetic theory of gases, all the equations that you do undergraduate starting at, it all the same thing and then will give much of it almost alone there. So this time average and ensemble average we all did that.

(Refer Slide Time: 08:56)



Postulate 2

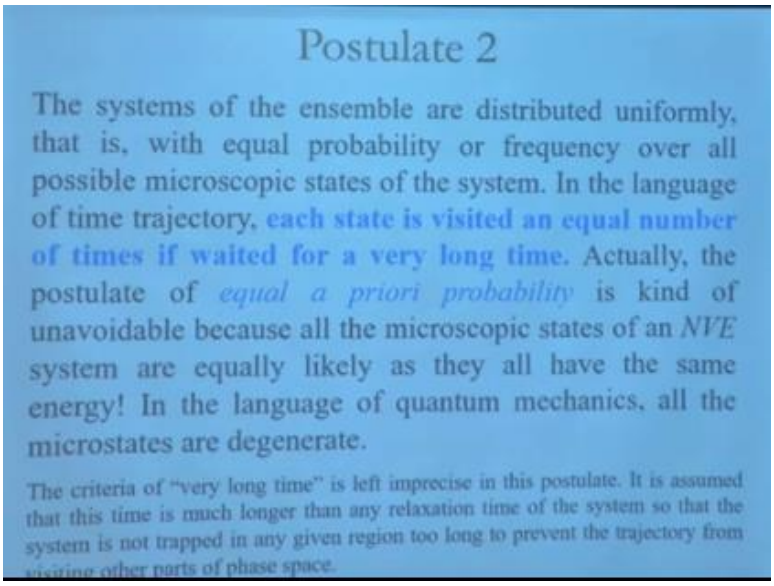
Schematic representation of different types of traps encountered by a particle during its movement. (a) The system may be trapped in some minima for a long time due to the large barriers, (b) the particle sampling a large number of microstates within a specified time due to the small potential barriers and (c) showing rapid change of position of the system.

One thing as this question asked is, why the problem is probably worked out if you have a system like that, let us see it stuck here. This is the energy landscape and the particle is executing a random walk here and if it gets stuck here, then we simulate it, stimulate it, stimulate it for years, we could not get a converged result. The guy was doing were not stupid that is because the system is larger, then you face larger and larger barriers, larger and minima and you are thrown out of the track.

We never get converged results. This is the reason, this is the thing you did in the Ergodic hypothesis. If Ergodic hypothesis, these system is called Ergodic, later I found out that there is a famous paper by Stein who said diffusion and these are beautiful paper by I go to Segai Sun and show got Bananji this issue but we were really put on the right track by Newman and Stein, two mathematicians sent from institute and current institute saying that one dimensional random.

This is called random energy landscape, diffusion in one dimensional random energy landscape is pathological in 1D. That is exactly what turned out to be correct.

(Refer Slide Time: 10:29)



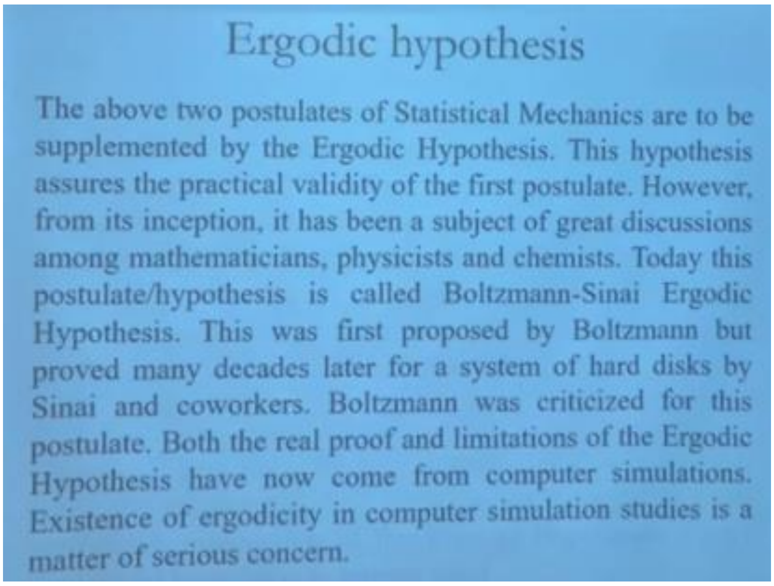
Postulate 2

The systems of the ensemble are distributed uniformly, that is, with equal probability or frequency over all possible microscopic states of the system. In the language of time trajectory, **each state is visited an equal number of times if waited for a very long time.** Actually, the postulate of *equal a priori probability* is kind of unavoidable because all the microscopic states of an *NVE* system are equally likely as they all have the same energy! In the language of quantum mechanics, all the microstates are degenerate.

The criteria of "very long time" is left imprecise in this postulate. It is assumed that this time is much longer than any relaxation time of the system so that the system is not trapped in any given region too long to prevent the trajectory from visiting other parts of phase space.

So the postulate of equal probability and then each state is visited an equal number of times if waited for a very long time. This is an equal probability, every state is an equal problem.

(Refer Slide Time: 10:42)



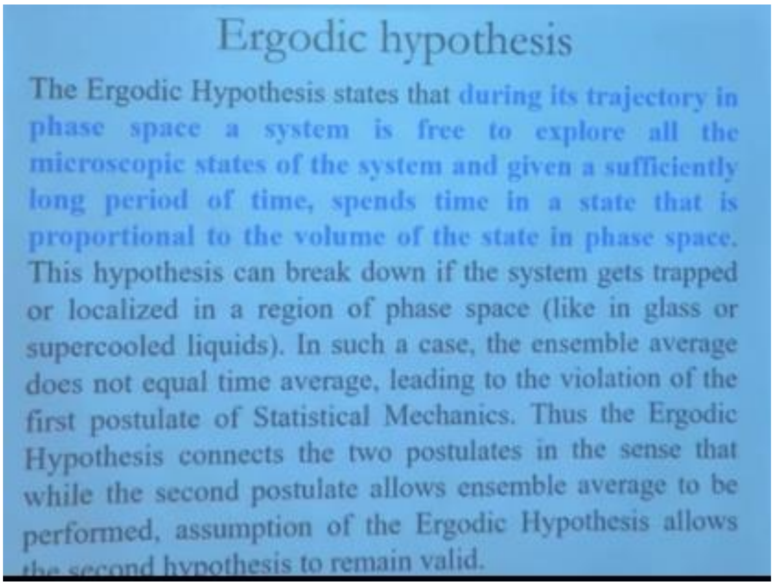
Ergodic hypothesis

The above two postulates of Statistical Mechanics are to be supplemented by the Ergodic Hypothesis. This hypothesis assures the practical validity of the first postulate. However, from its inception, it has been a subject of great discussions among mathematicians, physicists and chemists. Today this postulate/hypothesis is called Boltzmann-Sinai Ergodic Hypothesis. This was first proposed by Boltzmann but proved many decades later for a system of hard disks by Sinai and coworkers. Boltzmann was criticized for this postulate. Both the real proof and limitations of the Ergodic Hypothesis have now come from computer simulations. Existence of ergodicity in computer simulation studies is a matter of serious concern.

And then of course these two are connected, which is very important two postulates of Statistical Mechanics are to be supplemented by Ergodic Hypothesis. These I could assure the practical validity of the first postulate, without the Ergodic Hypothesis your first postulate as you are asking is mute mathematicians and physicists and this is done by sometimes called Boltzmann-Sinai.

Because Sinai is the one who first proved Ergodicity for a system of hard disks like million balls. But on a 2D he did that, real proof is amazing Rubinovich and Sinai, all mathematicians, system of hard disks, the beautiful thing that was done.

(Refer Slide Time: 11:27)

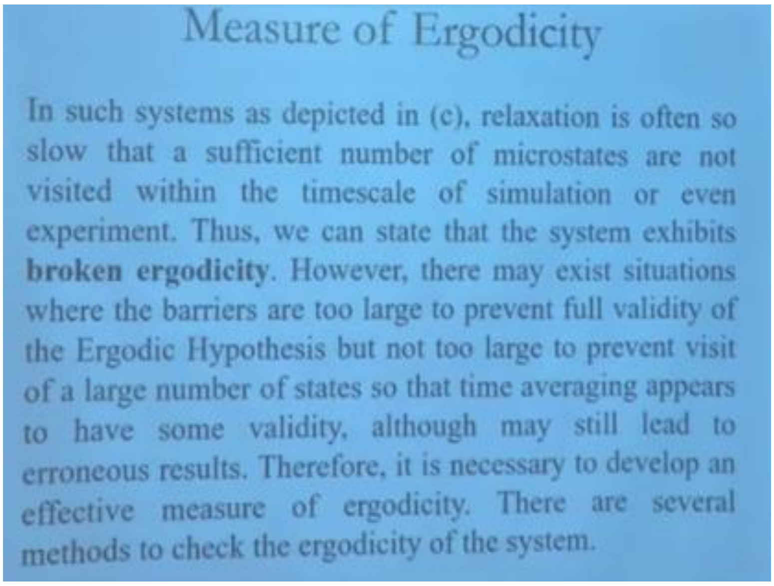


Ergodic hypothesis

The Ergodic Hypothesis states that during its trajectory in phase space a system is free to explore all the microscopic states of the system and given a sufficiently long period of time, spends time in a state that is proportional to the volume of the state in phase space. This hypothesis can break down if the system gets trapped or localized in a region of phase space (like in glass or supercooled liquids). In such a case, the ensemble average does not equal time average, leading to the violation of the first postulate of Statistical Mechanics. Thus the Ergodic Hypothesis connects the two postulates in the sense that while the second postulate allows ensemble average to be performed, assumption of the Ergodic Hypothesis allows the second hypothesis to remain valid.

And so the Ergodic states that during its trajectory in phase space a system is free to explore all the microscopes and has to be free. Here it is not free that guy is not really getting stuck there. So it has to be free for a sufficiently long period of time, and spends time in a state that is proportional to the volume of the state in phase space, that opens the room for NPT or any NVT ensemble where energy now plays an important role. So it is like that, I will stop here.

(Refer Slide Time: 11:58)

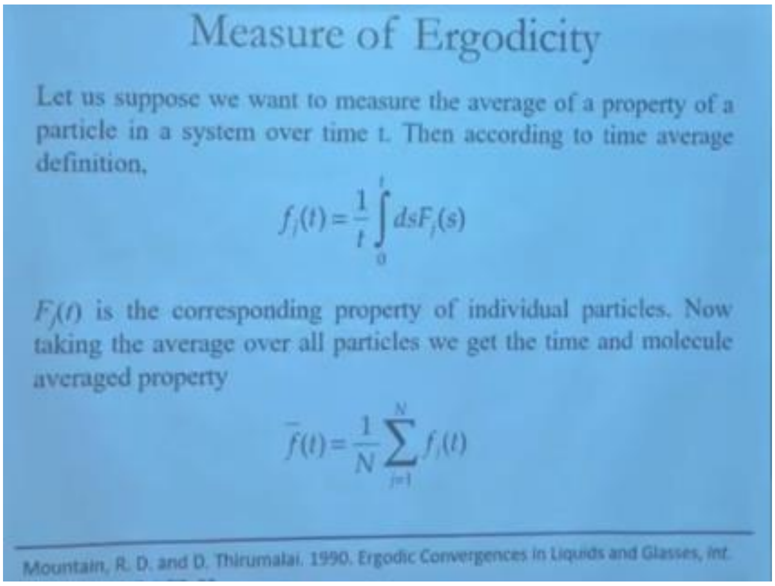


Measure of Ergodicity

In such systems as depicted in (c), relaxation is often so slow that a sufficient number of microstates are not visited within the timescale of simulation or even experiment. Thus, we can state that the system exhibits **broken ergodicity**. However, there may exist situations where the barriers are too large to prevent full validity of the Ergodic Hypothesis but not too large to prevent visit of a large number of states so that time averaging appears to have some validity, although may still lead to erroneous results. Therefore, it is necessary to develop an effective measure of ergodicity. There are several methods to check the ergodicity of the system.

Today, the measure of Ergodicity and all these things I am not going into.

(Refer Slide Time: 12:10)



Measure of Ergodicity

Let us suppose we want to measure the average of a property of a particle in a system over time t. Then according to time average definition,

$$f_j(t) = \frac{1}{t}\int_0^t ds F_j(s)$$

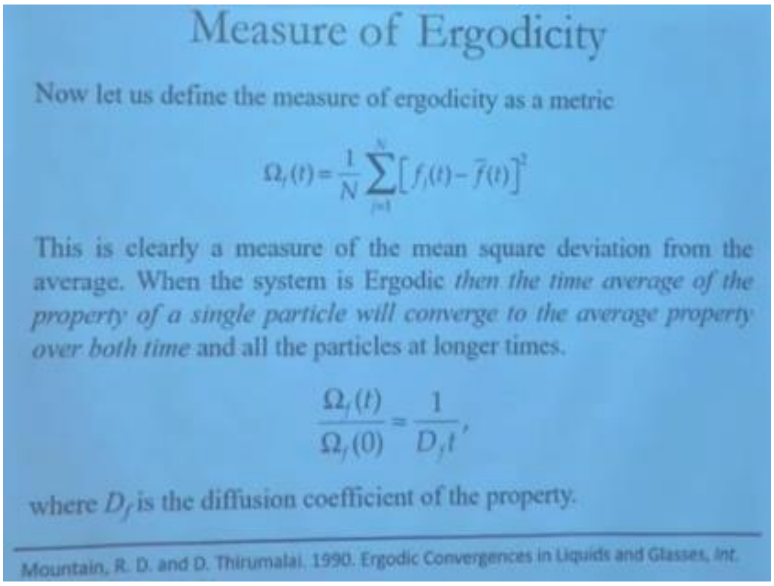
$F_j(t)$ is the corresponding property of individual particles. Now taking the average over all particles we get the time and molecule averaged property

$$\bar{f}(t) = \frac{1}{N}\sum_{j=1}^{N} f_j(t)$$

Mountain, R. D. and D. Thirumalai. 1990. Ergodic Convergences in Liquids and Glasses, Int.

But, I think today all these beautiful measures are;

(Refer Slide Time: 12:13)



Measure of Ergodicity

Now let us define the measure of ergodicity as a metric

$$\Omega_f(t) = \frac{1}{N}\sum_{j=1}^{N}\left[f_j(t) - \bar{f}(t)\right]^2$$

This is clearly a measure of the mean square deviation from the average. When the system is Ergodic *then the time average of the property of a single particle will converge to the average property over both time* and all the particles at longer times.

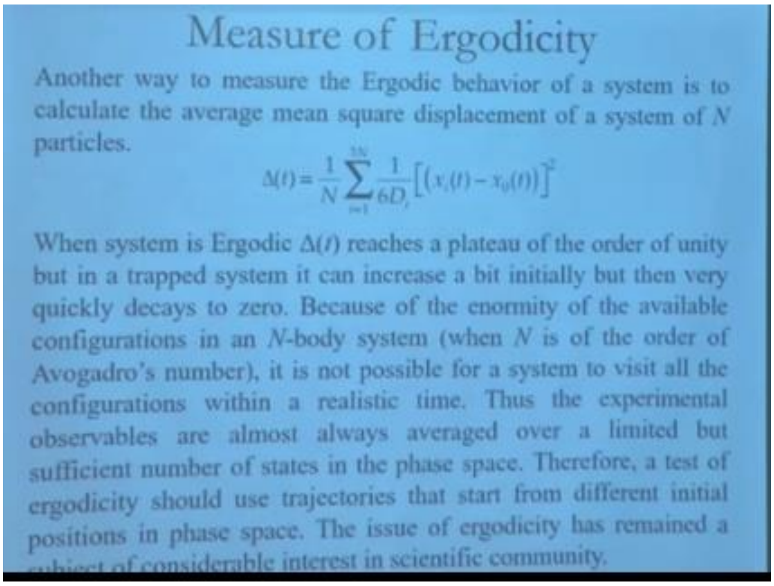
$$\frac{\Omega_f(t)}{\Omega_f(0)} = \frac{1}{D_f t},$$

where D_f is the diffusion coefficient of the property.

Mountain, R. D. and D. Thirumalai. 1990. Ergodic Convergences in Liquids and Glasses, Int.

There, this is essentially done by the Thirumalai and Mountain by doing how it is connected to diffusion, and is given in my book.

(Refer Slide Time: 12:22)



Measure of Ergodicity

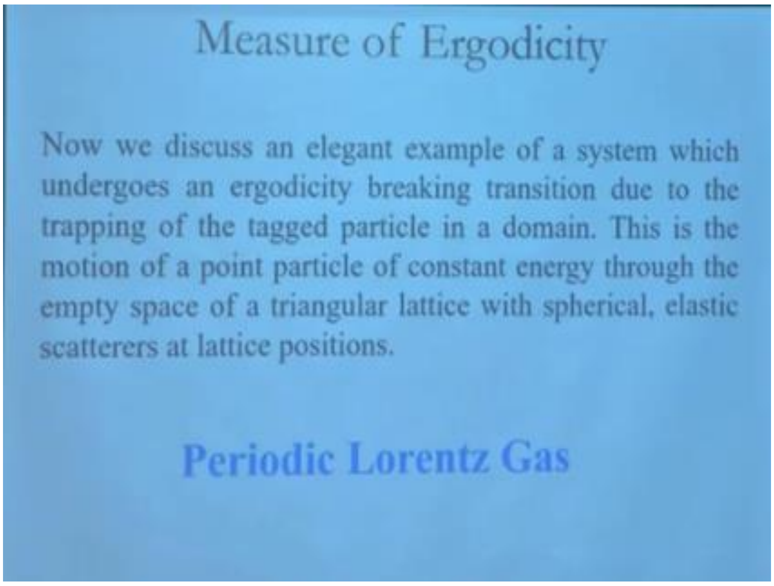
Another way to measure the Ergodic behavior of a system is to calculate the average mean square displacement of a system of N particles.

$$\Delta(t) = \frac{1}{N}\sum_{i=1}^{3N}\frac{1}{6D_i}\left[\left(x_i(t) - x_0(t)\right)\right]^2$$

When system is Ergodic $\Delta(t)$ reaches a plateau of the order of unity but in a trapped system it can increase a bit initially but then very quickly decays to zero. Because of the enormity of the available configurations in an N-body system (when N is of the order of Avogadro's number), it is not possible for a system to visit all the configurations within a realistic time. Thus the experimental observables are almost always averaged over a limited but sufficient number of states in the phase space. Therefore, a test of ergodicity should use trajectories that start from different initial positions in phase space. The issue of ergodicity has remained a subject of considerable interest in scientific community.

All the details and how you talk of diffusion is very interesting as I was telling in one of my lectures. Here if you want to talk of many body diffusions, the whole system is diffusing. Then you have this kind of quantity that is what Thirumalai and Mountain used to show the breakdown of Ergodicity as glass transition is approached but that means you are not talking about one particle, you are thinking of the whole configuration space of the system.

(Refer Slide Time: 12:54)



Measure of Ergodicity

Now we discuss an elegant example of a system which undergoes an ergodicity breaking transition due to the trapping of the tagged particle in a domain. This is the motion of a point particle of constant energy through the empty space of a triangular lattice with spherical, elastic scatterers at lattice positions.

Periodic Lorentz Gas

There are many other things but I will stop here to recap we started with the probability and statistics, central limit theorem and several other interesting things, then you went to phase space. We went to trajectory and discussed next what will happen starting with these postulates. So in my book I talked about realization of promises. We now go from microcanonical ensemble to canonical ensemble and when you go to fluctuation, you start deriving the beautiful equations like mean square fluctuation, specific heat and all these things.

And then the other systems will follow, so whenever you have orientation the phase space becomes larger. For example, when you are doing water molecules you have the orientation. At a level formula that does not pose any problem. The reason is that you just expand your notation X now has position and orientation and P will have no all kinds of momentum. So angular momentum is one reason that you know it decays very fast usually.

So its conservation hardly poses a problem for that one momentum conservation also doesn't pose too much of a problem in most of our calculations. But the formalism part nothing changes. This is essential in Schrödinger equation, you write down a wave function ‘Ψ’. You do not know when you're writing down a Schrödinger equation of a many body system. You do not think of solving it at that point.

You are writing and so all the theorems that you prove with a ‘Ψ’ and everything that is just formalism to you whether it has particles in a box or whether interacting systems and electron gas, nothing matters. So you have to separate out the formal part and once I was the good friend of a friend called Jim Lill, who was developing a theory of scattering with John light theory.

Reactive scattering I think is called light theory and he was writing this very difficult equation with momentum, angular momentum, position. So I always told him, ‘Jim, how are you going to put these things?’ He said, ‘Biman, let me develop formalism first’. He developed the formalism then he put in the computer and it became a very famous theory. So when you are developing the formalism.

You have to think of applications but do not get bogged down by applications at this stage. So when you are writing down phase space or these equations of partition functions, it does not matter whether your X has orientation or position. You have to be able to think like that in a very formal way but at the same time back of your mind you know when you're going to do applications, these formal things will become real things.

And that happens with that much faith you have to have. Science is always for optimist people, science is never for pessimists. I have already told you that this is the third lecture, fourth will start with the partition function. And then the valuable equation is there but I might not take the level equation too seriously. Level equation is the equation that allows you to track to generate the trajectory in phase space.

This is nothing but a Hamiltonians equation. I am not going to do that, instead I will continue with the ensembles. I will go to fluctuation and from fluctuation which is a wonderful chapter I tell you that from there we will do monatomic gas and diatomic gas. But everywhere it will be very practical like when I do monatomic gas, it will tell you about the use of that in modern day real life problems like protein DNA interaction, drug DNA intercalation.

And that has been used to find out the binding of chemotherapy diagnomycin to DNA. And then again we go to see the very interesting thing is that entropy comes with the monatomic gas beautifully. But the concept of rotational and vibrational entropy, those are very important. The rotational entropy in molecules is usually 30 percent of the total entropy that comes to diatomic.

And then all your normal modes, the fact that cV is 3/2R all these things comes from just a diatomic molecule. It is amazing that how much you can know from doing monatomic can just be diatomic. Then we will do the Ising model, which is the first monatomic gas; the non-interacting diatomic system will do the Ising model.