Indian Institute of Technology Madras

NPTEL

National Programme on Technology Enhanced Learning

Chemical Engineering Thermodynamics

by

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Lecture 34

Molecular basis of thermodynamics

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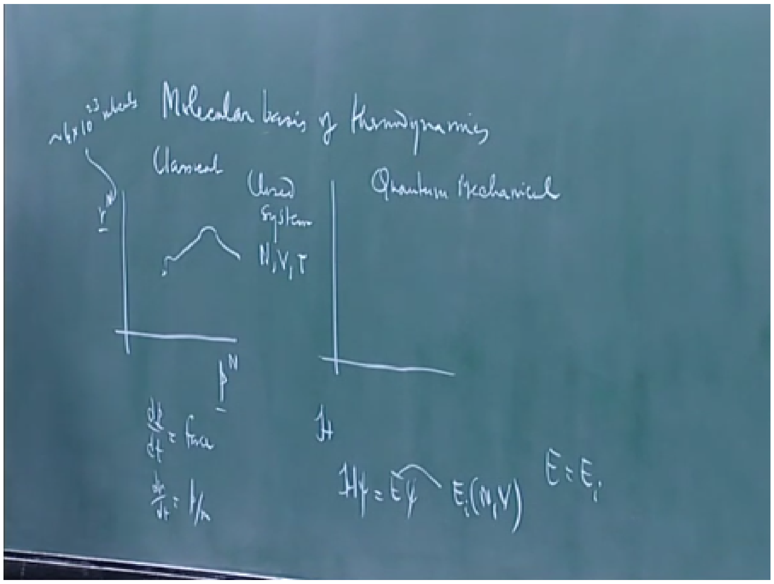

Let me start I want to discuss molecular basis of thermodynamics this is this is nothing true the exam straight away it is simply for information because I think it is important to know the basis if you look at there are two descriptions of the world one is the quantum mechanical description this is the classical description classical and quantum mechanical description in the quantum in the classic I am talking about essentially microscopic descriptions in the classical description what you do is to plot.

You if you plot the momentum and the position as a vector I am going to consider a phase space in which I consider it is not if it is two particles this would be 6 dimensional for one particle because px, py, pz and xyz and it would be six n-dimensional for n particles I have to take a mole of the substance you are talking of our guide row number of molecules, so your this is of the order of 6 x10^{23} molecules, let us say one mole of the substance then I have that many molecules I am putting down position the physical position xy.

Is that for each of these and the moment of px, py, pz to each of these particles then one point here represents a state of the system if I could go in and make all these measurements and in this 6x 10^{23} x 18 x 10^{23} space, if I can locate the point I would have then located the state of a system as it goes on in time each of these particles you have to solve Newton's laws of motion you have to say essentially dP/ dT is equal to force and the force will consist of the gradient of the potential energy.

And the potential energy will conserve all the interactions between all particles you are not trying to actually solve this and dR/ dT = P/m I have to write this set of equations for three components for 6 x 10^{23} even writing them down will tell you, but we have noted the short notation, so we will do this so in practice, if you could theoretically solve it you will have a trajectory that evolves in some way now in quantum mechanics what you do is solve Schrodinger's equation you write down the Hamiltonian and then you solve $H\psi = E\psi$ to get the stationary states of the system the only result.

We need from quantum mechanics here is that this e is a function of N and V if I have a closed system let us assume I am talking about a closed system a fixed number of molecules N a volume V and temperature this vector system in molecular thermodynamics mean a system in which NV and T are specified you can go to mixtures later let us talk about pure substances.

So while P and R in classical mechanics can vary continuously quantum mechanics says that this E is quantized E = Ei are the states that are permitted actually I should say Ei of N, V where the number of states in which the system can exist is countably infinite you can go on 1 2 3 0 E1 E2 E3 etc. And associated with each state is a probability that is the system will be in an energy E actually in classical thermodynamics if n V, T are fixed the energy is fixed he in this case is internal energy internal these also fixed.

What quantum mechanics says is the energy is never fixed in the system can exist in different states, but the energy that you see here is the average of those but I must again explain something here, so what you have is a discrete set of states in which if I position the state is actually it would not be I do not even draw this yeah this is energy what quantum mechanics tells me is that this can exist only in certain discrete values and I will say system exists in one of these with a certain probability.

And I can calculate an E bar Y bar is sum over Ei, Ei that basically Gibbs made to purse slits he said them actually Gibbs did not talk about quantum mechanical description at all but Gibbs made a certain number of parcelts.

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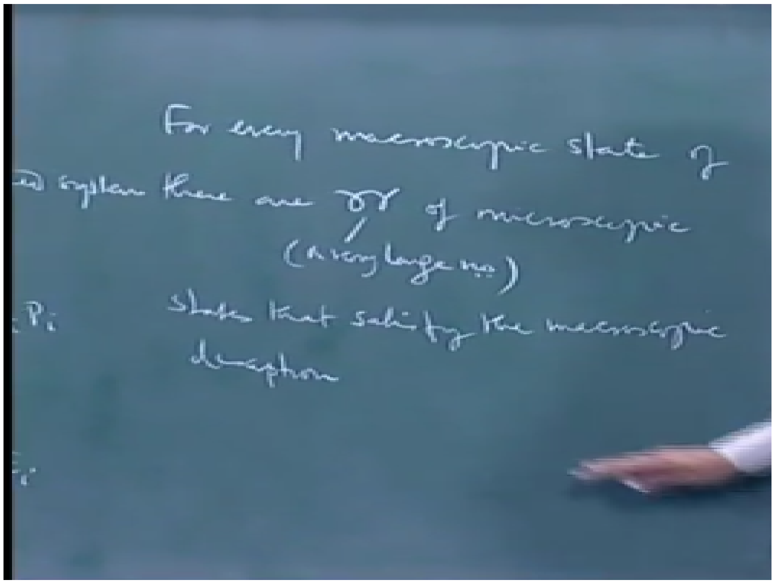

For every macroscopic state of a system there are $\mathcal{N}$ of microscopic (a very large no.) states that satisfy the macroscopic description

P_i

E_i

Gibbs said that for every this is not a parcel it is just a description for every macroscopic state of a closed system it could be anything I can also discuss this but to be very specific I will say for a closed system my closed system I mean number of particles is given the volume is given the temperature of a closed system there are the script n is used always a very large number by very large I mean even larger than this 10^{23} and very large number of microscopic states that satisfy a macroscopic description.

Let me explain what that means essentially what you are saying is if you fix me you are fixing the total volume within which molecules are moving as long as molecules move within a box you have satisfied the constraint of V, if you want to fix temperature you have to have fixed the average kinetic energy of the particles since there are 10^{23} particles you can vary the kinetic energies of all these particles in such a manner that the sum over m $iv^2/$ is a constant, so you can see the number of possibilities.

First of all I can just permute these Perkin switch from one particle to another and produce changes even if I do not switch I can alter the P, I can increase the P of one and decrease the P of the other and keep the kinetic energy constant total kinetic energy constant, so the number of possible states is clearly very large that is compatible with this I fixed here, so the number of such states in classical mechanics what it tells you is if the energy is a certain value if a combination of PS will give you.

There is a certain region of space that satisfies that satisfies these criteria within which the system can move as with time this is time evolution of a system and I am talking of time evolution of a system at equilibrium you might say nothing changes in equilibrium, but you know when I say a system is in equilibrium I mean all the measured macroscopic properties are constant to thing, but the molecules do not sit quietly the molecules keep moving around so the molecules change their state all the time.

If I take this glass of water the actual molecules luckily you cannot see it otherwise you will go mad if you can seem a little emotion luckily you see an average very quiet Placid glass of water that is sitting there doing nothing actually the molecules are bouncing off you have 10^{20} hitting this you can calculate that the average mean free path at this set room temperature is about let us say about 15 20 angstroms and you are talking of collisions the average velocity of a molecule at room temperature is 10^5cm/s and with an average mean free path of measured in angstrom say 10 angstroms.

Which is 10^{-7}cm/ 10^5 on an average every10 to the power minus 12 seconds you have a collision so the configuration changes visibly as soon as you have a collision, so the number of changes that are occurring here per second is of the order of 10^{12} 10^{13} so you are talking about million changes occurring through all this you are saying that water is doing nothing is just sitting there in you measure and give me macroscopic properties pressure volume temperature all those are constant.

So the idea is first of all what do you mean by a measurement this is this is not as this is a statement of fact if I go back here.

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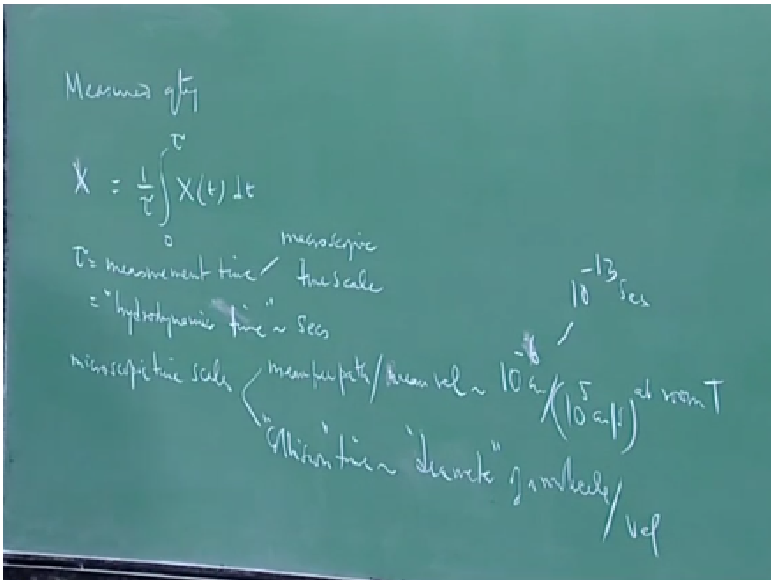

Measured qty

$$X = \frac{1}{\tau}\int_0^{\tau} X(t)\,dt$$

τ = measurement time / macroscopic timescale

= "hydrodynamic time" ~ secs

microscopic time scale ⟨ mean free path / mean vel ~ 10^{-8} cm / (10^{5} cm/s) at room T ~ 10^{-13} secs

"collision time" ~ "diameter" of molecule / vel

And ask what is measured quantity measured quantity if I look at any quantity let us look at some property x is simply the integral x as a function of time dT over a measurement time into1 / 2 where 2 is measurement time typically you may stick in a pressure gauge and measure the pressure takes you a few seconds measurement time will be a few seconds measurement time is sometimes called hydrodynamic tank hydrodynamics was pre molecular theory hydrodynamic thing.

So the word hydrodynamic time was used to describe time in units that are measured by people working in hydrodynamics they say the flow changes over seconds and so on so typically hydrodynamic time is of the order of seconds, we are only talking water of magnitudes but you have a microscopic thing there are actually two microscopic timescales this is sometimes called macroscopic time scale that is how do you measure time you measure it in second show do you measure microscopic time.

Scales you can consider two possibilities one is you can ask how often that is the configuration change and this could be in terms of number of coal every time a collision occurs concretely the configuration changes, so this will be approximately mean free path divided by average mean velocity this is of the order 10 $^{-7}$ which is centimeters which is the mean free path divided by

10^5cm/s this is at room temperature this will vary at room temperature this 10^5 order of magnitude.

I mean obviously if you take hydrogen and oxygen there will be a difference in the thing by a factor of 16 and so on or actually in the velocity by a factor of only 4, but the order of magnitude will be about 10^5 s this you can calculate, so this time is of the order of 10, 10^{-12}s then you talk of collision thing actually mean free path I should say 10^{-6} free path in gases for example is of the order of distance between collisions is of the order of 100 angstroms so you will get into or - 13 collision time on the other hand is the time this is again these are not concrete things these are this is a model you are looking at two molecules and ask you ask the question when are two molecules aware of each other is presence.

When there is a force between them typically if it goes beyond a certain size distance the other one molecule does not know the other molecule exists there these are weak forces these are van der Waals forces between two molecules and typically this will be of the order of again the mean they are diameter D of a molecule by velocity that is if I have for example.

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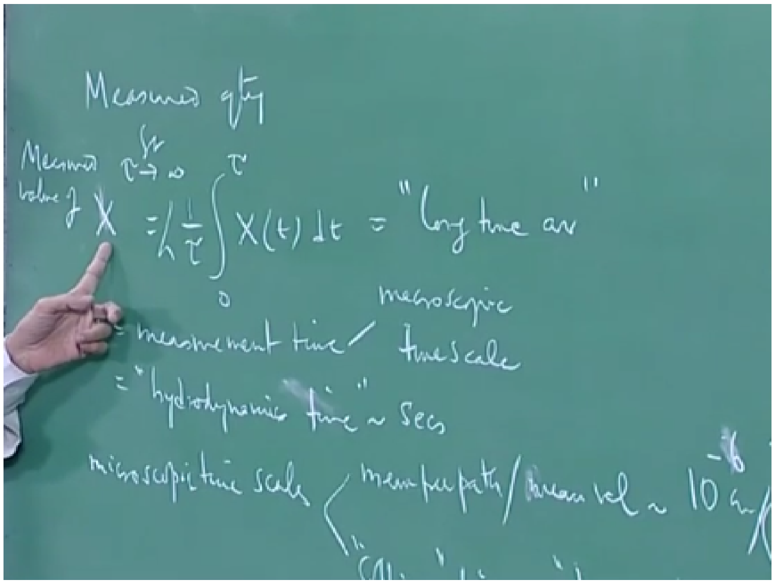

This collision time will depend upon the potential if you take for example an one or two potential I have molecule one here I have molecule two here, and I move molecule towards one when does one feel to actually in principle even at ∞ force is very weak in practice what you do is to say that when the force becomes a certain value first of all I must tell you some facts, if this molecule moves here up to this point it is attracted if there are only two molecules and one molecule is here the force here is attractive.

So this molecule will accelerate and you get faster and faster it will go here when there is no force at all but to go closer it will have to actually work against the intermolecular forces finally its kinetic energy that is the temperature of the system will determine its kinetic energy the kinetic energy will determine how close it gets before.

It is repelled right if a molecule comes very fast it may get as close as here because it may be able to resist this level of that is the kinetic energy is equal to this much potential energy, so how close it gets depends on temperature but this is a measure of size of the molecule this point this distance is called σ is usually denoted by σ and it is usually called the size of the molecule this distance where the intermolecular force between two molecules is 0 is usually denoted by R to indicate R minimum R is the distance between two molecules.

This r_m typically r_m is about 2^6 1/ 6 times σ if you do a Lennard-jones potential you can show that this r_m is approximately 2 to the1/ 6 times σ just so they are all both the same order of magnitude and this is the order amstrong is, so this molecular diameter is the order of 10^{-8} which is centimeters by 10^5 again, so this is of the order of 10^{-13} this is 11 I am sorry this is not 13 this is 11 6 - 5 is 11 sorry this is 10^{-13} incidentally this is called time of a coalition is 0 for hard spheres.

If you had hard spheres then this potential will be written this will be the hard sphere potential so the molecule will come in freely up to this point, if you experience no force it experiences an infinite force here and goes back you get an elastic collision between two molecules here again energy is preserved, so as the potential as the kinetic energy increases the potential energy will decrease will decrease to this point which is also gives you a measure of the kinetic energy then the potential energy here.

Increases so the kind little molecule will slow down till finally it bounces back but since σ and r_m are of the order of same order of magnitude what you do is to say that this can be cut off usually in all molecular theory you cut off the potential you do not write the potential like this you write the potential according to this law and then say 0 beyond this point, so your model is like this and it is a reasonable assumption to say when it gets to 2 σ or to essentially 2σ you say the potential energy is effectively 0.

Because the force falls off as 1 by r^7 the dispersion forces you cannot say that in the case of electrolytes alone in the case of electrolytes when you have two ions the force falls off is 1 by r^2 so the effective size or effective distance over which the intermolecular forces are felt the influence of 1 is felt on the other is much larger, so what do you mean by measurement now if you could go through an evolving system in classical mechanics and every 10^{-13}s you measure this property x all of this is apathetically you obviously cannot do it.

But let us assume you can then you measure it then you go to the next interval of time measure it again and so on and then you take an average over this is what you call a measured value if I measure for example the energy of the system or the pressure of the system I measure the pressure every 10^{-13} s over about 10^{13} of 10^{-13} s and then take the average, so essentially what Gibbs suggested was that x = is equal to actually he said this is actually the limit and store tends to ∞ but by ∞ he means infinite very large number in terms of microscopic time units.

So it is sometimes referred to as the long time average this is measured value of x this is sometimes referred to as long time average I will come back to quantum mechanical description we just look at classical statistical thermodynamics to begin with, so some statements I have made which are almost self-evident that the number of microscopic states compatible with a macroscopic state are very, very large because the number of molecules are very large and if that is true the measured value I must say x has to be what is called a mechanical variable.

For example x can be energy x can be pressure x cannot be entropy for example is not a variable that is defined in a given state in fact, if you had only one state the interview system is 0 the existence of multiple states and the choice is the system having a choice of going into one state or another is what produces entropy, therefore in strictly speaking I should talk about only mechanical variables and the two mechanical variables in thermodynamics would be pressure and energy.

In a closed system because volume and temperature are fixed already so let me come back here I have a measured value what Gibbs said was the following there are two things you should know there is an older hypothesis called the Ergodic hypothesis.

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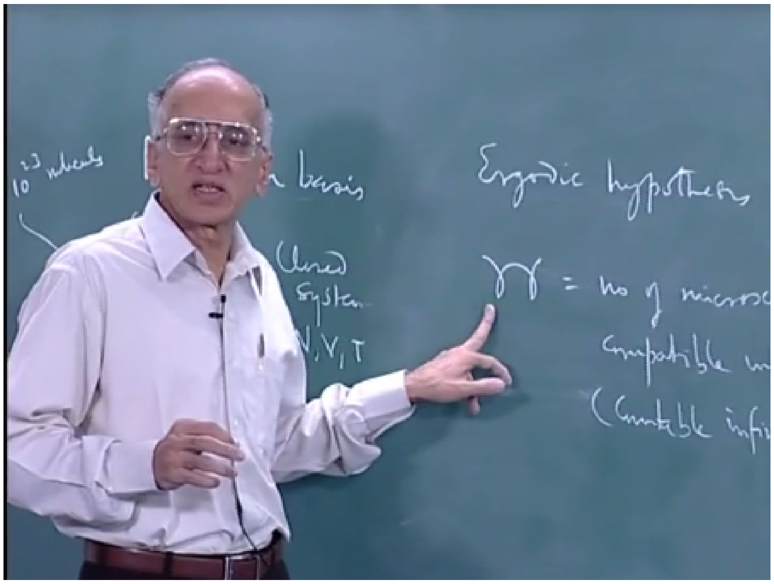

Which is accepted the Ergodic hypothesis says if you are lower system to evolve with time there is a finite probability that the system will come back to its original state or as close arbitrarily close to its original state as you pre determine, if you say want to come within 10^{-12} 5% of the original momentum and within the local occasion which is within a distance of whatever arbitrary distance you say that means you locate a point and you say system comes back to that point or as close to it as possible the hypothesis says given sufficient time the system will come back there.

The sufficient time may be for example for the universe they have calculated approximately in 10^{43} years there is a possibility this is only hypothetical, but this is it cannot be tested experimentally but it seems reasonable because if a system can exist in the states that is I am drawing all possible points which in which a system can exist compatible with N,V T I am looking at equilibrium systems there is a region of free space where there are many, many points that I told you any one of these points satisfies this condition.

So there is no reason why a system should not go through those points and this is actually this is a conjecture because of funk array but it is called the ergodic hypothesis and what it says is if your measurement time is sufficiently large then your microscopic state of the system will be in one of the states that is permissible in fact in one it will pass through all of the states that are permissible, so if I have if this is the number of states number of microscopic states compatible with N,V,T.

And is I am looking at an equilibrium system if some number of molecules is specified the volume is specified the temperature is specified, so what the ergodic hypothesis says is if your measurement time is large and as we have said we always say measurement time is very large its large in a microscopic sense if it's large the system has to pass through all these states, so when you take an average you are taking an average over all these states now how do you compute such an average.

So if we say this is the number of might when I write a German it is Krypton like this means a countable ∞ of states actually I am not asserting that there are infinite States, but even if there are they are countably infinite I can put label each state this comes from quantum mechanics because quantum mechanics tells you that equilibrium system has to satisfy hits a is equal to e say and Eψ the eigenvalues of this HS you know that Hamiltonian is simply potential energy plus kinetic energy.

And for the momentum do not ask me why I still do not have an answer but it says replace P/ -H bar / dX if you have px that is why there is the famous story of Heisenberg he said if I went to heaven he would ask God two questions why quantum mechanics and white turbulence and Heisenberg said God may have the answer for the first question he had a doubt whether God will have the answer about turbulence but even about the first one is doubtful that is it is not yet clear why you should mathematically make a transformation px2 – IH bar.

∂ /∂ x and the ∂ resulting answer should correspond with reality but they do so I do not know why this association occurs there are various reason various explanations given in textbooks, but nothing fundamental which convinces you it is a sort of a hypothesis but that has to do with quantum mechanics but what quantum mechanics just tells you and has been verified experimentally is that the number of states can be labeled if I have n and we.

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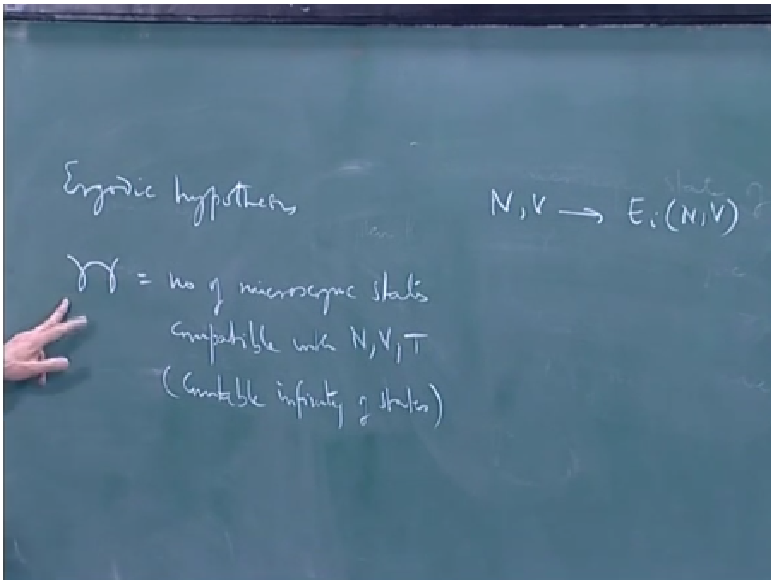

Then the eigen states the system can exist only in States E1 E0 E1 E2 eE3etc. Can be countably infinite but only one of those states is possible that is the quantization, so I can count the number of states therefore I call it is Krypton what Gibbs suggested was that he will put together what is called the un sampled the ensemble is a mental collection of all systems this is the ensemble has n systems in it all at all satisfying N, V,T in VP constraints that is he said instead of making a measurement like this over time which anyway is impossible.

Let us assume that I have a strange creature that can go in there every 10^{-13}s and make a measurement of the pressure then I would have taken this arrow taken the average order taken the limit I will go on measuring it till I get a steady value I will call that the pressure at that temperature at that point and actually notice that this is in an equilibrium system x is not a function of time.

It is not a function of macroscopic time that's why as to w increases x will remain constant but it is it is changing dramatically every 10^{-13} s, but its average for long time average will remain steady in an equilibrium system in a non equilibrium system I will have macroscopic time as well and will be a function of macroscopic time but microscopically it will still vary during a measurement time I will still have an average value incidentally in order to show that this is an average it is denoted by x bar now what Gibbs suggested was this is like a coin you toss a coin you count heads and tails you say what is the probability of heads you come up with 1/2 and so on instead of tossing one coin a million times you can toss a million coins simultaneously and that is the idea here instead of going.

Through these measurement painfully you collect these systems this is the mental collection because if you actually start collecting you will spend all your lifetime you would not have collected most of them. So the idea is to have a mental collection of all systems N,V,T systems that describe your physical prototype now what I want to do is to ask the probability of finding the one of these systems have to be in one of these states e1 e2 e3 etc.

So if I want to calculate e bar for this ensemble this is simply e I times the probability P I the sum over all the states this number of states would be because of my assumption to be scripted I sum over all the states I multiply the energy instate I by the probability of observing state I what Gibbs suggested was that this is also equal to the measured value I think I will call that XM instead of x-bar this is the measured value XM Gibbs first hypothesis that the longtime average of a property which is the measured value is equal to the ensemble average.

Because you are conceptualizing the system like as one that goes through time as time goes on it evolves through every possible state and you are doing the same thing by making a mental collection here.

So if I calculate the average value using the un-sampled I should get the measured value e I is known you solve the Schrodinger equation that is given actually right now actually I is known in all systems because you know the Hamiltonian and you know the potential energy if you do not know those you cannot proceed anywhere, if you know the potential energy and the Hamiltonian classically you would have had to solve these equations of motion you can never solve it you will you know even with the present computers if you do it for 10 to the power 23 molecules we will be doing it for a lifetime.

So the idea is not to do all this to develop a conceptual worm framework which finally gives you answers without actually doing these things he says what do you mean by a measurement you stick a thermometer you wait for it to read or you stick a pressure gauge you wait for the pressure gauge to read and then that time is hydrodynamic time your measurement time is never faster than a few seconds within then over those seconds the system has changed and about 13 10 over14 times.

So essentially you have sampled the entire space of possible states if you have done so this identification must be obvious you cannot prove it this is a hypothesis this is the first hypothesis of Gibbs that is he introduces the concept of an ensemble he introduces the concept of measurement as we understand it and he says the un-sample average should be equal to the more important question is how do you calculate PID?

That was again the genius of Gibbs his sake this is the first hypothesis this is the first postulate of statistical thermodynamics the first postulate says that the measured value physique is a is the long time average of a mechanical property which is equal to the ensemble average of the same property. Now in order to calculate the ensemble average I need to know PA, what Gibbs said was that in fact he did a very clever thing he said philosophically you have this socially the same principles apply everywhere the socialistic principle of equality and all that there is no reason to treat one state as being more probable than the other in an isolated system not in a closed system this is a closed system in a closed system some states may be preferred to other states I can find out I can go in and measure.

The only system for which I can make no measurements and therefore I am necessarily totally ignorant is an isolated system so Gibbs said all the microscopic states of an isolated system are equally probable that is the second postulate, and at this stage it is a postulate. So having made the postulate from that you have to deduce the properties of a closed system and then compare it with experiment.

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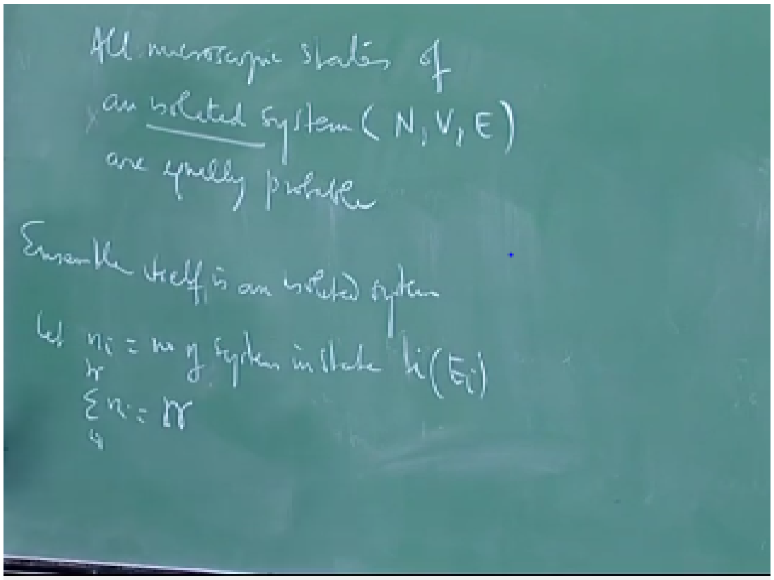

All microscopic states of
an isolated system (N, V, E)
are equally probable

Ensemble itself is an isolated system

let n_i = no of systems in state i (E_i)

$\sum_i^{\mathcal{N}} n_i = \mathcal{N}$

So the second postulate says remember that this P I are the pi is the probability is the P I is the probability of finding the given system in state I and I am talking about a given closed system so the second postulate does not relate to P I it simply says all microscopic states of an isolated system incidentally in classical thermodynamics an isolated system is described by n V and E energy is constant in an isolated system because and I by definition an isolated system cannot exchange mass or energy the energy is constant cannot exchange mass.

So the number of molecules is constant it does not do work therefore its volume is constant, so if you specify NV and D you specify an isolated system if you specify NV and t you specify a closed system if you specify V T and μ then you specify an open system because in an open system mass can change but the chemical potential at equilibrium the chemical potential with the external this thing will be the same as the chemical potential.

So let me get all the microscopic states of an isolated system are equally probably, the important word is the isolated system this P I is not the probability of an isolated system. Now given these two postulate here postulates he has to calculate the property of a closed system and compare it to the experiment or you need a procedure by which you can do this the procedure to calculate any X X bar Y bar is e I pi and I do not know PI but I know the probabilities in an isolated system.

So I have to go from isolated to this, so what Gibbs suggested and this is again once he does it sort of seems obvious what you should do, he said if I have got the entire collection here the ensemble here if you look at this ensemble this constitutes an isolated system because it includes all systems that are it is its N, V t it includes all systems are at the same temperature. So what I have here this ensemble itself and incidentally this is called the canonical ensemble the word canonical simply means as per rule and at that time most of the systems investigated with closed systems.

So closed systems were supposed to be the norm therefore the canonical ensemble represents the collection of all systems with the same nvt the micro he introduced the word micro canonical ensemble for isolated systems and the grand canonical ensemble for open systems. But let us talk about this if you look at the ensemble itself the ensemble itself is an isolated system, let ni b the number of systems in state ei and state I and a state in quantum mechanics of a closed system is characterized by the energy, if I specify for an N, V,T system by specify a I have specified the microscopic state of the system clearly sum over ni is n the number of systems is Krypton but sum over ni is also scripted that means some other nice will be 0 some of them will be large and so on.

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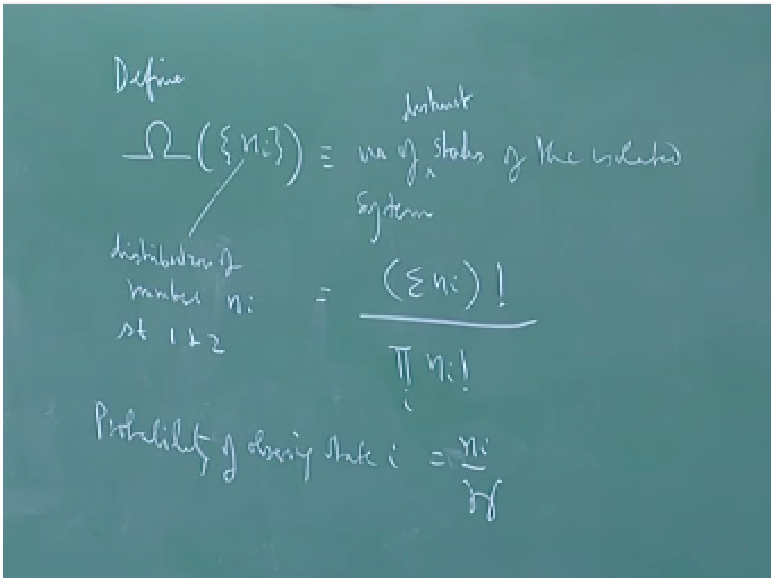

Define

$\Omega(\{n_i\}) \equiv$ no. of distinct states of the isolated system

distribution of numbers n_i st 1 & 2 $= \dfrac{(\sum n_i)!}{\prod_i n_i!}$

Probability of observing state $i = \dfrac{n_i}{\mathcal{N}}$

Now how do I find this probability of observing a state I, what I do is first write down I define Ω FN I Ω is simply the number of states this is defined as number of states of the isolated system ni is a distribution this is a distribution of numbers subject to this is one let me write down another constraint some over ni = ET ET is the total energy this ensemble is an isolated system reasons an isolated system is if I had one more NVT system that was not already inside this then I have been a mistake because by definition the unswayable is the collection of all systems at the same NVT right but in different microscopic states.

So by definition I have included all the systems here so there cannot be any system outside therefore this collection is an N, V is a isolated system and it's subject to a total energy and the total number of system these two are fixed so I will say sub distribution of numbers n I subject to 1 & 2 and what would this be equal to supposing I took all these systems and permuted them I have n capital script n systems script n factorial will be the number of permutations but suppose two of these systems were in the same state and I permitted them I would not know the difference.

So I have to correct for over counting by taking the fact taking into account the fact that permutations among the same systems among the systems in the same state will not be counted, so this number I can write down is simply sum over ni factorial in the number of ways of permuting all the systems divided by ni factorial product or I suppose I had only two states then I would have n-1 systems in state 1 n2 systems in state 2 in 1 +n 2 will be the total n 1 + n 2 factorial with the number of ways I can rearrange this configuration of that N 1 factorial will and n 2 factorial separately will not produce distinguishable States.

So the number of states of the isolated system let me say distinct states of the isolated system is given by ni factorial by this the probability of observing state I State I is simply ni by n but what is the probability of observing a distribution see ni by n is the probability given the distribution.

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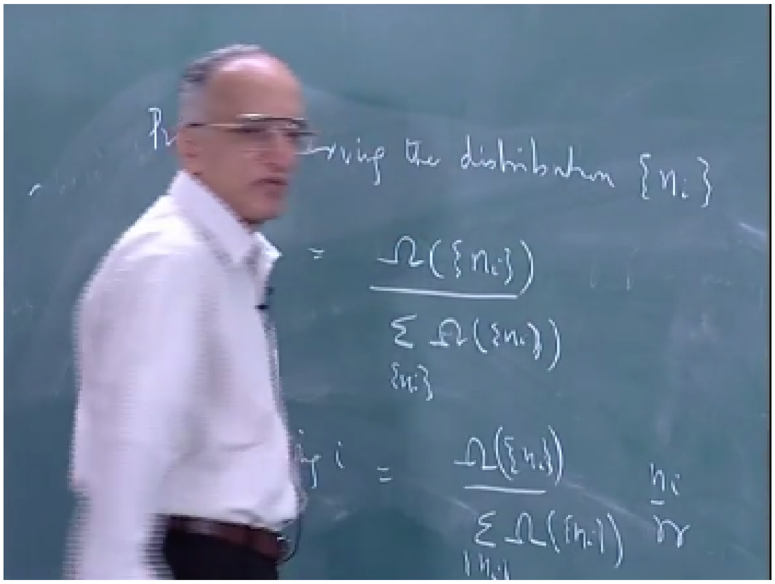

And again write down the probability of observing the distribution is simply Ω of n I which is the number of ways in which the distribution can manifest itself divided by the total number of ways in which all distributions can manifest I take the distributions n 1 + 2 + 3 etcetera, I can vary them as I please for every set of numbers N 1 n 2 n 3 etcetera there is a number of ways in which that distribution is observed this is the number of ways in which all distributions are observed.

So what is the probability of observing state I then this is the probability of observing I given the distribution if I give you the distribution n 1 + 2 + 3 etcetera, then ni by script n is the probability of observing I but the probability of observing the distribution itself is given by this, so I must multiply this by that to get the probability of observing I so this is simply equal to probability of observing nothing times ni by again at this stage the mathematics looks hopeless and Gibbs made an observation he said look you already know your classical thermodynamics you know if you fix N,V and P the energy for example is already fixed.

So he figured that there must be one EA which is much more probable than all other guys you have energy states e1 e2 e3 etcetera but there are some energy states that are close to e itself.

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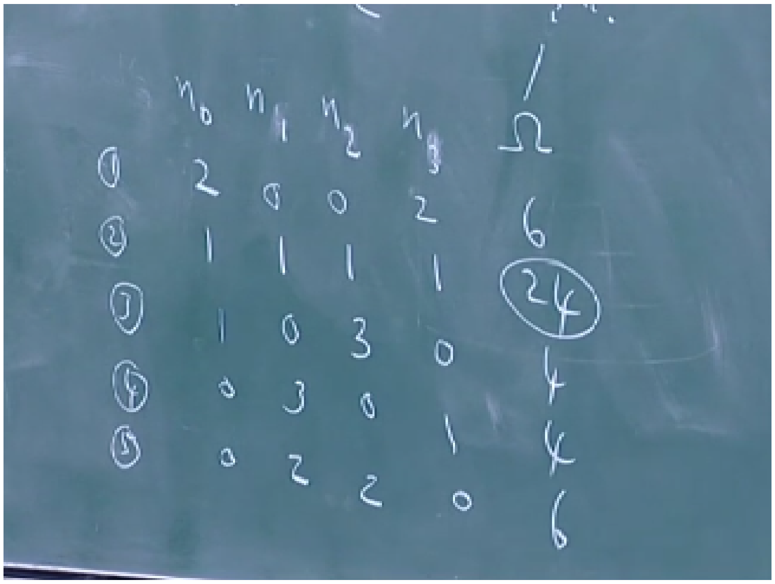

	n_0	n_1	n_2	n_3	Ω
①	2	0	0	2	6
②	1	1	1	1	24
③	1	0	3	0	4
④	0	3	0	1	4
⑤	0	2	2	0	6

So he figured that the distribution of energies for example if you look at the probability of observing I versus VI you will get something like you will get a normal distribution of some kind where this peak is around a bar, the probability will go up will be very high and then it will be very low on either side ideally if you are looking at a classical thermodynamic system with a large number of particles he expects this to get narrower and narrower till you have one value that you actually observe that is what you observe.

So what he suggested was that of all these distributions Ω F ni there is one distribution called the most probable distribution for which this term corresponding to the most probable distribution is much larger than all the other terms okay, this is it seems a little vague but I will do an actual calculation and show you let me take an example we will do a small example let us take a system with energy e VI equal to I into epsilon for convenience for example it may be 0 1 2 3 only four possible states let us say a particular system.

Can exist in let us assume that the number of particles or the number of systems number of states in which it can exist is let us say it is 4 that means this is the total number of systems in the ensemble these are the possible states the number of systems is for let us say the total energy is let us assume total energy I have to fix some number I will fix some number 6 then let me look at possible distributions.

I am going to put down values N 1 n 2 n 3 n 4 or sorry n 0 n 1 n 2 and n 3 subject to these two constraints the sum of these should be equal to 4 the sum of the energies energy this will be 6 epsilon I into epsilon this energy this is energy0 these are the systems with energy 0these are the systems with energy epsilon these are the system's energy to epsilon and 3 epsilon now what is one possible distribution for example is for let me start here let me start at the same this is 3 epsilon so I can have two systems.

Here which will make up 6 epsilon and the remaining two will have to be in zero energy those 200 is one possibility the other possibility is I have one system here I have to make up three I can have one here one here and one here this is the second possibility the third possibility let me calculate Ω here Ω for this is the distribution Ω for this distribution is the formula is this Ω is what 4! By product over I ni!

So it is 4! / 2! 0! 0! 2!, so it is 4 x 3 / 2 which is 6 Ω is 6 in this case clear, now if I have this is 4! is 24 / 1! 4 times so this will be 24, then it is possible for me to have three systems in energy level 2 that will make up 6 then the fourth will have to go to 0 this will be 4I suppose with one here I can do one more I can put three here I will do that then okay, sorry I should have put that down 1030 this is also a possibility is also 4 and.

If you start with the highest possible ones if there are two here then there can only be two at 0 energy if there is one here I can have one here one here or one here and three in energy one then I can have next one is 0 here put all of them into three of them in two and then one here this is the only possibility as far as I am concerned then this must be to this risk can be to this is zero now this is two is four I have made up and the other two are here this is again six if I have less than two here then I cannot make up the energy six I think these are the only ones.

So in this case there are five possible distributions of which one of them this is the most probable distribution so let me calculate the probability of the states if I now calculate the probability of observing P0.

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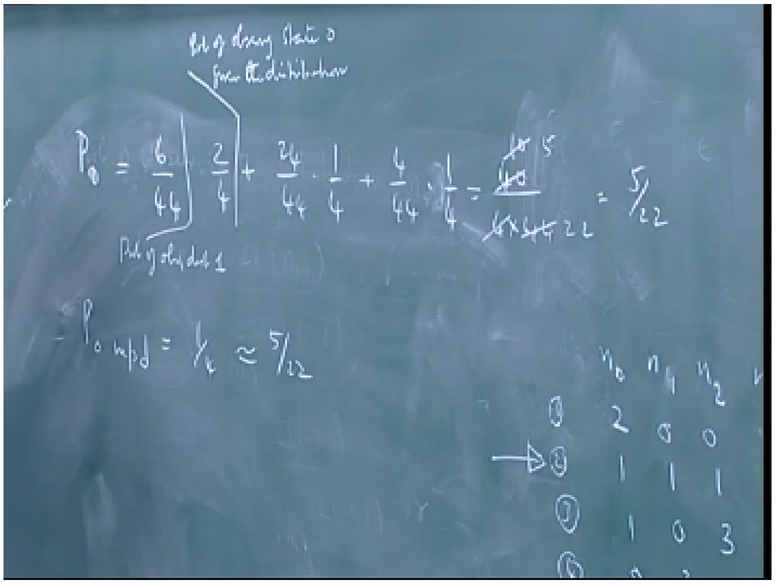

First of all the probability of observing the distribution the first distribution is 6 by what's the total here 20:44 right this is this has got several terms for the first distribution 6 by 44 this is probability of observing distribution 1multiplied by the probability of observing state 0 this is 2 by 4 given this distribution the probability that 0 is observed is 2 out of 4 total number of systems is for caring this is one term that is this is probability of observing state 0 given the distribution this is a conditional probability given the distribution this is the probability of separating state 0 I have to add several terms.

Now the probability of observing the second distribution similarly is 24 / 44 x 1 / 4 the next one is +4 / 44 x 1 / 4 the other two are 0 probability, so I do not have to take them too this is what does this come to 1236 + 440 so this comes to 40 / 4 x 44 okay now p0 most probable distribution, if I take the most probable distribution p 0 is 1 / 4 and as I take this distribution if this is if the most probable distribution is the only distribution then the probability of observing 0 energy is 1 / 4.

Because this is the most probable distribution in just English the distribution is the highest probability you are talking of only four systems and six energy total energy of 6 with that itself you get such a dominant probability if you do it for larger numbers in fact if you do an example with 10, 10 systems you will already find this probability is look at this number what is this come to this is 10/ 10 and 5 / 22 you are comparing 5 / 22 with 1 by 4 all I am saying is approximately equal to 5 / 22 in molecular similar system simulations molecular simulations we actually use only 30 particles and you can simulate a macroscopic system 32 particles you can show will simulate a microscope.

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