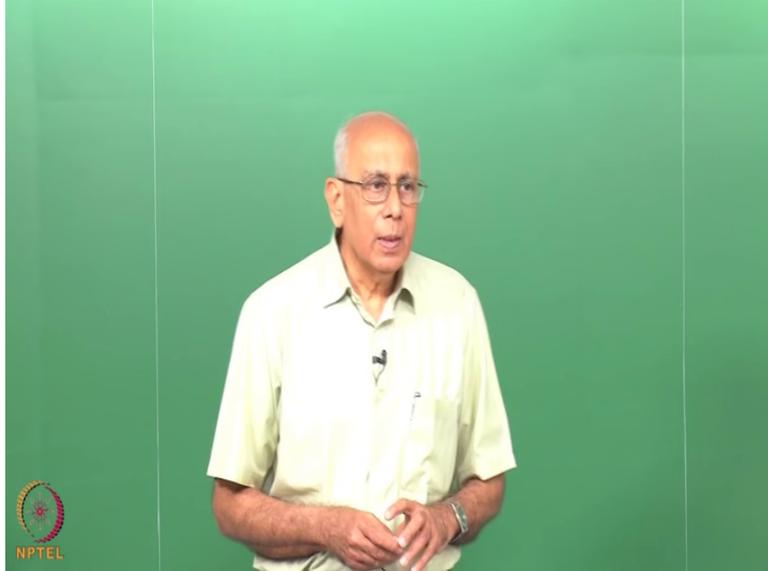


Nonequilibrium Statistical Mechanics
Professor V. Balakrishnan
Department of Physics
Indian Institute of Technology Madras
Lecture No 01
Recapitulation of equilibrium statistical mechanics

(Refer Slide Time 00:19)



So let's begin this course on non-equilibrium statistical physics or statistical mechanics with little bit of recap of equilibrium statistical mechanics which I presume all of you had a course in. Now if you recall, equilibrium statistical mechanics does not anywhere have time, the notion of time in it. The things are supposed to be in equilibrium, in thermal equilibrium. And when you deal with the averages of microscopic variables then you have this thing called thermodynamics. And when you include the fluctuations about the average, you need statistical mechanics of various kinds and various ensembles depending on the external conditions.

And that gives you all the information that you have, that you can find about the system, the microscopic system in thermal equilibrium. And just to recall to you, when you have a state of thermal equilibrium it does not mean a state of mechanical equilibrium. For instance if you take a container of gas and you put it at a fixed temperature, then even though the molecules are moving, the individual molecules are moving and there is lot of dynamics going on, overall microscopic quantities, certain microscopic quantities, certain microscopic quantities would not change with time.

The average values would not change with time. The variances would not change with time. No moments would change with time at all. So you can get away by removing t , little t , from consideration and dealing with everything in thermal equilibrium.

Now of course the systems that you look at are very complicated. Typically they have a very large number of particles or atoms or molecules of the order of Avogadro's number for instance and it is impossible, completely futile to write the equations of motion down for every one of these objects and try to solve these equations and calculate from the solutions whatever quantities you want to compute, microscopic quantities.

But the need for statistical physics is deeper than that. It is not just the fact that you have very large numbers of degrees of freedom. The fact is, that in almost all cases, if you look at classical systems for instance, the systems are chaotic in the classical dynamical systems point of view, in that sense. In other words even if you could write down all these equations and compute quantities you would soon find that your computational power is not sufficient to enable you to find out what happens to the system, for given initial conditions once sufficient amount of time has elapsed. It is impossible.

And that is true for very, very small systems. Even if you took a little box with a handful of particles in it, the system is in general chaotic. Even if you took 2 particles in it, the system is still generally chaotic. If you took just one particle in the box, even that can become chaotic depending on the shape of the box. If there are obstacles in between, if there are scatterers and so on, thick scatterers, then the system, future trajectory of the particle is chaotic and essentially not predictable, not computable in polynomial time.

So right away you know that there is need for some kind of statistical or probabilistic approach to the entire thing. But mercifully for us, fortunately for us, for instance, taking the example of a gas, the kind of question you ask of this system, the kind of information you want from the system does not in general, involve microscopic degrees of freedom. You are not really interested in finding out what is the velocity history as a function of time of the individual molecule. You are not interested in that.

You are interested, for instance, in the pressure exerted by this gas which means you would like to know what is the average force exerted by, on the wall per unit area and you are not interested in which particles are hitting the wall at any given instance of time and of course if you sketch the instantaneous force of the molecules on the wall, at the level of femtoseconds for example, you would find a very grainy kind of graph. It would be fluctuating very wildly. But if you look at on timescales which are more microscopic, say of the order microseconds or so, then you discover that so many collisions have occurred in your time span that things have averaged out and you get a certain average which is quite robust and doesn't change with time, Ok. Similarly you would like to know not what's the individual energy of a molecule but you would like to know what's the average kinetic energy of the system as a whole, what is the average internal energy and so on.

So the questions you ask of it are also questions about statistical averages. Now you can compute a statistical average in 2 different ways in such a complex system. You could for instance, follow a given particle and find out what its history is, and if there is a sufficient degree of mixing among the particles, then the time history of one particular particle is essentially the same as the history at the given time of all the particles.

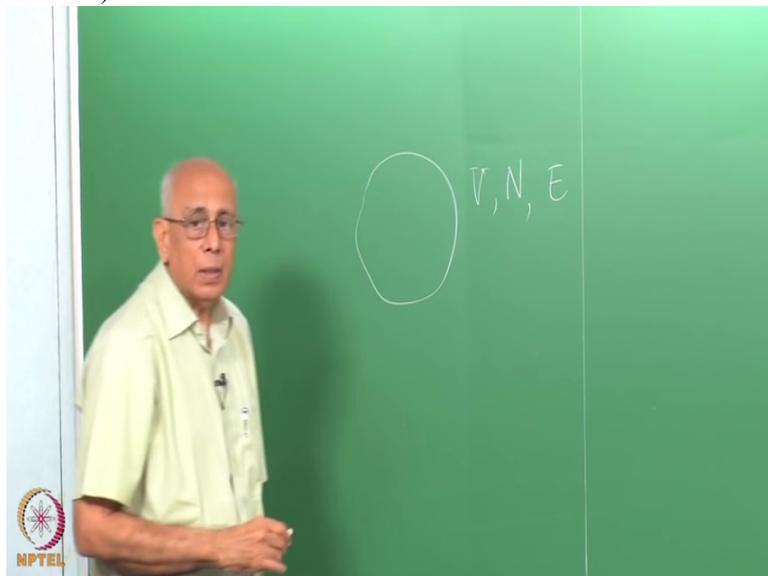
In other words, the time average over certain degrees of freedom would be the same as the ensemble average over the collection of particles. So the system in some sense self-averages as you go along, as time elapses, so which is the reason why you can eliminate time averages and use ensemble averages, Ok.

Now we will say much more about ensemble averages more carefully but this is just to give you a rough idea of what is involved in this business. Now of course once I say an ensemble average, you have to tell me an average over what distribution. So the whole of statistical mechanics is really a specification of what's the correct distribution function, probability distribution function over which the statistical averages are taken and which we believe will yield the same answer as long time or infinity time averages. So this equality of long time average and an ensemble average for suitable distributions over suitable distribution functions is what makes statistical mechanics work.

Then of course what specific average you have depends on the conditions to which you subject the system. If for instance, you had an isolated system, just for example, let's take a fluid with a given number of particles in some enclosed container, and let's say this container is isolated from the rest of the universe. It is completely isolated and is sitting somewhere without interaction and here it is, in this fashion.

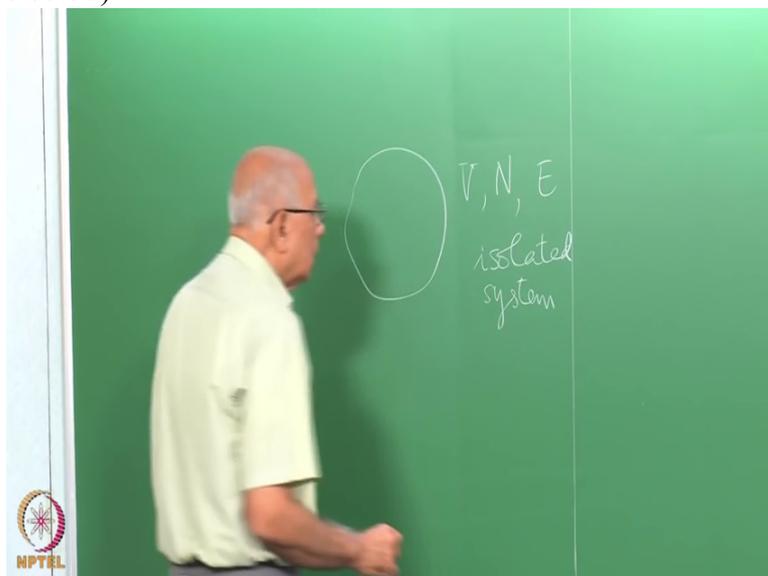
The number of particles is in volume V , the number of particles is N and let us say the total energy of the system is E .

(Refer Slide Time 07:26)



Then if this is completely isolated,

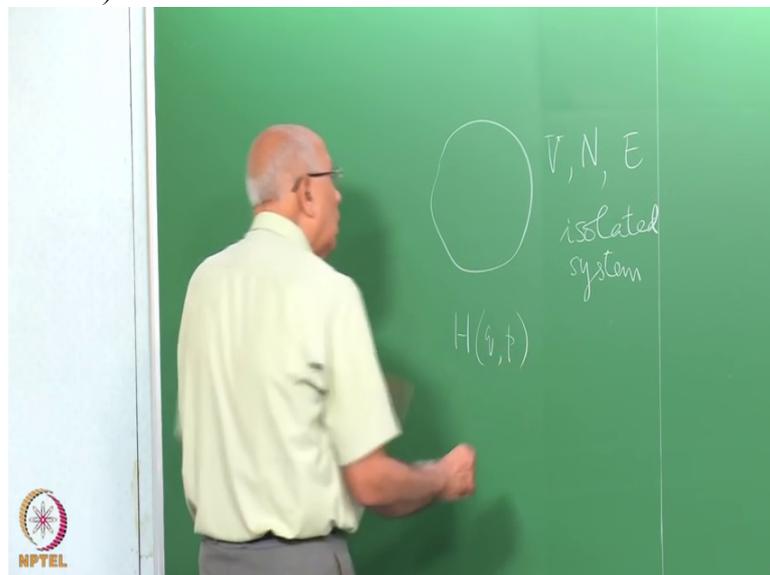
(Refer Slide Time 07:37)



no exchange of either matter or energy with rest of the universe, then in thermal equilibrium this system's energy doesn't change. It remains constant. That's a constant of the motion and then the way you would say, the kind of average you would take would be over a distribution which takes into account the fact that there is one constant of the motion in the problem.

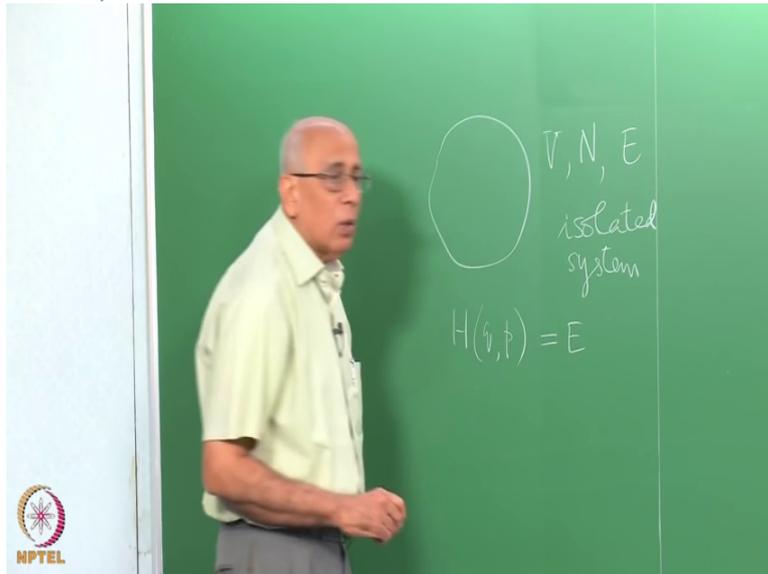
So whatever happens inside, we are not bothered about but the total energy of the system is constant. In other words, the Hamiltonian of the system and I presume that you are familiar with classical dynamics at the Hamiltonian level, which is specified by whole lot of generalized coordinates, generalized moment of all

(Refer Slide Time 08:21)



the particles, this quantity if it is a consolidated system, we make certain assumptions and we will make that more clear as go along, for such a Hamiltonian system which doesn't explicitly involve time, it is an autonomous system, this quantity, its numerical value remains

(Refer Slide Time 08:42)

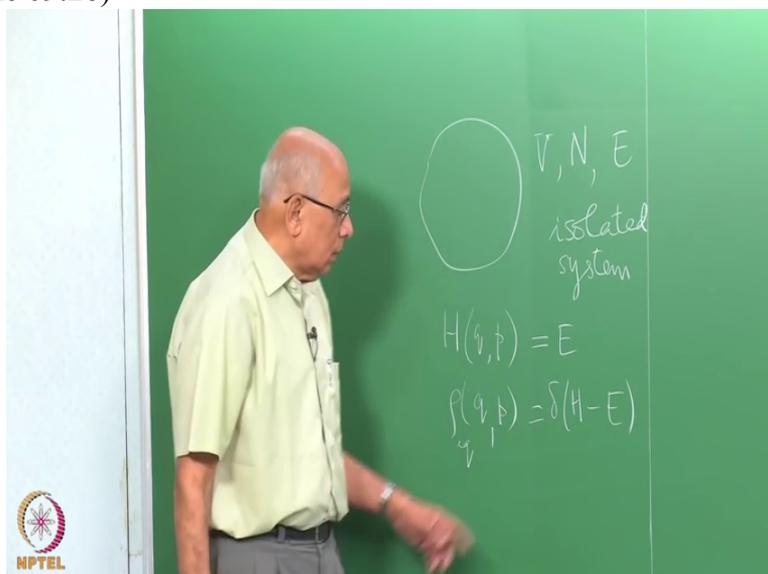


constant as a function of time.

So as the q s and p s change with time according to Newton's Laws or whatever equations of motion you have, this function of all the coordinates and generalized coordinates and momenta remains constant in this case.

So you could now ask what's the constant, what's the distribution that I am going to work with. What is the distribution in phase space as a function of all the q s and p s and of course a good first guess would be to say ρ of q s and p s in equilibrium, so let's put a little subscript here, this quantity must be equal to delta of H minus E ;

(Refer Slide Time 09:26)



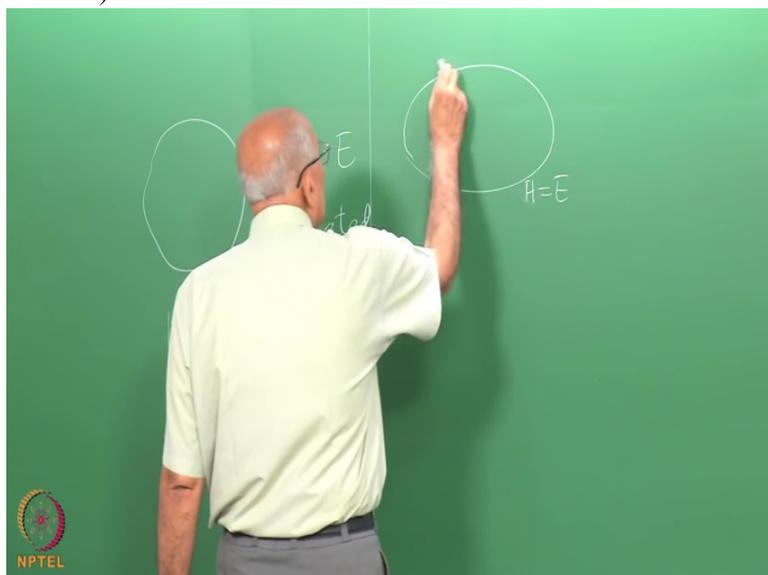
delta function, Dirac function which says that the total energy of the system remains constant. In other words the motion of the system is restricted to hyper surface on which this function H of q, p equal to a constant value, so prescribed value. So that's the equilibrium distribution function. Now of course you have subtle questions arising here, which is to say may be that there are other constants of the motion, may be total angular momentum is constant, may be the total linear momentum is constant. So there are other constants of the motion of that kind which you can identify even in the simplest of cases.

How come, how come, I am using a distribution function which depends only on the Hamiltonian and not on those other constants of the motion. That is a much more subtle question and I leave that as a question for you to ponder over for a moment and we will come back to this much later, Ok, at some stage we will answer it. But this is worth asking. Why is it that the other constants of the motion don't play the role? Ok. They actually do but it is not explicit here and I want you to think about it, Ok.

Now this distribution function is called the micro canonical ensemble, Ok. So for an isolated system you have the familiar micro canonical ensemble which is essentially saying that the motion is restricted to an energy surface, Ok. Well there is always a resolution in these matters. This is an energy of microscopic system so there is always some resolution.

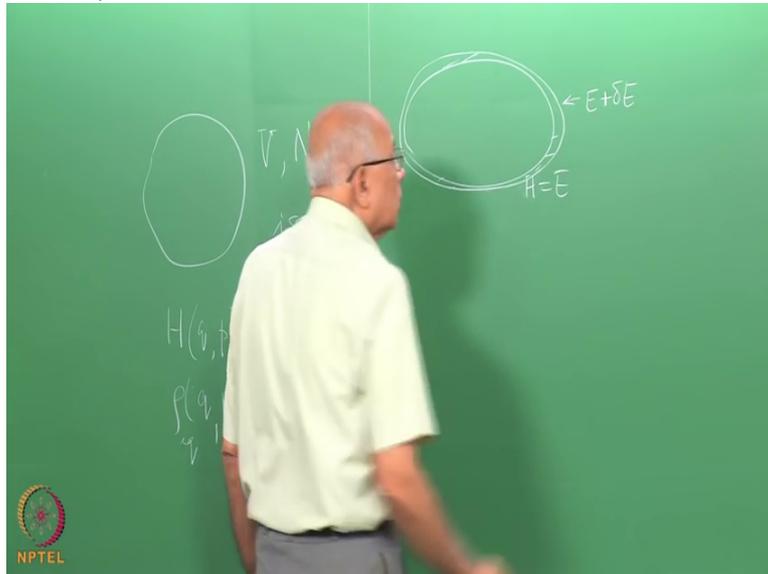
So if this schematically is the surface on which E , the energy is E ,

(Refer Slide Time 11:14)



what is really happening is that the system is restricted to a little shell on which the Hamiltonian here is E plus δE . So there is a certain

(Refer Slide Time 11:25)

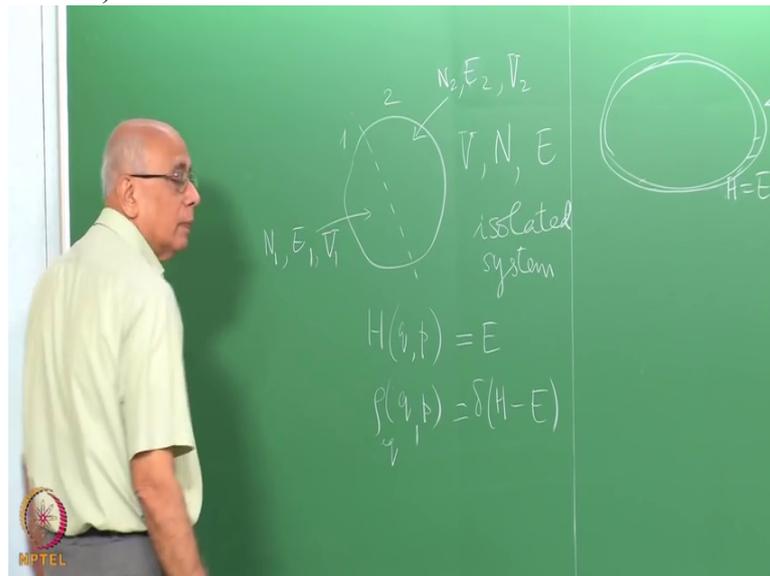


resolution δE and the system remains in this shell, it doesn't go inside, doesn't go outside and that's your distribution function essentially. And that's the simplest case.

Now as you know from equilibrium, statistical mechanics, the very fact that you have this conservation law here tells you a great deal. Once I have a system which is isolated and is in thermal equilibrium, in other words microscopic averages over this ensemble should not change as a function of time, then you can make a large number of deductions from it. And that's the business of equilibrium statistical mechanics.

Just to refresh your memories, the first thing you do is to say uh, uh, Ok, suppose I draw an imaginary partition out here in this case and break this into 2 roughly equal pieces for instance, so there is a system 1 and a system 2, and let's suppose that this has got N_1 particles and the energy is E_1 and this has got N_2 particles and the energy is E_2 and the volume is V_2 and here the volume is V_1

(Refer Slide Time 12:45)



and the system is in thermal equilibrium, then of course this energy E_1 is not constant because it is constantly suffering fluctuations from this side and vice versa.

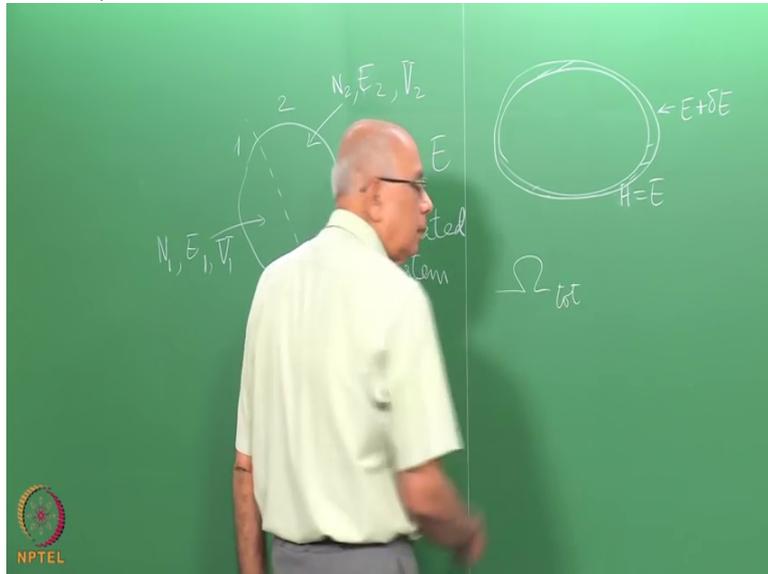
So particles from here are able to go there. Particles from there are able to go here. The energy of the system fluctuates. The energy of that system fluctuates and so on. So if you have taken the total number of degrees of freedom, broken it up into 2 partition, with an imaginary partition into 2 pieces, then you have 2 still microscopic systems but neither of them is an isolated system because each of them is in interaction with the other, this case.

But now we impose the condition that this be true, this thing be true, and now we ask what are the conclusions we can draw from the fact that these 2 systems are in equilibrium with each other? Ok. Then you need to introduce now the concept of the number of microstates that you have of this system.

Now what do I mean by microstate? Taking our example of particles, gas particles for instance, specifying the position and momentum, the three position components and momentum components of a particle specifies its state completely at any instant of time. We assume there are no internal degrees of freedom further. Then you have to do this for each one of the particles and that is the microstate of the system. If at any instant of time, you tell me what is the exact value of momentum of each particle; all the components and position of each particle then you have the microstate of the system, the entire system Ok.

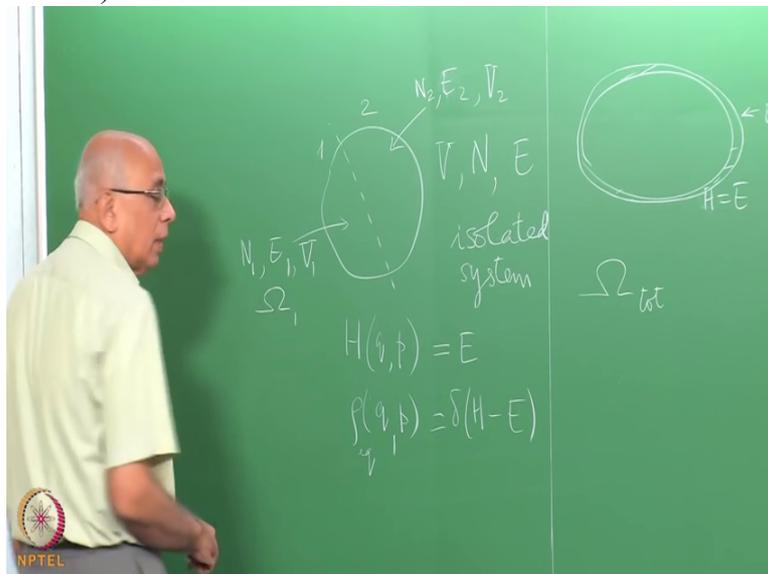
And now the question asked is how many microstates does this full system have? You assume that it has some total number of microstates Ω_{total}

(Refer Slide Time 14:33)



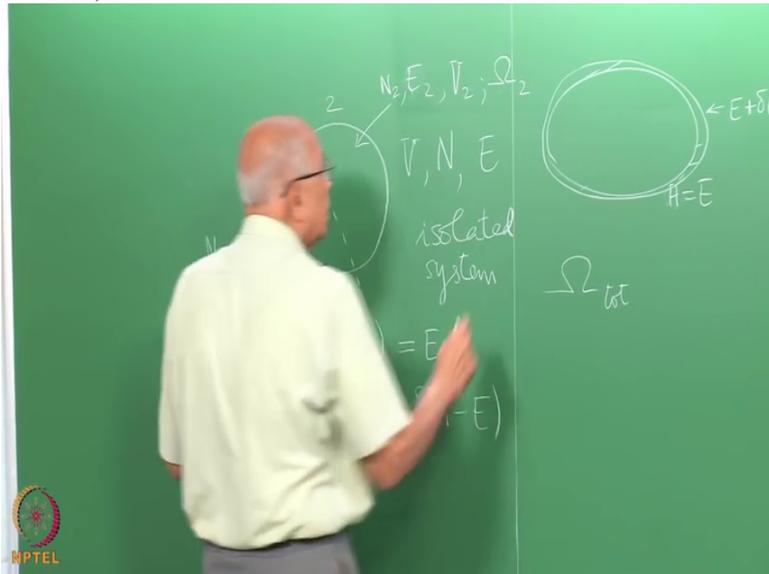
for the full system and with thing here, you have Ω_1

(Refer Slide Time 14:42)



microstates under these conditions and Ω_2 microstates under these

(Refer Slide Time 14:49)



conditions, then fundamental assumption is that total number of microstates of the system is essentially ω_1 times ω_2 because these are completely, these are both very large and then you can say, well there are some particles here in this partition which are the fellows actually exchanging energy or driving fluctuations into each system but that number is infinitesimal compared to ω_1 and ω_2 , Ok.

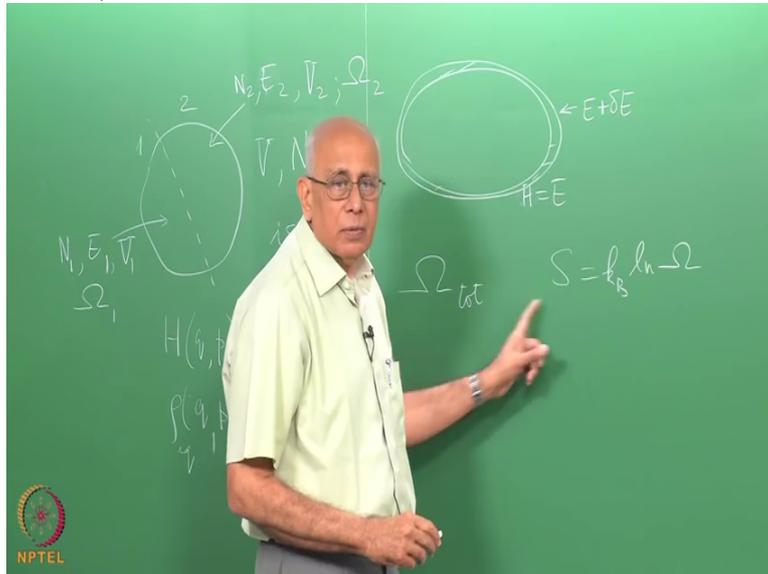
Because imagine for example, a partition, a box which is 1 cubic meter, you have 10^{24} particles in it, I put a little imaginary partition there and ask how many particles at any given time are passing through this point here. That would be of the order of 10^{24} to the power two thirds is proportional to the surface which is 10^{16} , and that is one part in 10^8 . So you see that the number of degrees of freedom which sort of talk to both systems is negligible to number of degrees of freedom here and here, so effectively ω_{total} is ω_1 times ω_2 .

And these are enormous numbers, huge numbers. For a liter of gas or something like that at normal temperature and pressure, the number of microstates would be probably of the order of 10^{30} or more, Ok because you have to take the full phase space, volume and then divide by h^3 which is the cell in phase space and then you end up with a very, very large number, Ok.

So you have the product of 2 large numbers and then it is convenient to take the log of it, so that it becomes additive completely. And that gives you a measure of how many microstates

there are on each side and as you know the entropy of the system, of any system is given by Boltzmann formula. This fixes the dimension of

(Refer Slide Time 16:48)

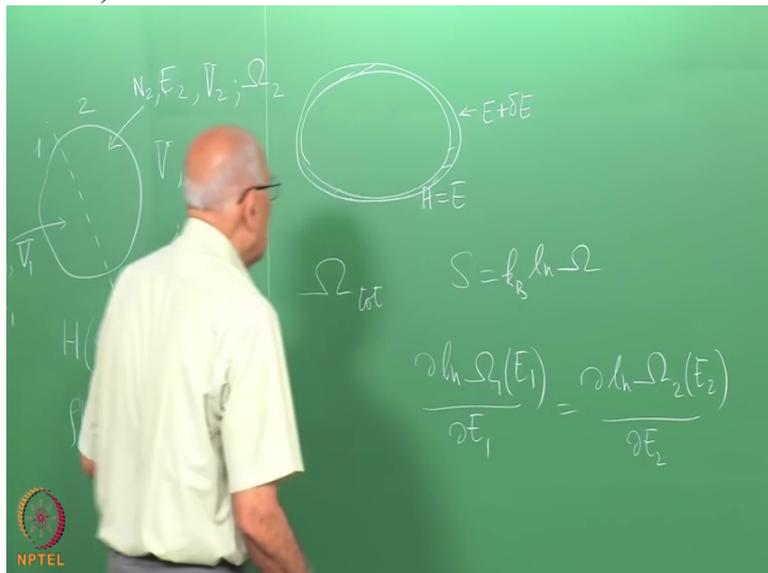


this entropy and this is essentially the log of the number of the microstates of the system, right and that's an additive quantity.

So what it is saying is that if the entropy of the system is a measure of the disorder here, then the total system has an entropy which is the sum of the two entropies here, Ok. So see, you see immediately that it is natural that this log of the number of degrees, of the number of accessible microstates appears naturally and then imposing the condition that this entire system will be in its most probable state, you immediately start getting information about it.

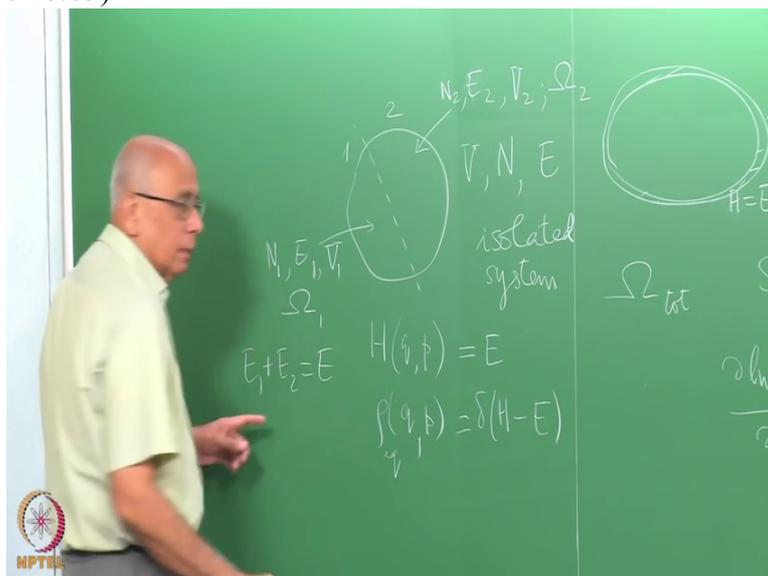
For instance the first piece of information you derive is that this omega is a function of the energy and of course of these two variables as well. And the first thing you derive is that $\frac{\Delta \log \omega_1}{\Delta E_1} = \frac{\Delta \log \omega_2}{\Delta E_2}$.

(Refer Slide Time 17:56)



By the way I should note that E 1 plus E 2 is equal to E.

(Refer Slide Time 18:03)



We know that total energy is conserved.

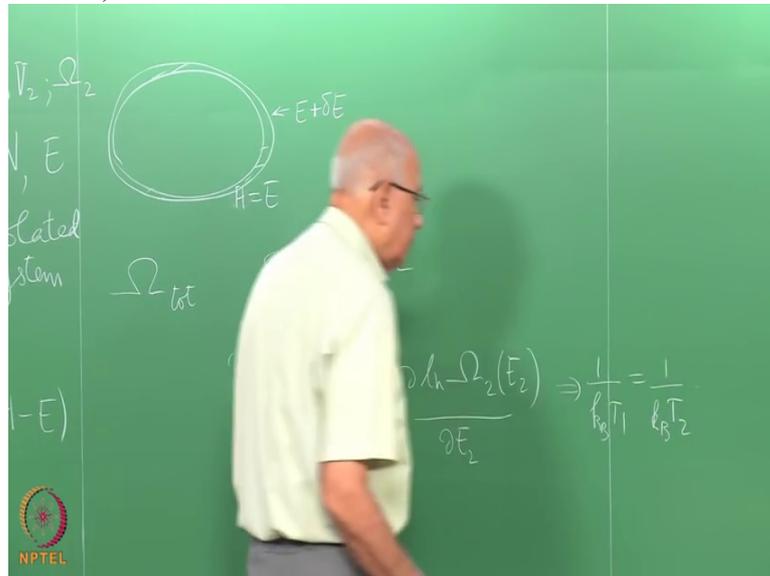
Again I neglect the interaction energy in-between here compared to the energies of these systems here. What do you call this quantity, the derivative of the log of the number of accessible microstates of the system with respect to its energy? Pardon me.

(Professor – student conversation starts)

Student: The inverse temperature

Professor: The inverse temperature, this has got dimensions of the inverse temperature. Energy is in the denominator. It essentially implies that 1 over k Boltzmann t 1 is 1 over k Boltzmann t 2.

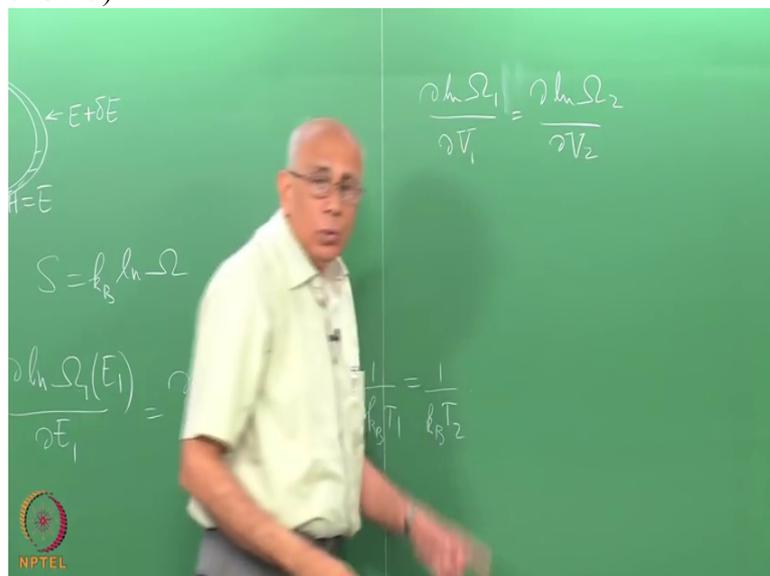
(Refer Slide Time 18:46)



It says that the temperatures on the two sides are equal, Ok. Similarly you could differentiate with respect to V , although I haven't written it explicitly. Ω is a function of V as well and you could ask what's the derivative with respect to the volume and with respect to the number as well.

What would those tell you? Ω_1 , let's just write here. Again

(Refer Slide Time 19:23)

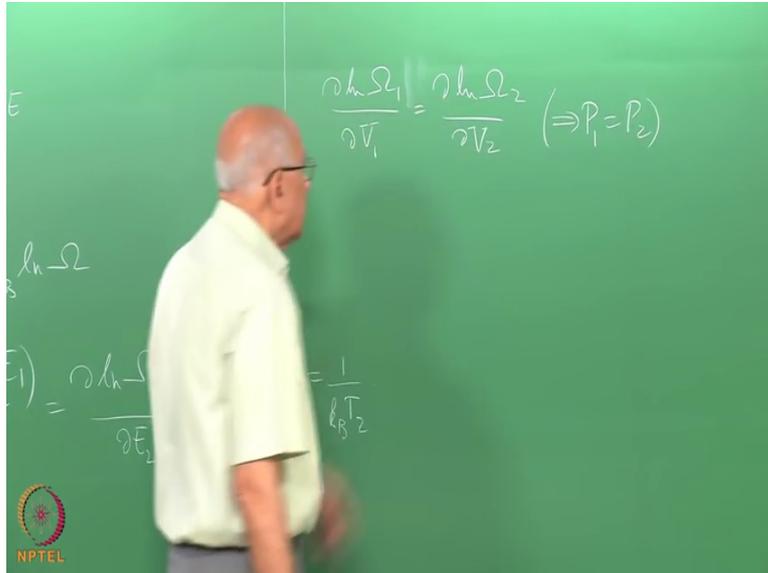


you use the constraint that V_1 plus V_2 is equal to V , Ok. What does this tell you?

Student: Pressure

Professor: Yeah, this essentially tells you the pressure on the two sides are equal.

(Refer Slide Time 19:39)



Now I leave you to verify that this is so by a very simple check. What you need to do is to use the fact that the entropy is given by the Boltzmann's formula, then of course you have the entropy here. And the derivative of the entropy with respect to volume will give you pressure because if you go back and look at the laws of thermodynamics this is exactly what it does.

(Professor – student conversation ends)

So let us write that so-called laws of thermodynamics. They follow from statistical mechanics but let us write this down. What is the, what is the first law of thermodynamics? Let us look at the fluid. So one molecular species, just a single molecular species at some volume V and some temperature T and fixed number of particles N . So what is the, what does the law of thermodynamics say about this? What does it say about the internal energy of the system?

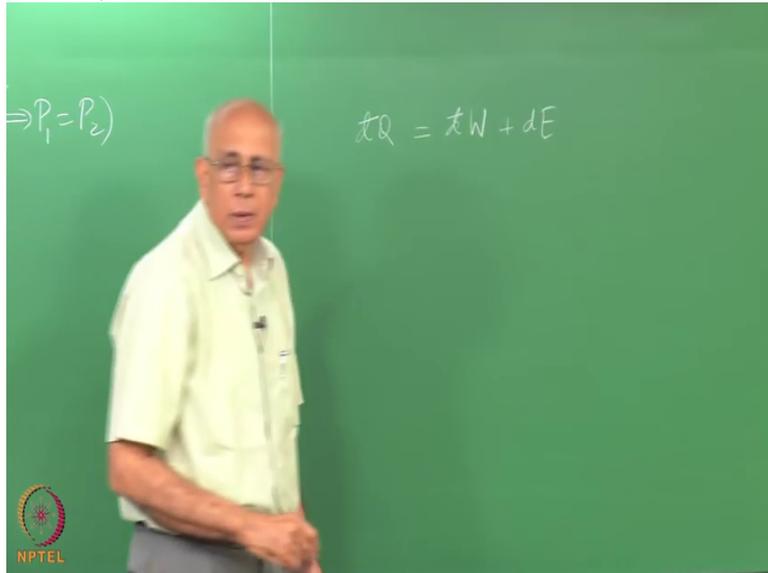
Well you start by saying that if I supply a certain amount of heat dQ to the system and that's an imperfect differential, this thing here will be equal to dW , another imperfect differential. This is the heat supplied to the system, an incremental piece of heat supplied to the system. That's the incremental piece of work done by the system. And what's left,

(Professor – student conversation starts)

Student: Internal energy

Professor: what's left is the internal energy of the system which is dE .

(Refer Slide Time 21:12)

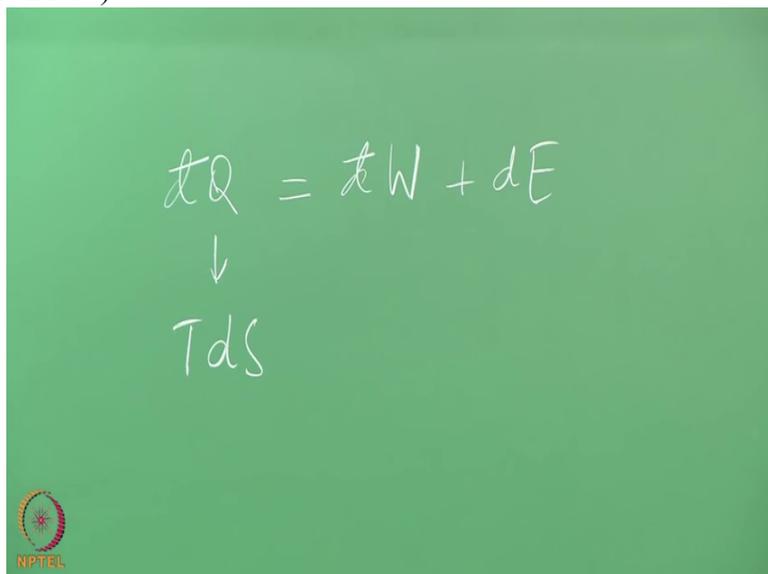


That is the perfect differential because E is a state function, Ok. On the other hand Q and W are not state functions which is why the differentials are imperfect till you multiply them by integrating factors and then you get perfect differentials, Ok.

(Professor – student conversation ends)

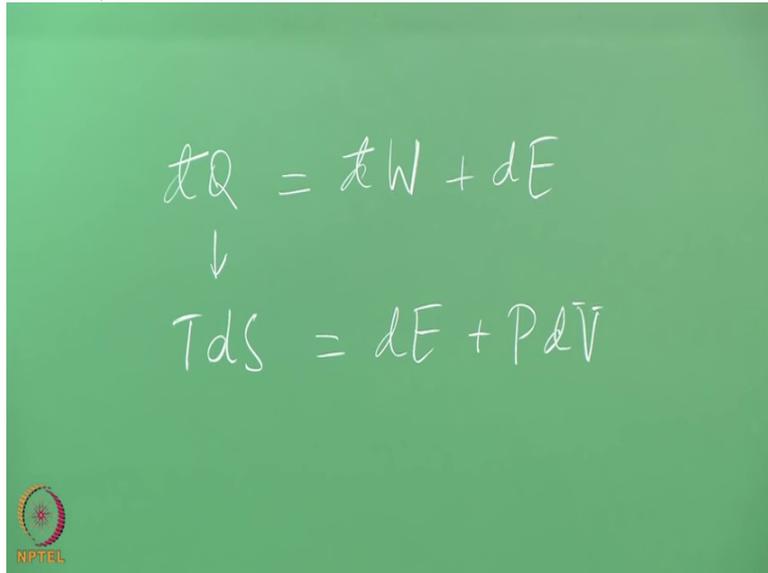
And what does the second law of thermodynamics say? It says for reversible processes this quantity is dS . In other words, if you take dQ and multiply it by $1/T$, that's the integrating factor

(Refer Slide Time 21:44)



which makes this dS a perfect differential, Ok. So on this side you have $T dS$ and on this side you have dE plus $P dV$,

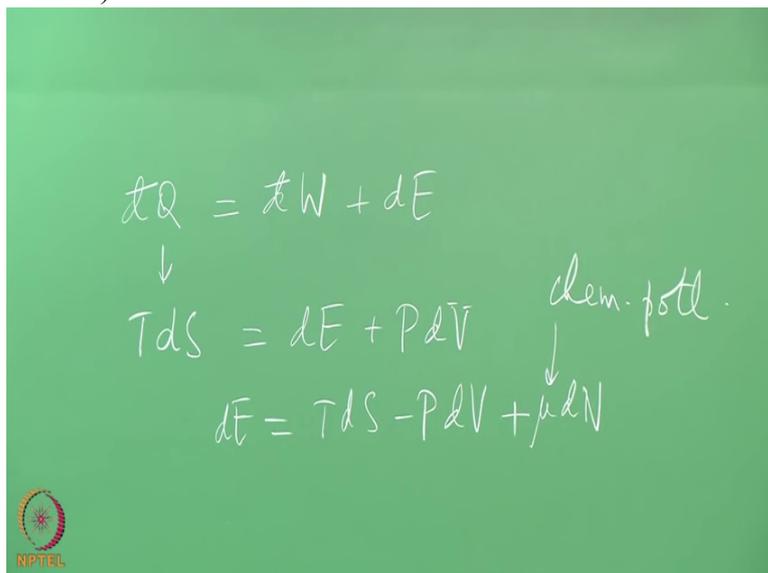
(Refer Slide Time 22:01)


$$\delta Q = \delta W + dE$$
$$\downarrow$$
$$Tds = dE + PdV$$

right? That's the familiar laws, of the first law and second law combined for reversible processes, Ok. Alright, Ok.

So this immediately says that dE equal to $T dS$ minus $P dV$. If you allowed the number of particles to change as well, then there would be another generalized force here on this side in addition to $P dV$. It costs a certain amount of energy to change the number of particles. And the cost and energy per particle is called its chemical potential, Ok. This is the chemical potential.

(Refer Slide Time 23:08)


$$\delta Q = \delta W + dE$$
$$\downarrow$$
$$Tds = dE + PdV$$
$$dE = Tds - PdV + \mu dN$$

chem. pottl.
↓

So it follows from here that since this is a perfect differential, it says delta E over delta S is T, or delta S over delta E is 1 over T and that's what I have written here. So it is completely consistent with thermodynamics, Ok.

Similarly it says delta E over delta V, this thing here is going to be proportional to the pressure and so on. So you can derive all the thermodynamic quantities and notice just, we I might, let me also point out that this thing here, this change in inte/integral, this is the generalized, this generalizes the laws of thermodynamics. You can add many, many other terms here, Ok.

In general what you have is, this is equal to T d S plus summation in this form, where these are generalized forces and these are generalized fluxes here. And the simplest of these is minus P here and a V here and then a mu here and d N there and so on, Ok.

(Refer Slide Time 24:21)

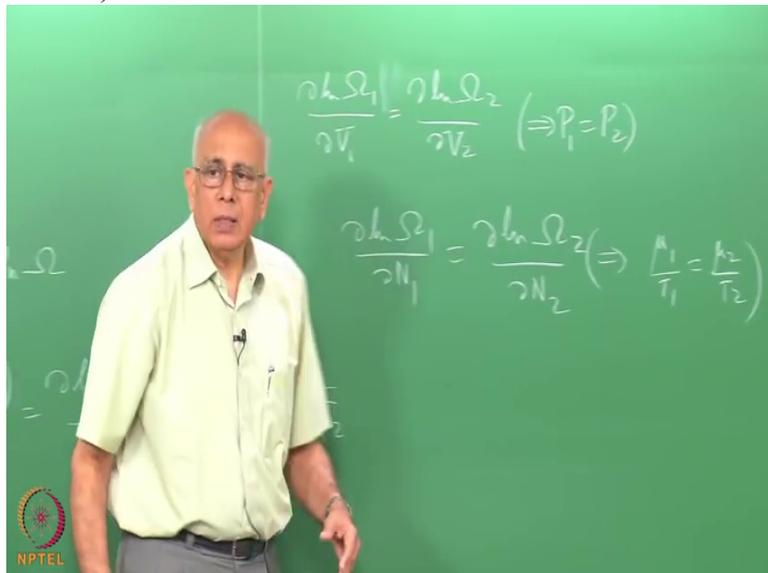
The image shows a green chalkboard with handwritten equations. At the top, it says $\delta Q = \delta W + dE$. Below this, an arrow points down to $TdS = dE + PdV$. To the right of this equation, there is a handwritten note "chem. pottl." with an arrow pointing down to the next equation. The next equation is $dF = TdS - PdV + \mu dN$, where dF is circled. Below this, it is written as $= TdS + \sum_i F_i dX_i$. In the bottom left corner of the green area, there is a small circular logo with the text "NPTEL" below it.

For instance if you applied a magnetic field the system would respond by changing the magnetization. So the force in this case is the magnetic field and the response is the magnetization, the extrinsic variable. You apply an electric field; the system could change its state of polarization. So again you have a generalized force which is the electric field and the response which is, or a flux which is the polarization and so on.

So now from this, it exhausts the contents of the laws of thermodynamics, you derive all sorts of relations using the fact that these are all perfect differentials. They are all state functions, Ok.

So to come back here, in the micro canonical ensemble, the fact that these two parts of the system are in equilibrium with each other immediately tells you that the temperatures have to be equal, the pressures have to be equal this side, and the chemical potentials have to be equal. So we can also write the same thing with $\Delta \log \Omega_1$ over ΔN_1 should be equal to $\Delta \log \Omega_2$ over ΔN_2 . This will imply that μ_1 over T_1 equal to μ_2 over T_2 .

(Refer Slide Time 25:41)



Since T_1 is equal to T_2 anyway already, the chemical potentials are also equal. So much for the micro canonical ensemble, Ok.

But now real life, we will, by the way, we will come back to this, we will come back to the laws of thermodynamics at 0:25:59.8 suitable intervals, there is one more piece of information that goes into thermodynamics which I have not put in here. While this says something about dS , dV and dN , you will express it as a perfect differential here, you could ask, can I make a statement about dF times x_i . Can I do that? Ok

And the answer is you need a little more physical input. You need a little more input about what this quantity is, this thing. What sort of dependence it has on S , V and N . You see it only

says that since dE is proportional to dS , dV and dN , it only says that E is the function of those three variables, Ok. It doesn't say what sort of function.

But now if you make assumption that it is proportional to these quantities, namely it is a homogenous function of these variables of degree 1, if you double the number of particles keeping other things constant, the internal energy doubles and so on. If you made that assumption of extensivity then you get a relation which also says $\sum x_i dF_i$ is zero and that's called the Gibbs Duhem relation, or the Euler relation in this case, and from that you derive the Gibbs Duhem relation and so on. The rest of thermodynamics proceeds that way, Ok.

But we are not interested in thermodynamics because first of all, it applies only in equilibrium and secondly it only deals with average quantities. It does not tell you anything about fluctuations about the average at all. In fact anything which involves fluctuations about statistical averages has to be put in as an input parameter, input information into thermodynamics.

Can you give me a notable example of such an input? Well when you deal with gases in thermodynamics, whether it is a real gas or an ideal gas, doesn't matter, you deal with that, there is no way you put in, you already have information of specific heats. You cannot compute specific heats within the framework of thermodynamics. Because specific heats involve the variance of the energy. And thermodynamics does not go to the level of the variance. It sticks at the level of the first moment or the average. So specific heat has to be put in as input parameter into thermodynamics.

Now in elementary courses in high school physics, you learnt that the ideal gas; the monatomic gas has a C_v which is three halves kT per particle and a C_p which is five halves kT Ok. Now you might say, uh, that's basic information. Where did that come from? It came in because in that particular case, you know the equation of state. We know that PV is equal to RT or n times RT . So once you know the equations of state of the system, it is just written down by the way empirically then matters become different altogether. One of the purposes of the whole business is to find the equation of state and if you give it to me, then that's it. I mean I can compute specific heats, Ok.

But in a real gas, for example the van der Waal's gas and so on, you don't have. If you have an equation of state, you can start trying to compute these quantities. But a priori in arbitrary thermodynamics system, given thermodynamic information you don't know what specific heats are. You don't know what susceptibilities are. You don't know what compressibility is. You don't know what response functions are. They are put in from outside, Ok.

(Professor – student conversation starts)

Student: But whenever we say something about inequalities at this side....

Professor: Yes, that's a good point. Thermodynamics will say however, the fact that you are in thermal equilibrium means that you are always at the minimum or maximum depending on how you define it, of some thermodynamic potential. And if it is supposed to be a stable equilibrium, then it gives you certain convexity properties, the fact that when you have a function of 2 variables, the parabolic bowl, the bottom of it is the state of stable equilibrium, right?

(Professor – student conversation ends)

So the fact that you have stability tells you that the various partial derivatives, second derivatives has specific signs. And that will tell you something about which quantities are positive, which quantities are negative. For instance you can show that thermodynamic stability implies that the specific heat at a constant volume of a system cannot be negative. The compressibility of a certain system cannot be negative and so on. So certain inequalities are obtained but you cannot find the actual, absolute values of these things.

For that you need a little more information. If you give me the Hamiltonian and you tell me how to do statistical mechanics then in principle if I can compute what is called the partition function of the system, then I can find all the thermodynamic variables, all the information that I need, all moments can be found, again in thermal equilibrium, in thermal equilibrium.

But now in this course, we are going to go out of thermal equilibrium. So even the fundamental postulate of equilibrium thermodynamics goes out of the window because as you know, the thermodynamics postulate defines in some sense what we mean by thermal equilibrium. It says that when you are in, I will come back to the definition, when you are in thermal equilibrium, it says all accessible microstates are equally probable for the system.

But now it still begs the question, what I mean by thermal equilibrium. Well, short answer is the state in which the distribution, all microscopic averages are time independent, Ok. And how is that achieved? It is achieved obviously by taking a probability distribution function which is itself time independent. Only then when you take averages with respect to it will everything be time independent, right.

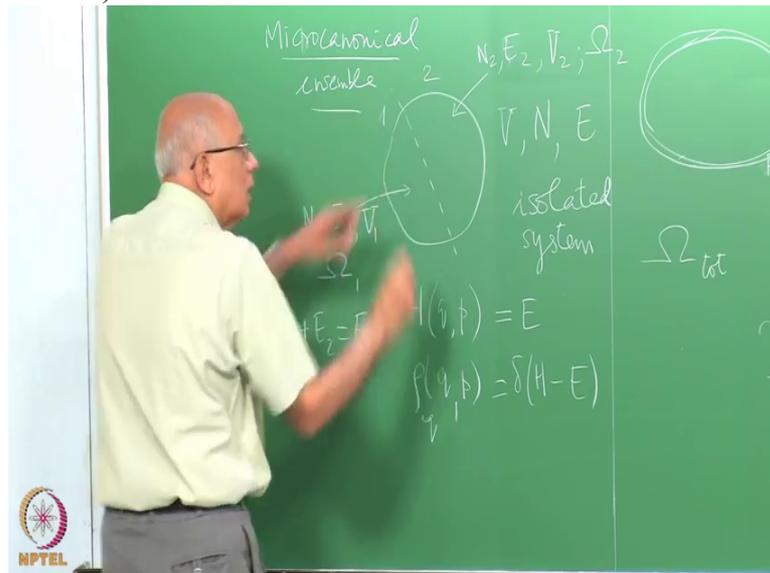
So the statement is, in thermal equilibrium which is defined by saying that the distribution function is time independent, all, all microstates, accessible microstates are equally probable, Ok. Now this is not derivable from mechanics; because if it were then we would go home. Statistical mechanics becomes a special case of mechanics, classical or quantum. No one has ever been to derive this. On the other hand people have been able to find sort of certain conditions under which it is true etc.

What we do know is that, if at any given instant of time, various averages are time independent, various averages are, well there should be another way of saying it, if at any instant of time you discover that all microstates are equally probable, accessible microstates are equally probable, then you can show that it will remain so at all times, Ok. That's the statement about the dynamics. So I repeat that if at any time you can show that in an isolated system, all accessible microstates have equal probabilities, then you are guaranteed that it will remain so for all times. Ok.

In other words this system is in thermal equilibrium. But we are trying to do the converse of it. We are trying to say, if the system is in thermal equilibrium, what can you say about the probabilities of various accessible microstates? And the postulate of the equilibrium statistical mechanics says that they are equally probable, Ok. So I want you to appreciate the fact that this is not derived from mechanics. This is an extra postulate that has gone in.

Alright. So let's get back to where we were. So this is what happened in the case of micro canonical ensemble. So the whole thing, all the thing I have said so far is in micro canonical ensemble, all this portion

(Refer Slide Time 33:58)

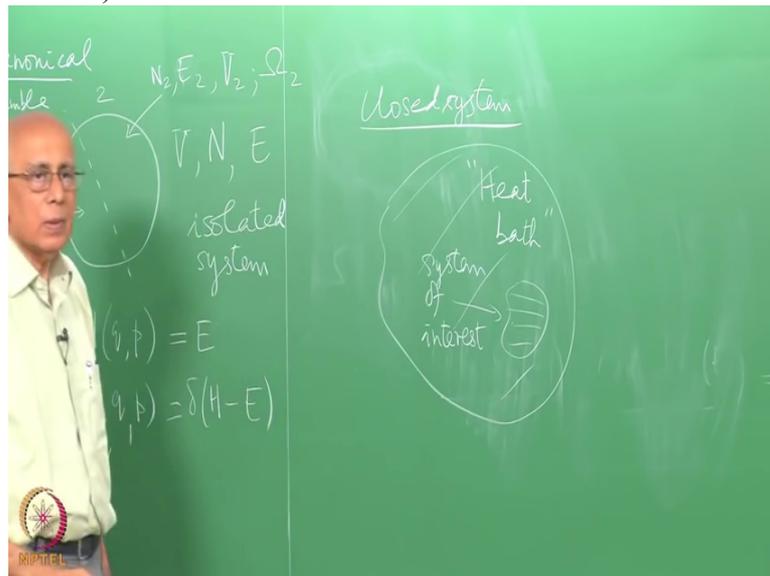


of it, yeah. Now you can say, look this is not very realistic because much more realistic physical situation is not a system in isolation from the rest of the universe, but the situation which is kind of interacting with this same environment.

Like a glass of water place on this table. It is certainly in thermal equilibrium with the external atmosphere, there is a system with a much larger number of degrees of freedom namely the atmosphere which is maintaining this system at equilibrium at some temperature. So one can then ask what is the correct ensemble; what is the correct distribution function in this case? So we have now an example of a system which is closed, so not an isolated system but a closed system in thermal equilibrium.

So we have in mind a huge heat bath or reservoir which is assumed, for example to be isolated and in thermal equilibrium and inside it you have your little system here which is the system of interest. This is the heat bath or reservoir, all the rest of it,

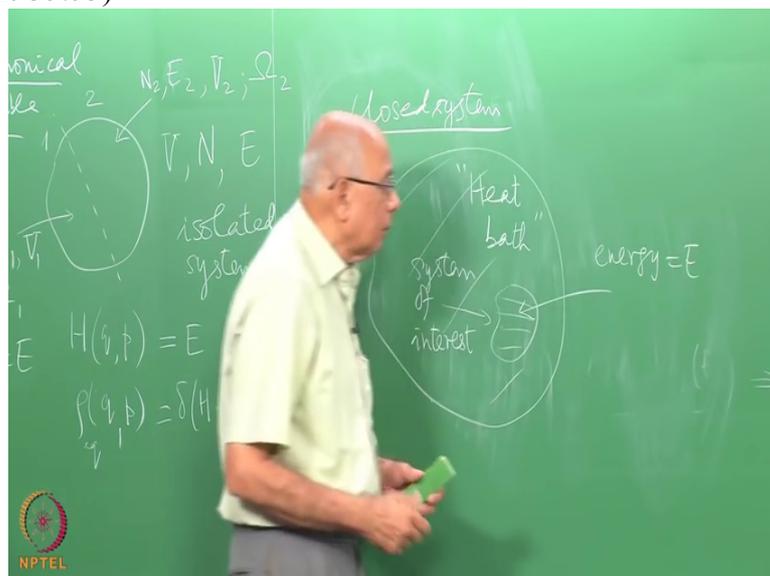
(Refer Slide Time 35:21)



Ok. And we will assume that this system has a fixed number of degrees of freedom, so it doesn't exchange any matter with the surroundings but certainly it can exchange energy. For example it could be a beaker of water which can be heated. We are assuming the number of particles remains the same, Ok. Then what happens in such a case? The energy of the system is no longer constant, Ok.

So let's suppose the energy is E

(Refer Slide Time 35:53)

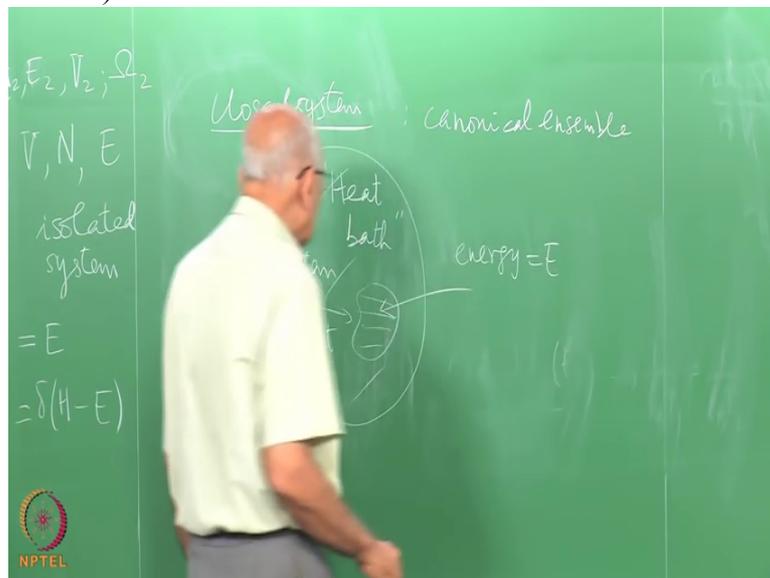


but that is fluctuating very rapidly as a function of time. And if this system is sufficiently small compared to the number of degrees of freedom here, then the fluctuations in this energy

can actually be quite large, can be enormous, Ok. So there could be a huge scatter of whatever average you have out there.

Then the question is what is the distribution function in this case; what is the equilibrium distribution function in this case? The temperature of the system is essentially decided by this guy. So the temperature of this is whatever this is, fixed. And in fact the ignorance is what is going on in the heat bath is summarized in the parameter called temperature which is the external bath sets the temperature, and then whatever internal dynamics happens here ensures which state the system would be in, etc. etc. This is called the canonical ensemble.

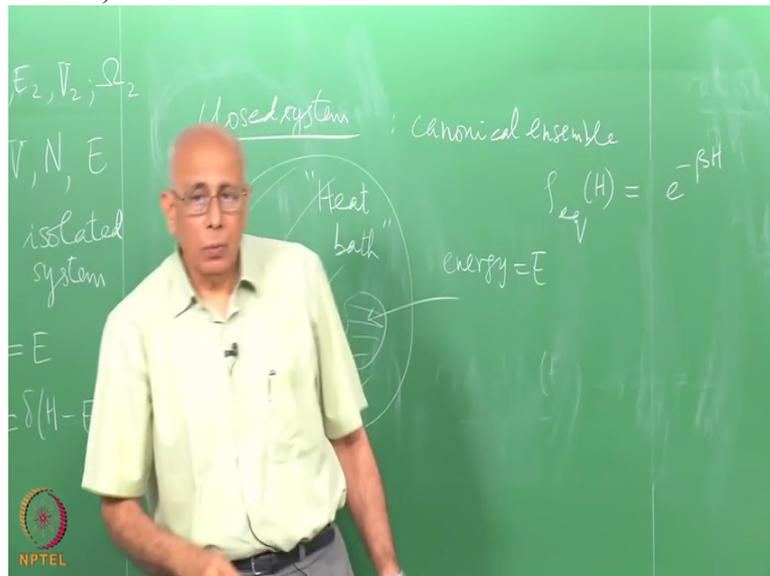
(Refer Slide Time 37:04)



And what would ρ equilibrium be in this case, here? Once again it turns out, that is the function of the energy of the system for reasons which would become clear when I talk about the Liouville equation. But now the question is, is it this? It is clearly not this because it is very clear that large energy fluctuations are driven into this system by the environment, some function of the Hamiltonian but certainly not the delta function at E .

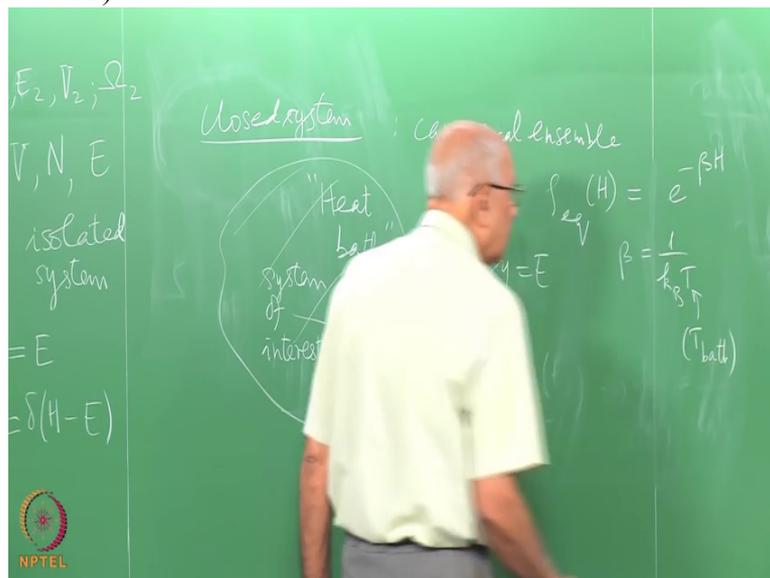
And then you have, you can derive this, you can actually take this case and make this smaller and smaller and ask what happens to this distribution and then you discover if this instance ρ equilibrium, it is the function of H , the Hamiltonian of the system, this is given by $e^{-\beta H}$

(Refer Slide Time 38:00)



where beta is 1 over k T. And this T is the T bath.

(Refer Slide Time 38:12)

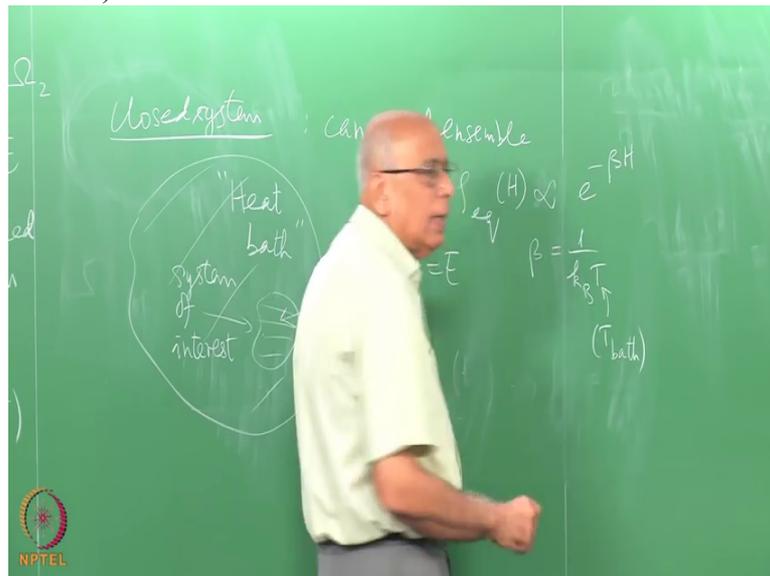


(Professor – student conversation starts)

Student: Is it proportionate?

Professor: It is proportionate.

(Refer Slide Time 38:25)

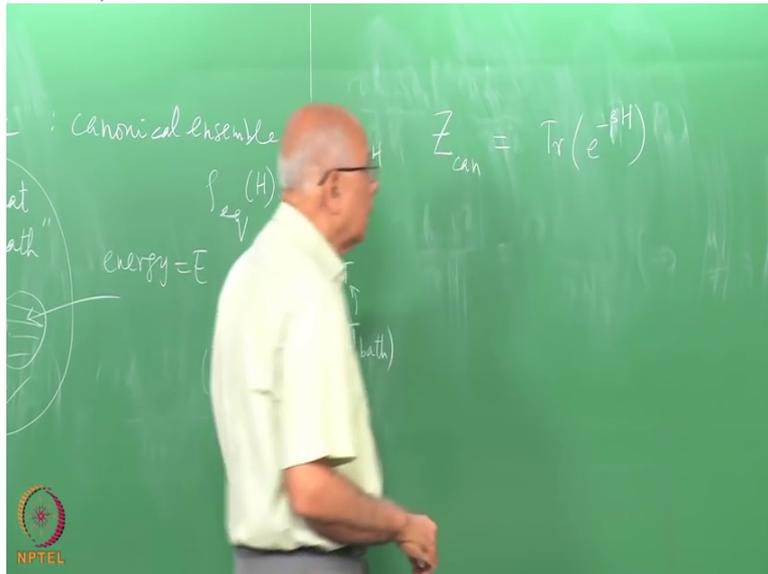


It has to be normalized, Ok. This is called the density operator. It is already written in somewhat abstract form, Ok. So I shouldn't do this. I will come back and tell you what the meaning of this is, more carefully, both classically and quantum mechanically. This is actually called the density matrix, the equilibrium density matrix or density operator. This is in general some operator but the more practical thing is 0:38:51.6 by what we mean by what is the partition function of the system, Ok.

(Professor – student conversation ends)

The partition function of the system is the canonical partition function is equal to the summation, well there is a formal expression for it, which is the trace of rho equilibrium, trace e to the minus beta H.

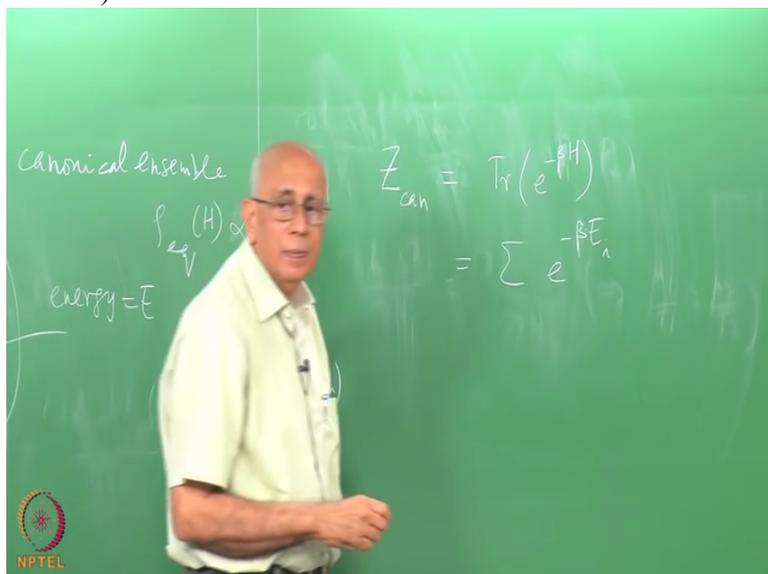
(Refer Slide Time 39:18)



By trace I mean all the sum of all the diagonal elements in some suitable basis, for instance in the basis in which the Hamiltonian has eigenvalues, specific eigenvalues and it is a diagonal operator, Ok.

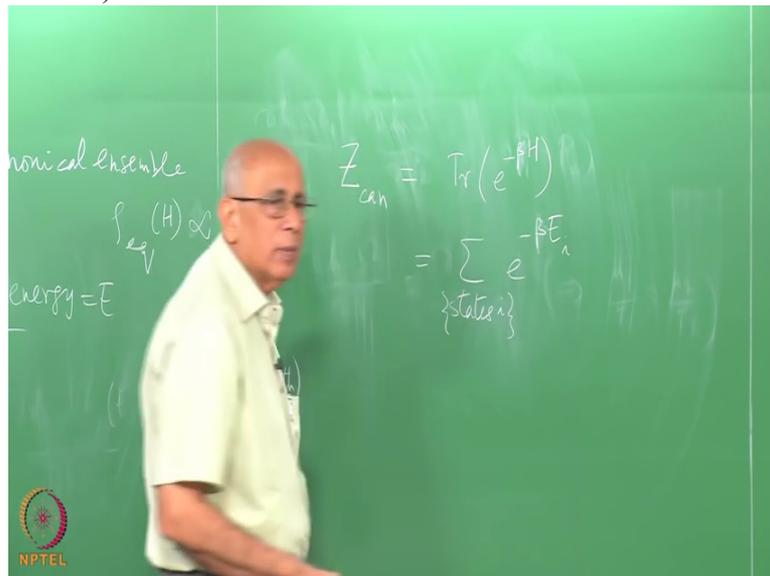
So written out in language which is familiar to you, this is equal to summation over e to the minus beta times the energy levels of the system,

(Refer Slide Time 39:44)



Ok. Actually it is sum over all the states, so states, let's write it properly. States, collection of states

(Refer Slide Time 40:10)



in the system, but it might so happen; I have written it in a discrete notation that states are assumed are E_1, E_2, E_3 in a denumerable way but whenever you have a continuous set of energy levels possible then you replace the summation by an integration in a straight forward way. But the question is this is over the states of the system. It might so happen that you have more than 1 state for a given value of the energy.

As happens for example in the hydrogen atom, where you know there are 3 quantum numbers which specify the state of the electron without spin being taken into account. And those are n, l and m . But for a given value of n , you have $2n^2$ possible states, right? So you have to sum over those and therefore you can write this as summation over levels, let us continue to call it i , $g_i e^{-\beta E_i}$ where this is the degeneracy of the state, of the energy level $E_{sub i}$.

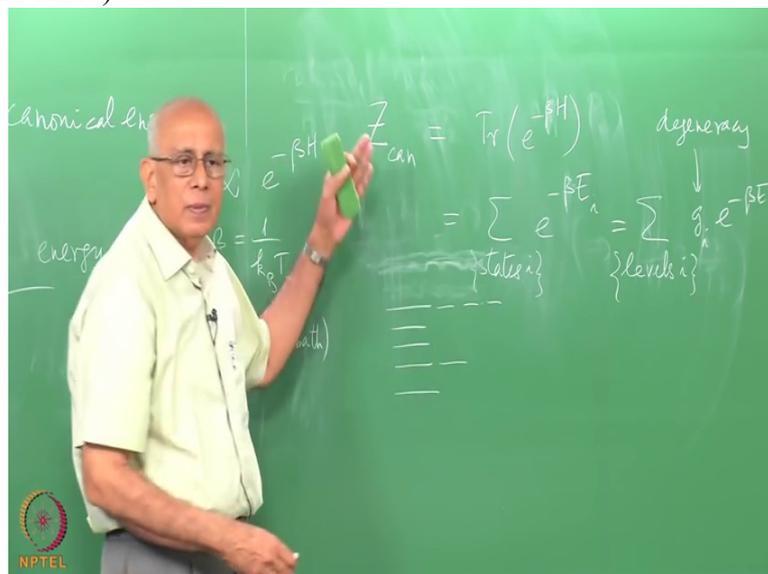
(Refer Slide Time 41:18)

$$Z_{can} = \text{Tr}(e^{-\beta H}) \quad \text{degeneracy}$$
$$= \sum_{\{states i\}} e^{-\beta E_i} = \sum_{\{levels i\}} g_i e^{-\beta E_i}$$

You have to count that particular energy level as many times as its degeneracy.

What happens when it becomes continuous spectrum? So this is fine as long as you have states looking like this, and you say at this energy level there are 2 possible states, at this energy level there are 4 possible states and so on. So you are including, counting over all these fellows here. But what happens if you have a continuum of energy levels?

(Refer Slide Time 41:49)

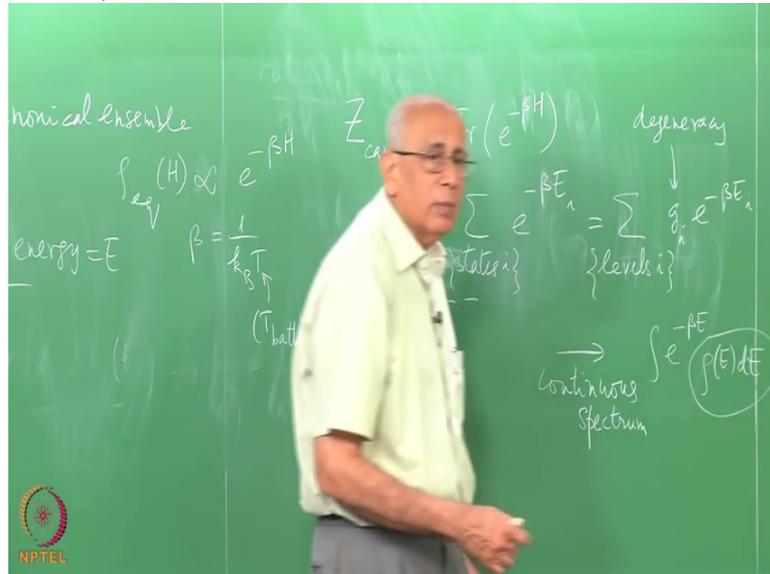


You must replace this summation with an integration and you have a certain resolution.

You ask now the question, how many states are there in an interval between E and $E + dE$? So this will go over for a continuous spectrum to an integral over E to the minus δE

times the number of states that are between E and E plus delta E and that's generally given by something like rho of E d E. This gives you the number of states that the system has

(Refer Slide Time 42:32)



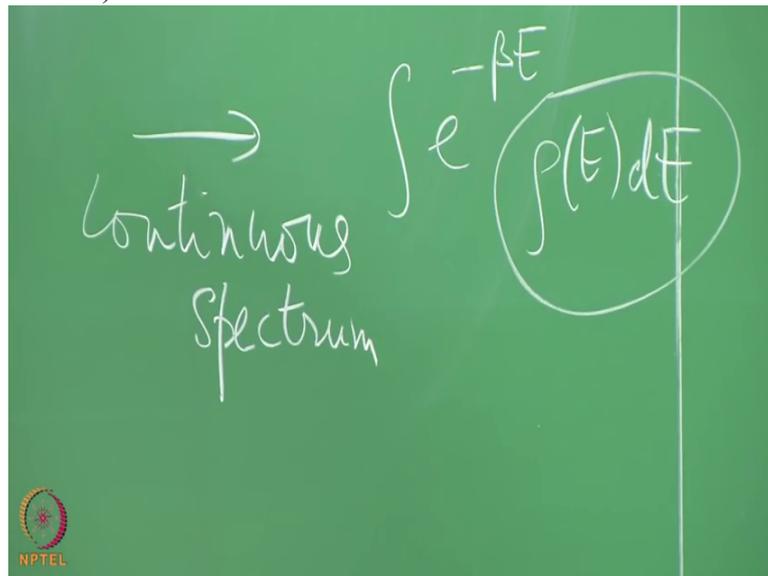
due to its dynamics between E and E plus delta E. And what would you call rho of E?

(Professor – student conversation starts)

Student: Density of states

Professor: The density of states. So you can now see that this Boltzmann's factor e to the minus beta E tells you the relative weight which is attached to the energy value E here. And the very fact that this decreases as a function of E increases tells you that at any given temperature, the higher energy states are

(Refer Slide Time 43:04)



less probable than the lower energy states, Ok, depending on this quantity here.

(Professor – student conversation ends)

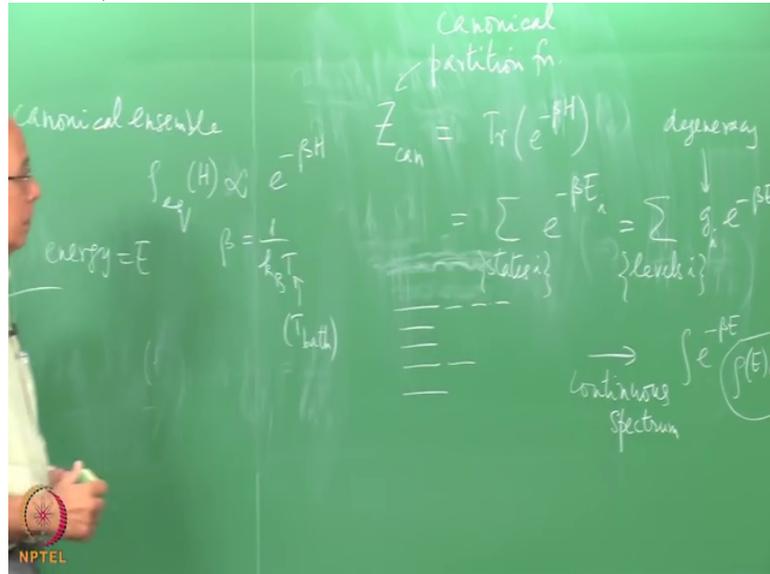
This quantity has got nothing to do with external heat bath. It has got nothing to do with temperature or anything like that. It's a property of your system. So that's got to be computed by doing whatever you do for the system, classical mechanics, quantum mechanics we don't care, whatever you do, the dynamics tells you what this density of states is. So this is where the mechanics part of it comes in and this is the statistical part.

This is the ignorance factor; this tells you we don't know what this external heat bath is doing to us at a detail level, but we do know that the relative probability with which an energy E value occurs for the system is proportional to the e to the minus beta E , Ok. This is nothing to do with classical or quantum mechanics. It is true for the canonical ensemble for both classical and quantum systems. So it's essentially, if the energy levels are bounded from below, go from zero to infinity. For example it would be like the Laplace Transform of the density of states. That is the partition function, Ok.

And the statement is that once you are in the canonical ensemble, then once you know the partition function then all quantities can be found. For instance if you take the log of this and differentiate with respect to beta and put a minus sign, you would get, to bring this E i down here, and then you get the average value of the energy etc.

So once you have the canonical partition function, all of the dynamics is derivable and more fluctuations about thermodynamics averages can also be derived. All moments are known. So once you have a knowledge of this quantity, the basic canonical partition function, canonical partition function,

(Refer Slide Time 45:12)



you have complete information about the equilibrium statistical properties of the system, Ok.

Now you can ask when do I work with this. When do I work with that? The answer is already clear. For isolated systems you would choose this, for systems in contact with the heat bath you choose this. So this is largely dictated by what are the conditions you put on the system here. And then of course you can go from one thermodynamics potential to another, just as when you have an isolated system in thermal equilibrium you would say that the internal energy of the system is at the minimum, Ok.

When you have a system which is at the fixed, at a given temperature, and the volume and the number are fixed, then you would say that the Helmholtz's free energy is at the minimum. If the pressure, temperature and number of particles is fixed, the Gibbs Free energy is at the minimum. And so on. So you choose appropriate thermodynamic variables to control the system, then depending on that, you want various ensembles, various kinds.

But the standard ones are the micro canonical and canonical ensemble and you generalize this a little bit more by saying that if this became an open system and could also exchange

particles with the surroundings, then you go towards what is called the grand canonical ensemble. Essentially you include the chemical potential in this Boltzmann's factor here. So you write here this as $\beta(E - \mu n)$ and that would be it, Ok.

You can find your own ensemble, depending on what problem you are looking at, doesn't matter, Ok. A deep question is will the answers that I get for a given physical system be the same if I compute in different ensembles? This is called the equivalence of the ensembles. It is not guaranteed, it is not guaranteed. There are exceptions to the rule.

And there are also the kind of exceptions which would violate this extensivity property here. Then the various ensembles are not equal to each other. The text book examples that you do in equilibrium statistical mechanics certainly satisfy this so people don't bother about which ensemble you compute things in, but there are cases where, many, many interesting physical cases where the ensembles are not equivalent to each other and physics will dictate the correct one that you need to choose.

So this is all I want to say about equilibrium statistical mechanics and most of the time we will work in this, canonical ensemble. The next question is, if I have a system in thermal equilibrium in the canonical ensemble, and describe it in the canonical ensemble, and I disturb it by putting an external force on it which might be time dependent. So I drive it out of equilibrium. What happens then? What happens to physical quantities? Is there a way in which I can compute it?

I can compute statistical averages. Is there a way in which I can find the time dependent probability distributions? And a very important question here, class of questions which we will spend a lot of time on is the following, suppose if I disturb this system away from thermal equilibrium and then switch off the disturbance, the system is in general expected if the disturbance was sufficiently small, expected under normal conditions to come back to equilibrium.

And a very interesting question is how does it relax to equilibrium? What are the time scales, how long will it take on the average to relax and what's the way in which it relaxes to equilibrium? That's the crucial question. Will it do so fast? Will it do so slow? What is the

characteristic time scale etc? This will of course, depend on the dynamics of what's going on inside. So the question is can we find a kind of general framework by which this question can be answered? A system moved a little bit away from equilibrium, how does it return to equilibrium?

First we got to assure ourselves that it does return to equilibrium because there could be cases, one small disturbance may move you out completely either to another state of equilibrium or somewhere else or to a multiple set of states. So we need to be assured about that. And even if you are assured about that, we need to know how does it return to equilibrium? What is the relaxation to equilibrium like?

So that's the first question we are going to look at, namely how do things relax to equilibrium when you make a small disturbance? So in some sense we will perturb it with a small perturbation, a time dependent part of the Hamiltonian which will not be a function of q s and p s but there is an external time dependent portion which is driving this system away from equilibrium. We will switch it on and off and see what happens in this case.

So first we can ask will it go to a new state of equilibrium if this force remains constant. And if I switch it off, will it come back to the old state? And if so how? How are these related to each other? So that's the business of linear response theory and that's the next question we will answer. So we will start with that tomorrow with the simple physical example which is not quite still linear response theory but it will give us, help us fix our ideas and see what's the general trick we are going to use to answer such questions? So we will start with that simple model of a single tagged particle, a colloidal particle in a fluid and then take it from there. We will stop here today.