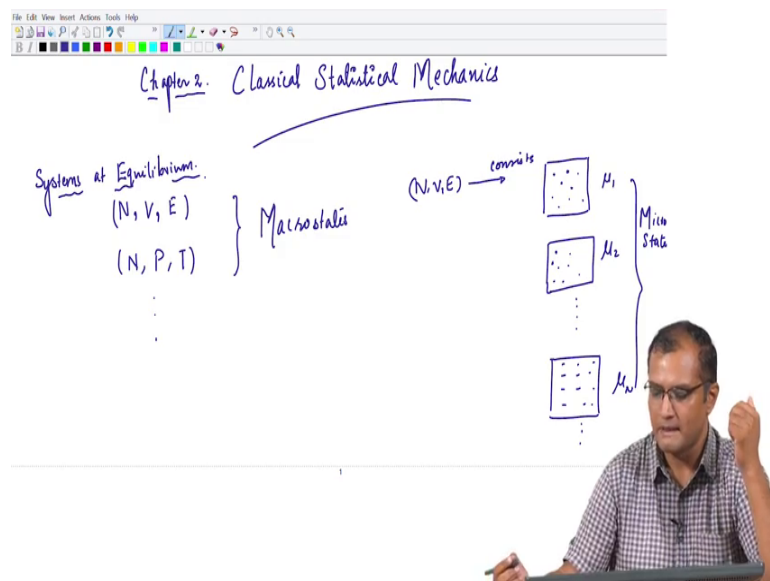


**Statistical Mechanics**  
**Prof. Ashwin Roy**  
**Department of Physics**  
**Indian Institute of Technology, Madras**

**Lecture – 11**  
**Microcanonical Ensemble**

Today we will start the second chapter on in this chapter in this course.

(Refer Slide Time: 00:23)



And we will now be, because we will be dealing with the classical systems, where quantum corrections are not required. So, this is the chapter that we will take on. And the subject of classical statistical mechanics is beautiful in the sense that, we are not really focused about exact time evolution of a trajectory of particles in the system ok.

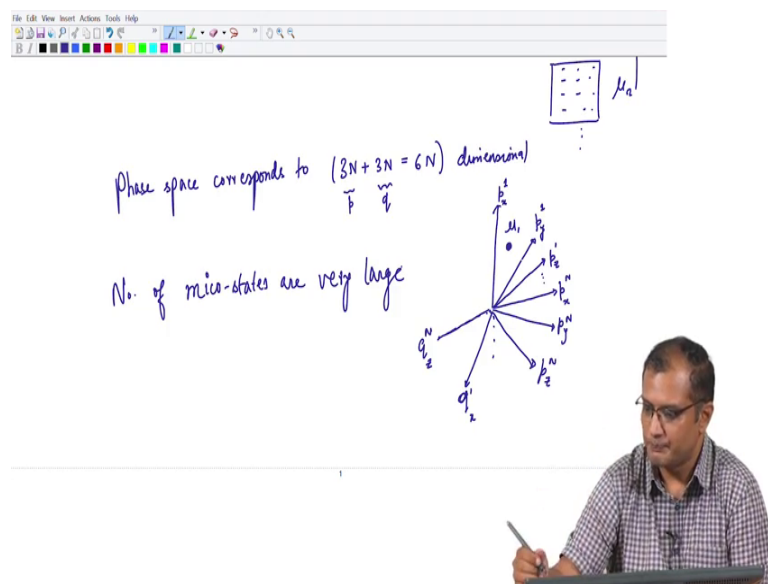
So, if you are looking at a let us say the particles of the gas in this room, I would be interested in understanding; what are the thermodynamic states accessible to the system ok. By thermodynamics states I am saying the macrostates available to the system. So, meaning for example, the values of number of particles, volume of the room and total energy of the room ok. So, this would be example of a macrostate. You could also say that you know I am interested in number of particles pressure in the room and the temperature of the room.

So, we are dealing with systems at equilibrium, and we are asking questions about states of the system which can be represented by the combinations of these variables that I have written down. So, these states are called as macrostates. And a macrostate by itself is basically characterization of system with very small number of variables. As you can see I have taken in macrostate I have taken only three variables.

But a given macrostate for example  $N V E$  which means if I take this room at a given value of  $N V$  and  $E$ . Then you can classify the system you can say that this particular microstate consists of a several micro states each different from the other, in terms of the location of the particles and their moment you know. So, I can take one macrostate and take the system in several different. So, these are basically micro states, ok.

So, this is like the specific arrangement of particles and momentum in the phase space. Now by phase space I mean, the system the coordinate in of their degrees of freedom in coordinates and degrees of freedom in a momentum coordinates.

(Refer Slide Time: 04:45)



So, phase space here corresponds to  $3 N$  momentum degrees of freedom for an  $N$  particle system, plus  $3 N$  position degrees of freedom. So, this is basically a  $6 N$  dimensional space this is coming from a momentum and this is coming from position. And in this phase space I can represent a micro state by a single point.

So, each of these  $\mu$  is that I have specified can be represented as a single point in this  $6N$  dimensional space. So, it is hard to visualize a this the space, but we can think of  $6N$  orthogonal axis. So, one of them could be the  $p_x$ ;  $x$  component of the momentum of the first particle then you can take another coordinate as a  $p_y$  of the first particle. And in this way you have taken you know you can take one more here. So, you can take  $3N$  degrees of freedom and now you can also take coordinates.

So, here a microstate here, it could be just one point its just one point here. So, I will say this is let us say micro state  $\mu_1$ ; well this is a only means that if I project this microstate on any of the axis let us say a if I project on the axis  $p_x$  then I will get the  $x$  component of the first particle. If I project it on the axis  $p_y$ , then I will get the  $y$  component of moment of the first particle and if I project it on  $q$  and  $z$ , I will get a  $z$  component of the  $n$ -th particle in the system. So, in the  $6N$  dimensional phase space, the system is actually just a single point and the evolution of system through these microstates. So, system can go from microstate  $\mu_1$  to microstate  $\mu_2$  all the way to  $\mu_n$  and these large number of micro states clearly  $n$  is very large here;  $n$  is not the number of particles I should use a different symbol here. The small  $n$  I will choose a small  $n$  because capital  $N$  is reserved for number of particles. So, I will use  $q_n$ .

So, clearly number of micro states are large, and is seem to sort of occupy these the phase space in such a way this is the projection of each microstate on the corresponding axis gives the coordinate of moment or the position of a particular particle, where a you are protecting the phase space point, where you are projecting the microstate on.

(Refer Slide Time: 09:33)

The slide shows a whiteboard with the following handwritten text:

Not required to time evolve the coordinates!

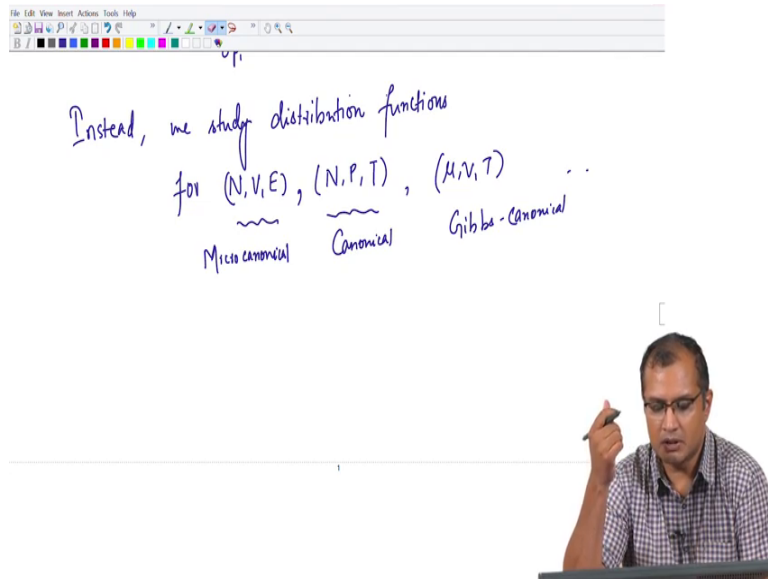
$$H(\{q_i, p_i\})$$
$$-\dot{p}_i = \frac{\partial H}{\partial q_i}$$
$$\dot{q}_i = \frac{\partial H}{\partial p_i}$$

Arrows point from the text to the variables  $q_i$  and  $p_i$  in the equations. In the bottom right corner, a man with glasses and a checkered shirt is sitting at a desk, looking at the slide.

So, basically what is being said here is that, it is not required to time evolve the coordinates, as you would do in classical mechanics, it is not required ok. That means, that in classical mechanics you would take an Hamiltonian, which is a basically function of a your position and momentum, and you would normally take the time evolution of a the position and momentum through the Hamiltonian.

So, the equation of motions that you will start with basically minus  $p_i$  dot as a  $\frac{\partial H}{\partial q_i}$  and  $q_i$  dot as a  $\frac{\partial H}{\partial p_i}$ . So, you do not require, you do not in statistical mechanics, you do not do a time evolution of your coordinates exactly.

(Refer Slide Time: 10:59)



So, what you do basically in any equilibrium system is basically, we study the distribution functions. I will describe what this distribution functions are. And for each of the equilibrium systems that I have discussed or I have described not described mentioned in the at the beginning of this lecture such as  $N V E$  systems at constant  $N V$   $N$  energy; this system is called as a microcanonical ensemble we will describe I will describe these ensembles in detail or when you specify the number of particles pressure and temperature which we call as the canonical ensemble. So, I will call this as the microcanonical ensemble. This is the canonical ensemble, or you could take Gibbs canonical ensemble.

So, instead of studying the exact Hamiltonian evolution you know or the evolution of the trajectory of particles, we will be concerned about the stationary properties of these systems. So, by that I mean that I will not be concerned about a single particles anymore, where the amount of information available is huge, but the problem also becomes intractable. Instead, we will go to the information of distributions. So, with that in mind I will take the first ensemble which is a micro canonical ensemble ok.

(Refer Slide Time: 13:17)

The slide contains the following handwritten text:

(1) Micro-canonical Ensemble:

Macrostate:  $\mathcal{H}(M) = E$

$$p_M = \frac{1}{\Omega(E, V)}$$

$$= 0 \quad , \quad \mathcal{H}(M) \neq E$$

Microstate:  $N, V, E$

$$N \sim 10^{23}$$
  
$$V \sim 100 \text{ L}$$
  
$$E \sim x \text{ Jol}$$

A small video inset in the bottom right corner shows a man with glasses and a checkered shirt speaking.

And the prototype system for each of this ensemble will be gas in a box. So, I am going to take for example, an ideal gas in this box and I am going to take this box with  $N$  particles volume  $V$  and total energy  $E$ . So, this is going to be my microcanonical ensemble.

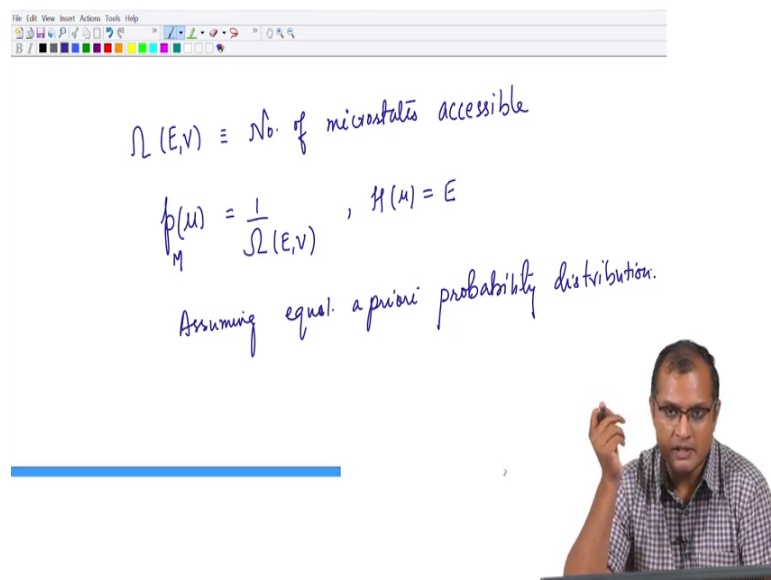
And as I said that,  $N V E$  represents a micro state here. So, you can specify a number of particles to be of the order of a you know  $10$  to the power of  $23$  you can specify the volume to be may be some  $100$  litres and you can specify some energy to be some joules ok; so  $x$  joules. And so, once you have specified this with the values of a number of particles, volume of the room and the total number of a and total amount of energy in this room. You are now basically in position to do some a statistical mechanics on the system ok.

So, by that I mean this is a system where a macrostate is specified by the condition that any macro state will have a Hamiltonian; that is nothing but the  $E$  that you specified ok. So, you have specified the energy to be  $E$  and the system could be in any micro state by micro state. I mean the exact position of the coordinates of the particles the momentum coordinates and the position coordinates. And as long as the Hamiltonian of the system is  $E$  which is the energy specified, then this probability of finding a system in that microstate corresponding to a macro state  $M$  would be nothing but  $1$  upon the total

number of microstates that the system has access to. And this will be the function of  $E$  and  $V$ .

So, if I increase the number of a particles or if I increase the volume, then the number of accessible states will also increase. And so, this is as long as your Hamiltonian is equal to the specified energy. And I know the moment we pick up a micro state where the Hamiltonian is not equal to  $E$ , then we will say that this is 0. So, the microstate has 0 probability if the energy corresponding to that micro state is nothing, but  $E$  ok.

(Refer Slide Time: 17:05)



$\Omega(E, V) \equiv \text{No. of microstates accessible}$

$p_M = \frac{1}{\Omega(E, V)}, H(\mu) = E$

Assuming equal a priori probability distribution.

So,  $\omega$  here corresponds to a number of microstates accessible to the system. And the fact that I have taken each micro state to have probability of  $1/\omega$ , this essentially means that; I am going to write it here the fact that I have taken the probability of any microstate corresponding to a macrostate  $M$  as  $1/\omega$  if  $H(\mu) = E$ . This means that I am assuming equal a priori distribution or equal a probability a priori probability distribution.

So, the meaning is if your macro state has  $\omega$  micro states then each microstate is has an equal probability for in that macrostate ok.

(Refer Slide Time: 18:51)



$$\text{Boltzmann Entropy: } S = k_B \ln \Omega$$

(1) Zeroth Law of Thermodynamics:



So, with that consideration, we can always write down the Boltzmann hypothesis for a entropy  $S = k_B \ln \Omega$  ok. So, this equal a priori probability distribution allows me to involve the Boltzmann's definition for entropy which is not nothing but a statement that the entropy is a you know is a negative extensive quantity and the calculation of entropy is a logarithmic related to a number of states accessible to the system.

So, armed with this important rule we can look at some cases interesting cases you can actually revisit some laws of thermodynamics. In fact, you can derive statistically laws of thermodynamics in the context of micro canonical ensemble. So, you are going to give strict to micro canonical ensemble, and give some discussion on laws of thermodynamics. So, the first law that I would discuss is the Zeroth law of thermodynamics ok. Now, I would not state the law straightaway in fact, I will present a small experiment, and the Zeroth law of thermodynamics will appear naturally at the end of it.



(Refer Slide Time: 20:57)

(I) Zeroth Law of Thermodynamics:

$\Delta E=0$   
 $\Delta V=0$   
 $E_A$   
 $S_A = k_B \ln \Omega_A$

$\Delta E=0$   
 $\Delta V=0$   
 $E_B$   
 $S_B = k_B \ln \Omega_B$

A, B are in thermal & Mechanical equilibrium

So, let me just take two systems at equilibrium ok. So, these are two systems that are let us call the systems as A and system B, and let us say that they are at equilibrium both thermal and mechanical equilibrium. Now, the meaning of this is that the systems are thermally isolated which means there is no exchange of heat with the surrounding. So, there is absolutely no exchange of heat with the surrounding and you have fixed walls that cannot move.

So, there is absolutely no way in which energy can leak out of the system and the walls are fixed. So, the volume cannot change. So, they are thermally and mechanically isolated. And the systems have energy content let us say the energy content of the system is  $E_A$  and the internal energy of the system is  $E_B$  ok. So, the systems are in thermal and mechanical equilibrium.

And if I ask you, what is the entropy of the system? So, you can individually say that the entropy of my first system would be  $k_B \ln \Omega_A$ ; where  $\Omega$  is the number of states in which our system A can exist and the entropy of the system will be  $k_B \ln \Omega_B$ . So, where  $\Omega_A$  and  $\Omega_B$  are the number of states in which systems A and B can exist.

(Refer Slide Time: 23:49)

Connect these systems

A, B can exchange Energy now.

$$S_A(E_A) + S_B(E_B) = \text{Total Entropy}$$

Now, let us you know connect the systems. So now, I am going to connect these systems ok. So, let me. So, this is my system B and this is my system A, I have connected these two systems in such a way that the system A and B can exchange energy ok, but they are shielded from the surroundings. So A, and B will not take or give any energy to the surroundings, they can exchange energy internally they can energy exchange energy between themselves, but they are still isolated both mechanically and thermally from the surroundings ok.

So, A and B can exchange energy now ok. Only energy the walls are all fixed. So, there is no volume exchange between the A and B. Now what happens to the; what can you tell about the joint entropy of the system? So, let us say immediately after you have connected the systems, the entropy of the joint system is  $S_A$  a function of  $E_A$  plus  $S_B$  a function of  $E_B$  this is the total entropy.

But wait the system is expand you know if the system is redistributing energy.

(Refer Slide Time: 26:29)

..... Wait to equilibrate.....

$S(E) = S_A(E_A^*) + S_B(E_B^*)$

So, you wait for sometime wait to equilibrate. So, you come back after sometime and now you see that the total entropy. Keep in mind that the total system is you know isolated which means our energy initially was  $E_A$  plus  $E_B$  it is still  $E_A$  plus  $E_B$  and I am call it as a the big  $E$ , that is my energy. So, I am going to underline this that my total energy was always been  $E_A$  plus  $E_B$ .

So, what has happened is, after waiting for a long amount of time I see that the energy of my system A has become  $E_A^*$  and the energy of my system B has become  $E_B^*$ . And if I call this as the equilibrium state of the joint system, I can write down the final entropy which is you know  $S$  the total entropy of the joint system and the joint system as energy  $E$  as the entropy of system A, but which is now sitting at energy  $E_A^*$  plus entropy of the system B which is now sitting at energy  $E_B^*$ , and this is actually a state of maximum entropy.

We can prove that is the state of maximum entropy, because if the systems had different energies and they exchanged energy between them after bringing them into contact. Then there is no way this system will go back to initial configuration on its own or spontaneously. Which means, this redistribution of energy was irreversible and when you say this energy was irreversible, this redistribution was irreversible the entropy of the system has definitely increased and we can find this out.

So, what we really mean here is, if you look at the change in entropy which is delta S. So, you can find out the change in entropy from.

(Refer Slide Time: 29:49)

$S(E) = S_A(E_A) + S_B(E_B)$

Q: What is the condition for equilibrium.

---

$$\delta S_A = \left. \frac{\partial S_A}{\partial E_A} \right|_{V_A} \delta E_A$$
$$\delta S_B = \left. \frac{\partial S_B}{\partial E_B} \right|_{V_B} \delta E_B$$

So, I am going to write down the question that, what is the condition for equilibrium. So, the condition for equilibrium is nothing but a certain state where this entropies of each subsystems a and b have maximized.

So, for that we must allow for establishment of identical temperatures on both sides and that is the condition that will derive as a consequence of a you know entropy maximization. So, you could basically say that the change in entropy the system A would be  $d S_A$  over  $d E_A$  at constant volume. And, you can think of change in entropy of system B as  $d S_B$  this would be total trophies. So, this would be ok.

(Refer Slide Time: 32:05)

$$\delta S = \delta S_A + \delta S_B = \left. \frac{\partial S_A}{\partial E_A} \right|_{V_A} \delta E_A + \left. \frac{\partial S_B}{\partial E_B} \right|_{V_B} \delta E_B$$

... Recall that  $E = E_A + E_B = E_A^* + E_B^*$

$$\delta E = 0 = \delta E_A + \delta E_B$$
$$\Rightarrow \delta E_A = -\delta E_B$$
$$\delta S = \left. \frac{\partial S_A}{\partial E_A} \right|_{V_A} \delta E_A + \left. \frac{\partial S_B}{\partial E_B} \right|_{V_B} (-\delta E_A)$$

And the overall change in entropy would be nothing, but delta S A plus delta S B which is nothing but delta S A upon S delta A E A plus this is the overall change in entropy. And now I am just going to recall the fact that, the total energy of the system is constant. So, I will write down E as E A plus E B its of course, also equal to E A star plus E B start the sum of final energies, but that is not required.

That means, I can write down my delta E which is 0 which is equal to delta E A plus delta E B which simply says that delta E A is equal to minus delta E B if you if you substitute it up stairs what you see here is that, the delta S comes out to be delta SA over delta E A into delta E A constant value would V A plus delta S B over delta E B at constant value of V B and I a substituting delta E B as minus delta E A and if you take a delta E A constant.

(Refer Slide Time: 34:21)

$$\delta S = \left( \frac{\partial S_A}{\partial E_A} \Big|_{V_A} - \frac{\partial S_B}{\partial E_B} \Big|_{V_B} \right) \delta E_A$$

thermal  
 If equilibrium is achieved,  $\delta S = 0$   
 arbitrary

Now, you are looking at the condition for equilibrium here. Like I said before if the evolution of your two systems after connection was such that they arose in reversible change ok. Some energy went from hot system to a cold system. Now this is an irreversible change, you cannot after the two systems have equilibrated, you cannot bring the energy back you know you cannot recover the initial configuration.

So, there is some amount of information that is lost, which is said as the change being irreversible. Now, when the change was irreversible, you will definitely expect a positive change in the entropy it will be greater than 0. But we are chasing a condition for equilibrium, which means if you are at equilibrium then there will not be any change in entropy any change of energy from any passage of energy from a from body A to B is reversible because you are at equilibrium. And if that is a case, then for any arbitrary energy change to make  $\delta S = 0$  I must demand at my pre factor here is 0 only then  $\delta S$  will be 0.

So, if equilibrium is achieved and by equilibrium I mean thermal equilibrium then I have to demand that the pre factor is 0.

(Refer Slide Time: 36:41)

then,  $\left. \frac{\partial S}{\partial E_A} \right|_{V_A} = \left. \frac{\partial S}{\partial E_B} \right|_{V_B}$

Defining  $\frac{1}{T_{A,B}} = \left. \frac{\partial S}{\partial E_{A,B}} \right|_{V_{A,B}}$

Condition for equilibrium:  $\frac{1}{T_A} = \frac{1}{T_B}$

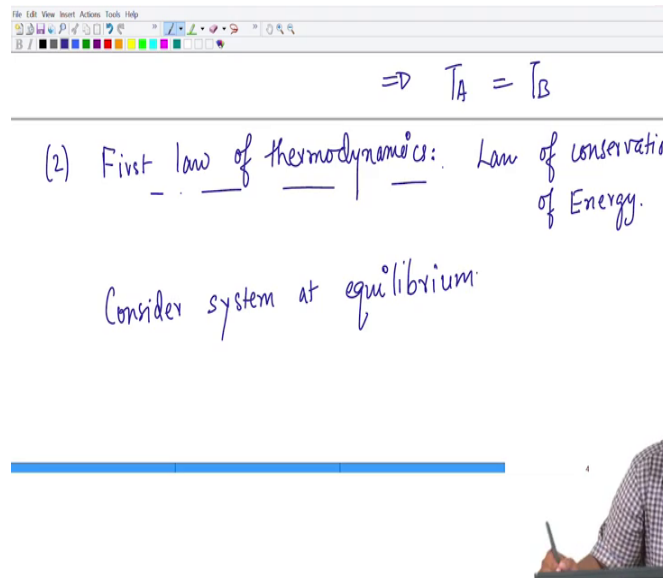
The pre factor is simply delta S over delta E A at a constant volume equals to. If the bracket is 0 which means these two values are equal. Now this is the condition for equilibrium.

And, I can now define empirically the empirical temperature as you know  $1$  upon  $T$ . So, if I define  $dS$  over  $dE$  as  $1$  upon  $T$ , then this quantity  $dS$  over  $dA$  at a constant value of a  $dS$  over  $dE$  A at constant value of the volume of system A is nothing but  $1$  over inverse temperature for the system A. So, I will say this is A comma B similarly this is A comma B, this is A comma B ok. So, the condition for equilibrium is simply equivalence of the two temperatures. So, remember how we derive this condition for equilibrium.

We just completed the change in entropy for a re distribution of energy between two systems. Now as long as we are away from equilibrium, this change in entropy will be non 0 which means your temperatures are not the same. The moment you reach equilibrium which could be let us say after an hour or after 2 hours or after 10 hours whatever be the case we come back. And now when we compute the change in entropy you will see that there is absolutely no change, because any energy that is exchanged across these two systems at equilibrium is basically a reversible change or reversible process.

And when that happens you take the entropy change to be 0 and this would be the condition of thermodynamic equilibrium between the systems A and B. So, this is like the zeroth law of thermodynamics.

(Refer Slide Time: 39:19)



The image shows a whiteboard with handwritten text. At the top, it says  $\Rightarrow T_A = T_B$ . Below that, it says "(2) First law of thermodynamics: Law of conservation of Energy." and "Consider system at equilibrium". A man in a checkered shirt is visible in the bottom right corner, writing on the whiteboard.

This is essentially says that the two systems will continue to exchange energy until the temperatures become equal ok. So for example, you connect them wait for a minute and ask the several question, has the equilibrium be achieved while you will see a are the two temperatures same?

If the two temperature are not same you will you know wait longer. Because, when the temperatures are not same any energy distribution any energy changed that has happened between the two is not reversible it is irreversible. And this irreversible exchange of energy will continue to happen until the two temperatures are same that is the condition for equilibrium. We can proceed from here and derive the first law as well.

So, we can candidate the first law which is essentially nothing, but I would say its book keeping of energy. So, you simply associate first law of a thermodynamics as a law of conservation of energy or bookkeeping of energy, you simply account for each mode of energy injection and work done and the first law of thermodynamics is nothing but a statement of a energy contribution. So, we shall see what that means. Suppose you take a system at equilibrium. So, consider a system at equilibrium ok.



(Refer Slide Time: 41:51)

The diagram illustrates a thermodynamic process. The top box represents the initial state with parameters  $N, V, E$  and entropy  $S(E, V)$ . The bottom box represents the final state after a small expansion, with parameters  $N, V + \delta V, E - P \delta V$ . A horizontal blue bar is drawn between the two boxes, indicating that the work done is not an exact differential. The text 'Allow Reversible work:' is written to the left, and the equation  $dW = -P \delta V$  is written below it. A vertical dashed line with arrows at both ends is labeled  $\delta V$ , representing the change in volume.

So, this is a system having some energy  $E$  and some volume and some number of particles, some volume in energy  $E$  and the system is at equilibrium now what we do is we allow. So, at this stage let us say the entropy of the system was a function of  $E$  and  $V$  we are keeping  $N$  constant. So, we can drop  $N$  and what I am doing is, am allowing the system to expand the little reversibly. So, there is some expansion of the system that I call as that I will address as  $\delta v$ .

So, some reversible work. And this reversible work is basically because is an exact differential, I am using horizontal bar here; means that this work cannot be traced the you know it is basically path dependent, it is not an exact differential and so, this is highlighted by this strike off and I call it as minus  $P$  into  $\delta v$ .

Now, the reason why I have taken a minus sign here is that, any work done by the system will lead to reduction energy and internal energy. So, if you would take an system and allow it to expand, there is a  $\delta v$  which is positive. So,  $P \delta v$  is positive, but minus  $P \delta v$  will be negative. So, its internal energy will be reduced, because the gas is has done some work. So, it is now sitting at a lower internal energy, it did work on account of its internally.

So, we are taking the convention as a minus  $p \delta v$  that explain the minus sign now what has happened after the small expansion is that,  $N$  has remain the same, but both  $V$

and E have changed ok. So, my system is now sitting at  $N V$  plus  $\delta v$  and energy  $E$  minus  $P \delta v$  fine. So, let us compute the change in energy the change in entropy.

(Refer Slide Time: 45:23)

Change in entropy:  $\delta S(E, V) = ?$

$$S(E - P\delta v, V + \delta v) = S(E, V) + \left. \frac{\partial S}{\partial E} \right|_V \delta E + \left. \frac{\partial S}{\partial V} \right|_E \delta v \quad \text{--- (1)}$$

Recall,  $\delta Q = 0$   
hence  $\delta E = \delta W = -P\delta v$

Show the change in entropy due to this reversible work that we did on the system is basically  $\delta S$  ok.

But I want to know; what is this  $\delta S$  as a function of  $E$  and  $V$ . We can compute this by a simple first order Taylor expansion. So, we can compute the entropy the final entropy by a simple Taylor expansion, we say that the energy after the work is equal to the energy before we did the work plus  $\delta S$  over  $\delta E$  at constant value of  $v$  in to  $\delta E$  plus  $\delta S$  over  $\delta v$  at constant value of  $E$  into  $\delta v$ .

So, this is the first order expansion of entropy around  $E$  and  $V$  is expanded around  $E$  and  $V$  as you can see that these derivatives are taken at  $E$  and  $V$  here. So, this is the first order expansion around energy  $E$  and volume  $V$  let us call this as equation 1. Now you recall that the system is thermally isolated ok. So, I will say that my data  $Q$  is 0; and so the only change in energy that can happen is due to the work that has been done on the system which is basically minus  $P \delta v$  ok.

The energy of the system can only changed due to the work done on the system, because the heat given to the system is 0 is thermally isolated.

(Refer Slide Time: 48:15)

hence

$$S(E - P\delta v, V + \delta v) - S(E, V) = \left. \frac{\partial S}{\partial E} \right|_V (-P\delta v) + \left. \frac{\partial S}{\partial V} \right|_E \delta v$$
$$\delta S = \left( \left. \frac{\partial S}{\partial E} \right|_V (-P) + \left. \frac{\partial S}{\partial V} \right|_E \right) \delta v$$

Recall that  $\frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_V$

So, in equation 1 I can substitute this thing and I can write down this equation 1 as  $S(E - P\delta v, V + \delta v) - S(E, V)$  on the left hand side. On the right hand side I will write as  $\left. \frac{\partial S}{\partial E} \right|_V (-P\delta v) + \left. \frac{\partial S}{\partial V} \right|_E \delta v$ .

And call the left hand side as the change in the entropy and the right hand side you can take  $\delta v$  outside common, and call this is as  $\left. \frac{\partial S}{\partial E} \right|_V (-P) + \left. \frac{\partial S}{\partial V} \right|_E$  into  $\delta v$  ok. And now, what we have learnt from the first law discussion that, the thermodynamic definition of temperature is  $\left. \frac{\partial S}{\partial E} \right|_V$ .

So, what we will do is, we will substitute this in this expression.

(Refer Slide Time: 49:49)

Recall that  $\frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_V$

$$\delta S = \left( \frac{-P}{T} + \left. \frac{\partial S}{\partial V} \right|_E \right) \delta V$$

This variation is due to reversible work,  $\delta S = 0$

$$\Rightarrow \frac{P}{T} = \left. \frac{\partial S}{\partial V} \right|_E \quad \text{--- (2)}$$

So, over delta S becomes minus P over T plus del S no in fact, I what I will do here is ok. Now, this is the variation in the entropy that is done very close that is done very slowly so that I am always at equilibrium. Because, if you remember this variation is due to reversible work which means I am always at equilibrium.

So, delta S must be 0 why? If data is not zero, then basically I have lost some information permanently and that is the indication that the process is not reversible. Then any loss of information is basically a consequence of an irreversible process you cannot recover it. So, that would be associated with a positive change in entropy. And if I am claiming that the process is reversible to be invest, then this delta is must be 0 no information is lost that means for any arbitrary delta v that I take ok.

This variation in volume is arbitrary I could have taken change in volume as per my liking, but any arbitrary volume displacement that I take such that the work done is reversible, and that should lead to 0 entropy change and that is only the possible if the pre factors here is 0. Because, delta v is not 0 it is arbitrary. The product of two numbers is always 0 one of them is arbitrary, while you will say the second number has to be 0 ok. So, I can take delta v to be non zero.

So, this is only possible the product will go to 0 only if the pre factor here which is what I have written in the parenthesis is 0. So, I will write down P over T is equal to del S over del v at constant energy. So now, you can compare equation 2 in equation 1 and re write

equation 1 ok. So, what I will do here is basically take the entropy on the right hand side left hand side and write down equation 1 again.

So, I am going to just. So, basically what I am going to do is you know I am just going to write down equation 1 again.

(Refer Slide Time: 54:09)

Rewriting eqn (1) using (2),

$$dS = \frac{\delta E}{T} + \frac{P}{T} \delta v$$

Now including all variations.

So, we just using equation 2 I can say that, delta S is basically you can write down d S over d E is 1 upon T. And if you look at the third term here is d S over d v at constant energy which is equal to P by T from equation 2 into derivation of volume V ok.

So, now including all variations which means you are no longer during this infinitesimal derivatives. If we include all variations I can write down this law as dS equals to d E over T plus P d v over T.

(Refer Slide Time: 55:19)

Now including all variations,

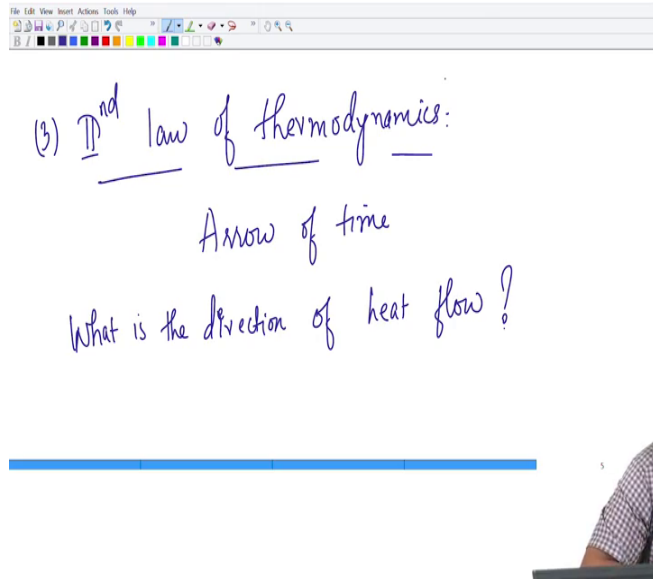
$$ds = \frac{dE}{T} + \frac{PdV}{T}$$

$\Rightarrow Tds = dE + PdV$  — 1<sup>st</sup> law of thermodynamics.

In other words I can write  $T ds$  it is the heat given to the system as a change in internal energy plus work done by the system. So, this is basically your first law of thermodynamics which if you see is nothing but an energy conservation statement that, if you give an amount of energy to the system which is  $T ds$ , it lonely increase the energy of the system by an amount  $dE$  plus if you allow the system to expand the work done would be  $P dv$  ok. So, that is the statement of the first law.

And with this we are now in a position to look at the second law of thermodynamics, which is basically a statement of a.

(Refer Slide Time: 56:33)



So, now I am going to discuss the second law of thermodynamics, which basically gives you the arrow of time and what is meant by the arrow of time? It simply means that now so far we have taken two systems and we have connected them and we asked the question what is the condition of equilibrium.

So, the condition of equilibrium is wait long enough such that the temperatures become the same, fine. But we do not have any idea as to what is the direction of flow of heat net direction of flow of heat from one body to the other, which is basically saying in which direction the time will forget.

So, in other sense we are basically asking question what would be the direction of heat flow, ok. So, what is the direction of heat flow? In a problem of a heat conduction; so we can give this direction of heat flow from the second law.

(Refer Slide Time: 58:21)

Total Entropy =  $S = S_A + S_B$

Right after connection      At equilibrium

$$S_A(E_A) + S_B(E_B) < S_A(E_A^*) + S_B(E_B^*)$$

∴ Change:  $\Delta S = S_A(E_A^*) - S_A(E_A) + S_B(E_B^*) - S_B(E_B) \geq 0$

So, you can basically say that the total entropy which is given as  $S$  that is nothing but  $S_A$  function of  $E_A$  plus  $S_B$  a function of  $E_B$ , you know which is basically soon after I just call as  $S_A$  plus  $S_B$  and give the independent variables very shortly ok. So, I am going to write down the situation all right. So, I will write down right after connection and at equilibrium. So, at equilibrium I know that the entropy would be  $S$  of  $A$  at  $E_A^*$  plus  $S$  of  $B$   $E_B^*$ , and right after connection was a  $S$  of  $A$   $E_A$  plus  $S$  of  $B$   $E_B$  and this entropy is definitely larger than the entropy to begin with ok.

So, that is the entire concept of a irreversible change. So, the initial entropy is definitely lesser than the final entropy, because you have lost some information. So, you have total entropy, change has to be positive. So, if I want to compute the change in entropy: the change could be  $\Delta S$  and that change will be nothing but  $S_A(E_A^*) - S_A(E_A)$  plus  $S_B(E_B^*) - S_B(E_B)$  and I know that this change will be greater than equal to 0, because I have you know the change is irreversible ok.



(Refer Slide Time: 61:03)

$$\therefore \text{Change: } \delta S = S_A(E_A^*) - S_A(E_A) + S_B(E_B^*) - S_B(E_B) \geq 0$$

Irreversible

$$\Rightarrow \left. \frac{\partial S_A}{\partial E_A} \right|_{V_A} \delta E_A + \left. \frac{\partial S_B}{\partial E_B} \right|_{V_B} \delta E_B \geq 0$$

$$\Rightarrow \frac{1}{T_A} \delta E_A + \frac{1}{T_B} \delta E_B \geq 0$$

So, if I write on this delta S. So, the right hand side basically means  $S_A(E_A^*) - S_A(E_A) + S_B(E_B^*) - S_B(E_B)$  is nothing but delta S A over E A into delta E A plus delta S B can this is greater than equal to 0, fine. So, basically what is meant is, this quantity is this thing and this quantity is this term. So, basically I am writing down the change in entropy as, the rate multiplied by the total change in energy. Now, this quantity is nothing but 1 upon T A from the definition of temperature into delta E A and I have 1 upon E B into delta E B which is greater than 0.

(Refer Slide Time: 63:07)

Since  $\delta E_A = -\delta E_B$  ( $E_A + E_B = E$  (const))

$$\Rightarrow \left( \frac{1}{T_A} - \frac{1}{T_B} \right) \delta E_A \geq 0$$

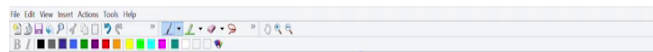
If  $T_B > T_A$  B is hotter than A.

$$\frac{1}{T_A} - \frac{1}{T_B} > 0$$

And since,  $\Delta E_A$  is equal to minus  $\Delta E_B$  that is because  $E_A + E_B$  is constant. You can rewrite this in equality as  $\frac{1}{T_A} \Delta E_A$  minus  $\frac{1}{T_B} \Delta E_B$  into  $\Delta E_A$  greater than or equal to 0. Now this is the beauty of the second law that it gives you the direction of heat flow. See the left hand side is a positive quantity. And that means, if you take  $T_B$  to be greater than  $T_A$ , so B is hotter than A. That means the quantity in the bracket will be definitely a you know a positive quantity.

So,  $\frac{1}{T_A} \Delta E_A$  minus  $\frac{1}{T_B} \Delta E_B$  will be positive because  $T_B$  is lesser than  $T_A$ . Now  $T_B$  is greater than  $T_A$  now to make the quantity positive overall quantity positive

(Refer Slide Time: 64:29)



If  $T_B > T_A$  B is hotter than A.

$$\frac{1}{T_A} - \frac{1}{T_B} > 0$$

implies  $\Delta E_A > 0$  A has received net flow of energy.



I want the  $\Delta T_A$  should be also greater than 0. Now what does this mean? Which means your object A has received a net flow or a net flow of energy, which is expected, because B was hotter than A you cannot have a hot body taking net flow of energy from a cooler body that is not possible.

So, the direction of heat flow is basically decided by the second law of thermodynamics, and that was naturally derived in the under the constraint of a you know the fact that the entropy of the system has to always increase if the process is irreversible ok. So, we had taken in case of a irreversible loss of information, and that has given as the condition that the heat flows from hotter body to a cooler body

So, that ends today's discussion. And next class we will start with the simple examples of a in microcanonical ensemble, and we will formalize the various concepts of a microcanonical ensemble.