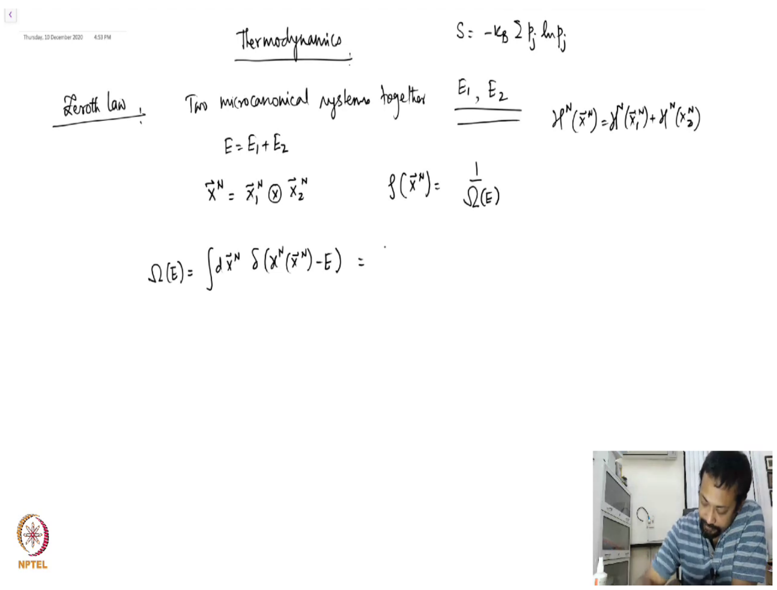
Statistical Mechanics
Prof. Dipanjan Chakraborty
Department of Physical Sciences
Indian Institute of Science Education and Research, Mohali

Lecture - 22
Microcanonical Ensemble

(Refer Slide Time: 00:20)



Thursday, 10 December 2020 4:53 PM

Thermodynamics :

$S = -k_B \sum p_j \ln p_j$

Zeroth law :

Two microcanonical systems together E_1, E_2

$\mathcal{H}^N(\vec{x}^N) = \mathcal{H}^N(\vec{x}_1^N) + \mathcal{H}^N(x_2^N)$

$E = E_1 + E_2$

$\vec{x}^N = \vec{x}_1^N \otimes \vec{x}_2^N$

$\rho(\vec{x}^N) = \frac{1}{\Omega(E)}$

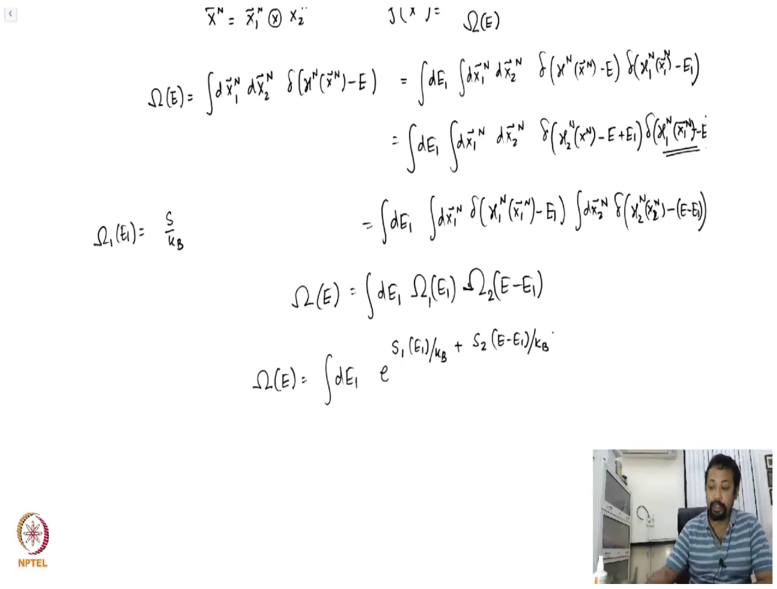
$\Omega(E) = \int d\vec{x}^N \, \delta(\mathcal{H}^N(\vec{x}^N) - E) =$

So, now we want to make the connection with thermodynamics. Although the first connection that we made with thermodynamics was with the expression minus K B sum over p j ln p j as the entropy because this has all the properties of the entropy that we encountered in thermodynamics. It is an additive quantity which means its an extensive quantity its monotonic function. So, everything is satisfied just as we just as we had seen in thermodynamics right.

Now, the first law of thermodynamics is the zeroth law and we have seen what the zeroth law essentially tells you that it brings in the concept of a temperature right. So, let us bring two microcanonical systems together, so that one of them have the energy E 1 and the other one has the energy E 2.

When you bring this together the total energy becomes E 1 plus E 2 right and you know the interaction between the parts. So, that the microstates becomes X 1 N outer product X 2 N correct your density rho of X N is 1 over omega times E. Where omega of E is now has to be carefully defined is essentially integral d of X N delta of h in X N minus E. And the Hamiltonian given these two energies the Hamiltonian of the system is combined system is X 1 N plus h n X 2 N correct.

(Refer Slide Time: 02:40)



$\vec{X}^N = \vec{x}_1^N \otimes x_2$ $\qquad$ $\rho(x) = \qquad \Omega(E)$

$$\Omega(E) = \int d\vec{x}_1^N \, d\vec{x}_2^N \; \delta(\mathcal{H}^N(\vec{x}^N) - E) = \int dE_1 \int d\vec{x}_1^N \, d\vec{x}_2^N \; \delta(\mathcal{H}^N(\vec{x}^N) - E)\, \delta(\mathcal{H}_1^N(\vec{x}_1^N) - E_1)$$

$$= \int dE_1 \int d\vec{x}_1^N \, d\vec{x}_2^N \; \delta(\mathcal{H}_2^N(x^N) - E + E_1)\, \delta(\mathcal{H}_1^N(\underline{\underline{\vec{x}_1^N}}) - E$$

$$\Omega_1(E_1) = \frac{S}{k_B} \qquad = \int dE_1 \int d\vec{x}_1^N \, \delta(\mathcal{H}_1^N(\vec{x}_1^N) - E_1) \int d\vec{x}_2^N \, \delta(\mathcal{H}_2^N(\vec{x}_2^N) - (E - E_1))$$

$$\Omega(E) = \int dE_1 \, \Omega_1(E_1)\, \Omega_2(E - E_1)$$

$$\Omega(E) = \int dE_1 \; e^{S_1(E_1)/k_B + S_2(E - E_1)/k_B}$$

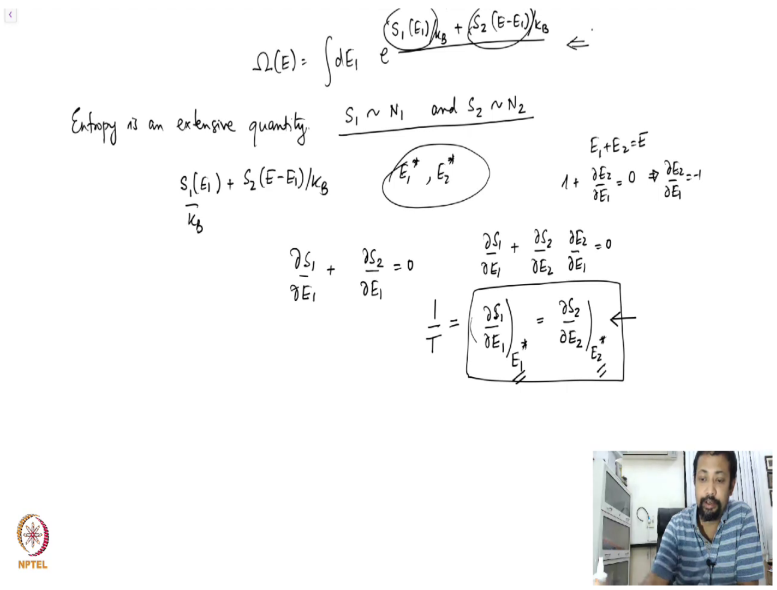
So, this becomes, so let us rewrite this carefully this is d X 1 N d X 2 N delta of H N X N minus E right good. So, now I let us recast this equation as d X 1 N d X 2 N delta of H N X N minus E delta of H 1 N X N minus E 1 these two the left and the right hand sides are identical there is no difference in that right.

But the moment you bring this one also has to write down this carefully. The moment you introduce this I can equivalently delta of H 2 N X N minus E plus E 1 delta of H 1 N X 1 N minus E 1. So, then the integral of E 1 will bring in the using the delta function if you know integrate of E 1 this E 1 is going to be replaced by this.

So, this clearly tells you that this is d X 1 N delta of H 1 X 1 N minus E 1 d X 2 N delta of H 2 X N X 2 N minus E minus E 1. And you quickly identify this to be d E 1 omega E 1 times omega E minus E 1 right. So, you bring two micro system microcanonical systems together each had energy one had energy E 1 another one had energy E 2 and then you bring them together. So, this is the total number of micro states for the joint system.

So, omega E is integral d E 1 this has to be omega 1 E 1 this has to be omega 2 E minus E 1 right, but omega 1 E 1 from the definition of entropy is S over K B. So, this is S 1 E 1 over K B plus S 2 E minus E 1 over K B correct.

(Refer Slide Time: 05:43).



$$\Omega(E) = \int dE_1 \, e^{\underline{S_1(E_1)/k_B + S_2(E-E_1)/k_B}} \Leftarrow$$

Entropy is an extensive quantity. $\underline{S_1 \sim N_1 \text{ and } S_2 \sim N_2}$

$$\frac{S_1(E_1)}{k_B} + S_2(E-E_1)/k_B \qquad E_1^*, E_2^*$$

$$E_1 + E_2 = E$$

$$1 + \frac{\partial E_2}{\partial E_1} = 0 \Rightarrow \frac{\partial E_2}{\partial E_1} = -1$$

$$\frac{\partial S_1}{\partial E_1} + \frac{\partial S_2}{\partial E_1} = 0 \qquad \frac{\partial S_1}{\partial E_1} + \frac{\partial S_2}{\partial E_2}\frac{\partial E_2}{\partial E_1} = 0$$

$$\frac{1}{T} = \boxed{\left(\frac{\partial S_1}{\partial E_1}\right)_{E_1^*} = \left(\frac{\partial S_2}{\partial E_2}\right)_{E_2^*}} \leftarrow$$

Now, entropy is an extensive quantity right. So, therefore, since S this would mean that S 1 is proportional to N 1 and S 2 is proportional to N 2 with the understanding that both N 1 and N 2 are very large. Consequently with this since this term scales with N 1, this term scales with N 2 this argument of the exponential is very very large. And I can evaluate this integral using a saddle point method at the extremum point of this expression.

And suppose I do that and this gives me two energies E 1 star and E 2 star which means what is being said here is that if once I bring the two systems microcanonical systems together they find a joint equilibrium by extremizing this quantity, correct? How will we extremize? Well del S 1 del E 1 plus del S 2 del E 1 is equal to 0 right.

So, which means del S 1 del E 1 plus del S 2 del E 2 del E 2 del E 1 is equal to 0. This is the saddle point you are trying to determine E 1 and E 2 star, but E 1 plus E 2 is the total energy

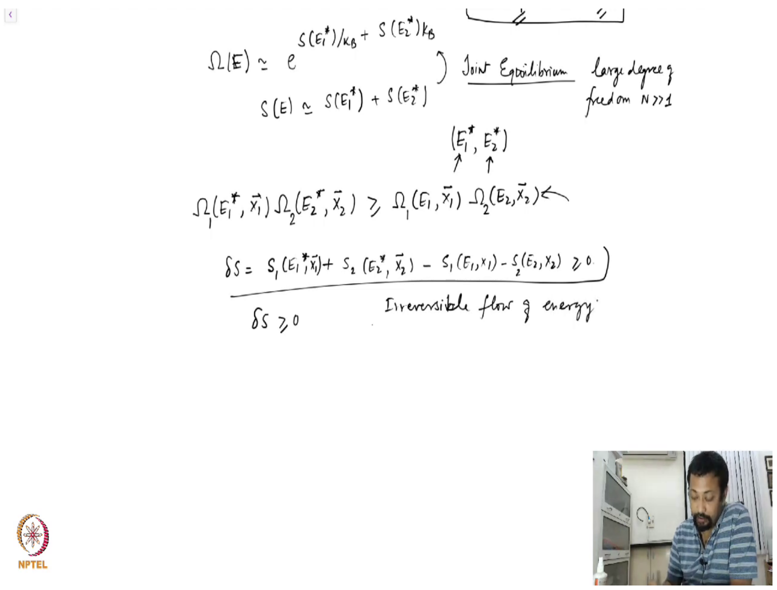
E. And therefore, del E 2 del E 1 is equal to 1 plus del E 2 del E 1 is 0 which means del E 2 del E 1 is minus 1 and therefore, you have del S 1 del E 1 at E 1 star is equal to del S 2 del E 2 and E 2 star.

This effectively tells you that when the two microcanonical systems have been brought together and they go into a joint equilibrium. And that joint equilibrium happens by extremizing this expression the entropy, which gives you E 1 star E 2 star and this condition is satisfied. And this from thermodynamics we know that is the inverse of the temperature. So, the joint equilibrium when they come to a joint equilibrium there is a thermodynamic property which becomes equal for both of them.

And this is essentially the sense of the zeroth law that if a, and b are brought together then b and c are brought together then are in equilibrium then a and c also are in equilibrium. So, therefore, we see that that we saw in the thermodynamics that the essence of the zeroth law was that it tells you that there is a common thermodynamic state function, when all the systems are in joint equilibrium and this is exactly also what we find out.

So, we bring the two microcanonical systems together bring them to a joint equilibrium and we see that these two derivatives must be equal at the joint equilibrium at these energies E 1 and E 2 star. And these two are essentially 1 by is the inverse of the temperature.

(Refer Slide Time: 10:11)



$$\left.\begin{array}{l}\Omega(E) \simeq e^{S(E_1^*)/k_B + S(E_2^*)k_B} \\ S(E) \simeq S(E_1^*) + S(E_2^*)\end{array}\right\}$$ Joint Equilibrium

large degree of freedom $N >> 1$

$$(E_1^*, E_2^*)$$
$$\uparrow \quad \uparrow$$

$$\Omega_1(E_1^*, \vec{x}_1)\,\Omega_2(E_2^*, \vec{x}_2) \geq \Omega_1(E_1, \vec{x}_1)\,\Omega_2(E_2, \vec{x}_2) \leftarrow$$

$$\delta S = S_1(E_1^*, \vec{x}_1) + S_2(E_2^*, \vec{x}_2) - S_1(E_1, x_1) - S_2(E_2, x_2) \geq 0$$

$$\delta S \geq 0$$

Irreversible flow of energy

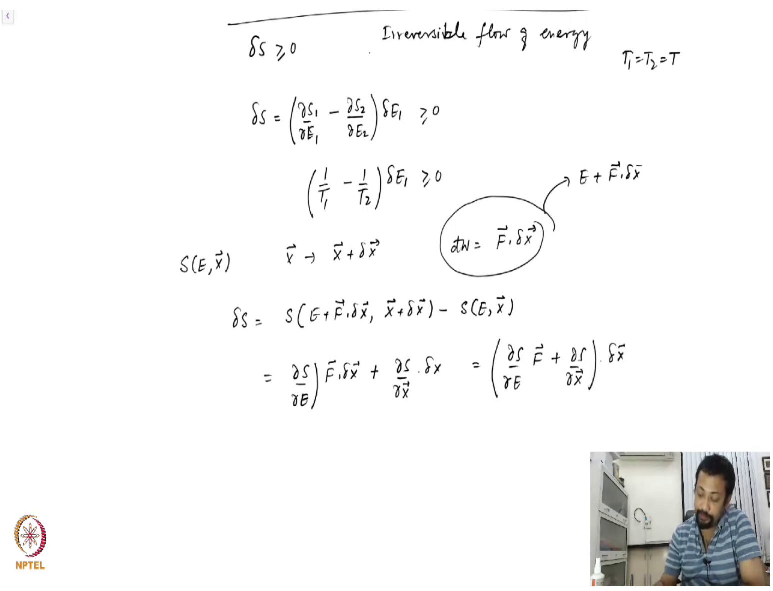
Further note that since we have evaluated this integral that we have written down over here using the saddle point our omega E oops omega E is approximately e to the power S of E 1 star over K B plus S of E 2 star over K B. So, that the entropy of the total system is approximately S of E 1 star plus S of E 2 star. This expression can be derived can you can arrive at this expression if you just take a log of this equation.

Now, the above definition of equilibrium of joint equilibrium essentially rests on the fact that there is large degrees of freedom and much much larger than 1 that makes it exponentially unlikely that the component energies of the system is anything other than E 1 and E 2 star.

Which deceptively means that the equilibrium point is such that larger number of accessible states are have the energies E 1 star and E 2 star than any other energies. So, essentially one can write down E 1 star comma X 1. So, I am replacing the generalized coordinates the v and the n by X 1 by the generalized coordinates X much much larger than omega E 1 X 1. We have to be careful with the notation, so omega 1 omega.

Now, this effectively means that delta S is S 1 E 1 star plus S 2 E 2 star, well the X 1 is also there comma X 1 comma X 2 minus S 1 E 1 X 1 minus S 2 E 2 X 2 is greater than equal to 0. This expression you arrive at by taking a law of this above equation. Therefore you have delta S is greater than equal to 0. So, that there is an irreversible flow of energy.

(Refer Slide Time: 13:24)



$\delta S \geq 0$ Irreversible flow of energy

$T_1 = T_2 = T$

$$\delta S = \left(\frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2}\right)\delta E_1 \geq 0$$

$$\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\delta E_1 \geq 0$$

$S(E, \vec{x})$ $\vec{x} \rightarrow \vec{x} + \delta\vec{x}$ $dW = \vec{F}\cdot\delta\vec{x}$ $\rightarrow E + \vec{F}\cdot\delta\vec{x}$

$$\delta S = S(E + \vec{F}\cdot\delta\vec{x}, \vec{x} + \delta\vec{x}) - S(E, \vec{x})$$

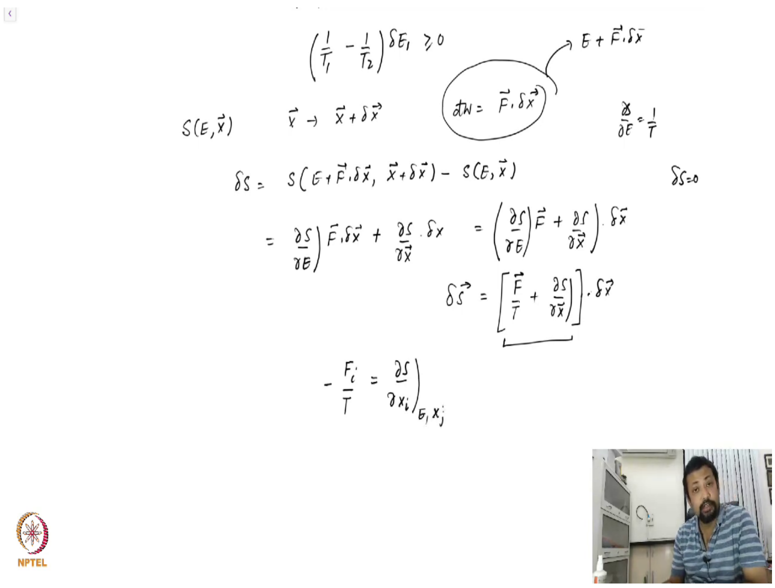
$$= \left.\frac{\partial S}{\partial E}\right) \vec{F}\cdot\delta\vec{x} + \frac{\partial S}{\partial \vec{x}}\cdot\delta x = \left(\frac{\partial S}{\partial E}\vec{F} + \frac{\partial S}{\partial \vec{x}}\right)\cdot\delta\vec{x}$$

Now, I can write down delta S when these two microcanonical systems were brought together without any work being done. Then I can write down then the equilibrium condition T 1 equal to T 2 equal to T is not satisfied. And therefore, my delta S is del S E 1 minus del S 2 E 2 times delta E 1 is greater than 0.

And this essentially means that 1 by T 1 minus 1 by T 2 delta E 1 is greater than equal to 0 that essentially tells you that the heat flows from a hotter to a colder body which is your clausiuss theorem. Now finally, we want to allow a variation in S of E comma x by changing the coordinates from X to X plus delta X.

So, that the work done d cut W is f dot delta X this is the generalized force as you are will aware of the description the language that we used when we did thermodynamics right. In which case your delta S is S of E plus f dot delta X, X plus delta X minus S of E comma X. So, this is equal to del S del E F dot delta x because this amount of work changes the energy from E to E plus f dot delta X right plus del S del X, which is del S del E F plus del S del X dotted with delta X.

(Refer Slide Time: 15:39)



$$\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\delta E_1 \geq 0$$

$$\xrightarrow{} E + \vec{F}.\delta\vec{x}$$

$$S(E,\vec{x}) \qquad \vec{x} \to \vec{x} + \delta\vec{x} \qquad \boxed{đW = \vec{F}.\delta\vec{x}} \qquad \frac{\partial S}{\partial E} = \frac{1}{T}$$

$$\delta S = S(E + \vec{F}.\delta\vec{x},\ \vec{x} + \delta\vec{x}) - S(E,\vec{x}) \qquad \delta S = 0$$

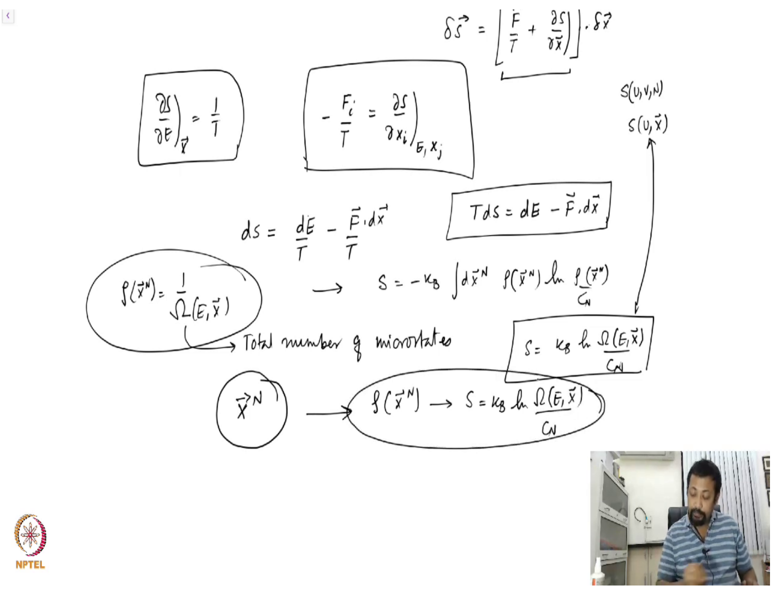
$$= \left.\frac{\partial S}{\partial E}\right)\vec{F}.\delta\vec{x} + \frac{\partial S}{\partial \vec{x}}.\delta x = \left(\left.\frac{\partial S}{\partial E}\right)\vec{F} + \frac{\partial S}{\partial \vec{x}}\right).\delta\vec{x}$$

$$\delta\vec{S} = \underbrace{\left[\frac{\vec{F}}{T} + \left.\frac{\partial S}{\partial \vec{x}}\right)\right]}.\delta\vec{x}$$

$$-\frac{F_i}{T} = \left.\frac{\partial S}{\partial x_i}\right)_{E,x_j}$$

Which we have just now seen that del S del E is equal to 1 by T is F by T plus del S del X dot right. Now, therefore, look at this expression of delta S, a spontaneous change is going to occur if this expression in the bracket is nonzero right. So, in order that at you are at equilibrium therefore, there is no spontaneous change delta S is 0 would mean that F i over T minus is del S del X i with E and X j being held constant.

(Refer Slide Time: 16:40)



So, we have now identified the derivatives of S del S del E at x held was 1 over T which we saw in the zeroth law. And this is the one we see that if we allow any variation in the coordinates, then my delta S is going to be like this, but since it is an equilibrium it is a joint equilibrium the delta S has to be 0 otherwise you are allowing a spontaneous change.

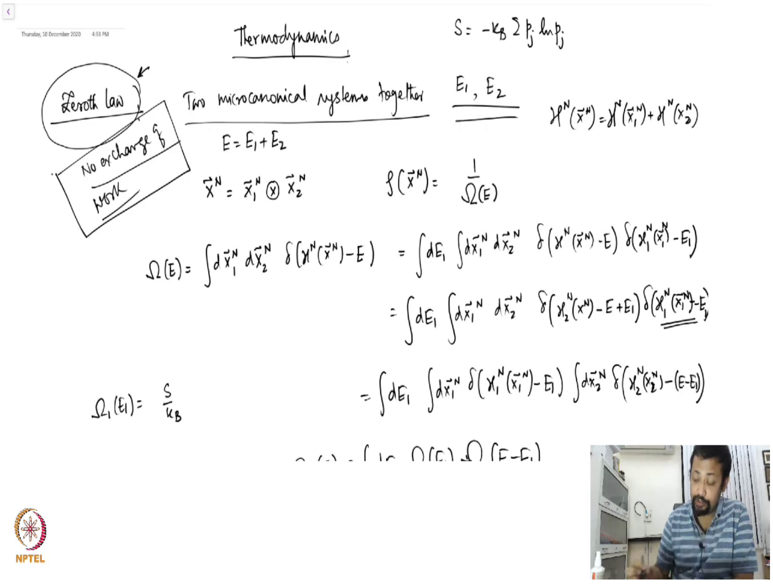
And therefore, your d S is since you know the variations in E this is d E by T minus F dot d X by T and you arrive at the first law which tells you that T d S is d E minus F dot d X right. So, in summary we started off with a probability density which we said was 1 over omega E comma X where this we said is the number of microstates the total number of microstates.

And using this definition of rho using this expression for rho we constructed the entropy as minus K B d X N rho X N l n rho X N divided by C N. So, that substituting for this becomes K B ln omega E comma X divided by C N. And we further showed that the connection this is really the entropy that we worked with or that we can link with the entropy that we had defined in thermodynamics.

In thermodynamics we have defined just the entropy as a state function which was a function of U, V, N or S as a function of U comma X. We see that these two have a very nice correspondence they not only have the properties that is satisfied by an entropy, but if we build in if we start looking at the laws of thermodynamics then indeed this expression for entropy satisfies gives me all the laws of thermodynamics. It gives me the zeroth law, it gives me the first law, it gives me the second law right.

So, therefore, starting from a microscopic picture where we will it where we were initially interested in the microstates of the system X N we have build something which is very much consistent with thermodynamics that we did earlier. The connection of course, comes in from this probability density that takes you to the entropy. Expression for the entropy l n omega E comma X divided by C N right.

(Refer Slide Time: 19:48)



Thursday, 10 December 2020 4:53 PM

Thermodynamics

$S = -k_B \sum_j p_j \ln p_j$

Zeroth law

No exchange of work

Two microcanonical systems together

E_1, E_2

$\mathcal{H}^N(\vec{x}^N) = \mathcal{H}^N(\vec{x}_1^N) + \mathcal{H}^N(x_2^N)$

$E = E_1 + E_2$

$\vec{x}^N = \vec{x}_1^N \otimes \vec{x}_2^N$

$\rho(\vec{x}^N) = \frac{1}{\Omega(E)}$

$$\Omega(E) = \int d\vec{x}_1^N\, d\vec{x}_2^N\, \delta(\mathcal{H}^N(\vec{x}^N) - E) = \int dE_1 \int d\vec{x}_1^N\, d\vec{x}_2^N\, \delta(\mathcal{H}^N(\vec{x}^N) - E)\, \delta(\mathcal{H}_1^N(\vec{x}_1^N) - E_1)$$

$$= \int dE_1 \int d\vec{x}_1^N\, d\vec{x}_2^N\, \delta(\mathcal{H}_2^N(x^N) - E + E_1)\, \delta(\underline{\underline{\mathcal{H}_1^N(\vec{x}_1^N)}} - E_1)$$

$$= \int dE_1 \int d\vec{x}_1^N\, \delta(\mathcal{H}_1^N(\vec{x}_1^N) - E_1) \int d\vec{x}_2^N\, \delta(\mathcal{H}_2^N(\vec{x}_2^N) - (E - E_1))$$

$\Omega_1(E_1) = \frac{S}{k_B}$

NPTEL

So, there is one thing that I should point it out and I should note that while we considered the derivation of the zeroth law. When we brought the two microcanonical systems together we only allowed an exchange of energy we did not allow any exchange of work there was no exchange of work this we did later on when we tried to when we derived the first law of this.

When we change the coordinate, so that over here when we change the coordinate from X plus X. So, that the energy now changes from E to E plus F dot delta X this you should keep it in mind.