Statistical Mechanics
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Lecture – 15
Canonical Ensemble

So, good morning students today, we will discuss the Canonical Ensemble in classical statistical mechanics. And this ensemble is in some sense more useful compared to the ensemble that we have studied so far which is the micro canonical ensemble.

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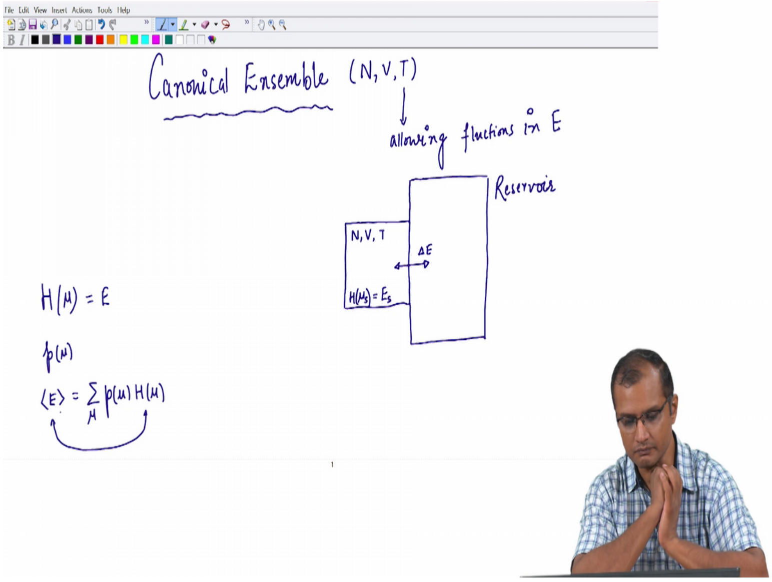

Canonical Ensemble (N, V, T)

$\downarrow$ allowing fluctions in E

$H(\mu) = E$

$p(\mu)$

$\langle E \rangle = \sum_{\mu} p(\mu) H(\mu)$

So, the canonical ensemble is your first ensemble that allows fluctuations. In your micro canonical ensemble, there were absolutely no fluctuations. It was ensemble of constant N, V and E. In this ensemble, I allow energy to fluctuate, thereby keeping temperature constant ok. So, this quantity T is kept constant by allowing energy to fluctuate. So, this is a first ensemble where are some fluctuations are allowed ok.

And just to help you understand I will draw a schematic diagram of a system in contact with a heat reservoir such as in this room where I am sitting and the temperature is comfortably kept to 26 degree centigrade by the thermostat which is the air conditioner. So, let us say this is our room and I am calling this as our system at constant N, V, and temperature T which is maintained by a reservoir. And the reservoir is purposefully taken to be much larger than the system, because I want the system to be driven by the reservoir not other way round ok.

So, otherwise if you take reservoir is smaller than the system, then the system acts as a reservoir to your thermostat ok. So, this is my reservoir thermal reservoir. And I am allowing for an energy exchange between my system and the reservoir. So, let us say that my system at some given instant is in a microstate mu ok, and the energy of this microstate is simply E. So, I am going to use subscript mu S to indicate this is a micro state of the system. And energy of the system is E s – instantaneous energy. So, the ham difference between Hamiltonian and energy is the following.

So, Hamiltonian is energy of a microstate; so, in some sense which is already carrying instantaneous information of the system. So, if I have microstate mu, I can say that the micro state has an energy which is E, but this is not an average energy. Suppose I know the probability of finding my system in that microstate, then the average energy is nothing but summation overall probabilities times the energy in that microstate, so that is the difference between E and H ok. So, H is an instantaneous energy for a microstate. And if you have the information of your probability distribution of microstates, you can compute the average energy that is the difference between energy and Hamiltonian, so that is just the small digression. Let us get back to a problem.

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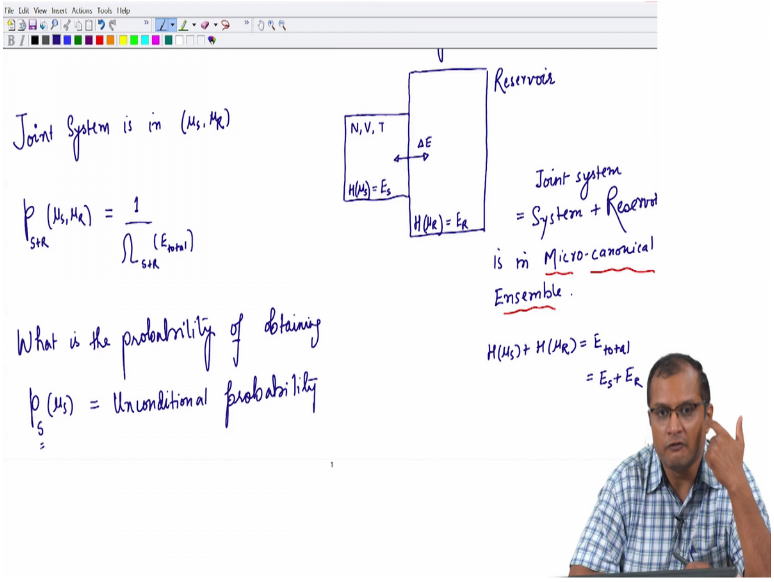

Joint System is in (μ_S, μ_R)

$$p_{S+R}(\mu_S, \mu_R) = \frac{1}{\Omega_{S+R}(E_{total})}$$

What is the probability of obtaining

$p_S(\mu_S)$ = Unconditional probability

=

Joint system = System + Reservoir is in Micro-canonical Ensemble.

$$H(\mu_S) + H(\mu_R) = E_{total}$$
$$= E_S + E_R$$

So, I am going to say that similarly my reservoir at some instant at the same instant let us say is in a microstate mu of R, and energy of this microstate is E of R ok. And because, the entire joint system which is my system plus reservoir is in micro canonical ensemble because, it is shielded from the surroundings ok.

So, my joint system is in a micro canonical ensemble. I can say that the energy instantaneous energy of my system plus the reservoir is equal to the total energy E that is fixed which is nothing but energy of the system plus energy of the reservoir which is fixed ok. Now, my system can exist in a large number of micro states and so does the reservoir. So, the joint system can exist in a microstate is in a micro state which is I will say a doublet of mu S and mu R. So, it jointly specifies mu S and mu R to specify the joint state of the system ok.

So, what I can tell is basically the probability or the joint probability of obtaining the subscript S plus R simply tells the, what is the joint probability of obtaining the system reservoir in some microstate mu S mu R that is a system is in mu S and the reservoir is in mu R ok. Well this is nothing but 1 upon total number of states accessible to the joint system at energy E total.

If you recall our micro canonical ensemble discussion, if we know the total number of accessible states to the micro canonical ensemble at N, V, E then the probability of finding a system in one of the micro state it is just 1 upon omega which is the total number of states. Now, the micro canonical ensemble here is the system plus reservoir. So, our total energy is E total in some sense N total, V total, E total is the micro canonical ensemble here. And this joint system can exist in omega sub S of R S plus R number of states. So, the joint probability of obtaining a system in a combination of mu S, mu R is nothing but 1 upon the total number of status accessible to my system plus reservoir and that is omega ok, this big omega.

So, I can ask now it myself what is the since I am interested in properties of my system, what is the probability of obtaining my system you know in microstate mu S you know that the probability of obtaining the joint system in mu S mu R is 1 upon omega S plus R. If omega S 1 upon S plus R is nothing but the total number of states accessible to the joint system. And each state is equiprobable each combination of mu S mu R is equiprobable. So, this probability can be computed by Bayes's theorem that we have discussed in the first chapter.

So, what is basically bring us is nothing but a unconditional probability that my system is in microstate mu S. I do not care about which state my reservoir is, give me the probability of finding my system if you look at the subscript, I am just using the subscript S, give me the probability of finding my system S in a micro state mu S ok.

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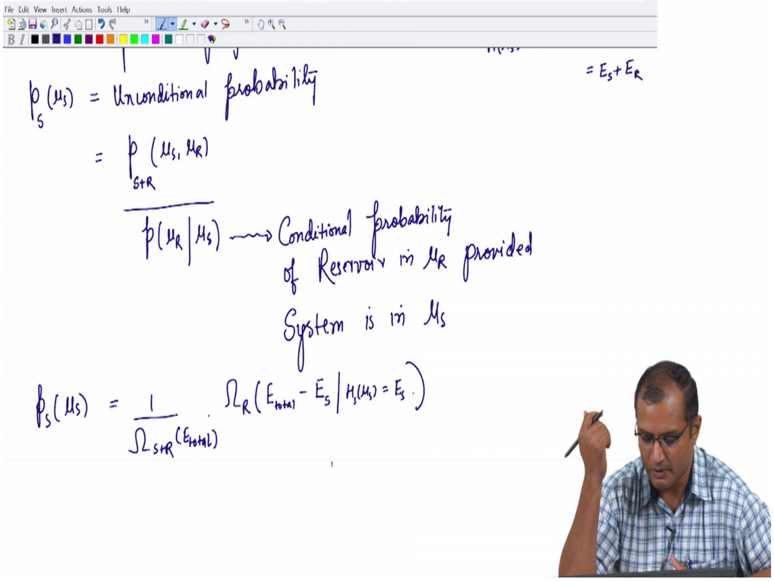

$= E_S + E_R$

$$P_S(\mu_S) = \text{Unconditional probability}$$

$$= \frac{P_{S+R}(\mu_S, \mu_R)}{p(\mu_R | \mu_S)}$$

$p(\mu_R | \mu_S) \rightsquigarrow$ Conditional probability of Reservoir in μ_R provided System is in μ_S

$$P_S(\mu_S) = \frac{1}{\Omega_{S+R}(E_{total})} \cdot \Omega_R(E_{total} - E_S \,|\, H_S(\mu_S) = E_S .)$$

And this can be answered by virtual Bayes's theorem is that if I have the total joint probability if you recall the Bayes's theorem, then I can simply say that this is nothing but the joint probability or total probability of obtaining the system in the this doublet divided by the conditional probability that my reservoir is in state mu R ok. Some reservoir sub provided the system is in this micro state mu S because the left hand side requires information of probability of finding the microstate mu S. So, the denominator has to be a condition probability of you know of finding a reservoir mu R mu R such that the system is it mu S, so that is the.

So, I will say that this is nothing but a conditional probability of reservoir in microstate mu R provided system is in mu of S ok. So, I can now write down my P of S the probability unconditional probability of finding the system in mu of S as nothing but 1 upon because, the numerator is nothing but 1 upon omega S plus R and some E total into the numerator is nothing but a probability of finding the reservoir number of microstates in which a reservoir can exist with the energy E total minus energy of the system at E s provided the system states at provided my systems instantaneous energy is E of s that is the denominator it as going in a in terms of number of states it has gone in the numerator ok.

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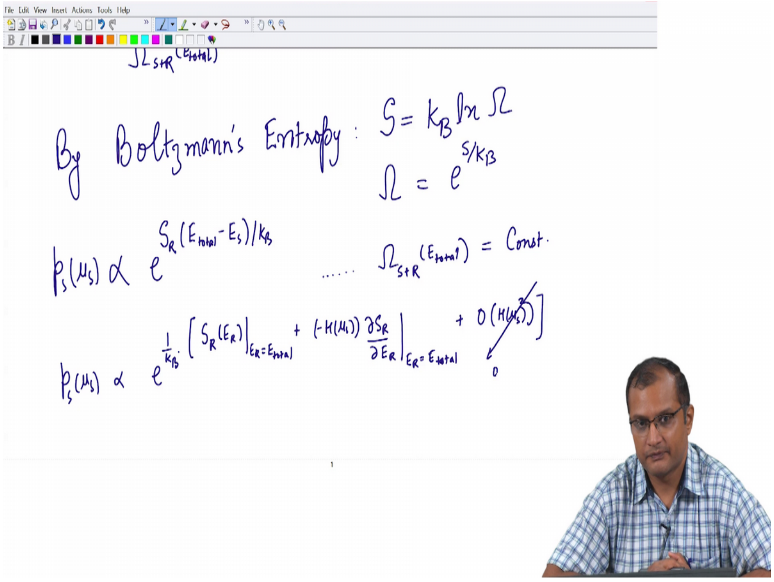

$\Omega_{S+R}(E_{total})$

By Boltzmann's Entropy : $S = k_B \ln \Omega$

$\Omega = e^{S/k_B}$

$p_s(\mu_s) \propto e^{S_R(E_{total}-E_s)/k_B}$ …… $\Omega_{S+R}(E_{total}) = \text{Const.}$

$$p_s(\mu_s) \propto e^{\frac{1}{k_B}\cdot\left[S_R(E_R)\big|_{E_R=E_{total}} + (-H(\mu_s))\frac{\partial S_R}{\partial E_R}\Big|_{E_R=E_{total}} + \underbrace{\cancel{O(H(\mu_s)^2)}}_{0}\right]}$$

Now, you can think of it in the following way that this you know by virtue of Boltzmann's entropy, I can always write down my S as k B ln omega if omega is a number of states. This give me omega always as you know it always goes as e to the power S over k B in spite in this case I am always write down equality here. So, I can write down my probability in terms of entropy as simply you know proportional to because, it is the denominator which is constant just e to the power entropy of the reservoir which is the function of E total reservoir is now and the energy E total minus E S over k B ok. Because my numerator is omega R, and you can write down that omega S of S plus R the total number of status assessable to the system is a constant ok.

So, I can write down my improbability of finding a micro state in mu S as simply proportional to E to the power S R over k B. And this is S R, which is the entropy the reservoir. And reservoirs energy is E total minus E s. And you can so you can you can basically say that this I can write down this p of s mu of s as simply proportional to e to the power, I can expand the numerator in powers of you know as a Taylor expansion so in powers of the energy of the system simply S of R as a function of E R.

So, I am going to expand entropy around the reservoir energy at E R equals to E total that will give me the leading term plus I am going to write down minus E of s which is nothing but because you are talking about instantaneous energy E of s is nothing but minus of H of mu S into delta S R over S E R at E R equals to E total plus higher order terms which I am going to draw because they are at least quadratic in powers of the Hamiltonian of the system, and that is very small compared to the energy of the systems I am going to drop it ok. So, we are going to basically not consider a terms quadratic and above in the powers of the systems energy.

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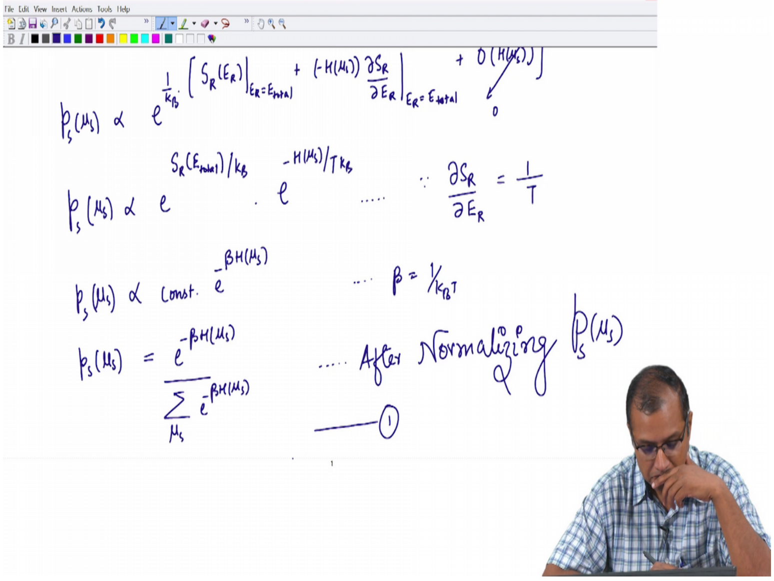

$$p_s(\mu_s) \propto e^{\frac{1}{k_B}\left[S_R(E_R)\big|_{E_R=E_{total}} + (-H(\mu_s))\frac{\partial S_R}{\partial E_R}\Big|_{E_R=E_{total}} + O(H(\mu_s)) \right]}$$

$$\xrightarrow{} 0$$

$$p_s(\mu_s) \propto e^{S_R(E_{total})/k_B} \cdot e^{-H(\mu_s)/Tk_B} \quad \ldots\ldots \quad \because \frac{\partial S_R}{\partial E_R} = \frac{1}{T}$$

$$p_s(\mu_s) \propto \text{const.}\, e^{-\beta H(\mu_s)} \quad \ldots\ldots \quad \beta = 1/k_B T$$

$$p_s(\mu_s) = \frac{e^{-\beta H(\mu_s)}}{\sum_{\mu_s} e^{-\beta H(\mu_s)}} \quad \ldots\ldots \text{After Normalizing } p_s(\mu_s) \qquad \text{——— ①}$$

So, this can be simply written as I can take this p of s mu S as simply proportional to e to the power S R E total over k B into e raise to minus H mu S and d S by d E is nothing but the temperature of the reservoir. So, I am going to write down from the thermodynamic definition of temperature that this quantity is nothing but 1 upon temperature of the reservoir.

So, now you can simply upon k B T of course, ok. So, you can you can simply say that the probability of finding the system in a microstate is simply equal to e to the power minus beta H mu S ok. You can think of you know you can basically substitute this beta as 1 upon k B T.

And look at the fact that I have converted the proportionality symbol into an equality which means I am going to divide this entire thing by summation overall microstates e to the power minus beta H mu S so as to normalize it to unity. This quantity is a constant because E total is fixed. So, it just cancel cancels off when you take the submission overall the exponentials, it cancels off in both numerator and denominator ok.

So, let me just be because it is appearing as to sudden it be do it in two steps, so that there is no confusion ok. So, I am going to simply for to make things simple do this in two steps ok. So, I am just going to maybe rub this off and simply write it as simply I will write it as some constant into e raise to minus beta H mu S. And the final step I am going to say that I have summed over all to normalize it. I am going to simply write it as e to the power minus beta H mu S over summation overall microstates e raise to minus beta H minus. So, this is basically after normalizing p of mu S. Now, let us call this as some equation 1 we have not labeled any equation so far.

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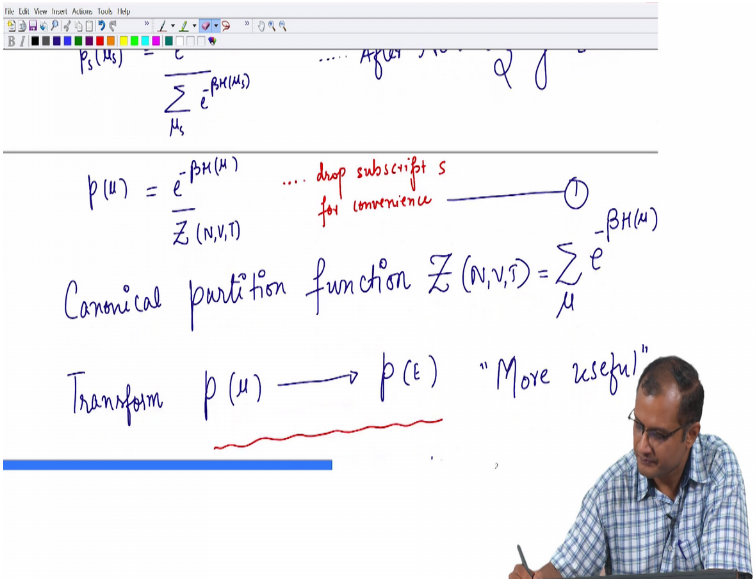

$p_s(\mu_s) = \frac{e}{\sum_{\mu_s} e^{-\beta H(\mu_s)}}$ ..... After

$$p(\mu) = \frac{e^{-\beta H(\mu)}}{Z(N,V,T)}$$ .... drop subscript s for convenience ——— ①

Canonical partition function $Z(N,V,T) = \sum_{\mu} e^{-\beta H(\mu)}$

Transform $\underbrace{p(\mu) \longrightarrow p(E)}$ "More useful"

Now, this quantity is basically the denominator is basically nothing but a partition function. So, we can actually write down this rewrite this for the sake of convenience as e raised to minus beta H over the canonical partition function at N, V and T. So, let me with your permission not call this is equation 1, I am going to call this as equation 1 ok. So, where this canonical partition function has been introduced just to remind that the macro state here is N, V, T, so the our partition function depends only on the macro state. And it is nothing but summation over all the microstates of a system of this Boltzmann factor e raise to minus beta H mu S. This is the definition of the canonical partition function.

Now, I am going to transform my probability distribution from microstate world to the energy world. So, I am going to write down this PDF in terms of energy E. Now, the reason why I want to do it is because a large number of microstates maybe degenerate may be sitting at the same energy ok.

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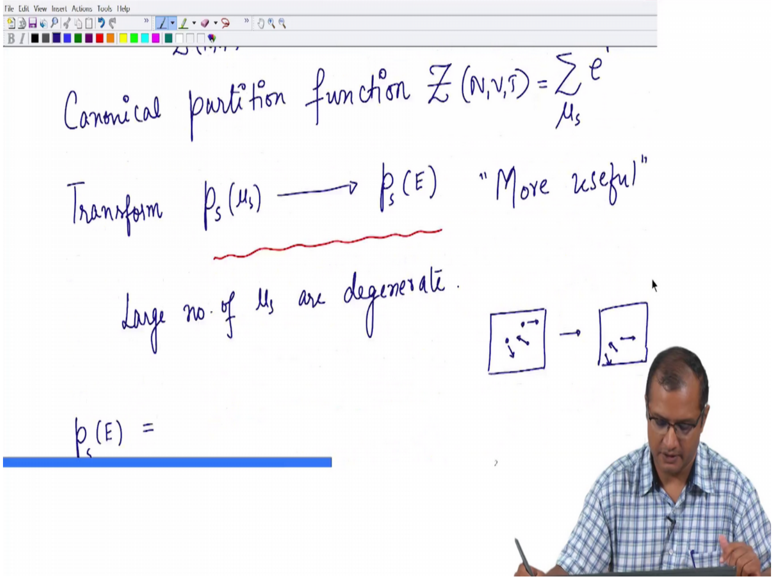

Canonical partition function $Z(N,V,T) = \sum_{\mu_s} e$

Transform $p_s(\mu_s) \longrightarrow p_s(E)$ "More useful"

Large no. of μ_s are degenerate.

$p_s(E) =$

For example, if you look at so I am going to write down the reason as you know this basically this construction is more helpful or more useful as a large number of microstates you know are degenerate. So, it is more helpful to look at the system from the viewpoint of energy than the microstate itself. So, you may ask yourself a question which energies are more probable and which energies are less probable instead of looking at the microstates themselves.

So, simple reason is if I take an ideal gas of particles and there are no there is no potential energy for example, then you know these particles as simply the energy of the system is simply kinetic. So, you know it does not matter if I take translate the entire pair you know to which is moving in some direction with some velocities. If I translate this entire pair to some other corner, then I get in different this another realization where the same velocities are possible, but energy is same. So, the kinetic energy is same in both the configurations, but this is a different microstate. So, you can construct large number of such microstates which correspond to the same energy.

And I am not interested in those microstates; I am interested in the energy distribution. So, I am going to transform my probability density probability distribution function from microstates to energy ok, so that can be done very easily by saying that if I want the probability distribution function in terms of energy, I can write it as since I have already used big E as the total energy. Have I used it? No, I have used E total as the total energy, fine. So, E here is the energy of all the system ok. So, you can you can this is the different symbol here maybe because you have used instantaneous energy as S.

So, I am going to use some let me use e itself. So, hear e is the energy of the system. And I am now going to drop the subscript mu as because now everything is related to system. So, I am going to drop the subscripts here, because we are only dealing with the system properties here ok. So, you can drop the subscripts purely for convenience. All quantities are now referred to as system quantities ok, so why do we keep S fine. So, I am going to simply drop these subscripts because, henceforth for tall quantities are system quantities.

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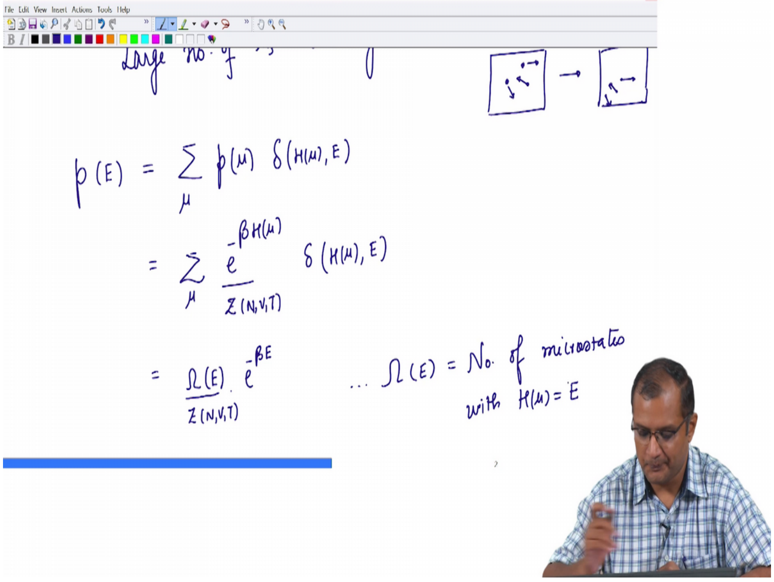

$$p(E) = \sum_{\mu} p(\mu)\, \delta(H(\mu), E)$$

$$= \sum_{\mu} \frac{e^{-\beta H(\mu)}}{Z(N,V,T)}\, \delta(H(\mu), E)$$

$$= \frac{\Omega(E)}{Z(N,V,T)} \cdot e^{-\beta E} \qquad \ldots\ \Omega(E) = \text{No. of microstates with } H(\mu) = E$$

So, this is nothing but so if you want to find out the PDF in terms of energy what you have to do is basically sum overall microstates of the system p of mu ok, and simply use the condition that whenever the energy of the system becomes E you take a count. And when it does not equal to you do not take a count. So, this is basically just a Kronecker delta function which when weight in your PDA, PDF mu of mu it gives you p of E.

So, I know the sum of all E should be 1. So, the right hand side simply tell tells me that I have to sum overall mu and sum overall E. For each E, I will sum overall mu and that will give me p of E. And when I sum overall E, I should get 1 ok. So, this will simply become if I substitute our expression for p of mu which is nothing but e to the power minus beta H of mu over the over the partition function that I am going to take outside ok. So, I am just going to maybe for the time being, I am going to write down this partition function in the denominator into delta of H mu, E.

Now, you can see that a large number of microstates that have energy E will contribute to the sum. So, first observation is that the partition function will come outside because it is it remains as is does not matter whether use the probability of finding the system in a microstate mu or you find the probability in terms of E partition function remains the same. And its summation simply captures all the states with energy E. So, I am going to say that this is omega with energy E, and e to the power minus beta E ok.

So, wherever H mu was E I picked up a sum and it will take e raise to minus beta H mu as e raise to minus beta E, how many times I did it omega E times. So, omega E is here is basically is the number of see every time this delta function picked one I have counted one. So, it has picked one omega E number of times. So, it is the number of microstates where the energy of the microstate was E, energy of the microstate of the system was E.

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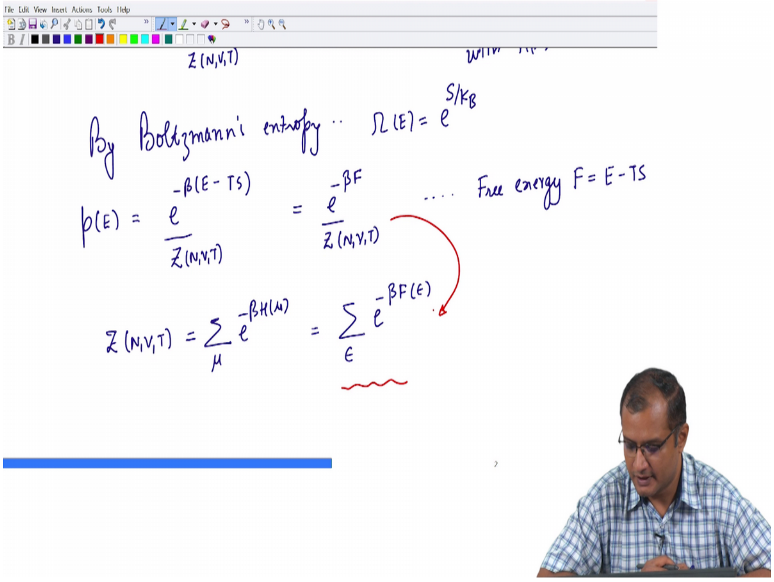

$Z(N,V,T)$

By Boltzmann's entropy .. $\Omega(E) = e^{S/k_B}$

$$p(E) = \frac{e^{-\beta(E-TS)}}{Z(N,V,T)} = \frac{e^{-\beta F}}{Z(N,V,T)} \quad \ldots \text{ Free energy } F = E - TS$$

$$Z(N,V,T) = \sum_{\mu} e^{-\beta H(\mu)} = \sum_{E} e^{-\beta F(E)}$$

And so now, since by virtue of again Boltzmann's entropy I can write on my omega of e as e to the power S over k B ok. So, my probability distribution function in terms of energy simply becomes e to the power minus beta E minus S over k B T ok. The two minus give you plus, I think I have to yeah. So, there should be carry, I have to write E minus T S, because beta itself is 1 upon k B T t and you just have 1 upon k v ok, but from thermodynamics I know that this is nothing but e raise to minus beta into free energy ok.

Since our free energy thermodynamic free energy or your Helmholtz free energy is e minus T S. So, of course, I am missing a partition function here which normalizes everything. So, our partition function that we have obtained in terms of microstates was nothing but summation overall mu's e to the power minus beta H mu. So, if you have all the microstates of the system then the Hamiltonians will give the information on the partition function.

Or in other energy if we have all the energy states in which the system can sit then the partition function can be computed as e raised to minus beta into free energy for that energy because this will normalize your probability distribution function p of E. So, the second definition of partition function here followers from here ok. So, I have to take the form of the E as summation overall energy is e raise to minus beta F because the numerator is e raised to the minus beta F that is an normalization I want to use to make my p of E normalized.

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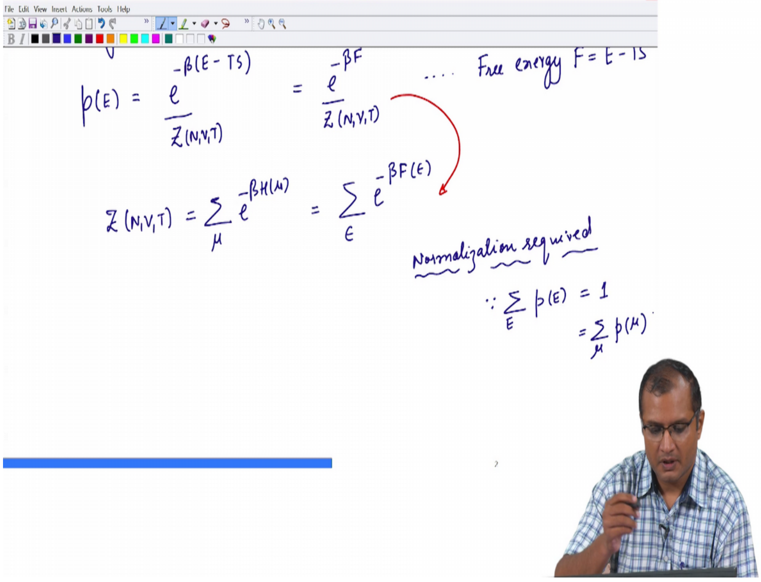

$$p(E) = \frac{e^{-\beta(E - TS)}}{Z(N,V,T)} = \frac{e^{-\beta F}}{Z(N,V,T)} \quad \ldots \text{ Free energy } F = E - TS$$

$$Z(N,V,T) = \sum_{\mu} e^{-\beta H(\mu)} = \sum_{E} e^{-\beta F(E)}$$

Normalization required

$$\because \sum_{E} p(E) = 1$$

$$= \sum_{\mu} p(\mu)$$

So, now I can I can write down this as you know the normalization required. So, the partition function is a normalization required to basically keep your probability distribution function well behaved ok, because we want summation overall energies p of E to be 1. All possible energy is that my system can take if I sum overall the probability, it should be 1 as shall be the probability of finding a system in a microstate ok. We break here. And when we come back we shall continue the discussion.

Thank you.