Basic Statistical Mechanics
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Lecture - 12
Canonical Ensemble Part – 2

So the first thing is done and this is all done by Gibbs: NVT that means energy is the first thing that will exchange. Because it is all-natural that a system will exchange energy with the surroundings.

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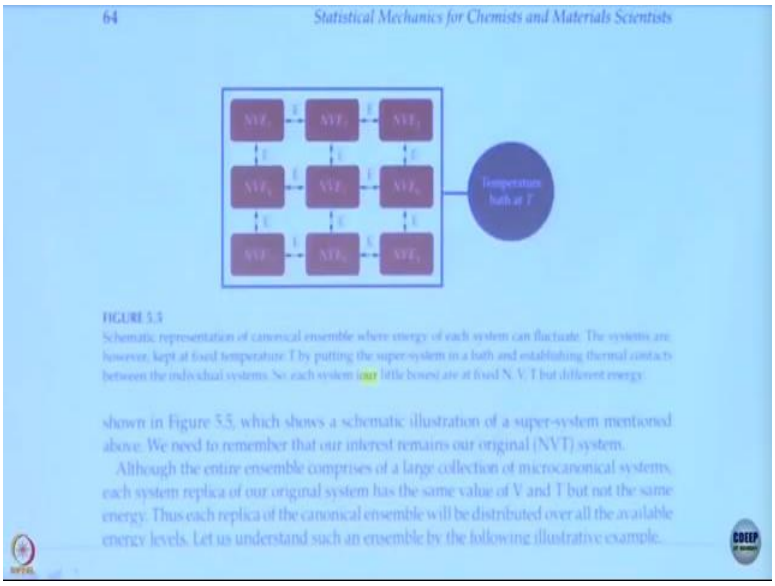

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FIGURE 5.5
Schematic representation of canonical ensemble where energy of each system can fluctuate. The systems are however, kept at fixed temperature T by putting the super-system in a bath and establishing thermal contacts between the individual systems. So each system (our little boxes) are at fixed N, V, T but different energy.

shown in Figure 5.5, which shows a schematic illustration of a super-system mentioned above. We need to remember that our interest remains our original (NVT) system.

Although the entire ensemble comprises of a large collection of microcanonical systems, each system replica of our original system has the same value of V and T but not the same energy. Thus each replica of the canonical ensemble will be distributed over all the available energy levels. Let us understand such an ensemble by the following illustrative example.

So that goes to give you NVT. Gibbs did these amazing things. He must have a very clear idea of what was going on. It must have been very- very interesting when you will think of it. There is a man alone sitting in Sterling laboratory in Yale. He once went to Europe and came back. The rest of his life, he never left. Many people gave him offer, but he never left. He did not marry.

In the morning, he used to go to his laboratory and in the evening used to come back to home. All his entire life, he lived with his sister, who took care of him and that is it. But these are very common those days. You know this kind of people like kind of ascetic, highly ascetic and dedicated life. So, sitting there he must have this huge clarity of vision that how to go.

So the first clarity and brilliant idea was to go to the ensemble. I give you, again and again, the example of the ten water glasses. You know they are all in different microscopic states but their properties are the same. So that would give you the idea of creating an ensemble because in one stroke he went from solving Newton's equation to a distribution function.

That was the whole idea of an ensemble. Then you go to distribution. As soon as you go to distribution you can define averages. As soon as you can define averages, you can start doing calculations; analytical calculation. Otherwise, you stuck, you cannot solve even 3-body problems. Okay? So that was the brilliant beginning of the whole of statistical mechanics: these ensembles.

Then he made those two hypotheses. First one was "time average equals to ensemble average." This, I have explained many times (it follows from the concept of the phase space which I think, I did in second-class or first-class). Then he had to make equal a priori probability because all these microscopic states have the same energy and there is nothing that we know about them other than that they have the same energy.

So there is no other option than that we assume they are equally probable. So there comes the equal a priori probability. But then he landed in trouble because the essence of ensembles is not taken care of. But who guarantees that the time average is equal to the ensemble average (the first postulate). Because for doing that my system, one system that has to go through all the microscopic states. So then all the microscopic states must be visited.

So the concept of dynamics or time-dependent came into Ergodic hypothesis. That is why there is a huge school of mathematics. Even today they were working on Ergodic hypothesis. A realistic system was shown to be Ergodic first time by a great mathematician Y. G. Sinai only in 1982. They said that the billiard ball model (2-dimensional discs) are Ergodic. That was the first time by showing the diffusion exists.

And the main thing is that two trajectories starting together, go over all the space. You might have heard beautiful things like chaos and the Lyapunov exponent. All these things are part of this Ergodic hypothesis and chaos. That is why so much interest in chaos. Okay?

Now coming back, so when you relax the constraint of energy, then again I do not have any next step to do. That is why I am saying he (Gibbs) must have a huge clarity of vision because the only thing that we have, is this thing. So what does he do? He said okay. I have my picture on here board. I put all these members of my ensemble, all the members of my canonical ensemble (very carefully, listen), all the systems in my canonical ensemble who are exchanging energy the surroundings, I put them against each other and then put them in a bath.

Let them attain an equilibrium. My humongous system (my super system is a homogeneous system) now equilibrates at a constant temperature but they are exchanging energy. So all of them are at different energy states. So, these now become my one super system. Now, I make an ensemble of this super system. So this super system is now isolated completely after the initial bath.

I hope you get the picture now. So, now I do a super ensemble of my super system. But the super system is now characterized by a constant number of particles (the total number of systems in my canonical ensemble, which is part of the super system, multiplied by the number of particles in each. Similarly volume, similarly the total number of particles. So there are constraints.

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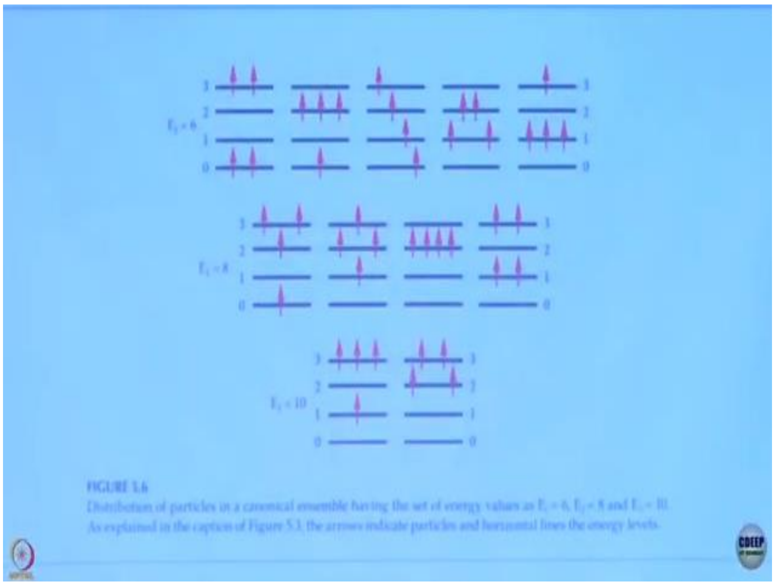

FIGURE 5.6

Distribution of particles in a canonical ensemble having the set of energy values as $E_1 = 6$, $E_2 = 8$ and $E_3 = 10$. As explained in the caption of Figure 5.3, the arrows indicate particles and horizontal lines the energy levels.

Now I want to write down the partition function. So this is the distribution, I discussed last time. This was the one are we considered in the microcanonical ensemble. In microcanonical ensemble, I have considered a system which is characterized by 4 energy levels, and also *N = 4*. Volume does not come here. It enters through these energy levels.

I hope you understand, like for particle in a box, remember, $\varepsilon = \frac{n^2h^2}{8ml^2}$, l is the length. So energy spacing comes through.

So, I have four systems, so this is my microcanonical ensemble with $\Omega = 4$, all right? Now I allow it to have different energies. As soon as I do that, these different states become available to it.

So canonical ensemble has many more states available to it. Now, immediately I realize that not all of them will have equal probability. So now I need to find out how to talk which is more probable, which energy is more probable.

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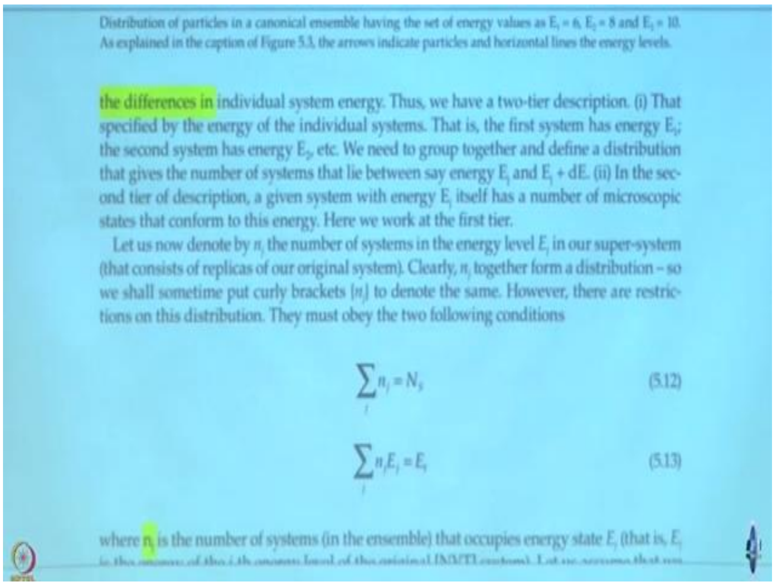

Distribution of particles in a canonical ensemble having the set of energy values as $E_1 = 6$, $E_2 = 8$ and $E_3 = 10$. As explained in the caption of Figure 5.3, the arrows indicate particles and horizontal lines the energy levels.

the differences in individual system energy. Thus, we have a two-tier description. (i) That specified by the energy of the individual systems. That is, the first system has energy E_1; the second system has energy E_2, etc. We need to group together and define a distribution that gives the number of systems that lie between say energy E_j and $E_j + dE$. (ii) In the second tier of description, a given system with energy E_j itself has a number of microscopic states that conform to this energy. Here we work at the first tier.

Let us now denote by n_j the number of systems in the energy level E_j in our super-system (that consists of replicas of our original system). Clearly, n_j together form a distribution – so we shall sometime put curly brackets $\{n_j\}$ to denote the same. However, there are restrictions on this distribution. They must obey the two following conditions

$$\sum_j n_j = N_s \tag{5.12}$$

$$\sum_j n_j E_j = E_t \tag{5.13}$$

where n_j is the number of systems (in the ensemble) that occupies energy state E_j (that is, E_j

And that is now done by saying okay; n is the number of particles in system j with energy E_j and add over that, you get the total energy in my super ensemble.

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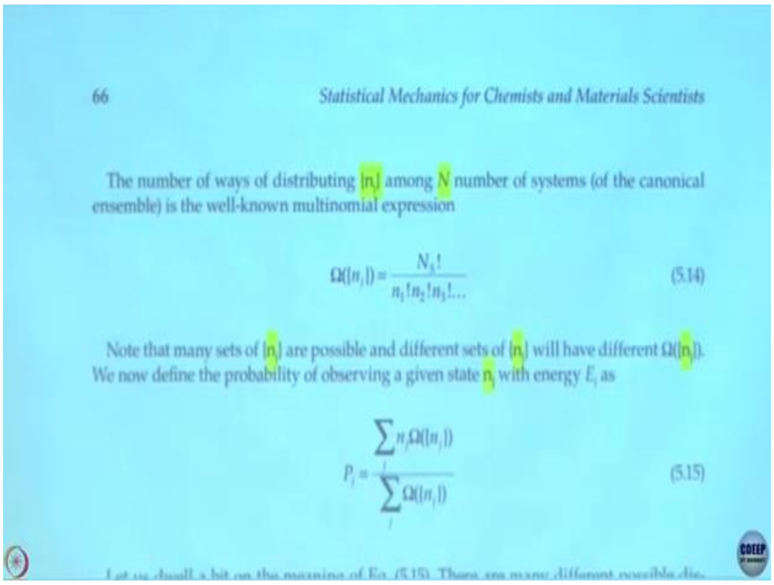

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The number of ways of distributing $\{n_j\}$ among N number of systems (of the canonical ensemble) is the well-known multinomial expression

$$\Omega(\{n_j\}) = \frac{N_S!}{n_1!n_2!n_3!\ldots} \tag{5.14}$$

Note that many sets of $\{n_j\}$ are possible and different sets of $\{n_j\}$ will have different $\Omega(\{n_j\})$. We now define the probability of observing a given state n_j with energy E_j as

$$P_j = \frac{\sum_j n_j \Omega(\{n_j\})}{\sum_j \Omega(\{n_j\})} \tag{5.15}$$

Let us dwell a bit on the meaning of Eq. (5.15). There are many different possible dis-

So *n*, remember *n* is again the number of particles in energy state E_j, in my super ensemble. It is a bit complicated because there are two layers that we are doing. n_j is the number of system in energy state E_j and then this is the way of combinatorics.

$$\Omega(\{n_j\}) = \frac{N_S\,!}{n_1\,!n_2\,!n_3\,!\ldots}$$

But these combinatorics has to be maximized with the constraints.

So these are the constraints:

$$\sum_j n_j = N_S$$

$$\sum_j n_j E_j = E_t$$

And I can define now the probability. Remember the question I was asking, so what is the probability? Now, all the energy levels are allowed, what is the probability? Now, what will be the condition that will determine what energy state is most probable in the system? So I have removed all the barriers, the system can be in different energy states.

I have still the constraint of number and volume in a super ensemble I have constructed. What is the condition that will tell me what is the probability of a given energy level? Now, energy levels are allowed energy levels are allowed. So what is the condition that will dictate? No, no that is the outcome. But without doing Boltzmann distribution, you take a guess, very simple, it will be the arrangement which will maximize this.

These are amazing things, really amazing and even now it never fails to surprise me that these holes with enormous accuracy one in 10^{23} or probably whatever that kind of number, this law of maximum entropy, the law of the maximum number holds such accuracy. It is just amazing! That because these are called laws of large numbers that come into play. So by the time you have some hundred particles or thousand particles, amazingly this distribution kind thing will be there. There is a force constant, of course, we will discuss that. That kind of zoom scene and it is essentially connected with a very deep level to the stability of the system and that is where Statistical Mechanics gives you a real insight into natural systems. That's how things work and is a mind-boggling.

So now I can define the probability of my system in a energy level, that is the probablility P_j. That is why I asked the question because I go for P_j and the only principle I have to maximize entropy (the maximum Ω). So this n_j is the number of systems in energy level E_j and now that particular energy level, my super ensemble can be distributed in the Ω ways. So then this is the normalization. This defines the probability P_j here.

$$P_j = \frac{\sum_j n_j \Omega(\{n_j\})}{\sum_j \Omega(\{n_j\})}$$

Take a look into that, it is not difficult. But I am saying that we are looking to a higher level and when I go to grand canonical ensemble even another high-level will come. But this is resting on microcanonical ensemble. Grand-canonical ensemble will be raised on canonical ensemble.

Let us say what we are trying to say. Ω is the number of ways, I can, like here. Omega (Ω) is the total number, they might be the same, let me work it out. So given an energy E_j, I have number of ways to define Ω_j. Alright now, so I now come there. I said it has to be weighted by Ω which is this. So the $\Omega\left(\left\{n_j\right\}\right)$ gives the weight of this. So in probability, how do you go about? We go about, we define a probability, as I did discuss little bit in lecture-2 (probability and statistics) which is given in my book, I think in chapter 2 itself, where you have the concept of the sample space.

What is the sample space? Sample space is the total number of space that is available to you. Like if I toss a coin, then the sample space is two: head and tail. If I throw a dice. then I have the sample space six. Then it is the total number of the sample space, that is so. Here, the sample space is defined by the total number of microscopic states that is available, not the total number of systems. So you remember the Venn diagram we draw so that is the reason should be Ω. Is it clear? It is a good question. now we have to go. What do we do?

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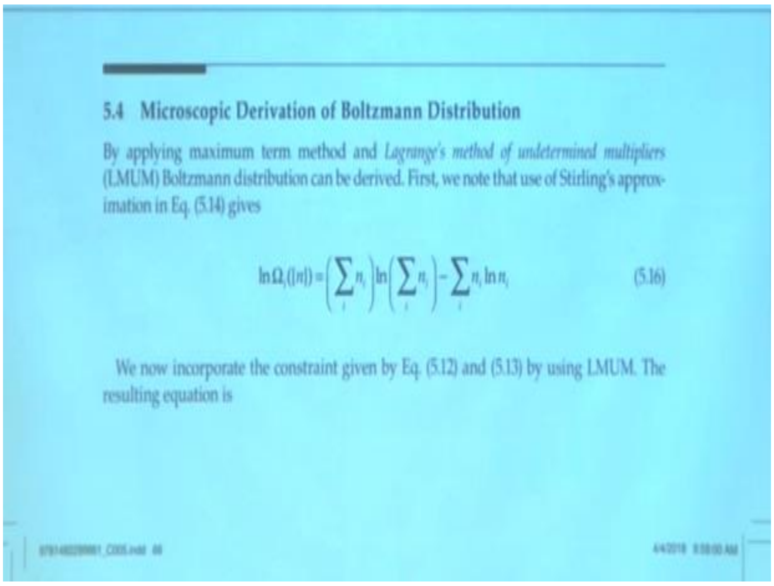

5.4 Microscopic Derivation of Boltzmann Distribution

By applying maximum term method and *Lagrange's method of undetermined multipliers* (LMUM) Boltzmann distribution can be derived. First, we note that use of Stirling's approximation in Eq. (5.14) gives

$$\ln \Omega_i(\{n\}) = \left(\sum_i n_i\right) \ln\left(\sum_i n_i\right) - \sum_i n_i \ln n_i \tag{5.16}$$

We now incorporate the constraint given by Eq. (5.12) and (5.13) by using LMUM. The resulting equation is

Now we have to go to what we did? Now we have to do Stirlings approximation ($\ln N! \approx N \ln N - N$). If you do that you get this quantity here,

$$\ln \Omega_i(\{n\}) = \left(\sum_i n_i\right) \ln\left(\sum_i n_i\right) - \sum_i n_i \ln n_i$$

This is the thing that we have to maximize but you have to maximize it with this constraint**.**

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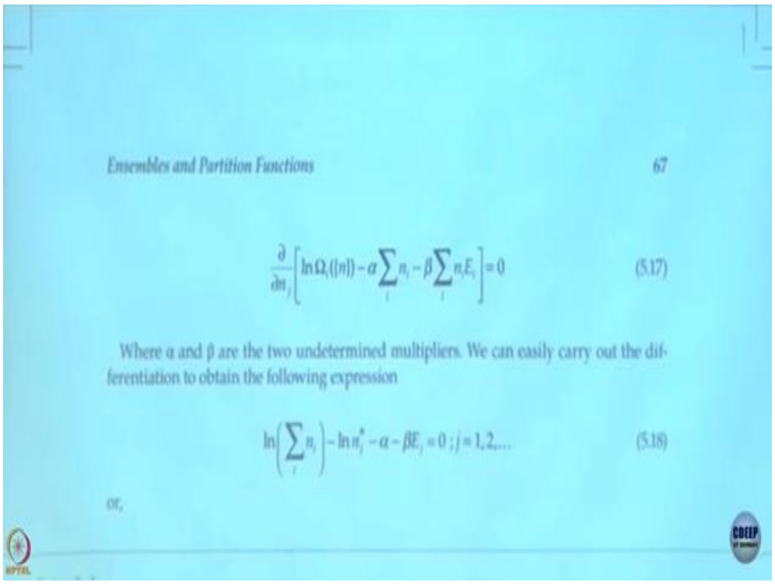

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$$\frac{\partial}{\partial n_j}\left[\ln\Omega_i(\{n\}) - \alpha\sum_i n_i - \beta\sum_i n_i E_i\right] = 0 \qquad (5.17)$$

Where α and β are the two undetermined multipliers. We can easily carry out the differentiation to obtain the following expression

$$\ln\left(\sum_i n_i\right) - \ln n_j^* - \alpha - \beta E_j = 0\,;\, j = 1, 2, \ldots \qquad (5.18)$$

or,

After that, we have the very important thing, which I would love to talk but it would take one class. This is called the method of constant variation or method of Lagrange's multiplier because it was done by Lagrange. This essentially says that you are maximizing something but you put a constraint to it.

For example, you want to have a certain distribution, but you put certain conservation condition of the distribution and these are the conservation condition. Now, the way that Lagrange's multiplier goes, is to put the constraint in the following form so that you can see very easily.

$$\frac{\partial}{\partial n_j}[\ln\Omega_i(\{n\}) - \alpha\sum_i n_i - \beta\sum_i n_i E_i] = 0$$

That this is these condition. If I take $\partial\sum_i n_i$ with respect to ∂n_j, this $\left(\sum_i n_i\right)$ is a constant, $\frac{\partial\sum_i n_i}{\partial n_j}$ will go to 0. This $\left(\sum_i n_i E_i\right)$ is constant because of the total amount of energy.

Because that is my super system, so the super system is the microcanonical system, that has constant energy, so $\left(\frac{\partial\sum_i n_i E_i}{\partial n_j}\right)$ will again be 0. So the way the Lagrange's multiplier works is that you put the constant in the following form, that the whole thing is. So this is the one you want to maximize but with respect to this constraint. In the book, in the appendix, I have described little better. So when you do that we get this equation when do we take this will go over because this quantity.

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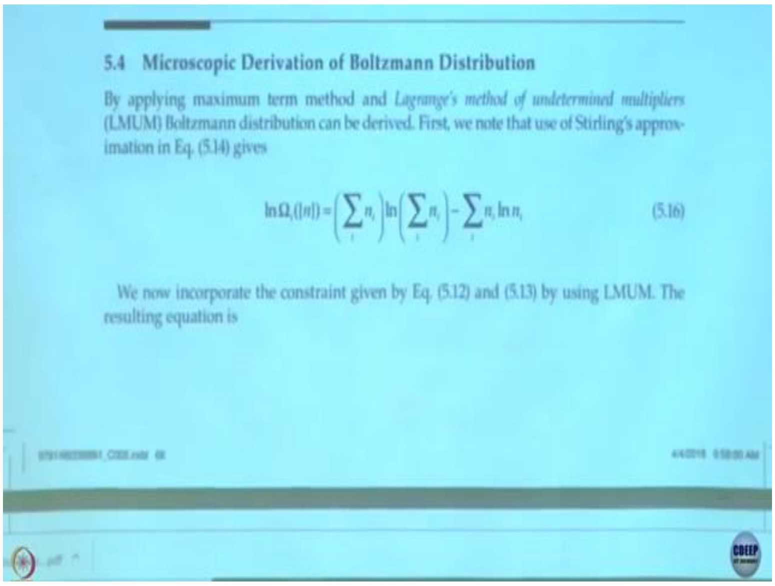

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$$\ln \Omega_t(\{n\}) = \left(\sum_i n_i\right) \ln \left(\sum_i n_i\right) - \sum_i n_i \ln n_i \tag{5.16}$$

We now incorporate the constraint given by Eq. (5.12) and (5.13) by using LMUM. The resulting equation is

Is this quantity and you can take the derivatives and then you get this is the condition taking the derivative this equation 17 then you get the 18 comes out.

$$\ln\left(\sum_i n_i\right) - \ln n_j^* - \alpha - \beta E_j = 0 \; ; \; j = 1, 2, \ldots$$

This is actually easier of the things that you have done here and then.

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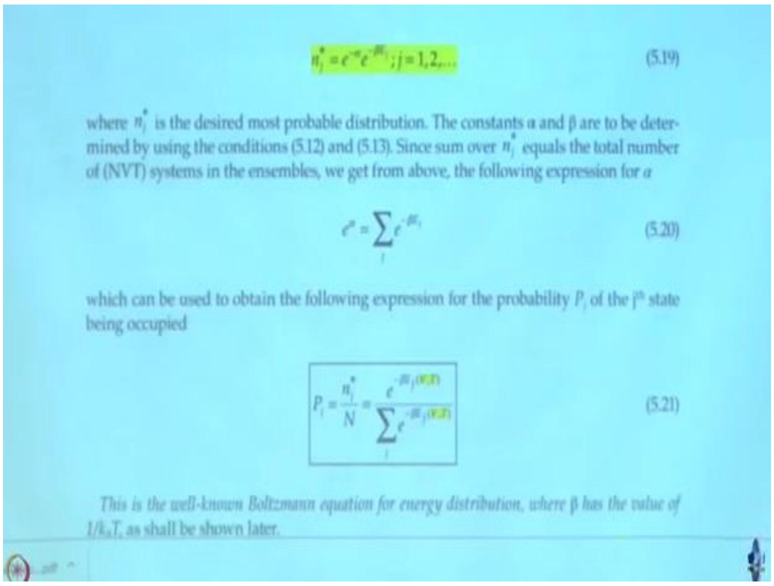

$$n_j^* = e^{-\alpha} e^{-\beta E_j} ; j = 1, 2, \ldots \tag{5.19}$$

where n_j^* is the desired most probable distribution. The constants α and β are to be determined by using the conditions (5.12) and (5.13). Since sum over n_j^* equals the total number of (NVT) systems in the ensembles, we get from above, the following expression for α

$$e^{\alpha} = \sum_j e^{-\beta E_j} \tag{5.20}$$

which can be used to obtain the following expression for the probability P_j of the j^{th} state being occupied

$$\boxed{P_j = \frac{n_j^*}{N} = \frac{e^{-\beta E_j(N,V,T)}}{\sum_j e^{-\beta E_j(N,V,T)}}} \tag{5.21}$$

This is the well-known Boltzmann equation for energy distribution, where β has the value of $1/k_BT$, as shall be shown later.

You can easily see that. This is the distribution that comes out because just I have taken *ln* of that and this that comes out.

$$n_j^* = e^{-\alpha} e^{-\beta E_j}\ ;\ j = 1, 2, \ldots$$

I sum over this. So, star (*) is there to denote that this is the most probable distribution. And at least, what I was telling that it was though it is the most probable, it works with the amazing accuracy. So I sum over that, I get the total N. and then

$$e^{\alpha} = \sum_j e^{-\beta E_j}$$

And then P_j, the probability is this

$$\boxed{P_j = \frac{n_j^*}{N} = \frac{e^{-\beta E_j(V,T)}}{\sum_j e^{-\beta E_j(V,T)}}}$$

So this is what the probability that you are telling that $\frac{n_j^*}{N}$ (N is the total number of systems in my microcanonical ensemble). So, you get now, this is the probability of getting my system in a j$^{\text{th}}$ energy state**.**

So j is the index of the energy state. So P_j is the probability. You recognize two things (a) this is the, our Boltzmann distribution. But we have not yet proved that $\beta = \frac{1}{k_B T}$, beta (β) is just in a constant parameter here.

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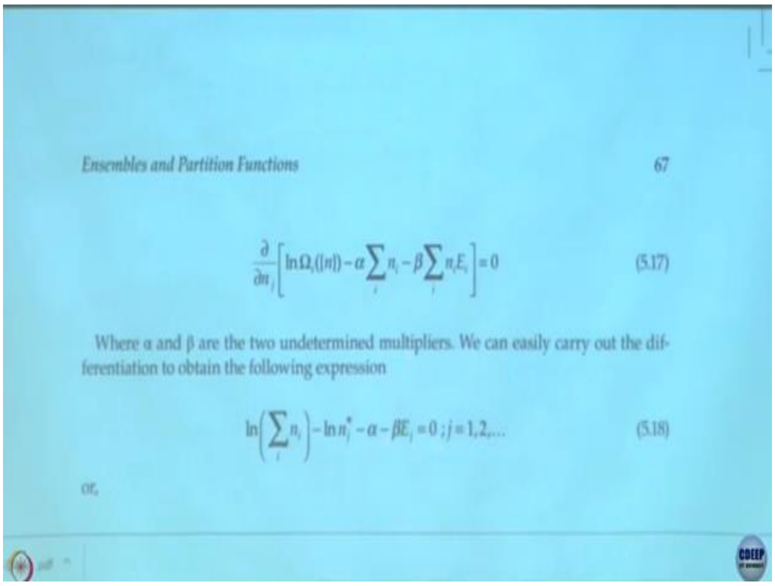

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$$\frac{\partial}{\partial n_j}\left[\ln \Omega_t(\{n\}) - \alpha \sum_i n_i - \beta \sum_i n_i E_i\right] = 0 \qquad (5.17)$$

Where α and β are the two undetermined multipliers. We can easily carry out the differentiation to obtain the following expression

$$\ln\left(\sum_i n_i\right) - \ln n_j^* - \alpha - \beta E_j = 0\ ;\ j = 1, 2, \ldots \qquad (5.18)$$

or,

That is why it is called the method of undetermined multipliers. At that level they are not determinative, they are introduced as constants and we have to determine them with the time. So, this is the quantity that comes here as the normalization is the partition function.

$$\boxed{Q_N(V,T)=\sum_j e^{-\beta E_j(N,V)}}$$

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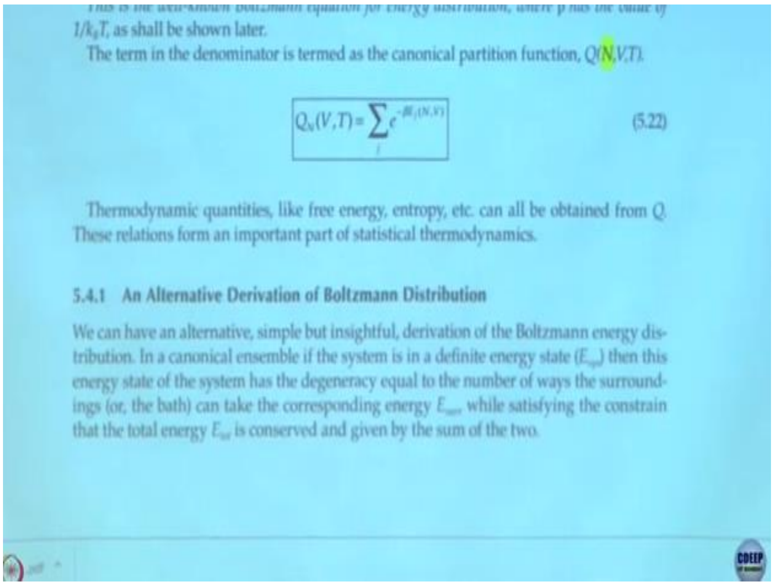

This is the well-known Boltzmann equation for energy distribution, where β has the value of $1/k_BT$, as shall be shown later.

The term in the denominator is termed as the canonical partition function, $Q(N,V,T)$.

$$\boxed{Q_N(V,T)=\sum_j e^{-\beta E_j(N,V)}} \qquad (5.22)$$

Thermodynamic quantities, like free energy, entropy, etc. can all be obtained from Q. These relations form an important part of statistical thermodynamics.

5.4.1 An Alternative Derivation of Boltzmann Distribution

We can have an alternative, simple but insightful, derivation of the Boltzmann energy distribution. In a canonical ensemble if the system is in a definite energy state (E_{sys}) then this energy state of the system has the degeneracy equal to the number of ways the surroundings (or, the bath) can take the corresponding energy E_{surr} while satisfying the constrain that the total energy E_{tot} is conserved and given by the sum of the two.

This is the one of the most important quantity in equilibrium statistical mechanics. But this is not just Boltzmann factor but sum over all the energy levels. The total weight is this

$$Q_N(V,T)=\sum_j e^{-\beta E_j(N,V)}$$

This is equivalent to Omega (Ω), exactly equivalent to Omega but in the canonical ensemble where the difference between this and microcanonical ensemble is that here I have all these different things.

And in microcanonical ensemble I just have Omega (Ω), total number of states but in canonical ensemble each of these states is weighted by beta (β). So they are weighted by beta and that is this is the weight. now I can have a degeneracy here, but that we will discuss later. So this I am not going to do.

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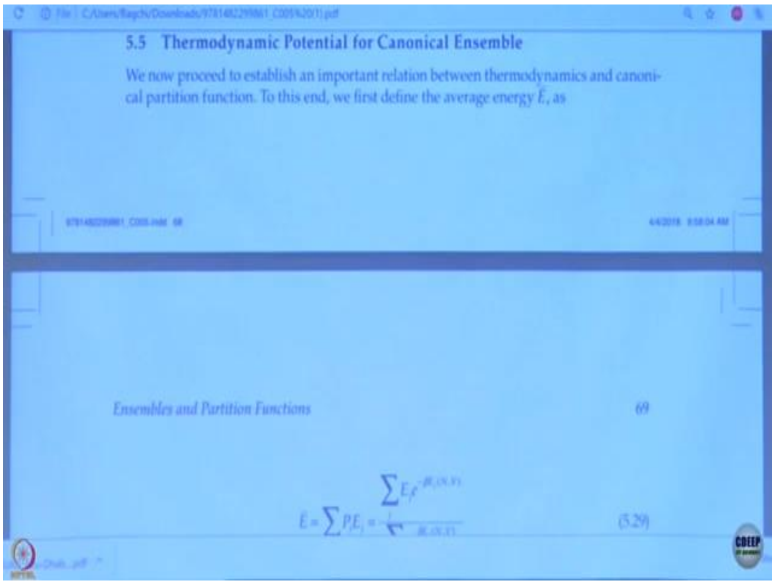

5.5 Thermodynamic Potential for Canonical Ensemble

We now proceed to establish an important relation between thermodynamics and canonical partition function. To this end, we first define the average energy $\bar{E}$, as

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$$\bar{E} = \sum_j P_j E_j = \frac{\sum E_j e^{-\beta E_j(N,V)}}{\sum e^{-\beta E_j(N,V)}} \quad (5.29)$$

So now the most important thing, which I think we will just do a little, then probably stop. Because I think how long this kind of heavy class can go on. So what the next thing is that so we have the following, this is microcanonical.

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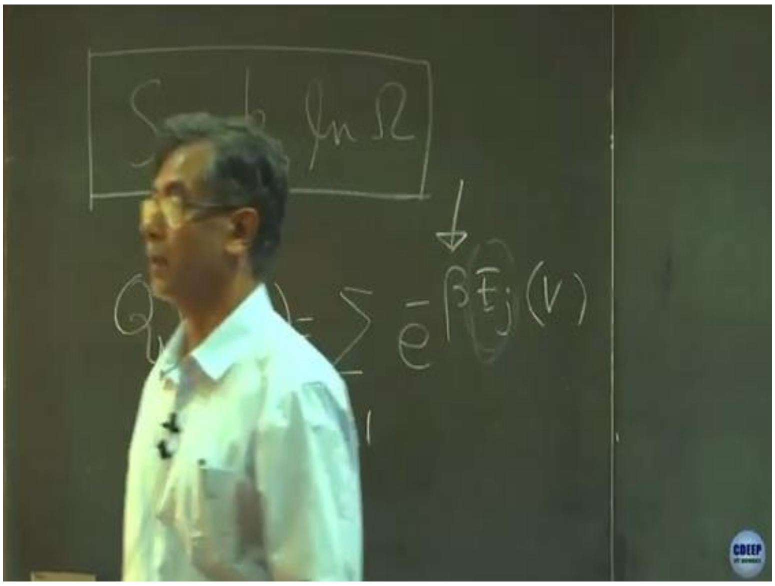

So then the way we write is $Q_N(V,T) = \sum_j e^{-\beta E_j(N,V)}$ this the common way of writing the canonical partition function. All the energy levels, you can have 1 or 0 does not matter. This is determined by V and so very interesting. So for temperature we will show that $\beta = \frac{1}{k_B T}$, the temperature comes through that. And the total number of particles is determined by the volume. This quantity (Q) is a lot of interest, a lot of insight can go into that but I will discuss a little later. So what we need to do now.

Two things we need to do: (a) that we have to establish the thermodynamic relations. We have done how thermodynamics follows from entropy. That was easy because we knew these things. Once we have the entropy, we can calculate other thermodynamic properties. Of course, we have to establish entropy by correspondence with Euler equation and the relation with Omega. but once we have that we know how to get temperature, $\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}$ is the temperature, that is a well-known relation.

Then we know the temperature, expression of pressure from entropy, expression of chemical potential from entropy. It is not the way you usually think about it but microcanonical ensemble gives you those relations. Now we have to define similar relations in the canonical ensemble.

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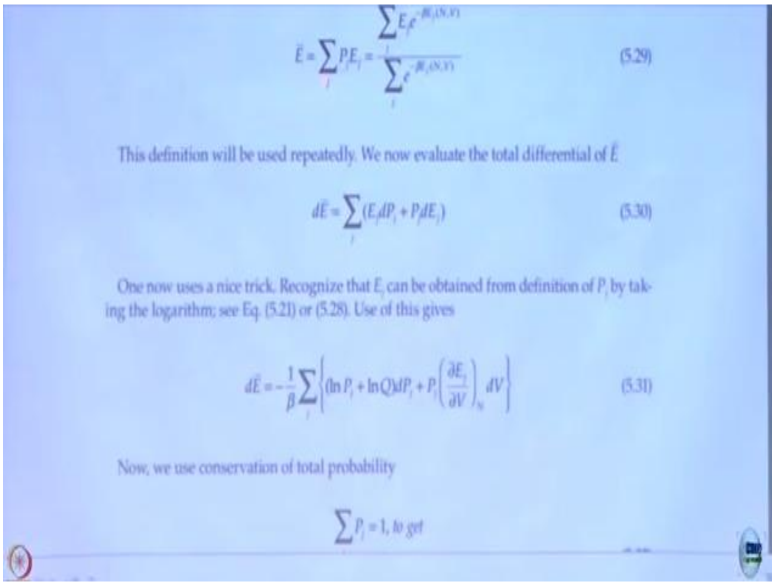

$$\bar{E} = \sum_j P_j E_j = \frac{\sum_j E_j e^{-\beta E_j(N,V)}}{\sum_j e^{-\beta E_j(N,V)}} \qquad (5.29)$$

This definition will be used repeatedly. We now evaluate the total differential of $\bar{E}$

$$d\bar{E} = \sum_j (E_j dP_j + P_j dE_j) \qquad (5.30)$$

One now uses a nice trick. Recognize that E_j can be obtained from definition of P_j by taking the logarithm; see Eq. (5.21) or (5.28). Use of this gives

$$d\bar{E} = -\frac{1}{\beta}\sum_j \left\{(\ln P_j + \ln Q)dP_j + P_j\left(\frac{\partial E_j}{\partial V}\right)_N dV\right\} \qquad (5.31)$$

Now, we use conservation of total probability

$\sum P_j = 1$, to get

So that is the idea now. So, we start with defining an average energy, so this is the average energy,

$$\bar{E} = \sum_j P_j E_j = \frac{\sum_j E_j e^{-\beta E_j(N,V)}}{\sum_j e^{-\beta E_j(N,V)}}$$

that comes out of my distribution and distribution is P_j. P_j is the probability of the system in energy level j, so this energy of the j^{th} energy level. These are the standard definitions. If this is the probability, then I have the partition function.

Again so, partition function Q is actually measure of the sample space. So all the averages will be determined with respect to this. This is the total weight of the sample space. So just like Omega is the weight of the phase space of the system (in microcanonical ensemble) and all our averages are calculated with respect to this quantity; in canonical ensemble, this (Q) is the weight of the system.

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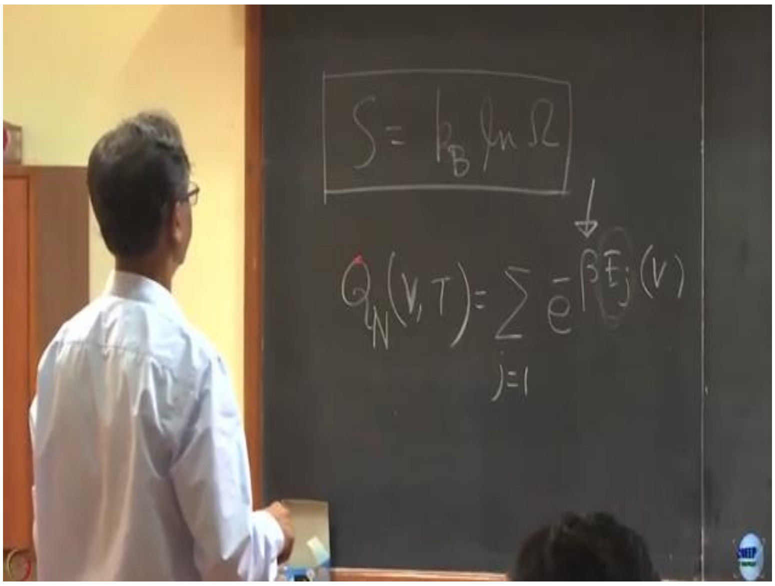

So, a system characterized by NVE has a weight, that weight is given by entropy or rather given by Omega, and then ln Ω is the entropy $\left(S = k_B \ln \Omega\right)$. Similarly in canonical ensemble, this (Q) is the weight of the system. So that is the way to talk of partition function. It gives you the weight of the system. That is why we maximize the weight or minimize the weight.

So now, we then again play a very interesting trick here that I will probably not get to do fully. But $d\bar{E}$ trivially from here to here.

$$d\bar{E} = \sum_j (E_j dP_j + P_j dE_j)$$

Now, as I say, one now uses a very nice trick, which is that we use the definition of *Pj*. and then Pj is defined by $P_j = \frac{e^{-\beta E_j(V,T)}}{Q_N(V,T)}$. So dP_j is then written as I can take d of the left hand side *Pj* then I get these two terms so *lnPj*, so *Ej* on the other side is in the numerator, the exponent, so this is in the exponent.

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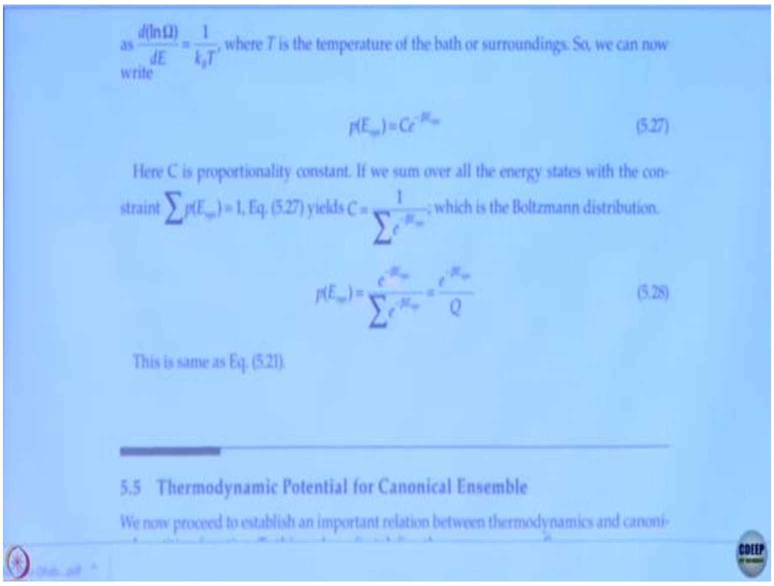

as $\frac{d(\ln\Omega)}{dE} = \frac{1}{k_B T}$, where T is the temperature of the bath or surroundings. So, we can now write

$$p(E_{sys}) = Ce^{-\beta E_{sys}} \quad (5.27)$$

Here C is proportionality constant. If we sum over all the energy states with the constraint $\sum p(E_{sys}) = 1$, Eq. (5.27) yields $C = \frac{1}{\sum e^{-\beta E_{sys}}}$; which is the Boltzmann distribution.

$$p(E_{sys}) = \frac{e^{-\beta E_{sys}}}{\sum e^{-\beta E_{sys}}} = \frac{e^{-\beta E_{sys}}}{Q} \quad (5.28)$$

This is same as Eq. (5.21).

5.5 Thermodynamic Potential for Canonical Ensemble

We now proceed to establish an important relation between thermodynamics and canoni-

So I can take *d* of that differential. Here so, then this comes out and then I get do I take log first then I took the differential I take the log so in ln P, the way E comes out beta E and become so beta ln Q so I have a expression for E that I put it here.

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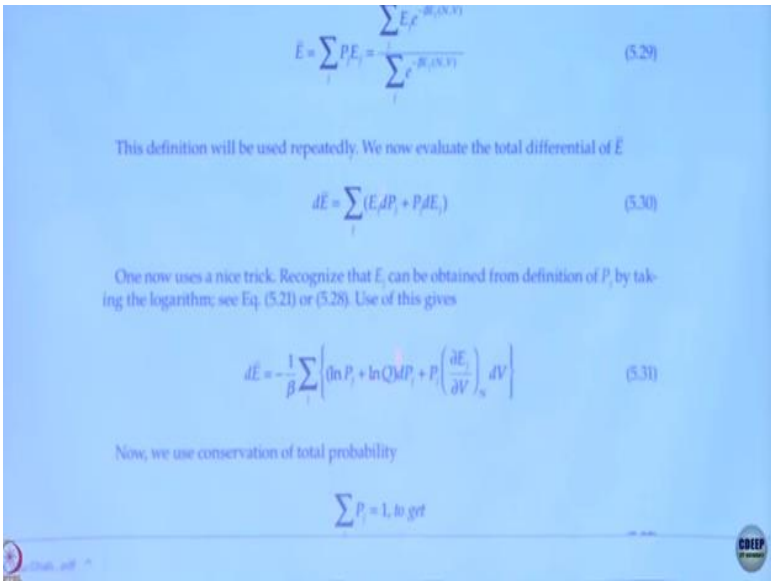

$$\bar{E} = \sum_j P_j E_j = \frac{\sum_j E_j e^{-\beta E_j(N,V)}}{\sum_j e^{-\beta E_j(N,V)}} \quad (5.29)$$

This definition will be used repeatedly. We now evaluate the total differential of $\bar{E}$

$$d\bar{E} = \sum_j (E_j dP_j + P_j dE_j) \quad (5.30)$$

One now uses a nice trick. Recognize that E_j can be obtained from definition of P_j by taking the logarithm; see Eq. (5.21) or (5.28). Use of this gives

$$d\bar{E} = -\frac{1}{\beta}\sum_j \left\{(\ln P_j + \ln Q)dP_j + P_j\left(\frac{\partial E_j}{\partial V}\right)_N dV\right\} \quad (5.31)$$

Now, we use conservation of total probability

$\sum_j P_j = 1$, to get

lnPj by lnQ then dPj comes the dPj the differential will come later then I have this term I write Pj as dEj.

$$d\bar{E} = -\frac{1}{\beta}\sum_j \left\{(\ln P_j + \ln Q)dP_j + P_j(\frac{\partial E_j}{\partial V})_N dV\right\}$$

And then, we know the condition that sum over Pj is 1 $\sum_j P_j = 1,$ because it has to be somewhere, because this is probability of being in the energy state. I had about everything that is normalized that is also come from this definition earlier. Tell me if you have any problem?

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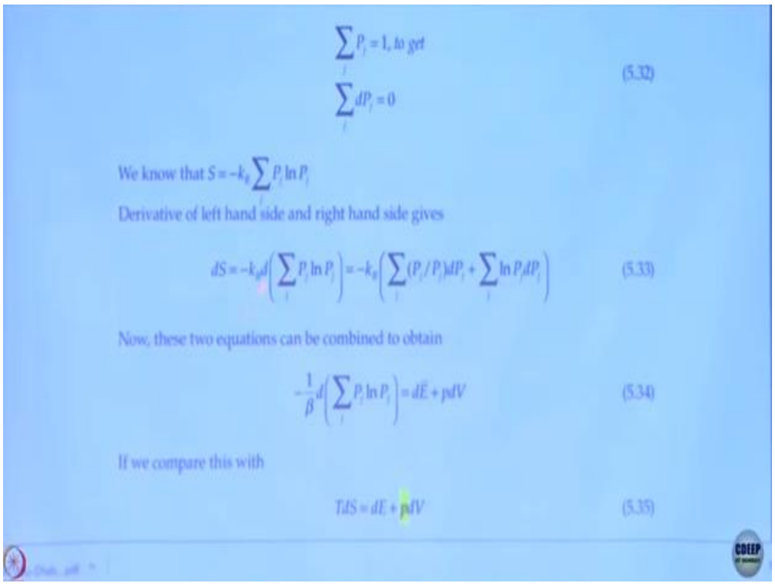

$$\sum_j P_j = 1, \text{ to get}$$

$$\sum_j dP_j = 0 \qquad (5.32)$$

We know that $S = -k_B \sum_j P_j \ln P_j$

Derivative of left hand side and right hand side gives

$$dS = -k_B d\left(\sum_j P_j \ln P_j\right) = -k_B\left(\sum_j (P_j/P_j)dP_j + \sum_j \ln P_j dP_j\right) \qquad (5.33)$$

Now, these two equations can be combined to obtain

$$-\frac{1}{\beta}d\left(\sum_j P_j \ln P_j\right) = d\bar{E} + pdV \qquad (5.34)$$

If we compare this with

$$TdS = dE + pdV \qquad (5.35)$$

And if that is so they sum over *dPj* is 0 $\left(\sum_j dP_j = 0\right)$, where I take *dPj* is 0. This is the thing we use constantly then we go back and we use, you know, the relation with entropy which same as this relation $S = -k_B \sum_j P_j \ln P_j$. You know this? Do I have to explain this or not? Yes or no? But tell me then, so this is the thing actually what happens. This is same as this because in microcanonical ensemble all are same.

This is what some information entropy and all the things but they are all the same in this kind of setup.

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

$$S = k_B \, N_E . \frac{1}{N_E} \ln \Omega$$

$$S = k_B \, \ln \Omega$$

So is it kind of it a same generalized of these things to be energy levels. And then I can do the dS this quantity, and I get this equation

$$dS = -k_B d\left(\sum_j P_j \ln P_j\right) = -k_B\left(\sum_j (P_j / P_j)dP_j + \sum_j \ln P_j dP_j\right)$$

One can work it out that you get how these things work. So these two equations, I believe as this can be combined to get this entropy is now written as TdS= dE + pdV.

Now, these two equations can be combined to obtain

$$-\frac{1}{\beta}d(\sum_{j} P_j \ln P_j) = d\bar{E} + pdV$$

If we compare this with

$$TdS = dE + pdV$$

We get,

$$TdS = -\frac{1}{\beta}d\left(\sum_{j} P_j \ln P_j\right)$$

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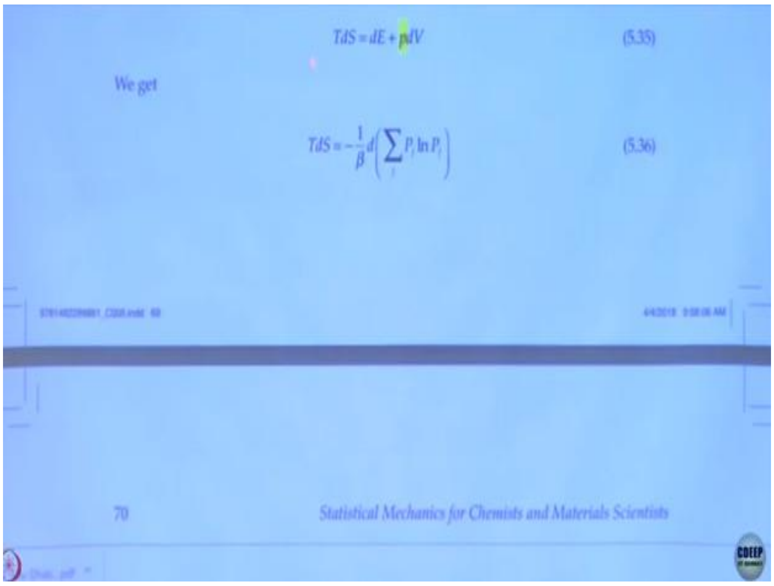

$$TdS = dE + pdV \qquad (5.35)$$

We get

$$TdS = -\frac{1}{\beta}d\left(\sum_{j} P_j \ln P_j\right) \qquad (5.36)$$

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Then the first relation with thermodynamics is

$$TdS = -\frac{1}{\beta}d\left(\sum_{j} P_j \ln P_j\right).$$

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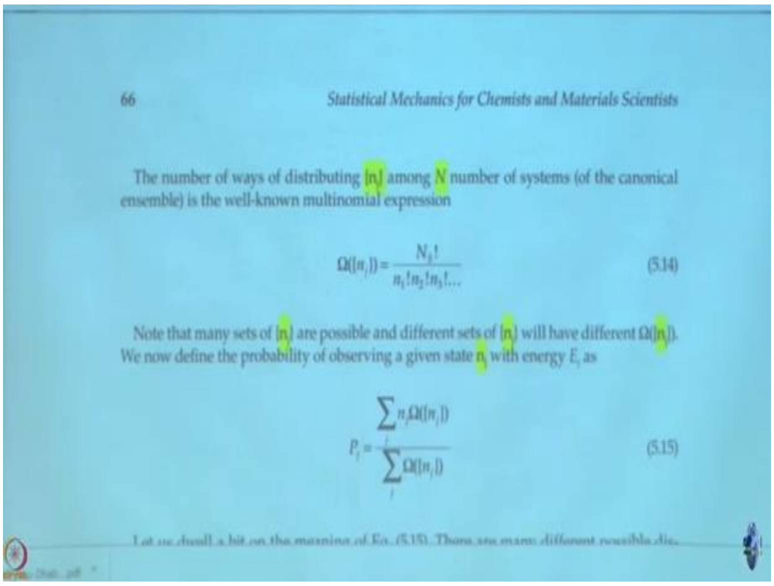

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The number of ways of distributing {n_j} among N number of systems (of the canonical ensemble) is the well-known multinomial expression

$$\Omega(\{n_j\}) = \frac{N_1!}{n_1!n_2!n_3!\ldots} \tag{5.14}$$

Note that many sets of {n_j} are possible and different sets of {n_j} will have different Ω({n_j}). We now define the probability of observing a given state n_j with energy E_j as

$$P_j = \frac{\sum_j n_j \Omega(\{n_j\})}{\sum_j \Omega(\{n_j\})} \tag{5.15}$$

Let us dwell a bit on the meaning of Eq. (5.15). There are many different possible dis-

At the end of the day, you are defining so what is this here let me describe this little bit, so as I was telling I forgot his name.

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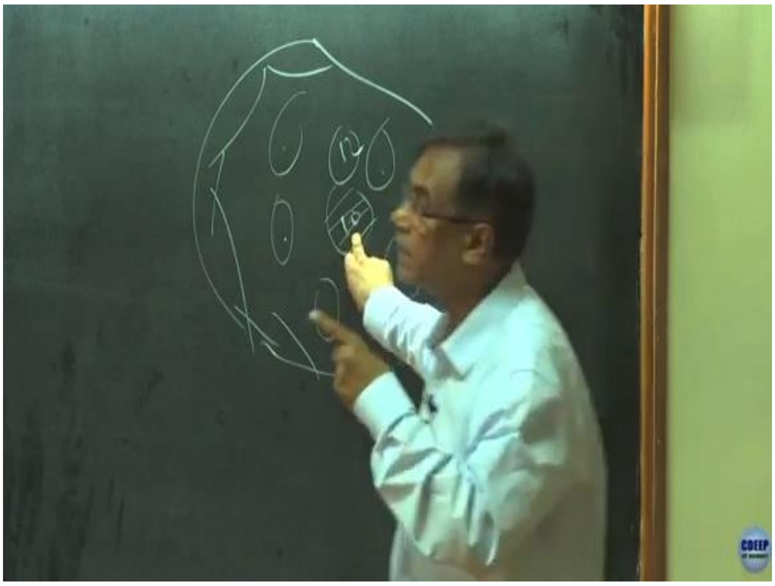

So, I have a phase space and what is the phase space as I explained that the total number of states in the system is a phase space always. Now that phase space is now partitioned. The total space constitutes, say I, for example, bias my coin if I bias my coin then I can make head and tail becomes different. And then there are two ways now look into it that the biasing that I do that probability has to add to something that is my sample space.

That is the question he was asking, that is also equal to total N and in this case, it will be two. So the but by the biased probability that had to add up to 1 also, total number of space so here this quantity is the giving that total number of space. So I have this is I have partitioned my system which is given to me that all the defined energy levels, I have partitioned my whole system in my configuration space so all different energy levels are there.

This is my sample space and each of them given by microcanonical ensemble because all of them is constant energy. So this is now if these are my microcanonical so I finding for each of them Omega each of them on finding Omega but now so this is an energy level say you want to say 10 this is 12 this is 14 all this so I say now go okay?
If I give you energy level 10 in my diagram. How many ways I can do it? That is this Omega.

So, now look at this so this partitioning so now I have to add up all the counts that I get here and that I have to get the total sample space like in Venn diagram that total sample space is this quantity now I have to go back and say okay this has a way these energy 10 has a number with it which is number of ways I can do 10 in microcanonical ensemble that quantity is this quantity.
Okay, this is very neat and clean where Stat. Mech. part is very clean, where one tends to get confused sometimes when the interface with the thermodynamics comes. Because they always think that Stat. Mech. interface is still a little rugged, there is always a little approximation that is made there, so that is where little bit ambiguity sometimes crop seen. o we will meet again at and we will start from the thermodynamics part and dS= dE + pdV. So we will finish canonical ensemble and start the Grand canonical today.

Tomorrow I will hopefully start doing the fluctuations, at least half towards the end of tomorrow morning. That is the most interesting thing in my a book in the initial title I have “realization of promises” that statistical mechanics has. See the difference between quantum Stat. Mech. is the following : in quantum, I do Schrodinger equation, no derivation is required. Then $H\Psi = E\Psi$, I can write H as $H = \frac{p^2}{2m} + V(x)$.

Then that is a differential equation. Now I put it in a V(x) equal to harmonic oscillator potential. I solve, I immediately get experimental observable quantities which is the vibrational spectroscopy, the lines. If I make a little distortion because of rotation, I get what is QR branch which is exactly experimental. Similarly you do particle in a box, you know, you go to conjugate polymer.

So at it almost trivial level you get results, which are connected to experiment and spectroscopy. That is why spectroscopy came first, quantum came later. Statistical mechanics, on the other hand, you have to do a lot of work, go through the whole postulates which is suddenly far more non-trivial than writing down Schrodinger equation. Of course, if you go how Schrodinger did it in his original paper, if you read, it will be a lot of fun.

That how we argued, which was given in the first edition of Berry, Rice and Ross. I used to have all his original papers at one time, that is why I knew that he did everything. He did it from De Broglie wavelength, De Broglie hypothesis. He does not do that operator, that was done by Dirac. History is this very interesting. So there was a formidable thing that went on, photoelectric effect, blackbody radiation, Planck's theory that led to quantum mechanics.

Here Maxwell, then Boltzmann but Boltzmann is so difficult we cannot work out Boltzmann equation in a class so we start with Maxwell.

Then okay Boltzmann tired and did $S = k_B \ln\Omega$. Then comes Gibbs, this formidable wall of the postulates, microcanonical, canonical, grand canonical then comes to applications. But the first applications are actually the fluctuations which just the I think one of the linear response, that is one of the most fundamental things of our natural science is the response functions that we will be able to do tomorrow.