Basic Statistical Mechanics

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Lecture - 11
Canonical Ensemble Part - 1

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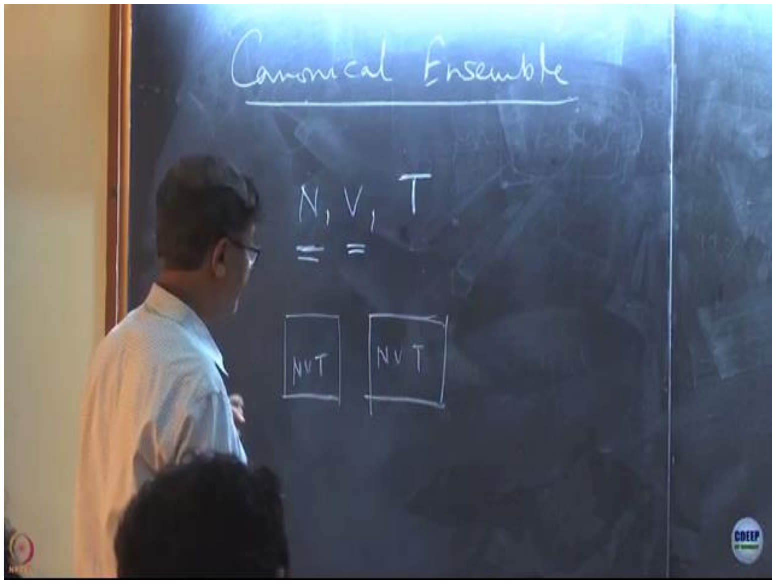

Canonical ensemble: So those are the relation between thermodynamics and micro canonical ensembles that I have given to you. I have given in the book certain problems and I should mention to you that the entire solution book, all the solution of the problems are I think one of you probably should work out in the class the problems, entire problem set that is now available online free if you have bought a book or anybody bought book, then we will be able to download this solution book.

So that solutions book itself is about 200 pages, because it is a huge number of problems in this book. But you need to do the solution because there are examples there are there problems which relate you calculate omega and they calculate the properties. So that is very essential part of the problem. Now going on to the canonical ensemble, canonical ensemble now is the ensemble where the system is characterized now by N V T.

So you cannot change number that is kept fixed, you cannot change volume kept fixed, so your volume fixed. Now so these are well the volumes are different in NVT, NVT all are the same and then think of systems of ensemble but the energy is changing now. So these systems are in a connected with a bath. Now we will do a beautiful mental construction that gives the, which is how to construct?

So basic strategy that gives it is the following: so here we have number fixed, volume fixed, but energy exchange is allowed. Energy exchange allowed such that temperature is constant. So you put it in a bath and we in chemistry always do these experiments. We put it in a bath, and to preserve the constant temperature. Then how did Gibbs do the calculation? Now let me first ask you one thing that when I let my energy constant go which is you know we grew up with the conservation of energy and constant energy we let it go and replace it by a constant temperature.

What is the change in this microscopic state of this system? Yes absolutely, so it can have many different energies. So conservation energy is gone, conservation energy is a huge constraint. All of them are constraints but we work in a natural system regular world with constraints. But here we let go the energy constraint. We were having in temperature, so we will let a macro variable go or extensive property go and replace it by an intensive property.

So, what will happen now to the number of microscopic states…. it will increase enormously, right? Now this is an example I believe is a very nice example.

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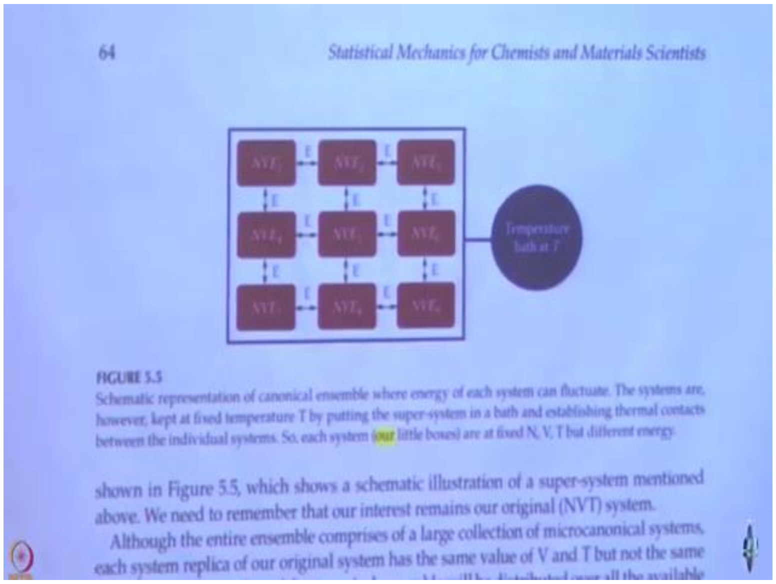

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FIGURE 5.5

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

So basic idea then is the following. These are not the best pictures, but we walked around with the pictures the way it is a canonical ensemble is NVE, so I have a huge number of systems I can put them together and I can, so I can, these are construction gives it so it comes to the construction minute this is I think one of the best thing in the whole of statistical mechanics.

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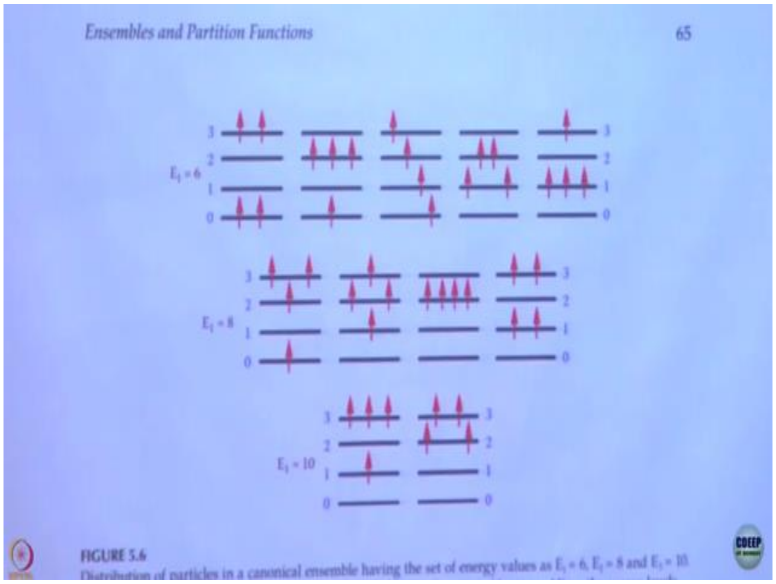

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FIGURE 5.6

Distribution of particles in a canonical ensemble having the set of energy values as $E_1 = 6$, $E_1 = 8$ and $E_1 = 10$

Here, now I have the same example; my four systems, but now I make the energy levels change. So, now here energy is 6, there 8, this 10. I have same energy levels, but now before I had only 4, right? I had only 4, but now I have these additional microscopic states. You are keeping the energy or temperature fixed from outside, you are putting it in a bath, you know, the temperature just like earlier I knew NVE that was my choice of my system, here my choice of variables is the NVT.

So, I have these systems which has same as number of each, in my system NVT that is you know this is very standard experiments we do that we have this number of volume and density fixed total number of in a beaker, total number of volume in a cell, volume is constant then he put it in a outside temperature. So as an experimentalist or in my thought experiment I can always keep these three fixed from outside.

So their phase from outside means what connection to both of you asked the questions that means I have freedom to vary these things I do not have freedom to vary other things, I have freedom to vary these things like I had freedom to vary NVE and as a varying NVE pressure is varying, here also I have these are my three independent variables. Now, I do not have energy (conservation of energy) constant.

However, I know if I keep the temperature fixed then energy is getting exchanged, the system is exchanging energy with the bath and the system is changing energy with bath, then I have different energies. So, as the different energies are there in the same number of microscopic states, because the system is the same I will have the microscopic energy levels, I will have many more, there I have 4, I have many more microscopic states, but of course let me ask you a question.

Of course, constancy of temperature and variation of energy allows very different states but there is a very powerful equation, very, very powerful equation actually one of the most important equation that comes out this testable mechanics that came out of Boltzmann works, that allows you to say which of this arrangement is more probable, which is that? So when I allow energy to change, listen carefully, I think that I am not formulating it well, I am telling you I am allowing energy to change, but systems always have spring in them.

Systems just like volume, there is a spring and in energy, there is a spring and I tell you the spring in energy is the specific heat. Spring in volume is the isothermal compressibility. These are all this spring, that is, which holds system together, and does not allow you to change. Actually, you can write down the free energy or any as a function expansion and you can see that there first order is zero because of the minimum energy free energy minimum condition.

Second term what this we call it response motion, which we deal with at quite extensively later that is one of the very important outcomes of this in my book when I wrote this chapter, I call realization of, from ensemble realizing, and the fluctuation of chapter, I say realization of the promises because that was first time stat-mech gave which was done by Einstein, the most remarkable prediction that comes.

So, I am asking you a question now, if I give you this kind of things in a more general sense many more energy levels much higher energy but in the system that which the energy is more probable, what is that? There is a distribution which will come out but all of you know that you know that from high school days Boltzmann distribution. So though energy is fluctuating across because of constancy of temperature there are a probable distribution of the energy.

So why do we when we relax the constant energy and in as a result of the constraint we get all these different energy base or different occupation of the microscopic state and different microscopic states there is some another there is a constraint that comes. So we relax a constraint but you get a constant in terms of distribution this happens again and again the same thing happens in the case of grand canonical ensemble or other ensembles.

But that is one of the beautiful ways of this thing. So go back let us see, how a constructed Gibbs went around with it. As I told you it is a beautiful construction that Gibbs state. So what Gibbs state, okay I assume that all my systems are at made at I put all my systems together, all my NVT together in contact with each other and then billions and billions of my micro canonical ensemble systems put together.

And then I put them in contact, then I put them in an isolated, I put a box around them and isolated constantly completely. So now, each of this system is the NVT system, this is NVT, this NVT, but I have put them in contact they are NVT, they can exchange energy. So instantaneously, each of the state is in different energies. Now I form a super ensemble, all of them I put in contact.

And I now added the energies all of them and is a very large number of ensemble of ensemble and I put I isolate them, then I can talk of, my super ensemble I insulate it, my super ensemble is a total number of N. So, I have these numbers of italicized N.

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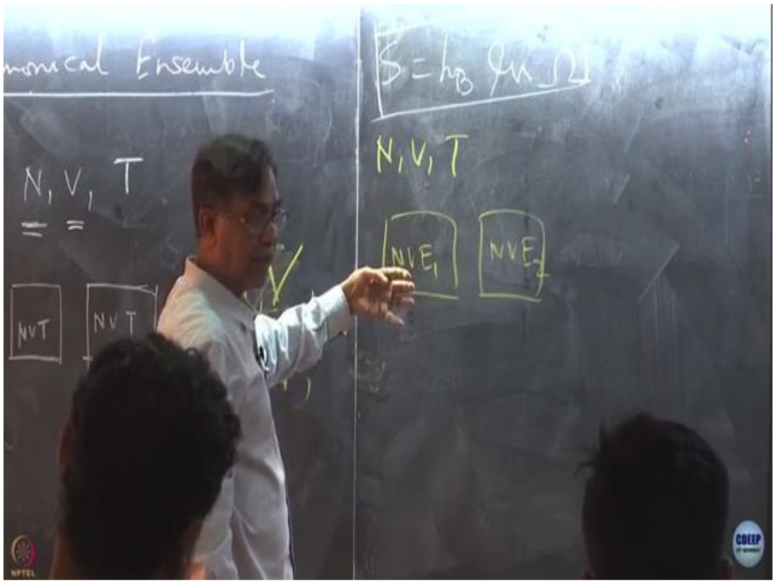

And, this is my total number of ensembles, total number of micro canonical ensembles in the system. So, now I put, I create an ensemble out of this ensemble. That means now my NVT each of my system here are at NVT, but instantaneously they are NVT, but they have different energies, right? So, when I put them together I have a huge n number of them I put them together, then isolate them.

Then I make ensemble out of that ensemble my super ensemble, then that my super ensemble each of them is also open ensemble, they themselves are in having these number of volume and these number of particles. But energy will have a sum, there is a constraint and this was then because the only thing that I have you have to understand, the only thing that I have is this formula. That is why I said that everything follows from that the only thing that I have this formula.

So now what I am trying to construct when I go to canonical ensemble I want to construct an ensemble of ensemble such that in my super ensemble, each ensemble is a micro canonical ensemble. Ensemble is a micro canonical ensemble. It is I was saying is one trying brilliant construction, it is very difficult. Then you know what one does there is if I have discussed it quite a bit here, but I just want to do the math.

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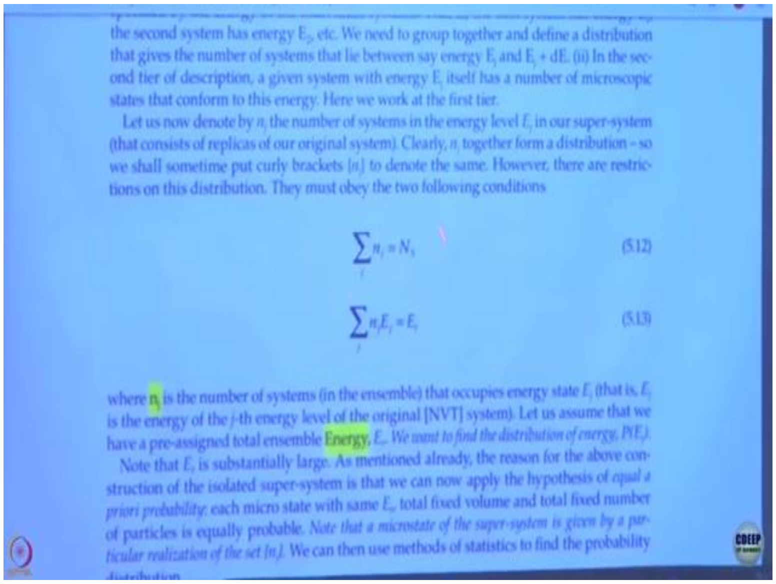

the second system has energy E_2, etc. We need to group together and define a distribution that gives the number of systems that lie between say energy E_i and $E_i + dE$. (ii) In the second tier of description, a given system with energy E_i itself has a number of microscopic states that conform to 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

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

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

where n_j is the number of systems (in the ensemble) that occupies energy state E_j (that is, E_j is the energy of the j-th energy level of the original [NVT] system). Let us assume that we have a pre-assigned total ensemble Energy, E_s. *We want to find the distribution of energy, $P(E_j)$.*

Note that E_s is substantially large. As mentioned already, the reason for the above construction of the isolated super-system is that we can now apply the hypothesis of *equal a priori probability*: each micro state with same E_s, total fixed volume and total fixed number of particles is equally probable. *Note that a microstate of the super-system is given by a particular realization of the set $\{n_j\}$.* We can then use methods of statistics to find the probability distribution

So now if I now have in my ensemble these the number of systems that have my energy here, then that has to be this is here the index is not capital n, it is total number in s and so then n_i total number, so let me denote this n by the number of systems energy. So then total number of things essential are the total number in my super ensemble and then the population n_j is an n_jE_j then multiply they got the total energy E_j.

So the notation I personally when I teach I actually Italicize n but here the italicized n has become capital N and capital E. So this is total energy E_j is energy of one of my systems in my ensemble and I have made I said micro canonical ensemble of the ensemble of ensemble and this is the condition because this is the total number. So, n is the total number of systems in my super ensemble and this is the total energy.

So each system in micro canonical ensemble constant temperature but they are in a different energy state. Is any confusion there? You are allowed to make the systems interact with each other and you are giving the condition that they themselves you keep that system for an equilibrium with long time with a bath. So that the temperature almost the way we do the simulations.

So, the temperature it comes to a constant level at temperature T, then you isolate it, insulate it completely and that is the super ensemble. That is how and then you call that super ensemble, number of particles of micro canonical system, you put together and construct a canonical a system in canonical ensemble NVT, then you put ensemble of these things and that has a constant total number of particles.

It is not the number of particles in one system is the total you know and then energy also in factually this is the constant, is it clear? This is not an easy construction. But what you get at the end of the day is of huge importance. This is a very serious business and usually this thing is not taught in the classes because it is a kind of complicated thing. Now we are going as i told you again and again whole throw.

We have created a super ensemble which is micro economical because I have nothing but on this equation to go.

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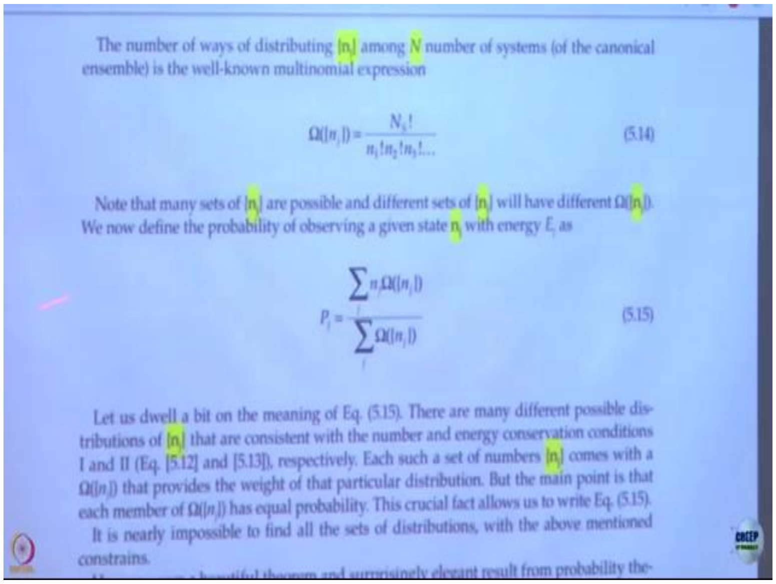

The number of ways of distributing $\{n_j\}$ among N number of systems (of the canonical ensemble) is the well-known multinomial expression

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

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_i with energy E_i as

$$P_i = \frac{\sum_j n_j \Omega(\{n_j\})}{\sum_j \Omega(\{n_j\})} \qquad (5.15)$$

Let us dwell a bit on the meaning of Eq. (5.15). There are many different possible distributions of $\{n_j\}$ that are consistent with the number and energy conservation conditions I and II (Eq. [5.12] and [5.13]), respectively. Each such a set of numbers $\{n_j\}$ comes with a $\Omega(\{n_j\})$ that provides the weight of that particular distribution. But the main point is that each member of $\Omega(\{n_j\})$ has equal probability. This crucial fact allows us to write Eq. (5.15).

It is nearly impossible to find all the sets of distributions, with the above mentioned constrains.

beautiful theorem and surprisingly elegant result from probability the-

So I have to go back to that equation, that is why I had to construct the micro canonical super micro canonical ensemble and I am working on the super micro canonical ensemble. So I had this super micro canonical ensemble where in is the total number of systems, so it is a total number of systems in my ensemble and total number of system each of the system it has in that energy level.

So in my super ensemble there is n_1 number of systems, not particles n_1 number of systems energy level 1, n_2 number of systems energy level 2 and then I can write total number like that. So, I do the commutation. Looks now, I can develop a saying and this is really extremely important, no one can now define that probability of observing a given state n_i in energy i, is this quantity. So here I have done it partition I have said okay,

I have in a n_i systems in energy level E_i, that has since they are in constant energy they are as an Omega associated with it. So, that is this Omega, then I this is normalization because I sum over all the energy levels, the total number of microscopic states is the total normalization, but this gives the probability of observing n_i particles in the a. So I am done an averaging here so this is a very important definition in the whole scheme, big scheme of developing the expression of micro canonical ensemble, is it clear?

So that means you have to think in terms of a little bit because this n_j is a number of systems at energy level j, since you getting, since you have fix these things as constant energy. I can talk of this and it makes sense because Omega is number of microscopic states of a system with a given N, V and energy. Now game we are going to play now so this is like you can guess what you are going to do?

So we have defined probability of observing a system with a energy E, E_j and we have the total number however we know internal number there are these two constraint. But, so this is not an unconstrained variable. So this is two constrained, so what is the way we do it?

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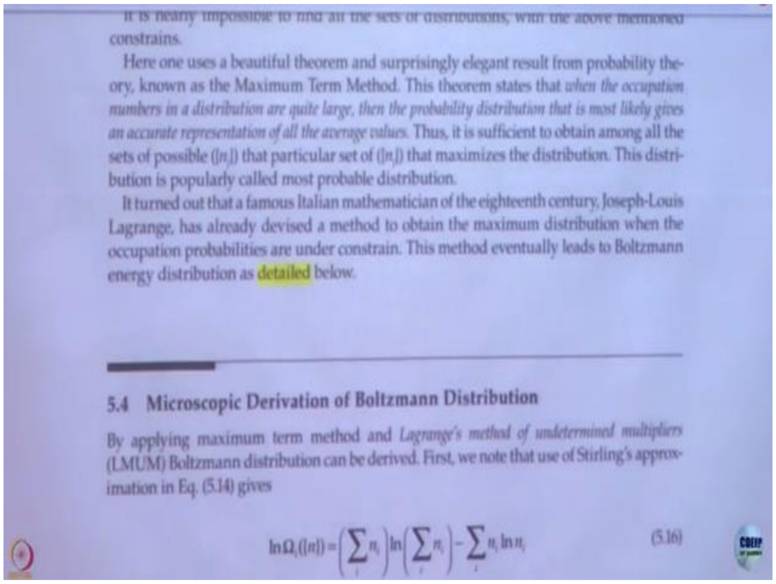

It is nearly impossible to find all the sets of distributions, with the above mentioned constrains.

Here one uses a beautiful theorem and surprisingly elegant result from probability theory, known as the Maximum Term Method. This theorem states that *when the occupation numbers in a distribution are quite large, then the probability distribution that is most likely gives an accurate representation of all the average values.* Thus, it is sufficient to obtain among all the sets of possible ($\{n_i\}$) that particular set of ($\{n_i\}$) that maximizes the distribution. This distribution is popularly called most probable distribution.

It turned out that a famous Italian mathematician of the eighteenth century, Joseph-Louis Lagrange, has already devised a method to obtain the maximum distribution when the occupation probabilities are under constrain. This method eventually leads to Boltzmann energy distribution as detailed below.

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

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

I so anybody has any clue how to go about it now. Just like before we are going to do, we will do the will maximize in an Omega and from the commutation I get this equation, any confusion there?

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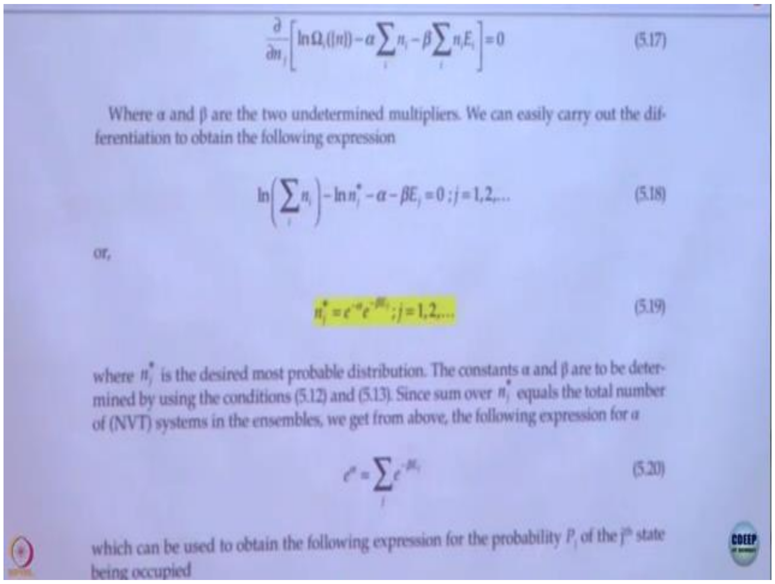

$$\frac{\partial}{\partial n_j}\left[\ln\Omega_i(\{n\}) - \alpha\sum_i n_i - \beta\sum_i n_i E_i\right] = 0 \quad (5.17)$$

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

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

or,

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

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

$$e^{\alpha} = \sum_j e^{-\beta E_j} \quad (5.20)$$

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

Now I want to maximize this quantity any confusion there? However, there is not the way you do that there is a way to do this there is a condition call they call the condition of Lagrange multiplier. When you have a variation but with subject to the constraint, so when I have these to constrain I have to put these two constrain into my these two constraints I have to combine with this equation of this equation with this quantity.

And you guys know the method of Lagrangian multiplier. This is the method of not a constant is a Lagrangian multiplayer is called method of Lagrangian multiplier off variation of constraints you have done that? No. So basic idea is that we have to maximize this quantity we have to find that distribution of n_j remember n_j is number of systems at energy level E_j. However even though I am allowing systems to vary over different energies there are priorities.

Because of NV and intermolecular interactions. There are some energy levels which are more populated than other energy levels, actually there is a Gaussian distribution and the coefficient of the Gaussian distribution is the specific heat but that comes later those very fundamental things comes later. Right now, we are trying to get I give you the energy levels I allow you to choose your energy but the system has a constrained system.

Because of this, total energy is conserved in super ensemble, total number is conserved in my ensemble. The variation so the Omega to that particular distribution so what I am talking of this area is a distribution and I am after this distribution. So n_j is number of systems in energy level E_j.

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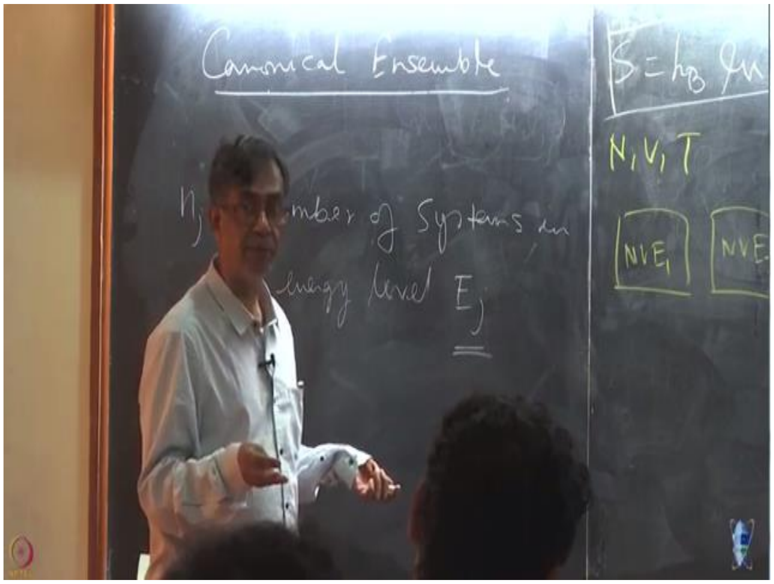

And I am allowing these energy levels to change because I do not have conservation of energy constants energy anymore. So these those my arrows, so I have many different energy levels however my systems prefer certain energy levels, all these energy levels are not when you do the computer simulation what do you see? You show the energy and the energy is fluctuating, but they fluctuate under value, that value is the average and also the most probable.

Now you plot a power distribution of the energy what do you find? You find the Gaussian distribution. Who determined what is the average value and who determines what is that there the width of the distribution? Width of the distribution is given by specific. Who determines that what average energy it will be it is by the intermolecular interactions and density and volume n energies, that determine your, so now those things must be there putting in a constraint and those are the constraint.

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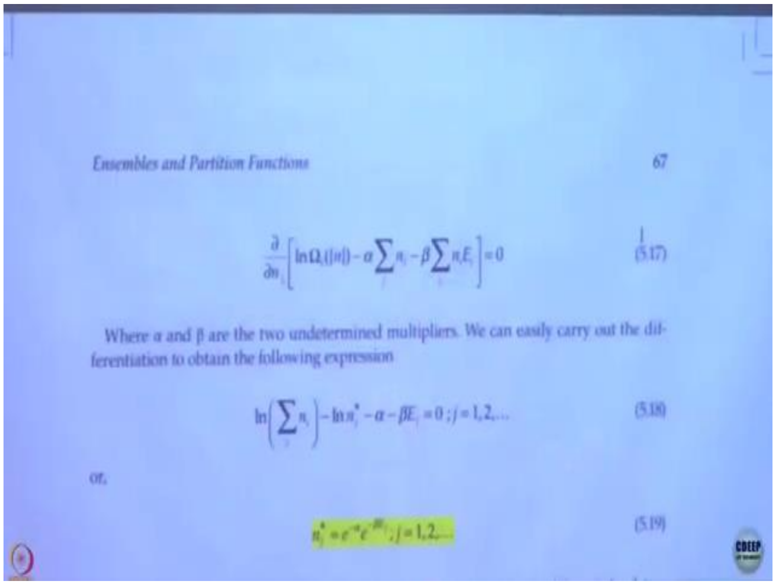

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$$\frac{\partial}{\partial n_j}\left[\ln\Omega(\{n\}) - \alpha\sum_j n_j - \beta\sum_j n_j E_j\right] = 0 \qquad (5.17)$$

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

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

or,

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

So a distribution is there which I have to maximize but that be any distribution will not do those distributions obey the total number of particles that I have, it is constant I have written those equations here, total number of my energy in the grand canonical after all I will be working in a grand my going back to my canonical ensemble. So the way that is done picking up a distribution of many distribution.

So I have a distribution of distributions picking up a distribution out of that distribution is that those distributions that follow this constraint and this is a method of Lagrangian multiplier. Please review that I have appendix on micro canonical and the Lagrangian multiplied in the book. So then we do this maximize with this constraint this is the way to meet up a Lagrangian multiplier and then you take this derivative you get Omega.

You put the Omega which we did here, this is the Omega and you do the starlings approximation and then you get these constraints and this is just a constant you can see now in J to the power alpha beta E. So nj stars become this quantity. So this is overall equation that comes out from these equations. Exactly that is very good question, actually that is an excellent question. So we will come to that. This is an excellent question.

This is the Boltzmann distribution. You are right and but I will come to that in minute. So I think we will probably with that answer of a question we will stop today as I said that you know one of the again the questions just like the questions you guys asked is the cause of confusion. So but you are okay with these now right? Now I have to get these quantities here, e to the power - r. So I do sum over nj if I do sum over nj and I sum over to a - beta j.

Then I kind sum over nj is the total number n and then this is the quantity it will be - beta j, E to the power alpha because this n is the a.

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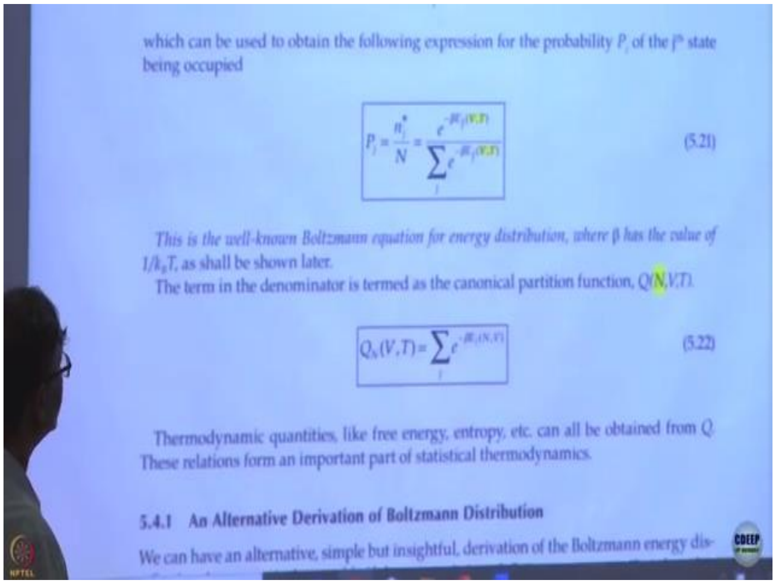

which can be used to obtain the following expression for the probability P_j of the j^{th} state being occupied

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

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

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 dis-

So then you get P_j is n_j by N from there you get to the $-\beta E_j$ by it is continuous quantities. We will just do sum over that so this is the definition that we started to do the probability of finding a system. so, because we want its systems number of systems energy ability it is not number of particles in its energy level either it is number of systems energy level and so the probability of observing a system again energy E_j is this quantity.

And this quantity is the canonical partition function and so if I write the canonical partition function here that has related then this is the one of the most fundamental equation of statistical mechanics which now tells you how we have not yet shown that beta is temperature but we will show that the beta is temperature for that we have to do an analysis very similar to what we did with all that equation in micro canonical ensemble.

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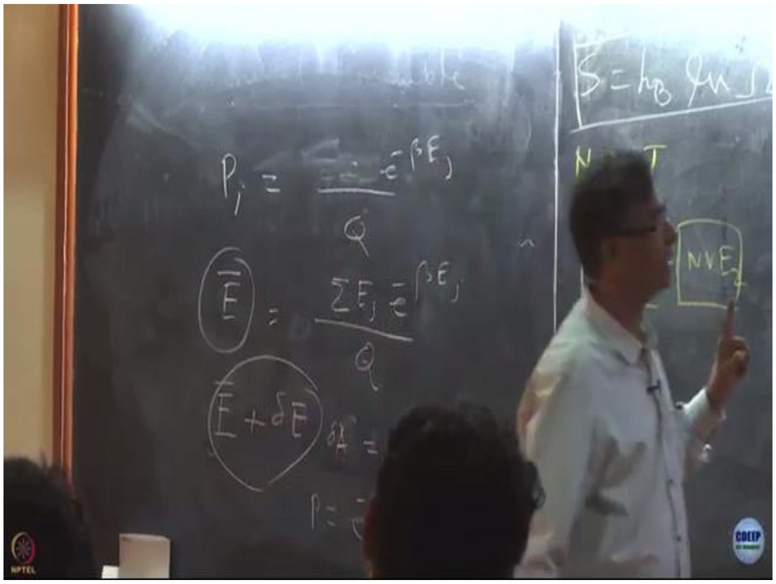

That we will do now I will just before you stop I will answer this very good question what you have to do now, in order to get out that so probability of P_j is you know P_j is $e^{-\beta E_j}$ now what do you do? You define the average energy E and then average energy E is this probability distribution. It is this quantity which is Gaussian. So now you consider your average energy is, this you make a fractionation ΔE and from here now you calculate that is exactly we will do later.

We calculate the variation of energy, so now you say since energy your average energy where the system is the one which minimizes the free energy. So fast derivative of that goes to zero, so you are in the energy then it is like that you energy E is; E average plus first derivative is zero then second derivative. So your variation of free energy and then because first derivative 0.

So now probability in this in easy to the power of minus Delta a, and that is e to the power minus it goes out and you get e to the power of minus Delta a square. So it is really very good question that volt even distribution has we need the Gaussian distribution but this is multiple distribution where you are asking what is the individual energy what is the population of individual intervals Gaussian that you observe is the total energy.

So in simulation when you find a Gaussian distribution of energy there is a total energy not the individual energy. Any observed system when you look at the observed total energy of system is the total energy average energy or in a observe energy that you are this is not the observed energy this is the one confusion is always that because when we do spectroscopy in quantum mechanics, we consider this is the energy that you observed in spectroscopically, but those are isolated single non interacting picture.

When you are allowing energies to exchange like in a macroscopic system or thermodynamics systems then this is Pj is the probability that your system is their energy Ej. We use that same they are also but when I talk about Boltzmann distribution is the total macro variable total macroscopic energy that is the Gaussian and that comes from there by same day and definition but you define the total energy by that equation.

And average energy of the equation then you say my free energy is the one that is minimum at the average energy E that property used and then you get the Gaussian distribution at equilibrium. Let us look at that. These are the construct we gave we did because as I told you there is only equation that you have is entropy $K_B \ln\Omega$ we did the construct made of a super which is microcanonical.

So we started with ensemble which is canonical then we put many canonical ensemble together and I put a super ensemble micro canonical ensemble, in the micro canonical ensemble I now can talk up number of system nj then I can do and construct your Omega now and that Omega has the constraint of total number of systems and total energy because I have a micro canonical. Micro canonical has constraint energy and constant n, I put those constraints by using a Lagrangian multiplier and I get that particle out.

That is Gibbs, that he played, Gibbs played. Now you are asking the Gaussian, energy is Gaussian, volume is Gaussian all these things, so in a computer simulation we are studying these you are talking of a single system but you are talking of trajectory for a long time or you can take a multiple Monte Carlo simulation where you are doing you are creating many, many configurations of this system which is same as creating many systems.

Now you are talking of average energy so when we plot, we plot the energy of the system either it is trajectory in Monte Carlo simulation and I have a histogram I have this many energy this many time my system is in its energy but that is the macroscopic total observed energy. This is not what you observe, this is what the microscopic occupation of the system and we find out from this distribution.

What is the energy? Average energy that just what I wrote down we will do it tomorrow and what is the entropy and what are the other properties. We have not done that we have just like in micro canonical ensemble we have done, we got that important that is a Boltzmann distribution and from there now will construct the rest of the things so that we will do tomorrow 10:30 right?