Lecture – 16
Fundamentals of Statistical Thermodynamics Part – I

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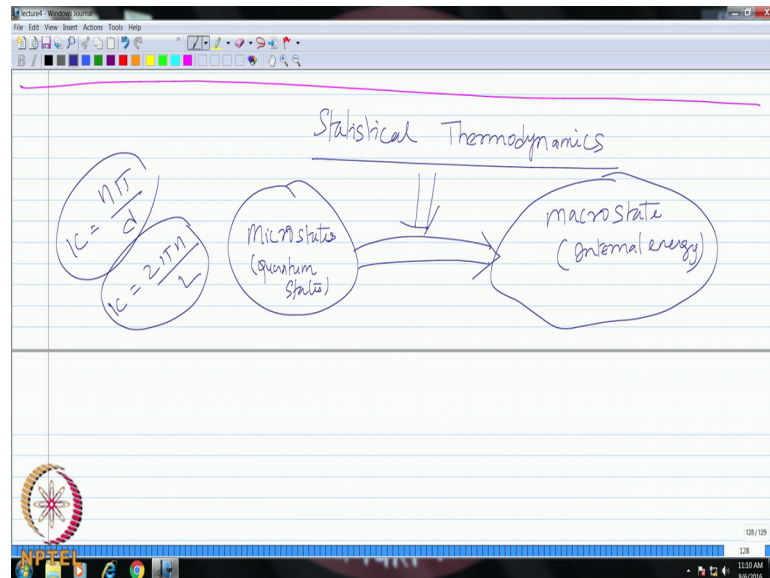
Good morning and today we will start a new topic, which is the statistical thermodynamics. Statistical thermodynamics is actually the bridge; you can say between the micro states that we had been dealing with so far the last so many classes, where we understand that in quantum mechanics, depending on whether you are looking at a simple particle in a quantum well or a potential constrained or, you are talking about electrons in a real crystal structure. You have several quantum states, which are also called as micro states. When I say micro states, these are corresponding to the discontinuous wave vector.

They can either be something like the N pi by D kind of quantization, where you put a particle in a potential energy constrained and get this or it can be in a real crystal where you are K can be 2 pi N by L. Never the less, what it means is you are having discontinuous values of K, which gives raise to discontinuous values of energy. These are called micro states. You have so many micro states and this are possible states where you know you can fill electrons and now in the macro scale picture in the continue picture,

you have 1 big you know macro state and what are the macro state that we are concerned with for example, internal energy, as a consequence you will have temperature.

Therefore, now we have to somehow link this information on so many micro states and we have to arrive at away of clearly defining the macro state or macro scale property for the system with so many numbers of micro states. This is where the role of statistical thermodynamics comes into picture. We are actually building what we called a bottom sub approach. We are now starting from the fundamental building blocks of individual energy carriers looking at the discrete nature of the energy states and now from there, we are trying to go to the continuum picture and trying to represent these micro states with some macro scale variables.

Then how do we do that? Statistical thermodynamic we cannot simply you know fill the electrons the way we want or fill phonons the way we want. There is a certain way that these electrons or phonons can occupy these energy states and these are represented by the distribution functions. Therefore, we have to respect the nature of these energy carriers and how they are supposed to occupy these energy states. Unless we do that, we cannot simply assume, the electrons and phonons to fill the micro states in a manner that we want to do. Therefore, statistical thermodynamics just 2 things, 1 it gives you the order in which these states are filled by the energy carriers number 1, number 2 then how do we transfer all these information from the micro scale to the macro scale.

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Eventually that is what we will do. Therefore, the first part is therefore, to look at the distribution of energy carriers. We have to understand, it is like some builder has built certain apartment complex say 100 apartments within the complex, each different size, you know different requirements, some 1 B H K 1 2 B H K, some 3 B H K and we do not know how people will fit in these apartments. Somebody may prefer 1 B H K somebody a 2 B H K. That is basically the distribution function and then finally, when you have you know find the right people, who can fit in this particular house, then you have known exactly how these apartments can be filled and this filled apartment now can be used to describe what we call the macro scale the aggregate of all these.

But to fill this, we have to look at all the micro states that are each and every apartment what kind of people can fit in this particular apartment and this is exactly how at the small scales, the energy carriers also preferred to occupy certain energy states and these are given by these distribution functions. Too quickly I mean I am sure many of you already took courses and probability and statistic. I am just going to directly go into the part of the matter and I will just assume that you know how to calculate the probability distribution function and so on. Now the question will be now for example, let us take 3 distinguishable particles.

I am just giving an example, you have 3 distinguishable particles and you have 4 energy states or four micro states. Let us say you have epsilon knot is a ground state. You have epsilon 1, epsilon 2 and epsilon 3 and now I am going to represent 3 scenarios, how these 3 distinguishable particles can possibly occupy these energy states. These are just examples. In scenario A, you have all the 3 particles occupying epsilon 1, like this. The other states are completely vacant and you can have a second scenario, where 2 particles or occupying epsilon knot and the third particle is occupying the highest state epsilon 3. How can you represent that?

The middle 2 are completely vacant. If 2 particles are occupying the lowest 1, they can occupy something like this, middle and the end of this energy state and you can have 1 particle which is like this. This is 1 combination. The other combination is you can have 1 on this end, 1 on this end. These 2 are vacant and here you can have the third particle occupying the middle. You have another possibility, where you can have these 2 occupying the left and the middle and the third particle occupying the right hand.

Therefore, when you have 2 particles occupying epsilon knot, 1 particle occupying epsilon 3, how many possibilities are there?

You have 3 possible combinations. If you are having only all the 3 distinguishable particles occupying only 1 energy level together, that means, only 1 combination is possible. Now you can go further and you can say you have 1 particle occupying epsilon knot, second occupying epsilon 1, third occupying epsilon 2. In that case how many different combinations are possible? You can have a scenario C. In which the highest energy state is not occupied, for example, the lower 3 once. You can have combination where 1 is occupying the left hand here the other is in the middle, third 1 is like this. Like this you can represent more states, you can all of you do that? 1 here, the other can be here, the other can be here.

How many such combinations are possible?

Student: (Refer Time: 10:30).

You freeze, you can first draw and check for yourself. You have 1 here, 1 here, 1 here then you have 1 here. So, you freeze these 2 positions, you move this.

Student: (Refer Time: 10:30) 37.

Let us draw all of them. Then you can have 1 here, the middle 1 towards this and 1 towards this. You should have 1 in the center now and 1 in right 1 towards left. If you want to calculate the probabilities, therefore, you can therefore, 1 2 3 4 5 6.

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Now, let us see how we can calculate the number of states or the number of arrangements possible. In case of scenario A, the number of arrangements, this is in the micro states. What we call as quantum states. These are representing the quantum states and you want to distribute particles into these quantum states.

The number of arrangements possible in scenario A is given by. You have 3 particles Therefore, 3 factorial divided by; in the first energy level you have 0 particles. 0 factorial second energy levels you have 3 particles, third energy level, you have 0 and fourth energy level 0. The general distribution is that you have N factorial divided by N 1, factorial N 2, factorial and so on. This gives you the distribution or number of arrangements totally that are possible for each scenario. In this case therefore, how many numbers of arrangements are possible? 3 factorial by?

Student: 2 1.

You have 1. This is what is given by this particular arrangement to all 3 basically occupying only 1 state, 1 micro state. That means, you can put them in only just 1 way.

Now if you apply this to the second case. You have 3 factorial divided by number of particles occupying the first level 2, 2 factorial second level.

Student: 0.

0, third level.

Student: 0.

0, fourth level 1. Therefore, this will be?

Student: 3

3. You have therefore, 1 micro state here. What we call and these are 3 micro states possible. That means, there are 3 possible combinations of these filling. Similarly, if you extended to the third scenario you have 3 factorial by 1 factorial 1 factorial 1 factorial and 0 factorial therefore, how many arrangements? 6. Now, this is giving you the probability. Therefore, usually what happens is the arrangements will always go towards the scenario of maximum probability.

The maximum probable distribution will be the most likely distribution. Therefore, the most probable distribution what you are talking about should correspond to the largest value of omega that means, we have to find the possible value of omega, which is highest that will give you the most probable distribution because the more number of states that you have more likely that, this will be the states occupied by these particles. These are actually not constraining like the way, we are constraining in scenario A B C. They try to occupy you know as freely as possible.

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That means, you have to find the most probable distribution at corresponds to the largest value of omega. This is basically the starting point of deriving these statistical distributions. What we will do first is just use the generic formula. In general if you have therefore, N number of particles and you have N subscript I particles in each energy state corresponding to the energy state epsilon I.

This is the more generic 1. Therefore, the probability for this distribution will be N factorial divided by N knot factorial N 1 factorial N 2 factorial till what we called N subscript R factorial. This R will be the maximum number of energy levels. There are totally R energy levels and you have a distribution N knot may be occupying the base level N 1, N 2, N 3, so on till the final energy level and you have totally N number of these particles. For any given scenario therefore, you can calculate the number of states micro states possible using this particular probability distribution. This can be also written as N factorial by product N I factorial ranging from I equal to 0 to R. This symbol is mean product.

And now what we will do is we have to find the most probable distribution. The most probable distribution is found out by maximizing omega. Corresponding occupancy will be determined. Now, what we will do is take log, natural log and both sides. You will have ln of N factorial minus ln of 0 to R N I factorial and since typically we are talking about I mean in a real case these particles are so large we are talking about so many number of electrons and phonons, there typically quite large and therefore, for large numbers of N Is, you can use the sterling's approximation, which states that your ln of some X factorial is equal to X ln X minus X. This is the sterling's approximation for large values of X.

Typically these particles are also too many. Therefore, we can apply the sterling's approximation. If you do that and you substitute into let us say this is equation 1. You have ln omega is equal to N ln N minus N. I applied sterling's approximation to this and similarly you can also apply the sterling's approximation. You can expand this and you can apply the sterling's approximation. How will you expand this? This is nothing, but ln of N N knot plus ln of N 1 plus ln of N 2 and so on and then you apply that.

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You can actually write this a summation. I equal to 0 to R N I ln of N I minus N I is that ok? This will be equation number 2. Now, there is a constraint on the system. Now suppose you assume that this is a close system, consisting of N particles and you have several of these micro states and these particles are now according to these combinations, there occupying the energy states.

They can occupy all these energy states under with following constrains, number 1 the total number of particles cannot change. Therefore, your N will be equal to a constant. You can do all these combinations, but you cannot alter the total number of particles That means, your N knot plus N 1 plus till N R should some up to always N, whatever combination you make or in other words summation I equal to 0 to R and I should be equal to N which will be equal to a constant. Therefore, the change in N which is equal to summation I equal to 0 to R. We can say that the change in N should be equal to 0, over all for the entire system and similarly if you look at the total system, the total internal energy should also be equal to a constant. If you are assuming this is a closed system, that means, it is not transferring any energy 2 and from this surrounding. The total internal energy as to be a constant, these particles can occupy any energy states, but it should also stratify this constraint.

In such a case you will have N knot epsilon knot plus N knot N 1 epsilon 1 and so on till you have N R epsilon R. This gives you basically the energy for particular micro state

number of particles occupying this particular energy level. Like the difference some all of them, you get the total internal energy.

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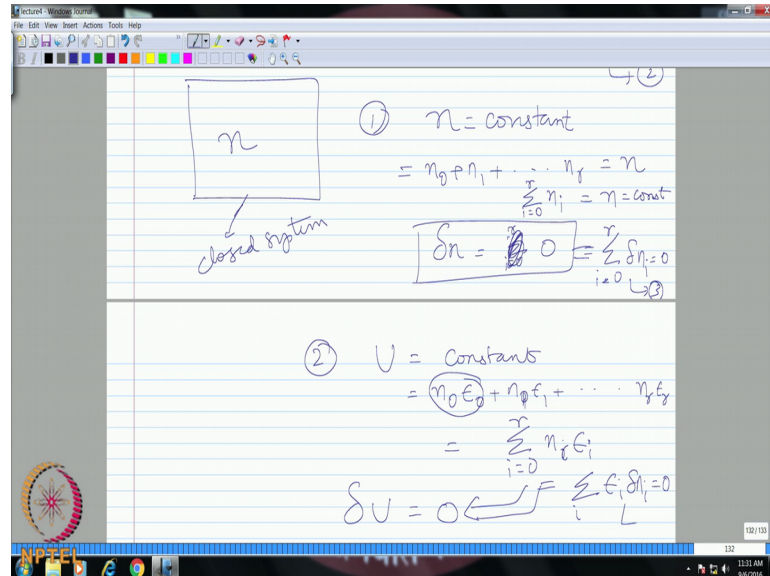
Also the condition now states therefore, this is equal to summation I equal to 0 to R N R N I epsilon I. This condition states that any inter change of particles can happen which conform to the fact that delta U is equal to 0. This also means, we can write this as summation I equal to 0 to R delta N I equal to 0 because of the fact that the total number of particles cannot change.

You can basically rearrange the particles within a given energy level, but the total number of particles cannot change and also the, at each and every energy level you know you can have a certain change in the number of particles, but when they all some these changes it should be equal to 0. Same way with this, we can write it as I epsilon I delta N I should be equal to 0 because of the fact that the internal energy cannot change. Let us call this as constrains 3 and 4.

If you are now going to find out the distribution, which is most probable distribution that is trying to maximize omega; that means, even if you inter change some particles among the energy levels, that is you allowing some delta N I, the value of omega should not change much because it is already close to the maximum probability.

You are looking at maximum probable distribution and you are also looking at the corresponding distribution of N at each energy level. Even amongst the energy levels you change. 2 particles here, 1 particle there and then you re arrange it that should not change the value of omega too much because this is already close to the maximum. Therefore, we can make an assumption that when we are looking at the maximum probable distribution even some small rearrangement should not affect your over all omega.

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Therefore, your delta ln of omega should be what, 0. Already you are going to the maxima. So, the condition therefore, that will ensure is that around this maxima your change will be negligible. You can there therefore, find the maxima by equating this to 0.

And therefore, what it means from equation number 2, say if you therefore, apply delta of this to equation number 2 and all of you please write it. Find delta of this entire equation. We are now maximizing value of omega to find the most probable distribution say if you take the delta of this entire equation now, what you will get on the right hand side first term? You will have delta N into ln of N correct. Now, delta N should be what, 0. Similarly you have delta N here. You have the first term on the right hand side going completely to 0. All of you please try it and I will just write the solution you check the later on. The second term on the right hand side, the delta of this will expand to this.

You have delta of N I ln of N I. Basically you can write this off, write this as delta N I ln of N I plus you have N I into delta ln of N I. If you differentiate ln of I, that is basically

D N I by N I minus delta N I. Therefore, again if you are applying this constraint, where the number of particles, total number of particles cannot change; that means, summation of delta N I should be equal to 0. What happens? This term and the summation of that you are going to 0. Therefore, essentially you are left with the fact that summation delta N I ln of N I should be equal to 0. This should give you the arrangements or distribution of particles which maximizes the probability, omega and which also satisfies the condition that the total number of particles cannot change during this rearrangement. From this we will introduce the concept of Lagrange multipliers.

So, the Lagrange multipliers, what we will introduce here? 1 we will introduce for the energy. We will introduce a constant which is having the units of reciprocal energy. We will apply this to our equation number 4, which is the constraint epsilon I summation of epsilon I delta N I equal to 0. What we will do is will multiply this by Lagrange multiplier beta, such that summation you have epsilon I delta N I equal to 0. This is just a constant. We can carry it inside the summation and we can simply multiply to equation 3. These now, let us call this as you know let us do we have a 4? Yes we have a 4. We are multiplying it to equation number 4. Let us call this as 5 now and 6.

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Similarly, we will introduce another Lagrange multiplier alpha, so that we will multiply equation number 3. We have alpha into delta N I equal to 0. This is equation number 7. This is just a constant no units. You do not have to worry about why we are doing this,

but later on we will see that for certain particle or a certain system these Lagrange multipliers can take certain parameters. We will just introduce that later on, but you can now assume. We are multiplying equation number 4 with the Lagrange multiplier which has 1 over the units of energy and the other 1 with equation number 3, which is just a constant without any dimensions. We have therefore, 5 6 7, will add all these together adding 5 6 and 7 summation I equal to 0 to R have ln of N I plus alpha plus beta epsilon I. Your delta N I is common. I am pulling this out. So, this should be equal to 0. Is that ok?

Now if you expand this, what it means? You have for example, ln of N knot plus alpha plus beta epsilon knot delta N knot plus you have ln of N 1 plus alpha plus beta epsilon 1 delta N 1 and so on and so forth. This all sum to be should be equal to 0 and now as we can see that your delta N knot delta N 1 by itself cannot be 0 because you have a certain change in the distribution. The sum of all these can be equal to 0, sum of delta N I can be equal to 0, but individually delta N 0 and delta N 1 delta N 2 their not 0. Therefore, in order to satisfy this, what should be the condition?

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Each of this should be equal to 0. Therefore, ln of N I plus alpha plus beta epsilon I individually should be equal to 0.

From this, we can write now, what is the distribution, the actual distribution which maximizes omega? This is distribution which is 1 by exponential alpha exponential beta

epsilon I. Is that ok? This is nothing, but exponential minus alpha plus beta epsilon I. This gives you the how they particles can be distributed at each energy level epsilon I corresponding to maximizing omega corresponding to satisfying the constraints that N should be constant and your U should also be constant. This is the most probable distribution most probable distribution of particles that maximizes omega, is it clear?

Till here whatever we did was purely you know statistics probability and statistics. For we have not really identified what kind of particles these are, but now what it tells is there is an exponential distribution of the particles, starting from the lowest energy level upwards. As and when your epsilon keeps increasing what happens to the number density? Decreases; more particles will occupy the lower energy states and then they will taper off as you go out to the higher energy states. How do we now apply this to particular particle? Whether it there electrons or phonons or photons or molecules. That is determined by the Lagrange multipliers alpha and beta. I am going to introduce some quick terminology here, let us not spent too much investigating them, but I am going to therefore, introduce 3 kinds of systems 1 is called micro canonical system micro canonical ensemble.

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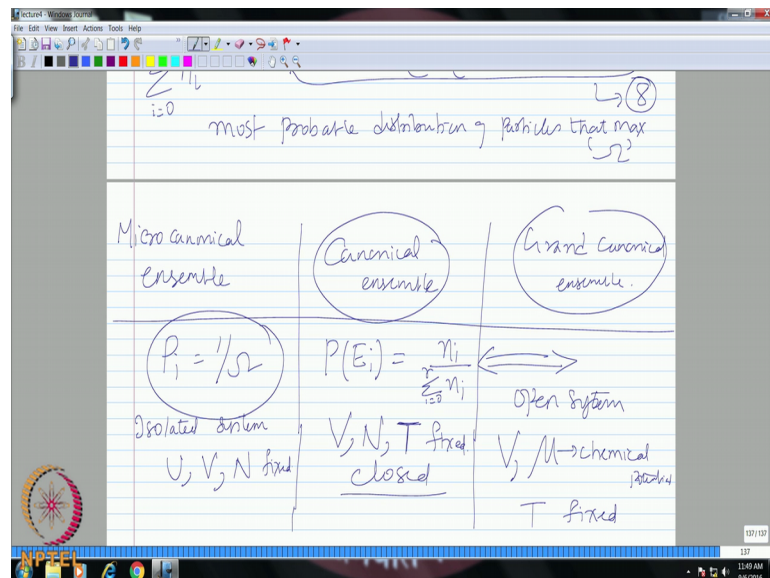
We will see what is this? This ensemble is nothing a statistical agglomeration of these distribution functions. We can use these ensembles to define the macro scale properties. We can how 3 different kinds of system, 1 is a micro canonical 1; the other is a canonical

ensemble. These are just terminologies the other is called the grand canonical ensemble. So in this case the question is what kind of particles fit where? For example, in the micro canonical and ensemble the probability will be or the distribution will be of equal probability. It is just given as 1 over omega, now this is a very simplistic approach and in this case, this is applied to an isolated system, in which your internal energy is a constant your volume is a constant and the number of particles are constants.

These are all fixed. Right now there is 1 more step I want to do. Now let us call this as equation number 8, this number distribution here. From this how can I calculate the probability distribution function? So, I have the number distribution 8. So, from this how can I calculate probability distribution function that is P corresponding to a particular energy?

Student: (Refer Time: 40:56).

N I divided by.

Student: (Refer Time: 40:56). This will give you the probability distribution function. In the case of micro canonical ensemble, it is say, that the probability to distribute particles is very simple. It is equally probable that all energy states can be filled whereas in canonical ensemble and grant canonical ensemble, it goes by the maximizing omega. Whatever we have derived here as equation 8, your P therefore, follows from equation 8.

Both here as well as the grand canonical ensemble, what kind of systems therefore, canonical ensemble can be applied? You have system where volume is a constant, the number of particles is fixed and it is also isothermal. Temperature is also constant. These are fixed. Typically this is a closed system. Therefore, your volume is fixed, number of particles is fixed, and temperature is also fixed. Now the difference between canonical and grant canonical is that this becomes and open system. Therefore, your N will no longer be constant. Your volume will be constant, what we instead of when we call what is call chemical potential mu will be a constant and if this is isothermal, you can also have T fixed.

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Now as a consequence, how do you differentiate the canonical and grand canonical? In both cases you use this particular equation to calculate the probability distribution.

However the values of the Lagrange multipliers will become different. For example, in the case of canonical ensemble the value of alpha will be equal to 0; beta will be equal to 1 by K B T, whereas the grand canonical, there alpha will be minus the chemical potential mu N I by K B T and beta will be still 1 by K B T. This is to summarize the different kinds of systems now for which we can extend our distribution function and apply the values of alpha and beta according to the kind of systems we are dealing with.

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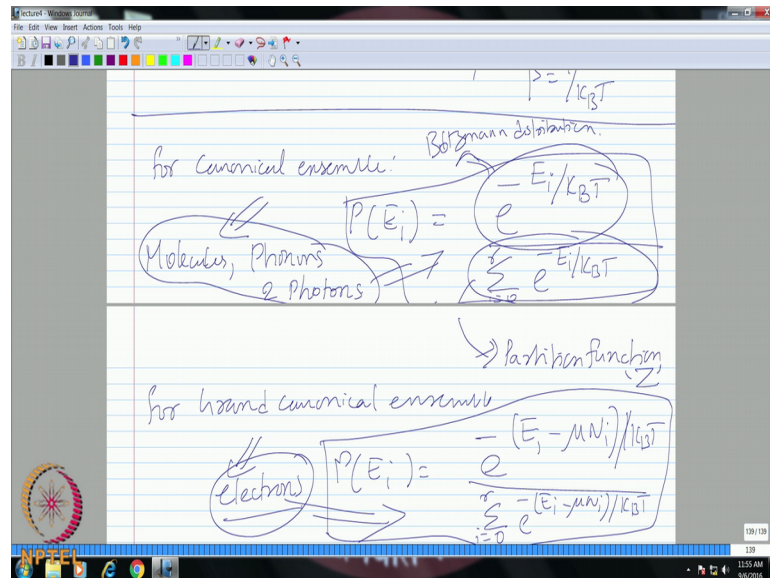
Therefore, if you write the distribution function in terms of probability distribution, for canonical ensemble your P probability will be exponential minus E I by K B T because alpha is 0. If you therefore, substitute into this, this becomes 1. You have exponential minus 1 by K B T to E I.

Therefore, divided by summation of E power minus E I by K B T, I going from 0 to R for grant canonical ensemble your probability, will be what? Substitute the alpha and beta what you get? E power minus.

Student: E I minus.

E I minus mu N I by K B T divided by summation E to the power minus E I mu N I by K B T. We will apply the canonical ensemble to system of molecules phonons and photons while the grand canonical ensemble is applied to system of electrons. Therefore, we have now come to a point, where we understand what is the distribution function? And second thing, we have also identified, what kinds of particles correspond to what kind of distribution function?

For example molecules phonons photons will correspond to the canonical ensemble electrons to the grant canonical, now the numerator that you have here. E power minus E I by K B T, this is called the bolds man distribution. The numerator, what we have here is the bolds man distribution and the denominator, the summation of all these across the

different energy levels. This is in statistical thermodynamics refer to as the partition function sometimes they use the nomenclature Z instead of writing this summation. This all the time replaces entire denominator with the nomenclature E Z, which is called the partition function, which is the summation of the distributions across the different energy levels. Based on this distribution function, now we will go ahead and derive the individual distribution functions for each energy carried.

For example, molecules in the case of molecules, what will happen to the energy? They are not discrete, they are continuous and if you are considering only a monatomic gas molecule. Only translational kinetic energy is there. In 3 dimensions you have 3 degrees of freedom, half M V X square plus V Y square plus V Z square. We can therefore, substitute for energy in terms of the translational kinetic energy and then we can calculate, what is the distribution probability distribution function for a molecules similarly for phonons, we can substitute the corresponding value of E I, what will be the E I for phonons?

Student: H mu.

H mu into N plus half, vibrational energy levels and if you look at electrons, we can also again substitute the corresponding value of E I. All this we will do in the next 2 or 3 classes you know starting from molecules. And once you derive them for apply them for molecules; they get the name Maxwell Boltzmann distribution. Similarly for phonons and photons they become the Bose Einstein distribution function and electrons they become Fermi Dirac. We will derived these distribution functions for the individual energy carriers and look at the nature, how they look and how they collapse? Actually even though the electron distribution function looks quite different from the phonon distribution function. They can actually collapse at some certain conditions and they will be looking similar. They will become collapse to Boltzmann distribution function.

Will see at what particular values they can do that then from these distribution functions. The part is achieved. We know how the particles are distributed, the next step is to therefore, calculate the macro scale properties. We are interested in internal energy. How do we do that? We know the distribution function; we have these corresponding values of energy, you have to take a cumulative. Therefore, we have to find the ensemble statistical ensemble of number of particles occupying each energy level based on this distribution

function from which we aggregate everything and calculate the total internal energy and once you know the internal energy, we can calculate the heat capacity.

From there, we should be able to now understand how the micro states or now transitioning and we get the macro scale properties. In the next, I think 1 or 2 classes we should finish the distribution followed by calculating the internal energy. About 2 to 3 classes know totally we should be able to complete this exercise and then we will be knowing you know at equilibrium systems how these particles are distributed, what kind of energies they posses and what is the contribution and so on. Then we will go on to cases of non equilibrium that is the transport of heat.

So, will stop here.