Statistical Mechanics
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Lecture- 29
Quantum of Classical Correspondance

All right. So, good afternoon students, today we will talk about the correspondence between quantum statistical mechanics and the classical statistical mechanics in the limit of high temperatures and low densities. This is the last subject of our discussion and an important discussion in the sense that, it tells you how to seamlessly connect quantum world with the classical world.

And of course, the only way to connect is when you start from quantum mechanics, you can take this high temperature low density limit and go to classical mechanics. You cannot do it vice versa and because quantum mechanics was constructed when classical mechanics failed to describe certain experimental phenomena.

So, it was a theory that was set up with certain principles and certain rules, axiomatic rules. And this makes this correspondence unidirectional in the sense that, there is no way you can start with the classical calculation and show a by some limit that quantum effects arise that is impossible; you can only start from quantum mechanics and take a classical limit and show a classical results. And I will explain this by starting with our is quantum statistics for both Fermi systems and Bose systems and take the high temperature low density limit especially when the system is very large because, this is where a natural classical to quantum correspondence occurs ok.

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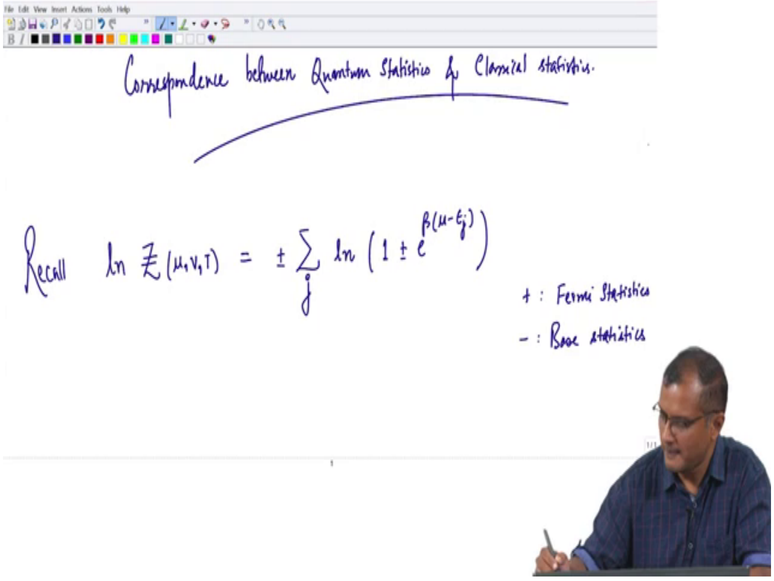

Correspondence between Quantum Statistics & Classical statistics.

Recall $\ln \mathcal{Z}(\mu, V, T) = \pm \sum_j \ln\left(1 \pm e^{\beta(\mu - \epsilon_j)}\right)$

$+$: Fermi Statistics

$-$: Bose statistics

So, today I am going to talk about correspondence between quantum statistics and classical statistics or can also be called as quantum to classical correspondence or classical statistics as a limit of quantum statistics whichever way you want to call it.

Now, I would like to start from a recollection that we have made in the context of partition functions of real particles. So, if you recall we had constructed the grand canonical partition function ok. So, I am writing down the logarithm of the grand canonical partition function, we can consult your notes for this particular expression, it was given as this expression where we summed over all possible energy states ok.

The plus minus sign here corresponds to the case where the system of particles is a Fermionic system or a Bosonic system ok. So, this is basically summation over all energy levels, lon of 1 plus or minus e raise to beta mu minus E j, where the plus is for the Fermi statistics and the negative is for Bose statistics ok.

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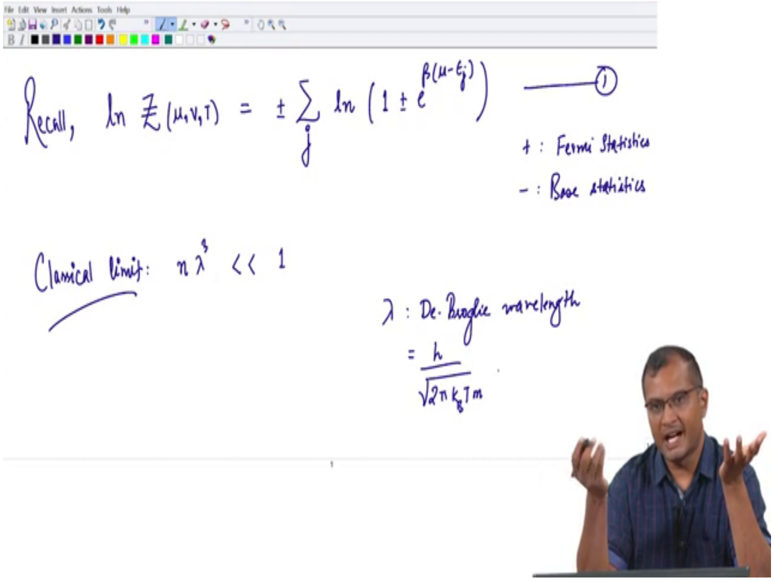

Recall, $\ln \mathcal{Z}(\mu, V, T) = \pm \sum_j \ln\left(1 \pm e^{\beta(\mu - \epsilon_j)}\right)$ —— ①

+ : Fermi Statistics

− : Bose statistics

Classical limit: $n\lambda^3 << 1$

λ : De-Broglie wavelength $= \frac{h}{\sqrt{2\pi k_B T m}}$

Let us label this equation as 1. If you do not recall this then its not a problem because you can derive this expression very quickly. If you want to derive it from first principles then we should know that a correct enumeration of states or enumeration of the partition function is very difficult if you want to; if you want to do this in canonical ensemble that is the ensemble of fixed n b and t. And then we said that this enumeration of states becomes very simple, if you allow the number of particles in a system to fluctuate.

Meaning that you do the calculation in grand canonical ensemble, which is the ensemble of constant chemical potential volume and temperature and then we had shown that the restricted sum becomes easier to compute because you allow in the total number of particles to fluctuate from zero to infinity, there by taking each term in the summation independently and you can construct this expression one very easily.

This was the subject matter of last lecture, I am just bringing it up as a recap. Anyway we will note our last lectures outcome which is the equation 1 our grand canonical partition function and proceed from here. Now how do we take classical limit? Classical limit is the limit as I keep saying, is the limit of high temperature in low density. Meaning if you take the number density, now this has the dimensions of 1 upon length cube, I want to construct a dimensionless number. So, which means I must multiplied by cube of some length now this is a dimensionless number ok. So, this dimensionless number if it is much much smaller than 1 then I am in the classical limit ok.

Now, how can I reach this? See either I can take n to be very small meaning I have blown the volume to be very large such that my density is become very small and this De Broglie wavelength here the De Broglie thermal wavelength has to be very very small. So, if both n and lambda become very small and lambda cube is much much smaller, then the product of these two small numbers will definitely be much smaller than 1. I know that De Broglie wavelength is given as some h over square root of 2 m 2 pi m kT.

So, it is not difficult to see why at high temperatures I will get a classical limit. So, if I temp if my temperature is very large, the De Broglie wavelength will basically be much much smaller it will go as 1 upon square root T. So, at high temperatures your De Broglie wavelength is much smaller lambda q becomes even smaller and I have also taken volume to be large. So, density to be less. So, high density low high temperature I am sorry low density high temperature limit naturally corresponds to the classical limit.

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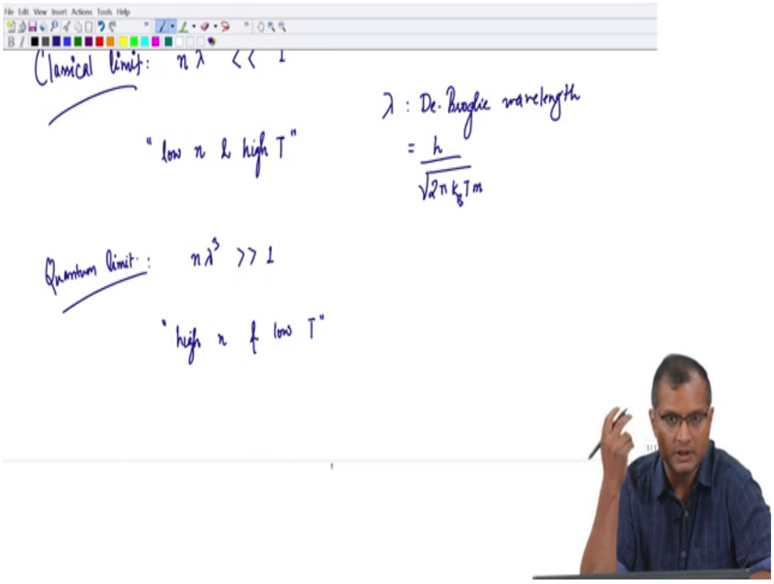

Classical limit: $n\lambda << 1$

"low n & high T"

λ : De-Broglie wavelength

$$= \frac{h}{\sqrt{2\pi k_B T m}}$$

Quantum limit: $n\lambda^3 >> 1$

"high n & low T"

So, you can reach the classical limit by low density and high temperature ok. The quantum limit is naturally the limit where we are doing our calculations and this is the limit where we expect n lambda cube to be much much larger than 1 and this limit can be raised reached by taking high density and low temperatures ok. So, this is like saying that at any temperature I can see quantum effects, if I go and increase my density. Similarly at any temperature I can see a classical effects if I keep my density sufficiently lower ok.

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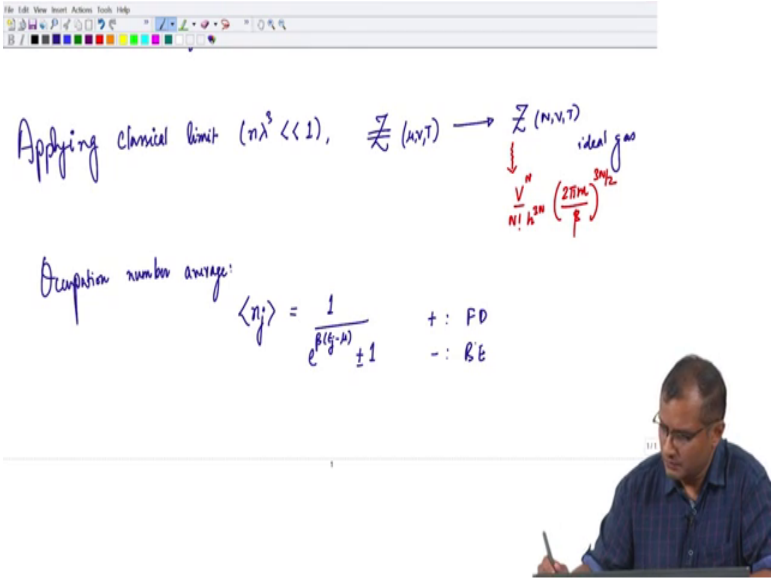

Applying classical limit $(n\lambda^3 << 1)$, $\mathcal{Z}(\mu,V,T) \longrightarrow Z(N,V,T)$ ideal gas

$$\downarrow \quad \frac{V^N}{N!\,h^{3N}}\left(\frac{2\pi m}{\beta}\right)^{3N/2}$$

Occupation number average:

$$\langle n_j \rangle = \frac{1}{e^{\beta(\epsilon_j-\mu)} \pm 1} \qquad \begin{array}{l} + : \text{FD} \\ - : \text{BE} \end{array}$$

So, you can take the classical limit here which is the subject matter of our interest and show that the partition function reduces to our well known canonical partition function. So, using classical limit or I would say applying classical limit ok, which is basically the limit n lambda cube being much much smaller than 1.

We will basically show that our grand canonical partition function reduces to our familiar partition function for an ideal gas which is if you recall it is nothing, but volume to the power N over let me use a different color here. If you remember the expression it is volume to the power N over N factorial divided by h to the power 3 N to 2 pi m over beta raised to 3 N by 2 this is our canonical partition function ok.

So, I am going to derive this from our quantum partition function in the classical limit. And in doing so, we will discover that the correct enumeration states which is this N factorial here which avoids over counting the microstates and hence gives you the correct definition of entropy is naturally embedded in your calculation, also the cell factor h also appears as a remnant of this quantum to classical correspondence.

So, both these factors which were sort of ad substitute in an adhoc fashion in classical mechanics are no longer you know substituted as adhoc they are embedded in the calculation and now you know why this h was called as Planck's constant because here h is Planck's constant and its high temperature low density limit reduces to a classical partition function where you had taken an edge keeping just the notion that I want to keep Z dimensionless and I want to have a some sort of a scale of the phase space.

So, I have taken an h which has a dimension is equal to action angular momentum is now realized as the Planck's constant. So, we will now say that h is Planck's constant, we could not have said Planck's constant earlier because this was a calculation done by Boltzmann and Gibbs, which predates all quantum mechanical work ok.

So, let us proceed from here. So, I am going to basically write down the occupation number or basically the average occupation number. So, this is nothing, but the ensemble average value of particles in some jth quantum level and we know that this is nothing, but 1 over e raised to beta e j minus mu plus or minus 1, where again these two signs correspond to whether the statistics is Fermi Dirac or Bose-Einstein ok.

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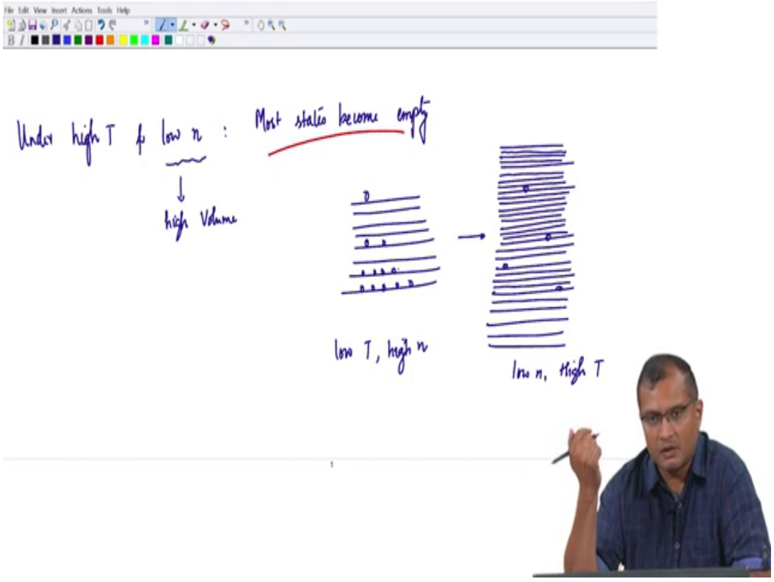

Now, we are taking a high temperature limit which means I am going to take. In fact, we are going to take both high temperature low density limit which is a classical limit. So, under high T and low density, I can safely say that most energy levels are unoccupied and the reason is the following at low density I have high volume, which means that the spacing between the energy levels will be almost negligible, these discrete states from a continuum now right.

Because your energy levels are proportional to 1 upon l square h cut square k square upon 2 m, k itself is 2 n pi by l. So, k square is 1 upon l square. So, if you calculate the difference between energy levels it will go as 1 upon l square or 1 upon l not 1 upon l square 1 upon it will go as 1 upon l.

So, you can think of the manifestation of large volume as the energy levels forming a continuum ok. So, now you have energy levels that are you know basically forming a continuum and there are large number of infinite number of them and now your temperatures are also very high. So, there is no in principle the particles can be anywhere and you have a large number of energy levels, which essentially gives you a picture that the average occupation number for any level would be a small number.

Because most levels are now empty; it is like you have one level here, another level here and the third level here you had some particles here and then you had some particles here. Now as I increase the volume of the system, I get more and more energy levels in between eventually what happens is as these particles can at the expense of very little energy difference and hop from one level to the other ok. So, you will now get a picture which is more or less like this.

Because the number of levels are now very large number they are very close to each other and because the temperature is very very high and these particles can practically go and sit at any level and they are infinite number of these levels with the separation between them almost negligible, you would expect that the average occupancy number would be a very small number ok.

So, a consequence of high temperature and low density is that, most states become empty this is the consequence. Suppose you had only lower density, but temperature was not high. So, you would have the right hand side picture where the states are very close ok, but since you kept the temperature low most particles would go and sit at the lowest possible states.

So, they would be more occupied. Then I cannot say that most states are empty, because the lower levels are now occupied. The fact that you made a large number of them closely start and you made the temperature very high which means now you are making most levels unoccupied, they will all go and sit at levels in such a way that you have only one particle per level at max on an average. So, you can see that I have a large number of states now on the right hand side which are unoccupied ok.

In the previous figure you can see that, I can you know at low temperatures I can at least see most particles and I would say high density. So, because I have taken high density the energy levels are not forming a continuum. So, volume is low ok. So, you can say that and the temperature is also low, so, most particles are taking the lower states. But as I go to low density and high temperature, I have a continuum of states and I give these particles you know a liberty to go and sit anywhere in this continuum. As a consequence of that most states are now unoccupied.

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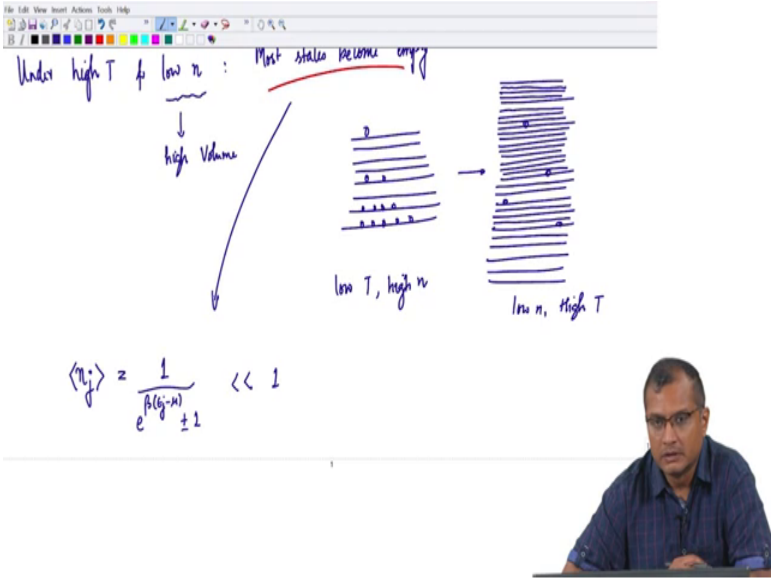

Under high T & low n : Most states become empty

high Volume

$$\langle n_j \rangle = \frac{1}{e^{\beta(\epsilon_j - \mu)} \pm 1} \ll 1$$

Which means that my average occupation number is which is given as 1 upon e to the power beta E j minus mu plus or minus 1 is much smaller than 1 as a consequence of this right. Now, what this means is that, the denominator should be dominating for this fraction to be much less than 1 my denominator should be dominating.

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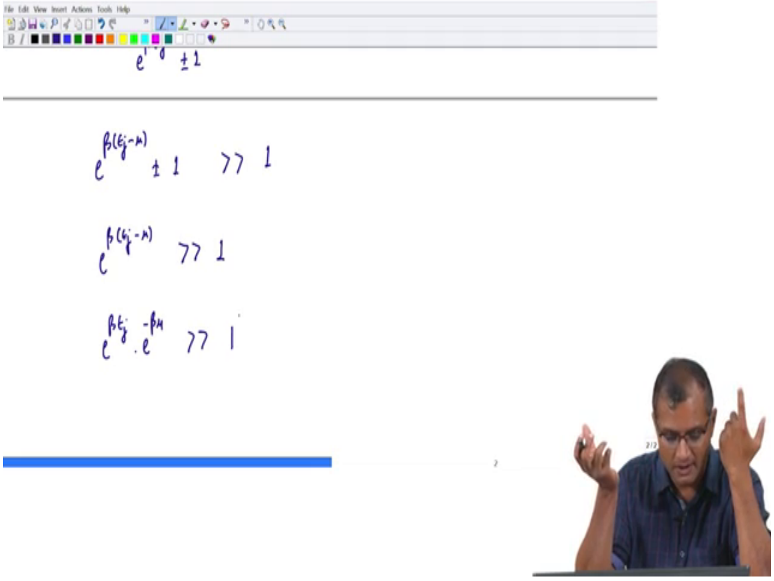

$$e^{\beta(E_j-\mu)} \pm 1 \gg 1$$

$$e^{\beta(E_j-\mu)} \gg 1$$

$$e^{\beta E_j} . e^{-\beta\mu} \gg 1$$

So, I can say that e to the power beta E j minus mu plus or minus 1 should be much much larger than 1 that is my denominator which only means that e to the power beta E j minus mu is much larger than 1 because I can ignore 1; 1 is a fixed number ok. So, x plus 1 is much larger than 1 means x is much lower than 1 ok. Now you can see that two things are here; one is that let me first plate it up. So, I will write it as you can see the left hand side of the inequality is j dependent the right hand side of the inequality is j independent, which only means that this energy level does not matter it is arbitrary any energy level will suffice or will satisfy this inequality.

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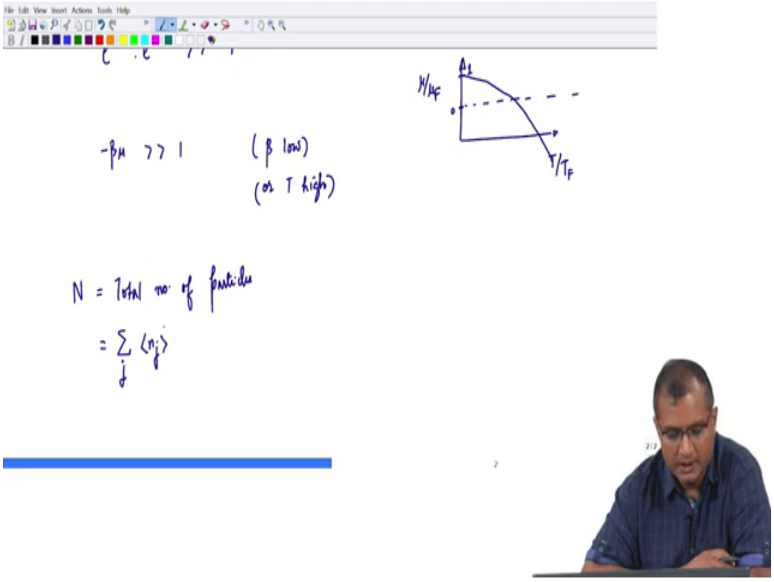

$-\beta\mu \gg 1$ (β low)
(or T high)

N = Total no. of particles
$= \sum_j \langle n_j \rangle$

Which can only mean that our minus beta mu is something which is much larger than 1. This is possible because this is actually true because at very low beta or high temperature, I know that my chemical potential is negative highly negative. So, minus beta mu has to be a number which is much larger than 1, if you recall your; if you recall your diagram or behaviour of chemical potential, mu over mu F versus T over T F you know that its somewhere starts from 1 T equal to 0 mu is mu F and it crosses 0.

So, this is the 0 point and then it takes a nosedive. So, at larger and larger temperatures, the chemical potential is more and more negative. So, minus beta mu as beta goes to 0 or temperature goes to infinity has to be a number which is much much larger than 1 ok. So, I am going to write down beta low or T high whichever is convenient to you ok.

So, this is our classical limit that minus beta mu is much much larger than 1. Of course, we have taken the liberty to assume that the system is in thermodynamic limit of course, that was that is not a bad assumption because most systems that we deal with in laboratory and already in the thermodynamic limit. So, with a large number of particles in large volume, the energy levels are very closely state. The classical limit just adds one more feature that I give every particle the liberty to go and sit anywhere. So, in the continuum is I tell anybody to sit anywhere, I can expect that most levels are unoccupied right.

If I keep if I do not give that liberty I will see that most of them are sitting at the lowest levels, and I cannot say that nj is much larger much much smaller than 1 for any j certainly for lower j s nj is not insignificant. But high temperature when I have given the liberty to go and sit anywhere in this infinite continuum of states, I can assume to a very good extent that average occupation number for any level would be much smaller than 1 ok.

So, this is the meaning of the classical limit in the large systems. So, now we can proceed from here and note that the total number of particles we just find it ok. We only increase the volume to sort of make an continuum of energy states and this is given as summation over all the states with the average occupation number of each state ok.

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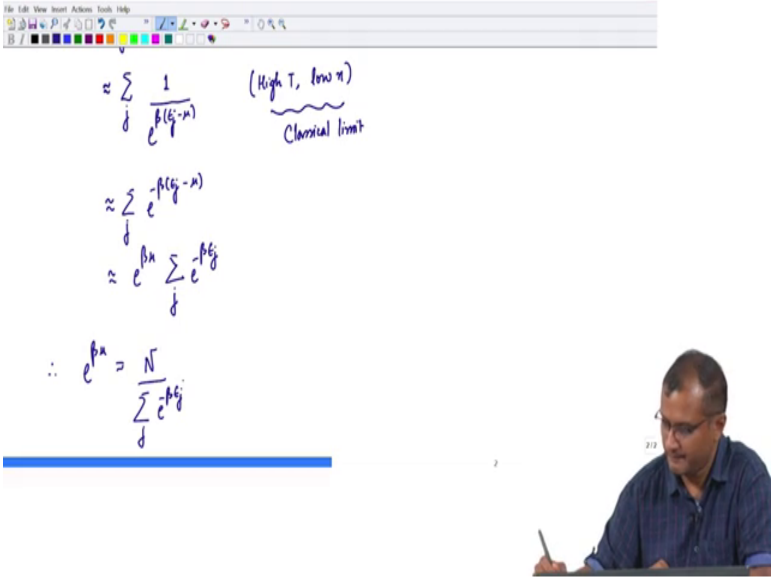

$$\approx \sum_j \frac{1}{e^{\beta(\epsilon_j-\mu)}} \qquad \underbrace{(\text{High } T,\ \text{low } n)}_{\text{Classical limit}}$$

$$\approx \sum_j e^{-\beta(\epsilon_j-\mu)}$$

$$\approx e^{\beta\mu} \sum_j e^{-\beta\epsilon_j}$$

$$\therefore\ e^{\beta\mu} = \frac{N}{\sum_j e^{-\beta\epsilon_j}}$$

And the average occupation number of each state has already been approximated. So, I will say this is approximated to you can look at the expression here. Because the exponent in the denominator is much larger I can write down this as just I can ignore the plus minus sign, which basically means that now it does not matter whether you have Fermi systems or if you are dealing at a Fermionic system or a base system. In the high temperature low density limit both the Fermi Dirac and Bose Einstein systems or both Boson system and the Fermi on systems behave identically.

So, I am going to write it as just 1 upon beta E j minus mu ok. The nearly equality sign should remind you that we are looking at the high T low density or classical limit. We have taken the classical limit of Bose Einstein and Fermi Dirac statistics ok. So, this can be simply written as summation over e to the power minus beta E j minus mu ok.

So, I can clearly take a couple of things outside here. So, I can say that this is e to the power beta mu into the summation j e raise to minus beta E j because this is a pre factor that does not depend on the index j and write down for e raise to beta mu as N over summation j e raise to minus beta E j ok.

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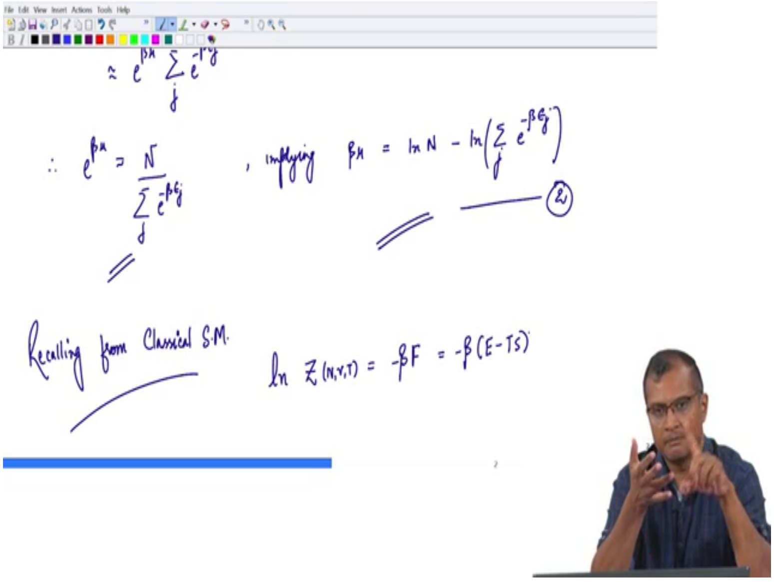

$$\approx e^{\beta\mu} \sum_j e^{-\beta\epsilon_j}$$

$$\therefore e^{\beta\mu} = \frac{N}{\sum_j e^{-\beta\epsilon_j}} \quad , \text{implying} \quad \beta\mu = \ln N - \ln\left(\sum_j e^{-\beta\epsilon_j}\right) \quad ②$$

Recalling from Classical S.M.

$$\ln Z(N,V,T) = -\beta F = -\beta(E - TS)$$

Also implying that I can take. So, I can also take a log on both sides and this will give me natural log ok. So, let us call this as a sum equation we have label datas equation 1. So, I am going to label this as an equation 2. So, equation 2 has two out as one is the left hand side which is basically this, the other is this both are the same equations. Now we can write down in some sense the partition function. So, if you recall your results from classical statistical mechanics.

So, we had a relationship between statistical mechanics and thermodynamics essentially the bridge that we constructed for every problem and this result was that the logarithm of the canonical partition function was related to the free energy by this expression ok. And I am going to write down this as minus beta and the free energy is the Helmholtz free energy. So, this is just a internal energy minus Ts ok.

Since our goal is to derive classical statistical mechanics from quantum statistical mechanics under this high temperature low density limit. It is sufficient that I derive the classical partition function starting from the quantum partition function because partition function is the bridge that connects thermodynamics to statistical mechanics. So, if I show that the quantum partition function reduces to the classical partition function, I would have done my job because from there I can derive all properties of my gas, entropy pressure so on and so forth.

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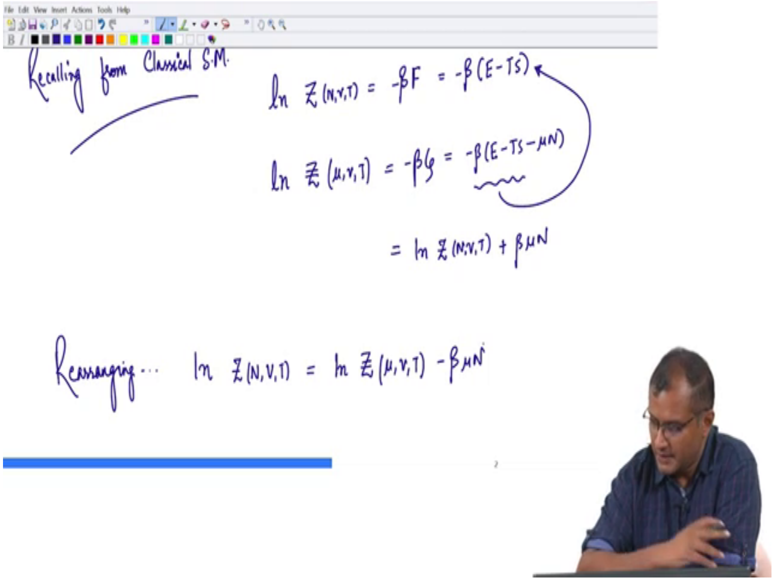

Recalling from Classical S.M.

$$\ln Z(N,V,T) = -\beta F = -\beta(E-TS)$$

$$\ln \mathcal{Z}(\mu,V,T) = -\beta \mathcal{G} = -\beta(E-TS-\mu N)$$

$$= \ln Z(N,V,T) + \beta\mu N$$

Rearranging… $\ln Z(N,V,T) = \ln \mathcal{Z}(\mu,V,T) - \beta\mu N$

So, a task simply reduces now to start from the quantum partition function which is the grand canonical partition function that is nothing, but I know the grand canonical partition functions logarithm gives me an energy scale which is the grand potential and that is equal to E minus Ts minus mu N I know this, but here is the thing. I know that beta times E minus Ts is also equal to lon of canonical partition function ok. So, I am going to write this as minus beta times. So, or I can just substitute the expression from there. So, this is the fun part. So, I can write it as a lon of the canonical partition function plus beta times mu N ok.

So, now you can you can see that I can write down I can just rearrange the terms and write down for the canonical partition function as right and now we just seems substitute for these quantities ok. So, we are just going to substitute for these quantities. So, first I am going to write down for lon of the grand canonical partition function which is nothing, but my equation 1 ok.

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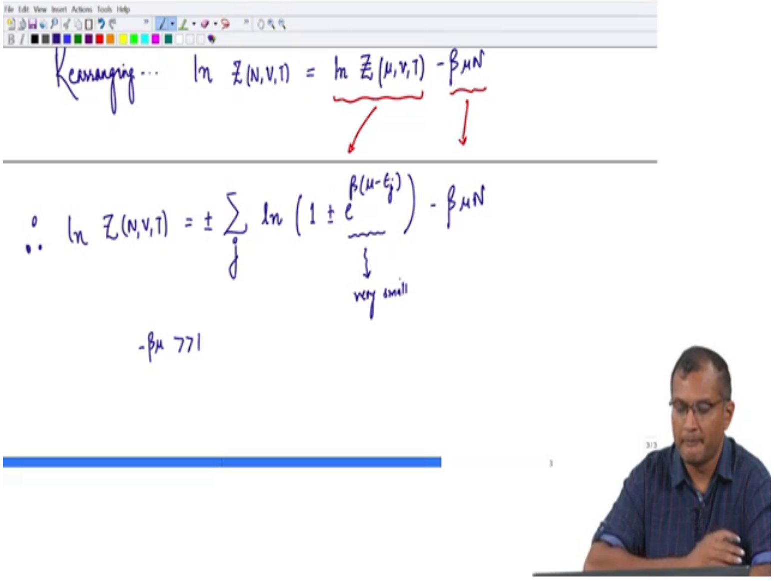

Rearranging… $\ln Z(N,V,T) = \underbrace{\ln \mathcal{Z}(\mu,V,T)} - \underbrace{\beta\mu N}$

$$\therefore \ln Z(N,V,T) = \pm \sum_j \ln\left(1 \pm \underbrace{e^{\beta(\mu-\epsilon_j)}}_{\text{very small}}\right) - \beta\mu N$$

$-\beta\mu \gg 1$

So, go back to equation 1 which is all the way here and substitute this. The second factor which is minus beta mu n fine. So, basically what I have done is I have taken as substituted for this term with this and I have written this term as is fine. Since we are in the classical limit, we are interested in the classical limit I have already I can already assume that my beta times mu or minus beta mu should be a number which is much much larger than 1 ok. So, I can safely put the exponent here to be a very small number turns out to be very small ok.

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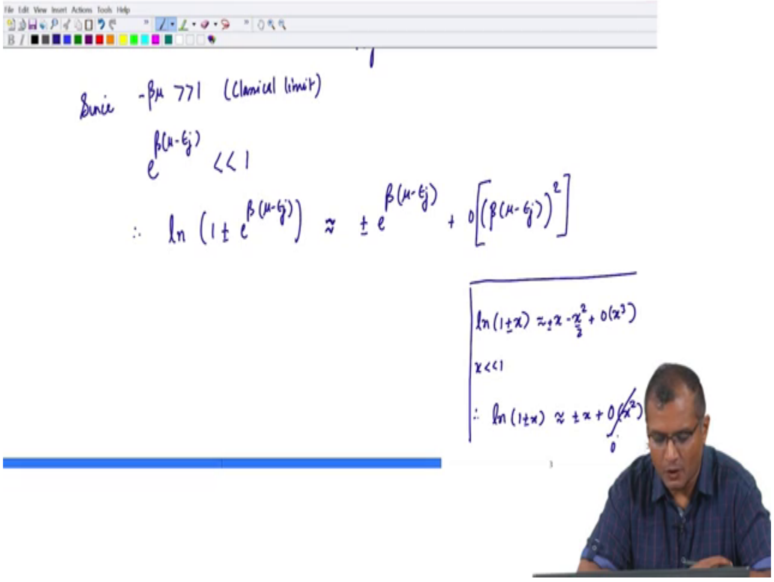

Since $-\beta\mu \gg 1$ (Classical limit)

$e^{\beta(\mu-\epsilon_j)} \ll 1$

$$\therefore \ln\left(1 \pm e^{\beta(\mu-\epsilon_j)}\right) \approx \pm e^{\beta(\mu-\epsilon_j)} + O\left[\left(\beta(\mu-\epsilon_j)\right)^2\right]$$

$\ln(1 \pm x) \approx \pm x - \frac{x^2}{2} + O(x^3)$

$x \ll 1$

$\therefore \ln(1 \pm x) \approx \pm x + \underbrace{O(\cancel{x^2})}_{0}$

So, then I can write down my right hand side. So, you will say that since minus beta mu is much much greater than 1 which is basically the classical limit, just to remind that we are in the classical we are interested in taking the classical limit; e to the power beta times mu minus E j is a number which is much much smaller than 1 ok.

Therefore, I can use the expansion since you know I can write down this lon of 1 plus minus e raise to beta mu minus E j and simply I can write it as plus minus e to the power beta into mu minus E j roughly and I can definitely ignore terms of the order beta times E, I can drop these terms.

This is nothing, but if I have to show it explicitly there is nothing, but if I have lon of 1 plus x, where x is very small, but smaller than 1, then I can write approximate this as x minus x square by 2 plus terms of the order x to the power 4 and so on like sorry right. Now definitely if I have minus x here, then I have to say this is plus or minus x, because the even powers of x do not suffer any sign change whether x is replaced with minus 6, but all the order powers will suffer the sign change.

So, I can say that to linear order if x is very small, I can approximate lon of 1 plus or minus x as simply plus or minus x and I will say that I am not interested in terms quadratic in above fine. So, that is what I have done. So, I have replaced lon of 1 plus or minus e raise to beta mu minus E j simply plus or minus e raise to beta times mu minus E j.

Now with that my right hand side becomes much simpler there is a plus or minus sign outside and each term in this summation this is coming with a plus minus sign which means I can now forget the plus minus sign, because if it is plus outside it is plus inside its minus outside its minus inside in either case I get plus only.

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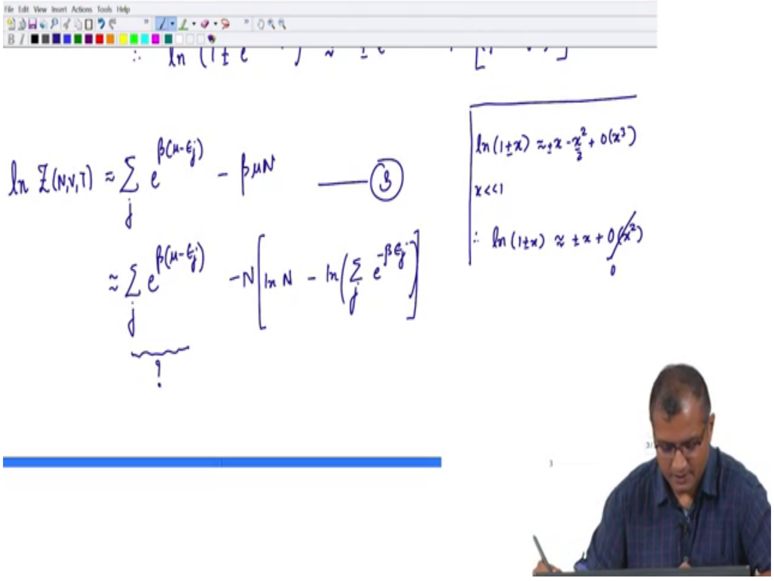

$$\ln Z(N,V,T) \approx \sum_j e^{\beta(\mu-\epsilon_j)} - \beta\mu N \quad ③$$

$$\approx \underbrace{\sum_j e^{\beta(\mu-\epsilon_j)}}_{?} - N\left[\ln N - \ln\left(\sum_j e^{-\beta\epsilon_j}\right)\right]$$

$$\ln(1\pm x) \approx \pm x - \frac{x^2}{2} + O(x^3)$$

$x << 1$

$$\therefore \ln(1\pm x) \approx \pm x + \underset{0}{\cancel{O(x^2)}}$$

So, this is a very promising scenario. So, I am going to write down as the left hand side as lon of my canonical partition function which is nearly equal to summation over j, each term was a lon of 1 plus minus x which is giving me plus or minus x only. So, I am just going to write down lon of 1 plus x as e raise to beta mu minus E j that is it, that is the first term in the right hand side. I have got one more guy that I have to take care of, which is minus beta times mu N. Now we make simple substitutions very easy sub once, but before that let us give this equation a name let us call this as equation 3 all right.

So, now you have to make very simple substitutions we will use this one substitution we will use as it is from here from equation 2. So, we are going to substitute for beta mu as this term. So, I am going to substitute this entire expression for beta mu, is that ok? This entire thing is for beta mu let us do that. So, I am going to write down the first term as it is. In fact, why do not we substitute ok? So, maybe we can do it in two steps its better that way. So, from the first term what I am going to do is basically take ok.

Let us write the first term as it is. So, it is just e raise to beta mu minus E j and I said that I am going to substitute for beta mu ok. So, I am writing minus N and for beta mu, I am going to substitute what I had written this term fine. Now let us try and do something with this term what can we substitute for this. Again let us go back upstairs.

So, if you look here this place. So, you can see that this is e to the power beta mu minus E j and you have the same thing here e raise to beta mu minus E j we just pulled out a minus sign and this is nothing, but N ok. So, we will substitute with N and you can refer upstairs. So, now let us write down the right hand side.

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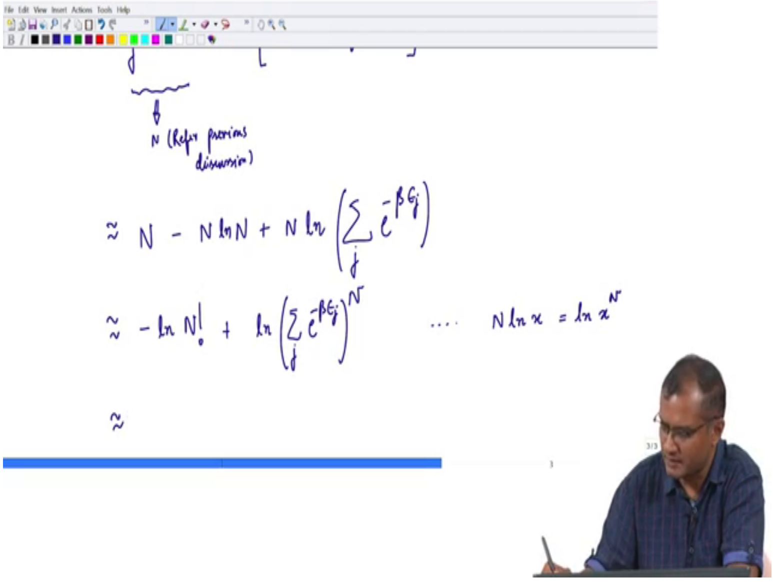

N (Refer previous discussion)

$$\approx N - N \ln N + N \ln \left(\sum_j e^{-\beta \epsilon_j} \right)$$

$$\approx -\ln N! + \ln \left(\sum_j e^{-\beta \epsilon_j} \right)^N \quad \ldots \quad N \ln x = \ln x^N$$

$$\approx$$

So, this becomes N minus N ln N, this is already looking like something plus N lon summation j e to the power minus beta E j. N minus N lon N looks like a familiar approximation this is a Stirling approximation of minus N factorial ok. So, this is the Stirling approximation of minus lon N factorial plus the second term I am simply going to write down as lon of summation j e to the power minus beta E j to the power N ok.

This is because you know its simply if I have N times lon of x this is nothing, but lon of x to the power N ok. So, this is what I have done to the second term I have taken N as an exponent because I want to combine all the logarithms. So, I can now combine my right hand side because both of them are log; log A plus log B is log of A times B.

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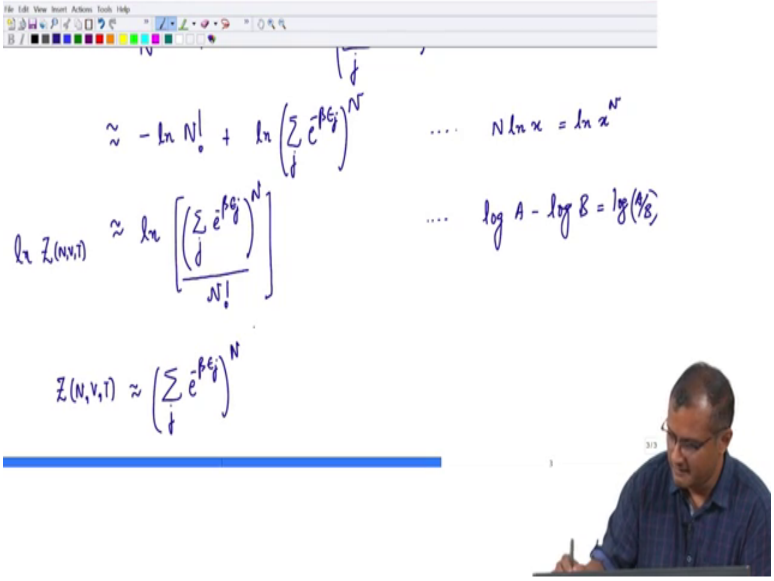

$$\approx -\ln N! + \ln\left(\sum_j e^{-\beta \epsilon_j}\right)^N \quad \ldots\ldots \quad N \ln x = \ln x^N$$

$$\ln Z(N,V,T) \approx \ln\left[\frac{\left(\sum_j e^{-\beta \epsilon_j}\right)^N}{N!}\right] \quad \ldots\ldots \quad \log A - \log B = \log(A/B)$$

$$Z(N,V,T) \approx \left(\sum_j e^{-\beta \epsilon_j}\right)^N$$

So, I can use this since I have a negative sign here. So, I am going to take log A minus log B its nothing, but log of A over B ok. So, I can write this as a natural log of summation e raised to minus beta E j the whole to the power N divided by factorial, what is on the left hand side? The logarithm of the canonical partition function.

So, I know my canonical partition function now, I can simply take anti log on both sides and that will give me an expression for the canonical partition function, the nearly equality is a remanence of the fact that we have taken the classical limit here and this is nothing, but summation of some kind of a Boltzmann factor to the power of N divided by N factorial.

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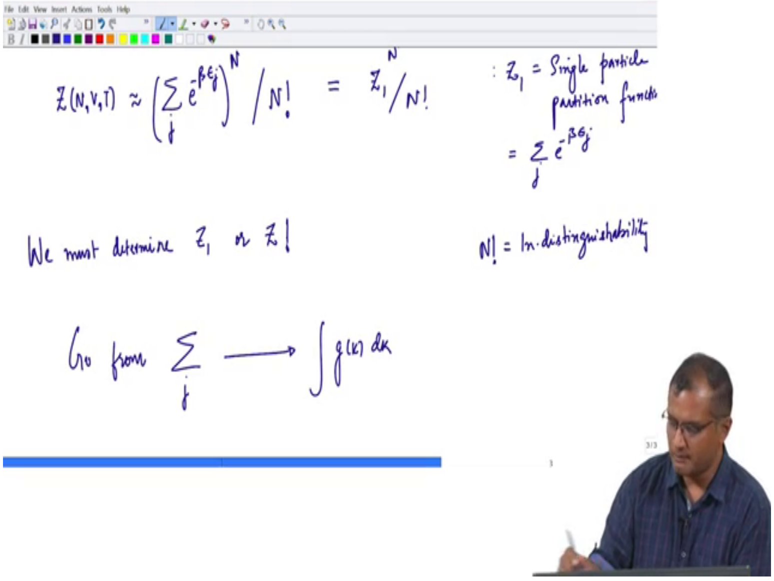

$$Z(N,V,T) \approx \left(\sum_j e^{-\beta\epsilon_j}\right)^N / N! = Z_1^N / N!$$

: Z_1 = Single particle partition functi

$= \sum_j e^{-\beta\epsilon_j}$

We must determine Z_1 or Z!

$N!$ = In-distinguishability

Go from $\sum_j \longrightarrow \int g(k)\, dk$

So, can I call this as nothing, but a single partition function raised to the power N divided by N factorial. So, this is like already the birth of the Boltzmann statistics. So, Z 1 is a single particle Boltzmann partition function. See its like you compute partition function for a single particle and raise it to N power, that will give you v to the power N and 2 pi m over beta to the power 3 N and so on so forth and there is 1 upon N factorial is the factor that comes due to the indistinguishability of N particles which you have to artificially plug in classical statistical mechanics to avoid Gibbs paradox, it here you do not have to do anything ok.

So, this N factorial was embedded in the wave function of the Fermions in the Bosons and when you take the high temperature limit, you get the correct statistic which requires no artificial plugging to save you from an entropy crisis. So, this is a single particle partition function let me complete my statement and this factorial here is because you got in distinguishability; what do you mean by in distinguishability? Particles are identical so, if I permute with N particles I have N factorial permutations, each one of them will have the exactly the same Hamiltonian and the wave function does not change which means I must not over count my microstates.

So, this is precisely the factor by which you would over count your microstates and get incorrect entropy. Well that is naturally avoided in quantum statistics because you do it in the grand canonical ensemble and you take into account the proper symmetrization and anti symmetrization of the wave function and so, this N factorial is already embedded in your calculation.

Anyway, it is relieving and it is I pleasing to see that everything falls in tact when you take the high temperature low density element of the quantum partition function. We are not there fully yet because we must determine Z 1 or if we determine Z 1 we will end up determining Z, because Z 1 to the power N by N factorial is your Z. So, that is the only agenda remaining ok.

So, let us complete this discussion and to do that all I have to do now is to basically go from discrete states to integration over a continuum of states. So, if you look at the Boltzmann partition function this Z 1, this is nothing, but the partition function that is written in for discrete degrees of freedom.

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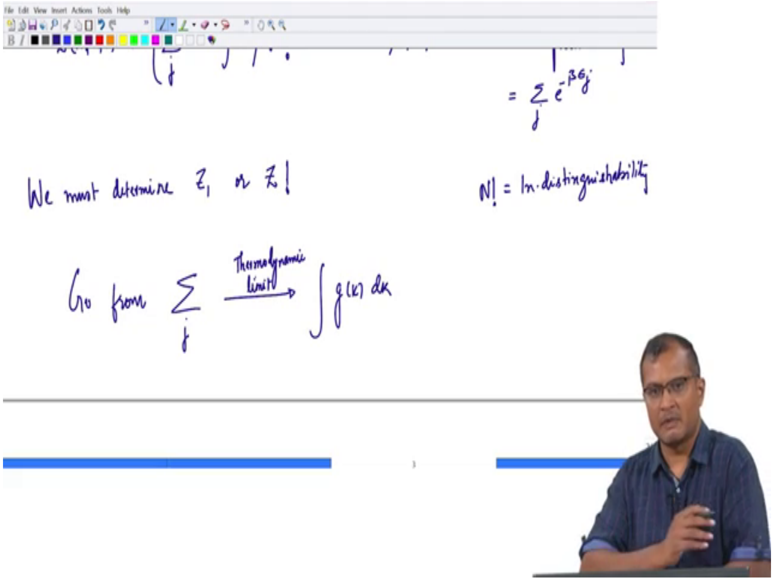

$= \sum_j e^{-\beta \epsilon_j}$

We must determine Z_1 or Z!

$N!$ = In-distinguishability

Go from $\sum_j \xrightarrow{\text{Thermodynamic limit}} \int g(k)\, dk$

So, we can go from discrete states to a continuum of states I will call this as a thermodynamic limit, as the number of states become squeezed so, tightly that the separation between the states disappears. So, you do not require you do not work with summation anymore what you would work now with is density of states.

So, the summation a must be replaced by density of states that is the logical thing to do when you have a continuum of states ok. Since we are taking a thermodynamic limit voluming very large, we must work with an integral representation, if you recall the partition function for an ideal gas you did not use a summation over all states. Because an ideal gas Hamiltonian you know is continuously is a continuous function, particles can go in any corner of the box with any momenta since position and momentum are continuous random variables, you would expect the Hamiltonian to be also continuously varying. So, you had the integral version of the partition function.

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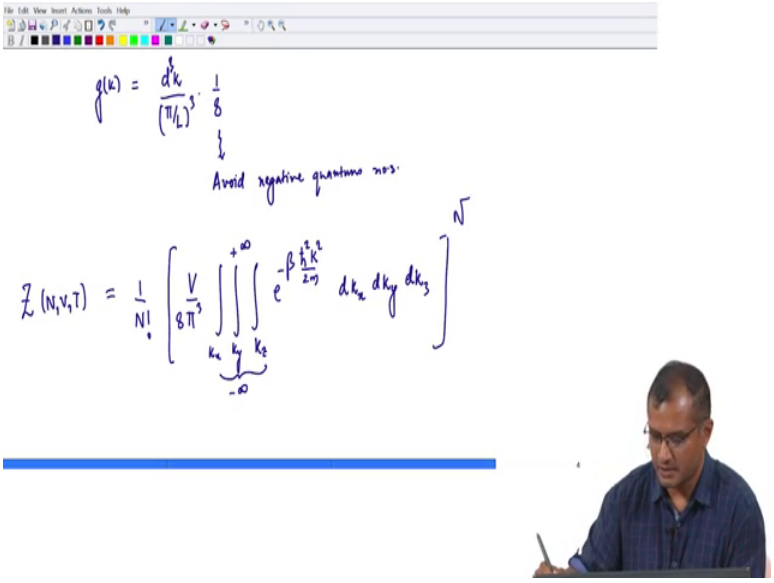

$$g(k) = \frac{d^3k}{(\pi/L)^3} \cdot \underbrace{\frac{1}{8}}_{\text{Avoid negative quantum nos.}}$$

$$Z(N,V,T) = \frac{1}{N!}\left[\frac{V}{8\pi^3}\underbrace{\int_{k_x}\int_{k_y}\int_{k_z}}_{-\infty}^{+\infty} e^{-\beta\frac{\hbar^2k^2}{2m}}\, dk_x\, dk_y\, dk_z\right]^N$$

So, I can compute this g of k as we have been doing all along, this is nothing, but you can write down this as d cube k over pi by L the whole cube and keep in mind that you have to take one eighth of the total volume, because you do not take negative excitation numbers avoid negative quantum numbers and just to remind you why we do not negative take negative quantum numbers?

Because taking a negative quantum number there is nothing spectacular to the system except apart from giving the wave function and overall negative sign and since wave function itself is nothing its just the probability amplitude, what is really meaningful is the probability density which is the wave function multiplied to its complex conjugate, and in that process a negative or a positive wave function gives you the same probability density. So, we work with only one eighth or one octant of the case space and to respect that observation we have taken a factor of 1 by 8th here ok.

So, now we can take this g of k and compute our partition function the last and final step. So, this is my left hand side and the right hand side is nothing, but I have 1 upon factorial

N already with me and that integral over the Boltzmann factors to the power N has now to be replaced with I can write down in this entire thing as an integral over I can write down this as a let me just write down this pre factors outside.

So, this becomes L cube and the numerator becomes just volume divided by pi cube and I am going to write down 8 here V upon 8 pi cube and I have a triple integral ok. So, this is like kx ky and kz going from minus infinity to plus infinity ok.

E to the power minus beta and energy is nothing, but h cut square k square over 2 m and this is nothing, but integrated over the volume element please look at here if to refresh your memory ok. So, this summation j over the Boltzmann factor is now my integral and the entire thing is raised to the power N which is basically this power and there is a 1 upon factorial N outside ok.

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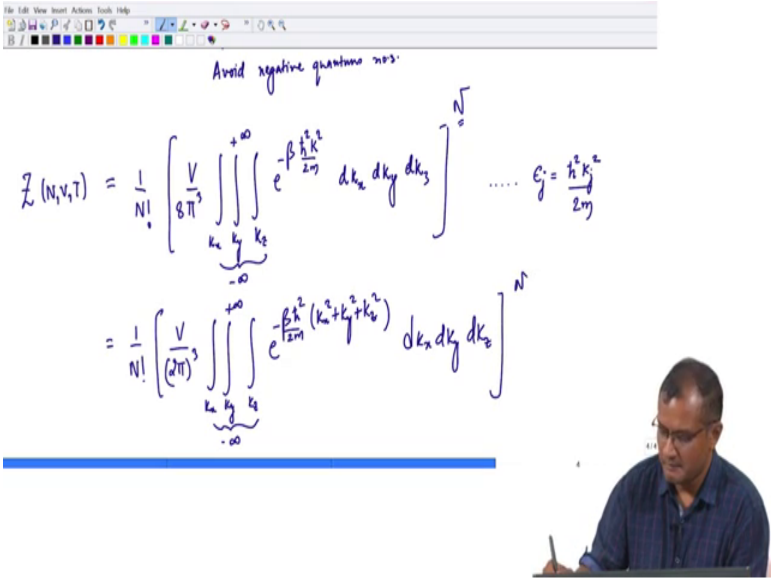

Avoid negative quantum nos.

$$\mathcal{Z}(N,V,T) = \frac{1}{N!}\left[\frac{V}{8\pi^3}\underbrace{\int\int\int_{k_x\,k_y\,k_z}}_{-\infty}^{+\infty} e^{-\beta\frac{\hbar^2k^2}{2m}}\,dk_x\,dk_y\,dk_z\right]^N \quad \ldots\ldots \quad \epsilon_j = \frac{\hbar^2k_j^2}{2m}$$

$$= \frac{1}{N!}\left[\frac{V}{(2\pi)^3}\underbrace{\int\int\int_{k_x\,k_y\,k_z}}_{-\infty}^{+\infty} e^{-\frac{\beta\hbar^2}{2m}(k_x^2+k_y^2+k_z^2)}\,dk_x\,dk_y\,dk_z\right]^N$$

And just to remind ourselves we have taken the liberty to replace energy of the j th state as h cut square kj square over 2 m ok. So, my Boltzmann factor is now e to the power minus beta h cut square k squared upon 2 m. Now you can see that these are nothing, but three independent Gaussian integrals I can write down one more step here.

So, I am going to write down this as 2 pi the whole cube 8 pi cube and the triple integral kx ky and kz all going from minus infinity to plus infinity e to the power minus beta h cut square over 2 m into kx square plus ky square plus kz square.

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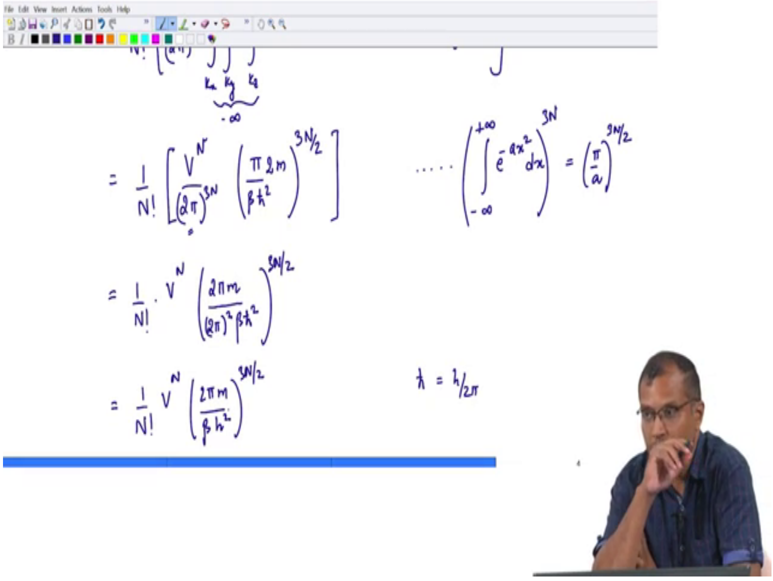

$$= \frac{1}{N!}\left[\frac{V^N}{(2\pi)^{3N}}\left(\frac{\pi 2m}{\beta\hbar^2}\right)^{3N/2}\right] \quad \cdots\cdots \left(\int_{-\infty}^{+\infty} e^{-ax^2}dx\right)^{3N} = \left(\frac{\pi}{a}\right)^{3N/2}$$

$$= \frac{1}{N!}\cdot V^N\left(\frac{2\pi m}{(2\pi)^2\beta\hbar^2}\right)^{3N/2}$$

$$= \frac{1}{N!}V^N\left(\frac{2\pi m}{\beta h^2}\right)^{3N/2} \qquad \hbar = h/2\pi$$

Since, the integration variable is dummy, there is nothing, but a single integral to the power 3 ok. So, I am going to write this as V to the power N over 2 pi to the power 3 N a single Gaussian integral is square root of pi by a. So, I am going to write pi over a; a is nothing, but beta h cut square into 2 m, this will give me a factor of 3. So, power of 3 because there are 3 integrals here and overall it will also be raised to an N because the there is a big N sitting outside. Of course, it is square root so, 3 N by 2 fine, little bit of recap.

So, minus infinity to plus infinity e raised to minus a x square dx is equal to square root of pi over a, I have a product of 3 of them. So, I will call this as pi by a to the power three half and if I have 3 N I will say that this is entire thing is nothing, but 3 N by 2 that is all. Let us rearrange the terms so, that it becomes familiar to our eyes. So, I am going to take 2 pi raise to 3 N inside this bracket which means I have to raise it to the power 2. So, I am going to write down 2 pi m in the numerator as it is and take this guy inside. So, if this should become 2 pi to the power 2 because there is a half also outside into beta h cut square raise to 3 N by 2 there is a square root sign.

So, I had to raise it to the power of 2 it was already raised to 3N. So, that does not get affected. So, this becomes now I can knock off a few things. So, h cut is nothing, but h upon 2 pi. So, 2 pi square h cut square is nothing, but just h square. So, this is nothing, but 2 pi m over beta h to the power 3 N by 2 square.

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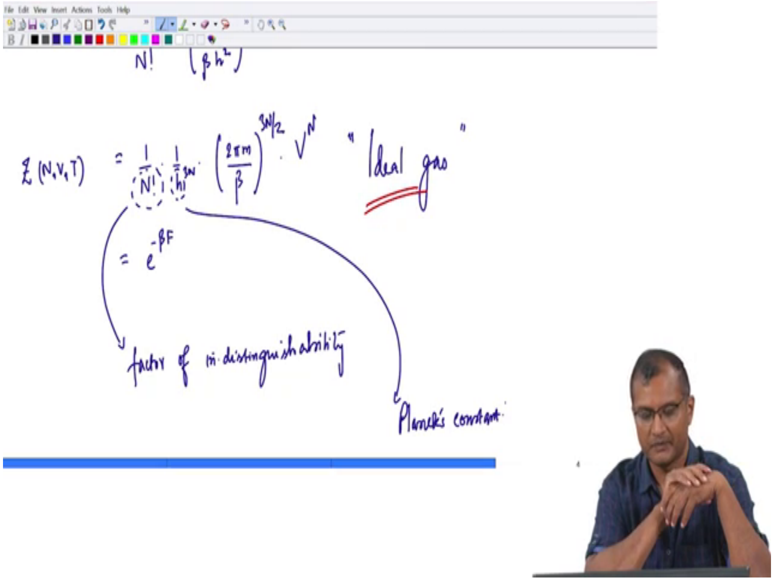

And let us take this h square also outside. So, what I get is 1 upon N factorial into 1 upon h to the power 3N into 2 pi m over beta to the power 3N by 2. This is my canonical partition function for an ideal gas classical ideal gas did I miss something? V to the power N what we started was for the system of Fermions and Bosons at low temperature?

So, we started from Fermi Dirac statistics and we systematically took the high temperature low density limit in the limit of large volume and what we ended up getting is a statistics where does not care whether you are looking at Bosons or Fermions particles are behaving ideally, their point size particles and everything is neat and intact.

This tells you that no matter whether you start from Bose Einstein statistics or Fermi Dirac statistics, the high temperature low density limit will take you to the ideal gas behaviour which is a beautiful correspondence. That I do not see any difference between the Fermi Dirac statistics or Bose Einstein statistics, they both behave like an ideal gas of non interacting particles.

So, I know for sure that this partition function is related to the thermodynamic free energy as e to the power minus beta F and so, this partition function will give me the correct values of you know the equation of state, the pressure, the entropy without any you know problems that we encountered in classical statistics mechanics, where we could not take the N factorial you know without an ad hoc substitution. So, here the expression that you get by this systematic process is the current expression, where the N factorial is a natural you know factor of indistinguishability, it did not have to be artificially plugged in this factor h is Planck's constant.

Again I did not have to take a Planck's constant and plug it artificially like I did in the classical stat mech, because I had to non dimensionalize a partition function in as an attribute some kind of a cell factor, the resolution of my phase space it had the dimensions of a action. Here h is the Planck's constant that came from the Bose Einstein or Max Fermi Dirac statistics.

So, the remnant h is the Planck's constant. So, we must call this h is Planck's constant because it came from quantum mechanics you do not get Planck constant in classical mechanics because Boltzmann and Gibbs would not have known this Planck's constant, because this was done only in the dawn of 20th century, when quantum mechanics was actually developed. Well as classical star trek predates quantum mechanics, it was done before quantum mechanics was developed.

So, the edge that is there in the Boltzmann and Gibbsian (Refer Time: 61:52) is not Planck's constant at least they did not know. They used a cell factor, they used non dimensionalizing factor something that has dimensions of angular momentum for action.

Now we know that this h is the Planck's constant, because we started from the quantum statistics and systematically derived classical statistical mechanics, which gives us the correct enumeration of states there is a factorial N sitting here which avoids over counting microstates and gives us the correct expression of entropy and so, is the expression dimensionless because of the h factor sitting in the expression. So, I will conclude this discussion of the quantum to classical correspondence. When we meet again we will discuss some working examples and that is the end of the course. So, we will stop it here.