Chemical Principles II
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Tutorial Problems - 12

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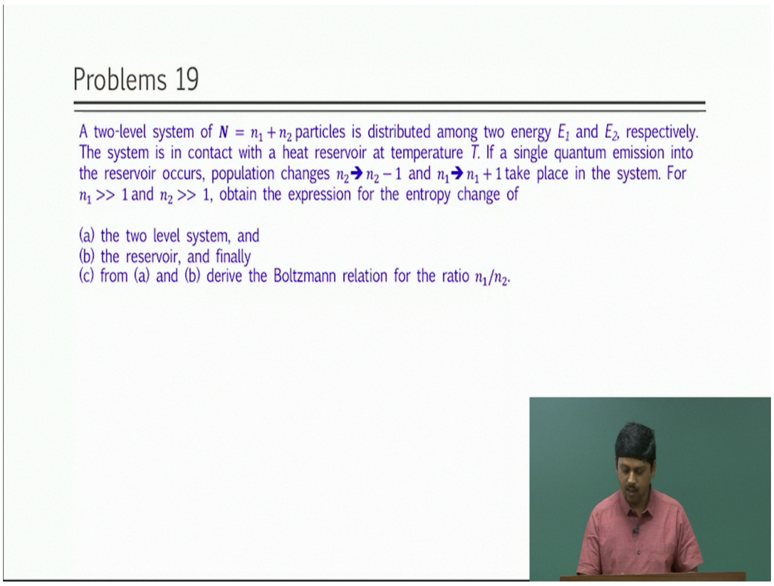

A two-level system where N equals to N1+ N2 particles is distributed among the two energies E1 and E2 respectively, that means N1 particles are there in energy level E1 and N2 particles are there in energy level E2, the system is in contact with the heat reservoir at temperature T. If a single quantum emission into the reservoir occurs, population changes from N2 to N2 -1 and N1 to N1+1 which means it goes from N2 to N1 rather, and N1 is much larger than 1 and N2 is much much larger than 1 obtain an expression of the entropy change of the two-level system, the reservoir and finally, from A and B derive the Boltzmann relation between N1 and N2 okay problem 19.

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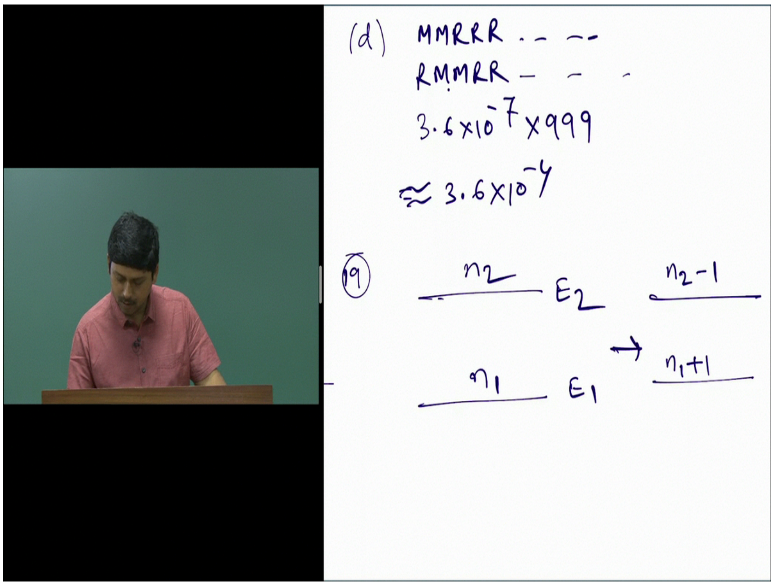

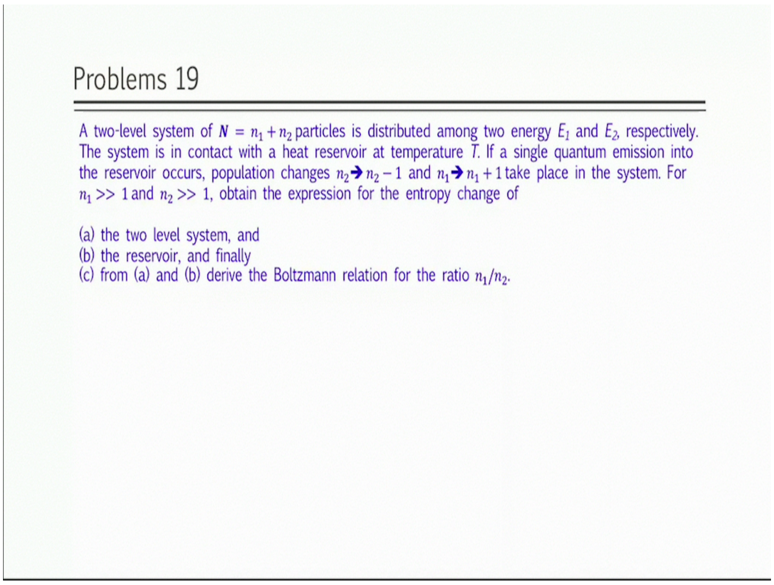

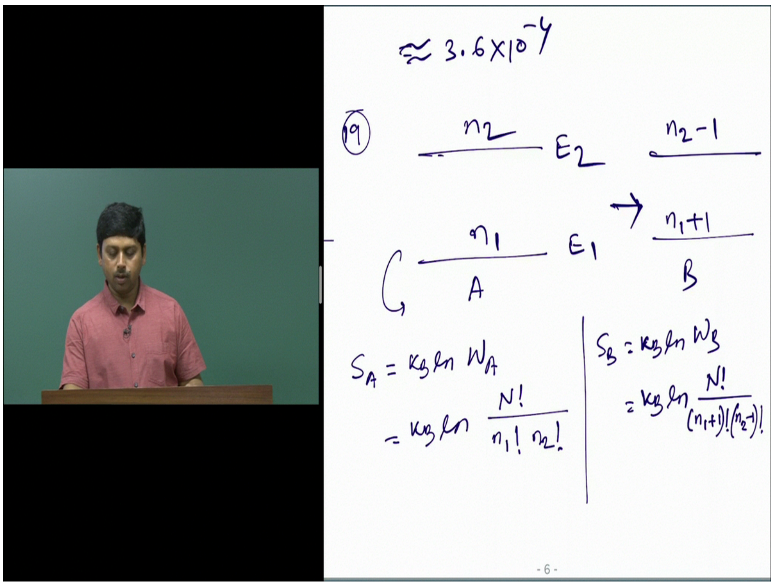

So this is a two-level system E1 and E2, there are N1 particles and N2 particles and suddenly goes to N2 -1 and here we get N1+1 this is the process that quantum emission is talking about, now question is obtained expression for the entropy change of the system, so the entropy of this previous system, let say it is goes from A to B, so entropy of the system A can be written as SA which is nothing but KBLWA, where WA is total N which is N factorial by N1 factorial and N2 factorial, where we know that N1+N2 equal to N, entropy of SB is KBLNWB, where it is factorial again by N1 +1 factorial and N2-1 factorial, where again N1+N2 equal to N.

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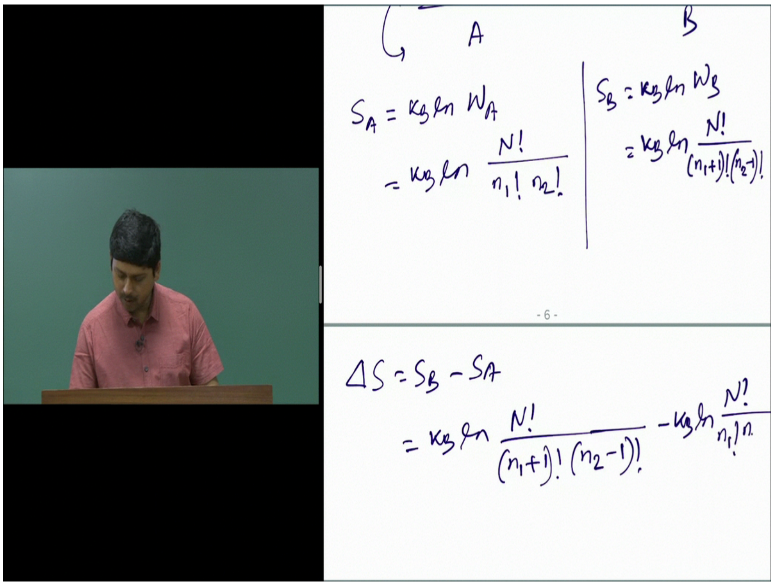

Now what is the entropy difference, entropy difference Delta S is nothing but SB minus SA, which is KBLN, N factorial by N1 +1 factorial, N2 -1 factorial minus KBLN N factorial by N1 factorial and N2 factorial.

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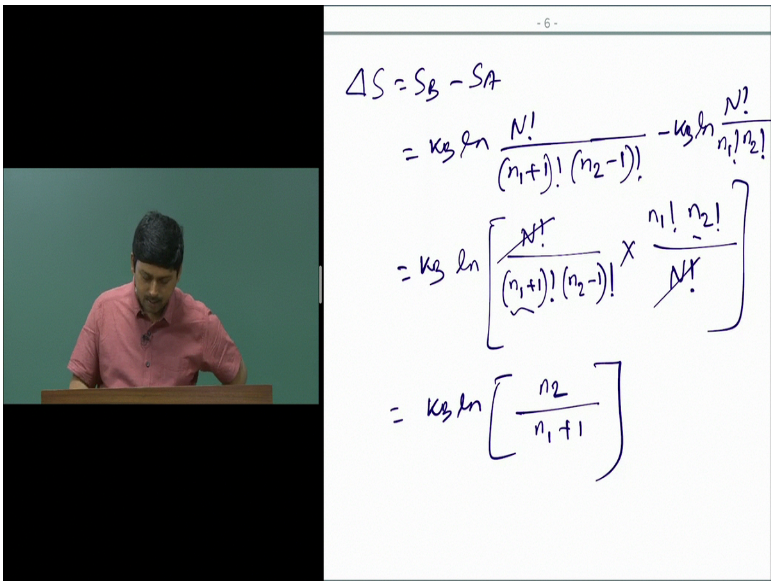

So therefore taking KB common LN, you can write as N factorial by N1 +1 factorial, N2 -1 factorial multiplied by N1 factorial, N2 factorial by N factorial, these cancel each other and we get N1+1 in the numerator and N2 in the numerator N2 and here N1 +1, so that will be the entropy change of the system, there we get.

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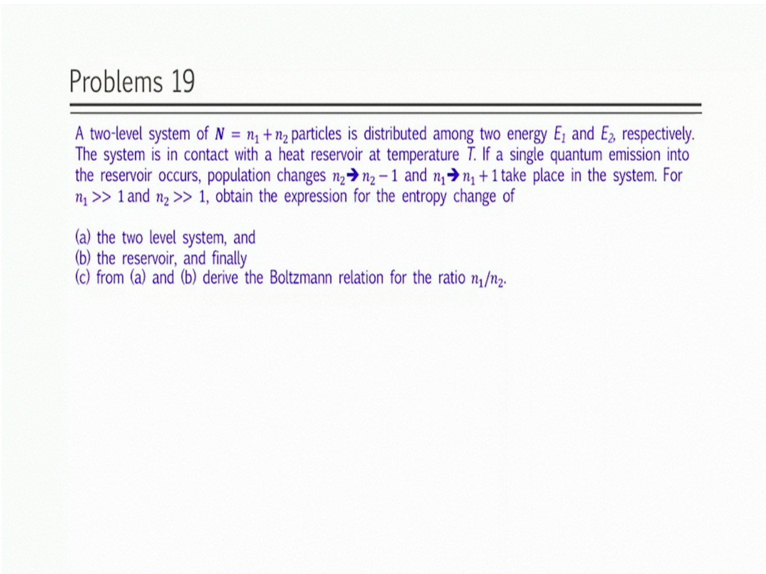

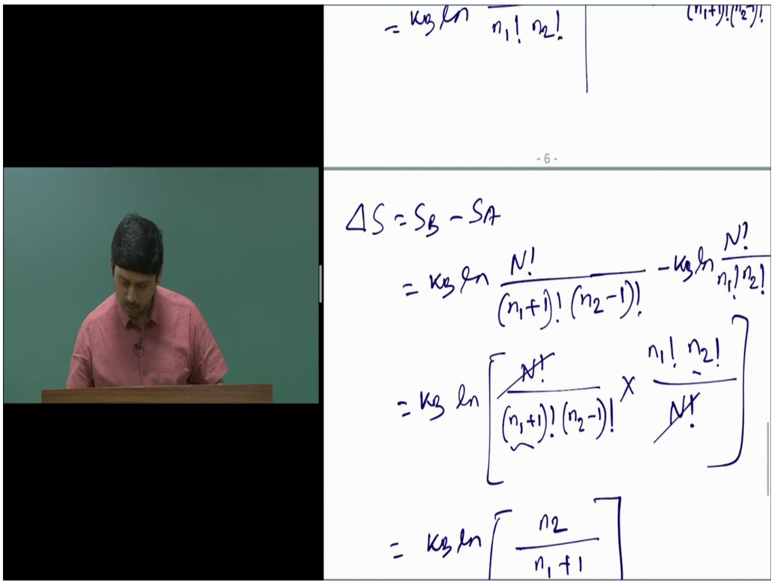

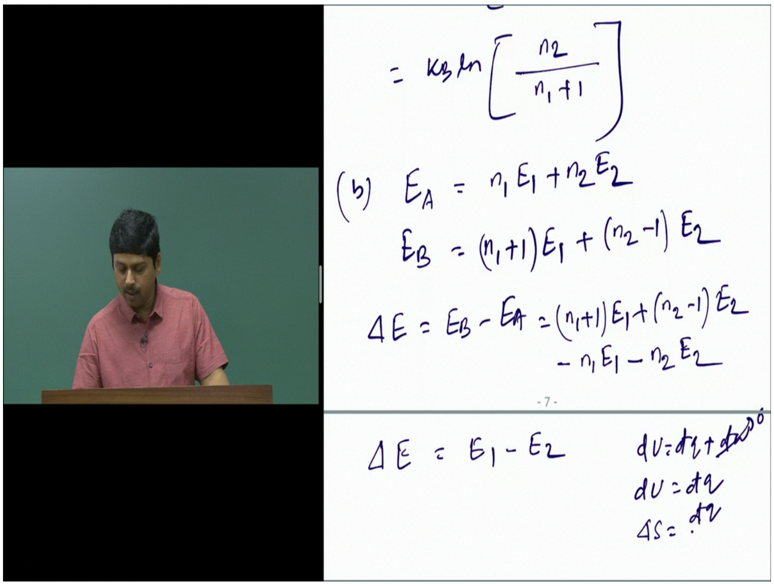

And now we have to see the second part of the question, obtain the expression the entropy change of the two-level system and the reservoir, second part of the question is at, how to calculate the entropy of the surrounding, so this was the entropy of the, entropy change of the system, two-level system and we have to calculate the entropy of the surrounding, now you know that entropy change of the surrounding is does not matter whether the process is reversible or irreversible and there were, the total image of the system earlier.

Let say EA which was N1 into E1 plus N2 into E2 and now energy of the system B is N1 +1 into E1 plus N2 -1 into E2, so therefore the changing the energy of the two system is EB minus EA, which would be given by N1 +1 E1 plus N2 -1 into, is it N2, yes -1, E2 minus N1 E1 minus N2 E2, so therefore Delta E is E1 and minus cancel each other, so it will be E1 minus E2, now that is a change in energy and you know the change in energy and change in heat is same, if the work done 0, so I just remind you that DV equal to DQ plus DW, now wherever there is DW equal to 0, the change energy is equal to change in heat and now entropy can be written as DQ by T.

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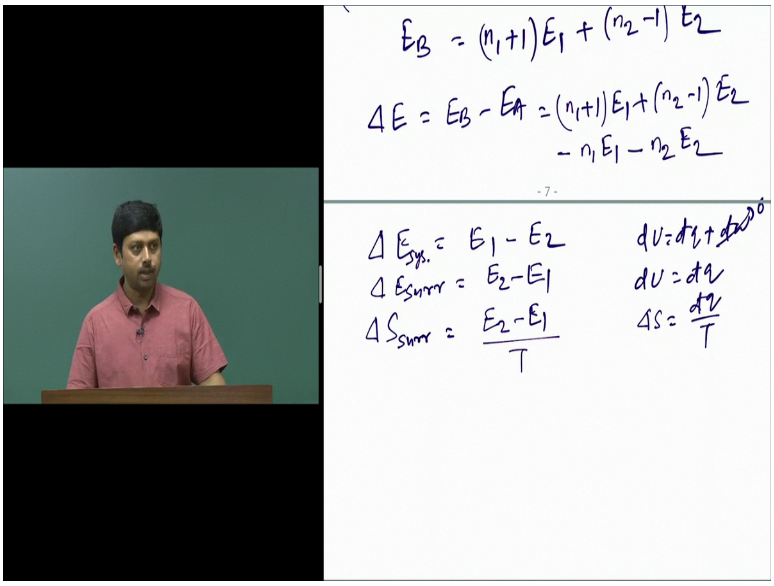

So let say the temperature of the system and surrounding is T, therefore Delta S of the surrounding will be Delta E by T, so that is the okay, by the way, this is the energy, the saved, this is the energy of the system, so therefore the energy change of the surrounding is E2 minus E1, so it is E2 minus E1 by T will be the entropy change of the surrounding.

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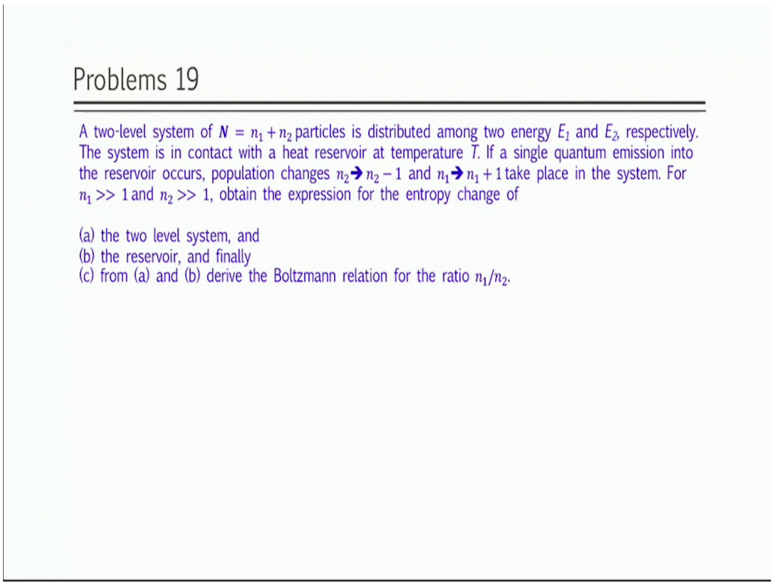

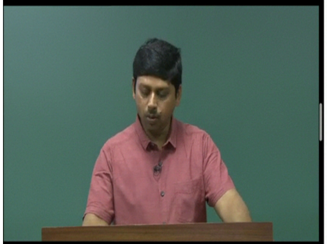

H → Correct base, $p = \frac{999}{1000}$

$= .999$

T → Mutated base, $(1-p) = \frac{1}{1000} = 0.001$

$$P(N=1000, n=0) = {}^{1000}C_0 \times (.999)^{1000} \times (.001)^0$$

$$= 1 \times 0.368 \times 1$$

$$= 0.368$$

$$P(N=1000, n=1) = {}^{1000}C_1 \times (0.999)^{999} \times (.001)^1$$

$$= 1000 \times 0.368 \times (.001)$$

$$= 0.368$$

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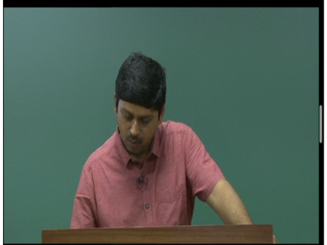


$$\Delta S = S_B - S_A$$

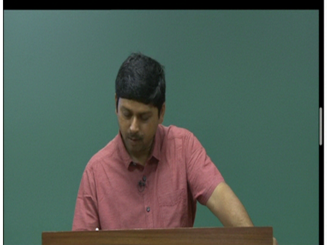
$$= k_B \ln \frac{N!}{(n_1+1)!\,(n_2-1)!} - k_B \ln \frac{N!}{n_1!\,n_2!}$$

$$= k_B \ln \left[\frac{N!}{(n_1+1)!\,(n_2-1)!} \times \frac{n_1!\,n_2!}{N!} \right]$$

$$= k_B \ln \left[\frac{n_2}{n_1+1} \right]$$

(b) $E_A = n_1 E_1 + n_2 E_2$

$E_B = (n_1+1) E_1 + (n_2-1) E_2$



$\Delta E_{sys.} = E_1 - E_2$ $\quad dU = dq + dw^{0}$

$\Delta E_{surr} = E_2 - E_1$ $\quad dU = dq$

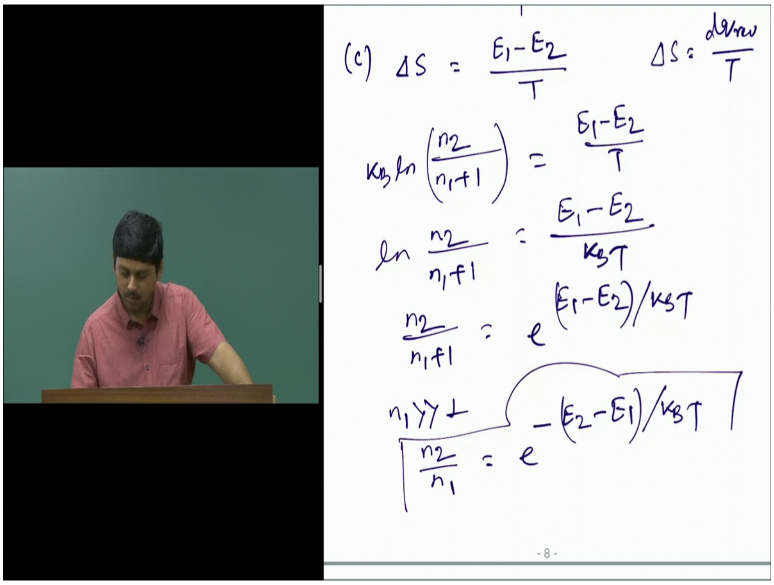
$\Delta S_{surr} = \frac{E_2 - E_1}{T}$ $\quad \Delta S = \frac{dq}{T}$

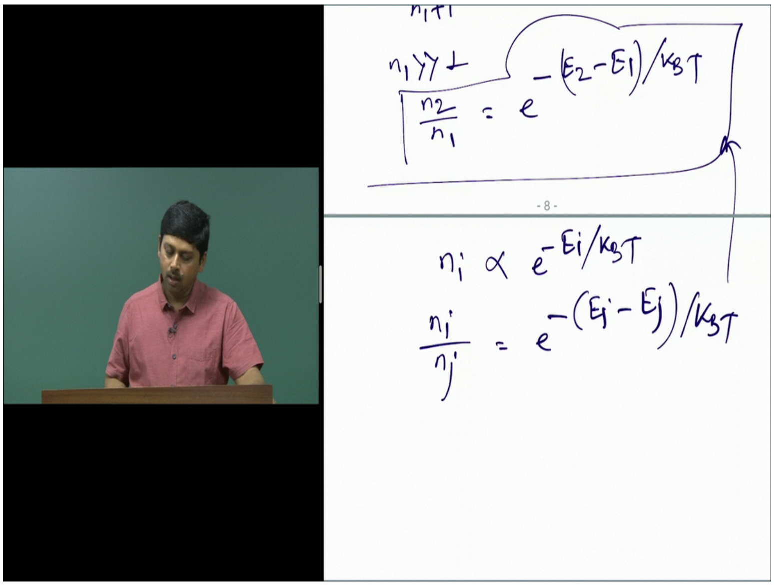
(c) $\Delta S = \frac{E_1 - E_2}{T}$ $\quad \Delta S = \frac{dq_{rev}}{T}$

$$k_B \ln \left(\frac{n_2}{n_1+1} \right) = \frac{E_1 - E_2}{T}$$

$$\ln \frac{n_2}{n_1+1} = \frac{E_1 - E_2}{k_B T}$$

$$\frac{n_2}{n_1+1} = e^{(E_1 - E_2)/k_B T}$$





Now coming back to the third part of the same question either from A and B derive the Boltzmann relation for the ratios of N1 and N2 okay, so now the third question demands that, we need to show the relation between these energy entropy, now you know that the distribution of particles in different levels follow Boltzmann distribution anyway what here the question demands that we show the Boltzmann distribution itself, but now for the we have to compare the entropy that we obtain from this energy calculation and also from the calculation of the Ws, now in order to show the relation between, we have to assume that the process is reversible, because if we assume that then only we can say that the entropy change of the system is nothing but E1 minus E2 by T.

That means the changing heat by T, if the processes not reversible, remember the Delta S is DQ reversible by T, it does not matter for the surrounding, though, so that is why for the surrounding this result is okay, however for the system is result will not be okay if the process is not reversible, so assuming that the processes reversible because without assuming that we cannot even do the calculation that is demanded, so assuming the processes reversible we can write the entropy as that and then we have already obtained relation of entropy as, as you can see here KBLN into by N1 +1.

So KBLN into by N1 +1 is E1 minus E2 by T and therefore LN, N2 by N1 +1 is E1 minus E2 by KBT, so therefore N2 by N1 +1 is E to the power E1 minus E2 by KBT and since N1 much, much greater than 1, we can write N2 by N1 is equal to E to the power minus E2 minus E1 by KBT and that is nothing but a Boltzmann distribution, where if you remember that NI proportional to the E to the power minus EI by KBT and therefore NI by NJ will be E to the power minus EI minus EJ by KBT that is the Boltzmann distribution, it is exactly the one that is on the, that is given there. Okay.

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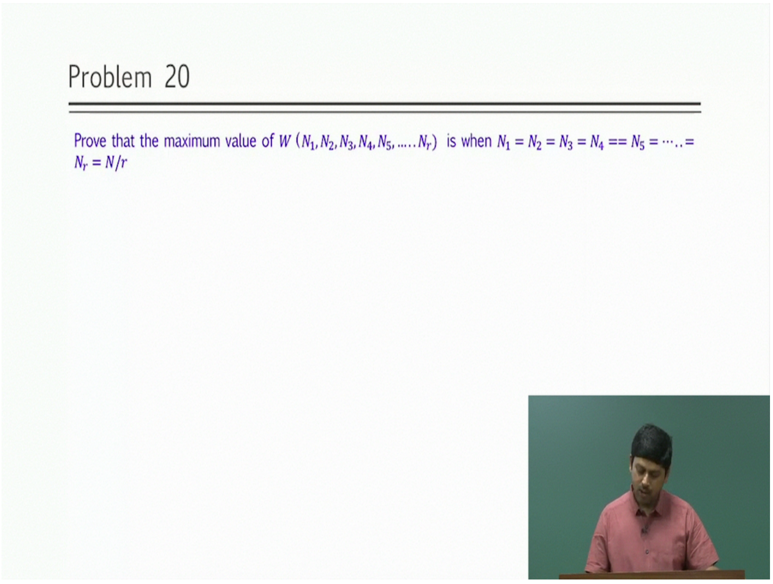

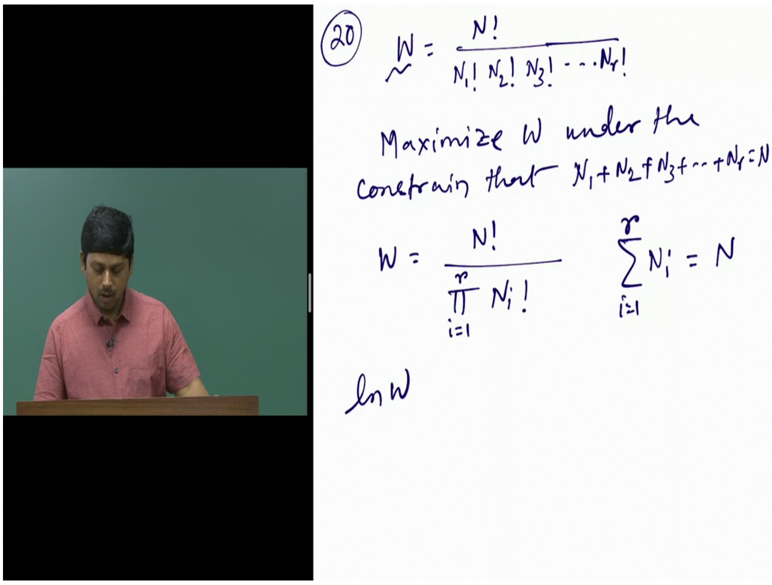

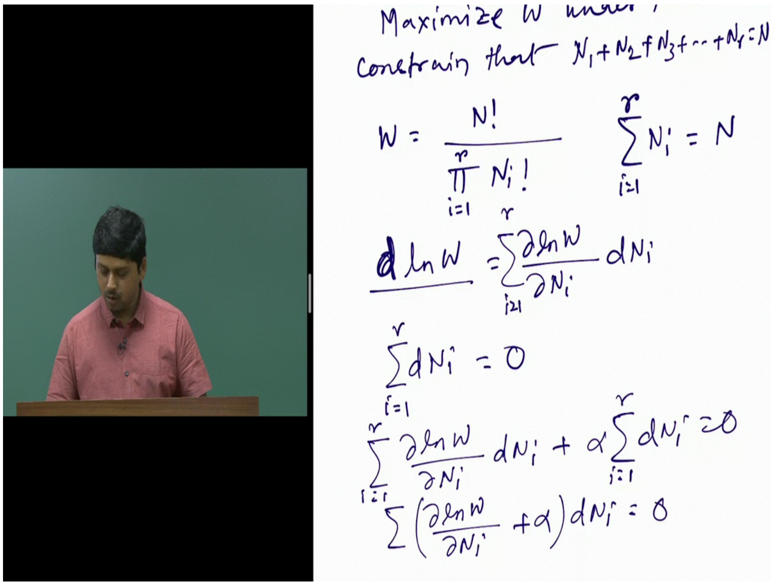

So when to the next question now, proof that maximum value of W is when N1, N2, N3 all are equal and N by R, so this is a multinomial distribution, problem number 20, so this is a multinomial distribution where W can be written as N factorial by N1 factorial, N2 factorial N3 factorial up to NR factorial, so there are this N is partitioned into R groups basically, so if partition is into two groups than we call it binomial because there are two groups and if there are like more than two then we call it multinomial distributions, so the question ask us to show that this multinomial distributions when maximize it, when you maximize the W, the maximum value will correspond to N1 plus N2 and N3 all as equal to N by R. Soc.

Now how do we approach that particular problem? So we have already derive the case of W when or maximize the W when we had a constraint of total energy and total number of particles but in this case there is no energy constraint present and only the constraint of particle present, so here we have to maximize W under the constrain that N1 plus N2 plus N3 plus NR is equal to N.

So let us do that, so W is N factorial by product of I equal to 1, R, NI factorial, so we have to maximize W, LNW and the sum of NI is a N where I goes from 1 to R, there is a can say that we have to satisfy, so as you know in our derivations when you give that, so we have to maximize LNW, so we have to do dell, dell NI under the constrain alpha that sum over NI is going to 0, so as you know the alpha is a Lagrange multiplier, Lagrange undermine multiplier, we have to determine the value of alpha such that this quantity holds, so you are maximizing the W, however we are constraining the value of NI.

So first we will do a or rather, so you have to maximize the W under the constraints of NI, so for that as you know that we can write DW or D, it is better to maximize LNW instead of W, so we are going to write DLNW as dell LNW by dell NI, DNI, so any exact differentiate you can write as sum over this quantities, I equal to 1 to R, similarly also varied NIs, remember NI is nothing N1, N2, N3 and all that, so you can vary N1 or vary N2 or vary N3, whatever you vary, might vary the sum or rather, each variations together is going to be 0, so now the quantity that you have to satisfies dell LNW by dell NI, DNI plus alpha DNI is equal to 0, I always goes to 1 to R, here also I goes to 1 to R or dell LNW where dell NI plus alpha DNI is going to be zero.

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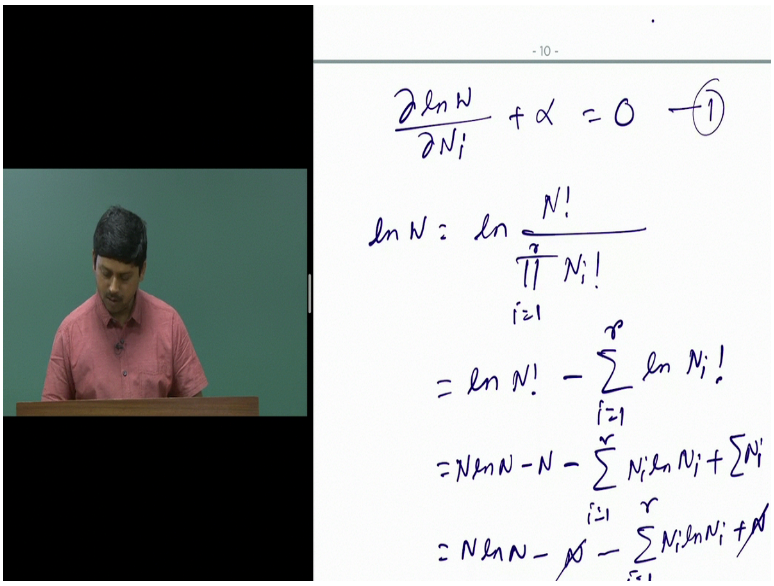

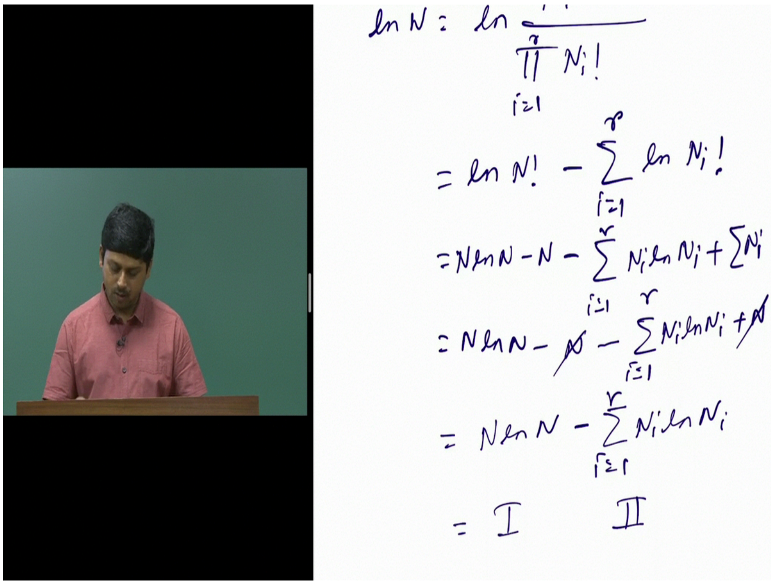

So, which we have to show that dell LNW by dell NI plus alpha is equal to 0, we have to not so but we have to use this particular constrain, use this particular format in order to show that it is equal to 0, now let us do that, now what is LNW? LNW is LN, N factorial by a product of I goes from 1 to R NI factorial, which is LN, N factorial minus sum over. I equal to 1 to R, LN NI factorial, we have discuss that before, so I am just going little bit faster on this.

Now let us do dell LNW by dell NI, before I do that I had to just satisfy some more things, let us just use the stylings approximation right here itself, that will be NLN minus N minus sum over I equal to 1 to R, NI LN NI plus sum over NI, which will give us NLN minus N minus sum over I equal to 1 to R, NI LN NI plus N, plus and minus cancel, giving us NLN N minus sum over I equal to 1 to R, NI LN NI, so this equation. I just give us 1 because there is very important, now this equation. I can write in two parts 1 and 2, or 1-2 because that is in minus, so let us put as 1-2.

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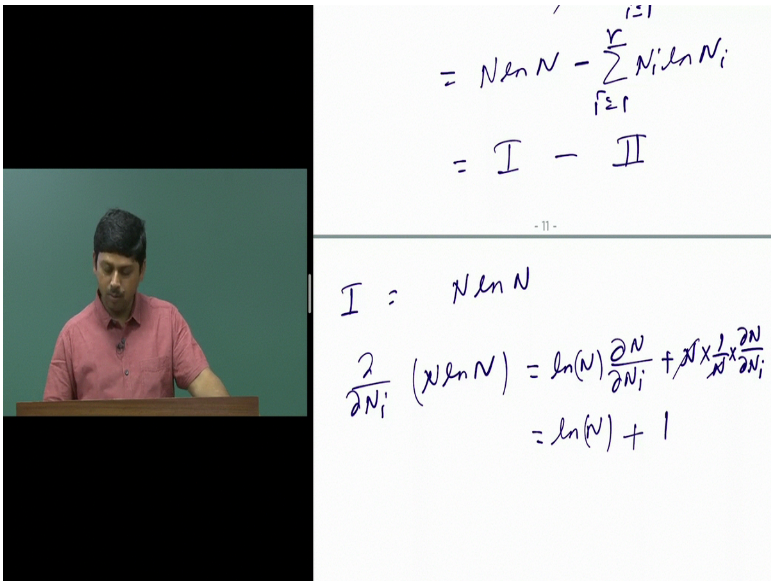

Now will do that separately, one is N LN N, so we take the derivative, therefore dell NI of N LN N, how do I do that, let us see it is a, you know, it is a differentiation for a product, let us do step-by-step it will be LN N dell N by dell NI plus N into 1 by N into dell N by dell NI, now LN N, dell N by dell NI, you know that N equal to N1 plus N2 plus N3 plus N4 plus N5 and all that right, so among which, whichever is matches with I will be 1 and rest of them will be 0, so therefore it is nothing but LN N, right inside this will cancel and this would also will give us just 1 rest of the term will go to 0, so it will be LN N +1.

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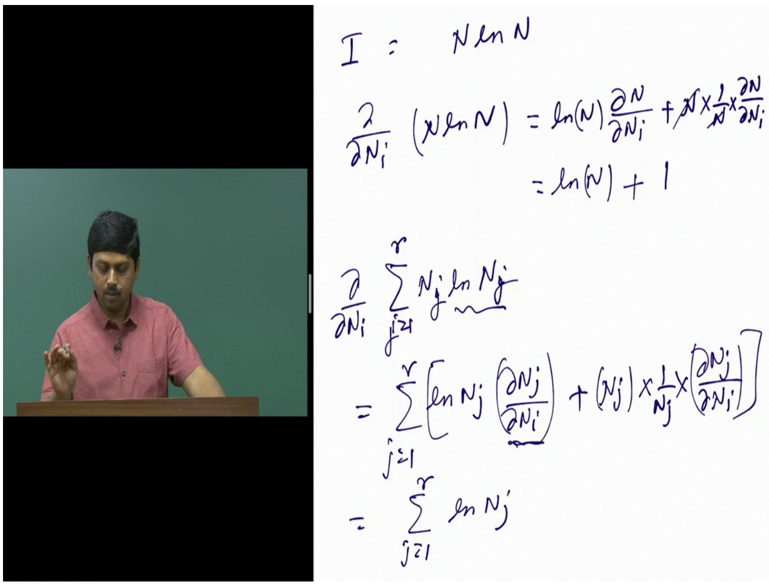
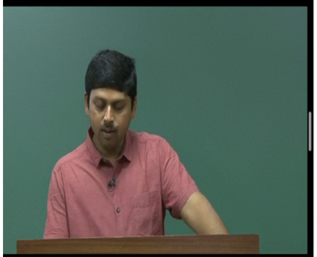




$I = N \ln N$

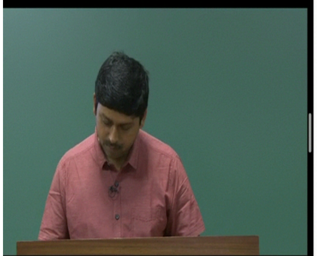
$$\frac{\partial}{\partial N_i}(N \ln N) = \ln(N)\frac{\partial N}{\partial N_i} + N \times \frac{1}{N} \times \frac{\partial N}{\partial N_i}$$

$$= \ln(N) + 1$$

$$\frac{\partial}{\partial N_i}\sum_{j=1}^{r} N_j \ln N_j$$

$$= \sum_{j=1}^{r}\left[\ln N_j \left(\frac{\partial N_j}{\partial N_i}\right) + (N_j) \times \frac{1}{N_j} \times \left(\frac{\partial N_j}{\partial N_i}\right)\right]$$

$$= \ln N_i +$$



∂N_i

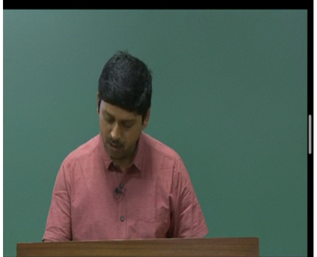
$$\ln W = \ln \frac{N!}{\prod_{i=1}^{r} N_i!}$$

$$= \ln N! - \sum_{i=1}^{r} \ln N_i!$$

$$= N \ln N - N - \sum_{i=1}^{r} N_i \ln N_i + \sum N_i$$

$$= N \ln N - N - \sum_{i=1}^{r} N_i \ln N_i + N$$

$$= N \ln N - \sum_{i=1}^{r} N_i \ln N_i$$



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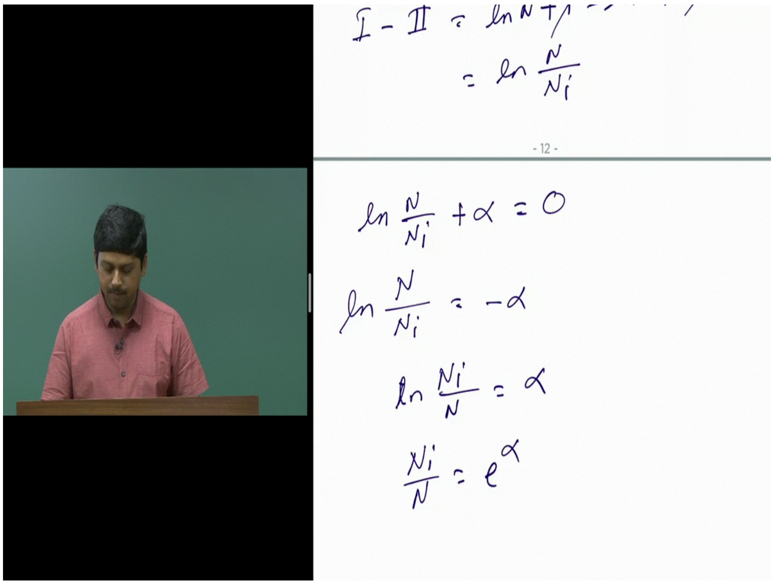
$I = N \ln N$

$$\frac{\partial}{\partial N_i}(N \ln N) = \ln(N)\frac{\partial N}{\partial N_i} + N \times \frac{1}{N} \times \frac{\partial N}{\partial N_i}$$

$$= \ln(N) + 1$$

$$\frac{\partial}{\partial N_i}\sum_{j=1}^{r} N_j \ln N_j$$

$$= \sum_{j=1}^{r}\left[\ln N_j \left(\frac{\partial N_j}{\partial N_i}\right) + (N_j) \times \frac{1}{N_j} \times \left(\frac{\partial N_j}{\partial N_i}\right)\right]$$



Now let us do the other one, this is NI LN NI, now in this case we can write the sum because I is a dummy variable, we can write sum as J itself, instead of I, let us write J because that will be helpful, now we are going to do the derivation of that and that will give us sum over J equal to 1 to R, so dell, dell, LN and J, dell NJ by dell NI plus NJ then I had to take derivative of LN and J, so it will be 1 by NJ and again dell NJ by dell NI and the sum is over the whole thing, then J equal to 1 to R, LN and J, now this quantity, what will be this quantity? So see the J can vary from 1 to R, and it dividing with some particular I, let say that is 2.

So only when it is dell N2 by dell N2 it will be 1, rest of the time it will be 0, so it will be just one quantity which is nothing but I, this is typically called chronical delta function IJ, but we are not going to in that detail, so that means the sum will be now replaced by just one down term which is just LN NI plus same thing will happen here also because you are only I term will survive, everything else will go and nothing but 1, so they are going to get just 1, so remember this is the first term and second term.

So from 1-2 we get LN, N +1 minus LN NI -1, 1,1 cancels giving us LN N by NI, now this one we got it from this quantity, this particular equation LNW, so we have maximised LNW now, so this we have done now plus alpha equal to 0, now we are going to put it back there, now that means LN N by NI plus alpha is equal to 0, which is N by NI is equal to minus alpha or LN by NI or NI by N is equal to plus alpha or NI by N is equal to E to the power alpha.

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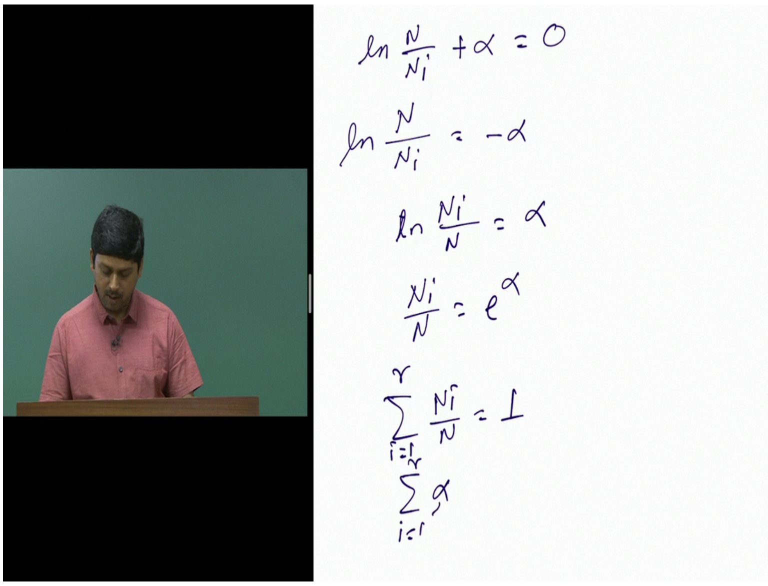

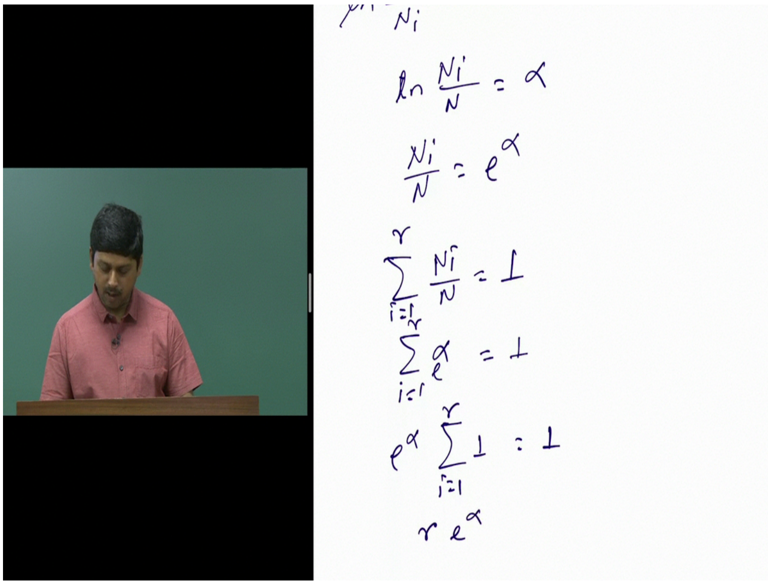

Now we know that if we sum over, so this is nothing but probability, if we sum over NI by N we are going to get 1, so which means if sum over alpha and the sum goes from again 1 to R, if we sum over E to the power alpha we are going to get 1, so the take E to the power alpha common because it is nothing but constant, it goes from 1 to R, this is nothing but just 1 is equal to 1, so there are R terms there, so R E to the power alpha is 1, so therefore E to the power alpha is nothing but 1 by R.

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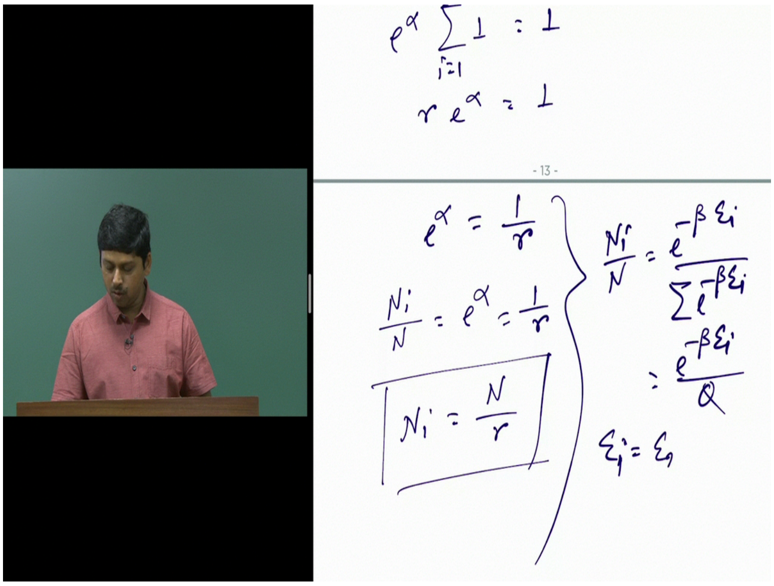

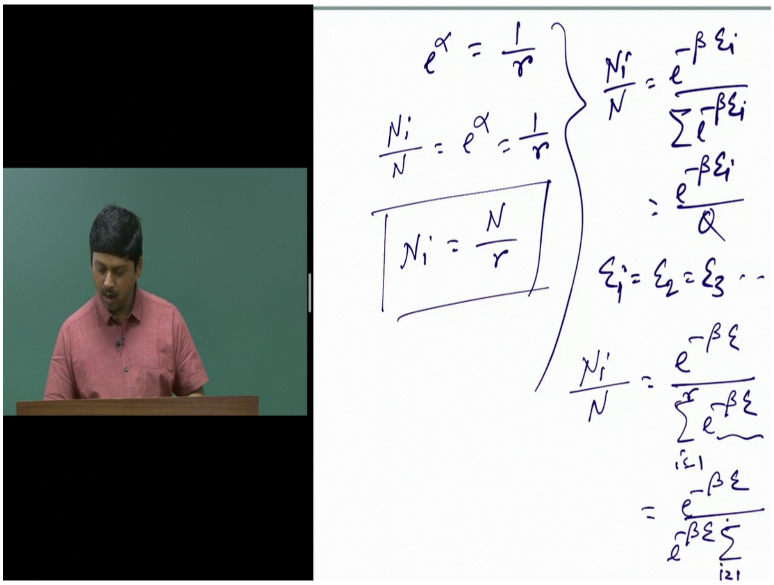

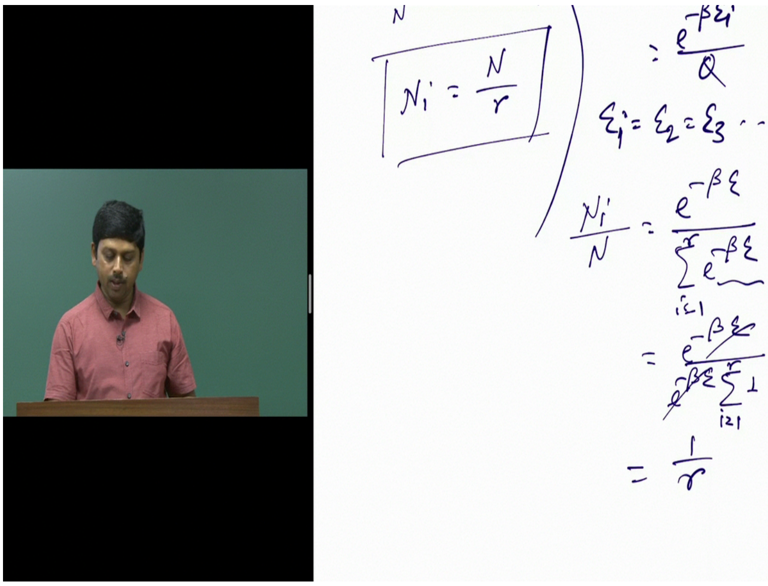

Now coming back here, what you got E to the power 1 by R, so NI by N E to the power alpha are nothing but 1 by R, so NI is nothing but N by R and that close the result, so we saw that if there is no energy constraints than the populations will be equally distributed, if there is energy constraint that means apart from alpha there is a beta constraints than will become exponential, so you have done both when there is why nature preference, population will be equally given.

Otherwise it will be an exponentially distributed and you have seen that exponential distribution, if the population are equally again go back to, so we can show that as well, you know that for a Boltzmann distribution NI by N E to the power minus beta EI by sum over E to the power beta EI or E to the power minus beta EI by Q that we no right, now if all the Es are same, they have the same value, if all EI are same, let say EI is equal to, E1 is equal to E2 is equal to E3 and things like that, then you know that NI by N it will be simply E to the power minus beta E, I goes from 1 to R.

So this is common, so will take it common, E2 the power minus beta E sum over I equal to 1 to R with 1 that is nothing but 1 by R, that is much easier, proof starting from a Boltzmann distribution, but we wanted to do that without knowing Boltzmann distribution and therefore we are arrive at that value as well. Okay.

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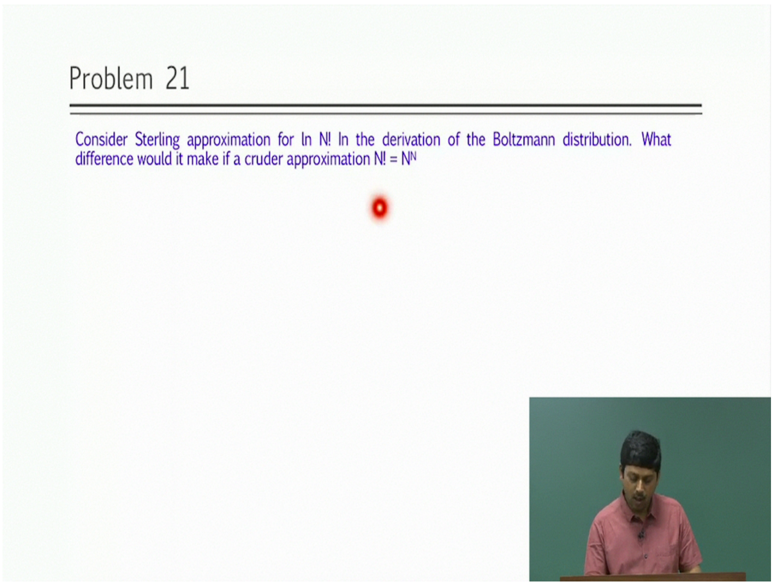
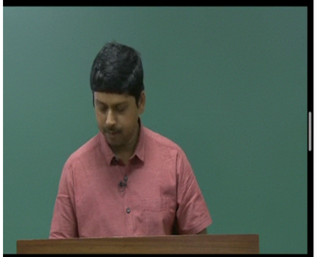




$$W = \frac{N!}{\prod N_i!}$$

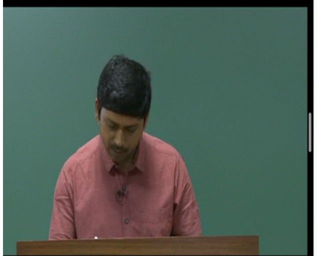
$$\ln W = \ln N! - \sum_{i=1}^{r} \ln N_i!$$

↳ Using Stirling's approximatⁿ

$$\ln W = N\ln N - N - \sum N_i \ln N_i + \sum N_i$$

$$= N\ln N - \cancel{N} - \sum N_i \ln N_i + \cancel{N}$$

$$= N\ln N - \sum N_i \ln N.$$



$$\ln W = \ln N! - \sum_{i=1} \ln N_i!$$

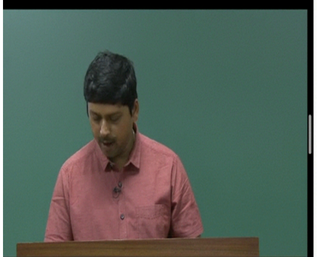
↳ Using Stirling's approximatⁿ

$$\ln W = N\ln N - N - \sum N_i \ln N_i + \sum N_i$$

$$= N\ln N - \cancel{N} - \sum N_i \ln N_i + \cancel{N}$$

$$= N\ln N - \sum N_i \ln N_i$$

Use Crude approximatⁿ



↳ Using Stirling's approximatⁿ

$$\ln W = N\ln N - N - \sum N_i \ln N_i + \sum N_i$$

$$= N\ln N - \cancel{N} - \sum N_i \ln N_i + \cancel{N}$$

$$= N\ln N - \sum N_i \ln N_i$$

Use Crude approximatⁿ

$$\ln W = \ln N! - \sum_{i=1}^{r} \ln N_i!$$

$$= \ln N^N - \sum_{i=1}^{r} \ln N_i^{N_i}$$

So now going to the next question, consider sterling is approximation for LN N factorial in the derivation of the Boltzmann distribution, what difference would it make if a cruder approximation of N factorial is equal to the N to the power N is taken, so now you see that, W is N factorial by NI factorial product, we have just seen that, so LNW is LN, N factorial minus sum over I equal to 1 to R, LN NI factorial, we have done that right, now here we are going to use both sterling approximation and the cruder approximation and going to see what happens to LNW, now using sterling approximation.

What do we get LNW equal to N LN N minus N minus NI LN NI plus NI which gives us N LN N minus N minus NI LN NI plus N and N, N cancels each other, giving us N LN N minus NI LN NI okay, now use crude approximation which is mentioned here, so then in that case will start from here, LNW is equal to LN, N factorial minus sum over LN NI factorial, I equal to 1 to R, now here we have to use N to the power N right, so LN N to the power N minus I equal to 1 to R, LN NI to the power NI.

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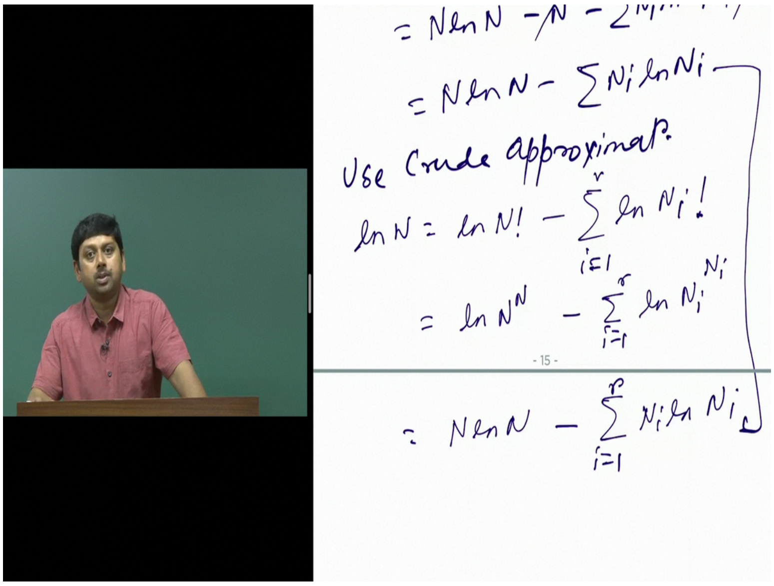

Once we do that we can write N LN N minus sum over I equal to 1 to R, NI LN NI, now you will see that this cruder approximation is exactly same as the sterling approximation for LNW, so sterling approximation give us N LN N minus sum over NI LN NI, cruder approximation give us exactly the same thing, so therefore this crude approximation would perfectly be alright, the reason is that when the number of particles are very, very large, see where is N factorial is used? Where we are placing the ball in the boxes without replacement and when, it is to the power, when you are placing the ball in the box with replacement.

Now when the N is very large, then those approximation is actually become equal and that is the reason here that Boltzmann distribution will exactly follow, even if you a cruder approximation was used as N to the power N.

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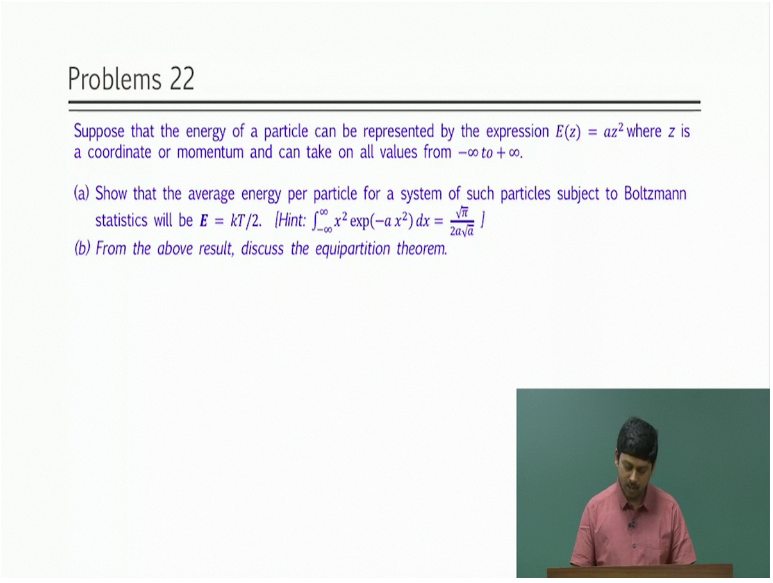

Another interesting question, suppose that the energy of a particle can be represented by the expression, EZ as AZ square, where Z is a coordinate or momentum and can take or all values from minus infinity to plus infinity, so that average energy per particle for a system of such particles subjected to Boltzmann distribution, Boltzmann statistics is KT by 2 and there is a hint also given and from the about result discuss the equipartition theorem.

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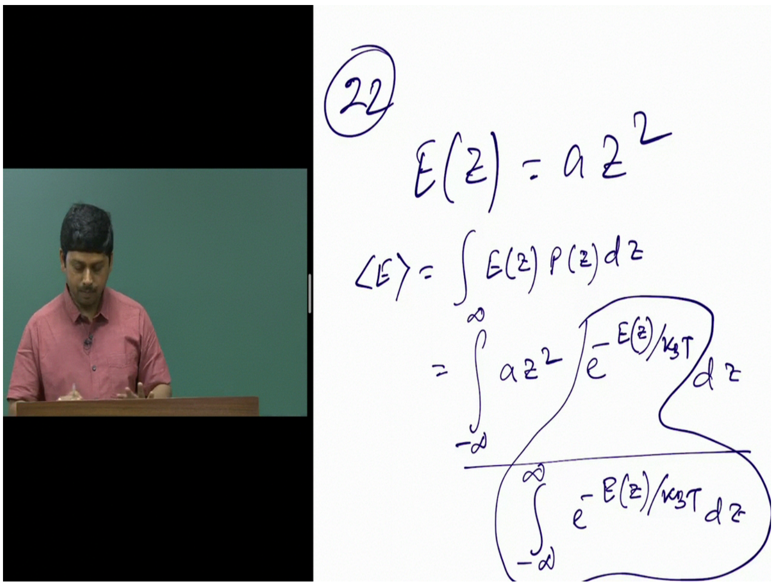
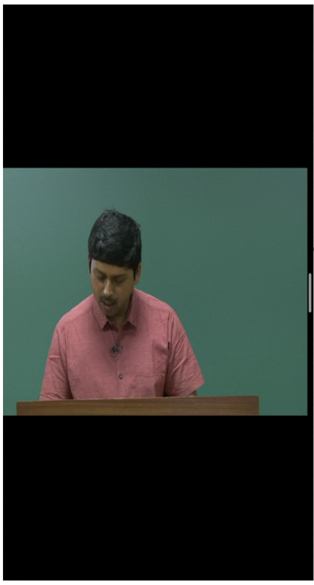


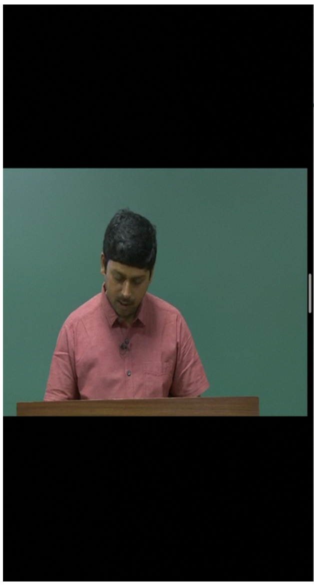


$$\int_{-\infty}^{\infty} e^{-E(z)/k_BT}\, dz$$

- 16 -

$$\mathcal{N} = \int_{-\infty}^{\infty} a z^2 e^{-az^2/k_BT}\, dz$$

$$= a \int_{-\infty}^{\infty} z^2 e^{-az^2/k_BT}\, dz$$

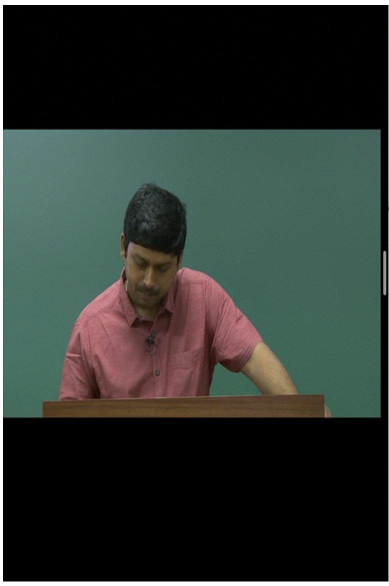


- 16 -

$$\mathcal{N} = \int_{-\infty}^{\infty} a z^2 e^{-az^2/k_BT}\, dz$$

$$= a \int_{-\infty}^{\infty} z^2 e^{-az^2/k_BT}\, dz$$

$$=$$



$$\int_{-\infty}^{\infty} e^{-E(z)/k_BT}\, dz$$

- 16 -

$$\mathcal{N} = \int_{-\infty}^{\infty} a z^2 e^{-az^2/k_BT}\, dz$$

$$= a \int_{-\infty}^{\infty} z^2 e^{-az^2/k_BT}\, dz$$

$$= A \times \frac{\sqrt{\pi}}{2\frac{a}{k_BT}\sqrt{\frac{a}{k_BT}}}$$

$$\sqrt{\pi}\,(k_BT)^{3/2}$$

You know that in order to calculate the average energy of a system E we have to write the probability, first of all the energy Z and the probability and DZ that is what we have to do, now. Okay, so PZ and now we write that is going from minus infinity to plus infinities, so it is AZ square and what is PZ? PZ is a E to the power minus EZ by KBT divided by integration of E to the power minus EZ by KBT, DZ and here we are going to get DZ.

So this is our PZ as you know, this is the PZ okay, so now we have in place the formal of the question, so let us right down the numerators and denominators, so numerator is minus infinity to plus infinity is AZ square E to the power minus AZ square by KBT DZ, take A out, it is Z square E to the power minus AZ square by KBT DZ, now here we are going to use help from the hint and take, and use the standard integral formula.

So that is, let see what it is says is that X square, E power minus AX square, X here is Z is root over pie by 2A into root over A, now here A is A by KBT, so we have to write A by KBT into root over of A by KBT is it alright, now, let see yes, so here is in the formula we have seen that Z is nothing but X and A in the formula is nothing but our A by KBT, so now it is okay, we get cancelled is A and we can write as root over pie by 2 root over A and here KBT by 3 x 2 yes, okay.

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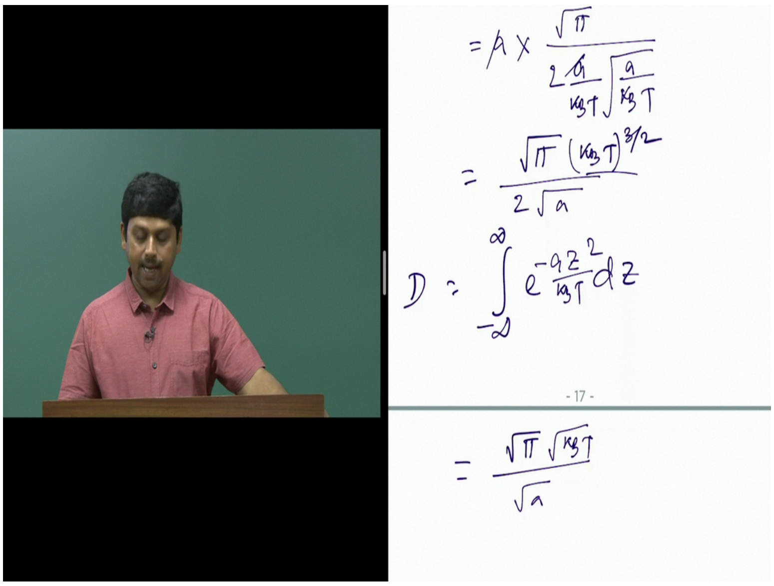

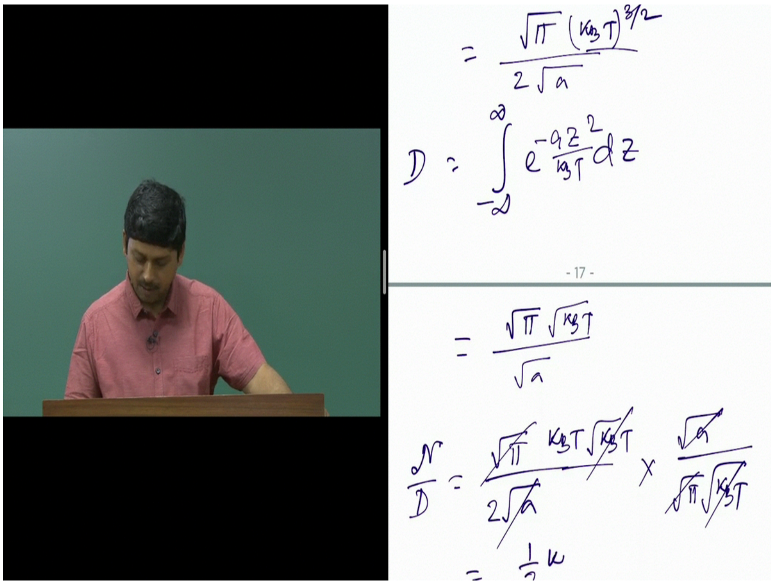

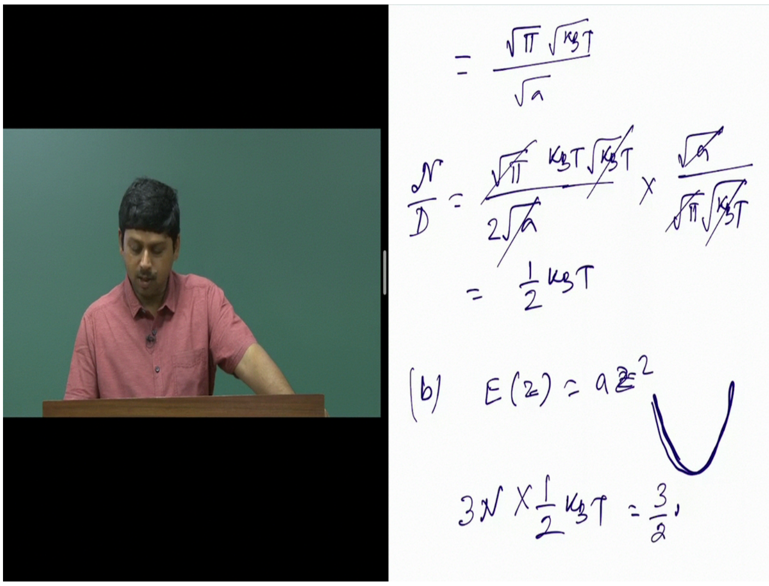

Now denominator, denominator is simple Gaussian integral minus infinity into plus infinity E to the power minus AZ square DZ, now what is the value for that, you know that, we already discussed if that is the case it is nothing but root over pie by A, so root over pie by root over A, again here this will be KBT for sure, A by KBT right, here again, it is root over A and root over KBT, because here A is nothing but A by KBT.

So now numerator by our denominator will become root over pie by 2 into root over A and KBT and root over of KBT, divided by the denominator, so root over A will go and root over pie and root over KBT will be here, so KBT and KBT cancels, root over A, root over A cancels, root over pie, root over pie cancels giving us half KBT.

So you see, now the first part is done, so average energy is half KBT and where did you obtain from? You obtain from the energy where EZ is written as AZ square and this type of energy, the question is typically call a parabolic potential and it comes from a quadratic potential, parabolic or quadratic potential and this particular potential give rise to as you can see half KBT of energy.

So equipartition theorem says that you know every quadratic energy will contribute to half KBT, so if there is a motion along X, Y and Z direction independently it will contribute to half KBT, plus half KBT, plus half KBT giving, erase to 3 x 2 KBT, so now basically every degrees of freedom will give rise to half KBT, so if you have N particles, you know, typically there will be 3N -6 vibration degrees of freedom, each of them will give half KBT, so each degrees of freedom will give you half KBT, so there are 3N degrees of freedom, giving you half KBT each, so for a system of N particles, nor interacting and the equipartition theorem will tell you that the energy of the system is 3 x 2 N KBT.