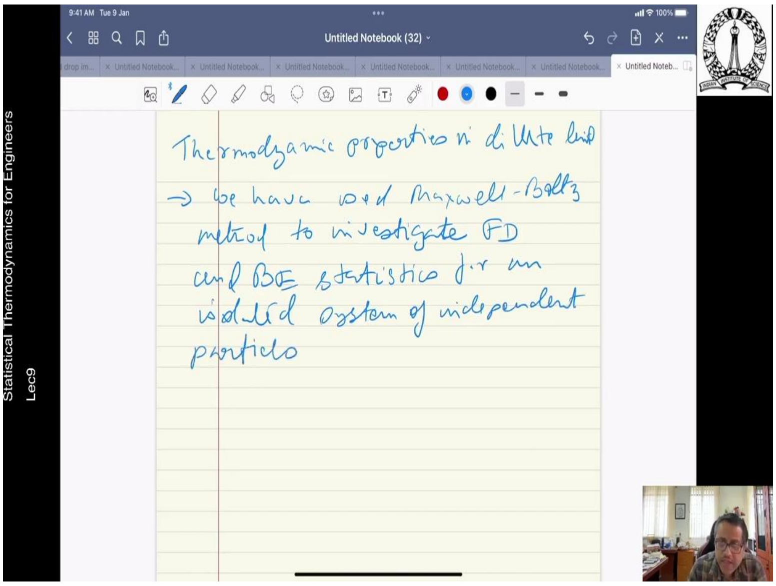
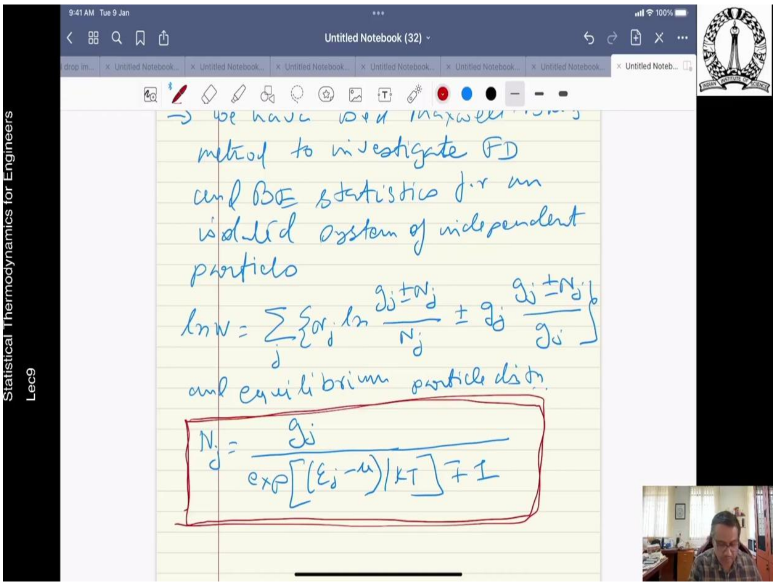
Statistical Thermodynamics for Engineers
Professor Saptarshi Basu
Indian Institute of Science, Bangalore
Lecture 12
The Dilute Limit and Concept of Molecular Partition Function

So, welcome to lecture 9. So, in this particular lecture, let us look into some more interesting stuff.

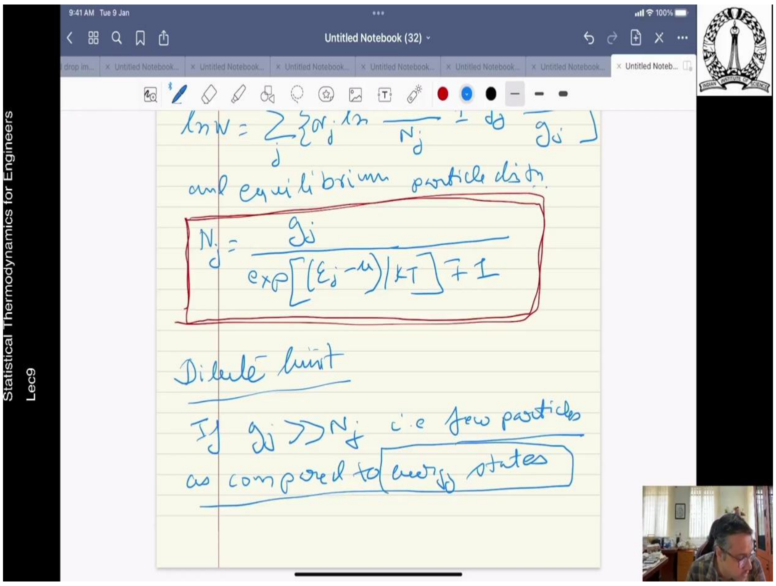
(Refer Slide Time: 0:12)





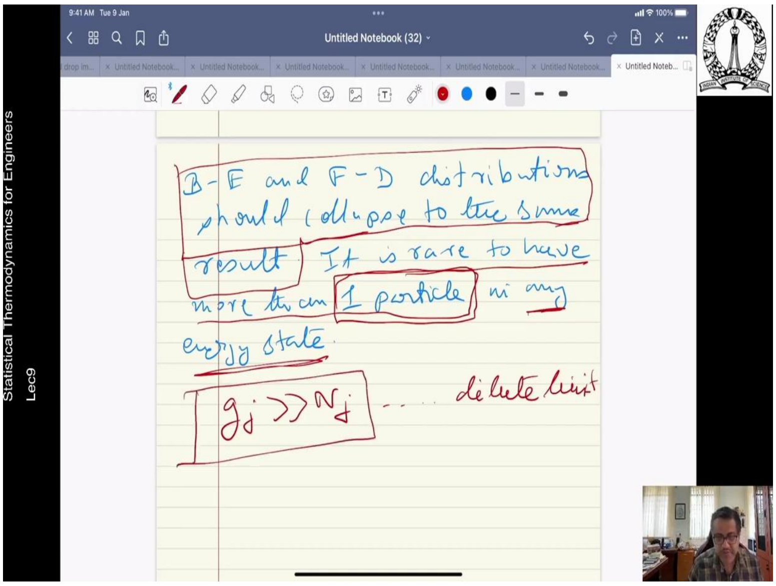
So, the topic of this lecture will be Thermodynamic Properties in Dilute Limit, so far what we have done is that we have used Maxwell Boltzmann method to investigate FD that is Fermi Dirac and BE which is Bose - Einstein statistics for an isolated system of independent particles. And what we got from that is this is the first expression that you got, (())(1:25) and the equilibrium distribution particle distribution which is also written as, N sub j is equal to g sub j divided by exponential E sub j minus mu by kT bracket closed minus plus 1. So, this is the equilibrium particle distribution and this was the number of particles distribution of particles or the thermodynamic (())(2:43).

(Refer Slide Time: 2:45)



Now in the dilute limit, we defined something called a dilute limit, so, what is that dilute limit, let us look at it carefully. If g sub j is much much greater than N sub j that means the degeneracy is much much greater than number of particles in that particular energy level that is few particles as compared to energy states, so, it is like a stadium where there are a lot of seats but only very poor attendance for example that means very few people have shown up. So, there are very few particles as compared to the energy states that are available.

(Refer Slide Time: 3:41)

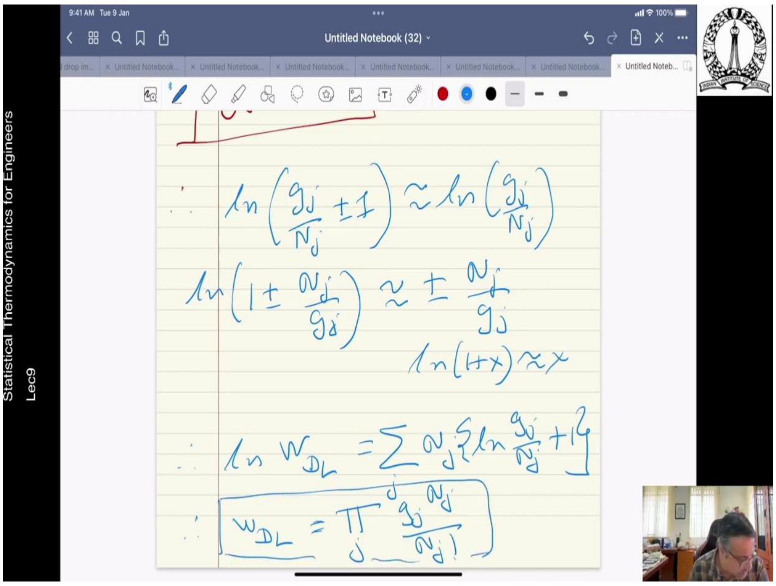


So, under this condition both Bose-Einstein and Fermi-Dirac statistics distributions should collapse to the same result. It is rare, why does it collapse because it is rare well to have more than one particle in many energy state in many energy state. So, the Bose-Einstein and Fermi-Dirac distributions should collapse to the same result. It is rare to have more than one particle in any energy state. It is almost impossible.

So, for the dilute limit to be valid g sub j must be much much greater than N sub j. This is the criteria for the dilute limit. So, as you can see that there are lots of seats available in our stadiums, it is unlikely that more particles I mean two people will start sitting on the same seat. So, they will probably occupy one seat at least because there are a lot of seats available.

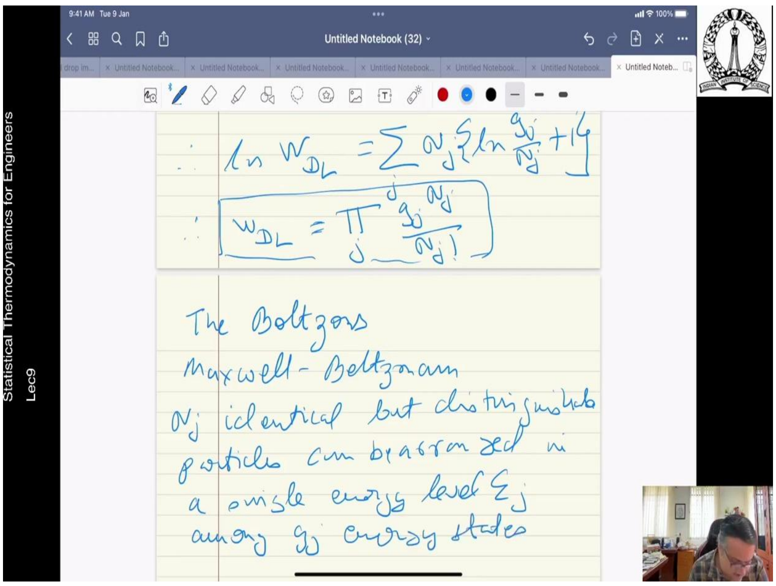
So, that is the reason why Bose-Einstein Statistics does not have any limits on the number of particles per energy state. But Fermi-Dirac statistics actually says it can be only one particle per energy state, but because there are lot of states available the Bose-Einstein statistics and the Fermi-Dirac statistics therefore collapse and they should give you the same result, but this will only happen when the degeneracy is much much greater than the number of particles in that particular energy level.

(Refer Slide Time: 5:55)



So, therefore, ln g by N sub j plus minus 1 is basically the same as ln g sub j by N sub j, and then of course, ln 1 plus minus N sub j by g sub j is almost equal to plus minus N sub j by g sub j this comes from the fact that ln 1 plus x is almost equal to x. So, therefore, ln in the dilute limit is basically nothing but summation over j N sub j ln g sub j by N sub j plus 1, so therefore in the dilute limit j sub g sub j raise to the N sub j by N sub j factorial. So, this is the final state that you get.

(Refer Slide Time: 7:14)



Statistical Thermodynamics for Engineers

Lec9

Maxwell-Boltzmann

N_j identical but distinguishable particles can be arranged in a single energy level ε_j among g_j energy states.

No limit on # of particles per state

$$w_j = g_j^{N_j}$$

$$\boxed{W_a = \prod_j w_j = \prod_j g_j^{N_j}}$$

Statistical Thermodynamics for Engineers

Lec9

No limit on # of particles per state

$$w_j = g_j^{N_j}$$

$$\boxed{W_a = \prod_j w_j = \prod_j g_j^{N_j}}$$

$\boxed{N_j! \text{ factor is off.}}$

Statistical Thermodynamics for Engineers

Lec9

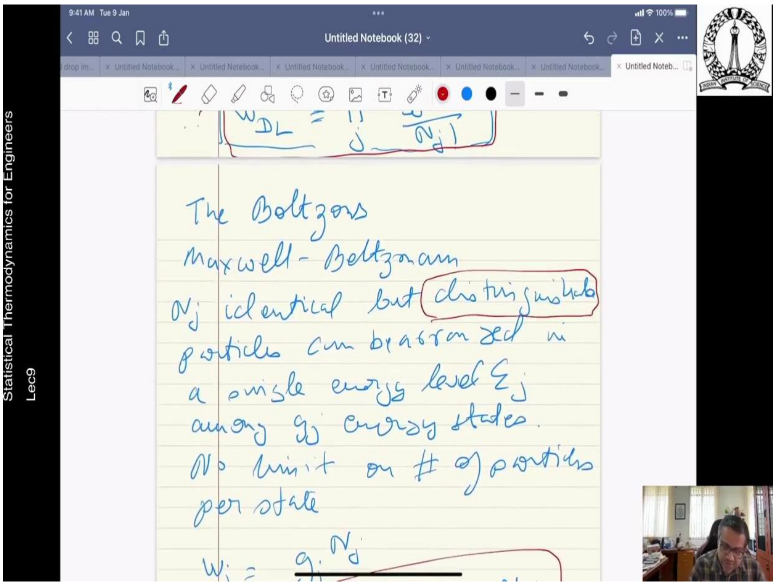
$$\ln W_{DL} = \sum_j N_j \left\{ \ln \frac{g_j}{N_j} + 1 \right\}$$

$$\boxed{W_{DL} = \prod_j \frac{g_j^{N_j}}{N_j!}}$$

The Boltzons

Maxwell-Boltzmann

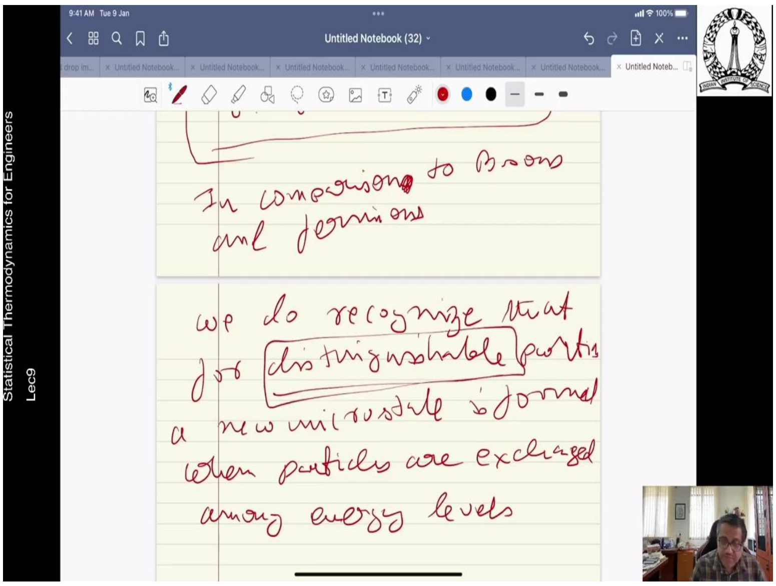
N_j identical but distinguishable particles can be arranged in a single energy level ε_j among g_j energy states.



So, this has got a what we can call this the Boltzons, so, Maxwell Boltzmann. So, N sub j identical but distinguishable particles can be arranged in a single energy level E sub j among g sub j energy states. There is no limit or number of articles per state. So, w sub j as we saw was g sub j to the power of N sub j, these are the Boltzons.

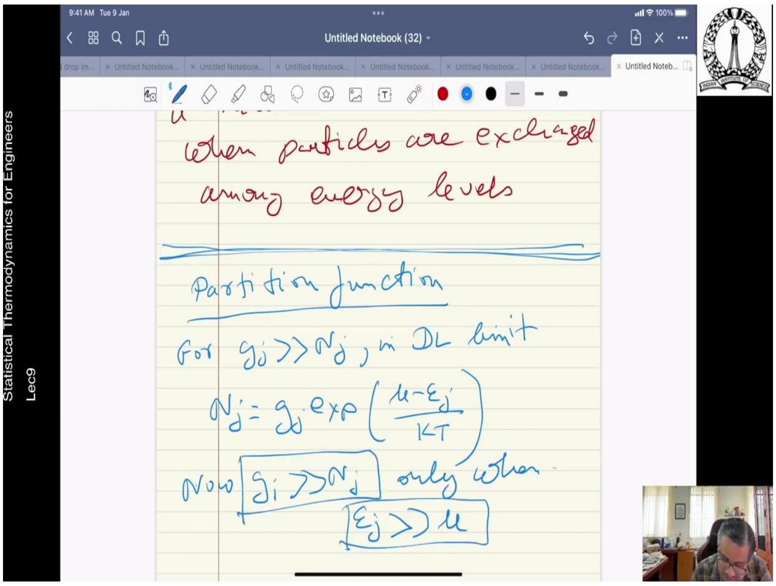
Now, if you compare this expression if you compare now this, this is what Boltzmann did. If you compare this expression with the one here energy dilute limit, you will see that basically there is a factor N sub j which is off. N sub j factor is off that is because in comparison to Boltzons and Fermions we do recognize the distinguishable particles a new micro state is formed where the particles are interchanged among the energy levels. So, this is where you know, Boltzmann got it wrong because he assumed that the particles were distinguishable.

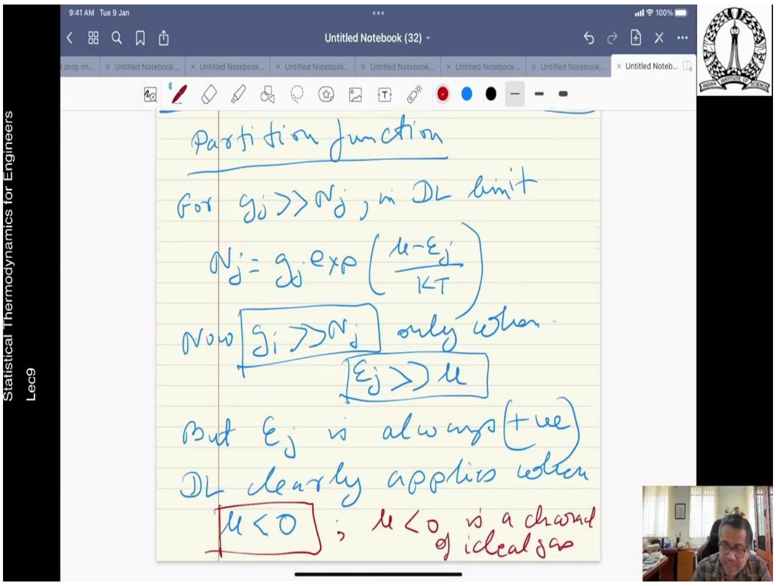
(Refer Slide Time: 9:36)



So, in comparison so, if you say this is where the Boltzons are different, what Boltzmann did in comparison to bosons and fermions, we do recognize that for distinguishable particles a new microstate is formed when particles are exchanged among energy levels because they are distinguishable that is where Boltzmann got it slightly wrong and that is why the results the Boltzons became very different.

(Refer Slide Time: 10:49)

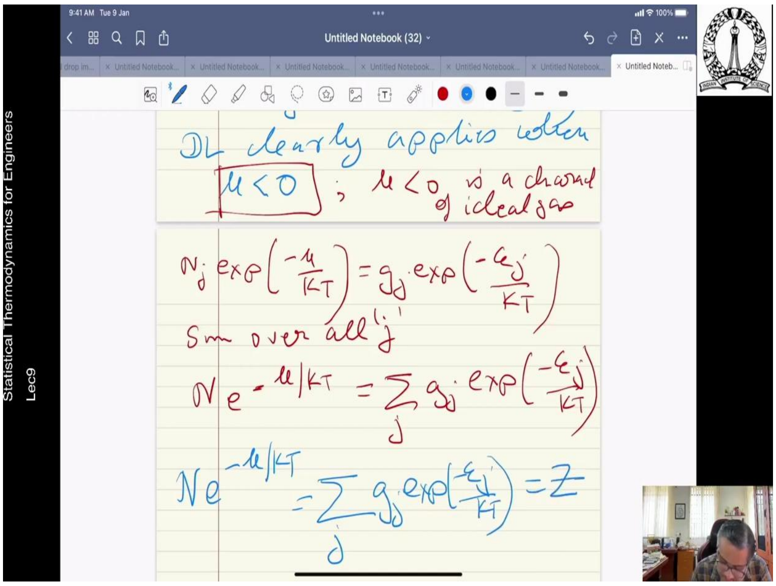


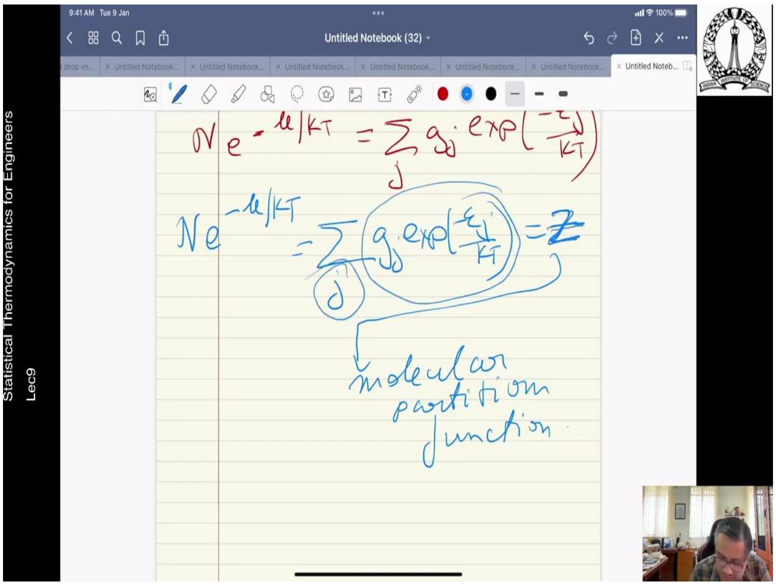


So, now that we have we have seen that what the dilute limit looks like and how the fermions and the bosons behave identically in the dilute limit. Let us look at a new definition now, which is called the partition function. So, once again for g sub j much much greater than N sub j in the dilute limit N sub j is equal to g sub j exponential mu minus E sub j divided by KT. Now g sub j is much much greater then N sub j only when E sub j is much much greater than mu, so g sub j is much much greater than N sub j but his happens only when E sub j is much much greater then mu.

But recognize that E sub j is always positive so, that dilute limit clearly applies when mu is less than 0 the chemical potential is less than 0. Therefore, mu less than 0 is a characteristic of ideal gas is a characteristic of ideal gas.

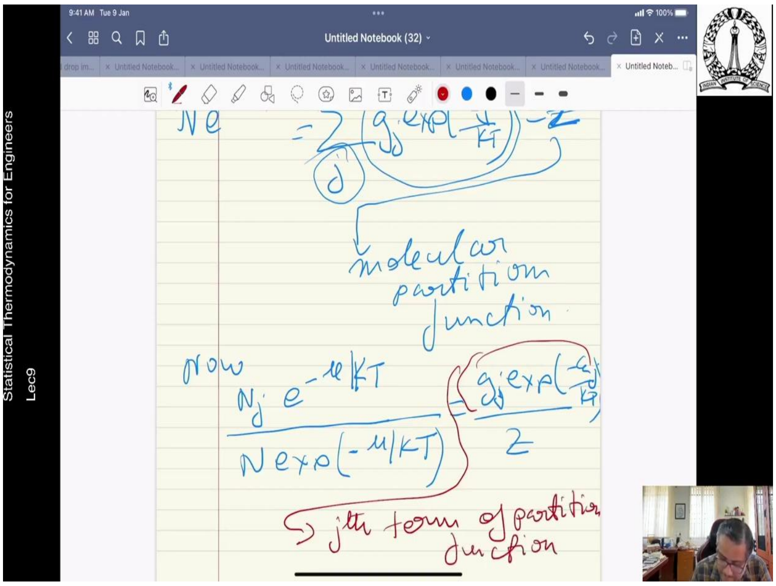
(Refer Slide Time: 12:48)





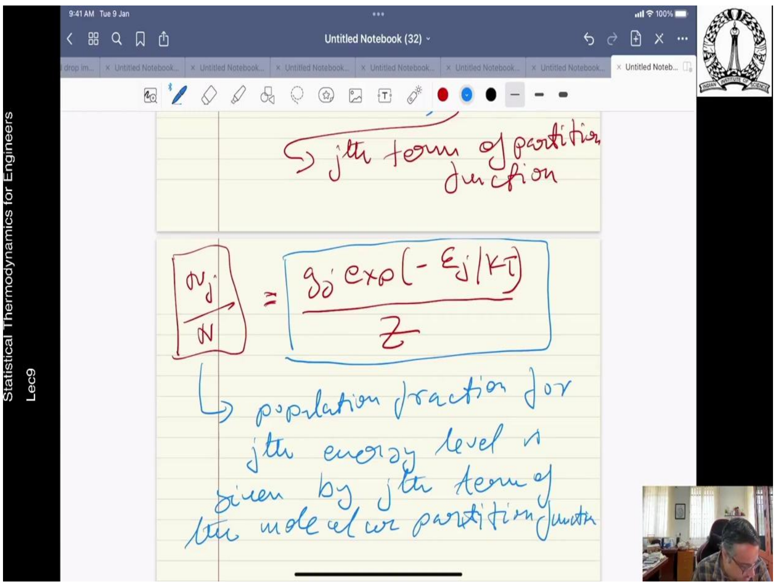
So, therefore N sub j exponential minus mu by KT is equal to g sub j exponential minus E sub j by KT. So, this is just a simple separation. Now some overall j that is sum overall energy levels what you see this N e to the power minus mu by KT because you have sum with overall energy levels. This side of course is j g sub j exponential minus E sub j by KT. Now, this particular term this is N e to the power minus mu by KT equal to let me write again g sub j exponential minus E sub j by KT. This is called Z where Z or Z is a molecule called the molecular partition function. So, molecular partition function is nothing but sum total of these terms over all energy levels.

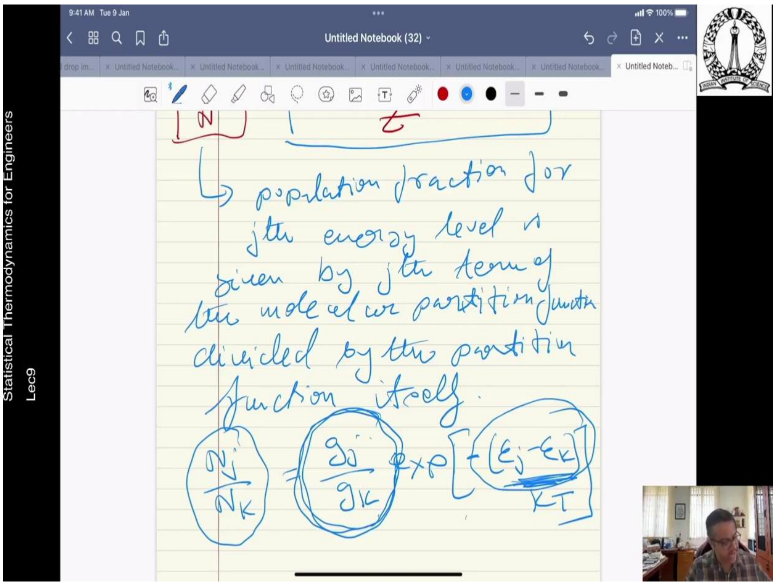
(Refer Slide Time: 14:27)

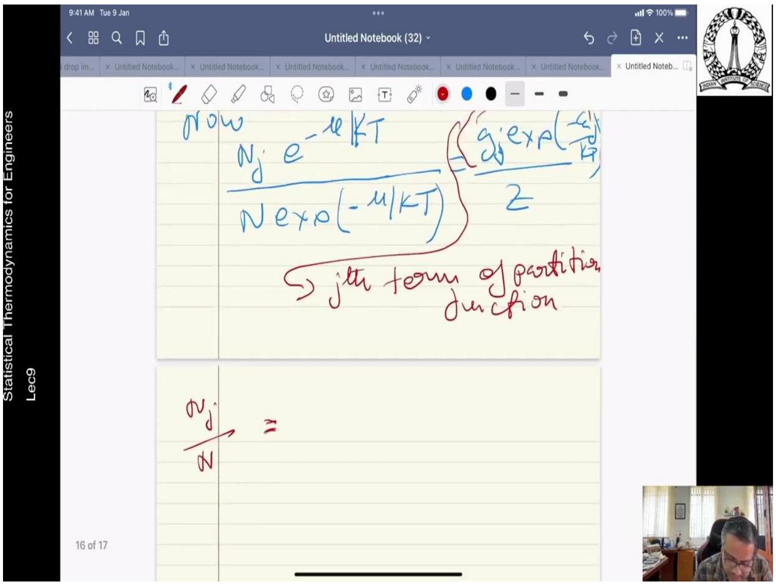


Now, if you take N sub j minus mu by KT divided by N exponential minus mu by KT that is nothing but basically g sub j into exponential minus E sub j by KT divided by Z. So, what is this particular term? This term that you see over here is basically the jth term of partition function is the jth term.

(Refer Slide Time: 15:28)



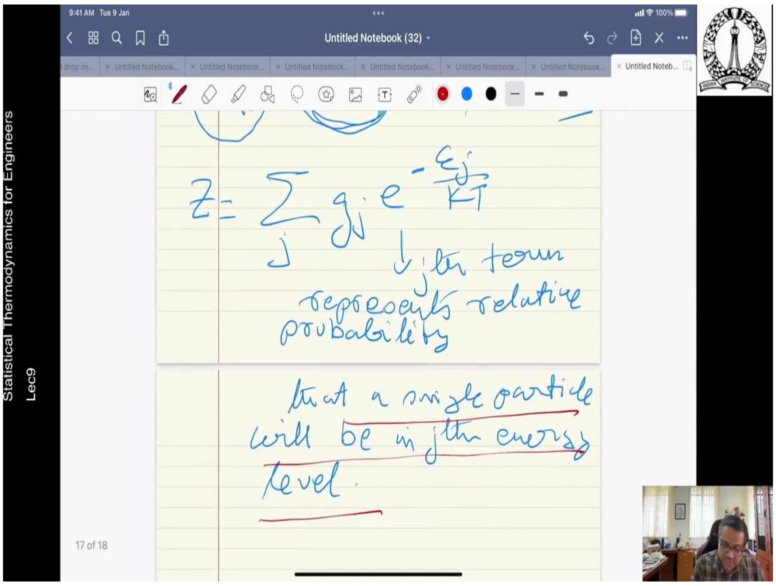




So, therefore, in other words N sub j exponential N sub j by N because this cancels out, N sub j by N is g sub j exponential minus E sub j by KT divided by Z. So, N sub j by N is actually given as this. Now, so, this means this is like this like a population fraction so, it is a population fraction is given by the jth term of the molecular partition function divided by the partition function itself, so if you call it so, this is population fraction for jth energy level is given by the jth term of the molecular partition function divided by the partition function itself.

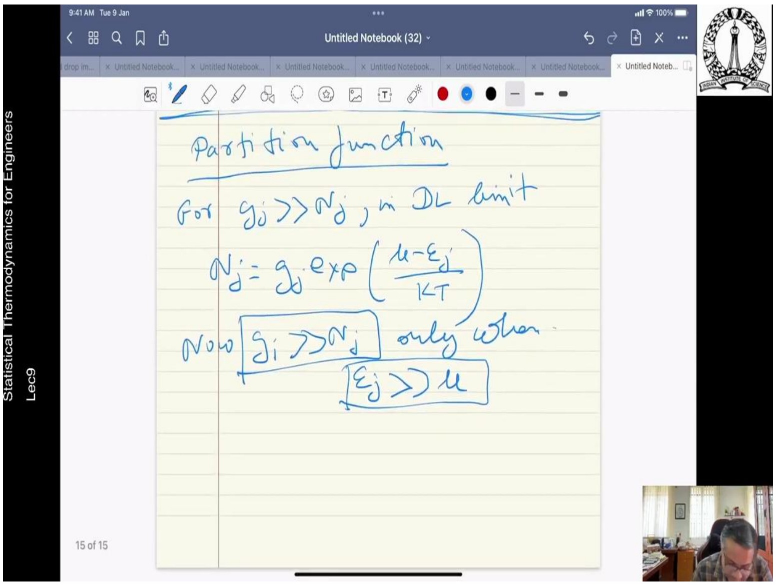
So, similarly, you can also write it as N sub j by NK. So, this is the relative population in energy level j and K are the ratio of the two is g sub j by g sub k exponential minus E sub j minus E K divided by KT. So, this is the relative degeneracy and this is the relative energy difference. So, this is like the ratio of the number of particles in energy level j versus energy level K which is equal to the ratio of degeneracy at those two levels and the exponential of the differential of energy between those two levels that E K energy level differential.

(Refer Slide Time: 18:14)



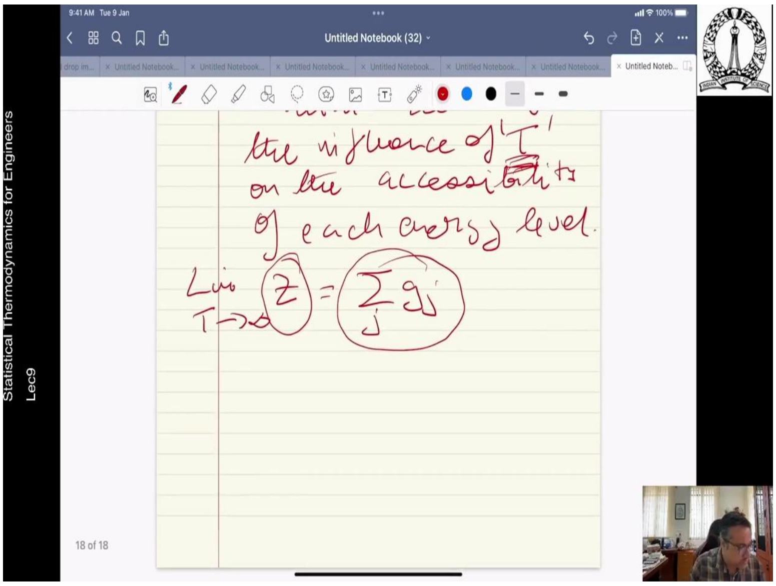
So, Z once again let us write it unequivocally in a very large fonts g sub j exponential E sub j by KT. So, if you look at it carefully that jth term, what does it physically imply of the partition function represents the relative probability that a single particle will be in jth energy level. So, this would be that a single particle will be the jth energy level is given by the jth term of the partition function. So, the jth term in terms of physical interpretation represents the relative probability that a single particle will be in the jth energy level. So, that is how you should interpret it.

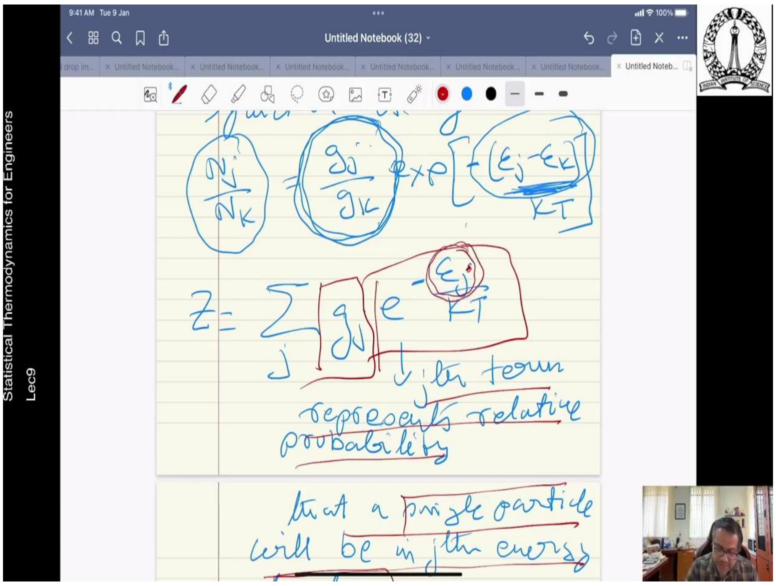
(Refer Slide Time: 19:35) wrong 20:26

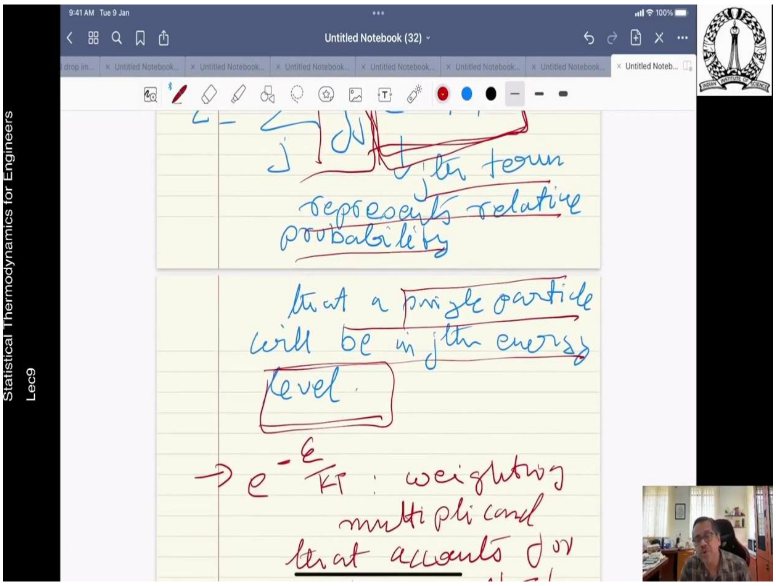


And what about this particular term this exponential term that you see So, this is e minus E by KT this particular term that is there in the exponent is basically like a weighting or a weighting multiplicand that accounts for the influence of temperature on the accessibility of each energy level. So, this is like this.

(Refer Slide Time: 20:29)



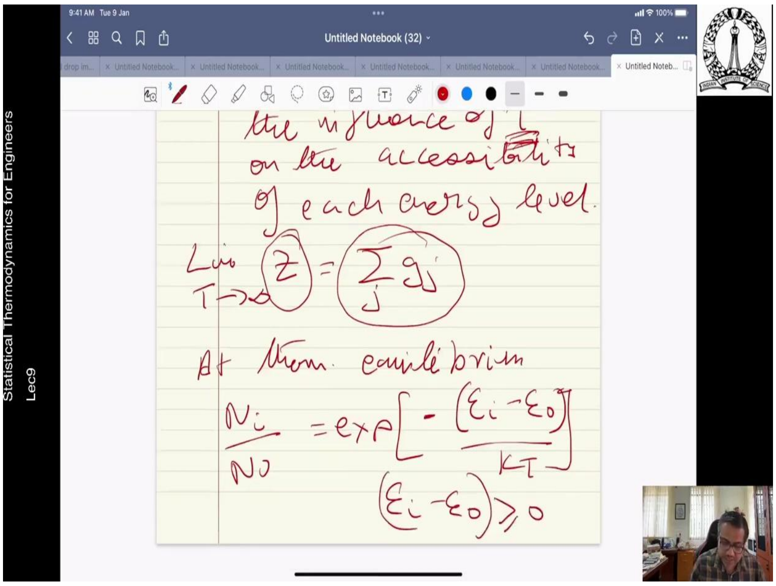


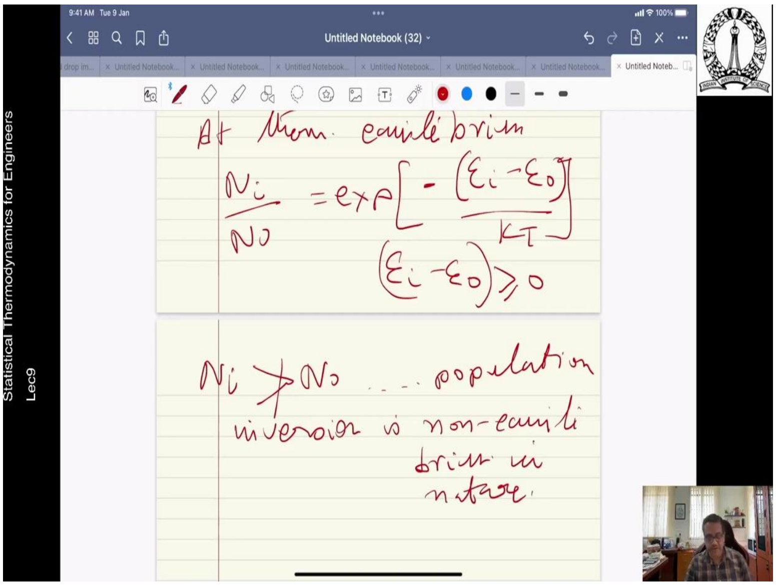


And in the limit when temperature goes to infinity this just becomes g sub j. So, what does this essentially imply that when if you look at this particular expression very clearly there is a degeneracy term and then there is a multiplicand which sits. This multiplicand is given by the energy so, higher is the energy, lesser is the probability of this particular term of energy in that particular way so, higher energy. So, that means, so, this would essentially translate to that this particular term is like a weighing fraction. So, not all energy levels has got equal probability which is kind of understandable the relative probability of a particle being at a higher energy level is comparatively a little lower.

Now, when this temperature however becomes in finite this means that this particular term essentially drops out and the partition function essentially becomes the sum total of all the degeneracy sum total of all the micro states. Now the role of temperature is essentially this particular role of temperature is essentially it regulates that whether the higher energy levels of energy all the energy levels are accessible to the particle or not. So, if it is low than the higher energy levels are comparatively less and less accessible, but when it is high, all the energy levels becomes equally accessible and therefore, you do not need this term at all, so this weighing fraction is no longer required when you actually have a situation like this.

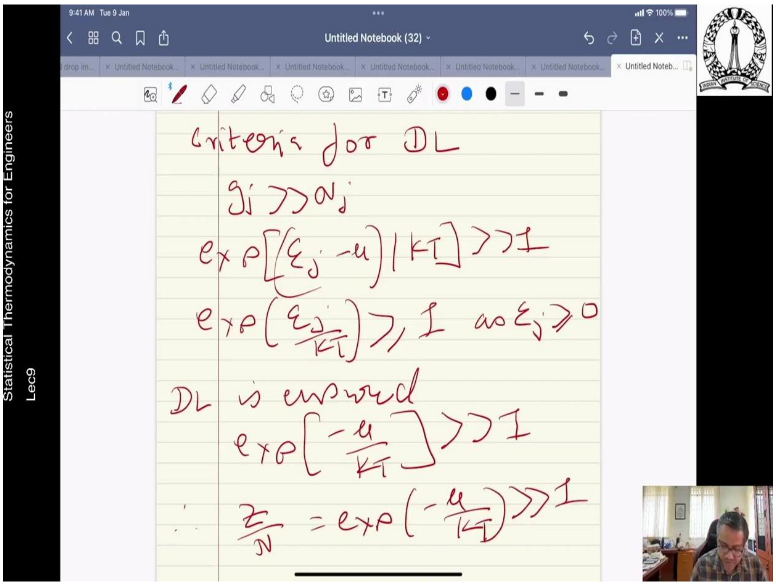
(Refer Slide Time: 22:14)





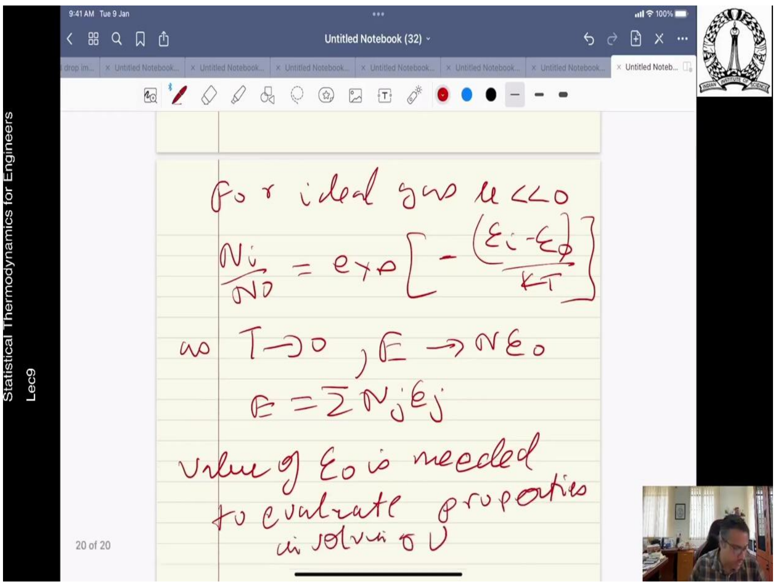
Now, at thermos dynamic equilibrium N sub i by N naught is equal to exponential minus E i by E naught divided by KT where E i minus E naught is definitely greater than 0. So, therefore, N sub i is N naught so, the population inversion is so, N sub i basically what does this implies is that in N sub i is therefore, cannot be more than N naught to begin with, the relative. So, the population this also implies that population inversion is non-equilibrium in nature is not an equilibrium situation, non-equilibrium in nature. I think this is quite clear from this particular estimate whatever we have shown here.

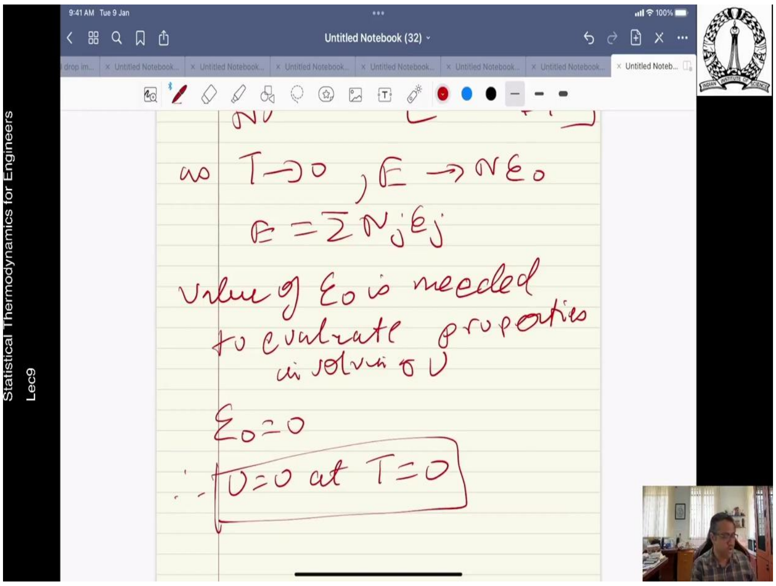
(Refer Slide Time: 23:34)



So, the criteria for dilute limit for D L is one is of course, your g sub j is much greater than N j and exponential j minus mu this also we get by KT is much much greater than the 1 that means exponential of e sub j by KT is much much greater than equal to 1 as e sub j is greater than equal to 0, so the dilute limit is insured if your exponential minus mu by KT is much much greater than 1. So, therefore, Z by N which is nothing but exponential minus mu by KT is much much greater than 1.

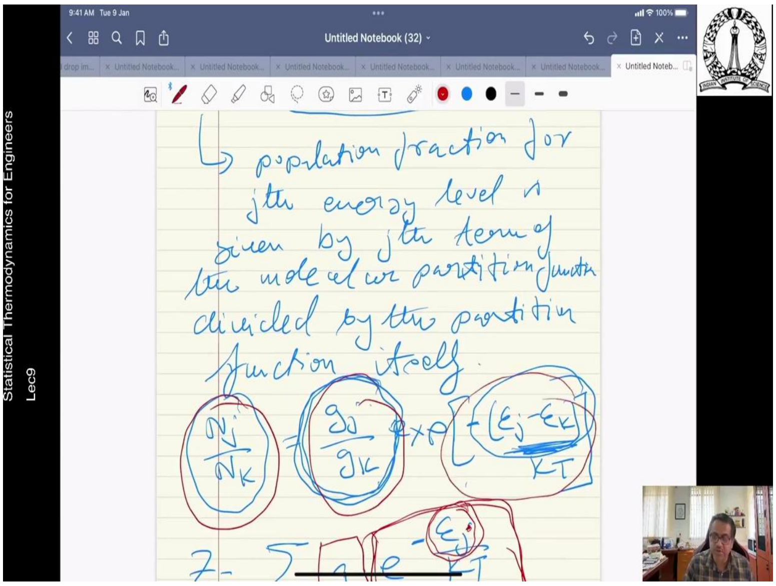
(Refer Slide Time: 24:37)

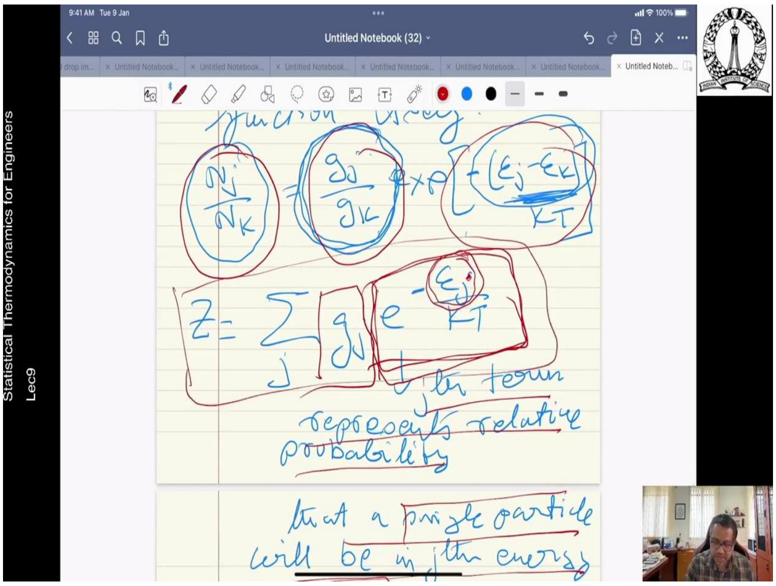


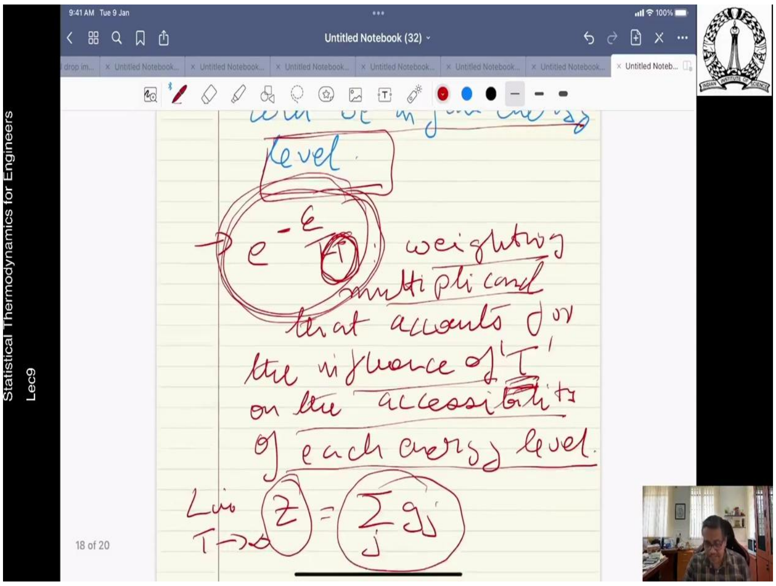


Now, for ideal gas, mu is much much less than 0. So, therefore, N sub i by N naught is equal to exponential minus E i minus E naught by KT (())(24:58) as T approaches 0 that means the temperature goes to 0, E goes to N E naught and E is further equal to N j into e sub j. So, the value of E naught is needed to evaluate any properties involving that involving mu. So, the value E naught is needed to evaluate any property (())(25:33) in properties involving mu. So, we take E naught is equal to 0 therefore, U is equal to 0 at T equal to 0. The E equal to 0 and T equal to 0.

(Refer Slide Time: 26:00)

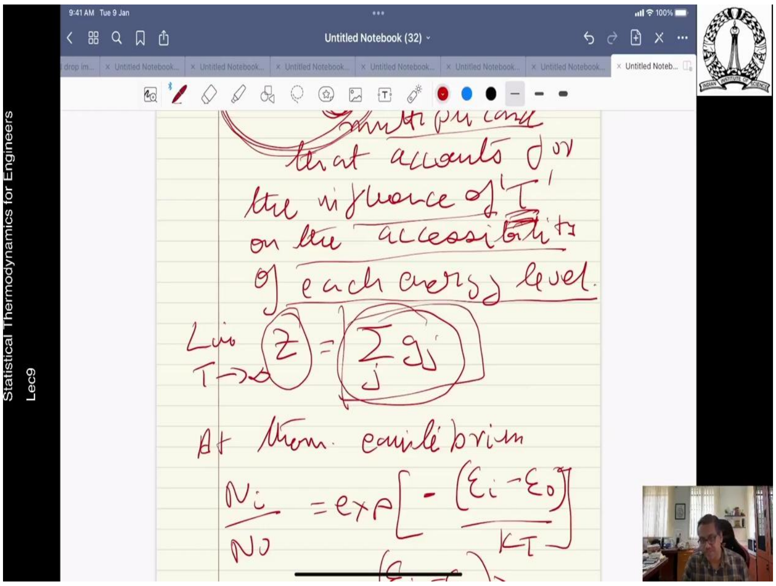


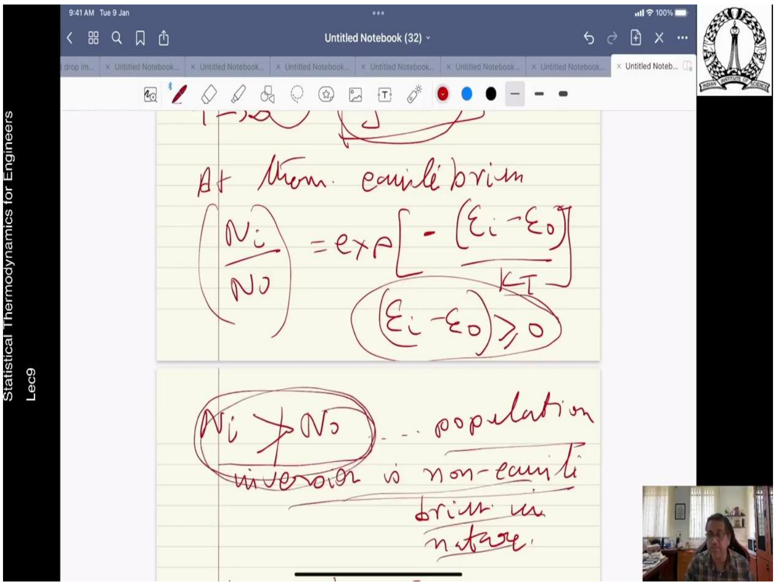




So, this is the time that we will in the next class do a problem on this degeneracy. So, we have understood gone through the steps now, just do a brief recap, this is the relative probability which is given by the ratio of the degeneracy and this ratio of the weighing fraction, this is the total molecular partition function and which represents like a relative probability of a single particle will be in the jth energy level and this acts like this particular exponential term is like a weighting multiplicand that accounts for the influence of temperature on the accessibility of each energy level. So, that is important.

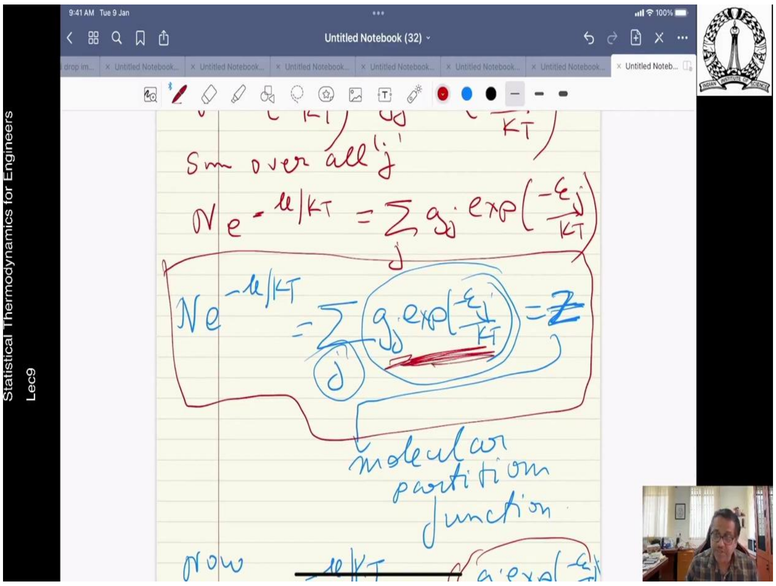
(Refer Slide Time: 26:48)

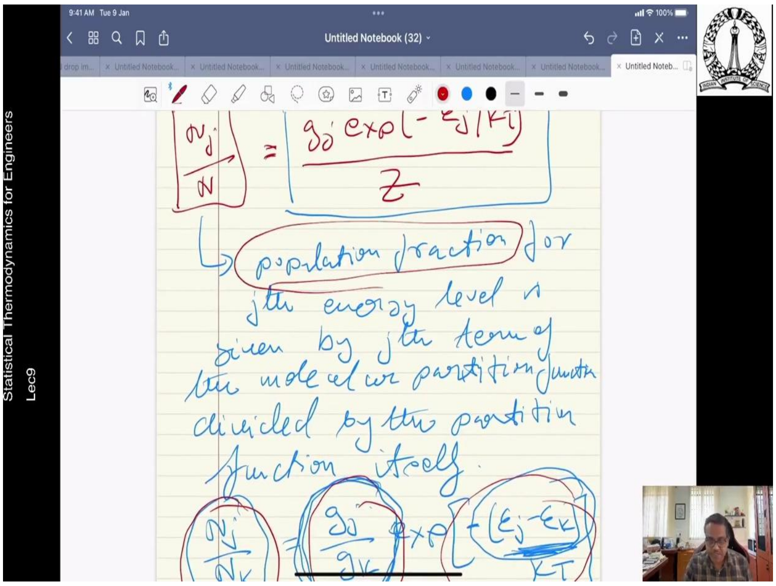


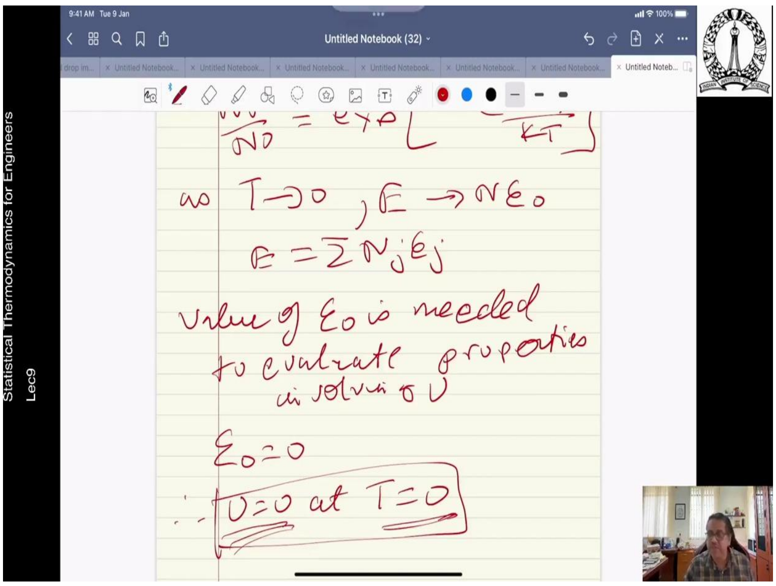


And at high temperature this particular becomes just a sum total of degeneres. And you can see from this expression that N sub i by N naught since this is always greater than 0, this actually proves that this cannot be valid. So, therefore, population inversion is a non-equilibrium process in nature.

(Refer Slide Time: 27:09)







And lastly, if you just do a bit of a recall that what is your partition function, so, this is the definition of your partition function. So, these are the terms of the partition function, it can also the jth partition function can represent is like a population fraction representation for the jth energy level.

So, these are the different quantities that you have. And this is also to note that at absolute zero, the internal energy is also equal to 0. So, we end that this particular lecture here which is lecture 9. And after that we will do a couple of problems on this partition function before we move any further. So, we will see you in the next class.