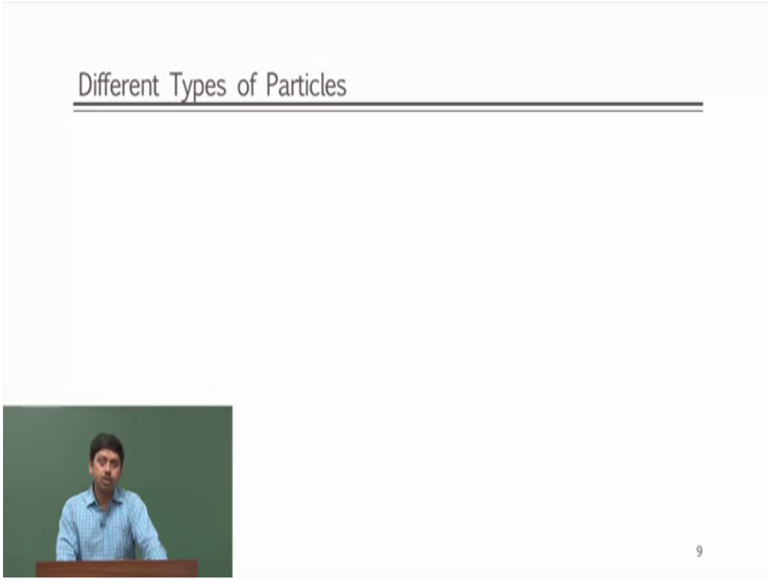
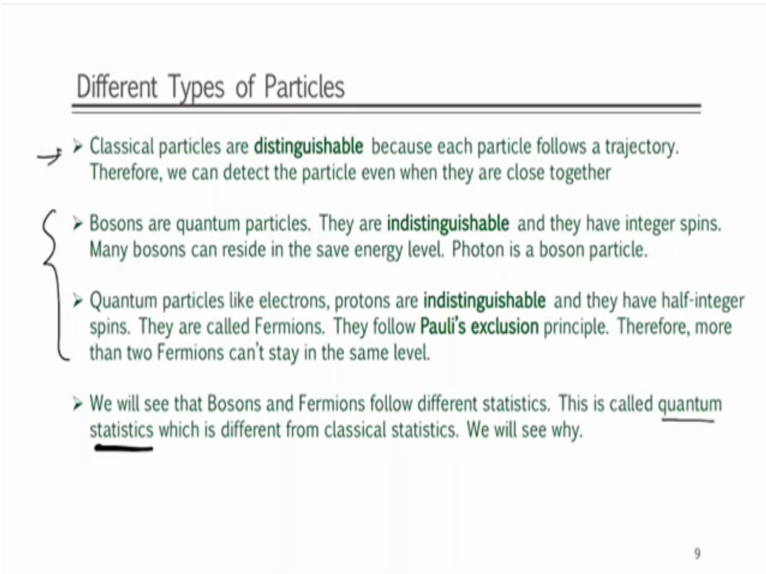
Chemical Principles II
Professor Dr. Arnab Mukherjee
Department of Chemistry
Indian Institute of Science Education and Research, Pune
Bose-Einstein, Fermi-Dirac and Maxwell-Boltzmann distribution

(Refer Slide Time: 00:16)



Now what will happen in the particles were in distinguishable and what is the (situa) what are the situation in which in distinguishable particle arise.

(Refer Slide Time: 00:26)



So as I said the classical particles are distinguishable because each particle follows a particular trajectory therefore we can detect the particle even when they are close together because the classical particles really will not like collapse onto each other, you know you can still there will be particles who even there even if they are come closer you can still say this is particle 1 this is particle 2 because we have been following that particle all along.

However for quantum particle for example bosons and fermions they are indistinguishable, so bosons there are two kinds of quantum particles are there one is called boson which are indeed you know there is those are indistinguishable and they have you know integral spins another characteristics of boson is that many of the bosons can reside in the same energy level, so photon is a boson particle like Higgs boson people know about a lot there is a as a you know boson that is a that has integral spins.

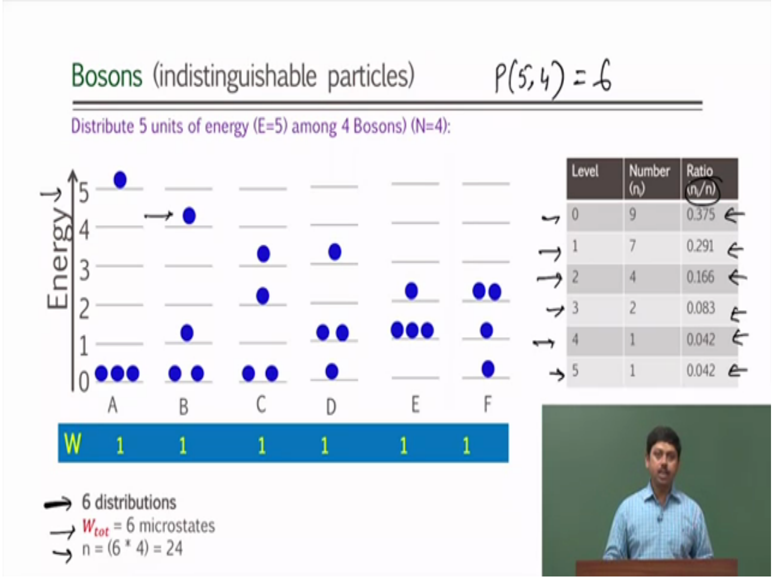
Similarly electron protons also are indistinguishable they are quantum particles and the reason they are in this simple is that when you know let us say you know hydrogen molecule when two electron come close together and form bond you can never distinguish which is electron 1 and electron 2, all that you write is a wave function associated with both the electrons together you do not identify.

So when they far apart maybe you know hydrogen atom has electron 1 hydrogen atom number 2 has electron 2 but when they are close then you cannot distinguish the electron anymore, so therefore electrons are indistinguishable particles and they are fermions because they have half integers spins and fermions have a speciality that not more than 2 fermions can stay in the same energy level due to Pauli is exclusion principle.

So for fermions the energy level can have either 0, 1 or 2 particle for bosons however you can have any number of particles however both fermion and bosons are indistinguishable particles unlike classical one which are distinguishable particles, so in that case then we have to still identify how to get the statistics? How to calculate W is? And how to get you know the distributions or probability distributions of the particles in different energy levels with respect to the energy.

So let us see that so we will see that bosons and fermions will follow different statistics and this is called quantum statistics it may be you know you know intimidating for you to knowing the term quantum statistics but in this particular course we are not going to go into mathematical detail of derivations of any of those quantum statistical formula all that we are emphasizing at this point is that this particles are indistinguishable and rest of the things are same as what we have discussed so and it will not be complicated as you can see soon.

(Refer Slide Time: 03:29)



So let us talk about bosons again we are going to talk about the same thing 5 units of energy 4 particle only thing the picture will look very different now, the picture will look like this all are blue particle remember the earlier ones where they had different colours, so colours were distinguishing the particles for us basically, so now we are putting all same colour so therefore you can no longer distinguish whether the green particle is up or red particle is up or which particle is up?

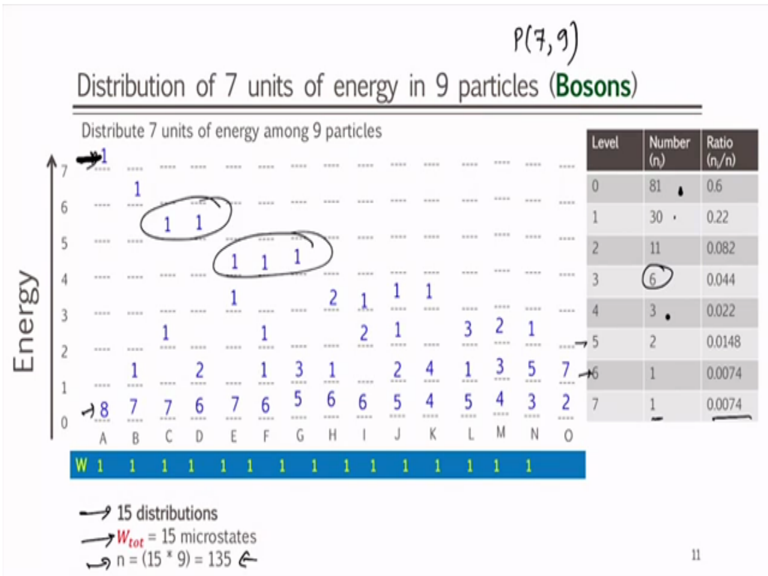
So the how many possible ways we can get this distribution only one possible way because either we bring whatever particle we bring we do not know each particle we are bringing up right so there can be only one way of getting so the number of microstates for distribution A is 1 remember however the number of distribution still remains to be P partition of 5 units of energy into 4 particle, so P 5 4 will be still 6 however individual (microstrip) microstates of individual distribution will be just 1 instead of n factorial by n 1 factorial into factorial because this is no longer distinguishable.

So these are all these are the 6 possible distributions that we had, we had shown you before but only thing is that in that particular case you had all different colours, now you have all same colour and because of that all the W is now are 1, you can no longer distinguish that whether which particle has gone up and which has gone down, so then automatically how what we get is that we get 6 distributions and we got only 6 microstates remember how many we got 56 microstates we got all total when the particles were distinguishable.

Now with indistinguishable particles we only get 6 possible microstates, so number of particles in all 6 possible microstates is 4 into 6 is 24, so total there are 24 dots in this graph and now we want to identify how many particles are there in which level? So for example you see that level one has 5 particles level sorry energy level 5 has 1 particle, energy level 4 also has only 1 particle, energy level 3 has 2 particle this one and this one, energy level 2 has 4 particle, energy level 1 has 1, 2, 3, 4, 5, 6, 7 particle and energy level 0 has 3 plus 2 5 plus 2 7, 8, 9 particles.

So you see each energy level we can just count from this distribution and we can get the number of particles in each energy level and now since we are combining all possibilities then we are dividing we have to divide this 9 by 24 to get the n i by n, so this is the probabilities n i by n as is shown here for each energy level. So now the same way we similarly what we got for distinguishable particles for bosons we get the same thing we get the similar distributions for bosons also and that is given by these numbers and we can plot them.

(Refer Slide Time: 06:45)

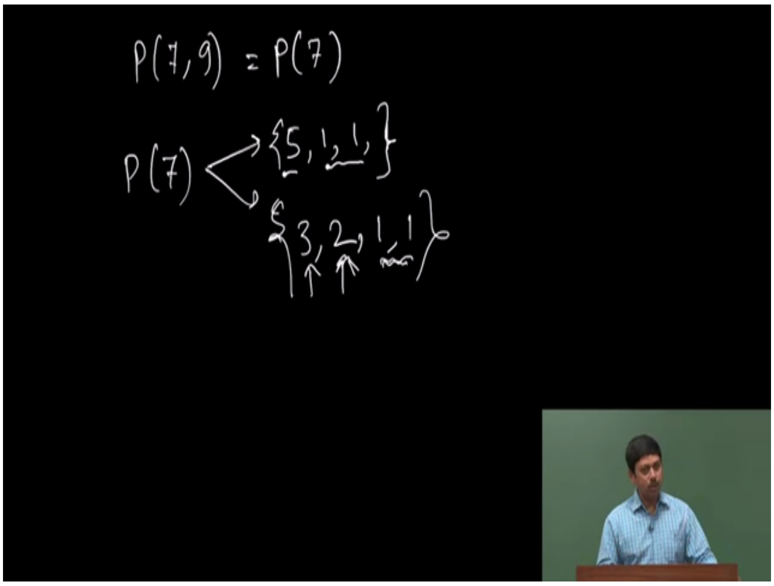


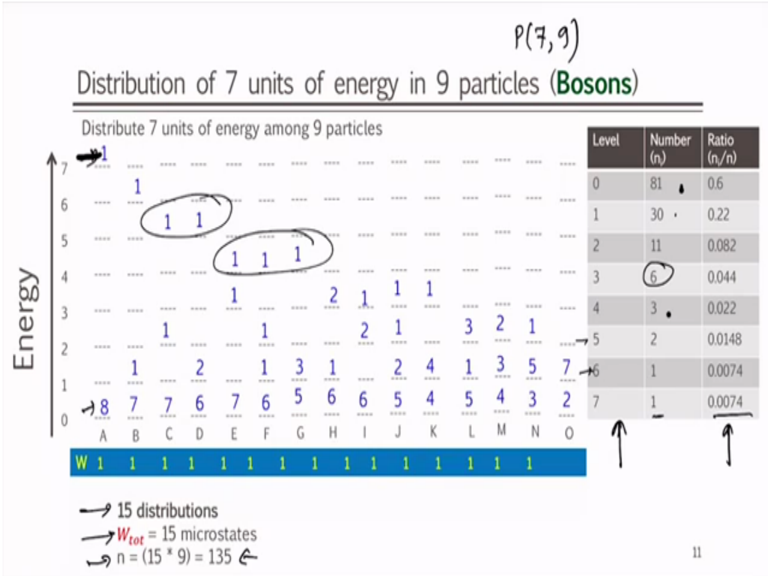
Before we do that, let us do for 7 units of energy in 9 particles in this particular case also the number of distributions will be same as 15 which we had before which is obtained from partition of 7 into 9 and here also we have similar distributions like A, B, C, D however here also the number of microstates for each of the distribution will be just one because particles are distinguishable note that we have not put with the dots because there is not enough space for putting eight dots here but this eight denotes just eight blue particle and this denotes just one blue particle for example here it denotes seven blue particle one blue particle, one blue particle so just imagine that they are all blue.

So earlier we did n factorial by n 1 factorial and all that here we cannot do that because they are all distinguishable indistinguishable therefore they are all just 1, now once you get that how many microstates then so 15 distributions each distribution give you 1 microstate so W tot is just 15, so total number of particles from all possible distribution is 15 into 9 because we have only 9 particles and 15 distributions, 15 into 9 is 135 now we can count how many particles are there in which level?

Let us start with 7, 7 has only 1 particle so 1 particle now probability is 1 by 135 which is given by this number, level 6 has 1 particle, level 5 has 2 particle as you can see from this level 4 has 3 particle as you can see from this and level 3 has 1 plus 2 3 plus 3 6 particle as you can see from here level 2 has 11 level 1 has 30 and level 0 is 81 you can count that.

(Refer Slide Time: 08:43)



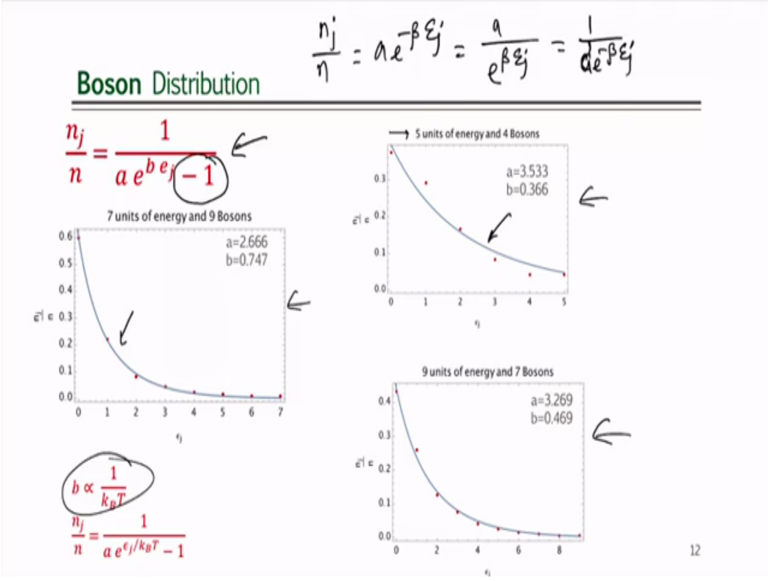


You know if you do not want to count then there is an easier way to do that is when you partition 7 into 9 which I will just show you one or two example let us say you partition 7 into 9 which is say which is nothing but 7 when you partition 7 into different parts let us say I do this partition 5, 1, 1, 1 no 5, 1, 1 that is the partition which means that I have 2 particles in level 1 and I have one particle in 5, so by now let us say I do one more 4, 3, 4, 2, 1, 1 this indicates that 1 particle having 4 energy to 1 particle having 2 energy and 2 particles is are having 1 in itself energy, so I am sorry this so we will just change that 4, 2, 1, is like 8 so we will just do 4, 3. 2. 1.

So which means that 1 particle is having 3 units of energy, 1 particle is having 2 units of energy and 2 particles having 1 in units of energy which means now if I get all the partitions and count how many 1 is are there we will get number of particles corresponding to 1, 1 units level if we count how many 2 is are there from all partitions then we will get number of particles having energy 2 like that we will get all possible values even without doing showing these particular distributions.

We can use partitions to get that and by then we can also count that how many particles are there in which level, once you do that again just count them and divide by the total number of n and we get we get this probability distributions with energy, so you see this is my energy level and this is the probability, we can plot that which we have done that.

(Refer Slide Time: 10:31)



We have plotted that here for 5 units of energy and for bosons 7 units of energy and 9 bosons and 9 units of energy and 7 bosons but the fit is not an exponential fit unlike the distinguishable classical particles this fit is this equation, so what was the difference from the earlier one if you see the Maxwell-Boltzmann one was n i by n was a e to the power minus beta epsilon j, so if I write it differently it will become a by e to the power beta epsilon j or I can write it as by bringing a down I can write is c to the power minus beta epsilon j you see here or a prime vacancy instead of c, a prime is nothing but 1 by a.

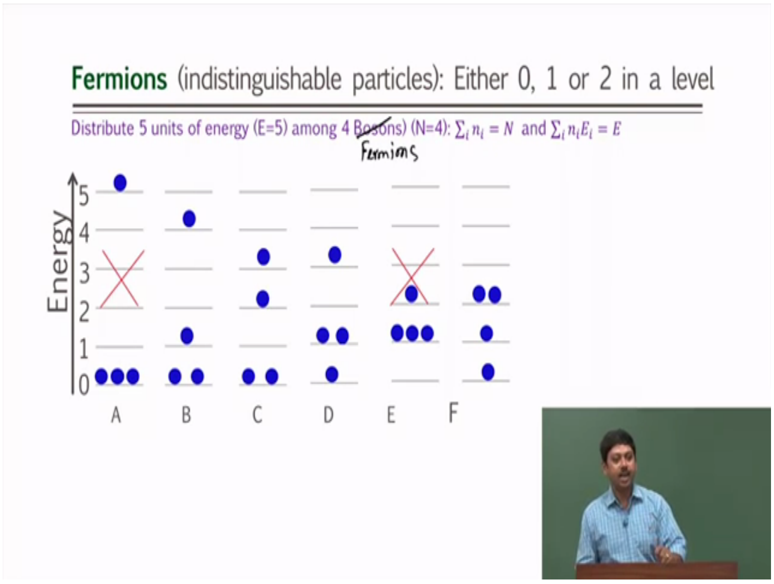
You see the only difference is that there is a minus 1 in the denominator this minus 1 was not there in case of Maxwell-Boltzmann distribution this minus 1 came because we are talking about now indistinguishable particles and especially bosons because bosons do not have restrictions to be many bosons can reside in the same level that is an important characteristics apart from being indistinguishable, these two characteristics one is indistinguishability another is many of them can recite and that will give rise to this particular statistics and I we have I have fitted that with that particular line although for 5, 4 it did not fit that well but you see it fitted really well for 7 units of energy and 9 bosons and also 9 units of energy and 7 bosons and it will fit very well when you increase the number of particles.

So you see that going from distinguishable particles to indistinguishable particles your statistics that means how the probability of occupying a particular energy level how it has changed from normal exponential distributions to something like this particular distributions which is an experimental observations that it will that distribution will follow this one. So now if something follows this one we know that they are bosons particle whether we had it we are able to distinguish or not that is a secondary aspect but if we get a statistics of particular distributions and it follows this one then we know that ok we are talking about bosons we are not talking about Maxwell Boltzmann.

Now the fact that classical particles follow Maxwell Boltzmann indicate that they are distinguishable but our eyes cannot may not be able to distinguish them we see all like you know incense let us say they say they look all the same colour we cannot distinguish them but our inability to in distinguish or distinguish has nothing to do with that whatever statistics we will get will tell us that what kind of particles we are dealing with and that is the thing.

So now we got bosons and again b is nothing but 1 by k B T which has a good implications we will talk about that later.

(Refer Slide Time: 13:29)



Now let us talk about fermions, now what is the speciality? Here we are talking about same blue particles except that since then electrons or protons and they have seen you know half integers spin more than 2 cannot reside in the same level so the number of occupants in any level is 0, 1 or 2. Now we are talking about 5 minutes of energy and 4 for boson for fermions so this is fermions.

So you see since we are talking about 5 units of energy and 4 fermions since we are talking about 5, 4 partition is the same as 5, 4 partitions as was there for other two (dist) you know (to pow) 2 particles also it will be again 6 possible distributions however all 6 are not right for fermions so can you tell me which one is not right?

Student is answering:

(())(14:26)

Professor:

First one is not going to be right because there are three particles in the level 0 and which else is not right?

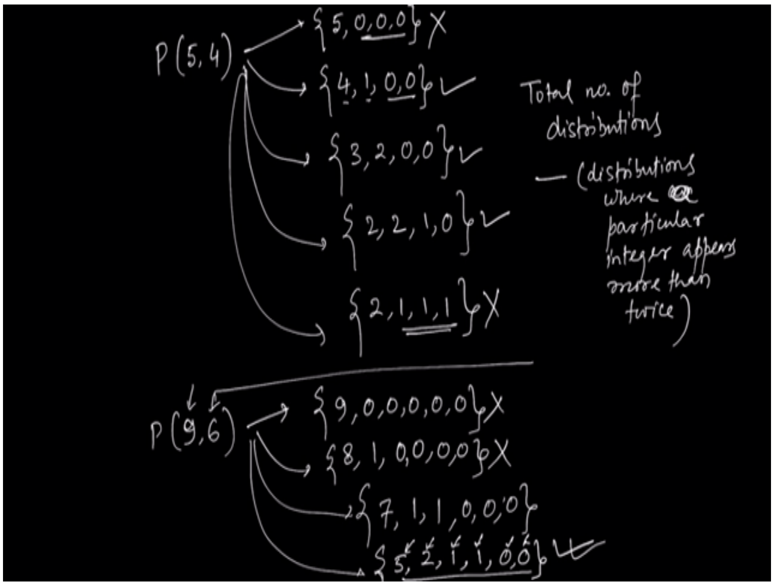
Student is answering:

E.

Professor:

Yes that also will not be right, so we land up not with 6 because of that restriction will land up with 4 distributions.

(Refer Slide Time: 14:46)

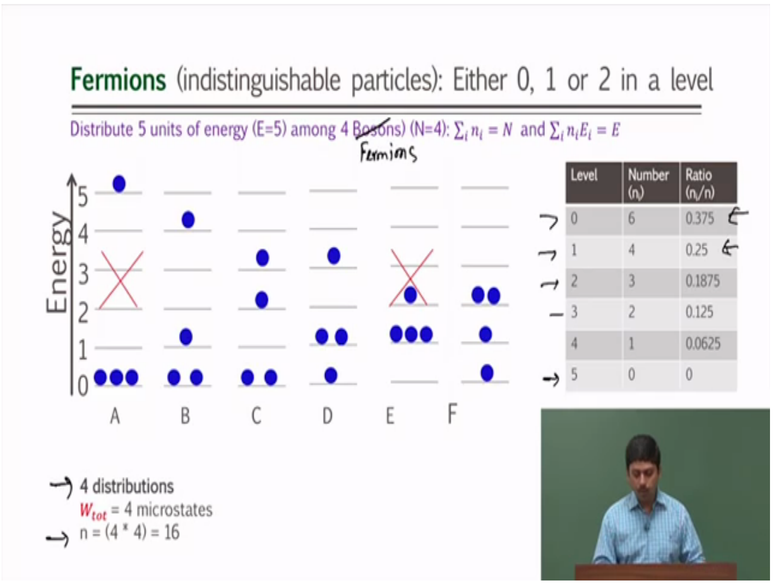


How do you get it from partitions? Let us say you have 5 units of energy and 4 particles, now you can partition the 5 minutes of energy among 4 particle in many different ways for example you put 5 party to 5 units of energy to be 1 particle and then rest of the 3 particles get 0 now this according to the rules of the Pauli is exclusion principle 3 particles will be in level 0 and therefore it will be not allowed.

Similarly you can break them into 4, 1, 0, 0 that is an allowed one because there are 2 particles on the level 0, 1 particle is in level 1 and 1 particle is level 4. Now if you do 3, 2, 0, 0 that is also allowed, if you do 2, 2, 1, 0 that is also allowed and if you do let us say 2, 1, 1, 1 and that is not allowed transition because there are 3 particles in level 1, so for bosons however everything is allowed because there can be more than 2 particles also in 1 level so therefore for fermions you have to first see that how many number of distributions, total number of distributions and then from this total number of distributions you have to subtract the distributions in which more the an integer number appearing more than twice distributions where and where a particular integer appears more than twice if you do that then you will be able to get the number of fermions.

You can try that for example with 9 units of particle 9 units of energy among six particles and then you can have let us say you can have 9 and then 5 zeros that will not be allowed that will not be allowed if you say 8, 1, 0, 0, 0, that is also not allowed then you have 7, 1, 1, 0, 0, 0 that is also not allowed but then if you have let us say 5 then 2 5 into 7, 7 plus 1 8 plus 1 9 and 0 and 0 that is an allowed one because the total energy is 5 plus 2, 7 plus 1, 8 plus 1 9, 6 particles 1, 2, 3, 4, 5, 6 and no integer is appearing more than twice so therefore this is an allowed fermions distribution where 9 units of energy distributed among 6 particles.

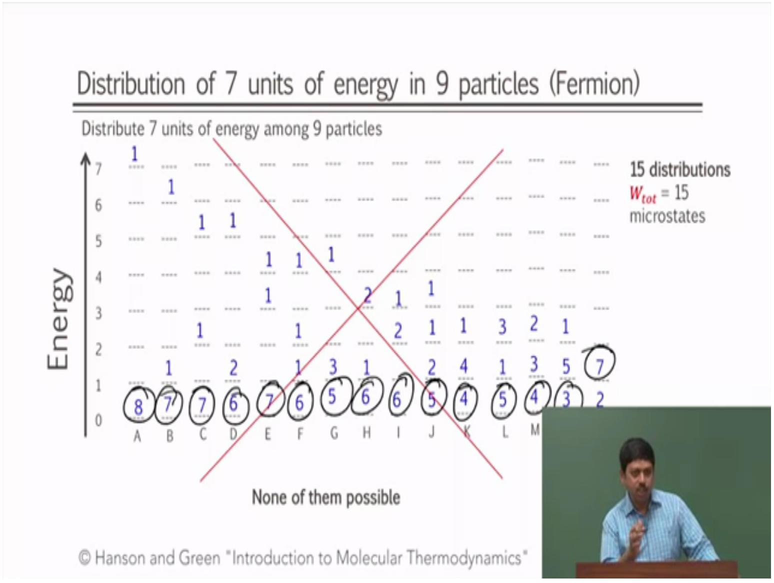
(Refer Slide Time: 18:04)



So now you see I am left with only 4 distributions not 6 only 4 distributions that mean is total number of particles in 4 distributions will be 16. Now let me count how many particles are there in which level. So for example level 5 has 0 particle because this distribution was not allowed so nothing can go to level 5, level 4 has 1 particle which is coming from this distribution B, levelled 3 has 2 particle coming from this and this distribution, level 2 has 3 particle coming from this one and this one, level 1 has 4 particle coming from this one, this one and this one and level 0 has 6 particle as you can see not coming from here but 2 plus 2 is 4, 5, 6.

So once we get that I divide 6 by 16 I get this number, I get divide 4 by 16 and get this number, so I get now again the probability with the energy levels.

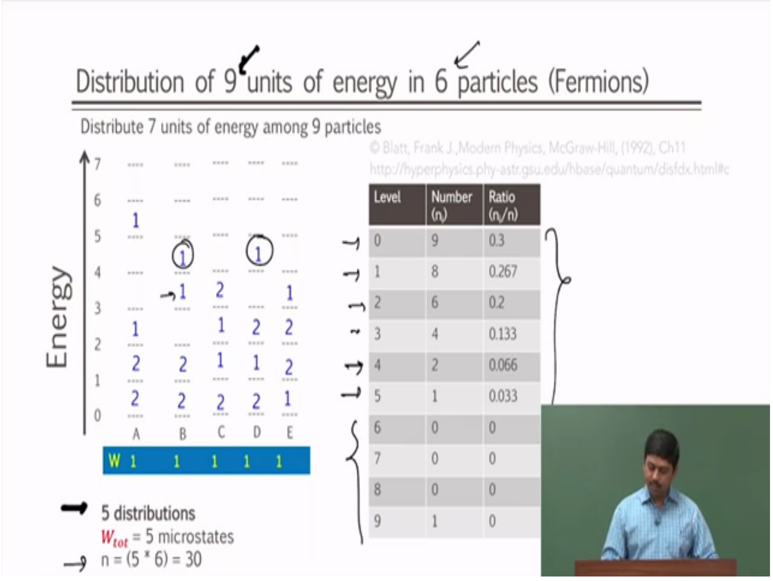
(Refer Slide Time: 19:07)



Similarly can you tell me which distribution so again I am now dividing 7 units of energy among 6 particles and I got the same I wrote down the same distribution as was in bosons and Maxwell-Boltzmann distribution. Now which of them is allowed can you tell me? actually none of them is allowed because in every distribution there is 1 level which has more than 2 particle for example here 8 is more than 2, here 7 is more than 2, 7 is more than 2, 6 is more than 2, 7 is more than 2, 6 is more than 2, 5 is more than 2 of course 6, 6, 5, 4, 5, 4, 3 and here 7, so I do not find any in which the number of particles is in every level is 2 or less.

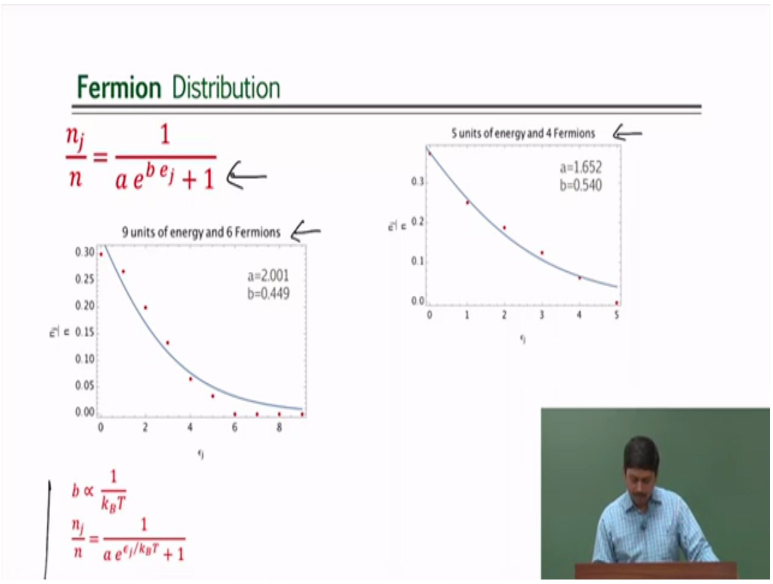
So, 7 units of energy cannot be distributed in 9 particles for fermions, so for fermions your energy level should be more than the number of particles, so let us switch it around.

(Refer Slide Time: 20:13)



Let us do it 9 units of an energy in 7 particle and you can see that there is only one possibility, you cannot change it to anything else only one distribution, only one microstate if you have 9 units of energy and 7 particles for fermions. Now if I reduce 1 particle 9 units of energy into 6 particle I get this many possible distributions 1, 2, 3, 4, 5 distributions I get, so now for five distribution I have total number of there are 6 particle so I have total 30 particles and I can count that how many (par) levels at which particle as you can see that 6, 7, 8, 9 will have 0 particle, 5 has only 1 particle, 4 has 2 particle, 3 has 4 particle, 2 has 6 particle and 1 has 8 and 0 has 9 particle and corresponding probabilities are given here.

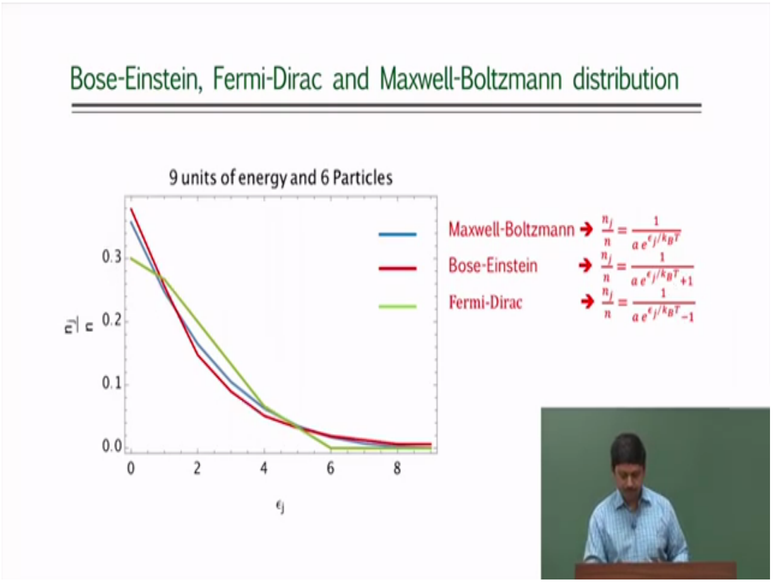
(Refer Slide Time: 21:23)



So we have plotted 5 units of energy into 4 fermions and 9 units of energy into 6 fermions because the other two are not possible 9 units of energy in 7 fermions well good gave us only 1 distributions which is statistically not good and 7 units of energy 9 particles did not give us anything, so you just line it up with these two and we have shown you but however in this case the fitting is not by any of the other two equations the fitting is done by these equations.

So remember for bosons it was minus for boson it was minus and for Maxwell distribution there was for Maxwell distribution this plus 1 or minus 1 was not there ok, so these are the three different statistics and again this is the same thing.

(Refer Slide Time: 22:08)



Now we compare all the three different statistics in the same graph so here we have taken 9 units of energy and 6 particles because that is you know that is working out for all the three different ones so we have done that and this in this we are showing the three different distributions Maxwell-Boltzmann distribution which does not have plus or minus 1 then Bose-Einstein distribution and Fermi-Dirac distribution all the three are shown here sorry I think this is plus and this is minus, this is minus.

And you see that they are they look more or less similar however they are not exactly same especially when you really increase the number of particles energy levels then they will differ you can see when the energy level is higher then of course they will follow the similar trend and when your temperature will become higher then also they will follow a similar trend and that is what it means however when the energy level is low or the temperature is low then the

Bose-Einstein Fermi-Dirac statistics or Maxwell-Boltzmann distribution they are all going to differ.

As you can see the difference is prominent you know in this intermediate region here we have not used any formula we have only used the our own ways of distributing the distinguishable individual particles having some fixed amount of energy and we land it up with some numbers for every given energy level and from there we got the statistics and that is what we are going to we have plotted and you have shown that how this is changing with different energy levels and that the fact that they are different for these three different types of particles that we discussed, ok.