Maxwell Boltzmann Statistics

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Lecture No. # 12

The Ideal Gas

Hello, welcome to this 12th lecture in this physics of materials course, physics of materials series of lectures. In the last class, last few classes we looked at the Drude model for conductivity of metallic materials. And as I have mentioned, the model is more general we have focused on conductivity. You can look at other properties, and how they are predicted using the Drude model as well so for example, this prediction of optical properties and so on. So, we have not really focused on that, we have picked up conductivity and thermal properties, thermal conductivity and electrical conductivity, and we saw its successes, we saw its failures.

And in the last couple of classes, we have been trying to narrow down on the reason for the failure. Because that is the way forward, we would like to understand, we start with the simple model, we would like to see why it as failed and on that basis, we will like to improve improvise on the model or improve the model. And if or if necessary try out the completely different model. As in the case with most things in science, we would like to settle down with the simplest explanation we can give for any phenomenon that we can see. So, simplest explanation you give, which completely adequately explains everything that you experience, is the explanation that we should go with this. So, this is the approach we wish to take.

So, in our search for the problem with the Drude model, what we sort of narrow down to was that, the manner in which the models predicts the distribution of energies in the system. Apparently there is some issue with that, because that is where the specific heat behavior begins to (( )) itself. The manner in which, those energy are there and the manner in which the system is able to absorb energy and so on. So, something to do with the energy is an issue with this model and also, something to do with the way in which the velocities are distributed within the system, which is again reflected in the way, the energy is distributed in the system.

So, so this was something that we narrow down to, as the place which we should focus on to identify the source of problem with this model right. Then we also looked at the fact that, we are dealing with very large system here. Large in the scene that, we may be still dealing with in a one meter cube, which which by itself it is not a very large piece of material, when you think of it that way, because it simply 1 meter by, 1 meter by, 1 meter. So, that is something that we can physically visualized, but in terms of the number of particle that are present their, the number of atoms that are present their and therefore, the number of free electron present their. We are looking at about 10 power 28 particles or the free electrons, that number is the very large number.

So, when you look at energy of the system, the velocity distribution within the system and so on. When you have such a large system, it is not physically feasible for you to actually independently measure the velocities and energies of each of those particles and then some how do an average. So therefore, as we discussed in the last class, our approach is to as statistical approach. So, and in that scene, we also looked at the few examples where we took the small amount of energy, some three energy levels and we had two particles, three particles and four particles which we took.

And we try to populate those energy levels of with those four particles; of with those number of particles that we had. Subject to some constrains that, the overall energy was fixed the volume of the system was fixed and of course, the number of particles that we have chosen has fixed. From that analysis, we concluded that as the number of particles increase, then there is something that, we would call as the most probable microstate. And and we are able to extrapolate and say that, as you reach very large numbers of particles, then of all the microstates available in the system. The most probable microstate is significantly more probable then all the other microstates combined.

So, that is the important thing, it is more probable than all the other microstates combined, not just more probable then the next most probable microstates. It is more probable, then the next most next most and the next most all combined, all the way up to zero. So, you do all possible additions, once microstates stands out in a huge way in that calculation, and that microstate then becomes the most probable microstate. And it is so significantly, it forms the other microstates that, when you take a snapshot of the system, you are more or less likely to find that system in that single microstate, which happens to be the most probable microstates. Statistical mechanics takes advantage of this concept or is based on this concept.

It is the fundamental idea of statistical mechanics, if you have set of rules which large system is following. Then you will based on the kinds of rule that the system is following, you may find situation where one microstate completely swamps all the other microstates. If that is the case, and in the kinds of system that we are discussing that happens to be the case, if that happens to be the case, then the equilibrium state of this system is simply the most probable state of the system. All the other states of system states that are available to the system, then become negligible, negligible and non effectively not available for the system from a statistical point of view. So, I take a snapshot you will find it in the most probable state.

So, this is the fundamental idea of statistical mechanics. So therefore, we find that given ours kind of system, the kinds of the sizes of the system that we are dealing with and this convenient very useful concept of statistical mechanics. It make scenes to as that may be want to talk in terms of energy of the system, when we want to talk in terms of velocity distribution in the system. Then statistical mechanics is the tool that, we should used to come up with the description for the system. So therefore, in our efforts to look at the energy distribution in the system and also the velocity distribution in the system, we will use the statistical mechanical approach. And more specifically, for the kind of particles that we have chosen which we described as identical, but distinguishable.

When you have a combination like that identical and distinguishable, the statistics for such a set of particles, a large collection of identical, but distinguishable particles has been worked out. And it has been worked out the credit for this is given to Maxwell and Boltzmann. So, there is statistical mechanical approach, call the Maxwell, which results in the statistics know as the Maxwell and Boltzmann statistics, which is applicable to the kind of system that we have described. Which is in ideal gas system and therefore, has been imposed also on the collection of electrons, that we have.

So, when we look at the Drude model, the concept we should be alert to is that, in the Drude model, Maxwell Boltzmann statistics have we imposed on those electrons or it is assumed that the electrons follow the Maxwell Boltzmann statistics. So, that assumption as we made, it is not stated upfront to you, but the moment we say that you know, we have taken ideal gas rules and ideal gas behavior and imposed state on the electrons or assumed that the electron behave like ideal gas of the molecules. Effectively we have also assumed that, the electrons in the solid obey Maxwell Boltzmann statistics. So, this is the key here. So, what we will do today is to derive the Maxwell Boltzmann statistics, we will derive the Maxwell Boltzmann statistics and this will lead as in fact, to further discussion later. Because it will enable as to better appreciate what alternate statistics can be used, when we look at the bunch of electrons.

So, first we will see what we have already done, which is the Maxwell Boltzmann statistics, we have imposed it already on our system. So, we are nearly going to look at what we have done effectively, even though we have done it without openly saying it, we have actually effectively impose the Maxwell Boltzmann statistics. So, we will drive that today and in subsequent classes, when we look at the give new characteristics to a particles, we will say that no no our particles are no longer going to have certain properties, they going to have the certain other properties.

When they have certain other properties, there is a other statistical mechanical drive statistics, which would be appropriate for that. Then we will impose the other statistics on the particles, then the prediction will change. And at that point we will see those new prediction are any better than the prediction we have currently made. So, with this kind of an introduction we will now actually drive the Maxwell Boltzmann statistics. So, that is what we do today.

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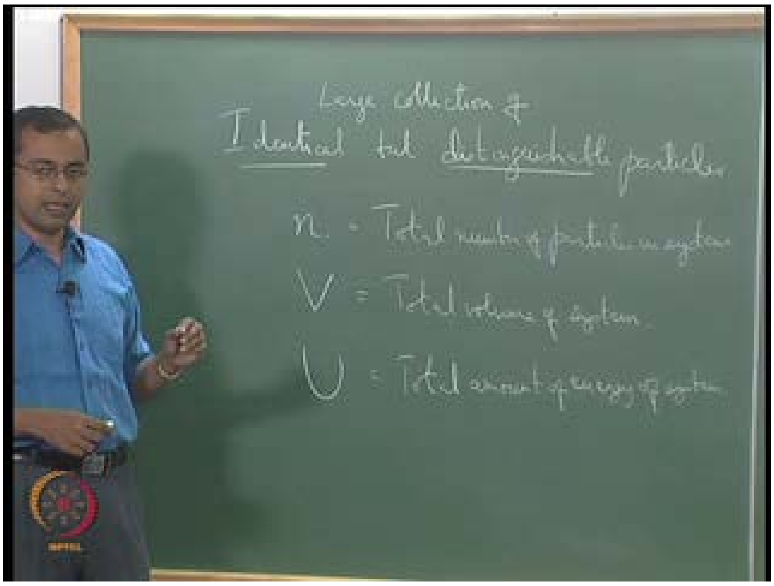

So, in our system we are saying that first of all it consist of identical, but distinguishable particles. I mentioned this in last class and I will alert you to it again, these are very important words which when stated in conversational scenes probably, convey something to you. But when it stated from the perceptive of statistics, the perceptive of behavior of particles, what they will do, what you can expect than to do, what you can expect than not to do. And therefore, make prediction on collections of large collections of particles these are very important words.

And in our very next class we will spend a significant amount of time specifically exploring what these words mean. What possibilities we have, what possibilities we have with respect to this two words and what are all those possibilities going to be, so that we will do in the next class. For the moment you just assume we will accept these words as they are and proceed to the derivation. So, we have a large collection of identical, but distinguishable particles. So, this is what we have. So, we will just say the total number of particles in our system is n.

(No audio from: 10:33 to 10:49)

We will say the volume of the system, total volume of the system is fixed total volume of the system is fixed. (No audio from: 10:58 to 11:07) And let say that, U capital U is the total amount of energy (No audio from: 11:15 to 11:28) total amount of energy available in the system. So, these are fixed, these are constants so, as to speak for our system. So, and I mentioned again last class important of V being constant for theoretical studies, because then that fixes the energy levels that are available in the system. That again, that itself is the concepts we will accept on face value for now.

Later on in our course we will actually convince our selves in a more detail manner that is the case. So, for now you just accept that, this is the case it is a confine system. So, as to speaks, total number of particles is fixed, total volume is fixed total volume is fixed, total amount of energy is fixed for our system right.

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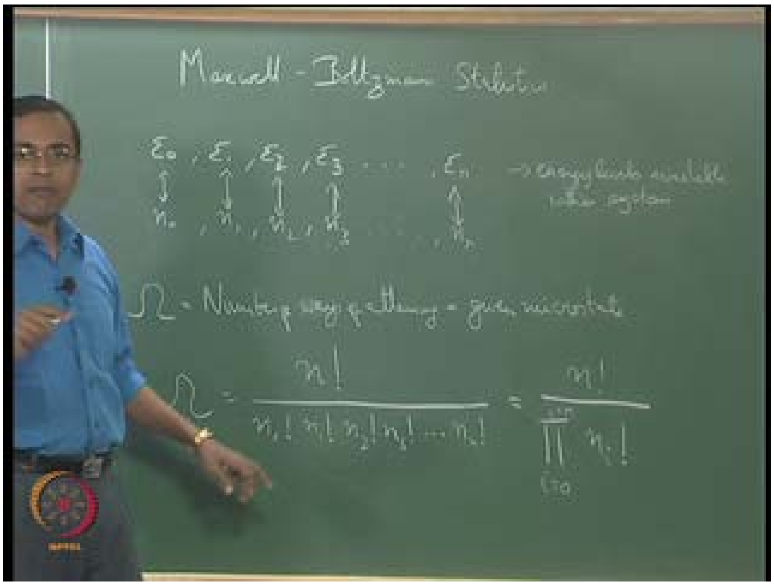

So, with this constrain we are going to derive the Maxwell Boltzmann statistics. (No audio from: 12:10 to 12:25) So, this is what we are going to do. So, to do this we will make some more assumptions about the details of our system. So, what we will say is that in the system see, we are saying upfront that you have a large collection of particles, there is the total energy there is the total temperature associated with that system and so on. And there is a distribution within the system. So, this is what we see, we wish to know if there is the range of energy available within the system, how many particles are at each of the energy level So, when we talk of distribution that is basically what we are looking at.

So, you have you now very small amounts of energy, very large amounts of energy available in a scale of energy. And then you may have very tiny amount of particles at lower levels of energy and tiny amount of particles of some other energy level. For example, we just do not know this is the case and we may have some other energy; some energy level which have high numbers of particles. So, when we take an average, you have to look at the number average of the energy and then that will give you the energy of the system so, as to speak right.

So, times the number of particles gives the energy of the system. So, we realize upfront that this information we seek. When we look at this kind of a system is how many particles or what fraction of particles is sitting at what energy level is the basic information we see. Once we have that, we have other information so, as to speak. So, we will get all the other information (( )) where the velocity distribution also come related to this information. So, although our total number of particles is fixed, what we have within the system, total energy is fixed we have. Let us say, within the system we have energy levels epsilon 0, epsilon 1, epsilon 2, epsilon 3 and epsilon r these are energy levels available within the system.

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So, this is fixed for the system, because we are said is the constant volume system and so on. So, these are all fixed values of energy. So, there is nothing that is changing about that we just have this energy. Now, at each of these energy levels, what we do not know is, how many particles are setting at these energy levels that are information that we do not know. So, for example, we will just say upfront we do not know. So, we will just say that there are n 0 particles sitting at e 0 energy level e 0, n 1 particles sitting at energy level e 1, n 2 particles sitting at energy level e 2, n 3 sitting at e 3 and so on, will be having n r particles sitting at energy level e r. So, this arrow is simply to show you that we which which energy level they are sitting at right.

So, we have n 0 particles at e 0, n 1 at e 1, n 2 at e 2, n 3 at e 3 and so on till we have n r at e r. We would like to get a sense of what are this values n 0, n 1, n 2, n 3 and so on or what is the fraction of them, I mean as the fraction of the total number of particles. So, that is the information that we see. So, in our system if you see many think are sitting constant, only this are the numbers that can change, only n 0, n 1, n 2, n 3, n 4 and so on till n r, those are the think that can change. Even this is fixed, the energy levels e 0, e 1, e 2, e 3,e 4 up to e r, they are all fixed values, there is no flexibility they are all fixed. So, only this can change right. So, this is what we wish to find out, what is what are these numbers right.

So, what we said is that the equilibrium state of the system, we want this numbers in the equilibrium state of the system, when the system reach an equilibrium what are this numbers you wish to now. So, the equilibrium state of the system is one which is the most probable microstate of the system. So, that is that is again something that the statistical mechanics tells us and we are assuming that, this system is following all those groups right. So, if you look at; if you now have a given set a given set of n 0, n 1, n 2, n 3, n 4 and so on up to n r. So, the let just say, we have one example of this collection one example of this collection.

Now, we would like to know in how many ways we can get this n 0 to be what it is, n 1 to be what it is and so on. So, the way that would occurs is the number of microstates, we will called at omega (No audio from: 17:07 to 17:14) number of ways of attaining this microstates, attaining a given microstate. And I will just put on the formula for it then, we will discuss what it is. Omega is n factorial divided by n 0 factorial, times n 1 factorial, times n 2 factorial, times n 3 factorial and so on times n r factorial. So, this is capital omega, which is the number of ways in which you can attain the particular microstate.

As I mentioned everything in the system is constant including e 0, e 1, e 2, e 3 e, e 4, e r they are all fixed. We only have a choose of what is the actual value of n 0, what is the actual value of n 1, n 2, n 3, n 4 and so on n r. So, at a; for a given microstate, we can have specific values of n 0, n 1, n 2, n 3 and so on, but if you chose another microstate those numbers would change. So, they are not; for a given microstate they are fixed. If you if you want to when I do this calculation for (()) microstate they are fixed. When when I can do the same of calculation for another microstate, where say n 0 may be two particles have been added to the n 0 and those particles have been removed from n 1.

So, in the new microstate this would be n 0 plus two that would be n 1 minus two everything else should be the same. So, like this you can keep on adding particles, removing particles from different different energy levels and for each possibility that you have, you can calculate the number of way of attaining that particular microstate. So, so in this example as I said, we have n factorial by n 0 factorial, n 1 factorial, n 2 factorial and so on. If as I as I mentioned, if I added removed two particles from n 1 and added them to n 0, the same calculation would have n factorial on top, it will have n 0 plus 2 factorial, n 1 minus 2 factorial and everything has should be the same.

So, this is the way in which we come up with the number of ways, in which you could attain a single microstate, a single combination or a single set of n 0, n 1, n 2, n 3, n 4 till n r. Now, also in terms of you know the way in which this equation is written been written up, it is the same as saying, in how many ways can you arrange n particles, which is the total number of particles in the system. Such that n 0 are of one kind, n 2; n 1 are of one kind, n 2 are of another kind, n 3 are of another kind, n r are of another kind, then you will come up with formula like this. What is the other kind here, they are all identical and distinguishable.

So, what we meant by other kind, simply that they are at the different energy level. This n 0 happen to be at e 0 energy level. So, they are of one kind so, as to speak. So, n 1 happens to be at e 1 so, they are of another kind. So, that is how we; if you want to compare it with something that you have done in high school (( )) that is how, you come up with this. So, this is the ways in which number of ways of attaining a given microstate. So now, our problem is simple we have now taken a very large system and from that system we have actually come up with the formula, which tells us the number of ways of attaining a given microstate in that system right.

So, this is the very useful piece of information for us. What we need to know is, what is that combination of n 0, n 1, n 2, n 3, n 4 till n r, what is that particular combinations which maximize the value of omega. So, that is all we see. We see to know, what is the combination of n 0, n 1, n 2, n 3, n 4 up to n r, which maximizes the value of omega. That that particular combination which maximizes the value of omega, then results in the in the; in that microstate becoming the most probable microstate right, we said upfront that if it is the most probable microstate, that is the equilibrium state, because it will swamp all other states combined.

So therefore, if we if we actually look at this, if there are any way in which you can find out the set which maximizes this omega, that is the set, that we are interested it. The moment you know that information, you know the distribution. Then you know that for that particular set some value, I will just give you some arbitrary value, may be 21, n 0 is

21, may be n 1 is 5000 something. So, you have 21 particles at e 0, you have 5000 particles at e 1, that is the equilibrium state of the system, from there you can get velocity distribution everything you can get from that right. So, that is just arbitrary numbers I thrown in a just give you some feel for what we are talking here. So, so our purpose is therefore, to maximize this right. So, this is what we wish to do.

So, to do that, we will do some we will make use of mathematical tools which are of convenient to us.

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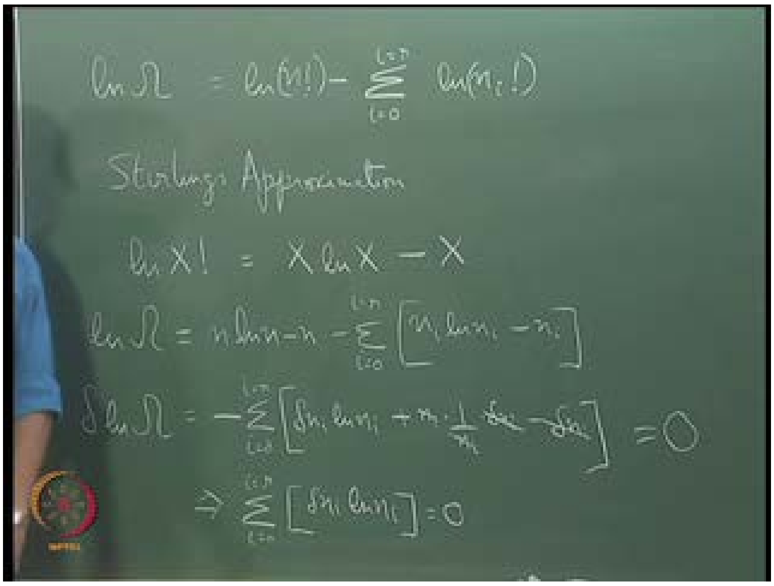

$$\ln \Omega = \ln(N!) - \sum_{i=0}^{i=r} \ln(n_i!)$$

Stirlings Approximation

$$\ln X! = X \ln X - X$$

$$\ln \Omega = n \ln n - n - \sum_{i=0}^{i=r} \left[n_i \ln n_i - n_i \right]$$

$$\delta \ln \Omega = -\sum_{i=0}^{i=r} \left[\delta n_i \ln n_i + n_i \cdot \frac{1}{n_i} \delta n_i - \delta n_i \right] = 0$$

$$\Rightarrow \sum_{i=0}^{i=r} \left[\delta n_i \ln n_i \right] = 0$$

So, what we will do first of all is write instead of dealing with omega directly you will deal with lon omega. So, quite simply this is simply lon n factorial minus incidentally, if you go back here, we can just to write to use the mathematical notation. This is the same as n factorial divided by pi of i equal to 0, i equal to r, n i factorial. Just as we write sigma for sum, we write pi for a product. So, just as we write sigma i equal to 0, to i equal to r of some bunch of terms. So, the same way if in this case, it is product of all this factorial n 0, n 1, n 2, n 3, n 4, n 5 up to n r. So, that product is represented by a pi instead of a sigma. So, this is what this compact notation is.

So, this compact notation we will now write here, you have lon n factorial up there minus. So, the bottom you actually in a denominator had product us, product of whole bunch of terms. So, if we take the logarithmic, the log of it the natural logarithmic of it, it would know be a sum of all those terms so, natural log of all those terms. So, therefore, we have minus sigma i equal to 0 to i equal to r lon n i factorial. So, this is what we have. So, we now; what why we choose lon omega is. If we look at the behavior of omega and lon omega, they behave similarly, in the scene that anything that maximizes omega also maximizes lon omega.

So, in that scene they are comparable and therefore, if you if you find a way of maximizing lon omega, that combination which maximizes the lon omega will also automatically maximize omega. So therefore, and mathematically this is more convenient to use, that is what, that is the reason why we go with natural logarithmic of the omega. So now, if you look at this we can rewrite this, we will make use of stirlings approximation. So, stirlings approximation is a way of approximating for log of a factorial. So, what it basically says is that (No audio from: 24:18 to 12:31) it basically says that lon X factorial is simply X lon X minus X.

So, lon of some numbers factorial is simply X lon, that number times the natural logarithm of the same number minus that number. So, this is all it means, and it turns out these is actually very good approximation even if you cross you now small numbers, you cross even 10 or something like that. Or some 10, 20 things like that small numbers you cross, this you will find if you just run the calculations you find this numbers workout very close. So, you do not have to go to very large numbers before you start working out well. But and it is it is indented at aimed at large numbers, at large values of X, but it turns out that even at small values of X this approximation holds to relatively small value.

I mean when you talk 20, 30 and all those are alternatively small numbers, it holds to. we are looking at a system again, as we mentioned many times 10 power 28 particles so obviously, this if you if you have any spilt up of it, chances are well pass this approximation. Well pass the range where above which the, this approximation holds therefore, this approximation is fine. So, the minimum range we would already cross and therefore, we will be this approximation would be valued. So, with this approximation we will rewrite this formula here.

Therefore, lon omega is now, n lon n minus n minus sigma i equal to 0 to i equal to r n i lon n i minus n i. So, this is the formula we have. Now, we want to maximize this right. So, essentially we would like to do, del lon omega by del lon n i effectively what we want to do. But what it also means that is that del lon omega and that should be 0, if I have reach the maximum. If we differentiated with respect to n I, which is that the only variable here is n i right. That is the only thing you can change, n is also fixed even though you have to keep track of that, in this formula n is fixed. So, this value n here is fixed lon n, this n lon n this are all fixed values, you do not have a choice only n i can change.

So, effectively del lon omega by del n i or if we just want to put it as del lon omega, it should be equal to 0. So, if you look at del lon omega, but this if it differentiate this with respect to n i it is going to be 0 any way because it is all constant. So, this is simply minus del n i lon n i plus n i into 1 by n i into del lon n i minus del lon n i and this is going to be 0, this is 0 right. So, if you look at it actually, if you look at this term, this n i and n i will get cancel and that will leave you del n i. So, plus del n i minus del n i. So, this will also get cancel. So, this entire term gets cancelled.

So, this be equal to 0 which is what we are going to have if you trying to maximize omega, will simply be imply sigma i equal to 0, i to equal to r del n i lon n i. The sum of del n i lon n i i equal to 0 to i equal to r is equal to 0. Actually, thus the minus sign here, but since it is equal to 0, it does not really matter, you have del n i lon n i equal 0 that is the sum of those terms is equal to 0 right. So, in our attempt to maximum lon omega, we find that we are run into one equation del n i lon n i equal to 0. So, we will make use of this equation right.

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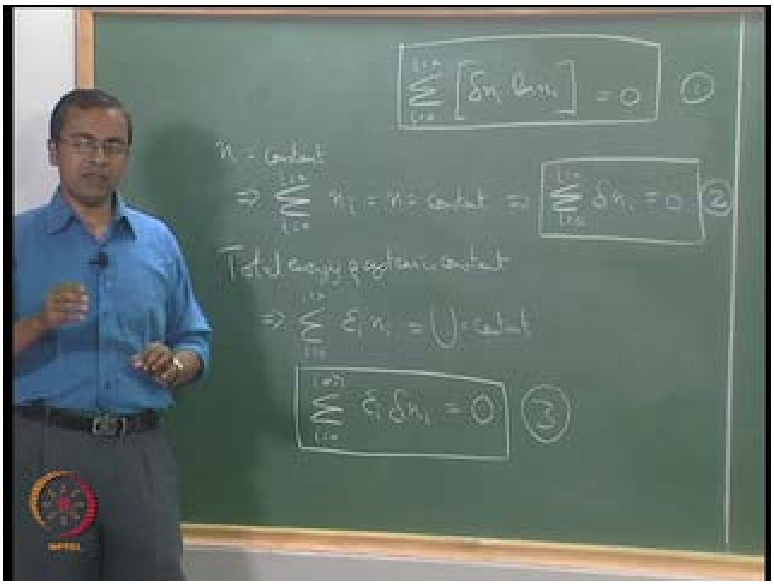

So, our equation now, I will just put that down here is sigma of i equal to 0 to i equal to r del n i lon n i equal 0 right. Now, we started off by saying that the total number of particles in the system is fixed, which is why therefore, n is fixed n equals constant right. We said n is equal to constant, but n i is not equal to constant right. So, because in that all those energy levels before the i energy level I mean r energy level that you have, you are going to move particles from one energy levels to another and so on. So, you have that freedom available to you. So, at a given point in time you do not know I mean at a given instant may be may have value of n i, but it is not fixed for the system it is it is a variable, but total number of particles is fixed.

So, therefore, if you remove a few particles from any one energy level, you have to put that many number of particles into all the energy levels put together combined. So, if it removes from one energy level, if you remove 10 particles. Then those 10 particles have to sit in have to be spread out across the other energy levels, you cannot just remove it from the system all together right. So similarly, if you add 10 particles into an energy level it has to come from within the system, you cannot this get it from somewhere. So, n is the constant therefore, the some of the so, this is the; which basically means, this implies sigma i equal to 0 to i equal to r of n i is what this n is equals n equals constant right.

So, this is what when we say n is equal to constant, the sum of all the particles available in all the energy level is the constant. So, that is what we (( )) which simply implies that any changes that you make in this I, which is you remove some particles from one, you have to put it somewhere else. So, this implies that sigma i del n i equal 0. So, in other words the total number of changes that you can make has to some up to 0, we remove 10 particles you have to add 10 particles somewhere, you cannot remove particles from a system. So, n being a constant means, the sum of all the changes has to total up to 0 right. So, that is what that equation is.

So, we have a second equation available for us and then finally, we have one more thing that we have constant that is the total energy of the system is fixed, (No audio from: 31:25 to 31:36) this implies some over i equal to 0 i equal to r epsilon i n i. This is the energy level epsilon i there are n i particles in it therefore, total contribution of the particles that are sitting at energy level is simply n i times epsilon i. And you have whole bunch of energy level i equals 0 to 1 2 3 4 5 6 up to r. So, the sum of them, the sum of all the energy levels times the number of particles that are sitting in those energy level is a constant, which is the total energy. So, we will call it U equals constant.

The energy levels themselves are fixed there you do not have any flexibility, but I can n i can change. So, that number of particles in that energy level can change therefore, this implies that, if you add particles or remove particles from any given an energy level and put it those particles are then put into other energy level. The sum of all those changes should workout to 0 in terms of energy associated with those changes. So, in other words if we differentiate this what we are basically saying is, sigma i equal to 0 i equal to r epsilon i del n i should equal 0.

Essentially differentiating this with respect to n I, if you do that it will work out to 0 and the physical significant of it simply, remove 5 particles from 1 energy level and you distribute them into 5 other energy levels. Then the total gain in energy of the system should equal to total loss of energy in the system. Therefore, the sum of changes in energy in the system should be 0. So, we have an equation here. So, we have three equation here, this is 1, this is 2 and this is 3.

So one way of describing the situation we have now is that, this is the equation that we are trying to maximize. In in our attempt to maximize the find the maximum the microstate with the maximum number of ways in which it can be attain, we got this equation. So, our attempt to get as the most probable microstate got as this equation, but that attempt is subject to this two constrains. The two constrains mean total energy total number of particles in the system is conserve. So, cannot be you cannot raise the number of particles or decrease the number of particles, total energy in the system is also conserve.

So, you cannot raise the energy of the system or decrease the energy of the system. So, we have we are trying to maximize the functions subject to this two constrains. Now, in the mathematics that you would have learn, we have learnt of you know maximizing function minimizing function and so on. So, that is something you are already familiar with, but we are add with slight twist here which is the, the fact that we have two constrains on that system. The physical way in which people describe this kind of situation is something like this. Let us say, you are an if you wanted to look at a analogue from say geography.

So, you have some kind of terrain. So, you have a terrain may be mountain side are something, that you are walking alone. Normally when we talk of maximum and minimum of function, it is like saying that what is the highest point in the mountain and what is the lowest point in that terrain. So, that is the maximum and minimum, but the fact that we have this two constrains is equivalent to saying that, I do not want to know the point which as the maximum height in the mountain or the minimum height in the mountain.

What I want to know is, in this mountain I first of all ask you to walk only along a particular path. So, you have big mountain, but I am asking you to walking along the particular path, which which may not go all the way to the top of the mountain. It just it is an arbitrary path, that I have determined I giving you some constrains saying you walk along this path only. In this path which is on that mountain, what is the highest point, what is the lowest point? That is the question that I want you to answer. You I mean, it is different from saying, which is the highest point in the mountain and which is the lowest point in the mountain.

The question is very specific. On this mountain so, it is not some arbitrary location. On this particular mountain, you have particular path that you have been assign to which may or may not take you to the highest point in the mountains. But regardless of where it is takes you, in that path what is the highest point, what is the lowest point that is what we are looking at. So, it is the same as saying that, you have you have a function which you want to maximize, but you are subject to this path, path given by this constrains. So, you are struck to that particular path, that this constrains give you. Within that constrains what is the maximum value that you are going to be, that is the question we are trying to answer. So, this is the mathematical problem that we are dealing with right.

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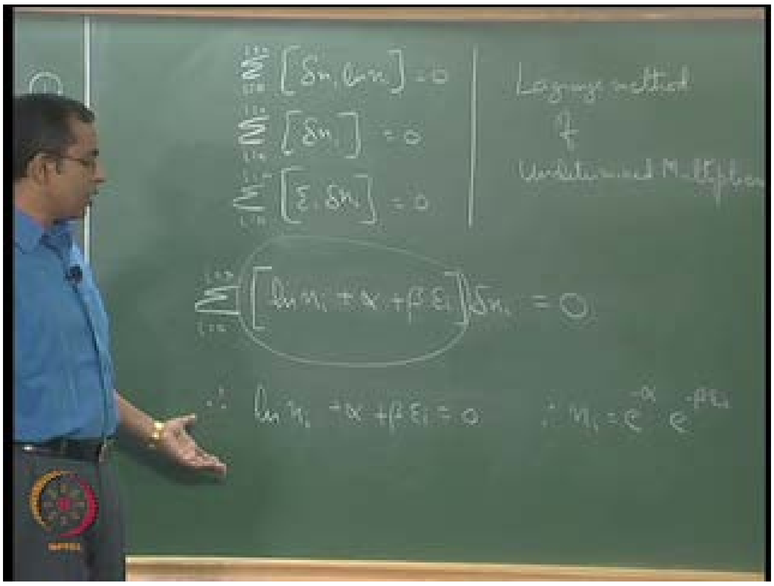

So, we will just rewrite only the final equations, then it will follow the method that we are using which is sigma over i (no audio 36:32 to 37:02) right. So, we have three equations that we wish to solve. The mathematical method that is used to deal with this kind of situation, where you have trying to maximize one function subject to certain other constrains. The mathematical approach taken for this is, referred to as the Lagrange method of undetermined multipliers. So, the mathematical method that is used for this purpose is referred to as the Lagrange method of undetermined multipliers. Incidentally, what we have done so far is the same methodology that we will use for two other statistical configurations that we will consider later in the course.

So, you will see this thing show up this kind of an approach show up later also, but the rules the system will follow somewhat different and therefore, the result will be quite different. But the concept we will use the approximation, we are using this method of undetermined multipliers that we using, all those things keep showing up again and again. So, this is called the Lagrange method of undetermined multipliers. So, you can look this up in mathematical book, in a book on graduate school engineering mathematics. But we will use it and so that degree we will even explain it here.

So, the basic idea is when you have a situation like this, one way of solving it is what this Lagrange method of undetermined multipliers is to simply say that, we will first of all we have three separate equation. So, we will first combine these 3 equations and before doing that, what we will do is we will do this undetermined multiplication. So, as to speak in other words what we will do is we will multiply this equation by alpha, where we do not know the value of alpha. So, we will arbitrarily multiply this equation by alpha we will arbitrarily multiply this equation by beta, then we will add them.

And the idea is that. So, we first do that, let us write that equation down where we have multiply this by alpha and we will multiply this by beta which the values of which we do not know at this point. And therefore, those alpha and beta are called undetermined multipliers because at this stage we are not determined. So, that is what this term, comes from undetermined, multipliers arbitrarily multiply by alpha and arbitrarily multiply by beta. So therefore, we have I will just write it down, then we will we will discuss this in (( )) lon n i plus alpha plus beta epsilon i del n i equals 0 right. So, these three are all equal to 0. So, if you just multiply this by a constant multiply this by some constant and then you add them, then they are all any way going to remain at 0. So, that we have done.

So, all I have done is, I taken this del n i out common. So, del n i come out you have only lon n I, this is alpha del n I, because I multiply this by alpha and I pulled out del n i which is out here so, I have alpha here. And you have beta epsilon i del n i in this equations again, I pulled out del n i. So, you have beta epsilon i. So, this is what we get. Now, the point is this sum has to be 0 right. Now, the logic behind this process is based on this idea that, this sum has to be 0 regardless of the value of del n i right. Because as we said in the beginning, this del n i are variable I mean is a variable, you can you can change the at a given for a, because i goes from 0 to i equal to r. In this system as we try to maximize the; I mean look for the condition that maximizes the microstate.

We are going to try varies values of n i and and so, at a given point in time we do not have control on exactly what each n i going to be, each del n i is going to be right. So, you are going to try changes where you going to add some particles here, you going to remove some particles there and so on. So, this has to be the sum has to work out to 0 regardless of the actual choice of the del n i. So, that is that is when you are actually satisfying this requirement, because to begin with you do not have control on the del n i effectively right. We do not have control in the sense that, I will put it this we have a lot of choice in what the del n i can be.

Therefore, for the sum to be to guarantee, the sum to be has to be a 0 we have to actually; what we are actually requiring is that this term to be 0. For this entire term to be 0, recognizing the fact that we have lot of choice on del n i and therefore, only accidently to become 0 if you are depending on del n i to make it 0. For you to grantee that it becomes 0, this term that precedes the del n I, that is what should become 0. So, this method uses this basic idea when you have this constrains, if you multiply them and put them all into multiply them by constant add them by all together. Then you sort of brought all the constrains into single equation, where you are now able to remove the variable and try to make it independent of changes on those variables.

So, therefore, this now is now required to be 0. So, this is the general idea of the Lagrange method of undetermined multipliers and like I said you can read this up more in the mathematics book, but this is what we will explain it also. So, therefore, we now require this to be 0 right. So, we now have change this entire mathematics to say therefore, lon n i plus alpha plus beta epsilon i should equal 0. Now, suddenly notice we are removed the sum. The sum is no longer relevant to us, regardless of the value of del n I, it has to be 0 therefore, this has to become zero. So, that is what this becomes all this preceding terms have to becomes 0.

Only then regardless of the del n i for all the possible values of del n i the final sum will always be 0, because the term that seen that is always 0. So, this is what we have. Therefore, we can now write, if you simply move alpha that side beta epsilon that side, both be a negative and we just convert this to so, n i will be e power all of this things. So, therefore, n i equal e power minus alpha and e power minus beta epsilon i right. So, we are now getting very close to be what we want. We have now n i which is the number of particles in the ith energy level, which is what we looking at.

We may we may convert that to a fraction. In fact, that is basically all going to do we are just going to convert this each of this into a fraction just for our convenient sake. But we now have it in terms of some alpha which we do not know at and some beta that we do not know at, but these are some kind some constants. And, but more importantly you have energy here. So, in terms of energy we have the number of particles, if you have an energy level, I can tell you, what is the number of particles, that are available at that energy level right and that is the information we want. And this is not some arbitrary number it is the number that corresponds to the most probable microstate.

We started all these calculation, we have done all these calculation with very first equation being the del n i lon n i equals 0, that sum of that. That sum that equation is the equation that maximizes the microstate, the number of ways in which you can get the microstate or corresponds to the most probable microstate. So, therefore, from there when you start and come up with a value for n i, this n i this n i e i combination for all the value of i that you can get, will then also give you the most probable microstate the distribution that corresponds to the most probable microstate fine. So, we will now just do some minor modification from this right.

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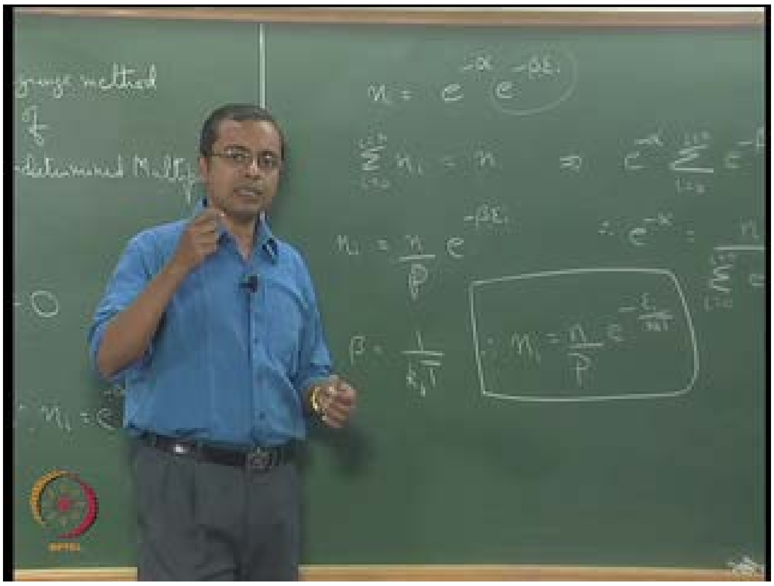

So, our equation finally, works out to n i equals e power minus alpha e to the power minus beta epsilon i fine. So, what we will do is now we will just try and make this in a form that is more convenient for us or more useful to us. So, we will just take advantage of the fact that, sum of all the n i should equal the total number of particles. This is i simply the number of particles at a given energy level, we have our energy level. So, if you some of all the particles you should get the total number of particles in the system, which is in your fixed.

So, this implies this is any way a constant. So, this is when we say sigma n i this means sigma of this this term here, because they are the same and in this term this is the constant, this nothing that changing here. So, effectively its only e i, that is in that sum. So therefore, it means e power minus alpha sigma i equal to 0 to i equal to r e to the power minus beta epsilon i equals n right. So, this and that n is the constant now, n is the total number of particles this alpha does not have any subscript i so, there it is outside the sum it is the constant effectively. Therefore, e power minus alpha is simply n divided by this sum. This sum in the denominator is actually called by a term called the partition function. So, it is this is the same as n by capital P, where P is the partition function.

(No audio from: 46:37 to 46:54)

Partition function, what it is it simply is that I mean stated that I will explain it in a moment. What it is going to do is, it is actually, if you look at original expression here, for every n i this term shows up right for every n i. Now, when I sum up for all of them this which is the term, that we are seeing here is simply the sum of that particular part of the n i term. And in a way it is like the, it is what actually that just gives you the fraction. So, that is effectively if you take for a given term the numerator you will have only one of those e i, in the denominator you will have the sum right. So, in the; which is what you have here, let us just put it back here then you can see it clearly.

Now, that you have e power minus alpha is n by P, what we are basically saying is that n i is simply n by P times e to the power minus beta epsilon i. So, what we have here n i so, we started with a expression for n i we took the sum for n using that we simplify and we got e power minus alpha as n by p which is simply n by this sum. And that n by p what I have put back here, instead of e power minus alpha I have put n by p here, e power minus beta epsilon i. This p here, is the sum of this e power minus beta epsilon i for all the epsilon I, that are available to us right.

So, it is it is in a way, it is the one that way sort of helps you come up with a faction so, as to speak. Because this is now some some across the all the all the energy states, this is for just this energy state. So, this is how you get this equation. So that therefore, it is called the partition function, it helps you get a sense of how the particles can be partition across all the energy levels right. So, and it terms out that this beta is simply 1 by k B T is a constant. 1 by k B T, k B is the Boltzmann constant, that a given temperature therefore, it works out to fixed value. So therefore, n i is simply n over P e to the power minus e i by k B T.

(No audio from: 49:13 to 49:21) So, we now have a function value for n i right. So, what have we got here, in by doing all the mathematics we have now got of expression for n i, which then tells us the number of particles that are available in the ith energy level. In the microstate, that is the most probable microstate and that is the information we were searching for right from the beginning. What is the most probable microstate and when we say what is the most probable microstate. Exactly, in fact the question we are asking is in that microstate how many particles are sitting at which energy level, because that is what defines the microstate it is not some arbitrary thing.

So, we now have an expression for that, what is that number of particles which are sitting in the energy level e i. The and in the; and this whole expression has been drive for the most probable microstate. So, this expression is then the Maxwell Boltzmann statistics expression. So, the Maxwell Boltzmann statistics actually, gives you this expression. If you wish to look at it some more, what it basically says is that, if we keep raising the energy level the number of particles will exponentially come down, because you have minus epsilon i here right. Epsilon i as a negative in the e power minus epsilon i by k B T. So, the higher this value goes exponentially the number of particles that energy level will decrease right.

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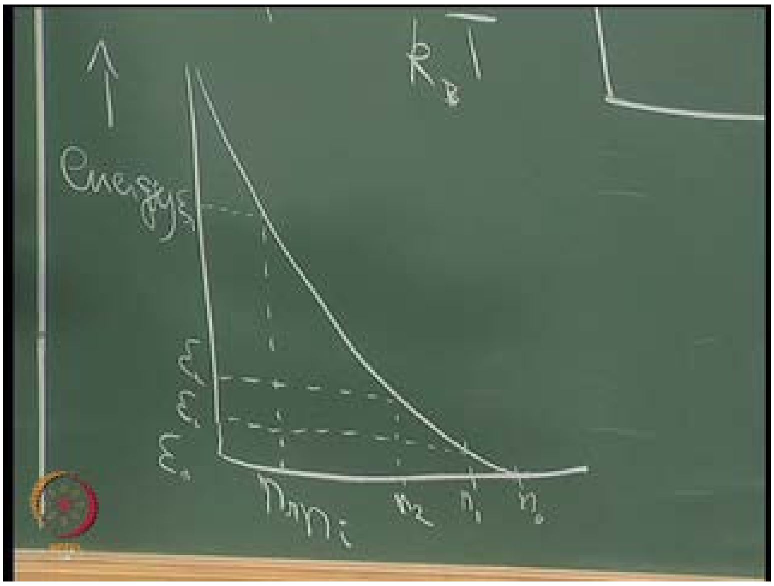

So in fact, if you want to make a plot of this function, you will simply see if you write the energy levels down. So, this is the number of particles and this is the energy (No audio from: 50:51 to 50:58) and this is number of particles n i and this would be n 0, n 1. Once you give I will just put it draw the diagram and then we can see. So, at e 0 we have n 0 particles, at e 1 we have n 1 particles some e 2 is somewhere here let us say we have n 2 particles and so on and then we have we now some e r we have n r particles right. So, this is what we have. So, this is the distribution of Maxwell Boltzmann that Maxwell Boltzmann gives.

So, Maxwell Boltzmann distribution is the manner in which particles are distributed across energy levels subject to the constrains that we have just discuss and you shows you that the particles are distributed like this. So, when we when we drive equations based on the assumption that we are using ideal gas laws, we are using that the particles are identical, but distinguishable and they follow all the rules of ideal gas laws and so on. Effectively the manner in which we are distributing energy amongst those particles is given by this distribution.

The manner in which we give velocity distributed, velocities and speeds are distributed across the particles will be a result of this distribution. From whatever we can calculate out of this distribution that is the manner in which the velocities and so on will be distributed. And this is then directly reflected on the translational kinetic energy of those particles, average translational kinetic energy of the particles, the kinds of behavior they show with respect to specific heat.

So, if you make predictions for specific heat and energy of those particles and it turns out that, there is some problem there. Then that problem translates to the fact that this distribution that we are seeing here is perhaps not applicable very well for electrons in the in a solid. So, this distribution of number of particles versus energy level is applicable very well for ideal gas particles, which follow the ideal gas behavior, kinetic theory of gases. But apparently is not as appropriate for particles such as electrons in a solid right.

So, we will in the next couple of classes in the very next class, we will actually look deeper into why why this is not correct and to do that specifically we will focus on those words identical and distinguishable. And see, what possibilities we have there and how suitable the possibilities are for with respect to what electrons display to us. And then we will take it from there and see what might be more appropriate way of doing it. And then eventually a few classes down the road, we will actually at that point after the next class we will have to deviate away and look at some other background material.

And then we will come back to a new statistical distribution, which would then be a more appropriate for a electrons. That stage we will come back to this distribution we have seen here and compare this distribution to the new distribution that we will come up with at a later stage. And see where is it that distribution gets it right, and where is it distribution gets it wrong and what is the problem that we have. That is the direction in which we will (( )). So, with this we will conclude today’s class and take it up in a next class. Thank you.