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Lecture - 17 Fundamentals of Statistical Thermodynamics Part 2

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So, good morning all of you, yesterday we looked at the Boltzmann distribution function, how we derived Boltzmann distribution function form simple probability assumptions, and the most important thing about this distribution function is that, it gives you what is the filling or number of particles that can occupy the energy levels, what is the order in which they occupy, so this is the most important consequence of the distribution function and also according to the kind of system that you are dealing with, you can talk about what we call as canonical or grand canonical these are the 2 most common ensembles, and we fit the system with phonons, molecules and protons to the canonical ensembles, and the electrons are usually assigned to the grand canonical ensemble.

So, accordingly we can write down the probability distribution function, for the canonical ensemble which looks like this and for the grand canonical ensemble like this. So, having now identified the corresponding distribution functions for the corresponding energy carriers, we will now apply this to derive the distribution function for each and every energy carrier.

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So, therefore, this is not just sufficient if you are looking at only the, know the probability of distribution of this particular energy carriers from this we have to first calculate the denominator which is the partition function, this is the summation term, this is still not complete and we have to also apply the corresponding energy levels. So, this is the generic form here. So, depending on your dealing with molecule or phonons or photons, appropriate values of energies have to be substituted. So we have to evaluate the partition function in the denominator and then come to the distribution function.

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So, today we will start with the applying this for first molecules. So, let us first start with molecules, which are more familiar, you do not even have to any quantum mechanics to understand the energies energy levels of these molecules, So these are basically continues energy levels, we do not have to apply any quantum mechanics principles for determining the energy levels here and if you are talking about monatomic atom, typically the one that will now consider monatomic atom. So, this is just one atom like this and it can have translational motion in all the three perpendicular directions, we can have V x, V y, V z.

So, therefore, the corresponding energy that possess by this particular atom, can be just half m, V x square, V y square plus V z square. So, it is three degrees of freedom for kinetic energy, translational kinetic energy. So, there are no vibrational modes, there are no rotational modes, purely translational Kinetic energy. So, therefore, you see this V x, V y, V z are continues energy levels. So, you can actually span from minus infinity to infinity depending on the direction that they are moving across.

So, now we will substitute into the definition of partition function, now we know which distribution to pick, so we look at molecules, therefore belong to the canonical ensembles, so we can therefore, calculate the partition function accordingly. So, your z will now be summation e power minus Ei by k B T. Now for a continuous function. So, we will use the integral, instead of the discreet summation here. So, this summation is good as long as you have discreet energy levels.

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But if you apply this for molecule, were you have continuous energy level. So, this can be replaced as a summation, and now what kind, how many integrals you have? You have three integrals, one in x, one in y, one in z. So you have minus infinity to infinity and you have e power minus m by 2, I am just substituting our kinetic energies into divided by K B T, and this integral is over d v x, d v y, d v z, is it clear.

So, we are just now evaluating the partition function. In the case of molecules, these are continuous and therefore we replace the summation with these integrals. So, if you evaluate this. In fact, you can actually try this in symbolic manipulation software like Mathematica, because this you cannot integrate by hand right now. So, you can perform this triple integral in a package like mathematica which will do numerical integration and give you the answer. So, that should come out to be m by 2 pi K B T, the whole power minus 3 by 2.

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So, this will be the result of this particular integration triple integral. So, this is your partition function z and therefore, what will be your probability distribution function P E of i.

Student: sir now we transfer that velocity v x, v y, v z that turns of x y. Yeah you already have the integrated this over minus these are for limits for v x, v y, v z. Student: but v x is the function over x. Correct, but all these are in v x space only, there is probability. All these are in momentum space you do not have any issue. So, we know the limits of the integral for v x, v y, v z.

So, all you have to do is plug it into some symbolic manipulation package like Mathematica and it will directly give you what is the result of this it will do a numerical integration for this. So, once you know the portion function now you can calculate your probability distribution. So, for this case it will be therefore, e power minus E i, let us write it in terms of E by K B T. So, this is what is there in the numerator, the denominator was the partition function now which we have evaluated. So, we will take this to the numerator, you will have m by 2 pi, K B T, the whole power 3 by 2.

So, therefore now what we need to actually evaluate, is not just the probability, but the distribution function, a number distribution. So, how much number of molecules can occupy by a particular energy level and So on. So, now once we know this probability the way, we are going to evaluate the distribution. So, this f here is the actually the number distribution function for energy carriers. So, we know that PE of i is nothing, but what actually it is n of i by summation n of i. Now we want to get back something like this. So, if you want to get the number distribution, so we will multiply the probability by the number density, that is the number of molecules in a unit volume of a system. For example, so this is a pure number, now what we are getting here is a density per unit volume, that is number of number of molecules per unit volume, it is a number density.

So, this distribution signifies number density here, where as this is just pure number count. So, therefore, for the entire volume, when you want to calculate the number density; so we will simply multiply the probability, with a corresponding number density. So, this we will call this as number density here, number density of molecules.

So, the way to interpret this is for a particular energy level, if these were discreet energy levels. So, this will tell you how many molecules can occupy that particular energy level. So, that will be the number density of molecules occupying that, and finally the distribution function will be an ensemble of this so; that means, you just sum over all these different energy levels and you allot the particular number to that particular probability and so on.

So, that will give you the total number distribution function for the entire system. So, in the case of molecules, these are anyway continuous and therefore, the number itself is just a constant value, it is not going to fit into one particular in a discreet energy level Ei, the way molecules and phonons are going to occupy. So, simply we can multiply this number of molecules or number density of molecules with the probability.

So, if you do that therefore, you will be just simply extending this as f is equal to n into m by 2 pi, K B T, whole power 3 by 2 e power minus this is again m by 2, v x square plus, v y square plus, v z square by 2 K B T. So, this gives you a number distribution function or this is your number distribution function for molecules. So, this distribution function is also called the Maxwell Boltzmann distribution function, so is that clear.

So, we started with therefore, the distribution of electrons at each energy level or each distribution of molecules, but now then we denote in terms of probability and now we are coming back to the distribution function, but now this are per unit volume. So, it is a number density function. So, therefore, we multiplied by the number of molecule per unit volume of the system. So, this n is nothing, but number density of molecule or this is you can interpret as number of molecules per unit value.

So this resulting distribution of molecule this will tell you; therefore for a system with volume v with n number of molecules. So, at what velocity levels like you have, p x particular value of v x, v y, v z, what will be the distribution of molecules in this particular band of v x, v y ,v z, these are continuous here. So, so continuous values of v x, v y, v z, it will tell you what will be the corresponding number of molecules that can occupy per unit volume of the system.

So, this is the classical distribution function, why because we do not have discreet values of energy levels here, ever thing is continuous. So, this is usually referred to as a classical distribution, because we do not have to start with any quantum mechanics to this derive distribution function, everything is continuous starting from the energies. So, all we did was put it into the Boltzmann distribution function, calculate partition function and that is it. So, there was there was no quantum mechanics into this, that is why this is called the Classical distribution function.

Now, if you apply this to the next energy carrier. So, we will do this for electrons, therefore in the case of electrons they obey the grand canonical ensemble.

 $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{e^{\frac{1}{2}(2k)log(\frac{1}{2})}}{P(E_i)} = \frac{e^{\frac{1}{2}(E_i - \mu N_i)}/k_B T}{Z}$ $N_i = O$ (empty) uyuu

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So, the probability of distribution of electrons will be e power minus E i minus mu n i by K B T by you have the partition function Z which is nothing, but summation of the numerator. So, for as the electron is concerned, were you are Z is equal to summation e power minus E i minus mu N i by K B T. So, when you look at the occupation of these energy levels by electrons. So, you have only 2 possibilities, you have a particular number for example, if you are talking about an energy level which is empty, so that means, this is equal to 0, if you are talking about an empty energy level.

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If your energy level is occupied this number will be just 1. So, only one electron can occupy an energy level. So, this will be a filled energy level, we cannot talk about multiple electrons occupying the same energy level. So, each energy level is occupied by one single electron therefore, you have 2 possibilities, one you have an empty energy level where you do not have any electrons and you have an energy level which is filled by only one electron.

So, therefore, in this case the calculation of z becomes relatively easy. So you have summation, this summation will run over the empty energy level and the filled energy level. So for the empty energy level, this particular portion will be 0. So, therefore, in this case the corresponding value of E i will also be 0. So, we can just write this as (Refer Time: 18:48) for the empty case minus 0, plus the filled case you have e power minus E i, this is the value of the filled energy level which is non0 minus mu N i by K B T. So, in this case N i will be equal to 1. So, essentially the value of Z becomes one plus e power minus E i minus mu by K B T. So, the way you have to interpret is, if there are no electrons basically there is no energy for that particular level. So, the energy possessed by the electron if there is no electrons it is 0.

Similarly if you are talking about a filled energy level, you have a particular value which is E i for the filled energy level, so, there are two possibilities, you have an empty energy level or you have a filled energy level. In the empty energy level there are no electrons, so, there is no energy in that case. So, if you substitute this you get the partition function which is now just 2 values, either you have an empty one or you have a filled one. So, it is a summation becomes pretty easy now. So after this we substitute back into the probability P of E will be, e power minus E i minus mu N i by K B T divided by you have one plus e minus E i minus mu by K B T. So, the next step would be to therefore, calculate the number distribution function.

Student: (Refer Time: 21:18).

Correct. So, this is just you are looking at one particular energy level. So, where only one electron can occupy this, unlike molecules, or phonons for examples Phonons many phonons can occupy an energy level whereas, in case of electrons your policy exclusion principle states that, depending on the spin again so spin will give you degeneracy, but if you have a plus half or minus half spin. So, this can occupy only one energy level.

So, therefore, it is like saying an electron with the spin of say either plus half or minus half, will occupy this. If there is nothing occupied there is nothing there. So, you have only two possibilities, either it is occupied or it is empty. So, depending on that we only get 2 terms in to the summation.

Student: Sir when the w function (Refer Time: 22:36) for a same time (Refer Time: 22:36) for different (Refer Time: 22:37) we get the same elegy even for the energy level for a (Refer Time: 22:37).

Right, but. So, for which concept you are talking about.

Student: wave function did for.

Wave function for.

Student: Electron for the entire.

For the electronic energy levels.

Student: If we consider that n point 2 value and l as a 2 different value 0 1 or minis 1 and r the base, that n value of plus or minus one is 0 and we get the same for energy given for a.

See, but that only the quantum mechanics will be tell you. I mean from that state. How the electrons can actually have these discreet energy levels, but suppose you want to fill these electrons into the spaces, you had only two possibilities, either you put one electron into one space or there is no electron filling one space. So, here what we are doing is we are allotting we have certain energy levels, from the quantum mechanics, but we are now putting the electrons into those fitting into those energy level. So, there are what it says now according to (Refer Time: 23:23) principle one electron has to go and occupy one energy level. So, there are only two chances. So, one it can be occupied or it cannot be occupied. So, only for those 2 discreet stats we can do the summation here, so therefore.

Student: (Refer Time: 23:44) piece of paper belonging to as sigma (Refer Time: 23:47).

Yeah, but we are summing in this case only the filled and empty once, the summation is only over the filled and empty once and the filled one will have particular value of energy e. So, what we will do is, will complete this exercise and then we will understand how it is going. So, now we have P of E, the next step is to therefore calculate what f is and how will be get f.

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 $7.1.0.9$ $1 \times P(E)$ $_{\circ}$ (ε ₁ - μ)/ k_{D} T $\overline{1}$ e or -5.56

So, we will be having the number density occupying a particular energy level multiplied by P E of i. So, therefore, based on this again you can take about 2 cases, one in which you have no occupancy 0. So, this will be 0 times P of E i, the other is fully occupied 1 times P of i.

So, therefore this f now becomes, this is completely 0. So, you have same as what we have written here E of i minus mu N i by K B T divided by plus e power minus i mu by K B T. So therefore if you multiply throughout by e power E i minus mu N i by K B T, the numerator and denominator, so the numerator becomes 1 and denominator will have e power E i minus mu by K B T plus 1. So, this resulting distribution function is called the Fermi Dirac distribution function.

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See I think your point is correct, but however, in the case of deriving the Fermi Dirac distribution it is however, I was also checking in a couple of texts and literature, they do not submit over the discreet energy levels of all the possible states. So, they only look at either an occupied state or unoccupied state and then they only summit over those two states. So, this is the characteristic of the Fermi Dirac distribution function.

So, unlike the case of Phonons, now when we do phonons, you will find that again we will be able to summit over the all the possible states, but in the case of electrons, to derive the Fermi Dirac, the summation is carried over only though either empty or filled state.

Student: (Refer Time: 27:25).

Correct. So, this is the grand this is the characteristic of grand canonical ensembles. So, I am not going in to all the details. So, I am only giving you the principle of now how these distributions functions are derived, but that is true. So, this is the basically the principle behind the (Refer Time: 27:52) canonical ensembles correct. So, ultimately now we are arrived at a distribution function for electrons, which looks quite different from the Boltzmann distribution function, now if you want to plot this because this is the very important distribution function. So, on the vertical access I have this number density distribution corresponding to particular energy E i and on the denominator I can plot for example, E of i, so that means, you have these discreet energy levels, for particular value

of E i you should know what is the number density that is occupying this energy level E i. So, that is given by this Fermi Dirac. So if you plot this for given temperature, because you see that this is also a function of K B T, so for a given value of temperature, let us say will start with 100 Kelvin, so this will look like this. So, this can be some value 0 and it can go up to say one.

So, now this is at temperature of 100 Kelvin and if you look at the distribution it should be kind of anti symmetric about the value of the chemical potential mu. Now this chemical potential will be equal to the Fermi level, if you are floating this for 100 Kelvin. So, at 100 Kelvin you would probably get something like this and at that particular value this will be equal to mu will be equal to E f at 0 Kelvin. So, this will be z equal to 0 Kelvin.

So that means, about the central, line central line here is given by the chemical potential. So, at 0 Kelvin this chemical potential will be equal to the Fermi energy level, so this distribution will be anti symmetric. If you continue plotting this for higher and higher temperatures, you will see that. For example, go to 300 Kelvin, you will be getting something like this. So, this will be at 300 Kelvin and it tends to become a straight line from the characteristic distribution like this at lower temperatures, it tends to go to straight line and finally, at when you say1000 Kelvin, it will be just straight line like this.

So, this is your typical Fermi Dirac distribution function. And for the case when you are E minus mu in the numerator for the limiting case, we can say when your E minus mu is much, much greater than K B T. So, what happens to the term compare to 1, exponential of this term will be very large and therefore, you can simply write this as e power minus E minus mu by K B T.

So, what is this? This is your Boltzmann distribution function. So, for the limiting case of E minus mu much greater than K B T, your Fermi Dirac distribution reduces to the Boltzmann distribution function. So, this is the typical nature of all though the Fermi Dirac looks like unique distribution function, we should also be aware that for large values of these energy, E which are much greater than your K B T. So, this can actually collapse into the normal Boltzmann distribution function.

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So, therefore, this is an important point, what we will do now is look at the final energy carrier, which is in the case of phonon. So now on similar lines, so we have to start with the corresponding probability distribution function for phonons and evaluate the partition function z by substituting the phonon energy that is the vibrational energy that we had derived.

So, you please start it, you try to evaluate what should be z because there are some mathematical steps involved in that, I will help you with that one. So, I will also once again give you what are your phonon energy levels, that h v times n plus half where n can be 0, 1, 2 till infinity. So, these are the discreet values of energy levels. So, this is your partition function.

So, we are now looking at canonical ensembles. So, it will be just e power minus E i by K B T and just e we have substituted into this. So, how do we evaluate this particular summation? So, we can just split this up into e power minus h nu by 2 K B T e power minus n h v by K B T. Am just splitting this into two terms.

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And therefore, you can write this as you can take out minus h nu by 2K B T, because this is independent of n, and then the summation can be apply to this other term and we can expand this summation. So, therefore, if you put n equal to 0, this will be 1, and then for n equal to one. So, you have e power minus h nu by K B T plus n equal to 2, you have e power minus h nu by K B T the whole square. So, basically e power minus 2 h nu by K B T can be written as e power minus h nu by K B T the whole square so on and so forth. So, you have all the other higher order terms till infinity. So, you have a now series expansion.

So, you can compare this to the Maclaunn series. So, you have 1 minus x inverse; can be expanded as 1 plus x, plus x square, plus x cube and so on. So, you can therefore, compare this series expansion to the Maclaunn's series and just hold on there. So, therefore, we can write z in terms of e power minus h nu by 2 K B T and from Maclaunn's series. So, therefore, this entire right hand side is equal to this. So, therefore, we can replace this with what 1 minus. So, x will stands for e power minus h nu by K B T. So, e powers minus h nu by K B T the whole inverse. So, this is the way we can evaluate the summation.

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Now you have the partition function. So, therefore, P E of i will be, e power minus h nu into n plus half by K B T divided by the partition function. Therefore if you knock of the common terms, you simplify what you get. So, minus e power minus h nu by 2 K B T can be cancelled off numerator and denominator. Therefore you will have e power minus h nu, n h nu by K B T in the numerator and this term we can take it to the numerator minus h nu by K B T is that clear.

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So, therefore, we need now the number density function f, which can be therefore written as your ensemble of your n which is nothing but summation n equal to 0 to infinity. This is your number density at each energy level corresponding value of probability you have to multiply and sum this over all the discreet energy states, from n equal to 0 to infinity.

In the case of electron we did this only for the occupied and the empty state. Now for the case of pronouns we are summing it over it is a canonical ensemble, will summit over all the discreet energy states possible. So, now therefore, if you put it into this you have again another summation coming up.

So, you have 1 minus e power minus h nu by K B T and the corresponding value of n is n i is nothing but, So you have, n e power minus n h nu by k b t. So, what we will do now is to again use the Maclaunn's theorem (Refer Time: 41:41) So, this should be written as 1 minus e power minus h nu by K B T you can take it out again this is independent of n, you have n equal to 0 to infinity in the summation and the summation is apply to this term right here.

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So, now we will just use a differentiation rule here. If you are talking about minus d by d x of summation n equal to 0 to infinity, e power minus n x let us say, where x can be h nu by K B T. So, I am just giving a differentiation rule, so if you differentiate this, what you should get; summation n equal to 0 to infinity, you have n e power minus n x. So, therefore, this term here is similar to the right hand side of this rule. So, therefore, we can replace this with minus d by d x of this. So, therefore, your f now is, 1 minus e power minus h nu by K B T into minus d by d x of some root infinity minus n h nu by K B T. So, now this summation of this 0 to infinity, e power minus h nu again coming back to how we did with this Maclaunn series, this entire summation of these terms 1 minus 1 plus e power minus h nu by K B T plus this square plus this, this is nothing, but Maclaunn series, 1 minus x to the power minus 1. So, therefore the same thing can be applied again to this term here, summation term we can apply the Maclaunn series again reduce it to.

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So, 1minus e power minus h nu by K B t times, you have minus d by d x and you have one minus e power minus h nu by K B t in the whole inverse, is that ok.

So, therefore if you differentiate this, can you complete it what you will get. So, this x is nothing but h nu by K B T. So, you can rewrite this as x, because I have written this as d by d x. So, it will be easy for you to differentiate in terms of x, this also you can write it in terms of x if you want to simplify it. So, therefore, you have 1 minus e power x and then you have to differentiate the next term. So, this will be e power minus x by 1 minus e power minus x the whole square. So, this term if you differentiate that will be e power minus x by 1 minus e power minus x the whole square.

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So therefore, if you cancel the common terms, Therefore you will be having finally, 1 by e power x minus 1. So, this will be 1 minus e power minus x. So, this will multiply and divide by e power x. So, I will be ending up with 1 by e power x minus 1. So, there is nothing, but 1 by e power h nu by K B T minus 1. So, lot of mathematical manipulations are required.

So, finally, therefore, we reach this distribution function for pronouns this is called your "Bose Einstein distribution function". So, if you want to plot this distribution function just like the way we plotted the Fermi Dirac, again this is the function of temperature right.

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So, on the y axis you can have the distribution f, the number distribution. On the x axis you can have what? In the case of electron we have energy, in this case we have the frequency, you can write this h nu also in terms of h bar omega; this is also h bar omega multiply and divide by 2 pi and you have modified plane constant times the angular frequency.

So, you can therefore, plot this as function of frequency either nu or omega is up to you ,in terms of hertz for example, and how does it vary with temperature. So, what say 100 Kelvin, you will have a function which is like, this is at 100 Kelvin, say at 300 Kelvin this will be looking like this, and as your temperature keeps increasing, so the number distribution will approach 0 for larger values of frequency. So this will be for 100 and if you are looking at 5000 Kelvin, so this is the way that the distribution function behaves and plotted as a function of frequency and temperature.

Once again similar to the Fermi Dirac case, for the limiting case was you have a h nu much greater than K B T. So, this term will be significant over. So, therefore, this will simply reduce to e power minus h nu by K B T, which will is nothing but again Boltzmann distribution. So for these limiting cases very high values of energy. So, that you are looking at values of nu which are very large or values of temperature which are very small like this. So, for these cases this distribution function will approach your Boltzmann distribution function. So, we will stop here, tomorrow we will summarise these distribution functions that we had derive their most important characteristics.

So, now that we have the number distribution, corresponding to each energy state, now we can do all these ensemble averaging to calculate the macro scale properties. So, we know what the number density is therefore, if you multiplied it with the corresponding energy you will know the energy of each state. And then if you sum them over you will get the total energy of the system. So, you have basically distribution function which tells you how many number of energy carriers can occupy particular state and now if you multiply it with that, energy of that state. So, it will give you the energy weighted average it is a weighted energy of that particular state and if you sum them over all the state, this will give you the total energy or the internal energy of that entire system.

So therefore, a micro state from the discreet microstate energies, now we can use this distribution functions to calculate the entire macro scale energies. So, we will do this exercise tomorrow, so will look at how to derive the internal energy for electrons phonons molecules.

Thank you.