ELEMENTS OF MODERN PHYSICS

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Lec 22: Quantum Statistics

We shall now try to make a distinction between the Maxwell-Boltzmann, Bose-Einstein and Fermi-Dirac statistics. They are in short called as MBB and FD statistics through an example, a simple example, say, for example, two particles and three energy states and so on. Then we'll talk about this theory of ideal gases and we'll derive the Maxwell-Boltzmann, Bose-Einstein and Fermi-Dirac statistics. We will talk about the fluctuations in the particle number and how we can get the classical limit of the quantum distribution. And we will also sort of list out the differences between these three statistics.

And so let us try to see that this MB statistics or the Maxwell-Boltzmann statistics. These are really for distinguishable particles. But then we take care of this indistinguishability by simply a Gibbs correction factor, which is 1 by n factorial. So we'll write down the partition function, the canonical partition function as 1 by n factorial. And then there is a sum over exponential minus beta ek.

And I just leave this sum without an index because whatever index this ek is characterized by, we have to sum over all of that. And this n factorial is important, which is the Gibbs correction factor. In the BE distribution, There is no such division by n particle and the partition function is simply the sum over exponential minus beta Ek. Now, this is basically a very large number of particles can occupy one quantum state.

and there is no and when they do they basically correspond to one state and similarly the FD also does not have any distinction of or rather there is a requirement of this dividing it by n particles and one can again write it pretty much same way as the Bose-Einstein distribution excepting that we have to keep in mind that there is an exclusion principle that comes into the picture, which prohibits two particles from occupying the same quantum state, okay? So, at most, one particle would be there in one quantum state. Unless you are talking about spins, then, of course, there is a degeneracy, and you can have an up and down occupying one quantum state, okay? So, let us take an example, and the example is one of the simplest examples that we can think of.

We take two particles and three energy states. And three energy states can be anything—it can be 0, epsilon 1, and epsilon 2; or 0, epsilon, and 2 epsilon; or even some of the bound state problems, you can have a minus epsilon, 0, and plus epsilon, anything. So, let me just denote them by epsilon 1, epsilon 2, and epsilon 3. And these two particles, although they are indistinguishable and identical particles, we will still call them A, B. So that, at least in the Maxwell-Boltzmann case, we know how to distribute the particles. Now, the question is to distribute them—them meaning the two particles—in the available three energy states.

MB $\quad Z = \frac{1}{N!} \sum e^{-\beta \epsilon_k}$

BE $\quad Z = \sum e^{-\beta \epsilon_k}$.

FD $\quad Z = \sum e^{-\beta \epsilon_k}$

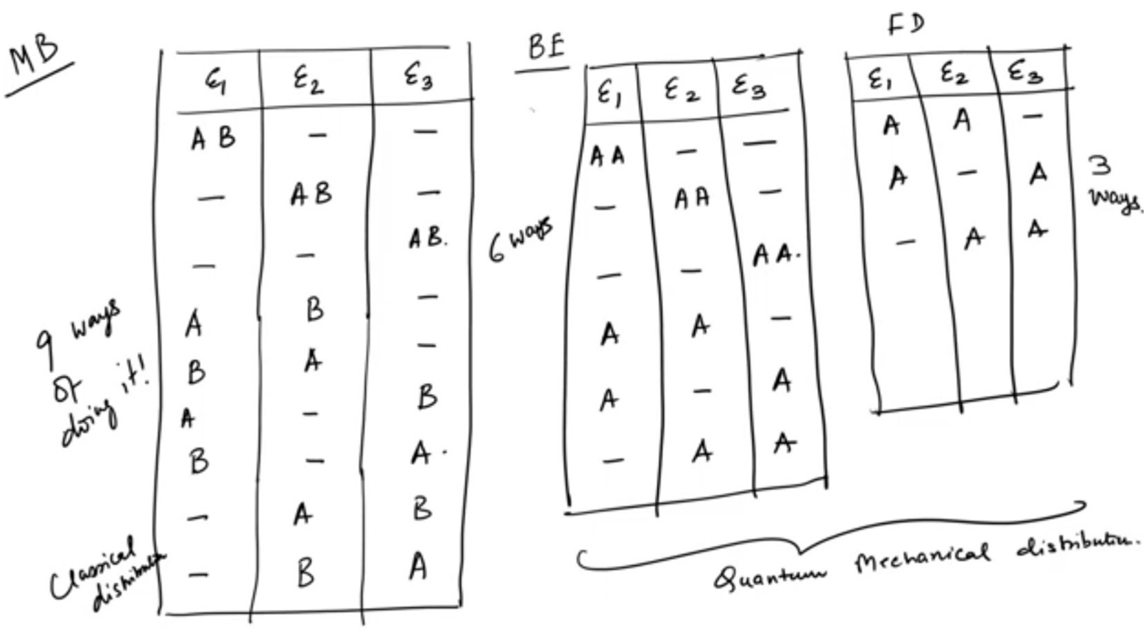
Example $\quad$ 2 particles, 3 energy states $\epsilon_1, \epsilon_2, \epsilon_3$.
(A, B.)
Distribute them in the available energy states.

All right, so this is the question that we have to deal with, and it is fairly simple. Let me just make a table to aid this discussion. So, we are talking about Maxwell-Boltzmann, where they are distinguishable, but the partition function will have a factor of 1 by n factorial—here, of course, n is 2. So, we have epsilon 1, epsilon 2, and epsilon 3, and these are like the slots or these are like the boxes in which we have to assign particles. And because they are distinguishable, we can write this as both of them in 1. That is epsilon 1, then it is epsilon 2, and then it is epsilon 3. Or we can have A in B and nothing here, or we can have BA and nothing here. We can have A, nothing here, and B here, or we can have B, nothing here, and A here, or we can have

Nothing here A and B, and nothing here under B and A; each of them is a distinct configuration for the problem. So, this is the total number of ways that it can be done. And as you can see, there are these 3 plus 4 plus 2, so there are 9 ways of doing it. Doing this distribution, and let me do it here for the B, and we sort of again make this thing, so there are these: epsilon 1, epsilon 2, and epsilon 3. Well, we are writing it slightly differently.

So, epsilon 1, epsilon 2, and epsilon 3, and now they are, of course, identical and indistinguishable. So, to take into account the indistinguishability, we will write both of them as A instead of A and B. But there is no restriction on the number of particles that can be assigned to a single energy state. So, one possibility is this; the other possibility is this. The third possibility is this; then we can have A, A, and nothing; you can have A, nothing, and A; and you can have nothing, A, A, okay.

So, clearly, there are six ways of doing it, okay, and do it on the same screen as for the FD case. And now, in addition to their indistinguishability, no two particles can occupy the same state. So, that sort of curtails the number. So, you have A, A, and nothing; A, nothing, A; and nothing, A, A; and hence there are three ways of doing it. So, see, there are a large number of ways of doing these distributions of particles among these three available energy states in the Maxwell-Boltzmann case because swapping the particles is treated as a distinct arrangement.



Like for these ones that you can see here, let me show it with the laser. So, you see AB and BA are two distinct ways. Similarly, you know here AB and BA are two distinct ways. However, they are not distinct in the quantum distribution. So, these are the classical distributions, and these two are the quantum mechanical distributions.

But we will show that both the quantum mechanical distributions that is both BE and FD distributions they actually boil down to the classical distribution either at large temperature or in presence of low density of particles. But let us first write down the partition function, so the canonical partition function We know that the canonical and the grand canonical are related, and you only have an extra factor, exponential beta mu, in the grand canonical distribution. It has to be properly incorporated. Okay.

But again, The grand canonical partition function really splits into or fragments into this exponential beta mu factor with this whole base to the power n, say for example, and then all these partition functions for the canonical case. So we have this as 1 by 2 factorial, and then it is an exponential minus 2 epsilon 1 plus exponential minus 2 epsilon 2 plus exponential minus 2 epsilon 3. plus twice of exponential minus—well, we are—this beta has to be there. So, let me write that beta here.

In fact, you should include that beta. So, it is beta into epsilon 1 minus epsilon. So, this is minus epsilon 1 plus epsilon 2. plus twice into x beta epsilon 1 plus epsilon 3 and plus twice of exponential minus beta epsilon 2 plus epsilon 3, and so on, okay. So, that is the distribution, and we have correctly divided by the number of particles, which is 2 here.

So, it is a 1 by 2 factorial. There are two distinct states or two distinct possibilities: one of them in epsilon 1, the other in epsilon 2, and vice versa. These were taken care of by the terms, the last three terms, which come with a factor of 2 because of this degeneracy. Okay. So, what is it for the B case, the Bose-Einstein?

As I have said, we do not need any factorial and factorial. So, we have an exponential minus 2 beta epsilon 1 plus exponential minus 2 beta epsilon 2, just like the Maxwell-Boltzmann case. And then it is exponential minus 2 beta epsilon. epsilon 3 plus there is a distinct state. So, it is exponential minus beta epsilon 1 plus epsilon 2 plus exponential minus beta epsilon 1 plus epsilon 3 plus exponential minus beta epsilon 2 plus epsilon 3.

So, these are the 6 terms that you get. there and for the FD it is simpler because you have only three possibilities and these three possibilities can be written as exponential minus beta epsilon 1 plus epsilon 2 plus exponential minus beta epsilon 1 plus 3 just maintaining the order in which we have written down this division of particles or distribution of particles. Plus exponential minus beta epsilon 2 plus epsilon 3. And that is the three canonical partition functions. So, you see that these are the different ways of distributing n particles in m available energy states.

So, if there are, say, m possible energy states instead of three, then let us write down how many states will be there or how many terms will be there. That is given by, this is for the fermions, for FD statistics, this will give rise to mc 2. So, let us call it NF. So, this will give rise to how many terms is what we are counting, and that is mc2.

So, that can be written as m into m minus 1 by 2. Which is nothing but m square by 2 minus M by 2. So, that is the number of particles, and if you are given an m, then you can just calculate this thing as m square by 2 and m minus m by 2. For BE, this NB is nothing but this is n Fermi plus m. So, this is m square by 2 because the number of two particle states for bosons would include all possible fermions and plus M states which have both particles in the same energy.

So, this is equal to m square by 2 minus m by 2 plus m. So, that gives you m square by 2 and a plus m by 2 instead of a minus m by 2. And similarly, for the m b distribution, so M B. So, this is n MB or classical; we can call it classical. Let us write it MB because C also stands for canonical. And this is equal to, you know, 1 by 2 factorial and N, which is classical.

$$Z_{MB} = \frac{1}{2!}\left[e^{-2\epsilon_1\beta} + e^{-2\epsilon_2\beta} + e^{-2\epsilon_3\beta} + 2e^{-\beta(\epsilon_1+\epsilon_2)} + 2e^{-\beta(\epsilon_1+\epsilon_3)} + 2e^{-\beta(\epsilon_2+\epsilon_3)} \right]$$

$$Z_{BE} = e^{-2\beta\epsilon_1} + e^{-2\beta\epsilon_2} + e^{-2\beta\epsilon_3} + e^{-\beta(\epsilon_1+\epsilon_2)} + e^{-\beta(\epsilon_1+\epsilon_3)} + e^{-\beta(\epsilon_2+\epsilon_3)}$$

$$Z_{FD} = e^{-\beta(\epsilon_1+\epsilon_2)} + e^{-\beta(\epsilon_1+\epsilon_3)} + e^{-\beta(\epsilon_2+\epsilon_3)}$$

If there 'm' possible energy states.

For FD $\quad n_F = {}^mC_2 = \frac{m(m-1)}{2} = \boxed{\frac{m^2}{2} - \frac{m}{2}}$

For BE $\quad n_B = n_F + m = \frac{m^2}{2} - \frac{m}{2} + m = \boxed{\frac{m^2}{2} + \frac{m}{2}}$

For MB $\quad n_{MB} = \frac{1}{2!}\, n_{classical} = \boxed{\frac{m^2}{2}}$

And this is equal to M square by 2. So in classical, it is just m square for M energy states, and because we have this Gibbs correction factor, that is 2 factorial, which is nothing but 2. But this is how these things work: for FD, you have m square minus m by 2; for bosons, you have m square by 2 plus m by 2; and for classical particles, you have m square by 2. So, these are the different ways of distributing particles and their corresponding canonical partition function. Now, let us derive the partition functions or, rather, the distribution functions, which we have not derived yet. So, we will write it as derivation of the distribution functions.

Derivation of the distribution functions.

$\bar{n}_i \,,\ \langle n_i \rangle$

$$E = \sum_i n_i \epsilon_i \quad , \quad N = \sum_i n_i$$

$$Z = \sum_{\{\}} e^{-\beta E} = \sum_{\{n_i\}} e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \cdots)}$$

We wish to calculate the average number of particles in a particular energy state —— Distribution function.

$$P = \frac{e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \cdots)}}{Z} \qquad \text{Boltzmann distribution.}$$

$$\langle n_i \rangle = \sum n_i P = \frac{\sum n_i e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \cdots)}}{Z}.$$

So, how do we derive it? I mean, it is not difficult to derive it. We just have to assume that the total energy is constant and remember that we are deriving it for the canonical sense or, rather, where the number of particles is constant, but it does not matter. You can just simply put a minus mu n, and we have told that a number of times that this grand canonical partition function and the canonical partition function. They are the same.

And then we'll see how these average number of particles or these distribution functions behave. By the way, the distribution function means that we want to calculate the average number of particles in a given energy state epsilon I. So, how many particles could be there? What is their distribution at a given temperature T? And this is called a distribution function. So, we calculate nothing but the average number of particles, and we know how to get the average number of particles from, say, for example, the partition function.

And this is what we will do. So, we assume that E is equal to some ni epsilon i and then there is a sum over i and also we have the total number of particles to be constant sum over i and we write down the partition function canonical partition function As we can just leave it, sum over whatever degrees of freedom that epsilon i has, and then we can write it as epsilon beta, and then we have this E, and this is equal to nothing but exponential minus beta. n1 epsilon 1 plus n2 epsilon 2, and so on and so forth. So, once again I just want to emphasize that this curly bracket that you see below the summation sign, I am not committing myself that what would be those summations over.

And that will depend upon the quantum numbers of the energy or the variables on the energy that it depends on and how those indices will take values. For example, now we can say that this is really a sum over ni because these n1, n2, they will take some values. pertaining to the condition that the total n i over all i should be equal to n. That is there. So, we want to calculate the mean number of particles. So, let me write that.

Mean or average—they mean the same thing. Particles in a given, in a particular energy state, and this is called a distribution function. Okay, so let me box it because this is an important thing. So, when one talks about a distribution, what does it mean? It means that we want the average number of particles that could be there in that in a given energy state so that that gives me an idea of internal structure of the system And finally, those internal structure will have to be translated to something that we get experimentally by doing thermodynamics, okay?

So, there is that internal structure or the microscopic structure is given by these distributions or these average values of these distributions, okay? So, the mean number of particles can be obtained by doing, you know, this P, where P is equal to that Boltzmann distribution. So, this is equal to N1 epsilon 1 plus N2 epsilon 2 and so on, divided by the canonical partition function. We have written this earlier; this is the Boltzmann distribution. is an important thing to notice that even the Wollman distribution as we have developed it belongs to classical physics, but this distribution at a given temperature T is equally applicable to classical and quantum statistics.

So, how do we calculate the mean number of particles, say ni? So, once again, I just want to make sure that sometimes I might have written it as ni bar and sometimes as this, but they really mean the same thing. Okay. So, throughout the course, if there is any of these symbols that you see, they would mean that average number of particles are being talked about. Okay.

So, this is equal to some, you know, again, this n i and that multiplied by p and this is nothing but, so, there is a n i and the exponential minus beta n 1 epsilon 1 plus n 2 epsilon 2, etc., etc., and then it is divided by z, okay. So, that is the average number of particles and that is what we want to calculate, okay. This is easy to calculate because we have already calculated something like this. It is 1 by z and then there is sum over these say ni's and there is a minus 1 by beta del del epsilon i and these exponential minus beta. n1 epsilon 1 plus n2 epsilon 2 and so on and then so this is that so 1 over z and this minus 1 by beta del del epsilon i and acting on this so that the epsilon i comes out and this is what rather the ni comes out sorry ni comes out and that is the expression that we you see it in the last line of this slide.

So, this is equal to that needs to be calculated and this is nothing but this is equal to 1 over minus 1 over beta z and nothing but a del z del epsilon i. So, n i then is equal to minus 1 by beta because this can be further simplified and can be written as del ln z del epsilon i okay. So, this is the formula for calculating the average number of particles and this is what we have seen earlier, right. So, you have the partition function, take the log of the partition function, take a derivative with respect to epsilon_i, and that would give you your average particle number, okay. So, this we will sort of use it for computing the distribution for all of these cases.

$$\langle n_i \rangle = \frac{1}{Z} \sum_{\{n_i\}} \left(-\frac{1}{\beta} \frac{\partial}{\partial \epsilon_i} \right) e^{-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + \cdots)}$$

$$= -\frac{1}{\beta Z} \frac{\partial Z}{\partial \epsilon_i}$$

$$\boxed{\langle n_i \rangle = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \epsilon_i}}$$

And let me just do it for the Maxwell-Boltzmann. Start from a new page here. So, we'll do it for the Maxwell-Boltzmann case. So Maxwell-Boltzmann, the distribution can be, you know, so the total partition function really for this non-interacting systems, they split into one particle partition function raised to the power n and Z1 is nothing but equal to, sum over i, say for example, exponential minus beta epsilon i. So, that tells you that log of z, which is equal to n log of z1, it is equal to n log of these things, exponential minus beta epsilon i.

So, that is the log of z. So, we got log of z and now go back to this expression that we have just derived which is you have to take this derivative with respect to epsilon 1 and that is the story that you have to follow. So, it is n i average is equal to minus 1 over beta del ln z del epsilon i. I write down the same expression once more and this is minus 1 beta 1 over beta and then there is a n and you have an exponential minus beta there is a minus beta. exponential minus beta epsilon i and then you have this as sum over i exponential minus beta epsilon i. So, I take a derivative with respect to epsilon i of this expression that you see above and then the beta minus beta comes out here and there are two minus signs okay so these two minus signs have to be you know written with care so this the minus signs will cancel and the beta will cancel as well and we get this as e to the power minus beta epsilon i divided by sum over i exponential minus beta epsilon i.

So, that is the distribution that you have and this is called as the Maxwell-Boltzmann distribution and if you want the distribution per particle then you can divide it by this. So, this average number of particles and if you divide it by the total number of particles writing Or if you simply, you know, work with the one particle partition function, then you will not get that n at all. Okay. So we implicitly sort of take care of that n and write it as exponential minus beta epsilon i and sum over i exponential beta epsilon i, assuming that we are working with.

Maxwell Boltzmann

$$Z = Z_1^N$$

$$Z_1 = \sum_i e^{-\beta \epsilon_i}$$

$$\ln Z = N \ln Z_1 = N \ln \left(\sum_i e^{-\beta \epsilon_i} \right)$$

$$\langle n_i \rangle = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \epsilon_i} = -\frac{1}{\beta} N \frac{(-\beta) e^{-\beta \epsilon_i}}{\sum_i e^{-\beta \epsilon_i}} = N \frac{e^{-\beta \epsilon_i}}{\sum_i e^{-\beta \epsilon_i}}$$

Dividing by the total number of particles.

$$\langle n_i \rangle = \frac{e^{-\beta \epsilon_i}}{\sum_i e^{-\beta \epsilon_i}}$$

(Assuming that we are working with the Single particle) the single particle partition function and why we can do that is that they are non interacting particles. So, there is no interaction between one particle with any other or any with the rest of the particles. So, we can deal with one of them and we can write down the we can write down the distribution function as this. So, this is called as the Maxwell Boltzmann distribution. Okay, so now we go to the Bose Einstein distribution.

Okay, so this distribution now will—so what we do is that we will split it up into a photon statistics. and a boson statistics, okay. They are the same things, of course—bosons, photons are bosons—but what we want to make sure is that one of them does not have a mu. This mu is equal to 0, and in general, mu is not equal to 0 for bosons, and in fact, it has to be positive. That is what we will see. But let us start with the photon statistics, which necessarily does not have a mu associated with it because we cannot keep the particle number constant, so that constraint completely goes away, and hence the Lagrange's undetermined multiplier goes away as well.

Okay, so we write down the photon statistics, and the way we can do it is that we write it down for—so our Z is equal to the summation over these ni's, and we have exponential minus beta n1 epsilon 1 plus n2 epsilon 2 plus and so on. So, you know, these n i's are really like 0, 1, 2, etc. for each of i's, for each i. Okay, and this sum has to be calculated, okay? And it is easy to see that this sum actually factorizes, and we can write down the partition function as n1, n2, and so on, and then exponential minus beta n1 epsilon 1 into exponential minus beta n2 epsilon 2 and so on, and all these brackets, okay.

Bose Einstein distribution.

(i) Photon statistics. $(\mu = 0)$

(ii) Bosons statistics. $(\mu \neq 0)$

(i) photon statistics.

$$Z = \sum_{\{n_i\}} e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \cdots\cdots)} \qquad n_i = 0, 1, 2 \ldots\ \text{for each } i$$

$$Z = \sum_{n_1, n_2 \ldots} \left(e^{-\beta n_1 \epsilon_1}\right)\left(e^{-\beta n_2 \epsilon_2}\right)\ldots$$

$$= \sum_{n_1=0}^{\infty}\left(e^{-\beta n_1 \epsilon_1}\right)\left(\sum_{n_2=0}^{\infty} e^{-\beta n_2 \epsilon_2}\right)\left(\quad\right)\ldots$$

And so, because of this factorization of the partition function, it is easy to evaluate it, and what one gets is the following. So, all these sums then I can write down as I can write down this as n1 equal to 0 to infinity and exponential minus beta n1 epsilon 1, then I open another one—this is n2 equal to 0 to infinity—exponential minus beta n2 epsilon 2, and all these brackets will simply, you know, be continued, and you have the product of the brackets, and if you can find out the product, then that is what you need. So, each term, if you see, is a GP series—each of the brackets that you see here is a GP series.

with the first term as 1 and the common ratio between the two is exponential minus beta epsilon i. Because between two successive terms, there is exponential minus beta i. So, that is a GP series. And geometric progression, we call it a GP series. And this GP series can be evaluated easily. And one gets the exponential minus beta n i epsilon i and over each of those n i equal to 0 to infinity as these 1 plus exponential minus beta epsilon i plus exponential minus 2 beta epsilon i and this is nothing but 1 divided by 1 minus exponential beta

epsilon i and of course my exponential minus beta epsilon i is less than 1 so this r the common ratio is less than 1 and that is why we can write it in this fashion. So the partition function the total partition function becomes all these brackets which are 1 minus exponential minus beta epsilon 1 1 divided by 1 minus exponential minus beta epsilon 2 and all of that, okay, for epsilon 3 and 4 and so on, okay. So, what you can do is that you can take a log of z and this is equal to minus log of, you know, so this is a product of this and log of 1 is equal to 0.

$$\sum_{n_i=0}^{\infty} e^{-\beta n_i \epsilon_i} = 1 + e^{-\beta\epsilon_i} + e^{-2\beta\epsilon_i} = \frac{1}{1-e^{-\beta\epsilon_i}}$$

$$Z = \left(\frac{1}{1-e^{-\beta\epsilon_1}}\right)\left(\frac{1}{1-e^{-\beta\epsilon_2}}\right)\left(\cdots\right)$$

$$\ln Z = -\sum_i \ln\left(1-e^{-\beta\epsilon_i}\right)$$

$$\langle n_i\rangle = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \epsilon_i} = \frac{1}{\beta}\frac{\partial}{\partial \epsilon_i}\ln\left(1-e^{-\beta\epsilon_i}\right)$$

$$= \frac{e^{-\beta\epsilon_i}}{1-e^{-\beta\epsilon_i}}$$

$$\boxed{\langle n_i\rangle = \frac{1}{e^{-\beta\epsilon_i}-1}} \longrightarrow \text{photon statistics.}$$

So, this is minus of log of 1 minus, exponential minus beta epsilon i and there is a sum over this i. So, that is the log of Z and now we know our prescription is clear that we need to calculate this thing by taking a derivative with respect to epsilon i in order to get the average number of particles in a given energy state. So, we get again n i average is equal to minus 1 by beta del ln z del epsilon i which is equal to 1 over beta. del del epsilon i log of 1 minus exponential minus beta epsilon i and this just one line it will give you exponential beta epsilon i divided by 1 minus exponential minus beta epsilon i. So, the photon statistics is this. exponential minus beta sorry so this is equal to that and your ns is equal to you can simplify this and you get you can divide numerator and denominator by exponential minus beta epsilon i so you get exponential minus beta epsilon i minus 1 and this is called as a photon statistics. In fact, this statistics was written down by Planck without a proper derivation later on Bose came and derived it and we have done the photon statistics.

Now, we will have to talk about bosons and like say for example, superfluid helium or helium-4 which are bosons with you know the number of electrons, protons and neutrons such that the total spin is an integer spin. So, there the thing that we need to take care of is we need to have a mu or the chemical potential in order to which really talks about fixing the number of particles or rather this condition that the total number of particles is a constant the total. number. So in order to incorporate that we need this mu which we have seen and we can simply you know write it here with put a bracket here and epsilon minus mu here. Let me show it by laser pointer.

So if you put a bracket here and put a minus mu that is going to work but then let us derive it for a better understanding. So, this is boson statistics and so we have a sum over i, n i average that should be equal to n. So now what we do is that we temporarily shift to the grand canonical distribution because the mu naturally originates there. We have seen that. So, we write down the ZG, which is nothing but the grand canonical partition function.

So, this is equal to this n1, n2, etc. from 0 to infinity, and we have these now the exponential of minus beta epsilon 1 minus mu. whole to the power n1 and exponential minus beta—well, this epsilon has to look the same—epsilon2. minus mu whole to the power n2 and so on all these brackets and we can write this down as a product term which is from i equal to 1 to infinity and we have all these brackets which are exponential minus you know beta epsilon i minus mu. And this hold to the power n i and we again get this product as 1 to infinity inside we can do a GP series sum and we get it at 1 minus Z F exponential minus beta epsilon i.

Boson statistics.

$$\sum_i \langle n_i \rangle = N.$$

$$Z_G = \sum_{n_1, n_2, \ldots = 0}^{\infty} \left[\exp\{-\beta(\varepsilon_1 - \mu)\}\right]^{n_1} \left[\exp\{-\beta(\varepsilon_2 - \mu)\}\right]^{n_2} \cdots\cdots$$

$$= \prod_{i=1}^{\infty} \left[\exp\{-\beta(\varepsilon_i - \mu)\}\right]^{n_i} = \prod_{i=1}^{\infty} \frac{1}{1 - z_f e^{-\beta\varepsilon_i}}$$

$$z_f = e^{\beta\mu}$$

$$\boxed{\langle n_i \rangle = \frac{1}{e^{\beta(\varepsilon_i - \mu)} - 1}.}$$

Bose Einstein distribution function.

You know that ZF is nothing but equal to exponential beta mu. So, combining this, we can write down this n_i average. Now, you know the prescription; we have done it a number of times. So, this can be written as exponential e to the power beta epsilon i minus mu minus 1, and this is called the Bose distribution function, or it is for Bosons, or it is also called the Bose-Einstein distribution function.

OK. And so, that's the average number of particles in a given energy state. And we have beta equal to 1 over KT. And this ZF, as you see here, is called the fugacity. And then, that is your distribution.

OK. So now, finally, let us do the Fermi-Dirac distribution. We will show all these distributions—the plots of this distribution as a function of, you know, epsilon minus mu or something—separately. We will do that in just a while after we do the Fermi-Dirac statistics. So here, keep in mind that Ni cannot be anything, but Ni can be either 0 or 1.

Either a single particle state will have no particles at all which is acceptable or at the most it can have one particle. So, this expression that you have which is equal to sum over ni, ni into exponential minus beta ni epsilon i divided by exponential beta epsilon ni epsilon i and all these are like ni's and so on. So, this has just two terms. So, n i is equal to 0 and 1 as I just wrote here. So, put

n i equal to 0 and 1 and what we get is so we have these the two terms they are so you have this okay so this n i equal to 0 and 1 is exponential minus beta n i epsilon i with n i factor here so this is 0 plus exponential minus beta epsilon i 0 plus epsilon i and then n i average will simply be equal to exponential minus beta epsilon i divided by 1 plus exponential minus beta epsilon i. you divide it by this things which will give you this 1 plus exponential minus beta epsilon i. If you divide top and bottom by exponential minus beta epsilon i, we have exponential minus beta epsilon i plus 1. And we will simply put this mu by hand here. So, we can just simply write it as mu.

And so, this is put by hand. Chemical potential. So, Ni becomes equal to Let me write it here, n i average is equal to 1 by exponential minus beta epsilon i minus mu plus 1 and that is called as the Fermi Dirac distribution function. sorry, there is this minus will not be there because you have divided by exponential minus beta epsilon i. So, this becomes exponential plus beta epsilon i. So, this is called as a Fermi-Dirac distribution function.

Fermi Dirac statistics.

$$n_i = 0, 1$$

$$\langle n_i \rangle = \frac{\sum_{n_i} n_i e^{-\beta n_i \epsilon_i}}{\sum_{n_i} e^{-\beta n_i \epsilon_i}}$$

Put. $\boxed{n_i = 0, 1.}$

$$\boxed{\langle n_i \rangle = \frac{1}{e^{\beta(\epsilon_i - \mu)} + 1}}$$

Fermi-Dirac distribution function.

$$\sum_{n_i = 0, 1} n_i e^{-\beta n_i \epsilon_i} = 0 + e^{-\beta \epsilon_i}$$

$$\langle n_i \rangle = \frac{e^{-\beta \epsilon_i}}{1 + e^{-\beta \epsilon_i}} = \frac{1}{e^{\beta(\epsilon_i - \mu)} + 1}$$

Put by hand

So, we have derived all these three distribution functions, which gives you the difference, you know, in the sense that the Bose distribution is, the Maxwell-Boltzmann distribution is simply exponential minus beta epsilon i. This is equal to 1, the denominator is equal to 1. So, it is simply exponential minus beta epsilon i and or you can put in the so you can also write it as n i which is equal to exponential minus beta epsilon i minus mu. So, now we have put it by hand. So, we would use this as a distribution now assuming this you know the particle number to be not constant or rather the total particle number to be constant.

So that mu enters into the problem. So it is exponential minus beta epsilon i minus mu. Then for the photon statistics is exponential 1 divided by exponential beta epsilon i. Once again, I do not have a minus sign. Let me just, yeah, so there is no minus sign there. Of course, you divide it by exponential minus beta epsilon i.

So, this gives rise to the photon statistics and this where there is no mu or mu is identical equal to 0 when we are talking about other kinds of bosons which that follow these statistics that they are identical but any number of particles can occupy any given energy state. And this is called as a Bose-Einstein distribution function, which is exponential 1 by exponential beta epsilon minus mu. minus 1 and and then we finally have the Fermi Dirac distribution function which is exponential beta epsilon i minus plus 1 minus mu plus 1 and so we can just write all of these distribution as n i is equal to 1 divided by exponential beta epsilon i minus mu plus minus a where a is equal to 0 for Maxwell-

Bolman distribution and a equal to minus 1 or rather a is equal to or we can just simply write it with a plus a not plus minus. So, it is for BE distribution

A is minus 1 and A equals plus 1 for the FD distribution, okay. So, that is the sort of writing it in a unified form, this distribution function, and we will see how these distribution functions are very important because we need to know the average number of particles and so on, okay. So, it is important to understand that for bosons, you know, you can have these—the mu has to be greater than 0 because otherwise, you will have negative occupancies or negative average number of particles, which does not make sense.

So, for bosons, epsilon—or rather, epsilon i minus mu—should always be greater than 0, or rather, mu should be greater than 0, which means now these epsilon i are the single-particle states. So, the epsilon i's take values, and we are talking about a non-interacting gas or non-interacting system. So, epsilon i's actually take values from 0 to infinity, and mu has to be greater than 0. So, that is an important thing that is additionally required.

So, with this, let us do the fluctuation in the number of particles. So, fluctuation on this Ni—whether all these fermions or bosons or classical particles—they like fluctuations, or what are their fluctuations, etc. So, what we mean—what we want—is that fluctuations in this particle number And we are really talking about the sigma squared equal to this n i squared minus n i average squared. So, n i squared average and n i average squared.

Now, we just got n_i average for all these distributions, but getting n_i square average is not difficult. You just have to take a double derivative with respect to epsilon_i of those distribution functions. And let us just do it in the grand canonical distribution. So, n i square is nothing but equal to 1 over ZG.. minus 1 over beta and there is a del del epsilon i square and a ZG and it is at a given fugacity and temperature.

$$\boxed{\langle n_i \rangle = \frac{1}{e^{\beta(\varepsilon_i - \mu)} + a}}$$

$a = 0$ for MB.
$a = -1$ for BE.
$a = +1$ for FD.

Fluctuations in the number of particles.

$$z_f = e^{\beta\mu}$$

$$\sigma^2 = \langle n_i^2 \rangle - \langle n_i \rangle^2$$

$$\langle n_i^2 \rangle = \frac{1}{Z_G} \left(-\frac{1}{\beta} \frac{\partial}{\partial \varepsilon_i} \right)^2 Z_G \Big|_{z_f, T}$$

So, ZF is again exponential beta mu. I am just using the relation that was derived earlier. and in fact this is quite useful to do that and so we get this as the sigma square as its n i square average minus n i average square and this is equal to minus 1 over beta del del epsilon i square log of ZG and ZF T and this is nothing but equal to minus 1 over beta del del epsilon i. I am just skipping a couple of steps which you can fill up. It is easy to see that and this is equal to ni and this is at a ZF and T and this is equal to exponential

beta epsilon i minus mu this divided by these exponential beta epsilon i minus mu plus a square. And you know what this A is: A equal to 0 for Maxwell-Boltzmann, A equal to minus 1 for Bose-Einstein, and plus 1 for Fermi-Dirac statistics or the particles. So these are n i squared is equal to exponential beta into epsilon i minus mu. and this is nothing but equal to 1 over ZF exponential beta epsilon i and this is nothing but equal to 1 by n i average minus a, okay.

So, the relative fluctuation again is inversely proportional to this average number of particles which it should be and so we have this sigma square by n i square, this is equal to 1 over n i For this, it is called the MB particles, and this is called the normal distribution. This is the normal distribution. where it's simply equal to 1 by ni average, which is a result that we have seen earlier, and then sigma squared by ni average squared, and you have a BE, which is 1 by ni plus 1 and this is called as the super normal distribution because this plus 1 that is why it is called super normal distribution and this for the other thing that is for the FD it is ni square is equal to or for the FD.

$$\sigma^2 = \langle n_i^2 \rangle - \langle n_i \rangle^2 = \left(-\frac{1}{\beta}\frac{\partial}{\partial \epsilon_i}\right)^2 \ln Z_G \Big|_{z_f, T}.$$

$$= -\frac{1}{\beta}\frac{\partial}{\partial \epsilon_i}\langle n_i \rangle\Big|_{z_f, T} = \frac{\exp\{\beta(\epsilon_i - \mu)\}}{\left(\exp\{\beta(\epsilon_i-\mu)\} + a\right)^2}$$

$$\frac{\sigma^2}{\langle n_i \rangle^2} = \exp\{\beta(\epsilon_i - \mu)\} = \frac{1}{z_f}\exp\{\beta \epsilon_i\}.$$

$$= \frac{1}{\langle n_i \rangle} - a.$$

$$\frac{\sigma^2}{\langle n_i \rangle^2}\Big|_{MB} = \frac{1}{\langle n_i \rangle}. \; ; \quad \frac{\sigma^2}{\langle n_i \rangle^2}\Big|_{BE} = \frac{1}{\langle n_i \rangle} + 1 \; ; \quad \frac{\sigma^2}{\langle n_i \rangle^2}\Big|_{FD} = \frac{1}{\langle n_i \rangle} - 1$$

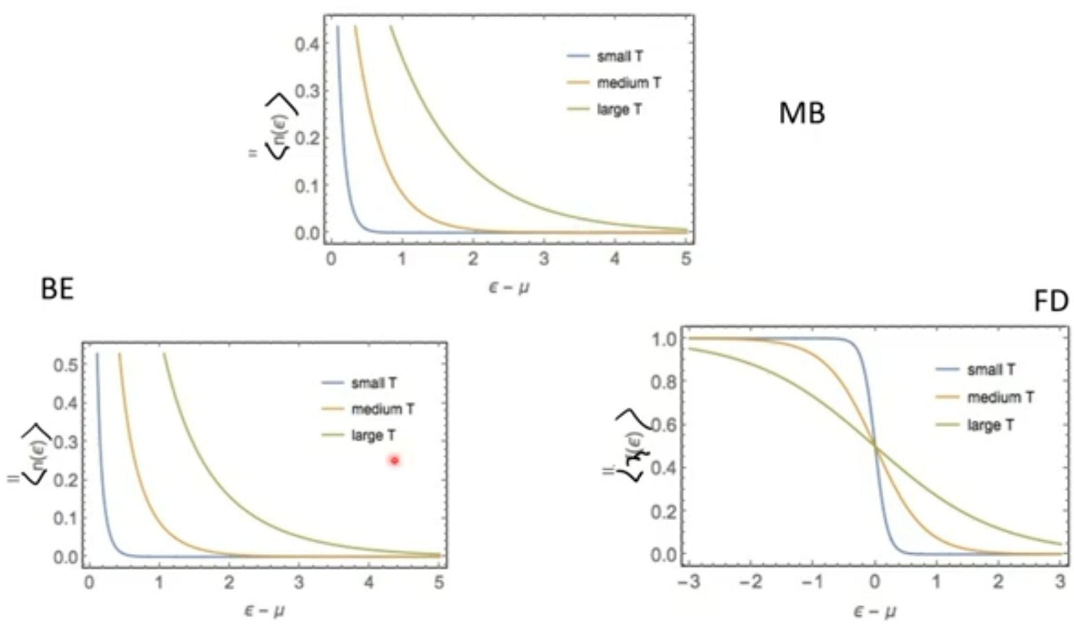
(normal distribution) (Super-normal) (Sub-normal)

This is equal to 1 by ni minus 1 and this is called as the subnormal distribution. Independent of the name, what it rather says is that the bosons actually promote fluctuations. In fact, if there are large number of particles in one given energy state, it will favor fluctuations or rather enhance fluctuations. And so that is why you see a super normal distribution for the sigma square by ni square. Whereas this hardcore condition, hardcore means this Pauli exclusion principle is often called as a hardcore which means that one particle does not like another particle and they strongly repel each other and it is not a possibility that two particles will occupy the same energy state.

That's the that's the distribution of that's the statistics. And that gives rise to a sort of these subnormal distribution. In fact, some of the experiments actually calculate or rather compute these some of these functions. Fluctuations in the particle number. Say, for example, the Hanbury Brown-Twiss experiment that looks at the particle number distribution for photons, okay.

We will not go into details, but there are experimental ways of determining that, okay. So, let me now quickly tell you that what are the classical limits, but before that let me show you this picture that we have. So, this is how the Maxwell Boltzmann distribution looks like where we are really talking about this average number of particles that is there well I mean this average number of particles and so on. So, the Maxwell-Boltzmann, it looks like that as a function of epsilon minus mu, you have the number of particles to increase as you go to epsilon closer to mu or epsilon minus mu going to 0. And in fact, the Bose distribution looks exactly the same, almost same.

It is only that as you come closer and closer to epsilon minus mu, There will be a large buildup of particles which is called as a Bose-Einstein condensation which is what we will see. So, these blow up is what we are talking about and there is a similar you know distribution or rather plot for as a function of epsilon minus mu. And these average particle number is also written as F at times you know, so that is some books will write it as F. So, they will show you this as the Maxwell Boltzmann and Bose Einstein which look very similar. And it is only that the Fermi Dirac looks absolutely dissimilar to the two, but there is one big similarity which one should notice.



is that as at the large, you know, the tail of that for each of the distributions, they are identical, which tells you that at large temperature or at large, you know, epsilon minus mu. So there has to be a beta factor that will make you understand this better. But in any case, we will show that the tail of the distribution that at very large values of epsilon minus mu, all these distributions give rise to same results, which means that as you go to larger and larger temperature or as you go to lower and lower density of particles, the quantum gases start behaving like the classical gases. They become distinguishable and the indistinguishability kind of fades out. and they start following the Maxwell-Boltzmann statistics.

So you see there is a nice taper-like function for very small t, and at t equal to 0, it is exactly a step or a very sharp step. And that tells you that all states which are in the negative epsilon minus mu, they are all occupied and all states which are greater than epsilon, these epsilon minus mu or epsilon minus mu equal to 0, they are unoccupied. But as you go larger and larger in temperature, there is these distributions kind of tapers down with more weight appearing in the larger energy regime. However, that happens at very high temperatures, okay? I mean, we have left it as small, medium, and large, but this large is enormously large because the temperature that we need for the distribution to fall to a value of half is very large—the actual value is very large, okay? And just to give you an idea of what a large number means, for example, for typical metals like copper or aluminum and so on, the Fermi temperature, which we will define later as a temperature corresponding to this epsilon minus mu equal to 0.

That Fermi temperature is of the order of 60-70,000 Kelvin. And you can understand that nothing can survive on Earth at that temperature. But that is the Fermi temperature. That is the scale of temperature for degenerate Fermi systems. So we will discuss the classical limit.

And what is the classical limit? So we write it down once again for the quantum distribution, now we do not need to write down the Maxwell Boltzmann, we will write only Bose-Einstein and Fermi Dirac which is e to the power beta epsilon i minus mu plus or minus 1, we know plus sign is for fermions and minus is for bosons. Okay, so this is the distribution—the average number of particles. So at low temperature or large beta, what happens? For fermions,

n i average is equal to 1, I mean it can be either 1 or 0, but only if epsilon i is less than mu, so low energies. So, we are talking about large beta or small temperature and for fermions it is equal to 0 if epsilon i is greater than mu, okay, so these large energies. Now for bosons, we have a similar thing excepting that this is equal to much much greater than 1 for low energies and this is almost equal to 0. for large energies, okay. So, it is the same thing for large energies, both the distribution they kind of give you 0.

But at low energies, one gives you 1, which is natural and the other gives you much greater than 1, okay. So, the bosons or rather the Maxwell-Boltzmann statistics, Ni is always much, much smaller than 1, okay. So, for MB particles, Ni is always much, much smaller than 1, okay. So the classical case corresponds to exponential beta epsilon i minus mu minus mu that should be much much greater than 1 for all i. Right?

Discussion on the classical limit.

$$\langle n_i \rangle = \frac{1}{e^{\beta(\epsilon_i - \mu)} \pm 1} \qquad \begin{array}{l} + : \text{ fermions.} \\ - : \text{ bosons.} \end{array}$$

At low temp (large β)

(i) for fermions $\langle n_i \rangle \simeq 1$ if $\epsilon_i < \mu$. (low energies)

$\langle n_i \rangle = 0$ if $\epsilon_i > \mu$ (large energies)

(ii) for bosons. $\langle n_i \rangle >> 1$ (low energies)

$\langle n_i \rangle \simeq 0$ (large energies)

for MB particles $\langle n_i \rangle << 1$:

Because it is only in that case that the one in the denominator would not matter and it is anyway much greater than this the first term would be much greater than the second term and then we can go back to the classical distribution. So, this is naturally the limit for the classical case. So, that tells you that ZF which is equal to exponential beta mu should be much, much smaller than 1 for this classical case to occur. So, we, let us try to derive it.

So, if you remember that log of ZG, either it is FD or BE, okay, so this is equal to plus minus sum over I log of 1 plus, plus minus exponential. Exponential minus beta epsilon i minus mu. So that is the log of ZG, and so we may actually calculate this expansion by noting that the plus sign is for fermions here and the minus sign is for bosons. Okay, so if you expand this above expression in a small parameter, a small exponential beta mu, because this is what we have just shown: that the exponential beta mu must be much much smaller than 1.

Classical case corresponds to

$$\exp\left[\beta(\epsilon_i - \mu)\right] >> 1 \quad \text{for all } i$$

$$z_f = e^{\beta\mu} << 1$$

$$\ln Z_G^{FD,\,BE.} = \pm \sum_i \ln\left\{1 \underset{\text{bosons.}}{\overset{\text{fermions}}{\pm}} \exp\left[-\beta(\epsilon_i - \mu)\right]\right\}$$

Expanding above for small $e^{\beta\mu}$

$$\ln x = x - \frac{x^2}{2} + \frac{x^3}{3} + O(x^4) .$$

If you do that and note that the log of x for x to be small is x minus x squared by 2 plus X cubed by 3 plus order x to the power 4 and so on. So, if you keep the first few terms for small x, then this log of ZG for FD and BE, this expansion can be written as log sum over i exponential minus beta epsilon i minus mu and a minus plus half of sum over i minus plus because initially the plus sign was for fermions and minus for bosons, but then the first term in the expansion is minus, so it sort of acquires another minus sign. So for fermions it is minus, and for bosons it is plus. So the top one is for fermion and the bottom one is for bosons, okay.

So, this is understandable, and this is exponential minus 2 beta epsilon i minus mu and so on, okay. These are the other terms, so which we neglect. So that is the log of ZG, and then of course your Ni for FD and BE they can also be expanded, so exponential minus beta epsilon i minus mu and then there is a 1 minus plus exponential minus beta epsilon i minus mu and so on, okay. So, this and plus this and so on, okay.

So, you see that we have expanded both the log of the partition function, grand canonical partition function and as well the distribution for small fugacity that is ZF to be much smaller than 1 and we get these expressions. So, the dominant term in the expression is what we need to deal with. So, for the log of ZG, the dominant term or the leading term is equal to the classical case. So, this classical term will give rise to a summation over i of exponential minus beta epsilon i minus mu.

$$\ln Z_G^{FD,BE} = \sum_i \exp\left[-\beta(\epsilon_i - \mu)\right] \mp \frac{1}{2}\sum_i \exp\left[-2\beta(\epsilon_i - \mu)\right] + \cdots$$

$$\langle n_i \rangle_{FD,BE} = \exp\left[-\beta(\epsilon_i - \mu)\right]\left\{1 \mp \exp\left[-\beta(\epsilon_i - \mu)\right] + \cdots\right\}$$

Dominant term ≡ classical case.

$$\left.\begin{aligned} \ln Z_G^{cl} &= \sum_i \exp\left[-\beta(\epsilon_i - \mu)\right] \\ \langle n_i \rangle_{cl} &= \exp\left[-\beta(\epsilon_i - \mu)\right] \end{aligned}\right\} \text{MB distribution.}$$

So, that is the classical case. We know that, and this n i classical again is equal to the exponential minus beta epsilon i minus mu and you know that these are nothing but coming from the MB distribution and everything makes sense that we at very small fugacity when the exponential beta mu is much much smaller than one you can do this expansion of the logarithms and these give you these expressions for the classical case or the Maxwell-Boltzmann case. So, if you take a particular scenario, that is, your epsilon i, which are the single-particle states, now I put epsilon k Epsilon i is equal to epsilon k because we have never specified the quantum number or the correct, you know, sort of quantity that expresses the single-particle energies. Let us specify this as epsilon k in this case, where k is the momentum.

And let us consider the free-particle partition function, or rather the energy, which is written as h cross square by h cross square k square by 2m. So, we are talking about the single-particle energies. So, log of ZG, let me see what we wrote classical here. So, classical is equal to I can do a So, and this is exponential minus beta h cross square k square over 2m minus mu, where m is the mass of the particle, and this is a d. You can write it as d cube k, or sometimes it is written as dk as well with a vector sign; they mean the same thing, okay.

So, you need to integrate over all k and again this is a very simple Gaussian integral and one gets it as V by 2 pi whole cube and exponential of beta mu and 2 pi m by beta h cross square and whole to the power 3 by 2. And if you want, you know, there are some other multiplicities, such as 2s plus 1 for the spin, to get in; all those things can be added, but they do not need to be here. So, we write this down as V over 2 pi whole cube. and ZF and a 2 pi m by beta h cross square by 3 by 2.

And so, this is for small ZF, ZF to be much smaller than 1, you get the log of ZG. And why we are writing the log of ZG would be clear just in a while, or rather in the next class, because this log of ZG is actually related to the thermodynamic parameter, which is PV over KT, and we will see that. that this equation of state really comes in. And the average number of particles, what will happen to that, or rather if you take this, then this is equal to a ZF del del ZF. I am using results that we have already, so ZG and classical.

$$\varepsilon_i = \varepsilon_k = \frac{\hbar^2 k^2}{2m}$$

$$\ln Z_g^{cl} = \frac{V}{(2\pi)^3} \int \exp\left[-\beta\left(\frac{\hbar^2 k^2}{2m} - \mu\right)\right] d^3k \leftarrow d\vec{k}$$

$$= \frac{V}{(2\pi)^3} \exp(\beta\mu) \left(\frac{2\pi m}{\beta\hbar^2}\right)^{3/2}.$$

$$= \frac{V}{(2\pi)^3} z_f \left(\frac{2\pi m}{\beta\hbar^2}\right)^{3/2}.$$

$$\left\langle \sum_i n_i \right\rangle = z_f \frac{\partial}{\partial z_f} \ln Z_g^{cl} = \frac{V}{(2\pi)^3} z_f \left(\frac{2\pi m}{\beta\hbar^2}\right)^{3/2} = N.$$

For this, we have a V by 2 pi whole cube and ZF 2 pi m by beta h cross square. whole to the power 3 by 2, and that should be equal to the total N, okay. And so we have taken this average number of particles and sum over all the energy states, and we know that the total number of particles will have to be N, so this is equal to N, okay. So, then what happens is that now we can take this expression and rather calculate this ZF here from this expression. So, we can calculate ZF because this fugacity is an important quantity in our discussion, and then the ZF comes out to be 0.

is equal to e to the power beta mu is equal to N over V h cube divided by 2 pi m kT whole to the power 3 by 2. Since ZF is much much smaller than 1, so classical limit would correspond to N over V that is the right hand side should also be much less than 1 and something that we have seen earlier is much smaller than 1. So, if you really think that this N by V or V by N, so V by N that is the total volume divided by the total number of particles is equal to something like A cube. Okay.

That's think of these, you know, the atoms or the molecules that are filling up this entire n number of them filling up the entire volume. And if you think of them as cubes, then it's just a cube equal to V by n. But if you think them as hard spheres, then it is, of course, there's a four third pi factor there, but we don't really worry about that. So, this is of the order of A cube or V over N whole to the power one third is like A. So, A is nothing but the interatomic or intermolecular distance. So that brings us that if you you know define lambda or sometimes it is written as lambda t let me write it with a lambda t which is equal to this is by this 2 pi m k t then that gives us so this is called as a thermal de Broglie wavelength. if you open up everything it has the dimension of length or wavelength.

$$z_f = e^{\beta\mu} = \frac{N}{V}\frac{h^3}{(2\pi m k_B T)^{3/2}}$$

Since $z_f \ll 1$, classical limit corresponds to.

$$\frac{N}{V}\frac{h^3}{(2\pi m k_B T)^{3/2}} \ll 1.$$

$$\frac{V}{N} = a^3 \quad \text{or} \quad \left(\frac{V}{N}\right)^{1/3} = a. \quad : \text{interatomic/intermolecular distance.}$$

$$\lambda_T = \frac{h}{\sqrt{2\pi m k_B T}} \quad \text{Thermal de-Broglie wavelength.}$$

So, A which is V over N whole to the power one-third must be much much greater than lambda. So, that tells you that the classical statistics dominates either at low densities that is particle densities at large temperatures And if both go in hand in hand, then of course, it is all the more better than the both the quantum statistics, they boil down to classical statistics. And that is what we have seen in the picture as well.

$$a = \left(\frac{V}{N}\right)^{1/3} >> \lambda$$

Classical Statistics dominates

(i) at low densities.

(ii) at large temperature.

Here you see that in the large energy regime, we can also, as I said, have the x-axis represented as beta times epsilon minus mu. They would all give you the same n_i, or rather the average of n, to be much, much smaller. So, we have derived the distributions. We now know that the quantum distributions have a classical limit, which merges with the MB distribution, with the Gibbs correction correctly taken into account. So, in a way, it appears that identical, indistinguishable particles lose their indistinguishability and become distinguishable at these low densities and large numbers of particles.

We will stop here and continue from the next class onward. Thank you.