Introduction to Statistical Mechanics

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Module No # 01
Lecture No # 04

Bose and Fermi Gases

Okay let us continue, if you recall we left off here where we prove that the entropy is an extensive function of its independent variables namely the total internal energy, volume and number of particles. So we have called this the fundamental relation of thermodynamics ,so what I want to do now is to see if I can go ahead and calculate this entropy function for specific examples.

So specifically I am talking about the entropy of ideal quantum gases, so just to point out that the, if you recall we had studied in quite significant detail the problem of you know marbles on a staircase. So specifically I have in mind an infinite staircase so imagine that there are N number of identical marbles on a infinite staircase. So I have already told you that identical particles is a characteristic feature of quantum mechanics.

So specifically in the case of marbles I have also suggested that there is no restriction on how many marbles can be placed on a single step. So this is an example of what are called Bosonic particles, so in quantum mechanics so when there is no restriction on how many particles can occupy certain energy levels that is called those particles are known as bosons and they are also non interacting particles in the sense that the energy of a certain level is an intrinsic property of that step.

It is not related to how many bosons are sitting on that step so this would not be the case for example if the bosons or the marbles had some kind of energy by virtue of the fact that there are other marbles next to it. So if that were the case then the energy of the marbles on the step would not be proportional to the number of marbles on the step so we are going to disregard this aspect and we are going to assume that if there is one marble per step.

So if so in other words then the energy of a step is just proportional to the number of marbles and the proportionality constant is independent of how many marbles there are. So this example would be called ideal Bose gas, an ideal collection of bosons specifically. So suppose you wanted to describe fermions, ideal fermions what you have to do is instead of you know saying that I do not restrict the number of bosons on each step.

You say that there is a severe restriction namely there is a maximum of one particle allowed per step. So in other words a step can accommodate either no particles at all or exactly one particle and no more. So in such a case the system that you would be describing is called an ideal Fermi gas ok. So now let me recall that we had started off I mean we had reached this point where we had tried to evaluate the entropy using the saddle point method.

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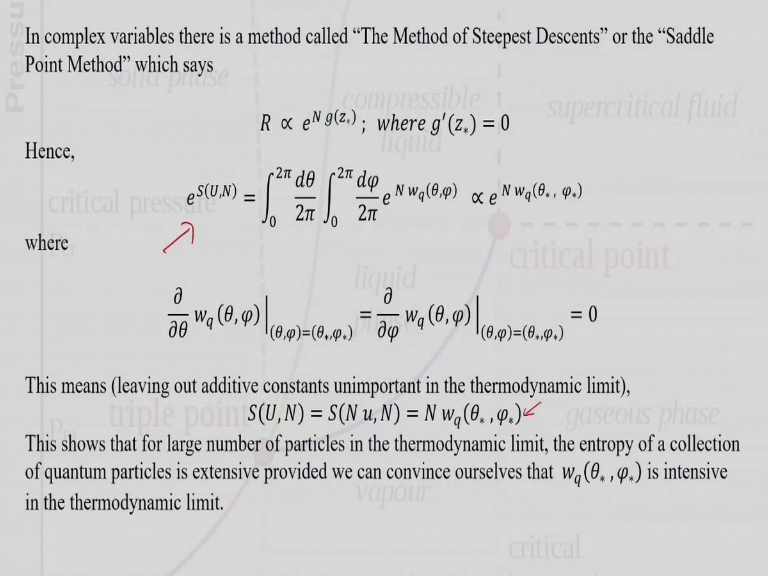

In complex variables there is a method called "The Method of Steepest Descents" or the "Saddle Point Method" which says

$$R \propto e^{N\,g(z_*)}\,;\ where\ g'(z_*) = 0$$

Hence,

$$e^{S(U,N)} = \int_0^{2\pi}\frac{d\theta}{2\pi}\int_0^{2\pi}\frac{d\varphi}{2\pi}\,e^{N\,w_q(\theta,\varphi)} \propto e^{N\,w_q(\theta_*,\,\varphi_*)}$$

where

$$\frac{\partial}{\partial\theta}w_q(\theta,\varphi)\Big|_{(\theta,\varphi)=(\theta_*,\varphi_*)} = \frac{\partial}{\partial\varphi}w_q(\theta,\varphi)\Big|_{(\theta,\varphi)=(\theta_*,\varphi_*)} = 0$$

This means (leaving out additive constants unimportant in the thermodynamic limit),

$$S(U,N) = S(N\,u,N) = N\,w_q(\theta_*\,,\varphi_*)$$

This shows that for large number of particles in the thermodynamic limit, the entropy of a collection of quantum particles is extensive provided we can convince ourselves that $w_q(\theta_*\,,\varphi_*)$ is intensive in the thermodynamic limit.

So we had reached this stage where we said that the entropy function is nothing but the saddle point value of this function W_q. So what I want to do in this lecture is I want to explicitly evaluate this for an ideal Bose gas and for an ideal Fermi gas. So I want to explicitly evaluate the entropy function for an ideal Bose gas and an ideal Fermi gas so let us see how to do that.

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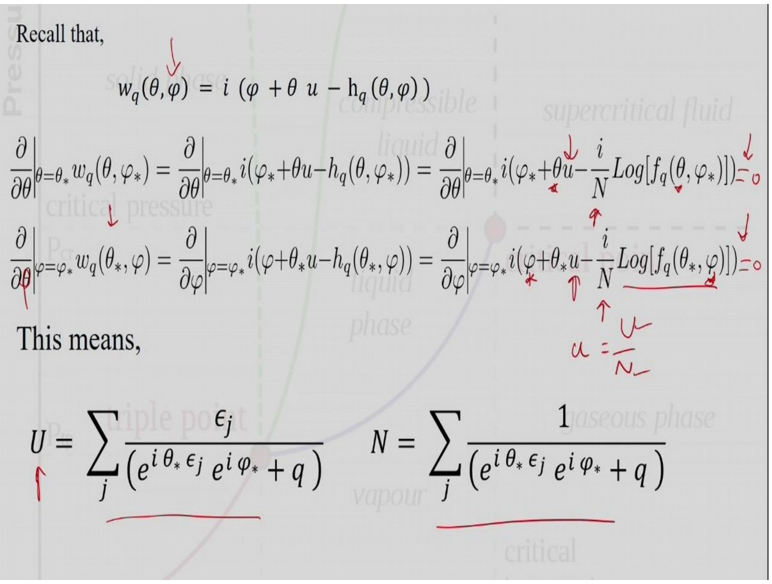

Recall that,

$$w_q(\theta,\varphi) = i\ (\varphi + \theta\ u - \mathrm{h}_q(\theta,\varphi))$$

$$\left.\frac{\partial}{\partial\theta}\right|_{\theta=\theta_*} w_q(\theta,\varphi_*) = \left.\frac{\partial}{\partial\theta}\right|_{\theta=\theta_*} i(\varphi_*+\theta u-h_q(\theta,\varphi_*)) = \left.\frac{\partial}{\partial\theta}\right|_{\theta=\theta_*} i(\varphi_*+\theta u-\frac{i}{N}Log[f_q(\theta,\varphi_*)]) = 0$$

$$\left.\frac{\partial}{\partial\theta}\right|_{\varphi=\varphi_*} w_q(\theta_*,\varphi) = \left.\frac{\partial}{\partial\varphi}\right|_{\varphi=\varphi_*} i(\varphi+\theta_* u-h_q(\theta_*,\varphi)) = \left.\frac{\partial}{\partial\varphi}\right|_{\varphi=\varphi_*} i(\varphi+\theta_* u-\frac{i}{N}Log[f_q(\theta_*,\varphi)]) = 0$$

$$u = \frac{U}{N}$$

This means,

$$U = \sum_j \frac{\epsilon_j}{(e^{i\,\theta_*\,\epsilon_j}\ e^{i\,\varphi_*} + q\,)} \qquad N = \sum_j \frac{1}{(e^{i\,\theta_*\,\epsilon_j}\ e^{i\,\varphi_*} + q\,)}$$

So the way you can do that is that you start with this definition of W and then you just try and see if you can first solve for the values of φ^* and θ^* and recall that those values are the ones that make the W an extremum, so in other words it is the saddle point itself. So θ^*,φ^* is precisely the saddle point and the value of W_q at the saddle point is proportional to the entropy function.

So now if you go ahead and evaluate this and remember that you have to set this equal to 0 in order to be describing the saddle point and then what you do is that you will be able to convince yourself that the total internal energy and total number of particles are going to be of this form. So now recall that we had defined the function that whose saddle point we have to find as W_q and the entropy function was nothing but the number of particles times this W_q at the saddle point.

Now in order to find the saddle point what you have to do is take this function and find the extremum, in other words the first derivative with respect to this parameter called θ has to be set to 0 and first derivative of this parameter W again, with respect to this with this functions sorry this is $\varphi = 0$. So when you do that you see is that you will be able to derive a formula for this. So you can eliminate this rather you can express U and N so notice that think of this as your unknowns and there are two unknowns and two equations and this f was derived earlier.

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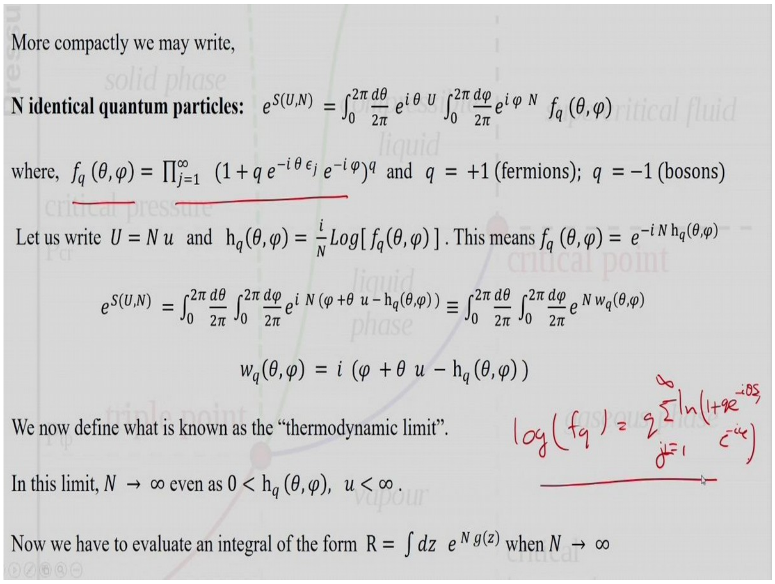

More compactly we may write,

N identical quantum particles: $e^{S(U,N)} = \int_0^{2\pi} \frac{d\theta}{2\pi} e^{i\,\theta\,U} \int_0^{2\pi} \frac{d\varphi}{2\pi} e^{i\,\varphi\,N}\; f_q\,(\theta,\varphi)$

where, $f_q\,(\theta,\varphi) = \prod_{j=1}^{\infty}\;(1 + q\,e^{-i\,\theta\,\epsilon_j}\,e^{-i\,\varphi})^q$ and $q\; = +1$ (fermions); $q\; = -1$ (bosons)

Let us write $U = N\,u$ and $h_q(\theta,\varphi) = \frac{i}{N} Log[\,f_q(\theta,\varphi)\,]$. This means $f_q\,(\theta,\varphi) = e^{-i\,N\,h_q(\theta,\varphi)}$

$$e^{S(U,N)} = \int_0^{2\pi} \frac{d\theta}{2\pi} \int_0^{2\pi} \frac{d\varphi}{2\pi} e^{i\;N\,(\varphi + \theta\;u - h_q(\theta,\varphi))} \equiv \int_0^{2\pi} \frac{d\theta}{2\pi} \int_0^{2\pi} \frac{d\varphi}{2\pi} e^{\,N\,w_q(\theta,\varphi)}$$

$$w_q(\theta,\varphi) = i\;(\varphi + \theta\;u\; - h_q\,(\theta,\varphi))$$

We now define what is known as the "thermodynamic limit".

$$\log(f_q) = q\sum_{j=1}^{\infty} \ln(1+q e^{-i\theta\epsilon_j} e^{-i\varphi})$$

In this limit, $N\;\rightarrow\;\infty$ even as $0 < h_q\,(\theta,\varphi),\;\; u < \infty$.

Now we have to evaluate an integral of the form $R = \int dz\;\; e^{\,N\,g(z)}$ when $N\,\rightarrow\,\infty$

So if you recall f was a way back here and this was my f here and so it is a function of θ and φ. So I am going to take the logarithm of that and if I take the logarithm of so

$$\log(f_q) = q\,\Sigma_j\,(1+q\,\mathrm{Exp}(-i\,\theta\,\varepsilon_j\,-i\,\varphi))$$

So that is what $\log(f_q)$ is going to be and I am going to use that directly here. So I am going to assume that I have used that here, so if I do that and if I think of u and N as my unknowns and recall that u is nothing but the energy density.

So energy per particle, so I have defined u as energy per particle so this is my u so I can finally read off just by thinking of u as my unknown and began as my unknown so effectively u and N as my unknowns. And you have two unknowns and two equations and when I solve it I end up getting this using the value of f that I had written down earlier. So I strongly recommend that you follow along with a notebook and pen and pause this video and try to fill in the gaps yourselves because it is quite tedious for me to explain all this steps.

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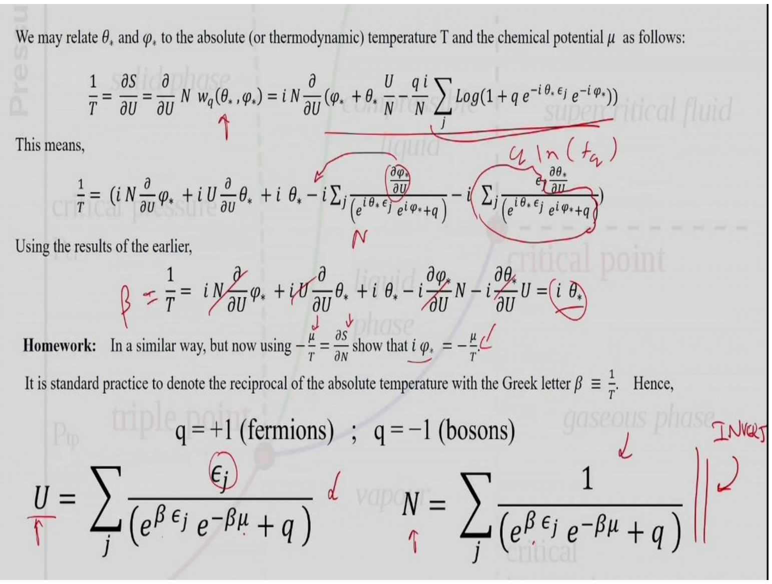

We may relate θ_* and φ_* to the absolute (or thermodynamic) temperature T and the chemical potential μ as follows:

$$\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{\partial}{\partial U} N\, w_q(\theta_*, \varphi_*) = i\,N \frac{\partial}{\partial U}\Big(\varphi_* + \theta_* \frac{U}{N} - \frac{q\,i}{N} \sum_j Log(1 + q\, e^{-i\,\theta_* \epsilon_j}\, e^{-i\,\varphi_*})\Big)$$

$q \ln(f_q)$

This means,

$$\frac{1}{T} = \Big(i\,N \frac{\partial}{\partial U}\varphi_* + i\,U \frac{\partial}{\partial U}\theta_* + i\,\theta_* - i\sum_j \frac{\frac{\partial \varphi_*}{\partial U}}{(e^{i\theta_* \epsilon_j}\, e^{i\varphi_*} + q)} - i\sum_j \frac{\epsilon_j \frac{\partial \theta_*}{\partial U}}{(e^{i\theta_* \epsilon_j}\, e^{i\varphi_*} + q)}\Big)$$

N

Using the results of the earlier,

$$\beta = \frac{1}{T} = i\,N \frac{\partial}{\partial U}\varphi_* + i\,U \frac{\partial}{\partial U}\theta_* + i\,\theta_* - i\frac{\partial \varphi_*}{\partial U} N - i\frac{\partial \theta_*}{\partial U} U = i\,\theta_*$$

Homework: In a similar way, but now using $-\frac{\mu}{T} = \frac{\partial S}{\partial N}$ show that $i\,\varphi_* = -\frac{\mu}{T}$.

It is standard practice to denote the reciprocal of the absolute temperature with the Greek letter $\beta \equiv \frac{1}{T}$. Hence,

q = +1 (fermions) ; q = −1 (bosons)

INVERT

$$U = \sum_j \frac{\epsilon_j}{(e^{\beta\,\epsilon_j}\, e^{-\beta\mu} + q)} \qquad N = \sum_j \frac{1}{(e^{\beta\,\epsilon_j}\, e^{-\beta\mu} + q)}$$

So not only am I interested in knowing a formula for u and N but notice that I have determined u and N implicitly in terms of the saddle point namely θ^* and φ^*. So now I am going to see if I can relate some of the saddle points to other parameters that I am more comfortable with such as temperature and chemical potential. So given the fact that the entropy function is nothing but total number of particles times this function W at the saddle point.

Now the reciprocal of the temperature as you very well known in thermodynamics is the slope of the entropy function as when plotted as a function of internal energy. So when you do this you will be forced to evaluate such a derivative and when you do that and you evaluate it at the saddle point and also you use this identity here. So it is a few steps are involved so you should bear with me so I am just substituting the value of W there and what I am going to do is so this is basically my you know log(f_q) if you recall and there was a q there.

So this q log(f_q) is what that is so I am forced to differentiate whatever is in this bracket with respect to U and you see that there everything depends on U even the saddle point depends on U. So I should not forget to differentiate the saddle point with respect to U and there is a U also outside the saddle point right there which of course I have to differentiate and when I do all that I end up with this.

And now I go ahead and I just recognize this, remember that this is nothing but you know it is basically the with that ε_j inside that is nothing but the total energy U and what is this if I pull this outside whatever remains is total number of particles. So now, so you see as a result this cancels out with this and I end up with this answer. The θ saddle point is simply related to the absolute temperature of the system.

So in a similar way you can convince yourself by using this identity or this definition rather of the chemical potential that the φ saddle point is very easily related to the chemical potential and of course temperature. So as a result now I do not have to write everything in terms of my saddle point which is a very mysterious object so instead of thinking of θ^* and φ^* which we will be hard pressed to you know attribute any physical meaning to unless we perform this calculation.

Now that we performed this calculation we know that the saddle point is directly related to the absolute temperature and the chemical potential. So I am going to go ahead and make use of this and write $e^{i\theta}$ as 1 / T and by the way I am measuring in this course as I perhaps told you that I will be measuring temperature in energy units. So as a result the Boltzmann constant is taken to be 1.

So in which case 1 / T is a inverse of temperature and there is a notation for this, a standard notation in thermodynamics and that is called β. So I am going to use this notation and rewrite these two expressions here in terms of β and μ so you see I am going to be able to do this. So and q is that numerical constant that determines whether I am talking about bosons and or fermions. So if q is 1 I am talking about fermions and q is -1 I am talking about bosons ,so where did this creep in? You should think about why suddenly a q creeped in it in fact it did not creep in it was there all along.

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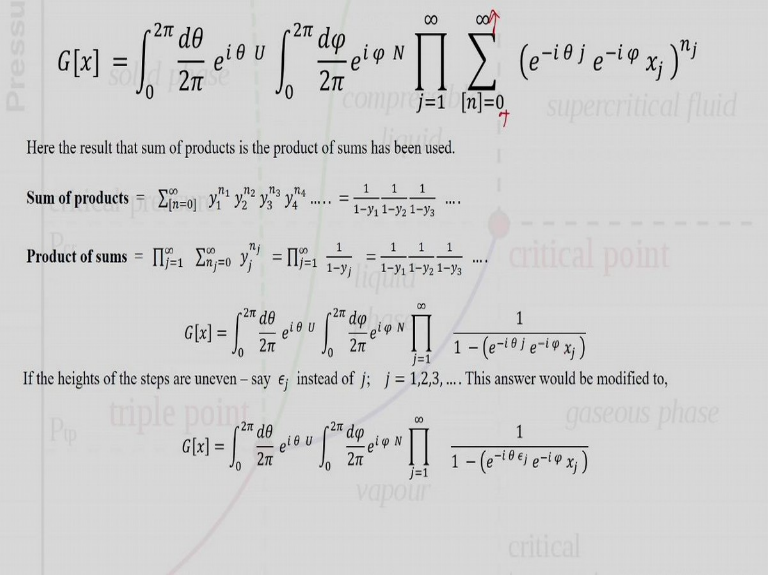

$$G[x] = \int_0^{2\pi} \frac{d\theta}{2\pi} e^{i\theta U} \int_0^{2\pi} \frac{d\varphi}{2\pi} e^{i\varphi N} \prod_{j=1}^{\infty} \sum_{[n]=0}^{\infty} \left(e^{-i\theta j} e^{-i\varphi} x_j\right)^{n_j}$$

Here the result that sum of products is the product of sums has been used.

Sum of products = $\sum_{[n=0]}^{\infty} y_1^{n_1} y_2^{n_2} y_3^{n_3} y_4^{n_4} \ldots\ldots = \frac{1}{1-y_1}\frac{1}{1-y_2}\frac{1}{1-y_3} \ldots.$

Product of sums = $\prod_{j=1}^{\infty} \sum_{n_j=0}^{\infty} y_j^{n_j} = \prod_{j=1}^{\infty} \frac{1}{1-y_j} = \frac{1}{1-y_1}\frac{1}{1-y_2}\frac{1}{1-y_3} \ldots.$

$$G[x] = \int_0^{2\pi} \frac{d\theta}{2\pi} e^{i\theta U} \int_0^{2\pi} \frac{d\varphi}{2\pi} e^{i\varphi N} \prod_{j=1}^{\infty} \frac{1}{1-\left(e^{-i\theta j} e^{-i\varphi} x_j\right)}$$

If the heights of the steps are uneven – say ϵ_j instead of j; $j = 1,2,3,\ldots.$ This answer would be modified to,

$$G[x] = \int_0^{2\pi} \frac{d\theta}{2\pi} e^{i\theta U} \int_0^{2\pi} \frac{d\varphi}{2\pi} e^{i\varphi N} \prod_{j=1}^{\infty} \frac{1}{1-\left(e^{-i\theta \epsilon_j} e^{-i\varphi} x_j\right)}$$

So I'll just remind you where it kind of started coming in it came all the way here when I was trying to, so if I decided to sum over all the particles up to infinity that means there is no restriction on the number of particles then I am going to get 1 over 1 – some quantity here. So however if I had decided that there was a restriction that is only up to 0 to 1 then it will be in the numerator it will become 1 + this quantity. So in other words if q is +1 it corresponds to fermions, if q is -1 it corresponds to bosons, so that is where that comes from that q.

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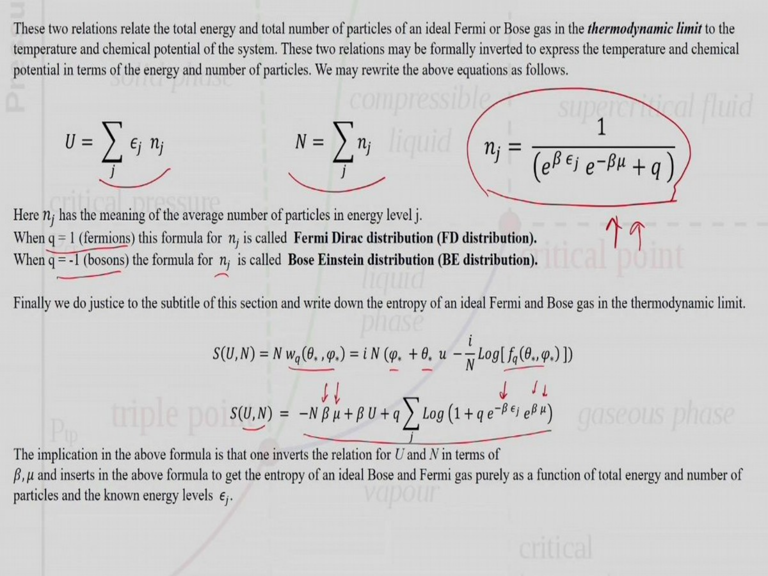

These two relations relate the total energy and total number of particles of an ideal Fermi or Bose gas in the ***thermodynamic limit*** to the temperature and chemical potential of the system. These two relations may be formally inverted to express the temperature and chemical potential in terms of the energy and number of particles. We may rewrite the above equations as follows.

$$U = \sum_j \epsilon_j\, n_j \qquad N = \sum_j n_j \qquad n_j = \frac{1}{\left(e^{\beta\epsilon_j} e^{-\beta\mu} + q\right)}$$

Here n_j has the meaning of the average number of particles in energy level j.
When q = 1 (fermions) this formula for n_j is called **Fermi Dirac distribution (FD distribution).**
When q = -1 (bosons) the formula for n_j is called **Bose Einstein distribution (BE distribution).**

Finally we do justice to the subtitle of this section and write down the entropy of an ideal Fermi and Bose gas in the thermodynamic limit.

$$S(U,N) = N\, w_q(\theta_*, \varphi_*) = i\, N\,(\varphi_* + \theta_*\, u - \frac{i}{N} Log[\, f_q(\theta_*, \varphi_*)\,])$$

$$S(U,N) = -N\,\beta\,\mu + \beta\, U + q \sum_j Log\left(1 + q\, e^{-\beta\epsilon_j} e^{\beta\mu}\right)$$

The implication in the above formula is that one inverts the relation for U and N in terms of β, μ and inserts in the above formula to get the entropy of an ideal Bose and Fermi gas purely as a function of total energy and number of particles and the known energy levels ϵ_j.

So now see recall that the entropy function strictly speaking is a function of in thermodynamics it is a function of the total internal energy, volume and number of particles. So however in this example we have been writing the entropy function in terms of the saddle point and of course we have shown that this saddle point is nothing but chemical potential and temperature.

So what we should do in other words is we should be able to invert these two relations and notice that here the left hand side are total internal energy and number of particles and the right hand side involves chemical potential and temperature. So what we should do is invert these two relations and rewrite temperature and chemical potential in terms of total internal energy and number of particles.

So if you do that then you can go ahead and substitute those expressions into your saddle point which is of course temperature, chemical potential and then you will be successful in expressing the entropy in terms of it is bonafide or genuine independent variables namely total internal energy and number of particles. So coming back to this point that so we can rewrite we can think of this U of the total internal energy as the sum of sum over all the energy levels.

Whatever I am summing is the energy level itself times a function called n_j, so I can think of this U and N as being this sort of sum where this n_j now has the physical interpretation of the average number of bosons or fermions in that energy level. So it has a interpretation of the average number of bosons or fermions because that is clear from this that if you sum over all the energy levels.

You get the total number of particles and you if you first multiply the energy of each level times the average number of quantum particles in that level and then you sum over all the levels of course you are going to get the total internal energy. So this is called Fermi-Dirac distribution if q is +1 and it is called the Bose-Einstein distribution if q is -1. So we have been successful deriving both the this is very important because you will see that in many statistic books.

They spend a lot of effort deriving this and but we have done it quite easily so you should, I should impress upon you that the derivation that I have presented in this series of lectures is somewhat novel that you would not find easily anywhere else, ok. So now I am going to also point out that of course the main quantity of interest was actually entropy all along. So remember I told you that is really the fundamental thermodynamic quantity of interest.

So now entropy function is simply related to this you know the function W whose saddle point we have decided to focus on. So now having found the saddle point we just go ahead and substitute the values of the saddle points I told you that they are related to temperature and chemical potential and then you put them back in and you get an expression of this sort. So this is my formula for the entropy function and of course you have to keep in mind that the independent variables are supposed to be only U and N.

But it appears that here it still involves β which is inverse temperature it still involves μ which is chemical potential so I also told you that there is a way to get rid of β and μ and rewrite it in terms of U and N and all you have to do is just invert these two relations here and here.

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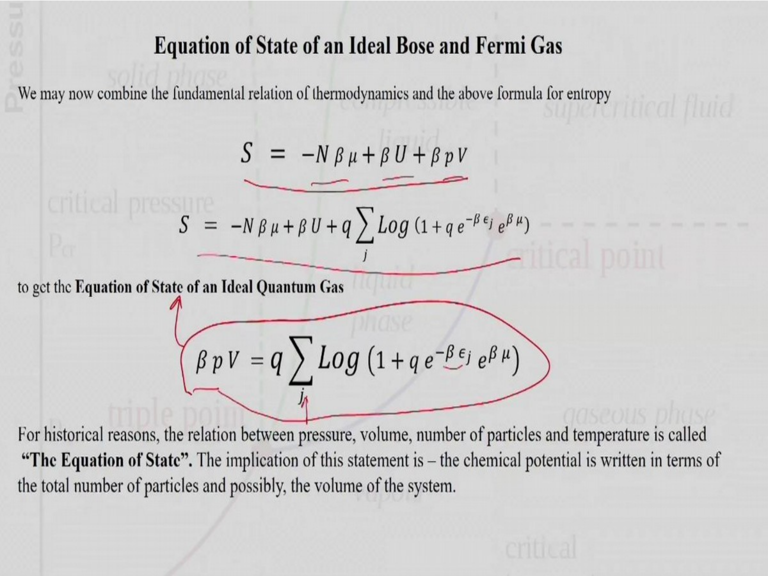

Equation of State of an Ideal Bose and Fermi Gas

We may now combine the fundamental relation of thermodynamics and the above formula for entropy

$$S = -N\beta\mu + \beta U + \beta p V$$

$$S = -N\beta\mu + \beta U + q\sum_j Log\,(1 + q\,e^{-\beta\epsilon_j}\,e^{\beta\mu})$$

to get the **Equation of State of an Ideal Quantum Gas**

$$\beta p V = q\sum_j Log\,(1 + q\,e^{-\beta\epsilon_j}\,e^{\beta\mu})$$

For historical reasons, the relation between pressure, volume, number of particles and temperature is called **"The Equation of State".** The implication of this statement is – the chemical potential is written in terms of the total number of particles and possibly, the volume of the system.

So now we can go ahead and derive something called the equation of state. The equation of state is nothing but a relation between pressure, volume and temperature and number of particles of a gas typically. So well in this case I won't be dealing with volume until a little later because I am still discussing marbles on a staircase so the notion of volume still does not have any concrete meaning here.

Until I actually commit myself to the describing a gas then only volume comes into the picture so I will do that a little later but now just use your thermodynamic identities and you know use your fundamental relation of thermodynamics and I use to compare these two we just derived this result and this is nothing but the fundamental relation of thermodynamics and you simply compare the two and you get what is called the equation of the state ok.

So this is the equation of state, so of whatever gas you want, so if q is +1 you are talking about the equation of state of ideal Fermi gas and if q is -1 you are talking about the equation of state of an ideal Bose gas alright.

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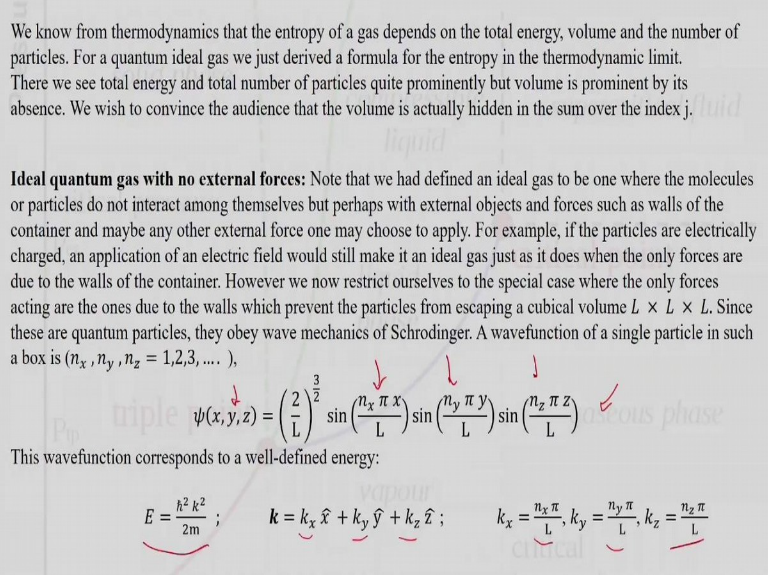

We know from thermodynamics that the entropy of a gas depends on the total energy, volume and the number of particles. For a quantum ideal gas we just derived a formula for the entropy in the thermodynamic limit. There we see total energy and total number of particles quite prominently but volume is prominent by its absence. We wish to convince the audience that the volume is actually hidden in the sum over the index j.

Ideal quantum gas with no external forces: Note that we had defined an ideal gas to be one where the molecules or particles do not interact among themselves but perhaps with external objects and forces such as walls of the container and maybe any other external force one may choose to apply. For example, if the particles are electrically charged, an application of an electric field would still make it an ideal gas just as it does when the only forces are due to the walls of the container. However we now restrict ourselves to the special case where the only forces acting are the ones due to the walls which prevent the particles from escaping a cubical volume $L \times L \times L$. Since these are quantum particles, they obey wave mechanics of Schrodinger. A wavefunction of a single particle in such a box is ($n_x, n_y, n_z = 1,2,3,\ldots.$),

$$\psi(x,y,z) = \left(\frac{2}{L}\right)^{\frac{3}{2}} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right)$$

This wavefunction corresponds to a well-defined energy:

$$E = \frac{\hbar^2 k^2}{2m} ; \qquad \mathbf{k} = k_x \hat{x} + k_y \hat{y} + k_z \hat{z} ; \qquad k_x = \frac{n_x \pi}{L}, k_y = \frac{n_y \pi}{L}, k_z = \frac{n_z \pi}{L}$$

So now I also want to go ahead and explicitly evaluate some of these in so I want to do this summation specifically so for a gas so I do not care about marbles anymore. So up till now this summation was over energy levels and the example was through a staircase with marbles, I still care about marbles of course they are bosons but I do not care about the staircase anymore.

So I am going to instead think of this as the energy levels of free particle confined to a box perhaps of a volume L X L X L so you have a box which have is a cubical box with sides L. Alright in that case so recall that I am discussing quantum particles so if I have a quantum particles I have also told you the ideal so ideal quantum particles means they do not interact with each other.

So they are independent particles so it is sufficient to solve a one body problem which we know from Griffiths how to do for a single quantum particle trapped in a box of cubical box of side L. And the wavefunctions are nothing but this so these are this is the wave function or rather this is the wave function as it is going to be described with by these three quantum numbers n_x , n_y and n_z and these quantum numbers are forced to be 1, 2, 3 etc., and so on.

Because 0 is excluded because if any one of them is 0 the wave function itself becomes 0 and then it violates normalization. You want the normal that total probability to be 1 and if it is the wave function itself is 0 the total probability can never be 1 and finally n's cannot be none of these n's can be negative. Because the if the wave function is you know flip sign it is basically it is like multiplying by an overall face and you know that two wave functions that differ by an overall phase is corresponds to basically the same state.

So now I am going to rewrite this so the energy of this wave function is really the energy of the free particle which is

$$E = P^2/2m$$

$$P = \hbar\ k$$

P is nothing but h bar times the magnitude of the wave vector which is k and the wave vector itself have three components k_x , k_y , k_z and k_x can be written in terms of the quantum number n_x and similarly k_y and k_z .

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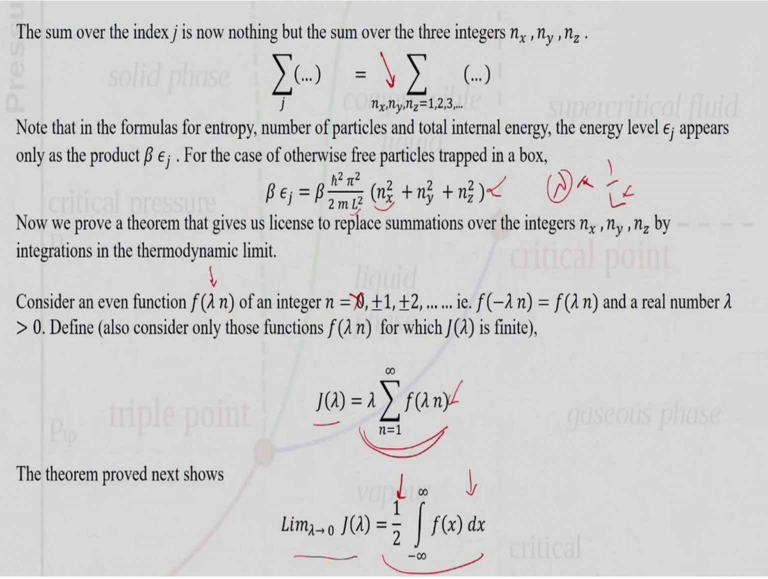

The sum over the index j is now nothing but the sum over the three integers n_x , n_y , n_z .

$$\sum_j (\ldots) \quad = \sum_{n_x, n_y, n_z = 1,2,3,\ldots} (\ldots)$$

Note that in the formulas for entropy, number of particles and total internal energy, the energy level ϵ_j appears only as the product $\beta\, \epsilon_j$. For the case of otherwise free particles trapped in a box,

$$\beta\, \epsilon_j = \beta \frac{\hbar^2 \pi^2}{2\, m\, L^2} (n_x^2 + n_y^2 + n_z^2)$$

Now we prove a theorem that gives us license to replace summations over the integers n_x , n_y , n_z by integrations in the thermodynamic limit.

Consider an even function $f(\lambda\, n)$ of an integer $n = 0, \pm 1, \pm 2, \ldots \ldots$ ie. $f(-\lambda\, n) = f(\lambda\, n)$ and a real number $\lambda > 0$. Define (also consider only those functions $f(\lambda\, n)$ for which $J(\lambda)$ is finite),

$$J(\lambda) = \lambda \sum_{n=1}^{\infty} f(\lambda\, n)$$

The theorem proved next shows

$$Lim_{\lambda \to 0}\ J(\lambda) = \frac{1}{2} \int_{-\infty}^{\infty} f(x)\, dx$$

So now the sum over the index j has to be now reinterpreted as the sum over the three quantum numbers n_x , n_y and n_z . Also I am going to finally rewrite this quantity $\beta\epsilon_j$ which appears all over the place, well it appears everywhere I am going to be able to I am going to use this idea to rewrite this in a more manageable way later on. So recall that I can rewrite ε_j in this fashion so when I substitute that here it is going to look like this.

So keep in mind that I want to study what is called the thermodynamic limit so I have a bunch of quantum particles that are trapped in a box, a cubical box of side L. But then I do not want my box to really have boundaries in the end, that I want it to be a you know uniform quantum gas. So how do I achieve that is to not have boundaries or first have boundaries and make the boundaries go so far away that any finite region of the box can be thought of as being especially uniform.

So that is the idea of thermodynamic limit, so what we are going to do is we are going to assume that the box is huge and the number of particles scales with the volume of the box so that the density of particles that is number of particles per unit volume remains fixed. So that is called the thermodynamic limit and we are going to work in the thermodynamic limit. So now it so happens that in the thermodynamic limit these summations which are really annoying because they are very hard to do can actually be converted to integrations which are easier to do.

So you do not have to do discrete sums in the thermodynamic limit because you can always convert them to integrations. So in order to do that I am going to prove the following theorem, so you will have to bear with me because again it seems rather technical but it is very important for you to follow along. Because I have noticed that especially this crucial idea that in the thermodynamic limit you can replace a discrete sum by integration is rarely explained in any of the books.

So typically you first encounter it in, you should encounter it typically for the first time in a statistical mechanics course but you also encounter it in solid state physics course and none of those books I feel do proper justice to this idea. So it is worthwhile to spend some time trying to prove this rigorously so that we will be fully convinced about its validity. So in order to do this consider an even function of this integer n.

So imagine that there is an integer n and this is an even function, well of course 0 is not really needed so in even function is 1 where you flip the argument you get back the same thing and now I am going to think of λn because I am going to think of this λ as a small quantity and that is because you see the n's, n^2 always come with an L^2 associated with it but in the denominator.

So in the thermodynamic limit what will happen is that my λ is really proportional to 1 / L where when in as L tends to infinity in the thermodynamic limit λ is a small quantity. So that is the whole idea of thinking about a function of a λn so now imagine that I perform this summation so I am going to define a quantity called j(λ) where j(λ) is nothing but this sum as defined.

So recall that I should not, I should exclude that n = 0 because then wave function itself becomes 0 so I start from one all the way upto infinity. Now I am going to ask myself is there a way I can avoid doing this summation or can I somehow replace this with something more manageable. So the answer is yes it so happens that you can prove or we are going to prove it right now that when λ → 0 this the summation rather this discrete sum can be replaced by this integration. So it is quite remarkable and this is a rigorous result that we can prove right now.

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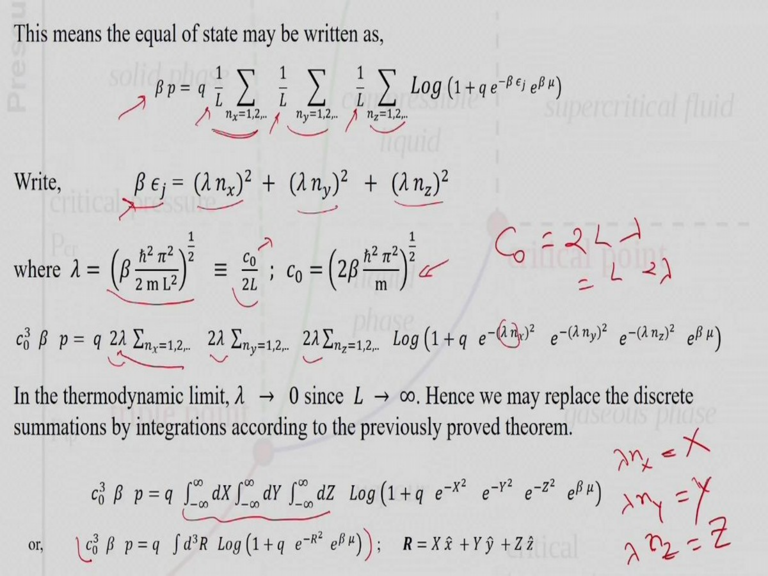

This means the equal of state may be written as,

$$\beta p = q \frac{1}{L}\underbrace{\sum_{n_x=1,2,..}}\ \frac{1}{L}\underbrace{\sum_{n_y=1,2,..}}\ \frac{1}{L}\underbrace{\sum_{n_z=1,2,..}} Log\left(1+q\, e^{-\beta\epsilon_j} e^{\beta\mu}\right)$$

Write, $$\beta\epsilon_j = \underbrace{(\lambda n_x)^2} + \underbrace{(\lambda n_y)^2} + \underbrace{(\lambda n_z)^2}$$

where $$\lambda = \underbrace{\left(\beta\frac{\hbar^2\pi^2}{2\,\mathrm{m}\,\mathrm{L}^2}\right)^{\frac{1}{2}}} \equiv \frac{c_0}{2L}\ ;\ c_0 = \left(2\beta\frac{\hbar^2\pi^2}{\mathrm{m}}\right)^{\frac{1}{2}}$$

$C_0 = 2L\lambda$

$= L\,2\lambda$

$$c_0^3\ \beta\ p = q\ \underbrace{2\lambda \sum_{n_x=1,2,..}}\ 2\lambda\sum_{n_y=1,2,..}\ 2\lambda\sum_{n_z=1,2,..} Log\left(1+q\ e^{-(\lambda n_x)^2}\ e^{-(\lambda n_y)^2}\ e^{-(\lambda n_z)^2}\ e^{\beta\mu}\right)$$

In the thermodynamic limit, λ → 0 since L → ∞. Hence we may replace the discrete summations by integrations according to the previously proved theorem.

$$c_0^3\ \beta\ p = q\ \underbrace{\int_{-\infty}^{\infty} dX \int_{-\infty}^{\infty} dY \int_{-\infty}^{\infty} dZ}\ Log\left(1+q\ e^{-X^2}\ e^{-Y^2}\ e^{-Z^2}\ e^{\beta\mu}\right)$$

$\lambda n_x = X$

$\lambda n_y = Y$

$\lambda n_z = Z$

or, $$c_0^3\ \beta\ p = q\ \int d^3R\ Log\left(1+q\ e^{-R^2}\ e^{\beta\mu}\right);\quad \mathbf{R} = X\,\hat{x} + Y\,\hat{y} + Z\,\hat{z}$$

Well we are going to prove it subsequently, so but let us use it right now instead of well we will postpone the proof for a little while later but I am going to use this now. So remember that in the equation of state I am forced to sum over all the j's and then sum over all the j's is nothing but summing over the n's. Now so as a result in the equation of state I will be forced to do this so I have put the V.

So remember there was a V there and V is nothing but L^3 and I have written L^3 as when it comes to this side to the right side becomes $(1 / L)^3$ and I have written $(1 / L)^3$ as 1 / L x 1 / L x 1 /L. So now I have this kind of a combination 1 / L times a summation. So now I am going to rewrite this

$$\beta\varepsilon_j = (\lambda n_x)^2 + (\lambda n_y)^2 + (\lambda n_z)^2$$

So then where λ is of course this we can just read it off because we know what this is and from there we can read of this λ and then I am going to define this c_0 in this fashion so as a result this is nothing but $c_0 / 2L$. So now if I multiply both sides by $(c_0)^3$ right so c_0 is nothing but so from here we can see that

$$c_0 = 2L\lambda$$

So what I am going to do is if I multiply by c_0 x c_0 x c_0 which is $(c_0)^3$ and $c_0 = 2L\lambda$ and L cancels with 1 / L so I end up with $(2\lambda)^3$. So now remember that

$$j(\lambda) = \lambda \Sigma_{n=1}^{\infty} f(\lambda n)$$

we just proved that this that is this quantity j. So $\lambda \Sigma_{n=1}^{\infty}$ is nothing but one half of the integration, right with respect to this whole thing called X.

So now we relabel λn_x as X, λn_y as Y and λn_z as Z. so it is like integrating over X, Y, Z and remember that there was a one half there and the three one halves and then there are 2 times 2 times 2 n all that cancels out and you end up with this result. So basically this is nothing but the volume integral of over this dimensionless vector whose components are X, Y and Z. So as a result I will be successful in rewriting the equation of state in this rather nice dimensionless form.

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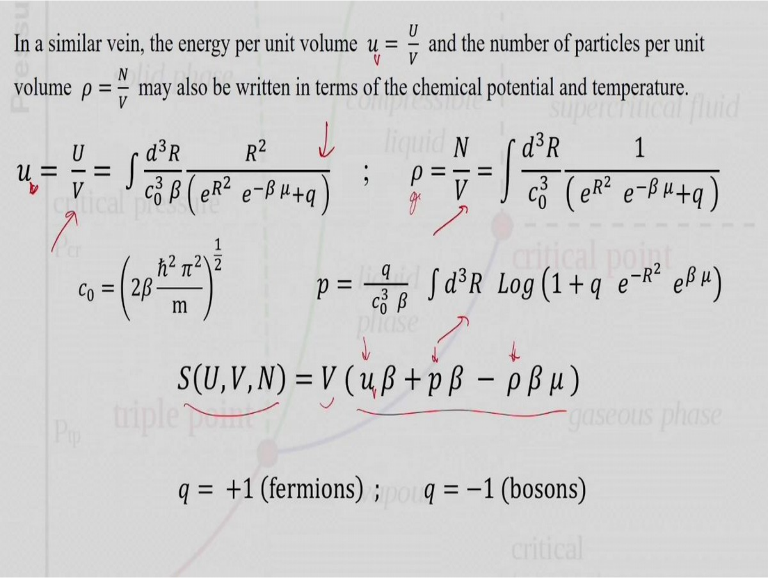

In a similar vein, the energy per unit volume $u_v = \frac{U}{V}$ and the number of particles per unit volume $\rho = \frac{N}{V}$ may also be written in terms of the chemical potential and temperature.

$$u_v = \frac{U}{V} = \int \frac{d^3R}{c_0^3} \frac{R^2}{\beta\left(e^{R^2}\, e^{-\beta\mu} + q\right)} \quad ; \quad \rho = \frac{N}{V} = \int \frac{d^3R}{c_0^3} \frac{1}{\left(e^{R^2}\, e^{-\beta\mu} + q\right)}$$

$$c_0 = \left(2\beta \frac{\hbar^2 \pi^2}{\mathrm{m}}\right)^{\frac{1}{2}} \qquad p = \frac{q}{c_0^3\, \beta} \int d^3R\ Log\left(1 + q\ e^{-R^2}\ e^{\beta\mu}\right)$$

$$S(U,V,N) = V\left(u_v\beta + p\beta - \rho\beta\mu\right)$$

$$q = +1 \text{ (fermions) };\quad q = -1 \text{ (bosons)}$$

You will have to excuse my misuse of notation here earlier I had used small u to be a number of total energy per particle now I have defined it as total energy per volume so maybe I should put as a subscript there. u_V implying that is the total energy per unit volume that is the energy density and the number of particles per unit volume is nothing but N / V. And as just as we were able to rewrite the equation of state in terms of this dimensionless integration over the dimensionless vector.

So all the summation over j have now in the thermodynamic limit been replaced by this integration over R which is a dimensionless vector. So we have expressions for the energy density, number of particles and the equation of state, all in terms of simple dimensionless quantities. And we can now go ahead and use this in our fundamental relation and we will be able to rewrite the entropy in terms of, suppose if I am successful in performing this integration which is likely to be far easier than doing a discrete sum over integers and not just one integer but three different integers and that is likely to be far more difficult than this.

So notice this here we can make use of spherical symmetry and even though technically there are three components but then there are no angles in the integrand and we can make explicitly use of that we are going to make explicitly use of that later on. Alright so now using that we can go ahead and substitute these intensive quantities, remember that these are intensive quantities in the sense that if I scale the number of particles by λ, scale the volume by λ because these two are extensive I end up getting a ρ which is independent of λ.

So as a result all these small case alphabets Latin and Greek they are intensive quantities and the uppercase alphabets are extensive quantities. So the entropy function is therefore the extensive volume times a whole bunch of intensive quantities where you have so this is the fundamental relation of thermodynamics and I am going to just plug in these p's, u's and ρ's ,ok so then I get this entropy function so if q is 1,

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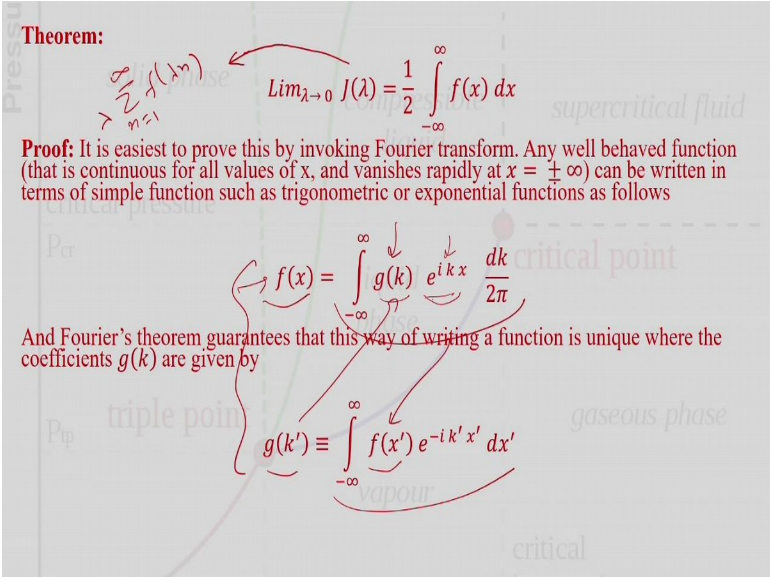

Theorem:

$\lambda \sum_{n=1}^{\infty} f(\lambda n)$

$$Lim_{\lambda \to 0}\, J(\lambda) = \frac{1}{2}\int_{-\infty}^{\infty} f(x)\, dx$$

Proof: It is easiest to prove this by invoking Fourier transform. Any well behaved function (that is continuous for all values of x, and vanishes rapidly at $x = \pm\infty$) can be written in terms of simple function such as trigonometric or exponential functions as follows

$$f(x) = \int_{-\infty}^{\infty} g(k)\, e^{ikx}\, \frac{dk}{2\pi}$$

And Fourier's theorem guarantees that this way of writing a function is unique where the coefficients $g(k)$ are given by

$$g(k') \equiv \int_{-\infty}^{\infty} f(x')\, e^{-ik'x'}\, dx'$$

I describe I am describing fermions you know non interacting fermions and q is -1 I am describing non interacting bosons ok, now let us come to the technical part. So even though this seems a little technical it is really nice to know this proof once and for all. So remember that I am trying to prove that this j which is nothing but $\lambda \sum_{n=1}^{\infty} f(\lambda n)$. So that is my that is what j is so if I take $\lambda \to 0$ this summation is I will be able to replace it by the integration.

So how do you prove this? It seems rather hard to prove except that if you realize that any function f can always be written in terms of simpler functions. So this can be as complicated as you want but however you can always according to Fourier, the mathematician Fourier, you can always write any function f(x) in terms of really simple functions e^{ikx}. So what is the beauty of this really simple function e^{ikx} is that as a function of x it is a very simple function because it is infinitely many times differentiable, it does not blow up anywhere ,it has no singularities, you can do whatever you want to do it pretty much whatever you do to it. It remains as it is it is like neutrino you know it just passes through so you can differentiate it once but e^{ikx}, apart from innocent pre factor like ik it remains the same function so you can integrate it again we get back the same function so that is the beauty of the exponential of x, so it remains you can do calculus very easily with it. So now it is very comforting to know that any complicated function that does not have those properties can still be rewritten you know not just of course as one of these but you know as a whole bunch of these.

So you will have to multiply this by an appropriate prefactor and then you have to add up a whole bunch of them, so adding in this context means integrating over that parameter k because you will be forced to take into account all the different k's there. If you want to mimic a general function f(x). Now it so happens that I well this is completely devoid of any meaning unless I am also able to tell you a prescription for how to get g(k).

So the idea is that you can get g(k) if somebody tells you what f(x) is then you can go ahead and perform this integral so this is the content of Fourier's theorem which says that these two put together are mathematically consistent. So that is another way of saying so if you take this expression you put this here because you change x to x' and you substitute here you should get an identity and the reverse is also true you take this put that there.

You are going to get an identity, so I am not going to do all that because of Fourier analysis is not part of this course so I am going to assume you already know this and if you do not please learn it yourself by reading the appropriate maths books.

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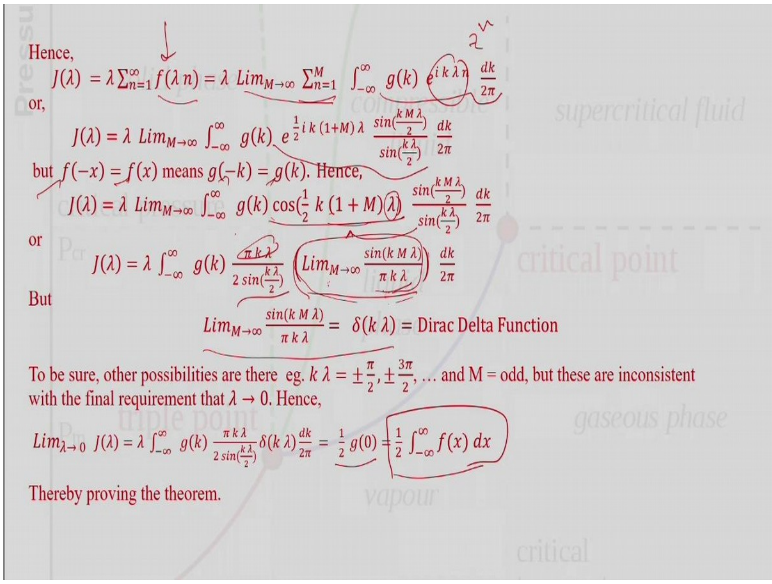

Hence,

$$J(\lambda) = \lambda \sum_{n=1}^{\infty} f(\lambda\, n) = \lambda\, Lim_{M\to\infty} \sum_{n=1}^{M} \int_{-\infty}^{\infty} g(k)\, e^{i\,k\,\lambda\,n}\, \frac{dk}{2\pi}$$

or,

$$J(\lambda) = \lambda\, Lim_{M\to\infty} \int_{-\infty}^{\infty} g(k)\, e^{\frac{1}{2} i\,k\,(1+M)\,\lambda}\, \frac{sin(\frac{k\,M\,\lambda}{2})}{sin(\frac{k\,\lambda}{2})}\, \frac{dk}{2\pi}$$

but $f(-x) = f(x)$ means $g(-k) = g(k)$. Hence,

$$J(\lambda) = \lambda\, Lim_{M\to\infty} \int_{-\infty}^{\infty} g(k) \cos(\frac{1}{2}\, k\,(1+M)\lambda)\, \frac{sin(\frac{k\,M\,\lambda}{2})}{sin(\frac{k\,\lambda}{2})}\, \frac{dk}{2\pi}$$

or

$$J(\lambda) = \lambda \int_{-\infty}^{\infty} g(k)\, \frac{\pi\,k\,\lambda}{2\,sin(\frac{k\,\lambda}{2})} \left(Lim_{M\to\infty} \frac{\sin(k\,M\,\lambda)}{\pi\,k\,\lambda}\right) \frac{dk}{2\pi}$$

But

$$Lim_{M\to\infty} \frac{\sin(k\,M\,\lambda)}{\pi\,k\,\lambda} = \delta(k\,\lambda) = \text{Dirac Delta Function}$$

To be sure, other possibilities are there eg. $k\,\lambda = \pm\frac{\pi}{2}, \pm\frac{3\pi}{2}, \ldots$ and M = odd, but these are inconsistent with the final requirement that $\lambda \to 0$. Hence,

$$Lim_{\lambda\to 0}\; J(\lambda) = \lambda \int_{-\infty}^{\infty} g(k)\, \frac{\pi\,k\,\lambda}{2\,sin(\frac{k\,\lambda}{2})}\, \delta(k\,\lambda) \frac{dk}{2\pi} = \frac{1}{2}\, g(0) = \boxed{\frac{1}{2} \int_{-\infty}^{\infty} f(x)\, dx}$$

Thereby proving the theorem.

So now I am going to use this, so remember that this is what I have to find as sum off now I am going to rewrite this f in terms of this Fourier coefficients. So I am going to write this as a Fourier transform, so now I am going to sum over all the n's and when I do I get this, this is a simple geometric series notice that this is nothing but something raised to n, well that something happens to $e^{ik\lambda}$.

So now when I sum over all the n's, well not all the n's from n = 1 to M but finally you know remember that I have to the infinite sum is formally defined like this where you sum from 1 to a certain value M and then you take the limit as $M \to \infty$. So remember that I have committed myself to an even function so that also makes the Fourier components even, that you can easily convince yourself of.

So now I am going to have to take this limit as $M \to \infty$ and so there is M sitting right there, so the idea is that if you take λ really really small this is kind of going to be bounded between 1 and -1. But however it is this quantity so I have rewritten it here and I have multiplied and divided so I put this outside there and I have multiplied and divided by this quantity and so now this is the singular thing that I have to worry about.

So when $M \to \infty$ if k is not 0 this thing oscillates and becomes 0 but if k is 0 so this thing only survives when k is 0 so when k is not 0 it becomes 0, so when k is 0 this Cos becomes 1 so I have been a little blase' here and kind of ignored altogether. I strictly should not have done that but it is kind of there it is lurking out here but the point is that you know if I stare at this ratio then I convince myself that this is nothing but the Dirac delta function.

And because of that this Cos becomes 1 and this becomes 1 half of g(0) and then I get back this result and g(0) is nothing but what is g(0)? g(0) is if I put k, k' = 0 I get this becomes 1 so g(0) is nothing but the integral of f. So it is (1/2) g(0) and I get this result ok, so as a result so this is the proof of this theorem of course it is not going to be fully convincing to a mathematics audience., because I've been rather sloppy in places but you get the idea that you can fill in the gaps yourself perhaps you can make it more rigorous if you wish. But this is the general sketch of the proof ok. So now I am in a position to derive the Maxwell Boltzmann distribution of a ideal classical gas. The reason is because we have taken a lot of trouble in deriving the Fermi Dirac and Bose Einstein distributions. Let us go to that and so remember that this is what that is so if q was +1, I am talking about the Fermi-Dirac distribution and q is -1, I am talking about the Bose-Einstein distribution.

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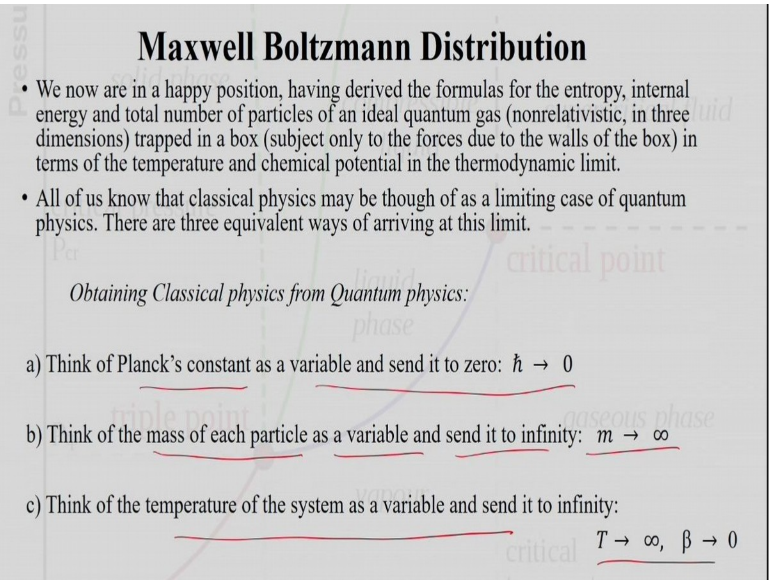

Maxwell Boltzmann Distribution

- We now are in a happy position, having derived the formulas for the entropy, internal energy and total number of particles of an ideal quantum gas (nonrelativistic, in three dimensions) trapped in a box (subject only to the forces due to the walls of the box) in terms of the temperature and chemical potential in the thermodynamic limit.
- All of us know that classical physics may be though of as a limiting case of quantum physics. There are three equivalent ways of arriving at this limit.

Obtaining Classical physics from Quantum physics:

a) Think of Planck's constant as a variable and send it to zero: $\hbar \rightarrow 0$

b) Think of the mass of each particle as a variable and send it to infinity: $m \rightarrow \infty$

c) Think of the temperature of the system as a variable and send it to infinity: $T \rightarrow \infty, \ \beta \rightarrow 0$

So the idea is that you know can I make use of this derivation that I have spent so much effort and deriving which is applicable to a quantum gas and see if I can take the sum appropriate limit and get a classical expression for it is classical counterpart and the reason why you can do that is because you all know that classical mechanics is just can be just thought of as a appropriate limiting case of quantum mechanics.

So how do you obtain classical physics from quantum physics? You can think of Planck's constant as a variable and send it to 0. So that is one way of thinking of obtaining classical physics from quantum physics and alternatively you can imagine the mass of a particle as variable and send it to infinity and lastly you can think of the temperature of the system as variable and send it to infinity even then you will be describing classical system even though you have started off with a quantum system.

So I will end here for this hour and I will get back to doing this namely I want to be able to derive the Maxwell Boltzmann distribution of a classical gas using the Fermi-Dirac and Bose-Einstein distribution that you have so painstakingly derived, alright thank you and hope you see you for the next hour.