

Introduction to Statistical Mechanics
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Module No # 02
Lecture No # 08
Specific heats of quantum gases

Ok ,so let us begin a new topic today and that is let us try and see if we can calculate the what are known as the specific heats of various gases. So specifically, I have in mind gases such as ideal gas and quantum fermi gas and quantum Bose gas. So let us start with ideal classical gas.

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Specific Heat at Constant Volume and at Constant Pressure

Specific heat at constant volume is defined as the change in (the most probable value of) internal energy per unit change in temperature.

Specific heat at constant pressure is defined as the change in enthalpy per unit change in temperature.

Classical Ideal Gas: Note that internal energy of a classical ideal gas is $\frac{3}{2} N T$. This means the specific heat at constant volume is $C_v = \frac{3}{2} N$. The enthalpy is $H = U + pV = \frac{3}{2} N T + N T = \frac{5}{2} N T$. This means $C_p = \frac{5}{2} N$. It so happens that while these results are peculiar to an ideal gas, the difference between these two is quite generally shown to be N . In terms of specific heats per particle,

Quantum Ideal Gas:

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

Handwritten notes on slide:
 $\frac{dU}{dT} = C_v$
 $\frac{dH}{dT} = C_p$
 $H = U + PV \rightarrow G = H - TS$
 $C_p - C_v = 1$
 $\int R^2 dR = 0$
 $q = +1 \rightarrow$ fermions
 $q = -1 \rightarrow$ bosons
 $q = 0 \rightarrow$ classical

So well regardless of which type of gas it is I can define the specific heat at constant volume as the rate of change of the internal energy of the system versus temperature. So it is the slope of the internal energy plotted versus temperature when you fix you know the density of particles is fixed and also the number of particles is fixed. So the volume and the number of particles are assumed to be fixed and you change the internal energy. So in other words you know that basically what I have in mind is the system that is in contact with a reservoir.

So they come to a thermal equilibrium at a common temperature and what I have for the system is that this system does not have really a well-defined internal energy but it certainly has a well-defined most probable value of the internal energy. So henceforth when I speak of internal energy of a system at constant temperature, I obviously mean that the most probable value ,ok.

So I have already told you that the most probable value is overwhelmingly likely in a system that is thermodynamically large.

So it is in the thermodynamic limit the most probable value is more or less the only possible value the other values are incredibly less probable. So given this state of affairs the total internal energy, the most probable value of the total internal energy is going to change if I decide to change the common temperature of the system and its surroundings. So the idea is that the specific heat is basically defined as the change in that most probable value of the internal energy and the ratio of that with the change in the temperature of the surroundings and therefore of the system.

So that is called the specific heat at constant volume because you are fixing the volume and of course the number of particles we are going to assume that anyway fixed but the volume is fixed so that the system does not have flexible walls. So that would correspond to specific heat at constant volume, ok. So that is what I have written here in this sentence. So this specific heat at constant pressure by contrast is defined differently because then you have to take into account the fact that the walls of the container move around and therefore you know some work additional energies are involved.

So instead of the internal energy the analog of the internal energy in the case of constant pressure is what is known as enthalpy. And enthalpy is defined as $U + PV$. So in fact it is instructive to understand why these definitions are the way they are. So, if you recall the Helmholtz free energy in case of systems that have constant volume and constant number of particles but variable energy was defined in this fashion.

So we defined it as the internal energy minus TS . So this is basically telling you something interesting physically. So what it is telling you is that the free energy that is available to you to do work is not the entire internal energy of the system but less than this less by this amount called TS . So TS is the amount of energy that it kind of gets wasted in terms of entropy. So in another word it is some kind of random energy that you cannot really make use of that is always present in the system that you can never make use of.

So the energy that you can eventually make use of is the free energy which is the total energy in the system minus the random energy which you cannot make use of. So which is why we end up defining specific heat as the rate of change of internal energy with temperature which is the quantity that is sitting here. So similarly, in the case of a system that constant pressure, so if you recall that was actually defined in a similar way that instead of internal energy there was enthalpy sitting here.

So similarly, the role played by the internal energy in the case of constant volume is taken up by enthalpy in the case of constant pressure. So this would correspond to a specific heat at constant pressure and the rate of change of internal energy with respective temperature is called specific heat at constant volume. So now let us go ahead and see if I can evaluate these quantities for various gases. Let us start with the classical ideal gas.

So you know that in the classical ideal gas the total internal energy is $\frac{3}{2} N k T$ which we have just derived some time back and as a result the specific heat at constant volume is just the rate of change of this with temperature which is $\frac{3}{2} N$. Remember that I have put Boltzmann constant is 1 in all my lectures. So as a result but we also know for a instance that the equation of a state for a classical ideal gas is $pV = NT$. So if I add the $U + pV$ which is the definition of enthalpy I get $\frac{5}{2} NT$

So now the rate of change of enthalpy with temperature is $\frac{5}{2} N$. So now if you take the difference between the two I get something proportional to N and of course this upper case C refers to the specific heat of the system as such whereas the lower case c refers to the specific heat of the system per particle so that is the only difference. So for the specific heat of the system per particle constant pressure minus the specific heat of the system per particle at constant volume is 1 for a classical ideal gas only.

Ok so that that was easy and in fact it is quite uninteresting as well because everything is very simple. So now let us get to something slightly more interesting and that would respond to quantum ideal gases. So remember that I speak of when I speak of ideal gas whether it is quantum or classical I mean a gas where the constituent particles do not interact with each other

but rather only interact with the walls of the container maybe or the surrounding or whatever they do not interact amongst each other.

But of course in quantum mechanics that is a little bit hard to pin down in the sense that you know if you talk about fermions you know that you cannot really put two fermions in the same state because Pauli exclusion principle and you could you know raise your hand and say well that is the sort of the interaction as well how can you ignore that I mean this after all it is an interaction in the sense that the fermions is sensing the presence of another fermion it is not allowing two fermions to occupy the same state.

So in that sense it is true that there is some kind of interaction so when we talk of ideal quantum gases we of course mean something over and above that. So these type of interactions which are due to fundamental laws of nature which is regardless of the nature of the other forces involved so you know such interactions that are always present they are called statistical interactions so they are always present.

So for bosons there is a you know also a statistical interaction caused by the fact that you can you know they are all indistinguishable and you can put as many as you want in the same state. So now let us get to quantum ideal gases and if you recall I had written down general expressions for the energy density that is energy per unit volume and the number density which is the number per unit volume of quantum gases. So if q was $+1$ it corresponded to fermions and q was -1 it corresponded to bosons.

So now you could actually go ahead and perform this integration so you do not have to you know scratch your head about how to do this because after all it is a very simple integral you know this is a R is you know just a scalar quantity and this implies a spherically symmetric integrand. So I can always write the volume element as $4\pi R^2 dR$ and I integrate from $R = 0$ to $R = \infty$. That is what I could be doing here and there.

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Using Mathematica commands such as (set $z = e^{\beta\mu}$),

$$\rho = \text{Integrate}\left[\frac{4\pi R^2}{(e^{R^2} z^{-1} + q)c_0^3}, \{R, 0, \infty\}\right]$$

we get $\rho = -\left(\frac{m}{\beta \hbar^2}\right)^{\frac{3}{2}} \frac{Li_3(-qz)}{2\sqrt{2}\pi^{\frac{3}{2}}q}$; $u_V = -\left(\frac{m}{\beta \hbar^2}\right)^{\frac{3}{2}} \frac{3 Li_5(-qz)}{4\sqrt{2}\pi^{\frac{3}{2}}q\beta}$

where $Li_s(z) = z + \frac{z^2}{2^s} + \frac{z^3}{3^s} + \frac{z^4}{4^s} + \dots$ is the PolyLog function.

Well you can do it by hand I mean by you can try to do it by hand but you will find that you know you will be stuck with the certain function that you would not be able to handle beyond a certain point and so you will end up with the function which is what is known as a poly logarithmic function so poly log function. So these are tabulated and in fact the definition of poly log function of z with index s is defined in this fashion $Li_s(z)$ so this is poly log.

So we can tabulate these for various values of s . So that values of interest in the case of three dimensional gases quantum gases is when s is $3/2$ for density and when s is $5/2$ for energy density. This for number density we will have to calculate this poly log function for $s = 3/2$ and for the energy density we need the poly log function for $s = 5/2$. So you do not have to get scared about these functions I said well I do not know what they are how would I learn this subject.

Nowadays there is no need to worry about all these there nobody takes any pride in doing integration anymore because there are lots of symbolic algebra packages out there that do it for you. So all I have given such a example here in mathematica. The language mathematica you can just use this as an example and just insert this command in the mathematica language and then out comes this answer. So you do not have to worry too much about even if you do not know how to do an integral nowadays there is lot of packages that do it for you.

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The formula for pressure is

$$p = \frac{q}{c_0^3 \beta} \int d^3R \text{Log}(1 + q e^{-R^2} e^{\beta \mu}) = - \frac{q \pi^{\frac{3}{2}}}{\left(2\beta \frac{\hbar^2 \pi^2}{m}\right)^{\frac{3}{2}} \beta} \text{Li}_{\frac{5}{2}}(-q z)$$

Taking the ratio we obtain quite generally,

$$\frac{p}{u_V} = \frac{q \pi^{\frac{3}{2}}}{\left(2\beta \frac{\hbar^2 \pi^2}{m}\right)^{\frac{3}{2}} \beta} \frac{1}{\left(\frac{m}{\beta \hbar^2}\right)^{\frac{3}{2}} \frac{3}{4\sqrt{2} \pi^{\frac{3}{2}} q \beta}} = \frac{2}{3}$$

Ok so we can similarly write down the answer for pressure. So the pressure also involves such a integral over these R's and then this also involves the poly log function for 5/2 ok so this was 5/2 as well. Now that is interesting because that is telling you something, so regardless of whether what q is I can so remember that if q was + 1 it was fermions. So if q was + 1 it was fermions, if it was -1 it was bosons, and -1 q = + 1 fermions -1 was bosons.

And I mean let me be little mischievous and say q = 0 well they are strictly not allowed because q was supposed to be + or -1. So let us let us try to become a little greedy and say what is q = 0 correspond to. Well that is certainly going correspond to something which we are familiar with because if this goes away remember that if we ignore this q altogether that corresponded to classical Boltzmann statistics or classical ideal gas and that is what it is. So it is classical ideal gas.

So I mean so you can take one or the other point of view namely you can either say that well in certain limits q can be ignored altogether and therefore this only this survives or alternatively I forcibly put q = 0 which is the same thing. So now so regardless of what that q is you can see that if I take the ratio of the pressure which I have calculated in terms of this poly log function which has an index 5/2 and the internal energy density. The energy density of the gas in terms of the same parameters so that also has index 5/2.

And if I take the ratio, I get a whole bunch of constants which then simplified to this incredibly simple fraction which is $2/3$. So that is very interesting, notice that this two thirds should not be taken to be that universal. In fact, it is universal in the sense that it is applicable to Bose gas, Fermi gas and classical ideal gas. However, it is only applicable if those gases live in three dimensions and the energy momentum dispersion is parabolic. So that means I am talking about nonrelativistic free particles.

So in other words the E vs p is $p^2 / 2m$, it is only then this works and also I have to live in 3 spatial dimensions. So I have to believe that the gases are existing in three spatial dimensions. So if you have a situation where you can have a for example a metal where the conduction electrons can be modeled as a fermi gas a gas of fermions and these days you can create a two dimensional conductor which is basically you know you can think of the conduction channels of a MOSFET two dimensional or even one dimensional sometimes depending upon the situation.

So you can have a lower dimensional fermi gases which are realizable in practice quite easily. So these days there is a subject called, I mean there is a subject where you trap atoms, so it is called laser cooling or trapped atom. So you trap atoms in artificial lattices created by criss-crossed laser beams and you can kind of coax those atoms to behave like ideal Bose gas or ideal fermi gas and nearly ideal Bose gas nearly ideal fermi gas and you can test many of. So you can reduce the dimensionality by choosing your lattice to be deliberately two dimensional and you can study various properties.

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This means for quantum ideal gases (and a fortiori for classical ideal gases) with energy-momentum dispersion being parabolic the pressure in the thermodynamic limit is related to the total internal energy through the relation

$$pV = \frac{2}{3} U$$

Fugacity expansion: The formal answers in terms of the Poly Log function is not very illuminating. The alternative is to evaluate approximately by performing expansions – typically low temperature or high temperature expansions. In the present case it is more convenient to expand in powers or inverse powers of the fugacity $0 < e^{\beta\mu} = z < \infty$. Consider the integral ($n = 0, 1$)

$$g_n^q = \int d^3R \frac{R^{2n}}{(e^{R^2} z^{-1} + q)}$$

So as a result I am able to write down this really nice equation of state type of expression which tells me that pressure times volume is two thirds the internal energy. So I do not have to, you know in order to obtain equation of state I do not have to re do any calculation. All I have to do is find the total internal energy and that immediately gives me equation of state ok. So now well that was the absolutely correct answer without any further qualifications or comments.

But it is also completely useless because I do not know what this function looks like or how it behaves. So I cannot really get any physical insight from this. So in order to gain physical insight I really have to make sure that I do not use these functions that I do not know how to deal with. So it is better if I expand in a certain in terms of a certain parameter that I choose to regard as being small or you know I have to select a certain parameter which I feel is small and then expand in powers of that and see how things behave as a result as a function of that parameter.

So that is called a controlled approximation and we want to make such a controlled approximation we want to expand in powers of something we can you know have a handle on, something we know we can control. So one such approximation in this context is what is known as the fugacity expansion. Where if you recall a fugacity is defined as $e^{\beta\mu}$. Given that β and μ are real and β is positive. So this means therefore that said which is the fugacity can never be negative it is always real and positive.

So now so let us go ahead try to see if we can evaluate an integral of the sort. So remember that if n is 1 that would correspond to I would be calculating the density of particles when n is 0. So when n is 1 I would be calculating the energy density because if you go back here so if this is R^0 there, and this is R^2 . So that if it is if I write it as R^{2n} . So n is 0 corresponds to calculating density and n = 1 actually corresponds to calculating energy density. This n=0 corresponds to calculating particle density n=1 corresponds to calculating energy density.

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Fermions: $q = +1$, $g_n^1 = \int d^3R \frac{R^{2n}}{(e^{R^2} z^{-1} + 1)}$

Small z expansion: $g_n^1 = 2^{-n-\frac{1}{2}} \pi (2^{n+\frac{3}{2}} - z + \dots) z \Gamma(n + \frac{3}{2})$

$u_V = \frac{g_1^1}{c_0^3 \beta}$ $\rho = \frac{g_0^1}{c_0^3}$

$\frac{U}{N} = \frac{u_V}{\rho} = \frac{g_1^1}{g_0^1 \beta} = \frac{3}{2\beta} + \frac{3z}{8\beta\sqrt{2}} + \dots$

where $z = \frac{c_0^3 \rho}{\pi^2}$ where $c_0 = \left(2\beta \frac{\hbar^2 \pi^2}{m}\right)^{\frac{1}{2}}$

Handwritten notes: $z = e$, $\rho(n \dots) = n!$, $c_0 = [L]$, $= \text{Thermal wavelength}$, λ_T

Ok so now let us go ahead and calculate this so I am going to start with fermions, so in fermions q is + 1. So now I can go ahead and expand in powers of z. Let us assume that you know z is really small compared to 1. So in other words z is positive and close to 0. So in which case there is a well-defined expansion that you can do and clearly you know the leading term is proportional to z because if you take the z upstairs the leading term is going to be proportional to that the next term is. So you can just go ahead and evaluate this.

So you will have the answers in terms of the Gamma function. So if you remember the

$$\Gamma(n-1) = n! , \text{ if } n \text{ is integer}$$

When n is not integer you will have to generalize this definition. So I am going to assume you know how to do all this, if you do not, please look it up. Just go to any maths book that tells you how to define Gamma function and it will tell you how to generalize it to any complex number.

Alright so now given that I am able to write down this answer the this integral in terms of fermions in terms of an expansion I can now go ahead and calculate the energy density and the number density. So it comes out to be this expansion for instance if I take that ratio that is interesting because if I take this ratio u energy density divided by number density that is just the energy per particle. So because you can it is $(U / V) / (N / V)$. So the V 's cancel out and you get U / N .

So now the advantage of doing this is that a whole bunch of things is cancel out as a result and then you get this result. So keep in mind that if you have a situation where you fix the number of particles. So remember that this method actually is it is kind of it tells you thing that I do not want to know for instance it tells me. So the original formulas really tell me something which I do not care about that much.

It tells me the energy density in terms of chemical potential. What is chemical potential? So in chemical potential appears only when you have a system where the number of particles is not fixed. So I am allowed to exchange the number of particles with my reservoir or surroundings and what is fixed is the average number of particles. So it as if the number of particles is fluctuating.

But remember that I have told you that in a thermodynamically large system I can you know go back and forth between a description where the number of particles is truly fixed and the number of particles is fixed only in the sense of most probable value. And these I can go back and forth between these two points of U without paying any penalty only if the systems are thermodynamically large which means I am entitled to ignore fluctuations.

So I am going to always assume that, that is the case that I can ignore fluctuations. In which case so conceptually their equivalent, the conceptually studying a system that where the number of particles is truly fixed is equivalent to studying a system where the number of particles is fixed only on an average in the sense of most probable value. So now that conceptually there is no problem but then practically the problem is that I really have my I want all my answers in terms of things that I can put my finger on which is the number density of particles.

I really do not know or do not care too much about what the chemical potential of my gases. I just want to know that on an average I have these many particles in this volume and can you tell me what is my energy density. So what this is telling you is this formalism telling you that a given that this is fixed. You somehow do this integral and calculate this $1/z$ in terms of the number of particles per unit volume and then go ahead and plug that in here and that will tell you the energy density it is a lot of work.

But unfortunately you have to do that work because this formalism comes out immediately and easily only in this language where I allow everything to exchange that is I allow energy to fluctuate and the number of particles to fluctuate so things become very easy in this case. So that is the reason why I have temperature because energy is allowed to fluctuate, I trade energy with temperature and I allow number of particles to fluctuate so I trade the number of particles with chemical potential.

So now if I want to revert back to energy and number of particles I have to work in the sense of the most probable values. Ok so with that long preamble let me get back to where I was and that is here. So as a result so keeping in mind what I just told you that I really do not care about writing my answers for my energy in terms of the chemical potential after all what is z ?,

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

and μ is the chemical potential may be I do not care about this.

So what I should be doing is rewriting my z in terms of things I do care about which is the density of particles. And so happens that his expression is simple enough that it allows me to invert it. So remember that when z is small I can throw away this all these other terms and then the inversion becomes straightforward and it is a linear relationship.

And so recall that z is small implies so if at fix density, so if I fix my density if I fix the number of particles and my volume and so on, so on an average that is. So if I fix it then the only way I can fiddle around with z I mean if I have to make z smaller and smaller in order for the scheme to become more and more accurate. The only way I can fiddle around with this is by making c_0 . By the way c_0 has dimensions of length and it is sometimes called thermal wavelength.

So this has a name this is called thermal wavelength. And in fact, this is not the standard notation for thermal wavelength. The standard notation is actually λ_T . Because remember it depends on β which is the inverse temperature. So there is a standard notation which I have been for some reason unwilling to use. But you see many books refer to it as λ_T that is my c_0 . So it is called thermal wavelength.

So thermal wavelength is inversely proportional to the square root of the temperature of the system. So because it is inversely related to temperature and z is cubed of that so it is so z becomes smaller and smaller as the temperature of the system becomes larger and larger. So this is basically the semi classical limit. So if you remember I have told you earlier the three ways of thinking about the classical limit is either you make h Planck's constant go to 0 keeping everything else fixed or you make the mass of each constituent go to infinity keeping everything else fixed.

The third alternative is you keep everything else fixed and make the temperature go to infinity. So either of these possibilities allow you to study the classical limit of a quantum gas. All right so that is precisely what we are doing now this small z expansion is just code word for classical expansion. So keeping that in mind I can go ahead and substitute this formula for z in terms of ρ .

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The total energy is given by

$$U = \frac{3}{2} N T + 3 N \pi^2 \rho \frac{\hbar^3}{4 m} \sqrt{\frac{1}{m} \frac{1}{T^2}} + \dots$$

and the equation of state is

$$p V = N T + 2 N \pi^2 \rho \frac{\hbar^3}{4 m} \sqrt{\frac{1}{m} \frac{1}{T^2}} + \dots$$

The above represent the semi-classical expansions for the energy and equation of state of an ideal Fermi gas.

Large z expansion: Write $z = e^{\beta \mu}$ and $R = \sqrt{\xi \beta \mu}$ so that,

$$g_n^1 = (\beta \mu)^{\frac{3}{2}+n} \int_0^\infty \xi^{\frac{1}{2}} d\xi \frac{2\pi \xi^n}{(z(\xi^2+1))}$$

Handwritten notes: $h \rightarrow 0$, $m \rightarrow \infty$, $T \rightarrow \infty$, $n=0 \rightarrow 2P$, $n=1 \rightarrow 4V$

And I get this kind of an expansion of semi classical expansion for the energy density of a quantum fermi gas at high temperatures. So remember this is semi classical as high temperatures.

So high temperatures is the leading contribution to the energy is the classical ideal gas result which is $U = 3/2 NT$ and then you also have quantum corrections. So notice that the Planck's constant appears prominently in the numerator.

So it is inviting you to make that tend to 0 and get back your classical results. So if you make Planck's constant go to 0 you get back your classical result which is total energy is $3/2 NT$. So same here for equation of state so the leading contribution is the classical equation of state which is $pV = NT$ and then you can either choose to make Planck's constant go to 0 or you can choose to make the temperature go to infinity which is the same thing or you can make the mass go to infinity.

See all these possibilities are there for you to stare at explicitly. So you can recover the classical equation of state using either of these three methods. So you either make $h \rightarrow 0$ or you make $m \rightarrow \infty$ or you make $T \rightarrow \infty$. So all these three are equivalent and they all make this thing go to 0 and you get back your classical equation of state. So but then if you choose not to do that what you are essentially calculating is the quantum corrections to the classical equation of state and classical energy of a gas.

So the quantum corrections also have hidden in them information about the nature of the underlying statistics or the quantum nature of the particles. So if it is fermions only if it is fermions it has this particular form. If it is not fermions if it is bosons if this formula is going look very different I mean if it is going to look their same here but then it is going to look different there.

Ok so now let us get to the more interesting problem of the large z expansion. So I told you that the small z expansion is nothing but a semi classical expansion. So you get back something close to the classical ideal gas results. So now the reverse is what is known as the large z expansion or the ultra-quantum expansion. So in the ultra-quantum expansion you are actually making the temperature go to 0 instead of go to infinity. So it is the other extreme limit.

So in order to do this what we have to do is that I am going to reparametrize my integration variables remember there was some R which was dimensionless. I am going to rewrite in terms of another dimensionless quantity called ξ okay so I am going to redefine R to be this. The

advantage of doing this is I can explicitly extract the temperature dependence outside and then finally I end up with an integral that only depends on some numerical values n.

So remember this n was either 0 well n was 0, so n was 0 if I wanted to calculate ρ and n was 1 if I wanted to calculate energy density. Ok so I am going to use this now and so remember when z is very large so when z is very large so here is z. So when z is very large then most of the contribution comes when $\xi - 1$ is negative. So when, see if $\xi - 1$ is positive then z to the power positive is very large and that very large is in the denominator and it is going to do suppress the whole thing.

However if $\xi - 1$ is less than 0 so it is going to be z raise to something less than 0 and if z is very large that whole quantity is going to become very small and that is going to tend to 0 and so that dominant term will be 1 and so that is you get an answer which is not vanishingly small. But what I can first do is that given this the fact that there is a natural you know the interval between 0 to infinity can be naturally split up into interval from 0 to 1 and from 1 to infinity.

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When $z \gg 1$, the dominant contribution comes from $0 < \xi < 1$. Hence we may write,

$$g_n^1 = (\beta \mu)^{\frac{3}{2}+n} \int_0^1 \xi^{\frac{1}{2}} d\xi 2\pi \xi^n - (\beta \mu)^{\frac{3}{2}+n} \int_0^1 d\xi \frac{2\pi \xi^{n+\frac{1}{2}}}{(z^{-(\xi-1)} + 1)} + (\beta \mu)^{\frac{3}{2}+n} \int_1^\infty d\xi \frac{2\pi \xi^{n+\frac{1}{2}}}{(z^{(\xi-1)} + 1)}$$

So from 0 to 1 I can rewrite it like this so I will rewrite like this. So this is a mathematical identity, I've just re written in terms of just split it up from 0 to 1 and from 1 to infinity. Ok this is what you will have to take my word for it so this is how it looks like. So now I can now make expansions that in the last two integrals it says that the dominant contribution comes from the region near $\xi = 1$ and why is that? Because see if z is since $z \gg 1$ always.

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In the last two integrals the dominant contribution comes from the region near $\xi = 1$. Hence we may write $\xi = 1 + \xi'$,

$$I_1 = \int_0^1 d\xi \frac{2\pi \xi^{n+\frac{1}{2}}}{(z^{(\xi-1)} + 1)} = \int_{-1}^0 d\xi' \frac{2\pi (1+\xi')^{n+\frac{1}{2}}}{(z^{-\xi'} + 1)} \approx \int_{-\infty}^0 d\xi' \frac{2\pi (1+\xi')^{n+\frac{1}{2}}}{(z^{-\xi'} + 1)} \approx \int_{-\infty}^0 d\xi' \frac{2\pi}{(z^{-\xi'} + 1)} + \int_{-\infty}^0 d\xi' \frac{2\pi \left(n + \frac{1}{2}\right) \xi'}{(z^{-\xi'} + 1)}$$

Similarly,

$$I_2 = \int_1^{\infty} d\xi \frac{2\pi \xi^{n+\frac{1}{2}}}{(z^{(\xi-1)} + 1)} \approx \int_0^{\infty} d\xi' \frac{2\pi}{(z^{\xi'} + 1)} + \int_0^{\infty} d\xi' \frac{2\pi \left(n + \frac{1}{2}\right) \xi'}{(z^{\xi'} + 1)}$$

Therefore,

$$I_1 = \frac{\pi \text{Log}[4]}{\text{Log}[z]} - \frac{(2n+1)\pi^3}{12 \text{Log}[z]^2} ; I_2 = \frac{\pi \text{Log}[4]}{\text{Log}[z]} + \frac{(2n+1)\pi^3}{12 \text{Log}[z]^2}$$

So if $z \gg 1$ so recall that here in this integration limit $0 < \xi < 1$. So if it is less than 1 this exponent is positive. So as a result this whole thing gets suppressed. So the only way it does not get suppressed is when ξ is close to 1. So if ξ is close to 1 this becomes close to 0 and so somehow this thing will still survive when ξ is close to 1. So this integral will survive you know will contribute dominantly only in the regions where ξ is near 1.

So as it goes from 0 it is like integrand I mean the integration contributes negligibly from 0 all the way up to something close to 1. So from somewhere from $1 - \epsilon$ to 1 then only in this region it sort of contributes you know all other regions it kind of does not contribute. So I am going to explicitly make use of this idea. Here also you can see that because z is much larger than 1 always in this example I mean remember I am taking the other extreme limit.

I have already studied the z small limit so I am now taking the z large limit. So the z large limit, so again because ξ is no larger than 1 in this part of the integration. So this whole thing is going to be again suppressed unless ξ is again close to 1. So in this integration when I integrate from 1 to ∞ , I have to be you know I can get away by integrating it from 1 to some $1 + \epsilon$. I do not have to go all the way up to infinity because it is not going to contribute much.

So I am going to make you use of this and I am going to rewrite because I can get away with this like this. So I can rewrite in terms of so ξ is always close to 1 so I can write it as $1 + \xi'$. And now

notice that ξ' so I have split it up into this one this integration. So I have split it up into the integration, not split it up rewritten it in terms of ξ' . So that is what I have done here. So I have rewritten in terms of ξ' .

So now notice that because of this integrand is substantial only when ξ' is close to 0. So therefore, when ξ is close to 1 so I do not care what is this I mean it might as well be minus infinity it is not going to make any difference. As I told you most of the integration is going to contribute for ξ' close to 0. So it does not matter whether I call this - 1 or call this- 2 or -3 it is not going to contribute much I mean it is not going to affect my answers that much.

So I am going to be bold and make it all the way to $-\infty$ because I know that it is not in fact it is going to contribute less and less as it becomes more and more negative. So I might as well do that. So if I do that then I can use my expansion so remember this is I can use my binomial type of expansion and rewrite it like this. So that is the story for this integration the first term here which I have called I_1 I call this I_1 . So now I can do the same thing for this integration which I am going to call I_2 .

So the I_2 is similarly I am going to write it like this. So now notice that in case of I_1, ξ' was close to 0 at negative but in the case of I_2, ξ' is close to 0 but positive. So here I have to go from 0 so here I am in a happy position this is already infinity so I might as well go to infinity. So then I can go ahead and do the same type of expansion and this is $\xi = 1 + \xi'$ and then I expand and get this.

So when I do this integration I finally end up with this, these results explicit result for I_1 and I_2 they look pretty ugly. But that is fine I am going to be able to use them now. So I am going to substitute that back in so remember that ones I get my I_1 and I_2 I put them back here because this was I_2 and this was I_2 and I put them back there and I get this expression.

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$$g_n^1 = (\beta \mu)^{3+n} \frac{4\pi}{3+2n} - (\beta \mu)^{3+n} \left(\frac{\pi \text{Log}[4]}{\text{Log}[z]} - \frac{(2n+1)\pi^3}{12 \text{Log}[z]^2} \right) + (\beta \mu)^{3+n} \left(\frac{\pi \text{Log}[4]}{\text{Log}[z]} + \frac{(2n+1)\pi^3}{12 \text{Log}[z]^2} \right)$$

or,

$$g_n^1 = (\beta \mu)^{3+n} \frac{4\pi}{3+2n} + (\beta \mu)^{3+n} \frac{(2n+1)\pi^3}{6 \text{Log}[z]^2}$$

$$u_V = \frac{U}{V} = \int \frac{d^3R}{c_0^3 \beta} \frac{R^2}{(e^{R^2} e^{-\beta \mu + 1})} = \frac{g_1^1}{c_0^3 \beta}$$

$$\rho = \frac{N}{V} = \int \frac{d^3R}{c_0^3} \frac{1}{(e^{R^2} e^{-\beta \mu + 1})} = \frac{g_0^1}{c_0^3}$$

$$c_0 = \left(2\beta \frac{\hbar^2 \pi^2}{m} \right)^{\frac{1}{2}}$$

And then when I simplify it these two terms cancel out ok. So these two terms cancel out and I end up getting this. So the leading contribution is this and the next leading contribution is this. This is the next leading because remember that I am doing a large z expansion, so this is the same thing here same thing there but then there is a $\log[z]^2$ in the denominator. So this is less important compared to this.

So now remember that this is what u_V was as usual ok in terms of thermal wavelength. So this was u_V which is energy per unit volume when this was the number per unit volume. So as usual I told you that there is an annoying feature which is common to all these approaches that I have discussed so far and that is that instead of expressing everything in terms of energy density, it is expressing everything in terms of chemical potential which I do not care about. So $z = e^{\beta \mu}$ and μ is chemical potential I do not care too much about it.

So I have to make this uncomfortable but necessary calculation or I have to perform this step where I convert my chemical potential back in terms of the number of particles per unit volume. So I have to use this as a kind of dictionary where I translate the chemical potential language back into the number density language. So unfortunately, it has to be done and it has to be done on a case by case basis because for fermions the details are different for bosons were details are very different.

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When the density of fermions is fixed (independent of temperature) then the Chemical potential has to be adjusted and made to depend on temperature such that this is achieved. Given that the large z expansion is same as low temperature expansion, we may write,

$$\mu = \mu_F (1 + x); \text{ where } x \ll 1$$

Here μ_F is the chemical potential at zero temperature. Write $\mu_F = \frac{\hbar^2 k_F^2}{2m}$ so that,

$$\rho = \frac{k_F^3}{6\pi^2}$$

$$\frac{k_F^3}{6\pi^2} \approx \frac{\left((\beta\mu_F)^{\frac{3}{2}} \frac{4\pi}{3} \left(1 + \frac{3}{2}x\right) + (\beta\mu_F)^{\frac{1}{2}} \frac{\pi^3}{6} \right)}{\left(2\beta \frac{\hbar^2 \pi^2}{m} \right)^{\frac{3}{2}}}$$

Handwritten notes:
 $p_F = \hbar k_F$
 $\sim \frac{\hbar^2 k_F^2}{2m}$
 $(1+x)^{3/2} \sim (1 + \frac{3}{2}x)$

So for fermions it so happens that absolute 0 the chemical potential actually freezes to a certain value which I called μ_F . So remember that the large z expansion is same as low temperature expansion. For reasons that are obvious because large z means $e^{\beta\mu}$ is large and you know you can think of μ as something fixed and then make β large. And β large is same as temperature is small.

So if you believe my assertion, ofcourse let us make this assertion and then convince ourselves that it is correct and namely that at large z expansion or low temperature expansion I am entitled to write the chemical potential as something μ_F which is the chemical potential at 0 temperature times term which is going to be small as temperature tends to 0. Okay so I am going to also introduce a new quantity called k_F which is basically called a fermi wavenumber.

So the fermi wavenumber is defined as the chemical potential at absolute 0 when it is expressed in terms of $p_F^2 / 2m$ and where p_F is the fermi momentum which is defined as

$$p_F = \hbar k_F$$

So this is nothing but $p_F^2 / 2m$ so if I rewrite my chemical potential at 0 temperature in terms of this that is what it is. So I can re-express my density in terms of k_F .

Now that I have been able to do this I can go back and rewrite this formula. So this formula if I rewrite in terms of k_F and I plug this back in into this formula here. So I put $n = 0$ and I put this in here I get this rather ugly looking expression which I have to solve, ok. So keep in mind that

in this case x is really small and because of that I have expanded μ to the $3/2$. I have written as in fact I got something like this which I have approximated as $1 + 3/2$ and so on that is what I have done here.

Ok so other than that I have not done anything else. So now if you stare at this you will see that after simplification I will be able to write down an answer for x , you see this term so basically what is going to happen is that this term will see because when β is very large, so low temperatures ok. So there is a $\beta^{3/2}$ sitting here so that is very important.

There is a $\beta^{-1/2}$ so that is less important but then this will one can suspect there will be you know $1/\beta$ sitting all over the place in x also x is depends on β . So that will be $1/\beta$ to the power of something some positive number. So this is also because it is x is small at low temperatures. So this term is going to be as small as this term. So the important I mean the terms that is most important is this one.

And by construction this term is the same as this one I mean when all put together everything put together this term and this this everything put together is this. So that is how I have constructed it. So as a result I can equate the rest of it to 0 when I cancel out the zeroth order term the first order terms also have to cancel out. So that will tell me the relation between x and the rest of it. So the answer comes out to be this.

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Hence $x = -\frac{\pi^2}{12} \left(\frac{T}{\mu_F}\right)^2$ or

$$\mu = \mu_F \left(1 - \frac{\pi^2}{12} \left(\frac{T}{\mu_F}\right)^2\right)$$

$$\frac{U}{N} = \frac{u_V}{\rho} = \frac{g_1^1}{c_0^3 \beta \rho} = \frac{(\beta \mu)^{\frac{5}{2}} \frac{4\pi}{5} + (\beta \mu)^{\frac{1}{2}} \frac{\pi^3}{2}}{\rho c_0^3 \beta} = \frac{3}{5} \mu_F \left(1 + \frac{5\pi^2}{12} \left(\frac{T}{\mu_F}\right)^2\right)$$

$$C_V = N \frac{\pi^2 T}{2 \mu_F}; \quad C_P = \frac{5}{3} C_V$$

EQUATION OF STATE: $pV = \frac{2}{3} U = \frac{2}{5} \mu_F \left(1 + \frac{5\pi^2}{12} \left(\frac{T}{\mu_F}\right)^2\right)$

So I mean instead of rambling on and on I think what you should do is not allow me to ramble on and on, what you should do is pause this video and you know go ahead and verify all these steps on your own right now and just pause the video just go ahead and take a piece of paper or several pieces of paper and a pen and workout all the steps until you are sure about what you are doing and what I was saying.

Make sure that what I was saying was right and it is right but make sure it is right. So convince yourself that it is right. Ok, so I am going to allow you to do that and now let me stop here because I am going to continue discussing how to get the equation of state and the energy density of an ideal fermi gas explicitly in terms of temperature by completing this calculation.

And later on what we will do is we will learn how to repeat this calculation for an ideal Bose gas. And once we do that we will be in a position to consolidate all these results we have obtained in one big slide and we will be able to stare at them. So remember we have succeeded in studying the classical ideal gas which was really simple but then we also succeeded in studying the quantum fermi gas both at low and high temperatures.

And later on we will study the quantum ideal Bose gas at low and high temperatures also and then we will be able to you know put down all these results in one slide and stare at them. And when we stare at them we will notice a pattern and that pattern will enable us to introduce what is known as a virial expansion of the equation of state. So let us get to that gradually so we are going to study that and that is very interesting and very useful. Ok so I am going to stop here, thank you.