Statistical Mechanics
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Lecture - 17
Classical Ideal Gas (Canonical Ensemble)

Hi, so good morning students. Today, we will talk about system of continuous degrees of variables a continuous degree of freedom. And this will be system under Canonical Ensemble.

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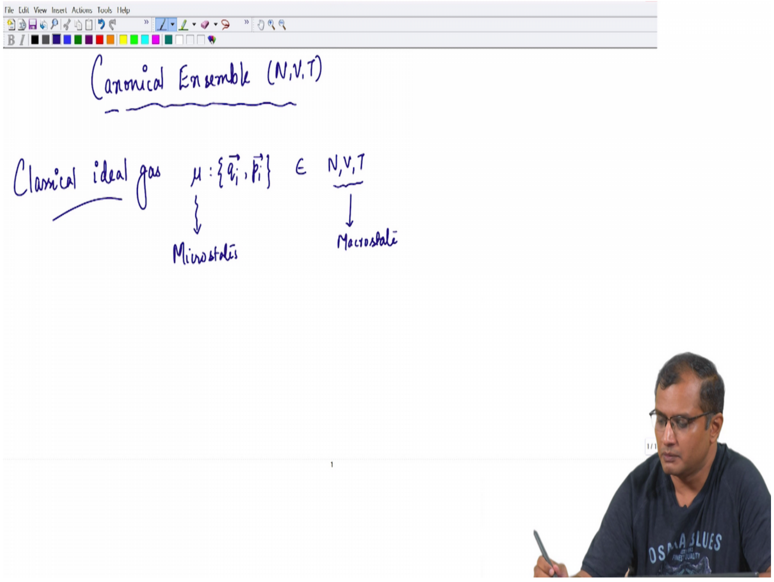

So, the case study would be of an ideal gas, where the degrees of freedom are continuous random variables. So, I am going to take case study of classical ideal gas. We had taken this case study of the ideal gas under constant energy condition that was the micro canonical ensemble.

So, today I am going to take the same gas where particles are to be treated ideally in the sense that they do not have any interaction potential. So, micro state typically of a classical ideal gas is composed of a set of coordinates and momenta, these constitutes a single micro mu. And the microstate belongs to our macro state N, V, T ok. So, this is your micro state and there are large number of micro states. And this is our macro state the specified value of N, V, T ok.

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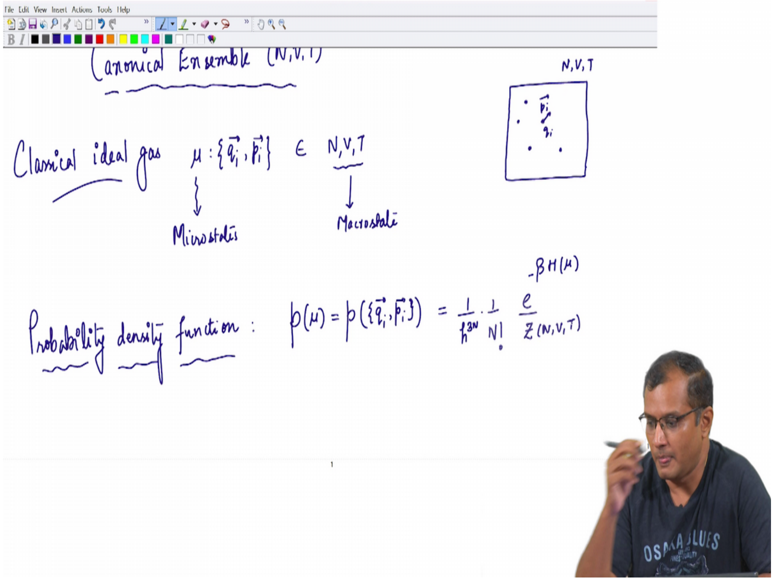

Canonical Ensemble (N, V, T)

Classical ideal gas $\mu : \{\vec{q}_i, \vec{p}_i\} \in N, V, T$

Microstates

Macrostate

Probability density function : $\rho(\mu) = \rho(\{\vec{q}_i, \vec{p}_i\}) = \frac{1}{h^{3N}} \cdot \frac{1}{N!} \frac{e^{-\beta H(\mu)}}{Z(N,V,T)}$

So, now, you can think of this ideal gas as a system which is enclosed in a container and you particular particle here is having momenta of pi and location is some q i and so on and so forth ok. So, this is a box of volume V, there are N particles in the box and it is in contact with the heat reservoir at temperature T, which means I can write down the probability density function. Remember we do not have probabilities here because degrees of freedom are continuous. So, we need a some continuous version of our probabilities which is density function. Now, this is to be realized as function which when integrated over the entire volume of phase space accessible to my system is unity ok.

So, I can define my PDF of a particular microstate which means the microstate here is nothing but a particular set of values for momentum and positions which keeps continuously changing. So, this is one microstate and I want to know its probability density. So, this would be 1 upon h to the power 3 N into 1 upon N factorial e to the power minus beta times the Hamiltonian of the microstate over the canonical partition function.

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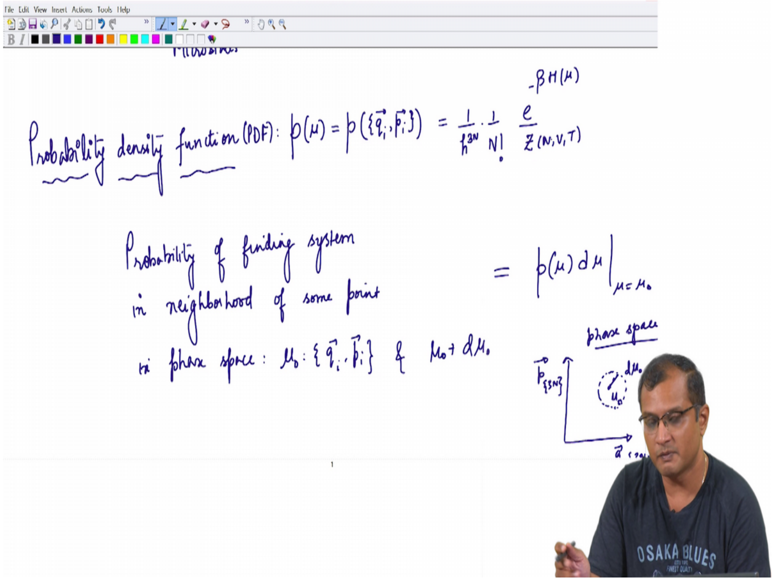

Probability density function (PDF): $p(\mu) = p(\{\vec{q}_i, \vec{p}_i\}) = \frac{1}{h^{3N}} \cdot \frac{1}{N!} \frac{e^{-\beta H(\mu)}}{Z(N,V,T)}$

Probability of finding system in neighborhood of some point in phase space: $\mu_0 : \{\vec{q}_i, \vec{p}_i\}$ & $\mu_0 + d\mu_0$ $= p(\mu)\, d\mu \big|_{\mu = \mu_0}$

Now, as you can see here what is meant by the probability density function is that I can ask myself what is the probability now of finding our system in a in the neighborhood of see if I basically ask yourself, ask you a question that the neighborhood of some in the neighborhood some part of phase space. So, some value q and p in the phase space of some point now this is momentum and this is you know then basically what is what is meant by here is that I would like to write this you know some of the phase space point as some point in the phase space.

Let us say let us call that point in the phase space as some point as a mu naught which is given by some specified values of you know these all the particles ok. So, all q i's are specified and all p i's are specified. And the neighbor[hood] of a neighborhood of this point mu naught means that in the vicinity of mu naught and that is basically number of states between some mu naught and mu naught plus d mu naught ok. And that probability is given as simply p of mu d of mu at mu equals to mu naught that is the meaning of probability density. So, you go to your 6 N dimensional phase space.

And so this is basically 3 N momentum coordinates and I have 3 N position coordinates. In the 6 N dimensional phase space, if I select a point as mu naught you know some microstate and if I want to ask what is the probability of finding a system in a small cell of volume you know in a small shell around this mu naught, then basically of volume ok. So, in some sense this would be; this would be like in the neighborhood of this mu naught and so this would be like some distance d mu naught. See you can volume around this mu naught then your answer is this probability that I have written here ok.

So, let us from the definition of this probability density function or PDF, compute the partition function. Say if you look at the definition of the PDF you can think of the canonical partition function simply as a normalization of your PDF.

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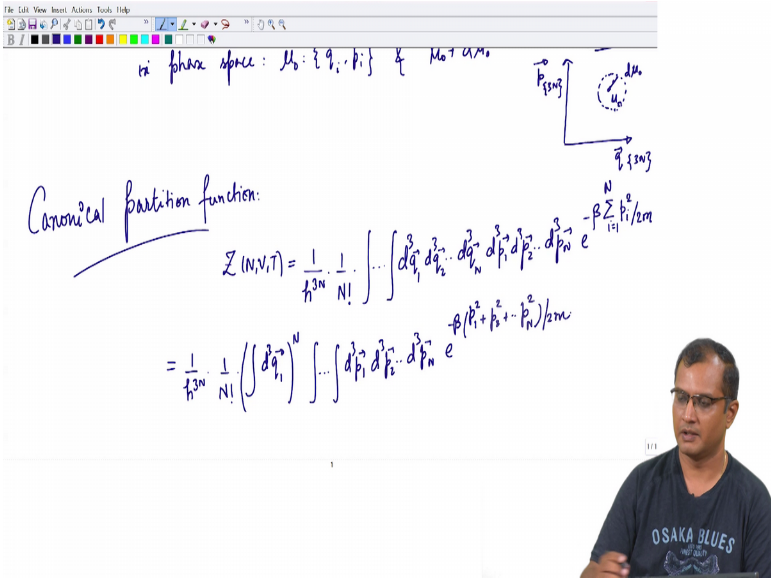

in phase space : $\mu_0 : \{q_i, p_i\}$ & $\mu_0 + d\mu_0$

Canonical partition function:

$$Z(N,V,T) = \frac{1}{h^{3N}} \cdot \frac{1}{N!} \cdot \int \cdots \int d^3\vec{q}_1 \, d^3\vec{q}_2 \cdots d^3\vec{q}_N \, d^3\vec{p}_1 \, d^3\vec{p}_2 \cdots d^3\vec{p}_N \; e^{-\beta \sum_{i=1}^{N} p_i^2/2m}$$

$$= \frac{1}{h^{3N}} \cdot \frac{1}{N!} \cdot \left(\int d^3\vec{q}_1 \right)^N \int \cdots \int d^3\vec{p}_1 \, d^3\vec{p}_2 \cdots d^3\vec{p}_N \; e^{-\beta (p_1^2 + p_2^2 + \cdots p_N^2)/2m}$$

So, I can write down the canonical partition function which is the norm of this PDF. So, this partition function by the definition of p of nu that have taken you know is simply the norm of this so which is nothing but partition function normalizes our PDF. So, it is simply by this definition given as 1 upon h to the power 3 N into 1 upon N factorial into these N-dimensional 3 N dimensional position integrals to conserve the space.

So, I will use the space done below to write it down. This is the cell volume h to power 3 N, the N factorial here reminds us that we are looking at the case of ideal gas where particles are all identical. So, to avoid over counting of the microstates because particles are indistinguishable. There are precisely N factorial microstates for each arrangement of unpacked particles. So, I need to divide the partition function by N factorial to avoid the over counting.

And then I have these integrals over the entire phase space. So, I am going to write down d cube q 1 into d cube q 2 to all the way to d cube q N, then I have these momentum integrals of the our Boltzmann factor which is e raised to minus beta the Hamiltonian of a microstate is nothing but summation overall particle momenta, where i will go from 1 to N p i square by 2 m ok. So, p i square is nothing but the sum of squares of momentum of each particle and there are N particles in the system.

So, straightaway I can see that the position integrals and the volume integrals are independent. So, I can integrate them separately. So, the position integrals will give me its position integral will give me, so I can write down this as a integral d cube q 1. And since each one of them is separate I can say that this is nothing but to the power N yes I will take just one of them and raise it to the power N because, they are all the same and they are independent. And the same applies for the momentum integrals. So, let me just write them after small manipulation here. So, I am going to write down this as a integral d cube p 1 into d cube p 2 all the way to the d cube of p N into e raised to minus p 1 square by 2 m correct.

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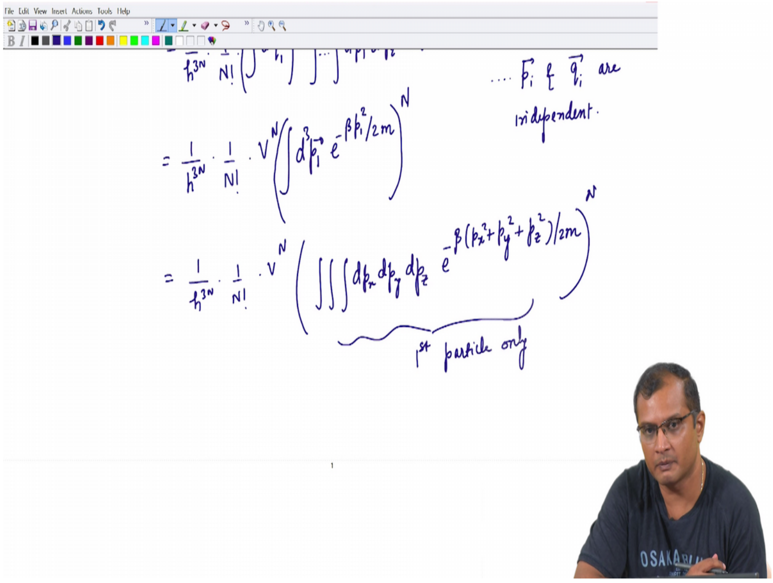

.... $\vec{p}_i$ & $\vec{q}_i$ are independent.

$$= \frac{1}{h^{3N}} \cdot \frac{1}{N!} \cdot V^N \left(\int d^3\vec{p}_1 \, e^{-\beta p_1^2/2m} \right)^N$$

$$= \frac{1}{h^{3N}} \cdot \frac{1}{N!} \cdot V^N \left(\underbrace{\iiint dp_x \, dp_y \, dp_z \, e^{-\beta (p_x^2 + p_y^2 + p_z^2)/2m}}_{1^{st} \text{ particle only}} \right)^N$$

So, now I can write this simplify this further I can write this is 1 upon x to the power 3 N into 1 by N factorial. The single volume integral would give me V, but I have raised it to the power N so, it gave me V to the power N. And look at the momentum integrals since they all these p i's are independent of each other. So, I can write this as a single integral over one particle and raise this to the power N, in case since all these particle momenta are independent. You can basically write that momentum and positions are independent.

Now, you can write this as so the momentum integral that I have written is if you look at p 1 square is the sum of squares of the components of momentum of the first particle ok. So, this can be written as I can write down this as d cube p 1 can be written as week triple integral d p x d p y and d p z of e raised to minus beta p x square plus p y square plus p z square of the first particle ok. And I can raise the entire thing to N ok. So, I am going to write down this as for the first particle itself. So, a single particle contribution has to be raised to power N that will give you the contribution coming from N particles.

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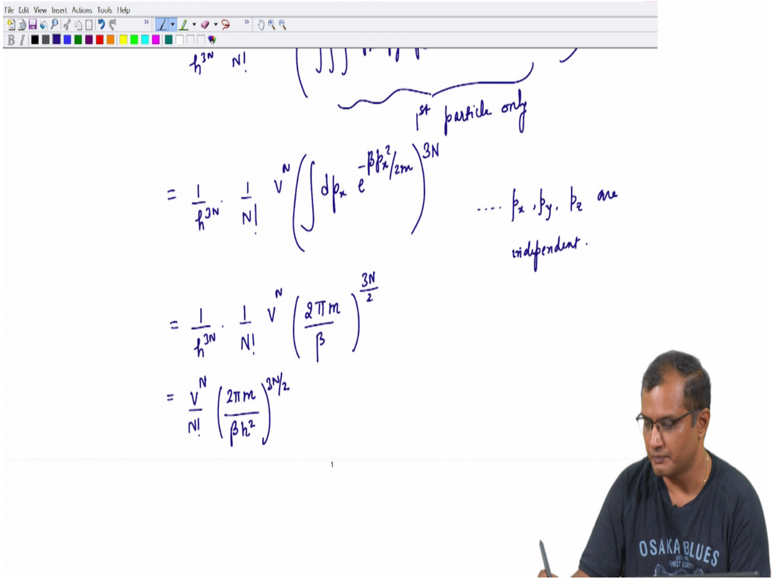

1st particle only

$$= \frac{1}{h^{3N}} \cdot \frac{1}{N!} V^N \left(\int dp_x \, e^{-\beta p_x^2/2m} \right)^{3N}$$

.... p_x, p_y, p_z are independent.

$$= \frac{1}{h^{3N}} \cdot \frac{1}{N!} V^N \left(\frac{2\pi m}{\beta} \right)^{\frac{3N}{2}}$$

$$= \frac{V^N}{N!} \left(\frac{2\pi m}{\beta h^2} \right)^{3N/2}$$

Now, you can see that each component of the momentum of any particle is independent of the other component which means I can write this as further simplification is possible here, I can write this as simply integral d p x e raised to minus beta p x square by 2 m, but now I have to raise it to power 3 there was already a power N sitting outside ok. Since p h, p y and p z are independent that is the definition of a vector its components are linearly independent.

So, then I know that the now the integral that is sitting inside bracket is a simple Gaussian integral, which is just square root of pi by a, a being the pre factor p x square. So, I can write this as V to the power N square root of pi by a, a being the pre factor of p x square. So, I just have beta here and 2 pi m. But this entire thing is raised to the power 3 N by 2. So, I am going to the entire thing is raised to 3 N. So, I am going to write this as just one half that comes from the Gaussian integral and 3 N which is already sitting outside ok. So, this is the canonical partition function. And let us just simplify it a little bit. So, what I can do is I can write down this be V raised to N upon N factorial and take the h inside this parenthesis. So, I can write this as 2 pi m upon beta h square raised to 3 N by 2 ok.

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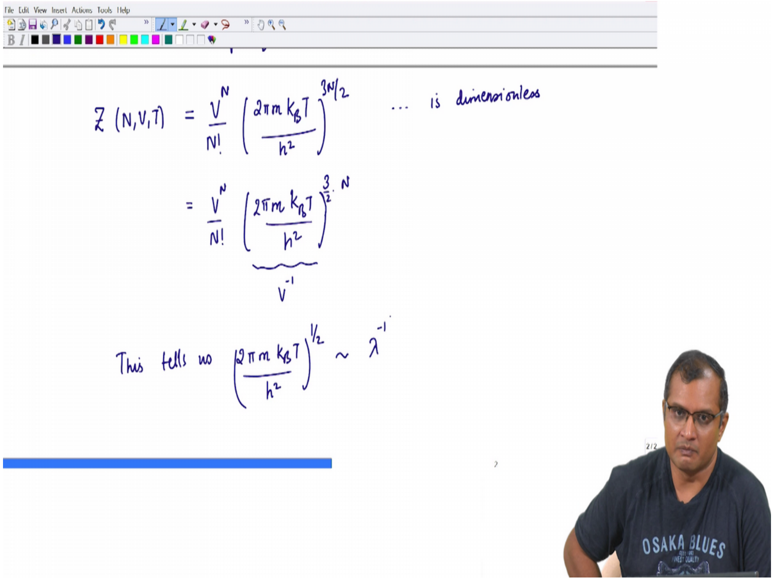

$$Z(N,V,T) = \frac{V^N}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2} \quad \ldots \text{ is dimensionless}$$

$$= \frac{V^N}{N!}\underbrace{\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}\cdot N}}_{V^{-1}}$$

This tells us $\left(\frac{2\pi m k_B T}{h^2}\right)^{1/2} \sim \lambda^{-1}$

So, this is my canonical partition function. And I can write it as V raised to N upon N factorial beta is just 1 upon k T. So, I can write this as 2 pi m k B T upon h square to the power 3 N by 2, now 2 pi m k T upon h square is related to a length scale. Why do I say it because partition function is dimensionless it has to be here we are going to take a logarithm of this to compute pre energy and build bridge that connects to the thermodynamics very soon I am going to construct that bridge. But let us know that let us be aware of the fact that Z has dimensionless which means I have got a volume to the power N already, N factorial is dimensionless, which means this guy if I write it like V to the power N upon N factorial into 2 pi m k T upon h square raised to half raised to N. So, this quantity should have the dimensions of the V to the power minus 1, because there is a V raised to N as a pre factor, so unless this 2 pi m k T upon h square root.

Student: That whole raise to 3M right so.

Right, though.

Student: (Refer Time: 20:06).

Right, right. So, this has to be so I am going to write it as. So, the entire 2 pi m k T upon h square to the power 3 by 2 should have the dimensions of 1 upon volume, because then raised to the power N it has the dimensions of 1 upon volume to the power N ok, so that will cancel with the dimension it will cancel with the dimensions of V raised to N.

Now, which tells me that since volume is constructed as a cube of a length scale, I have to take this tells us that the entire thing that I have indicated as V raised to minus 1 is a cube of a length scale. So, I can tell that 2 pi m k B T upon its square raised to just the one half is related to some length to the power minus 1, because now if I raise both to the power minus 3, there comes lambda to the power minus 3, which is like a 1 upon volume that is what I want ok.

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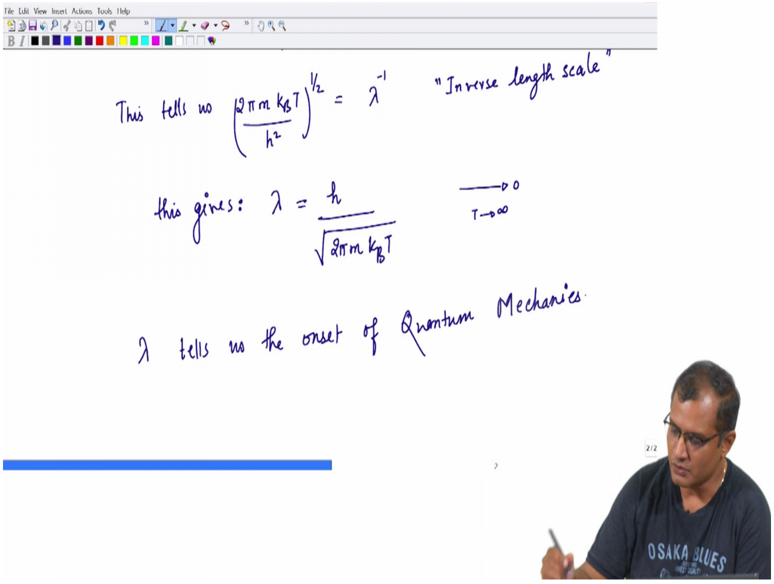

This tells us $\left(\frac{2\pi m k_B T}{h^2}\right)^{1/2} = \lambda^{-1}$ "Inverse length scale"

this gives: $\lambda = \frac{h}{\sqrt{2\pi m k_B T}} \xrightarrow[T\to\infty]{} 0$

λ tells us the onset of Quantum Mechanics.

So, if I call this as the some 1 upon length scale ok, some inverse length scale and I am going to tell you that this is an important length scale. So, let us this gives let us workout what it gives; my lambda as simply h upon square root of 2 pi m k B T. Now, this length scale very clearly you know it goes to 0 as the temperature goes to infinity. And this length scale becomes larger and larger as the temperature goes to 0. So, this is very important length scale which goes by the name of de Broglie scale length, it sort of manifests the onset of quantum mechanics at low temperature. So, one has to associate lambda that at what temperatures one has to consider quantum mechanical effects naturally, lambda alone will not tell us the onset of quantum mechanics, you have to compare lambda with some other length scale.

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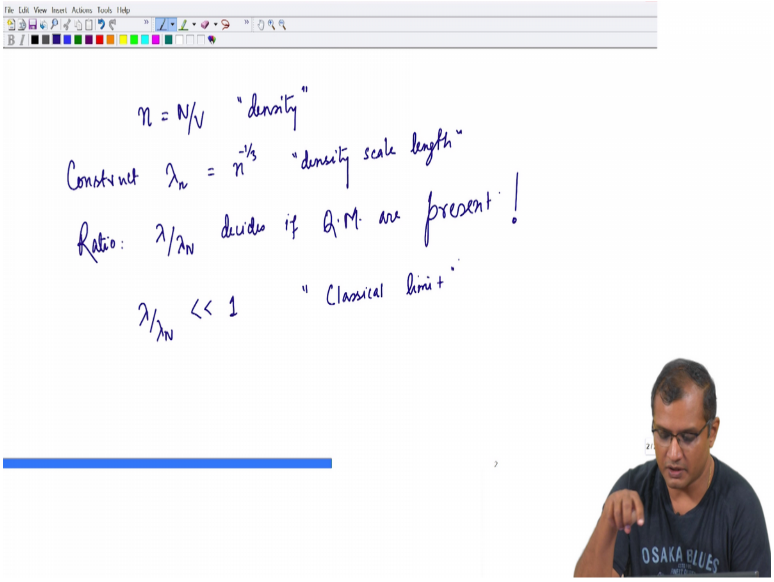

$n = N/V$ "density"

Construct $\lambda_n = n^{-1/3}$ "density scale length"

Ratio: λ/λ_N decides if Q.M. are present!

$\lambda/\lambda_N << 1$ " Classical limit"

So, let me come give you a some comparison. So, if you have a density, so there would be a length scale that you can construct from density. So, I would say that there is a construct some no, I am going to tell you how quantum mechanics sort of how can you tell that quantum mechanic effects are arising in your system.

So, construct some length scale from density which is something like material property of a system, because density is once you decide the density for your system, it remains as it is ok. So, N particles in a box of volume V fixes your density. Now, you can play with the temperature and hence play with your de Broglie wavelength and see how does your de Broglie wavelength compare with your density length scale.

So, let us say you have a density which is fixed ok. So, construct some density land scale lambda sub N which is nothing but n to the power minus 1 by 3 roughly if you take an inverse cube root of density, it will give you a length scale which is I am going to call as a density length scale.

Now, the ratio of your de Broglie wavelength over lambda N decides if quantum mechanical efforts are present. So, if lambda is over lambda N becomes a number which is much smaller than 1, you know that lambda N is dominating here which means your density scale lengths are much much larger compared to your de Broglie wavelength. So, you will not be using quantum mechanics here at all, when will lambda by lambda N become a smaller than 1, well certainly when your either your density is very.

So, lambda by lambda; lambda over lambda N to the power N simply tells me that you know this is the classical limit, where your lambda is much larger than lambda N. So, here density is fixed to some length scale. Now, if your de Broglie wavelength is much much smaller, which means the temperature is too high at the high temperature limit. So, your quantum mechanical efforts are almost gone.

Student: Anyone this length scale can be (Refer Time: 26:27) about distinguishability or distinguish between it will save the length scale we can talk about the.

So, distinguishability is embedded in quantum mechanics from the property of the wave function itself. So, for example we know that for fermions and bosons have wave functions that are either anti-symmetric or symmetric, depending upon whether they are Fermi wave functions or a wave functions bosons.

So, in distinguishability is embedded in quantum mechanics from the beginning and so we do not have to introduce N factorial in the calculations that is totally separate argument from whether you are in classical limit or quantum limit. So, the every system can be pushed to quantum limit by increasing density or reducing temperature both have the same effects; see if I increase the temperature density my length scale lambda N reduces.

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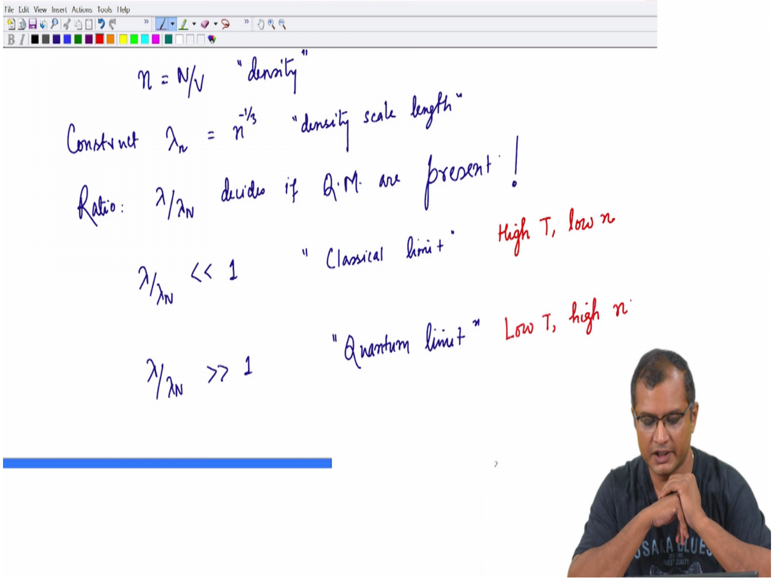

$n = N/V$ "density"

Construct $\lambda_n = n^{-1/3}$ "density scale length"

Ratio: λ/λ_N decides if Q.M. are present !

$\lambda/\lambda_N << 1$ " Classical limit " High T, low n

$\lambda/\lambda_N >> 1$ "Quantum limit" Low T, high n

So, let me write down first. So, the other limit of course yes, when you are in much larger than 1 and I am going to say that this is a quantum limit. Now, let us see both the cases. See you have in your hand two things; temperature and density; if you take high temperature and low density, high temperature would make lambda smaller de Broglie wavelength smaller, so your numerator in the first case is getting smaller.

And the fact that you have taken low density will push a lambda N to larger values, a particles are now separated further and further, because you are at low density. So, numerator is smaller, denominator is larger what is this ratio make become numerator is smaller denominator is large?

Student: (Refer Time: 28:16).

Numerator is small denominator is large the ratio becomes much smaller ok, so that is your classical limit. Now, quantum limit for the system can come if you go to high density and low temperature, which means if you go at low temperature, your de Broglie wavelength will inflate, it will become larger and larger, because it goes as 1 upon square root T. So, low temperature means de Broglie wavelength will go up. So, look at your expression. So, de Broglie wavelength is going to larger and larger values, because a temperature is taken to lower and lower values. What happens to the denominator?

Student: When density is very small.

When density is small, now the particles are basically closer to you know when the density is large not small. So, the classical limit high T and low density and the quantum limit is sitting at I am going to use different colour and this is sitting at low temperature and high density. Now, think when the numerator which is lambda depends on temperature. So, if you go to low temperature what happens to the numerator?

Student: (Refer Time: 29:47).

And if you go to high density what happens to the denominator?

Student: Decreases.

So, what happens to the ratio?

Student: (Refer Time: 29:53) greater than.

Because 10 by 100 is definitely much larger than 100 by 1, which is much larger than 1000 by 0.1 and so on and so forth, so you are making this ratio larger and larger. So, the de Broglie wavelength that I have written here he tells us the onset of quantum mechanics if you have another length scale to compare. So, I have argued here that the length scale to compare is the density length scale.

You cannot just say by looking at high temperature and say that you know, classical effects are expected. Now, you have to also look at density because that will give you another length scale, the density length scale with which you can compare and tell whether classical effects are seen or quantum effects are seen ok. So, you need a reference density scale length being the reference in this scale ok. So, your system can go to the appropriate limit depending upon whether depending upon the ratio of these length scale ok. So, the ratio is important.

Now, let us get back to our calculation. So, we have reached the stage where the partition function is ready for use and as I have always been telling that partition function exists for a certain purpose, it helps us to establish a connection with thermodynamics.

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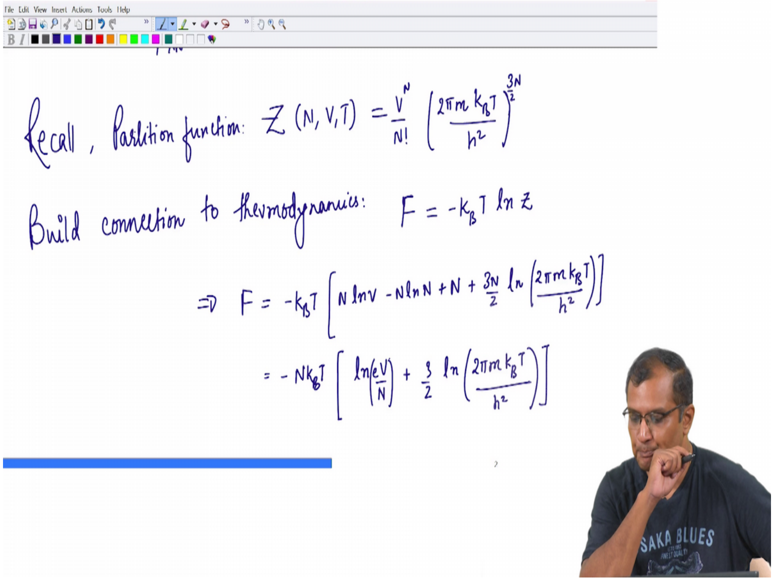

Recall, Partition function: $Z(N,V,T) = \frac{V^N}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3N}{2}}$

Build connection to thermodynamics: $F = -k_B T \ln Z$

$$\Rightarrow F = -k_B T \left[N \ln V - N \ln N + N + \frac{3N}{2} \ln\left(\frac{2\pi m k_B T}{h^2}\right)\right]$$

$$= -N k_B T \left[\ln\left(\frac{eV}{N}\right) + \frac{3}{2} \ln\left(\frac{2\pi m k_B T}{h^2}\right)\right]$$

So, let us make that connection. So, the partition function in the canonical ensemble was given as fine. So, now I am going to build connection to thermodynamics. And the starting point is the computation of free energy. So, the connection from classical mechanics classical statistical mechanics to thermodynamics is obtained by connecting the microscopic world that is residing in your logarithm of Z to the microscopic world which is in free energy is a thermodynamic average to thermodynamically average quantities. So, they represent micro macro states or macro states information.

So, now I can write down my free energy as simply minus k T and logarithm of Z would simply give me N log V these are natural logs to the base e and since N factorial is large I am going to use a Stirlings approximation here. So, it is minus N lon N plus N and the parenthesis as 3 N by 2 lon 2 pi m k T over x square. And so you can sort of simplify for you know for the sake of convenience, so you can take can pull out the number of particles and write it as minus N k T.

And the first two logarithms can be written as logarithm V by N. And you have one here when you pull out an N, so you get a one here that is lon e to the base e. So, I am going to club that e here ok. And this is simply 3 by 2 lon 2 pi m k B T over h square fine. So, let me just write it slightly. Now, so let us call this as expression 1.

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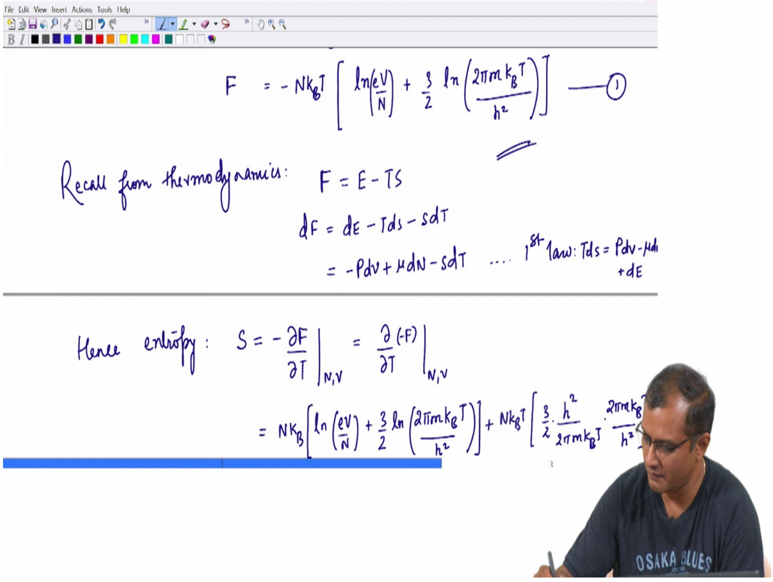

$$F = -Nk_BT\left[\ln\left(\frac{eV}{N}\right) + \frac{3}{2}\ln\left(\frac{2\pi m k_B T}{h^2}\right)\right] \quad \text{——} ①$$

Recall from thermodynamics: $F = E - TS$

$$dF = dE - Tds - sdT$$

$$= -Pdv + \mu dN - sdT \quad \ldots\ 1^{st}\ \text{law}: Tds = Pdv - \mu d$$

$+dE$

Hence entropy: $S = -\left.\frac{\partial F}{\partial T}\right|_{N,V} = \left.\frac{\partial(-F)}{\partial T}\right|_{N,V}$

$$= Nk_B\left[\ln\left(\frac{eV}{N}\right) + \frac{3}{2}\ln\left(\frac{2\pi m k_B T}{h^2}\right)\right] + Nk_BT\left[\frac{3}{2}\cdot\frac{h^2}{2\pi m k_B T}\cdot\frac{2\pi m k_B}{h^2}\right.$$

So, you recall from thermodynamics that your free energy is given as E minus T S ok. So, you can easily write it in differential form and this simply becomes and from first law, we can write d minus Tds as minus P dv plus mu dN.

So, if you recall the 1st law of thermodynamics, we can write down the heat given to a system as work done by the system minus mu dN. And there is also change in internal energy, so you can write down plus dE ok. So, if you write down dE minus Tds, it is minus P dv plus mu dN.

Now, I can use this to get an expression for entropy. So, the entropy here is nothing but you know a partial derivative of free energy with respect to temperature at constant N and V conditions constant N, V conditions. So, my entropy is nothing but minus dF over dT at constant N, V conditions constant number of particles and constant volume. I can also write this as d by dT of minus F at constant N, V conditions ok.

Now, your expression for F is here equation 1 ok. So, this is your free energy F fine, which is obtained by taking logarithm of the (Refer Time: 38:18) partition function. So, you can take the derivative of free energy or minus F as you take it there are two terms. So, if you take the derivative the first term, what you get is just N k B ok. And you write down the entire term, which is lon ev by N plus 3 by 2 lon 2 pi m k B T over a h square.

Now, you take the first term which is just N k B T and take the derivative of the second now lon ev upon N has no temperature unit. So, from the second term you get 3 by 2 as a pre factor, then 1 upon the argument of the log, which is h square by 2 pi m k B T. And you have to take the derivative of the pre argument with respect to the temperature that will give you another 2 pi m k B over h square lot of things are going to cancel of here.

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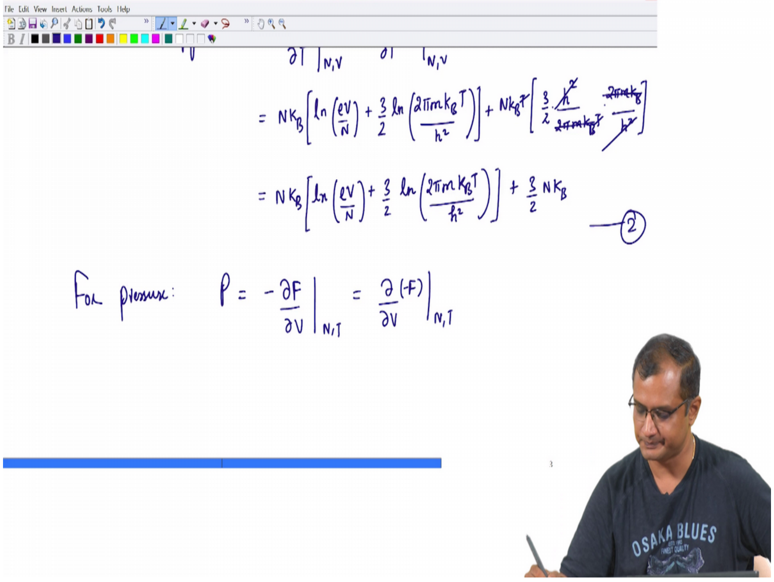

$$= Nk_B\left[\ln\left(\frac{eV}{N}\right) + \frac{3}{2}\ln\left(\frac{2\pi m k_B T}{h^2}\right)\right] + Nk_B\cancel{T}\left[\frac{3}{2}\cdot\frac{\cancel{h^2}}{\cancel{2\pi m k_B T}}\cdot\frac{\cancel{2\pi m k_B}}{\cancel{h^2}}\right]$$

$$= Nk_B\left[\ln\left(\frac{eV}{N}\right) + \frac{3}{2}\ln\left(\frac{2\pi m k_B T}{h^2}\right)\right] + \frac{3}{2}Nk_B \quad \text{②}$$

For pressure: $P = -\left.\frac{\partial F}{\partial V}\right|_{N,T} = \left.\frac{\partial(-F)}{\partial V}\right|_{N,T}$

So, we can knock off the x square h square with x square, you can knock off 2 pi m k B with 2 pi m k B here and you can knock off this temperature T with this temperature T ok. So, just 3 by 2 N k B is remaining there, which is particularly I pleasing, because it can give you the internal energy of a gas at constant N, V, T conditions as we shall see. So, this is nothing but 2 pi m k B T over h square plus 3 by 2 N K, because everything else got cancelled. Let us call this as expression 2.

So, we now have an equation for the entropy of an ideal gas. From this you can construct lot of other things. And as you can already see that the entropy here is extensive in nature thanks to the fact that we have taken care of the in distinguishability. So, if I scale N, V by lambda N and lambda V my entropy is scales by lambda times S, so it is purely extensive. And it is also a monotonically increasing function of temperature as expected.

And what I am going to do here now is basically compute the pressure of ideal gas ok. So, from the ideal gas you know equation of state I already know that pressure is equal to N k T upon volume or P v equals to N k T, but can we derive it here. You derived this in the case of kinetic theory of gases we are using the approach of kinetic theory. But, using the statistical mechanics approach also you can get the equation of state for an ideal gas as very simple.

Just look at this equation that I have written here for the incremental change in free energy this equation. So, if I look at the incremental change in free energy, I can write down the pressure as negative derivative of free energy with respect to volume at constant N and T ok. So, I am going to use this equation to my advantage and compute the equation of state.

So, I am going to write down for pressure, I am going to write it as negative derivative of free energy with respect to volume at constant N, T conditions, number of particles and constant temperature, which is nothing but derivative with respect to volume of minus F at N, T conditions constant N and constant T conditions.

Now, if you look at the expression for Helmholtz free energy, you can see that only the first term in the square parenthesis has a volume dependence, the second term does not have the dependence ok. So, what I am going to do is just take the product of N k T in to lon ev by N as the free energy term that will give me.

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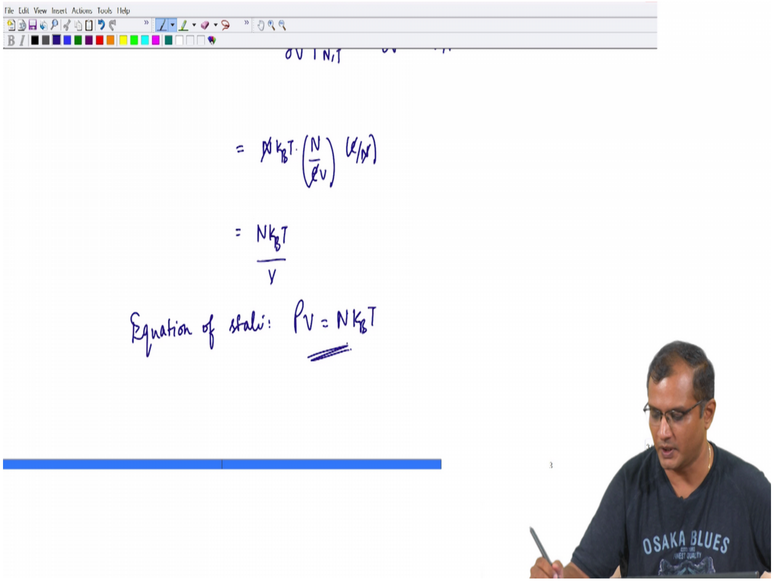

$$= \cancel{N} k_B T \cdot \left(\frac{N}{\cancel{e}V}\right) (e/\cancel{N})$$

$$= \frac{N k_B T}{V}$$

Equation of state: $\underline{\underline{PV = N k_B T}}$

So, if you take the derivative of free energy with respect to in this expression with respect to volume, so what you will get is just N k T, because I need derivative of with respect to volume of minus F, so just N k T that is the pre-factor, it is volume independent here ok. And lon ev by N simply gives me N by ev that is the 1 upon argument of the log. And if you go and see the pre-factor of so if you see the argument, it is ev by N. So, it will give me ev one more ev and 1 by N derivative with respect to so.

Student: (Refer Time: 44:47).

With respect to volume right. So, it just e by N absolutely right. So, you can see that this is nothing but so you can see that this e knocks off and this N will knock off. So, what you will have is just N k T over V ok. So, this will equation of state of an ideal gas ok.

So, now you can also compute internal energy of an ideal gas, so that the fact that we have computed pressure and entropy you can also compute what is the internal energy of the ideal gas. Now, there are two ways to compute internal energy. So, one is the one way which is the easier way is to basically use the thermodynamic law that connects free energy with internal energy. So, I am talking about basically from here ok.

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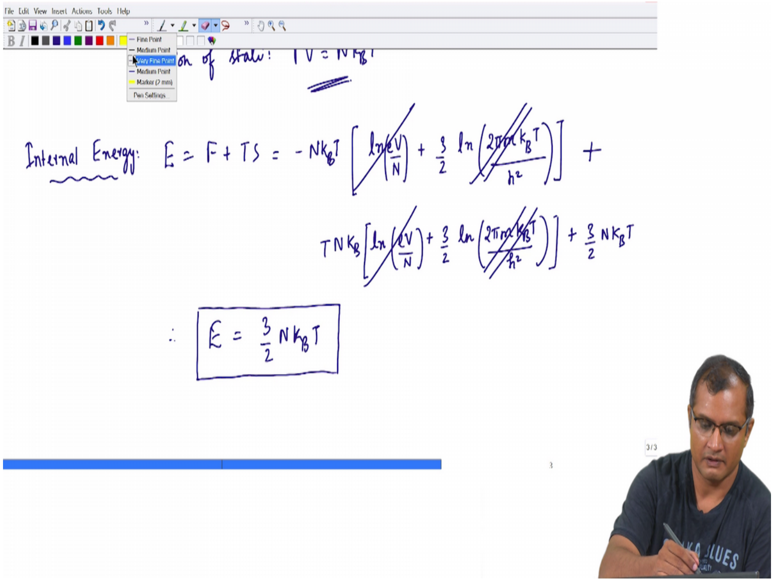

…on of state: $PV = Nk_BT$

Internal Energy: $E = F + TS = -Nk_BT\left[\cancel{\ln\left(\frac{eV}{N}\right) + \frac{3}{2}\ln\left(\frac{2\pi mk_BT}{h^2}\right)}\right] +$

$TNk_B\left[\cancel{\ln\left(\frac{eV}{N}\right) + \frac{3}{2}\ln\left(\frac{2\pi mk_BT}{h^2}\right)}\right] + \frac{3}{2}Nk_BT$

$\therefore \boxed{E = \frac{3}{2}Nk_BT}$

So, we can write down the internal energy as F plus T S. And for F I can substitute the entire expression first going to copy it. So, this is the expression for the free energy F, so this is just the expression for free energy and I need to take the expression for T S. So, let us copy the expression for S, so this is the expression for S.

So, we are supposed to add T S, so I am going to add T S here. So, as you can see the first term clearly knocks off with the first term in the second parenthesis. So, this term will knock off with this term, because the free factor is just N k T in both the terms. And very easily you can see that this term will also knock off with this term, what were left with just 3 by 2 N k T.

Student: (Refer Time: 48:42).

So, here I need to multiply T here, because this is T S. So, therefore, I can write down E as 3 by 2 N k B T. So, this is another important result that goes by the you know in the contacts of the ideal gas, this is the internal energy of the ideal gas. We already obtained the equation of state, which is P v equals to N k T. We also obtained the entropy and the free energy was already obtained to build the connection with the thermodynamics.

Now, what you can also obtained is if you look at the incremental free energy, you can also obtain chemical potential of an ideal gas at under N, V, T condition. So, if you look at this relationship, you can write down for mu as dF by dN at constant volume and temperature ok. So, so you can take the derivative of free energy with respect to N at constant volume and temperature and that will give you mu.

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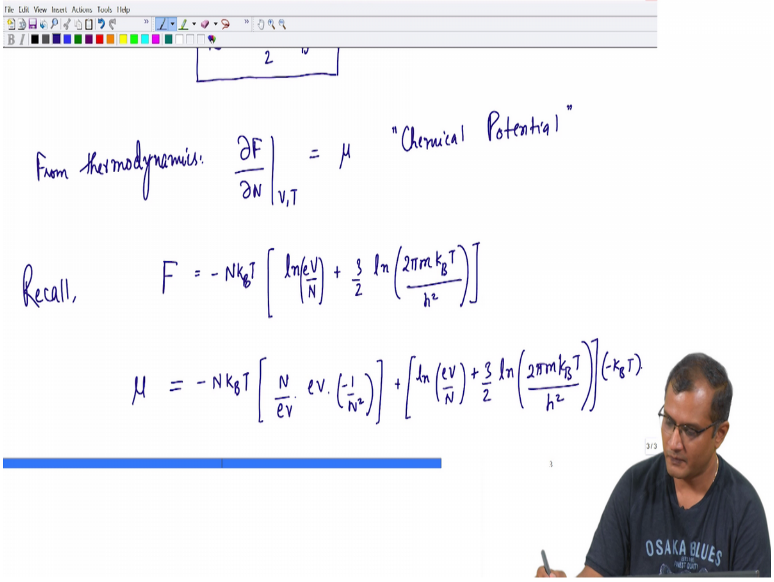

From thermodynamics: $\left.\frac{\partial F}{\partial N}\right|_{V,T} = \mu$ "Chemical Potential"

Recall, $F = -Nk_BT\left[\ln\left(\frac{eV}{N}\right) + \frac{3}{2}\ln\left(\frac{2\pi m k_B T}{h^2}\right)\right]$

$$\mu = -Nk_BT\left[\frac{N}{eV}\cdot eV.\left(\frac{-1}{N^2}\right)\right] + \left[\ln\left(\frac{eV}{N}\right) + \frac{3}{2}\ln\left(\frac{2\pi m k_B T}{h^2}\right)\right](-k_BT).$$

So, from thermodynamics dF by dN at constant volume and temperature should give me the chemical potential ok. So, you can compute the chemical potential as if you look at the function free energy, so let us copy the free energy, so that we can use it readily. So, this is the free energy functional formula, I think this is already there as F plus T S so if you will use it, so this is its already in front of me. So, this quantity is F, let me copy it anyway so.

Student: (Refer Time: 51:29).

In fact, all other not just here as a good question. So, let me just finish this computation hold on to a question for a second. And so this is my free energy expression, so you recall that your free energy is basically this expression ok. And from here if I want to compute the chemical potential, I have to take the derivative with respect to N at constant V and T. Let us do that first.

So, again you can see here that so I am going to do it So, let us let me take the first term, which is N minus N k T and the derivative of log ev by N is nothing but N by ev into e v, and this will be minus 1 by N square and that is it, second term does not have any N plus lon ev by N plus three half ln 2 pi m k B T upon h square into minus k T.

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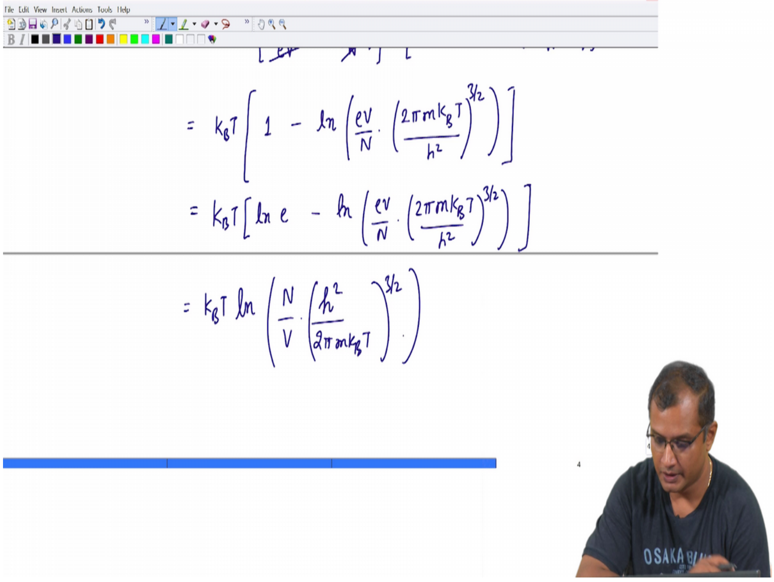

$$= k_B T \left[1 - \ln\left(\frac{eV}{N} \cdot \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right) \right]$$

$$= k_B T \left[\ln e - \ln\left(\frac{eV}{N} \cdot \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right) \right]$$

$$= k_B T \ln\left(\frac{N}{V} \cdot \left(\frac{h^2}{2\pi m k_B T} \right)^{3/2} \right)$$

So, if you see you can knock off this ev with this e, one N with this N square and so what you have is nothing but minus just k T. So, I can take k T from this common you just have k T here, because this entire N square will cancel. There is an N square you know 1 upon N square you know. So, this N square will cancel, there is one N here and this one N here ok, and minus becomes positive.

So, if I take k T outside, then I have 1 minus logarithm of if I take the these two logarithms are combined, what do I get? I get e v upon N into 2 pi m k B T to the power divide by h square to the power 3 half fine by clubbing the two logs. And the minus k T is coming with the minus sign here, because I have taken k T outside.

One more step I can write down this one as lon e ok. So, this is like k T I can visualize this one as lon e to the base e. So, it will simply become let me write it as ln e to the base e minus ln ev by N into 2 pi m k B T by h square to the power 3 half is the end of the logarithm is the end of the square bracket fine, we will be one more step and we are we have reached our goal, which is lon. So, I do not need a bracket anymore, because now these two logs will be combined to one. So, this becomes just N by V into h square by 2 pi m k B T the whole raised to a 3 by 2 fine.

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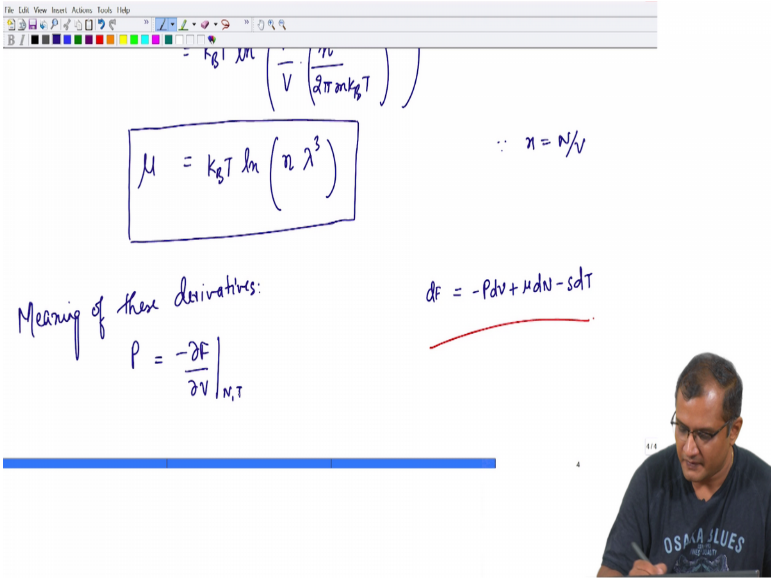

$$\boxed{\mu = k_B T \ln\left(n \lambda^3\right)}$$

$\because n = N/V$

Meaning of these derivatives:

$$P = -\frac{\partial F}{\partial V}\bigg|_{N,T}$$

$$dF = -PdV + \mu dN - SdT$$

Now, you can think of this N by V as sum density N by V as sum density. And h square by 2 m k T the whole square root is nothing but our d by wavelength or d by scale factor, this entire thing is raise to the power 3 ok. So, now we can see in some sense the role of chemical potential here. And the there are two length scales coming one is the d by length scale and the other is the density length scale n. And that is whose logarithm decides the chemical potential in our case.

So, let me write down the three results would be obtained here. So, we obtained the chemical potential, we obtained the internal energy, and we obtained the question of state for the ideal gas. Now, let me write down the differential form first law and till you the meaning of it. I am going to copy this, and this is important. So, the entire derivations of you know the meaning of these thermodynamic derivatives, which derivatives these derivatives. So, let me sort of push it on the right side, because I need some space.

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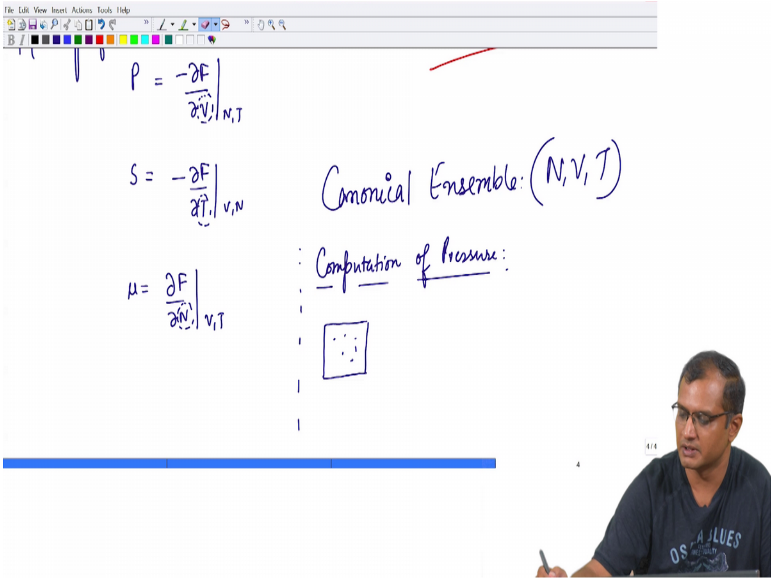

$$P = -\left.\frac{\partial F}{\partial V}\right|_{N,T}$$

$$S = -\left.\frac{\partial F}{\partial T}\right|_{V,N}$$

$$\mu = \left.\frac{\partial F}{\partial N}\right|_{V,T}$$

Canonical Ensemble: (N, V, T)

Computation of Pressure:

So, this is our this basically provide provided us with tool to construct all these derivatives. So, we constructed, for example for pressure we said that it is minus dF over dV at constant N and T. And same thermodynamic law give us the expression for entropy as minus dF over dT at constant V and N. And same chemical potential gives us the expression as dF over dN at constant V and T.

Now, the question is I have computed these three quantities pressure, entropy and chemical potential by taking a derivative with respect to V, derivative with respect to temperature and derivative with respect to N. But, in my canonical ensemble these are the three quantities preserved or conserved a micro state is specified by the triplet N, V, T and I am taking derivative with respect to N, V and T.

So, what does that mean, well it simply means that you have to construct canonical ensemble at different values of V key thing N and T constant. And simply tell how free energy changes with volume that will give you the pressure of that system, what does that mean for pressure for example, so for computation of pressure, I want to take the first case only and that will that should be enough to explain how entropy and mu can be computed.

So, you create different canonical ensembles. So, let us say you create this ensemble at N, T and volume V1 ok. This is one system call it as a system S1. You take another canonical ensemble, this time you do an experiment with another canonical ensemble. So, let me sort of make the system in contact with the heat reservoir.

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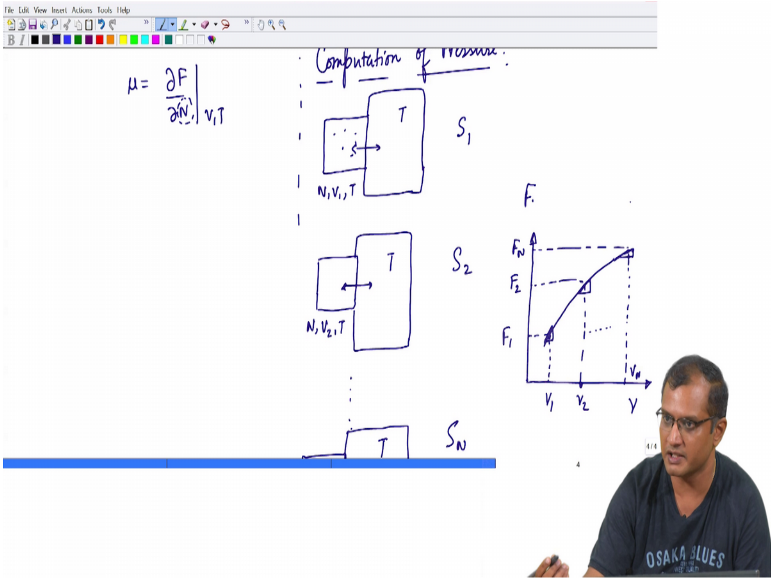

So, this is in contact with some heat reservoir it is exchanging energy. And this system is maintained at N, T and V 1 or you want to call it as N, V 1, T. So, the volume of the system is V 1, we are taking n particles at volume V 1 and temperature T ok, call it as system 1. Then you do an experiment with another system. This time this new system is connection in is in is in contact with another reservoir, but at a same temperature, the number of particles are same, but the volume of the system is V 2, this is my second system. You took you are free to choose any volume. So, you choose you chose the volume v 2 number particles and temperature are kept the same. This way you constructed large numbers of systems varying only in volume with respect to each other with number of particles and temperature are taken to be constant.

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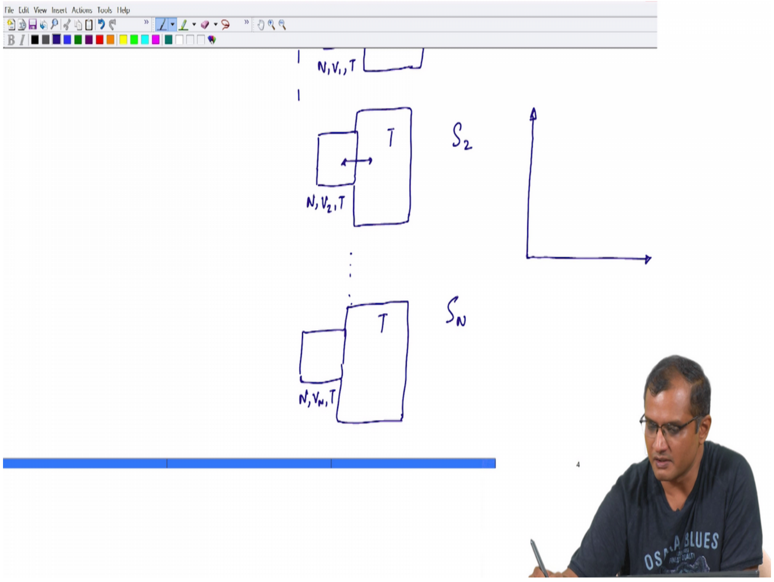

Now, from all the systems let me call let me let me show the nth system also the Nth system is also connected to a reservoir temperature T. We have the same number of particles. The volume of this system is taken as V N some value I do not know. And now from all these N systems you basically construct you compute their you compute their free energy versus volume. So, this would be like something like this. So, this is your V 1 and this was the free energy of the first system, this was the volume of the second system and that is the free energy of the second system and so on this way you simply extended. And somewhere at on the line you have the volume of the Nth system and correspondingly you have its you know free energy. You simply done a bookkeeping of this and you call this as F N. And in the end you have just opening your book and plotting these values fine.

And I am saying that the pressure of system one is nothing but the slope here which is dF by d dV. The pressure of the system at V 2 is nothing but the slope here and the pressure of the system nth system is nothing but the slope here. The slopes here nothing but dF over dV which is what I have shown here negative of that slope. Similarly, you can construct systems at various temperatures keeping N and V the same. And after you have constructed large numbers of such systems varying by small temperatures. You compute you plot f versus T and take the derivatives at the value of temperature you want to take and that would give you the entropy of the system fine, so that is the meaning of these derivatives. So, do not be alarmed when you see the derivatives they have a simple meaning.

So, I am going to call this as simply this derivative as simply dF by dV at V 1 which is giving me minus pressure fine ok. So, we break here and when we meet again we will discuss the Gibbs canonical ensemble which is ensemble that is constructed by allowing one more thermodynamic variable to fluctuate which is either volume or magnetization. So, if you allow volume to fluctuate, you can control pressure, so where in ideal gas this will lead to an N, P, T ensemble. For magnet in contact with magnetic field in presence of a magnetic field this should also be a N, V, T ensemble. So, we will discuss the Gibbs ensemble in the next lecture.

Thank you.