# Statistical Mechanics
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## Lecture – 19
## Classical Ideal Gas (Gibbs Canonical Ensemble)

So, Good Afternoon students. Today, we will start with the case of Classical Ideal Gas as discrete degree of freedom example of the Gibbs Canonical Ensemble. So, like always do in this course, I choose examples having both continuous degrees of freedom and discrete degrees of freedom.

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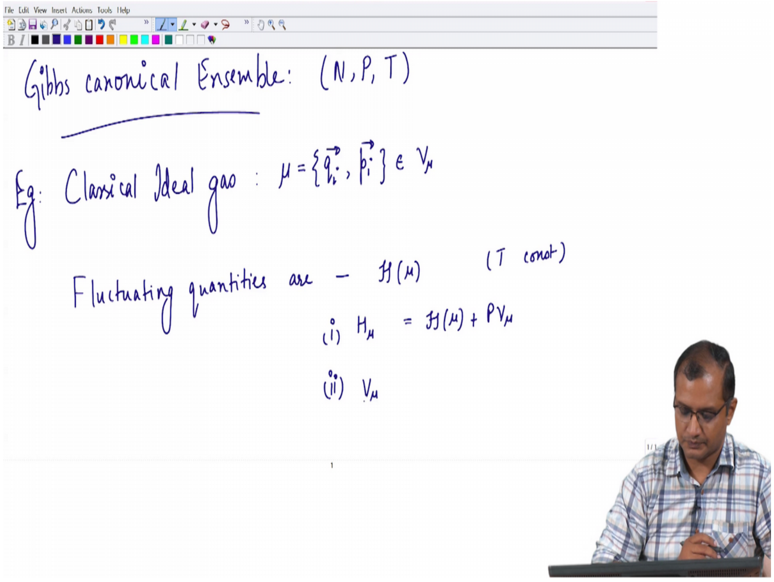

Gibbs canonical Ensemble: (N, P, T)

Eg: Classical Ideal gas : $\mu = \{\vec{q}_i, \vec{p}_i\} \in V_\mu$

Fluctuating quantities are – $\mathcal{H}(\mu)$ (T const)

(i) $H_\mu = \mathcal{H}(\mu) + PV_\mu$

(ii) $V_\mu$

So, in the case of Gibbs canonical ensemble, I am going to take the example of classical ideal gas, where a micro state is basically specified as the set of values of positions and momentums of the gas particles, in a volume which also depends on the microstates states. So, this is a system where you allow volume to fluctuate in order to keep pressure constant. So, volume of a microstate is also a variable that keeps fluctuating in addition to the energy of the system.

So, I just recall that the fluctuating quantity in these systems are basically the Hamiltonian. So, if you fix the volume, then you allow you have to allow for energy exchange in order to keep the total temperature constant ok. So, T is constant, so have to fluctuate allow for fluctuations in the Hamiltonian. But, if Hamiltonian is fluctuating, I will have a fluctuation in the enthalpy of the system. So, the enthalpy is basically the energy of that microstate plus the pressure volume work that the system does in order to maintain constant pressure. So, this is one fluctuating quantity, which is the enthalpy I call it has the enthalpy of the microstate ok.

And the second quantity is as I have said is the volume ok. So, I have to change the letter here, this is the microstate here is specified as mu. So, I am going to call it as the enthalpy of the mu state. And similarly we are denoting V mu as the volume of the mu th microstate. So, both the enthalpy and the volume are fluctuating quantities ok.

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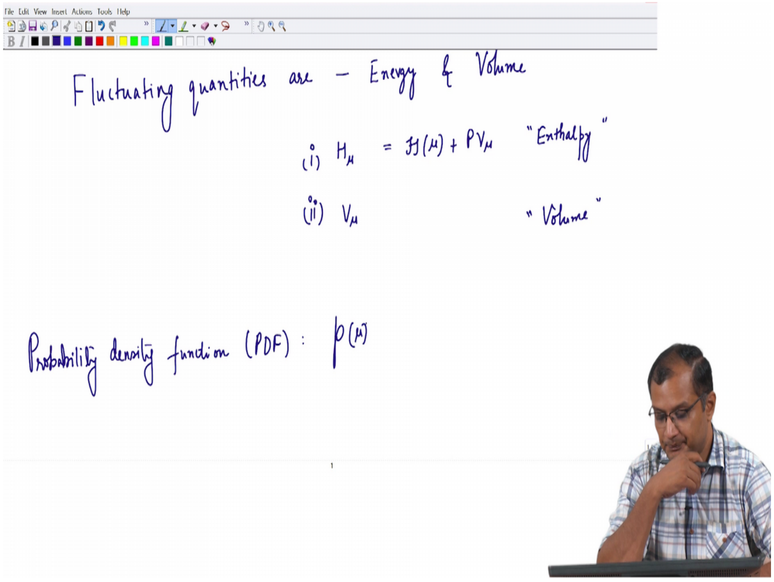

Fluctuating quantities are – Energy & Volume

(i) $H_\mu = \mathcal{H}(\mu) + PV_\mu$ "Enthalpy"

(ii) $V_\mu$ "Volume"

Probability density function (PDF) : $\rho(\mu)$

So, you can you can include the in this discussion the write down the fluctuating quantities are energy and volume. And we have written down the relevant thermodynamic variables whose average is that we have calculated ok. So, we have calculated the average of the enthalpy, and the average the volume. So, this is nothing but the enthalpy of the microstate, and this is nothing but that volume of the microstate, and also call them as the instantaneous volume or the instantaneous enthalpy ok.

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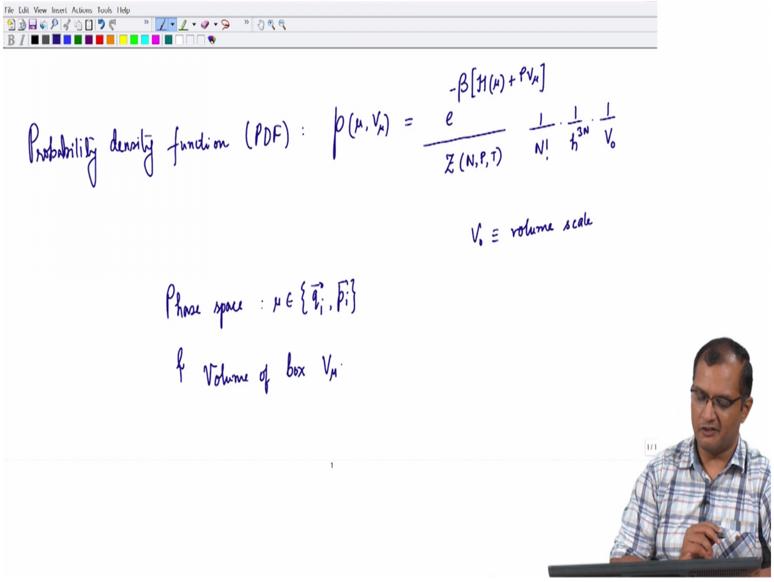

Probability density function (PDF) : $p(\mu, V_\mu) = \frac{e^{-\beta[\mathcal{H}(\mu) + PV_\mu]}}{Z(N,P,T)} \frac{1}{N!} \cdot \frac{1}{h^{3N}} \cdot \frac{1}{V_0}$

$V_0 \equiv$ volume scale

Phase space : $\mu \in \{\vec{q}_i, \vec{p}_i\}$

& Volume of box $V_\mu$.

Now, the ideal gas is in the canonical ensemble Gibbs canonical ensemble can be specified by a probability density function, which has to give the probability of finding a microstate in the vicinity of from mu. And that can be that is given as a p of mu, and you can write down this PDF has 1 upon. So, we can just write it down as a the Boltzmann factor into H to the power into in a Boltzmann factor, which is e to the power minus beta into the energy of the microstate ok. And to normalize this I have to divided by the partition function.

Now, this is not yet probability density function, because it is not the dimensions of the phase space volume. So, I am going to divided by N factorial that takes case into account the fact that the particles are indistinguishable. So, there are roughly exactly N factorial permutations that you can do on N particles. And if I do not divide by N factorial, I would be over estimating the number of state we precisely that factor. So, taking into account the in distinguishability, I have divided by N factorial.

And as I was saying that I have to non-dimensionalist in order to not I have to make the dimensions one upon phase space volume. So, so I am going to divided by few more factors. So, one factor is the self-factor that is the smallest volume you can have in the phase space with N particles that is called to the cell factor. And in addition to this, I am also going to divided by some volume scale. So, we not here is some volume scale, and this is because my phase space now has the additional degree of freedom, which is the volume of a microstate ok.

So, as you can see my phase space is not just you know, it is not just composed of particle coordinates and moment. The phase space now involves information of the volume microstate also the physical volume of the box ok. So, I am going to say that my phase space here. So, the overall degree of freedom is movement in phase space, which is due to the microstate and volume of the box for given value of mu ok, so that is why I have to divide by a volume scale to not demonize my partition function.

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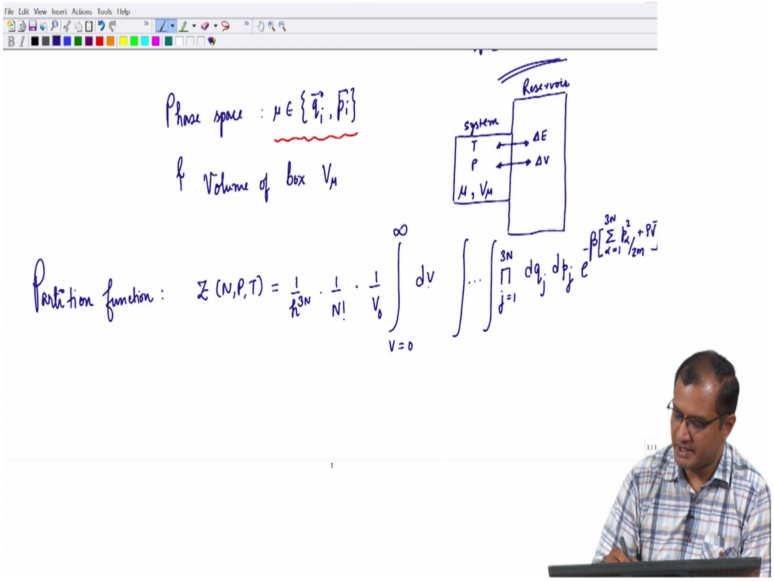

Phase space : $\mu \in \{\vec{q}_i, \vec{p}_i\}$

& Volume of box $V_\mu$

Partition function : $Z(N,P,T) = \frac{1}{h^{3N}} \cdot \frac{1}{N!} \cdot \frac{1}{V_0} \int_{V=0}^{\infty} dV \int \cdots \int \prod_{j=1}^{3N} dq_j \, dp_j \, e^{-\beta\left[\sum_{\alpha=1}^{3N} p_\alpha^2/2m + P\bar{V}\right]}$

So, now I can write down the partition function looking at this equation 1, I can directly write down my partition function as Z N P T ok. So, it to understand the preceding argument that my phase space and volume of the box together constitutes the overall you know scenario is to visualize the our system.

So, at some instant the system is in a microstate mu. So, mu here is basically the set of coordinates that has specified here ok, so that is my mu. And corresponding volume of the system is view of mu. And the system is constantly exchanging energy in order to keep my temperature constant, it is also exchanging volume.

So, there is a constant amount of constant interaction of the system with the reservoir mechanically. So, it is continuous mechanical interaction, which is manufactured in the exchange of volume, and that keep my pressure constant ok. So, thermal interaction is necessary to keep temperature constant and mechanical interactions necessary to keep pressure constant.

So, then the partition function of the system can be written as you know including all those pre factors needed for non-dimensionalist in my partition function upon N factorial for in distinguishability raise to the power 3 N is to as for the phase space volume, in I am going to divided further by a volume scale, because this going to be a integral over all the possible volumes system can take. So, my system can take volumes from 0 to infinity ok. Do not be surprised with these limits, because both these volumes have very lower very low probability of occurrence as shall be seen in a write down the Boltzmann factor.

And so this will be a volume integral. And then we have a phase space integral, where I will have six n dimensional phase space integral over all the momentum and positions. So, I have removed the vector inside, because I have taken some over 3 N ok. As you see now their components already, each particle has three components of momentum, and three components of position. So, my summation is not over 1 to N, it is now directly return from 1 to 3 N ok. So, I will not write down d cube q and d cube p into the Boltzmann factor, which is e raise to minus beta the Hamiltonian of the microstate.

Now, the Hamiltonian of the microstate is nothing but summation overall momentous, because that is the only energy system can have, it is an ideal gas. So, I am going to use some new symbol. Let me use alpha goes from 1 to 3 N p alpha square by 2 m plus P V ok. This V is the volume integral that we are going to perform ok.

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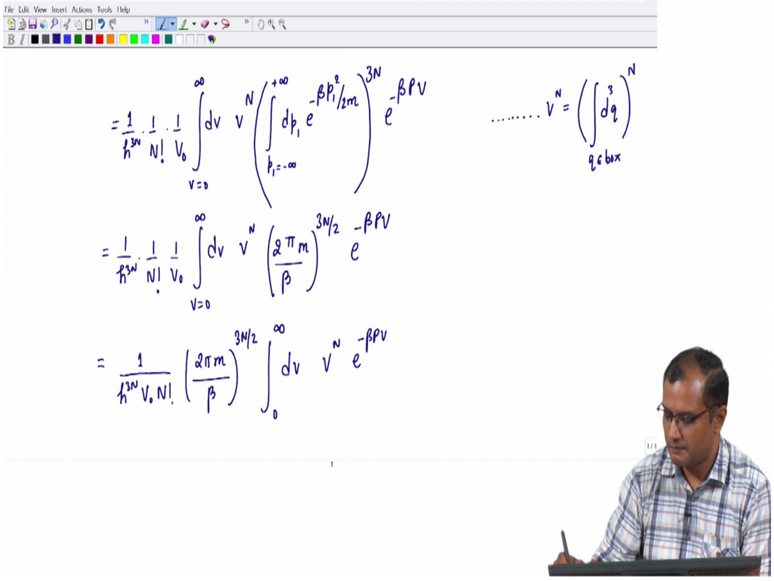

$$= \frac{1}{h^{3N}} \cdot \frac{1}{N!} \cdot \frac{1}{V_0} \int_{V=0}^{\infty} dV \; V^N \left( \int_{p_1=-\infty}^{+\infty} dp_1 \, e^{-\beta p_1^2/2m} \right)^{3N} e^{-\beta P V} \qquad \ldots\ldots\ldots \; V^N = \left( \int_{q \in box} d^3q \right)^N$$

$$= \frac{1}{h^{3N}} \cdot \frac{1}{N!} \, \frac{1}{V_0} \int_{V=0}^{\infty} dV \; V^N \left( \frac{2\pi m}{\beta} \right)^{3N/2} e^{-\beta P V}$$

$$= \frac{1}{h^{3N} V_0 N!} \left( \frac{2\pi m}{\beta} \right)^{3N/2} \int_{0}^{\infty} dV \; V^N e^{-\beta P V}$$

So, now you can where this as 1 upon h to the power 3 N into 1 upon N factorial into 1 upon some volume scale integral V going from 0 to infinity d v, well you can straight away see that the position integrals will give me V raise to N ok. So, position integrals are giving me V to the power N.

And all the momentum integrals can be written as just integral d sum you know p 1 momentum degree of freedom of first particle into a raise to minus beta p 1 square by 2 m, where p 1 will take the values from minus infinity to plus infinity. And the entire thing will be raised to the power 3 N. These V raise to N has come because of the fact that I have written V raise to N as integral d q 1 d q 2 d q so I will go I am going to write it as. So, it is better that I write it as just integral d cube q, where q belongs to the box whole to the power N ok.

So, a single particles volume integral over d cube q 1, d cube q 2, and d cube q 3, which is integral over d cube q is just volume V, there are N such integrals, so this is just V raise to N ok.

Student: (Refer Time: 16:57).

Right. So, so there is one factor that I have is there let me just write down that factor, I am going to write it here and instance specific so, let me just move everything on one side. And I am going to write it as e to the power minus beta P V that is it fine.

So, you can write this as 1 upon h to the power 3 N into 1 upon N factorial into 1 upon V 0 integral V goes from 0 to infinity d v V raise to N. And this Gaussian integral will simply give me square root of pi by a, so it is given a pi by a. a is already beta by 2 m, and so it will give me in 3 N by 2 into e raise to minus beta P V. So, I can bring out the constant outside. So, what I will have is basically just 1 upon h to the power 3 N V 0 N factorial into 2 pi m upon beta is to 3 N by 2 into volume integral V raised to N e raise to minus beta P V.

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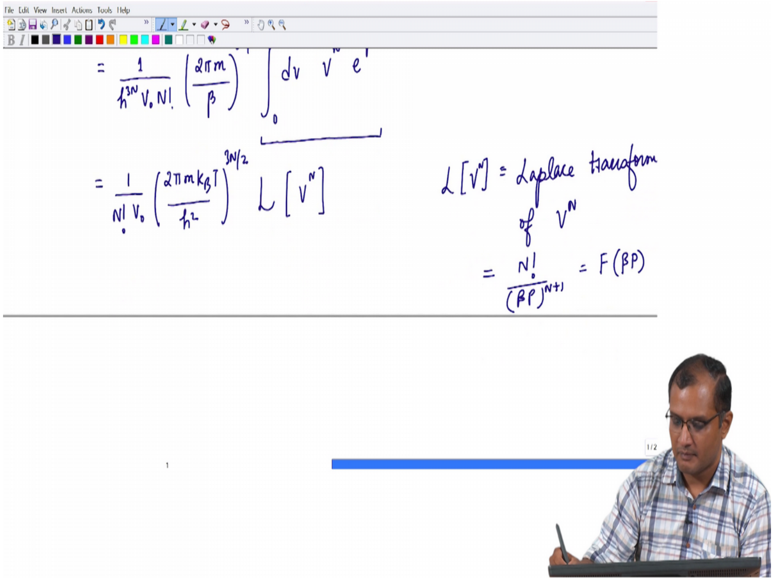

$$= \frac{1}{h^{3N} V_0 N!}\left(\frac{2\pi m}{\beta}\right) \underbrace{\int_0 dv \; V^{N} e}$$

$$= \frac{1}{N! \, V_0}\left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2} \mathcal{L}\left[V^N\right]$$

$\mathcal{L}[V^N]$ = Laplace transform of $V^N$

$$= \frac{N!}{(\beta P)^{N+1}} = F(\beta P)$$

So, the pre factor here can now be written as 1 upon h to the power 3 N. So, I am going to take h inside the parentheses, I am going to write it as 1 upon N factorial into V 0, I am going to write as 2 pi m K B T upon h square to the power 3 N by 2 ok. And if you noticed that, this is nothing but there is nothing but a Laplace transform of V to the power N except that the fact that I have taken the SCR of the transformers beta P.

So, this is called as the Laplace transform of V to the power N that we already know is the result of Laplace transform as N factorial over a to the power N plus 1 or a here is beta P ok. So, the variable a or s that you take in the Laplace transform is actually you know this is a function of beta P is already beta P here.

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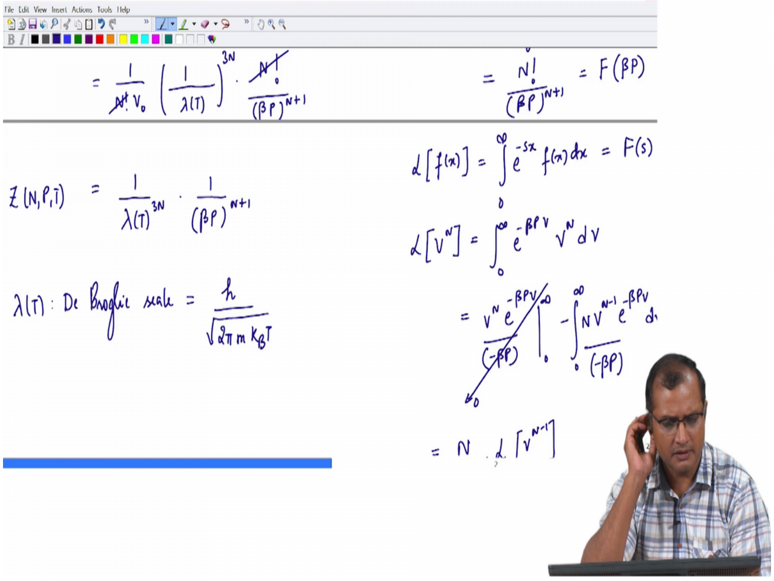

$$= \frac{1}{\cancel{N!}\, V_0} \left(\frac{1}{\lambda(T)}\right)^{3N} \cdot \frac{\cancel{N!}}{(\beta P)^{N+1}}$$

$$= \frac{N!}{(\beta P)^{N+1}} = F(\beta P)$$

$$Z(N,P,T) = \frac{1}{\lambda(T)^{3N}} \cdot \frac{1}{(\beta P)^{N+1}}$$

$$\mathcal{L}[f(x)] = \int_0^\infty e^{-sx} f(x)\, dx = F(s)$$

$$\lambda(T) : \text{De Broglie scale} = \frac{h}{\sqrt{2\pi m k_B T}}$$

$$\mathcal{L}[V^N] = \int_0^\infty e^{-\beta P V} V^N dV$$

$$= \cancel{\frac{V^N e^{-\beta P V}}{(-\beta P)}\Bigg|_0^\infty} - \int_0^\infty \frac{N V^{N-1} e^{-\beta P V}}{(-\beta P)} dV$$

0

$$= N \cdot \mathcal{L}[V^{N-1}]$$

So, if you do not remember Laplace transforms, you can recall that if there is a function f of x, then its Laplace transform is nothing but integral 0 to infinity e raise to minus s x f of x dx, and because a different integral x, it is only a function of s ok.

Now, our function was V raise to N, so Laplace transformer of V raise N is we can define it as e raise to minus beta P into beta P V into V raise to N d of v so fine. So, if you want to find out its answer it is nothing but you take V raise to N has the first function, because it is success of derivatives will reduce the order.

So, if I take V raise to N is the first function, you can I am just going to write down two steps, and then it will be clear to you how to do it. So, it is V raise to N e raise to minus beta P V dived by minus beta P, the limits 0 to infinity minus integral derivative of the first into integration of second ok.

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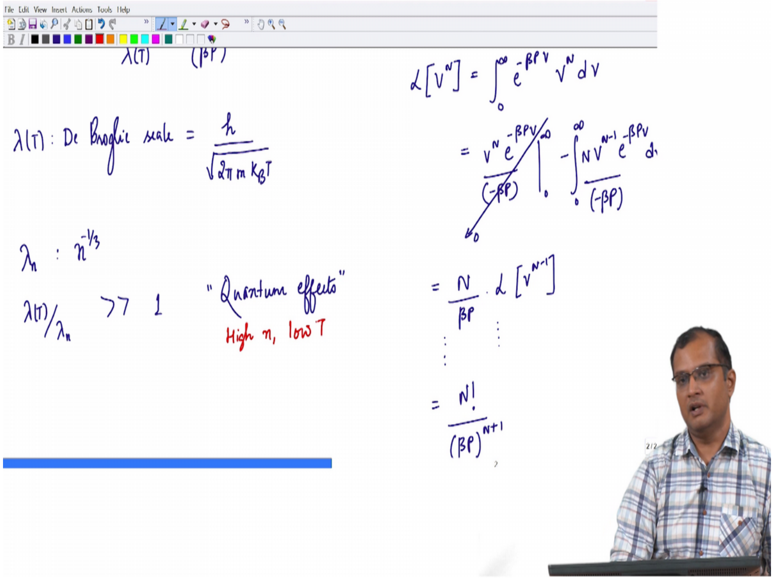

$\lambda(T)$ $(\beta P)$

$\lambda(T)$ : De Broglie scale $= \frac{h}{\sqrt{2\pi m k_B T}}$

$\lambda_n : n^{-1/3}$

$\lambda(T)/\lambda_n >> 1$ "Quantum effects"

High n, low T

$$\mathcal{L}[V^N] = \int_0^\infty e^{-\beta P V} V^N dV$$

$$= \cancel{\frac{V^N e^{-\beta P V}}{(-\beta P)}\Bigg|_0^\infty} \to 0 - \int_0^\infty \frac{N V^{N-1} e^{-\beta P V}}{(-\beta P)} dV$$

$$= \frac{N}{\beta P} \cdot \mathcal{L}[V^{N-1}]$$

$$\vdots \qquad \vdots$$

$$= \frac{N!}{(\beta P)^{N+1}}$$

So, you can see their limits will give this 0 here, because at infinity e raise to minus beta P V will dominate, and it 0 V raise to N will dominate. So, this goes to 0, what you have is just N upon beta P into Laplace transform of V raise to N minus 1. So, if you continue like this, until you get Laplace transform of one which is s, so that would be just N factorial. So, next term would be N into N minus 1, and so this can be written as beta P the whole raise to N plus 1 ok, when you end. The last term here would be a Laplace transform of 1; it is 1 upon beta P or 1 upon s. Anyway, so there is a short discussion of how you do a Laplace transform.

So, I am going to write down the result here, which is 1 upon N factorial V 0. And look at this pre factor, it already looking like length scale to the power 3 N. So, I am going to write it has 1 upon our De Broglie wave length temperature dependent wavelength to the power 3 N into N factorial divided by beta P to the power N plus 1 ok.

And you can knock off these two N's here now N factorials. So, what you have is just 1 upon lambda to the power 3 and into 1 upon beta P to the power N plus 1. And this is your Gibbs canonical partition function ok.

So, notice that we have defined our De Broglie length as upon square root of 2 pi m K B T, which as we discussed in the few lectures ago indicates the onset of quantum mechanical effects, provided you have references skill that comes from density. So, if you have one length scale, I will call it is a density dependent length scale, which is some kind of n to the power minus 1 by 3.

Then when you have the De Broglie wavelength for exceeding this density dependent length scale, then you basically have a quantum mechanical effects, which is basically a fact that you are density is so large that your density dependent length scale becomes very small. A large density would mean the density dependent scale for inter-particle separation is very small, particles are very close to each other, which means our lambda n will be very very small.

And if you have low temperature, then our de by wavelength would be very large, because it behaves as 1 upon square root T, it increases as inverse square root temperature. So, the quantum efforts will arise in the limit of high density, and low temperature. Low temperature will make my numerator large, and height high density will make my denominated small, which means the ratio will be much larger than 1, let us called as the quantum limit.

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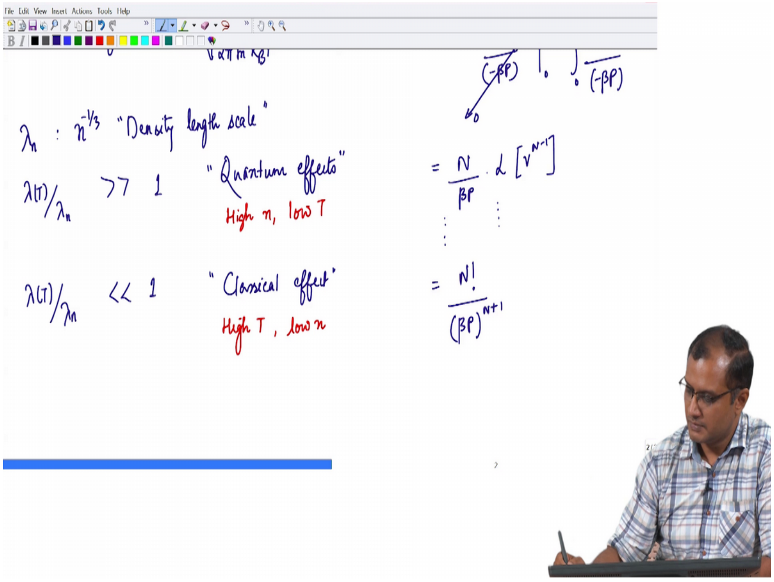

$\lambda_n : n^{-1/3}$ "Density length scale"

$\lambda(T)/\lambda_n \gg 1$ "Quantum effects"

High n, low T

$\lambda(T)/\lambda_n \ll 1$ "Classical effect"

High T, low n

$= \frac{N}{\beta P} \cdot \mathcal{L}\left[V^{N-1}\right]$

$= \frac{N!}{(\beta P)^{N+1}}$

And similarly, when you have this ratio was smaller than 1, you have classical effects or you have a classical limit. So, here you are talking about high temperature that will make your De Broglie wavelength very small, because it will go as 1 upon square root T. And you will talk about low density, so in the low density limit my denominator will be very large, because the particles are will be there separation would be much larger, there would be inter-particle separation would be very large. So, the ratio becomes smaller and smaller and becomes negligible, let us the onset of classical mechanics.

So, the de by De Broglie wavelength that have taken here is a very important length scale in that sense ok. So, I am going to call this as a lambda n or the density scale. And let us proceed with our calculation, so we will stop that the expression of the partition function. See if I look at the partition function, it has basically all the information available to connect statistical mechanics to thermodynamics, which is actually the goal of this lecture. And we can start off by computing the Gibbs free energy ok. So, I for the sake of convenience, I am going to copy this expression, because I am going to use it immediately here.

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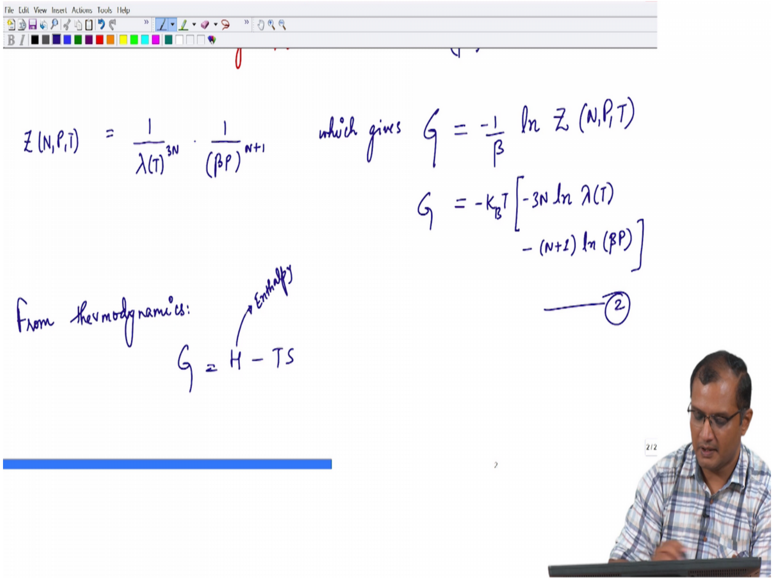

$$Z(N,P,T) = \frac{1}{\lambda(T)^{3N}} \cdot \frac{1}{(\beta P)^{N+1}}$$

which gives $G = \frac{-1}{\beta} \ln Z(N,P,T)$

$$G = -K_B T \left[ -3N \ln \lambda(T) - (N+1) \ln (\beta P) \right] \quad ②$$

From thermodynamics:

$$G = \overset{\text{Enthalpy}}{H} - TS$$

So, so I can so which gives me degree which gives me the Gibbs free energy that is minus 1 upon beta logarithm of the Gibbs canonical partition function, and that is nothing but minus K B T and if you take the log of this, what you basically get here is. So, I am going to take the logarithm of this minus 3 N ln of lambda T minus N plus 1 ln of beta P ok, fine.

Now, I already know that my Gibbs free energy. So, let me call this as equation 2. From thermodynamics I know that my Gibbs free energy is written as H minus T S, where H is the thermodynamic enthalpy ok.

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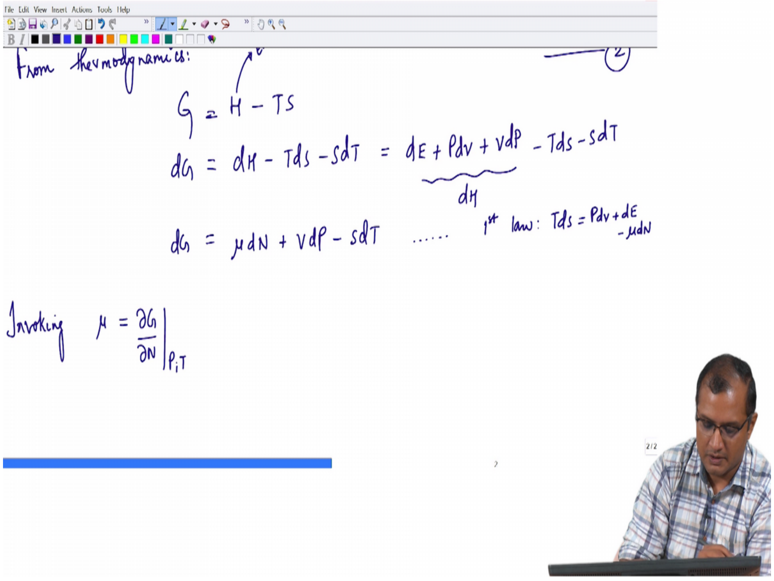

From thermodynamics:

$$G = H - TS$$

$$dG = dH - Tds - sdT = \underbrace{dE + Pdv + vdP}_{dH} - Tds - sdT$$

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

Invoking $\mu = \left.\frac{\partial G}{\partial N}\right|_{P,T}$

②

So, you can write down the differential form of this as the H minus T d S minus S d T. And this can be written as if I know, if I write down H S E plus P V, so this is d E plus P d V plus V d P this is nothing but my d of H ok, minus T d S minus S d T ok. So, you can now write down from the first law of thermodynamics, you write down for d E plus P d V minus T d S ok.

So, you can now write it as just mu d N plus V d P minus S d T, because I have use the first law as T d S equals to P d V plus d E minus mu d N. So, then I can write down each of this quantity is mu V and S by invoking the appropriate derivative. So, by invoking the appropriate derivatives I can compute chemical potential as d G over d N at constant value of pressure and temperature.

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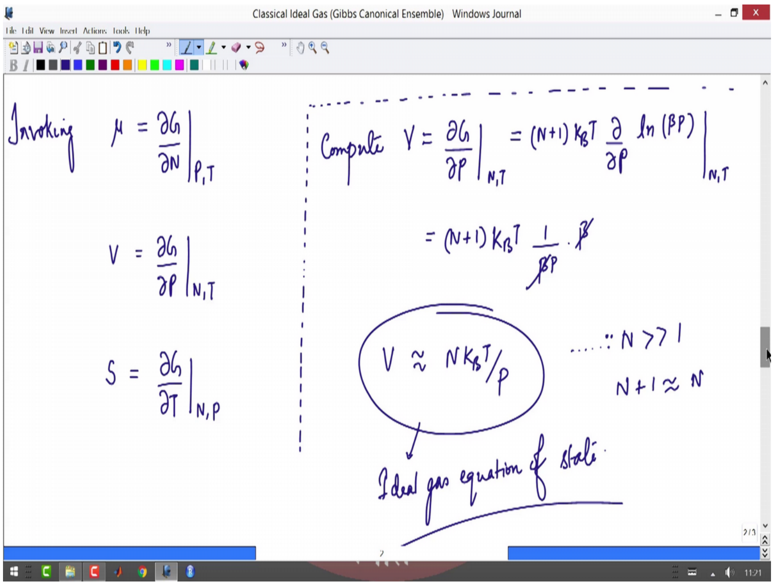

Invoking $\mu = \left.\frac{\partial G}{\partial N}\right|_{P,T}$

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

$S = \left.\frac{\partial G}{\partial T}\right|_{N,P}$

Compute $V = \left.\frac{\partial G}{\partial P}\right|_{N,T} = (N+1) K_B T \left.\frac{\partial}{\partial P} \ln(\beta P)\right|_{N,T}$

$= (N+1) K_B T \frac{1}{\cancel{\beta} P} \cdot \cancel{\beta}$

$\boxed{V \approx N K_B T / P}$ ..... $\because N >> 1$, $N + 1 \approx N$

Ideal gas equation of state.

I can also invoke the derivative with respect to pressure to compute volume, but then I have to fix number of particles and temperature. And I can also compute entropy by invoking derivative with respect to temperature, but holding number of particles and pressure is constant. So, you can compute these three thermodynamic variables easily. I am going to compute only one and leave the others as homework ok.

So, I am going to demonstrate how to compute one of them. So, let us compute volume ok. So, so volume is derivative of free energy with respect to pressure holding N and T tight. So, let us look at the expression for the Gibbs free energy. So, if you hold temperature and pressure temperature and number of particles constant, then I can see that the first term in the Gibbs free energy does not contribute to volume, because it depends only on number of particles and temperature, the de Broglie wavelength is purely a function of temperature.

Now, the only term that contributes here is the second term. And that constant temperature and N number of particles, I can write it as N plus 1 into K T into d over d P of l n beta P at constant N T fine. Now, you can see that I can take the beta outside; it does not depend on pressure ok. So, so this can be very easily computed. So, you can write it as N plus 1 K B T and derivative of ln beta P is just 1 upon beta P into beta, you can knock of these betas.

And write down the final answer as just N K B T over P, this is because N is very very large compared to 1. So, N plus 1 is the same as 1, N plus 1 is same as N ok, you can write down since this the case. So, then this is the ideal gas law equation of state alright.

So, now we have the equations for the chemical potential volume and entropy from which you have already computed the volume. And I have left it computation of the chemical potential and entropy as an exercise. So, I will just finished the entire calculation by computing enthalpy.

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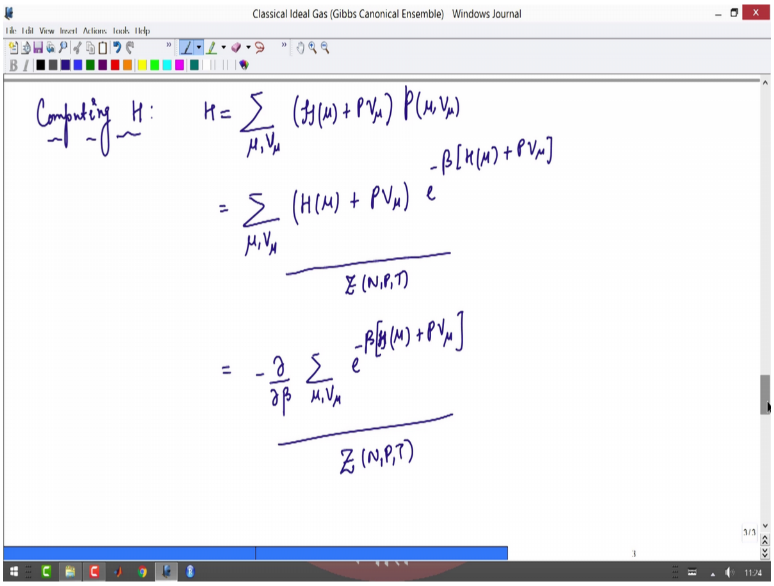

Computing H:

$$H = \sum_{\mu, V_\mu} (\mathcal{H}(\mu) + PV_\mu)\, P(\mu, V_\mu)$$

$$= \frac{\sum_{\mu, V_\mu} (H(\mu) + PV_\mu)\, e^{-\beta[H(\mu) + PV_\mu]}}{Z(N,P,T)}$$

$$= \frac{-\frac{\partial}{\partial \beta} \sum_{\mu, V_\mu} e^{-\beta[\mathcal{H}(\mu) + PV_\mu]}}{Z(N,P,T)}$$

So, the thermodynamic enthalpy. So, this is a task that can be done by saying that you can compute the average of the instantaneous enthalpy. So, you some over all the microstates. So, this is a microstate mu with a volume V mu, and you take the enthalpy of this microstate which is the Hamiltonian plus P V and you to sample it in the distribution of the microstates ok.

And this is nothing but summation over the entire microstates of so we going to sample the enthalpy in this distribution. So, I am going to write down the distribution that we already know for our system will be energy scale, that is the partition function the sum over all the probabilities, and to pull out H plus P V mu, I need to just derivate it with respect to beta just once.

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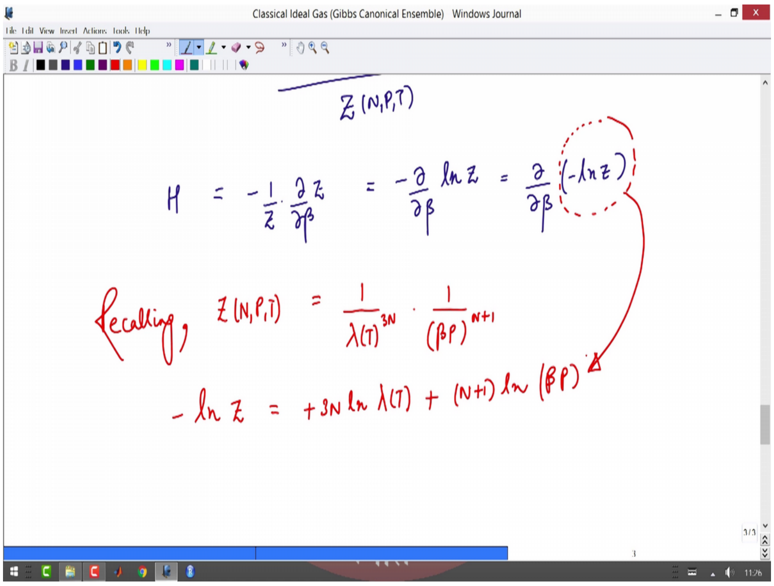

$$Z(N,P,T)$$

$$H = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta}\ln Z = \frac{\partial}{\partial \beta}(-\ln Z)$$

Recalling, $Z(N,P,T) = \frac{1}{\lambda(T)^{3N}} \cdot \frac{1}{(\beta P)^{N+1}}$

$$-\ln Z = +3N\ln\lambda(T) + (N+1)\ln(\beta P)$$

So, I am going to take a negative derivative with respect to beta of. And just minus 1 upon Z d by d beta of Z, which is nothing but minus d by d beta of ln Z. Now, we know that the patrician function is given here. So, I am just going to copy the expression for the partition function. So, for just a convenience.

So, what are just obtained is basically the equation for my enthalpy ok. And if I recall that my partition function is given by this expression. So, I can compute ln of Z, as simply minus 3 N ln of lambda T minus of N plus 1 ln of beta P, which means minus ln Z will become plus on both the terms.

And what is required here to compute the enthalpy, I am just going to substitute for in fact I am going to just I am going to just a substitute 4 minus ln Z. So, I can rewrite this as d by d beta of a minus ln Z. And for this minus ln Z, I am going to substitute this expression that you have just computed. So, I am going to substitute for this minus ln Z this expression.

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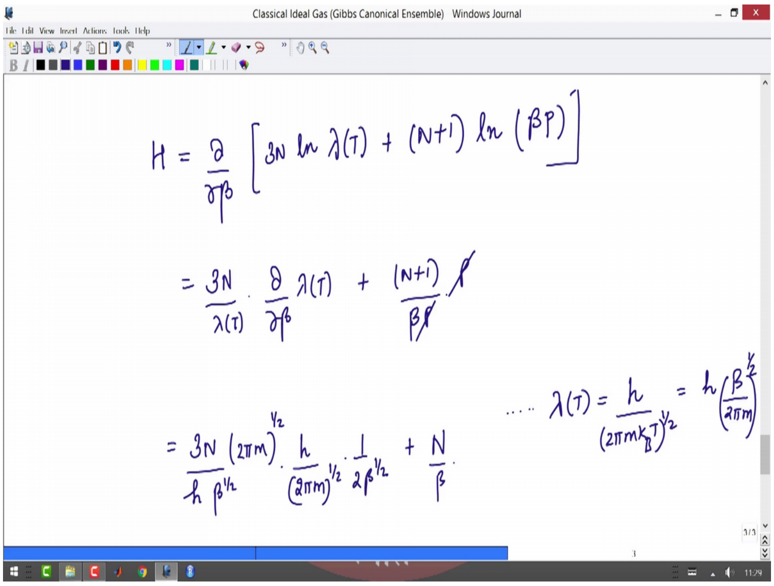

$$H = \frac{\partial}{\partial\beta}\left[3N \ln \lambda(T) + (N+1)\ln(\beta P)\right]$$

$$= \frac{3N}{\lambda(T)} \cdot \frac{\partial}{\partial\beta}\lambda(T) + \frac{(N+1)}{\beta \cancel{P}} \cdot \cancel{P}$$

$$\ldots\ \lambda(T) = \frac{h}{(2\pi m k_B T)^{1/2}} = h\left(\frac{\beta}{2\pi m}\right)^{1/2}$$

$$= \frac{3N}{h\,\beta^{1/2}}(2\pi m)^{1/2} \cdot \frac{h}{(2\pi m)^{1/2}} \cdot \frac{1}{2\beta^{1/2}} + \frac{N}{\beta}.$$

And this will make my enthalpy as d by d beta of thrice N ln lambda plus N plus 1 ln beta P ok. And this can be very easily computed, so 3 N comes outside, what I get is basically 3 N by ln of lambda T into the derivative of lambda t plus N plus 1, which is a constant divide by beta P and into P; so that completes the derivative we can straight away knock off this these two p's.

And since our de Broglie wavelength was given as h upon square root of 2 pi M K B T, I can also write this as a so just to save some space here. I can also write it as h into beta point 2 pi M the whole square root ok.

So, then the simply becomes 3 N and I am going substitute the value of lambda here, which is h upon h into square root of beta into 2 pi M square root. And the derivative here simply becomes h upon 2 pi M the square root, and derivative of square root be there is just 1 upon 2 square root beta plus the second term I am going to write it as N times 1 upon beta, because N plus 1 is equal to N as N is very large.

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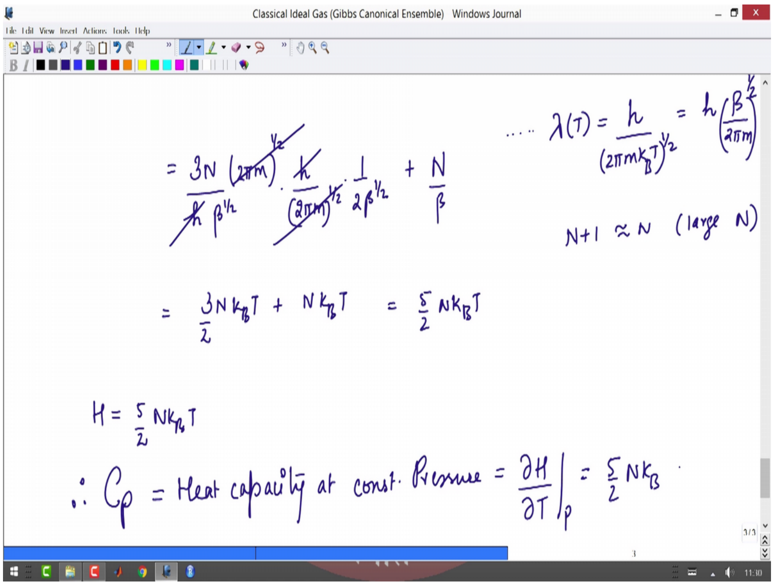

$$= \frac{3N}{\cancel{h}\,\beta^{1/2}} \cancel{(2\pi m)}^{1/2} \cdot \frac{\cancel{h}}{\cancel{(2\pi m)}^{1/2}} \cdot \frac{1}{2\beta^{1/2}} + \frac{N}{\beta}$$

$$\ldots\ \lambda(T) = \frac{h}{(2\pi m k_B T)^{1/2}} = h\left(\frac{\beta}{2\pi m}\right)^{1/2}$$

$N+1 \approx N$ (large $N$)

$$= \frac{3}{2} N k_B T + N k_B T = \frac{5}{2} N k_B T$$

$$H = \frac{5}{2} N k_B T$$

$$\therefore C_p = \text{Heat capacity at const. Pressure} = \left.\frac{\partial H}{\partial T}\right|_p = \frac{5}{2} N k_B$$

So, we are doing thermodynamics, so it is all in the thermodynamic limit. So, if you knock off these terms that cancel you are left with nothing but 3 by 2 N k B T plus N k B T which is nothing, but 5 by 2 N k B T. This is your thermodynamic enthalpy. Therefore, you can compute the heat capacity at constant pressure as simply derivative of enthalpy with respect to temperature at constant pressure and this is nothing, but 5 by 2 N k B T and this is larger than heat capacity constant volume as it should be.

This is because you have to understand that the energy skill in the problem is enthalpy. So, there right derivative to take is derivative of enthalpy not the total energy and that gives us the heat capacity at constant pressure because you have taken the pressure constant in this ensemble.

So, this completes the discussion on the Gibbs canonical ensemble and case study at a particular case study of the ideal castor gas which is the system of a you know with degrees of freedom that are continuous. In the next lecture, we will discuss system which is a magnetic system of n spins. And we will continue from here, and look at the thermodynamic properties of a magnetic system of n spins ok. So, we close the lecture here.