Statistical Mechanics
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Lecture – 22
Ideal Gas (Grand Canonical Ensemble)

Good morning students. Today we will discuss an example of the Grand Canonical Ensemble and I am taking the example of an Ideal Gas which is basically a system with continuous degrees of freedom.

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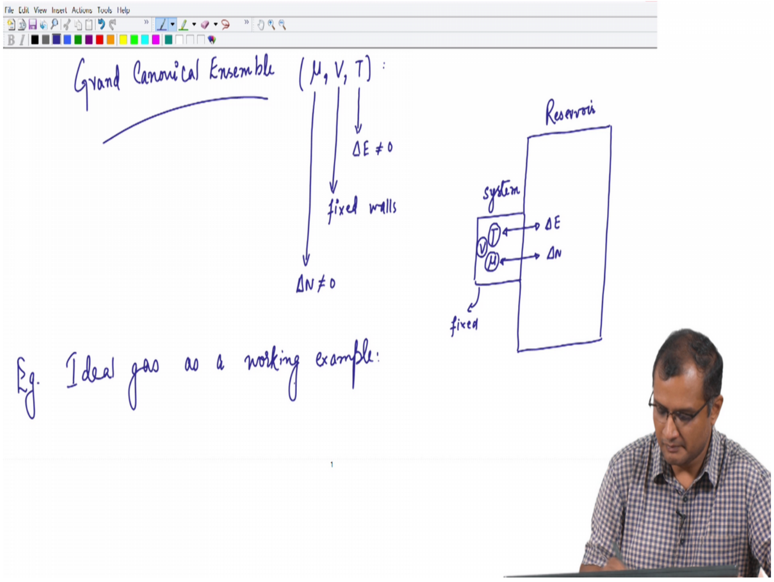

So, in the last lecture we had done the theoretical formulation of this very important ensemble that is going to be used in quantum statistics. And, this is the ensemble of constant chemical potential volume and temperature.

And just to recall the important results this temperature T was controlled by allowing exchange of energy with the reservoir and volume was kept fixed by using fixed walls. And the chemical potential was kept fixed by allowing number of particles, you know allowing for exchange in the number of particles between the system and the reservoir. So, delta N and delta a represent here exchange of the thermodynamic variable.

So, we have drawn schematic in the last lecture which applies in the present case as well. So, this is our system and this is in contact with reservoir whose purpose is to key power system at a constant temperature and chemical potential. So, let us indicate the exchange of energy between the reservoir in the system that maintains by temperature T and indicate the number of particles that are exchanged between the system and the reservoir and that maintains my chemical potential.

And I have fixed walls. So, that maintains constant V ok. So, there are 3 variables mu, V and T that are maintained using this technique or using this reservoir, this using this ensemble ok. So, now I am going to take a system which is an ideal gas. So, ideal gas as a working I would say as a working example.

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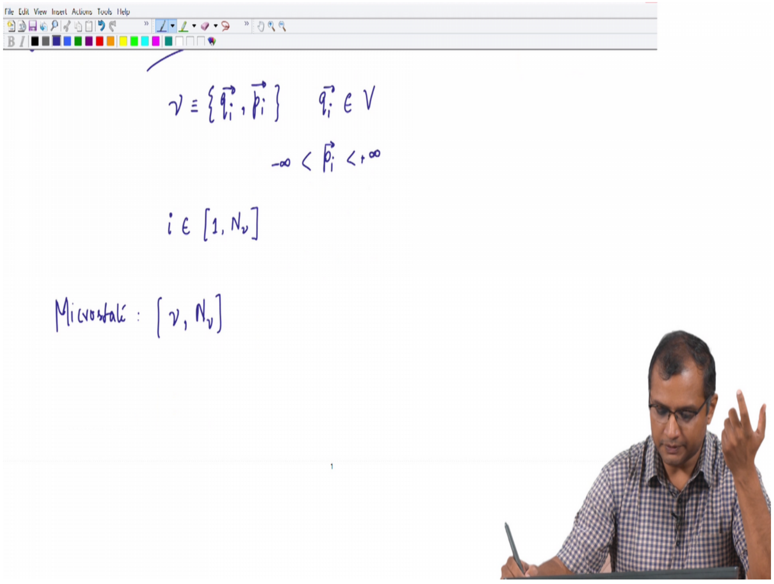

$\nu \equiv \{\vec{q}_i, \vec{p}_i\}$ $\quad \vec{q}_i \in V$

$-\infty < \vec{p}_i < +\infty$

$i \in [1, N_\nu]$

Microstate : $[\nu, N_\nu]$

Now, you know an ideal gas is basically system whose microstate is represented at any instant as nothing but the set of positions and momentum where the positions are all inside the box of volume V that is not you know move. And all the momentous are basically allow to take a values between minus infinity to plus infinity, the extreme values that are excluded. Now, one has to keep in mind that this is a system where N is constantly varying. So, the microstate is now jointly represented by the set of q i's and p i's such that my i, the index to the particle is between 1 and N nu.

Precisely meaning that the number of particles in the mu th microstate is also a number that fluctuates ok. So, you cannot just use nu as your microstate, you have to use a doublet of microstate that is a set of q and p, but with number of particles being N nu.

So, this is the this doublet here jointly represents a microstate ok. So now, I am going to write down the probability density function.

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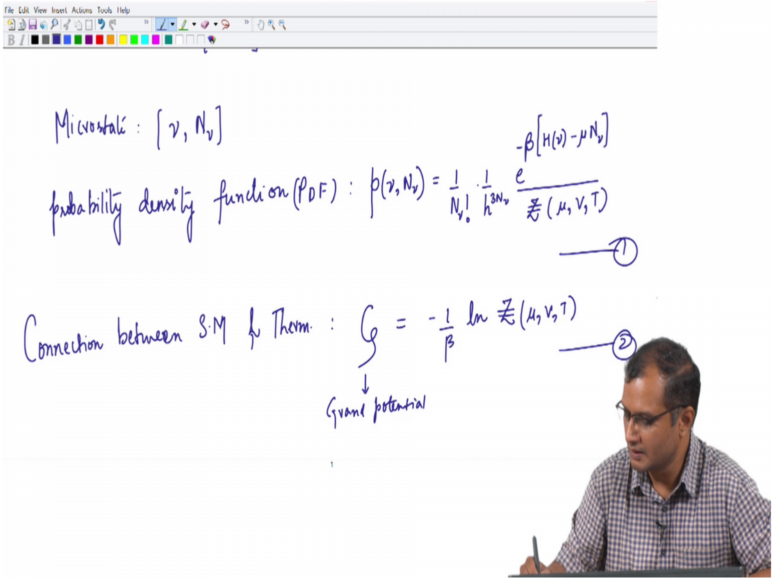

Microstate : $[\nu, N_\nu]$

probability density function (PDF) : $\rho(\nu, N_\nu) = \frac{1}{N_\nu!} \cdot \frac{1}{h^{3N_\nu}} \frac{e^{-\beta[H(\nu) - \mu N_\nu]}}{\mathcal{Z}(\mu, V, T)}$ ——①

Connection between S.M & Therm. : $\underset{\downarrow\ \text{Grand potential}}{\mathcal{G}} = -\frac{1}{\beta} \ln \mathcal{Z}(\mu, V, T)$ ——②

So, the probability density function like we saw in the last class which written for a discrete system, but here we have to make sure that the PDF has the dimensions of 1 upon phase space volume. So, I am going to write the probability of finding the system is now microstate nu probability density with number of particles N nu is basically 1 upon N nu factorial. This is to accommodate the fact that for each microstate which has N nu particles there are precisely N nu factorial permutations which are absolutely identical because, the particles are indistinguishable.

So, one has to divide this by N nu factorial so, as to avoid over counting of the microstates ok. So, there is a factorial N reminds this of this over counting that we have to avoid. Now, I am also going to take the cell factor h to the power 3 N nu where h is the our familiar action having the dimensions of angular momentum and this solely exists here to enable us to count the number of microstate. So, I have some sort of a volume that I am going to very soon take and in that volume the resolution the highest resolution on the smallest cell factor that I can accommodate is h to the power 3 N and hence I can do accounting of the microstates.

So, this cell factor is basically it is has 2 purpose. One is that it enables us to count; second it makes our partition function dimensionless. So, then I have to take the our

Boltzmann factor e to the power minus beta and the relevant energy scale of the problem. The relevant energy scale of the problem with the Hamiltonian corresponding to the micro state that we are focusing minus the chemical work which is the chemical potential that is held constant by reservoir in to the number of particles in that microstate.

So, our total energy scale is not the internal Hamiltonian alone which would have been the case if this was a just canonical ensemble, but here over and above the internal Hamiltonian you have a chemical work that is done by the reservoir to keep the chemical potential constant. Now this is the Boltzmann factor; obviously, this is not normalized. So, I have to divide by the norm which is our partition function and that is nothing but the grand canonical partition function.

So, this completes my in probability density function for the system in the grand canonical ensemble. Now, I have to find out the partition function for the simple reason that if you remember we had in the last lecture derive the connection between statistical mechanics and thermodynamics as a this very beautiful relationship, in the form of an energy scale which we called as the grand potential given as a minus k T or minus 1 over beta logarithm of the grand canonical potential.

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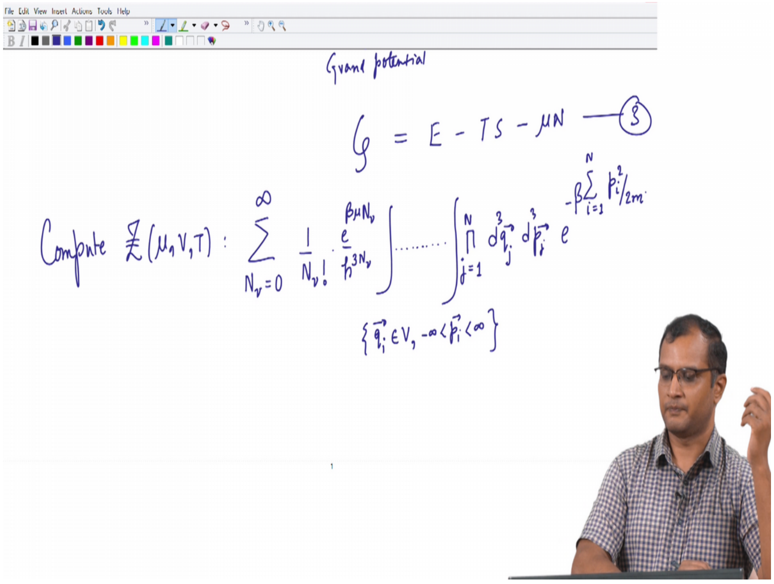

Grand potential

$$\mathcal{G} = E - TS - \mu N \;—\; ③$$

$$\text{Compute } \Xi(\mu, V, T) : \sum_{N_\nu=0}^{\infty} \frac{1}{N_\nu!} \cdot \frac{e^{\beta\mu N_\nu}}{h^{3N_\nu}} \int \cdots\cdots \int_{\{\vec{q}_i \in V,\, -\infty < \vec{p}_i < \infty\}} \prod_{j=1}^{N} d^3\vec{q}_j \, d^3\vec{p}_j \, e^{-\beta \sum_{i=1}^{N} p_i^2/2m}$$

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Why does this provide a connection with statistical mechanics and thermodynamics is because, the grand canonical potential or the grand potential is also related to thermodynamic quantities by this relationship that is the definition that we have adopted for the grand potential. So, I can connect equation 2 and equation 3 to compute various important properties of my ideal gas and in this lecture I shall demonstrate how to do it because this is as a this is being taken as a this task is being taken as a working example.

So, let us look at equation 1, 2 and 3. From equation 1, I can work out an expression for the partition function because this is a norm of the probability density function. So, if you can obtain the partition function for the classical ideal gas under grand canonical ensemble, you can then use equation 2 and 3 to connect the statement with thermodynamics. So, the first task is to compute partition function ok. So, let us compute the partition function then we shall be in the position to utilize equation 2 and 3.

So, compute the partition function and this is very simple look at the form of equation 1. To normalize my PDF, partition function here has to be sum over all the degrees of freedom. The degrees of freedom here being momenta and position, there is one more degree of freedom which is N nu; number of particles in the particular microstate. So, you have to sum over N nu also.

So, I am going to sum over all possible so, this is if we wish to say this is some kind of a restricted integral that is going to come inside. So, I am going to sum my N nu from 0 to infinity and take the entire numerator inside. So, this would be like 1 upon N nu factorial into 1 upon h to the power 3 N nu and like we did for this discrete case we had a restricted some inside I will have a restricted integral. So, for each N nu that is outside I will sum over all my degrees of freedom in that N nu k. So, let me take some more space here to indicate what I mean by this restricted integral.

So, now this is the integral over my entire face space. So, I have integral over all coordinates, position coordinates and momentum coordinates subject to the criterion that my position coordinates are all inside the box V and my momentums are all between minus infinity to plus infinity. So, I am allowing for all the possible momentas. So, the integral limits on the momentum are going from minus infinity to plus infinity for each component of the momentum.

And naturally I have all the momentum volume and you know coordinate volume. So, let me indicate that with this product symbol. So, here the product symbol would be sum j going from 1 to N and I will have a d cube q j and I will have a d cube p j for all N particles.

So, this is the volume element for the N particle system into the Boltzmann factor which is here and the Boltzmann factors chemical work has to be taken outside because that is independent of position and momentum. So, that comes outside. So, which gives us just e to the power beta a mu N nu that comes outside this is independent of position and momentum. And what is leftover is just e raise to minus beta into the Hamiltonian.

Look here Hamiltonian of the mu th microstate and this is an ideal gas which means is Hamilton is purely kinetic. So, observing that the Hamiltonian of a ideal gas is purely kinetic energy and I will write down the Hamiltonian which is I am going to use let us say some i going from 1 to N pi square by 2 m ok.

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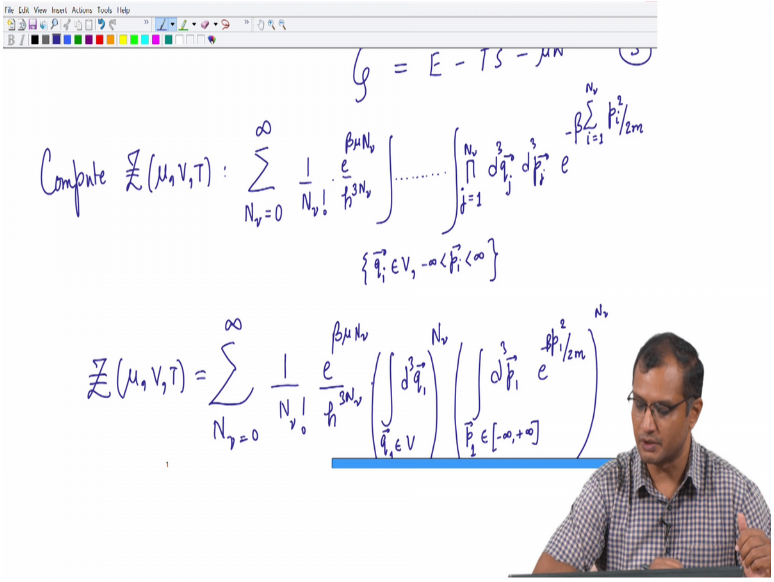

$$\mathcal{G} = E - TS - \mu N$$

$$\text{Compute } \mathcal{Z}(\mu, V, T) : \sum_{N_\nu=0}^{\infty} \frac{1}{N_\nu!} \cdot \frac{e^{\beta\mu N_\nu}}{h^{3N_\nu}} \int \cdots\cdots \int_{\{\vec{q}_i \in V, -\infty < \vec{p}_i < \infty\}} \prod_{j=1}^{N_\nu} d^3\vec{q}_j \, d^3\vec{p}_j \, e^{-\beta \sum_{i=1}^{N_\nu} p_i^2/2m}$$

$$\mathcal{Z}(\mu, V, T) = \sum_{N_\nu=0}^{\infty} \frac{1}{N_\nu!} \frac{e^{\beta\mu N_\nu}}{h^{3N_\nu}} \left(\int_{\vec{q}_1 \in V} d^3\vec{q}_1 \right)^{N_\nu} \left(\int_{\vec{p}_1 \in [-\infty, +\infty]} d^3\vec{p}_1 \, e^{-\beta p_1^2/2m} \right)^{N_\nu}$$

Now, if you recall so, this is basically my grand canonical partition function. So, I am going to write down the first few pre factors which is N nu going from 0 to infinity 1 upon N nu factorial e to the power beta nu N nu over h to the power 3 N nu.

And if you see the momentum integrals here can be performed independently with the position integrals ok. Each particles momentum integral it is d cube q will simply give me a volume ok. So, this is exactly the canonical partition function that we have already computed ok. So, each momentum degree of freedom when integrated in 3 dimension will give me 2 pi m by beta to the power 1 half and because there are 3 N such momentum coordinates it will give me the power of 3 N by 2.

So, I am going to write down first the position contribution to listen to you which is simply I can I can either I done the result directly or I can do it into steps. So, let us do it into steps. So, I will write down the momentum and position integrals separately. So, let us do it for the position integral. It is nothing but integral for let us say some particle 1 in the box V d cube q 1 and there are precisely N such integrals. So, this is to the power N and for the momentum I can write down integral I can write it as a integral 3 integrals I will write down.

So, I can write down as p 1 some momentum belonging to the range minus infinity to plus infinity d cube p 1 e to the power minus p 1 square by 2 m and again there are N such integrals.

Student: Sir into beta.

Into beta of course, ok. Now, this can be written as summation N nu going from 0 to infinity 1 upon N nu factorial into 1 upon h to the power of 3 N nu into e raise to beta nu N nu, the volume integrals will simply give me V to the power N.

Student: (Refer Time: 17:54) N nu.

e to the power N nu of course, and the similarly either summation here goes from 1 to N nu and the product also goes from 1 to N nu absolutely yes. And so, this is V to the power N nu.

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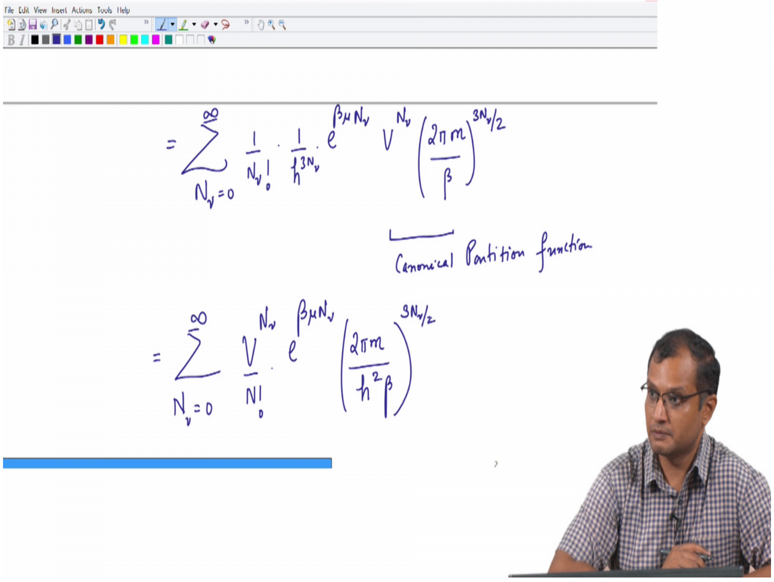

$$= \sum_{N_\nu=0}^{\infty} \frac{1}{N_\nu!} \cdot \frac{1}{h^{3N_\nu}} \cdot e^{\beta\mu N_\nu} \underbrace{V^{N_\nu} \left(\frac{2\pi m}{\beta}\right)^{3N_\nu/2}}_{\text{Canonical Partition function}}$$

$$= \sum_{N_\nu=0}^{\infty} \frac{V^{N_\nu}}{N!} \cdot e^{\beta\mu N_\nu} \left(\frac{2\pi m}{h^2\beta}\right)^{3N_\nu/2}$$

Because, this is the number of particles in the nu th microstate which is summed over outside and the momentum integrals will simply give me 2 pi m over beta to the power 3 by 2. And there is so, this is the momentum integral that is written inside the bracket and there is an N nu outside. So, I am going to write it as 3 by 2 N nu.

Each degree of freedom will give me 2 pi m by beta half raised to the power half there are 3 degrees of freedom. So, it gives me 2 pi m by beta raise to 3 half and there are N nu such integrals. So, the overall result is 3N nu by 2 ok. You could also say that this part is purely remnant from the canonical partition function and I will agree to it ok, let remind this is the canonical partition function. Nevertheless, we can proceed from here and the compute write down the final form of it.

So, I am going to club a few things here and there. So, why do not we write it as N nu going from 0 to infinity V to the power N nu divided by N factorial. And, I am going to write down e to the power beta mu N nu and h I am going to take inside and write it as 2 pi m over h square to the power 2 pi m upon beta h square to the power 3 N nu by 2 ok.

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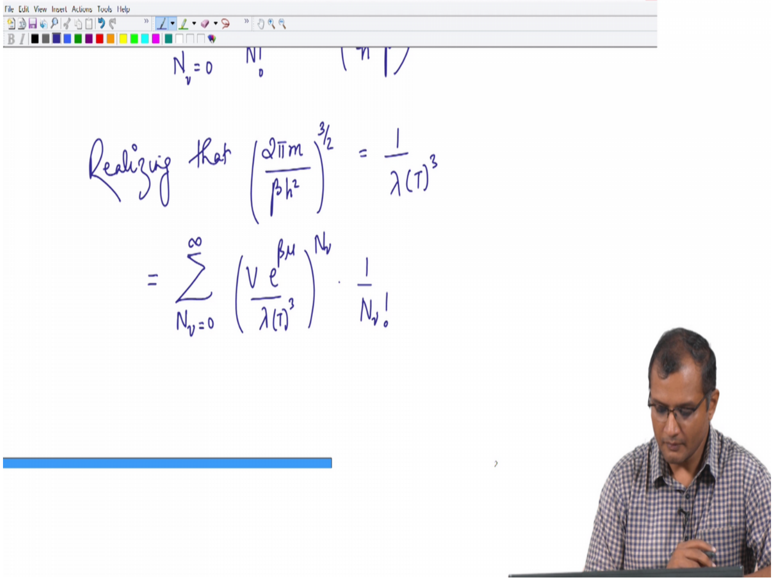

$N_\nu = 0 \quad N!$

Realizing that $\left(\frac{2\pi m}{\beta h^2}\right)^{3/2} = \frac{1}{\lambda(T)^3}$

$$= \sum_{N_\nu=0}^{\infty} \left(\frac{V e^{\beta\mu}}{\lambda(T)^3}\right)^{N_\nu} \cdot \frac{1}{N_\nu!}$$

And realizing that our 2 pi m by beta h square to the power half is nothing but the 1 upon De Broglie wavelength which means 2 pi m. If I raise it to the power 3 this become just a De Broglie wavelength to the power 3 ok. So, then I can rewrite my previous expression as the I can just take the common power N and multiply all these factors. So, what I will get is basically V into e raise to beta mu divided by lambda T to the power 3 and the entire thing raise to the power N nu into 1 upon N nu factorial, fine.

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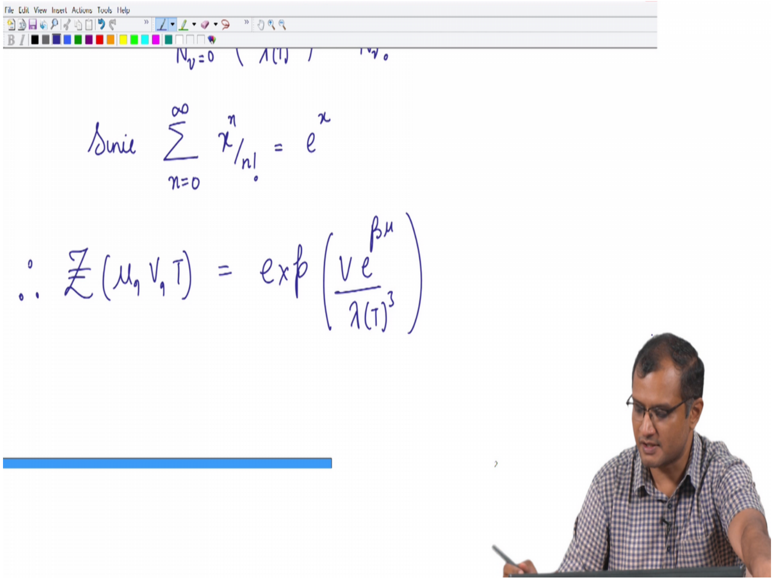

Since $\sum_{n=0}^{\infty} x^n/n! = e^x$

$$\therefore \mathcal{Z}(\mu, V, T) = \exp\left(\frac{V e^{\beta\mu}}{\lambda(T)^3}\right)$$

So, you know that this summation x raise to n divided by n factorial ok. So, if you recall that this is nothing but an expression for e to the power x ok. So, I can write down my partition function or I can write down my grand canonical partition function. So, I can write down my grand canonical partition function as nothing but e to the power V e raise to beta mu over lambda T to the power 3.

So now, I have the partition function for the classical ideal gas under grand canonical ensemble. So, now, I can develop all thermodynamic quantities very easily because look at z is already with me now. If you go back and look at the expressions 2 and 3 the equation 2 will allow me to construct the grand potential and grand potential is related to all the quantities S, mu and pressure through the equation number 3 ok. So, let us first compute the grand potential ok.

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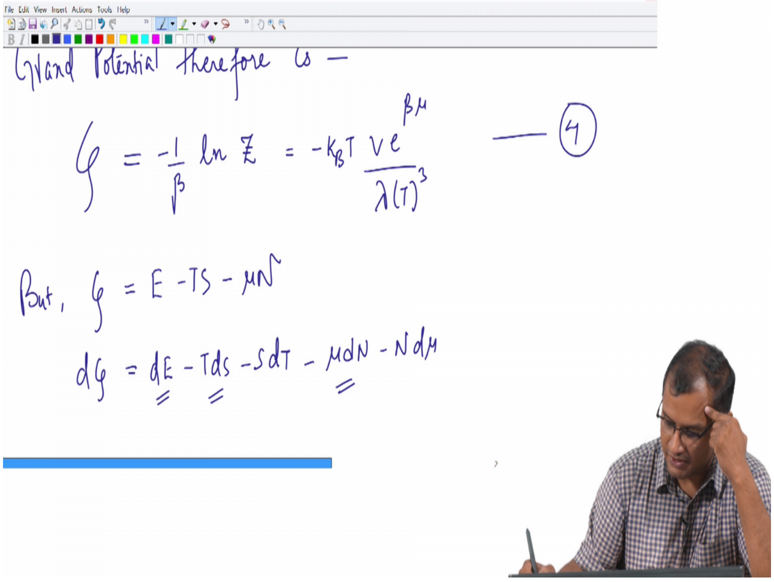

Grand Potential therefore is —

$$\mathcal{G} = -\frac{1}{\beta}\ln \mathcal{Z} = -k_B T\,\frac{V e^{\beta\mu}}{\lambda(T)^3} \qquad — ④$$

But, $\mathcal{G} = E - TS - \mu N$

$$d\mathcal{G} = \underline{\underline{dE}} - \underline{\underline{Tds}} - SdT - \underline{\underline{\mu dN}} - Nd\mu$$

So, the grand potential here is nothing but so, the grand potential is nothing but minus 1 upon beta logarithm of our grand canonical partition function. So, this would be nothing but minus K B T into lan of this is nothing but V e raise to beta mu over lambda T to the power 3 ok; natural log of the exponent is nothing but 1. So, now, let us call this is equation 1, 2, 3, 4. So, this is our grand potential.

So, if you look at equation 3 here ok, so, I am just going to write down the equation 3, but we know that x i is equal to E minus T S minus mu N. So, I am going to take a small differential and that is how I develop all connections fine and then you can substitute for d E minus TdS minus mu dN from first law. You can substitute for this as minus PdV because, from the first law we know that the way we have been writing our first law is that the heat supply to the system is always taken as the increase in the internal energy.

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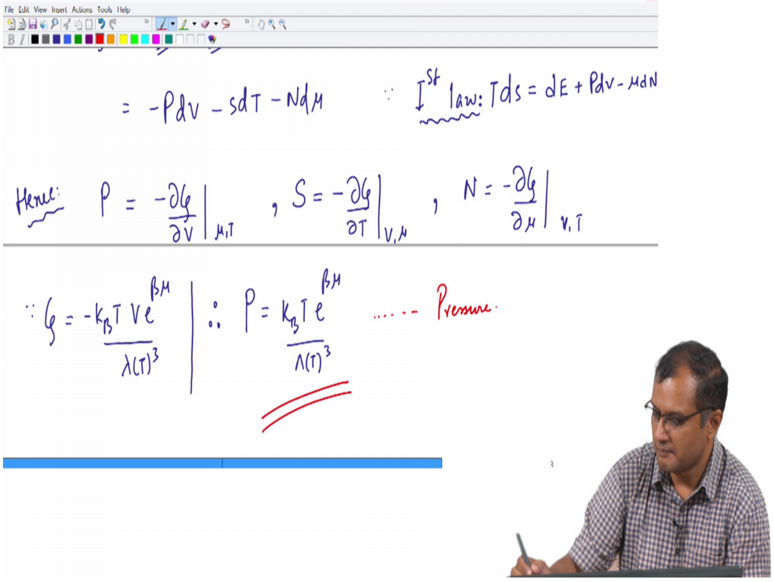

$$= -Pdv - sdT - Nd\mu \qquad \because \ \text{I}^{st} \text{ law: } Tds = dE + Pdv - \mu dN$$

Hence: $P = -\frac{\partial \mathcal{G}}{\partial V}\Big|_{\mu,T}$, $S = -\frac{\partial \mathcal{G}}{\partial T}\Big|_{V,\mu}$, $N = -\frac{\partial \mathcal{G}}{\partial \mu}\Big|_{V,T}$

$$\because \mathcal{G} = -\frac{k_B T V e^{\beta\mu}}{\lambda(T)^3} \ \Big| \ \therefore P = \frac{k_B T e^{\beta\mu}}{\Lambda(T)^3} \ \ldots\ldots \text{Pressure.}$$

Suppose, we give heat to the system it will lead to increase in the internal energy. System may also do some work. So, both that both of them are taken as positive; work done by the system and internal energy is raise plus there is some contribution that comes from chemical interaction. If you allow particles to leave the system or enter the system then you have nu dN, otherwise you just have d and PdV. So, our this is the grand canonical on symbol.

So, we allow for 3 different ways in which heat given to a system can manifest. It can increase the internal energy which is Te, heat up the particles. The system may you know expand or contract and the system may actually allow for some exchange of particles so, that is mu dN.

Now, we can we can now compute all these quantities. So, I can compute the pressure. This is what we mean by computing thermodynamic quantities. So, hence there were thermodynamic quantities are pressure which is nothing but negative d psi by dV at constant mu 1 T. And, I can compute entropy as negative d psi by d T at constant V 1 mu and I can also compute number of particles as negative d psi by d mu at constant volume and temperature ok.

So, if you have the expression with you can compute all these things. So, minus k T I am going to write down minus k T V. So, let us just write down the expression for the grand canonical potential is that right, yes. So, therefore, I can write down for P pressure as so, the only thing that is basically, there is only one variable that is volume in the expression. So, it is simply minus-minus turns into positive because there is already a minus sign in the grand potential.

So, it is simply k T e raise to beta mu over lambda T the whole cube ok. So, as you can see this is the pressure of our gas at constant mu e T condition. So, I am going to sort of underline it. So, this is the first expression or pressure ok.

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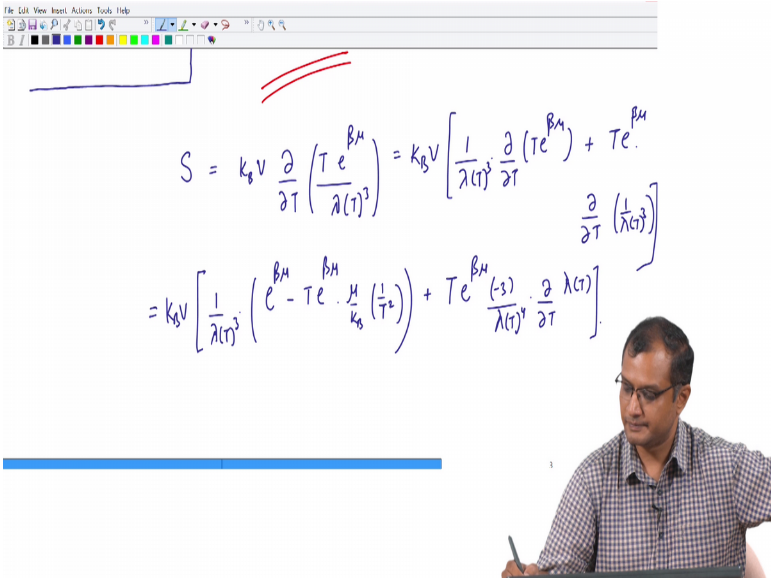

$$S = k_B V \frac{\partial}{\partial T}\left(\frac{T e^{\beta\mu}}{\lambda(T)^3}\right) = k_B V \left[\frac{1}{\lambda(T)^3} \cdot \frac{\partial}{\partial T}\left(T e^{\beta\mu}\right) + T e^{\beta\mu} \cdot \frac{\partial}{\partial T}\left(\frac{1}{\lambda(T)^3}\right)\right]$$

$$= k_B V \left[\frac{1}{\lambda(T)^3} \cdot \left(e^{\beta\mu} - T e^{\beta\mu} \cdot \frac{\mu}{k_B}\left(\frac{1}{T^2}\right)\right) + T e^{\beta\mu} \frac{(-3)}{\lambda(T)^4} \cdot \frac{\partial}{\partial T} \lambda(T)\right].$$

You can compute the entropy which is basically temperature derivative. So, then basically we have to be careful for the temperature derivative. So, what comes out is basically just the Boltzmann constant and the volume.

So, I am going to first write down the temperature derivative of T e raise to beta mu over lambda T into the power 3. So, k B into Boltzmann constant will come out. So, we can we can do it in few steps. So, we will first write it as a T e raise to beta mu into so, I am going to write it as a plus. So, this will be nothing but so, this will give me plus this is your first product. So, e raised to beta mu when taken derivative for temperature.

I have just written e raise to beta mu and mu by k B is the factor and 1 over T is derivative is minus 1 over T square and our this is not yet complete. So, I will take the second derivative as well and here noting that our lambda T is I can write it as minus 3 upon lambda T to the power 4 into d by d T of a lambda T fine.

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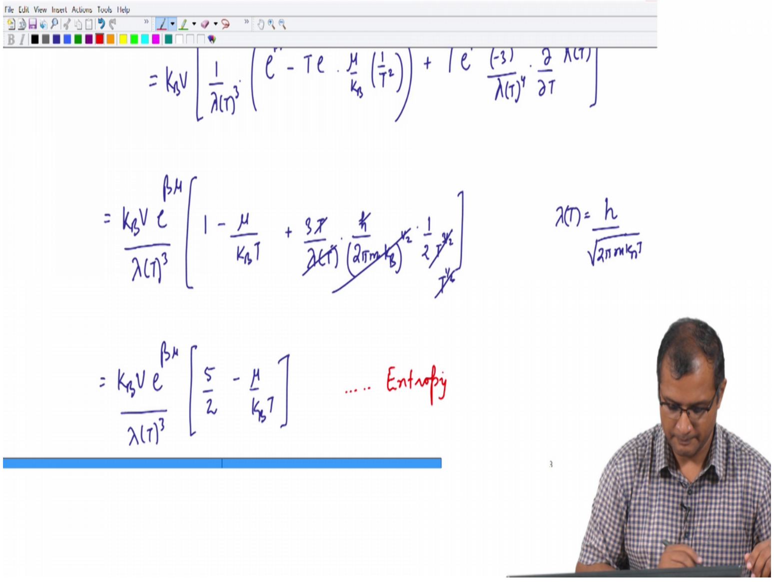

$$= k_B V \left[\frac{1}{\lambda(T)^3} \left(e - Te \cdot \frac{\mu}{k_B}\left(\frac{1}{T^2}\right) \right) + Te \, \frac{(-3)}{\lambda(T)^4} \cdot \frac{\partial}{\partial T} \lambda(T) \right]$$

$$= \frac{k_B V e^{\beta\mu}}{\lambda(T)^3} \left[1 - \frac{\mu}{k_B T} + \frac{3\cancel{T}}{\cancel{\lambda(T)}} \cdot \frac{\cancel{h}}{\cancel{(2\pi m k_B)^{1/2}}} \cdot \frac{1}{2 \cancel{T^{3/2}}} \right] \quad \cancel{T^{1/2}}$$

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

$$= \frac{k_B V e^{\beta\mu}}{\lambda(T)^3} \left[\frac{5}{2} - \frac{\mu}{k_B T} \right] \quad \ldots\ldots \text{ Entropy}$$

So, this is then so, what I will take out is basically lambda T to the power 3 outside ok. If I can take quite a few things outside; so, what I am going to take out side is basically say I can take e raise to beta mu outside everywhere and I can also take lambda T to the power 3 outside. So, what I get in the first term is basically just 1 minus mu over k T ok. And from the second term I will get minus 3 T over lambda T into derivative of lambda T. So now, lambda T is basically h over 1 upon square root of 2 pi m k B T.

So, this would simply be h over 2 pi m k B and this would be just you can get 1 upon 2 raise to T raise to 3 by 2 ok. So, then I will have to take in a few terms here and there. So, what I am going to do is basically knock of this T where 3 by 2 and so, this will become I just T raise to 1 half and that would be nothing but just lambda T in the numerator. So, that will cancel of with this term and what I will have is just 3 by 2 in the second term.

So, this is just k B V e raise to beta mu upon lambda T to the power 3 and this would be just it will just give me 5 by 2 minus mu by k T. So, let us just check of the expression is correct ok. So, now, let us compute the pressure we have already computed the pressure. So, let us compute the number of particles. So, this is the entropy, but you have just computed and to compute the number of particles.

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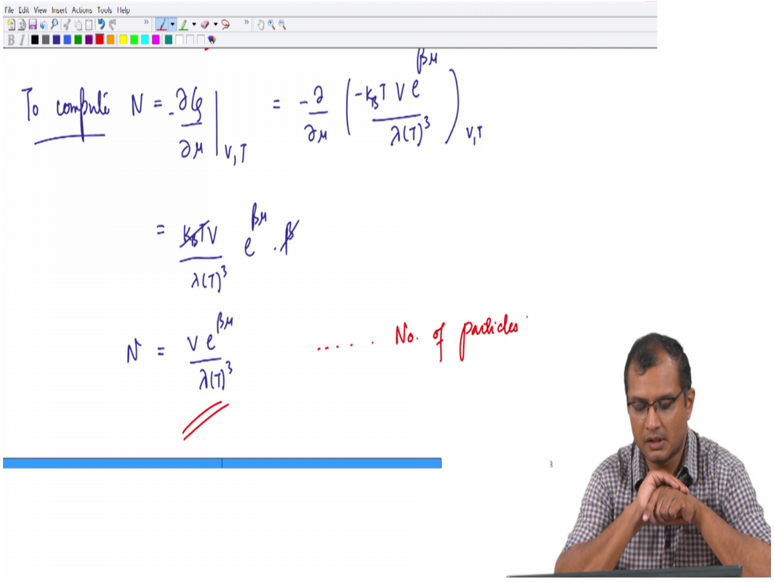

To compute $N = -\frac{\partial G}{\partial \mu}\Big|_{V,T} = -\frac{\partial}{\partial \mu}\left(\frac{-k_B T V e^{\beta\mu}}{\lambda(T)^3}\right)_{V,T}$

$= \frac{\cancel{k_B T} V}{\lambda(T)^3} e^{\beta\mu} . \cancel{\beta}$

$N = \frac{V e^{\beta\mu}}{\lambda(T)^3}$ ..... No. of particles

I have to take the derivative with respect to mu, but constant V and T and let us just look at this expression for G which is minus k T v into so, this is I believe negative derivative yes ok. So, this is basically a negative derivative of if you look at the expression fine. So, if you take this derivative you get k B T into V outside no issues there.

In fact, what you will get is also lambda T to the power 3 outside and this would just give you e to the power beta mu into beta. So, we shall cancel of with this k T. So, what you have for number of particles is just V over V into e raise to beta mu over lambda T to the power 3 ok. So, that is the expression for the number of particles.

So, this is just the entropy and this is the number of particles. So, with this our discussion of the classical ideal gas under grand canonical ensemble comes to an end and this also ends our chapter 2 on classical statistical mechanics. So, when we meet in the next class we will start to discussion on quantum statistical mechanics. We will take a few important cases of electrons in a gas.

We also take boson gases and also electrons in the solid. So, we will take some nice cases in quantum statistical mechanics and you will also see how this grand canonical ensemble becomes the natural distribution or the natural ensemble to compute properties in quantum mechanics. So, we end it here and begin the discussion on quantum statistics in the next lecture.