Statistical Mechanics
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Lecture – 21
Grand Canonical Ensemble

So, good morning students; today we will discuss the last ensemble in this chapter which is the Grand Canonical Ensemble.

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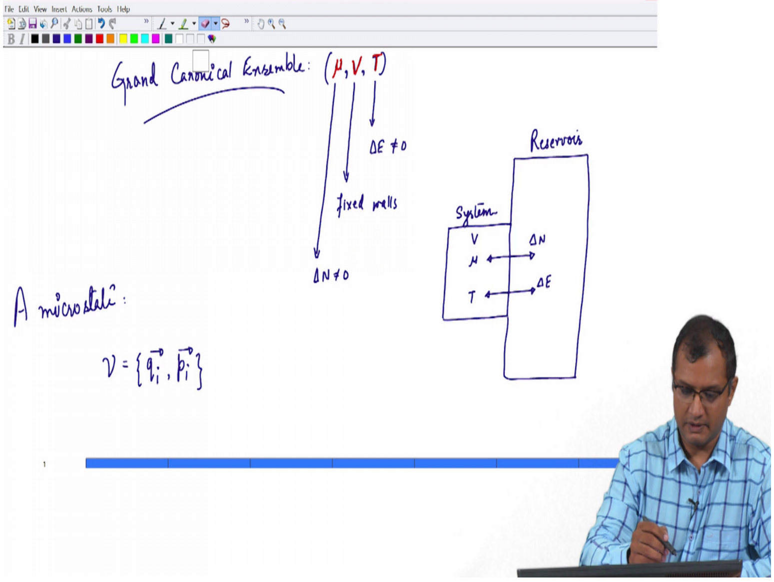

And this is a very important ensemble in the fact because, it allows for the correct enumeration of states when you go and do the calculation in quantum statistical mechanics. So, the natural ensemble to do calculations in quantum systems is the grand canonical ensemble. And so why not finish this chapter on classical stat make with the discussion of this grand canonical ensemble.

So, the ensemble is basically collection of systems or microstates all specified by the macrostate mu some generalize variable x I have taken volume here and temperature T ok. So, you can maintain temperature by allowing exchange of energy with the reservoir, you can maintain volume by keeping fixed walls. So, the system is mechanically isolated. And you can maintain chemical potential in a system by allowing particle interactions with the reservoir ok. So, these interactions are non-zero which means a system is going to exchange both energy and number of particles to maintain constant mu and constant T ok.

So, let us draw a schematic that will help us understand what is going on. So, I am going to draw my system here. So, this is going to be my system in contact with the reservoir and as usual the joint system and reservoir is in microcanonical ensemble which is always the case ok. The system is not isolated the reservoir is not isolated, but system plus reservoir is isolated. So, the system is maintained at constant volume and that is because I have taken fixed walls their walls are not moving. So, volume can be maintained constant, but now the walls between system and reservoir are porus.

So, they allow for interaction of you know chemical interaction or you allow for exchange of particles between system at reservoir in order to keep mu fixed. So, this fixes mu and you allow for interaction in energy to keep the temperature constant. So, whenever there is a fall in you know whenever the systems temperature is below the offset below the set temperature; the reservoir will give energy and bring the system back to the temperature T. And whenever the systems temperature is above the reservoir it will act like a sink and withdraw energy to bring the system back to temperature T.

So, after a long time of contact with the reservoir the systems temperature is set to T and the chemical potential is set to the chemical potential or the reservoir. So now, we have a system which it constant mu V and T. So, we would be interested in looking at the probability distribution function of the microstates. So, I have define the macro state here it is the specified value of mu V and T this is my macro state.

A microstate here would basically correspond to you know I am going to use the microstate with a different symbol here, because mu is already reserved to the chemical potential. And I am going to write down the microstate as collection of momentum coordinates, position coordinates, and momentum coordinates. We will restart it, no it is simple I do not want this light it will I mean this is it is going to throw so, much glare on my screen yeah. So, let us start it again I mean I am sure of it broke the flow is this also off, off yes.

Start from beginning.

Yeah we will start from the beginning, it is a button also.

So, good morning students today we will talk about the last ensemble in our course ok. There is already not going well alright. So, good morning students we will start discussion on the last ensemble in our course which is the Grand Canonical Ensemble.

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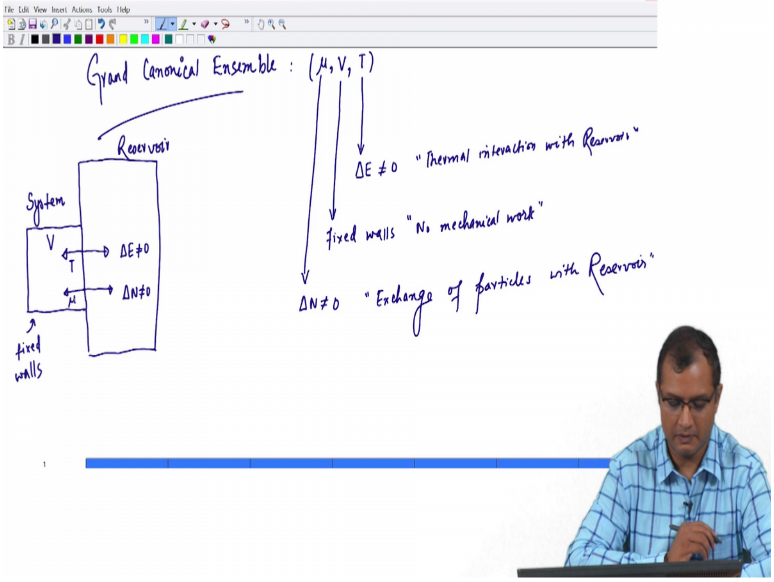

Grand Canonical Ensemble : (μ, V, T)

$\Delta E \neq 0$ "Thermal interaction with Reservoir"

fixed walls "No mechanical work"

$\Delta N \neq 0$ "Exchange of particles with Reservoir"

So, this is the ensemble where the member systems are all specified by a macro state at constant chemical potential volume and temperature. So, you can instead of volume you can take any other generalized variable such as magnetization for example, for spins in constant magnetic field.

Let me also tell you that this is the most important ensemble in statistical mechanics in the sense that it, it naturally provides for the correct enumeration of states for systems in quantum mechanics. So, you will realize in chapter 3 that the most natural ensemble to do calculations in quantum systems with the grand canonical ensemble. So, I am going to spend the last part of my lecture precisely on this issue on this ensemble which is the ensemble at constant chemical potential volume and temperature.

So, the grand canonical ensemble is maintained by fixing temperature and I know I can fix temperature by allowing for energy interactions with the reservoir. And I can fix volume in any system by just having fixed walls. So, there is no work mechanical work. So, walls do not move and there is no mechanical work and I can fix the chemical potential by allowing exchange of particles with the reservoir. So, this is called as thermal interaction with the reservoir and this is called as you know exchange of particles with the reservoir.

So, if you allow for energy interaction it keeps temperature constant, if you allow for exchange of interactions exchange of particles with the reservoir you can keep the chemical potential constant. Now the keep fixed walls do not allow them to move then at would just fix your volume there by saying that there is no mechanical work done on the system. So, I can draw a schematic here to show what is going on by drawing my system and connecting it with the reservoir ok.

So, you can say that the system is in constant volume because the walls are fixed ok. So, the walls are fixed and you allow for interaction of energy. So, there is exchange of energy with the reservoir, that keeps my temperature constant ok. And you also allow for particles to be exchanged because the walls can be made to be porous. So, that would keep my chemical potential constant ok. So, now let us look at the typical microstate that the system can rest in.

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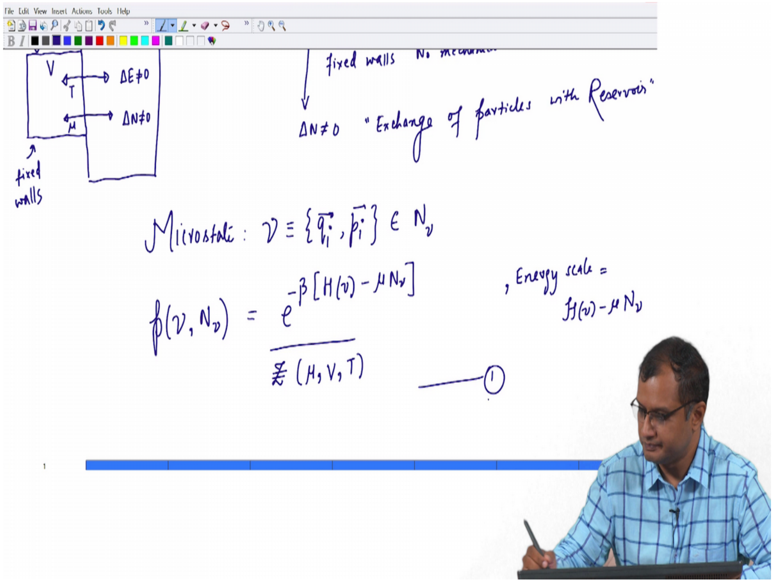

$\Delta N \neq 0$ "Exchange of particles with Reservoir"

Microstate : $\nu \equiv \{\vec{q_i}, \vec{p_i}\} \in N_\nu$

$$p(\nu, N_\nu) = \frac{e^{-\beta[H(\nu) - \mu N_\nu]}}{\mathcal{Z}(\mu, V, T)} \quad \text{——— ①}$$

, Energy scale = $H(\nu) - \mu N_\nu$

So, a microstate here is basically specified by a label nu I am going to use a label nu because mu is already reserved for chemical potential. So, a microstate here is nothing, but the set of position and momentum coordinates; it belonging to a certain instant when the number of particles is N nu because the number of particles are also changing. So, i here belongs to you know the one of the N nu particles in that particular nu at microstate ok. So, our microstate is not just a q i and p i for a fixed N and itself is varying from microstate to microstate ok.

So, that is the definition of a microstate here which been which tells me that the probability of finding my system in a microstate nu such that the number of particles are N nu ok; is nothing, but the Boltzmann factor e to the power minus beta into the energy scale which in this problem is the Hamiltonian for the nuth microstate; where you have N nu particles minus an energy scale which is due to the constant chemical potential which is nu times N nu that is the energy scale for the problem ok.

So, the energy scale for the problem is not the Hamiltonian alone, it is H nu the Hamiltonian for the nuth microstate minus the chemical work that you are allowing to be done on the system and N here is the number of particle in the nuth microstate ok. Well naturally this PDF is not normalized we have to normalize it. And so, the factor the norm is the grand canonical partition function and I am going to give it a different label with the double horizontal strikes. So, this is the partition function of the system in the grand canonical ensemble ok. So, let us call this as equation 1. Now you can easily see what should be the expression for the partition function.

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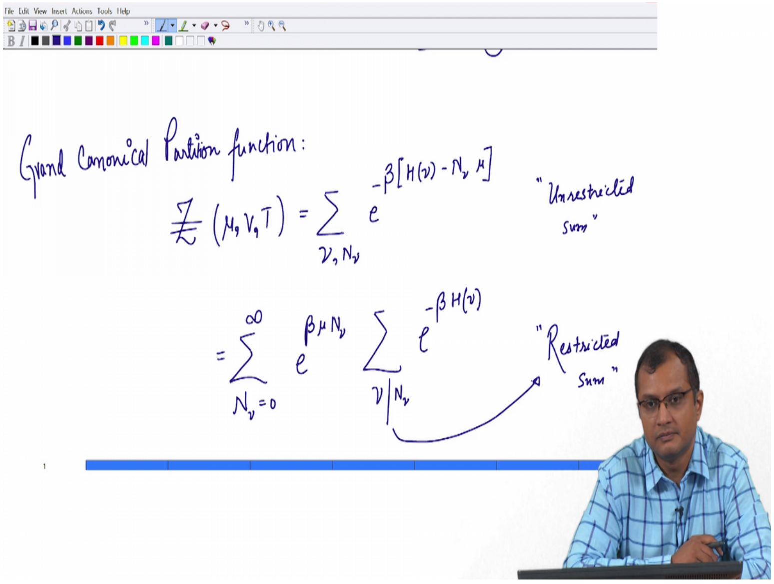

Grand Canonical Partition function:

$$\mathcal{Z}(\mu, V, T) = \sum_{\nu, N_\nu} e^{-\beta[H(\nu) - N_\nu \mu]}$$

"Unrestricted sum"

$$= \sum_{N_\nu = 0}^{\infty} e^{\beta \mu N_\nu} \sum_{\nu | N_\nu} e^{-\beta H(\nu)}$$

"Restricted sum"

So, the grand canonical partition function that provides the link with thermodynamics can be very easily obtained as simply summation over all microstates of this Boltzmann factor ok. So, let us do that so we will take summation overall the microstates. Now microstates is the doublet of nu N nu ok; that is a combination with specifies a single my microstate and I am going to sum over the Boltzmann factor which is e raise to minus beta the energy scale ok.

Now this is a double summation so it is in some sense unrestricted sum. So, all possible values of N N nu are taken, but I can convert this into a restricted sum and do this calculation easily. So, what I am going to say is that let me first compute the sum over all possible number of particles ok. So, that would be saying that I am going to take the summation over N nu ok. So, here the N nu will go from 0 to infinity all possible number of particles. The extreme values of N nu who would have a probability that is very very small as can be seen ok. So, once you have fixed your N nu you can compute the inner sum overall micro set such that it takes the value N nu from the previous sum ok.

And for each N nu that is set in the outer sum you compute all possible microstates. And so I have to take e to the power beta outside because that does not depend on the microstate nu ok. So, this will be acting only our e to the power beta mu N nu because this is just the variable here is just the number of particles in the microstate. And the inner sum would now be on the microstates such that the number of particles is fixed to N nu by the outer sum summation over e raise to minus beta H nu is it ok. So, now is like changing from unrestricted sum to restricted sum.

So, this thing is a restricted sum ok. So, you for example, you in the outer sum N nu could be 50. So, your 50 particles in your system for these 50 particles compute all possible microstates by arranging the particles in the box and that is your inner sum then you change 50 to 51, and then compute all possible microstates for these 51 particles and compute the inner sum. So, this way you take the number of particles in the outer sum from 0 to infinity and compute the inner sum ok. Now, if you pay attention to this inner sum it is looking very familiar ok.

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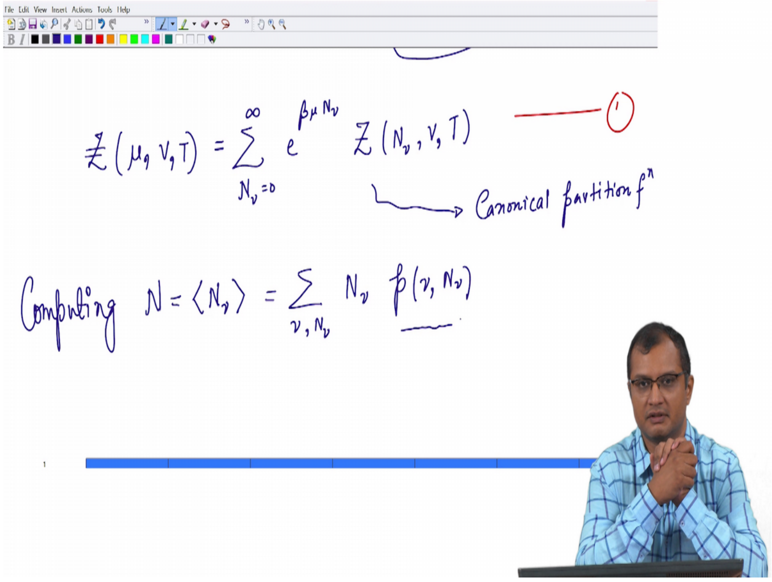

$$\mathcal{Z}(\mu, V, T) = \sum_{N_\nu=0}^{\infty} e^{\beta\mu N_\nu} \underbrace{Z(N_\nu, V, T)}_{\longrightarrow \text{ Canonical partition } f^n} \quad \text{———} ①$$

$$\text{Computing} \quad N = \langle N_\nu \rangle = \sum_{\nu, N_\nu} N_\nu \, \underline{p(\nu, N_\nu)}$$

So, it already looks familiar in the sense that this is nothing, but the summation over the Boltzmann factor for N nu particles ok. So, I am going to call it as the canonical partition function with N nu particles. If we recall this is the canonical partition function for N nu particles because the only thing that is. So, the inner sum is at constant temperature at constant volume ok. And now it is at the N nu so this is a partition function for N V T or the canonical partition function.

N is not varying for the inner sum it is constant. So, it is a partition function for the canonical ensemble. So, that restricted sum is nothing, but the canonical partition function. But now we can also. So, I am going to write this as. So, my grand canonical partition function is this expression summation overall N e raise to beta mu N times the canonical partition function ok. So, I am going to call this as equation 1 ok. And now you can compute averages of various quantity in our system. So, you can compute for example, average number of particles in the system because N is a fluctuating quantity to keep chemical potential constant like I said for every fluctuating random variable we are interested in it is moments.

So, the first moment to compute is it is average. So, to compute average number of particles which is like saying what is the expectation value of N. Now this is simple this is nothing, but summation overall nu N nu e to the probability distribution function which is nothing, but fine which is like saying my PDF here is going to tell me what is the probability of finding a microstate with N nu particles and having moment and position which is given by nu. So, you simply sample your N nu in that PDF and the result would nothing be would be nothing, but your average number of particles. So, when you do this sampling what you get you have the, you have to do the sampling.

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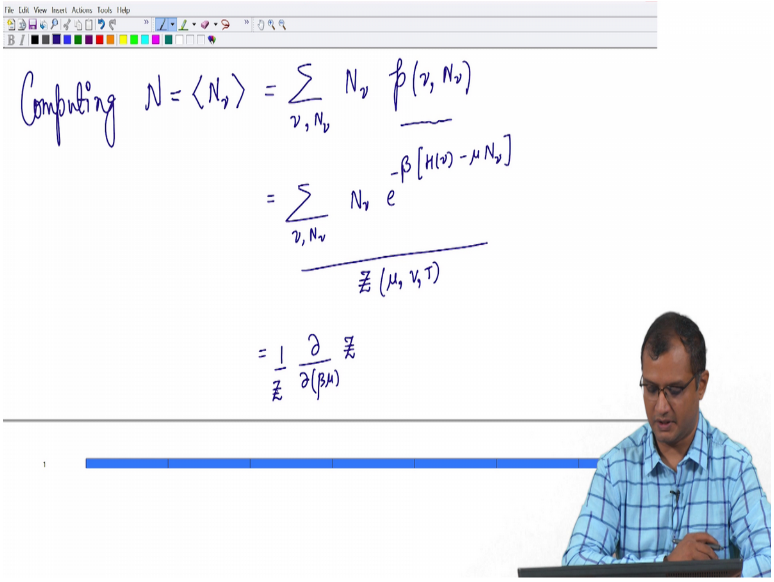

Computing $N = \langle N_\nu \rangle = \sum_{\nu, N_\nu} N_\nu \, \underline{p(\nu, N_\nu)}$

$$= \frac{\sum_{\nu, N_\nu} N_\nu \, e^{-\beta[H(\nu) - \mu N_\nu]}}{\mathcal{Z}(\mu, V, T)}$$

$$= \frac{1}{\mathcal{Z}} \frac{\partial}{\partial(\beta\mu)} \mathcal{Z}$$

And this would be nothing, but N nu and your PDF is nothing, but e to the power minus beta H nu minus mu N nu over the grand canonical partition function fine. Now you can pull out N nu by simply taking a derivative with respect to beta mu ok. So, we can write down that I will take a derivative with respect to beta mu of the grand canonical partition function ok. And the denominator already has a grand canonical partition function ok.

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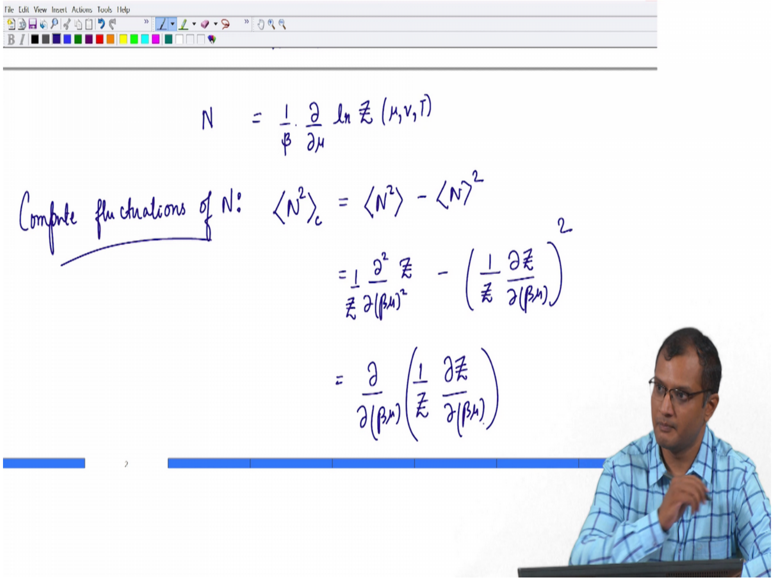

$$N = \frac{1}{\beta}\cdot\frac{\partial}{\partial\mu}\ln \mathcal{Z}(\mu,V,T)$$

Compute fluctuations of N: $\langle N^2\rangle_c = \langle N^2\rangle - \langle N\rangle^2$

$$= \frac{1}{\mathcal{Z}}\frac{\partial^2 \mathcal{Z}}{\partial(\beta\mu)^2} - \left(\frac{1}{\mathcal{Z}}\frac{\partial \mathcal{Z}}{\partial(\beta\mu)}\right)^2$$

$$= \frac{\partial}{\partial(\beta\mu)}\left(\frac{1}{\mathcal{Z}}\frac{\partial \mathcal{Z}}{\partial(\beta\mu)}\right)$$

So, this is nothing, but you can write it as a 1 upon beta d by d mu of lon z where z is nothing, but the grand canonical partition function. So, it is have a function of mu V and T ok. So, this is the expression for average number of particles in your system ok. So, look at your partition function which is nothing, but the sum over all degrees of freedom. And the degrees of freedom here are not just the position moments, but they also the number of particles in a given microstate. So, this is the number of particles in the system also called as the mean N. You can also compute fluctuations of N. So, these are nothing, but the second cumulant of the random variable N. And that is nothing, but you take the second moment minus the square of the first moment.

And then it is very simple to see that it is nothing, but you can you can already see that this is d over d beta mu you have to pull out N two times. So, it is the second derivative of this your canonical grand canonical partition function over the grand canonical partition function; minus square of the first derivative ok. So, if you see this will the terms in bracketed term is nothing, but the mean N and a first time is nothing, but the mean of N square ok. And you can write this as nothing, but d over d beta mu of you can write it as 1 upon z d z over d beta mu is it. So, by chain rule it will expand to the previous equality.

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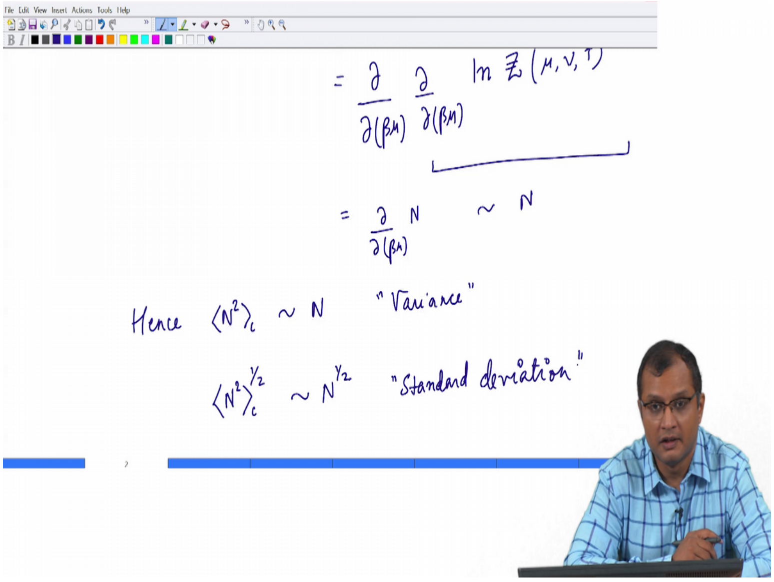

$$= \frac{\partial}{\partial(\beta\mu)} \underbrace{\frac{\partial}{\partial(\beta\mu)} \ln \mathcal{Z}(\mu, V, T)}$$

$$= \frac{\partial}{\partial(\beta\mu)} N \quad \sim N$$

Hence $\langle N^2 \rangle_c \sim N$ "Variance"

$\langle N^2 \rangle_c^{1/2} \sim N^{1/2}$ "Standard deviation"

And if you pay attention to the fact the term in the parentheses is nothing, but logarithm of the derivative of the logarithm of z. So, this is nothing, but d over d beta mu of I can write this as fine so, but now this term has already been computed ok. So, this term is already been compute. So, this is over here. So, this is nothing, but your N itself. So, this is d over d beta mu of N.

So, now, you can see that this thing scales as N because beta mu in intensive quantity N scales is N ok. So, your variance scales as N ok. So, our variance scales as N this is my variance or the second cumulant. That tells me that the standard deviation which is square root of my variance will scale as a square root, which is the standard deviation.

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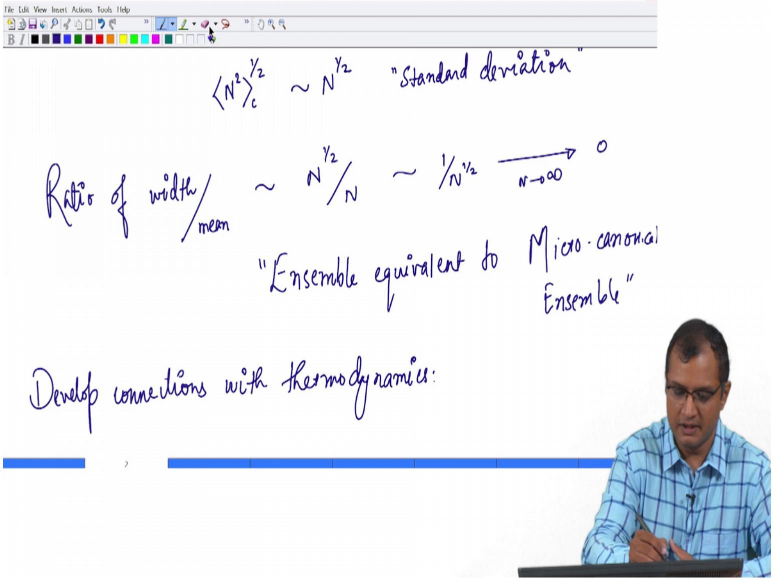

$\langle N^2\rangle_c^{1/2} \sim N^{1/2}$ "Standard deviation"

Ratio of width/mean $\sim N^{1/2}/N \sim 1/N^{1/2} \xrightarrow[N\to\infty]{} 0$

"Ensemble equivalent to Micro-canonical Ensemble"

Develop connections with thermodynamics:

Now we can see that the ratio of standard deviation over mean which is basically a quantification of ensemble equivalence diminishes in the limit of large N. So, the ratio of width over mean which will always signify how sharp your distribution is in the thermodynamic limit. So, this will be square root N over N which is nothing, but 1 upon square root N and that will diminish or go to 0 in the thermodynamic limit. So, this is called as the ensemble equivalence. That means, our grand canonical system in the limit of N going to infinity; suppose this is a large you know room or a hall or an auditorium which is in grand canonical ensemble would have it is number of particles fixed.

So, it would actually be a system looking very similar to a canonical ensemble, its number of particles are fixed, no longer fluctuating. Well, you can argue that the there is a fluctuation and as you increase a system size the width also increases of the distribution. But I am going to ask: what is the proportion of your width to mean and that proportion would be diminishing value in thermodynamic limit. So, essentially it has features of a microcanonical ensemble as N goes to infinity ok.

So, it is the equivalent not equal to it is equivalent to addition using is equivalent to micro canonical ensemble, the ensemble where N is fixed. In your ensemble the N is not fixed, but it is the relative width over mean is the diminishing value. So, essentially it is features are like that of a micro canonical ensemble as N goes to infinity. Now we can develop connections with thermodynamics as usual, in all ensembles we can develop connections with thermodynamics and this connections these connection are always established through the partition function. So, I am going to bring down my partition function which is a very important derivation. So, let us export our canonical grand canonical partition function downstairs and build a connection with thermodynamics ok. So, let us export it here fantastic.

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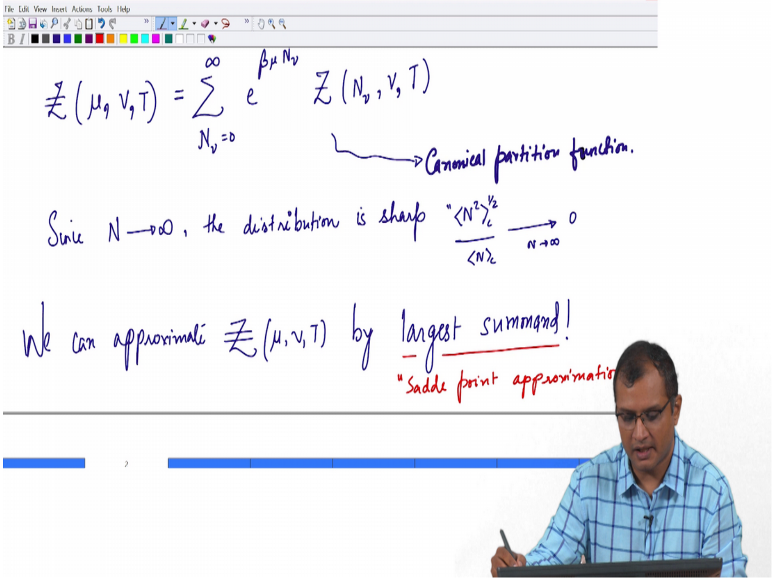

$$\Xi(\mu, V, T) = \sum_{N_\nu=0}^{\infty} e^{\beta\mu N_\nu} Z(N_\nu, V, T)$$

$\longrightarrow$ Canonical partition function.

Since $N \to \infty$, the distribution is sharp "$\frac{\langle N^2\rangle_c^{1/2}}{\langle N\rangle_c} \xrightarrow[N\to\infty]{} 0$

We can approximate $\Xi(\mu, V, T)$ by largest summand!

"Sadde point approximatio

So, we now have a our and just to remind you that this is the canonical partition function ok. Now, I need an approximation of this partition function because again computing the summation over infinity is difficult. So, can I approximate it now you can approximate using a technique called as saddle point approximation since N is very large. So, this is approximation technique that is discussed in our appendix so you can refer to it. Since N is very large we can take a large number of particles in the system and distribution is sharp by sharp distribution. I mean I have already shown that the ratio of width over mean has gone to 0 as N goes to infinity is the meaning of sharp distribution ok.

I can approximate the summation in the above expression we can approximate this grand canonical partition function by largest summand. So, grand canonical partition function is already a sum over so many terms ok. If you look at the right hand side of the grand canonical partition function it is a sum over. So, many terms the idea here is to not take the entire sum the idea here is to use the saddle point approximation ok. So, this is called as the saddle point approximation. So, the sum will now be replaced by the maximum of the summand this technique has been discussed in detail in the appendix. So, you can now write down the partition function.

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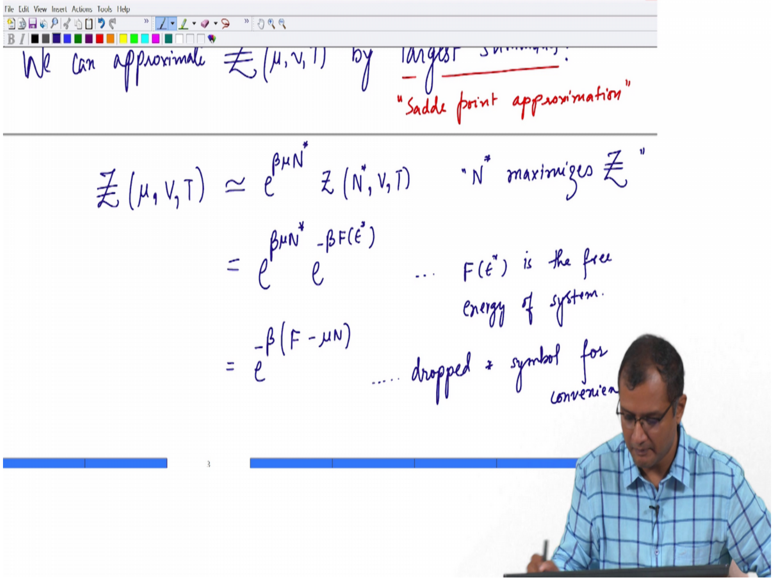

We can approximate $\mathcal{Z}(\mu, V, T)$ by largest

"Sadde point approximation"

$$\mathcal{Z}(\mu, V, T) \simeq e^{\beta\mu N^*} Z(N^*, V, T)$$

"N^* maximizes $\mathcal{Z}$"

$$= e^{\beta\mu N^*} e^{-\beta F(\epsilon^*)}$$

... $F(\epsilon^*)$ is the free energy of system.

$$= e^{-\beta(F - \mu N)}$$

..... dropped * symbol for convenien

The grand canonical partition function approximated by the maximum summand ok. Now it is not an exact equality it is an approximation. So, the maximum summand here the first term would be e to the power beta mu N star here N star is the value that maximizes the exponential and I have to also take it is a product of two values. So, I have to take maxima of both of them. So, I am going to take the maxima of z itself the canonical partition function also ok.

So, I will say that the N star here maximizes the grand canonical partition function ok. So, it has to maximize both the exponent e raise to beta mu N and the canonical partition function z. And this is nothing, but if you look at our derivations the canonical partition function. If you recall was already approximated the maxima of this was e to the power minus beta into free energy. If you recall where f is free energy of system ok;so, here e star is the free energy that minimizes the e star is the energy that minimizes free energy.

And hence, we take that free energy here and so then you can write it as basically drop all the stars because now they are all the thermodynamic variables. So, we have dropped all the subscript and you can write it as e to the power minus beta into the free energy minus mu N. So, now all the quantities are stress wise. So, we have dropped the asterisk symbol for convenience ok because, these quantities are thermodynamic in nature. So, N star here the thermodynamic N that maximizes it e star is also thermodynamic.

So, I am going to drop the symbols for convenience because otherwise we will have a star on each symbol inside; so, dropping symbol star with the understanding that all energies and all number of particles are already in the thermodynamic limit. So, N here in the final expression is the thermodynamic N e star is a thermodynamic e f is a thermodynamic f free energy and so on.

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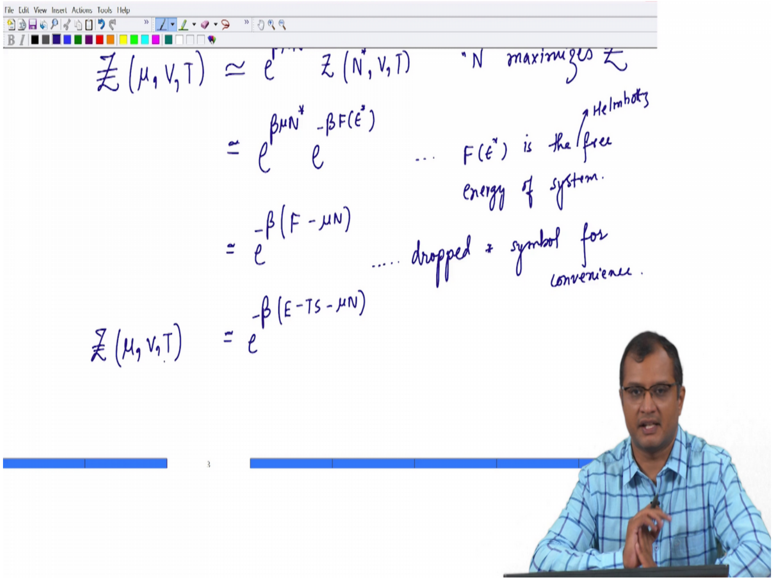

$$\mathcal{Z}(\mu, V, T) \simeq e \; Z(N^*, V, T)$$

$^*N$ maximizes Z

$$\simeq e^{\beta\mu N^*} e^{-\beta F(E^*)}$$

… $F(E^*)$ is the free energy of system.

↑ Helmholtz

$$\simeq e^{-\beta(F-\mu N)}$$

….. dropped * symbol for convenience.

$$\mathcal{Z}(\mu, V, T) \simeq e^{-\beta(E-TS-\mu N)}$$

So, I can write down this final equality as e to the power minus beta the thermodynamic free energy or the Helmholtz free energy. I am going to write it as Helmholtz free energy is nothing, but the sum of internal energy minus temperature entropy work minus mu N. So, E minus T S is F.

So now, we what we have is basically all these are approximations. So now, if you look at this is my grand canonical partition function, and it is basically e to the power minus beta into some energy scale E minus T S minus mu N. So, we can label this as some equation number, let us label it as equation number 2.

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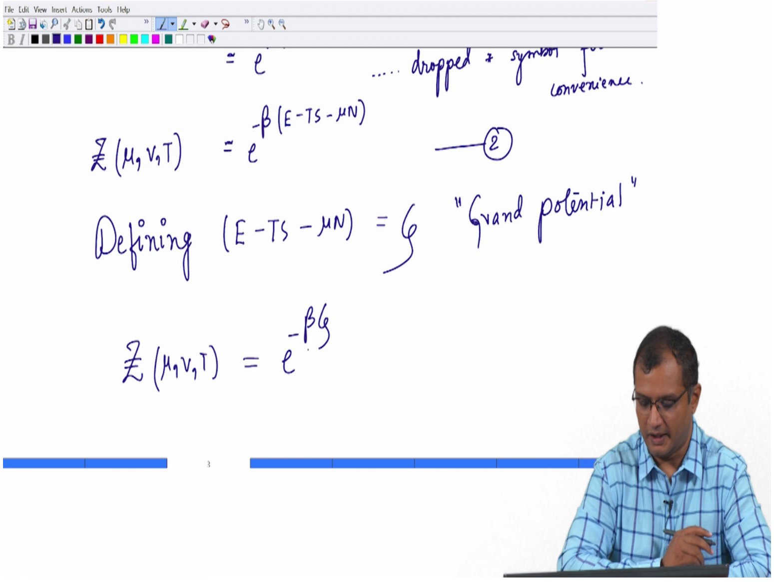

$= e$ ..... dropped * symbol for convenience.

$$\Xi(\mu, V, T) = e^{-\beta(E-TS-\mu N)} \quad \text{——} ②$$

Defining $(E - TS - \mu N) = \xi$ "Grand potential"

$$\Xi(\mu, V, T) = e^{-\beta \xi}$$

So, if we define it is in our hands to define this energy scale. So, I am going to define it, this energy scale just for convenience sake as some grand potential ok. So, this is the energy scale that will build connections with thermodynamics ok. So, I am going to define my energy scale in this Boltzmann factor as grand potential. So, I can write down my grand canonical potential, as e to the power minus beta xi ok. And now you can see that the connections from thermodynamics can be established by simply taking a logarithm, so my thermodynamic energy scale is xi.

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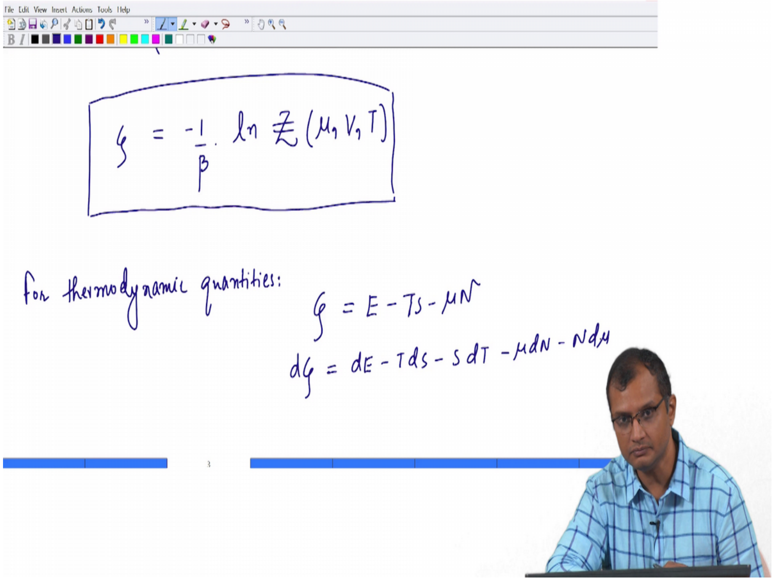

$$\boxed{\xi = -\frac{1}{\beta} \cdot \ln \Xi(\mu, V, T)}$$

For thermodynamic quantities: $\xi = E - TS - \mu N$

$$d\xi = dE - TdS - SdT - \mu dN - N d\mu$$

So, this will be nothing, but minus one upon beta ln the grand canonical potential. Compare this with the connection that you established in the context of the Gibbs canonical ensemble. So, there are the relevant energy potential was the Gibbs free energy, in the canonical ensemble the relevant energy scale was the Helmholtz free energy. And, here you have the grand potential that sets of that connection from the statistical mechanics to thermodynamics. So, this is the very important result. So, if you know how to compute the partition function for a system then you can use this relationship to compute various thermodynamic quantities.

What do I mean by that? Well I mean, but if you know partition function then you can invoke appropriate derivatives of the partition function and compute the thermodynamic quantities. For instance our energy scale here is for thermodynamic quantities; I am going to stop after this and take the example of an ideal gas in the next lecture, but just to sort of end the discussion I want to explain what I just said ok. How do I invoke appropriate derivative. So, look at this energy scale that is in front of you the grand potential.

So, this is E minus T S minus mu N ok. So, you start with that and take the incremental derivatives ok; so, the differentials on the thermodynamic law. So, what you have is the following expression fine. Now, you can use the first law of thermodynamics and do something with d E minus d S T d S minus mu d N. So, I can write this as I can substitute for d E minus T d S minus mu d N as a simply minus P d v.

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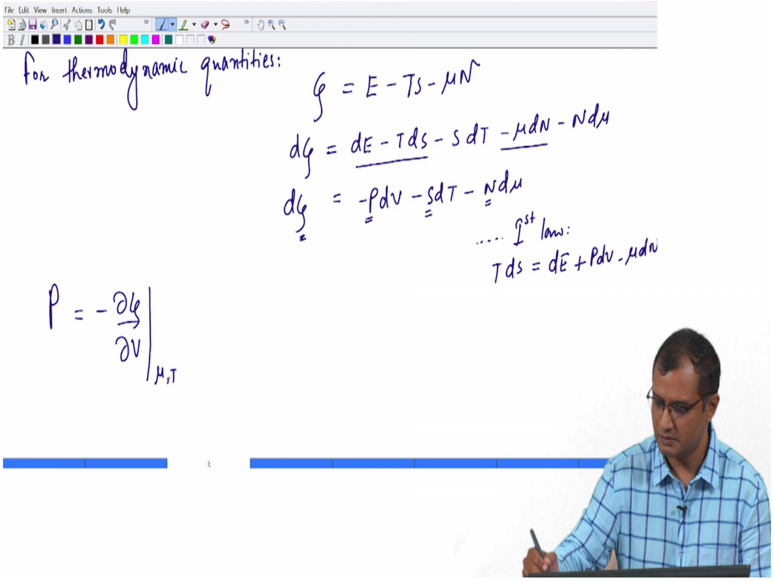

For thermodynamic quantities:

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

$$d\mathcal{G} = \underline{dE - Tds} - S\,dT \underline{- \mu dN} - N d\mu$$

$$\underline{\underline{d\mathcal{G}}} = -\underline{\underline{P}}dV - \underline{\underline{S}}dT - \underline{\underline{N}}d\mu$$

..... I^{st} law:

$$T ds = dE + PdV - \mu dN$$

$$P = -\frac{\partial \mathcal{G}}{\partial V}\bigg|_{\mu, T}$$

Because, the first law allows me to write down the heat energy as that goes into the system as the rise in internal energy plus pressure volume work done by the system minus the chemical work ok. So, minus P d v will simply be what I have substituted for. So, then if I look at this if I look at this expression in front of me I can compute pressure entropy and number of particles by invoking the appropriate derivatives of the grand potential ok.

So, I can write down pressure as a negative derivative of the grand potential with respect to volume ok. So, let me write this again, I can write it as negative derivative of the grand potential at constant chemical potential and temperature.

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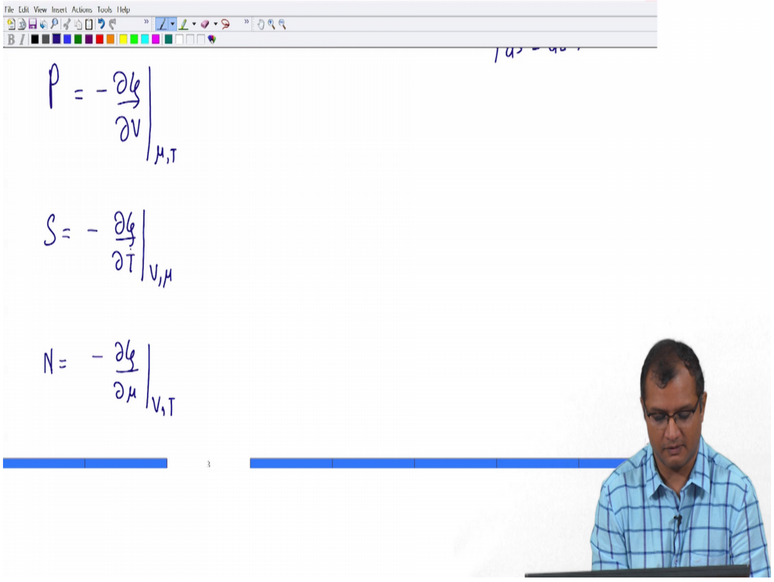

$$P = -\frac{\partial \mathcal{G}}{\partial V}\Big|_{\mu,T}$$

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

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

And, I can compute entropy as a minus derivative of the grand potential at constant temperature at with respect to temperature at constant volume and chemical potential. And finally, I can compute number of particles by taking derivative with respect to chemical potential, fine. So, you can compute so you are look into this your system is it constant mu V and T and derivative with respect to this thermodynamic variables of the grand potential provides the connection with thermodynamics.

So, I can compute the pressure of my system entropy of my system, a number of particles of my system, using these appropriate derivatives. So, you can substitute for xi in these derivatives from this expression and compute all these quantity. So, if you have the knowledge of xi you can compute all this derivatives and invoke and compute the thermodynamic quantities.

So, in the next class we will take the examples, I will take a working example in the class and take the ideal gas as one system. And do this calculation and compute pressure entropy and number of particles at equilibrium. So, we break here and when we meet in the next class I am going to discuss the ideal gas under grand canonical ensemble. And we will compute various thermodynamic quantities that we have just discussed in this lecture.

Thank you.