Statistical Mechanics
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Lecture –18
Gibbs Canonical Ensemble

Good morning students. Today we will start about and discuss the grand the Gibbs Canonical Ensemble.

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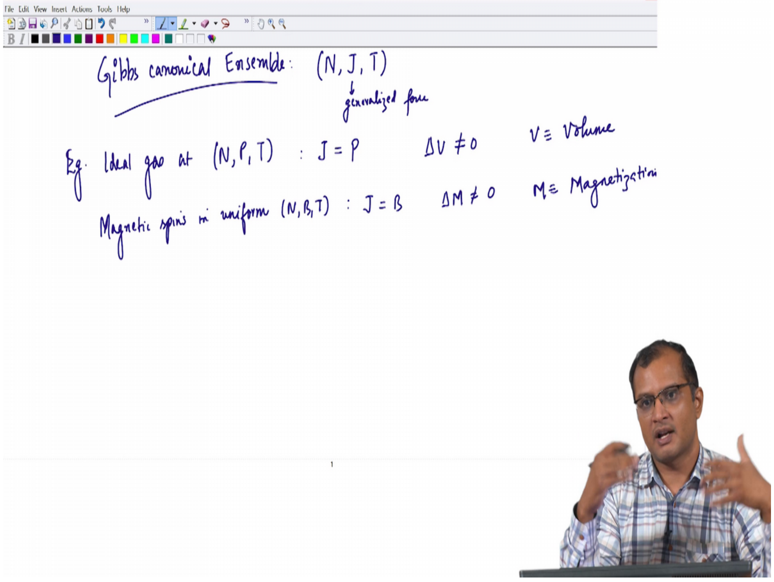

Gibbs canonical Ensemble: (N, J, T)

$\downarrow$ generalized force

Eg. Ideal gas at (N, P, T) : $J = P$ $\Delta V \neq 0$ $V \equiv$ Volume

Magnetic spins in uniform (N, B, T) : $J = B$ $\Delta M \neq 0$ $M \equiv$ Magnetization

And here three variable that I have chosen to keep constant are the number of particles in a system to generalize force J and the temperature t ok. So, examples of such a system are you know an ideal gas at some constant values of NP and T. So, of taken the generalized force as pressure P ok. So, J is the generalized force, so the system as to do work against the generalized force in some sense. You could also take magnetic systems in some uniform magnetic field, uniform field.

So, that would be N B and T at some constant number of spins magnetic field B and temperature T. So, in this case I have taken the generalized force to be magnetic field. So, in contrast to the canonical ensemble where we allowed only energy to be exchanged in order to keep temperature constant; for this ensemble I must allow for extra extensive variable to x to fluctuate. The extensive variable that I am allowing to fluctuate corresponds to volume if I want to keep pressure constant. So, there is a fluctuation of volume in the system and if I want to keep magnetic field constant then I must allow for fluctuations in magnetization ok. So, V here is the volume and M stands for magnetization.

Please note that both volume and magnetization are extensive variables which means they scale with system size. If you increase the volume by you know if you want to keep the density constant, and you increase number of particles by some factor lambda then you have to increase volume by the same factor to keep the density constant the same applies to magnetization. So, a larger system will have larger magnetization.

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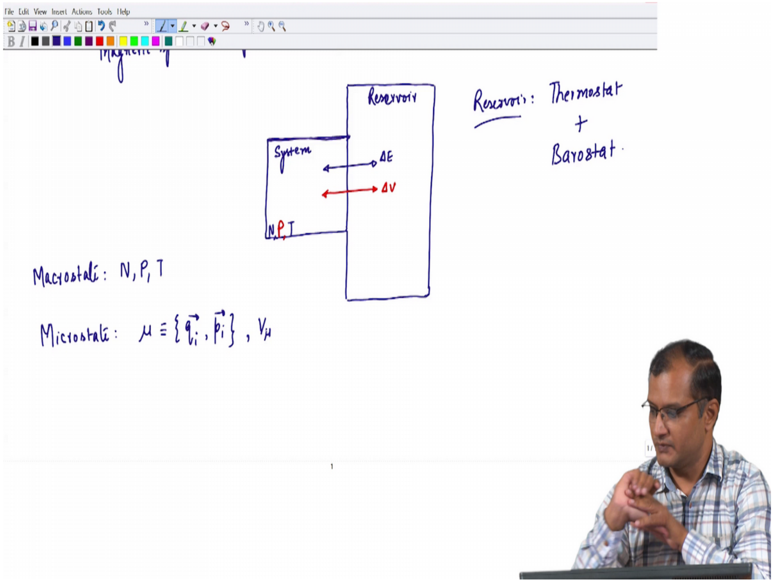

Macrostate: N, P, T

Microstate: $\mu \equiv \{\vec{q}_i, \vec{p}_i\}, V_\mu$

So, let us draw a schematic here to take an example. So, this is going to be my system and I have taken the case of an ideal gas let us say I am taking the case of ideal gas ok. In contact with reservoir and let us say that this reservoir allows you know this system is allowed to exchange energy with the reservoir. So, the system is exchanging energy with the reservoir in order to keep the temperature T constant.

And similarly, you can allow exchange of volume to keep pressure constant and since we are not allowing any number of particles to escape the system or reservoir N is naturally conserved ok. So, that is the meaning of keeping N PNT constant. So, this reservoir is basically nothing, but a combination of thermostat because it keeps temperature constant in the system and it is also acting as a barostat which means it is keeping pressure constant.

So, that the reservoir for us combination of thermostat plus barostat. Now for such systems you can say that a microstate. So, let us first describe our; we already know the macrostate as NPT the specified value of the NP and T. The corresponding microstate, then there are large number of these microstates they are specified as some mu which is nothing but the set of values of position and momentum. So, these are nothing, but the set of values of the position and momentum.

But now, this is also specified together with the volume of the microstate, because at any instant if you come back to the system and observe it you will see that positions in momentum are positions are free to take any values in the box which is the system. And the momentum is free to take any values between 0 to infinity, but now you have to also specify the volume of the box because that is fluctuating.

So, in the given volume all possible momentum and positions constitute one microstate which is already a large number, then when the volume fluctuates and becomes a mu volume you have to again allow for all the particle degrees of freedom to change and those are the microstates in that volume. So, microstate is jointly specified for a given volume and the set of values of q and p ok. So, you have one additional degree of freedom which is the volume of the microstate that is very important thing to be remembered here.

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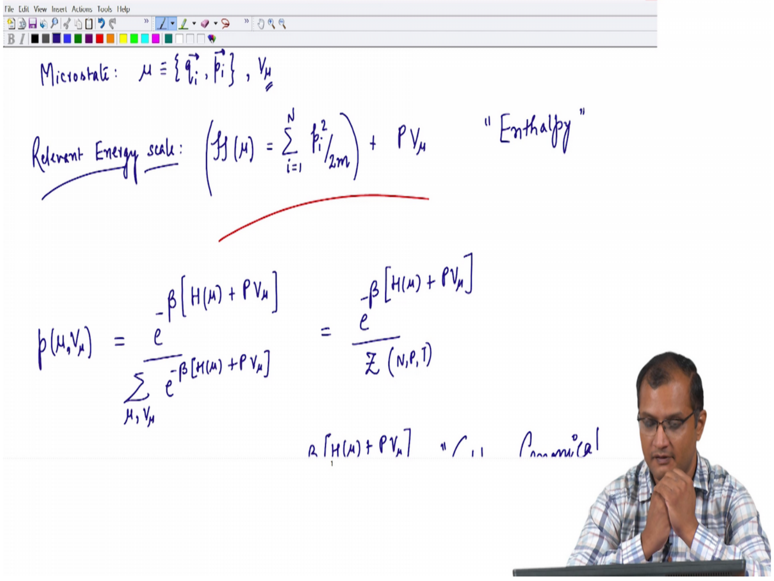

Microstate: $\mu \equiv \{\vec{q}_i, \vec{p}_i\}, V_\mu$

Relevant Energy scale: $\left(\mathcal{H}(\mu) = \sum_{i=1}^{N} p_i^2/2m\right) + PV_\mu$ "Enthalpy"

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

$\beta[H(\mu)+PV_\mu]$ " Canonical

Now, just in the similar spirit, if I want to write down the probability of finding my system in a microstate which is instantly, and that particular instant is in volume V of mu V mu meaning volume of that microstate. Then I have to say that this is nothing, but e to the power minus beta into some energy scale; now what is that energy scale? So, let me write down this energy scale. So, before we write down the probability distribution let us write down the energy scale that is relevant here.

So, relevant energy scale here is not just the total energy that comes from the Hamiltonian, like in the canonical ensemble the relevant energy scale was just the energy of the microstate mu. Now which was basically nothing, but for an ideal gas you could write down this as 1 to N pi square by 2 m; this is not energy scale. The relevant energy scale is the Hamiltonian for a given microstate plus the pressure volume work that the system has done against the barostat ok.

So, the system is now constantly trying to you know maintain its you know the its pressure see this is a PV amount of energy that one must associate with this is not a system it is mechanically isolated. PV work will not be there if the system is mechanically isolated the system is being constantly held at a pressure P. And one must in involve the pressure volume work because the system is not mechanically isolated so, pressure volume work has to be there. So, this is my total energy scale now ok.

So, I must write down my probability of finding the system in a given microstate mu at volume V mu as a Boltzmann factor. Now the Boltzmann factor here is a e raise to minus beta into the energy scale ok. The energy scale is now as we have discussed H mu that is nothing but pi square by 2 m summed over all particles; if it is an ideal gas plus, the pressure volume work which the system has done against the reservoir, this is my Boltzmann factor. And, I know that this is not a normalized probability density or probability distribution function I must write it with a nom which is nothing, but e raise to minus beta H mu plus P of P mu.

Now, this makes my probability distribution function properly behaved and I am going to call this denominator as the partition function, but partition function for my NPT system. So, partition function is specified for a microstate this is Gibbs canonical partition function.

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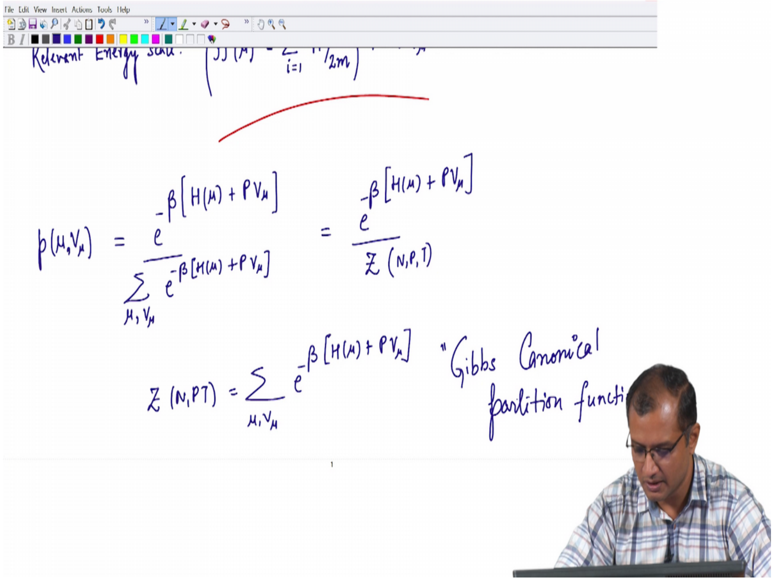

Relevant Energy scale:

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

$$Z(N,PT) = \sum_{\mu, V_\mu} e^{-\beta[H(\mu) + PV_\mu]}$$ "Gibbs Canonical partition functi

So, you can think of you can write down your Z of NPT which is nothing, but our summation overall all microstates e raise to minus beta H mu plus P of V mu as the Gibbs canonical partition function. We can of course, write down an integral version of this that I am going to use in the next lecture, but suppose you can enumerate the number of states this is also a representation nice representation.

Of course, before we proceed I am going to call this relevant energy scale as enthalpy ok, because this is energy plus PV and that from thermodynamics its an enthalpy. So, in the ensemble of Gibbs where you are controlling pressure in addition to temperature the relevant energy scale is not the total energy itself it is the enthalpy of the system ok. So, the Boltzmann factor will not have energy it will have enthalpy ok. So, that is something that you need to keep track of that our energy scale has changed from Hamiltonian to enthalpy. Now like in the canonical ensemble I wanted to know; what is the average value of the energy?

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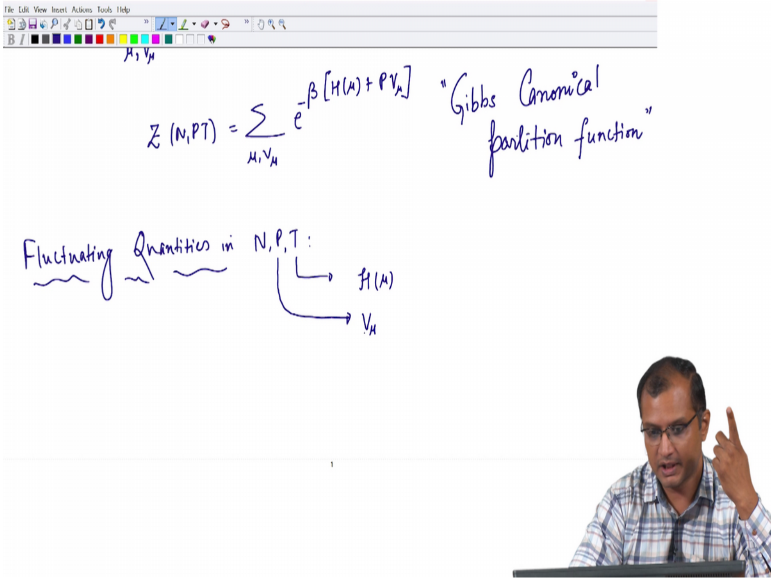

μ, V_μ

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

"Gibbs Canonical partition function"

Fluctuating Quantities in N, P, T :

$\to \mathcal{H}(\mu)$

$\to V_\mu$

Here, I have two quantities that are fluctuating what are the fluctuating quantities in this system? In our Gibbs canonical ensemble to maintain this macrostate I know there are two quantities that are fluctuating to maintain temperature I have to allow for energy fluctuations. So, there are two quantities that are fluctuating; one is energy or I will say the Hamiltonian that fluctuates, and there is one more thing that fluctuates to maintain pressure I must allow for fluctuating in the; I must allow for fluctuations in the volume ok.

So, there are two quantities that are fluctuating in my system the Hamiltonian or the energy and volume these are two fluctuating qualities. And actually when something is fluctuating you will be talking about their averages because, their quantities themselves now have no meaning the instantaneous values of meaning what you really require is the quantity in the thermodynamic limit or the average of this quantity.

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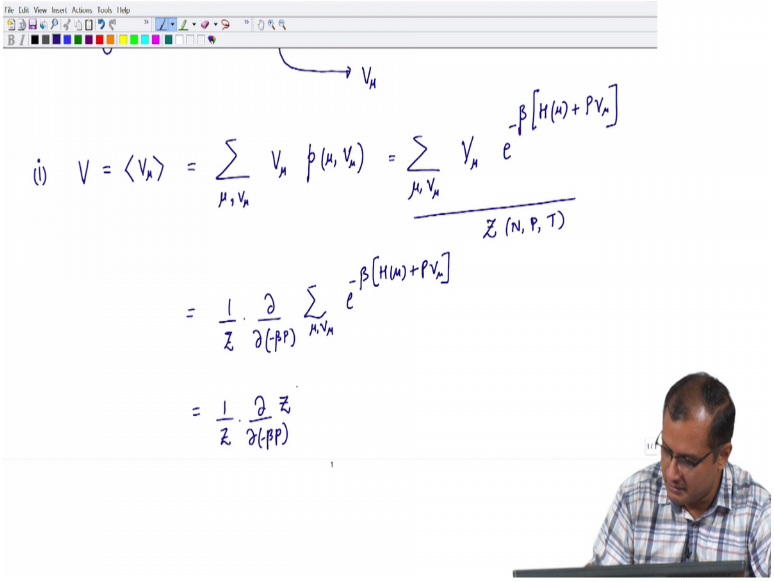

$$\rightarrow V_\mu$$

$$\text{(i)} \quad V = \langle V_\mu \rangle = \sum_{\mu, V_\mu} V_\mu \, p(\mu, V_\mu) = \frac{\sum_{\mu, V_\mu} V_\mu \, e^{-\beta[H(\mu) + PV_\mu]}}{Z(N, P, T)}$$

$$= \frac{1}{Z} \cdot \frac{\partial}{\partial(-\beta P)} \sum_{\mu, V_\mu} e^{-\beta[H(\mu) + PV_\mu]}$$

$$= \frac{1}{Z} \cdot \frac{\partial Z}{\partial(-\beta P)}$$

So, the first average that you can think of is that of volume average ok. So, I am going to call V as the average of the instantaneous volume. So, this is nothing but you have to sample this volume among all the microstates and this is the sampling you sample is the instantaneous volume in your probability distribution. So your probability distribution is p of mu and V of mu this is your probability distribution function , and you sum over all mu and V and sample here, your volume this will give the average volume of the system fine.

So, let us proceed with this calculation this is nothing but summation over all the microstates the volume of the microstate and your probability density function which is e to the power minus beta in the energy scale which is enthalpy instantaneous enthalpy. So, H mu plus PV mu this is root enthalpy energy scale, over your Gibbs canonical partition function which is nothing but summation over all probability; so that this is normalized.

So, I can write down this as 1 upon Z into to pull out a V mu all I have to do is basically take a derivative with respect to minus beta P of the Gibbs canonical partition function ok. So, if you want to write down in two steps you can do that. So, I am going to write this as; this is what you would do. So, the summation is overall microstates and for each microstate you had pressure is fixed. So, beta (Refer Time: 14:41) any way fixed.

So, they are independent of the microstate. So, this derivative will go inside the summation and derivative each term and from each term what you it will pullout is basically a V of mu that is under the summation. And you will get the numerator in the previous expression. The denominator is just a Z that I have taken outside and this is nothing, but 1 upon Z d over d minus beta P of the Gibbs canonical partition function.

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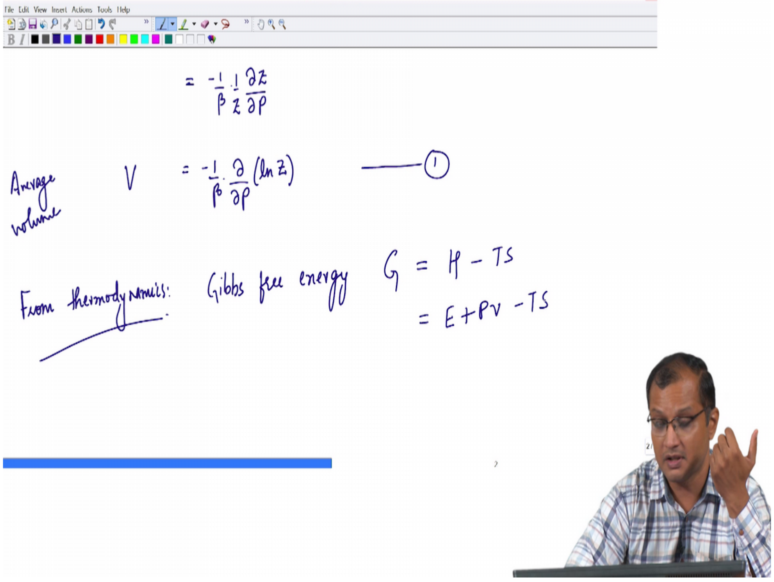

$$= -\frac{1}{\beta}\cdot\frac{1}{Z}\frac{\partial Z}{\partial P}$$

Average volume $V = -\frac{1}{\beta}\cdot\frac{\partial}{\partial P}(\ln Z)$ —— ①

From thermodynamics: Gibbs free energy $G = H - TS$

$= E + PV - TS$

Since, beta is anywhere constant here. So, I am going to take it out as minus 1 over beta dZ by dP and there is a 1 upon Z here ok, this is pressure not small p's I am going to use a capital P here ok. So, every were I have to use a capital P. So, this is nothing, but if you look at minus 1 over beta d by dP of lon Z. So this is the average volume or thermodynamic volume of your system, the system is fluctuating in its volume, but it has some average volume. So, this is the thermodynamic average volume that is computed in terms of the partition function ok.

Now you could also construct this thermodynamic average volume from thermodynamics. Sorry, I already know from thermodynamic that there is a energy scale which goes by the name of Gibbs free energy. Now that is specified as enthalpy thermodynamic enthalpy minus the temperature in entry temperature entropy energy. So, I can write this as a E plus PV minus TS these are all thermodynamic quantities by the way.

So, they are already averaged fine, what I am going to do is basically write down volume in terms of thermodynamic variables and compare my equation 1 where I have written thermodynamic volume connected to statistical mechanics. The comparison of these two expressions will reveal yet another bridge between statistical mechanics and thermodynamics. So I am say that suppose you were doing thermodynamics not stat-mech you could still compute the volume of your system by appropriate thermodynamic derivatives this is what I am going to do now.

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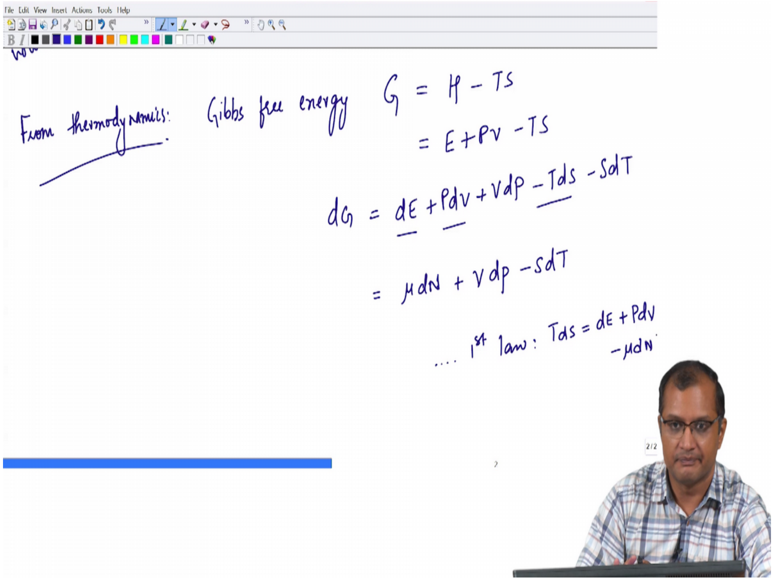

From thermodynamics: Gibbs free energy $G = H - TS$

$$= E + PV - TS$$

$$dG = \underline{dE} + \underline{Pdv} + Vdp \underline{-Tds} - SdT$$

$$= \mu dN + Vdp - sdT$$

.... 1st law: $Tds = dE + Pdv - \mu dN$

So, I am going to write down the differential form for this law as a dE plus Pdv plus Vdp minus Tds minus Sdt. And here, you can substitute from first law I can write down dE plus Tds dE plus Pdv minus Tds as simply mu dN and remaining quantities I am going to write down as Vdp minus Sdt. Because, from first law of thermodynamics, I already know that the total heat given to the system is just a book keeping a law of conservation of energy appears as summarise in internal energy plus some pressure volume work minus mu dN some chemical work; if you allow N to exchange ok. So, if I substitute the value of dE plus Pdv minus Tds it is simply mu dN which is what I have done ok.

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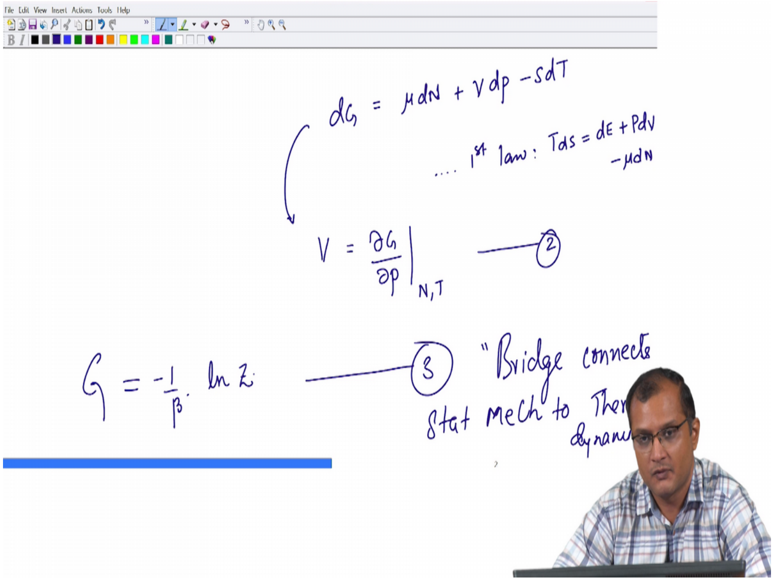

$dG = \mu dN + Vdp - SdT$

$\ldots$ 1st law : $TdS = dE + PdV - \mu dN$

$V = \left.\frac{\partial G}{\partial p}\right|_{N,T}$ ——— ②

$G = -\frac{1}{\beta} \ln Z$ ——— ③

"Bridge connects Stat mech to Ther dynam

So, now you can look at this differential form of the thermodynamic law and write down what is the value of volume. So, this gives me for volume as dG over dP at constant N and T and this is exactly my system. So, my T and N are constant and I want to see how my Gibbs free energy changes with pressure. So, if I compare this equation 2 with the equation 1 just look at the left hand side they are both volumes thermodynamic volumes right hand side is dG over dP and right hand side is the dG over dP of 1 upon beta lon Z.

So, I can compute I can equate my Gibbs free energy with 1 upon beta lon Z. So, this is the bridge that connects stat mech to thermodynamics. So, the quantity on the right hand side has information of all the degrees of freedom in a microstate information which is embedded in Z. Let us see your partition function you summed overall probabilities to make it normal it has information of your microstates your Hamiltonian all the microscopic world information is inside Z. The left hand side quantity is nothing to do it is just the thermodynamic quantities g that you measure in any process in for a system in which has very very large degrees of freedom in the thermodynamic limit.

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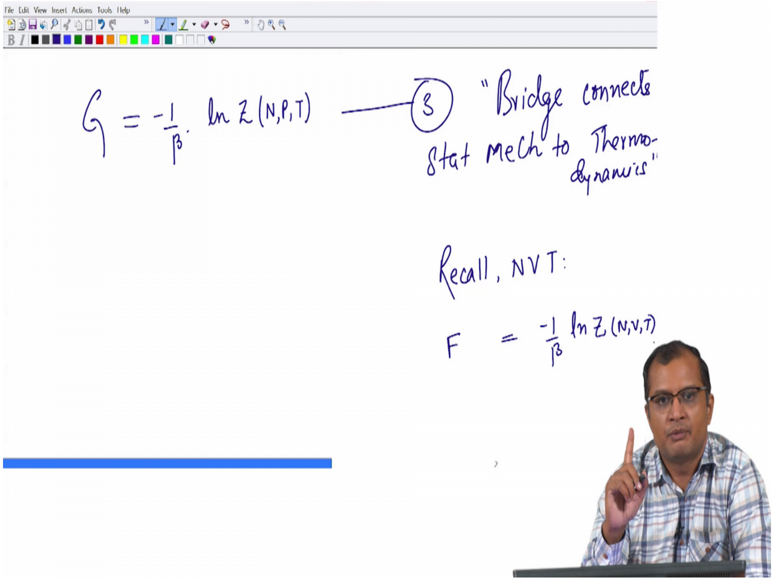

$G = -\frac{1}{\beta} \ln Z(N,P,T)$ — ③ "Bridge connects Stat Mech to Thermodynamics"

Recall, NVT:

$F = -\frac{1}{\beta} \ln Z(N,V,T)$

So, this is a beautiful connection similar to the connection that we had in the canonical ensemble recall that for the canonical ensemble you had this 1 over beta lon Z connected to the free energy. So now, what you have here is Gibbs free energy not the Hammond's free energy simply because, you now have pressure volume work instead of the total energy instead of the Hamiltonian. So, I am going to write down just to remind the audience that this is the how to differentiate, because the right hand side is similar know both of them 1 upon beta lon Z.

So, this is the partition function for the macrostate NPT where as this is a partition function for the macrostate NVT please note the distinction here these are different partition functions. Now, we have already computed one average which is volume average we can compute another average which is the average of the enthalpy.

Remember our total energy is no longer just the Hamiltonian it is the Hamiltonian plus PV. So, like I said there are two fluctuating variables I have already computed the average of V I am now interested in computing the average of H plus PV, because that is what is the new energy scale in the problem ok.

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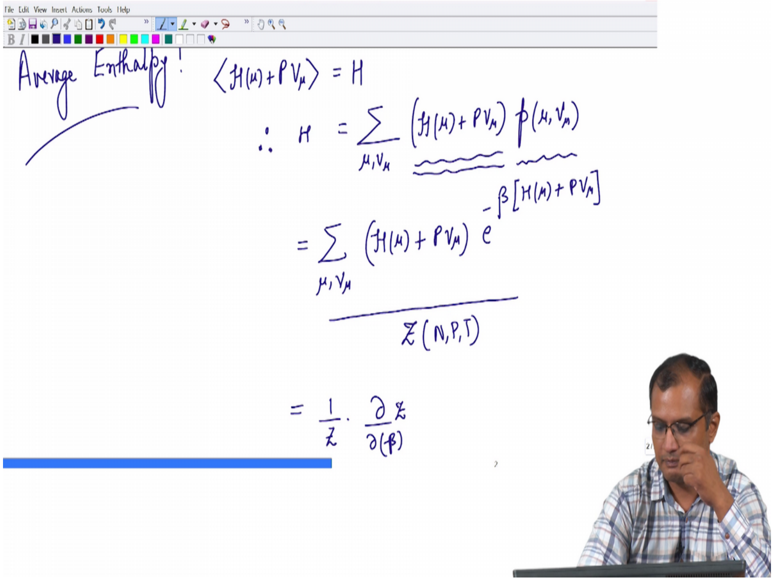

Average Enthalpy!

$$\langle \mathcal{H}(\mu) + PV_\mu \rangle = H$$

$$\therefore\ H = \sum_{\mu, V_\mu} \underbrace{\left(\mathcal{H}(\mu) + PV_\mu\right)}\ \underbrace{p(\mu, V_\mu)}$$

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

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

So, so, average enthalpy because enthalpy is your with new energy scale is given as you know you have to take the average of the energy scale and this will be your average enthalpy I am calling it is H. So, this is nothing but. So, I can write down my H as summation over mu.

And the volume this is my joint jointly mu and V we will represent a microstate and summing overall microstates. And basically in weighing this variable thermodynamic variable I will take the weight of this variable in this distribution. Remember, our distribution is now jointly specified by the microstate and the volume so this is my distribution and in this distribution I am going to sample my variable which is the enthalpy. And at the end of the sampling what I will get is the average value of my variable that I have sampled in this distribution ok. So, this is going to give me nothing but summation over V mu H of the Hamiltonian plus PV mu e raise to minus beta H mu plus PV mu. Over the Gibbs canonical partition function which is I am going to call as Z of NPT. In the same similar way since I have to pull out H plus P mu I am going to take a derivative with respect to the numerator is nothing but the derivate of my partition function with respect to minus beta ok.

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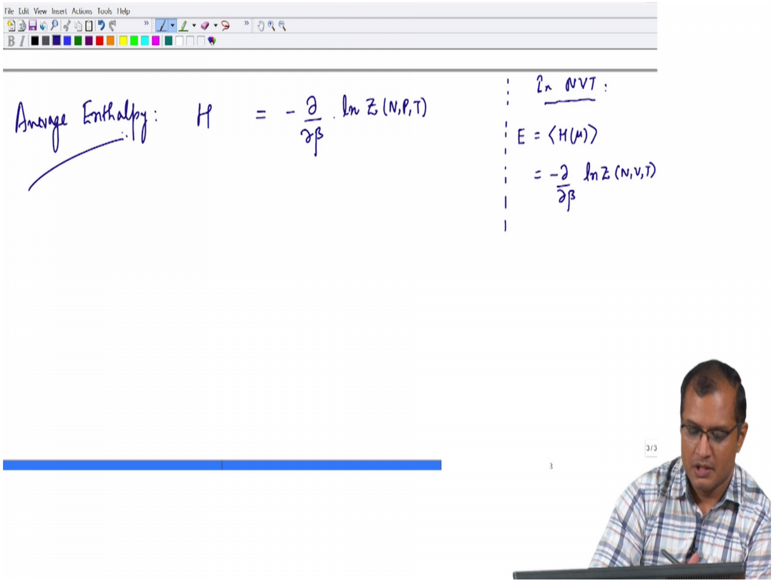

Average Enthalpy: $H = -\frac{\partial}{\partial \beta} \ln Z(N,P,T)$

In NVT:

$E = \langle H(\mu) \rangle$

$= -\frac{\partial}{\partial \beta} \ln Z(N,V,T)$

So, this is if you look at is nothing, but if I pull out a minus sign it is nothing, but going to just use new space here. So, this is nothing but minus d by d beta of lon Z and the quantity that I was basically computing was the average enthalpy this was the energy scale this is the energy scale in our NPT on symbol.

And its average value is related to is directly given as negative derivative of lon Z with respect to beta. So this Z here is nothing but the Gibbs canonical partition function. Now compare this with your canonical result there the relevant energy scale was just the total internal energy or the average of the Hamiltonian, we obtained it as the average of the Hamiltonian. And we saw that this is equal to minus d over d beta of lon Z look at the beautiful symmetry here this is the same relationship, but this Z was the canonical partition function where as the Z that is here in the current problem is a Gibbs canonical partition function.

So here there are beautiful symmetries here relevant energy being Hamiltonian, relevant energy being the enthalpy and its relation to the its relationship with the partition function is symmetric its exactly the same ok. So, we are not learning newer things we are just encountering the same thing, but we need to keep track of the relevant energy scales in the problem. Now, once I have determine the average enthalpy have been I will be interested in enthalpy fluctuations.

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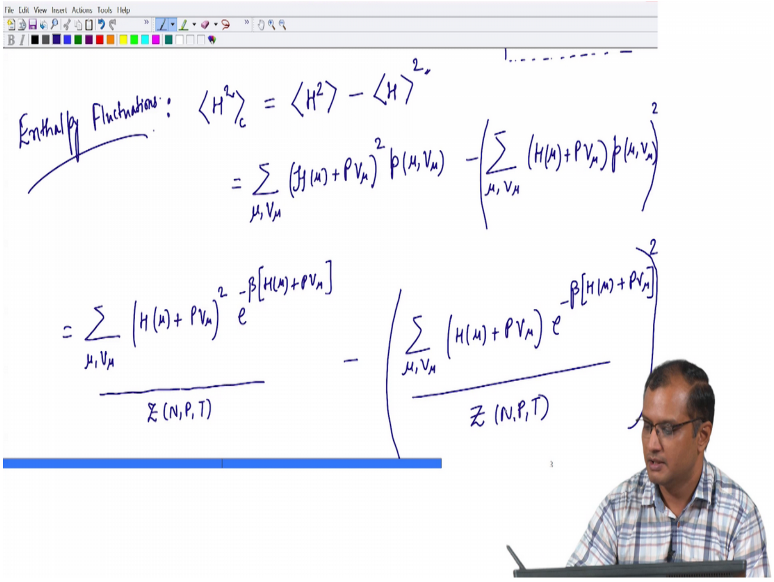

Enthalpy Fluctuations: $\langle H^2 \rangle_c = \langle H^2 \rangle - \langle H \rangle^2$

$$= \sum_{\mu, V_\mu} (H(\mu) + PV_\mu)^2 \, p(\mu, V_\mu) - \left(\sum_{\mu, V_\mu} (H(\mu) + PV_\mu) \, p(\mu, V_\mu) \right)^2$$

$$= \frac{\sum_{\mu, V_\mu} (H(\mu) + PV_\mu)^2 \, e^{-\beta[H(\mu) + PV_\mu]}}{Z(N, P, T)} - \left(\frac{\sum_{\mu, V_\mu} (H(\mu) + PV_\mu) \, e^{-\beta[H(\mu) + PV_\mu]}}{Z(N, P, T)} \right)^2$$

You can see where this is going, I computer energy fluctuations in the canonical ensemble, and show that the energy fluctuations in NVT or canonical ensemble are related to heat capacity at constant volume. I am going to show similar to energy fluctuations in canonical ensemble there is enthalpy fluctuation in our Gibbs canonical ensemble, and it is also related to a material property which is heat capacity at constant pressure ok.

So, after average enthalpy I am going to talk about enthalpy fluctuations because ensemble enthalpy fluctuates how does it fluctuate? Well of course, I am going to write it as second cumulant of the enthalpy ok, which is the measure of the variants in enthalpy or the fluctuations in enthalpy, size of the fluctuations.

Well, this is given as the second movement minus square of the first movement and let us write it down its a very simple calculation just little bit tedious. So, please do not you know be discouraged with the expressions that are going to get longer the calculations extremely simple and very straight forward. So, the average here means I am sampling H square in some distribution.

So, this is nothing, but sampling in our microstates distribution H which is the instantaneous enthalpy is nothing but its mu plus PV mu. But we have to take it square in the distribution p mu V mu that is the first term minus the second term is nothing but the sampling of H which is enthalpy which is nothing but H mu plus PV. So, this will give me just mode of the enthalpy, but I am going to take a square of this because the second term is the square of the average the quantity inside the bracket is the average enthalpy the outside square is this square.

So, next that is inside P ok. Now, we know that our probability distribution function is nothing but I am going to write it since I need I am going to require more space let me shift equality on the extreme right side left side. So, the first term is nothing, but summation mu V mu. And I can write this as H mu plus PV mu whole square e raise to minus beta H mu plus PV mu divided by the Gibbs canonical partition function minus; I am going to write down summation overall the microstates the quantity inside the bracket is the average of the enthalpy and there is a square outside this bracket.

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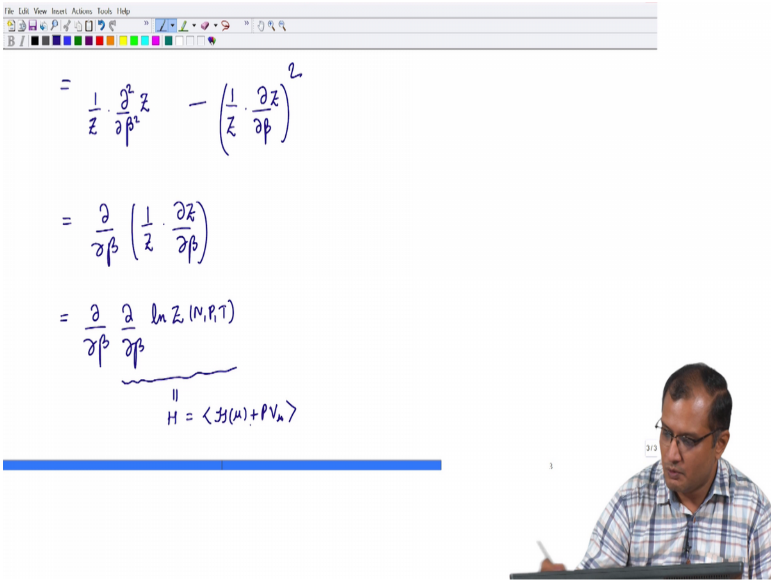

$$= \frac{1}{Z}\cdot\frac{\partial^2 Z}{\partial\beta^2} - \left(\frac{1}{Z}\cdot\frac{\partial Z}{\partial\beta}\right)^2$$

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

$$= \frac{\partial}{\partial\beta}\underbrace{\frac{\partial}{\partial\beta}\ln Z(N,P,T)}_{\overset{\shortparallel}{H = \langle \mathcal{H}(\mu)+PV_\mu \rangle}}$$

So, what you can do here now is simply you can write down the first term as nothing but 1 upon Z which is I am going to take the denominator outside. And the numerator if you carefully see is nothing but the instantaneous enthalpy pulled out twice from the partition function. So, to pull it out once you have to take a derivative with respect to minus beta to pull it out twice you have to take two derivatives which is nothing but d by d d square by d beta square of the partition function.

So, one derivative with respect I will pull out minus enthalpy one more derivative will pull out another minus enthalpy minus minus becomes plus and that is your second derivative and here the second term would be you have just pulled out one term. So, it is going to be 1 upon Z into the d by d beta of the partition function and you square it ok. So, if you take one derivative with respect to beta it will pull out a minus H, but look there is a square outside.

So, it makes it if you could take out a minus sin and square it become positive the other minus sign is because of the fact that the entire second term is taken negative, right. What I mean to say is that I could have taken derivative with respect to minus beta to pull out an H, but this minus sign taken outside of the square poses no issue. So, I am going to just write it as just d by d beta if that is your concern it poses no issue. So, then I can see that this is nothing but d by d beta of 1 upon Z dZ by d beta. So, if I apply the chain rule to get the first term minus the second term because, 1 upon z derivative is minus 1 by Z square and this is nothing but if you look at the quantity in the parenthesis is nothing, but d by d beta of lon Z.

But this should ring a bell in your minds that this quantity is already been calculated what is this quantity? This quantity is nothing but average enthalpy. So, this quantity was the computed as the average enthalpy H the average of.

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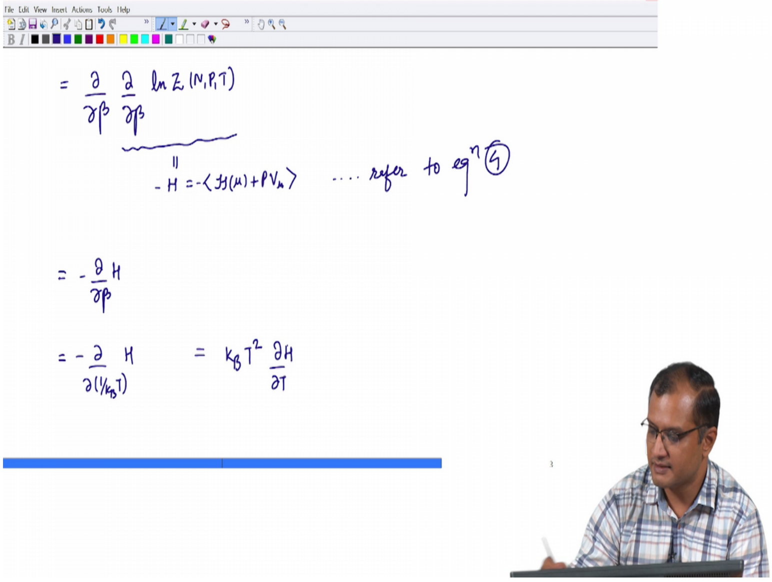

$$= \frac{\partial}{\partial\beta}\underbrace{\frac{\partial}{\partial\beta}\ln Z(N,P,T)}_{\overset{\parallel}{-H = -\langle \mathcal{H}(\mu) + PV_\mu \rangle}} \quad \text{.... refer to eq}^{n}\ \textcircled{4}$$

$$= -\frac{\partial}{\partial\beta}H$$

$$= -\frac{\partial}{\partial(1/k_B T)}H \qquad = k_B T^2 \frac{\partial H}{\partial T}$$

So, what you are getting here is nothing, but d over d beta of the average enthalpy H. So, if you refer let me put the equation number have I named it no I have not given any equation number. So, let me given equation number we are given 1 2 3; so, let us call this as equation number 4. So, this is like refer to equation 4.

Beautiful result because what you see in front of you is that is there a minus sign missing correct. So, this is basically minus of H so, I will pull out minus H here. So, I am going to write down this to be used to correct it myself that this is related to. So, I am going to write it as minus of H or minus of both sides I need to put a minus sign ok.

So, then you can think of it this way that d over d beta is nothing, but minus d over d of 1 by KBT of enthalpy which is nothing, but if I pull out KB in the numerator it simply becomes KBT square d by dT of your enthalpy. And this enthalpy is temperature derivative is called as the heat capacity at constant pressure ok.

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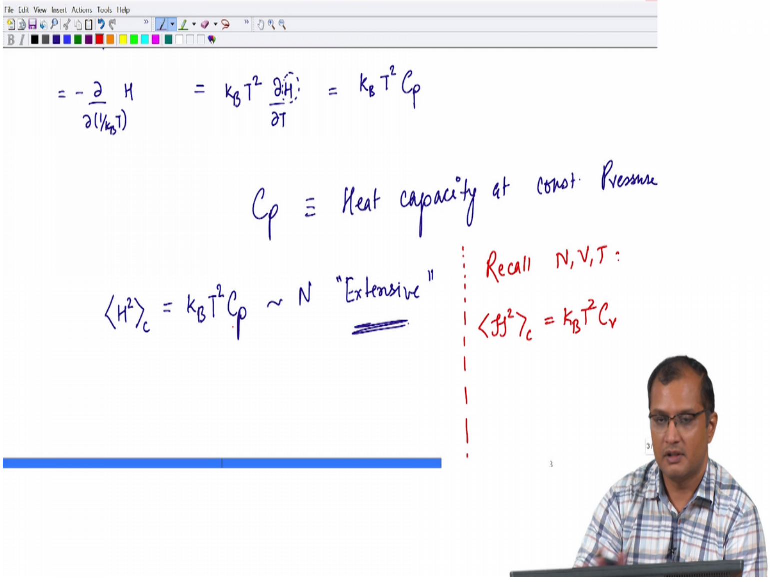

$$= -\frac{\partial}{\partial(1/k_BT)} H = k_B T^2 \frac{\partial H}{\partial T} = k_B T^2 C_p$$

$C_p \equiv$ Heat capacity at const. Pressure

$\langle H^2 \rangle_c = k_B T^2 C_p \sim N$ "Extensive"

Recall N, V, T :

$\langle \mathcal{H}^2 \rangle_c = k_B T^2 C_v$

So, CP here is the heat capacity at constant pressure and let me just write down what is CP? CP is the heat capacity at constant pressure. So, the temperature derivative of the energy scale is the heat capacity that we already know, but what we ended up proving is that the quantity that we are computing from the beginning the left hand side is nothing but enthalpy fluctuations. So, these are all enthalpy fluctuations. So, in the end I must write down that the enthalpy fluctuations similar to energy fluctuations in canonical ensemble are related to the heat capacity at constant pressure.

So, this is also a quantity that scales with system size of this is also extensive remember these are heat capacity not specific heat. So, they are extensive in nature, you can think of this variable here H which is enthalpy with that itself is extensive, all the quantities in this are intensive ok. So, this is the relationship that is very important and just to recall you are not saying something that is new. If we call from your NVT there we had seen that the energy fluctuations are related to energy fluctuations they are referred to as the have the fluctuations in the Hamiltonian.

So, there the energy fluctuations in the Hamiltonian was shown to be related to heat capacity at constant volume here we are showing that the heat capacity at constant pressure is related to enthalpy fluctuations. So, there is this beautiful correspondence between these two ensembles and that in itself is a beautiful observation that if to know about the material properties which is heat capacity you can find it out by the fluctuations in the system. So, fluctuations reveal a lot more about the properties of the system than we actually think you know. So, here the fluctuations are telling us how the heat capacities are; you know what are the heat capacities in the system I should say it that way.

So, we end the lecture here, and we meet in the next class will talk about some examples we take one discrete example. In fact, we will take two discrete examples one is the case of an ideal gas, when is the case of magnetic spins in a uniform magnetic field that is going to be the case of a discrete degree of freedom example. And I am going to take another example which is a classical ideal gas which is a continuous degree of freedom example, both under Gibbs canonical ensemble. So, when meet in the next class we will carry forward and discuss these two examples.