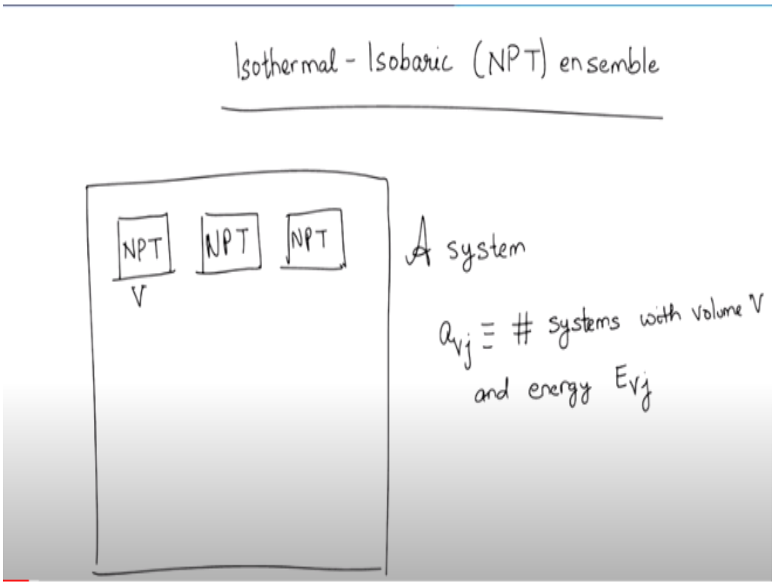
Advanced Thermodynamics and Molecular Simulations
Prof. Prateek Kumar Jha
Department of Chemical Engineering
Indian Institute of Technology-Roorkee

Lecture - 19
Isothermal Isobaric Ensemble

Hello, all of you. In the last lecture we have been discussing the grand canonical ensemble. And before that we have discussed the canonical and micro canonical ensemble. In this class we will discuss the very last ensemble that is called the isothermal isobaric ensemble for which the Gibbs energy is a thermodynamic function is one of the most commonly used ensembles for the purpose of molecular simulations and also it is more relevant to the experiments because in experiments we typically keep temperature and pressure as controlled variables.

So the process in which we will build the equations for the ensemble will be the same as we have been doing except that we will have a new definition of the partition function corresponding to the isothermal isobaric ensemble and the average properties will again be written in terms of partition functions, but for this new partition function that we determine for the isothermal isobaric ensemble.

(Refer Slide Time: 01:32)



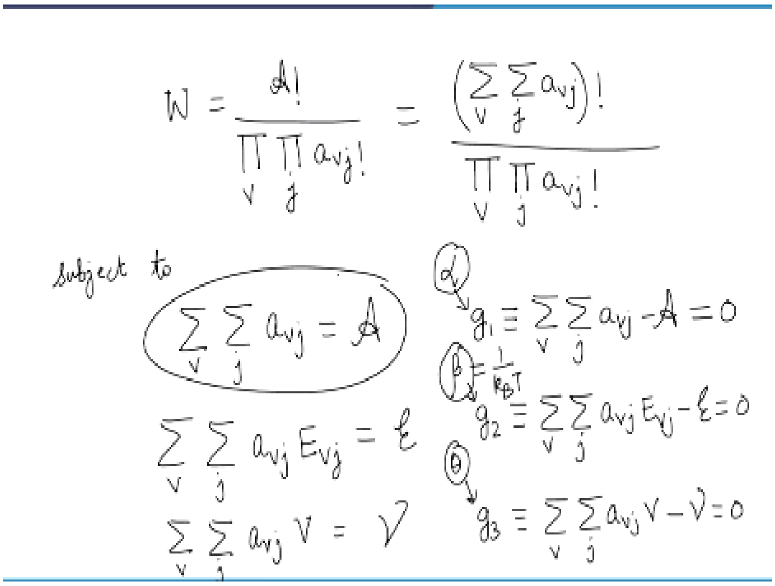
Isothermal - Isobaric (NPT) ensemble

$a_{Vj} \equiv$ # systems with volume V and energy E_{Vj}

So the basic idea for the isothermal isobaric or the NPT ensemble is the following. So pressure is a control variable that means, if I look at systems in the ensemble, the conjugate variable volume will not be constant. The volume can vary in the systems, but the pressure will be constant. So in this case unlike say the canonical ensemble when the NVT was the control variable and therefore, volume was a control variable, in this case what we will have is NPT will be the control variable we are controlling the number, the pressure and the temperature but again we will have a large number of systems in the ensemble let us call it ‘A’ systems but now they are going to have different volumes every system will have a different volume unlike the previous case.

So therefore, we can now define the occupation number as something like a_{vj} that corresponds to the number of systems with volume V the volume can vary and energy and we are offering total energy that is E_{vj}, right. So now we can determine the number of ways of distribution for this particular and ensemble by this formula.

(Refer Slide Time: 03:35)



$$W = \frac{A!}{\prod_v \prod_j a_{vj}!} = \frac{\left(\sum_v \sum_j a_{vj}\right)!}{\prod_v \prod_j a_{vj}!}$$

subject to

$$\sum_v \sum_j a_{vj} = A$$

$$\sum_v \sum_j a_{vj} E_{vj} = \mathcal{E}$$

$$\sum_v \sum_j a_{vj} V = \mathcal{V}$$

$$\alpha \rightarrow g_1 \equiv \sum_v \sum_j a_{vj} - A = 0$$

$$\beta = \frac{1}{k_B T} \rightarrow g_2 \equiv \sum_v \sum_j a_{vj} E_{vj} - \mathcal{E} = 0$$

$$\theta \rightarrow g_3 \equiv \sum_v \sum_j a_{vj} V - \mathcal{V} = 0$$

So W is going to be-

$$W = \frac{A!}{\prod_V \prod_j a_{vj}} = \frac{\left(\sum_v \sum_j a_{vj}\right)!}{\prod_v \prod_j a_{vj}!}$$

And now we will have certain constraints. The first constraint is the same as what we have been doing that is if I sum over the occupation numbers, we should get the total number of systems in the ensemble that is capital A. That is-

$$\sum_v \sum_j a_{vj} = A$$

Same applies for the energy so if I sum over the energy of all the systems in the ensemble that is going to be –

$$\sum_{v}\sum_{j} a_{vj}E_{vj} = E$$

And finally, we can also sum over the volumes in this case. So if I sum over volume of all the system that is equal to some large V.

$$\sum_{v}\sum_{j} a_{vj}V = V$$

Keep in mind that whenever we define these constraints, we assume that for the total system, if I sum over all the volumes, if I sum over all the energies that should be a constant variable that is on the assumption that there is an infinite bath and the systems together with the bath become like an isolated system, because I am considering both the system and its surrounding. Systems interact with the bath that is how we get constant temperature and pressure but systems do not interact between themselves so as to speak. So therefore, I can define three constraints. Let me call it g 1, g 2 and g 3.

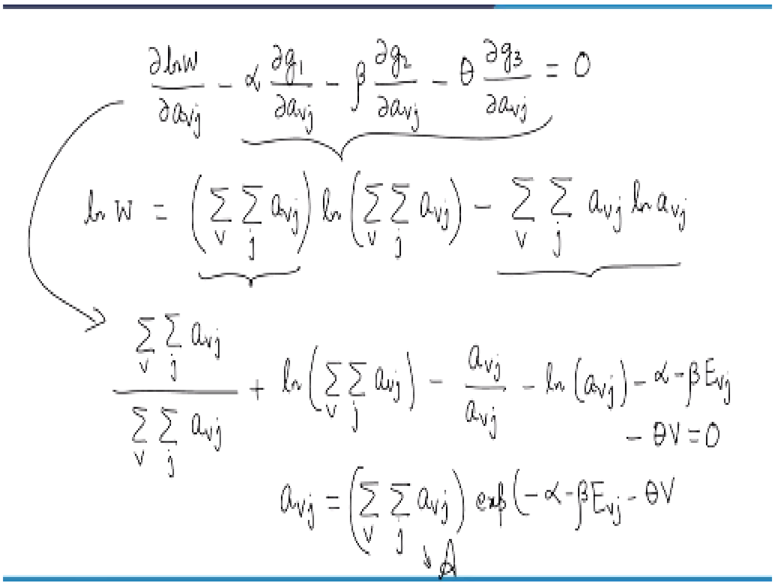
$$g_1(\alpha) \equiv \sum_{v}\sum_{j} a_{vj} - A = 0$$

$$g_2(\beta) \equiv \sum_{v}\sum_{j} a_{vj}E_{vj} - E = 0$$

$$g_3(\theta) \equiv \sum_{v}\sum_{j} a_{vj}V - V = 0$$

Now these constraints will appear as a Lagrange multiplier in the maximization problem. So let us define the multipliers as α, β and some θ. This β is equal to 1 by k_B T as earlier, because the energy constraint is going to be the same as the canonical ensemble that we have done earlier. So the β the multiplier is also going to be the same. However, this θ is a new multiplier that come here. A existed as λ1 in the previous problem, but in any case, this will come from the first constraint later in the derivation. So anyway, the α will not appear in the final formula, but β and θ will appear.

(Refer Slide Time: 07:25)



$$\frac{\partial \ln W}{\partial a_{vj}} \underbrace{- \alpha \frac{\partial g_1}{\partial a_{vj}} - \beta \frac{\partial g_2}{\partial a_{vj}} - \theta \frac{\partial g_3}{\partial a_{vj}}} = 0$$

$$\ln W = \underbrace{\left(\sum_v \sum_j a_{vj}\right)} \ln\left(\sum_v \sum_j a_{vj}\right) - \underbrace{\sum_v \sum_j a_{vj} \ln a_{vj}}$$

$$\frac{\sum_v \sum_j a_{vj}}{\sum_v \sum_j a_{vj}} + \ln\left(\sum_v \sum_j a_{vj}\right) - \frac{a_{vj}}{a_{vj}} - \ln(a_{vj}) - \alpha - \beta E_{vj} - \theta V = 0$$

$$a_{vj} = \underset{\downarrow A}{\left(\sum_v \sum_j a_{vj}\right)} \exp(-\alpha - \beta E_{vj} - \theta V$$

So therefore, the maximization problem is-

$$\frac{\partial \ln W}{\partial a_{vj}} - \alpha \frac{\partial g_1}{\partial a_{vj}} - \beta \frac{\partial g_2}{\partial a_{vj}} - \theta \frac{\partial g_3}{\partial a_{vj}} = 0$$

And this has to be set equal to zero for the most probable distribution.

So now the ln W can be written as using a Stirling formula as-

$$\ln W = \left(\sum_v \sum_j a_{vj}\right) \ln\left(\sum_v \sum_j a_{vj}\right) - \sum_v \sum_j a_{vj} \ln a_{vj}$$

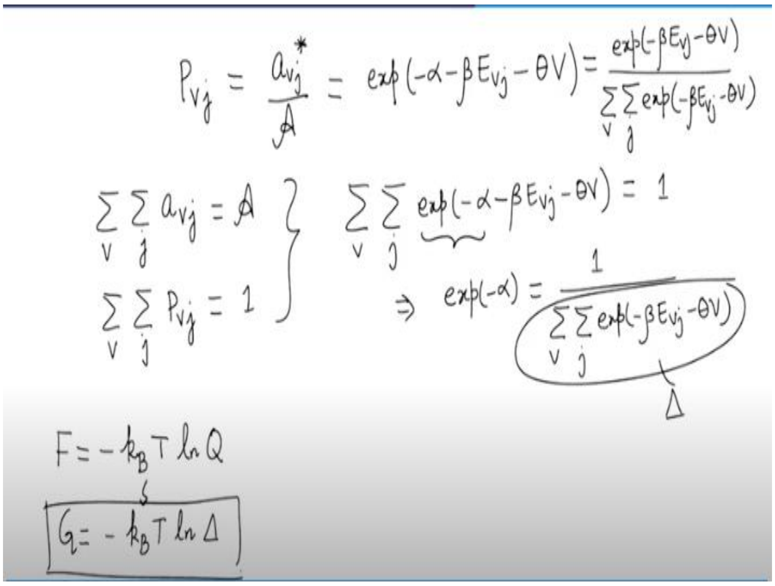
So therefore, if I use the maximization formula, what do I get here is-

$$\frac{\sum_v \sum_j a_{vj}}{\sum_v \sum_j a_{vj}} + \ln\left(\sum_v \sum_j a_{vj}\right) - \frac{a_{vj}}{a_{vj}} - \ln(a_{vj}) - \alpha - \beta E_{vj} - \theta V = 0$$

So if I solve this what I have is-

$$a_{vj} = \left(\sum_v \sum_j a_{vj}\right) \exp(-\alpha - \beta E_{vj} - \theta V)$$

(Refer Slide Time: 10:55)



$$P_{vj} = \frac{a^*_{vj}}{A} = \exp(-\alpha-\beta E_{vj}-\theta V) = \frac{\exp(-\beta E_{vj}-\theta V)}{\sum_v\sum_j \exp(-\beta E_{vj}-\theta V)}$$

$$\left.\begin{aligned}\sum_v\sum_j a_{vj} &= A\\ \sum_v\sum_j P_{vj} &= 1\end{aligned}\right\} \quad \sum_v\sum_j \underbrace{\exp(-\alpha-\beta E_{vj}-\theta V)}_{} = 1$$

$$\Rightarrow \exp(-\alpha) = \frac{1}{\underbrace{\sum_v\sum_j \exp(-\beta E_{vj}-\theta V)}_{\Delta}}$$

$$F = -k_B T \ln Q$$

$$\boxed{G = -k_B T \ln \Delta}$$

So therefore, I can define the probability of having the volume V and energy level E_{vj} as-

$$P_{vj} = \frac{a^*_{vj}}{A} = \exp(-\alpha - \beta E_{vj} - \theta V)$$

So therefore, we have got the expression for the portability. So first thing we do is to find this Lagrange multiplier. So the first one α will come from the normalization that is-

$$\sum_v \sum_j a_{vj} = A$$

$$\sum_v \sum_j P_{vj} = 1$$

And therefore,

$$\sum_v \sum_j \exp\left(-\alpha - \beta E_{vj} - \theta V\right) = 1$$

$$\exp(-\alpha) = \frac{1}{\sum_v \sum_j \exp\left(-\beta E_{vj} - \theta V\right)}$$

So if I put this thing right above the first equation what we get is-

$$P_{vj} = \frac{a^*_{vj}}{A} = \exp\left(-\alpha - \beta E_{vj} - \theta V\right) = \frac{\exp(-\beta E_{vj} - \theta V)}{\sum_v \sum_j \exp\left(-\beta E_{vj} - \theta V\right)}$$

So now as we have been doing, the denominator becomes the partition function. So in this case, this quantity is the partition function for the isothermal isobaric ensemble. And let me call this some Δ that is the partition function for this ensemble. So just like what we had for the canonical ensemble that my Helmholtz free energy was minus kB T ln of the partition function for the canonical ensemble.

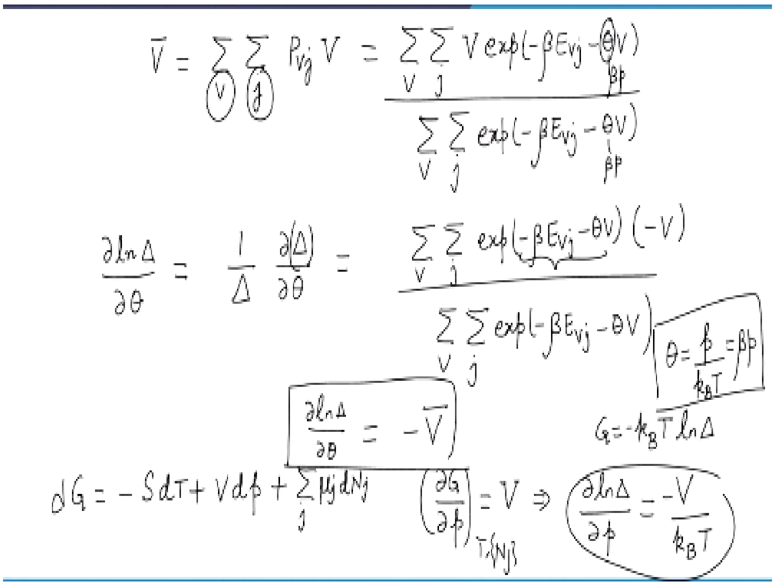
$$F = -k_B T \ln Q$$

If I am doing it for the grand canonical ensemble, we already know that the corresponding thermodynamic function is the Gibbs free energy. And that should be equal to minus k_B T ln of the Δ that is the partition function for the isothermal, isobaric ensemble.

$$G = -k_B T \ln \Delta$$

Now we can go ahead and try to find the average properties in this particular case. So let us say for example, I am interested in the average volume.

(Refer Slide Time: 14:11)



$$\bar{V} = \sum_{\textcircled{v}} \sum_{\textcircled{j}} P_{vj} V = \frac{\sum_v \sum_j V \exp(-\beta E_{vj} - \underset{\beta p}{\textcircled{\theta}} V)}{\sum_v \sum_j \exp(-\beta E_{vj} - \underset{\beta p}{\theta} V)}$$

$$\frac{\partial \ln \Delta}{\partial \theta} = \frac{1}{\Delta} \frac{\partial(\Delta)}{\partial \theta} = \frac{\sum_v \sum_j \exp(\underbrace{-\beta E_{vj}}-\theta V)(-V)}{\sum_v \sum_j \exp(-\beta E_{vj} - \theta V)}$$

$$\boxed{\theta = \frac{p}{k_B T} = \beta p}$$

$$\boxed{\frac{\partial \ln \Delta}{\partial \theta} = -\bar{V}}$$

$$G = -k_B T \ln \Delta$$

$$dG = -S dT + V dp + \sum_j \mu_j dN_j \qquad \left(\frac{\partial G}{\partial p}\right)_{T,\{N_j\}} = V \Rightarrow \frac{\partial \ln \Delta}{\partial p} = \frac{-V}{k_B T}$$

So the average volume will be-

$$\bar{V} = \sum_v \sum_j P_{vj} V$$

that is multiplying the probability to realize the volume with the probability. So keep in mind that I am summing over all the energy levels and all the volumes that is the mean value or average value of energy we obtain that is equal to-

$$\bar{V} = \sum_{v}\sum_{j} P_{vj}V = \frac{\sum_v \sum_j V \exp\left(-\beta E_{vj} - \theta V\right)}{\sum_v \sum_j \exp\left(-\beta E_{vj} - \theta V\right)}$$

Now this would come from the derivative of the ln of the partition function that is what we have seen in the earlier case as well. So in this case, if I do-

$$\frac{\partial \ln \Delta}{\partial \theta} = \frac{1}{\Delta}\frac{\partial \Delta}{\partial \theta} = \frac{\sum_v \sum_j \exp(-\beta E_{vj} - \theta V)(-V)}{\sum_v \sum_j \exp(-\beta E_{vj} - \theta V)} = -\bar{V}$$

So now if I compare that with the differential form of dG the Gibbs free energy what we see is that-

$$dG = -SdT + Vdp + \sum_{j} \mu_j dN_j$$

It does not matter if you are doing for a multicomponent system, because the derivative does not apply to the last term in this case. So what we have is-

$$\left(\frac{\partial g}{\partial p}\right)_{T,\{N_j\}} = V$$

As we have already established-

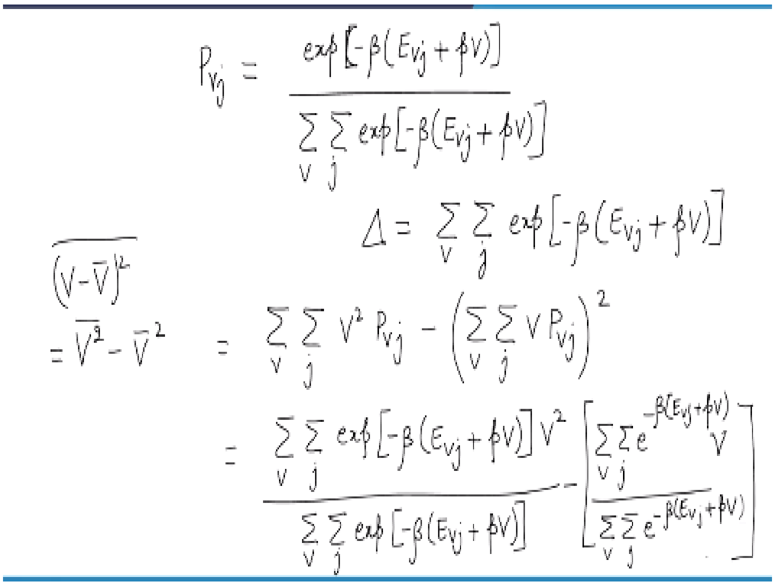
$$G = -k_B T ln\, \Delta$$

Therefore,

$$\frac{\partial \ln \Delta}{\partial p} = \frac{-V}{k_B T}$$

Why is that? Because I am putting G is equal to minus k_B T ln Δthere. So minus, so there will be a minus sign right here.

(Refer Slide Time: 18:34)



$$P_{vj} = \frac{\exp[-\beta(E_{vj} + pV)]}{\sum_v \sum_j \exp[-\beta(E_{vj} + pV)]}$$

$$\Delta = \sum_v \sum_j \exp[-\beta(E_{vj} + pV)]$$

$$\overline{(V-\bar{V})^2} = \overline{V^2} - \bar{V}^2 = \sum_v \sum_j V^2 P_{vj} - \left(\sum_v \sum_j V P_{vj}\right)^2$$

$$= \frac{\sum_v \sum_j \exp[-\beta(E_{vj} + pV)] V^2}{\sum_v \sum_j \exp[-\beta(E_{vj} + pV)]} - \left[\frac{\sum_v \sum_j e^{-\beta(E_{vj}+pV)} V}{\sum_v \sum_j e^{-\beta(E_{vj}+pV)}}\right]$$

So therefore, what we have is my P_{vj} can be set equal to-

$$P_{vj} = \frac{\exp\left[-\beta\left(E_{vj} + pV\right)\right]}{\sum_v \sum_j \exp\left[-\beta\left(E_{vj} + pV\right)\right]}$$

Or in other words, the partition function for the isothermal isobaric ensemble is-

$$\Delta = \sum_v \sum_j \exp\left[-\beta\left(E_{vj} + pV\right)\right]$$

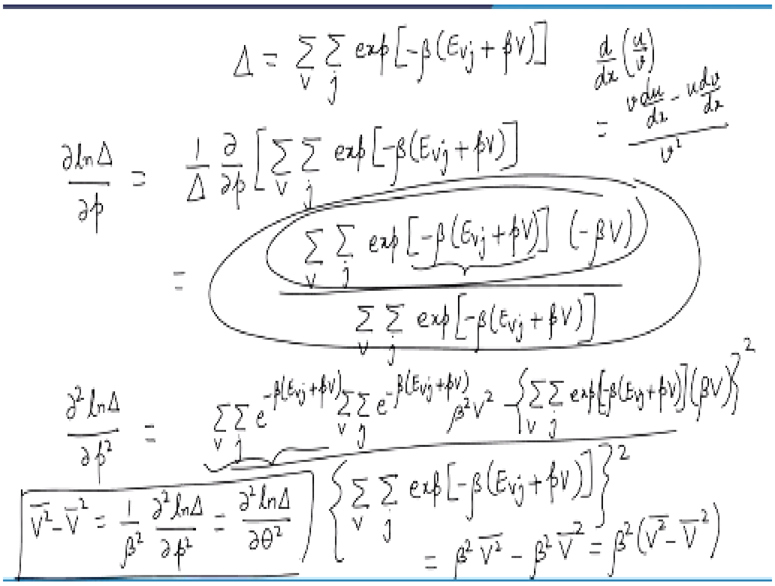
Now let us say if I am interested in the fluctuation in the volume in this case. So now since volume is a variable we will have an average value and we will have a fluctuation. That we can define again as-

$$\overline{(V - V)^2} = \overline{V^2} - \bar{V}^2 = \sum_v \sum_j V^2 P_{vj} - \left(\sum_v \sum_j V P_{Vj}\right)^2$$

$$= \frac{\sum_v \sum_j \exp\left[-\beta\left(E_{vj} + pV\right)\right]^2}{\sum_v \sum_j \exp\left[-\beta\left(E_{vj} + pV\right)\right]} - \left[\frac{\sum_v \sum_j e^{-\beta[E_{vj}+pV]} V}{\sum_v \sum_j e^{-\beta[E_{vj}+pV]}}\right]$$

So you will find a lot of similarity in the math. So if I look at the grand canonical ensemble, we were looking at the fluctuation in the number of molecules. The kind of formula that we had was similar to this except that we had N in place of V. But the basic schematic the basic way in which we are doing the math is very similar to what we have been what we have been doing. So this should be equal to the second derivative of the ln Δ that is the partition function in this case. So let us see if it is indeed true.

(Refer Slide Time: 21:49)



$$\Delta = \sum_V \sum_j \exp[-\beta(E_{Vj}+pV)]$$

$$\frac{d}{dx}\left(\frac{u}{v}\right) = \frac{v\frac{du}{dx} - u\frac{dv}{dx}}{v^2}$$

$$\frac{\partial \ln \Delta}{\partial p} = \frac{1}{\Delta}\frac{\partial}{\partial p}\left[\sum_V \sum_j \exp[-\beta(E_{Vj}+pV)]\right]$$

$$= \frac{\sum_V \sum_j \exp[-\beta(E_{Vj}+pV)]\,(-\beta V)}{\sum_V \sum_j \exp[-\beta(E_{Vj}+pV)]}$$

$$\frac{\partial^2 \ln \Delta}{\partial p^2} = \frac{\sum_V \sum_j e^{-\beta(E_{Vj}+pV)} \sum_V \sum_j e^{-\beta(E_{Vj}+pV)}\beta^2 V^2 - \left\{\sum_V \sum_j \exp[-\beta(E_{Vj}+pV)](\beta V)\right\}^2}{\left\{\sum_V \sum_j \exp[-\beta(E_{Vj}+pV)]\right\}^2}$$

$$= \beta^2\overline{V^2} - \beta^2\overline{V}^2 = \beta^2\left(\overline{V^2}-\overline{V}^2\right)$$

$$\boxed{\overline{V^2}-\overline{V}^2 = \frac{1}{\beta^2}\frac{\partial^2 \ln\Delta}{\partial p^2} = \frac{\partial^2 \ln\Delta}{\partial \theta^2}}$$

So let us say if I start with Δ-

$$\Delta = \sum_v \sum_j \exp[-\beta(E_{vj} + pV)]$$

Then,

$$\frac{\partial \ln \Delta}{\partial p} = \frac{1}{\Delta}\frac{\partial}{\partial p}\left[\sum_v \sum_j \exp[-\beta(E_{vj} + pV)]\right]$$

$$= \frac{\sum_v \sum_j \exp[-\beta(E_{vj} + pV)]\,(-\beta V)}{\sum_v \sum_j \exp[-\beta(E_{vj} + \beta V)]}$$

And therefore, we pretty much get the result as earlier. Keep in mind that earlier we were doing with respect to theta but θ is equal to β multiplied with the pressure.

Now let us say if I do the second derivative. So I have to differentiate whatever result we have obtained with respect to the pressure again. So you will have the denominator multiplied with the derivative of the numerator minus the numerator multiplied with the derivative of the denominator divided by denominator whole square. Essentially I am using the formula for division which is equal to-

$$\frac{d}{dx}\left(\frac{u}{v}\right) = \frac{v\frac{du}{dx} - u\frac{du}{dx}}{v^2}$$

Let us see what it gives me-

$$\frac{\partial^2 \ln \Delta}{\partial^2 p} = \frac{\sum_v \sum_j e^{-\beta(E_{vj}+pV)}\beta^2 V^2 - \left\{\sum_v \sum_j \exp\left[-\beta\left(E_{vj}+pV\right)\right](\beta V)\right\}^2}{\left\{\sum_v \sum_j \exp\left[-\beta\left(E_{vj}+pV\right)\right]\right\}^2}$$

After cancellations we get-

$$\frac{\partial^2 \ln \Delta}{\partial^2 p} = \beta^2 V^2 - \beta^2 \bar{V}^2 = \beta^2\left(\overline{V^2} - \bar{V}^2\right)$$

And therefore, I can write my fluctuation as-

$$\left(\overline{V^2} - \bar{V}^2\right) = \frac{1}{\beta^2}\frac{\partial^2 \ln \Delta}{\partial p^2} = \frac{\partial^2 \ln \Delta}{\partial \theta^2}$$

So using that what we have been able to establish is that, we have a general protocol once we know the partition function. And there is a way the partition function is being defined. The partition function is always defined by summing over the Boltzmann factors, but then there is some correction to the Boltzmann factor depending on the ensemble under consideration and in fact, all the partition function to that extent is also related because I could as well have written this Δ for example-

$$\Delta = \sum_v \sum_j \exp\left[-\beta\left(E_{vj}+pV\right)\right]$$

$$\sum_v \left[\sum_j \exp\left(-\beta E_{vj}\right)\right] \exp(-\beta pV)$$

(Refer Slide Time: 27:28)

$$\boxed{\Delta = \sum_{V} \sum_{j} \exp\left[-\beta\left(E_{Vj} + pV\right)\right]}$$

$$= \sum_{V} \underbrace{\left[\sum_{j} \exp\left(-\beta E_{Vj}\right)\right]}_{Q} \exp\left(-\beta pV\right)$$

deSo first of all the partition function are the normalizing functions and generating functions they can be used to generate not only the average value, but also the fluctuations of the quantity. Now the key thing to remember is that our ability to find the fluctuations will depend on the ensemble under consideration. So let us say for example, if I talk about volume fluctuations, it means that volume is not a control variable that is only possible when we are doing the isothermal isobaric ensemble out of all the ensembles that we have considered. In all the cases we have considered the volume was a control variable. So the volume fluctuation is only defined in this particular ensemble. So this idea of computing this will only make sense when I am looking at the isothermal isobaric ensemble in the all the ensembles that we have done so far.

Similarly, if I talk about fluctuations in the number of particles, that will make sense only in the grand canonical ensemble and therefore, in that case we should use the grand canonical partition function. So ultimately, the basic scheme or the way to think about any thermodynamic problem is first to identify what is the appropriate ensemble for this problem.

Let us say for example, I am interested in the behavior where I am performing experiments at a constant temperature and a constant pressure what this means is that we have an ability to control temperature and pressure that is the confusion people always have that when I say constant temperature and pressure, it does not mean that temperature and pressure are being held fixed for that experiment forever. It only means that I can do it at different temperatures. I can do it at 20, I can do at 30 we have a mechanism to control temperature and to run experiment at a constant temperature.

Similarly, the same applies for the pressure thing. So if I am saying that I am doing at a constant pressure it means that we can do at any pressure value in any experiment we have ability to control the pressure variable. So if for example, we are doing at constant temperature and pressure or controlled temperature and pressure, then in that case, I will seek to find the isothermal isobaric ensemble partition function that is the Δ in this case.

If for example, we are not doing experiments at constant temperature and pressure, let us say we are doing at constant temperature and constant volume in that case, we will go for the canonical ensemble partition function. And in that case, the Helmholtz free energy would make sense unlike the Gibbs free energy in the previous case when I was doing constant temperature and pressure. Similarly, if for example, I am working with constant number, constant volume and constant energy, in that case entropy becomes a thermodynamic function and we are talking about the micro canonical ensemble partition function.

So therefore, the key idea that I want to reemphasize is that for any thermodynamic problem, the first objective is to find what are the control variables in this problem. And once we have done that, the next part is to find what is the partition function. We have not so far discussed how to get the partition function, because even if I have said the delta is this, I do not know what these E_{vj} values are. These energy values will depend on the discrete energy states. So in principle, it comes from quantum mechanics. We have not said how it comes there. We have not even said how will I find the pressure and volume all of this can be found, once I know the partition function, but we do not know the partition function itself we know what properties it should satisfy.

If I know partisan function, I can generate the average properties. I can generate the fluctuations. But all I have is an expression of the partition function in terms of the energies that is still unknown to me and therefore, we need to find a way to find that particular partition function.

So in the next lecture, I will say how that partition function is derived from the what is known as the molecular partition function. We take an ideal gas example and so how can we derive the partition function for this case. But going further, I will also discuss what is known as a lattice model that is a simplified way of estimating the partition function.

It turns out that for all complex scenarios, the partition function is highly non trivial because you can just imagine, if I have millions of molecules or billions of molecules, in reality we are talking about systems having moles of molecule that is 10^{23} or higher molecules. So in that case, we can imagine there will be like a large number of possible states. So whenever I put this simple looking sum over all the volume and all the j, that sum will contain a very large number of terms that corresponds to the number of possible confirmations. So even though once I know this partition function and I can find everything, getting the partition function it is a challenging affair.

It turns out that we can have some ways to estimate the partition function or some ways to approximate the partition function that is one way of doing it. And the other way of doing it is to use the molecular simulations, where we will see how we smartly handle our ability to not compute the partition function and we can still get the average properties.

So with that, I conclude this lecture. Thank you.