Advanced Thermodynamics and Molecular Simulations
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Lecture - 17
Partition Function of a Dense Gas; Grand Canonical Ensemble: Partition Function, Most Probable Distribution

Hello, all of you. In the last lecture we have been discussing the canonical ensemble and how can we compute the properties using the partition function. And finally, we discussed the example of an ideal gas partition function and how can we derive the equation of a state of an ideal gas.

So in this lecture, we will take the argument further and we first discuss one more example that is the Van der Waals equation of state that is true for dense gases and then finally, I will discuss how to do it for the grand canonical ensemble that is when the chemical potential are the control variables that is like an open system kind of an arrangement.

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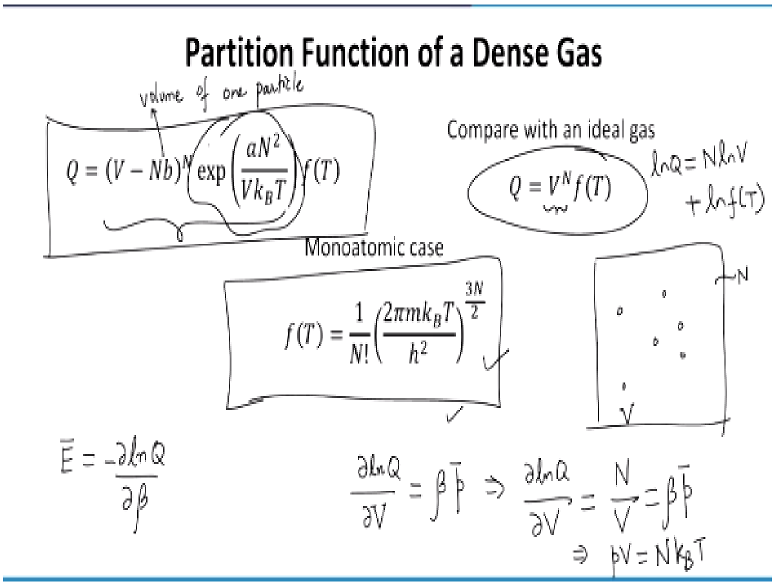

Partition Function of a Dense Gas

volume of one particle

$$Q = (V - Nb)^N \exp\left(\frac{aN^2}{Vk_BT}\right) f(T)$$

Compare with an ideal gas

$$Q = V^N f(T)$$

$$\ln Q = N \ln V + \ln f(T)$$

Monoatomic case

$$f(T) = \frac{1}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3N}{2}}$$

$$\bar{E} = -\frac{\partial \ln Q}{\partial \beta}$$

$$\frac{\partial \ln Q}{\partial V} = \beta p \Rightarrow \frac{\partial \ln Q}{\partial V} = \frac{N}{V} = \beta p$$

$$\Rightarrow pV = Nk_BT$$

So essentially, we are doing the ideal gas case. And I defined the partition function of an ideal gas. I did not derive it, I told you that to derive it, it has to be a different kind of a theory but we had some intuition that since the particles can pretty much be anywhere in the volume V.

$$Q = V^N f(T)$$

So there are and most like V ways or the number of ways of placing one particle is proportional to V that is the volume. And so if I have N particles, we have V to the power N number of ways of distributing it proportional to that and then there has to be a function of T. If one does the derivation for an ideal gas, it turns out that the function f T is given by this.

$$f(T) = \frac{1}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3N}{2}}$$

And using that, we already have established that if I do for example-

$$\frac{\partial \ln Q}{\partial V} = \beta \bar{p} = \frac{\partial \ln Q}{\partial V} = \frac{N}{V} = \beta \bar{p} = pV = Nk_B T$$

So now we can also find other properties using the ideal gas model. For example, if I am interested in the average energy of an ideal gas that is given as-

$$\bar{E} = -\frac{\partial \ln Q}{\partial \beta}$$

And in that case, the function of f (T) has to be differentiated with respect to β. So we will do that in a minute but then we can also extend the ideas to other kinds of gases for which the ideal gas model is not true. For example, one of the model for a dense gas is the following where Q is given by this-

$$Q = (V - Nb)^N \exp\left(\frac{aN^2}{Vk_B T}\right) f(T)$$

The function f (T) remains the same, if the gas is mono atomic and the same is true for the ideal gas as well only for the mono atomic gas we have this particular function. But then, if you look at the first and second term, that is quite complicated than compared to what we had here and the reason is in a dense gas, we no longer assume that the particles are of zero size they occupy some volume, roughly speaking b is the volume of one particle and therefore, once I place that particle that volume is occupied. So the other particle can only come in the other part of the space, not in that space. And therefore, the number of ways does not go like V to the power N. It goes to a lower number that is something like V - Nb to the power N. And all of this is true only when N is large.

Then there is one more factor, again I am not deriving how it is coming. But essentially it is coming because of the fact that the molecules cannot really overlap or the particles cannot really overlap that also gives some penalty when this overlap starts to occur that is, it is stopped as soon as there is an overlap. So we will not really go into the details right now of how it is derived but just for this value of Q also we can compute the property.

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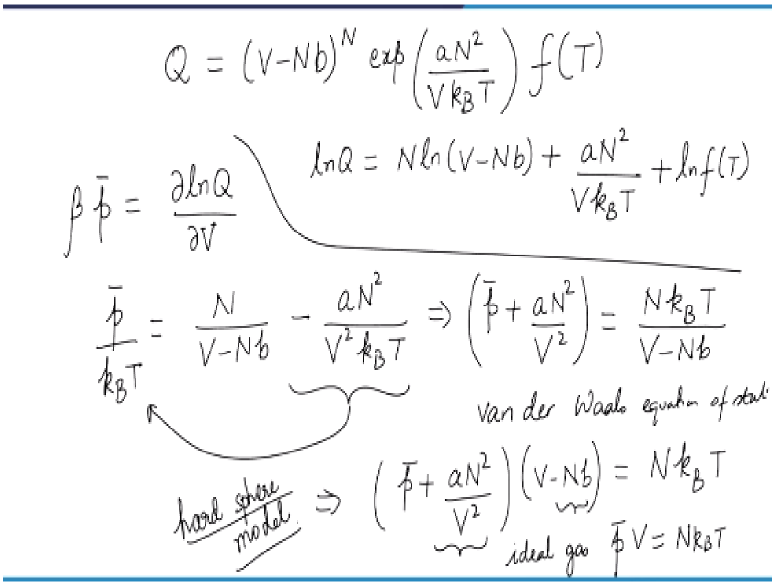

So let us first start with the equation of state for a dense gas model. So my Q is-

$$Q = (V - Nb)^N \exp\left(\frac{aN^2}{Vk_BT}\right) f(T)$$

So now if I am interested in the average pressure, the average pressure is again given as-

$$\beta\bar{p} = \left(\frac{\partial \ln Q}{\partial V}\right)$$

So ln Q in this case will be-

$$\ln Q = N\ln(V - Nb) + \frac{aN^2}{Vk_BT} + \ln f(T)$$

So if I take this derivative with respect to volume, what I get is-

$$\frac{\bar{p}}{k_BT} = \frac{N}{V - Nb} - \frac{aN^2}{V^2k_BT}$$

$$\bar{p} + \frac{aN^2}{V^2} = \frac{Nk_BT}{V - N_b}$$

$$\left(\bar{p} + \frac{aN^2}{V^2}\right)(V - N_b) = Nk_BT$$

what I essentially get is known as the Van der Waals equation of state. So if I compare with ideal gas model, so for an ideal gas it was-

$$\bar{p}V = Nk_BT$$

If I compare these two, you see that the right hand side is the same, but in the left hand side we have some correction to the pressure and some correction to the volume and the correction to volume is coming because now we attribute some size to the particles. So every particle cannot just be anywhere. They only will be in the places where other molecule is not coming and because of that, there is also some repulsion between the particles or we cannot allow overlap of particle and that also gives me an additional pressure so as to speak.

What is interesting about this Van der Waal equation of state is as we will see in the later part of this course, is that if I simply account for this particular correction, this model of the gas can also liquefy that means, I can show that, if I lower the temperature, this thing will go from a gas state to a liquid state. So as you know the liquid state you have lesser entropy than compared to gas and then there is more structure so as to speak that there is more interaction between the molecules that result in the liquid phase.

In the ideal gas model since we start with assuming that there is no interaction, there is no difference so as to speak between a gas state or a liquid state or in other words, we cannot describe the gas to liquid transition because the interaction that will appear when the gas becomes liquid is simply not accounted for in the model. However, in this case, you have an interaction even if the interaction is only resulting when there is a close contact or an overlap, even that itself is sufficient to explain the liquefaction of a gas. So we will come to that point again but keep in mind that this particular model is also referred as a hard sphere model and this becomes particularly important when we are doing molecular simulations this particular model can explain the phase transitions like gas to a liquid and so on. In fact, one of the first computers or supercomputers in those days, were used to perform molecular simulations on these hard sphere systems containing barely 200 particles. And even that was, I would say very big discovery back in those days, because it shows a potential to get equation of state using molecular simulations.

So we will come back to this model also in the molecular simulation part of this course but keep in mind that we are not really deriving the partition function in all these cases. I simply start with a partition function. The derivation of partition function itself is a whole different story. But once we have partition function, we can get the equation of state. Not only the equation of state, we can also get properties like average energy and specific heat.

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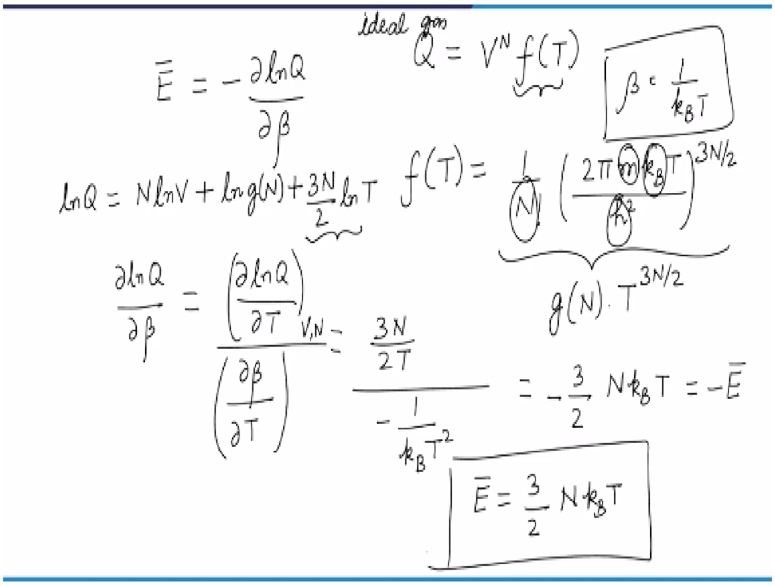

$$\bar{E} = -\frac{\partial \ln Q}{\partial \beta} \qquad \overset{\text{ideal gas}}{Q} = V^N f(T) \qquad \boxed{\beta = \frac{1}{k_B T}}$$

$$\ln Q = N \ln V + \ln g(N) + \frac{3N}{2} \ln T \qquad f(T) = \underbrace{\frac{1}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2}}_{g(N)\cdot T^{3N/2}}$$

$$\frac{\partial \ln Q}{\partial \beta} = \frac{\left(\frac{\partial \ln Q}{\partial T}\right)_{V,N}}{\left(\frac{\partial \beta}{\partial T}\right)} = \frac{\frac{3N}{2T}}{-\frac{1}{k_B T^2}} = -\frac{3}{2} N k_B T = -\bar{E}$$

$$\boxed{\bar{E} = \frac{3}{2} N k_B T}$$

So we already have seen that my average energy is given as-

$$\bar{E} = -\frac{\partial \ln Q}{\partial \beta}$$

So for ideal gas-

$$Q = V^N f(T)$$

And now if I am interested in the derivative with respect to β, in that case, the derivative of (f) will come into picture, because temperature essentially is related to β. β is equal to-

$$\beta = \frac{1}{k_B T}$$

. So therefore, let me write the form of my f (T) from what I have started with. So-

$$f(T) = \frac{1}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3N}{2}}$$

Here, m is the mass, N is the number of particles, h is the Planck's constant, k_B is the Boltzmann constant and therefore, I can write this as some constant that is a function as-

$$f(T) = g(N).T\text{^}(\frac{3N}{2})$$

That is true for a monoatomic gas. And now if I do-

$$\ln Q = N \ln V + \ln g(N) + \frac{3N}{2} \ln T$$

So now if I compute the doh ln Q by doh T, what essentially I will get is the first term will not contribute because now I am taking partial derivative with respect to temperature. So the volume is held constant here. So essentially what we have and the second term also will not contribute because N is held also constant.

$$\frac{\partial \ln Q}{\partial \beta} = \frac{\left(\frac{\partial \ln Q}{\partial T}\right)_{V,N}}{\left(\frac{\partial \beta}{\partial T}\right)}$$

So essentially you will have only the third term contributing and that will give me-

$$\frac{\partial \ln Q}{\partial \beta} = \frac{\frac{3N}{2T}}{-\frac{1}{k_B T^2}} = -\frac{3}{2}Nk_BT = -\bar{E}$$

So E bar for a monatomic ideal gas is given as-

$$\bar{E} = \frac{3}{2}Nk_BT$$

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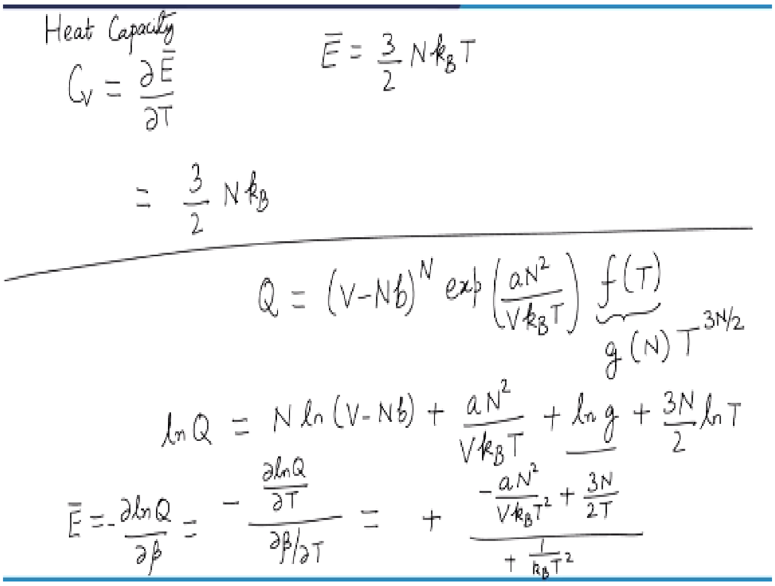

Heat Capacity

$$C_V = \frac{\partial \bar{E}}{\partial T} \qquad \bar{E} = \frac{3}{2}Nk_BT$$

$$= \frac{3}{2}Nk_B$$

$$Q = (V-Nb)^N \exp\left(\frac{aN^2}{Vk_BT}\right) \underbrace{f(T)}_{g(N)\,T^{3N/2}}$$

$$\ln Q = N\ln(V-Nb) + \frac{aN^2}{Vk_BT} + \underline{\ln g} + \frac{3N}{2}\ln T$$

$$\bar{E} = -\frac{\partial \ln Q}{\partial \beta} = -\frac{\frac{\partial \ln Q}{\partial T}}{\partial \beta/\partial T} = +\frac{-\frac{aN^2}{Vk_BT^2} + \frac{3N}{2T}}{+\frac{1}{k_BT^2}}$$

So let us say if I am now interested in the specific heat. So the specific heat as we have discussed is given as-

$$C_v = \frac{\partial \bar{E}}{\partial T}$$

That is the definition of specific heat. And since we are doing it at constant volume, so it is specific heat at constant volume. Actually, it is the heat capacity, I am sorry not the specific heat. When I define specific heat, it is per unit number of particles. In this case, we are doing the heat capacity that is extensive in nature, it depends on quantity.

So E bar we already have seen it is-

$$\bar{E} = \frac{3}{2}Nk_BT$$

And therefore,

$$C_V = \frac{3}{2}Nk_B$$

We could have also got it starting from the partial derivative of the partition function. Then we will have a second derivative of the ln Q with respect to βgiving me by specific heat that is what we did in the last lecture.

So now let us do the same thing for the Van der Waals model. So in the Van der Walls model, my Q is-

$$Q = (V - Nb)^N \exp\left(\frac{aN^2}{Vk_BT}\right) f(T)$$

And f (T) I already have written as some function as-

$$f(T) = g(N)T^{\frac{3N}{2}}$$

So if I do a ln Q here what I essentially have is-

$$\ln Q = N\ln(V - Nb) + \frac{aN^2}{Vk_BT} + \ln g + \frac{3N}{2}\ln T$$

Just like what we had in the earlier case the last term is the same for both the Van der Walls or dense gas and for an ideal gas. And therefore, if I am now interested in E bar, E bar is-

$$\bar{E} = -\frac{\partial \ln Q}{\partial \beta} = \frac{-\frac{\partial \ln Q}{\partial T}}{\frac{\partial \beta}{\partial T}} = \frac{\left(-\frac{aN^2}{Vk_BT^2}\right)\left(\frac{3N}{2T}\right)}{\frac{1}{k_BT^2}}$$

And then you see there is some correction to the energy that is coming in the case of the dense gas, the correction with respect to the. If I simply had this it was for the ideal gas. So there is some additional correction that will come because of the additional interactions introduced in the hard sphere model or the Van der Waals model. So we can also go ahead and find the specific heat and so on. And this is pretty much tells me how given a partition function, I can compute the properties.

So whole apparatus where I am finding the thermodynamic behavior remains the same irrespective of what definition of partition function we are using. Every partition function will give me a different equation of state naturally but the way that we are doing the computation, the basic formula of the ensembles remain the same irrespective of the definition of the partition function. So therefore, the broad objective if I am interested in the thermodynamic behavior is to find the partition function and we have not so far discussed how to do that and we will come to that later but before we really go there, let us now think of couple other ensembles such as the grand canonical ensemble and the isothermal isobaric ensemble.

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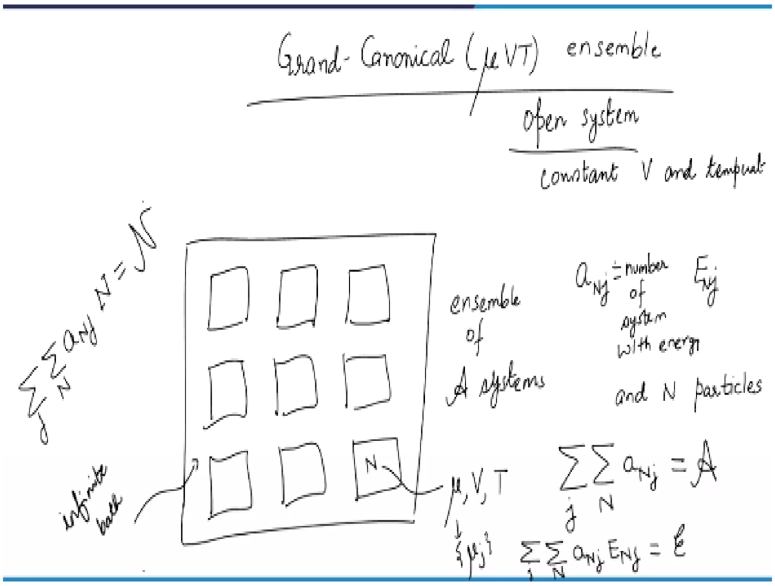

So there is something called the grand canonical or the μVT ensemble, which is pretty similar to ensemble that we have been doing the NVT ensemble except the N is no longer a control variable, μ is a control variable. So this refers to systems which are open, that is the number of molecules can change, but still at constant volume and temperature.

So if I think of the grand canonical ensemble the way we think about it is still the same, we consider that we have an ensemble of some ‘A’ states or systems and each of these ‘A’ systems now have the same value of the chemical potential, the volume and the temperature, although we can extend it to more than one component. In that case, you will have a μ_j here. I am right now doing it for only one component where there is only one chemical potential. We have been discussing that chemical potential is more useful when we have a multi component system, but the basic derivation still applies. A simple extension will be that you will replace the μ with μ_j of all the components. In fact, it can be somewhere in between where one of the component you are controlling the chemical potential and other component you are controlling the number of molecules. In that case, we can call it a semi-grand canonical ensemble. One example is let us say if you have a polymeric system with polymer and solvent and polymer part of it is having the same number of molecules in every system, but the amount of solvent is changing in different systems. In that case, we can control the chemical potential of solvent and the number of molecules of polymer that will be somewhere between the grand canonical and canonical ensemble, and that is referred as a semi-grand canonical ensemble.

But in this particular simple case, we are assuming that we have only one component and therefore, we have only one chemical potential. So now in the canonical ensemble case, I defined a_j as the number of systems having energy E_j. But now both N and energy becomes a variable. So therefore, now we will define the occupation as something like aN_j that is the number of systems with energy and let me call the energy EN_j, because now the number of molecule is also changing with the systems. And N molecules are in general particles.

So now there are two variables that are changing, one is the energy and one is the number of particles in the systems. So now in this particular case, if I look at the summation over a, we have to sum over both the number of molecules and the energy levels of systems. And that will be equal to my total number of states in ensemble A.

$$\sum_{j}\sum_{N} aN_j = A$$

Also if I look at the energies, we can look in the same way. We can sum over all the energy levels and all the number of molecules and the occupation number multiplied with energy of a system containing N particles and that is the j^{th} energy level of that. So this is equal to again some constant E.

$$\sum_{j}\sum_{N} aN_j E_{Nj} = E$$

The other assumptions remain the same, we are assuming that it is an infinite bath such that the temperature is being maintained. The systems cannot still exchange energy, but the number of molecules and systems can change subject to the constraint that we have got here. So finally, since the total system, we can still assume the mass is conserved or system plus the surrounding or the bath, the mass is conserved. So there is one more constraint here, that is –

$$\sum_j \sum_N a_{Nj} N = N$$

So now we have three constraint, one for the number of state, one for the number of particles and one for the energy of the systems and all the constraints basically tells me that the total energy of the entire ensemble, the total number of molecules of entire ensemble, and total number of states of the entire ensemble is fixed in this particular system.

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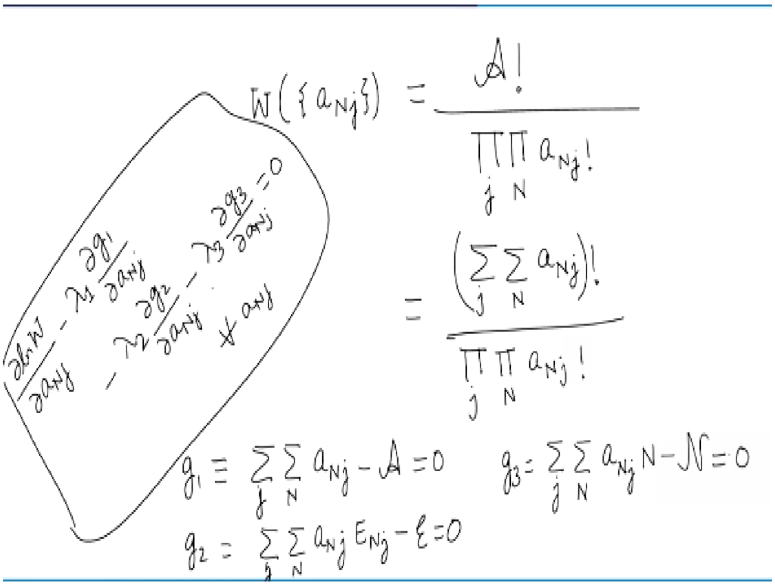

$$W(\{a_{Nj}\}) = \frac{A!}{\prod_j \prod_N a_{Nj}!} = \frac{\left(\sum_j \sum_N a_{Nj}\right)!}{\prod_j \prod_N a_{Nj}!}$$

$$\frac{\partial \ln W}{\partial a_{Nj}} - \lambda_1 \frac{\partial g_1}{\partial a_{Nj}} - \lambda_2 \frac{\partial g_2}{\partial a_{Nj}} - \lambda_3 \frac{\partial g_3}{\partial a_{Nj}} = 0 \quad \forall\, a_{Nj}$$

$$g_1 = \sum_j \sum_N a_{Nj} - A = 0 \qquad g_3 = \sum_j \sum_N a_{Nj} N - \mathcal{N} = 0$$

$$g_2 = \sum_j \sum_N a_{Nj} E_{Nj} - \mathcal{E} = 0$$

So what is going to be the number of ways of distribution in this case is like for a given distribution of aNj, we can think that the number of ways will be A factorial. And now for canonical ensemble we did a product over aj's, but now since we are doing a grand canonical ensemble, so therefore, we will do two sums here, one over j and one over N. That is the product over all this factorials. And I can also replace the numerator with summation of j summation over N aNj factorial and I can also write my constraints again.

$$W(\{aN_j\}) = \frac{A!}{\prod_j \prod_N aN_j!}$$

$$= \frac{(\sum_j \sum_N aN_j)!}{\prod_j \prod_N aN_j!}$$

So one constraint is for the number of states-

$$g_1 = \sum_j \sum_N aN_j - A = 0$$

The other constraint is for the energies-

$$g_2 = \sum_j \sum_N a_{Nj} E_{Nj} - E = 0$$

And the last constraint is for the number of molecules-

$$g_3 = \sum_j \sum_N a_{Nj} N - N = 0$$

And now the minimization problem is going to be-

$$\frac{\partial \ln W}{\partial a N_j} - \lambda_1 \frac{\partial g_1}{\partial a_{Nj}} - \lambda_2 \frac{\partial g_2}{\partial a_{Nj}} - \lambda_3 \frac{\partial g_3}{\partial a_{Nj}} = 0$$

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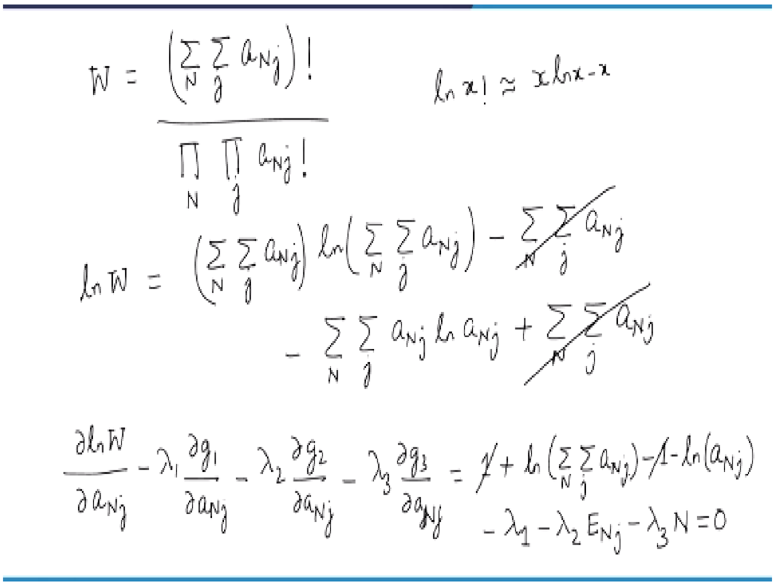

$$W = \frac{\left(\sum_N \sum_j a_{Nj}\right)!}{\prod_N \prod_j a_{Nj}!} \qquad \ln x! \simeq x \ln x - x$$

$$\ln W = \left(\sum_N \sum_j a_{Nj}\right) \ln\left(\sum_N \sum_j a_{Nj}\right) - \cancel{\sum_N \sum_j a_{Nj}} - \sum_N \sum_j a_{Nj} \ln a_{Nj} + \cancel{\sum_N \sum_j a_{Nj}}$$

$$\frac{\partial \ln W}{\partial a_{Nj}} - \lambda_1 \frac{\partial g_1}{\partial a_{Nj}} - \lambda_2 \frac{\partial g_2}{\partial a_{Nj}} - \lambda_3 \frac{\partial g_3}{\partial a_{Nj}} = \cancel{1} + \ln\left(\sum_N \sum_j a_{Nj}\right) - \cancel{1} - \ln(a_{Nj}) - \lambda_1 - \lambda_2 E_{Nj} - \lambda_3 N = 0$$

So let us first find the W.

$$W = \frac{(\sum_N \sum_j a_{Nj})!}{\prod_N \prod_j a_{Nj}!}$$

And now if I take a ln W, I will have using the Stirling approximation for large x, this can be approximated as-

$$\ln W = \left(\sum_N \sum_j a_{Nj}\right) \ln\left(\sum_N \sum_j a_{Nj}\right) - \sum_N \sum_j a_{Nj} - \sum_N \sum_j a_{Nj} \ln a_{Nj} + \sum_N \sum_j a_{Nj}$$

And therefore, if I do-

$$\frac{\partial \ln W}{\partial a_{Nj}} - \lambda_1 \frac{\partial g_1}{\partial a_{Nj}} - \lambda_2 \frac{\partial g_2}{\partial a_{Nj}} - \lambda_3 \frac{\partial g_3}{\partial a_{Nj}}$$
$$= 1 + \ln\left(\sum_N \sum_j a_{Nj}\right) - 1 - \ln(a_{Nj}) - \lambda_1 - \lambda_2 E N_j - \lambda_3 = 0$$

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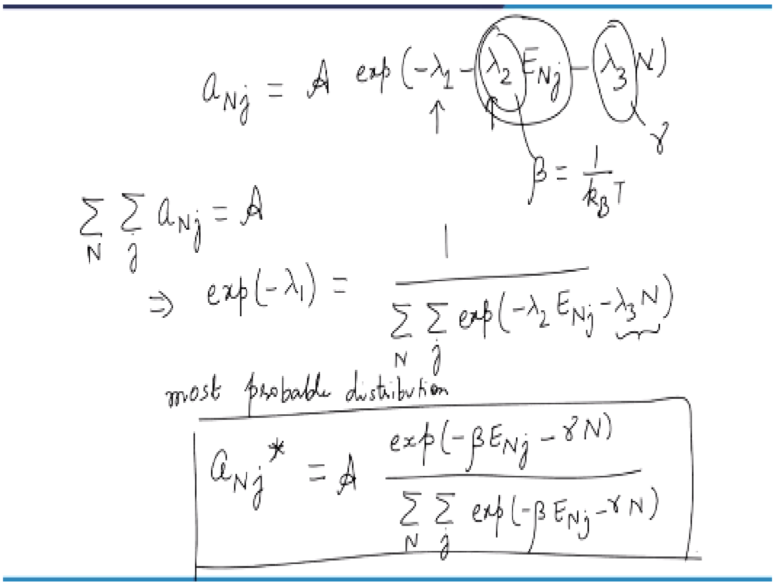

$$a_{Nj} = A \exp(-\lambda_1 - \lambda_2 E_{Nj} - \lambda_3 N)$$

$$\beta = \frac{1}{k_B T}$$

$$\gamma$$

$$\sum_N \sum_j a_{Nj} = A$$

$$\Rightarrow \exp(-\lambda_1) = \frac{1}{\sum_N \sum_j \exp(-\lambda_2 E_{Nj} - \lambda_3 N)}$$

most probable distribution

$$\boxed{a_{Nj}^{*} = A \frac{\exp(-\beta E_{Nj} - \gamma N)}{\sum_N \sum_j \exp(-\beta E_{Nj} - \gamma N)}}$$

So if I do simplifications here, what I essentially will get is-

$$a_{Nj} = A\exp(-\lambda_1 - \lambda_2 - \lambda_3 N)$$

So now if I look at this particular expression, there are a few things we can notice here that until the first and second part, it bears similarity with the canonical ensemble. And actually the first λ1 we can get by using the constraint as I got for the canonical ensemble-

$$\sum_N \sum_j a_{Nj} = A$$

If I do this in this case, what I get is-

$$\exp(-\lambda_1) = \frac{1}{\sum_N \sum_j \exp(-\lambda_2 E_{Nj} - \lambda_3 N)}$$

And second thing is that since this pretty much refers to the same constraint as the canonical ensemble case, we can think of this λ to be same as the β that is beta equal to 1 by k_B T. We will see in the next class that it indeed works out correctly when we do that. The last constraint is a bit unknown here, so let me call it some γ.

So as of now we have a Nj at for the most probable distribution and let me use it like a Nj star to indicate that. This is already found by maximizing the W in this case and therefore, this is already the most probable distribution. So this is given as-

$$a_{Nj}^{*} = A\,\frac{\exp\left(-\beta E_{Nj} - \gamma N\right)}{\sum_N \sum_j \exp(-\beta E_{Nj} - \gamma N)}$$

So in the next class we will start from this particular point and I will tell you how the properties are evaluated in the grand canonical ensemble just like what we have done for the canonical ensemble.

So with that I stop here. Thank you.