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

Lecture - 18
Computing Properties in Grand Canonical Ensemble

Hello, all of you. So in the last lecture, we started doing the grand canonical ensemble that is when the chemical potential volume and temperature are the control variables that refer to an open system and we derived the expression for the most probable distribution. So we will take that discussion further this day and find how can we find the average properties for the grand canonical ensemble.

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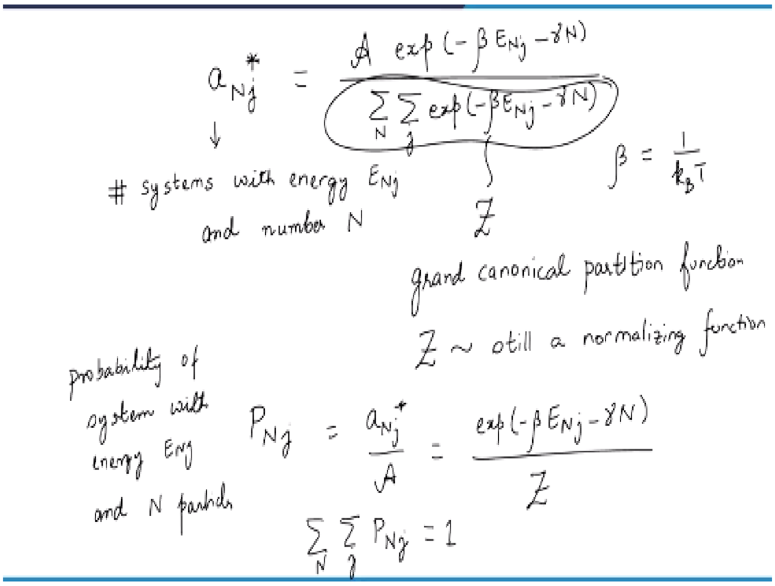

$$a^*_{Nj} = \frac{A \exp(-\beta E_{Nj} - \gamma N)}{\underbrace{\sum_N \sum_j \exp(-\beta E_{Nj} - \gamma N)}_{Z}} \qquad \beta = \frac{1}{k_B T}$$

$\downarrow$ # systems with energy E_{Nj} and number N

Z grand canonical partition function

$Z \sim$ still a normalizing function

probability of system with energy E_{Nj} and N particles

$$P_{Nj} = \frac{a^*_{Nj}}{A} = \frac{\exp(-\beta E_{Nj} - \gamma N)}{Z}$$

$$\sum_N \sum_j P_{Nj} = 1$$

So essentially what we have discussed so far is the most probable distribution that is given as the number of systems with energy EN$_j$ and number N is given as-

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

β is argued to be same as-

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

because the constraint for the energy is the same as the canonical ensemble. γ we have not discussed so far that it is a Lagrange multiplier, but we do not know what exactly it signifies until so far in the discussion.

So even though the function is defined a bit differently in the canonical ensemble, the properties of the function remains the same as in the canonical ensemble case, that is Z is still a normalizing function and that we can see because the probability of a state or a system having EN$_j$ energy and N molecules or N particles is given as-

$$P_{Nj} = \frac{a^*_{Nj}}{A} = \frac{\exp(-\beta E_{Nj} - \gamma N)}{Z}$$

It ensures that the probabilities add to 1. That is if I do summation of N summation over j, P N$_j$, then the numerator will have the same summation as denominator, they will cancel and this will be equal to 1.

$$\sum_N \sum_j P_{Nj} = 1$$

So by using this partition function, we can still normalize the probabilities. And it is still also a generating function and we will see how it works out in this case. So let us say if I start with Z as-

$$Z = \sum_N \sum_j e^{-\beta E_{Nj} - \gamma N}$$

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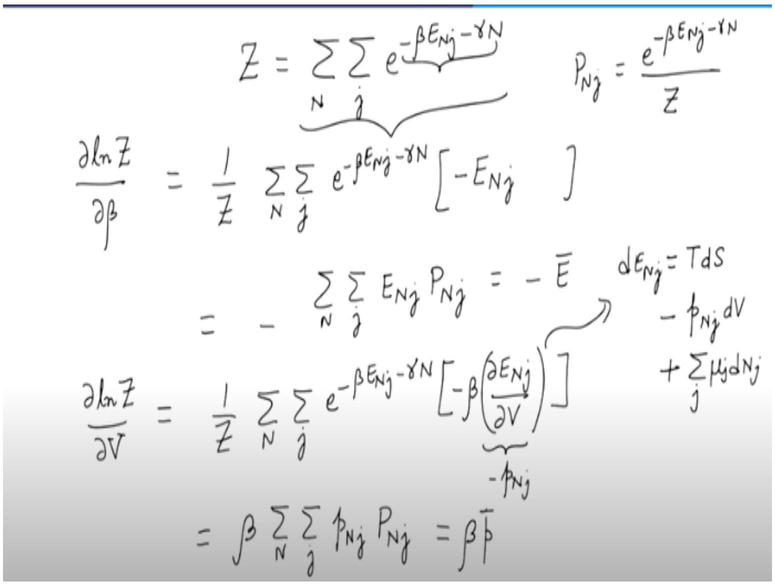

$$Z = \underbrace{\sum_N \sum_j e^{\overbrace{-\beta E_{Nj} - \gamma N}}}$$

$$P_{Nj} = \frac{e^{-\beta E_{Nj} - \gamma N}}{Z}$$

$$\frac{\partial \ln Z}{\partial \beta} = \frac{1}{Z} \sum_N \sum_j e^{-\beta E_{Nj} - \gamma N} \left[-E_{Nj} \right]$$

$$= - \sum_N \sum_j E_{Nj} P_{Nj} = -\bar{E}$$

$$dE_{Nj} = TdS - p_{Nj} dV + \sum_j \mu_j dN_j$$

$$\frac{\partial \ln Z}{\partial V} = \frac{1}{Z} \sum_N \sum_j e^{-\beta E_{Nj} - \gamma N} \left[-\beta \underbrace{\left(\frac{\partial E_{Nj}}{\partial V} \right)}_{-p_{Nj}} \right]$$

$$= \beta \sum_N \sum_j p_{Nj} P_{Nj} = \beta \bar{p}$$

In the earlier case we said that doh ln Q by doh β is minus of the average energy, right. In the grand canonical case it will be simply Q replaced with Z. So doh ln Z by doh β happens to be minus of average energy. Let us see how it is true. So if I take the-

$$\frac{\partial\, ln\, Z}{\partial \beta} = \frac{1}{Z}\sum_N\sum_j e^{-\beta E_{Nj}-\gamma N}\left[-E_{Nj}\right]$$

$$= -\sum_N\sum_j E_{Nj}P_{Nj} = -\bar{E}$$

So although the ensemble has changed, the control variables has changed, but the relation between the average energy and the partition function is the same. The partition function itself is different for the grand canonical ensemble, but the relation relating the average energy with the partition function is the same. We can still use partition function to generate the properties of interest, in this case the average energy.

We can also do it for other properties. So let us say if I do-

$$\frac{\partial \ln Z}{\partial V} = \frac{1}{Z}\sum_N\sum_j e^{-\beta E_{Nj}-\gamma N}\left[-\beta\left(\frac{\partial E_{Nj}}{\partial V}\right)\right]$$

This E is still the internal energy and we know that-

$$dE_{Nj} = TdS - p_{Nj}dV + \sum_j \mu_j dN_j$$

So if I take-

$$\frac{\partial E_{Nj}}{\partial V} = \beta\sum_N\sum_j p_{Nj}P_{Nj} = \beta\bar{p}$$

So it is the same relation that we have got with Q replaced by Z in this particular case. Now since there is a γ appearing here, we can also compute a derivative with respect to γ that we could not do in the earlier case because there is a new variable coming in the grand canonical case. So let us see what that gives us.

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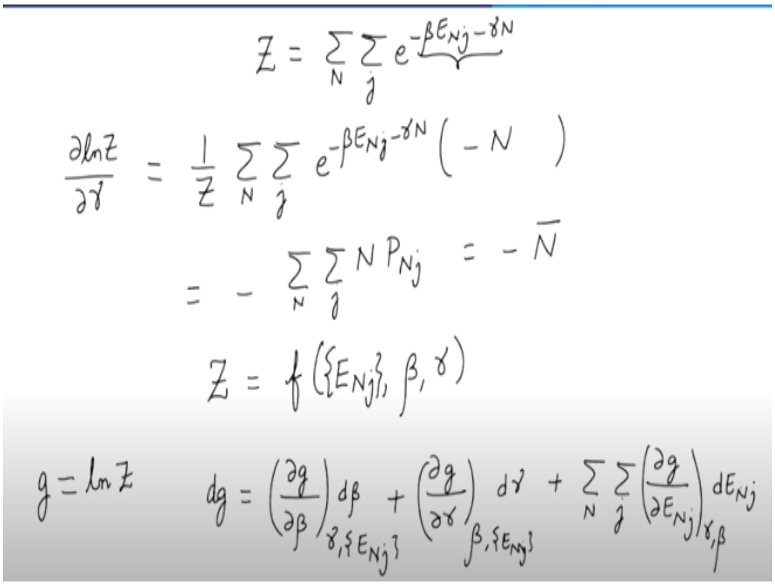

$$Z = \sum_N \sum_j e^{\underbrace{-\beta E_{Nj} - \gamma N}}$$

$$\frac{\partial \ln Z}{\partial \gamma} = \frac{1}{Z} \sum_N \sum_j e^{-\beta E_{Nj} - \gamma N} \left(- N \quad \right)$$

$$= - \sum_N \sum_j N P_{Nj} \quad = - \overline{N}$$

$$Z = f(\{E_{Nj}\}, \beta, \gamma)$$

$$g = \ln Z \qquad dg = \left(\frac{\partial g}{\partial \beta}\right)_{\gamma, \{E_{Nj}\}} d\beta + \left(\frac{\partial g}{\partial \gamma}\right)_{\beta, \{E_{Nj}\}} d\gamma + \sum_N \sum_j \left(\frac{\partial g}{\partial E_{Nj}}\right)_{\gamma, \beta} dE_{Nj}$$

So if I start with the same Z –

$$Z = \sum_N \sum_j e^{-\beta E_{Nj} - \gamma N}$$

and if I compute-

$$\frac{\partial \ln Z}{\partial \gamma} = \frac{1}{Z} \sum_N \sum_j e^{-\beta E_{Nj} - \gamma N} (-N)$$

$$= - \sum_N \sum_j N \, P_{Nj} = -\overline{N}$$

So in this case we can also find the average number of molecule in the systems or average number of particles in the system as the derivative of ln Z with respect to γ. In this case this N is also a variable. So you will have fluctuations in N and you will have some average value of N that also can be computed using the partition function.

So essentially until so far I have demonstrated that even for the grand canonical ensemble Z works like the both the normalizing function and the generating function. And the same idea is true for also other ensembles that we discuss later. So always keep in mind that if I know Z, then I can find all the properties of interest, but the properties themselves that we can evaluate from there depend on the choice of ensembles. Let us say average number of particles does not have any meaning in the canonical ensemble case, because the number of particles was the control variable in this case number of particles can fluctuate or vary between state and therefore, average number of particle is a meaningful variable in this case, and that we can evaluate using the partition function.

Now if I go a bit further from there, we can also notice that this Z is actually a function of my E_{Nj} β and γ. And again, it is like for all possible values of E_{Nj} that is like a multiple energy values and β and γ are single values. So now I can define a quantity ln of Z. Let me call that quantity g. So I can define the total derivative d (g) as-

$$g = \ln Z$$

$$dg = \left(\frac{\partial g}{\partial \beta}\right)_{\gamma,\{E_{Nj}\}} d\beta + \left(\frac{\partial g}{\partial \gamma}\right)_{\beta,\{E_{Nj}\}} d\gamma + \sum_N \sum_j \left(\frac{\partial g}{\partial E_{Nj}}\right)_{\beta,\gamma} dE_{Nj}$$

And we can evaluate this partial derivatives. Let us see how we can do that. So-

$$\frac{\partial g}{\partial \beta} = \frac{1}{Z} \sum_N \sum_j e^{-\beta E_{Nj} - \gamma N}(-E_{Nj}) = -\bar{E}$$

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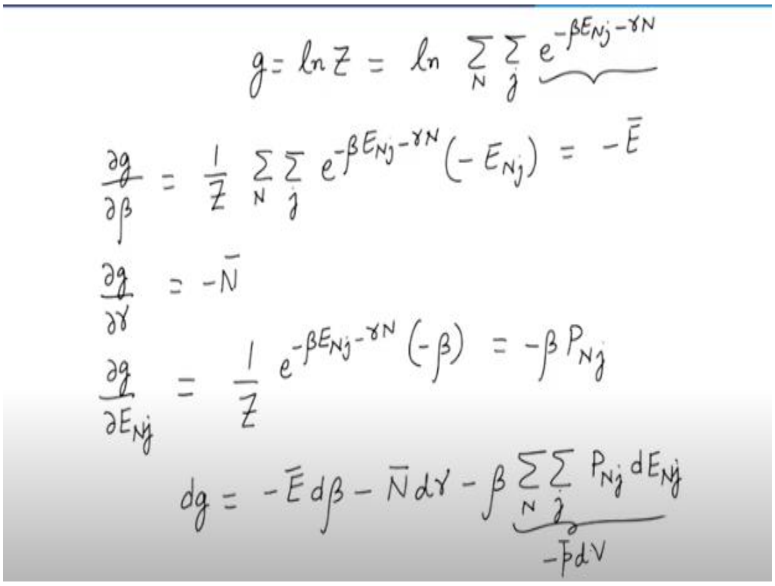

$$g = \ln Z = \ln \sum_N \sum_j \underbrace{e^{-\beta E_{Nj} - \gamma N}}$$

$$\frac{\partial g}{\partial \beta} = \frac{1}{Z} \sum_N \sum_j e^{-\beta E_{Nj} - \gamma N}(-E_{Nj}) = -\bar{E}$$

$$\frac{\partial g}{\partial \gamma} = -\bar{N}$$

$$\frac{\partial g}{\partial E_{Nj}} = \frac{1}{Z} e^{-\beta E_{Nj} - \gamma N}(-\beta) = -\beta P_{Nj}$$

$$dg = -\bar{E}\, d\beta - \bar{N}\, d\gamma - \beta \underbrace{\sum_N \sum_j P_{Nj}\, dE_{Nj}}_{-\bar{p}\, dV}$$

Similarly,

$$\frac{\partial g}{\partial \gamma} = -\bar{N}$$

The last one doh g by doh E_{Nj} that will be equal to so now this will apply only to one of the terms right here and that term is when energy is equal to E_{Nj} for all the other value in summation this will not contribute to the derivative. So this will be-

$$\frac{\partial g}{\partial E_{Nj}} = \frac{1}{Z} e^{-\beta E_{Nj} - \gamma N}(-\beta) = -\beta P_{Nj}$$

That is the probability of that particular state. So therefore, I can write my dg as-

$$dg = -\bar{E} d\beta - \bar{N} d\gamma - \beta \sum_N \sum_j P_{Nj} dE_{Nj}$$

Now the last term is something that relates to the work done in the in this particular case and why is that because every state will gain energy with dEj. And therefore, the net change due to the work is given by P_{Nj} d_{Ej} just like what we had for the canonical ensemble and microscopic term, this is equal to - p bar dV. That is the work done, right. The same thing that we have done for the canonical ensemble as well in this case, the only difference is that we have an extra summation over N just because we have varying number of molecules, but the argument remains the same as earlier.

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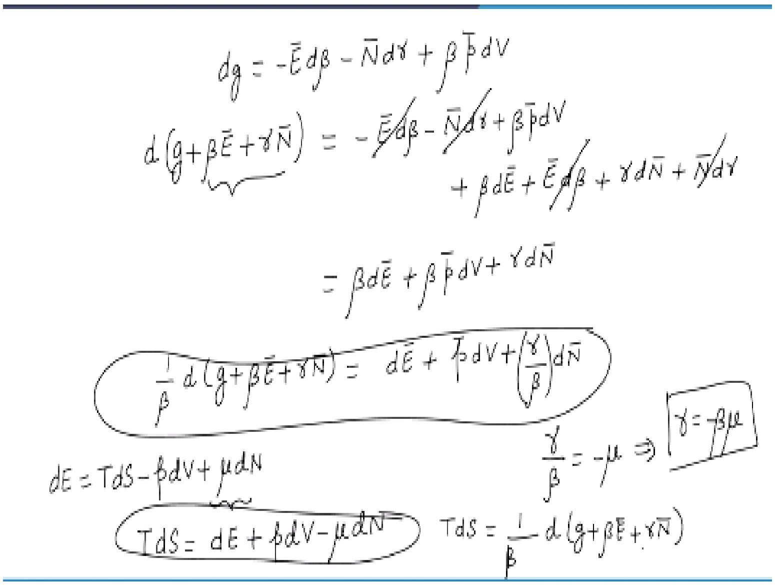

$$dg = -\bar{E}d\beta - \bar{N}d\gamma + \beta\bar{p}dV$$

$$d(g+\beta\bar{E}+\gamma\bar{N}) = -\cancel{\bar{E}d\beta} - \cancel{\bar{N}d\gamma} + \beta\bar{p}dV + \beta d\bar{E} + \cancel{\bar{E}d\beta} + \gamma d\bar{N} + \cancel{\bar{N}d\gamma}$$

$$= \beta d\bar{E} + \beta\bar{p}dV + \gamma d\bar{N}$$

$$\frac{1}{\beta}d(g+\beta\bar{E}+\gamma\bar{N}) = d\bar{E} + \bar{p}dV + \left(\frac{\gamma}{\beta}\right)d\bar{N}$$

$$\frac{\gamma}{\beta} = -\mu \Rightarrow \boxed{\gamma = -\beta\mu}$$

$$dE = TdS - pdV + \mu dN$$

$$TdS = dE + pdV - \mu dN \qquad TdS = \frac{1}{\beta}d(g+\beta\bar{E}+\gamma\bar{N})$$

So therefore, what we have is dg is-

$$dg = -\bar{E}d\beta - \bar{N}d\gamma + \beta\bar{p}dV$$

Now let us define a quantity-

$$d(g + \beta\bar{E} + \gamma\bar{N}) = -\bar{E}d\beta - \bar{N}d\gamma + \beta\bar{p}dV + \beta d\bar{E} + \bar{E}d\beta + \gamma d\bar{N} + \bar{N}d\gamma$$
$$= \beta d\bar{E} + \beta\bar{p}dV + \gamma d\bar{N}$$
$$\frac{1}{\beta}d(g + \beta\bar{E} + \gamma\bar{N}) = d\bar{E} + \bar{p}dV + \frac{\gamma}{\beta}d\bar{N}$$

Now let us compare with the definition of dS that we have used earlier. So basically we can write dE as-

$$dE = TdS - pdV + \mu dN$$

Keep in mind that we had a summation earlier, but now we are looking at only one component, so I only have µdN. If we are doing a multi component case, we simply have to also put a summation in this term over the number of species. So this will give me-

$$dS = dE + pdV - \mu dN$$

So if I compare the above two expression, we can say that-

$$\frac{\gamma}{\beta} = -\mu$$

And therefore,

$$\gamma = -\beta\mu$$

γ which was not well defined so far, it was Lagrange multiplier, but there was no physical significance actually is related to the chemical potential. It is minus β multiplied with the chemical potential and if I compare the left hand side, what we have is-

$$TdS = \frac{1}{\beta} d(g + \beta\bar{E} + \gamma\bar{N})$$

which is essentially I can write my dS as-

$$dS = \frac{1}{\beta T} d(g + \beta\bar{E} + \gamma\bar{N})$$

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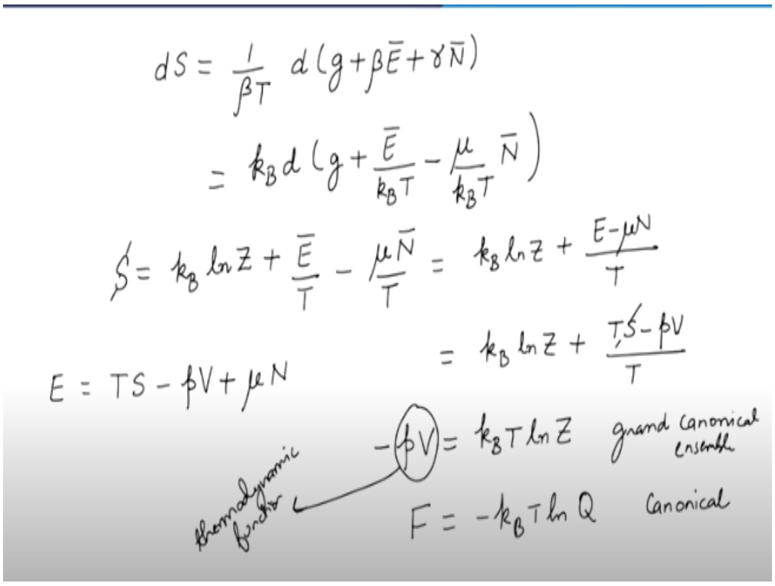

$$dS = \frac{1}{\beta T} d(g + \beta\bar{E} + \gamma\bar{N})$$

$$= k_B d\left(g + \frac{\bar{E}}{k_B T} - \frac{\mu}{k_B T}\bar{N}\right)$$

$$S = k_B \ln Z + \frac{\bar{E}}{T} - \frac{\mu\bar{N}}{T} = k_B \ln Z + \frac{E - \mu N}{T}$$

$$= k_B \ln Z + \frac{TS - pV}{T}$$

$$E = TS - pV + \mu N$$

$$-\boxed{pV} = k_B T \ln Z$$ grand canonical ensemble

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

And as we know-

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

So this will give me-

$$dS = k_B d(g + \frac{\bar{E}}{k_B T} - \frac{\mu}{k_B T}\bar{N}$$

So if I compare this what we have is-

$$S = k_B \ln Z + \frac{\bar{E}}{T} - \frac{\mu N}{T}$$

If I now compare with the absolute value of internal energy that we have found earlier, we have found that-

$$S = k_B \ln Z + \frac{\bar{E}}{T} - \frac{\mu N}{T} = k_B \ln Z + \frac{E - \mu N}{T} = k_B \ln Z + \frac{TS - pV}{T}$$

$$E = TS - pV + \mu N$$

$$-pV = k_B T \ln Z$$

If I compare with the earlier case what we had was

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

for the canonical with what I am getting in the grand canonical ensemble, you may say that just like my Helmholtz energy was the thermodynamic function that we had to minimize for the canonical ensemble, pV becomes the thermodynamic function in the case of a grand canonical ensemble. So that is simply-

$$-pV = k_B T \ln Z$$

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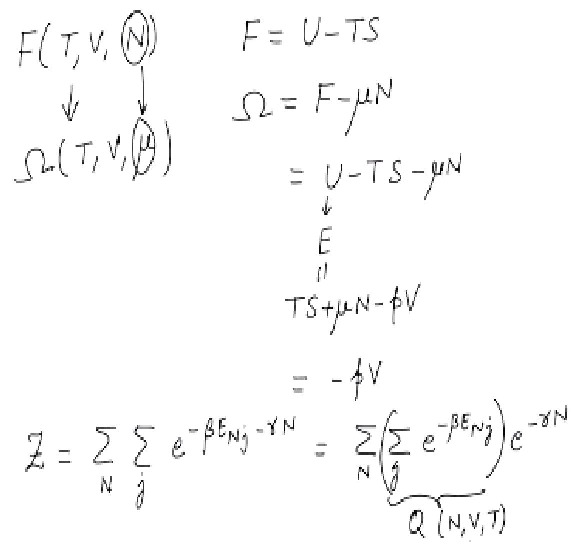

$$\begin{tikzcd} F(T,V,\textcircled{N}) \arrow[d] \\ \Omega(T,V,\textcircled{\mu}) \end{tikzcd}$$

$$F = U - TS$$

$$\Omega = F - \mu N$$

$$= \underset{\substack{\downarrow \\ E \\ \parallel \\ TS + \mu N - pV}}{U} - TS - \mu N$$

$$= -pV$$

$$\mathcal{Z} = \sum_N \sum_j e^{-\beta E_{Nj} - \gamma N} = \sum_N \underbrace{\left(\sum_j e^{-\beta E_{Nj}}\right)}_{Q(N,V,T)} e^{-\gamma N}$$

So we can also get it by using Legendre transformation. Let us see how it works. So basically, we have to go from the Helmholtz free energy that is a function of T, V, N to some potential Ω let us call it Ω as a function of T, V, μ. So essentially N has to be replaced with μ here and that thing is coming from the Legendre transformation. So first of all we know that-

$$F = U - TS$$

$$\Omega = F - \mu N$$
$$= U - TS - \mu N$$

We have been using the notation E for the U in our case and E is equal to-

$$E = TS + \mu N - pV$$

So this pretty much gives me in this particular case-

$$\Omega = -pV$$

So therefore, what we have been able to establish is that, for the grand canonical ensemble the thermodynamic function that we can also get by Legendre transformation gives me a value that is equal to - k_BT ln of Z. So the thermodynamic function essentially relates to the partition function in pretty much the same way, in every ensemble. In the canonical ensemble the thermodynamic function was F. In the grand canonical ensemble the thermodynamic function is Ω that is equal to - pV, which is still - k_BT ln of the partition function, just like what we had for the canonical ensemble F = -k_B T ln Q.

The definition of partition function has changed but the relation between the thermodynamic functions and the partition function has not changed. The relation between the averages of properties with the partition function has not changed and therefore, once we do this kind of a toolkit for a particular ensemble the same toolkit can be more or less employed for every different ensemble just keeping in mind that the partition function in there have changed. In fact, the partition function Z relates to the canonical partition function we can see how it happens. So Z is-

$$Z = \sum_N \sum_j e^{-\beta E_{Nj} - \gamma N}$$

This I can as well write as-

$$Z = \sum_N \left(\sum_j e^{-\beta E_{Nj}} \right) e^{-\gamma N}$$

And this quantity $\sum_j e^{-\beta E_{Nj}}$ in the above equation actually is my canonical partition function Q.

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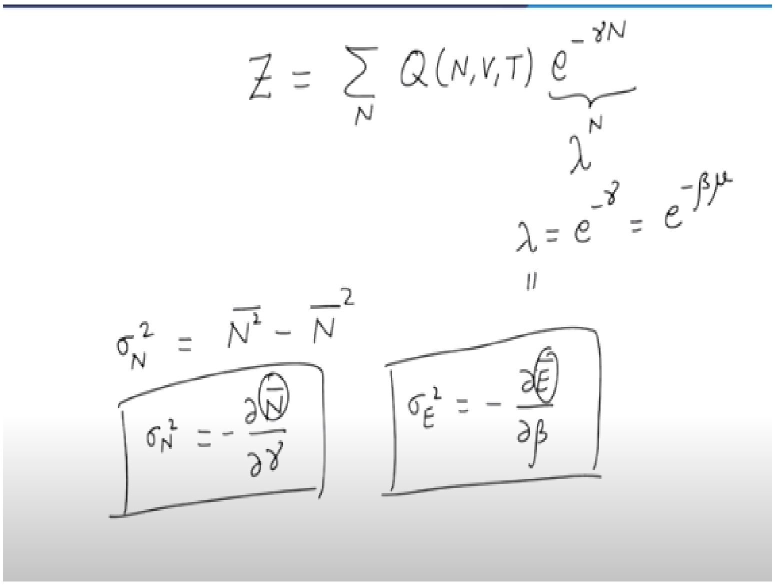

So therefore, my grand canonical partition function is simply a summation of N of the corresponding canonical partition function when n was held constant multiplied with exponential of minus γN.

$$Z = \sum_N Q(N, V, T)e^{-\gamma N}$$

And γ we have already discussed, it relates to the chemical potential. In fact, this can be related to something that is known as the activity of the system. So we can represent this as something like-

$$e^{-\gamma N} = \lambda^N$$

And,

$$\lambda = e^{-\gamma} = e^{-\beta\mu}$$

This is what is referred as the activity of the system, right. So we can also go back to thermodynamics and find the different ways in which chemical potential is represented and all of this essentially come from the definition of the partition function.

So to conclude the discussion, what we have done in this particular case is that we have derived the partition function of grant canonical ensemble. We showed that the properties you could evaluate for the canonical ensemble, we can still evaluate in the grand canonical ensemble using more or less the same definition. In addition to that, you also have the average number of molecule that is meaningful in the case of grand canonical ensemble that also we can get from the partition function. And finally, grand canonical partition function is related to the canonical partition function.

In the last bit, what we can also show that the fluctuation in the number of molecules is also related to the partition function in pretty much the same way the fluctuation in energy was related to the partition function in there. All that will change is that now I am looking at N in place of E. So you will have-

$$\sigma_N^2 = \overline{N^2} - \bar{N}^2$$

And we can pretty much do the same math as we did for the σE^2 in the canonical ensemble and find that my σN^2 is given as simply-

$$\sigma_N^2 = -\frac{\partial \bar{N}}{\partial \gamma}$$

In fact, σE^2 is also related to the average energy with pretty much the same formula that we had for the canonical ensemble.

$$\sigma_E^2 = -\frac{\partial \bar{E}}{\partial \beta}$$

So in the similar way, we can find the fluctuation of quantities, also using the partition function and why I am saying that because this N bar and E bar can be evaluated again as the derivative of the partition function. So essentially, the fluctuations or the variance is characterized by the second derivative of the partition function in the non-canonical ensemble and the same was true for the canonical ensemble.

In the next class, what we will do is we will discuss what is known as an isothermal isobaric ensemble, in which case the control variables are the number of molecules, pressure and temperature. And in that case, until so far what we have done is the volume was constant, but in that case, the pressure will be constant or the pressure will be the control variable in that particular case and as you know we expect to get the Gibbs free energy as the thermodynamic function and we will have a partition function for that particular ensemble that will be clearly different from the partition function for ensembles we have done so far. But it will still be a generating function and where we are evaluating the average properties are still going to be the same in the isothermal, isobaric ensemble.

So with that I conclude here, thank you.