Foundations of Computational Materials Modeling
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Lecture 18
Introduction to Statistical Mechanics-3

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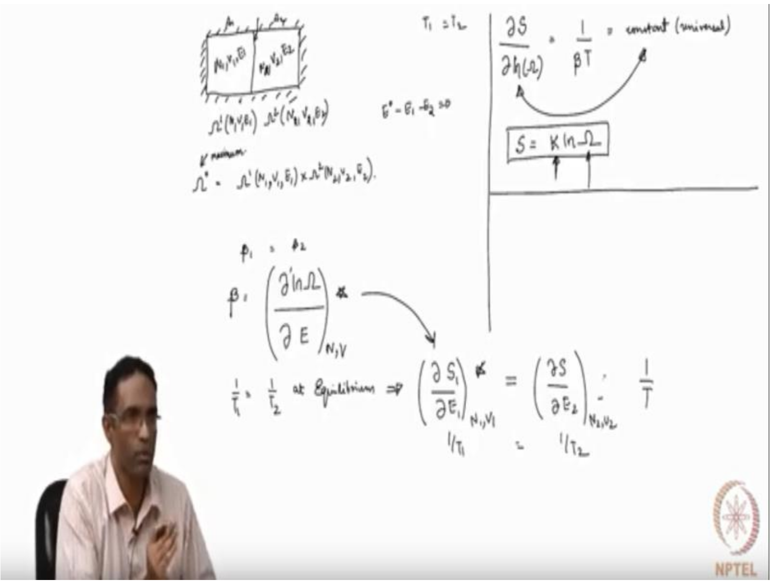

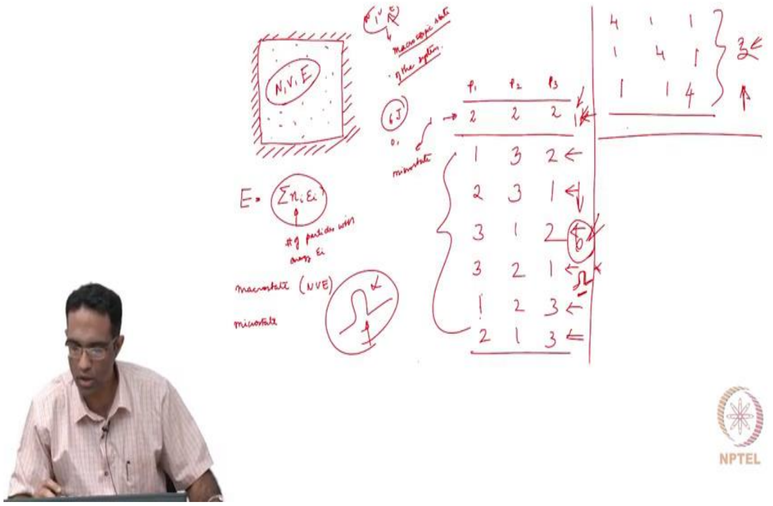

So, what did we do last class? Let us have a small recap of that, so we considered a system and we said that there is a thermal wall in between these two systems. N2 V2 and E2 are basically the number of particles, the volume and the corresponding energy of each of these two systems A1 and A2 and we talked about what is referred to as a complexion or a micro state which is basically the number of ways that this particular macro state can actually be reached by the system.

And I give you an example that, we had a box with say n different particles or three I think which we took an example of three different particles and we said that the total energy is six joules and we wrote down you know how many combinations or how many ways such an energy or such a macro state can actually be obtained. And so, what we saw was, there was only one way that this system could take the energy two to true, whereas there were six different ways where it could take the energy combinations one three and two.

So, each of these is actually a micro state, each of these is actually a micro state which corresponds to a certain given a macro state. That was basically to introduce the terminologies, micro state and macro state. Then, we went ahead and instead of trying to calculate what this number omega is going to be for a typical system, we tried to understand in what way if you knew that, the thermodynamics of the system actually automatically falls out.

So, for that we actually consider this consider the system right here, and we said that if omega 1 is the total number of ways you can have N1, V1, E1 and omega 2 is the total number of ways the system can be in N2, V2 and E2, then we did a thought experiment where we said that this would be a thermal wall where the system is capable of exchanging energy, but not the particles or not the and it would not move, it is not a movable piston or anything like that, and we asked the question, at what point of time will this energy transfer stop?

So, from classical thermodynamics, all of you immediately told me that T1 is equal to T2, but we do not want to do classical thermodynamics, we want to see how thermodynamics actually can fall out from the microscopic nature of the material that is there inside this, basically the gas or whatever you want to call it. So, and we said that this particular function becomes a maximum once equilibrium is reached, this omega naught becomes a maximum.

So what the idea or the philosophy behind that is the following, any system left to itself, if you put up it and leave it, then naturally the system evolves in such a way that it wants to maximize the total number of ways it can actually reach such system, reach that micro state, that is its natural tendency. Its natural tendency to do that is to maximize the number of ways it can actually attain that particular macro state. That is the something that I am telling you without proof I am asking you to accept that. Without accepting that can be difficult for us to do anything in statistical mechanics.

So, we accept that at equilibrium the number of the system will be in such a state that the total number of micro states that it has is going to be the highest for a given macro state. Therefore, we maximize this, but we have to subject it to a constraint that E naught minus E1 minus E2 is actually equal to 0 because this is actually a closed system, and during the process of exterminations, we derived a condition for this to happen as beta 1 should be equal to beta 2, where beta 1 or beta is actually equal to dou non-omega by dou E keeping the number of species and the volume actually a constant.

And then we had to invoke classical thermodynamics to see what relationship this omega maybe having to the real thermodynamic variables that we are acquainted with, and so we said that beta 1 should be equal to beta 2 or 1 by T1 should be equal to 1 by T2 at equilibrium, which from classical thermodynamics boil down to saying that dou S by dou E E1 at N1, V1 must be equal to dou S by dou E2 at N2, V2 and looking at this expression right here, and this expression right here which is equal to 1 by T or one this is equal to 1 by T1 must be equal to 1 by T2 at equilibrium.

So, looking at these two expressions right here, this one and this one, there was we wrote down dou S by dou log of omega, must be equal to 1 divided by beta T and that has to be a constant universal constant. So, this relationship essentially helps us write S which is one of the thermodynamic properties of the system, in terms of K which is constant the Boltzmann constant and omega, which is basically the number of ways the system can actually reach that particular state, S is equal to K log omega. So, we have derived S as a function of some micro state.

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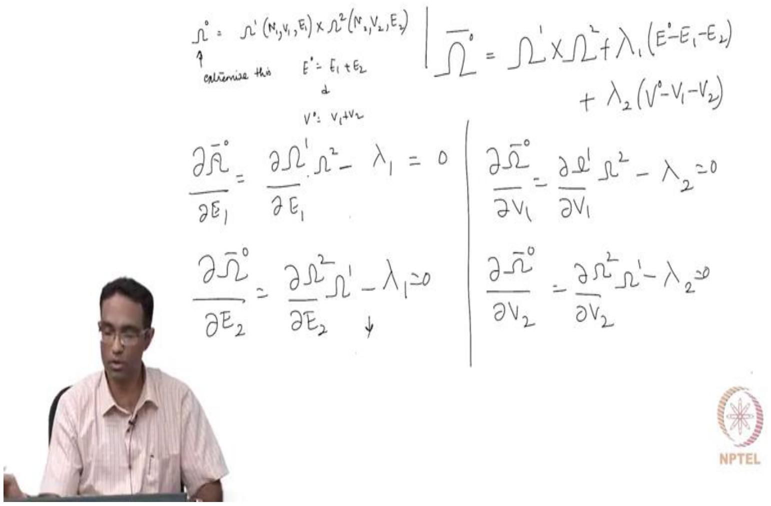


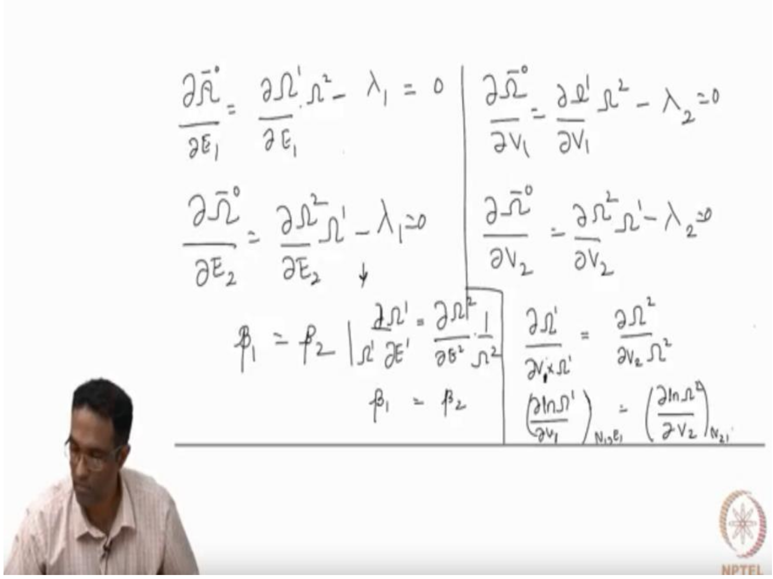
$\Omega^0 = \Omega^1(N_1, V_1, E_1) \times \Omega^2(N_2, V_2, E_2)$

extremise this $E^0 = E_1 + E_2$ & $V^0 = V_1 + V_2$

$\bar{\Omega}^0 = \Omega^1 \times \Omega^2 + \lambda_1 (E^0 - E_1 - E_2) + \lambda_2 (V^0 - V_1 - V_2)$

$$\frac{\partial \bar{\Omega}^0}{\partial E_1} = \frac{\partial \Omega^1}{\partial E_1} \Omega^2 - \lambda_1 = 0 \qquad \frac{\partial \bar{\Omega}^0}{\partial V_1} = \frac{\partial \Omega^1}{\partial V_1} \Omega^2 - \lambda_2 = 0$$

$$\frac{\partial \bar{\Omega}^0}{\partial E_2} = \frac{\partial \Omega^2}{\partial E_2} \Omega^1 - \lambda_1 = 0 \qquad \frac{\partial \bar{\Omega}^0}{\partial V_2} = \frac{\partial \Omega^2}{\partial V_2} \Omega^1 - \lambda_2 = 0$$



$$\frac{\partial \bar{\Omega}^0}{\partial E_1} = \frac{\partial \Omega^1}{\partial E_1} \Omega^2 - \lambda_1 = 0 \qquad \frac{\partial \bar{\Omega}^0}{\partial V_1} = \frac{\partial \Omega^1}{\partial V_1} \Omega^2 - \lambda_2 = 0$$

$$\frac{\partial \bar{\Omega}^0}{\partial E_2} = \frac{\partial \Omega^2}{\partial E_2} \Omega^1 - \lambda_1 = 0 \qquad \frac{\partial \bar{\Omega}^0}{\partial V_2} = \frac{\partial \Omega^2}{\partial V_2} \Omega^1 - \lambda_2 = 0$$

$$\beta_1 = \beta_2 \qquad \frac{\partial \Omega^1}{\Omega^1 \partial E^1} = \frac{\partial \Omega^2}{\partial E^2} \frac{1}{\Omega^2} \qquad \beta_1 = \beta_2$$

$$\frac{\partial \Omega^1}{\partial V_1 \times \Omega^1} = \frac{\partial \Omega^2}{\partial V_2 \Omega^2}$$

$$\left(\frac{\partial \ln \Omega^1}{\partial V_1}\right)_{N_1, E_1} = \left(\frac{\partial \ln \Omega^2}{\partial V_2}\right)_{N_2, E_2}$$

Next, we will see what now happens, instead of actually allowing this wall to be only thermal, only allowing the temperature to actually live for exchange of energy to take place. Let us see what happens when we also allow it to actually move. Let us see what happens when we allow it move. So then when we allow it to move, we still have omega not equal to omega 1 N1, V1, E1 times omega 2, N2, V2, E2, but now we have to extremize this, subjecting it to the constraint that and we have to extremize with respect to both the variables V and V1 and V2 also, because this piston can now move.

So, when we do this, what happens is the following. So, we get something that looks like maybe I will do it, so dou omega 0 by dou E1 omega bar because we need to find a composite function, so we will actually extremize a composite function omega 1 times omega 2 plus lambda 1 times E naught minus E1 minus.

Student: Sir, you in your right side there are three mistakes.

Professor: I am very sorry. So, 1 times omega 2 minus lambda 1 times E naught minus E1 minus E2 minus lambda 2 times V naught minus V1 minus V2. Now we have to extremise this function omega naught bar with respect to E1, E2, V1 and V2. Consequently, when we do that what happens is…

Student: Sir does the sign of lambda matters here plus or minus.

Professor: Does not matter, that sign can get absorbed into lambda. So, if you want to put up plus here, and then will get a minus here equal to 0 and then now you need to still differentiated with respect to V1 and V2 and that will give you.

So, this aspect continues to tell you what, this one this condition here we will continue to tell you that beta 1 should be equal to beta 2 for equilibrium, this is that is what, are you able to follow that? From here how you get here, is nothing but you know dou omega 1 by omega 1 times or 1 by omega 1 or dou omega 1 by dou E1 equal to dou omega 2 by dou E2 into 1 by omega 2 which can be written in the terms log like I pointed out last class, which turns out to be beta 1 is equal to beta 2.

This one turns out to be dou omega 1 by dou V1 times omega 1 is equal to dou omega 2. Now, this is again dou log of omega 1 with respect to dou V2, but this time clearly during the process of differentiation, you have kept the number of particles and the energy fixed.

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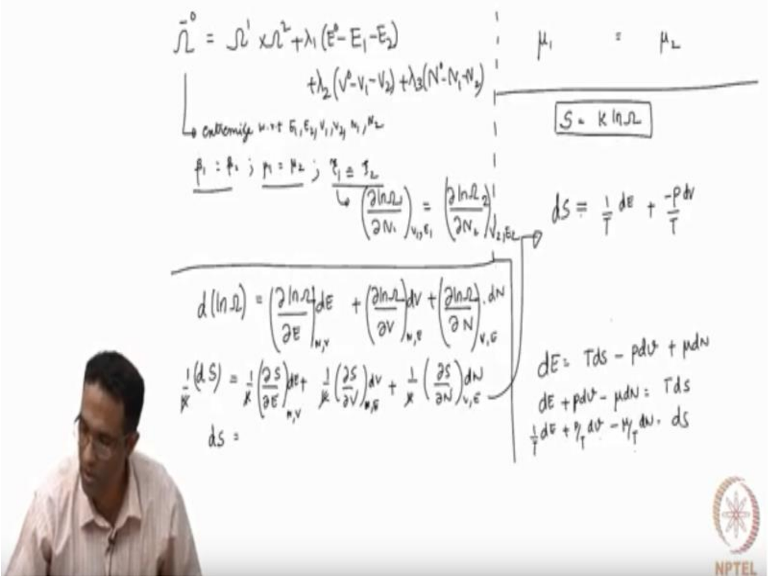

$$\bar{\Omega}^0 = \Omega^1 \times \Omega^2 + \lambda_1(E^0 - E_1 - E_2) + \lambda_2(V^0 - V_1 - V_2) + \lambda_3(N^0 - N_1 - N_2)$$

→ extremize w.r.t $E_1, E_2, V_1, V_2, N_1, N_2$

$\beta_1 = \beta_2$; $\mu_1 = \mu_2$; $\xi_1 = \xi_2$

$$\left(\frac{\partial \ln\Omega_1}{\partial N_1}\right)_{V_1,E_1} = \left(\frac{\partial \ln\Omega_2}{\partial N_2}\right)_{V_2,E_2}$$

$\mu_1 = \mu_2$

$\boxed{S = k\ln\Omega}$

$$dS = \frac{1}{T}dE + \frac{-p\,dV}{T}$$

$$d(\ln\Omega) = \left(\frac{\partial \ln\Omega}{\partial E}\right)_{N,V} dE + \left(\frac{\partial \ln\Omega}{\partial V}\right)_{N,E} dV + \left(\frac{\partial \ln\Omega}{\partial N}\right)_{V,E} . dN$$

$$\frac{1}{k}(dS) = \frac{1}{k}\left(\frac{\partial S}{\partial E}\right)_{N,V} dE + \frac{1}{k}\left(\frac{\partial S}{\partial V}\right)_{N,E} dV + \frac{1}{k}\left(\frac{\partial S}{\partial N}\right)_{V,E} dN$$

$dS =$

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

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

$$\frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN = dS$$

This one, let us call it as some, so at equilibrium, if the pistons are allowed to move, then the condition that we must have at equilibrium is this mu1 must be equal to mu2 where mu1 is basically dou log omega 1 by dou V1 and dou log omega 2 by dou V2. In a similar spirit, now let us not have the membrane, only exchange energy, it is allowed to move in addition to that I am going allow it to be permeable so that it can also exchange the species. That means that, two species gas N1, N2 can actually intermix once the, so I remove this constraint also, the only constraint that was now present is that that is impermeable to the movement of the molecules.

Now, I remove that constraint also and we see what condition that brings about, and then later on just like all we related beta 2 temperature, we will see what this mu1 and mu2 is going to be, so obviously it is going to be related to pressure and the chemical potential. So here what happens? You do exactly the same thing, I am not going to repeat the entire derivation. You do exactly the same thing with this as the composite function, obviously N naught is basically the total number of particles which should be fixed because it cannot move out of the box.

So, now you have to extremize this with respect to E1, E2, V1, V2, N1, N2. Now we already did with respect to E1, E2, V1, V2 and we got the following results. So we should have beta 1 should be equal to beta 2 and we should have, say mu1 must be equal to mu2 and now this one will essentially have some C1 equal to C2 and as you can guess this C1 is supposed to be dou log omega 1 by dou N1 keeping the volume and the energy fixed and V C2 is going to be dou log 2 by dou N2, V2, E2.

Now this suffix 1 or super fix 1, do not get confused, there is nothing to get confused there, so whether I write it below or above it just omega 1, please do not I I find it hard to keep track of that I wrote the previous super fix so omega1 is omega1 whether 1 is appearing as a super fix or as a suffix.

So, now how do these things actually related relate to actual thermodynamics? So, in order to see that, let us now accept only one thing, we just say S is equal to K times log of omega, this is known now, we showed that from the first exercise. Now let us write d of log omega, omega is now a function of N V and E so this becomes dou log omega by dou E into dE plus dou log omega by dou V into dV dou log omega by dou N into dN.

Obviously, here I am keeping the other two variables constant. So, if I am dou E means I am going to keep the number and volume constant, here I am going to number and energy constant, here I am going to keep the volume and the energy constant. So, now so I know that S is equal to K log omega, so this actually can be written in terms of my entropy, so this is S over K so d of S over K is equal to this again. So, 1 over K S by dou E plus 1 over K times dou S by dou V dou N plus.

So, what was dou S by dou E from our initial analysis? Dou S by dou E was dou log omega or dou, this one is what? Dou S by dou V from classical thermodynamics? 1 by P, is it 1 by P isn’t it minus P dV by T, you will get a 1 by T over there also. Let us write down the expression and derived from that, so the dE is equal to Tds minus Pdv plus mu dn.

So you have the dE plus Pdv minus mu dN is equal to Tds or 1 by T into or 1 by T into dE plus P by T into dv minus mu by T into dN is equal to dS, which means dou S by doe E at constant N and V is actually equal to 1 by T and dou S by dou V at constant N and E is actually equal to P over T, is that right? And dou S by dou N at constant V comma E is actually equal to minus mu over T.

So, if you compare these expressions, if you compare these expressions to this and if you compare these expressions to your mu1 mu2 and C1, C2 what do you get? So, you get so dou S was so from here, let us take this expression here, which implies, so what is this? Dou log K into dou log omega by dou V was what was actually our mu or mu was nothing but P divided by K times T.

So, if you have mechanical equilibrium, then you have mu1 equal to mu2 or P1 by KT1 equal to P2 by KT2, but at equilibrium, we have already shown that T1 is equal to T2 which essentially implies P1 is equal to P2. So, both the whole idea here is that both from the by considering omega or by considering entropy, you are essentially getting the same results that the systems the same conditions that the system should satisfy in order to have equilibrium, that is the whole idea here.

In a similar spirit, if you do it for the other variable, you would get mu1 equal to mu2 or mu by KT is equal to mu by KT mu1 by KT1 should be equal to mu2 by KT2, since T1 is equal to T2 you will have mu1 is equal to mu2, is that clear? So, what follows from this whole exercise is, if you knew your omega, the total number of complexions or how it is going to vary with the macro state specified for the system.

Then it is possible for you to derive the entire thermodynamics from it by just taking by doing S is equal to K log omega and then taking the appropriate derivatives to get the pressure, to get the temperature and to get the chemical potential, but you should know how the omega is as a function of N ,V and E.

Right now, we are not yet seen how this omega looks or what value it should have, but even without that, we were able to accept one basic postulate and derive the entire thermodynamic from it. So right now, do you have any questions? Are there any questions that you have? Is this clear?

This is a chemical potential mu, that is a a good point. So, what else, can we use all the chemical potential? Let us say mu mu dN, in this expression, mu is a chemical potential, but here this mu is not the chemical potential. It is just term here dou log omega1 by doe V1, in fact it is closer more closely related to the pressure than the chemical potential, is that ok? Or is it? Maybe I can change it to alpha.

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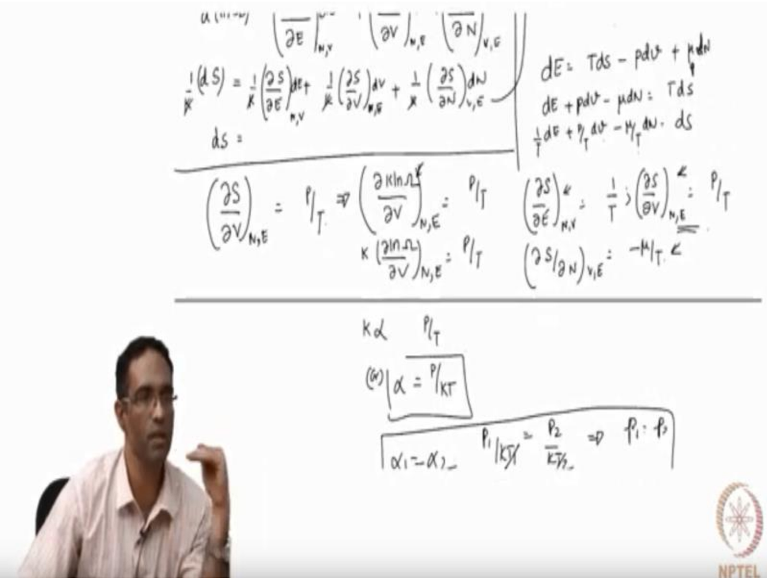

$$\frac{1}{\cancel{k}}(dS) = \frac{1}{\cancel{k}}\left(\frac{\partial S}{\partial E}\right)_{N,V} dE + \frac{1}{\cancel{k}}\left(\frac{\partial S}{\partial V}\right)_{N,E} dV + \frac{1}{\cancel{k}}\left(\frac{\partial S}{\partial N}\right)_{V,E} dN$$

$$dS =$$

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

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

$$\frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN = dS$$

$$\left(\frac{\partial S}{\partial V}\right)_{N,E} = p/T \Rightarrow \left(\frac{\partial k \ln \Omega}{\partial V}\right)_{N,E} = p/T$$

$$k\left(\frac{\partial \ln \Omega}{\partial V}\right)_{N,E} = p/T$$

$$\left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{1}{T};\ \left(\frac{\partial S}{\partial V}\right)_{N,E} = p/T$$

$$\left(\partial S/\partial N\right)_{V,E} = -\mu/T$$

$$k\alpha \quad p/T$$

$$(\alpha)\ \boxed{\alpha = p/kT}$$

$$\alpha_1 = \alpha_2 \quad p_1/kT_1 = \frac{p_2}{kT_2} \Rightarrow p_1 = p_2$$

Alpha 1 is equal to alpha 2 and consequently here I will have a mu will be equal to PT and I should expect alpha 1 equal to alpha, this is ok this is fine.

For the chemical potential equivalence, you will get, is ok? Are there any doubts here? Anything, any step that is confusing or something that you want me to repeat? By comparing the expressions that arise from the microscopic details like the omega, we are able to actually draw a similarity between what happens there and what happens in the classical thermodynamic sense, that is the whole idea.

So, basically the recipe for statistical mechanics is, if you find this omega, then you are basically done, but apparently the determination of this omega is not a very easy thing. It is extremely complicated, and it is possible for us to obtain analytical solutions for omega only for very simple systems like ideal gas and things like that, we will do that also. We will do it for an ideal gas and show you how you can actually get the ideal gas law by finding of omega for the ideal gas.