

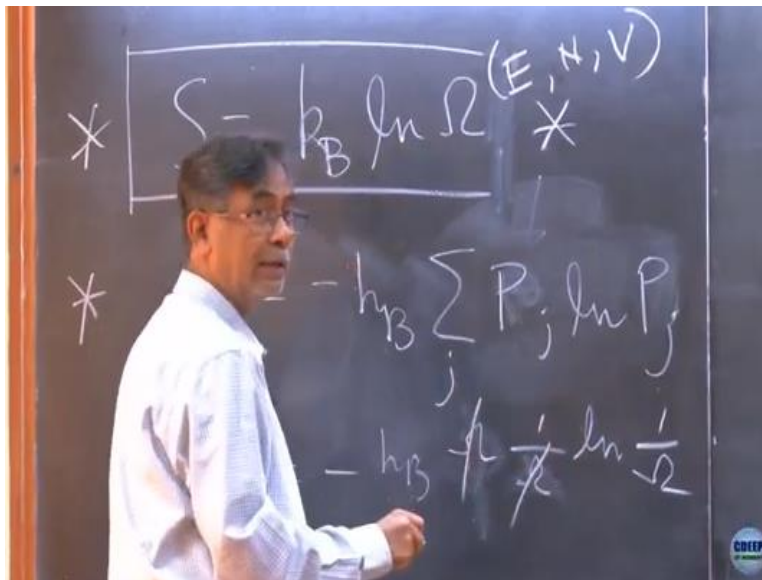
Basic Statistical Mechanics
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Lecture - 13
Thermodynamic Potential for Canonical Ensemble

In the continuing saga of statistical mechanics that we are trying to develop this course, we walk till now in the micro canonical ensemble and we start in the canonical ensemble we defined the partition function the canonical ensemble and what you are going to do now the very first we derived the most important equation of the canonical ensemble, and then we will go on doing some more of thermodynamics with canonical partition function.

So that required certain amount of calculations. So first thing to do that the generalization of micro canonical ensemble.

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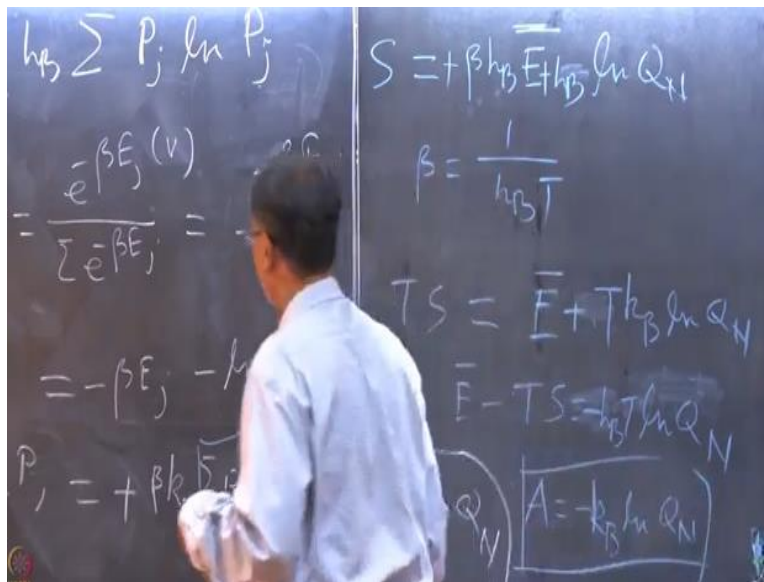
As I told you this is the most important equation where everything starts from, these are microcanonical and these are function of the E, N and V. The generalization of that to canonical ensemble is this thing is the entropy they come out of the sum then you have this is 1 over Ω sum gives this Ω , so this becomes $-k_B$. So now this sum gives Ω this Ω cancels this Ω $\ln 1$ Ω is 0.

$$\begin{aligned}
 S &= -k_B \sum_j P_j \ln P_j \\
 &= -k_B \Omega \frac{1}{\Omega} \ln \Omega \\
 &= k_B \ln \Omega
 \end{aligned}$$

So this is the generalization of this to canonical ensemble where probability of energy level P_j . They should be regarded as equivalent to each other so this is the again you have to regard as best way as I said regard it as a none such or starting point of statistical mechanics does to be two postulates.

And one should be clear about it that every great theory or every framework starts with certain postulates and certain assumptions. The validity of them are seen by the agreement of the predictions with the experiments just like in quantum mechanics we start with Schrodinger equation and all kinds of things that we assume one of the major thing is the P square it is this one operator representation in coordinates. Now so I will just do this upstairs and I told you I will derive what is the most important thing of the partition function.

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So that is, I mentioned that nobody has an explanation why k_B is what value that it takes.

$$P_j = \frac{e^{-\beta E_j(V)}}{\sum_j e^{-\beta E_j}} = \frac{e^{-\beta E_j}}{Q_N}$$

Now I am going to take ln of that this I mentioned meet in the morning then I get $-\beta E_j - \ln Q_N$, do not be too much concerned about the subscript and all these things but canonical partition function which in VT ensemble you always put N as a subscript and then write TV or VT here.

$$\ln P_j = -\beta E_j - \ln Q_N$$

$$-k_B \sum_j P_j \ln P_j = +k_B \sum_j P_j \beta E_j + k_B \sum_j P_j \ln Q_N$$

$$S = k_B \beta \bar{E} + k_B \ln Q_N$$

$$S = \frac{\bar{E}}{T} + k_B \ln Q_N \quad \left(\beta = \frac{1}{k_B T} \right)$$

$$\bar{E} - TS = -k_B T \ln Q_N$$

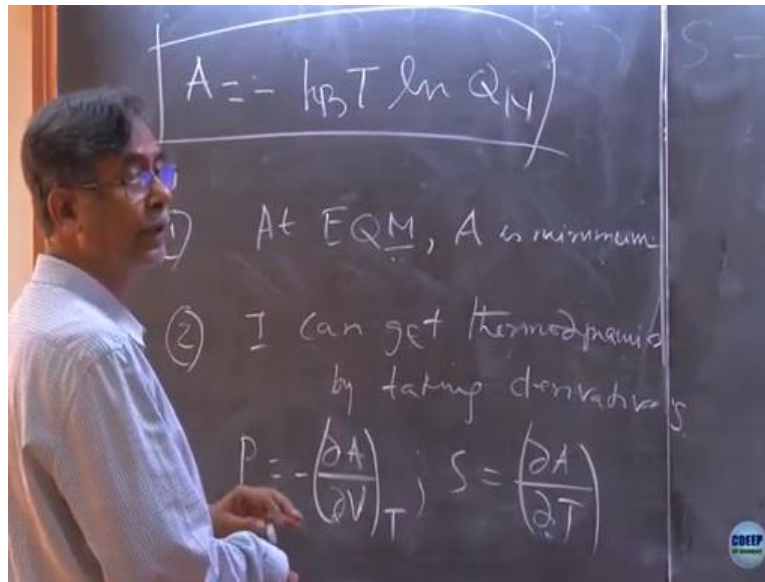
$$A = -k_B T \ln Q_N$$

I tend to write TV but many books like VT I think there is not much in it. Now I want to go over here so I multiplied by P_j , I sum over j then I multiplied by $-k_B$ this my right hand side now. I do that here, I do $-k_B$ and another $-k_B$ so $\beta k_B P_j E_j - P_j \ln Q_N$. So this is my S left-hand side for entropy S is equal to now $P_j E_j$ sorry you should have told, you tell me when I am writing anything wrong $P_j E_j$ because I sometime you think ahead or you do not think your hand thinks ahead and so this is E average $-\beta k_B E$ average and this is $-\ln Q_N$.

Now $-k_B$, I have multiplied by k_B so this also become $+$, I have multiplied by $-k_B$ this is the whole thing that I multiplied to this quantity so $-k_B$ and this $-k_B$ so I will have a $+k_B$ and both and this will also be $+$, now so I will show a little later but for the time being I put the value and work it out a little later there is not much more detail derivation, so when I do that my βk_B is $1/T$ so I get $TS = E$ average $+ k_B \ln Q_N$.

I bring this on the right hand side and these on the left and these on the right so $E - TS = -k_B T \ln Q_N$, when I do $\beta k_B T$ βk_B is $1/T$ $1/T$ goes there you guys are not following $1/T$ comes here. You might as TS then $k_B T -k_B T$ this is the problem this $\ln Q_N$ because this transfer here these goes here that goes there so $E - TS$ is the free energy $A = -k_B T \ln Q_N$. So this is the as I have been saying this is the most important just like we had entropy equal to $k_B \ln \Omega$ in canonical partition function.

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So $A = -k_B T \ln Q_N$ the most important relation in the canonical partition function and probably can be considered as the most important relation in the Statistical Mechanics because this is the one we use. Why this is so important? As to qualify that statement, the most important the reason is that beauty of Helmholtz free energy there is any property of Helmholtz free energy which can you tell me what is the unique property?

So this derivation is smooth and nice and bit elegant at the end of the day this nice little and smooth easy flowing derivation gives us this great result. Now I am asking you, you must tell me (since all of you have done some posts in statistical mechanics) why this is so useful and so universally used? In all theoretical calculation and analytical calculation we go Helmholtz free energy.

Analytical calculation unless you have kind of inhomogeneous systems and phase transition we do not go to grand canonical, so you have to now tell me why . Yeah, that is a good point is a minimum, it is the same it is actually if it is not there as I told you I should have in front of it that is the maximum, so basic condition is the maximum because the entropy is maximum, it follows from the same thing.

So one property is that at equilibrium A is minimum, we always use that. That is used in all theories for example Landau phase transition so there is and one more very important property that is why it because that is shared by all partition functions because partition function has to be maximum. It is the partition function which is maximum because partition function is the weight of the system so the condition is the partition function is the maximum, like entropy is the maximum.

Now there is something extremely important. Absolutely, but there is more general than that you can get every property, equation of state, entropy, pressure by just taking derivative. It is far easier to take derivative because when you try to do integration like equation of state is far more complicated so you can get thermo dynamic properties. So uniqueness or unique advantage of this one is that I can get thermodynamics by taking derivatives.

$$P_A = -\left(\frac{\partial A}{\partial V}\right)_T \quad S = -\left(\frac{\partial A}{\partial T}\right)_V$$

Like as you just said P_A equal to $-dA/dV$ this board we can get entropy S from $-dA/dT$, then I can get compressibility by second derivative, specific heat by second derivative. So again tell loudly $-dA/dV$ is interval has two be positive free energy increases with temperature it should be a positive. But you are right there should be T in front of it not the sign that I might be missing so check that.

But this is a very, very important as I said that much of the things that we do essentially already for Monte Carlo simulations or all these things are essentially attempted to get the partition function. Now we will go and do that derivation which is a little bit messier and with this blackboard which is small and I need space now I am going to show that β is 1 over $k_B T$.

Remember β is a one of the undetermined Lagrangian multipliers in the constraint, β comes with the constant of energy (very important to remember). Alpha came with the number on the total number sum over in energy level E_j sum over in j of all these systems because I went from canonical to micro canonical by building a super system which is micro canonical.

So in my super system which is microcanonical each member is canonical then each member of my canonical which has a different energy E_j that operation allows me to define a distribution P_j there are many layers here and in that process I had to put when I maximize the Ω the total number of ways I introduced Lagrangian method of undetermined multipliers β is one of the undetermined multipliers.

So what is that we need to find now? And as I said this is a little bit messy so I did it today but I much warn you that I am still missing a factor of T , so now we are going to do this determine the Lagrangian undetermined multiplier and as I told you, little messy and in this respect I want to make a comment of the kind of mathematics we do in statistical mechanics and the kind of mathematics we do in quantum mechanics. You guys are quite familiar with the mathematics we do in quantum mechanics.

Because as I told in the morning that is whatever I do I will end up with a partial differential equation $d^2/dX^2 \chi$ and then $+V X$ equal to $d \chi / dX_i$ and that that then is a partial differential equation which we solve this put in the boundary conditions. And these are depending on what $V X$ you have they either become hermite polynomial or Legendre polynomial or Laguerre polynomials and boundary condition is the quantity that makes your energy levels discrete.

It is very important to know that and that is the hallmark of quantum mechanics. So it is essentially solving these differential equations and then when you go to numerics again you solve the same differential equation with a potential you may introduce a grid and when you want to be excite a states then you know then you have to complexity because you have to deal with the nodes and many individual function and many other things with derivative taking the second derivative.

That you have to do of the wave function makes these numerical calculations demanding, that is why an army of chemists physicist do not do this kind of game anymore. But if you chemists are doing it because of the molecules and molecules the wave function changes rapidly across the bond and all these things for your problem. In statistical mechanics however the mathematics is a different nature we do have many partial differential equation.

We solve but one of the things that we work with probability, and many times you need to like we had the confusion in the morning how the sample phase comes. So much of the mathematics is conceptual and because it is probabilistic and many times the mathematics is rather subtle and one major thing that is in statistical mechanics in this subject is highly mathematical, that is one thing you have to know why people in particular in chemistry find difficult to do statistical mechanics analytical work because it is highly mathematical.

Very soon you will land in doing the complex analysis of the partition function in the complex plane, which gives rise to the singularity, even at that level you will see there are lot of manipulations with the probability theory which are kind of tricky. So with this prelude, I start with the derivation of β .

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To show: β

$$P_j = \frac{e^{-\beta E_j}}{\sum e^{-\beta E_j}} = \frac{e^{-\beta E_j}}{Q_N}$$

$$\sum E_j P_j = \frac{\sum E_j e^{-\beta E_j}}{\sum e^{-\beta E_j}}$$

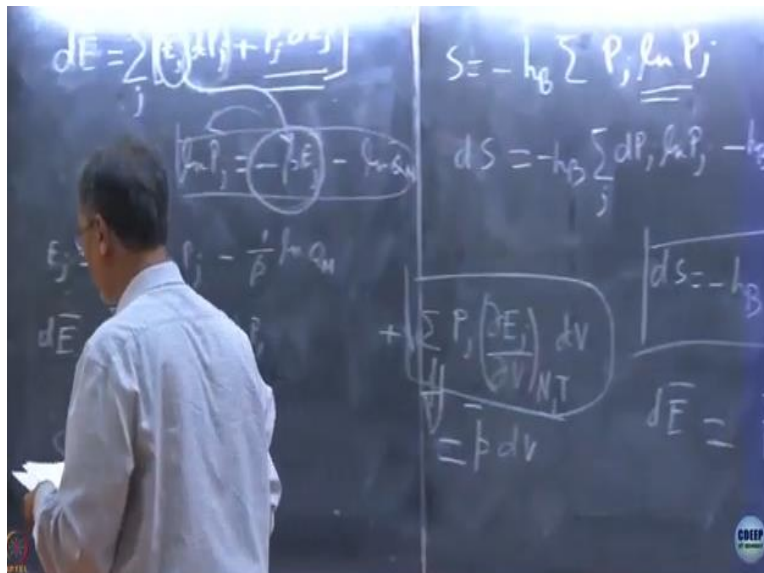
$(E_j, dP_j + P_j dE_j)$

So I start again with $P_j e^{-\beta E_j}$ and I have little bit difficulty with a limited portion of the board but I probably will use the other side now but then I cannot see a problem that side to this side. So I start again the same way I did before. This is given there also but I am not too satisfied with the one the sequence of equation that is given there. Because book is problem is that you go back over equation 5.1 and then 5.10 and that is a little difficult.

$E_j P_j$ so all right, correct? Because I have the $P_j E_j$ sum over J sum over J everywhere now I do one thing you realize both in the micro canonical and grand canonical ensemble there also we start with S . Then we made dS because all these thermodynamic Euler equations we went to differential form of the Euler equation the differential form of the Euler equation because we want to use essentially fundamental what I call the fundamental equation.

Which is the fundamental relation of thermodynamics is $dE = TdS - PdV$ that kind of relations that comes in, so dE this quantity it is little tedious but need to be done. Now this is the relation we will need I am going to put it upstairs.

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Now I go to definition of P_j that I had the P_j equal to e to the power $-\beta E_j$ by partition function

$$P_j = \frac{e^{-\beta E_j}}{Q_N}$$

I take the log of that so $\ln P_j$ so this equation let me write down then I will erase that a P_j definition is e to the power $-\beta E_j$ by Q_N I take logarithm of that I get $\ln P_j$ equal to $-\beta E_j - \ln Q_N$. So E_j is, I bring it on that side one of the main thing is to do a long analytical calculation that you continuously clear your board.

Or you are doing calculation continuously change your sheet of paper go from one to the other, this is one of this I see the students make the mistake they continue working on the same sheet of paper and do all these things and they get confused. You have to keep your things very clear. So E_j then from here I bring it on the other side take on the other side so then I divide by β so -1 over $\beta \ln P_j$, so this has come to this side this remains so -1 over $\beta \ln Q_N$.

So now there is a D and there is a E_j so what I am going to do; I am going to put this E_j this value of E_j here. So, I now going to -1 over $\beta \ln P_j - \ln Q_N$ into dP_j . Let me write down a little bit more clearly this quantity dE sum over $j - 1$ over β sum over let me put dP_j this is dP_j in front so dP_j and then $E_j P_j - 1$ over $\beta \ln P_j - 1$ over $\beta \ln Q_N$, there is dP_j in front. Now I have -1 over β .

So I have this $\ln P_j - \ln Q_N$, so dE is E_j . I have 1 over it so I put the E_j here, so I have be careful about the sign that $\ln Q_N - 1$ over $\beta dP_j \ln Q_N$. So I have dE this is the $P_j dE_j$ I have put in and this is $P_j dE_j$ and so I have $\ln P_j$. so I solved from that for E_j and E_j will come on the left hand side and that will bring one over β on the other two terms. Now I have to put this E_j back here so then that I put E_j both of them on over β .

So I have this one over $\beta \ln P_j$, $\ln P_j$ is this thing there β so there is a β coming here. You have taken it out. That is correct? That one over β stays here Now what happened? On the right hand side $dP_j \ln Q_N$ is. So $\ln Q_N$ is there that I think is. Very important thing that I am going to do now P_j equal to 1, so now that means dP_j equal to 0, correct? So that means this term is going to be 0.

But I have to keep remembering that. So now I have the following relation now that dE , I still have $P_j E_j$ so $dE dP_j$. You guys should have told me I still have these quantity. So E_j is this but this is still there. So dE is this term is there but dE this term is correct because I am replacing $\ln P_j$ I have replaced $\ln P_j$, so what I have done I have touched this term, how I touched this term? I have replaced this thing I got from this but I have left these untouched.

So d will not come with any β or anything it is just $P_j dE_j$, no now this term dE_j can be written as $dE_j dV$ at constant N you can if you want constant $T dV$. Now so this now let me work it to that this is the quantity you know micro canonical we have seen either when energy level is changing

with volume that is the partial pressure P_j . So we have $P_j dV$ now this is the definition of average pressure.

So I have this term done is $+ P$ average dV , so this is taken care of so this quantity is equal to PdV that part is done. Now I have to take care of this part, now we know that dP_j the $\ln Q_N$ that this term has when dP_j is equal to 0. So I am left to it $dP_j \ln P_j$. Alright? Now on my entropy I am going back to my again the derivation of entropy little $-k_B P_j \ln P_j$. So my I now have to work on this equation.

I have to work on this term and then S equal to this quantity, so now dS is equal to $-k_B$ I take B inside so, of the sum I get $dP_j \ln P_j - k_B P_j$ one over P_j . I work on that and get dP_j . Yes all right $\ln P_j$ I work on that I will get one over $P_j dP_j$. So they cancelled I have sum over dP_j I already showed sum over since P_j equals to one conservation condition sum over dP_j equal to 0. So these one drops out.

So I am now $dS = -k_B dP_j \ln P_j$. Now I already have the following relation here, that $dP_j \ln P_j$ is dE and $dP_j \ln P_j -- +$ I already had dE and β , so my dE is and there is one more term which is this term, which is PdV . So I have this is outside sitting outside. I have here $dE = PdV$ and then I have that term $+ 1$ over βP_j 1 over term $dP_j \ln P_j$. $\ln P_j dP_j$. $dP_j \ln P_j$ is dS by k_B , so that I now get $dE = PdV$ and $+ 1$ over β .

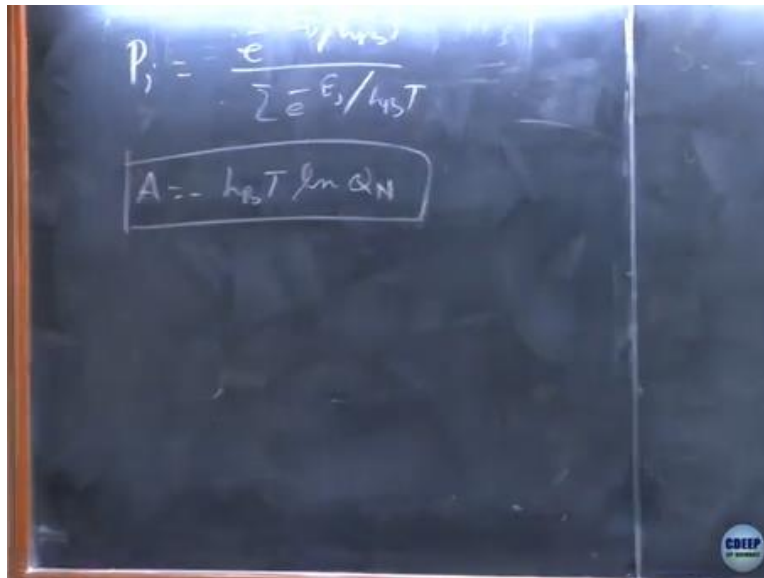
Then I have a $-dS$ by k_B . dS k_B that is okay, no it is not that simple, so this becomes so I do not know what is beta remember that. I do not know what is beta so I have $-\beta k_B dS$. Now I compare with these thermodynamic relation dE equal to $PdV - TdS$ correct!. One over beta k_B now yes that moment so now compare that there then I get 1 over beta k_B equal to temperature. And that means beta equal to 1 over $k_B T$.

So that, the my second Lagrangian multiplier undetermined multiplier that one determines by going through these somewhat elaborate forces. Is that clear now? So that is actually fairly neat derivation but you know this is what I was gave this little lecture on mathematics in statistical

mechanics that there is a lot of interplay with probability theory and the conservation of probability.

So all these things you have to bring in and do that, so now we can go back so we have put $\beta = 1/k_B T$.

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$$P_i = \frac{e^{-E_i/k_B T}}{\sum_j e^{-E_j/k_B T}}$$
$$A = -k_B T \ln \Omega_N$$

Now I can write by Boltzmann distribution at P_j and then now complete my proof that I had started with $-k_B T$ then when I prove this thing I did not tell you because I proved as one over beta I did not tell you that bit is one over $k_B T$ so then this is the most important relation in the canonical partition function.

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Using Eq. (5.33) for dS in the above equation, we find

$$\beta = \frac{1}{k_B T} \quad (5.37)$$

Use of the canonical definition of P , into the above equation, and simultaneous use of the well-known thermodynamic relationship between entropy, internal energy and Helmholtz free energy, when number of particles are fixed, gives

$$S = \frac{E}{T} + k_B \ln Q = \frac{E}{T} - \frac{A}{T} \quad (5.38)$$

This gives an important relation between Helmholtz free energy and the canonical partition function

$$A = -k_B T \ln Q(N, V, T) \quad (5.39)$$

This equation serves as one of the most fundamental and useful equations of Statistical Mechanics!

So these two proofs that we did kind of complete the major part of canonical partition function but they take $1/k_B T$ and then this is the one. I did first because it is very neat I did not want to bring the most important equation at the end of this rather elaborate and a bit tedious derivation so that is what I did these derivation first in the form of $k_B T \ln Q_N$ and we already discussed the properties of this partition function.

So then the important thing that we already discussed the beauty is that we can get how come you were right now there is a - sign. If I increase temperature either free energy increases, how much free energy know $-k_B T$ is there that probably why because if I increase temperature then partition function would increase, but the free energy decrease. So that is I always think in terms of partition function because that is the weight of the system.

So yes there is a- here as you pointed out and so that essentially this is the entropy this is the pressure and this is the beauty of canonical partition function this is the canonical partition function done, so you have done micro canonical we have done canonical.