Foundations of Computational Materials Modelling
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Canonical ensemble; Partition function
Lecture 24

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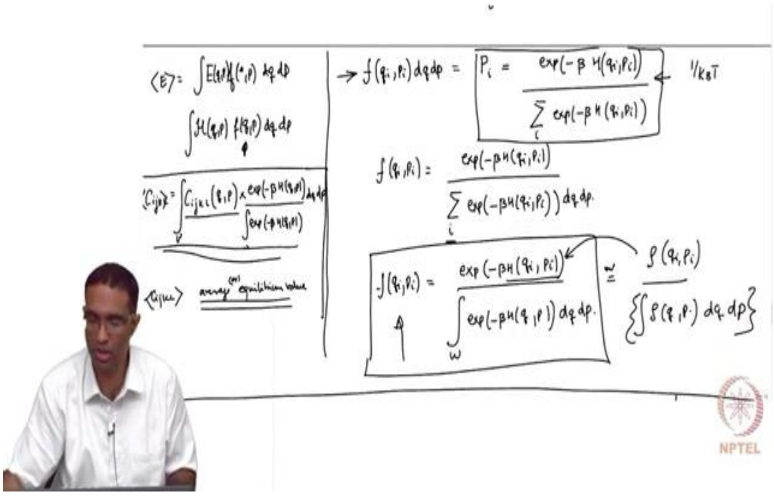

Trying to see if we can have an alternative way of deriving this expression here, what is the probability that the energy is E i? We made some intuitive arguments and showed that, it turns out to be this expression right here where beta is basically 1 by kb T, Boltzman Constant time temperature.

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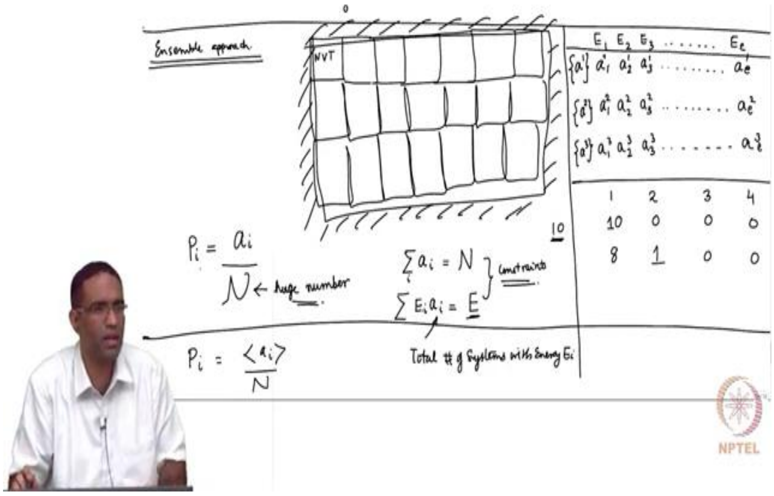
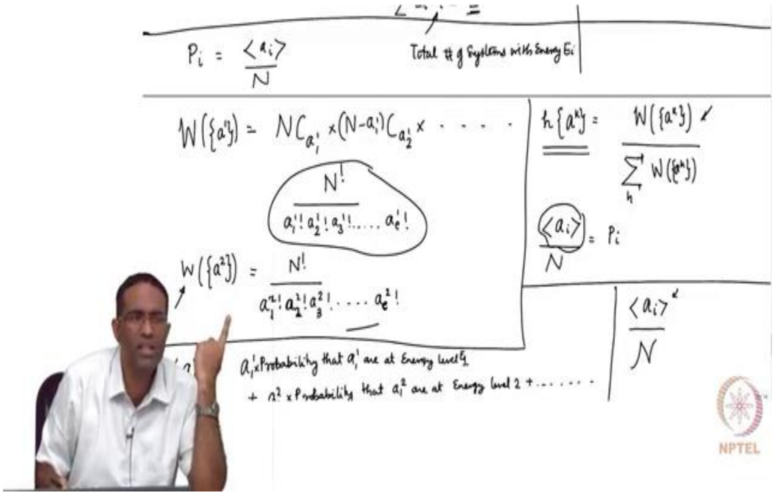




$P_i = \frac{\langle a_i \rangle}{N}$

Total # of Systems with Energy Ei

$W(\{a^1\}) = {}^{N}C_{a_1^1} \times {}^{(N-a_1^1)}C_{a_2^1} \times \cdots$

$\frac{N!}{a_1^1!\, a_2^1!\, a_3^1! \cdots a_e^1!}$

$W(\{a^2\}) = \frac{N!}{a_1^2!\, a_2^2!\, a_3^2! \cdots a_e^2!}$

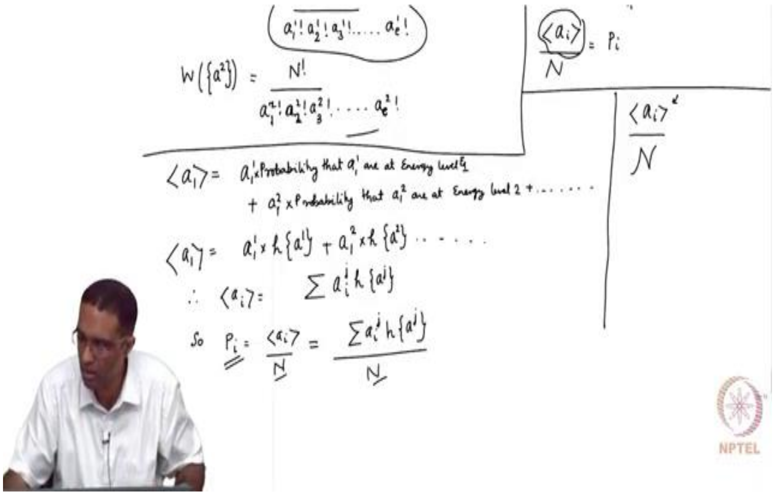
$h\{a^k\} = \frac{W(\{a^k\})}{\sum_h W(\{a^k\})}$

$\frac{\langle a_i \rangle}{N} = P_i$

$\frac{\langle a_i \rangle^2}{N}$

$a_1^1 \times$ Probability that a_1^1 are at Energy level E_1

$+\ a^2 \times$ Probability that a_1^2 are at Energy level 2 + ...



$\frac{N!}{a_1^1!\, a_2^1!\, a_3^1! \cdots a_e^1!}$

$W(\{a^2\}) = \frac{N!}{a_1^2!\, a_2^2!\, a_3^2! \cdots a_e^2!}$

$\frac{\langle a_i \rangle}{N} = P_i$

$\frac{\langle a_i \rangle^2}{N}$

$\langle a_1 \rangle = a_1^1 \times$ Probability that a_1^1 are at Energy level E_1

$+\ a_1^2 \times$ Probability that a_1^2 are at Energy level 2 + ...

$\langle a_1 \rangle = a_1^1 \times h\{a^1\} + a_1^2 \times h\{a^2\} \cdots\cdots$

$\therefore \langle a_i \rangle = \sum a_i^j h\{a^j\}$

So $P_i = \frac{\langle a_i \rangle}{N} = \frac{\sum a_i^j h\{a^j\}}{N}$

And we were trying to now we were doing something else were we took a different approach were we considered various ensembles each of which are in the same macro state, however they are all in a different micro state and they are all exchanging energy with each other and they are satisfying these constraints.

Summation over a i is equal to N, were N is the total number of ensamples in the system and summation over E i times a i is equal to E and a suffix i means the total number of systems with energy, E i. That is what it means. A i is .... E i. So, then in order to actually get this probability, what we essentially need is, we need the average number of systems with energy E i divided by the total number of ensembles in the system and that would essentially give us P i.

So, A i is essentially given number of average number of systems with energy E i and if you divide it by the total number of systems present here, you would get the probability that the system has energy E i., okay? In order to do that, we first started enumerating the various possible distributions that the system can have. So, E1, E2, E3, E4 and so on are the various energies that it can have until Ee.

Then a 1 which is represented through this flower bracket so, flower bracket a 1 means, a particular distribution, a particular way by which the system can achieve the energy,... The associated energy that it is supposed to have. That is this energy. That is this energy, right?

So, you can have a 1 1, the super fix 1 represents the, is the label for the distribution that I am talking about whereas the suffix here represents the energy level that is occupied by that system. So, a 1 1 means, in this example that we talked about here, it turned out to be 10 and in the second example, it turned out to be 8 and so on. Is this aspect clear so far?

So, this was okay. So, now what is the total number of ways you can achieve a certain distribution so, for example, what is the total number of ways you can achieve the distribution a 1 or the flower bracket a 1? So, that is nothing but, N ensembles taken a 1 1 at a time so, you have taken a 1 1 of these and put it in the basket of E1. The remaining has to be put in the basket of, a 2 1 has to be put in the basket of E2 and so on.

So, basically combination problem, right? So, is nothing but N taken a 1 1 at a time times N minus a 1 because you are you have removed a 1 1 samples times from this you are taking a 2 1 and putting it into energy E2 and you continue to do that, and this is what is what you will get, right? You have studied this in your lower classes, right?

Similarly, there is a different distribution, the total number of ways this distribution can be attained is given by that and you can keep going. Consequently, the total number of ways, the probability that you can get any one particular distribution is, total number of ways you can get that distribution divided by total number of ways all possible distributions can be realised, right. So, that is represent that probability is being represented by this h. h flower bracket a k means, what is the probability that I can get this distribution a k? That

$$\underline{\underline{h\{a^k\}}} = \frac{W(\{a^k\}) \checkmark}{\sum_h W(\{a^k\})}$$

is what it means.

Now, what do you want again reiterating the fact that what I essentially need is, the average number of samples or systems with energy E i divided by total number of systems will give me the probability that the system has energy E i. So, I need to find this out. How will I find this out? Let us take for example, the average number of systems with energy E1, average number of energy E1.

What would that be? That would be a 1 1 times the probability that I can have a 1 1 system at energy E1 plus a 1 2 times the probability that I can have a 1 2 systems with energy E1 and a 1 3 times the probability that I can have the system with energy I can have a 1 3 systems with energy E1 and so on.

Which is what I have written down here so, average number of systems in a 1 is nothing but a 1 1 times the probability that a 1 1 systems are at energy level E energy level 1 or E1, a 1 2 times the probability that so on and so on. So, now what is the probability that a 1 1 systems are at energy level E1? It is nothing but the probability that the a 1 distribution is realised. Is not it?

So, this is nothing but a 1 1 times h of a 1 plus a 1 2 times h of a 2 and so on. Therefore, the average number of systems with energy E i is nothing but a i j times h of a j and that if I divide by N, I get actually P i.

$$P_i = \frac{\langle a_i \rangle}{N} = \frac{\sum a_i^j h\{a^j\}}{N}$$

But still this is still not in the form that we saw previously, we are expecting to see the same expression right here, something like e to the power minus beta e divided by summation over all possible energy states exp, exponent minus beta e. That is what we are trying to see. But we still do not have it.

Now, what happens is that, we have to make the same arguments that we made several classes when we actually started statistical mechanics. What we said was, when the system is basically at equilibrium, there is one specific distribution of energy states that it would take such that, this that particular distribution has this number to be such a large value such a large value that for that special distribution, this h or the probability that the distribution is realised is very-very close to 1, right we made that argument, right, when we started talking about statistical mechanics.

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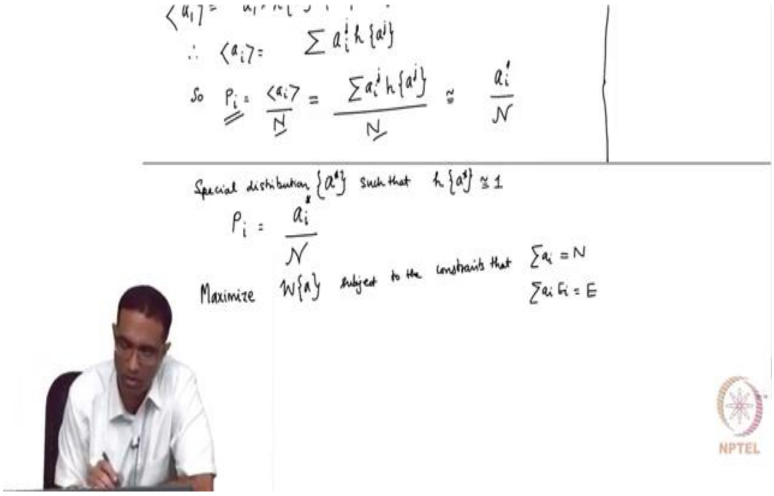


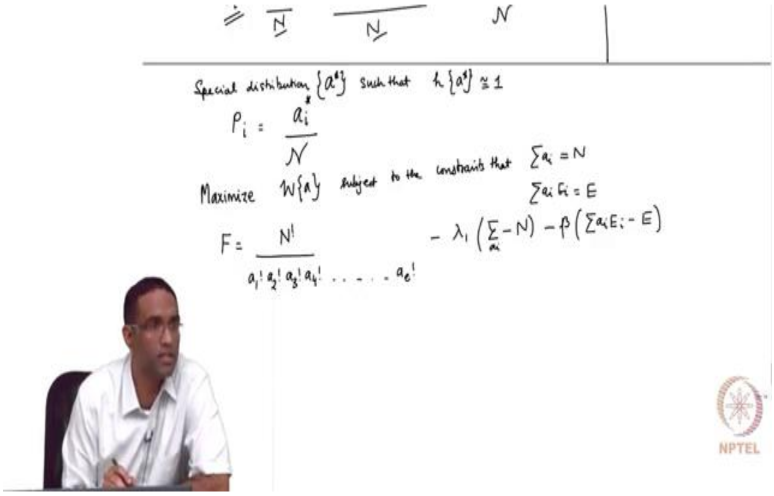
$$\therefore \langle a_i \rangle = \sum a_i^j h\{a^j\}$$

$$\text{So } P_i = \frac{\langle a_i \rangle}{N} = \frac{\sum a_i^j h\{a^j\}}{N} \approx \frac{a_i'}{N}$$

Special distribution $\{a^*\}$ such that $h\{a^*\} \cong 1$

$$P_i = \frac{a_i^*}{N}$$

Maximize $W\{a\}$ subject to the constraints that $\sum a_i = N$, $\sum a_i E_i = E$



Special distribution $\{a^*\}$ such that $h\{a^*\} \cong 1$

$$P_i = \frac{a_i^*}{N}$$

Maximize $W\{a\}$ subject to the constraints that $\sum a_i = N$, $\sum a_i E_i = E$

$$F = \frac{N!}{a_1!\, a_2!\, a_3!\, a_4! \ldots a_e!} - \lambda_1 \left(\sum_{a_i} - N\right) - \beta\left(\sum a_i E_i - E\right)$$

So, it so happens that, there is a special distribution a star such that, is approximately equal to 1 or very-very equal to 1 and all the other distributions are basically irrelevant or 0. So, for all practical purposes, we could consider P i to be only that special distribution because h of a star is actually equal to, close to 1.

Right, this is approximately equal to at equilibrium, all the other hs become 0 and there is one special distribution for which h of that distribution is close to 1. So, I have a i star divided by N, that would basically give me my equilibrium distribution,ok?. Now, the problem is, we still do not have this as a function of the energy of the system. But we can get it by performing a maximization, okay.

What we say is that, if the distribution that it takes is essentially the one that will basically maximize this quantity. If this number of ways can be achieved so large then this is a very large number and consequently that is almost close to the total number of ensembles present and the probability that it is seen is highest. So, what we have to do is, we have to maximize W of a, that means we have to find the number of systems in energy E1, number of systems in energy E2 in such a way that this quantity omega W of a is a very-very large number. So, what is, so that is we are working with that special we are trying to find out that special system, we are simply throwing out all the other systems because we know that they are going to be irrelevant.

There are better proofs to show that they are irrelevant and that is that it peeks that this distribution actually peeks about that special distribution and everything else is 0. But we are not going to do that in this class. So, we are just gone to maximize this. But we have to subject to the constraints that all the a i summation of all the a i must be equal to 1 and a i, E i must be equal to, must be equal to some E. So, so our composite function that we have to maximize is nothing but so, we have to maximize with respect to what? The a i’s, right, we have to find the value of a i, we maximizes this entire function. So, how would you maximize it? You take dou F by dou a i and equate it to 0 and keep dou a 1, for dou F by dou a 1, dou F by du a 2 and so on and equate it to 0 to find a condition that is necessary to maximize the function subject to these two constraints.

But the whole problem is when you are trying to maximize things with factorial, it becomes a problem right, unless you use what is referred to as the Stirling Approximation.

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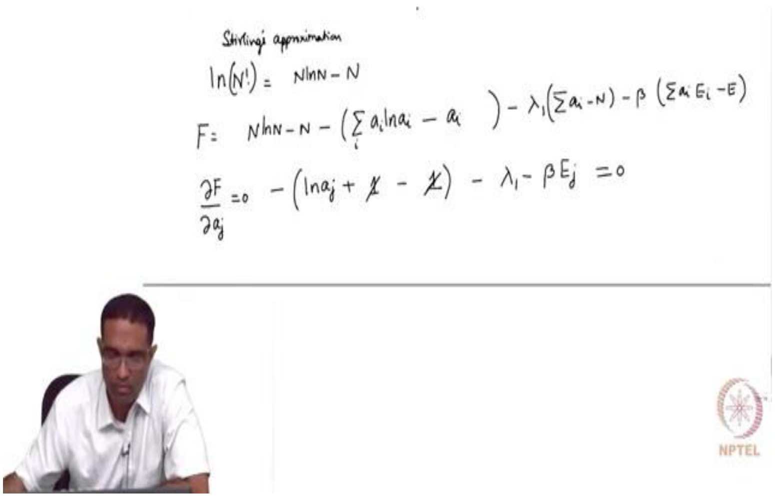
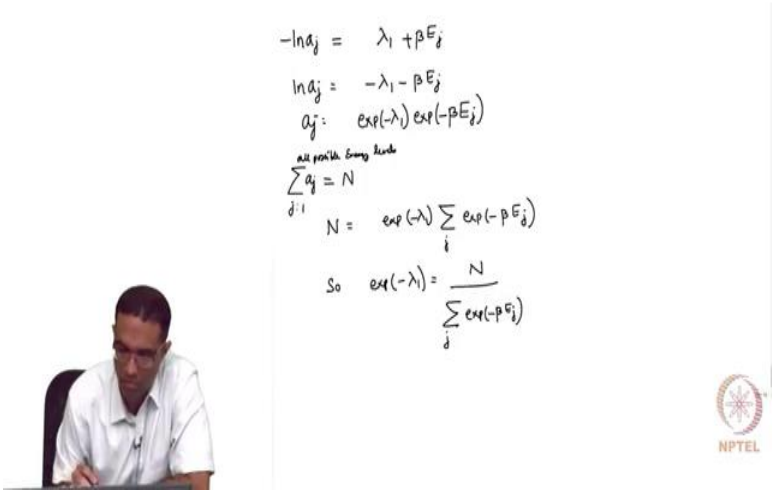


Stirling's approximation

$\ln(N!) = N\ln N - N$

$F = N\ln N - N - \left(\sum_i a_i \ln a_i - a_i\right) - \lambda_1\left(\sum a_i - N\right) - \beta\left(\sum a_i E_i - E\right)$

$\frac{\partial F}{\partial a_j} = 0 \quad -\left(\ln a_j + \cancel{1} - \cancel{1}\right) - \lambda_1 - \beta E_j = 0$



$-\ln a_j = \lambda_1 + \beta E_j$

$\ln a_j = -\lambda_1 - \beta E_j$

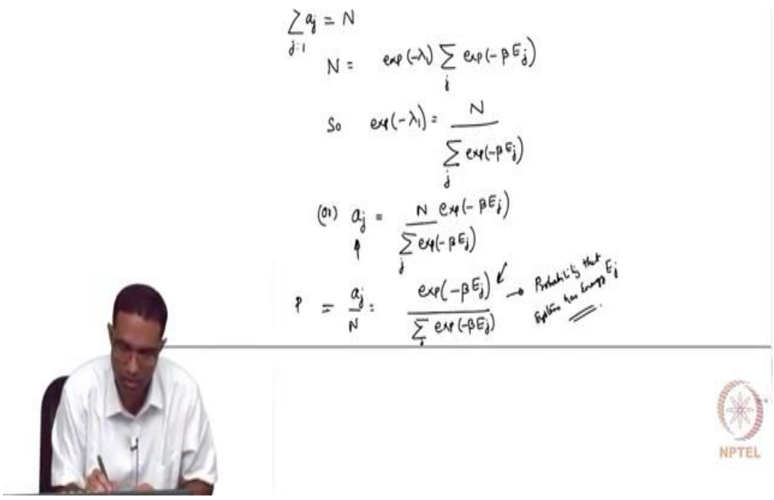
$a_j = \exp(-\lambda_1)\exp(-\beta E_j)$

all possible Energy levels

$\sum_{j=1} a_j = N$

$N = \exp(-\lambda)\sum_j \exp(-\beta E_j)$

So $\exp(-\lambda_1) = \frac{N}{\sum_j \exp(-\beta E_j)}$



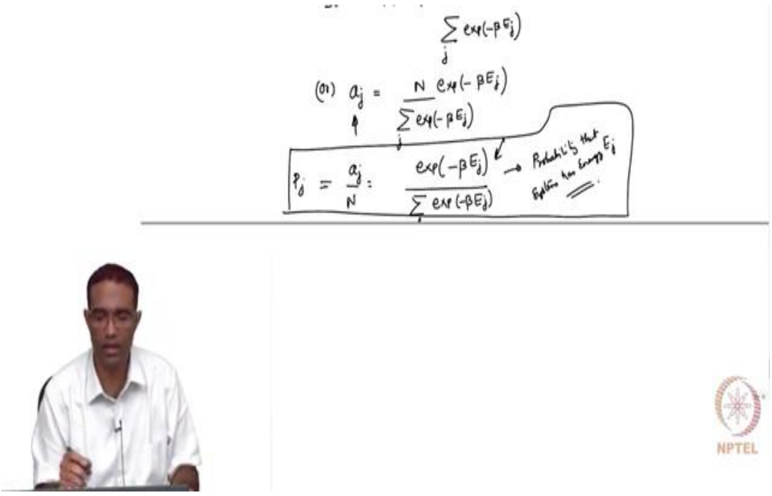
$\sum_{j=1} a_j = N$

$N = \exp(-\lambda)\sum_j \exp(-\beta E_j)$

So $\exp(-\lambda_1) = \frac{N}{\sum_j \exp(-\beta E_j)}$

(or) $a_j = \frac{N \exp(-\beta E_j)}{\sum_j \exp(-\beta E_j)}$

$p = \frac{a_j}{N} = \frac{\exp(-\beta E_j)}{\sum_j \exp(-\beta E_j)}$ → Probability that System has Energy E_j



$$\sum_j \exp(-\beta E_j)$$

$$\text{(or)}\quad a_j = \frac{N\exp(-\beta E_j)}{\sum_j \exp(-\beta E_j)}$$

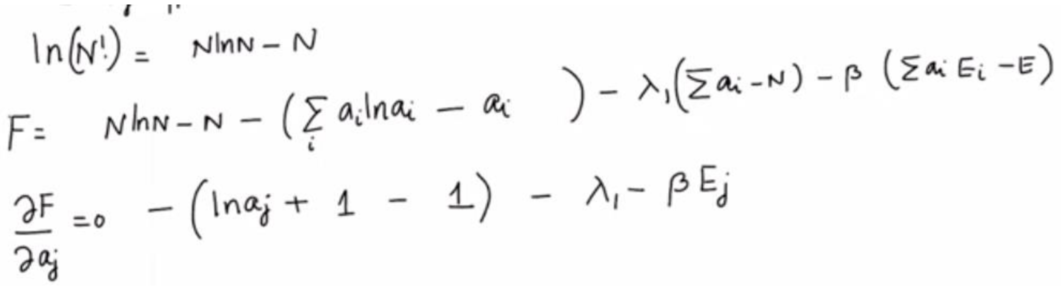
$$\boxed{p_j = \frac{a_j}{N} = \frac{\exp(-\beta E_j)}{\sum \exp(-\beta E_j)}}$$

→ Probability that system has energy E_j

So, we use the Stirling approximation which is excellent for when the value of N is very-very large, right? So, for in Stirling approximation, N factorial is nothing but N ln N minus N. So, let us rewrite this based on Stirling approximation, you will get N ln N minus N minus of summation over all I, a i ln a i minus a i, because in each of the denominator you would have a i ln a i minus a i. Is this right?

No-no wait, 1 minute. I need to, I think this is Stirling approximation. So, this is not Stirling approximation, Stirling approximation is ln of N factorial is N ln N minus N. so, instead of extremizing, I made a small mistake here, instead of extremizing this function needed extremize the ln of the function, right? Otherwise it would be impossible for us to extremize it. So, then you have writing this down properly you would get N ln N minus N minus of summation over i a i ln a i minus a i, right?

But this has to be minus lambda 1 times summation, so let us do the following, dou f by dou a j must be equal to 0 where a j is anything here. So, these things do not depend on a j. Therefore, you have here minus of only the derivative with respect to the jth thing will actually survive here, right? So, you will have here, ln of a j plus a j plus actually plus 1 because it is going to be plus 1 minus 1, right? Minus lambda 1 into minus lambda 1 minus beta into E j.

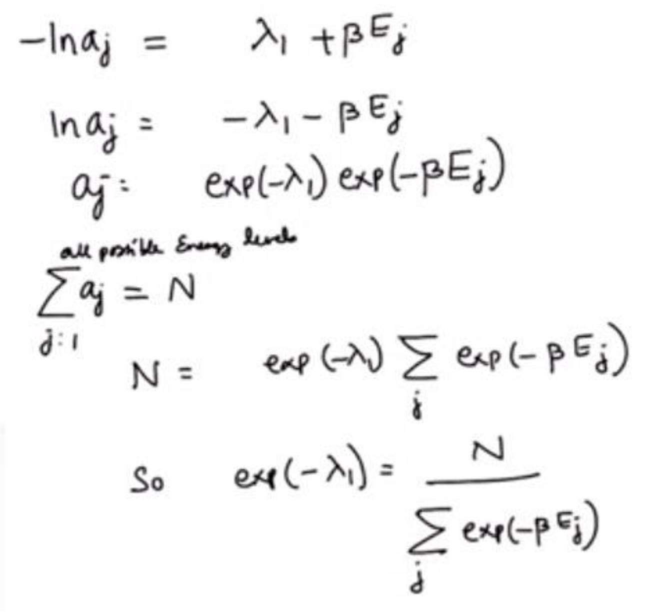


$$\ln(N!) = N\ln N - N$$

$$F = N\ln N - N - \left(\sum_i a_i \ln a_i - a_i\right) - \lambda_1\left(\sum a_i - N\right) - \beta\left(\sum a_i E_i - E\right)$$

$$\frac{\partial F}{\partial a_j} = 0 \quad -\left(\ln a_j + 1 - 1\right) - \lambda_1 - \beta E_j$$

Is this you are able to follow this step? Because the idea is that only this, the terms here will survive or the ones which will be differentiated with respect to a j, all the others will be 0, right. So, this basically reduces to this has to be equal to 0 for extremization. Right, I am just taking the ln however one of the things that you should understand is that a j must be equal to N, j equal to 1 to all possible.



$$-\ln a_j = \lambda_1 + \beta E_j$$

$$\ln a_j = -\lambda_1 - \beta E_j$$

$$a_j = \exp(-\lambda_1)\exp(-\beta E_j)$$

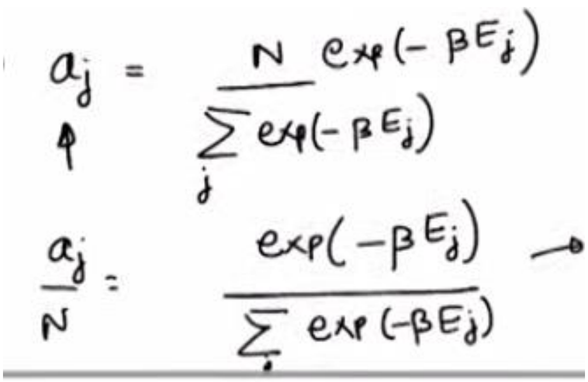
all possible Energy levels

$$\sum_{j=1} a_j = N$$

$$N = \exp(-\lambda_1)\sum_j \exp(-\beta E_j)$$

$$\text{So} \quad \exp(-\lambda_1) = \frac{N}{\sum_j \exp(-\beta E_j)}$$

So, that means, right? So this is the number of ensembles with energy level E j. The probability that, it is at that energy level is nothing but, a j divided by N and you get exp minus. These are probability that the system has the energy E j.



$$\underset{\uparrow}{a_j} = \frac{N\exp(-\beta E_j)}{\sum_j \exp(-\beta E_j)}$$

$$\frac{a_j}{N} = \frac{\exp(-\beta E_j)}{\sum_j \exp(-\beta E_j)} \longrightarrow$$

If you look at this expression, so this is clearly P j from what we had derived previously. This one, correct?

$$\boxed{P_i = \frac{\exp(-\beta E_i)}{\sum_i \exp(-\beta E_i)}}^{\,i}$$

Yes or no? Except that, I cheated by just writing this one of the multiplier is beta without proving it. There is no, I did not provide an explicit proof and tell, to tell you that, this beta is in fact to the same beta which is 1 by K T, which occurs here and everywhere in thermodynamics basically 1 by k times T.

So, the derivation or to prove that you know it is possible, I am not going to go over the derivation. It is it is a little long derivation. It will take another one class to just do that. Instead, I am going to make the derivation and put it up in the notes and you can actually take a look at it. So, now we have this and I told you that I will derive one expression for the Helmholtz free energy.

So, again this again you know, E j is nothing but can be written in terms of the Hamiltonian, in terms of q i and p i like what we talked about in the last class. And now we want to talk about deriving the Helmholtz free energy. Before that are there any questions? Yes.

Student: after applying Sterling Approximation, I think within N power n minus M within bracket you have to write summation of a i on a i minus summation a i.

Professor: Yeah-yeah, yes, so we will do some thermodynamics now.

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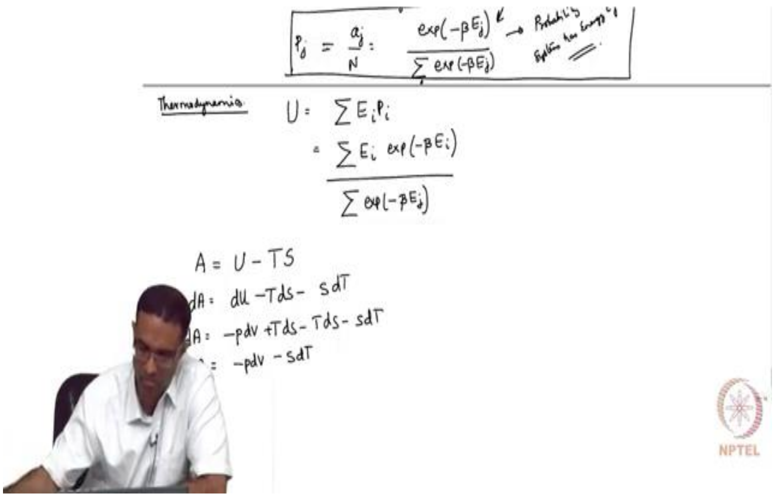
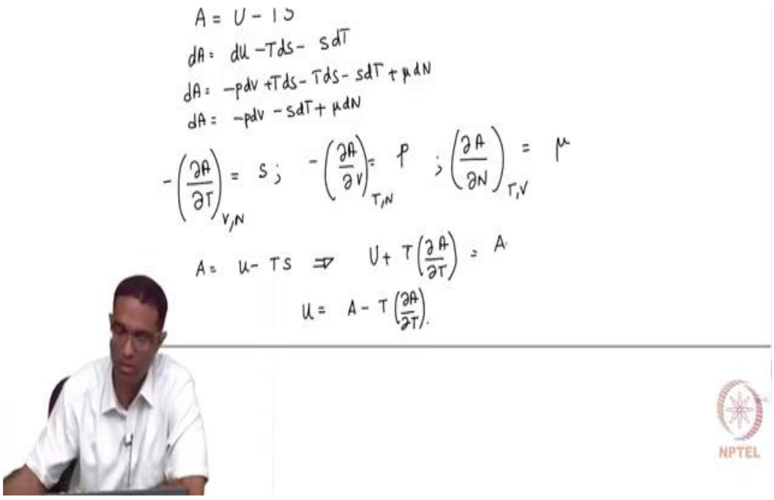


$$\boxed{p_j = \frac{a_j}{N} = \frac{\exp(-\beta E_j)}{\sum \exp(-\beta E_j)}} \rightarrow \text{Probability system has energy}$$

Thermodynamics

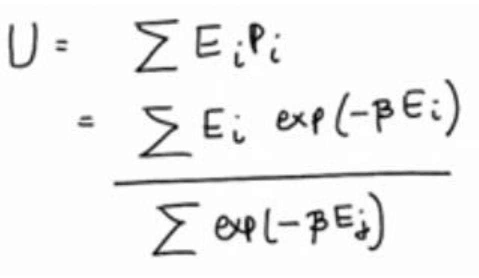
$$U = \sum E_i P_i$$
$$= \frac{\sum E_i \exp(-\beta E_i)}{\sum \exp(-\beta E_j)}$$

$$A = U - TS$$
$$dA = dU - Tds - sdT$$
$$dA = -pdv + Tds - Tds - sdT$$
$$= -pdv - sdT$$



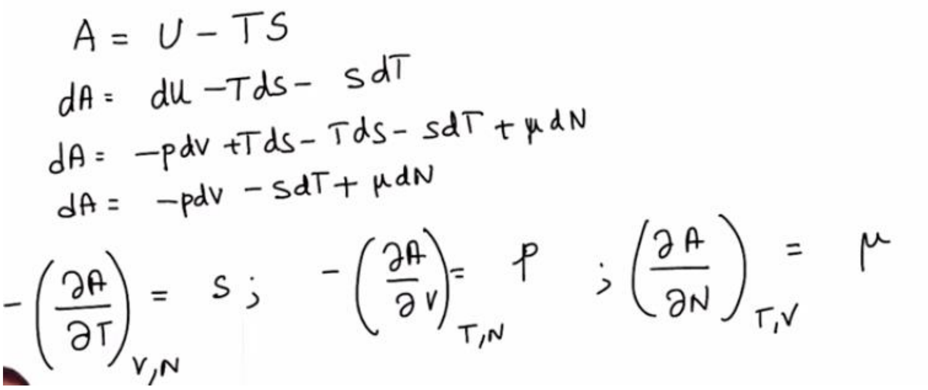
$$A = U - TS$$
$$dA = dU - Tds - sdT$$
$$dA = -pdv + Tds - Tds - sdT + \mu dN$$
$$dA = -pdv - sdT + \mu dN$$
$$-\left(\frac{\partial A}{\partial T}\right)_{V,N} = S; \quad -\left(\frac{\partial A}{\partial V}\right)_{T,N} = P; \quad \left(\frac{\partial A}{\partial N}\right)_{T,V} = \mu$$
$$A = U - TS \Rightarrow U + T\left(\frac{\partial A}{\partial T}\right) = A$$
$$U = A - T\left(\frac{\partial A}{\partial T}\right).$$

What is the average internal energy of the system? What is internal energy of system at equilibrium? If I if I knew the probability that the system is at energy E, if I knew the probability of whatever the probability is, for the system to be at energy E i. What would be the average internal energy of the system? Or what was the internal energy of system at equilibrium? That is it, right? This is same as summation...



$$U = \sum E_i P_i$$
$$= \frac{\sum E_i \exp(-\beta E_i)}{\sum \exp(-\beta E_j)}$$

Now, let us, what is Helmholtz free energy? What is the expression for Helmholtz free energy? Say Helmholtz free energy is A, yeah right. U minus TS. So, which is correct? Or like we do in thermodynamics, we can write dou A by dou T minus is equal to S and obviously dou A by dou V is equal to P dou A by dou T, you are maintaining T constant. And maintaining and holding T constant. Ofcourse, you will if you are also considering the chemical potential of the system, you would continue to have a plus Mu dN, not here, here, from here you would have a Mu dN and there, you have dou A by dou N, so you are keeping N constant here, N constant here. And differentiate it with respect to N at constant T and V will be equal to the chemical potential of the system.



$$A = U - TS$$

$$dA = dU - Tds - sdT$$

$$dA = -pdv + Tds - Tds - sdT + \mu dN$$

$$dA = -pdv - sdT + \mu dN$$

$$-\left(\frac{\partial A}{\partial T}\right)_{V,N} = s \; ; \quad -\left(\frac{\partial A}{\partial v}\right)_{T,N} = p \; ; \quad \left(\frac{\partial A}{\partial N}\right)_{T,V} = \mu$$

So, now we just want to show how this A turns out to be a function of p and q that is our goal here. So, there are couple of tricks that we have use here in order to do that. So, first we again write this A to be equal to U minus TS which implies the average energy or the internal energy of the system minus T times S which is dou A by dou T which is equal to A.

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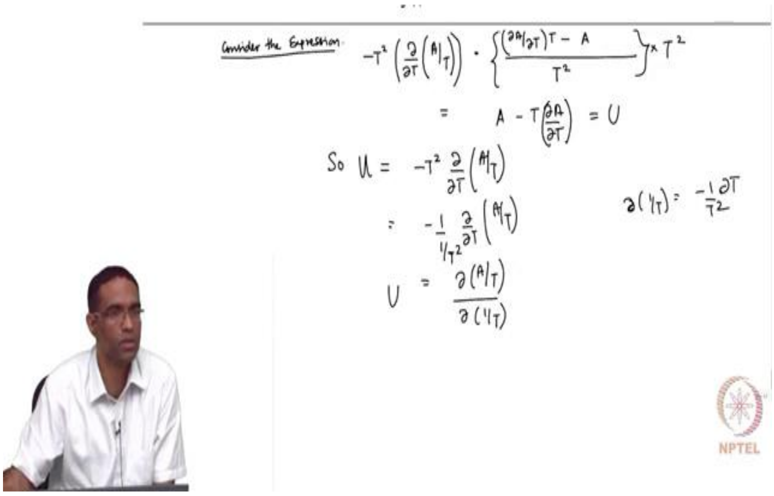


Consider the Expression: $-T^2\left(\frac{\partial}{\partial T}\left(A/T\right)\right) \cdot \left\{\frac{(\partial A/\partial T)T - A}{T^2}\right\} \times T^2$

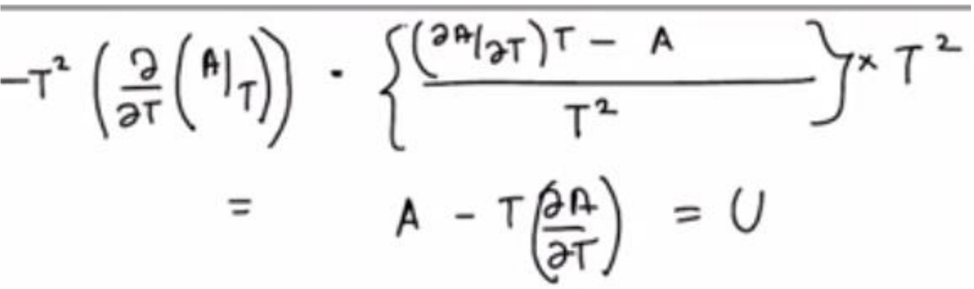
$= A - T\left(\frac{\partial A}{\partial T}\right) = U$

So $U = -T^2 \frac{\partial}{\partial T}\left(A/T\right)$

$= -\frac{1}{1/T^2}\frac{\partial}{\partial T}\left(A/T\right)$

$\partial(1/T) = \frac{-1}{T^2}\partial T$

$U = \frac{\partial (A/T)}{\partial (1/T)}$



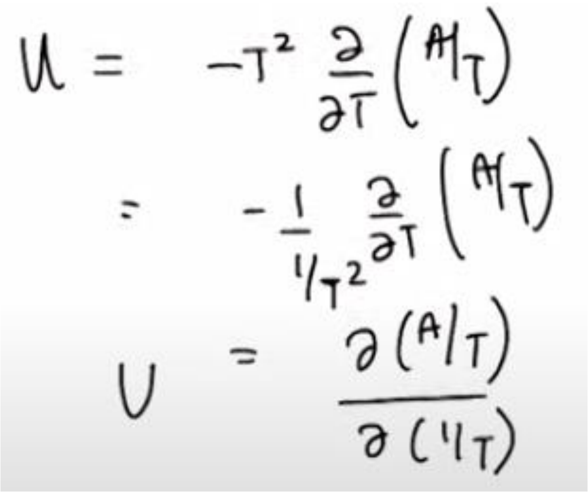
$-T^2\left(\frac{\partial}{\partial T}\left(A/T\right)\right) \cdot \left\{\frac{(\partial A/\partial T)T - A}{T^2}\right\} \times T^2$

$= A - T\left(\frac{\partial A}{\partial T}\right) = U$

Now, now consider the expression, so what does this turn out to be? Which is nothing but, right? I am just taking, I just, I have to manage and do some manipulations so, just look at this expression here, minus 1 by T square dou by dou T of A by T is nothing but this using your basic calculus, which turns out to be A minus T into dou A by dou T and which is nothing but U, correct?

So, U can also be written as minus T square dou by dou T of A by T, which can also be written as minus of 1 over T square which is same as,... now dou of, what is dou of 1 by T?

Minus 1 over T square, dou T, right. So, this term here becomes dou of this is also, okay. Any questions on that step? No.



$$U = -T^2 \frac{\partial}{\partial T}\left(A/T\right)$$

$$= -\frac{1}{1/T^2}\frac{\partial}{\partial T}\left(A/T\right)$$

$$U = \frac{\partial(A/T)}{\partial(1/T)}$$

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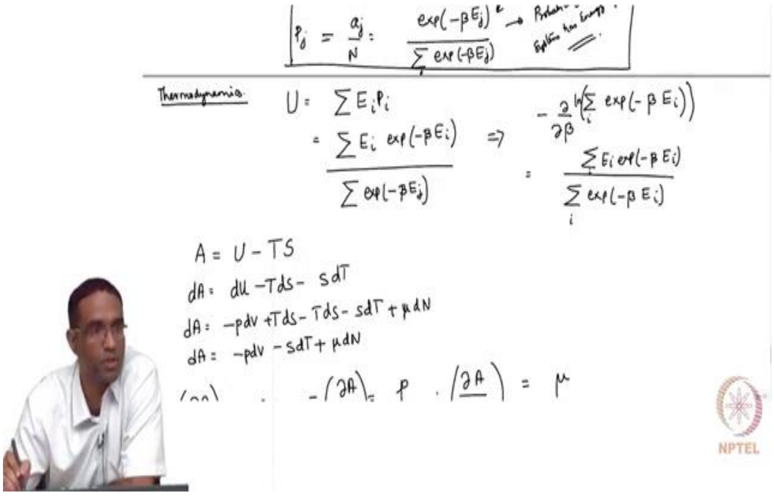

$$p_j = \frac{a_j}{N} = \frac{\exp(-\beta E_j)}{\sum \exp(-\beta E_j)}$$

Thermodynamics

$$U = \sum E_i P_i$$

$$= \frac{\sum E_i \exp(-\beta E_i)}{\sum \exp(-\beta E_j)} \Rightarrow -\frac{\partial}{\partial \beta} \ln\left(\sum_i \exp(-\beta E_i)\right) = \frac{\sum E_i \exp(-\beta E_i)}{\sum_i \exp(-\beta E_i)}$$

$$A = U - TS$$

$$dA = dU - Tds - sdT$$

$$dA = -pdv + Tds - Tds - sdT + \mu dN$$

$$dA = -pdv - sdT + \mu dN$$

$$-(\partial A) = p \quad (\partial A) = \mu$$

Now let us take a look at our energy, average energy of a system. This can be written as minus dou by dou beta summation over i exp minus beta times E i. Let us take the derivative with respect to beta sorry ln on this quantity. I am saying that this U can also be written like this. So, let us verify it.

What happens, in the denominator you get i, exp minus beta times E i. And at the numerator, you have to differentiated the exponent function minus beta times E i but then you have to differentiate it with respect to beta so, I would get a minus E i, okay. Since there is a minus right in the front of it already, it cancels with the minus that comes from this beta and you get back exactly the same expression, okay.

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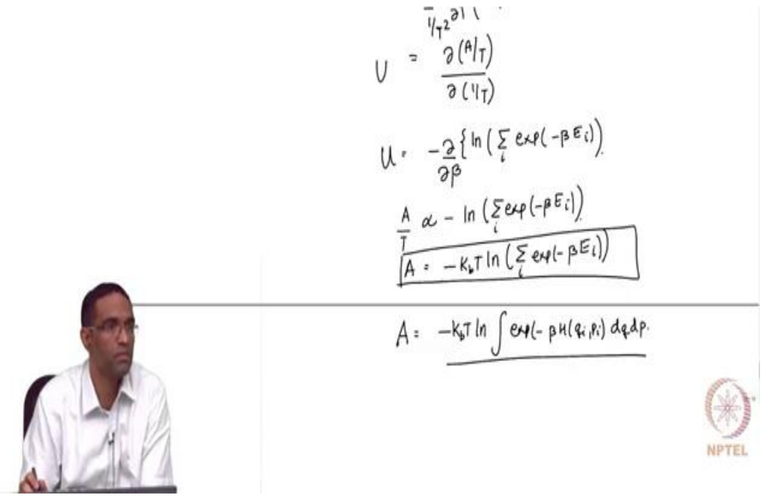


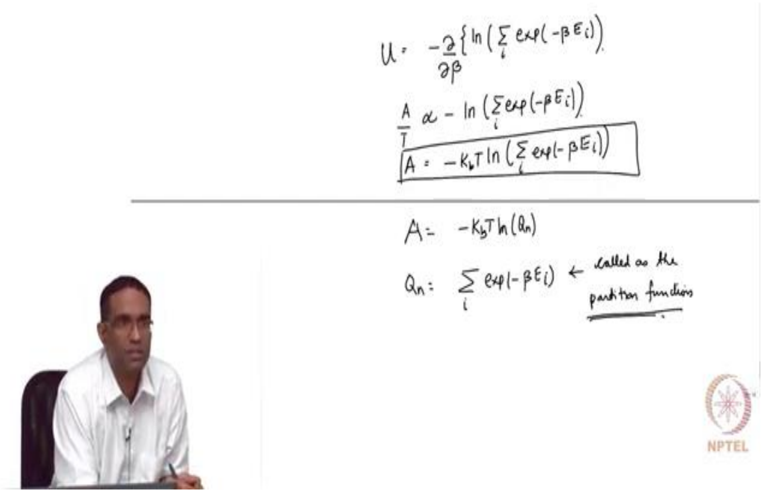
$$U = \frac{\partial(A/T)}{\partial(1/T)}$$

$$U = -\frac{\partial}{\partial\beta}\left\{\ln\left(\sum_i \exp(-\beta E_i)\right)\right.$$

$$\frac{A}{T} \propto -\ln\left(\sum_i \exp(-\beta E_i)\right)$$

$$\boxed{A = -K_b T \ln\left(\sum_i \exp(-\beta E_i)\right)}$$

$$\underline{A = -K_b T \ln \int \exp(-\beta H(q_i, p_i))\, dq\, dp.}$$



$$U = -\frac{\partial}{\partial\beta}\left\{\ln\left(\sum_i \exp(-\beta E_i)\right)\right.$$

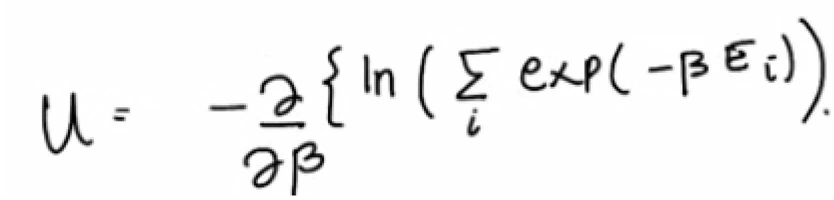
$$\frac{A}{T} \propto -\ln\left(\sum_i \exp(-\beta E_i)\right)$$

$$\boxed{A = -K_b T \ln\left(\sum_i \exp(-\beta E_i)\right)}$$

$$A = -K_b T \ln(Q_n)$$

$$Q_n = \sum_i \exp(-\beta E_i) \leftarrow \text{called as the } \underline{\text{partition function}}$$

So, now we make a comparison between the two. Any doubts? You have a doubt? So, okay? So, make a comparison between these two expressions.



$$U = -\frac{\partial}{\partial\beta}\left\{\ln\left(\sum_i \exp(-\beta E_i)\right)\right.$$

So, what should you get? It appears that A by T is proportional to minus ln.... .... right? Or A is equal to some constant but again that constant turns out to be the Boltzmann constant times ln of .... Expression for the Helmholtz free energy.

$$U = -\frac{\partial}{\partial \beta} \{ \ln \left(\sum_i \exp(-\beta E_i) \right).$$

$$\frac{A}{T} \propto - \ln \left(\sum_i \exp(-\beta E_i) \right).$$

$$\boxed{A = -K_b T \ln \left(\sum_i \exp(-\beta E_i) \right)}$$

Now, this is again although this is just E i, this can be written as minus K b T ln of the integral ... and for obvious reasons, if you are going convert the if you are going to consider the classical system., you need to be careful and have the quantity what quantity should you have? H power 3 N and N factorial should be present here. If you are talking about the classical system.

So, we will we will leave it at this. We will leave at this expression right here. This A is equal to minus K b T minus Q n and this Q n or ln of Q n is equal to this and it is called as a partition function. It will occur over and over again so, there is a name given to it.

$$A = -K_b T \ln (Q_n)$$

$$Q_n = \sum_i \exp(-\beta E_i)$$

So, now once you have your Helmholtz free energy like I have mentioned in the last class, once you have your Helmholtz free energy as a function of energy or in another words as a function of the Hamilton, Hamiltonian, it becomes a function of the positions of the momenta.

And if you have other quantities which are also functions of positions in momenta, you take appropriate derivatives to derive any thermodynamic quantity in terms of the positions and the momenta of the velocities of the system okay, that would be and then you will have to properly average it if you are using statistical mechanics.

However, if you are using molecular dynamics stimulations, you will not do phase averaging but rather you would do, what would you do? Time averaging, okay. So, with these, I think we should stop with statistical mechanics and we should start doing introducing you to some molecular dynamics stimulations, okay.