Statistical Mechanics
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Lecture - 35
Grand Canonical Ensemble Ideal Gas- Part II

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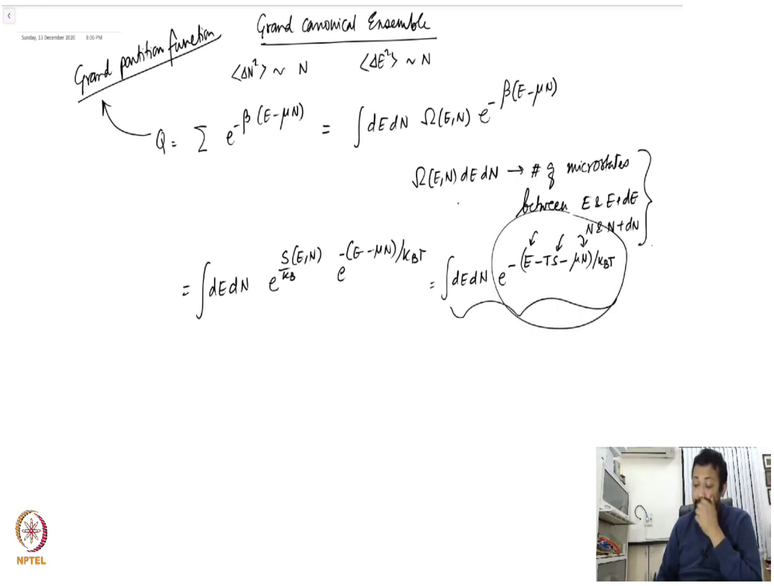

So, now our job is essentially to relate to the; to relate to thermodynamics right. So, in grand canonical ensemble and we have already established that delta N square goes as N delta E square goes as N. So, all the averages are meaningful and now I want to relate to thermodynamics. For that we once again go back and start with our grand partition function this Q is called a grand partition function.

Unfortunately, we have used capital Q for a single particle function in the canonical ensemble, but we will modify that syntax later on right. So, this quantity is some over all state is minus beta E minus mu N which is integral dE dN omega E comma N e to the power minus beta E minus mu N, where omega E comma N dE dN is the number of microstates between E and E plus dE N and N plus dN.

Again, this root is pretty straightforward as we had done a little bit more elaborate because now we have two variables is E to the power S E, N over K B minus E minus mu N over k B T times e to the power E minus mu N over k B T. So, that this becomes integral dE times dN e to the power minus E minus TS minus mu N over k B T.

Once again you see that the energy internal energy E the entropy S and the particle number N are all extensive quantities and therefore, they scale as N and therefore, I can try to figure out this particular integral using a subtle point approximation, where I maximize the quantity in the argument of the exponential.

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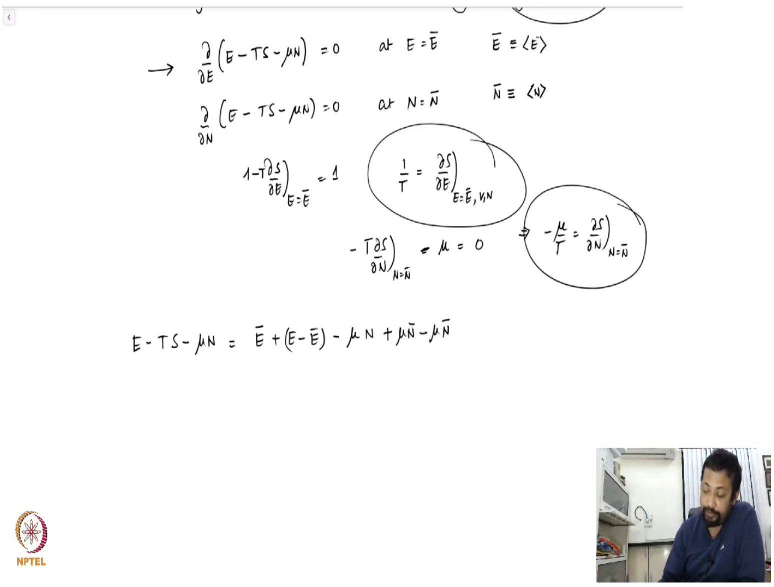

Which means I will have del del E of E minus TS minus mu N is equal to 0 at E is equal to E bar and del del N of E minus TS minus mu N is equal to 0 at N is equal to N bar sorry right. So, please note that this E bar is identical to average of E. We will interchangeably use this symbols would not get confused that they are something different right.

So, therefore, this condition the first condition gives you 1 minus T del S del E at E equal to E bar is equal to 1 and you recover the thermodynamic relation 1 by T is del S del E at E equal to E bar with V and N held constant.

The second relation gives you T del S del N at N equal to N bar is going to be minus mu is equal to 0, which implies minus mu by T is del S del N at N is equal to N bar so you recover the two thermodynamic relation. Then let us write down E minus TS so minus mu N around E bar and N bar and that idea is very straightforward we have done this E minus E bar minus mu N minus plus mu N bar minus mu N bar.

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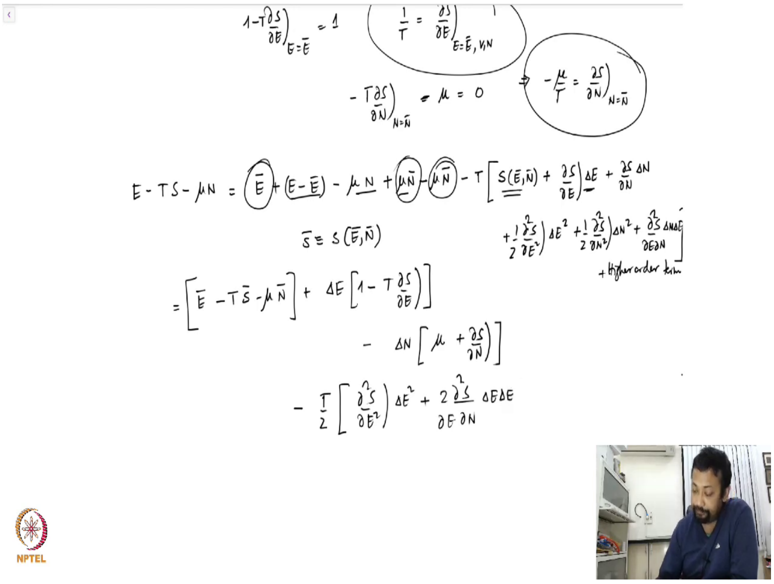

Plus sorry minus T S of E bar times N bar plus del S del E delta E plus del S del N delta N plus del 2 S del E 2 delta E square plus del 2 S del N 2 delta N square there is going to be a half factor here plus del 2 S del E del N delta N delta E. Of course, you will have higher order terms which we will ignore. So, this expansion essentially assumes that your system size is very very small and delta E.

Since it is exponentially unlikely to find the system in a state other than E bar N bar therefore, the fluctuations in delta E are extremely small. So, this gives you E bar plus mu minus mu N bar. So, that you have and this quantity we denote as S bar where S bar is identical to S of E bar comma N bar.

The first term is this, this is delta E and I have a delta E over here so this becomes delta E times 1 minus T del S del E minus mu N and plus mu N bar gives you minus mu delta N not mu delta N we will take delta N outside this gives you mu and plus del S del N. And then you have minus T by 2 del 2 S del E 2 delta E square plus 2 del 2 S del the mixed derivative delta E delta N.

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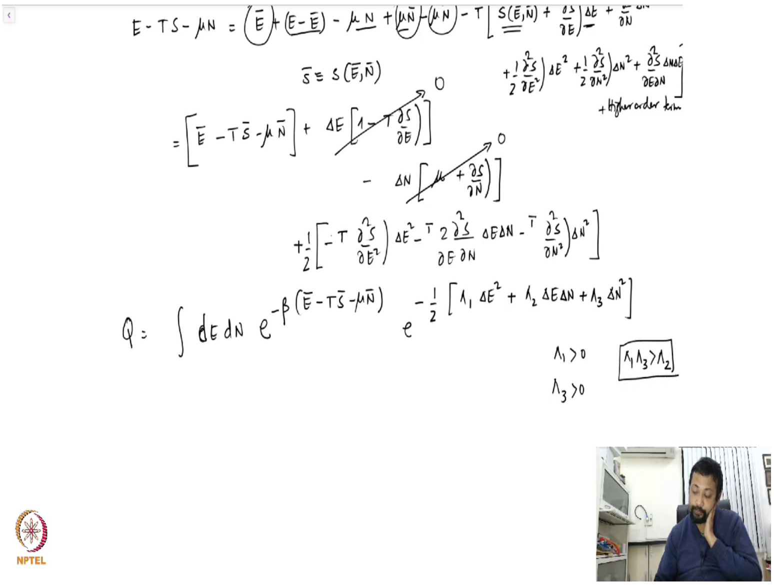

Plus del 2 S del N 2 delta N square. What we will do is will make this plus and bring a minus sign all in front of it. In fact, we will also absorbed T inside. So, that [vocalized- noise] will cost this expression as minus T by 2 T by 2 with a minus sign T by 2 with a minus sign sorry not the half we will keep the half outside so, that the structure remains as a Gaussian fluctuation, right.

So, your omega of this is 0 from the thermodynamic relation that we have calculated. So, your Q of E N this becomes integral e to the dE dN e to the power minus beta E bar minus T of S bar minus mu of N bar times e to the power minus half lambda 1 delta E square plus lambda 2 delta E delta N.

I made the mistake here this should not be delta E delta E, but delta E delta N plus lambda 3 delta N square. So, one can easily do the calculations a little bit more to realize that lambda 1 is positive lambda 2 lambda 3 is positive and lambda 1 lambda 3 is greater than lambda 2 this you can do. This is the conditions kind of we derive when we did stability criteria.

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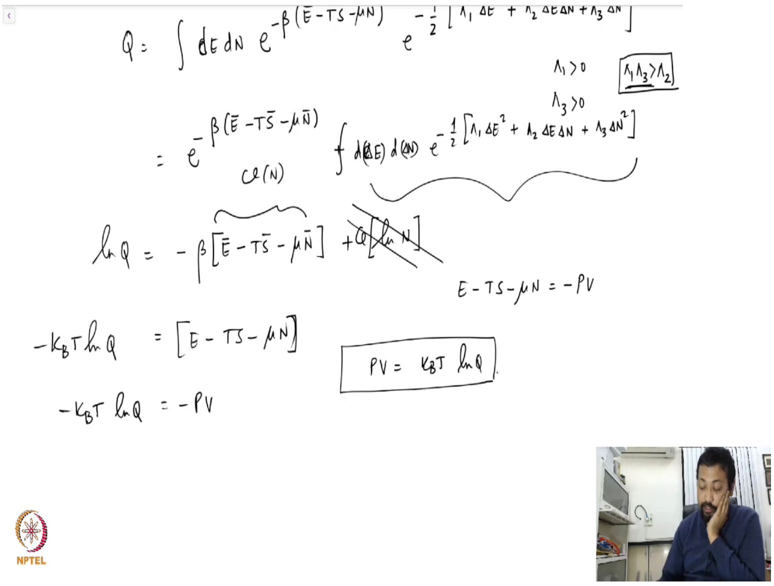

So, this becomes minus beta E bar minus T of S bar minus mu of N bar integral dE one can now convert it to d of delta E d of delta N because this is a shift of variables e to the power minus half lambda 1 delta E square plus lambda 2 delta E delta N, lambda 1 would be the inverse of the specific heat lambda delta N square will be the del N del mu that we did.

The coefficient of delta N square will be the del N del mu del mu that we did and one can verify this very easily right. So, these fluctuations essentially this is a Gaussian probability distribution Gaussian distribution of joint distribution of E and N and this can be integrated very very easily and the integral you see that is going to be a function of is going to be dependent on N because delta E square because you have lambda 1 lambda 2 and lambda 3 which are all dependent on N therefore, the integral is going to be an extensive quantity.

If you take a log in contrast this gives you minus beta E bar minus TS bar minus mu N bar plus log of N, we will write this is as order of log of N whereas, this quantity is of the order of N because all of them are extensive quantity and in the thermodynamic limit I can drop out this term, this term does not mean compared to the first term.

So, I will remove the bar and I will write that minus k B T ln Q is E minus TS minus mu N where all these quantities referred to your averages and therefore, you see that E minus TS minus mu N is going to be minus P of V. So, this becomes minus P V is minus k B T ln Q. So, that pressure times volume is k B T ln Q and this is the connection with thermodynamics.

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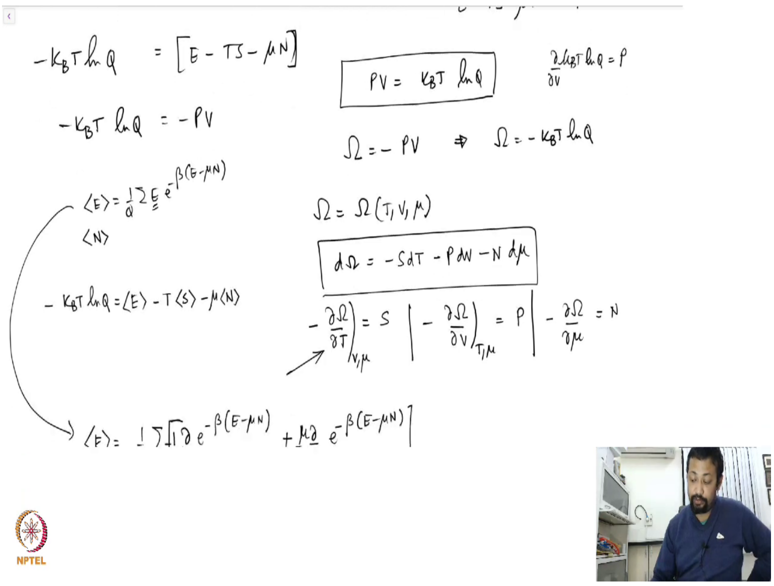

But we do not usually stop here I mean I know that the grand potential omega is minus P times V and this implies that omega is minus k B T ln Q, but what is omega function of omega is what? Is a function of T, V and mu and therefore, d omega is going to be minus SdT minus PdV minus N d mu. Recall from your thermodynamics that this is the differential in omega looks like.

So, that del omega del T is minus of that is the entropy del omega del V what is being held constant V comma mu is being held constant del omega del V T comma mu is being held constant is minus of P and del omega del mu minus of that is going to be N right. So, I have three relations one can validate it also from starting from the fundamental relation right because I know the expression for average E, I know the expression for average N, correct.

You also know that k B T ln Q is minus k B T ln Q is average E minus T average S minus mu average N.

So, this is going to be sum over 1 by Q E e to the power minus beta E minus mu N and this E one has to be careful now is average of E is going to be 1over Q sum over del del beta of e to the power minus beta E minus mu N. But then that actually brings out if you take a derivative with respect to beta that actually brings out a factor which is E minus which is plus E minus plus mu N. So, one has to subtract del del mu 1 over beta e to the power minus beta E minus mu N.

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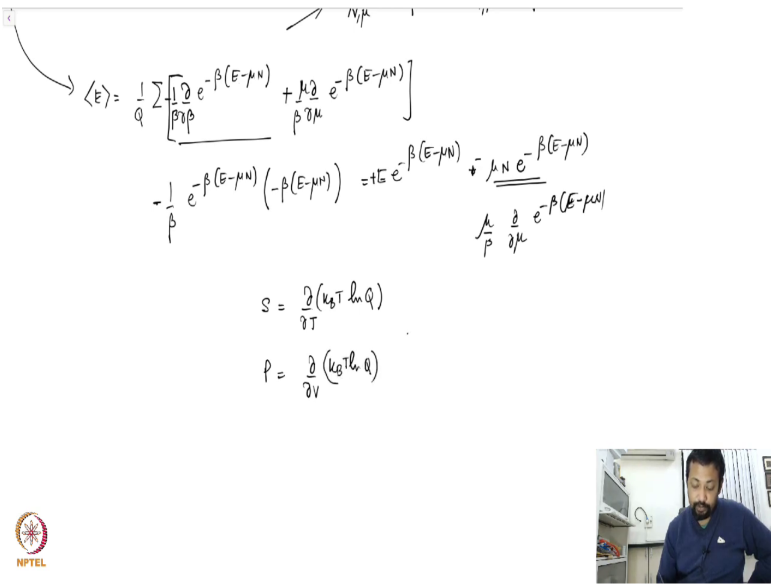

Let us see whether we are correct in our hypothesis if I do this then this gives me e to the power minus beta E minus mu N times minus beta E minus mu N. So, first of all this has to be divided by 1 by beta right. So, 1 by beta of this is going to be e to the power minus beta E minus mu N E minus E plus mu over beta sorry beta has been taken care of so mu times.

So, if I do it with a minus beta over here then you see minus of beta is this is plus and this becomes minus. So, I have to add this particular term and this particular term is essentially mu times del del N mu over beta times del del N of minus beta E minus mu N. So, then if I am doing a minus over here this has to mu over beta del del mu of minus beta E minus mu N right.

So, this should be your average E and you can manipulate this similarly you can also write down average of N and you can see that this is the relation that you are going to come up with.

So, straightforward S is going to be del del T of k B T ln Q, pressure is going to be del del V of k B T ln Q which is very very straightforward to validate over here because del del V of the left hand side gives you pressure and this is the right hand side you see k B T ln Q is equal to the thermodynamic pressure.

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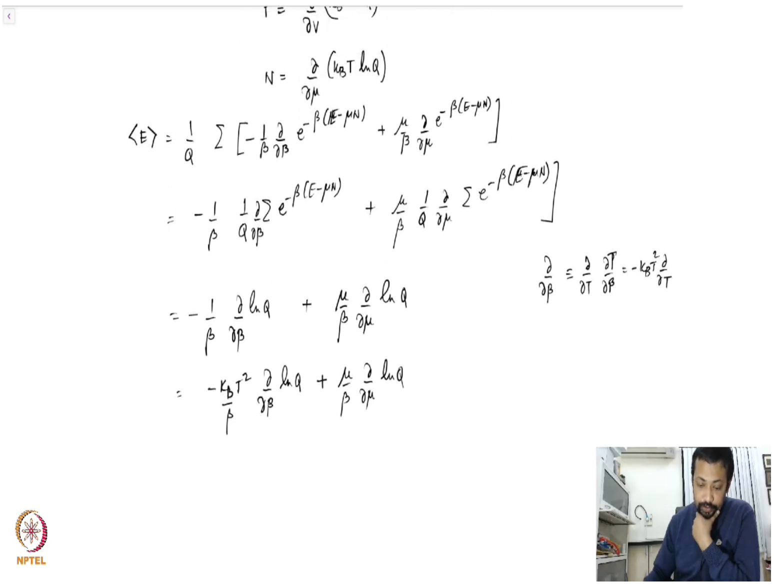

And finally, N is going to be k B T del del mu of k B T ln Q right good. So, one can continue this relation average of E is 1 by Q sum minus 1 over beta del del beta of e to the power minus e to the power beta mu E minus mu N plus mu over beta del del mu of e to the power minus beta E over mu N right.

And this you see is going to be minus 1 over beta 1 over Q sum of a del del sorry del del beta of e to the power minus beta E minus mu N plus mu over beta 1 over Q del del mu of sum over e to the power minus beta mu minus E minus mu N. This is very straightforward this becomes del del beta of ln Q plus mu over beta del del mu of ln Q right.

But del del beta is identical to del del T del T del beta which is minus k B T square del del T. So, this becomes minus k B T square del del beta ln Q plus mu over beta del del mu ln Q. However, we did not observe this is somewhere horribly wrong because I have a 1 by beta over here because then it makes me k B T cube. So, when did we go wrong so, let us go back and check our calculation once again and we see that here is where we went wrong this beta factor is not going to be there.

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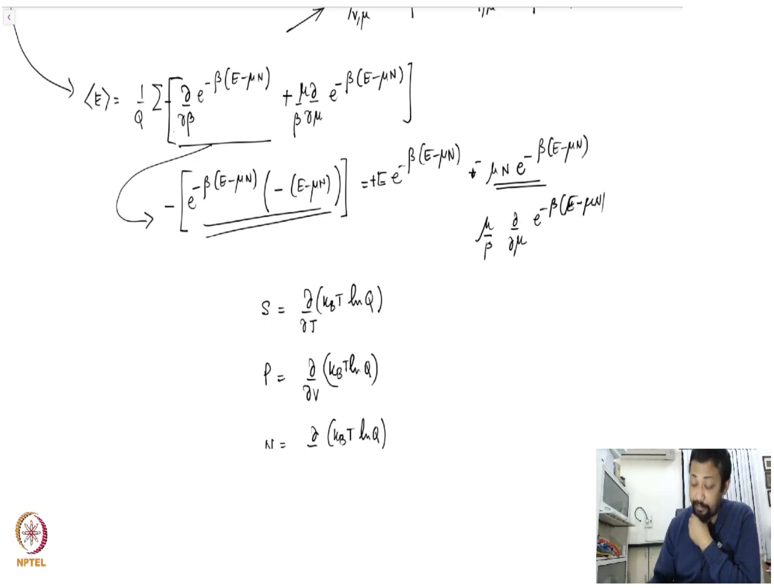

So, we are going to remove this beta factor and we are going to keep it as minus, minus. So, this 1 by beta vanishes over here and the rest of it is fine because if this is the case then you see minus of e to be power minus beta del del beta of this is going to be. So, just this particular term is going to be minus of this right.

And that becomes e e to the power minus beta E minus mu N and then you have a minus mu N e to the power minus beta E minus mu N, but this particular term is del del mu e to the power minus beta E minus mu N because if you take a derivative with respect to mu now, you will bring out bring down beta times N.

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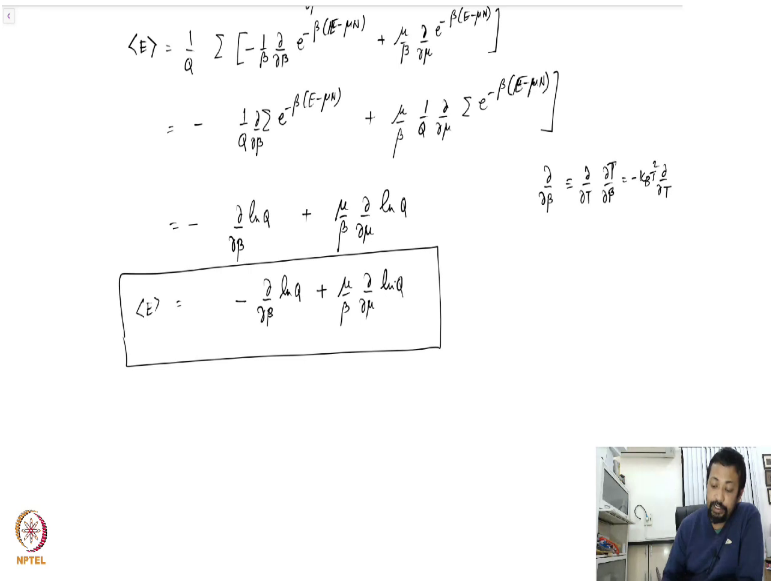

And so I am dividing by beta and therefore, this is not going to be there and the answer in simplest form is average energy is going to be minus this is the simplest form it is going to be minus del del beta ln Q plus mu over beta del mu del n Q good.

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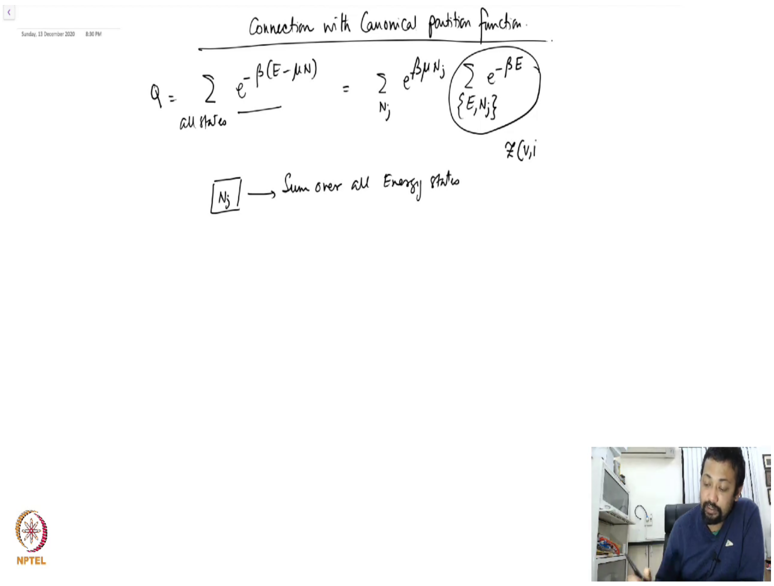

Our final task in this part in this lecture is to look at connection with canonical partition function. So, Q is sum over all states e to the power minus beta E minus mu N right, which means that this is going to be N j e to the power beta mu N j times sum over E all the possible energy states times beta E right, but this particular well to be very explicit over here one has to be saying that E comma N j.

So, this sum I can split into two sums right what does this mean that means, I take a system with a fixed number of particles N j and then I sum over all energy states and once I have taken this I sum over the second step is to I sum over than all possible system sizes which means you sum over the particle numbers right. But this quantity is very very familiar to us and this quantity is nothing, but the canonical partition function we will say Z V comma N.

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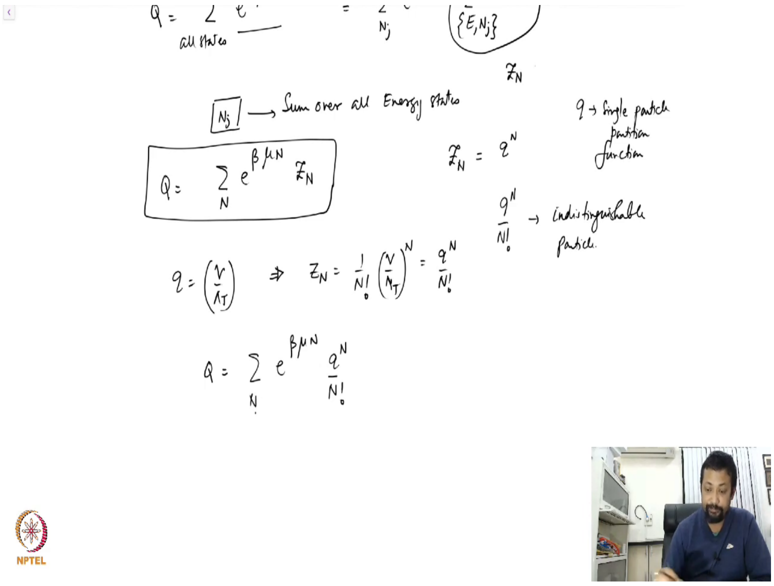

So, we will simply denote this by Z N. So, therefore, you see we have come up with a very nice thing that this is e to be power by beta mu N times Z N. Now, recall in the canonical form ensemble we did non interacting systems and in the non interacting systems we said that for an N particle partition function or can be expressed in terms of a single particle partition function, where q is my single particle partition function where q is the single particle partition function.

Note: here is where I am changing the notation when we did canonical ensemble I had represented this single particle partition function with capital Q right and depending on whether you have a distinguishable set of particles you will have q to the power N or you will have q to the power N over N factorial for indistinguishable particle right.

So, for example, when we looked at an ideal gas my q was V over lambda T and therefore, this will imply that Z N was 1 over N factorial V over lambda T raised to the power N which will simply write as q over N raise to the power N factorial and therefore, your grand canonical partition function become e to the power beta mu N q to the power N over N factorial sum over N.

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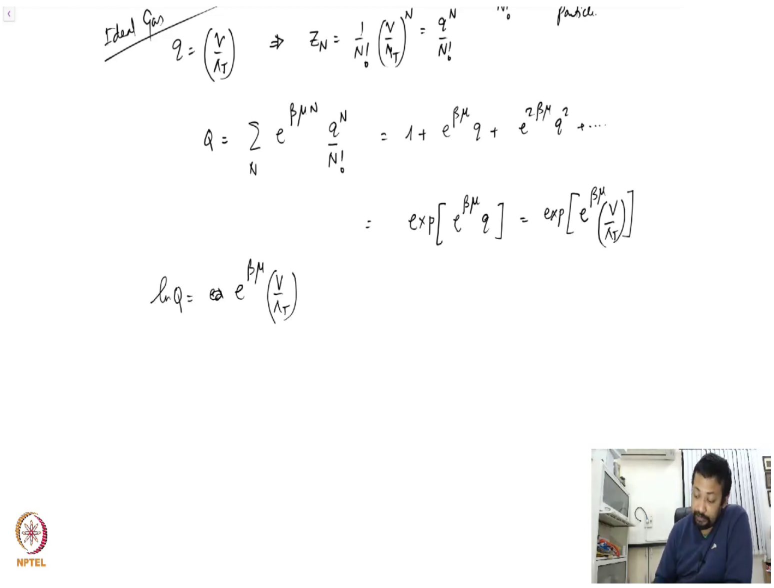

If I expand this sum this is going to be 1 plus e to the power beta mu let us say q plus e to the power 2 beta mu q square so on and so forth, and this is going to be e to the power we will write exponential of e to the power beta mu times q which is exponential e to the power beta mu V over lambda T, ln Q is going to be e to the power of beta mu V over lambda T right. So, this is the case for an ideal gas in the grand canonical ensemble right good.

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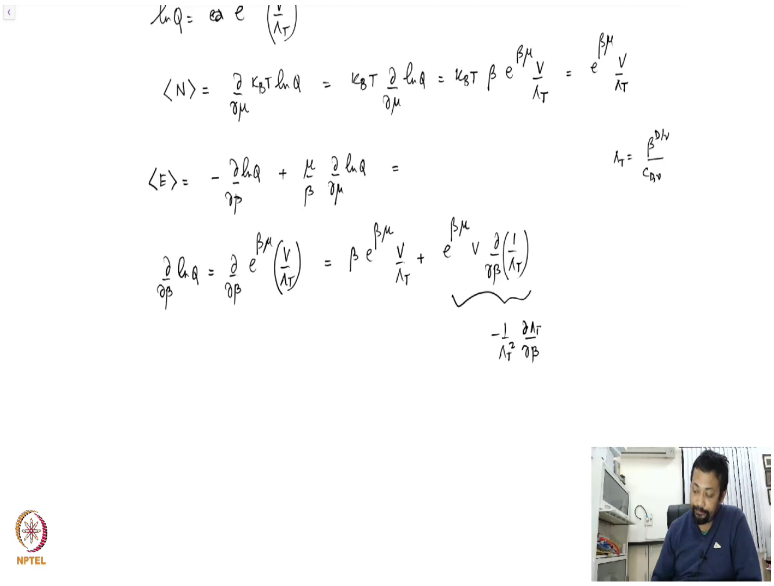

Then we will just work out one simple thing which is average of N was del del mu of k B T ln Q. So, this is k B T times del del mu of ln Q which takes it to beta e to the power beta mu V over lambda T. So, that this is just e so, the average particle number is given by e to the power V over lambda T. Average of the energy was minus del del beta of ln Q plus mu over beta del del mu of ln Q.

Now this is where things are going to get nasty, but we will see. So, del del beta let us do it very clearly del del beta of ln of Q is going to be del del beta of e to the power beta mu V over lambda T. Now remember your lambda T is also a function of beta right. So, you know that lambda T was defined as beta over D of nu divided by C D comma nu correct.

And therefore, this is going to be beta e to the power beta mu V over lambda T plus e to the power beta mu V del del beta of 1 over lambda T. Now, del del beta of 1 over lambda T is the one which we have to carefully do. This derivative is minus 1 over lambda T square del lambda T del beta.

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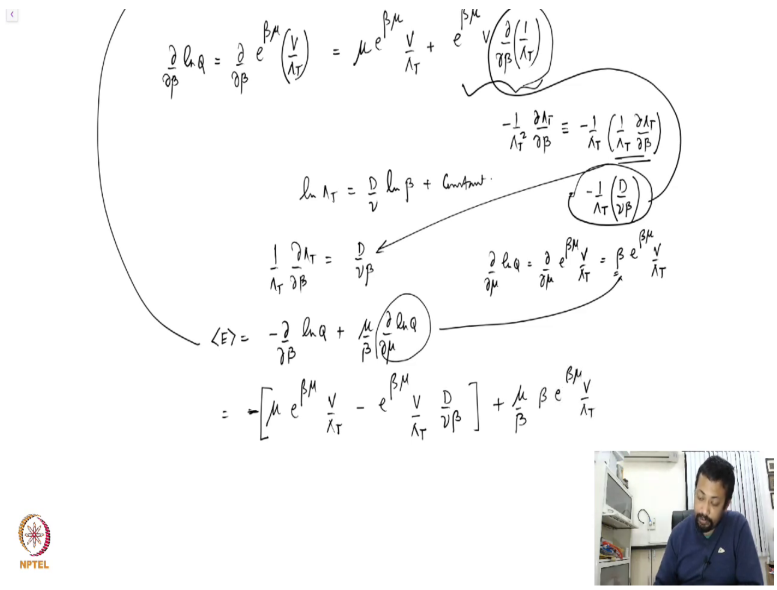

Log lambda T is going to be D over nu l n over beta plus a constant which we are not worried about. So, therefore, del del beta 1 over lambda T is going to be del lambda T is going to be D over nu beta. So, which means this I can write as minus 1 over lambda T 1 over lambda T del lambda T del beta correct. I am little bit worried about the negative sign yeah that is ok that is ok.

So, this means this derivative is now minus 1 over lambda T D over nu beta, because this is the derivatives which we are plugging in from here. So, therefore, the average energy if you take the expression over here from top is minus del del beta of ln Q plus mu over beta del del mu of ln Q del del mu of ln Q is quite trivial to do is del del mu of e to the power beta mu V over lambda T neither volume depends on the chemical potential neither lambda T depends on the chemical potential.

And therefore, you just have beta times e to the power beta mu, V over lambda T right. Wait, I think there has been some mistake over here because this beta does not I am terribly sorry because this is del del beta of beta mu so that this is going to be mu times this.

So, you have mu e to the power beta mu plus this and this is correct. So, therefore, you have mu e to the power beta mu V over lambda T plus e to the power beta mu V there is a minus sign outside. So, we have to take care of this we will use this term and put in back as the derivative. So, that V over lambda T there is a minus sign. So, the plus become a minus and then I have D over nu times beta plus mu over beta and this derivative comes from over here beta e to the beta V over lambda T.

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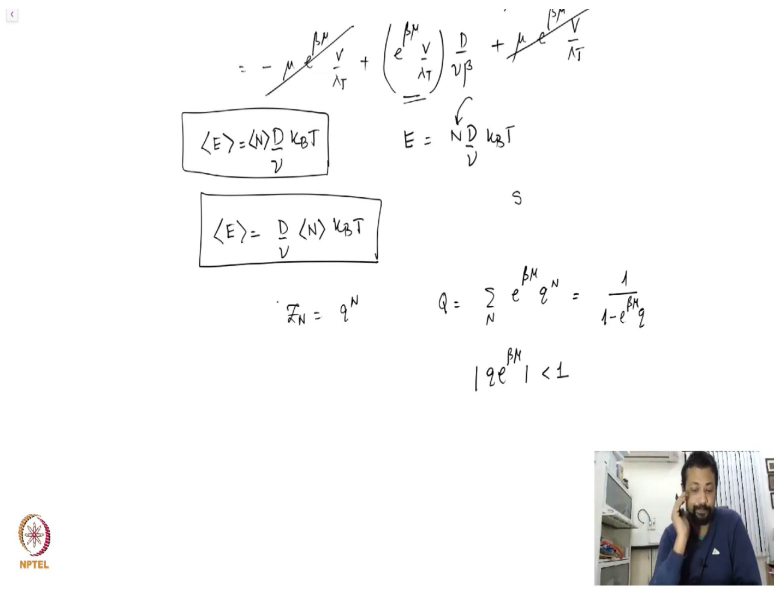

This, this gets cancelled out and you have minus mu e to the power beta mu V over lambda T plus e to the power beta mu V over lambda T. We will enclose in bracket you will see in a movement why this is so D over nu plus beta plus mu e to the power mu V over lambda T. This and this cancels out and if you recall just a little while ago the quantity within the brackets within the parenthesis is nothing, but the average N.

So, essentially your average energy then becomes D over nu average of N times k B T. In the canonical ensemble you had N times D over nu k B T because your N was fixed right. Here, this relation is replaced by average of E is D by nu average of N k B T. So, this is how the relation gets modified in the grand canonical ensemble. I invite you to calculate the entropy and you will see the same phenomenon that averaged the N that and the E is replaced by average E and the average N.

Finally, very quickly if my single particle partition function is just sorry if my N particle partition function Z of N is just q to the power N then, the grand canonical partition function becomes sum over N e to the power beta mu q to the power N, which is 1 by 1 minus e to the power beta mu times q with the understanding that e to the power beta mu q is less than 1 right. So, we will conclude the our section on canonical ensemble here.