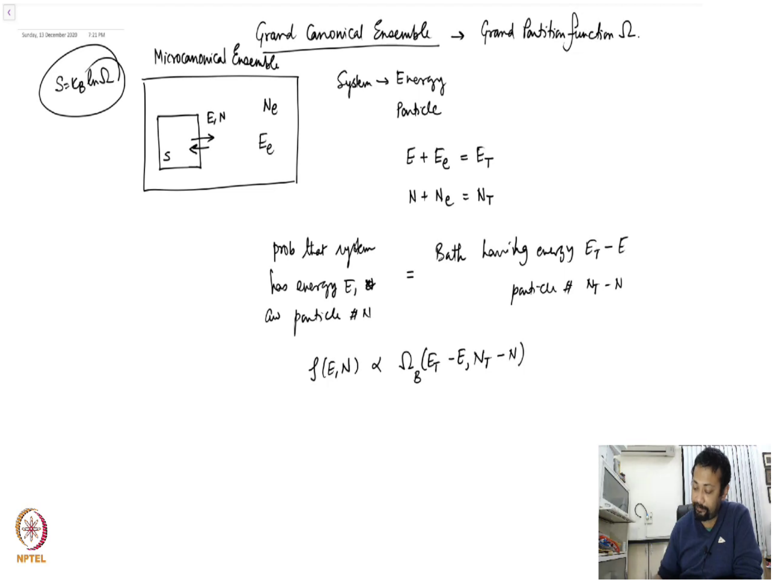
Statistical Mechanics
Prof. Dipanjan Chakraborty
Department of Physical Sciences
Indian Institute of Science Education and Research, Mohali

Lecture - 34
Grand Canonical Ensemble Ideal Gas – Part I

(Refer Slide Time: 00:23)



Welcome back. So, we were discussing the Canonical Ensemble and we will discuss a different type of a canonical ensemble which is called the Grand Canonical Ensemble and we will show that this particular ensemble is connected to the grand partition function omega, right.

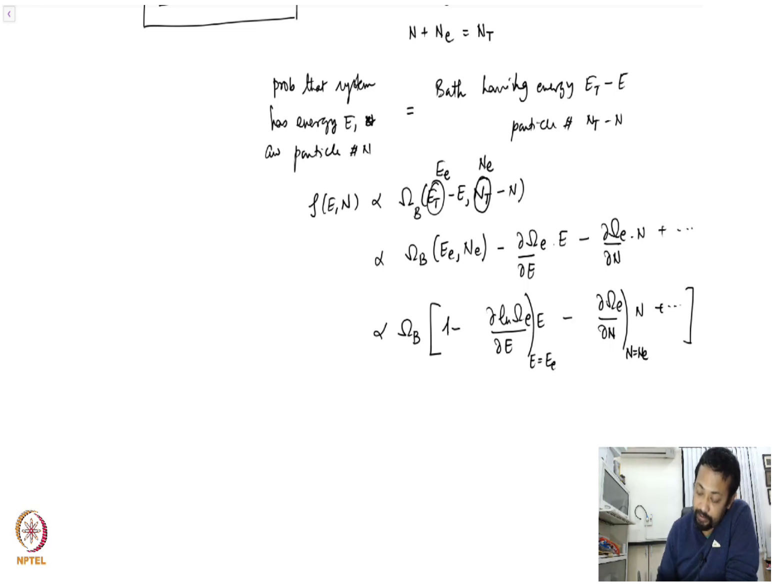
So, we start off with our system which can not only exchange energy, but also can exchange particle number. So, the system can exchange energy and particle number. So, it is a hydrostatic system which means that you can imagine that you have N number of particles which is contained within a box of V, but that just that N is not fixed in time, it is fluctuating in time.

There is a big bath surrounding this with which particles can go to and enter like this with which the system and exchanges particles as well as energy. So, let the bath have the energy E e and particle number N e, so that again just as we had done in the canonical ensemble we will assume that the bath plus the system acts as a micro canonical ensemble.

See, in the earlier lectures, whenever when we did the canonical ensemble we said that look we could derive the distribution of the probability in find of finding the system in the energy state E from the fundamental relation in statistical mechanics and if you are wondering what their fundamental relation is it is s equal to K B ln omega this is what connects everything right.

So, in this particular case we have E plus E e is equal to the total energy E total and N plus N e is equal to the total energy N T. So, that the probability of let us shorten the writing probability that S has probability that the system has energy E and particle number N and particle number N is equal to the bath having energy E total minus E and particle number N total minus sorry, N e sorry N. So, therefore, we will write this as rho E comma N is proportional to omega E T minus E N T minus N.

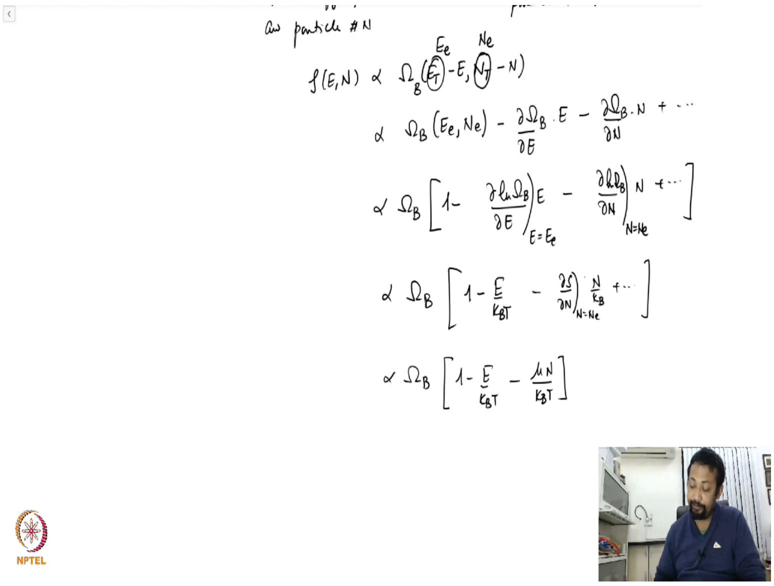
(Refer Slide Time: 03:41)



And, once again we say that the bath is so huge compared to the system that we can literally replace this E t by E e and N t by N E which is E e is the energy of the bath and N E is the particle number contained in the sorry bath. So, again we follow the same strategy that we did minus del omega E del E times E minus del omega E del N times N plus higher order terms which we will ignore.

So, this becomes omega B 1 minus del ln omega E over del E times E minus. So, this E is equal to minus del omega E del N plus higher order terms. Sorry, there is an this is going to be ln omega E; because once I bring I have changed notations here terribly sorry, for that.

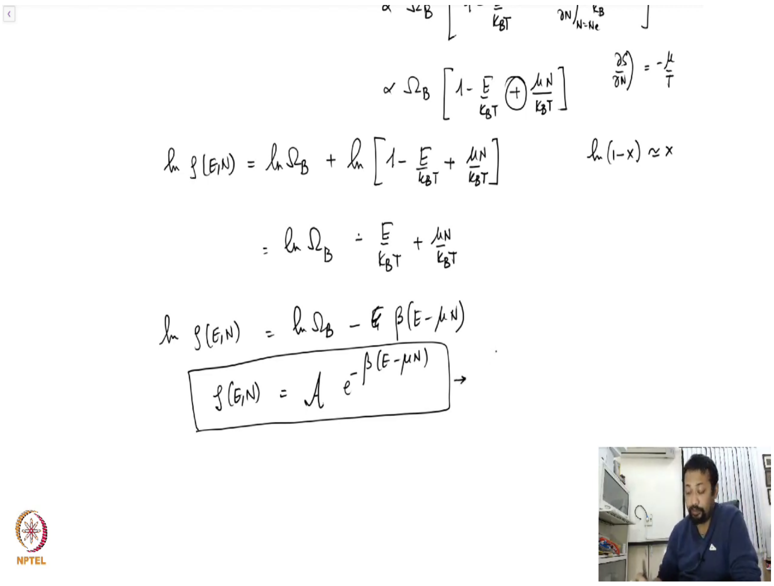
(Refer Slide Time: 05:01)



This has to be omega B, this has to be omega B and this has to be also omega B and since I have taken omega B outside that is where the log comes in just as in the canonical case. So, you have proportional to omega B, the first one I know. So, E over this omega B is S over K B. So, I have E over K B T for just as we go in the canonical case and this becomes del S del N, N equal to N e N over K B.

And, from thermodynamics we know that this is going to be 1 minus E over K B T minus mu N over K B T, right.

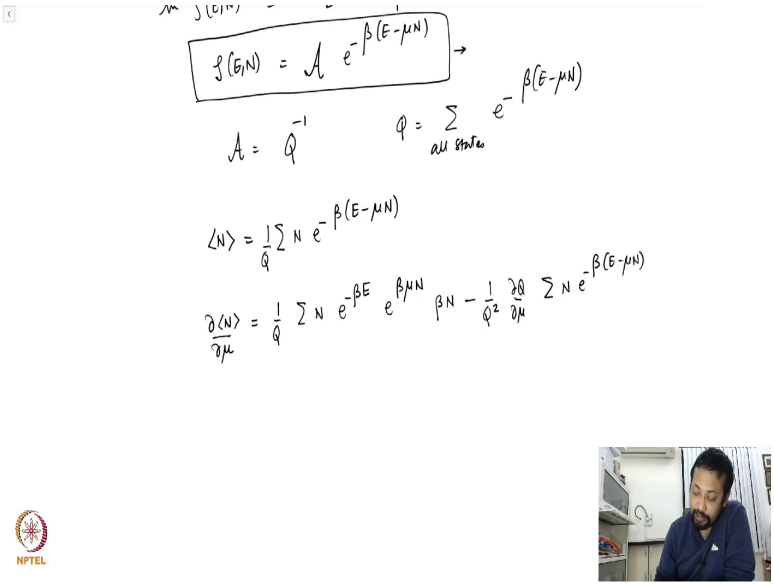
(Refer Slide Time: 06:07)



If I now take a log of rho E comma N; that means, this is going to be ln omega B plus log of 1 minus E over K B T minus mu N over K B T, am I right? Yeah, this sign is not right because del S del N is equal to minus mu over T. So, this becomes plus so that I will use the expansion of this approximately X, then this becomes minus E K B T plus mu N over K B T which means ln of rho E comma N is ln of omega B minus beta E minus mu N.

If I now exponentiate this, then I have log rho of E N is a normalization A e to the power minus beta E minus mu N. So, I have now derived the probability that the system would be in the energy state E comma N and with the particle number.

(Refer Slide Time: 07:43)

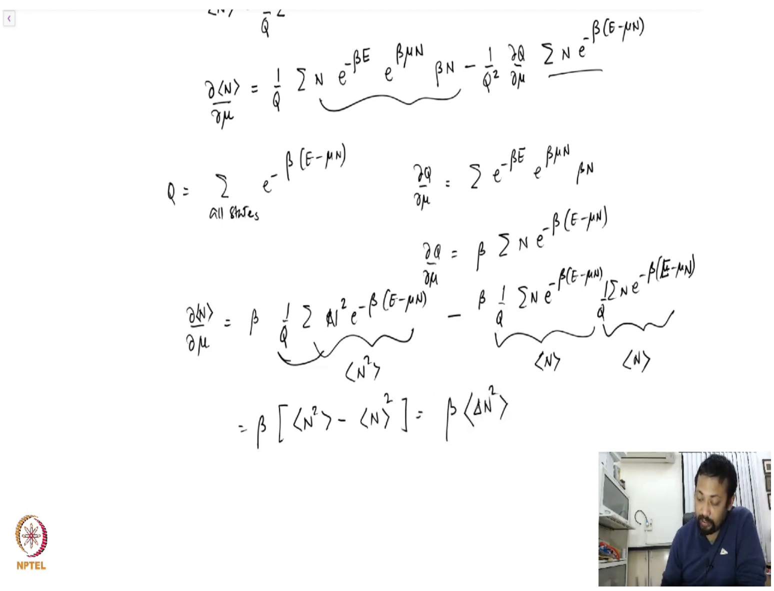


The normalization again as usual is given by z N. So, Q inverse where, Q is sum over all states e to the power minus beta E minus mu N. So, before the standard root now is to connect it to thermodynamics and before we connect it to thermodynamics the first thing that we check is that we know that even here also since we are talking about a fluctuating energy and fluctuating particle number therefore, both of this will have a certain mean, right. And it is this mean that I want to connect to thermodynamics.

So, in thermodynamics I had the internal energy u and this I will connect it to the mean of the energy and I had the particle number this I am going to connect it to the average of this N, right, but are the average is meaningful, right. So, for that I want to first check the following average of N. Average of N is 1 over Q N e to the power minus beta E minus mu N which means this is going to be.

So, if I now take del N del mu then N e to the power minus beta E e to the power beta mu N times beta N right, plus sorry, I know I have to take care of this as minus 1 over Q square del Q del mu sum over N e to the power minus beta E minus mu N.

(Refer Slide Time: 09:56)

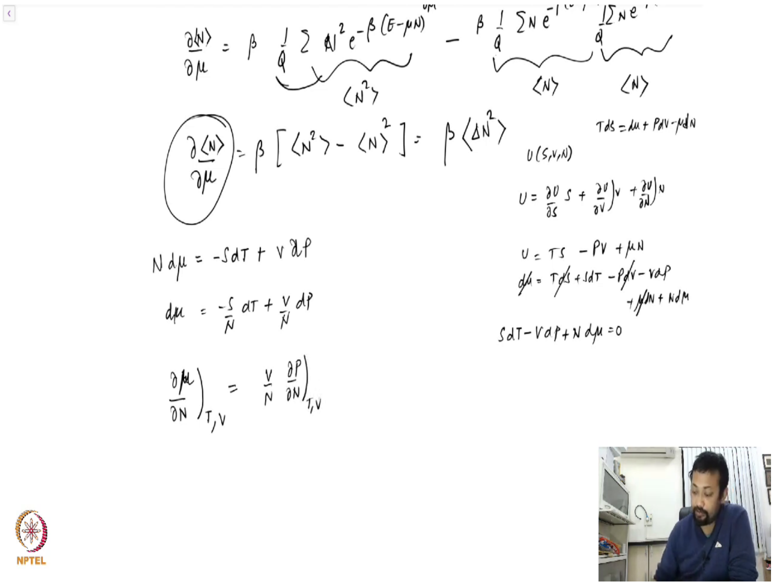


Q is sum of a all states e to the power minus beta u minus mu N. So, that del Q del mu is sum I will not always write all states, it is understood that I am summing over all state is minus beta E e to the power beta mu N beta N. So, that I have this as beta times N E to the power minus E minus mu N.

If I look over here I can simplify this as 1 over Q beta over Q well let us write it in mu 1 over Q sum over E to N square e to the power minus beta E minus mu N minus the 1 over Q square I can distribute. So, there is going to be a beta factor that comes from the derivative of this and then I have 1 over Q sum over N minus beta E minus mu N and then I have this term which is sum over N E to the power minus beta mu E minus mu N.

Both of this sorry, both of this is average of N and this you recognizes average of N square together with the Q. So, you have beta average of N square minus average of N whole square which is beta times delta N square average.

(Refer Slide Time: 11:56)



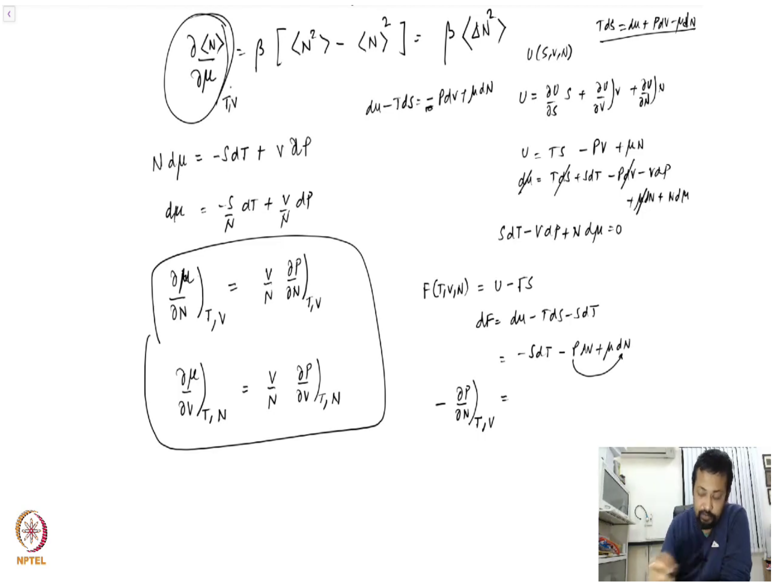
And, this quantity is del N del mu, good. Now, one has to express the left hand side because I understand that this represents the fluctuations, but del N del mu might not be an easily accessible quantity. So, in the experiments for example, right I only know that my response functions are positive, but how do I know that my del N del mu is also a positive quantity?

Of course, one can argue that look delta N square is a positive quantity. Therefore, del N del mu also has to be a positive quantity understood, but let us see. So, we want to look I mean it is. So, use the (Refer Time: 12:34) relation. So, U for a hydrostatic system I know that U is a function of S, V, N and therefore, if I use the homogeneity property then I know that this is going to be del U del S times S del U del V times V plus del U del S times N.

Further, I also have T d S is the first law plus P d V minus mu d N. So, that del U del S is TS and del U del V is going to be minus PV and this is del U del m is going to be plus mu N. So, the differential gives you T d S plus S dT minus P d V minus V d P plus mu d N minus plus N d mu. So, d U cancels with T d S minus P d V plus mu d N.

So, your left out with S dT minus V d P plus N d mu is equal to 0. So, if you take it to the other side you have N times d mu is equal to minus S dT plus V d P, right. So, therefore, d mu is minus S over N dT plus V over N d P, right. Now, del mu del N temperature held constant volume held constant is V over N del P del N, right; temperature held constant, volume held constant.

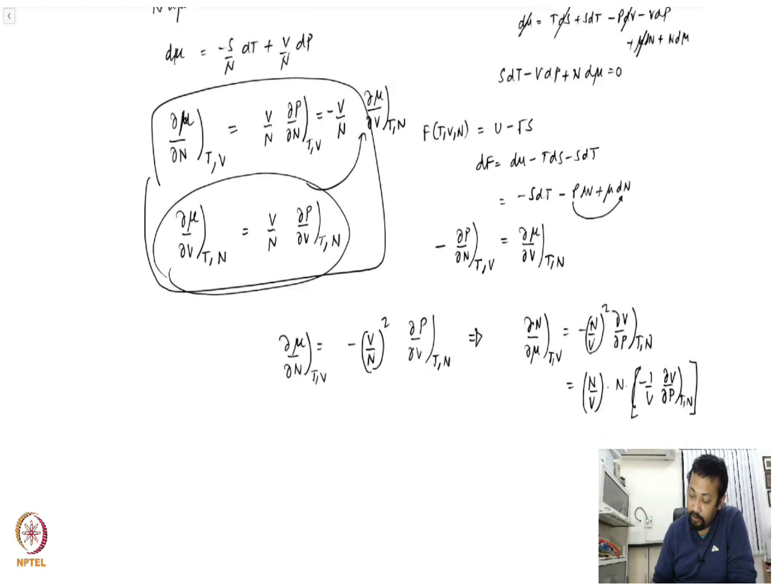
(Refer Slide Time: 14:30)



And, del mu del V temperature held constant N held constant is V over N del T del V T comma N, right. So, now, once again this del mu del N is related to del N del mu, but it is not very useful because I have a del P del N. For that we looked at the Helmholtz free energy which gives me d F is del F del T.

Well, if you are uncertain about things you always do it as U minus TS which is d F is equal to d U minus T d S minus S dT and from the first law I have d U minus T d S is equal to minus P d V plus mu d N. So, I have minus S dT minus P d V plus mu d N. So, that immediately you see that del P del N T held constant T comma V with a minus sign is going to be what here also you realize that T and V are being held constant.

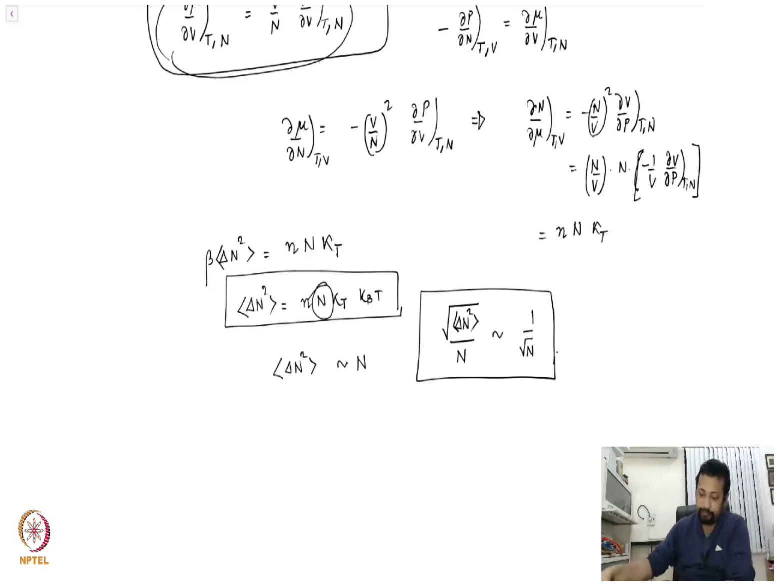
(Refer Slide Time: 16:06)



Del P del N T comma V is going to be del mu del V T comma N. So, you immediately see that this quantity is V over N del mu del V T comma N with the minus sign, right and therefore, you have del mu del N T comma V as minus V over N whole square. You substitute this over here del P del V T comma N.

Let us simplify it over here itself because this would imply that del N del mu T comma V is minus N over V whole square del V del P T comma N. I will keep bring out one N and then I will manipulate this as N by V times N times minus 1 by V del V del P T comma N.

(Refer Slide Time: 17:33)

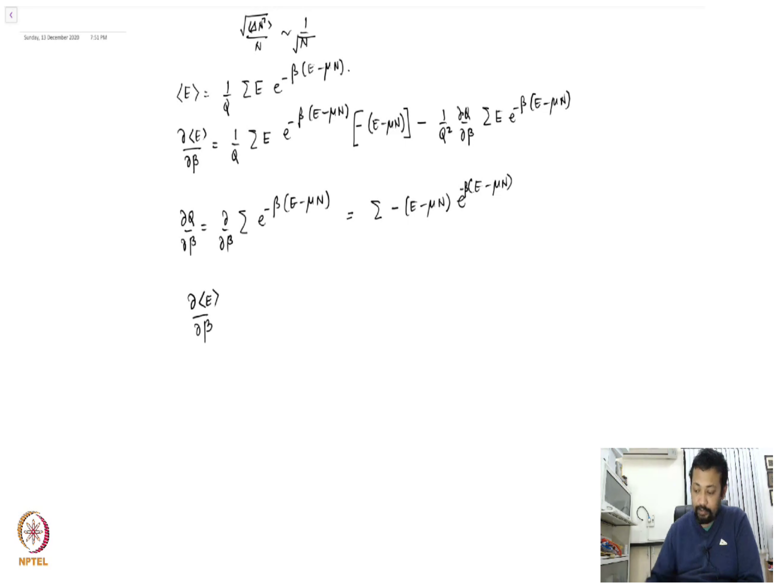


And, all of these are familiar to us this is the number density which is an intensive quantity, this is capital N and this quantity is again an intensive quantity which we know it as a compressibility. So, you immediately see that my delta N square. So, beta time delta N square average is n N kappa T.

So, that delta N square the average of the number fluctuations is n N kappa T times K B T and therefore, delta N square will go as N because I have a N sitting over here all the rest of them are independent of N or does not scale they are intensive variables now. So, square root of delta N square over N will go as 1 over square root N.

So, in the thermodynamic level when I have a large enough system my distribution of N which is a fluctuating particle number becomes very very sharp peak because you see that the width of this distribution becomes vanishingly small, right. So, your mean is well defined and therefore, you are in a good position to connect it to thermodynamics by saying that look the average of my N corresponds to the N that we did, good.

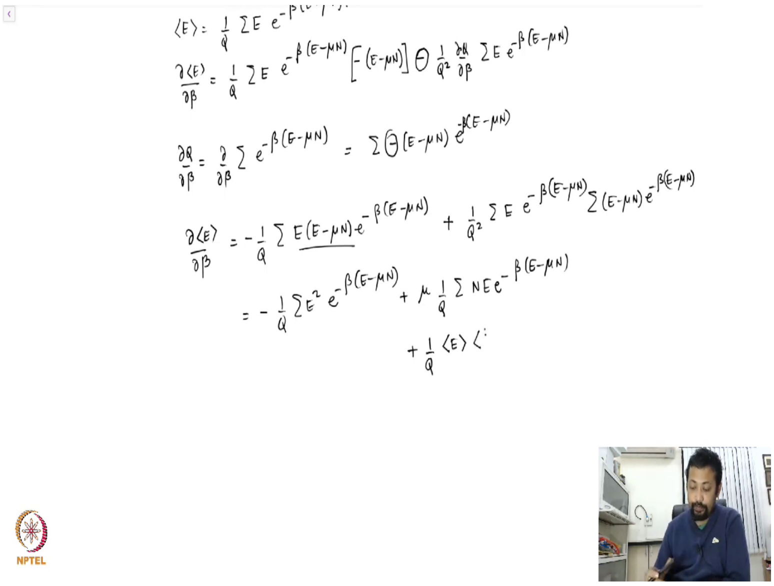
(Refer Slide Time: 19:14)



So, now that we have delta N square the square root of delta N square average over average in going as 1 over square root N. What about the energy? So, the average energy is 1 over Q sum over E e to the power minus beta E minus mu N. So, del E del beta is going to be 1 by Q sum over E 1 has to be careful now, minus beta E minus mu N minus E minus mu N minus 1 over Q square del Q del beta sum over E e to the power minus beta E minus mu N.

It is once again it is a same laborious calculation that one has to do, but it is not very difficult to do. Let us look at del Q del beta is del del beta of sum E to the power minus beta E minus mu N which is going to be sum over minus E minus mu N times e to the power E minus mu N with a minus beta in front, right.

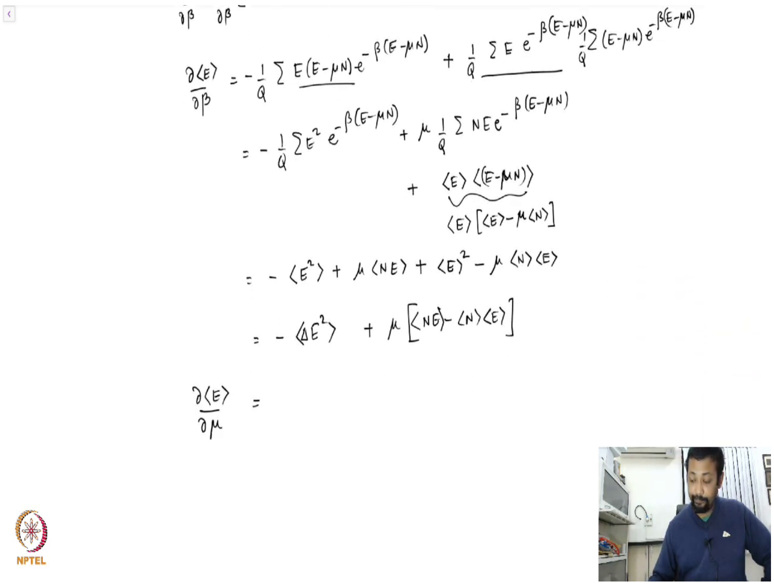
(Refer Slide Time: 20:55)



So, del E del beta is going to be 1 by Q the minus comes outside sum over E E minus mu N minus beta E minus mu N minus and this becomes a plus together with this minus and this minus this becomes a plus 1 by Q square sum over E e to the power minus beta E minus mu N times sum over E minus mu N e to the power minus beta E minus mu N.

Let us expand this minus 1 over Q sum over E square minus beta E minus mu N plus mu 1 over Q sum over N times E e to the power minus beta E minus mu N. The second term is 1 over Q average of E times average of we will remove the 1 by Q square.

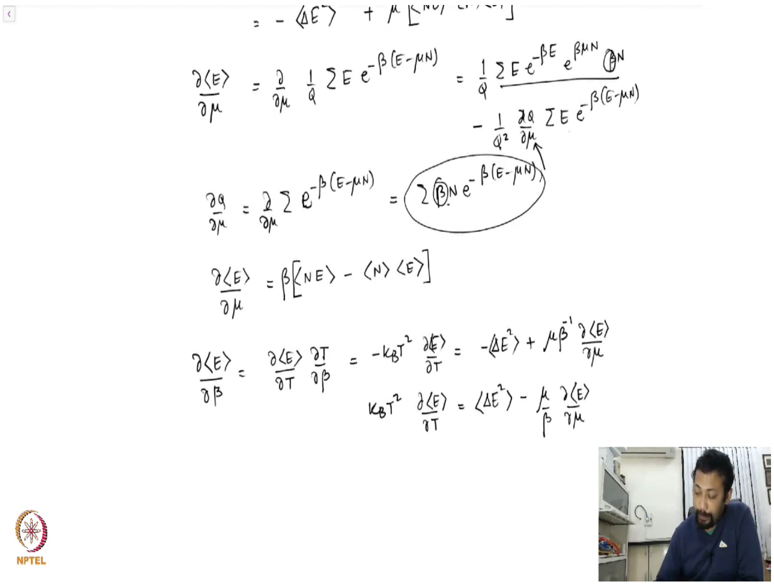
(Refer Slide Time: 22:25)



And, you can distribute the 1 by Q from here and 1 over Q over here. So, that this becomes average of E and this becomes average of E minus mu N so that this term is average of E times average of E minus mu average of N. And, therefore, the first term is average of E square plus mu average of N E plus average of E whole square minus mu average of N average of E.

So, that we have minus delta E square average plus mu NE minus average of N average of E, right. We are not done yet with this, we have to take a little more steps.

(Refer Slide Time: 23:50)



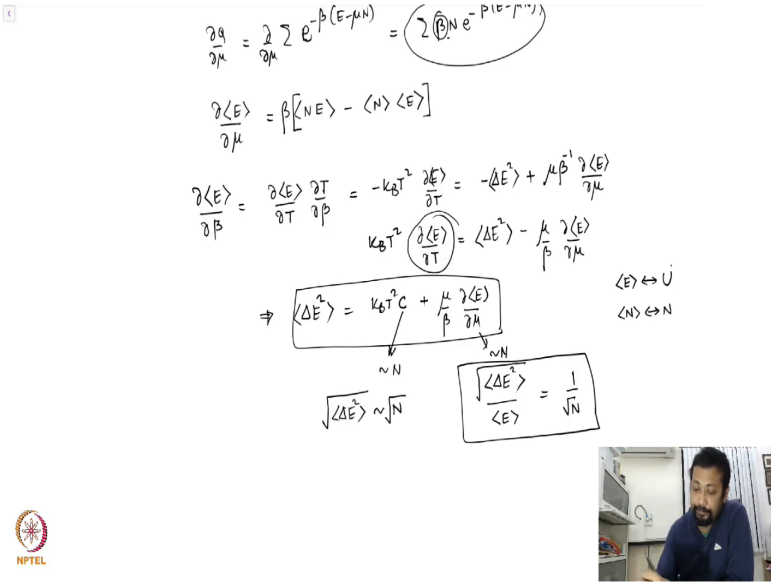
You want to calculate del average E del mu and that quantity if I look over here is del del mu of 1 over Q sum over E e to the power minus beta E minus mu N which is going to be 1 over Q sum over E e to the power minus beta E e to be power beta mu N; now, I am taking a derivative with respect to this therefore, I should have beta N minus 1 over Q square del Q del mu sum over U minus beta E minus mu N.

But, del Q del mu we have already done. Del Q del mu is just del del mu of sum over E to the power minus beta E minus mu N which is going to be sum over N beta N E to the power minus beta E minus mu N, right. So, you put back this over here again distribute the Qs. So, that you have del average E del mu is going to be.

This term is average of N times E and this times this is average N average E right, except now I have a beta factor common in both cases. So, I have to multiply this with beta. So, that del E del beta which is del E del T del T del beta is equal to minus K B T square del E del T is going to be equal to minus delta E square plus mu over P sorry, mu beta because del E del beta inverse.

So, that K B T square del E del T is going to be delta E square minus mu over beta del E del mu.

(Refer Slide Time: 26:52)



This implies we have the fluctuations in the energy is given by this quantity is your specific heat. This K B T square times C plus mu over beta del E del mu. We believe this calculation up to here noting that this will scale as N because it is a derivative of temperature the derivative of the internal energy with respect to the temperature and E being a extensive quantity. Therefore, this should scale as N.

And, similarly this is a derivative of the internal energy with respect to the chemical potential and this will also scale with N. So, your delta E square average scales with N which mean square root of this in scale with square root of N and again you recover the result over average of E is equal to 1 over square root of N.

So, in the thermodynamic limit your fluctuations your distribution of the energy becomes a very sharply peeked function. Your fluctuations in that distribution decay as 1 over square root N and as you go to larger and larger systems size you will see that the width of this distribution becoming narrow and narrow so that you can immediately relate the average of the quantity to the internal energy that we did in the thermodynamics and average of N with N.