Statistical Mechanics

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Lecture - 29

Canonical Ensemble

So, now, what we want to consider now that we have dealt with micro Canonical Ensemble. Now, typically micro canonical ensembles are the ones which refer to the isolated system the language of thermodynamics, but isolated systems are very very rare in real life.

Normally, we always see that our system is either in the presence of the heat bath the reservoir all around us either in a thermal reservoir or it is connected to the open air; therefore, there is a barrel step that maintains a constant pressure in the system so on and so forth.

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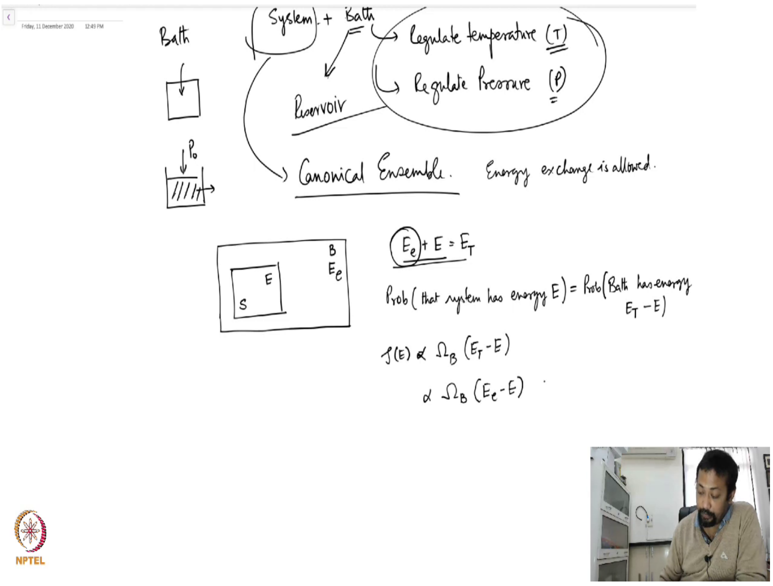

$E_e + E = E_T$

Prob (that system has energy E) = Prob (Bath has energy $E_T - E$)

$\rho(E) \propto \Omega_B (E_T - E)$

$\propto \Omega_B (E_e - E)$

So, essentially we always have system plus a bath. Now, this bath can regulate temperature, can regulate pressure; for example, I can keep a small container and leave it outside. So, let us heat up the container there is a liquid or gas which is contained in that container you heat it up and you leave it outside and come back after a day you will see that the container has the same temperature as a, outside temperature.

So, essentially the whole environment surrounding this container acts as a bath. I can also leave the container open in which case the pressure in the container is kept constant and is equal to the atmospheric pressure P naught. So, a bath is typically it is a heat reservoir or essentially the other languages it is a reservoir that can be used to maintain temperature in high pressure.

Now, such a system when it is connected to a bath is what is statistically (Refer Time: 02:12) canonical ensemble. So, in the first canonical ensemble that we considered the possibilities are that of course, I will keep the temperature fixed which means only energy exchange is allowed, right.

So, the system and I want to find out the probability distribution of the density for the system to be in the energy state E the system has an energy E and it has it is in connected to a bath which has an energy let us say E e, the environment. So, that the total energy E e plus E is a constant quantity right.

Now, probability that system has energy E is equal to the probability that the reservoir or the bath has energy E T minus E, right. Therefore, we write rho of E which is the probability for the system to be in the energy state E as proportional to the total number of microstate of the bath with the energy E T minus E.

However, also note that energy being an extensive quantity the bath is so large, the reservoir is so large that in this equation the dominance is of this energy E e. So, what we will do as our next step is we will approximate this as E e minus E right.

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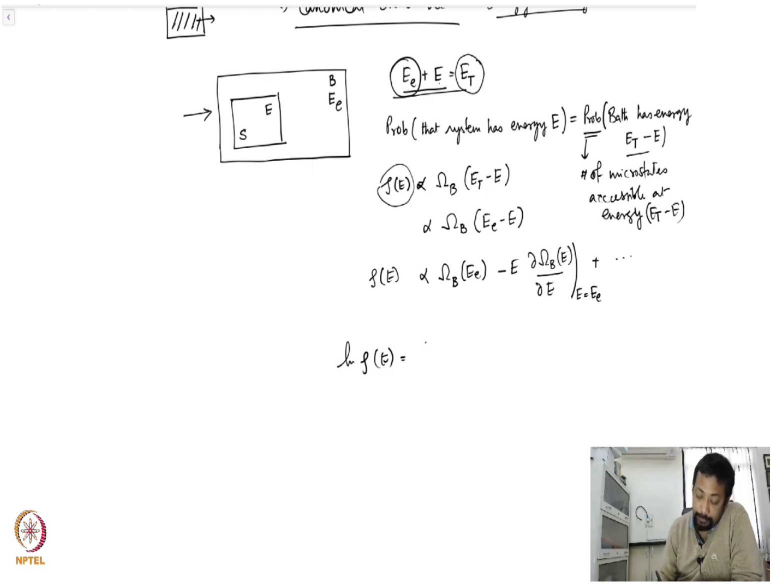

$$\boxed{E_e} + E = \boxed{E_T}$$

Prob (that system has energy E) = Prob (Bath has energy $E_T - E$)

# of microstates accessible at energy $(E_T - E)$

$$\boxed{\rho(E)} \propto \Omega_B (E_T - E)$$

$$\propto \Omega_B (E_e - E)$$

$$\rho(E) \propto \Omega_B(E_e) - E \left.\frac{\partial \Omega_B(E)}{\partial E}\right|_{E=E_e} + \cdots$$

$$\ln \rho(E) =$$

Therefore, so, E since E is negligibly small one can clearly approximate this to minus E del omega B del E evaluated at E is equal to E e plus higher order terms which will ignore because E is so small. So, again just a very briefly to say that I have a system which is connected to a bath and which is allowed to exchange energy right. So, the systems energy can actually fluctuate.

Now, but the total energy which is E total and is a sum total of E e the energy of the bath plus the energy of the system. You should note that this bath plus the system is a micro canonical ensemble and therefore, when the bath is so large compared to the system the probability that the system has an energy E is the probability that the path has the energy E total minus E.

Now, the bath is so large that it itself is like an isolated system and therefore, this probability or rather the right hand side is proportional to the number of microstates accessible at energy E t minus E right. So, then I have rho of E is equal to this.

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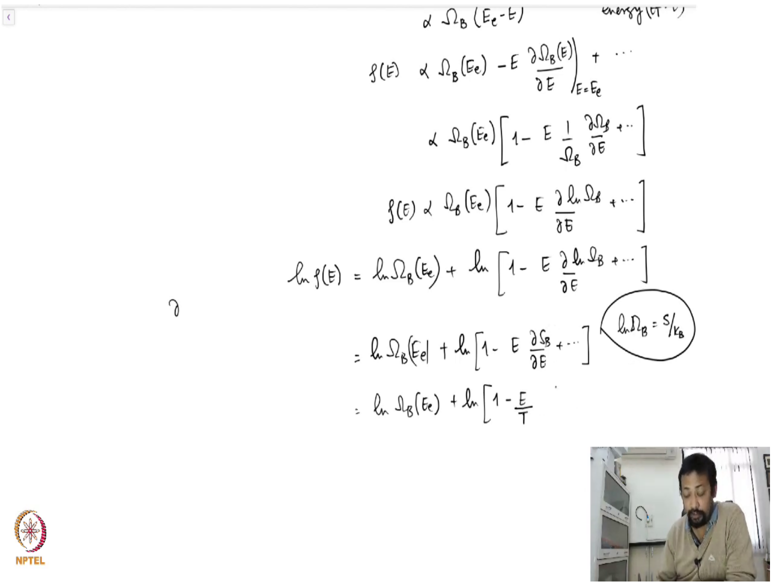

$$\propto \Omega_B(E_e - E) \qquad \text{energy}$$

$$\rho(E) \propto \Omega_B(E_e) - E \left.\frac{\partial \Omega_B(E)}{\partial E}\right|_{E=E_e} + \cdots$$

$$\propto \Omega_B(E_e)\left[1 - E\,\frac{1}{\Omega_B}\frac{\partial \Omega_B}{\partial E} + \cdots\right]$$

$$\rho(E) \propto \Omega_B(E_e)\left[1 - E\,\frac{\partial \ln \Omega_B}{\partial E} + \cdots\right]$$

$$\ln \rho(E) = \ln \Omega_B(E_e) + \ln\left[1 - E\,\frac{\partial \ln \Omega_B}{\partial E} + \cdots\right]$$

$$\partial$$

$$= \ln \Omega_B(E_e) + \ln\left[1 - E\,\frac{\partial S_B}{\partial E} + \cdots\right] \qquad \boxed{\ln \Omega_B = S/k_B}$$

$$= \ln \Omega_B(E_e) + \ln\left[1 - \frac{E}{T}\right.$$

If I take a log of this is proportional to now is going to be, but well before I take a log I want to just simplify this a little bit more so that I can write down this as proportional to omega B E of e 1 minus E 1 by omega B del omega B del E plus higher order terms. So, this becomes omega B E e 1 minus E del ln omega B del E plus higher order terms. This is my probability of finding the system in the energy state E.

Therefore if I now take a log of E this becomes ln omega B E plus ln 1 minus E del ln omega B del E plus higher order terms. But, del; so, first note that ln omega B is S over K B right is entropy of the reservoir.

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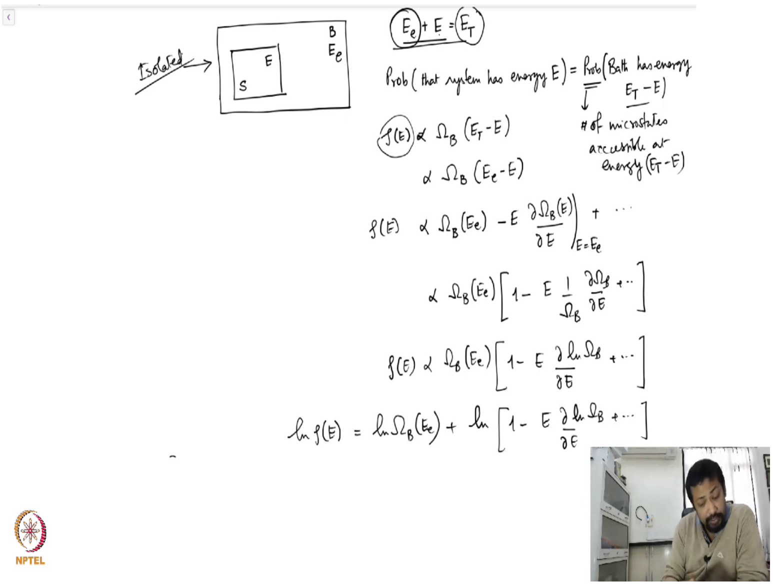

$\boxed{E_e} + E = \boxed{E_T}$

Prob (that system has energy E) = Prob (Bath has energy $E_T - E$)

\# of microstates accessible at energy $(E_T - E)$

$$\boxed{\rho(E)} \propto \Omega_B (E_T - E)$$

$$\propto \Omega_B (E_e - E)$$

$$\rho(E) \propto \Omega_B(E_e) - E \left.\frac{\partial \Omega_B(E)}{\partial E}\right|_{E=E_e} + \cdots$$

$$\propto \Omega_B(E_e)\left[1 - E \frac{1}{\Omega_B}\frac{\partial \Omega_B}{\partial E} + \cdots\right]$$

$$\rho(E) \propto \Omega_B(E_e)\left[1 - E \frac{\partial \ln \Omega_B}{\partial E} + \cdots\right]$$

$$\ln \rho(E) = \ln \Omega_B(E_e) + \ln \left[1 - E \frac{\partial \ln \Omega_B}{\partial E} + \cdots\right]$$

Because the reservoir is so large the reservoir plus the system both totally is this acts as an isolated system and one can apply metro canonical ensemble to this system plus reservoir. But, since the reservoir is so large and the bath is a tiny fraction of the reservoir is small therefore, I can use this expression.

So, then this becomes ln omega B E e plus ln 1 minus E del S B del E, right plus higher order terms which would then approximate to not approximate to which will write to 1 minus E del S E over T and this T is the temperature of the bath not the system right, good.

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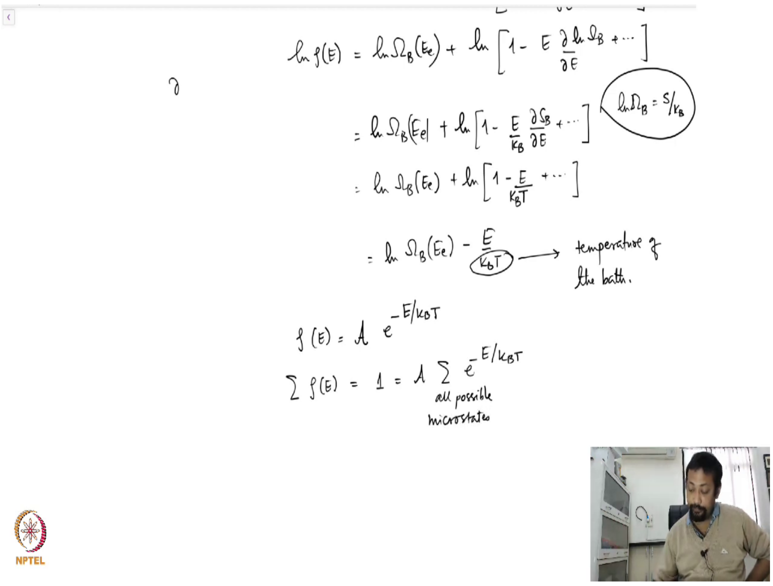

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$$\ln \rho(E) = \ln \Omega_B(E_e) + \ln\left[1 - E\frac{\partial \ln \Omega_B}{\partial E} + \cdots\right]$$

$$= \ln \Omega_B(E_e) + \ln\left[1 - \frac{E}{k_B}\frac{\partial S_B}{\partial E} + \cdots\right]$$

$$\boxed{\ln \Omega_B = S/k_B}$$

$$= \ln \Omega_B(E_e) + \ln\left[1 - \frac{E}{k_B T} + \cdots\right]$$

$$= \ln \Omega_B(E_e) - \frac{E}{\boxed{k_B T}} \longrightarrow \text{temperature of the bath.}$$

$$\rho(E) = A\, e^{-E/k_B T}$$

$$\sum \rho(E) = 1 = A \sum_{\substack{\text{all possible}\\ \text{microstates}}} e^{-E/k_B T}$$

I can expand the log omega B times E e minus sorry, this has to be S over K B T right E over K B minus E over K B T. Note, this is the temperature of the bath, right. So, that rho of E is a constant we will call A e to the power minus E K B T. So, the probability of the system to be in the energy state E is given by this expression.

The A is obtained from the normalization. So, if I just do sum over rho E which is going to be one which means A e to the power minus E over K B T, but what am I summing over? I am summing over all possible micro states right.

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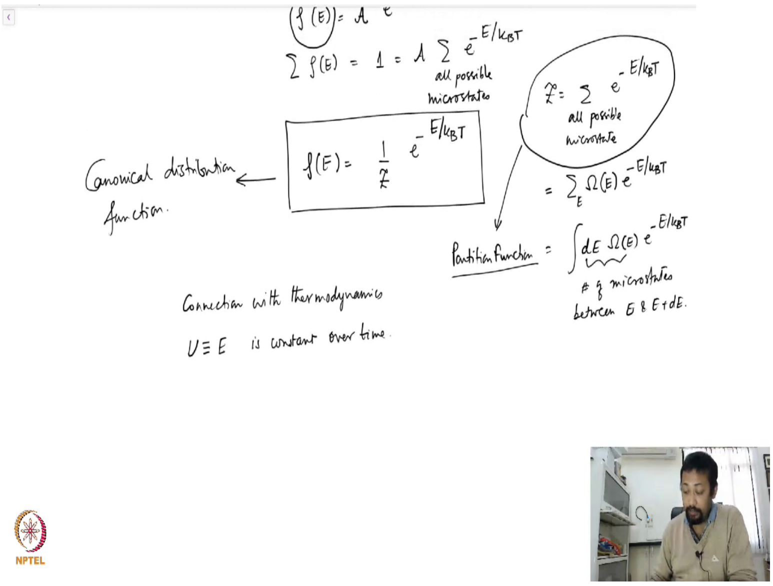

$\rho(E) = A\, e$

$\sum \rho(E) = 1 = A \sum_{\substack{\text{all possible} \\ \text{microstates}}} e^{-E/k_BT}$

Canonical distribution function. ← $\boxed{\rho(E) = \frac{1}{Z} e^{-E/k_BT}}$

$Z = \sum_{\substack{\text{all possible} \\ \text{microstate}}} e^{-E/k_BT}$

$= \sum_E \Omega(E)\, e^{-E/k_BT}$

Partition Function $= \int \underbrace{dE\, \Omega(E)}_{\substack{\#\text{ of microstates} \\ \text{between } E\ \&\ E+dE.}} e^{-E/k_BT}$

Connection with thermodynamics

$U \equiv E$ is constant over time.

And, rho of E takes the form 1 by Z e to the power minus E over K B T, where we have written Z as sum over all possible microstates e to the power minus E over K B T, right. This I mean omega E one can also write as this where omega E is the number of microstates with energy E and sum over E.

If you want to look at in a continuum way then this is going to be d E omega E e to the power minus E K B T depends on the system you are looking at. And, omega E d E is the total number of is the number of microstates between E and E plus d E, right. This is what is called a canonical distribution function right and we shall work with it.

The central quantity of interest is this one z which is called a partition function. In canonical ensemble the whole trick is involved is to evaluate this partition function, right. But, all of this is fine. So, all of this has been derived from the fundamental postulate of statistical mechanics that you started off with in an isolated micro canonical. Isolated system use the principle the language or the work I mean the theory that we did for the micro canonical ensemble you use that thing.

And then essentially distribute determine the probability density for the system to be in the energy state E, right. Now, the biggest part is I have to make the connection with thermodynamics. Now, to build the connection with thermodynamics we note the first thing is that in thermodynamics the quantities that we have dealt with are essentially quantities which are constant right.

For example, the energy U which is equivalent to E in the in our description in the statistical description of a system is a constant over time. These are microscopic quantities which show no fluctuations connect. But, clearly what we have over here is the energy of the system fluctuates because we are describing it in terms of a probability density, right.

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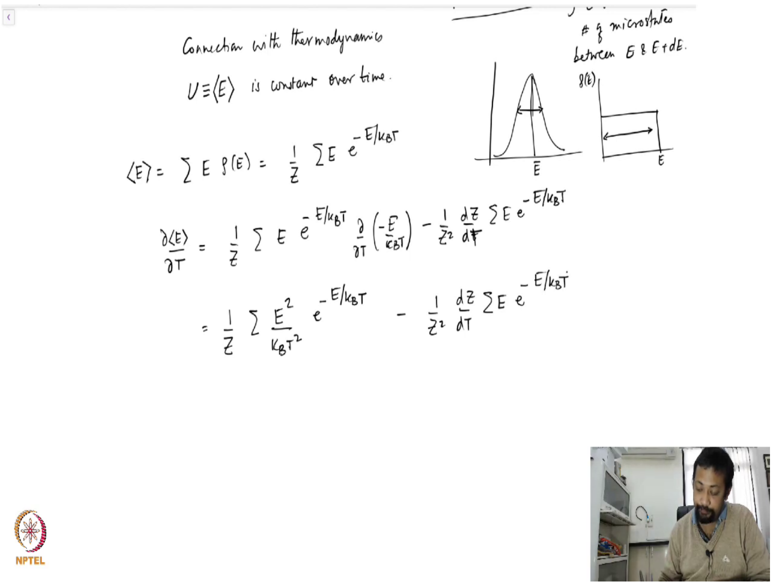

Connection with thermodynamics

$U \equiv \langle E \rangle$ is constant over time.

$$\langle E \rangle = \sum E \rho(E) = \frac{1}{Z} \sum E e^{-E/k_BT}$$

$$\frac{\partial \langle E \rangle}{\partial T} = \frac{1}{Z} \sum E e^{-E/k_BT} \frac{\partial}{\partial T}\left(-\frac{E}{k_BT}\right) - \frac{1}{Z^2}\frac{dZ}{dT} \sum E e^{-E/k_BT}$$

$$= \frac{1}{Z} \sum \frac{E^2}{k_BT^2} e^{-E/k_BT} - \frac{1}{Z^2}\frac{dZ}{dT} \sum E e^{-E/k_BT}$$

So, how do we bridge the gap or how do we make the connection? The first thing that we note is that the energy that we the internal energy that we had in thermodynamics is identical to the average energy in statistical mechanics, right. But, the mean or the average is only meaningful if the distribution is sharply peak when you have a well defined mean, right.

So, for example, if I have a distribution of energy which looks like this then this is a relevant quantity then everything is meaningful because you see the width and the distribution the mean are well defined. But, if I have a distribution which is like this for the energies rho of E, then I am in a little bit of trouble.

Because this width of this distribution spreads all across this range and therefore, range of allowed ranges of E and therefore, the meaning is not the meaning of mean the average is not very meaningful right. So, let us see the average of energy in our in a canonical ensemble is essentially sum over E rho E which is 1 by Z sum over E e to the power minus E over K B T and the sum is over all state.

So, now, let us take a derivative of this average energy with respect to temperature. Then the first term is sum over E e to the power minus E over K B T del del T of minus E over K B T plus sum over E e to the power minus well, we will put it later on let us say.

So, we write this as minus 1 by Z square minus 1 by Z square d Z dt sum over d t capital T sum over E e to the power minus E over K B T which is equal to 1 by Z sum over E square over K B T square. This is comes from the derivative e to the power minus E over K B T minus 1 over Z square d Z dT sum over E e to the power minus E over K B T.

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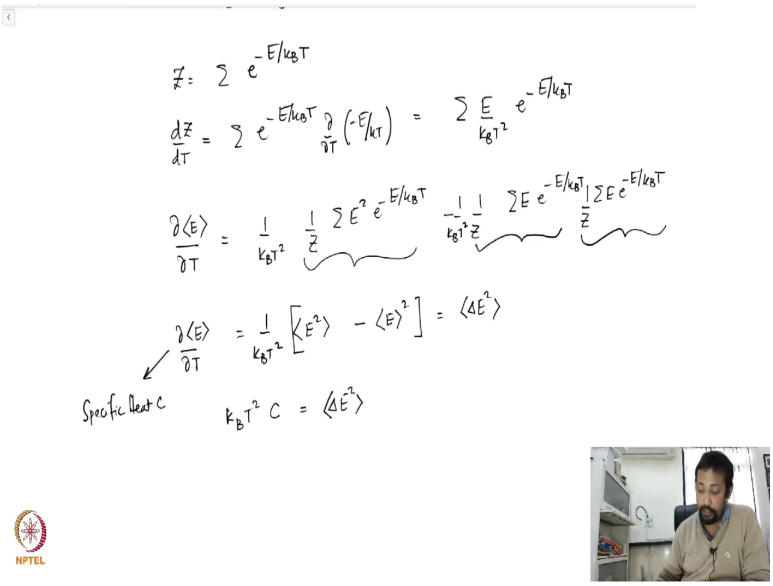

$$Z = \sum e^{-E/k_BT}$$

$$\frac{dZ}{dT} = \sum e^{-E/k_BT} \frac{\partial}{\partial T}\left(-E/kT\right) = \sum \frac{E}{k_BT^2} e^{-E/k_BT}$$

$$\frac{\partial \langle E \rangle}{\partial T} = \frac{1}{k_BT^2} \underbrace{\frac{1}{Z} \sum E^2 e^{-E/k_BT}} - \frac{1}{k_BT^2} \underbrace{\frac{1}{Z} \sum E e^{-E/k_BT}} \underbrace{\frac{1}{Z} \sum E e^{-E/k_BT}}$$

$$\frac{\partial \langle E \rangle}{\partial T} = \frac{1}{k_BT^2}\left[\langle E^2 \rangle - \langle E \rangle^2\right] = \langle \Delta E^2 \rangle$$

Specific Heat C

$$k_BT^2 C = \langle \Delta E^2 \rangle$$

Now, Z the partition function is sum over all states e to the power minus E over K B T. And, therefore, d Z d T if I take a time temperature derivative of this partition function is sum over e to the power minus E over K B T del del T of minus E over K B T which is again sum over E over K B T square e to the power minus E over K B T, right.

So, our expression for del E del T is equal to 1 over, let us first take out 1 over K B T square then 1 over Z sum over E square e to the power minus E over K B T minus 1 over Z square 1 over K B T square and then I have d Z d T which is going to be sum over E e to the power minus E over K B T, then an another sum over E e to the power minus E over K B T.

1 over K B T square this you clearly see is the average over E square minus if you look over here I can now take the Z square and write it like this. But, this is average over E this is average of E, so that I have average E whole square with the bracket outside. So, therefore, this quantity is delta E square average is equal to del E K del T.

So, that, but this quantity on the left hand side is nothing, but the specific heat C. So, I have K B T square times C is equal to delta E square.

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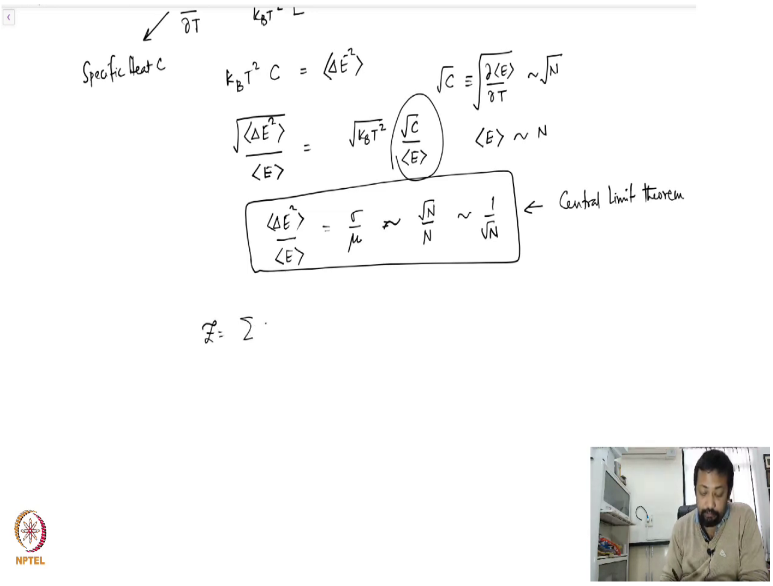

Specific Heat C

$$k_BT^2 C = \langle \Delta E^2 \rangle$$

$$\sqrt{C} \equiv \sqrt{\frac{\partial \langle E \rangle}{\partial T}} \sim \sqrt{N}$$

$$\frac{\sqrt{\langle \Delta E^2 \rangle}}{\langle E \rangle} = \sqrt{k_BT^2}\,\frac{\sqrt{C}}{\langle E \rangle}$$

$$\langle E \rangle \sim N$$

$$\boxed{\frac{\langle \Delta E^2 \rangle}{\langle E \rangle} = \frac{\sigma}{\mu} \sim \frac{\sqrt{N}}{N} \sim \frac{1}{\sqrt{N}}} \leftarrow \text{Central Limit theorem}$$

$$\mathcal{Z} = \sum$$

So, delta E square of this divided by average of E is going to be K B T square C not K B square, but K B T square times C divided by average of E. This is the term which is not very interesting to me, but it is this ratio which is important. C sorry, this is wrong. Since I have taken the square root this is going to be square root K B T square, square root C over average of E it is this ratio which I am interested.

Now, C which is identical to del E del T is an extensive quantity and therefore, it will scale with N. So, square root of C, the specific heat is going to be square root N. In contrast, average of E is going to be scaling as N, right, is an extensive quantity.

So, therefore, delta E square over average of E which is essentially the ratio of sigma over the mean the standard deviation over the mean is going to be square root N over N. So, we will just write down this will go as 1 by square root N. Now, this is a remarkable result essentially that tells you that if you keep on increasing the number of particles in the system your distribution of energy which is a fluctuating quantity in the canonical ensemble becomes sharper and sharper so that the sigma of a mu will scale as 1 over square root N.

It is a consequence of what is the central limit theorem? Because the total energy is essentially sum total of energies of the individual particles which are itself random, right. Now, what we do next? Well, we take the partition function and we write down.

Now, the first thing we have cleared of is that look in our description in our statistical description is clearly meaningful, that this expression that we have derived and all the derivations that we have done starting from the fundamental postulate of statistical mechanics which is S equal to K B l and omega is really meaningful.

Because in a sense what I am getting it at is that if in the thermodynamic limit where I really have a large number of particles in the system my distribution becomes sharply peaked. So, the mean is truly meaningful and this average I can connect to the internal energy in thermodynamics. But, we have still a little more to go.

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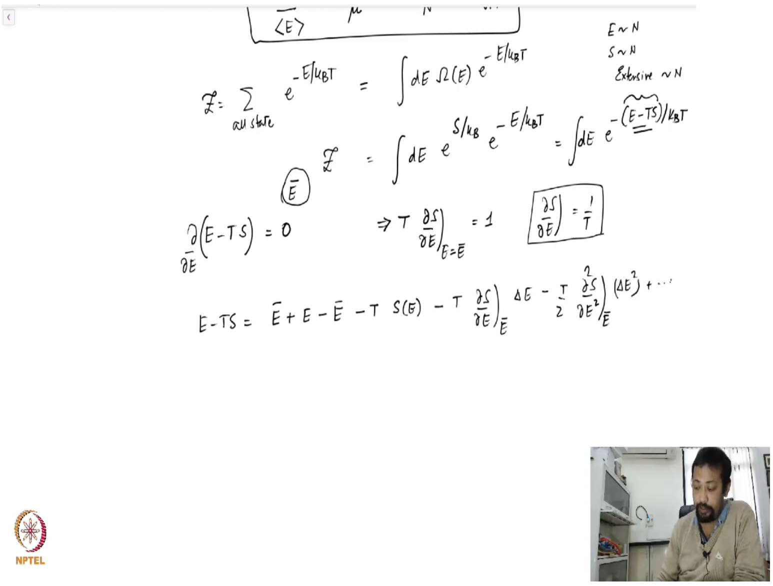

$\langle E \rangle \quad \mu \quad N$

$E \sim N$

$S \sim N$

Extensive $\sim N$

$$Z = \sum_{\text{all state}} e^{-E/k_BT} = \int dE\, \Omega(E)\, e^{-E/k_BT}$$

$$\boxed{\bar{E}} \quad Z = \int dE\, e^{S/k_B} e^{-E/k_BT} = \int dE\, e^{-\overbrace{(\underline{\underline{E-TS}})}/k_BT}$$

$$\frac{\partial}{\partial \bar{E}}(E - TS) = 0 \quad \Rightarrow T \left.\frac{\partial S}{\partial E}\right)_{E=\bar{E}} = 1 \quad \boxed{\left.\frac{\partial S}{\partial E}\right) = \frac{1}{T}}$$

$$E - TS = \bar{E} + E - \bar{E} - T\, S(\bar{E}) - T \left.\frac{\partial S}{\partial E}\right)_{\bar{E}} \Delta E - \frac{T}{2} \left.\frac{\partial^2 S}{\partial E^2}\right)_{\bar{E}} (\Delta E^2) + \cdots$$

So, let us look at the let us start again with the partition function where this was all over all states e to the power minus E over K B T. So, we start off with the partition function, where I have Z as a sum over all states E to the power minus E over K B T and which we write d E omega E if there is energy states at a continuum e to the power minus E over K B T.

So, that this integral is d E e to the power S over K B e to the power minus E over K B T which is integral d E e to the power minus E minus TS over K B T, right. Now, note that E minus T S is an extensive quantity because E also scales with N, S also scales with N therefore, this quantity is an extensive quantity extensive that scales with N.

And, therefore, in the long thermodynamic limit we can use the saddle point to calculate evaluate this partition function, right which would mean that we minimize E minus T S, right del del E of this, to give me the minimum energy or to the energy at which the system is likely to happen is going to be 0, right.

So, this means that T del S del E at E is equal to E bar is going to be 1 which gives me the thermodynamic relation that del S del E is going to be 1 by T, correct. Now, once I have this E bar I want to write down this part in terms of this. So, E minus T S is E bar plus E minus E bar.

So, what I am trying to do over here is, I am trying to write down this argument of the exponential around this energy E bar minus E bar minus T of S E minus T del S del E evaluated at E bar times delta E minus T by 2 del 2 S del E 2 E bar delta E square plus higher order terms, right.

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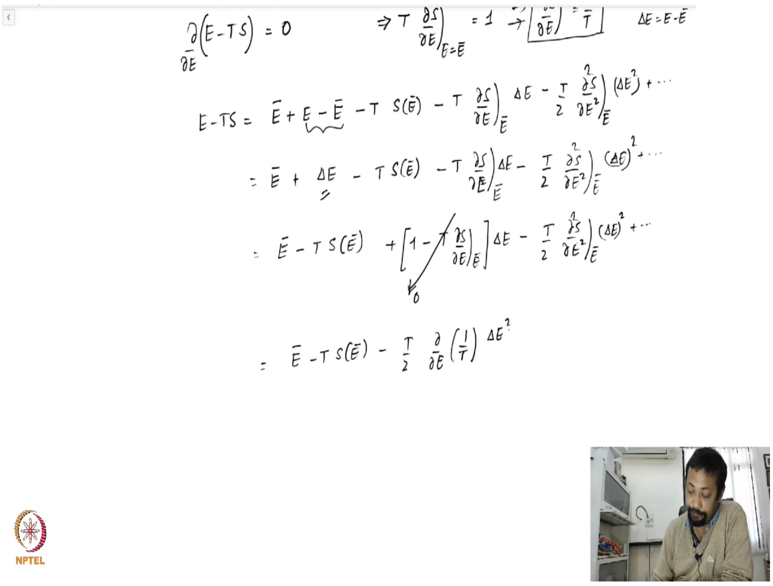

$$\frac{\partial}{\partial \bar{E}}(E-TS) = 0 \qquad \Rightarrow T\left.\frac{\partial S}{\partial E}\right)_{E=\bar{E}} = 1 \rightarrow \boxed{\left.\frac{\partial S}{\partial E}\right) = \frac{1}{T}} \qquad \Delta E = E-\bar{E}$$

$$E-TS = \bar{E} + \underbrace{E-\bar{E}} - T\,S(\bar{E}) - T\left.\frac{\partial S}{\partial E}\right)_{\bar{E}}\Delta E - \frac{T}{2}\left.\frac{\partial^2 S}{\partial E^2}\right)_{\bar{E}}(\Delta E^2) + \cdots$$

$$= \bar{E} + \Delta E - T\,S(\bar{E}) - T\left.\frac{\partial S}{\partial E}\right)_{\bar{E}}\Delta E - \frac{T}{2}\left.\frac{\partial^2 S}{\partial E^2}\right)_{\bar{E}}(\Delta E)^2 + \cdots$$

$$= \bar{E} - T\,S(\bar{E}) + \left[1 - T\left.\frac{\partial S}{\partial E}\right)_{\bar{E}}\right]\Delta E - \frac{T}{2}\left.\frac{\partial^2 S}{\partial E^2}\right)_{\bar{E}}(\Delta E)^2 + \cdots$$

$$0$$

$$= \bar{E} - T\,S(\bar{E}) - \frac{T}{2}\frac{\partial}{\partial E}\left(\frac{1}{T}\right)\Delta E^2$$

So, that I have E bar plus this 2 makes it delta e. So, here the delta E that I have used is E minus E bar minus T of S E bar minus T of del S del E evaluated at E bar minus T by 2 del 2 S del E 2 E bar delta E square plus higher order terms.

Let us take the term constant T minus S E bar that is the first term that I have. So, there is a delta E over here. So, I can group that with this delta with this delta E to write down T del S del E at E bar times delta E minus T by 2 del 2 S del E 2 evaluated at E bar delta E whole square plus higher order terms, good.

This term vanishes because of this condition that we have just derived right because E bar is given by this. So, I have E bar minus T of S E bar minus T by 2 del del E of 1 by T since del S del E is 1 by T times delta E square, correct.

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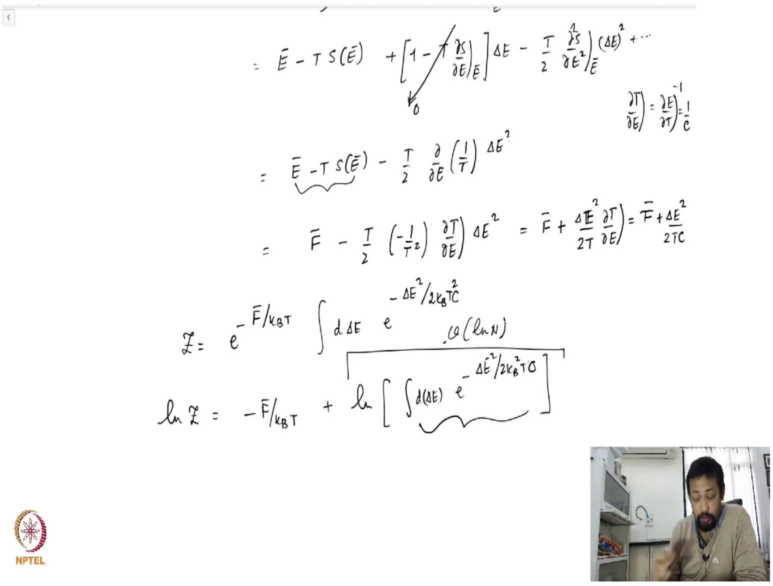

$$= \bar{E} - TS(\bar{E}) + \underbrace{\left[1 - T\frac{\partial S}{\partial E}\Big)_{\bar{E}}\right]}_{0}\Delta E - \frac{T}{2}\frac{\partial^2 S}{\partial E^2}\Big)_{\bar{E}}(\Delta E)^2 + \cdots$$

$$\frac{\partial T}{\partial E}\Big) = \frac{\partial E}{\partial T}\Big)^{-1} = \frac{1}{C}$$

$$= \underbrace{\bar{E} - TS(\bar{E})} - \frac{T}{2}\frac{\partial}{\partial E}\left(\frac{1}{T}\right)\Delta E^2$$

$$= \bar{F} - \frac{T}{2}\left(-\frac{1}{T^2}\right)\frac{\partial T}{\partial E}\Big)\Delta E^2 = \bar{F} + \frac{\Delta E^2}{2T}\frac{\partial T}{\partial E}\Big) = \bar{F} + \frac{\Delta E^2}{2TC}$$

$$Z = e^{-\bar{F}/k_BT}\int d\Delta E\; e^{-\Delta E^2/2k_BT^2C}$$

$$\ln Z = -\bar{F}/k_BT + \overbrace{\ln\left[\underbrace{\int d(\Delta E)\; e^{-\Delta E^2/2k_B^2TC}}\right]}^{\mathcal{O}(\ln N)}$$

So, we will call this F this quantity minus T by 2 minus 1 over T square del T del E delta E square, right. So, I have F bar minus this becomes plus, this becomes 1 over 2T del T del E, but del T del E is essentially inverse of the specific heat. So, I can write down. So, there is a delta E square over here of course.

I can write down this as F bar plus delta E square 2TC the specific heat, right. So, del T del E is equal to del E del T inverse rule of partial derivatives if you recall and this is 1 by C, good. So, therefore, your partition function Z is e to the power minus F bar over K B T integral over d of delta E e to the power minus delta E square over K B TC, right is this correct?

Let us just see. Sorry, there has to be a T square over here. So, that ln of Z is going to be minus F bar over K B T plus log of this integral d of delta E e to the power minus delta E square over twice K B T square C. But, this integral is a Gaussian integral and if you evaluate this integral you are going to get a term which is going to depend only on C. Therefore, this whole term is of the order of log of N.

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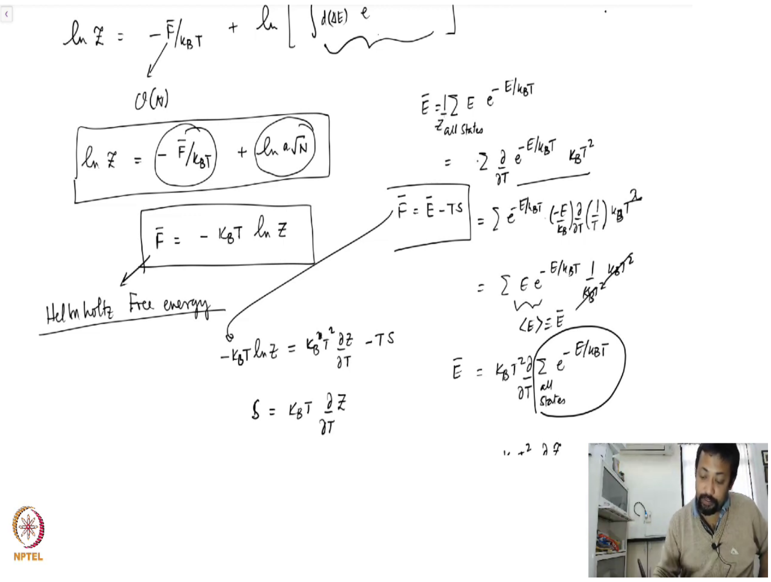

$$\ln Z = -\underbrace{\bar{F}/k_BT}_{\mathcal{O}(N)} + \ln\Big[\underbrace{\int d(\Delta E)\, e}\Big]$$

$$\boxed{\ln Z = -\bar{F}/k_BT + \ln a\sqrt{N}}$$

$$\boxed{\bar{F} = -k_BT \ln Z}$$

Helmholtz Free energy

$$\boxed{\bar{F} = \bar{E} - TS}$$

$$-k_BT \ln Z = k_BT^2 \frac{\partial Z}{\partial T} - TS$$

$$S = k_BT \frac{\partial Z}{\partial T}$$

$$\bar{E} = \frac{1}{Z}\sum_{\text{all States}} E\, e^{-E/k_BT}$$

$$= \sum \frac{\partial}{\partial T} e^{-E/k_BT}\, k_BT^2$$

$$= \sum e^{-E/k_BT}\left(\frac{-E}{k_B}\right)\frac{\partial}{\partial T}\left(\frac{1}{T}\right) k_BT^2$$

$$= \sum \underbrace{E\, e^{-E/k_BT}}_{\langle E\rangle \equiv \bar{E}} \frac{1}{\cancel{k_BT^2}}\cancel{k_BT^2}$$

$$\bar{E} = k_BT^2 \frac{\partial}{\partial T}\sum_{\text{all states}} e^{-E/k_BT}$$

$$k_BT^2 \frac{\partial Z}{}$$

In contrast, if you see over here this term is of the order of N because this term by definition is E bar minus T S of E bar, right. This is extensive, this is extensive therefore, this quantity is also extensive. So, in the thermodynamic limit essentially what we will have is ln Z ok let us just write it down as F bar over K B T plus if you look at this if you integrate this then this is going to be ln square root of N.

So, in the thermodynamic limit there is going to be some factor, but we will not worry about that, but it says well we will just write down this as a times ln N square root and to be correct where a is to be determined after you evaluate this integral. But, in the thermodynamic limit this you can ignore compared to the first term, the second this term you can ignore compared to this term so that you have F bar as minus K B T ln Z.

And, this quantity we have already encountered E minus TS we have already encountered in thermodynamics. If E is identical to your E bar is identical to your internal energy and S is the entropy therefore, this is the Helmholtz free energy. So, once you calculate the partition function Z, you calculate the root to thermodynamics is provided by this relation you. First calculate the Helmholtz free energy F and from there you calculate all the quantities that you need.

For example, once you know F, F is E bar minus T S, right. So, let us just see. So, now, we will remove the distinction between bar and this we will just say that F is E minus T S, right. What is average of E? The E which is ok let us put the bar, so that it is understood, average of E is sum over E e to the power minus E over K B T, correct.

Now, sum over all states, is it possible to manipulate in terms of the partition function, that is all one has to figure out. So, if this I can write down sum over del del T of e to the power minus E over K B T, but then this if I do a del del T it is going to get me an additional 1 by T square. So, I have to multiply this by K B T square if you do not believe me, then you can explicitly do this we have done this earlier it is going to be e to the power minus E over K B T times minus E over K B del del T of 1 by T times K B T square, ok.

So, let us writing down properly I have 1 over T times K B K B T square. So, this is sum over E e to the power minus E over K B T 1 over K B T square times K B T square and then I have basically this as the average of the energy identical to E bar right. So, this is the expression I have. Now, from this I can pull out K B T square outside E bar as K B T square sum over I can take out the derivative also del del T of e to the power minus E over K B T, where the sum is over all states again, but this is the partition function.

So, essentially you have 1 over K B T square del del T of Z right. So, this quantity is minus K B T ln Z the Helmholtz free energy the left hand side and this is K B T square del del Z del T minus TS. So, I can take I can divide throughout sorry, K B T square I can divide throughout by temperature to give me S is equal to K B T del del T of Z ok. I am sorry, I have missed 1 thing this has to be there has to be 1 by Z.