Statistical Mechanics
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Lecture- 15
Two Level System
(Microcanonical Ensemble)

So, good morning to all of you; so, today we will start a discussion on case study on Microcanonical Ensemble. So, in the last class we looked at what is meant by a micro canonical ensemble.

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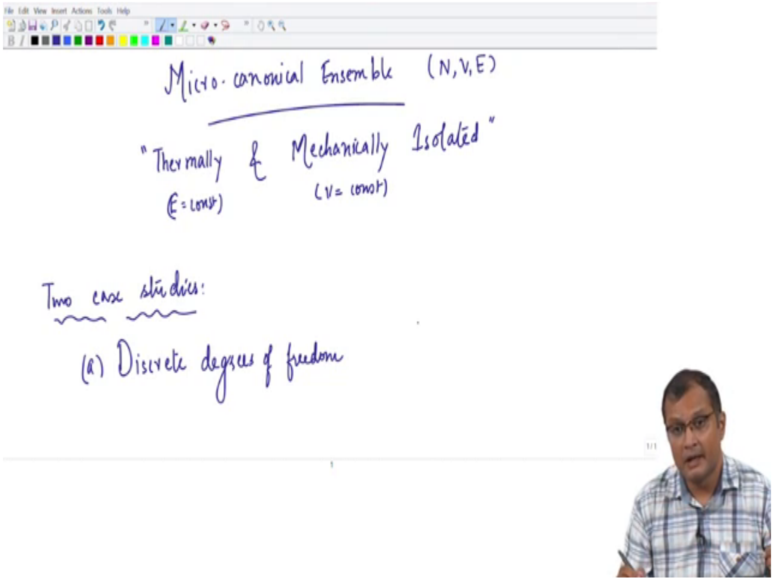

Micro-canonical Ensemble (N, V, E)

"Thermally & Mechanically Isolated"

(E = const) (V = const)

Two case studies:

(a) Discrete degrees of freedom

So, this is the ensemble of fixed N V and E and these are systems which are thermally and mechanically isolated. Thermally means you have the energy constant and mechanically means you have the volume constant. And I would like to discuss a few case studies of you know micro canonical ensemble. So, I will take two case studies. So, one case study would be the study of discrete degrees of freedom. So, I will take an example from the world of discrete degrees of freedom and examples here would be particles with energy levels.

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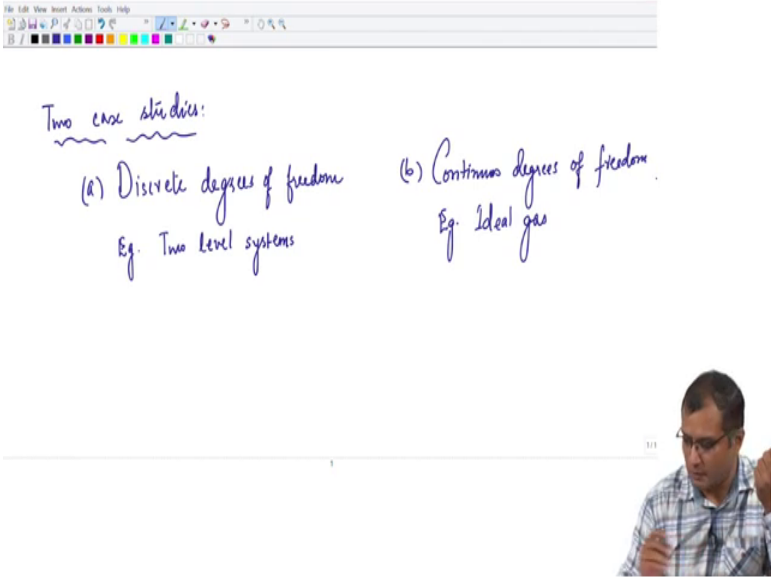

Two case studies:

(a) Discrete degrees of freedom

Eg. Two level systems

(b) Continuous degrees of freedom

Eg. Ideal gas

So, I will take the simplest case of a two level system, where the particles in the system can exist only in one of the two levels ok. For the case of continuous degrees of freedom, and we shall visit this case study in the next lecture, I will take the example of an ideal gas. Now we say that the ideal gas is continuous degrees of freedom because the particles in an ideal gas can take any value of energy from 0 to infinity.

So, we consider this and a system with continuous degrees of freedom; the momentum degrees of freedom are continuous whereas, in the discrete degrees of freedom trace the particles can take energy is only in these two levels that we are going to talk about.

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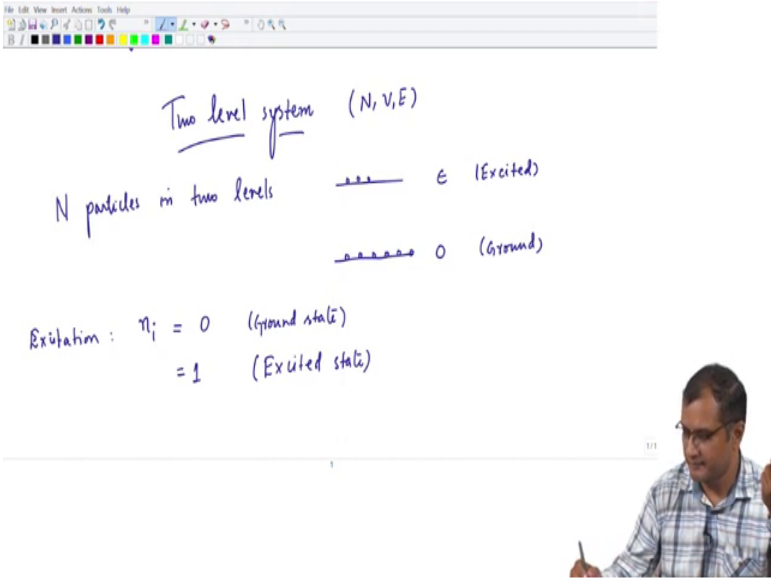

Two level system (N, V, E)

N particles in two levels

ε (Excited)

0 (Ground)

Excitation : $n_i = 0$ (Ground state)

$= 1$ (Excited state)

So, today we will discuss the case of the discrete degree of freedom or the two level system in micro canonical ensemble ok. So, we will take the case of a two level system in the micro canonical ensemble.

Now, this means that we take N particles in two levels. So, the two levels I mean that we take two energy levels with values 0 and epsilon these are the two energy levels, and you can put particles in these you can distribute these N particles like this, some of them being in the excited states some of them being in the let us say the ground state ok. And, naturally we can call the occupation number or the excitation I would say the excitation state ok

So, the excitation number the excitation can be taken as either 0 basically mean it stays in the ground state that the i th particle is in the ground state, we can take the excitation of the i th particle as 1 that only means that this is in the excited state ok.

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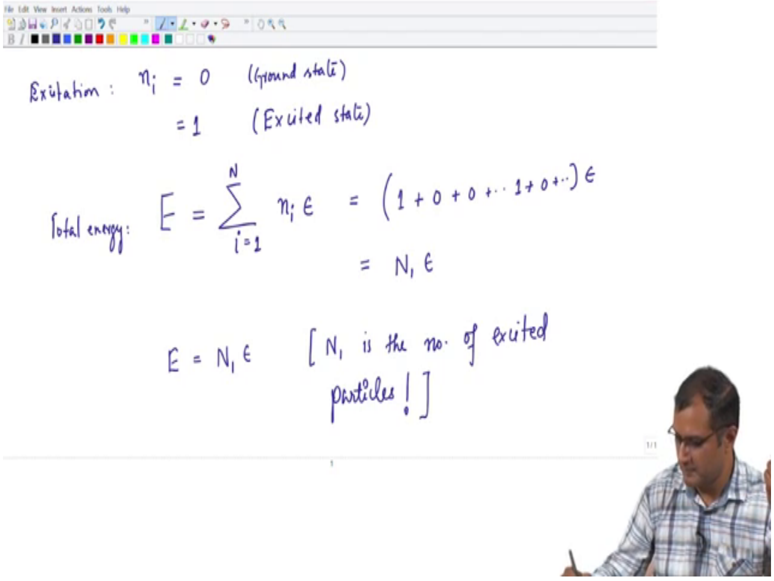

Excitation : $n_i = 0$ (Ground state)

$= 1$ (Excited state)

Total energy: $E = \sum_{i=1}^{N} n_i \epsilon = (1+0+0+\cdots 1+0+\cdots)\epsilon$

$= N_1 \epsilon$

$E = N_1 \epsilon$ [N_1 is the no. of excited particles!]

So, this way if I compute the total energy, which will come out to be summation over all particles, the state in which the particles are and the energy level. So since I have taken the energy level the 0 and epsilon, the total energy summation of summation over all particles the excitation state times epsilon. So, this will suppose you are first particle is in excited state you will take n i is 1 the next particle is in ground state and the next is also in ground state and so, on and so, forth you will have 1’s and 0’s. And, in the end what you will have is basically the sum as sum N1 times epsilon where N 1 is clearly the number of ones that you have ok. So, you can write down the energy as total energy as N 1 times epsilon, where N 1 is the number of excited particles.

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Only for two level system; so, if you had three level systems you would have you have to take 0 epsilon and probably epsilon 1 or something. So, in that case your energy levels will have one more energy state.

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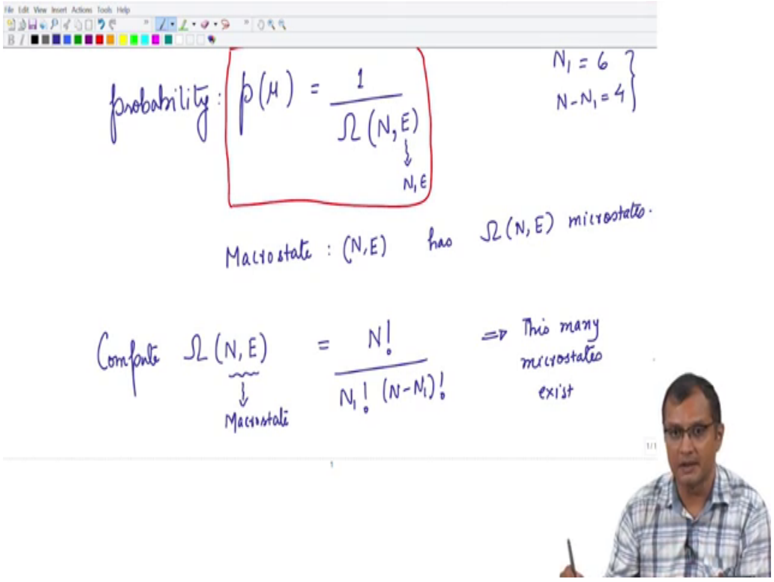

probability : $\boxed{p(\mu) = \frac{1}{\underset{\downarrow\, N,E}{\Omega(N,E)}}}$

$\left.\begin{matrix} N_1 = 6 \\ N - N_1 = 4 \end{matrix}\right\}$

Macrostate : (N,E) has $\Omega(N,E)$ microstates.

Compute $\underset{\substack{\downarrow \\ \text{Macrostate}}}{\Omega(N,E)} = \frac{N!}{N_1!\,(N-N_1)!}$ ⇒ This many microstates exist

So, now we can think of the probability of finding the system in a certain microstate mu. Now microstate mu here is a certain combination of these a excitation values. So, you say that the set of n i’s. So, if I take N 0 has 2 and you take N 1 as 1 then basically these are this is the this is a microstate for a three particle system ok. So, the set of particular set of n i’s that you take constitutes a microstate ok.

So, you can take for N equal to let us say 10 particles, we can take the ground state number of particles in the in the in the ground state ok. So, as simply I am going to take this as a let us say I am going to take N 1 has let us say 6 and N minus N 1 in the exited state as 4. So, this is basically particular microstate. So, you can change these microstates and obtain the values of you know and the system at you can construct system and different microstates

And I am going to write down this probability of finding a system in a particular microstate as just 1 upon the total number of states accessible to system ok. Because each microstate is equiprobable and in this way I can write down the micro state as a function of total number of particles and the energy E ok. So, inside this energy E is the information of number of particles in the excited state.

So, N is the total number of particles, N 1 is the excited particles. So, N and N 1 together constitute the total number of microstates in the system. So, then what we have is basically right. So, this is the probability of a particular microstate corresponding to a macrostate N 1 or N comma E. So, N comma E specifies a macrostate has which has basically omega of N comma E microstates.

So, if you so, the above expression says that if you have these many microstates for a macrostate N comma E, then the probability of finding a system in one of the microstate is as essentially 1 upon omega because these macro states because these microstate are equiprobable fine. So, if there are 10 microstates then the probability of each microstates is 1 by 10 is it right. So, then we can compute this would be clear.

So, you compute the total number of microstates for this particular macrostate ok. So, we have basically this is a macrostate and omega which is the number of microstates is nothing, but the number of ways in which we can arrange N 1 particles in the excited state ok. So, these many basically these many microstates exist in this one microstate of N comma E ok.

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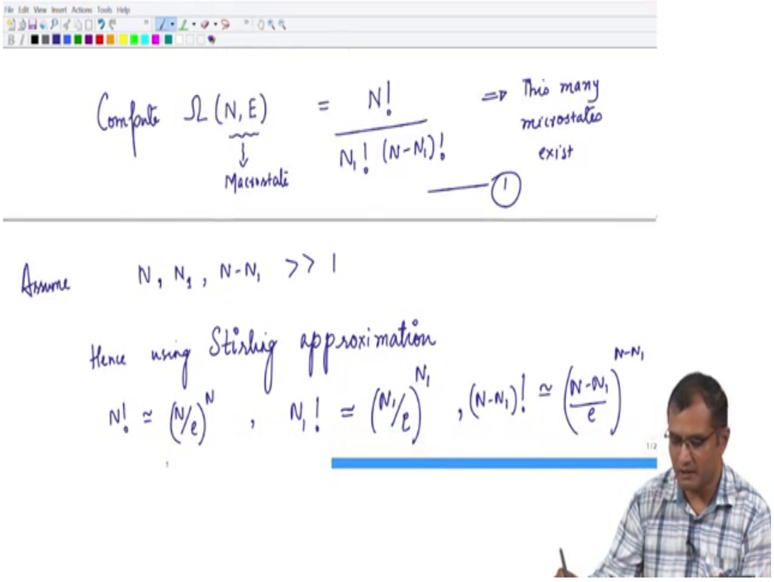

Compute $\underbrace{\Omega(N, E)}_{\downarrow \text{ Macrostate}} = \frac{N!}{N_1!\,(N-N_1)!}$ ——— ① $\Rightarrow$ This many microstates exist

Assume $N, N_1, N-N_1 >> 1$

Hence using Stirling approximation

$N! \simeq \left(N/e\right)^{N}$, $N_1! \simeq \left(N_1/e\right)^{N_1}$, $(N-N_1)! \simeq \left(\frac{N-N_1}{e}\right)^{N-N_1}$

Now, we assume that these N, N 1 and N minus N 1 there all very large let us say then our N particle system has large number of particles and hence large number of particles in the excited state. So, these values of number of particles in both excited state and ground state as well as the total number of particles are very large. So, under that assumption I can approximate these numbers using Stirling approximation.

I can use the Stirling approximation and write down our N factorial as N by e to the power N factorial and to the to the power N and N 1 factorial as I am going to use the approximation symbol here because these are approximations as N 1 by e to the power N 1 and finally, I can write down N minus 1 whole factorial as N minus N 1 divided by e to the power N minus N 1.

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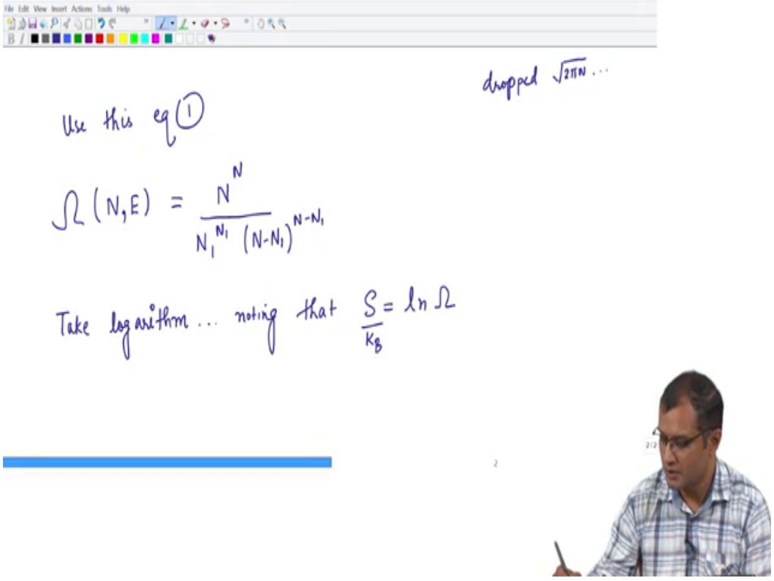

dropped $\sqrt{2\pi N}\ldots$

Use this eq ①

$$\Omega(N,E) = \frac{N^N}{N_1^{N_1}\,(N-N_1)^{N-N_1}}$$

Take logarithm ... noting that $\frac{S}{k_B} = \ln\Omega$

These are Stirling approximations of course, I have dropped terms which are quadratic in which are I have dropped terms and the pre factors of the order 2 pi N, but that is not necessary here. So, if you use these Stirling approximations in your equation let us label this as equation as equation 1 we can write down our omega, number of microstates in this macrostate N comma E as N to the power N upon N 1 to the power N 1 into N minus N 1 to the power N minus N 1 ok.

The exponential cancel and now I can take logarithms on both sides and noting that the entropy is related to logarithm of omega by the Boltzmann's expression.

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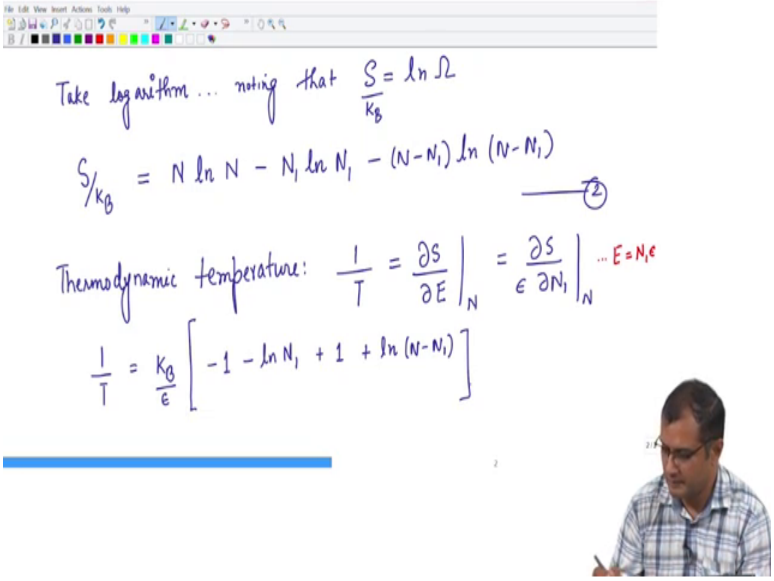

Take logarithm ... noting that $\frac{S}{k_B} = \ln \Omega$

$$S/k_B = N \ln N - N_1 \ln N_1 - (N-N_1)\ln(N-N_1) \quad ②$$

Thermodynamic temperature: $\frac{1}{T} = \frac{\partial S}{\partial E}\Big|_N = \frac{\partial S}{\epsilon\, \partial N_1}\Big|_N$ ... $E = N_1\epsilon$

$$\frac{1}{T} = \frac{k_B}{\epsilon}\left[-1 - \ln N_1 + 1 + \ln(N-N_1)\right]$$

So, I can write down my entropy S over KB as N log N this is a logarithm to the base e natural log minus N 1 log N 1 minus N minus N 1 lon N minus N 1 is it fine. Let us call this is equation 2. Now we know from previous lecturers that the value of thermodynamic temperature is nothing, but the derivative of entropy is a function of energy ok. So, we know that the temperature is given by this thermodynamic expression in this case we have the constant number of particles as the extensive variable. So, I am going to take the derivative of equation 2 and get temperature.

So, I am going to write down my 1 upon temperature as simply KB times and just for this reason for the time being note that, I can convert this derivative to a derivative on N 1 by simply taking an epsilon outside since you by noting that the total energy is a variable of purely N 1. So, I can write down this derivative in terms of just N 1. So, that gives me this derivative as. So, I can write this as KB upon epsilon and the first term is constant because it is totally a function of N and N is a constant.

So, the second term will give me minus 1 minus lon N 1 then I will get plus 1 that the derivative of lon N minus N 1 and finally, I will get plus lon N minus N 1.

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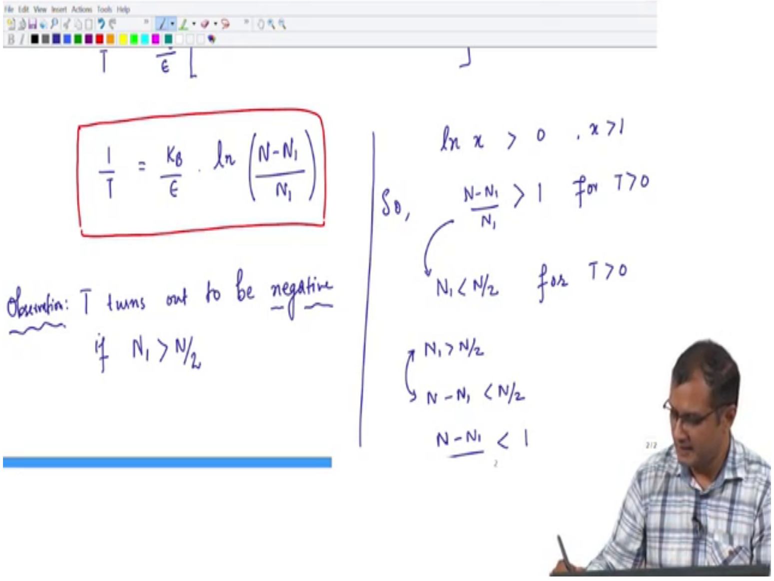

$$\boxed{\frac{1}{T} = \frac{K_B}{\epsilon} \cdot \ln\left(\frac{N-N_1}{N_1}\right)}$$

Observation: T turns out to be negative if $N_1 > N/2$

$\ln x > 0 \quad , x > 1$

So, $\frac{N-N_1}{N_1} > 1$ for $T > 0$

$N_1 < N/2$ for $T > 0$

$N_1 > N/2$

$N - N_1 < N/2$

$\frac{N-N_1}{} < 1$

So, now you can knock off this one and that one and write down your temperature as KB over epsilon into logarithm of N minus N 1 upon N 1; other beautiful relationship which tells you something very important. You see in this expression I know that lon of any quantity is greater than 0 if x is greater than 1. The moment x becomes less than 1 logarithm becomes negative. So, for this logarithm to stay positive I must demand that N minus N 1 upon N 1 should be greater than 1 for T to be positive for the logarithm to be positive enhance temperature to be positive.

Ah We must demanded N minus N 1 upon N 1 should be greater than 1. So, this basically tells you that your N 1 should be always less than N by 2 because if you put N 1 as N by 2 N minus N 1 by N 1 becomes 1 exactly 1 and the moment your N 1 becomes larger than N by 2 the numerator becomes smaller than N by 2, denominators already larger than N by 2. So, N by N minus N 1 by N 1 will become smaller than 1. So, I will say that N should remain less than N by 2 for temperature to be positive right.

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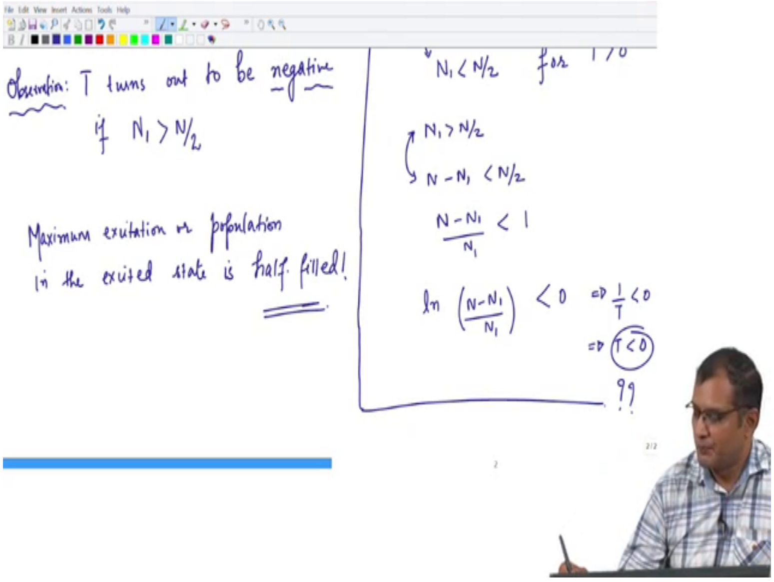
Observation: T turns out to be negative if $N_1 > N/2$

Maximum excitation or population in the excited state is half filled!

$N_1 < N/2$ for $T > 0$

$N_1 > N/2$

$N - N_1 < N/2$

$\frac{N - N_1}{N_1} < 1$

$\ln\left(\frac{N-N_1}{N_1}\right) < 0 \Rightarrow \frac{1}{T} < 0$

$\Rightarrow \boxed{T < 0}$

??

So, if you if you simply say that if N 1 exceeds N by 2 what happens? N minus N 1 will be less than N by 2 because the total is N the denominator is N 1 is already greater than N by 2. So, I can write that N minus N 1 by combining these two I can say that N minus N 1 by N 1 has become smaller than 1. And, hence logarithm of N minus N 1 by N 1 has turned negative thereby turning my left hand side negative which is 1 over temperature. So, implies that 1 upon T has become negative which implies that my temperature has become negative what is going on.

So, I will tell you what is going on in a short while, but this expression it is you know gives us the conclusion let us proceed by making this not conclusion let us proceed by making this observation, that our maximum number of particles is N by 2 in the excited state and this means that our T turns out to be negative if excitation or number of particles in the exited level is greater than half the number of total particles ok. So, this is the observation that we have made here ok. So, that is the observation we made here and I am going to proceed with the discussion by saying that the maximum excitation or population in the excited state appears to be half filled.

So, in a two level system by raising the temperature of the system you can only increase the number of particles and excited state to be half the total number of atoms that is the maximum we can do. And we can see that by inverting this expression ok. So, I will invert this expression for energy and show that the maximum we can do is just a half filled in the excited state ok. So, let me pull this expression here ok.

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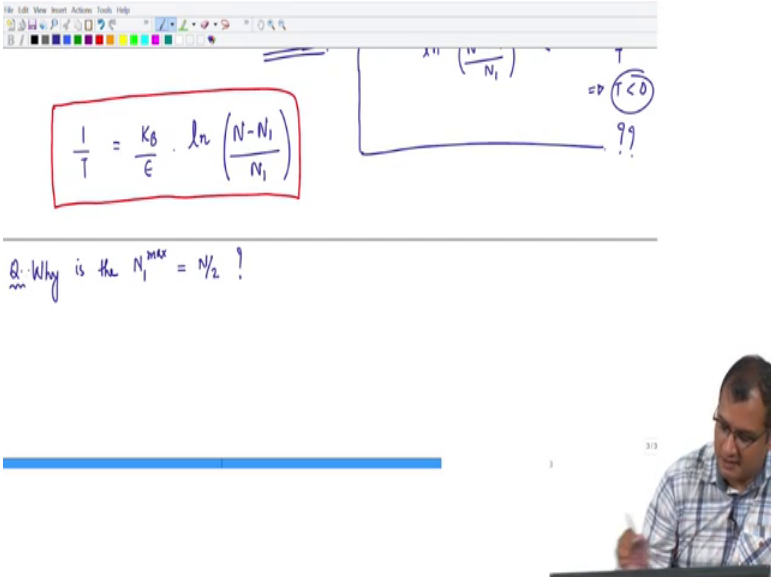

$$\boxed{\frac{1}{T} = \frac{K_B}{\epsilon} \cdot \ln\left(\frac{N-N_1}{N_1}\right)}$$

$\Rightarrow \boxed{T<0}$??

Q. Why is the $N_1^{max} = N/2$?

So, I am going to explain this maximum excitation to be half filled and not more than that in two ways ok. So, I will explain this using. So, the question is why is the N 1 max equal to N by 2 in these two level systems. So, this question will be answered using two argument.

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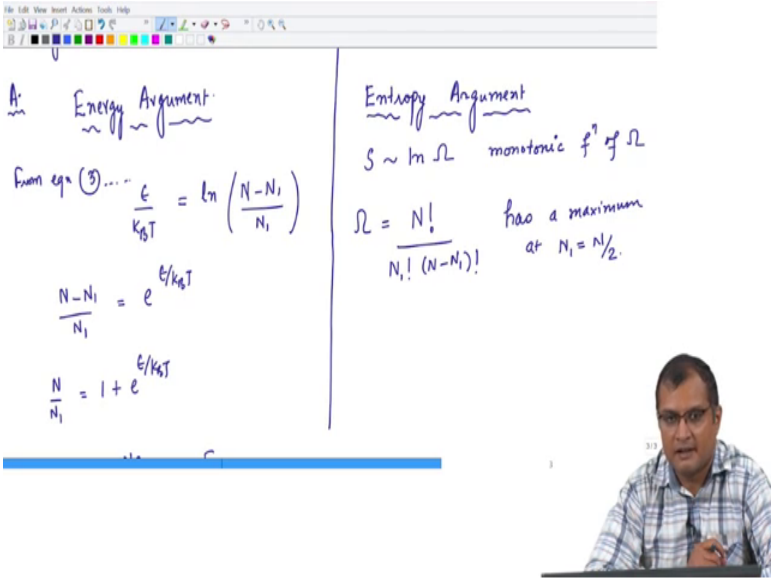

A. Energy Argument

From eqn (3)... $\frac{\epsilon}{K_B T} = \ln\left(\frac{N-N_1}{N_1}\right)$

$$\frac{N-N_1}{N_1} = e^{\epsilon/k_B T}$$

$$\frac{N}{N_1} = 1 + e^{\epsilon/k_B T}$$

Entropy Argument

$S \sim \ln \Omega$ monotonic f^n of Ω

$\Omega = \frac{N!}{N_1!\,(N-N_1)!}$ has a maximum at $N_1 = N/2$.

So, I will use one argument which I will say as the energy argument, which is perhaps easier to understand at this moment for immediately understandable. And the other augment that I am going to use is basically the argument of disorder or entropy argument. Entropy is a measure of disorder. So, it is delightful scenario to basically understand why I cannot more increase the population in the excited state by more than half using two different methods by the argument of energy and by the argument of entropy.

So, let us use the energy argument which is straightforwardly obtained from the last expression on the temperature. So, if I invert this expression for energy what can I do is basically I can say that my from the let us call this as some equation third fourth, let us call it as third. So, I can say from equation 3 I can write down the value epsilon upon K BT as just the logarithm of N minus N 1 upon N 1 which means I can say N minus N 1 over N 1 is e raise to epsilon upon K BT and I can simply say this is N by N 1 equals to 1 plus e raise to epsilon upon K BT and finally, I am going to write it as N 1 equals to N upon 1 plus e raise to epsilon upon K BT.

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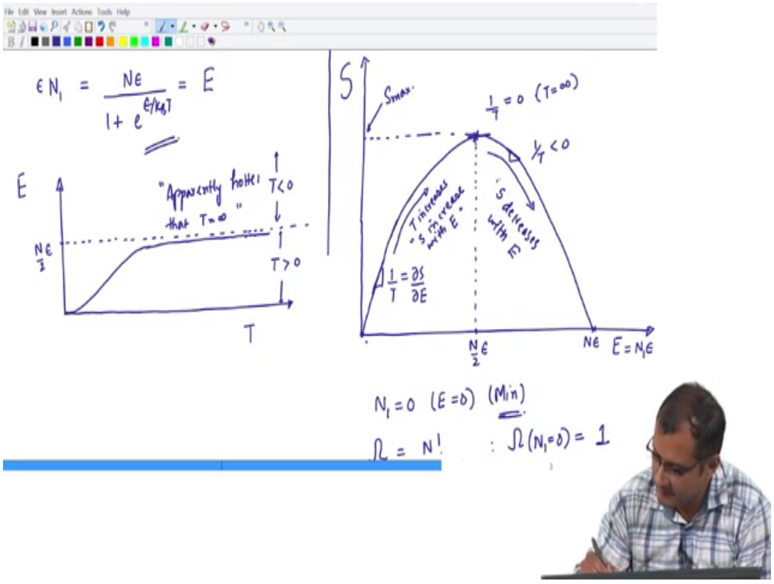

Just simple transposing terms on both sides now I will multiply epsilon both sides which is nothing, but the expression for energy because, epsilon into N 1 is my energy ok. So, let us write it as ok. So, this is basically my energy. So, the energy is epsilon N upon 1 plus e to the power epsilon over KT now let us plot this we learn a lot from sketchers ok.

So, let us sketch it. So, I am going to sketch my energy versus temperature ok. Now as you can see at T equals to 0 the denominator becomes e raised to infinity plus 1 which is infinity and 1 upon infinity is 0. So, my energy is 0.

And at T goes to infinity I have e to the power 1 by infinity which is 0 which is e raise to 0 which is 1. So, I have the maximum energy as N by 2 into epsilon. So, let me construct this maximum value of energy. So, my energy as a function of temperature will monotonically rise and its maximum value is suppose to be just N by 2 epsilon. And as you can see that I can go to this is called any entire region below this dash line is called as the region of positive temperature ok.

And I know that if I try to push the number of particles more than half to the excited state it goes to the region of negative temperature. So, I am going to call this region as the region of negative temperature. Now we can see why negative temperatures are hotter than the infinite temperatures. So, the to if I start from a system which has less number of particles in the ground state, I continue increase in the temperature of the system I and go to infinite temperatures yet I will not be able to push the number of particles more than half to the exited state.

One the other hand if I somehow start whether system which has more particles in the exited state then the ground state, when the system is already in the negative temperature state. So, I will say that the negative temperature state is hotter than the infinite temperature case, because even with infinite temperature I could not exit more than half of the number of particles. So, somebody has given me more than half which means he is giving me a hotter system, but I know his system is in the infinite temperature state. So, it apparently is hotter than you know T equals to infinity because I have put more particles in the excited state.

So, this is the reason why if you start with positive temperature you cannot go to more than half filled precisely because, the amount of you know the highest possible temperatures we can reach in your system is by is you know we will only take the excitation to 50 percent in your system. And so, that is the reason why you cannot go to negative temperatures by simply heat in the system. The other argument that you can give is the entropy argument.

So, this argument means that you know our S behaves like logarithm of omega and this is monotonic function in the sense that if omega monotonically increases, then my entropy will also monotonically increase with omega. Now I know that my omega is basically the number of microstates and that is N factorial upon N 1 factorial into N minus N 1 factorial, you know this has a maximum at half filled excitation ok. So, the binomial multiplicity peaks at the value N by 2 ok. You know this result that the maximum value of N c r is at N c N by 2.

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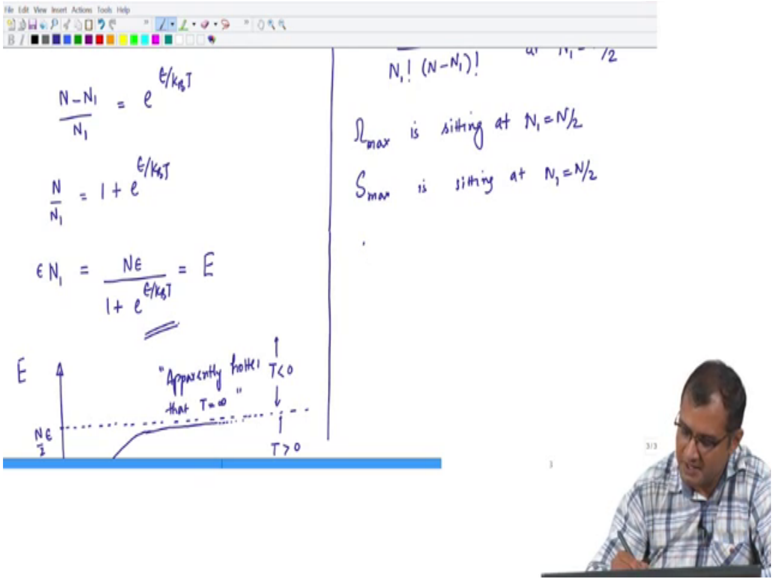

$$\frac{N-N_1}{N_1} = e^{\epsilon/k_BT}$$

$$\frac{N}{N_1} = 1 + e^{\epsilon/k_BT}$$

$$\epsilon N_1 = \frac{N\epsilon}{1+e^{\epsilon/k_BT}} = E$$

$$N_1!\,(N-N_1)!$$

Ω_{max} is sitting at $N_1 = N/2$

S_{max} is sitting at $N_1 = N/2$

So, it has a maximum N by 2 which means my omega max is a sitting at. So, I can expect my entropy which is monotonic function of lon omega is also sitting at N by 2 because entropy is a monotonic function of you know omega. So, which means I can plot the I am going to use a bigger figure here because this is the beautiful argument the disorder argument.

So, I am going to plot this as a function of E and noting that E is nothing, but purely a function of N 1 I am going to plot S versus E. I know at N 1 equals to 0 and hence E equal to 0 my entropy should be 0.

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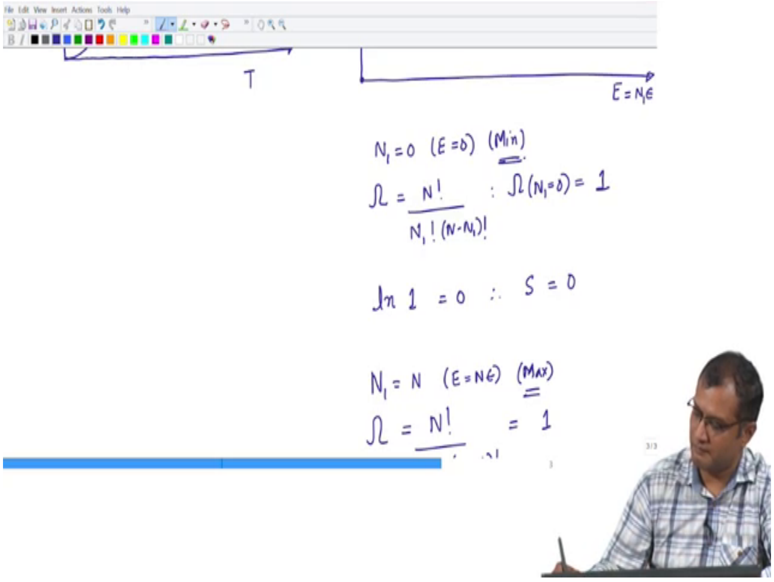

$N_1 = 0 \quad (E = 0) \quad \underline{(\text{Min})}$

$\Omega = \frac{N!}{N_1!\,(N-N_1)!} \quad : \Omega(N_1=0) = 1$

$\ln 1 = 0 \quad \therefore \quad S = 0$

$N_1 = N \quad (E = N\epsilon) \quad \underline{(\text{MAX})}$

$\Omega = N! \quad = 1$

Because when N 1 is 0 or our energy is 0 omega is nothing, but N factorial by N 1 factorial into N minus N 1 factorial. At N 1 equal to 0 omega at N 1 equals to 0 is nothing, but 1 because its simply becomes N factorial upon N factorial and what is lon of 1? 0.

Therefore our S becomes 0. So, I have a point here and the maximum number of N 1 I can have is basically N. So, I will say this is the minimum this scenario where excitation is maximizer is there all of them are excited. Again here I can say that omega as a function of N 1 is nothing, but N factorial upon N 1 factorial into N minus N 1 factorial you put N 1 as N this is nothing, but 1 again because now you have N factorial upon N factorial again which means my entropy which is logarithm of omega is again 0.

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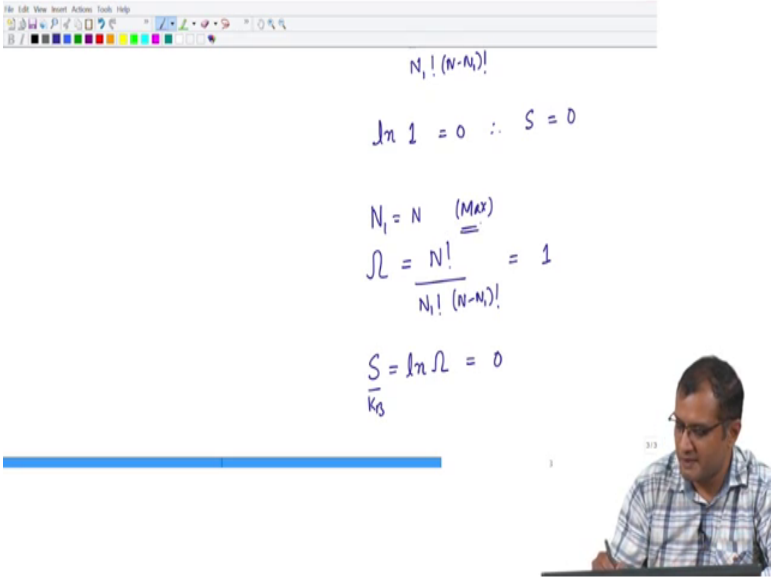

$N_1!\,(N-N_1)!$

$\ln 1 = 0 \;\therefore\; S = 0$

$N_1 = N \quad (\underline{\underline{MAX}})$

$$\Omega = \frac{N!}{N_1!\,(N-N_1)!} = 1$$

$$\frac{S}{k_B} = \ln \Omega = 0$$

So, this was the case of maximum this was the case of minimum N 1. So, I will go I will basically is to be symmetric in my. So, I am going to write it as simply means N equals to E equals to this is the case of maximum. So, basically I am again back to 0 when my energy is N times epsilon and I am 0 here and somewhere at the peak at the value when N 1 becomes N N by 2. So, the energy is basically by 2 epsilon have a peak. So, I am going to draw function which has a maximum.

So, this is the maximum value of entropy and as you can see from thermodynamics the slope is basically 1 upon T because it is ds over d E this is the slope ds over dE. And you can see as you increase your energy you are slope reduces. So, this is the direction in which slope reduces which means your T increases. So, 1 by T reduces which means T increases finally, when you reach this peak the slope 1 by T is 0 which means this is the regime of infinite temperature.

So, when you reach in the energy here you would have reached in the entropy picture here when the slope becomes 0 or temperature becomes infinity. Now if you try to go on the other side, the slope 1 by T has turned negative. So, what you are trying to do is basically in this side. So, I will say that my T increases or S increases my disorder also increase, but on this side I will see that my disorder decreases. So, what is happening is that above the maxima if I try to put in more energy my system becomes more and more disordered.

So, if I try to increase energy from 0 to N by 2 epsilon the system gets more and more disordered all the way up to infinite temperature which is the point here at the maximum you cannot cross this. Now moment you try to cross it by you know artificially pumping particles in the excited state more than half filled, you go to the other side of the curve where your entropy begins to decrease. So, this is like I am putting more energy. So, this would be the region where you know.

So, I will say that S decreases with energy and here S increases with energy. And this is not possible I mean you cannot these are this is we had scenario that you are trying to increase energy in a system and created more ordered. It would be like asking a bunch of students who are more hyperactive you know an expecting them to be more ordered hyperactivity means, they have more energy they will be constantly jumping up and down, but apparently this group of students who are hyperactive are more ordered then this group of students which are normal and you know not hyperactive there more disordered. So, this is the entropy argument that you cannot exceed the number of particles in the exited state more than N by 2.

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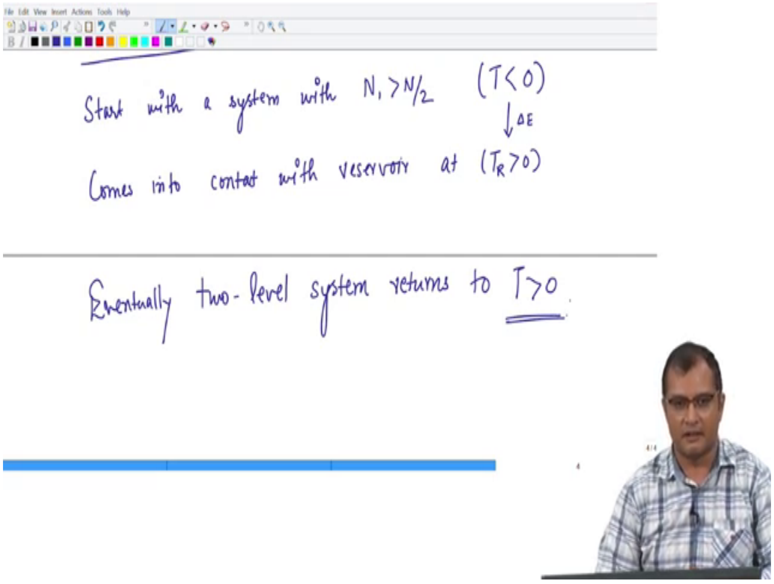

Start with a system with $N_1 > N/2$ $(T<0)$

$\downarrow \Delta E$

Comes into contact with reservoir at $(T_R > 0)$

Eventually two-level system returns to $T>0$.

So, the only way to exceed you know beyond N by 2 is to start with a system with N 1 greater than N by 2 which means you have already started with a negative temperature state. And as soon as the system you know comes in contact with a reservoir at positive temperature, with a reservoir you know at some positive temperature let us say T R is greater than 0.

There will be in exchange of energy between these two systems. In fact, this system would only lose energy, any excess energy that it has it will lose that energy to the reservoir and come back to positive temperature and thereby you know after this it will come back. So, eventually you can say that this two level system returns to positive temperature. So, we can start with more particles in the excited state then the ground state, but this would be a metastable state. You should not be a system that will stay in negative temperature forever

So, as soon as the system comes into contact with the reservoir at finite temperature, it will come down to positive it will come down to a lower energy such that its temperature turns positive. And this is the manifestation of negative temperature states you can you can think of a negative temperature state to be an exceptional state, where putting more energy yields more order into the system thereby making the slope ds by d negative. So, in the next class will proceed with the system with continuous degree of freedom and discuss the case of ideal gas in the context of micro canonical ensemble. So, the break here and give me it in the next class.