Introduction to Molecular Thermodynamics
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Lecture - 15
Statistical Ensembles

Molecular thermodynamics is actually a very special application of statistical mechanics, which is one of the fundamental corners of condensed matter physics. Now in today's lecture what we are going to do is, we are going to look at the fundamental aspects of statistical mechanics; that is going to be extremely important as far as our discussion of molecular systems are concerned.

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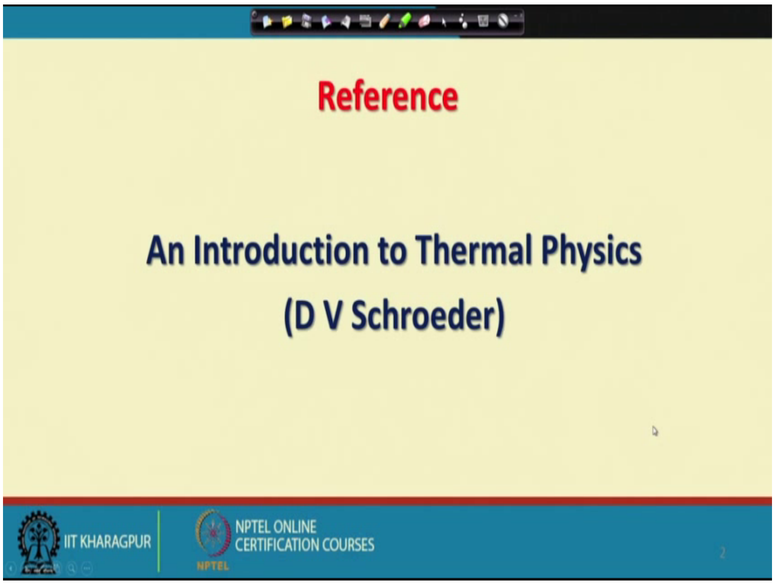

Reference

An Introduction to Thermal Physics

(D V Schroeder)

Now, for the part that I am going to discuss today; i would like to put as reference a very simple book which is an introduction to thermal physics by D V Schroeder, which gives you a lot of insight or rather detailed insight into the connection between the thermodynamics that we observed, and the microscopic states underlying each of our observation.

So, now let us start by outlining the hypothesis of statistical mechanics.

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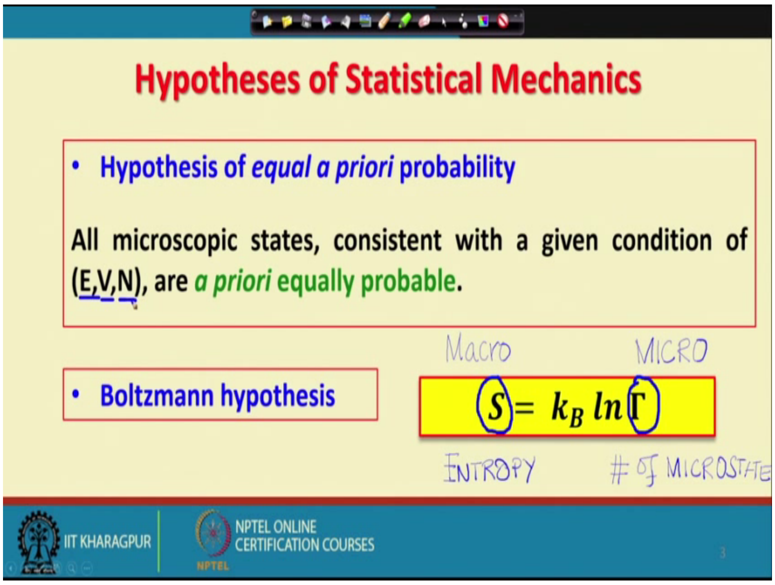

Hypotheses of Statistical Mechanics

- **Hypothesis of *equal a priori* probability**

All microscopic states, consistent with a given condition of (E,V,N), are *a priori* equally probable.

- **Boltzmann hypothesis**

Macro MICRO

$$\boxed{S = k_B \ln \Gamma}$$

ENTROPY # of MICROSTATE

As the title suggests, these are hypothesis when the scientists were faced with the task of formulating a general description of systems comprised of a very large number of particles, where you would like to start from the molecular model, and try to predict the property that you are going to measure in the real microscopic world. Certain hypothesis needed to be proposed to start building this theoretical description.

The first one of this hypothesis is known as the hypothesis of equal a priori probability. So, when I say a priori, it means that I am not at all assuming anything. I am just starting from the stretch. So, to say, and this hypothesis says that if you have a given condition of a given energy, given volume and a given number of particles. Then at this point we know that there are several microscopic states associated with one given condition of this three thermodynamic variables. And this hypothesis says that all the microscopic states that are associated with a given condition or given values of E V and N are a priori equally probable.

So, I do not have any basis of trying to explain why these kind of statement is coming. All we can say is, this appears to be a very important starting point for the formulation of the principles of statistical mechanics. So, once you can, let me remind you that this is a hypothesis. This cannot be proved rather later on we can try and understand why this is a justifiable hypothesis, but we can never prove it.

There is another hypothesis which gives us the other cornerstone of statistical mechanics and that is the Boltzmann hypothesis, and this hypothesis is once again associated with a famous scientist Boltzmann, who gave us probably the most important mathematical relationship that gave rise to application of basic theoretical physics to a very large number of systems with real practical applications. So, let us go back and have a look at this one single equation that probably has single handedly changed the way we model real interacting systems.

Now, what do I have in the Boltzmann hypothesis, this equation. It has two sites. In the first site, what I have is the quantity S, this is nothing, but the entropy of the system. So, when I say this is the entropy I understand that I am talking in terms of the thermodynamic properties of the system. So, which means that this is a macroscopic property.

On the other hand, I find on the right hand side this quantity gamma we have seen. What gamma is. Gamma is the number of microstates number of microstates possible, and as a result you see that we are here talking in terms of the microscopic model for a given system. We also know that if I specify the value of e v and n, which in other words if I have an isolated system, then at equilibrium the entropy of the system has a fixed value. And now the Boltzmann hypothesis is connecting this thermodynamic property to the number of possible microscopic states, that are associated with this given condition.

Here instead of gamma what we have, is the log of gamma. You would understand why, because gamma is a huge number, and therefore, the log of gamma probably is a much more physically intuitive quantity that is going to enter into this relationship.

Now, what is k B? K B is known as the Boltzmann constant. So, this subscript b is actually signify the name of Boltzmann. So, S is proportional to l n gamma. So, the situation is, you have a system where it is an isolated system, you have defined its thermodynamic state at equilibrium by specifying a given value of its internal energy volume and number of particles.

We have already seen in this course, that under such condition we can find out the number of possible microscopic states. And if N is very large if the, it is a macroscopic system, and the available amount of energy is also very large. We know that the number of microscopic states gamma is going to be very large.

Now, if I know what the natural logarithm of this number gamma is, according to Boltzmann hypothesis I can immediately write down that entropy of the system is proportional to the log of gamma, and the proportionality constant is now known as the Boltzmann constant. So, as you understand that the Boltzmann hypothesis gives us an extremely important relationship, which does the very crucial task of connecting the microscopic system property information to the macroscopic properties of the system.

Now, let me try and have a demonstration of how these concepts are relevant to all the discussions that we had till now in this course.

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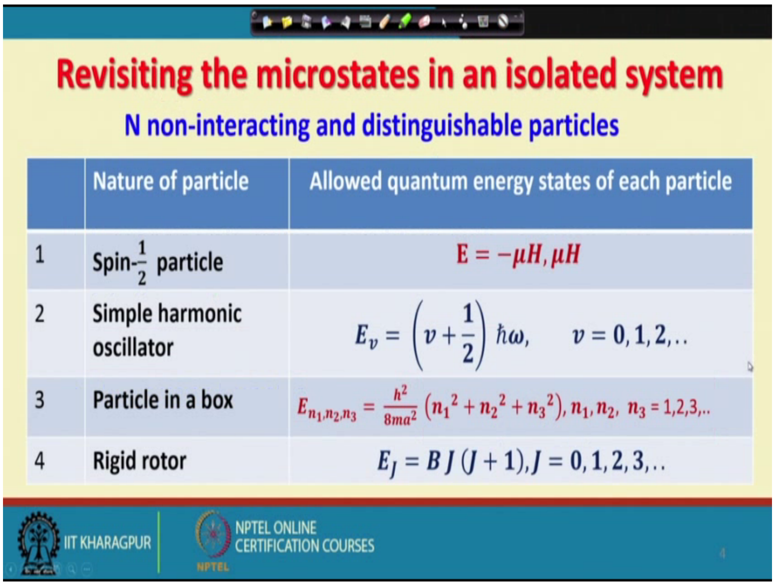

Revisiting the microstates in an isolated system

N non-interacting and distinguishable particles

	Nature of particle	Allowed quantum energy states of each particle
1	Spin-$\frac{1}{2}$ particle	$E = -\mu H, \mu H$
2	Simple harmonic oscillator	$E_v = \left(v + \frac{1}{2}\right)\hbar\omega, \quad v = 0, 1, 2, ..$
3	Particle in a box	$E_{n_1,n_2,n_3} = \frac{h^2}{8ma^2}\left(n_1{}^2 + n_2{}^2 + n_3{}^2\right), n_1, n_2, n_3 = 1,2,3,..$
4	Rigid rotor	$E_J = B\,J\,(J+1), J = 0, 1, 2, 3, ..$

So, let us revisit the microstates in an isolated system, and the system is comprised of capital n non-interacting and distinguishable particles we can, as well have indistinguishable particles as we have seen in the last lecture. And if I have a single particle like a spin half particle or a simple harmonic oscillator, or a particle in a box or a rigid rotor. I know that I can define the microscopic states in each of these cases by knowing the solution of the Schrodinger equation. And also I can find out that if I fix the total energy of the system, I can count the number of possible microscopic states for a given value of the total energy, the total number of particles and the volume of the system.

Now, let us go one step ahead and remind you of a specific system that I am going to use to demonstrate to you. The two hypothesis that I have introduced to you in this lecture. the first one.

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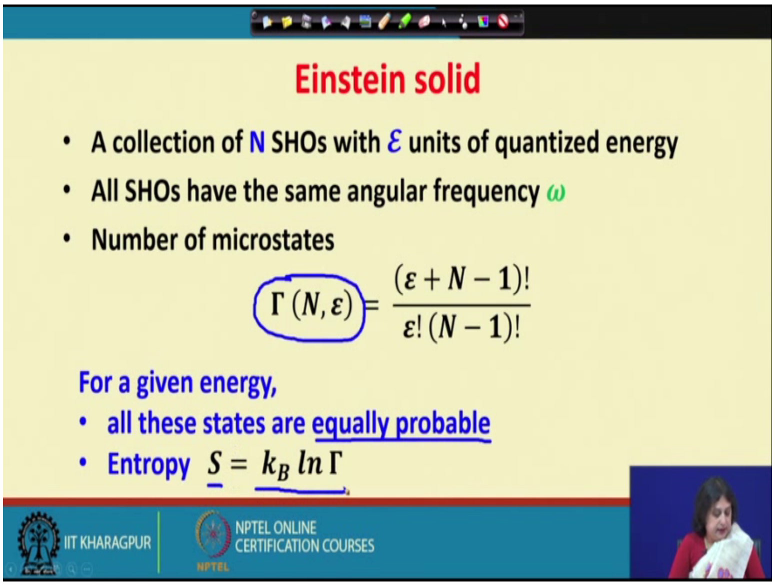

Einstein solid

- A collection of N SHOs with $\mathcal{E}$ units of quantized energy
- All SHOs have the same angular frequency ω
- Number of microstates

$$\boxed{\Gamma(N,\varepsilon)} = \frac{(\varepsilon + N - 1)!}{\varepsilon!\,(N-1)!}$$

For a given energy,

- all these states are <u>equally probable</u>
- Entropy $\underline{S} = \underline{k_B \ln \Gamma}$

So, let us once again remind ourselves that; what is an Einstein solid. And Einstein solid is a collection of capital n simple harmonic oscillators which are not interacting with each other, and they have epsilon units of quantised energy. And all the simple harmonic oscillators have the same angular frequency omega. So, if these collection of simple harmonic oscillators are placed in a constant volume v, then it is an isolated Einstein solid, and then the number of microscopic states can be very easily calculated like this.

So, what the two hypothesis tell us from this expression are as follows. First if e and n are fixed, then these many microscopic states are possible, and all these states are equally probable for the given values of E N and V. And if you can compute what gamma is. Immediately you can find out for this isolated system. The entropy value is going to be k B l n gamma.

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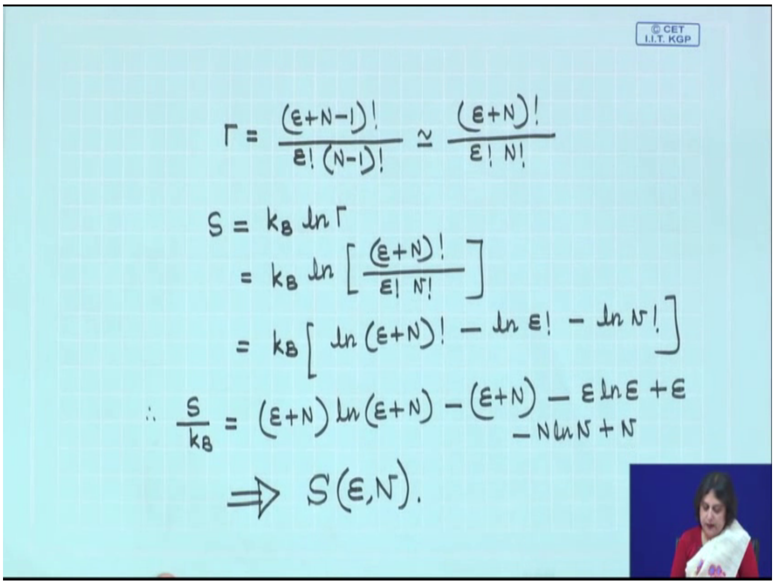

$$\Gamma = \frac{(\varepsilon+N-1)!}{\varepsilon!\,(N-1)!} \simeq \frac{(\varepsilon+N)!}{\varepsilon!\,N!}$$

$$S = k_B \ln \Gamma$$

$$= k_B \ln \left[\frac{(\varepsilon+N)!}{\varepsilon!\,N!} \right]$$

$$= k_B \left[\ln(\varepsilon+N)! - \ln \varepsilon! - \ln N! \right]$$

$$\therefore \frac{S}{k_B} = (\varepsilon+N)\ln(\varepsilon+N) - (\varepsilon+N) - \varepsilon\ln\varepsilon + \varepsilon - N\ln N + N$$

$$\Rightarrow S(\varepsilon, N).$$

Then therefore, I would say that if gamma is equal to epsilon plus N minus 1 factorial divided by epsilon factorial by N minus 1 factorial for large values of epsilon, and N this is approximately equal to epsilon plus N factorial divided by epsilon factorial and N factorial, then; what is the entropy of the system.

Entropy of the system is S equal to k B l n gamma, and therefore, this is equal to l n of epsilon plus n factorial divided by epsilon factorial by n factorial. And you can now write this as l n epsilon plus N factorial minus l n epsilon factorial minus l n N factorial. Now this looks pretty familiar, because if the individual numbers epsilon and N are large, you can use the stirlings approximation, and then very easily write down that I must be having in this case this simplification, and; obviously, this kind of algebraic expressions can be simplified, and the net result is going to be, that I can obtain an algebraic expression for s in terms of epsilon and n right. And therefore, this actually is a big lift in the challenge for modelling complex systems, where there is a very large number of particles present.

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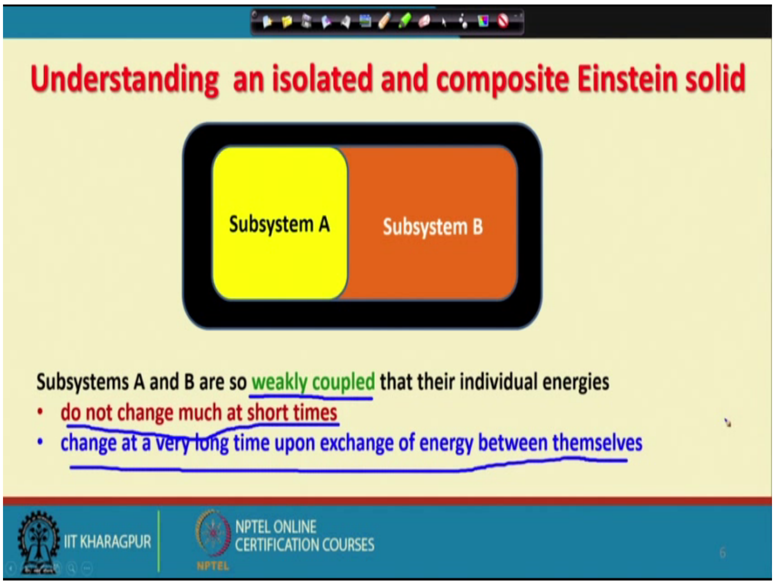

Understanding an isolated and composite Einstein solid

Subsystems A and B are so weakly coupled that their individual energies

- do not change much at short times
- change at a very long time upon exchange of energy between themselves

Now, let us next to go, and have a little more complicated situation and the situation is an isolated and compose it Einstein solid. Now before this we have always been talking about one single block of Einstein solid, which is comprised of capital N simple harmonic oscillators non-interacting and distinguishable.

Now, what I have done is, I have taken this big block and divided it into two subsystems. There is the subsystem 1 and there is this subsystem 2, and what I am going to do is, to start with. I will not allow any interaction between subsystem A and B, but for my current purpose, what I am going to do is, I am going to assume certain things. It says that the subsystem A and B, they are extremely weakly coupled. So, that the individual energies of the system do not change much at short time, but change at a very long time, upon exchange of energy between themselves.

So, what are the ways in which I can design an experimental situation like this? So, once again following the original representation I have taken an insulated box.

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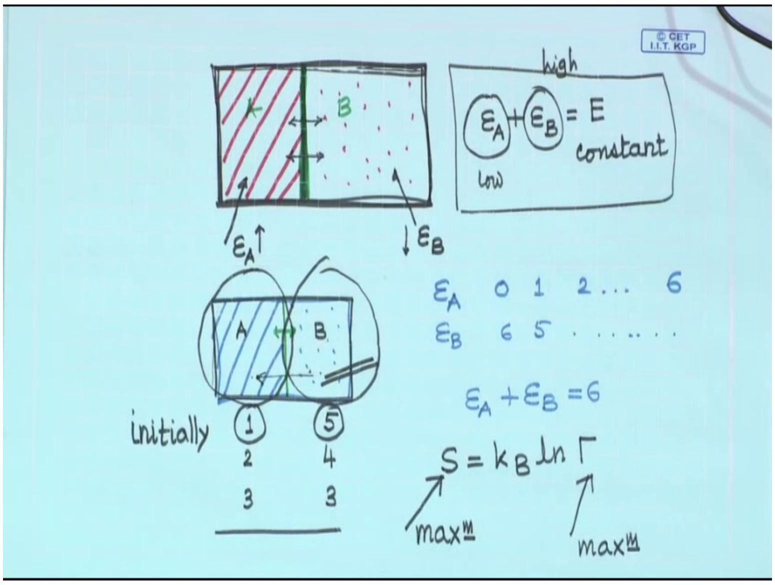

So, this insulated box or this big block of solid box, which is rigid impermeable and adiabatic, so that there is no exchange of energy volume or particles with the surrounding.

Now, I have constructed a partition in this box, and this partition is such that it is highly non adiabatic rigid, as well as impermeable. And therefore, the solid material that I have on the two sides. Let me shade them like this, and let me shade them like this. Although they are the same solid, I would say that there will be no exchange of either energy or volume or mass between them.

Now, I am going to alter this model a little bit. I am going to make the separator weekly adiabatic. So, what do I mean by weekly adiabatic. It means that the system if I measure, if I had some method of measuring the energy of the system at short times, the energy of this subsystem would be epsilon A and energy of this subsystem would be epsilon B and by the given condition. Since my entire box is insulated, and it is an isolated system and this is equal to capital E which is a constant ok.

Now, I had since I have made this separator weekly diathermal, which means that these two systems can now exchange energy between themselves, but the separator being weekly diathermal one. What will happen is. At any given instance of time if you measure the energy of either the compartment A or the compartment B, you will find that they have more or less constant value of energy, but if you wait for a long time, because of this nature of weak coupling between them, and the possibility of very small exchange of energy, what will happen is. There will be, let us say epsilon will go on increasing and epsilon B will go on decreasing. If to start with epsilon A was low and epsilon B was high. So, with this exchange epsilon A with will increase epsilon B will decrease. Keeping this condition that epsilon A plus epsilon B is always a constant.

So, that is the basic idea behind designing this kind of system, and then there are certain points that I would like to highlight over here, and they are as follows.

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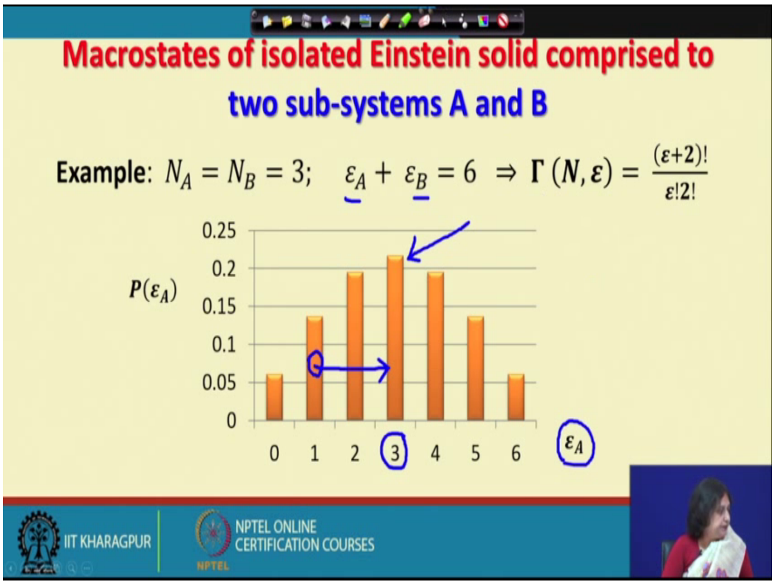

Macrostates of isolated Einstein solid comprised to two sub-systems A and B

Example: $N_A = N_B = 3$; $\underline{\varepsilon_A} + \underline{\varepsilon_B} = 6 \Rightarrow \Gamma(N, \varepsilon) = \frac{(\varepsilon+2)!}{\varepsilon!2!}$

if I look at the macro states of the isolated Einstein solid comprised of these two subsystems A and B. Let us say the compartment A, I have three simple harmonic oscillators. And in the compartment B I have three simple harmonic oscillators. So, it is a system comprised of 6 simple harmonic oscillators distributed equally on the two sides of the compartments three each. And we also have in this Einstein solid, the total energy is 6 quantum. So, that epsilon A plus epsilon B is equal to 6.

And then depending on what we know that depending on what the value of this N and epsilon are, I can find out gamma. And if I now calculate the number of microstates gamma and the probability of observing a particular microstate where the energy of the compartment A, is epsilon A. We have already seen this kind of pictures.

Now, what is these kind of picture. Tell me there are several observations that we can make over. Here we find that epsilon A can take a values from 0 to the maximum, which in this case is 6 and the probability of the some sub-compartment A, to have the value of energy epsilon equal to 0 is much less compared to the situation, where it has an energy value equal to 3.

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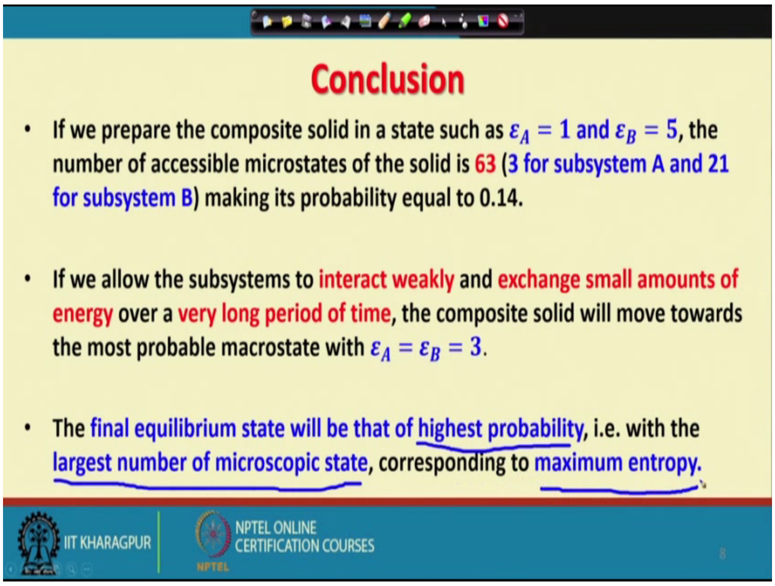

Conclusion

- If we prepare the composite solid in a state such as $\varepsilon_A = 1$ and $\varepsilon_B = 5$, the number of accessible microstates of the solid is 63 (3 for subsystem A and 21 for subsystem B) making its probability equal to 0.14.
- If we allow the subsystems to interact weakly and exchange small amounts of energy over a very long period of time, the composite solid will move towards the most probable macrostate with $\varepsilon_A = \varepsilon_B = 3$.
- The final equilibrium state will be that of highest probability, i.e. with the largest number of microscopic state, corresponding to maximum entropy.

Now,. So, this tells us that if we prepare the composite solid in such a state that epsilon A is equal to 1, and epsilon B equal to 5, then the number of accessible microstates of the solid is 63, making its probability somewhere equal to 0.14.

So, if I go back. So, I am talking about epsilon A and epsilon B in such a way that epsilon A is equal to 1. So, automatically epsilon B is equal to 5. So, I have started with a system, started with a state of the system, where epsilon A is equal to 1 and I am here, and the probability of this state, starting state is 0.14.

Now, if I go down and check once again that what is going to happen? If we allow the subsystem to interact weakly, and exchange small amounts of energy over a very long period of time. This composite solid will move towards the most probable macro state, why is it. So, that is because once again let us look at the situation, where I have these two compartments separated by this weakly diathermal separator, which allows in the long time, a small exchange of energy between the compartment A and compartment B.

Initially I started with how many quanta of energy in a one quantum of energy in B 5 quanta of energy. Now if I allow them to exchange energy as I have said before, then B being at higher energy is in a position to lose some energy to 1. So, this number will go up to 1 2 3 so on and so forth, and correspondingly this number will come down to 5 4 3 and so on and so forth.

Then the question that we are asking here is, if we allow this weak exchange the composite system will move from this less probable, less probable state, when it has had a probability equal to 0.14 to some other macro state. So, in which direction will it go. It is going to go towards the direction that increases epsilon A and decreases epsilon B. now when will it stop; obviously, we understand that this process will stop, only when the energy epsilon A is equal to energy epsilon B. This is a total energy of the some compartments A and B respectively.

Now, if we go back and look at the probability distribution once again for the system, that we are talking about. Therefore, all we are saying is. If I start from a system like this, then I am going to ask the system is allowed to exchange energy. I am going to go spontaneously in this direction increasing epsilon A and; obviously, decreasing epsilon B at the same time. And where will I stop. I will stop when the energy is epsilon A and epsilon B are equal. Under what condition will these two energies be equal; that is when epsilon A equal to epsilon B equal to 3.

Now, interestingly what we find is that, it is this condition where the distribution of P epsilon A is associated with the maximum number of microscopic states, or this is the most probable macro state of this composite Einstein solid, this then can be very easily concluded that. Well the composite solid on being allowed to move interact weakly over long times of long periods of time. It will move towards that state that is associated with a maximum number of microscopic states.

And we can also conclude that the final equilibrium state will be that of the highest probability. Now which equilibrium. If the equilibrium state has the highest probability, it must be associated with the largest number of microscopic states. And according to the Boltzmann hypothesis, if you have a macroscopic state that is associated with the largest number of microscopic states, then that must be the macro state having the maximum entropy.

So, now we see the different loop points started converging in one direction. So, what I had. Was I started off with a block of solid? It is a macroscopic block of solid subsystem A, is still macroscopic subsystem B, is still macroscopic, and I am saying that the energies of epsilon A and epsilon B can have discrete quanta values. Like epsilon A can have values from 0 1 2, up to 6. And since epsilon A plus epsilon B is equal to 6. Therefore, automatically the values of epsilon B are fixed accordingly ok.

Then I said to start with. I prepare my system in such a way that epsilon A is having energy of 1 quantum. Epsilon B is having energy 5 quantum, and then I allow these two systems to exchange energy vary slowly, when the exchange energy; obviously, you understand that there initial equilibrium state is disturbed. So, your question would be what will happen to these macroscopic bodies, when they try to attain a new equilibrium state then I have. As I said that the compartment having the higher energy will try to provide some energy to the compartment which is having the lower energy.

So, the spontaneous change in state is going to be the one, where the system passes on thermal energy in the form of heat from the region of higher energy to the lower energy. Here as you see, and then equilibrium is reached when there is no more such heat flow. So, this we find, is this process, or the attainment of the equilibrium to be associated with attainment of that macroscopic state; that is associated with the highest number of microstates, and this is exactly what the Boltzmann hypothesis was trying to tell us.

The equilibrium state in an isolated system, when it has undergone some internal change, some constraint, internal constraint has been removed. It will readjust itself and settle in a new equilibrium state; such that its entropy is maximum in terms of the microstates. We find that this new equilibrium is associated with a maximum number of with a state associated with a maximum number of microstates. Therefore, we justify the use of Boltzmann hypothesis, saying that well S is equal to k B l n gamma. So, at equilibrium when gamma is maximum, I understand at the same time S is also going to be maximum.

So, as we see that by introducing the Boltzmann hypothesis, they are not violating any of the concepts that we are familiar with from our previous experience, with thermodynamics. Let us go move and go to one step further.

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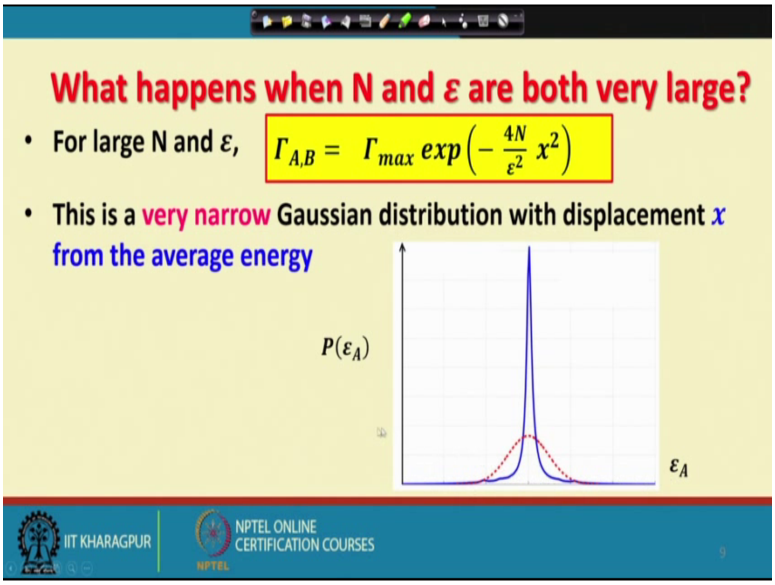

What happens when N and ε are both very large?

- For large N and ε, $\boxed{\Gamma_{A,B} = \Gamma_{max} \exp\left(-\frac{4N}{\varepsilon^2}x^2\right)}$
- This is a very narrow Gaussian distribution with displacement x from the average energy

And say that. Well what happens when both the number of particles and the quanta of energy available to this Einstein solid composite Einstein solid. Both of them are very large.

Then what find is once again we have work this out in some previous lecture, that this becomes a very sharp distribution right. So, the number of possible values of epsilon A is going to be a very wide range, and we have already seen that. Then the probability peaks around some value depending on the kind of system that you have. And the probability of being in a state characterised by some value of epsilon A much different from this peak position is vanishingly small.

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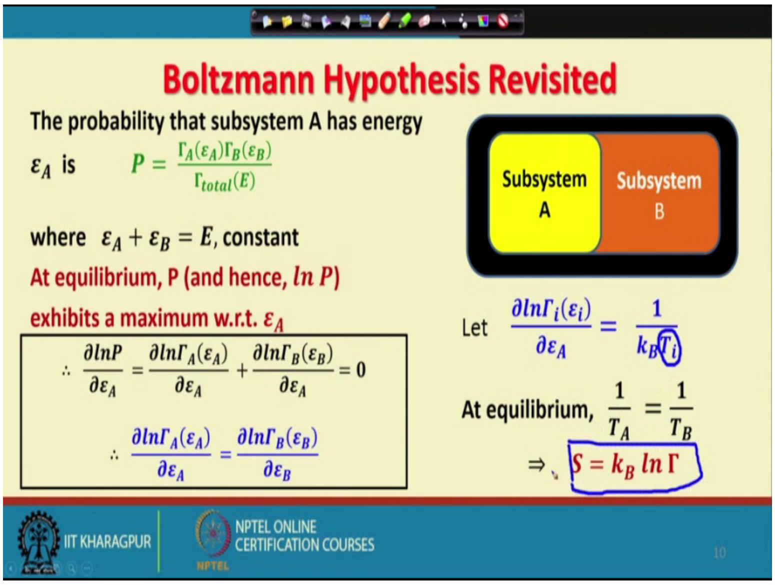

Boltzmann Hypothesis Revisited

The probability that subsystem A has energy ε_A is $P = \frac{\Gamma_A(\varepsilon_A)\Gamma_B(\varepsilon_B)}{\Gamma_{total}(E)}$

where $\varepsilon_A + \varepsilon_B = E$, constant

At equilibrium, P (and hence, $ln\,P$) exhibits a maximum w.r.t. ε_A

$$\therefore \frac{\partial lnP}{\partial \varepsilon_A} = \frac{\partial ln\Gamma_A(\varepsilon_A)}{\partial \varepsilon_A} + \frac{\partial ln\Gamma_B(\varepsilon_B)}{\partial \varepsilon_A} = 0$$

$$\therefore \frac{\partial ln\Gamma_A(\varepsilon_A)}{\partial \varepsilon_A} = \frac{\partial ln\Gamma_B(\varepsilon_B)}{\partial \varepsilon_B}$$

Let $\frac{\partial ln\Gamma_i(\varepsilon_i)}{\partial \varepsilon_A} = \frac{1}{k_B T_i}$

At equilibrium, $\frac{1}{T_A} = \frac{1}{T_B}$

$\Rightarrow \boxed{S = k_B\, ln\,\Gamma}$

So, what is it that we are concluding from here we are concluding that, that is exactly what is to be expected from the Boltzmann hypothesis?

Now, let us revisit the Boltzmann hypothesis is once more, and try and see that if it matches with other concepts that the concept of heat flow from one region of the system to the other, and this is how we propose to do it. Now given this composite Einstein solid, I would say that the probability that the subsystem A has some energy epsilon A is given by this probability P.

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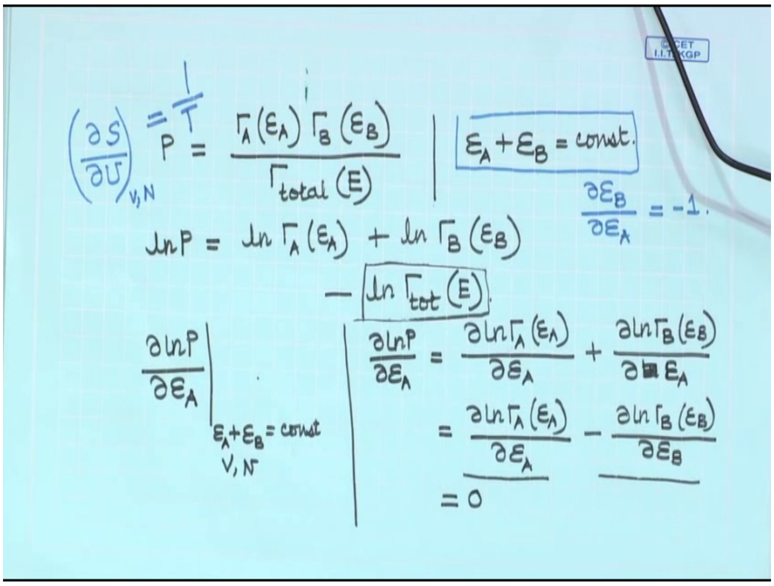

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T}$$

$$P = \frac{\Gamma_A(\varepsilon_A)\,\Gamma_B(\varepsilon_B)}{\Gamma_{total}(E)}$$

$$\boxed{\varepsilon_A + \varepsilon_B = const.}$$

$$\frac{\partial \varepsilon_B}{\partial \varepsilon_A} = -1.$$

$$\ln P = \ln \Gamma_A(\varepsilon_A) + \ln \Gamma_B(\varepsilon_B) - \boxed{\ln \Gamma_{tot}(E)}$$

$$\left.\frac{\partial \ln P}{\partial \varepsilon_A}\right|_{\substack{\varepsilon_A+\varepsilon_B = const \\ V,N}}$$

$$\frac{\partial \ln P}{\partial \varepsilon_A} = \frac{\partial \ln \Gamma_A(\varepsilon_A)}{\partial \varepsilon_A} + \frac{\partial \ln \Gamma_B(\varepsilon_B)}{\partial \varepsilon_A}$$

$$= \frac{\partial \ln \Gamma_A(\varepsilon_A)}{\partial \varepsilon_A} - \frac{\partial \ln \Gamma_B(\varepsilon_B)}{\partial \varepsilon_B}$$

$$= 0$$

And this is equal to gamma A epsilon A into gamma B epsilon B divided by gamma total E. We have seen before how to calculate this quantity P for a given value of epsilon A and epsilon B, and an given number of particles.

Now, please remember that epsilon A plus epsilon B once again is a constant. Now we can once again say that at equilibrium this probability. And hence the natural logarithm of this probability must exhibit a maximum with respect to epsilon A if that is. So, then I can very easily say that if I write down what l n P is l n P is going to be l n gamma a gamma total epsilon.

So, in order to find out the condition under which this l n P exhibits. So, maximum what I can do is. I can take a derivative of this l n P with respect to del epsilon A, keeping epsilon A plus epsilon B constant. And not only that the volume of the system is constant, and the total number of particles is also constant, and the result is going to be given by a condition like this. So, basically what you are saying is as follows. So, del l n P del epsilon A; that is going to be equal to del l n gamma A which is a function of epsilon A divided by dell epsilon A plus dell l n gamma B which is a function of epsilon B divided by dell l n dell epsilon A. As you see that this number is fixed for given total energy volume and number of particles. So, that is not going to vary with epsilon A. So, I have not written this number, but please remember that I already have this restriction on the system. Therefore, I can very easily write down that del epsilon B dell epsilon A that is equal to minus 1 right.

And therefore, this expression now turns out to be del l n gamma a del epsilon A minus dell l n gamma B, which is a function of epsilon B divided by dell epsilon B and for l n P to have a maximum with respect to epsilon A, this must be equal to 0. This means these two terms here, and here must be equal when the maximum appears and that the condition then of equilibrium, that this particular quantity that I have shown here which is a derivative of the log of number of microscopic states in the subsystem a, that must be equal to the corresponding quantity for the subsystem B.

Now, what does it mean is this, something that we would physically expect the answer, actually is very simple. Now look at what we can know from introducing some quantity T. So, let me say that this temperature t is related to this derivative, as I have shown in the context of the equilibrium condition. Then what is the equilibrium condition. The equilibrium condition now turns out to be that 1 by Ta is equal to 1 by T b ok.

Now, this means that what I am talking about, is the fact that if entropy is k B ln gamma. In that case what I have is. I am taking a derivative of this l n gamma with respect to energy, and I am coming up with some kind of a parameter temperature. Now if S is related to this, what is the derivative of entropy with respect to energy. If you remember that in the case of. Well while we talked about the thermodynamics in an isolated system dell S dell U V N, this is equal to 1 by T. So, what is T. There T is a temperature.

So, now what I see here is that, if I look at this derivative these two derivatives become equal to each other with respect to these subsystems a and b. So, now, this is a post justification of the existence of a relationship like this. Now let me repeat the kind of argument that I have been trying to post here. First of all I said that there are two parts of an isolated system. I remove some kind of an internal constraint and allow the system to undergo a change in state. So, that it spontaneously goes to a new equilibrium state.

The new equilibrium state is going to be the one associated with a maximum number of microscopic states, then I said, fine. Now I understand in terms of the microscopic states, I should be getting the condition in terms of the fact that dell l n gamma for the compartment A dell epsilon A that must be equal to dell l n gamma B to compartment B.

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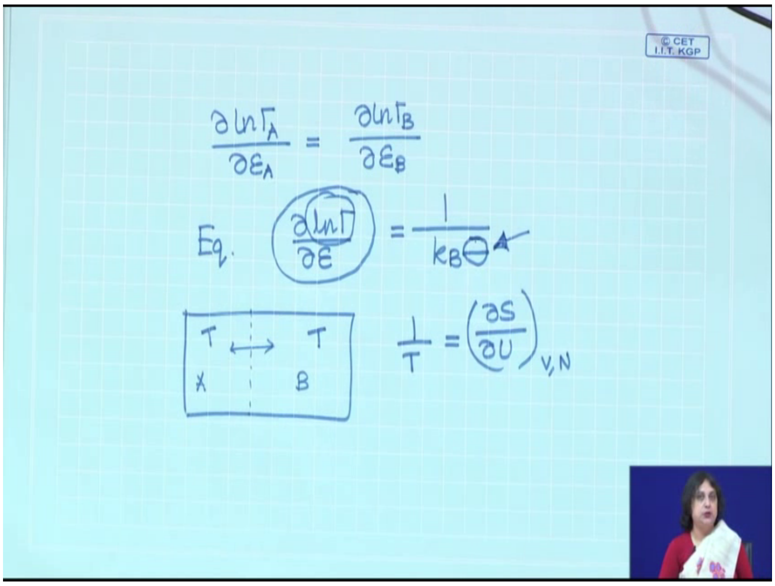

$$\frac{\partial \ln \Gamma_A}{\partial \varepsilon_A} = \frac{\partial \ln \Gamma_B}{\partial \varepsilon_B}$$

$$\text{Eq.} \quad \frac{\partial \ln \Gamma}{\partial \varepsilon} = \frac{1}{k_B \Theta}$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}$$

So, basically the equilibrium condition now depends on dell l n gamma dell epsilon this derivative, but if in the real world if you have an isolated system, and then you allow exchange of energy between the two compartments when will the composite body at in a new equilibrium when the temperature of the system is uniform throughout and therefore, if and only if this quantity can be mapped onto the real physical temperature, you can say that whatever we are say saying. So, far has some logical implication.

Now, if that is. So, if I define this as some kind of a function of what I call say I call it theta right then the presence then I understand that this theta is related to dell epsilon of l n gamma. Now I know that temperature 1 by T is equal to dell S dell U V N. Therefore, this quantity has to be related to entropy. So, that theta can be the quantity related to temperature and that is exactly what has been shown in this slide, it says that if I allow energy exchange they will attain a thermal equilibrium at thermal equilibrium you must be having temperature of subsystem A and equal to the temperature of the subsystem B.

And then here you have shown that equality of these two quantities determined the equilibrium between the subsystems A and B. Therefore, this dell l n gamma dell epsilon must be related to the temperature and if that is. So, then by retracing my route back I would say that l n gamma this quantity must be related to the entropy of the system, because del S del U is related to the temperature of the system.

So, now that we have discussed the basic principles of statistical mechanics and I have shown to you how you justify using especially the Boltzmann hypothesis. From the next lecture we will go straight ahead and think of ensembles of collections of microscopic states in a given system, in a given thermodynamic state, and try to derive the thermodynamic properties starting from the microscopic Hamiltonian.

Thank you.