**Classical Physics**
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**Lecture No. # 24**

Yes so, let us continue with where we left off yesterday, we did a quick recap of thermodynamics and we will come back to thermodynamics and then try to derive equations of state such as the ideal gas equation of state, from the laws of statistical physics. So, let me go back little bit to statistical physics. And now, try to understand what the distribution of energy is in a system in a large isolated system in thermal equilibrium.

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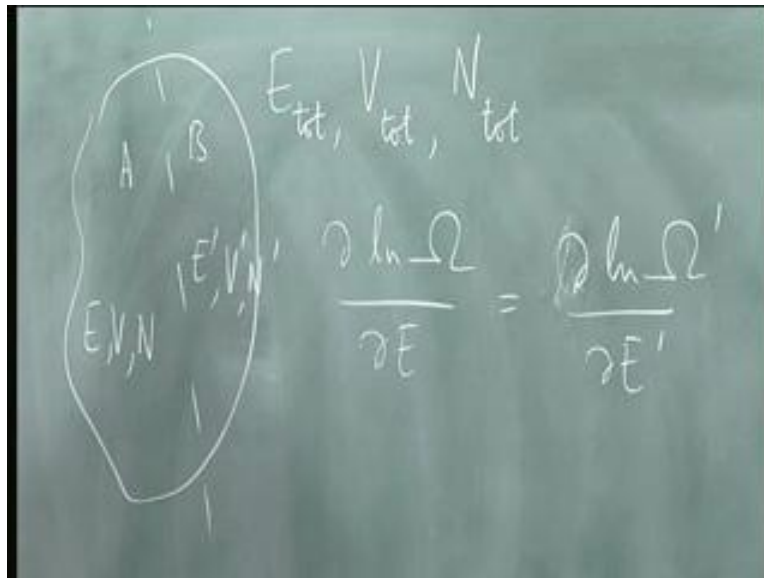


So, if you recall we had a large system a total system in thermal equilibrium, isolated system with some total energy E, total volume V, total and number of particles N total. And then I said well, if you draw an imaginary partition here and call these two sub systems A and B, which are in thermal equilibrium with each other, then the statement made was that the conditions of equilibrium, imply that, delta log omega over delta E on the 1 side is del delta log omega prime over delta E prime on the other side. Where this has energy E, volume V, number of particles N and these are prime variables this side. And we have 2 other conditions for the partial derivatives with respect to volume and the number as well.

And I pointed out that these are really the statements that the temperatures on the two sides are equal by definition, the pressures are equal and the chemical potentials are equal. That was just a statement, because I did not really establish that what I identified as delta log omega over delta V was in fact the pressure over temperature. I just made the statement there that this is called the pressure, but I have to really show that and to do that we have to make contact with thermodynamics which we have not done at all. But before, we do that it is going to be a little bit of claim before we do that because, this is not the best way till which to do that.

It turns out you need a slightly more, slightly better way of making contact with thermodynamics. Although, in principle it can be done from here which is little too elaborate so, we will choose a easier route.

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But before, we do that we should ask after all we started by asking, what is the probability P that the energy of the system A was equal to some number E between 0 and E total? And then of course, I said this quantity was equal to the number of microstates of the system A corresponding to energy E and volume V and number N and so on, multiplied by corresponding number of microstates for the system B divided by a normalization factor omega total of E total.

With this statement, the idea of equal apriori probabilities of the full isolated system has been exhausted, the content of that is exhausted. And there is a further assumption, that the interaction between these 2 sub systems is such that the number of degrees of freedom engaged in this interaction at any instant of time is negligible compared to N and N prime. And therefore, the total number of microstates of the total system corresponding to energy E for the subset system A can be written in this product form, 2 independent systems all together.

So, these were the two assumptions that went there. Now, the question arises, what is P of E? What is the formula for P of E? And this, we can derive in a regress way but I am going to do this by a sort of hand waving way, just to show you what will happen?

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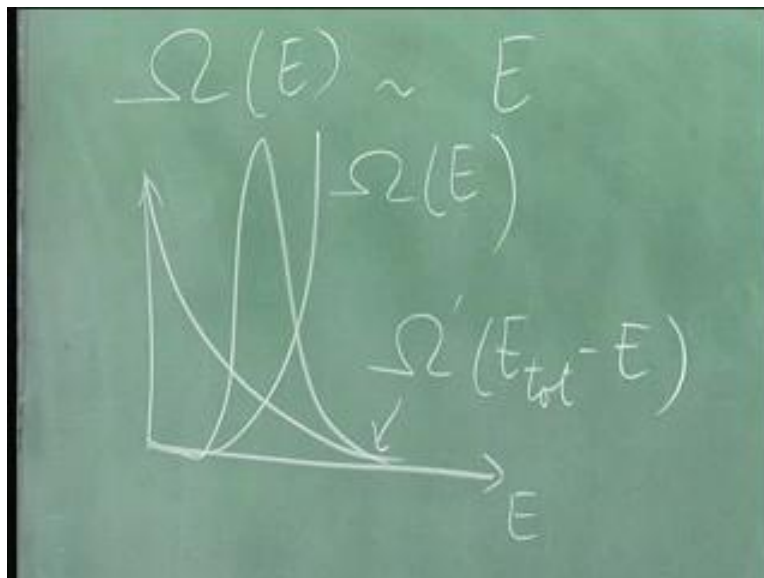


You see, I already pointed out that omega of E is going to go like E raised to the power N its really going to increase with the energy its a number of accessible microstates of the system at some energy E and that going to increase as the energy increases like a very large power of E. And this quantity here, is omega prime of E total minus E because, the sum of the 2 is equal to E total, assuming that the interaction energy at any instant is negligible compared to the energy E and E prime. And therefore, this quantity here is a rapidly decreasing function of E, because it starts at E equal to 0 at some number and then as E increases towards 0 this function decreases.

So, on the 1 hand you have a function that is increasing very rapidly from 0 on the other hand, you have another function that is decreasing rapidly.

So, as a function of E this guy is going up extremely fast, this is omega E and the other 1 is coming down extremely fast. And this is omega of omega prime of E total minus E, we are looking at this as a function of E that is the variable you can run from 0 to E total and your product of it rapidly increasing function and a rapidly decreasing function. This means, that the product itself is essentially 0 here thus it crosses 0 very rapidly here and its essentially 0 out here this side and this function is going to start looking like this, the product is going to look like that in between.

And this is easy to verify, that the only place where it can have any significant departure from 0 would be somewhere near the maximum of this function, right start looking like a very sharply peak function here. And if that is the case, then what is this going to look like? Well, instead of looking at P of E, which involves very, very large numbers E to the power 10 to the 23 is a sort of not very manageable.

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Let us look at log P of E as we always do take a log here. Then log of this plus log of that and we could ask what does this function look like, I have already sort of waved my hands and said this

function goes up and comes down. So, let us expand it about the mean value about this peak value and let us call this peak value some E bar and my assumption is, it can be justified regressly, that this function is essentially 0 but there is a huge peak at E bar and then it goes back to zero. So, this thing here if I expand about E bar this is equal to log P of E bar plus E minus E bar delta log P of E over delta E at E bar plus E minus E bar whole square over 2 factorial the second derivative plus etcetera.

And of course, if you are expanding about the maximum this quantity is 0 by definition, because E bar is an extreme of this function and that leaves you as a first correction apart from a constant it leaves you this quantity here. But this is a maximum, which implies that this function here, this number here is a negative number, because you are at a maximum.
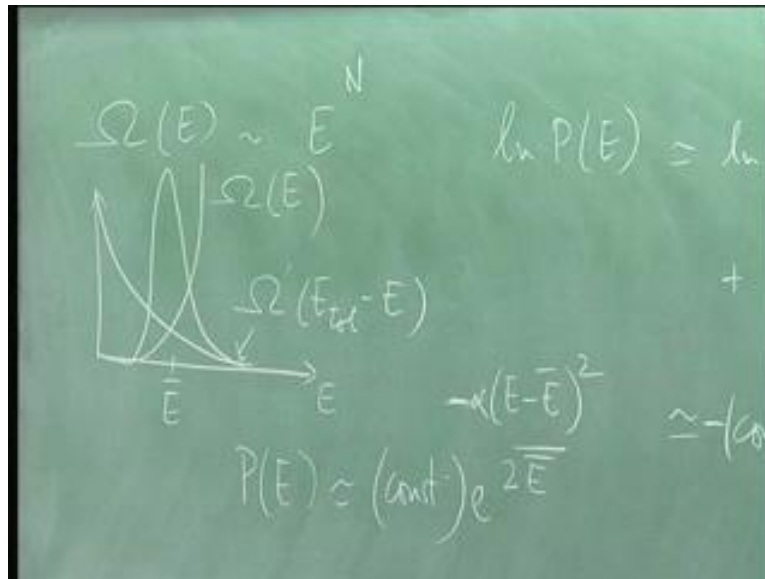
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So, this whole thing goes like some constant, minus some positive constant time E minus E bar the whole square plus higher order terms plus corrections and when you exponentiate this, it gives you a Gaussian shape immediately.

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So, this says P of E is like some normalization constant E to the power minus E minus E bar whole square and there is a scale factor there is this factor 2, and then there is this constant here there is some kind of scale factor with correct number of dimensions physical dimensions so, that this exponent is dimensionless. As you can see, P of E is dimensionless it is a probability and you have a 1 over energy square sitting here and therefore there is some number here which is of dimension energy square. So, some constant so, let me just call it minus alpha something of the other; and that is a Gaussian, E to the minus X square is a Gaussian in X. So, this says that you have an extremely sharply peak quantity.

If you did this, a little more carefully then you discover that what you have here, let me put that factor N is in fact proportional to E bar itself; so proper derivation would tell you that you have a variance; remember that for a Gaussian whatever appears in the denominators E to the minus X square over 2 sigma square appears, and whatever is appearing down there. So, let us even put the 2 here, apart from some numerical constant you get a variance, which is proportional to the mean value itself.

Now, you are already familiar with the probability distribution, where the variance is proportional equal to the mean the Poisson distribution. This is a Gaussian which has come from Poisson by a kind of a route that I mentioned earlier, from the binomial you go to the Poisson

and then you go to the Gaussian. So, something like that has happened here too and essentially you have a variance which is not independent, but its proportional to the mean energy itself. Our purpose here is not to worry about this too much because this is not the distribution, we are going to use for practical calculations.

But I want to show you that it is formed on simple physical ground is of this kind, it is a Gaussian very, very sharply peaked. It is so sharply peaked we cannot draw this on this scale that is the reason I use the log in order to be able to even represent this function.

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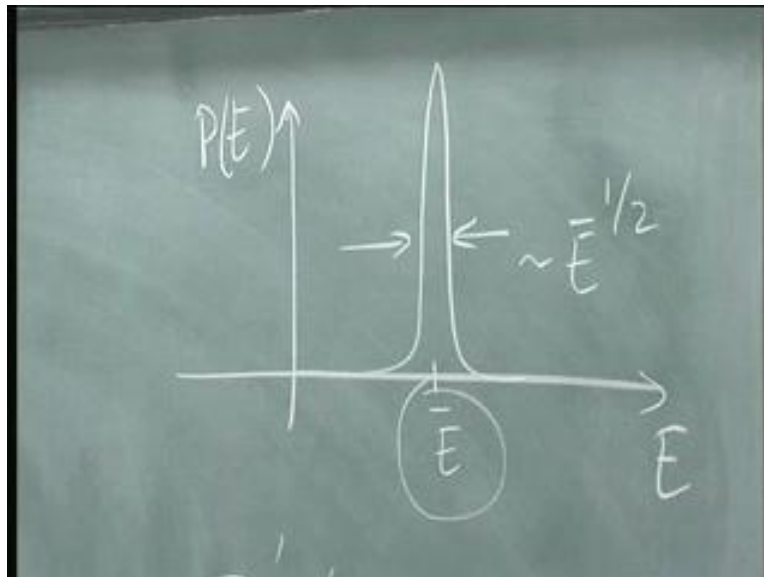


Now, this is at root of thermodynamics because, if you know that you have a peak. So, here is E and here is P of E purely this system, isolated since thermal equilibrium, if you look at junk of it here. You have guaranteed by these arguments, that the energy distribution is something of this kind about some E bar and it has a width which is proportional to E bar to the power half square root of E bar. So, this width to this the ratio goes like 1 over square root of E bar. And if E bar is proportional to the number of degrees of freedom, by the equi partition kind of argument then you can see that in a thermodynamic system, the fluctuations about the average value are indeed negligible. They go like 1 over the square root of the number of degrees of freedom.

So, if you have the 10 to the 24 particles, then the fluctuations in thermal equilibrium about the mean value of the energy would be of the order 1 over 10 to the 12, and therefore completely negligible. And that is the reason thermodynamics is able to get away we just talking about average values, and what I call E yesterday in thermodynamics is really E bar. So, they even did not talk about fluctuations about average, just call it the average energy just call it the internal energy.

So, but once you come to statistical mechanics then E is a random variable and you have to really talk about its average and so on. But this is the quantity that appears in thermodynamics called the internal energy. But then this is of course true for systems of this kind here, and this is what is called the micro canonical ensemble in which doing calculations is a little tedious, because we need to have this system also a very large system, very large number of degrees of freedom but this may not happen, I might want to look at what happens to 2 atoms, embedded in a much bigger medium or a single atom or a few molecules or a very small object embedded in a big heat bath or some kind.

So, this is not a useful ensemble in that respect and what you would like to ask is, what happens to this graph? If I start making this system a smaller and smaller such that, essentially A is a small sub system sitting inside a huge heat bath. Inside a huge system which is driving fluctuations into this small sub system, what happens to this probability distribution? Let me give the answer right away and then we will justify it, we will do it right away. What happens to this is? This curve no longer remains a delta function it shifts to the left and slowly becomes an exponential of this kind.

So, it really becomes an exponential distribution in the energy which is very different from a very sharply peaked Gaussian distribution. But that would then apply, even if the system a was very small and it had large energy fluctuations in it. It is obvious, that if you looked at single atom in this room, its energy fluctuations would be extremely large. There could be instance, when it is traveling with practically 0 velocity, there could be instance when it got with very, very high velocity much higher than the average velocity.

Both these are possible and therefore the actual fluctuations are very, very severe, how does 1 take that into account? Well by doing exactly what we want to do now, which is to ask what happens?

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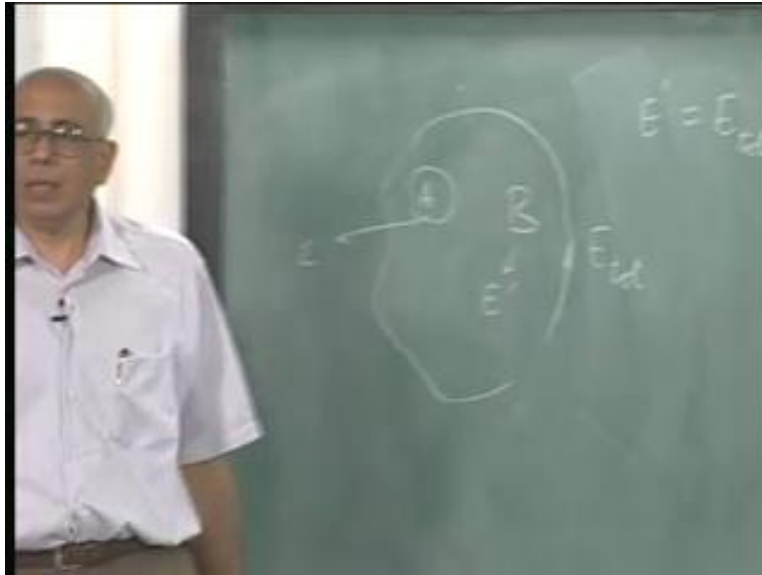


If this thing here is no longer, again I (( )) the total system of this kind, but I say this guy here A is out here and the rest is B everything else is B. And just to keep track of the fact that A could be a very small subsystem immersed in a huge heat bath this is called heat bath now.

Let us assume, that this has an energy epsilon use the symbol epsilon here instead of E, could be a large number but the assumption is that the subsystem a has a number of degrees of freedom much smaller than the number of degrees of freedom in the A in the bath outside in B. So, again the total energy is E total, this B has energy E prime and E prime plus epsilon is equal to E total. So, now I ask, what is the probability that the energy of A is epsilon? Same question as before. What is P of epsilon equal to?
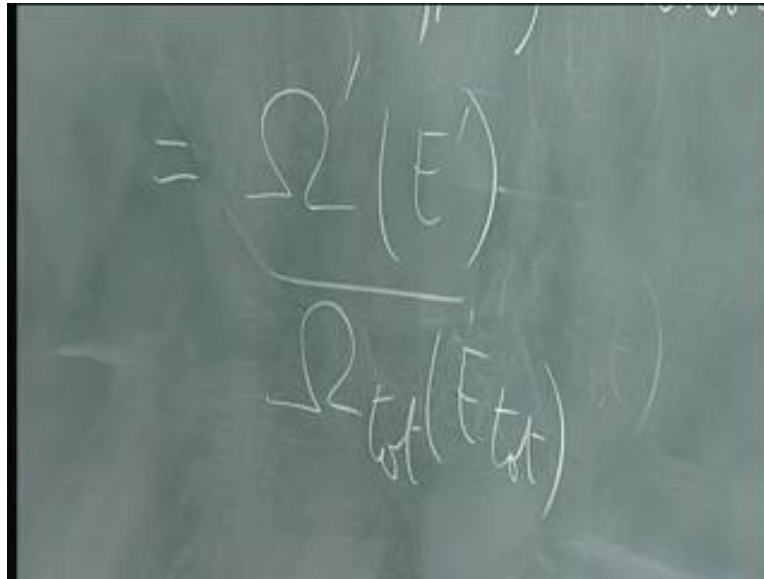
I can no longer assume that this and that are independent of each other, I certainly cannot do that. I cannot assume, that the total number of accessible microstates of the full system total system, such that the energy of A is equal to epsilon, is just the product of number of microstates of A times those of B, this is no longer possible. In fact its B that is driving everything, its controlling everything since, epsilon is much, much smaller even its much smaller than E total really it is much smaller.

So, what would this be? This thing here is equal to number of microstates of the total system such that the energy of A is epsilon divided by total number of total number of microstates. This if you recall is normalization constant its omega total E total. So, this by definition is true once again because, the total number of microstates of the full system they are all equally probable because that system is isolated in thermal equilibrium.
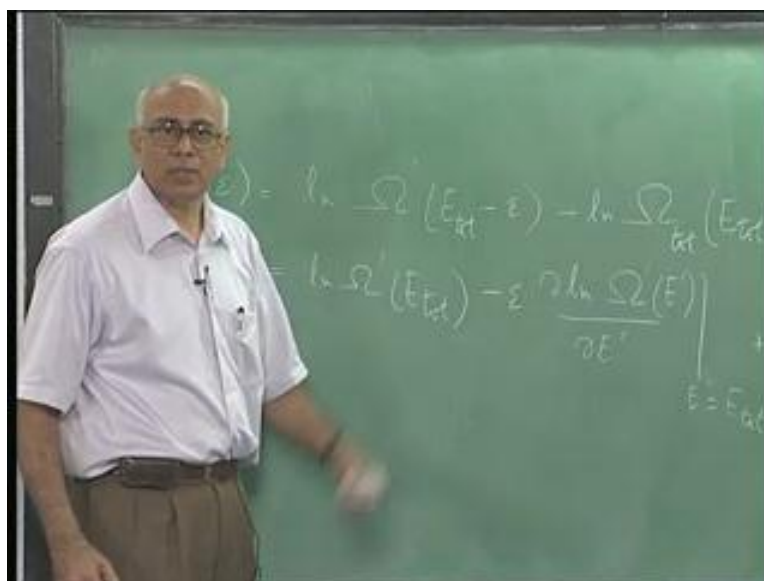
$$= \frac{\Omega'(E')}{\Omega_{tot}(E_{tot})}$$

But what is this equal to appear? This is simply equal to omega prime, because now the fundamental physical assumption is that this system is strongly affected by B but this system is not affected by A at all. If you look at the 10 molecules out of 10 to the 24 molecules its clear, that whatever happens to these 10 molecules is not going to do anything to the 10 to 24 molecules it is not going to change its statistical particles. So, because of that this is equal to omega prime of E prime divided by normalization factor divided by this constant, but then we will see, how cleverly one can eliminate it? Omega total of E total; that is your P of E. As before, you have ratio of 2 very large numbers so, let us just take logs and see what happens?

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Therefore, if you do that you get log P of E equal to log omega prime of E total P of epsilon that is in now E total minus epsilon this is E prime and E prime has to be E total minus epsilon, minus log a constant omega total E total. Now, what does this suggest immediately? It says that since, E total is much bigger than epsilon expand this function in a Taylor series about the point E total.

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And the first term is equal to log omega prime of E total minus epsilon delta log omega prime of E prime over delta E prime at E prime equal to E total plus higher orders and then a constant minus log to omega total E total. There is no question of maximum or anything like that, you have a very large number and you are expanding and you want to find the value of this function at epsilon less than E total. And therefore, the value is equal to value at E total minus epsilon times the first derivative and second derivative and so on so forth and mind you this is in the log.

And the higher order terms are negligible because this term here is going to dominate completely to first order in epsilon and then what happens? This is a constant this quantity here is a constant.
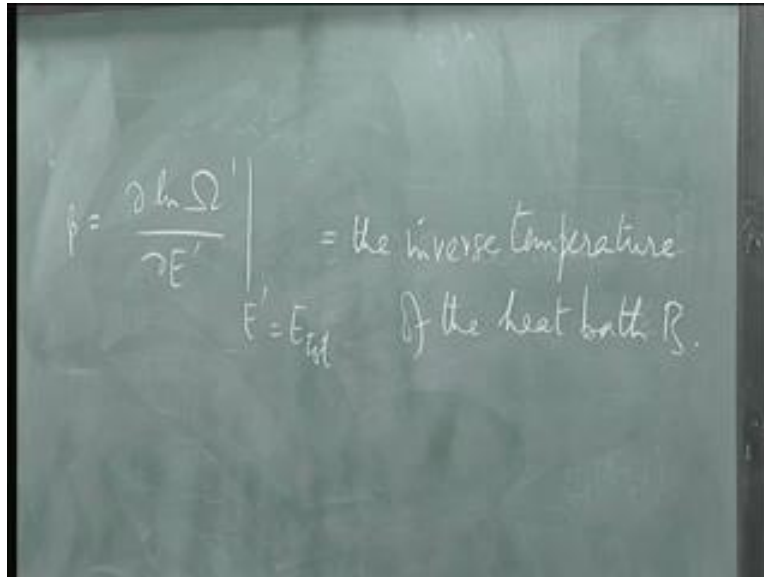
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So, this says this implies that P of epsilon equal to some constant E to the power minus, there is a number here which says take this system, take this bath here, take the derivative of number of its accessible microstates with respect to its energy at value of energy equal to the total energy, and what you call that? We gave it a name; we called it the inverse temperature. It was called it is a number and it is called the inverse temperature, of what? Of this system so, this system is governing the temperature of the full system. Its driving large fluctuations into the sub system A the energy of A is fluctuating rapidly, we have got a probability distribution but the probability distribution is E to the minus energy epsilon multiplied by a number, that number comes from this heat bath around.

So, let us call this minus beta epsilon and this beta is in fact, beta is equal to delta log omega prime over delta E prime at E prime equal to E total equal to the inverse temperature of the heat bath B. In the sense of, what happens in the heat bath? This we are not interested in that sub system at all is buried in a single number, the temperature of that system. And then the probability distribution, is just constant E to the minus beta epsilon. But the beauty of this is we do not know this constant, it involves the total system, which involves the knowing something about this system B and its degrees of freedom and so on. But the point is, we do not need it we do not need it, and this is the clever part of statistical physics. Because, this constant which starts out by saying well you should know this function, you should know that and so on, is not necessary. Because, after all this probability has to be normalized, over all possible values of epsilon.

So, if you tell me what are all the possible values of epsilon? I am going to impose the condition that if you sum over all those values you have to get 1, and that is the clever part. So, that normalization constant is fixed by the sub system properties alone and you eliminate it what happens outside, to make this clearer, let me write this in the following way. Let us suppose for a moment just for ease of illustration, that this sub system A has discrete energy levels like a quantum system.

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So, let us suppose its energy levels are epsilon zero, epsilon 1, epsilon 2 up all the way. These are the energy levels of the sub system A. So, here is a ground state first excited state second excited state and so on. And let us assume, for a moment that these are discrete and are countable, we will relax this assumption in a minute.

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Then what is P of epsilon? It is says P of epsilon equal to E to the minus beta epsilon but now, we have talked about not the energy being epsilon but energy being either this or this or this or that. So, you have to talk about the particular value of the energy and ask, what is the probability that the energy is that particular value? So, P epsilon i probability of epsilon i equal to this, but we must require that when you sum over this, set of indices i set of levels you must get 1 and therefore this must be equal to summation over j equal to 1 up to whatever level E to the minus beta epsilon j. That is the normalized probability.

And by doing this very clever trick, you have eliminated the need to know anything more about this bath do not need any information about it. There is only 1 piece of information you need from the bath and that is what is its temperature? And once, you tell me that temperature, how the temperature is obtained? I do not care, whether it is an oil bath or a water bath or an fluid bath, whatever we do not care. The fact is if this is in thermal equilibrium with the rest of this heat bath, this reservoir drives strong fluctuations in energy into this sub system here it also will drive fluctuations in number and so which we will come through.

But the probability that it attains any one of its energy levels is just an exponential function of this kind, with the ignorance factor being put in here. We have not interacted and then neglected anything, there are strong interactions. The question is a good deep one because it says, have we neglected any interactions?
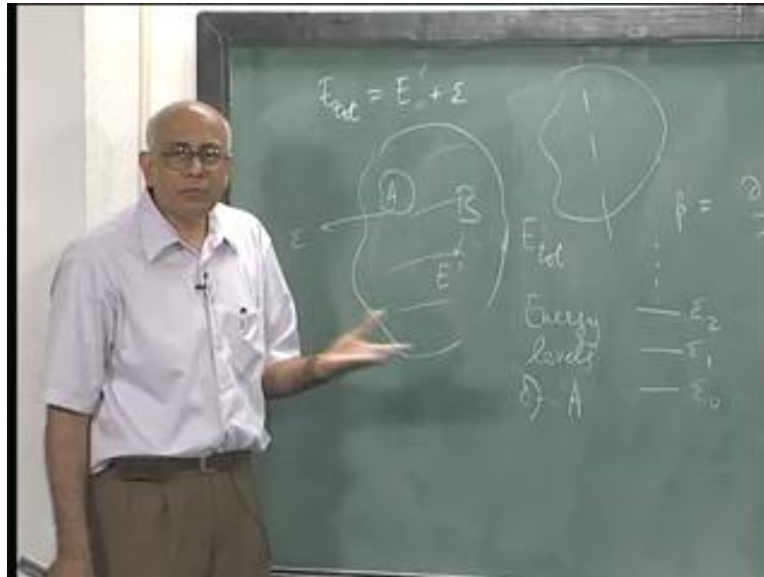
Earlier what I said was, if you had a thing like this then the number of degrees of freedom here participating in it interaction at anytime was negligible and I wrote the total system, as a sum the total energy I wrote as a sum of this quantity plus that. Now again, the problem arises if I look at this thing here, can I write E total equal to E prime plus epsilon? Can I do that or not. The point is this epsilon is strongly fluctuating. And now this way of looking at it, these are the prescribed values for epsilon, if the system A is in vacuum. These are the energy values let us say, these are given values which I find from the dynamics of the system. Then I take that and put it inside this heat bath, what happens next? Well the energy is going to jump back and forth due to what, due precisely to the interactions.

So, the outside system is driving fluctuations in this system and for a moment I have said, let us say that it has got these energy levels and it is fluctuating between these energy levels. And the question I ask is, what is the probability? That it is at this point or this point at any instant of time. Now, what you have to appreciate based on her question right away, is that at any instant of time the system is not in a specific energy state, it would be if it were just left alone and it is a stationary state. But it is not so, it is got a probability distribution so thermal system and thermal equilibrium of this kind is not in a fixed energy state. If it were a quantum system, it is not in a pure state at all. Not even in a usual superposition of pure states of energy eigen states. It is in what called a mixed state and when we do quantum physics next semester, I will explain this at

greater detail. But for the moment, this is the physical assumption that this system here has strong fluctuations being driven into it from the outside and we are in fact finding the probability distribution. What is true, is that this probability distribution does not change with time and that is because, we assumed that system to be in thermal equilibrium, that is the only statement. If on the other hand, I take a single atom in a particular quantum state I prepare it and then insert it into this heat bath, the question is, how soon will it go into this distribution? Starts off with 1 level and will it equilibrate, that is a separate question.

That is answered by asking, what is the relaxation time? What is the equilibration time? That is the different question altogether. But now, I am assuming that this is already in thermal equilibrium and you are in a steady state. Then the interactions occur, they are very strong, they drive very strong fluctuations in my sub systems. The only assumption made is, I have written down the energy levels of the sub systems based on, its own dynamics without leak outs to any heat bath or anything like that.

Now the question asked is, is it discrete? And that need not be so, what happens if its continuous? There is another question you have to ask and that is, how do I know that these levels are not degenerate? How do I know that there are 2 states corresponding to this energy of 3 corresponding to this, if its hydrogen atom certainly there is degeneracy right.

So, I should be careful, I should write very carefully states j not levels, because there could be 2 states, there could be this and this and could be this this and this and so on. So, I should sum over all possible states of a system and not over the levels. What is does it mean to be in 2 states at the same time? This question is, what does it mean to be in 2 states in 2 or more states at the same instant of time? If you have in quantum mechanics, if you have an energy eigen state and you put some in the energy eigen state, then in the absence of all perturbations and influences from outside. By definition, the system will remain in that state, if it is in an energy eigen state more precisely, if it is in eigen state of the Hamiltonian of the system.

But if it is in any other state, which is an eigen state of some operator which does not commute to the Hamiltonian, then in that state you cannot make a sharp precise statement as to what the energy is? So, as far as energy states are concerned, it is in a super position of such energy eigen states. I have assumed for purpose of illustration, that the energy levels namely, the eigen states of the Hamiltonian of the system form a discrete set, which I have labeled by epsilon knot, epsilon 1 and so on.

We are going to relax that assumption, we can make it a continual, you could make it a partially discrete, partially continuous to do that so, that is not a serious problem. The whole point is, the point I am emphasizing is, you are allowing for a summation over all possible states of his

system with that weight factor, E to the minus beta times the energy of that system, of that state that is all. For instance, the angular momentum here, may be different from the angular momentum there. But they would appear with the same weight factor for the energy, if their energies are equal that is all its being set.

Then, what does thermal equilibrium mean? I started with an operational definition I started by saying the averages of all macroscopic quantities observables are independent of time, that was my statement of thermal equilibrium. And then I made a fundamental postulate, which said for an isolated system at thermal equilibrium all its accessible microstates are equally probable. And then I said what does that imply? It implies that different portions of this system are certain quantities are constants, I call them the temperature, the pressure and so on.

And then, we said what happens if I have a much smaller system embedded in a much larger 1 here? Then the conclusion, we have arrived at is that the temperature of this heat path plays a primary role and the distribution of the energy in this subsystem is governed by its energy levels with a certain weight factor, in which this constant beta appears. So, the ignorance of the heat bath is completely subsumed in the knowledge of one constant namely the temperature, and it is this very specific exponential form; that appear everywhere.

Does this mean that the probability of being here or here or here is exactly the same? This depends on the weight factor which I have to associate with these degenerate states; I have not done so yet. So, these states themselves could form various subsets and some of them could be weighted more, some could be weighted less, it depends on how many states they are? There are so, let us write this down right away, let us put that down right away.

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This is equal to by the way this quantity here has a name, because it appears as a normalization factor everywhere and we will see that that is all that matters. And everything is derivable from it, quantity is called Z, capital Z the so called canonical partition function.

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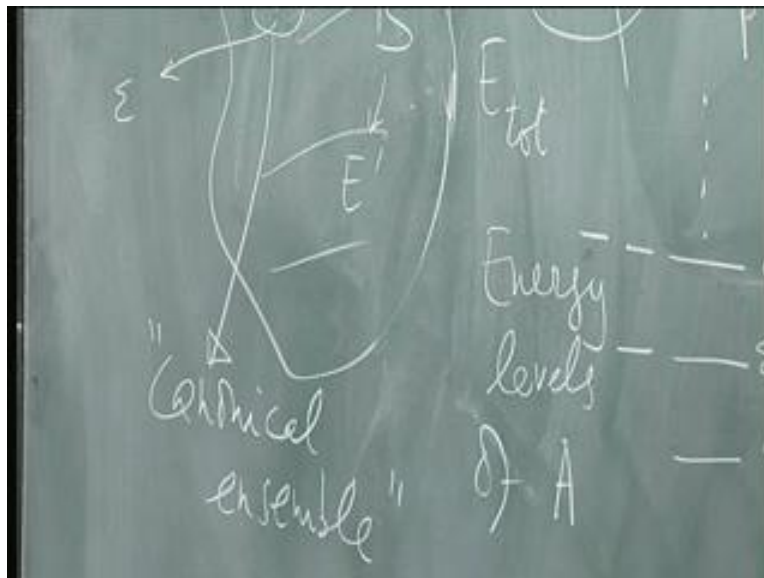


And this situation is called the "canonical ensemble". Then where you have a system inside the heat bath in thermal equilibrium, it is called the canonical ensemble. So, what we have succeeded

in doing is in obtaining a probability distribution function. So, now when I want to find average values, I am going to average over that distribution function appropriately. But the functional form of this distribution function is not a Gaussian, but it is a damp exponential decaying exponential.

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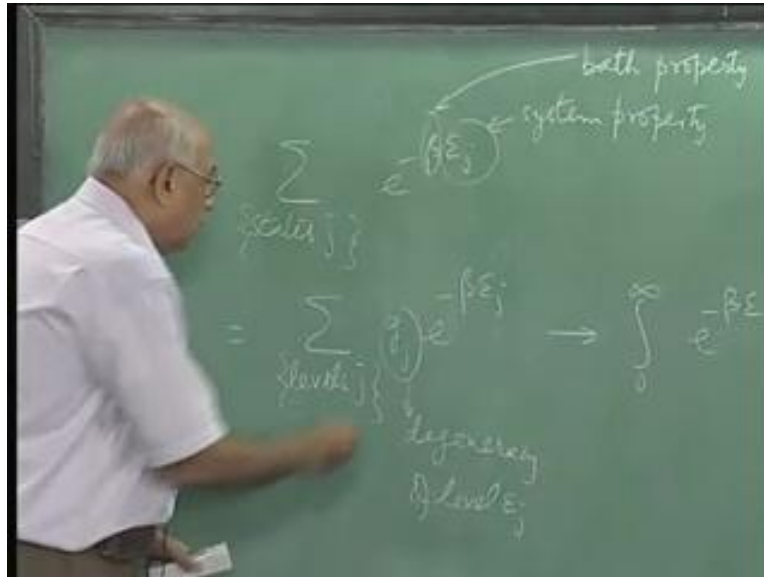


Now, let us look at this canonical partition function a little more carefully so, what is this equal to? Z canonical sometimes I put it as Z canonical here, just to tell myself remind myself its canonical, this is equal to states all the states, the set of states j the full set of states j E to the minus beta epsilon j.

I emphasize once again, this is a system property and this quantity here is a bath property. It comes from the heat bath, from the external world surrounding the system. But if I would like to write this in terms of energy levels, then I should say levels and just for ease of notation and let me continue to call them j. Let me use the symbol j for it once again, it is equal to E to the minus beta epsilon j but I must count the level j as many times as it appears. I must multiply therefore this level should be counted 3 times. So, its equal to G sub j and this is called the degeneracy of another level epsilon j.

Now, of course it is good turn out that you have a continuous spectrum so, now imagine that these energy levels really start at 0 and go all the way up completely. Then what would you do while it is clear instead of a summation, you would have an integration. And the integration would go like an integral, from whatever level upwards from 0 upwards say so, without loss of generality let us assume, for the moment that our energy levels are all bounded from below, which is important and then goes up all the way to infinity .

But as you can see, things are going to get more and more improbable as you go up. Because, if epsilon increases in its positive numbers either the minus beta epsilon becomes very, very small if epsilon is very large for any given beta.

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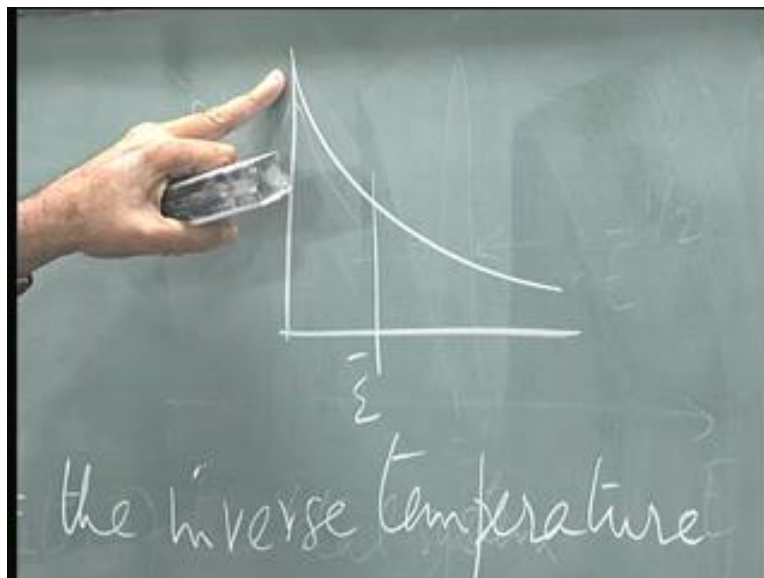


So, it is already telling you, that this distribution is an exponential distribution or may be a histogram following this pattern here and there is some mean energy epsilon bar, but there this most probable value is actually the lowest energy state. But because of the fluctuations you are not at the most probable value but, you really are distributed completely. And then, what would this be? It would be 0 up to infinity in general, if I assume it goes all the way up to infinity; and then E to the minus beta epsilon that is a continuous variable.

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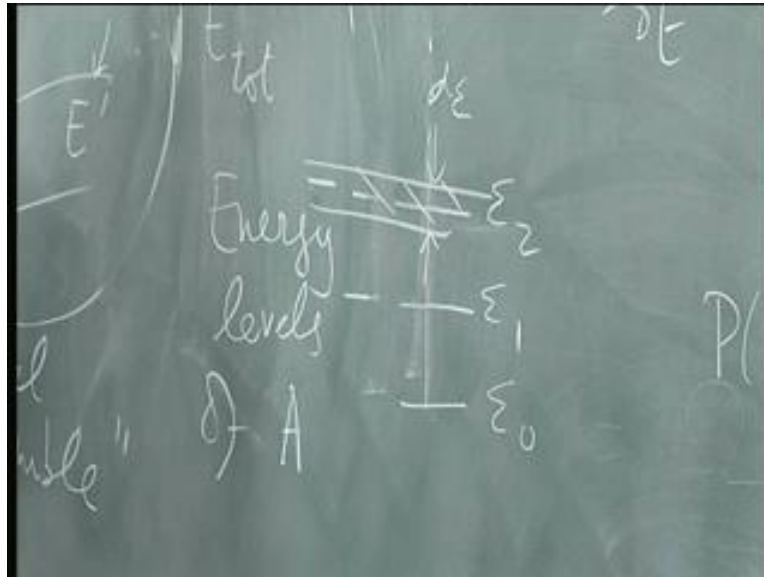


And now, what should I do instead of G j instead of this counting this, I should ask in an energy interval d epsilon, how many energy levels are there? So, I should replace the degeneracy factor by a rho of epsilon d epsilon, where rho of epsilon is density of states.

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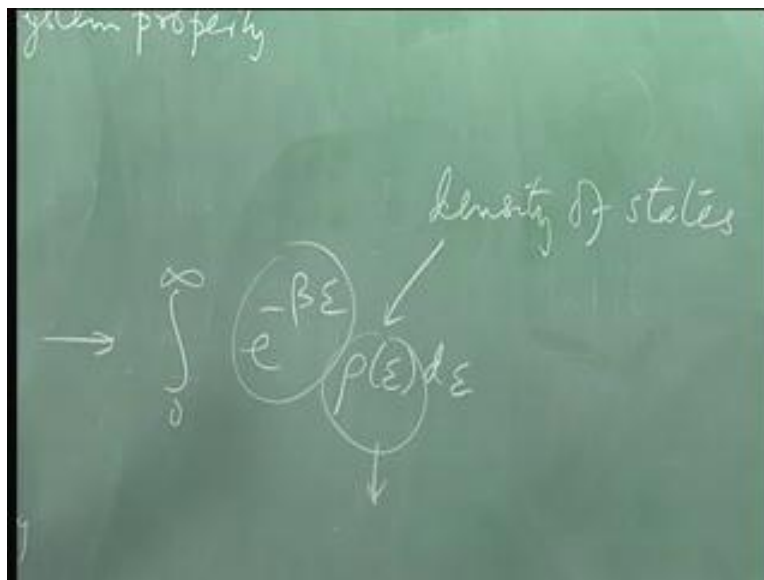


So, this tells me it includes all the effects of degeneracy and dynamics and so on and so forth and of course, it is a continuous variable so, rho of epsilon d epsilon is the actual number of states in

this thing here and then you integrate over all of them. So, you either use this or you use that but, it turns out for an instance if it turns out that this system as a few discrete levels and beyond certain stage it becomes, a continuum then you have to sum over these discrete levels and integrate over the continuum that is a matter of detail. But, this is the general formula for the partition function canonical partition function.

What does it remind you of? It reminds you of a Laplace transform; it looks exactly like a lap lace transform of the function rho of epsilon. In which the transform variable is the inverse temperature of the heat bath and the time usual time is replaced by the energy. So, looks very much like a laplace transform. And that is what it is, it generates now all the moments because, this is going to tell you this generates moment generating function, the lap lace transform is another word for a moment generating function for continuous variables, and this is exactly what it is?

By the way, there is an interesting thing you have to examine and look at here. This quantity here comes from the system properties. What does the actual dynamics of the system? Classical quantum we do not care, the mechanics of what is going on inside? This comes from the weight factor comes from heat bath. So, the statistical aspects of the system of these averages, statistical aspects are here in the mechanical aspects are here statistical mechanics so, everything is sort of split off.

So, it says in some sense since, I know E to the minus beta epsilon is a known function, the unknown is rho of epsilon. So, from different system from system to system, what it will change is rho of epsilon? And therefore, the reason why different systems behave differently is because, there are density of states is different. So, it really it says things about system but the way they would behave if you put them in a heat bath and put them in thermal equilibrium, this is the weight factor got many fancy names it is called the Boltzmann Gibbs factor or the Gibbs measure and so on and so forth.

But that is what appears, this is the basic thing that appears here. And it is very different from the Gaussian we had earlier. Now the path is little downhill because all we have to do is ask we have this, what do we do next? What can we find next from this? And then of course, the whole of statistical mechanics if you accept this is calculation now based on this partition function here.

For instance, the first question you would ask is that is very nice but, what is average energy? First thing is what is the average energy of this system? How do you answer that?

Let us start doing that, sometimes I am going to use capital E instead of small epsilon, if the system I am looking at itself is quite big. If its glass of water in the atmosphere in this room then, it certainly has smaller number of degrees of freedom than the atmosphere, but it is still it is in thermal equilibrium and fluctuations could be driven into it, but then it is not a single microscopic system so, I would use E for it.

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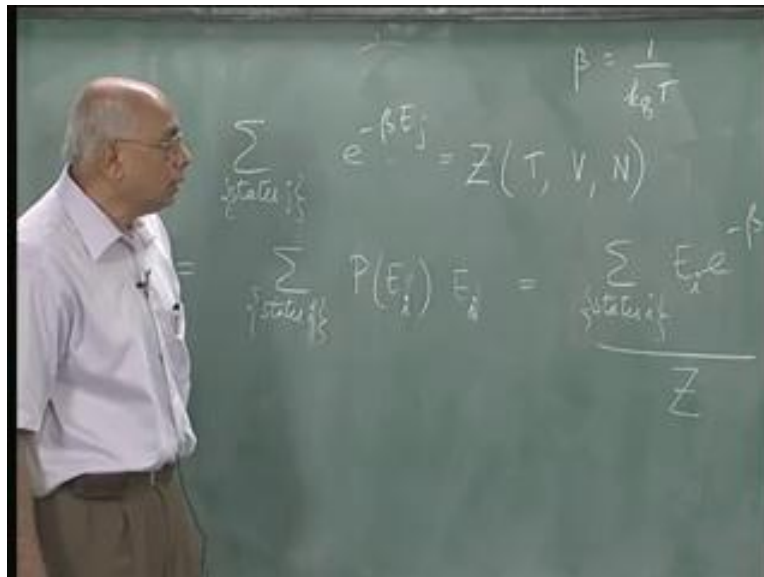


So, let us do that and let us write Z equal to summation for the moment I retain a sum, states j E to the minus beta E j, you can write it in this form and I ask, what is the average value of it? I use this symbol for average, what is this equal to? By definition, this is equal to summation over states j, the probability of the state E j multiplied by E j itself by definition. And the probability is here probability of E i is E to the minus beta E i over this (( )). So, let us write it in that form probability to E i multiplied by E i just to keep this index clear, this is equal to summation states i set of states i E to the minus beta E i and Ei divided by z. This by the way is nothing to do with E i, it is a number which j has been summed over so, it is a constant in what is the z of function of? What is the Z of function of?

What can this possibly be a function of? Z of what, it is certainly a function of beta which I will call T. So, now let us leave all our hesitation out and simply write beta is 1 over K T and I call T the temperature of heat bath and K Boltzmann is the Boltzmann constant which converts from energy to temperature. So, it is a function of T what else it is a function of? Is it the function of E j, no that is summed over; it is gone, all the system properties are gone, they are summed over completely. So, what would be a function of?

The other thermodynamic variables, it would certainly be a function of this, of the num, of the volume of the system of the number of particles. Those are the macroscopic variables which are given to you. So, it certainly be a function of those quantities but, it is not a function of the individual energy levels because, that is been summed over completely. So, that point you have to appreciate, its only thermodynamic variables that appear and what is this equal to?

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This I could write as over Z but then I could write this as summation states i E i e to the minus beta E i divided by summation states j e to the minus beta E j. You see I started by saying I am going derive, what the pressure is? So, I started by saying, that my system is specified by its energy, volume and number and everything else is presumed to be given from that, which is what will happen for the kind of systems we look at? Otherwise, you have to find that is a deep question, what are the independent thermodynamic variable, which is specify your macroscopic

system? So, you need a set of state variables specified and pressure is certainly one of them, I could look at an ensemble, in which I work here tacitly I am working in an ensemble in which I am the free energy is the Helmholtz free energy tacitly assume that.

But of course, you can work in the pressure ensemble in which case you must write T P and N and so forth. So, this is the most convenient 1 because, I started the micro canonical ensemble with this and then we said pressure is a derived quantity so, we retain that but you do not have to do it. So, what can I simplify this? And the answer is yes of course, because this is equal to if I take this quantity and beta is a variable and I differentiate with respect to beta and I am going to get minus E j.

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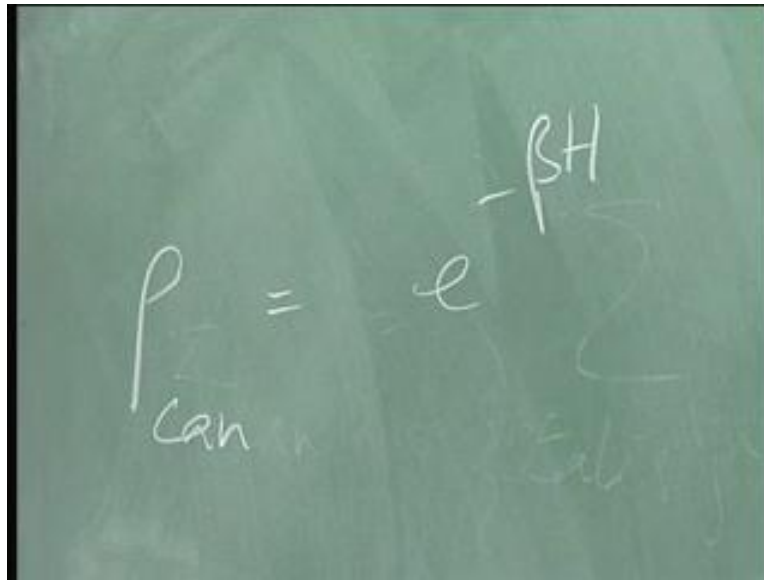


So, certainly you can write this as equal to minus delta over delta beta log z. So, you differentiate log z you get a 1 over z and then you differentiate z itself, you get a minus beta outside and you calculate the minus E i you kill then minus sign with this.

So, you have an extremely convenient formula for the average value of energy of a system in thermal equilibrium in the canonical ensemble, It is just the derivative of the partition function the log of the partition function, with respect to the inverse temperature with a minus sign. This is going to be the most basic formula of all may be use this repeatedly, what do I call this E? It is

the internal energy of the system, it is the average value. I want to be even more sophisticated here, I will not call it E, but I would like to say it is the Hamiltonian of the system.

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You have a system with a Hamiltonian, then the way you say it is, you say that the density operator rho canonical is equal to E to the minus beta times the Hamiltonian of the system. Once, you write that in terms of the Hamiltonian then all these proportions about the levels and so on are taken care of, it is only writing this density operator in some particular representation. So, when we do quantum statistics, quantum mechanics then we will use that formula there. But for the moment let us just continue with this its minus delta over delta beta log z here. So, you give me z and I tell you, what the average energy is of this system?

We can compute it for all sorts of things, and of course, if this by the way this had nothing to do with whether it was a summation or not, even for an integration exactly the same thing would go through and you would have this formula here. And this is what you call the internal energy of the system? More precise way of writing it is to say that it is the expectation value of the Hamiltonian of the system. So, when we do quantum physics we say this is what H that is what you call U in thermodynamics, is precisely this quantity here? But having found the energy the average energy, the next question is what about the scatter? How scattered is it? What is the

variance of the energy? So, the next thing we have to do is to find out what is the variance of energy?

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So, we would like to ask the variance of energy E is equal to E square minus E average square by definition it is the mean square minus the square of the mean. But as you know, this is a non negative quantity it is also equal to E minus E average the whole square by definition, it is also equal to this.

It is the mean value of the square of the deviation from the mean and what is that equal to? Well, for that you need to know for this quantity is, how do we compute that? $E$ square itself equal to I have to put $E_i$ square here, which means I have to differentiate twice with respect to this. So, what happens next, what its equal to take I delta 2z over delta beta 2 I do this then, if I take z and differentiate it I get an $E_i$ I differentiate it second time I get $E_i$ square and then i sum over this, but it must be normalized and therefore, its equal to 1 over z this.

Therefore, this variance is equal to 1 over z delta 2z over delta beta 2 minus 1 over z square delta z over delta beta square. Because, $E$ average itself was equal to 1 over z delta z over delta beta. So, this is the expression I get but, this as you can see can also be written as take out 1 over z and then you could write this as equal to can you simplify this a little more. You can certainly write it as a second derivative over delta beta 2 of log z. Because, the first time you differentiate this you are going to get 1 over z delta z by delta beta.

And we differentiate it the second time, we are going to get minus 1 over z square delta z by delta beta square and then, 1 over z delta 2z over delta beta 2 then. So, that is a very compact way of writing the variance of energy. Just the second derivative in this, can we rewrite this again because, I know that, where was that formula? I know this. So, you could write this as minus, check the minus signs please. And also write it as the derivative with respect to beta of the internal energy or average energy

But suppose you write it as a function of temperature, what would happen? This is equal to minus delta over delta T E delta T over delta beta. Now, what is delta T over delta beta? T is equal to 1 over $k_B$ beta so, let us write delta beta over delta d beta over d T equal to minus 1 over $k_B T$ square.

So, we want the reciprocal of that and therefore, this quantity is equal to $k_B T$ square and the minus sign goes away. What you call this delta U over delta T, $C_v$ it is the specific heat at constant volume. Because, everything else is kept constant so, we finally have this is equal to $k_B T$ square $C_v$ for these systems. So, you see the variance of the energy has a direct physical implication. The variance in the canonical ensemble is directly proportional to Cv.

What is the immediate conclusion? Well we know that, C v cannot be negative because, the variance has to be positive. So, that as a proof now that this specific heat at constant volume is in fact non-negative possible definition. The second point, is that in thermodynamics where you deal with averages alone, there is no way of finding out what the distribution is? Because given just the average values and therefore, you cannot calculate C v.

C v in thermodynamics is an input, it is an input parameter. But in statistical mechanics, you have a way of calculating it once, you give me the energy levels I plug it into this formula and I compute what C v is from the variance of the energy. So, that is why I mentioned that, this quantity which looks like an input parameter in thermodynamics is in fact calculable from fundamental first principles in statistical physics.

Because, you can calculate any moment you like and you have the distribution itself. And the variance or the fluctuations about the mean it is not that they do not appear in thermodynamics they do but, they appear as input parameters. That is constants which you have put in, unless the system is such that you know its equation of state, if you can know the ideal gas equation of state then of course, you know the system you put it in empirically and therefore, you can compute C v in principle otherwise, there is no way of doing it.

So, I stop here today and we take this up and now go on to the question of, what about the other quantities? What about computing pressure? For instance, so are the chemical potential and so on. In principle, we should be able to compute everything now that we have a distribution and this is what we will do and we have to soon make contact with the ideal gas equation of state. So, we know that the beta we are talking about is in fact the same as thermodynamic in temperature.