Classical Physics

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Lecture No. # 22

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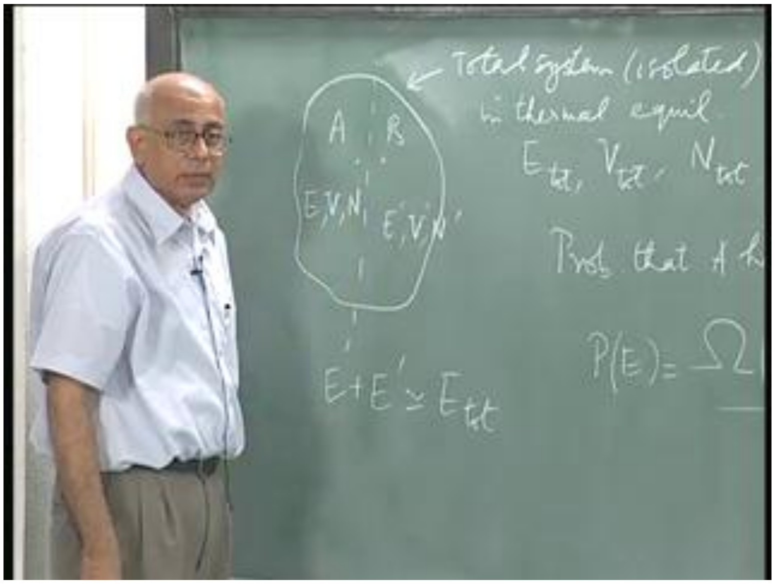

Let me resume, where we left off we were talking about the micro canonical ensemble, I go over this argument again, because it is a delicate argument. And it goes as follows, we have a large system A total the total system total system, which is isolated and in thermal equilibrium. And we are going to assume, that it has some stated total energy E total, the total volume V total, and the total number of particles N total; and it is in thermal equilibrium, the energy is constant. And then I said if we imagine partitioning this system into two pieces, and I call them A and B, these are sub systems which are in thermal equilibrium with each other, when the energy of either of these systems is not fixed, because there are fluctuations.

And if I now say that, the energy of this is E, V and N these are variable quantities some sense, and then this is E prime, V prime and N prime. What we going to do is ask, given the postulate of a equal periodic probabilities for all the microstates, accessible microstates of the total system, what can we say about the probability distribution or for instance the energy in this system, this is the question we are asking.

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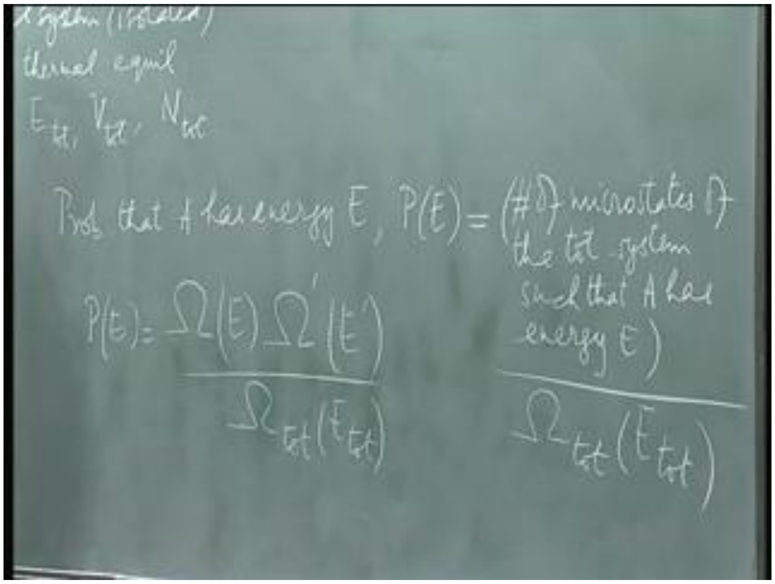

system (isolated)

thermal equil

$E_{tot}, V_{tot}, N_{tot}$

Prob that A has energy E, $P(E) = \dfrac{(\#\text{ of microstates of the tot system such that A has energy } E)}{\Omega_{tot}(E_{tot})}$

$$P(E) = \frac{\Omega(E)\,\Omega'(E')}{\Omega_{tot}(E_{tot})}$$

And I said the probability that A has energy E, and I call this P of E this was equal to in the absence of any further information, simply the fact that all the microstates of the total system are equally probable, this is obviously that fraction of the total number of microstates of the total system. For which A has energy E and therefore, B has energy E prime minus E E total minus E, so this is equal to the number of microstates of the total system such that, A has energy E divided by the total number of microstates of the total system, with energy E total or whatever it is.

And that I denoted as sigma omega total of E total, this is the normalization factor, and this is more or less obvious; but now, comes the physical assumption that these two systems, have very large numbers of degrees of freedom each of them. And that the number of degrees of freedom in interaction, on either side at any instant of time is very small compared to the of degrees of freedom, in the bulk in A and B.

Then this quantity factors into P of E, factors into omega, which stands for the number of accessible microstates of the system A corresponding to energy E multiplied by the number of microstates of the system B, which is omega prime with energy (E prime). And of course, we know that E plus E prime is approximately equal to E total, what I have left out , is the interaction energy, which cannot be apportioned uniquely into either the energy of A or B.

And my argument was that the number of degrees of freedom in this partition, is very small compared to these guys and therefore, the actual interaction energy at any instant of time is very small, and is neglected. So, this was P of E divided by of course, by the normalization factor; so this is where the physics has gone in, that the total number of microstates of the full system is simply the direct product of the number of microstates of this, times the microstates number of microstates of that, which is true if these are independent systems.

But they are actually in interaction with each, and again I repeat the assumption is that the interaction energy is negligible, compared to the energy of these two systems right, then this is true, this is the fundamental idea. Now, some idea of how big, by the way this thing is a function also of V and N, I have omitted writing that we will just for gravity, but there are E prime N prime, and whatever other macroscopic parameters you need, in order to specify this system, all of them are sitting there.

You see, if there are if there is a particle here, which is attracting the particle there, then there is a potential energy of attraction, and now I am going to assume that these forces are short range forces, and therefore a particle here, is not going to attract a particle there, essentially negligible. But, close to the partition at any instant of time, there will be some potential energy, which cannot be apportioned as energy of this or that uniquely. And that energy is definitely needed, that is what is creating interaction between these two subsystems, but it is itself negligible compared to E or E prime, so this is the assumption.

Parameters are required to completely specify the matrix.

We do not know yet we do not know yet I am tending towards thermodynamics systems where it would depend on the energy the volume and the number, because I would like to discuss fluids, I would like to make contact with thermodynamics of course, if this is precise of charged particles, the electric fields, magnetic fields you will need all of them. And we will add all of those as we go along, but right now I would like to aim towards the elementary loss of thermodynamics, which would normally write down for fluids or gases or something like that.

So, just to be definite I have said let us take E, V and N, I might need more, so given this let us have some idea of how big these numbers are, how big this is likely to be…

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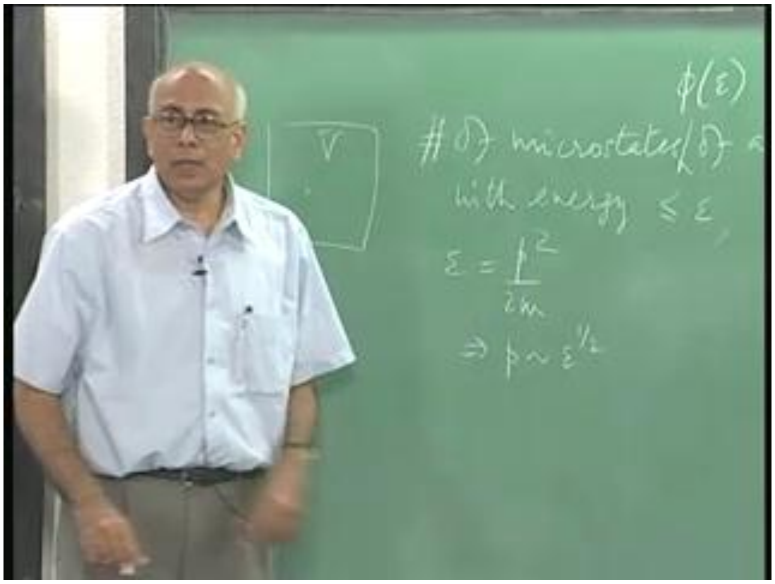

And let us do that by asking, suppose I take a particle, a single particle and put it in a volume V and there is a particle moving around in this volume V. Let us calculate, how many microstates it has what is the number of microstates this object would have, well it depends on the energy and the number of microstates is the number of cells in phase space, of this object here. And of course, phase space is actually infinite dimensional as you can see, because the momentum of this particle can run all the way from 0 to infinity in magnitude; although the physical volume runs from 0 to capital V, it is inside capital V the phase space volume is actually infinite.

So, we have to make the question a little more precise, I asked how many, number of microstates of a particle of mass, with energy less than equal to some number epsilon, so I prescribe an energy and I ask you, within in this energy epsilon and its free particle inside a single particle no forces on it, what is the total number of microstates I could have. Well, what you do is to find the volume of the phase space, corresponding to this total energy, and all you have to do is to recognize that epsilon is P squared over 2 m, its only kinetic energy.

So, I prescribe a limit and ask within this energy epsilon, how many states do I have, and it is quite clear, that the number of microstates, and let me call this omega let me call this omega omega would correspond to a particular energy, so let me call this number of microstates phi of epsilon. So, this gives me the number of microstates of the particle such that, the energy of the particle runs from 0 to epsilon.

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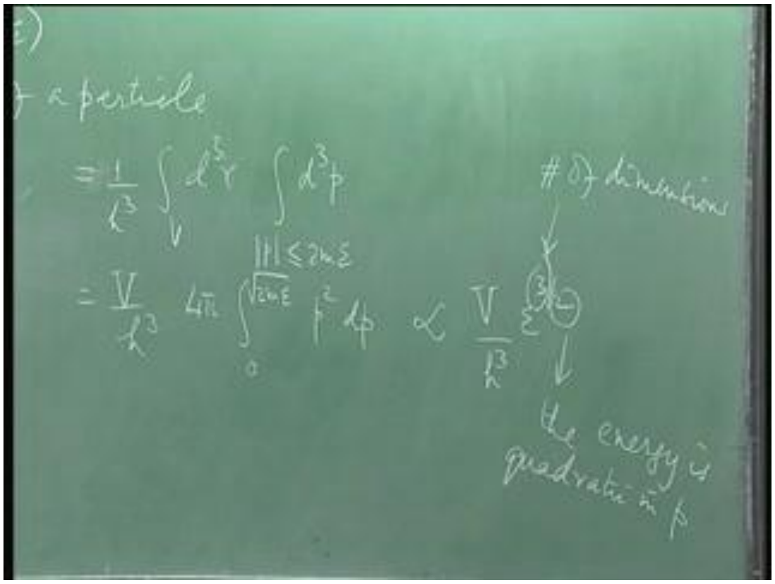

a particle

$$= \frac{1}{h^3}\int_V d^3r \int_{|p| \le 2m\varepsilon} d^3p$$

$$= \frac{V}{h^3}\, 4\pi \int_0^{\sqrt{2m\varepsilon}} p^2\, dp \propto \frac{V}{h^3}\, \varepsilon^{3/2}$$

# of dimensions

the energy is quadratic in p

This number is equal to, and integral over a volume element over v that is the d x, d y, d z to run over this volume element V, and then in momentum, so let me write this as d 3 r to show that it is a three dimensional volume , in coordinates d 3 r. I could write this is any coordinate system I like spherical polar in polar, we have Cartesian whatever, times d 3 p in momentum space d 3 p of what, that is it this is the volume, this is the volume here.

Such that, this d 3 r is restricted to the volume V and such that, modulus P is less than equal to 2 m epsilon, so you integrate all directions of momentum such that, the magnitude of this momentum is less than equal to the number 2 m epsilon, where epsilon is what you prescribe, that is it. But this is an infinite number of points really, because each point is an element is a possible state of the system, but we already said that we are going to counts this in phase space, and you cannot specify x and p to better than planks constant in precision.

And therefore, this is divided by into 1 over planks constant cube, because you are in three dimensions and each Cartesian component is an uncertainty planks constant, and its one over h cube. Now, mind you could have taken h over 2 pi or I could have taken square root of three times planks constant etcetera, so this is only giving you orders of, its not giving you the actual number which is irrelevant to you; and what is this equal to, this is equal to V over h cube.

Because, this just integrates out the V is just V times this guy here, and what will I get here, how should I do this integral, since the magnitude of P has been fixed, it is clear I am must use spherical polar coordinates; in momentum space. And then the angle is irrelevant, completely irrelevant, so this says this is equal to 4 pi times an integral from 0 to square root of 2 m epsilon p squares d p. The magnitude of momentum I call it P without any vector, and the three dimensional volume element is P square d p in three dimensions, and then the angular in integration has done that is the 4 pi, and the upper limit of integration is square root of 2 m epsilon.

So, this is equal to apart from some constants, this is proportional to V divided by h cube back sitting there, and then the relevant portion is not the square root of 2 m and so on, which we will fix later on, but p square d p, and if you integrate this you get p cubed over 3. But, the upper limit of integration is epsilon to the half here, and therefore epsilon to the power 3 by 2 and that is the key point.

That the number of accessible microstates of this particle with energy less than equal to some number epsilon, goes with epsilon like epsilon to the 3 half's, and where did this 3 come from, in this 3 half, where did the factor 3 come from; it came on integrated p square d p, but where did the p square come from, three dimensions. So, this 3 is in measure of the dimensions, the number of dimensions you are in, if you restricted it to a plane this would become p d p and that would become p square and so on. So, this 3 here is directly the number of dimensions, physical dimensions.

And where did the 2 come from, well the 2 came, because of this relation the half came, because this implied that p was proportional to epsilon to the half; the relation between energy and momentum, the energy was a quadratic function of the momentum, so the 2 came from there.

The reason I am saying this is, because if you change these assumptions then that will change automatically, so this 2 actually came from the fact, that the momentum the energy is quadratic, in P.

That is a very good question, is this true only in three dimensions or is it valid in all dimensions, it is valid in all dimensions; for a particle of non zero rest mass, its valid in all dimensions, where did that come from eventually, it came from the fact that the right relation between energy and momentum for a free particle is in fact the following.

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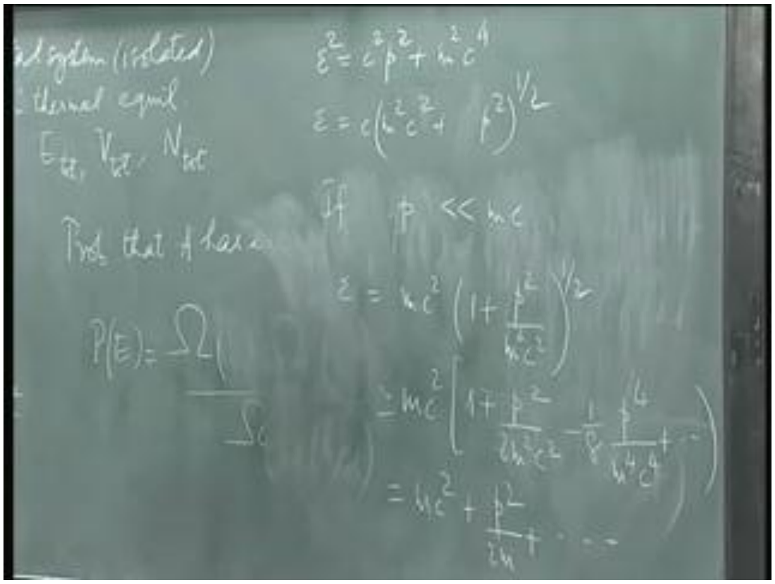

It is E squared, is c squared p squared plus m square c to the power 4, that is the right relation between energy and momentum for a free particle; for a classical free particle, in any number of dimensions. The momentum you have this, this by the way is the rest mass of the particle; I am not going to denote this by m naught and so on, because then it gives you the wrong impression that mass changes with velocity, this is not true it is not true; the mass is a constant it is the rest mass that is it. It is just that the relation between energy and the velocity, and momentum is a not a linear relation and relativity.

So, since we are going to do relativity later on, we will get the proper discipline and just write a constant m, m stands for the rest mass of the particle. Now, of course you also know immediately that this is epsilon is equal to m square c 4 plus c square p square to the power half. And if if it should so turn out, I take out the c by the way, so we can write this c and write this as m square c square plus p square, if p is much, much less than m c, because the rest mass multiplied by the speed of light is a natural scale of momentum for a free particle; and it is called the compton momentum, that provides a scale of momentum for a particle.

If the magnitude of momentum the particle is much, much less than m c, then you can do a binomial expansion here, and you could write this epsilon equal to c times I take out an m c, so there is an m c square multiplied by 1 plus p square over m square c square to the power half. And that is approximately equal to m c square times 1 plus e squared by 2 m square c square, that is the first term in the binomial expansion, plus half times half minus 1 over 2 factorial, that is equal to minus 1 8 minus 1 8 p 4 over m 4 c 4 plus dot dot dot. And you can see that this becomes equal to m c square plus miraculously p squared over 2 m plus higher orders.

So, there is a constant energy here, called the rest energy of the system plus an energy due to its motion with a momentum p, and that is p square over 2 m plus terms which involve the speed of light. And if you set the speed of light equal to infinity as you do in non relativistic physics; and you ignore this rest energy, because that is something you keep forever matter cannot be destroyed or created in non relativistic physics.

Then the book keeping for the kinetic energy is just p square over 2 m, that is where you get this, so this is the origin of this p squared over 2 m.

In in how many dimension

N dimension

In N dimensions in N dimensions again you need to have spherical polar coordinates in N dimension, and the way you do it is there are n minus 1 angles of various kind, which are around from 0 to 2 pi. One of them runs 1 to 2 pi 0 to pi, and the other ones run 0 from 0 to 2 pi or whatever.

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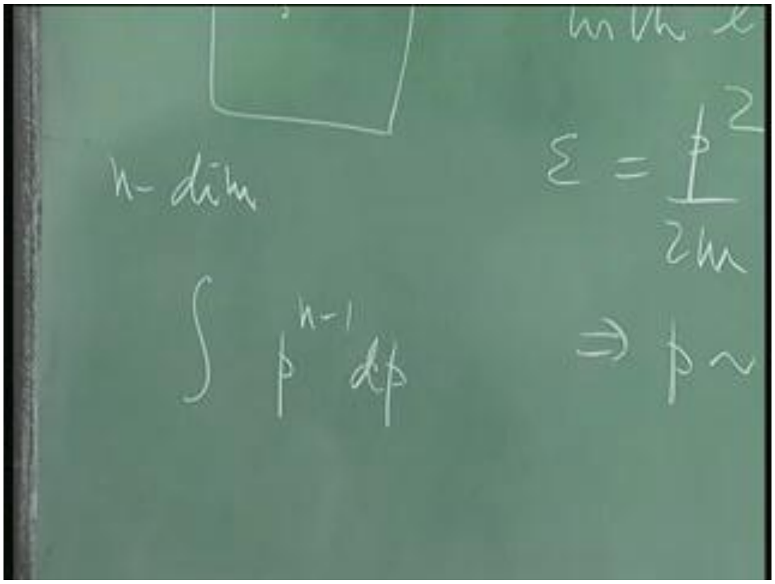

And then, apart from some angular factor, which we can write down finally you would have in n dimensions, n spatial dimensions you would have p to the n minus 1 d p, that is the radial coordinate and therefore, when you integrate this out you get the epsilon to the power n over 2 automatically.

Sir, this is the total energy, because of the potential and kinetic energy

No, no this is free particle, so I have not added to it the energy that it might have due to the due to experience in field or something I have not added that, at all its just a free part as it stands.

That is the content of Einstein theory of relativity says that mass is equivalent to energy, mass and energy are really two words for the same thing, it is not quite so simple as that, I will get back to this. When I do this relativity but, the point is this this thing here, since it is not created or destroyed in non relative physics, you keep that aside, it is just it gets out of the book keeping both in the debit and credit side of the ledges since, this is always there you will note it completely. But, if there is a possibility of converting it or extracting that energy, then of course you have to keep track of it.

This 0 of energy is arbitrary for non relativistic physics, but that is not so in relativistic physics, this was 0 has a definite meaning, so it is good to know that this 3 half comes this 3 come where this come from by dissecting it, the three comes from the number of physical dimensions. And this 2 comes from the quadratic relation between energy and momentum, if you should change this, then of course that whole thing changes for instance, if we work in two dimensions.

Then it becomes 2 over 2, if you work in two dimensions with a system, which has got a linear relation between energy and momentum, then that 2 goes away and you get an epsilon square there and so on. So, each time, we will be free with this we will keep this in mind, that this is where it comes from and now, you see you can ask what is this number of microstates for a given energy shell.

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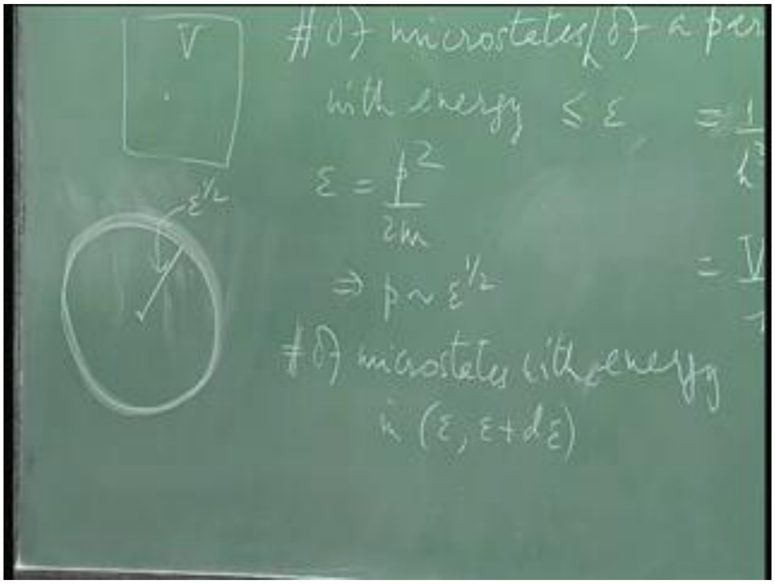
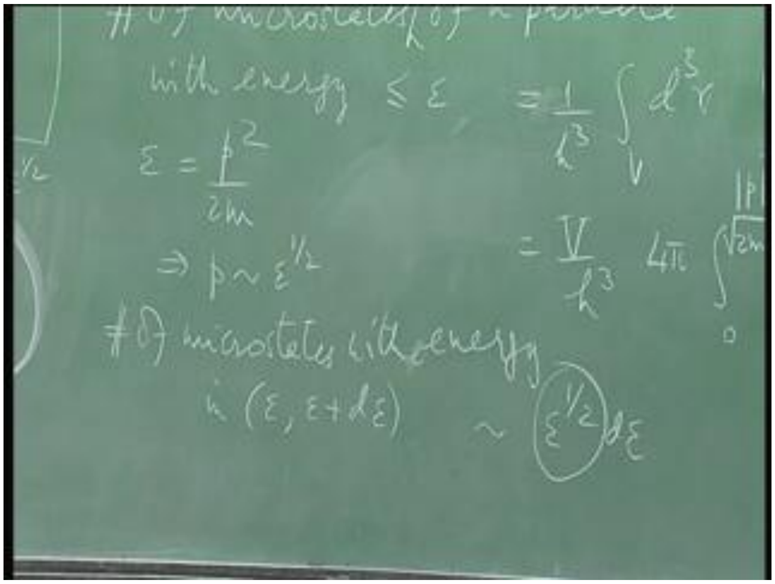


# of microstates of a per
with energy $\leq \varepsilon$ $= \frac{1}{h^3}$

$\varepsilon = \frac{p^2}{2m}$ $= \frac{V}{}$

$\Rightarrow p \sim \varepsilon^{1/2}$

# of microstates with energy
in $(\varepsilon, \varepsilon + d\varepsilon)$



Now, you see what is happening is, in energy space if this in momentum space, if this is the magnitude of the momentum and the momentum can point in any direction, the radius here was proportional to epsilon to the power half. And that is the reason the volume is proportional to epsilon to the power 3 half. Now, if you ask how many states are there, in a little shell of between energy epsilon and epsilon plus d epsilon, what would your answer be, it is a surface here and therefore, it is a derivative of that quantity there, with respect to epsilon.

So, the number of microstates with energy in epsilon, epsilon plus d epsilon, in a little shell of thickness d epsilon about this, would be equal to the volume of the shell, which would be the surface area here, multiplied by this thickness here. And what is the surface area that is proportional to the epsilon to the half, you differentiate this with respect to epsilon, and it is equal to its proportional to epsilon to the half d epsilon apart from factors 2 pi and so on.

The crucial thing is this, that gives you the number of microstates in unit energy interval, when you multiply it by the thickness d epsilon, you get the actual number of microstates in that shell.

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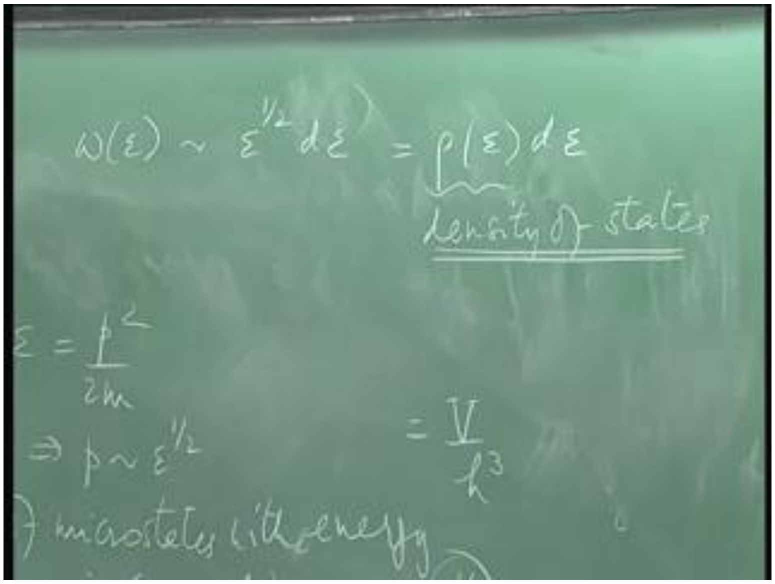

$$\omega(\varepsilon) \sim \varepsilon^{1/2} d\varepsilon = \underbrace{\rho(\varepsilon)}_{\text{density of states}} d\varepsilon$$

$$\varepsilon = \frac{p^2}{2m}$$

$$\Rightarrow p \sim \varepsilon^{1/2}$$

$$= \frac{V}{h^3}$$

microstates with energy

And this has a name in a continuous spectrum, this quantity here omega of epsilon is epsilon to the half d epsilon and this is equal to rho of epsilon d epsilon and this is called the density of states, very important concept. It is the number of microstates, apart from a constant of proportionality it is the number of microstates per unit energy interval at energy epsilon; and that is growing like a square root of energy, in three dimensions.

What would it do in two dimensions, this would become a 2 had we lived on a plane this would become a 2, and this would just become an epsilon, and what is happens to the density of states becomes a constant the density of states becomes a constant, and this is of crucial importance for all these quantum hall effects, fraction of quantum hall effects and so on. Because, there the electrons in these are actually effectively in a plane due to an intense magnetic field, that confine to a plane and then, the density of states of independent of the energy has performed physical implications.

What would happen in one dimension suppose, we lived on a line and that is important and that are actual quantum systems with effectively one dimensional, then this would have become a half, and if I differentiate it you would get 1 over square root epsilon. So, therefore, the density of states actually increases as energy becomes smaller and smaller, if you were in one dimension things get more crowded, and so on, so all these are practical implications in condensed matter physics.

But, for our present purposes, all we need to recognize is that, this idea of density of states this guy here is proportional to square root of the energy. Of course, you may say look we are going to this next, when we do quantum mechanics you put a particle inside a box, then the energy level are not continuous they are actually discrete.

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So, where is the question of square root of epsilon as number of density of states, anything like that, the answer is that in those cases, if you plot the number of states if you plot the phi of epsilon as a function of epsilon, in the true quantum case what would happen is there is no state at all, there is a ground state. And then the first excited state is a little bit away from it another first excited state, and the number just remains at that. So, you start off for 0 energy there may be no state at all, and then there is a finite ground state, so somewhere here it starts this is 1, and it continues like this till you hit the next energy state level and then it becomes 2, and keeps going in this fashion.

As the energy increases the number of states degeneracy is, increase the number of state increase and so on, and so forth. But, what is the prediction made here, classically says proportional to epsilon to the 3 half, which is a curve like this, so what is really happening is that as you get into higher and higher energies, then this ladder thing essentially starts mimicking your continuous curve.

So, the whole idea of density of states, continuum of energy, continuum of possible states arises, only if you have a sufficiently large number of quantum quantum numbers quantum numbers are large enough that you have many, many states. Otherwise, a continuum picture breaks down rarely, so if you close absolute to 0 may be only the first few excited states are involved, and then this is not a very a accurate picture, but we are now going to do classical statistical physics, which is at high temperature, sufficiently high temperatures, so I assume that things are continuous energy is continuous. I have not got in complications of discrete energy levels at the moment, but I did bring in the fact that the number of cells and phase space is countable, and I did that by dividing by h cube.

So, that was for operational reasons, so I ignore all those factors I have described here, epsilon to the 3 half.

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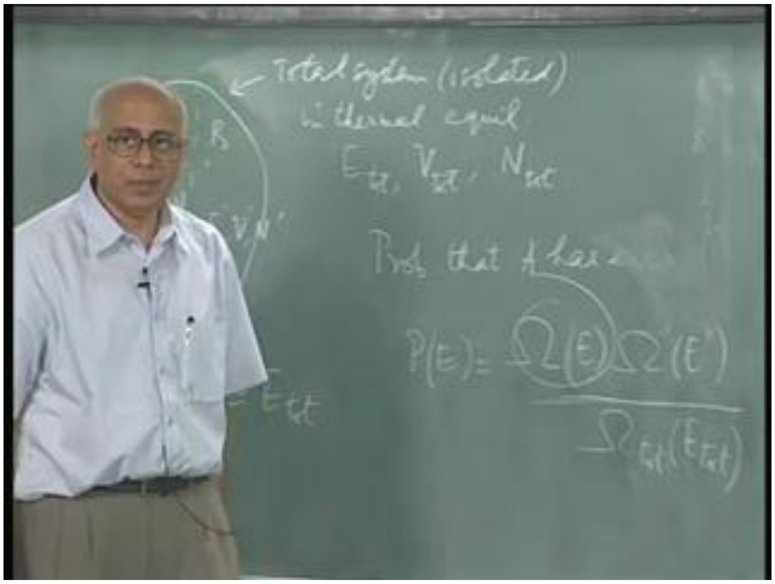

And now let us come back and ask what is this guy, what is this going to look like omega of E omega prime of E prime over total of E total, what is this going to look like, what does this number look like, if you do not know anything else. Well, there is a very large number of particles inside, n of them and if you assume these are all free particles, then you can write the total energy as the sum of energies of each of these particles. And then what would this look like notice, I am using small omega there, I am using capital omega here.

So, single particle I will use small omega small epsilon and so on, and for big thing here for the full system I will use a corresponding capital letters. So, what would this omega be like I know what this little guy is like, goes like this thing here, what would the big thing be once again it is clear.

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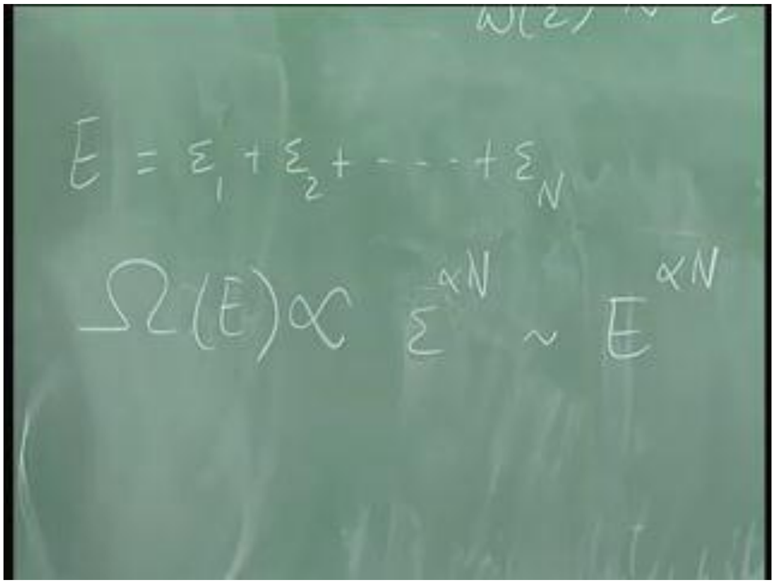

That if I write the total energy, if I write the total energy of the system as the first particle plus energy of the second particle plus its plus epsilon n, there are n particles approximately I write it in this fashion. Then what is the total number of states, that I would have, if these are all independent and the first particle can take 100 states, and second can take 100 states it is clear, that together they could take a 100 squared states; the number of possible microstates is 100 square.

So, it is quite evident that E is proportional to omega of E is proportional to E raised to a large power, this guy here raised to a large power epsilon epsilon raised to a very large power, and if I say all the particles have approximately the same energy, on the average. Then N times epsilon is equal to capital E and therefore, instead of epsilon I will write capital E over N and right now, I am interested in the E dependence, so this goes like epsilon to something which is N here.

In fact, since each of them is a half this is N over 2, but N is so large I am interested in orders of magnitude at the moment, so let me just write this as epsilon to some alpha N, alpha could be half or 3 half or 5 half depending on how I count, it does not matter but, the fact is it is proportional to N. And in fact, if I write E epsilon in terms of N this goes like N sorry, E to the power half, this is the crucial point. So, let me repeat this argument, each particle in this volume v has a large number of possible states, if its energy is some epsilon, then we know that the number of possible states it has is proportional to epsilon to the half multiplied by that resolution E epsilon.

Now, I have N of these particles, and I am assuming that these N particles most of the energy of this system consist of individual energies, and the potential energy is negligible. If this is the case, which is not always true but, if that is the case then I can write the total energy in this form, and if on the average all this energies are of the same order of magnitude epsilon, then the total number of states is epsilon raised to the number of particles.

But, epsilon itself is capital E over N the first order to the good approximation, so the whole thing is proportional to the energy raised to some constant of order unity multiplied by the number of degrees of freedom or number of states. And that is a very rapidly increasing function of N of E, so this is the lesson that we need to know, these are astronomically large numbers, this thing here is of order Avogadro’s number macroscopic systems.

And that is what you have to deal with here, so we have very large numbers this is a huge number that is a huge number, and when you have such huge numbers then it is clear that what we should do, is to work in term of log so that you bring things into a controllable fashion. And now what is going to be the most probable state, the most probable one is that state for which P of E is at a maximum and that would be my equilibrium state.

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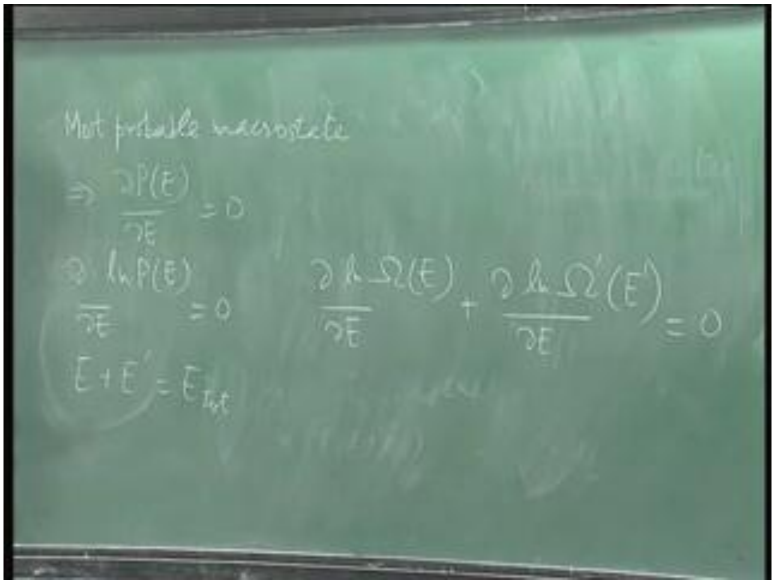

Most probable macrostate

$$\Rightarrow \frac{\partial P(E)}{\partial E} = 0$$

$$\Rightarrow \frac{\partial \ln P(E)}{\partial E} = 0 \qquad \frac{\partial \ln \Omega(E)}{\partial E} + \frac{\partial \ln \Omega'(E')}{\partial E} = 0$$

$$E + E' = E_{tot}$$

The system which has the largest number of accessible microstates, that is the macro state which is most probable therefore, to compute the most probable macro state most probable macro state implies delta P of E over delta E equals to 0 it is an certain extreme. Of course, you should say you should immediately object and say well, you should ensure it is a maximum and not a minimum, we do that next, we will do that subsequently, but first it is an extreme means delta P of E over delta E is 0.

And that is what I would say is going to happen in equilibrium, but then what does this mean is this is huge numbers here and therefore, since the log of a number is a monotonically increasing function of this number, I could as well take the logs and then take the delta. So, its same as saying delta log P of E over delta E is equal to 0, now that make things much more manageable, because it brings this huge exponent N down.

And what does that give you that tells you, when that delta log omega of E over delta E plus delta log omega prime of E prime over delta E equal to 0, because this is constant, the denominator is constant, if I take a log here, this goes away, so log constant does not get differentiated. So, you see the normalization constant has gone off and I am left with that condition there, but I also know that E total E plus E prime equal to E total therefore, E prime is

E total minus E. And derivative with respect to E is minus with derivative with respect to E prime, because of constants because, they two add up to a constants.

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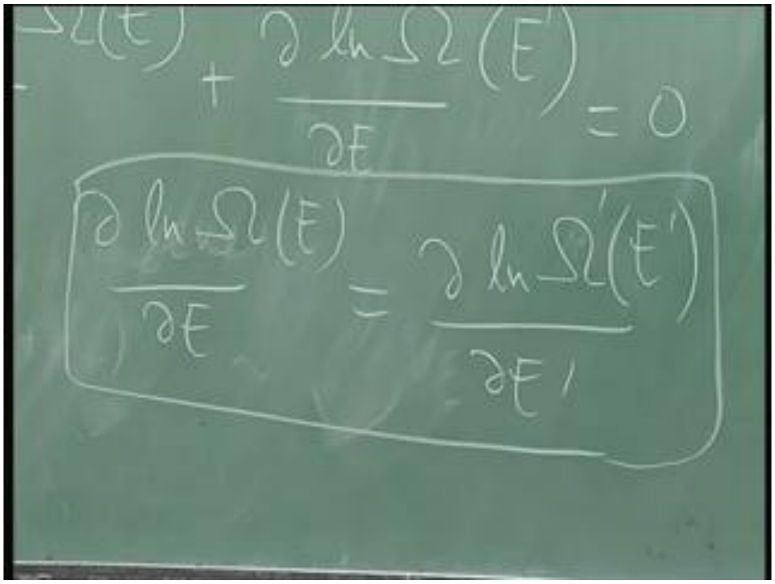

$$\Omega(E) + \frac{\partial \ln \Omega(E')}{\partial E} = 0$$

$$\boxed{\frac{\partial \ln \Omega(E)}{\partial E} = \frac{\partial \ln \Omega'(E')}{\partial E'}}$$

So, therefore I can finally write this condition as delta log omega of E over delta E equal to delta log omega prime of E prime over delta E prime, so that is the condition for the most probable macro state, that is what is going to obtain in the equilibrium. Now, note is the left hand side refers only to properties of A, the right hand side refers to the properties of A prime; the right hand side may be a physically different system from the left hand side, you could have jar of oil in equilibrium with an atmosphere, and that is fluid and this is gas that does not matter.

The corresponding quantities are equal on both sides, the rate of change of the log of the number of accessible micro states of system A, is equal to exactly the same function on the right hand side, for system B. So, it is a some system property of A is equal to this N system property for B, this system property is called the inverse temperature, this is the definition of the temperature.

So, we define a function

This is the definition of the temperature, and now of course I have to show you that this definition is the same as the thermodynamic definition, what you call the absolute scale of temperature, which was defined by saying the absolute scale of temperature is defined in thermodynamics by saying there exist a thing called classical ideal gas, whose pressure times volume is proportional to the absolute temperature. So, I must show that this is the same as the ideal gas temperature, then thermodynamic definition and this statistical mechanical definitions are identical.

We are not done that yet.

This is the definition for equilibrium, it defines the temperature here, so I am going to define temperature and then say in equilibrium the temperature of A is equal to the temperature of B that is the condition, so we define it. But what is the physical dimension here? The physical dimension is not that of temperature, omega is a number of micro states, so its dimensionless log is of course dimensionless; but this is a 1 over energy.

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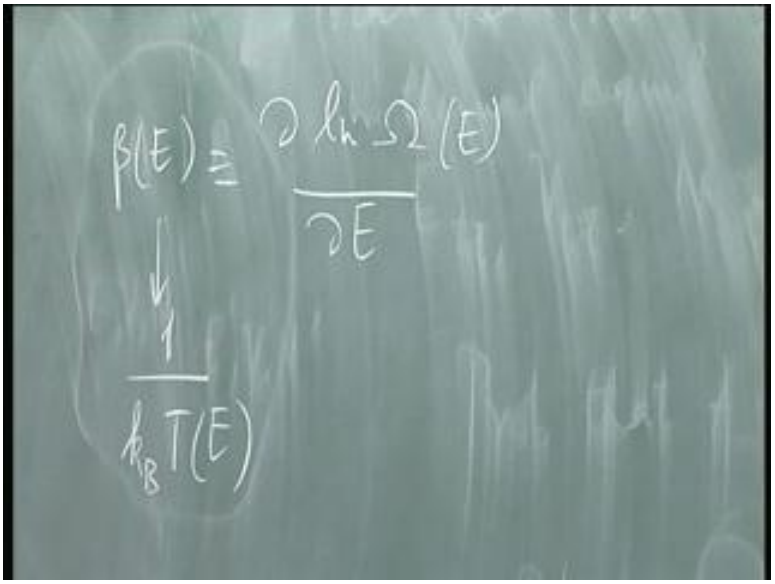

$$\beta(E) \equiv \frac{\partial \ln \Omega(E)}{\partial E}$$

$$\downarrow$$

$$\frac{1}{k_B T(E)}$$

So, I define a function beta of E equal to definition delta log omega of E over delta E, and that is the inverse temperature, so this beta of E is in fact 1 over k Boltzmann times T of E. Since, we made the historical mistake of defining, temperature rather than inverse temperature is what we should have defined, I call it 1 over k, and k Boltzmann is a conversion factor which converts from energy to temperature units. So, you see unlike thermodynamics, where the energy is a function of temperature in general the average energy, in statistical mechanics the temperature is a function of the energy, and that is the right way to do it.

So, this quantity beta the inverse temperature, I am going to use very frequently I will use this symbol beta here, but it is really 1 over k T over here.

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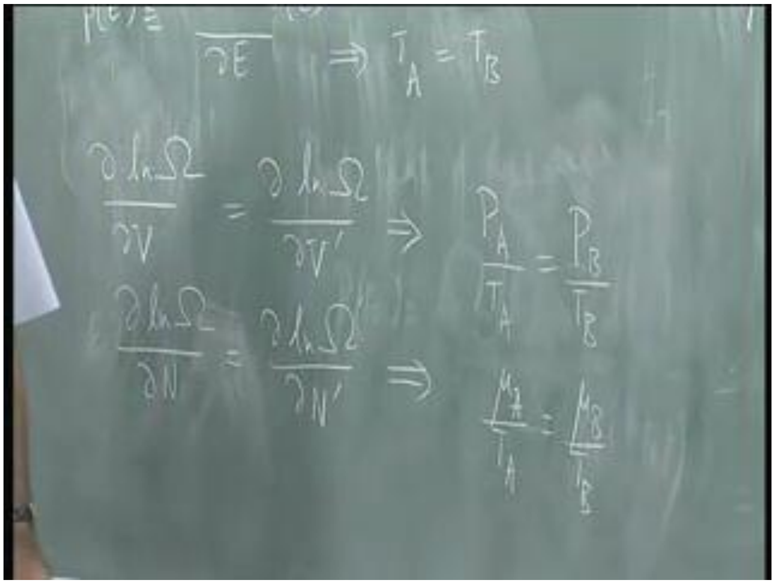

So what we are saying is that by definition in equilibrium the temperature of A is equal to the temperature of B. Now, this is the first condition, that when you have a large system, isolated system in thermal equilibrium; the temperatures of any two parts of it are the same.

Assuming of course that each part is large enough, for you to talk about a temperature, if it is just one particle, then of course I cannot talk about temperature for it, so I have already assumed that both A and A B are sufficiently large with a large number of degrees of freedom; so that I can define the temperature, which is a statistical concept here. So, I assume that omega of E is a continuous function of E and so on and so forth. By the way this definition here permits you to go further, then the normal definition of temperature would.

Because, you see there is nothing to stop you, from having a situation in which this omega of E, which is after all the number of states that you have suppose it goes up and comes down, then the temperature could in fact becomes negative. Because, there is nothing that says omega of E must be a monotonically increasing function of E, for free particles yes, it was increasing like E to some power; but there could be some other systems, which have some energy levels and then there is an upper bound on the energy levels.

So, you have lots of energy levels in between and then it stops, so the number of states would in fact go up, and then come down again, and then the slope would become negative. So, the possibilities of negative temperature are already built in into this, and indeed there are systems, which display would display negative temperature in this sense. So, this is the statistical mechanical definition of temperature, it does not make much sense at the moment, till we show that this is exactly the same as the temperature as defined in thermodynamics.

Now, once we do that, then we know that you are on right track then we go further, but is this all the information we get, no we get more information from here, because exactly the same argument would go for the other variables on which, this omega depended, and the other variables here as I have written it here, are the number and the volume.

So, in fact, we can show now that delta log omega over delta V on both sides must be equal, and in fact delta log omega over delta N is equal to delta log omega over delta N prime. And in thermodynamic terms, which we will see this here, this guy implies that this would imply that the pressure on this side divided by temperature, must be the pressure on this side divided by the temperature, I will show that this here really is the pressure over temperature. And what would this imply what would that imply, so in thermal equilibrium for a very large system in an isolation, the temperatures on the two sides of two parts of it are the same, the pressures are the same.

What would this imply, this would imply that the chemical potential of this side would be the chemical potential on that side.

We have did defined entropy, we have not yet defined entropy but indeed your right, am going to define this quantity multiplied by Boltzmann constant and so as to get rid of this 1 over k t, the k Boltzmann I am going to define that as the entropy. Yes, so jumping ahead a little bit.

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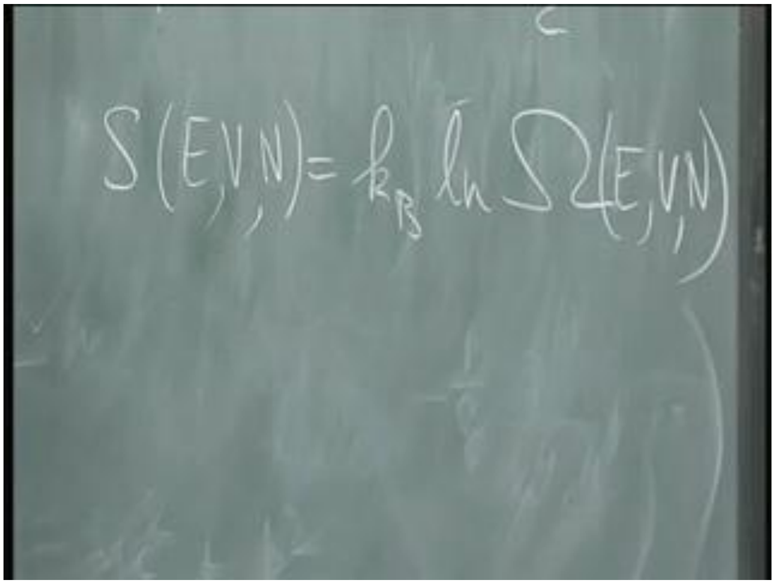

$$S(E,V,N) = k_B \ln \Omega(E,V,N)$$

I am going to define the entropy of the system S of E as equal to k Boltzmann log omega, so define the entropy in this fashion. Why do I do that, because everywhere in physical in in physical applications, its log omega that appears, not omega itself therefore, its useful to have a name for log omega and it is called the entropy.

It is a definition once again, and of course immediately you realize that this since, if this is the function of E, V and N, so is this a function of E, V and N equal to, so in general that is certainly true for such systems. But that is a good point, since he raised it, this is good time to ask what is the connection with thermodynamics, so let us ask what is the connection with thermodynamics, I am going to assume that all of you have studied thermodynamics, you already know this subject yes, fair assumption, so we do thermodynamics in 15 minutes and then we leave.

All you need to know

So what I am saying is that in thermal equilibrium, system is in steady state and so on, and so forth, I made the assumption that all microstates where equally probable, period. The consequence of that, consequence of that was that certain partial derivatives of the left hand side must be equal to the corresponding partial derivatives on the right hand side, I could partition it further, so every piece of the system if I define this function log omega, its derivative with respect to these thermodynamic variables must be the same in all subsystems.

And those derivatives are now associating with physical quantities, thermodynamic variables, like temperature, pressure, and chemical potential, and so on. Of course, these are definitions as it stands, but the proof of the coding is that I am going to relate them to thermodynamics; so one way of doing this would be axiomatically start from here, and say this is my definition of P A, this is my definition of mu A, and to show you from here that you in fact get the ideal gas equation of state and so on.

But, we would not do that instead of that, I will start with thermodynamics and show you get exactly the same relations, so it matches on both sides, I will in fact calculate this entropy which you cannot do in thermodynamics, compute this term, because we have the machinery to calculate it, because we know how to go phase space and count cells, and therefore we know how to calculate it, which you do not do in thermodynamics.

So, let us go and do thermodynamics in a nutshell 15 minutes, I am not sure what is your impression of thermodynamics is, but it is a very basic science, it is a science of energy, which is the most fundamental quantity of all, so it is useful to know few things about it. And going beyond the level of imaging that it is just a practice give you practice in writing partial derivatives or something, little more than that.

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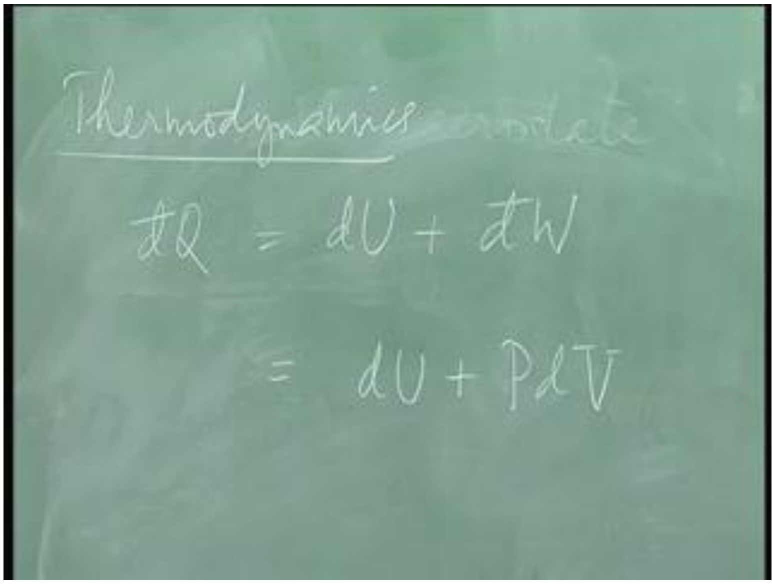

Thermodynamics

$$\text{đ}Q = dU + \text{đ}W$$

$$= dU + PdV$$

So, let us write down thermodynamics in a nutshell, we will do thermodynamics for a simple fluid which is a usual thing; we do it for in turn we will try to make it general for the complicated systems. I am going to assume the loss of thermodynamics, of course the loss of thermodynamics are derivable from here explicitly, but we are going to assume it and just make sure that matching is right. Now, what is first law of thermodynamics which essentially conservation of energy, and what is it essentially say it says, that if you supply some heat to a system, you call it d q is the amount of heat infinitesimal increment in heat that you supply to a system.

This heat goes into doing two things, first the system does some work possibly and the second thing it does is to change its internal energy; this is a statement. So, d q is d u plus d w this way you write it, now of course this term tells you a lot of experience, the whole of 19th century tells you, that unfortunately d q is not a perfect differential. In other words, you cannot specify the heat of a system q without saying how it reach that state, so specifying the value of q, at some values of thermodynamics parameters is not going to tell you anything.

Similarly, for w but, not true for u, which is a state function which means, if you tell me the dependent independent variables perhaps S, V and N or whatever it is, then I can tell you a unique q, but that is not true for d q and d w. And you recognize that by putting little slash as here to show, these are imperfect differentials, is about perfect differentials; but the miracle is the difference between d q and d w is a perfect differential. So, that is why more sensibly, it is better to write this d u here, as d d u equal to d q minus d w which is this difference, but this is how it was got ridden initially, so we will leave it.

Now, what is this d w, this is equal to d u plus, it is equal to p d v for a simple single component fluid, let us put that down plus p d v since, we are familiar with that, so let us put down plus p d v. But, actually this system could do other kinds of work, it could be charged then it would do work against an electric field for example, you apply an electric field it would do work or it magnetic, you apply magnetic field its magnetization could change, so there are lots and lots of kind of work that you have.

And in general this thing here, has a better way of writing it you should write it as some force times the displacement, this is essentially what p d v is some force times the displacement of some; but then, the way it is being written it is clear that if you, if d v is positive p decrease as you know, if you compress something you increase the pressure the volume decreases.

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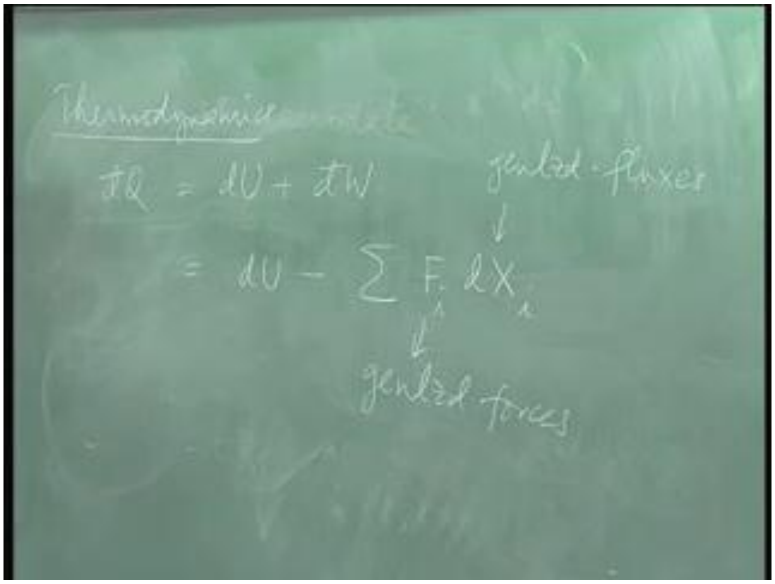

And therefore, this p d v is got a wrong sign in some sense, the right way to do this is to write this as d u minus a summation over all possible forces with their conjugate variables, thermodynamic variables.

So, let me write this is F i d x I, and these quantities are generalized forces, and these fellows are generalized fluxes, of the forces p is a very important example, and the corresponding d x is minus d v. So, there are other terms that are possible, you could for example have a force that is not physical at all called the chemical potential, and then what changes is the number of particles.

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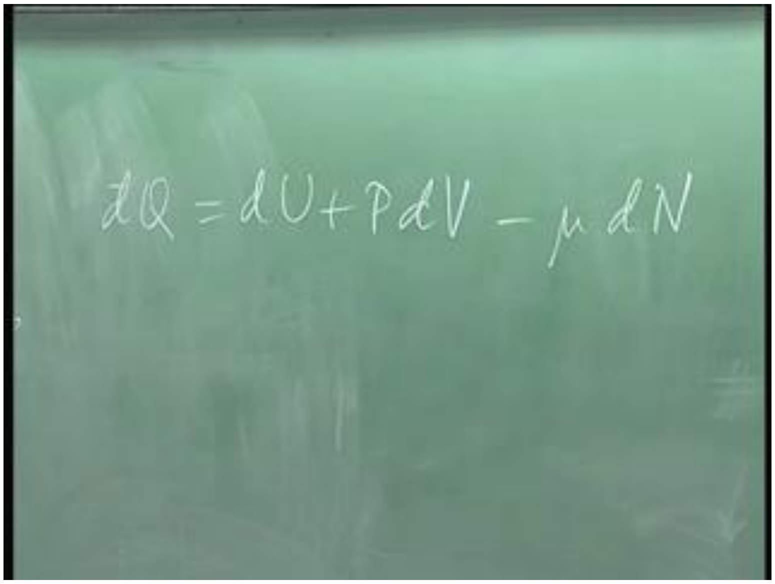

$$dQ = dU + PdV - \mu dN$$

So, you have a term like where um simple single components simple fluid would be d q equal to d u plus p d v minus mu d n, that is the simplest generalization of the most elementary way of writing thermodynamics, for a single component fluid. There the only work to do is the p d v kind of volumetric strain, for incident you what is p, what is p, what does it stand for?

The pressure, but its macroscopic body, so you really have stresses and strains, and stress is a tensor of rank 2, because you can have stresses, and you can have shear stresses and what is this p then, it is a volumetric strain, it is a volumetric um hydrostatic stress in other words, it is a trace of the stress tensor, trace of the stress tensor. So, you really have a stress tensor sigma i j sigma 1 1 would correspond to pulling in the 1 direction, 2 2 would be in 2 direction and 3 3 would be in the 3 direction, and then sigma 1 2 would be a shear perpendicular to 3 direction and 2 3 and 3 1.

So, you have a lot of these it is a symmetric tensor of rank 2, but if you took sigma 1 1 plus 2 2 plus 3 3, that is the hydrostatic stress, it is the trace of the stress tensor. Now, the trace is independent of rotations, right therefore the pressure is a scalar, since its independent of rotations you have exactly the same value, no matter how you orient your coordinate system; that is why if you put inside a fluid you put a little volume area element, does not matter in which direction you pull it, but the force per unit area is same.

What you call that, what you call this rule, where the pressure inside is same in all directions Pacsal’s law Pascal’s law Pascal’s law is the statement that stress, that the pressure is a scalar, because it is the trace of the tensor, stress tensor. And follows directly from there, the medium is isotropic as in the liquid and then immediately it follows that the trace is independent of how you orient it.

Otherwise, you would you have to different pressures in different directions, should have in a non isotropic medium, so that is the pressure we have here, and then there is chemical potential and so on, and so forth. But remember this is the generalized form of writing, for the moment let us write this a single component thing.

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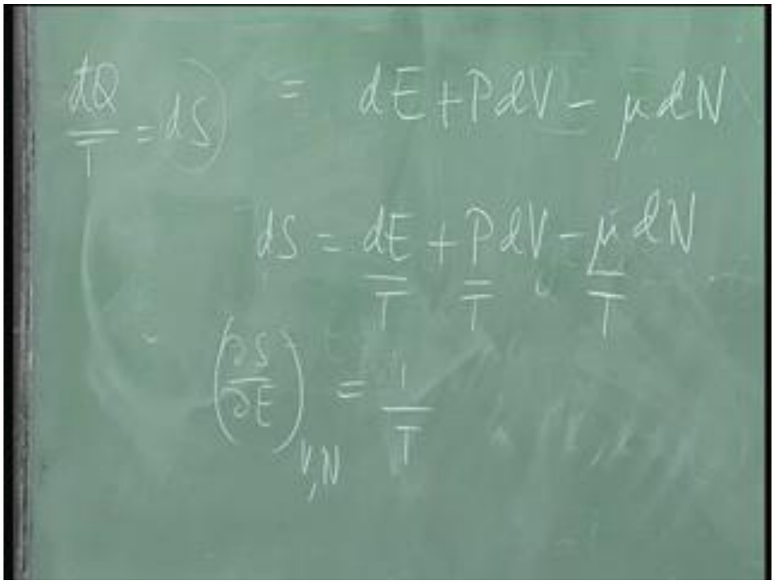

So, du plus p d v minus mu d N, by the way let me call this the energy E, and not u because, u i should like to reserve which is the same thing in thermodynamics, for the average energy. So, let me just make clear, that this is energy E, so write it as E E, when you do thermodynamics, and when you have average energies then it is exactly equal to what you call the internal energy, but to remind myself that is it is the energy I write E.

And on this side, what this equal to, what is d q the second law of thermodynamics says that d q, d q we know is an imperfect differential, but in the case in which I have reversible processes, then I can use an integrating factor on d q, to convert it in to a perfect differential. And in thermodynamics that integrating factor is called 1 over the temperature, because we know that d q divided by t becomes d s, the change in the thermodynamics entropy.

That is the definition of the entropy, the increment of entropy in thermodynamics, so if I put that in, it says T d S equal to de plus P d V minus mu d N, which I will write in the following form, d E over T P over T minus mu over T. Now

Yeah it is reversible, so I am going to assume we are talking about reversible processes, otherwise I do not know how to define entropy in thermodynamics.

We are going to assume that everything is in quasi static equilibrium, everything is reversible and so on otherwise, you cannot even point in the p v plane, and you cannot even write these things. So, everything is in thermal equilibrium quasi static processes and so on, very slow compared to the equilibration times, and then this is certainly true. And by the way, what does this tell you, this tells you that delta S over delta E keeping V and N constant is equal to 1 over T.

And if S is k log omega, and I bring the k down, then it says delta log omega over delta E keeping V and N constant is 1 over k T and that is exactly we have here. So, this is built, this is tailor to make sure that, you get that right or rather that follows from this, follows immediately from this, this not a regress proof, but you would see that later. And incidentally that is the reason; I got P over T and mu over T, because they are just partial derivatives of this entropy with respect to V and N; this is called the entropy representation of the micro canonical ensemble. Because it writes the infinitesimal it writes the differential of S, in terms of the differentials of E V and N.

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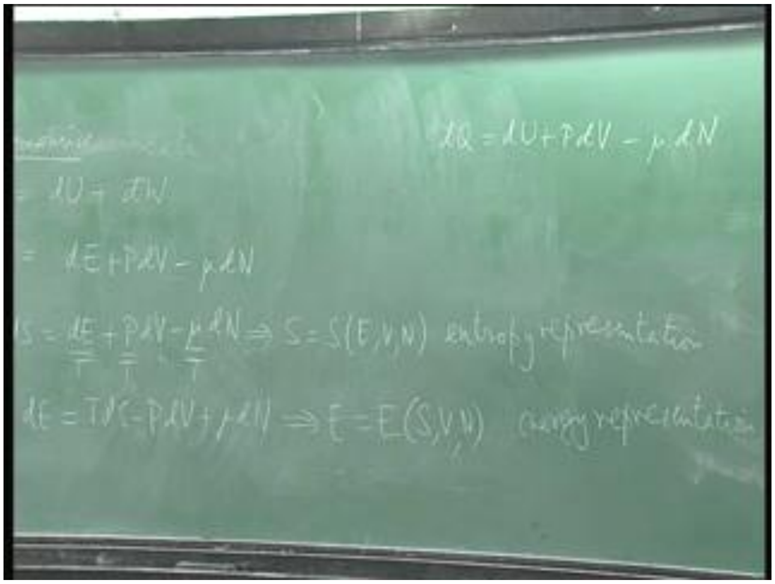

$dQ = dU + PdV - \mu dN$

$= dU + đW$

$= dE + PdV - \mu dN$

$S = \frac{dE}{T} + \frac{P}{T}dV - \frac{\mu}{T}dN \Rightarrow S = S(E,V,N)$ entropy representation

$dE = TdS - PdV + \mu dN \Rightarrow E = E(S,V,N)$ energy representati

So, this says S equal to S of E V and N, and this is entropy representation. You could rewrite this in another way you could write this as de equal to t d s minus p d v plus mu d n you could write that too just as good and this is called the energy representation of the micro canonical ensemble, which you choose is a matter of taste then of course, you have all these partial derivative relations it says immediately delta S over delta E at V N constant is 1 over T.

Similarly, definition of P and definition of mu and ditto here, you can write delta E over delta S is a definition of temperature, and not its reciprocal and so on, so all the usual relations could be written down. So, much for the first law there, but notice one thing, notice that when you write this, when you write the increment in the energy in terms of quantities here on the right hand side thermodynamic quantities it occur, they occur in pairs conjugate pairs almost like your p's and q's in Hamiltonian dynamics.

They occur in conjugate pairs, there is a T and S, P and V, mu and an N the product of the 2 has dimensions of energy always; so the product of a generalized force times the generalized flux has dimensions of energy.

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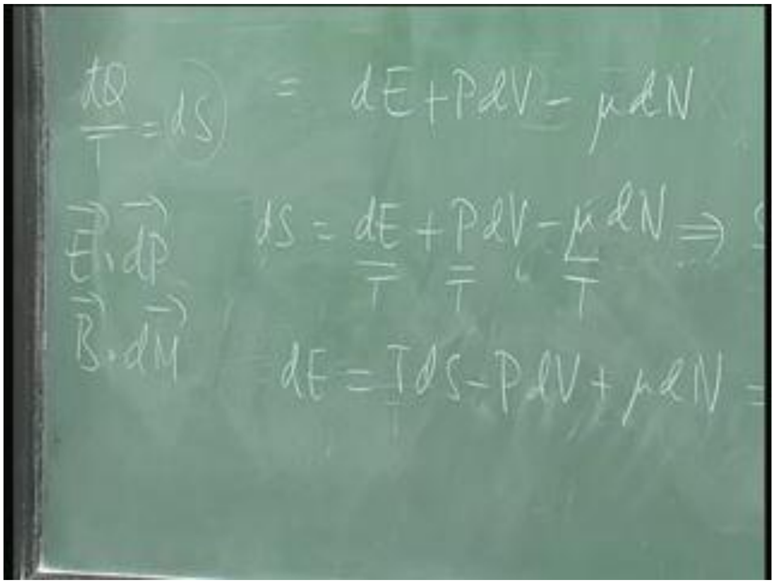

$$\frac{dQ}{T} = \boxed{dS} = dE + PdV - \mu dN$$

$$\vec{E}\cdot d\vec{P}$$

$$\vec{B}\cdot d\vec{M}$$

$$dS = \frac{dE}{T} + \frac{P}{T}dV - \frac{\mu}{T}dN \Rightarrow$$

$$dE = TdS - PdV + \mu dN$$

But the individual force flux may have all kinds of physical dimensions, similarly you could add terms to this if you have an electric field you would have E dot d p, the energy the electric field times the polarization that will have physical dimension of energy. Similarly, B dot d m, where B is magnetic field, m is the magnetization would have physical dimensions of energy and so on, but in the simplest case this is the rule that is written down here, these are conjugate variable in that sense.

But there is another very crucial thing, that you notice and that is some of these variables change with system size, some variables do not, and always they occur in pairs, if I take the container containing volume V number N particles, and double the volume, double the number of particles, keeping the density constant; then the density does not change, the temperature does not change, these are intensive variables.

Things which become proportional to the volume or the number of particles are extensive variables, and this breaks up neatly into intensive times extensive, pressure is an intensive variable, chemical potential is an intensive variable, the entropy, the volume, the number, the energy are all extensive variables. So, we immediately have a break up into intensive and extensive variables, the other thing is there are certain things, you apply as generalized forces, and certain things you measure as fluxes as responses.

So, immediately you see that there is a response, stimulus response to the relationship here, T, P, mu are called field variables, and S, V, N are called state variables, they are extensive variables. So, it is like you apply the field variables and do measure the state variables, of course this distinction is not always rigid, if you take a container of gas I could put a piston on it, I could do two things, I could increase load, and change the pressure and thereby change the volume, I could also remove the piston change, the volume and thereby change the pressure.

So, which one you call the force, and which you call the flux is actually a little, it is up to you, but in general you would call the field variables, the intensive variables the field variables and the extensive variables the state variables, and they current pairs here. So, this is it, for the for the thermodynamics all the Maxwell relations can all be written, but there is one crucial input that is missing, this is not telling you enough; and that is we have not used the fact, that the energy is an extensive variable.

If I simply double the number of particles double the volume etcetera, and do not do anything else, I would in general change the energy, and it is an extensive variable I am going to put that in next time, as an input. Am going to assume, that the energy is an homogeneous function of degree 1 in those variables, S, V and N. And then use Euler's theorem from calculus to derive the rest of thermodynamics, so that is it and once you put that along with this, the job is essentially done. And then we make contact with what we come back here, and make contact with this, the rest is a matter of detail as we go along, but this is in the target; so we meet next time and then I do this.