Classical Physics

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Lecture 25

Our aim now is to try to derive some of the standard results of thermodynamics such as, the classical ideal gas and its equation of state from statistical mechanics. We already have some mechanism laid in place for the partition function, and then now the task is to show its connection with thermodynamics. Now there are several ways of doing this and I have been debating as to which is the best or simplest model system in which one can do this; still I do not think there is an unambiguous answer to this. The classical ideal gas is in fact, it is a very simple system but it requires further physical input we have to make several approximations which I would have to justify which we will do. And this might give the impression that this theory is extremely approximate which is not true. On the other hand, there are other problems where the energy levels are discrete in a quantum mechanical situation, and then the calculation becomes easier, calculation looks more transparent. So, I am still at in two minds as to which one to start with, but probably we should stick to traditional path and go to the classical ideal gas and look at that.

So, let us do that; this is our aim. But in between I will also just of course in between some discussion on probability distributions, because this is something we have been promising for a while, so might be we will take a little digression do that and then come back to this main problem. So first, we need to make a connection with thermodynamics between what we have been doing so far so that is crucial and let us try to do it.

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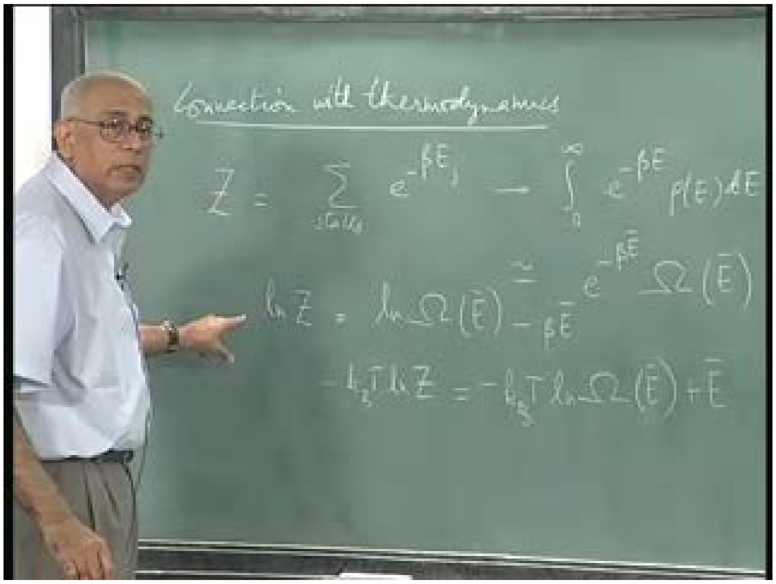

And again I do this in sort of heuristic way and our aim is to actually compute quantities and not so much to go into the formulism itself, therefore I am going to give short shift to formal derivation and simply do things by more or less heuristic arguments, wherever they will not affect the results and whenever we need to be very careful and certainly be. So, recall that the canonical partition function Z was equal to a sum over states e to the minus beta times the energy of each state for any given system in thermal equilibrium with the heat bath at some temperature T which is beta inverse. We also wrote this as a kind of um laplace transform in the continuous case it was equal to d E e to the minus beta E. I will write this as this e to the minus beta E rho of E d E from some lower bound to an upper bound whatever it was zero to infinity in general. Now of course, the kind of gas the kind of system we are looking at, I already pointed out would be one where this density of states is a very rapidly increasing function of the energy goes like for a collection of particles will typically go like the energy raised to the number of particles which is an extremely rapidly increasing function.

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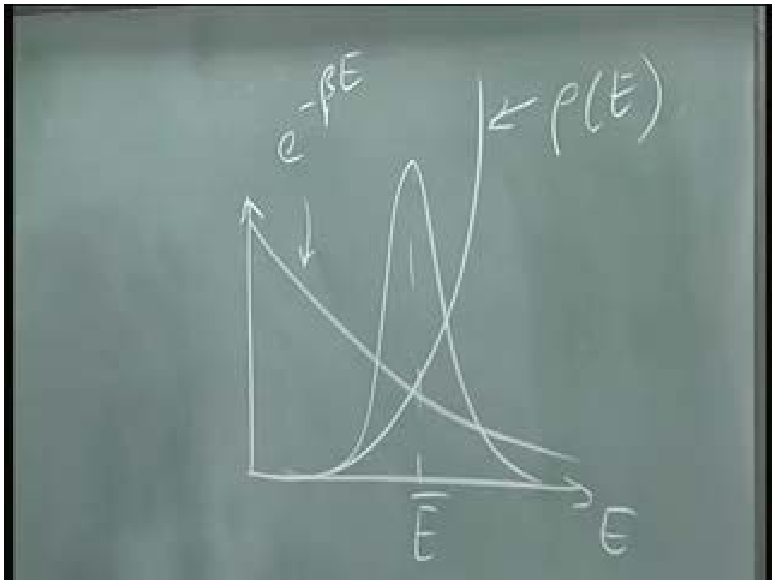

So, although that is the exact partition function, if you plot this quantity as a function of E I will look at what this integral does when you see except in quantum mechanical situations, where you have to be extremely careful and compute this number this thing here this rho of E is a very rapidly increasing function of E and therefore it goes up in this fashion which is typically rho of E. On the other hand e to the minus beta E is a decreasing function and falls off exponentially, so the same argument as before decrease exponentially and when you multiply the two together the dominant contribution is going to be from some point in between where the curves intersect and this quantity integrand e to the minus beta E rho of E is in fact going to look like this the product is going to look like this peaked about some point E bar, therefore to a very good approximation this is also equal to e to the minus beta E bar multiplied by this number here this gives you the number of states in an interval dE, some finite resolution about this point here and therefore this is nothing but omega of E bar. So, that is what the total number of states accessible microstates.

Now E bar is some kind of average energy but look at what this formula implies, if I take log on both sides it says log Z and then is equal to log omega of E bar minus beta E bar and I multiply through by kT which is beta and take a minus sign here and you end up with minus k boltzmann T log Z is equal to k boltzmann T log omega at e bar minus e bar itself.

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But now in statistical mechanics the entropy is defined by boltzmann formula. So, let us write that down boltzmann formula says, S is defined as k boltzmann log omega. So, what does this tell you an E bar is the average energy which you are used to writing as U, so it is really telling you that U, this quantity here did we miss a minus sign it becomes a plus here plus minus, because I took a minus here minus k B.

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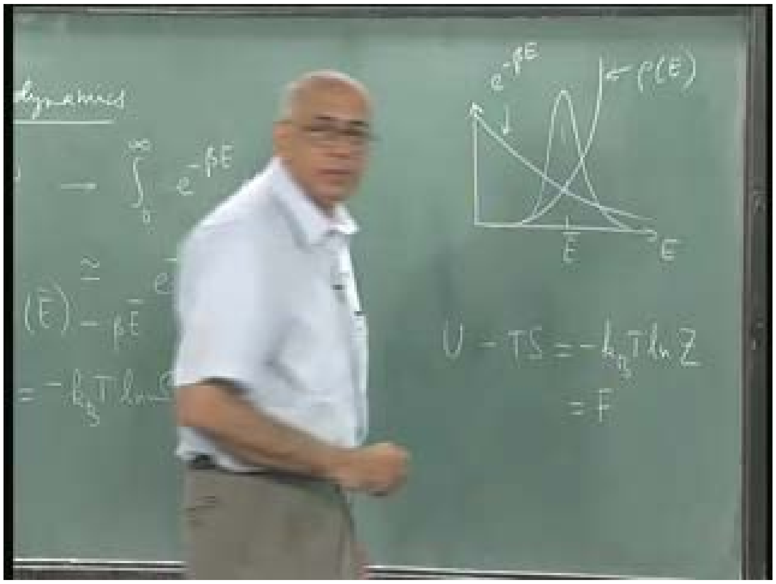

It says U minus TS is equal to this quantity but of course this is a quantity for which we have already got a name in thermodynamics. This is equal to the helmholtz free energy F, so this what establishes the connection with thermodynamics namely you should say that this Z which is a sum of exponentials can also be written as equal to e to the minus beta times, you see its e to the minus beta times the whole lot of energies and these energies have nothing to do with the temperature their system properties, but if I say the sum of exponentials which is not a negative quantity can be written as e to minus as an exponential itself e to the beta times some effective energy this quantity is some effective energy it is got dimensions of energy because one over kT has dimensions energy. So that effective energy if I call it F that is what the helmholtz free energy is… So, the whole idea of writing helmholtz free energy is to say can I write this positive quantity as e to the minus beta times an effective energy that is the free energy that effective energy ofcourse will depend on the temperature, ofcourse because you cannot say its e to the minus beta e one plus e to the minus beta e two and so on.

e one e two are independent of temperature, but if I insist on writing it as e to the minus beta times the single energy then ofcourse this will be a function of temperature very complicated function of temperature and other variables like volume number and so on. So, this is how the helmholtz free energy is defined in statistical mechanics, for a free particle that does not what happens at all it increases like e to the power three half or something like that, rho of e the density itself increases like e to the power half, because the its infinite you have lots and lots of states but as we know the probability with which this thing is going to occur is going to keep decreasing.

So, you have lot of possibilities available, but the probability of taking on any of them is going to be sharply cut off by e to the minus beta e, that is the whole point because what is the physical reason for that because in a crude way what is happening is the fluctuations in this system are being driven by the environment which has maintained a certain temperature T. The moment you have a temperature T it is a kind of bath and this temperature T implies that on the average each bath degree of freedom has an energy of the form kT. So, one of them goes and punches your sub system and transverse energy kT and then there is interaction mutual back and forth etcetera.

Now, in order to pump this system up to an extraordinarily high energy you must have a coherent punch from all the bath degrees of freedom, same time that is improbable very improbable. So, it goes one at a time little jumps here and there and therefore the average energy is maintained at some finite value and its very improbable that very high energy is it that is the reason for this minus here, this is really where this came it says it is very improbable that you will have a coherent punch from a random thermal bath and that is why you end up with this very damp very large damping factor at high energies of course this increases no problem, this is an exponential cut off and that is more powerful than a power law increase here, no matter how high the power law and therefore the partition function will be finite so in a way this real summarizes everything although it is not a proof by any means.

I actually work backwards, I use the same symbols but the whole idea the proof of pudding is in the eating, if with this identification of S and this identification of F I run through this machinery and produce for you the correct classical ideal gas equation, then you know the things are consistent completely. So, I have again avoided formal derivations in order to motivate things, tell you in a physical form what the meaning of this kind of statement is this one and what is the idea behind the helmholtz free energy its simply writing this partition function as an effective e to the minus beta times an effective energy. So, F is minus kT log Z, we are going to use that because our claim now is that if you go ahead with this from the helmholtz free energy we can derive all sorts of thermodynamic relations we should be able to derive everything we need what is our strategy going to be well lets rub this down I know that F. So, now I will without any hesitation instead of e bar use a symbol U which is what we know in thermodynamics.

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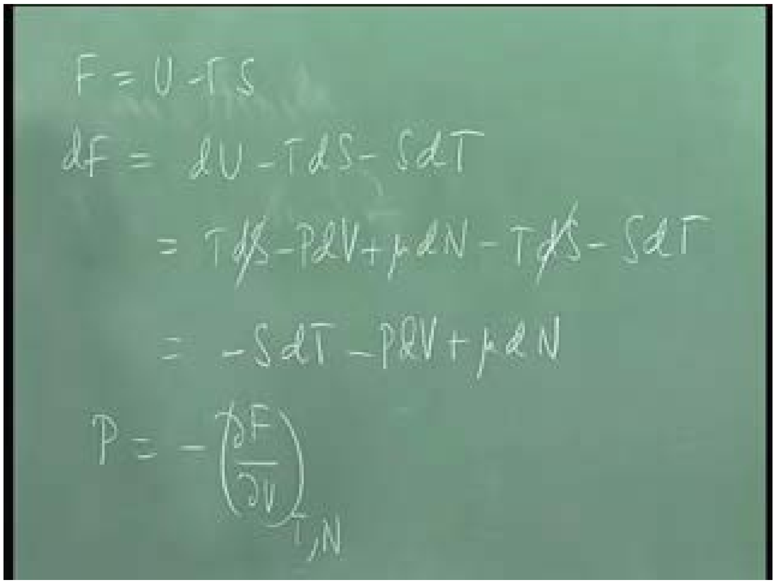

$$F = U - TS$$

$$dF = dU - TdS - SdT$$

$$= T\cancel{dS} - PdV + \mu dN - T\cancel{dS} - SdT$$

$$= -SdT - PdV + \mu dN$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$$

So, F is U minus TS this implies d F is dU which is dU minus T dS minus S dT and of course dU is equal to T dS minus P dV plus mu dN and then minus T dS minus S dT. So, it is just a legendre transform and therefore this is equal to um minus S dT minus P dV plus mu dN and one of the things we want to calculate is the pressure which is equal to minus delta F over delta V keeping T and N constant. So, all we have to do is to find out what this F is compute it and we will do that from statistical physics starts from this formula, we find what Z is then compute minus kT log Z and after that you put that in here differentiate with respect to volume and out should come the pressure and if you get P equal to rT over V or N k boltzmann T over V for N particles, then we know we are right completely so that is the strategy. We are going to use this formula which is a general one.

I want to appreciate that, it is obvious but I wanted to appreciate that all these relations are independent of classical ideal gas, they have nothing to do with it they are completely general statements, just that now I am going to go ahead and derive the equation of state for a classical ideal gas I emphasize this particularly, because there is often an impression that the only thermodynamics system in the universe is the classical ideal gas and everything has an equation of state PV equal to RT and of course that is not true, there is no classical ideal gas it is an idealization and it cannot as we will see it cannot be consistent as a description of anything down to absolute zero it is completely impossible for reasons which will become clear.

We are going to use this and then I come back to that formula and do that. So, now let us try to write what is the partition function for a classical ideal gas, I am going to do this in a sloppy way first and then depending on the kind of question that arise we will become more and more careful. So, I am going to push many things under the rug and depending on how alert you are, we will come back and justify things.

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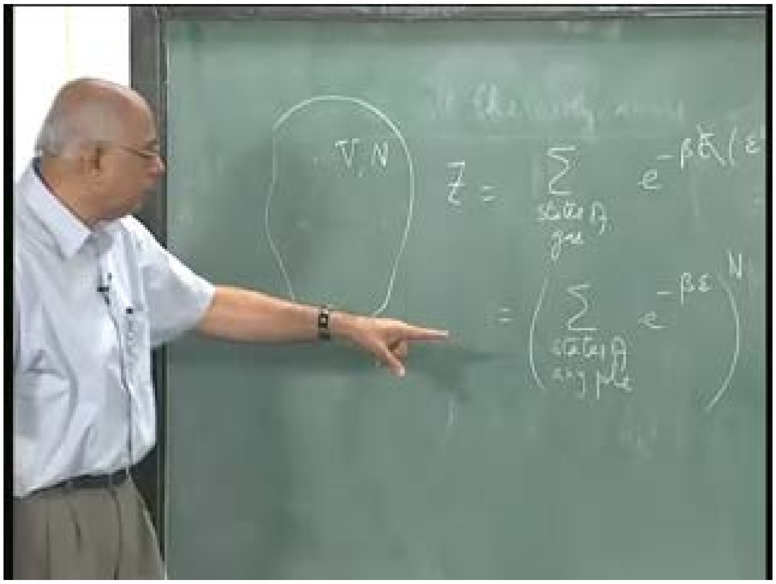

I have this volume V with N particles and the assumption is you have point particles of equal mass m and they are zipping around and they undergo elastic collisions with each other nothing more and this whole system is in contact with some heat bath which maintains the system at temperature T. Then what is the partition function Z equal to and I start by arguing that all these particles are independent of each other and therefore since I want to compute a sum over the number of states over the states of gas, that mean states of all the particles all the microstates that are accessible e to the minus beta times the energy of each state.

Now, I argue that because there is no interaction between the particles, the energy is in fact the sum of energies of course that is not true at the instant of collision but now, let us look at time scale the collisions are practically instantaneous. So, they are really a set of measures zero any time, I look at this gas you cannot find anything actually touching and now what does it physically mean there is a time scale involved the collisions are due to electromagnetic interactions finally between the molecules and electromagnetic interactions have a time scale typically of the order of ten to the minus fifteen seconds or less.

So, that is a such a short time scale compared to the time scales, we are talking about here compared to the no time scale at all thermodynamic means everything is stable and stationer. So, very long time scales that we neglect that so we assume that collisions are instantaneous as a matter of fact in this room each gas molecule is actually undergoing collisions the interaction time itself is ten to the minus fifteen seconds or less but even the time between collisions is very short, it is of the order of tenth of a pico second. So, in a pico second it already has undergone ten collisions and has forgotten its initial velocity completely, so this is really an very fast equilibrating system. So, if I write this as equal to e to sum over states, so therefore this e can be written as the energy of particle one plus the energy of particle two plus etcetera where the superscript labels the particles.

Then each particle is independent of all the others and therefore takes on exactly the same possible energies, there is no preference between the particles and this immediately factorizes the number of states of the entire gas factorizes this product factorizes into sum over states of any single particle times e to the minus beta epsilon where epsilon is the energy of that single particle raised to the power N, this is a great advantage of having the probability distribution which is an exponential, because if that exponential is sum then of course the probability distribution factors, now you see this is very reasonable it says since these particles are all identical and they are moving around and assuming their distinguishable, so right now there is no question of quantum physics at all.

The total partition function can be written as the N eth power of what you could call the partition function of a single particle then the task is to find this thing here and this particle can be anywhere inside this volume and it has only kinetic energy no potential energy at all.

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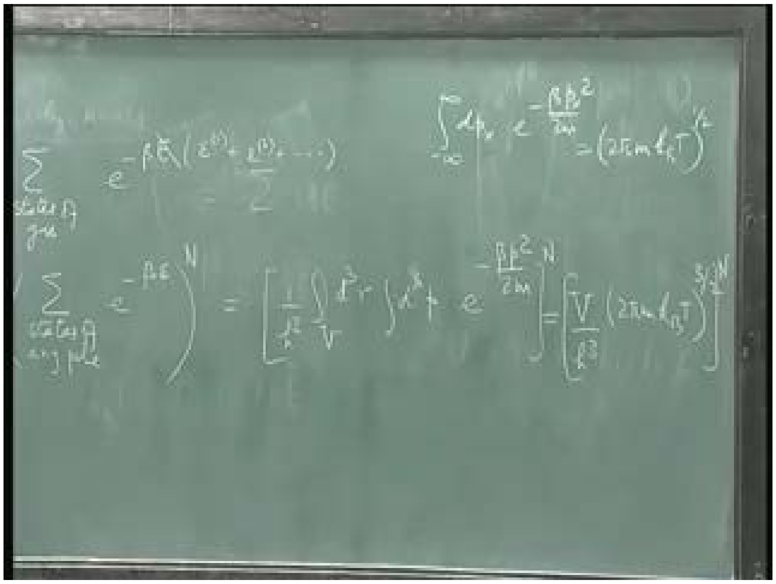

Therefore, m you could write this as equal to an integral, because now its phase space of this particle which is this volume times momentum space. So, d 3 r over the volume V can be anywhere in the volume d 3 P which is the momentum space, because it is in the phase space both x and P are involved in three dimensions e to the minus beta P square over two m because that is the kinetic energy. P square over 2m, but this is the volume of phase space available integral over the entire phase space available to a particle weighted with this e to the minus beta e factor the boltzmann factor, but that is not the number of states we have to really sum over the number of states and the number of states is found by as you know by a partitioning phase space into cells of size h planks constant in each connection it could be a multiple of h it does not matter, because we are going to take the log anyway and then that is going to disappear, remember our physical quantities would come from taking the log of that Z finding F and after that finding partial derivatives with respect to microscopic variables.

So, constants like planks constants would disappear from the way completely even the mass of the particle is likely to go away unless appears in very specific places notice the mass of the molecule has appeared here, now what is this equal to this is equal to the volume divided by h cube because there is no term here in the boltzmann constant which involves the coordinates when would that fail? If you had interaction between the particle, then of course the coordinates of different particles would appear and you cannot do this anymore. So, this is why the classical ideal gas is very simple or if I put the whole system in some field in gravitational potential for example then there would be a term here which would involve also the potential energy and then you cannot do the integral over the volume so easily.

So, we will look at a problem of that kind too because then it is clear that the air in this room, if its subjected to gravity the density at the bottom is greater than the density up there and that factor is missing now, because there is no gravitational field or any other field, so it is a free gas and we have V over h cube and you have to do this integral this is a three dimensional integral; you can do it many ways but obviously the simplest way to do it is to simply write this as dp x dp y dp z and use the fact that you have e to the beta p x square p y square p z square so this also factors and a typical integral be minus infinity to infinity dp x e to the minus beta p x square over two m and similarly for y similarly for z and its just multiplied but this is a Gaussian integral and what's this equal to we know e to the minus a x square is square root of pi over a where a is positive and a is now here beta over 2 m therefore this is equal to 2 m k boltzmann t to the power a half two pi and you have three of them in each case so this is 2 pi m k boltzmann t to the power three half in 3 dimensions and the whole thing has to be raised to the power N what happens next we have to find F.

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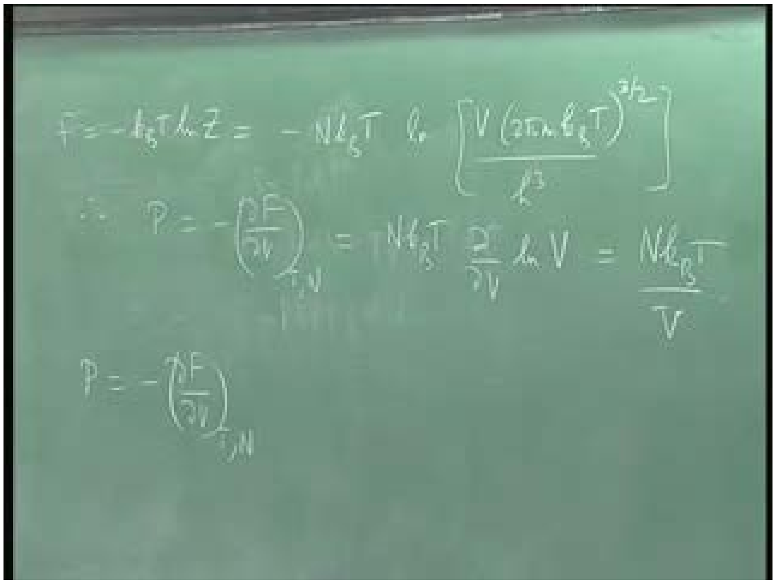

$$F = -k_B T \ln Z = -N k_B T \ln \left[\frac{V (2\pi m k_B T)^{3/2}}{h^3} \right]$$

$$\therefore P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = N k_B T \frac{\partial}{\partial V} \ln V = \frac{N k_B T}{V}$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$$

And therefore F equal to minus k boltzmann T log z which is equal to minus N k boltzmann t log V times 2 pi m k boltzmann T to the power three half divide by h cube. i hope i am right ya so i am taking log of this to the power N is N log the same thing so that’s it and then therefore p equal to minus delta F over delta V T, N this is equal to N k boltzmann T delta over delta V of log V keeping T and N constant so this is kept constant and i differentiate only with respect to V and you have delta over delta v log um and the minus sign goes away this minus goes away against this minus sign and therefore this is equal to N k boltzmann T by V which is the classical equation of state. this pv equal to N k boltzmann T if you have one mole of it then N is N Avogadro and k time boltzmann is the gas constant r.

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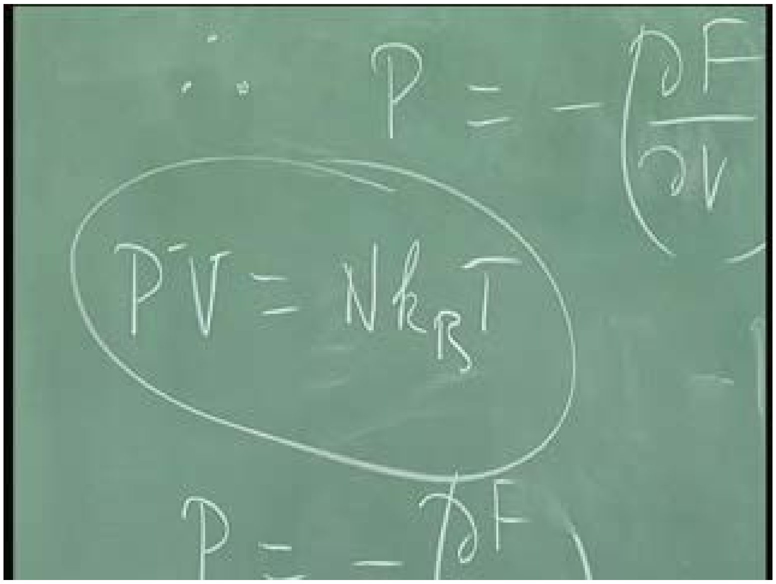

So, we have indeed derived the classical equation of state and that is come out correctly. I am asserting that this tells me now that this connection be made with thermodynamics is and this T indeed, is the T the statistical, T is the thermo dynamical T, the statistical entropy is the thermodynamic entropy and so on. There are other collaborations independent collaborations which one can do, for example you should ask, what is the average energy this is immediately a question that arises what is the average energy and that is not hard to compute.

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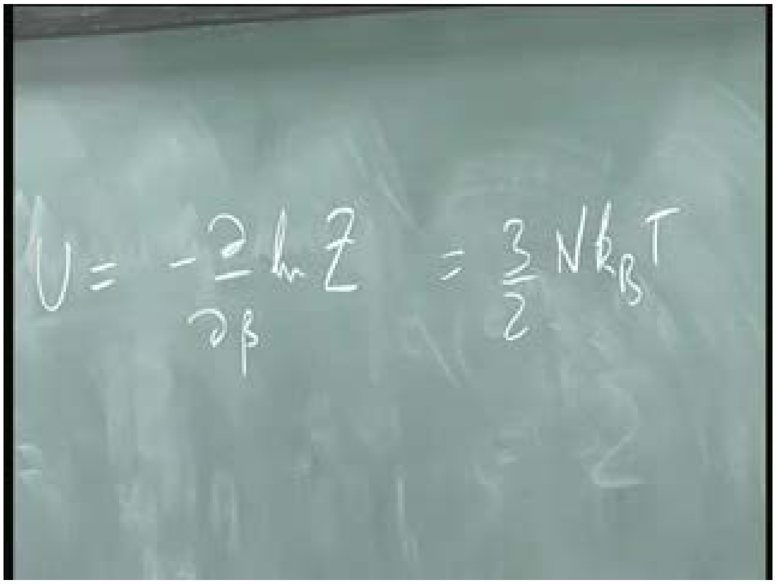

Because you already have formula for it, our formula was U equal to minus delta over delta beta log Z. We have the general formula for the average energy and we have a Z, so we have this guy here.

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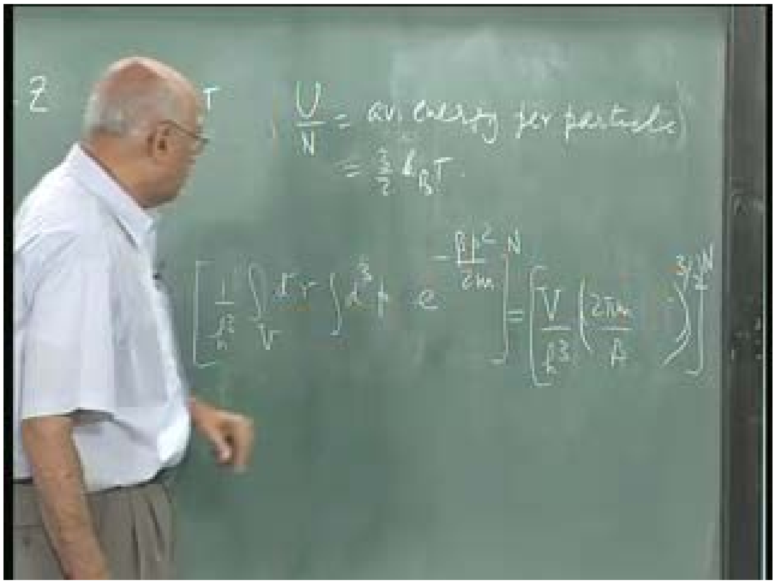

And kT is one over beta, so we put a beta here and you have to do a delta over delta beta log this and the power that comes out is three over two N over beta and this already has a minus because it is in the denominator those two cancel and what does this give you. It says three half N k boltzmann T one over beta, if you take log beta and differentiate it which is the same as kB T which is correct too, because this immediately says that U over N equal to average energy per particle equal to three half k boltzmann T divide by N and then I get three half k boltzmann T which is the equipartition theorem each degree of freedom has half kT. Now let us dissect this a little bit where did this three half come from where did this three half come from it came from here and where did this come from it came, because I am in three dimensions um and where did the half come from it came from the Gaussian integral um this half came from the Gaussian integral directly and why did that come because you why did this become a Gaussian integral because the energy is quadratic in the momentum.

That is the genesis of this three halves, here the reason you got half k T per degree of freedom, because that degree of freedom appeared in the Hamiltonian as the quadratic function of the corresponding dynamical variable you got a p squared and then you integrate it e to the minus p squared and you got that half so this tells you that every quadratic contribution to the Hamiltonian, will give you exactly the same answer a half. So for instance, if you have a vibrational degree of freedom you pretend this is an oscillator then there is a p square from the kinetic energy and there is an x square from the potential energy and that is also quadratic and therefore for each vibrational degree of freedom the average energy would turn out to be per particle would turn out to be half kT plus half kT, which is one k T.

So, if you recall when you do specific heats of diatomic molecules and you look at vibrational degrees of freedom you had a kT there not a half kT per degree of freedom, but this whole thing comes from the fact that every term every dynamical variable in the Hamiltonian which is appears in a quadratic form is going to contribute a half kT due to this mechanism here had that been different, suppose I had oscillators for which the kinetic energy is p square over two m plus the potential energy and suppose this were an harmonic oscillators in the potential energy was x to the power four, then what would happen is that kinetic energy would give you an answer half kT on the average.

But the potential energy would give you a quarter kT and then per degree of freedom the total energy would three quarters kT. So, although factors are some time they have deep implications, so this is where this thing came three half three half came the three is the three dimensions two is the energy momentum relationship is quadratic T is proportional to the square of the momentum.

We are going to do black body radiation then we do quantum statistics later on and then we will see that this is completely thrown out of the window you are still in three dimensions. So, that three would still appear but then the energy is linearly proportional to the momentum T equal to cp for a photon and therefore that would turn out to be different this two would not appear at all. But there are further complications you have what is called bohr statistics applied by that particle and therefore this would turn out to be about three to the power four completely changed.

But for classical particles this is where equipartition theorem comes from it comes from the fact that every degree of freedom which appears in the square form in the Hamiltonian is going to contribute half kT to the average energy per particle. Now, with these two we have actually seen what the classical ideal gases can do I mean this is it.

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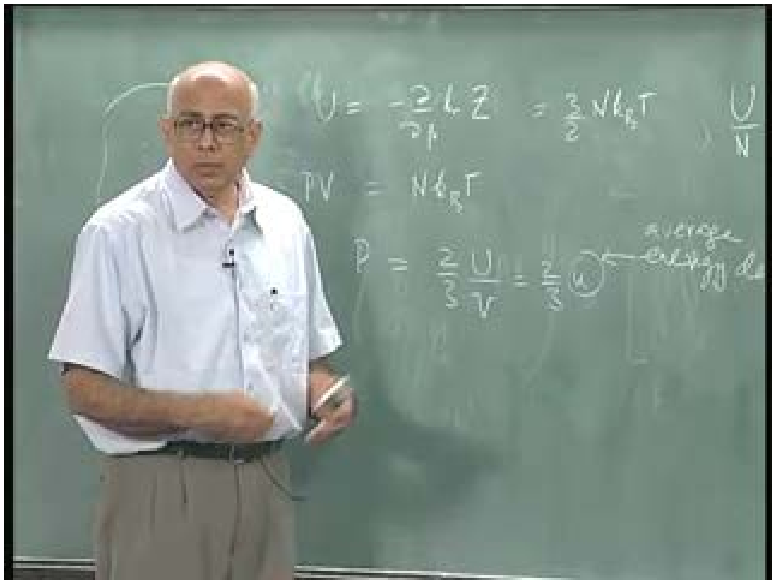

So, if you actually put these two together you have U is this and PV equal to N k boltzmann T. So, this immediately implies that PV P is equal to n kT but n kT is two-thirds U and I divide by V so it is two thirds U over V which is two-thirds U. This is energy density average energy density, the average energy per particle per unit volume, sorry per unit volume, this quantity has exactly the same dimensions as force per unit area which is pressure and the right way to write down the equation of state for the system is to say that the pressure is two thirds of the energy density internal energy density the two comes from the quadratic relation energy is the square of the momentum and the three comes from the dimensionality this relation remarkably will be true, this kind of relation is going to be true even for quantum gases provided they are ideal gases and then it will turn out that, if you have photons for example this would become a one and this would remain three and you would have one third U and this would indeed turn out to be the case.

So, although P would have a complicated formula U would have a complicated formula the ratio turn out to be very simple and for all ideal gases this kind of relation is to P is some number times U and you can read of things from this number U. Now what is the assumption I made in deriving this, we can go on to derive other things, which we are going to do and we will run into a problem very shortly, but what is the assumption I made here, the main assumption I made was I could write the energy as a sum of all those guys independently and then I said I just sum over each one of these fellows separately, but you have to also ask is this really true how many states are actually available what kind of error, have I made in doing this and did I take into account the fact that different molecules are indistinguishable I did not.

One molecule is exactly the same as another, so kind of schematically you have to pay attention to this, because the fact is the physical fact is these molecules are indistinguishable from each other whereas I pretended they are not and that is going to lead to some trouble.

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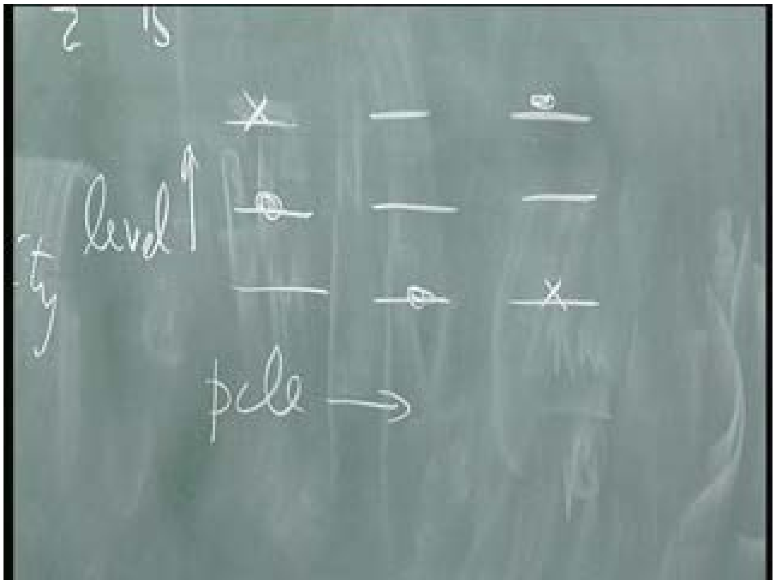

Because if for a moment, I write the energy levels in a discrete form; so this is particle one’s ground state, second, third etcetera. This is the first excited state, third excited state etcetera, just for illustration and say the first particle is in the first state here the second one is in its ground state the third one is up there and so on am counting over all these possibilities, but if these particles are indistinguishable then even if they do not interact with each other, if you have the first particle instead of this you had it here and instead of that you have am sorry instead of this you had it there and therefore instead of this fellow is exchanged here and goes here this configuration is not distinguishable from the earlier configuration it has to contribute exactly the same thing in fact it is the same state in some sense and we have over count it by saying these fellows are independent we have over count it.

There are other ways of saying this and when we do quantum statistics. I will come back and fix this problem we will be very careful about how change this method of counting one thing is very clear instead of saying that this is particle and this is level our book keeping has gone by saying says where is the first particle, where is the second where is the third one we sum over all these possibilities and then multiply the whole thing together, but if they are indistinguishable we should really ask how many fellows are sitting in this level how many are sitting in this level how many are sitting in this level and so on and in the nutshell the difference between classical and quantum statistics is to do instead of a column wise tally you do a row wise tally you do that you get quantum statistics.

Now that is why you talk about occupation numbers in quantum statistics you are not worried about which particle is occupying a given level you do not even worried about how many of them are there and that is it and that will give you the correct counting statistics. We will see this problem crop up even classically and then we will try to fix it subsequently, we are going we are recourse to this kind of argument for the moment let us go ahead and do the other thing namely and I would not do this and point out the problem here and we will come back to it.

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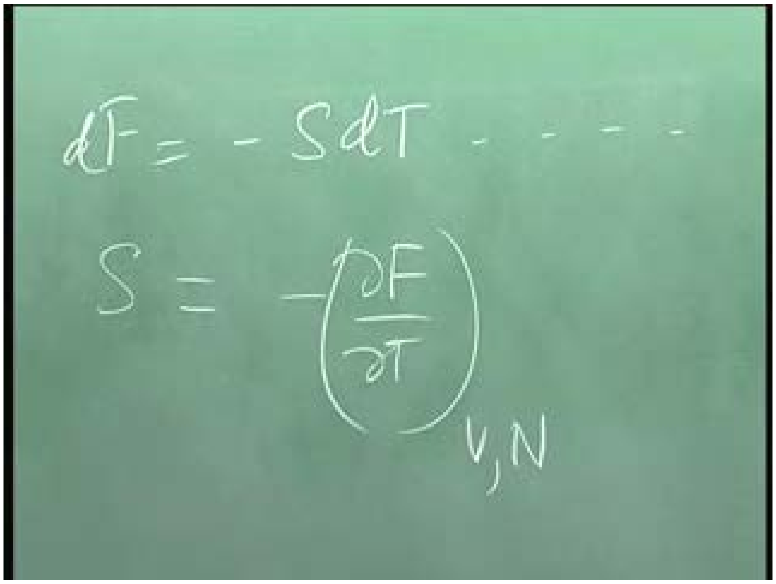

$$dF = -S\,dT - - - -$$

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

Notice that F was also equal to dF was equal to minus S dT dot, dot, dot. Therefore, S is equal to minus delta F over delta T keeping V and N constant. So, in principle I should be able to take this F and difference which I have got out there differentiate it and get the entropy of the classical ideal gas, but what is going to happen I did that.

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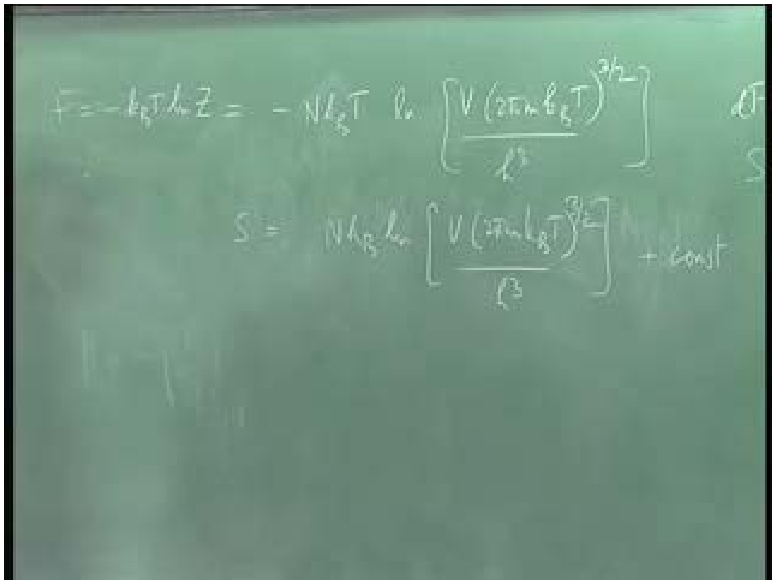

$$F = -k_B T \ln Z = -N k_B T \ln\left[\frac{V(2\pi m k_B T)^{3/2}}{h^3}\right]$$

$$S = N k_B \ln\left[\frac{V(2\pi m k_B T)^{3/2}}{h^3}\right] + \text{const}$$

So, this is equal to s is equal to by differentiate this um there is a term which is N k boltzmann log V times two pi N k B T to the three half over h cube, that differentiate this quantity and then there is a plus some constant, because if I differentiate log T with respect to T, I am going to get a one over T that cancels against this and then there is some constant this thing, this is not good news, because if I go to T equal to zero, this goes up and its unphysical, of course you would argue against it by saying, look I know that the classical ideal gas is a theoretical construct and it certainly cannot be expected in real life to go right down to absolute zero, because I know in real life whenever you take condensed matter or a gas and then you cool it down, it would condense it would become beyond a certain temperature it become a liquid and then it becomes a solid.

And therefore this whole thing is out of the window completely, there are interactions definitely there are interactions and as the temperature gets lower and lower this tendency for interactions would dominate would increase and things would condense and therefore it is not fair to do this, I agree with that this is a good argument that this thing cannot be extrapolated down to zero, but there is a more serious problem with the formula for the entropy here, which we will fix subsequently it is called the Gibbs paradox and we will fix it and it has to do with this counting of states with indistinguishability. So, it says really you cannot get away with this, but for the moment let us leave it in this form and see what happens as you proceed, so we could do the rest of it we can compute chemical potential for example: because we know how to differentiate respective N and let us do that let us compute what the chemical potential is…

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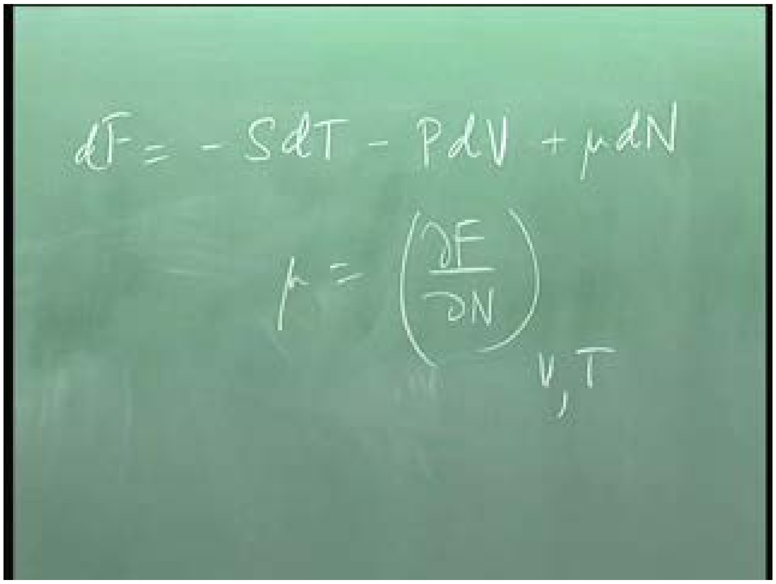

$$dF = -S\,dT - P\,dV + \mu\,dN$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T}$$

So, dF is S dT minus P dV, then was it a plus mu N mu dN or a minus mu dN, the plus mu dN. So, we know that mu is delta F over delta N keeping V and T constant. Let us compute that.

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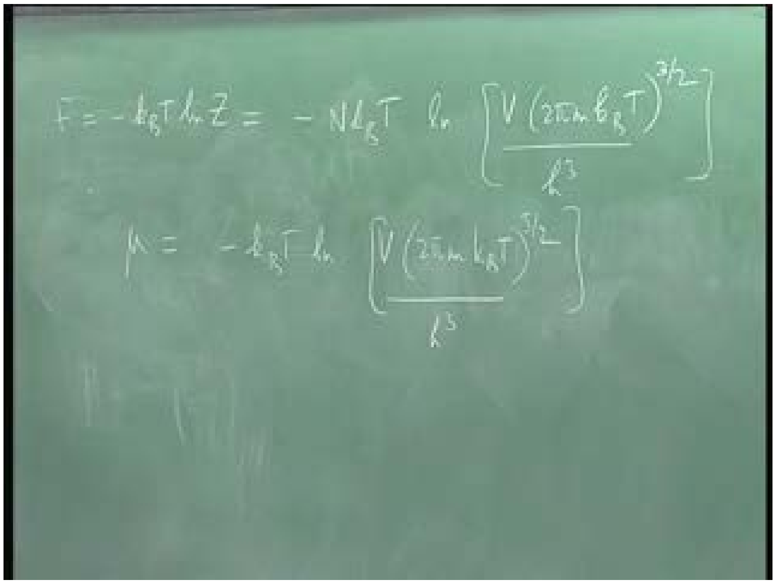

$$F = -k_B T \ln Z = -N k_B T \ln \left[\frac{V (2\pi m k_B T)^{3/2}}{h^3}\right]$$

$$\mu = -k_B T \ln \left[\frac{V (2\pi m k_B T)^{3/2}}{h^3}\right]$$

So, mu for the classical ideal gas equal to derivative with respect to N and that is equal to minus k boltzmann T log V two pi n k B T three half by h cube. So, this is what it looks like as it stands, but I am not too happy with this formula either and the reason this is not a very sensible formula is that what do you think is wrong, with this formula what do you think is wrong, with this formula itself this is a serious problem here or a multiple of it and so on. But then you could always argue saying that this formula is not very true very low temperature. So, this is not the difficulty but there is a serious problem here even with ordinary thermodynamics and that problem is related to the Gibbs paradox, I talked about you see the fact is, I expect this free energy to be an extensive quantity.

I expect that, if I double the volume, I double the number of particles keep the temperature exactly the same nothing should happen. So, the free energy should be simply proportional to N and then whatever else multiplies it should depend on intensive quantities, but there is this very uncomfortable V sitting here, had this been V divided by N. I would be very happy, it would depend on the density, because the N proportionality is outside, but that V is sitting inside and this is a serious. So, there is something wrong here, this is not cannot be the right counting this cannot be the right counting and we have to fix that problem. So, even the chemical potential turn out to be wrong and cannot come out right.

So, we have to fix the fact that, we make two drastic approximations somewhere and this has to be stated out. Now, what was the approximation we made we said these fellows are all completely independent of each other and therefore the partition function is simply the N eth power of the partition function for a single particle, but we did not take into account the fact that these particles are indistinguishable. Now, how many ways can you take N particles and arrange them among various levels um how many permutations are there of these particles N factorial. So, one way of fixing this would be to simply divide the answer for the partition function by N factorial and say I over counted. So, I divide by N factorial that is the number of ways in which you can mix these guys, but that is not, that is too simplistic said because of the following fact.

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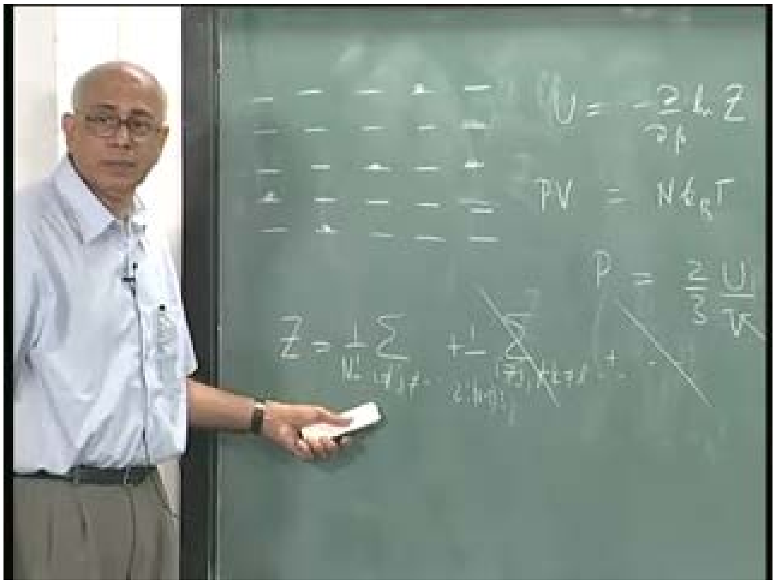

Had the particles been like this and now let us be honest. Now, these are the possible energy levels of each particle had the particles been like this, there is one here, there is one, there is one there, there is one there and there is one. It is free I need one more there is one there and so on when this argument is perfectly right, because it says whether this guy is in level two and this fellow is in level one or vice versa does not matter and there are N factorial ways of doing this and therefore I can divide the answer by N factorial and be and be done with it but what about a possibility like this what about the possibility that this fellow is also here then the division by N factorial is not correct answer. What I should do is except these two particles the remaining fellows are all in different levels and therefore I divide by N minus 2 factorial and these two particles trying to change is the two factorial that comes out.

So, whenever there are coincidental levels I have to treat that separately and ofcourse you can imagine now, when this becomes a continue and you have a huge number of levels possible the question is what factor are you going to divide by then I have to separate the partition function into a contribution where all the particles are in different levels plus a contribution, where all of them are in different levels except two of them and then except three of them four of them and then there are different levels and so on and becomes virtually impossible to count, but luckily for us luckily for us if the number of levels available is much larger than the number of particles you put in then the probability that any two of them is in the same level is going to be negligible and now for the gas in this room that is exactly what happens. So, I want to say this again.

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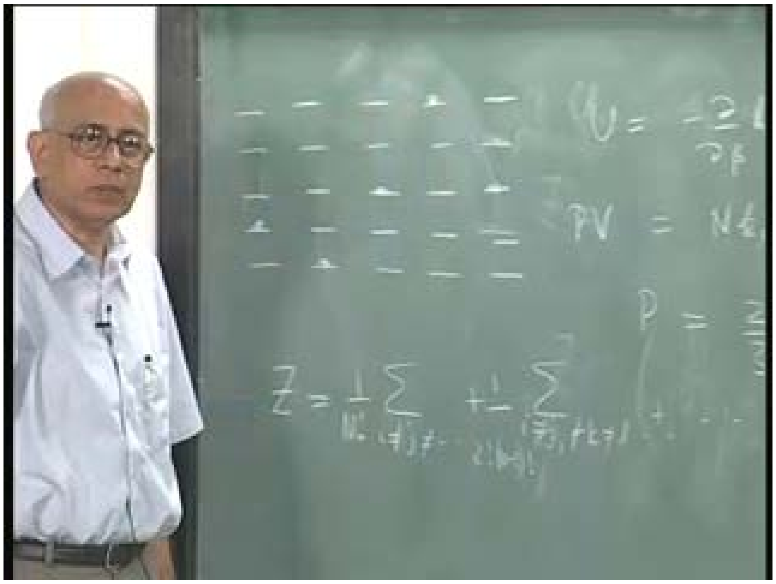

The true partition function Z is equal to some sigma over all the particles in which the level i is not equal to level j not equal to etcetera, where i j refer to levels of particle one divided by N factorial a contribution, where i not equal to i equal to j but not equal to k not equal to l etcetera and then divided by two factorial N minus two factorial plus dot, dot, dot infinite number of such huge number of such terms. Now, if the number of levels is much larger than the number of particles and I toss these particles in then the probability of this or that or that happening, if it is negligible I can throw out all these guys throw out all these guys and do this alone but here you got to be careful that you do not count the possibility that two of them would be in the same level. If you do then you over counted again but once again the correction to that the mistake you make by doing, so counting would be negligible.

So, again we remove this restriction and sum over all levels possible for each of them. So, there are two compensating mistakes that are made in the classical ideal gas and really the numbers are such that there is no mistake at all effectively, because we will see we will make a count for the gas in this room, for example nitrogen hydrogen and normal temperature and pressure the number of levels available will be of the order of ten to the thirty two for one mole of a gas the number of particles is ten to the twenty four twenty three. So, you have nine orders of magnitude away and therefore, if you have this factor of ten to nine what is the or ten to the seven even what's the probability that two of them would be in the same level, one part in ten to the fourteen that three of them were in the same level as one part in ten to twenty one and so on therefore completely negligible.

So, this is the reason why this crude way of fixing the problem works completely, but we need a criterion for when it is going to work and let us give that criterion, we talked about this criterion related to the chemical potential, but I want you to understand that there is really not a very bad approximation all it is a very good approximation provided, this is statement I made is valid namely the number of levels available is much larger than the number of particles so what you have to check is, is that true, is that true to that accuracy statements I am going to make are true. So, let us put the fix in and see what happen I correct this by this fudge factor, instead it was fudge factor because this was done before the advent of quantum mechanics and it was done by these two people Sackura and Tetrode and this is the correction that he made that they made and worked.

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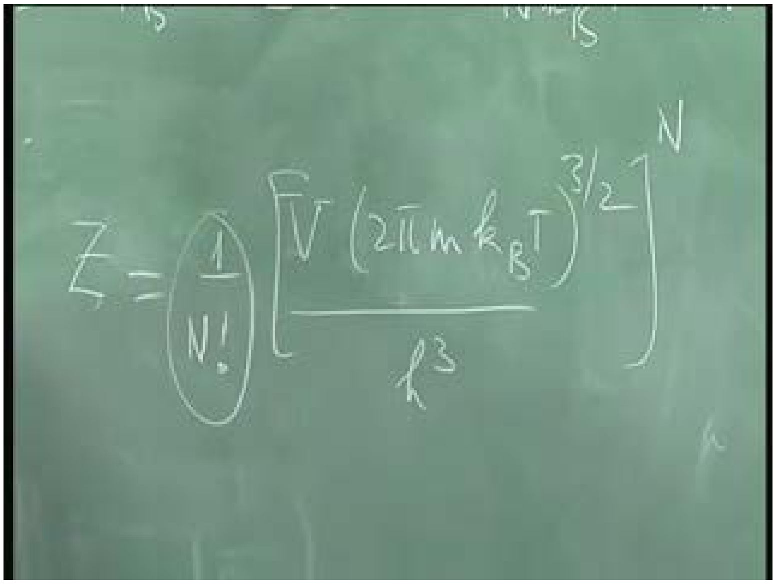

$$Z = \frac{1}{N!}\left[\frac{V\,(2\pi m k_B T)^{3/2}}{h^3}\right]^N$$

So, the idea was that you took Z equal to e over V times two pi m k boltzmann T over three half over h cube to the power N and divided by N factorial.

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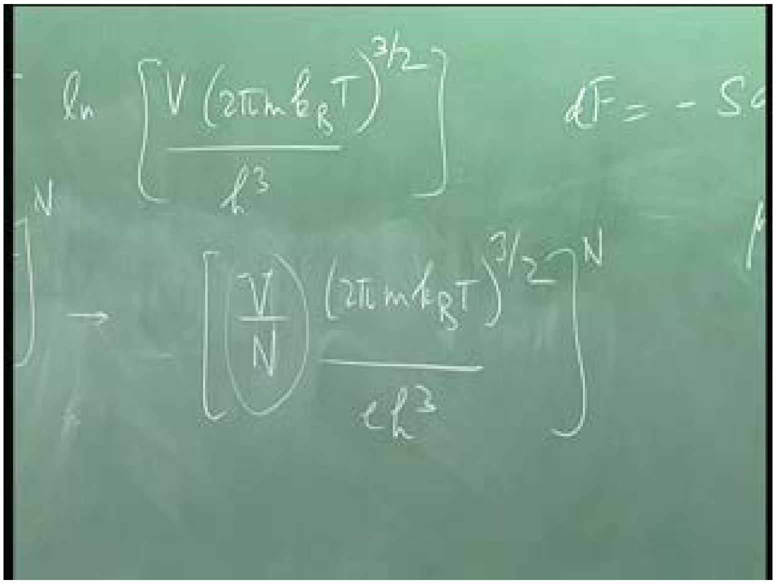

$$\ln\left[\frac{V\,(2\pi m k_B T)^{3/2}}{h^3}\right] \qquad dF = -S$$

$$\rightarrow \left[\frac{V}{N}\,\frac{(2\pi m k_B T)^{3/2}}{e h^3}\right]^N$$

So, once you do that you are in great shade, because this N factorial. We can use sterling's formula for the N factorial and replace it by N power N e to the minus N. So, you can certainly write this as equal to V over N two pi N k boltzmann T over three half over e h cube to the power N where e is the base of the natural logarithm, not the charge now you could ask what about the square root of two pi N and so on. It is irrelevant because the whole thing is completely you are going to take the log and that is completely negligible its completely irrelevant but notice this magic has been affected, namely this guy here this V has been replaced by V over N and that is an intensive quantity. So, all the problems with the classical ideal gas except serious problems of what happens as anyway go to absolute zero are fixed are completely fixed.

Of course, it will not give you the correct entropy of the system as you go to absolute zero, because the system is not going to be a classical ideal gas as you go to towards absolute zero but this problem of the paradox and so on are going to be resolved as we will see, now what is the criterion I will end with that what the criterion that we need in order to settle this. Well, the criterion is as follows its really buried in quantum mechanics once again, because as I kept saying even counting the number of states and phase space requires you to put a planks constant in there, it did not play much of a role, because when I take these logs it disappears I could have multiplied it by three instead of planks constant square root of three times planks constant would have done exactly the same thing would disappear.

But if I want absolute number then I have to worry about it, I really have to start up and do this and that cannot be done at the classical level, because we know that I have brought up ultimately these are quantum objects, so we really have to use quantum physics from the beginning and derive things completely and pass through the classical limit subsequently, but let us see when we expect the classical limit to be valid what is going to happen well two things first of all the particles are indistinguishable and secondly in quantum mechanics we know that the position and momentum of a particle cannot be specified with arbitrary precision at any instant of time.

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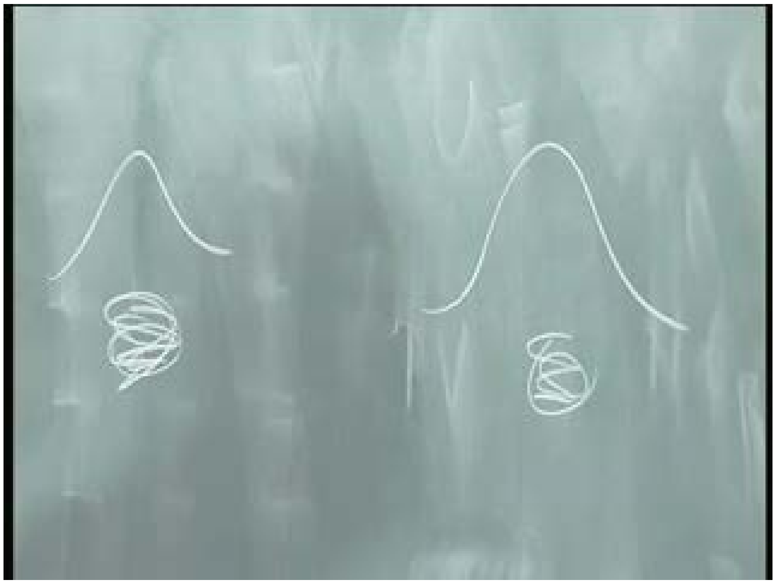

Therefore, in some vague way these particles are really some fuzzy objects some wave function which tells you particle is in there with high probability and you have another of these guys out here and so on, if it turns out that the average distance between these wave packets is much larger than the spread of the wave packet itself then you can say this is particle one is here particle two is here, now of course you cannot say that when they interact, because when they collide and go off is a little black box coming in there.

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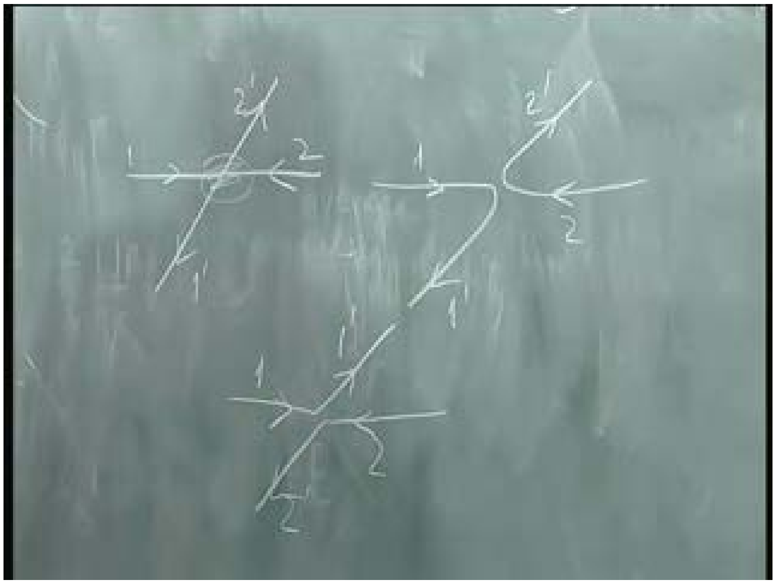

So, if you have an incident in which two particles collide and out comes this and that so this was particle one and this was two and this is one prime and two prime, what has happened here is one comes along and gets scattered two comes along and gets scattered in this fashion, but if this is a black box to you whatever is happening inside there, then it is clear that this incident could also have happened and this is the particles are exchanged here and you cannot tell which is which, so this is the reason why even in the dilute approximation when the de broglie wavelength of these particles is much smaller than the inter particle separation, you can get away with this classical approximation you do not have to do with classical statistics but you have to still take into account the indistinguishability factor by putting there - N factorial, by putting that n here because of this possibility even just instantaneous collisions could do this for you but in general you don’t have to worry about quantum mechanics itself any further, if this is the situation and what is the criterion for this situation to happen, I would like this distance to be much smaller than this distance I would like the inter particle separation r sub s.

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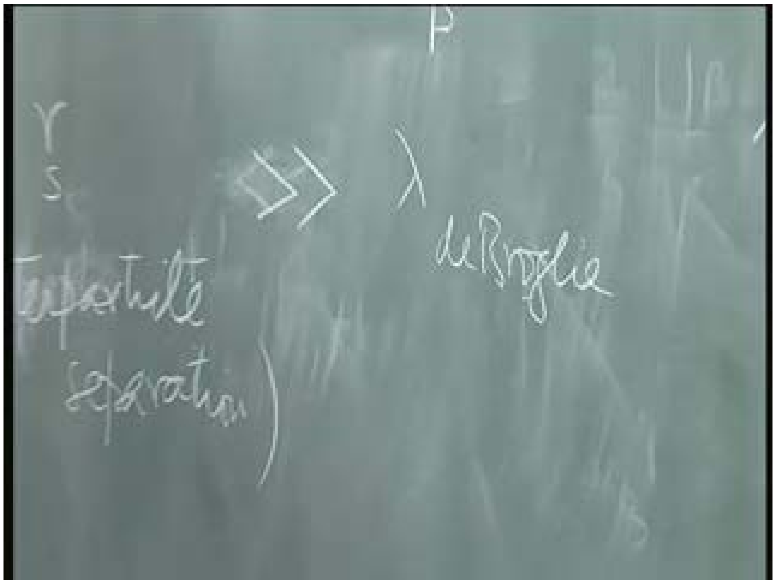

Inter particle mean inter particle separation to be much greater than lambda de broglie wavelength, if that is true I say, I can get away with classical statistics with that fixed factor otherwise I have to do quantum statistics genuine quantum statistics, but let us compute what this is this lambda de Broglie really depends on the energy of the particle and we use very elementary considerations. So, this is saying r sub s now what is the inter particle separation.

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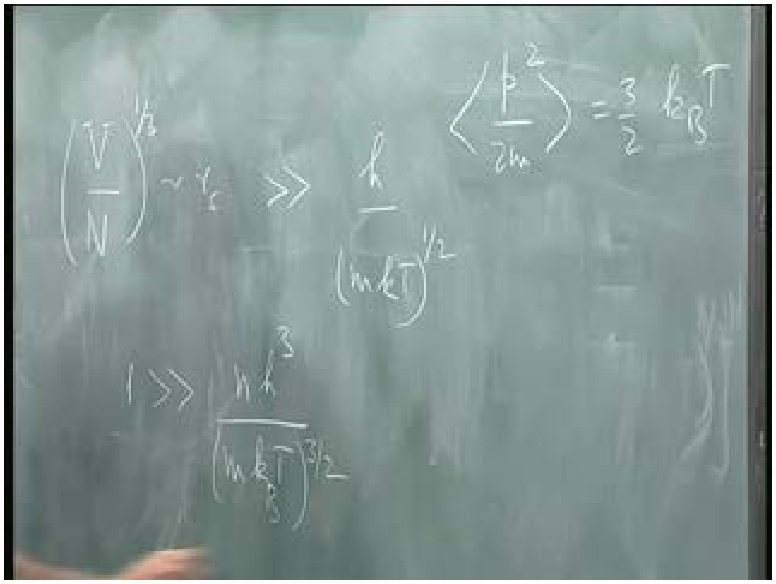

If you are going to put in a volume V, you are going to put n particles then the volume available for each particle is V over N and therefore what is the linear dimension available for each particle the cube root of this guy cube root of this is r sub s and this must be much greater than the de broglie wavelength, the de broglie wavelength is planks constant divided by the momentum, so what are we going to do for the momentum well the momentum can run over all possible values but on the average the momentum is given by the equipartition theorem it says at temperature T P squared over two m average value equal to three half k boltzmann constant T, this implies that P is of the order of m kT to the power half modulo factors three half two and all that, but m we have to put in k boltzmann this also we have to put it, this is the root mean square momentum.

If you write now this side, you have V over N and therefore it says one is much greater than this N over V is the number density N and with that lets cube this whole this over m kb t over three half or this is much less than one, this is the criterion. So, that is the criterion for classical statistics it is very simple physical argument completely, it says if this is true put that N and see what happens then for a glass classical statistics is valid. I want you to put in the numbers for nitrogen for air at normal temperature and pressure k is three ten to twenty, ten to the minus twenty three T is the ten to power two three hundred Kelvin, the mass of a particle the mass of molecule is like what ten to the minus twenty six kilograms um for a nitrogen molecule h is ten to the minus thirty four and there is a cube appearing there and then what is N, the number density well you can find out, because you know that one gram mole of each gas with normal temperature and pressure occupies whatever it is twenty two point four something or the other so put that in and then you discover this number will be of the order of ten to the minus seven or something like that okay so that's exactly why it works.

But the moment that this is changed its going to flunk the moment the density increases certainly when it becomes liquid density, this is gone completely or what is the other instance in which its going to change if this guy is low if the temperature is low its tending towards absolute zero this is going to go the other way, this number ,this quantity here it is called, it is what is it it is the ratio of the inter particle separation, it is the ratio of the de broglie wavelength of thermal wavelength this is called the thermal wavelength. Because I put in h over thermal energy there is much smaller than this inter particle separation this is called the degeneracy factor, yet another misuse of the word degeneracy. So, it is a it is not a very nice too many things are called degenerate but this is one more of them.

If this quantity, it becomes of order unity then of course you need quantum statistics and I might as well tell you. Now, we will discover that if you look at electrons in a metal they are absolute zero of temperature, this factor goes the other way becomes the order of ten to the three is much bigger than one. So, it is smaller than one, if you go to neutron star the density is so high that this factor becomes the order of ten to the power six or seven and so on. Then it is the extreme quantum limit completely, the other way if you go to super fluid helium at four Kelvin then this guy, here if you go to helium at very low temperatures then this here again changes the inequality flips over and you need quantum statistics once again.

You cannot apply this as it stands to photons for the simple reason that I assumed m was not zero you redo this whole business and then you discover you never going to be able to do it, because in the case of photons you cannot localize them at all have zero rest mass. So, this argument is not valid and it is to start with intrinsically quantum mechanics, so we will come to that, but the check here is going to be precisely this by the way, I want you to verify after putting in that N factor that this is essentially this is closely related to the chemical potential of the classical ideal gas you need a log somewhere and check this out. So, I hope I tried to give you some idea of what is the assumption that I have gone in into deriving the classical equation of state, what is the physics that has gone in and how good the assumptions are and they really are very excellent as far as normal conditions are concerned, but we must be alive to the possibility that as soon as this changes you have to apply the full power of quantum statistics and the idea in quantum statistics would be to put it in a nutshell to do a row wise tally of the energy level of the possibilities rather than a column wise standard and that will help us find out what happens. So, let me stop here.