Mechanics, Heat, Oscillations and Waves

Prof. V. Balakrishnan
Department of Physics
Indian Institute of Technology, Madras

Lecture – 38
The Classical Ideal Gas

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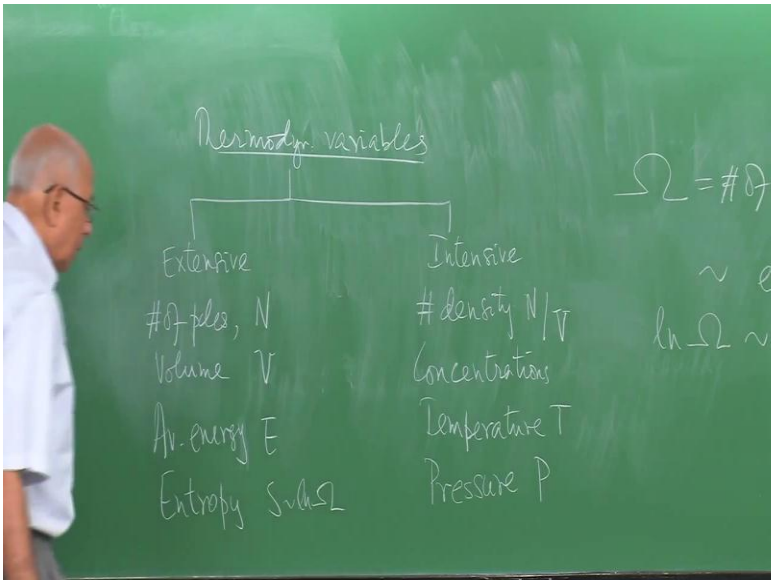

Let me point out right away, that I mentioned last time that the entropy was also an extensive quantity, I have not define the entropy yet properly, I will do so, but I must explain why this is so. This is a measure of the disorder of the system and without making misty of it by tell you, where this formula, why it becomes extensive it clarifies matters a lot. I have already mentioned that if you have a macroscopic system with a large number of degrees of freedom, we can ask how many micro states it has and this number of micro states if I call omega equal to number of micro states of a system with N elementary consequence, capital N particles for instance or molecules.

Then, this is typically of the order of the exponential of N, it does not matter what is exponential it, but it is the exponential of N here. So, this means that log of this omega is like N apart from various constants here, always and this entropy S is like, is proportional to the log of omega that is the statistical mechanical definition given by Boltzmann for the entropy. It is not the thermodynamic definition which I will come to little later, but this definition here tells you immediately that this quantity too is proportional to N for an ordinary systems and that is why it is an extensive quantity and we have a whole list of extensive quantities.

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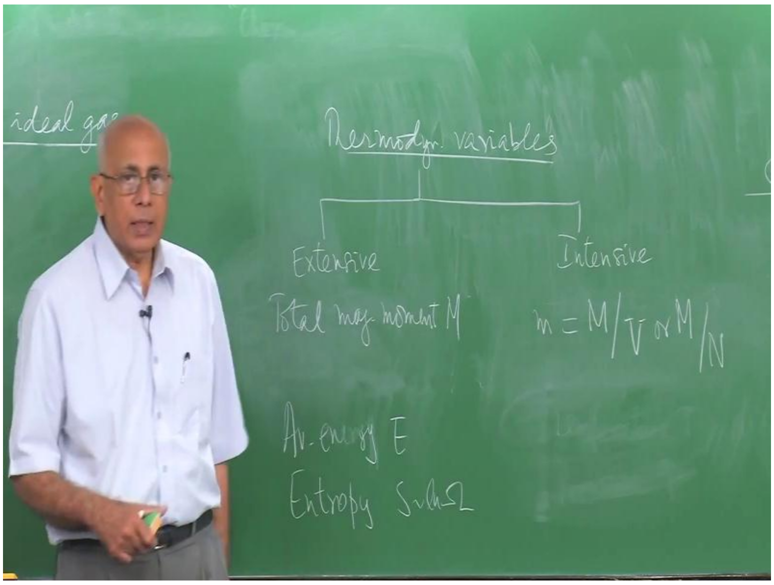

For instance, if I magnetizes a sample, then the net magnetic moment out here, total magnetic moment M is an extensive quantity, because if I add more particles, more particles to the system, more atoms which have got magnetic dipoles, I get a larger magnetic moment. On the other hand, the corresponding intensive quantity would be the magnetization M per unit volume, M divided by V or M divided by N, the magnetization per particle or per atom would be an intensive quantity like the density or the concentration.

So, every time you have an extensive quantity, you can in principle divide by the number of particles or volume of the system for a given density and make it into an intensive quantity here, but the distinction between the two should be kept in mind. Now, it also turns out that in thermodynamics it also turns out that the energy of the system in general comes in pairs, it comes in products for some reason, for good reason in the following sense.

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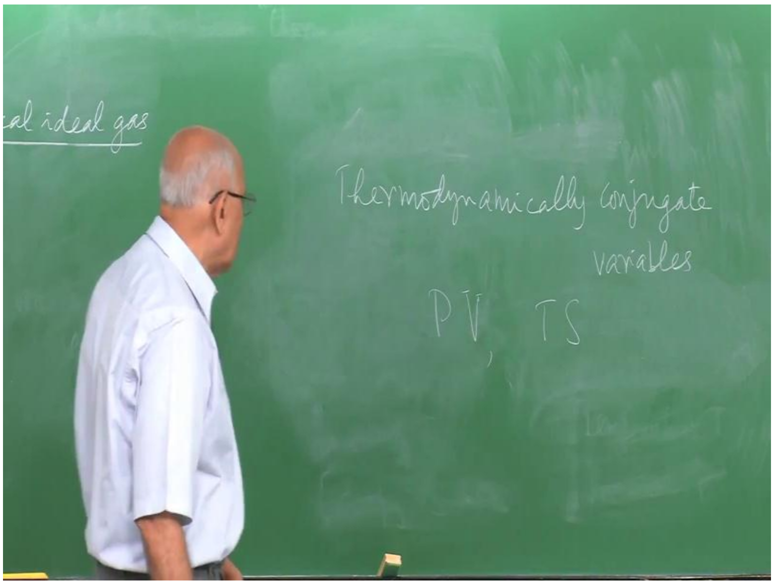

But, the energy of the system is expressible in terms of products of an extensive variable and a conjugate intensive variable and these are said to be thermodynamically conjugate variables and the most common of them all is that the pressure, which is an intensive variable multiplied by the volume of the system which is an extensive variable has the physical dimensions of an energy and in fact, it is related to the internal energy of the system here.

So, these form a pair, thermodynamically conjugate pair; very like in mechanics a coordinate and the momentum, the corresponding component of the momentum form a conjugate pair in a very specific sense. Here in a somewhat different sense, these form thermodynamically conjugate variables here, the other famous pair is the entropy and the temperature. These two also physically of the dimensions, product has a physical dimensions of an energy and appear in this combination in various expressions for different kinds of energy of the system.

So, there is always one intensive variable and one extensive variable here and the system requires that you must specify at least one extensive variable, otherwise you do not describe the actual system itself and the rest of them are could be intensive variables. But, you cannot describe the system purely in terms of intensive variables, because then you would not have any information on how big this system was, how many particles there are etcetera.

This is a technicality, but it is worth point in out at this stage and it explains, why these combinations appear in various places. Now, have in said this, let me say a few things about the laws of thermodynamics. As I said thermodynamics has now, is now understood in terms of a small number of laws rather small number of laws here, which give a great deal of information. The question is, are these fundamental laws.

I have already pointed out, I have already mentioned that these are not fundamental laws in the sense of Newton second law of motion; it is a fundamental law of mechanics, this is not on the same footing. The laws of thermodynamics are actually derived from those of equilibrium statistical mechanics, where there is a fundamental postulate of equilibrium statistical mechanics, which is not itself derivable from mechanics either classical or quantum, but has to put in as an extra postulate at least as of now.

And then, the rest of the laws of statistical mechanics follow and so do the laws of thermodynamics and as a consequence, all the other physical consequences of these laws follow. So, it all follows from a certain fundamental postulate of equilibrium statistical mechanics, you are not going to get into that here, we will operate at the level of the laws of thermodynamics themselves here. Now, the laws of thermodynamics got established before historically, well before equilibrium statistical mechanics itself got established and there is a long historical progression of ideas throughout the 19th century, when people are trying to come to Gibbs with the idea, what really he means, what is meant by he and this was mind you at a time when the very molecular or atomic constitution of matter was not very clear.

In fact, the two problems were very closely linked with each other and few people like Boltzmann and Maxwell and Gibbs understood at a very deep level and Einstein understood at a very deep level, what was implied by having a large number of microscopic constituents interacting with each other and where statistics came in and where probability came in and so on. But, it took a while to recognize that heat is a form of molecular motion, random molecular motion.

In the process, a lot of empirical rules were evolved and the rules of thermodynamics themselves got evolved as these empirical rules based on experimentation here. Now, it was in all pure experiment, it also termed out that we had one very important theoretical laboratory in which we could try out various things in understanding the whole idea of thermodynamics and subsequently statistical mechanics and that is the classical ideal gas here. What happen was that when people did experiments on real gases like oxygen and nitrogen and so on and so forth, they came across a couple of laws which were empirical, purely empirical in nature.

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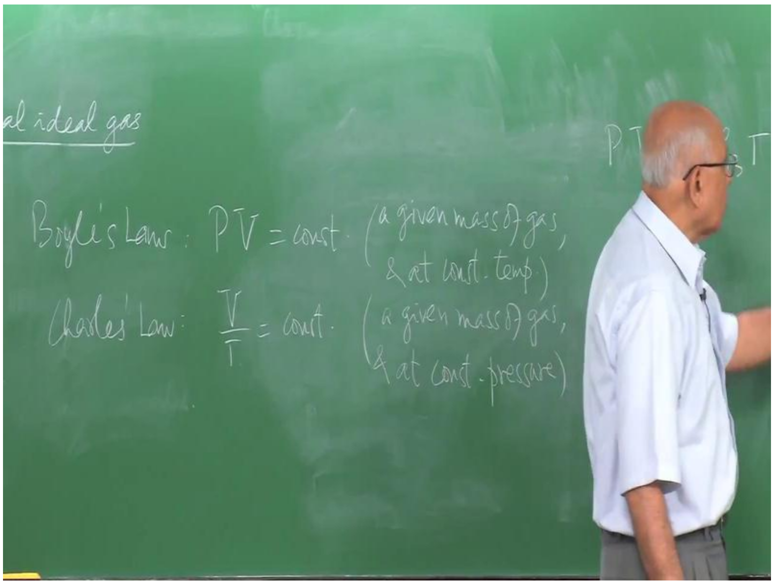

And these laws called most notable among them is Boyle's law, it said that the pressure times the volume was equal to constant under certain conditions for a gas, essentially constant for a given mass of gas and at constant temperature. So, that was one empirical observation, they were of course, deviations from it and as we know today real gases do not obey this exactly, but to a good approximation they do at sufficiently high temperatures. And the other law was Charles's law, which said that V over T was equal to constant for a given amount of gas, given mass of gas and at constant pressure.

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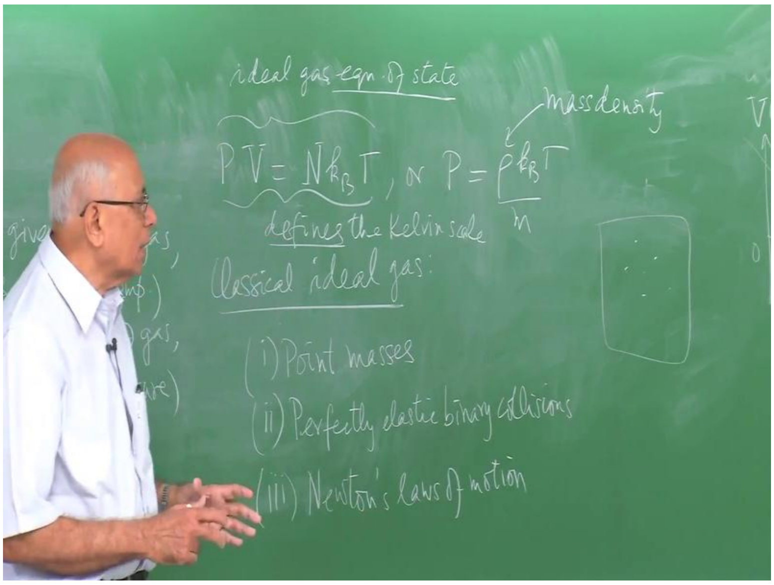

Together, these two laws could be subsumed into a single law which today we know as P V equal to n times R T, which I will write in a slightly different way. I will write this, since I want to emphasize the number of particles N times k Boltzmann times T. So, together these two laws let to this law here, which as I have already mentioned could also be written as that mass density times k Boltzmann T over m, this is the mass density. I should write it P equal to, I should write it as or P equal to rho k Boltzmann T over m and this is the mass density, says the pressure is directly proportional to the density at a fixed temperature and so on.

Now, this is what is called the ideal gas equation of state, an equation of state in this context is a relation which tells you what the pressure of this system is, given it is volume and it is temperature or it is density and it is temperature. So, where is this come from? Well, essentially it came from this thing here, but today by Einstein we know what it corresponds to. It corresponds to saying that you have a gas in which the interactions between the molecules are of a very specific nature and these assumptions are the following.

The interaction as we know is essentially into molecular interaction, but in this case is so called ideal gas, classical ideal gas and I will say why I call it classical. It corresponds to saying that you take a set of particles, put it in a container and the only interaction that you assume between the particles are two body elastic collisions, perfectly elastic collusions. So, one point masses, two perfectly elastic binary toward a time, between the particles and between any particle and the walls of the cavity and three, each particle obeys Newton’s laws of motion.

So, this is classical dynamics at the molecular level, the assumption of point masses and toward a time collisions, these three assumptions today enable us to derive from first principles, this equation of state. This is called the ideal gas equation. In general, for a gas for a given amount of gas, if you write the pressure as the function of the density and the temperature, that is called an equation of state and the other equations of state of which are make one brief mention of a non ideal gas a little later, but the ideal gas equation of state is a simplest thing, you can write down and it is derivable from statistical mechanics.

But, in the context of thermodynamics it is an input, empirical input from these laws which were experimental laws here. So, much so, that temperature in thermodynamics is defined why are the ideal gas equation are state, this says to define the absolute scale of temperature, so this thing here defines the Kelvin scale. Now, what is this assumption actually mean that you have only elastic binary collisions and no other interaction.

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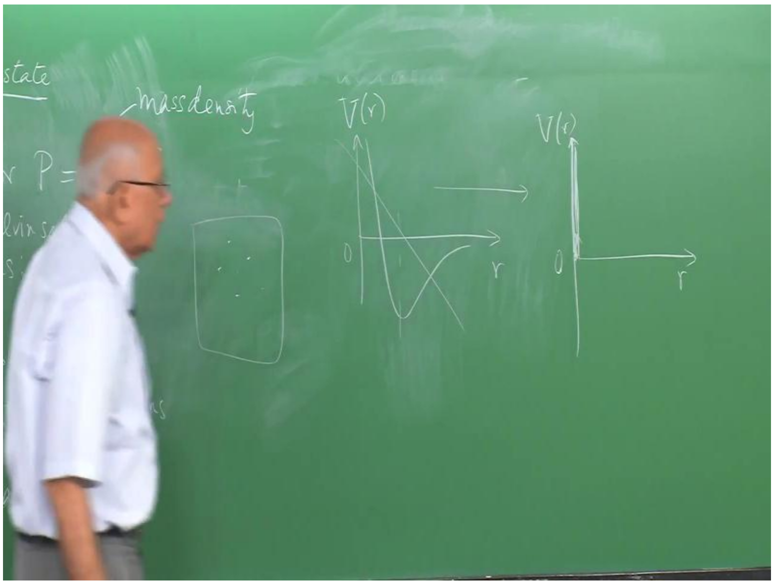

Well, what it means is if you go back toward, we have talked about earlier namely the intermolecular potential for neutral objects, neutral molecules is generally of this form. The potential energy of a molecule which is at a distance little r away from another molecule which is at the origin is given by shape of this kind, it is got short range repulsive force and a long range attractive force, because still this point here the force is repulsive, because the slope of this graph is negative.

So, minus a slope is positive which pushes it outwards and the slope beyond this point is positive, which means minus the slope is negative or there is an attractive force here. And we also saw, I pointed out that one simple model would be to say that this goes like 1 over r to the power 12 goes to infinity like that as r goes to 0 and that D case to 0 like 1 over r to the 6 called the Vander Waals force or potential here. Now, that is replaced, these thing is replaced by the assumption that you completely neglect the attractive force and the repulsive force acts only at the origin namely point forces.

So, the potential is infinite at r equal to 0 plus infinitely and it is 0 everywhere else and that is the graph, it is not a very good approximation, but remarkably enough, it terms out to be good enough for most real gases at sufficiently high temperatures and sufficiently low densities. This is true; this I think works quite well, the ideal gas equation of state works quite well. So, in that sense the ideal gas equation of state is a great help to us in thermodynamics, because it has helped us the fact that this gas is existed and under suitable conditions they satisfy an equation approximately of this form, has help as a great deal in unraveling the subject of thermodynamics and statistical mechanics itself.

It is then like a problem which you could solve, like the two body problem or the harmonic oscillator problem in mechanics, the fact that you can solve these explicitly see dissert the solutions see, what it looks like and so on has helped us in this instance also by providing as vector thing of this kind. Now, we know more about the system, we know more about the ideal gas system, we know something very important about it, we actually know what the average energy of this gas is, of gas of N particles is.

So, remarkably even though these are all using about and so on ((Refer Time: 16:43)), under these conditions here of a perfectly elastic binary collisions and so on, we can actually write down in expression for the average energy of the system. And the average energy of the system, let me write this down and the same ideal gas, it is very important to write this down.

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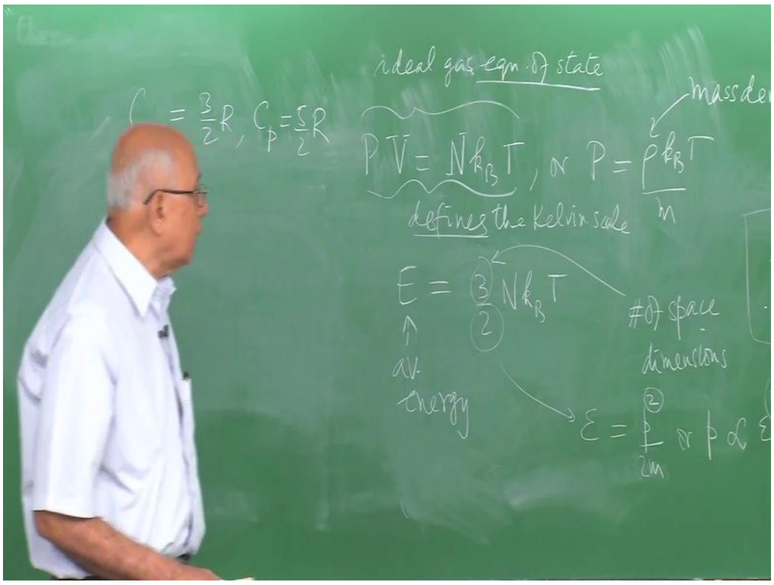

Here, the average energy 3 half N k Boltzmann T, the 3 reflects the fact that the molecules are moving in three dimensions, the 2 is a little more shuttle, it arises from the fact that the relation between the energy the kinetic energy and the momentum of each particle is a quadratic relationship. So, this let me just make these statements without justifying them further, this is the number of dimensions, number of space dimensions and these two comes from the fact that the energy of each particle, the kinetic energy of each molecule is a quadratic function of the momentum of the particle.

So, these two appears here in the denominator, but it comes directly from the fact that r p is proportional to Epsilon to the power half. So, it is the same half that appears here, this place here, so essentially the same half. So, even though this looks like an arbitrary statement, that the statement made in elementary treatments which says that the average energy per degree of freedom is half k T called the equally partition of energy.

It really comes from the fact that the momentum is the square root of the energy here proportional to the square root of the energy, so that is the half that reflects itself here. Now, the fact that we know this energy and you know this, says that you know pretty much everything about this system, not true in general in thermodynamics. Thermodynamics generally deals with systems whose equation of state you do not know, we may guess what it is, we have good approximations to it, but we do not really know what it is exactly, we do know the equation of state exactly.

On the other hand the ideal gas is a simple model, where this knowledge is available to assign therefore; we can make a further progress here. For instance, once you know this you can deduce a property of the ideal gas, which you cannot deduce in thermodynamics, for normal thermodynamic systems and let me explain what that property is. The specific heat of a system, whether it is a constant volume or constant pressure or any other condition, is not derivable from thermodynamics from the laws of thermodynamics.

It is an input parameter, the specific heats are always input parameters and the reason for it is because is a very deep one, it is because the specific heat is related not to the average energy, but to the variance of this energy, namely the square of this energy mean square minus the square of the mean to the variance or standard deviation of the energy, that goes beyond thermodynamics. I have already mentioned that thermodynamics is a science of average quantities; the fluctuations about this average to the thermal noise are neglected in thermodynamics and not directly taken into account.

But, this does not mean the thermodynamics does not involve any quantities, which involve the higher moments of the energy or other physical quantities. Fluctuation are important, they are crucial they in fact, are responsible for the system being in equilibrium. On the other hand thermodynamics does not directly deal with them, it deals only with average quantities. But, anything which involves, any physical quantity which involves something beyond the average like the standard deviation is an input parameter into thermodynamics and that is what it is for most systems in thermodynamics.

You have to tell me, what the specific heat of the system is at constant volume or constant pressure or otherwise in most cases, but the fact that in the ideal gas situation alone. We can actually write an explicit expression down for this energy tells us that we can write down what the specific heat also is and that is why, as you all aware in thermodynamics in elementary treatments. We have the statement that the specific heat per mole of the gas at constant volume is 3 halves r and at constant pressure it is 5 halves r, for a monotonic classical ideal gas one mole of a monotonic ideal gas.

So, I repeat specific heats of input parameters in thermodynamics except in the case of the ideal gas, where you actually have detailed information, because we know what not only what the equation of state is, but we also know what the internal energy of the system is explicitly. Then, we know all the other properties of it as well. Once again I repeat that this equation, although it is written down empirically in thermodynamics and is used to define the temperature, absolute scale of temperature this equation is derivable from statistical mechanics, fairly easily using these assumptions ((Refer Time: 22:23)).

What we need are these assumptions that these are point particles that the potential, ((Refer Time: 22:29)) the interaction between particles is of this kind and that around the binary collisions here, completely elastic binary collisions that suffice to actually deduce what the equation of state of this system is here. We can go further, you can also deduce what the entropy of the system is, we can find out all the thermodynamic properties of the system from equilibrium statistical mechanics.

I might as well mention that right here, but we are not going to do that, we simply going to take this equation here and ask, what information can we get from it? What is the most general thing we can do with it and so on and so forth. Having said this about the ideal gas, this is a good time to also ask what happens if the gas is not an ideal gas. This is the correction beyond the ideal gas and a great deal of effort was spent in the 19th century in trying to find out, whether there exist a kind of universal equation of state which will describe real gases or non ideal gases, the classical non ideal gasses. We will come to that in a second.

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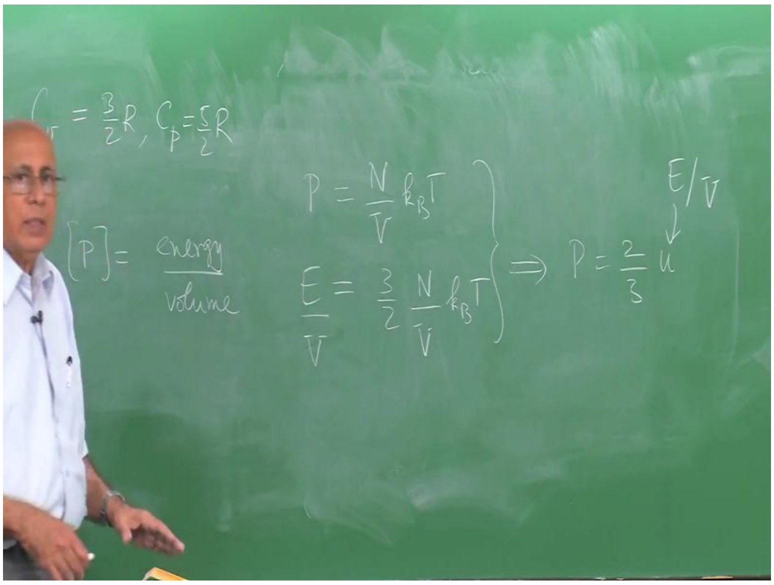

But, before that I want to point out another fact which is the, notice that the pressure the physical dimensions of pressure is force per unit area or energy per unit volume. So, it is like the energy density, ((Refer Time: 24:10)) on the other hand this thing here can also be written as an expression for the energy density here, you can see that it is 3 half N k T. So, once again if I introduce the number density E over V is 3 half N over V k Boltzmann T, on the other hand the pressure P equal to N over V k Boltzmann T and today the, these tell you at once that it is clear that the pressure is the energy per unit volume and the only energy we have in this problem, the energy per unit volume is a energy density itself.

So, these must be related to each other and this equation are state explicitly tells you that two-thirds the pressure equal to two-thirds, little u this is the energy per unit volume here. I point out again, that this relation specific here in this case to the classical ideal gas, the 2 comes from the quadratic relation between the energy and momentum of an individual molecule, the 3 comes from the fact that the molecules move in three spatial dimensions and those facts become clear, when one does a statistical mechanics.

But, this is yet another way of writing down the equation of state directly in terms of the energy density here, because that is the only quantity which has the correct dimensions, the same dimensions as the pressure itself here. What else, can we say immediately from this in a great deal, one can for instance compute what is the compressibility of this gas, in we have already done a little bit of elasticity. So, we can find out what the bulk modulus of this classical ideal gas is, it is a fluid it is got a pressure and find out what the bulk modulus is.

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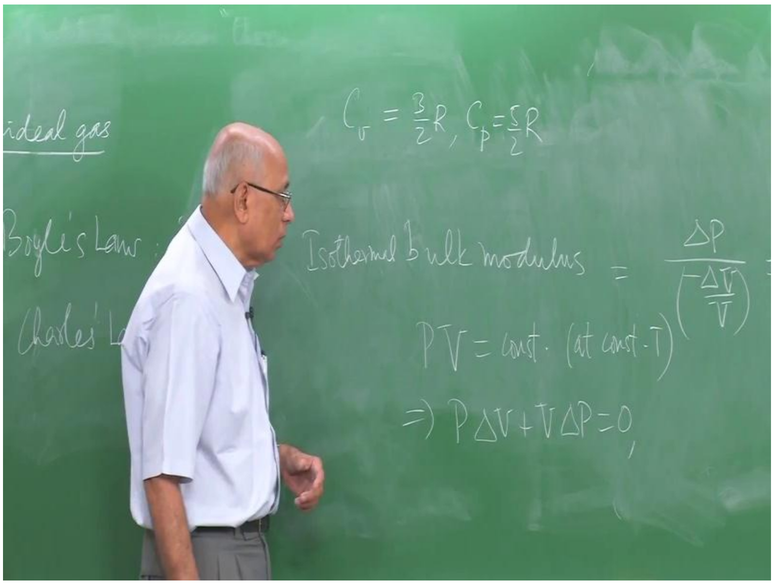

The bulk modulus as you know has the physical dimensions of a stress, a strain a stress divided by strain; the strain of course, does not have any dimensions. So, under a change delta P it is minus delta V over V, this is dimensionless and that is the bulk modulus then. What we need to do is to compute, what this quantity is for a classical ideal gas in the case when these become infinite decimals here. Now, it is got to have that dimensions of pressure, which is got to have the dimensions of an energy density.

The only quantity which has dimensions of pressure in this problem is a pressure itself. So, I would actually expect that this thing terms out to be the pressure itself and indeed it does. When we looked at the speed of sound in the isothermal approximation, we discover the bulk modulus was equal to the pressure itself and let us we derive this again, because you have P V equal to constant. At constant T, this implies that P delta V plus V delta P equal to 0 and that immediately tells you that this quantity is equal to P, the pressure itself.

So, the compressibility of this gas which is defined as 1 over the bulk modulus, I should really call this the isothermal bulk modulus. It is the pressure itself and the isothermal compressibility of this gas which is the reciprocal of the bulk modulus is 1 over the pressure here, where the fact that the compressibility is a reciprocal of the pressure, is the reason why when you inflate air in the tyre, a rubber tyre you kick it to see how reject this object is, to how resistant it is to compression and what you really measuring is the pressure directly.

So, the fact that you kick a tyre in order to see if it is inflated properly is really a measure of the pressure inside the gas. What you are doing it is through the compressibility by estimating the compressibility. The adiabatic, we have not talked about adiabatic here, but the adiabatic compressibility is also easily found, what you need to use is P V to the gamma equal to constant. We will come back to this and look at the properties of the ideal gas, when we look at processes other than isothermal processes here.

I will also make a mention at that time of a, how you go beyond the ideal gas and what is the first kind of correction one would think of and this is what Vander Waals state in his famous equation.