Mechanics, Heat, Oscillations and Waves
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Lecture – 37
What is Thermo Dynamics

The last topic we are going to cover in this course, in this very short course is a brief description of a very important subject namely that of Thermodynamics. Now, we begin this course by understanding a little bit about the mechanics and dynamics of individual particles, single particle, two particles or a collection of particles and so on. We went on to understand, what happens when you have a wave motion, when you have waves in a continuous medium such as the string or air or solid medium and then, we also studied a little bit about the dynamics of fluids namely, what the equation of motion of a fluid is, what it is consequences are and so on.

So, logically the next thing to do is to ask what happens when you have a very large number of collections of particles and this is what matter generally is. Because, we know that matters consists of atom and molecules and we know that the number of these molecules or atoms in any normal size sample of matter is exceedingly large, astronomically large. In fact, it is bigger than astronomically large, because it is of the order of Avogadro's number typically, which is of the order of 10 to the 23 or 10 to the 24.

So, we are faced with this problem that we need to be able to understand the collective behavior of an exceedingly large number of elementary consequence, whether they are atoms or molecules, does not matter, but we need to be able to come to cribs with this problem of describing system with very large number of elementary constituents or a very large number of degrees of freedom in technical terms.

This requires totally different techniques from the once that we have been talking about so far and thermodynamics is one such technique. In fact the subject itself, when I am going to say a large number of things in words today, I am going to do a lot of talking, because it is a deep subject, it has very profound certainty in it and it is good that we understand, what is involved in this subject very clearly before we begin to understand or carry out the mathematics involved in the subject.

I want to make a special point of this today, because the general impression that the beginning student gets from courses, elementary courses on thermodynamics or statistical mechanics is that, it has to do with a lot of partial differentiation, partial derivatives, using the calculus in various ways and so on without much physical content. Nothing could be further from the truth, the subject is an extremely physical one, it is based on physical postulates, it describes real physical system and is in some sense a very fundamental subject.

Finally, say so there is several definitions of thermodynamics possible, the one that seems most suitable here would be to say that it is in fact, the study of transfer of energy from one system to another if you like or the energetic of systems. And as you know, energy is one of the most fundamental physical quantities with which we are pre occupied by most of the time. So, in that sense it becomes crucial to understand how to deal with systems with a very large number of degrees of freedom.

Most of what I am going to say today will be quantitative, will be statements that I make and I will try to the extent possible to write them down on the board even at the expands of a being very slow as I go along in terms of coverage of material. Because, I think the issues involved are so deep and so settled, that it is good to spend time and understand them clearly write from the beginning.

Throughout, I am also going to be pointing out that thermodynamic itself is not a fundamental subject in that sense, it is derived from a deeper subject called equilibrium statistical mechanics, which is outside the preview of this course, but which is needed in order to understand the loss of the thermodynamics. And let me say it, write out in the beginning the loss of thermodynamics a very small set of loss tell you a huge amount of information about systems, large systems, but the loss themselves are not really fundamental loss, these loss are derivable from a mode, from deeper considerations from what is called the fundamental postulates of equilibrium statistical mechanics. We probably will not get to that in this course except that passing dimensions, but it is good to remember that the thermodynamic is a derived subject in a very, very specific and precise manner which I will explain.

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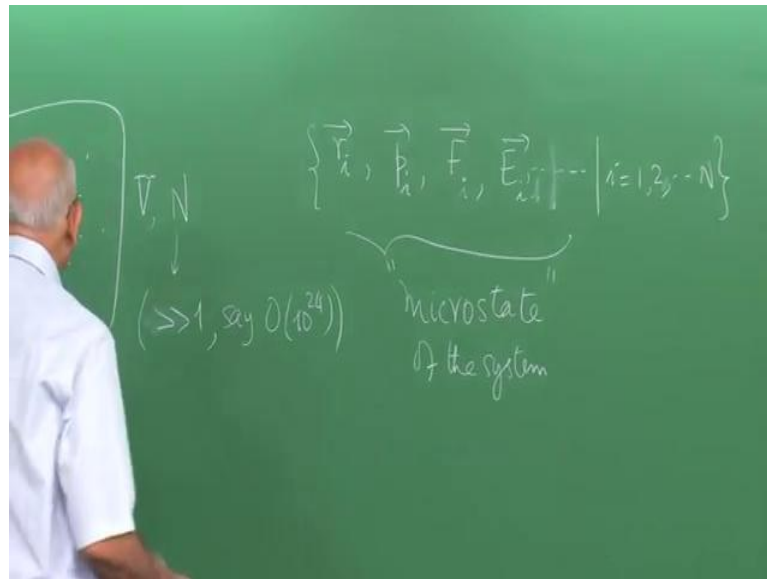
So, our first problem is to ask what happens if you took a container of some specified volume V and you put N particles in it, where this N is very large. So, much, much greater than 1, say of the order of 10 to the 24 or something like that and you have these particles moving above in this container, if it is a container of gas interacting with each other and we would like to know what physical information we can get from this system, how to understand the physics of this system of particles which are interacting with each other.

You can see immediately based on our experience in mechanics, we wrote down the equations of motion for one particle or two particles in a center force problem. Even that was formidable and quite difficult to solve. When I pointed out, that when you have three or more particles, you really do not have enough constants of the motion to solve code and code the problem analytically in closed form. So, when you have 10 to the 24 particles, it is completely hopeless to do this, but still in principle we could ask, what is it that we need in order to understand the physics or the dynamics of the set of particles.

What you need is of course, the coordinates of all these particles, where i labels the particles 1 to N if you like, you would need to know the moment of p i, you would need to know the forces on all these particles due to every pairs. So, you need to know what is the force, net force on the particle i F sub i and what is it is angular momentum and what is it is energy and so on and so forth.

You would need to know all these dynamical variables at any given instant of time and then, in principle you would solve Newton's equations of motion for each particle and write down the solutions for all the dynamical variables at any subsequent instant of time. Now, this is; obviously, in practical if you have 10 to the 24 particles, not only is it in practical, it is virtually impossible; not only is it virtually impossible, it is actually useless in some sense.

Because, at the end of the day, when you look at the system like this, the questions we ask of the system do not require a detailed knowledge of these quantities here. The questions we would ask, for instance if this is a gas would be, how much should I heat this gas in order to make it to a certain amount of work, what is the energy input that I can give to this gas in order to extract some work, how much heat comes out of this gas when I do some work on it and so on.

So, these are questions which have nothing to do with individual particles at all, the clearly question which have to do with on a much larger coarse-grained scale. For instance if I want to know what is the pressure of this gas, what I would do is to ask what is the force per unit area on the walls of this gas on the average. I do not worry about, what happen every peak of second, because the particles interact, they hit the walls etcetera and the action is actually happening in peak of seconds or less, that is not what I am measuring.

What I am measuring is, over a larger times scale I am measuring some kind of average force here. So, the key word here is average, I am always averaging overall the possibilities of what the elementary consequence can do. So, this is the whole point that the knowledge of these variables which I should called microscopic variables, I am going to use this term microscopic in a very specific sense.

By microscopic, I mean the variables pertaining to each individual elementary constituent of the system namely each molecule or each atom of this system, those are the so called microscopic variables. And if I do this for all the variables, a specification of all these tells me everything in principle that I need to know about this system at any given instant of time and I would call that a microstate of the system.

A microstate involves knowing this for the full set up particles, so dot, dot, dot for i equal to 1, 2 all the way up to N. So, microstate involves a great deal of information in it,

it involves knowing completely the state of each elementary constituent of the system at any given instant of time and; obviously, for a system like this, the number of microstate is enormous. For instance, even if each particle, instead of a particle imagines replacing it with the coin or something like that, a coin has only two stage, there is a head and there is a tail.

So, if you have a n coins, the number of possible head and tail combinations that you can form from the set of n coins is 2 to the power N, it is already exponentially large in the number of particles N and that is what happens in a real system. The number of possible microstate is truly astronomically large; it is exponentially large in the number N here that is important to the number here. So, even listing all these states can be quite of formidable task in general, but in principle we can think of doing so and we know that there are large numbers of microstates of the system. On the other hand, I already said that the kind of questions we ask of such a system would be average questions. There will be questions about what is the average total energy of the system.

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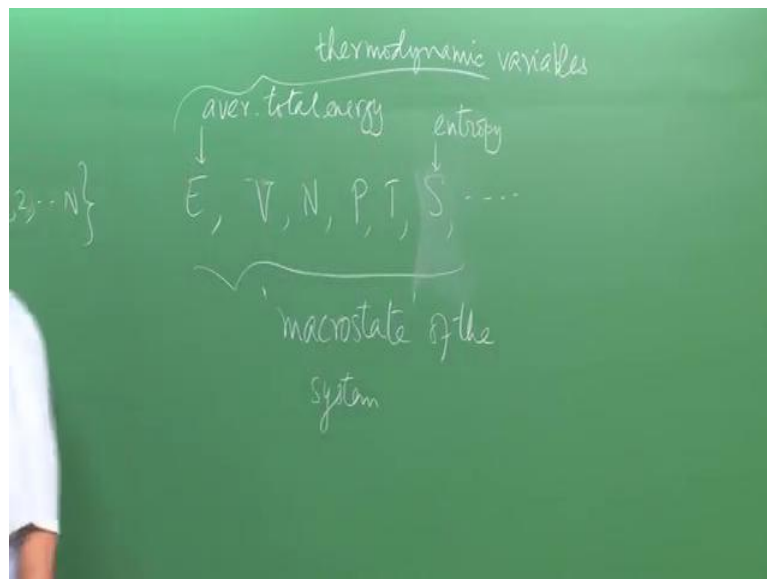
So, let us write down some of these variables, average total energy. What is the volume of this system? What is the number of particles in the system, the total number of particles here and then, we could ask more detail questions like, what is the pressure of the system, what is the temperature and so on. We have to define these quantities yet, but

we have a whole lot of these things here, we also know that if it is a thing like a gas or a liquid or something like that, they would be a lot of disorder.

Then, we have to specify what is meant by this disorder, we must have a quantitative measure of this disorder and that is called the entropy of the system. I will write the symbol down for it and explain what it is little later, so there is the symbol and so on. So, we have a whole collection of these variables, which have not, which are in principle related to these microscopic variables, but in practice would be some kind of averages over various possibilities for these microscopic variables here and what would one call these, I call them microscopic variables and a specification of this would be specifying a microstate of the system.

And the statement I am making now is that, in thermodynamic and in general for such system we are interested microstate of the system. We trying to find out here, what certain average properties are like for the system and then, extract as much information as possible from it and what thermodynamics does is to study these average quantities, if you like these are thermodynamic variables, these set of variables are thermodynamic.

There are several other thermodynamic variables, we will talk about a few of them, but you should appreciate right away the distinction between these microscopic variable pertaining. There is nothing to do with a microscope, the word is used only in the sense that these are the variables corresponding to the very small constituents, individual constituents of our system and these variables or the microstates are specified by specifying all these microscopic variables, whereas the thermodynamic state of the system is specified by specifying the macroscopic variables, the thermodynamic variables.

Next point, the whole science of thermodynamics, the word is a misnomer unfortunately. It should have been called thermo statics, because there is no time dependence in the thermodynamics; not at this level, in any case. Thermodynamics deals with systems in thermodynamic equilibrium and let me so important definition that we need to write it down.
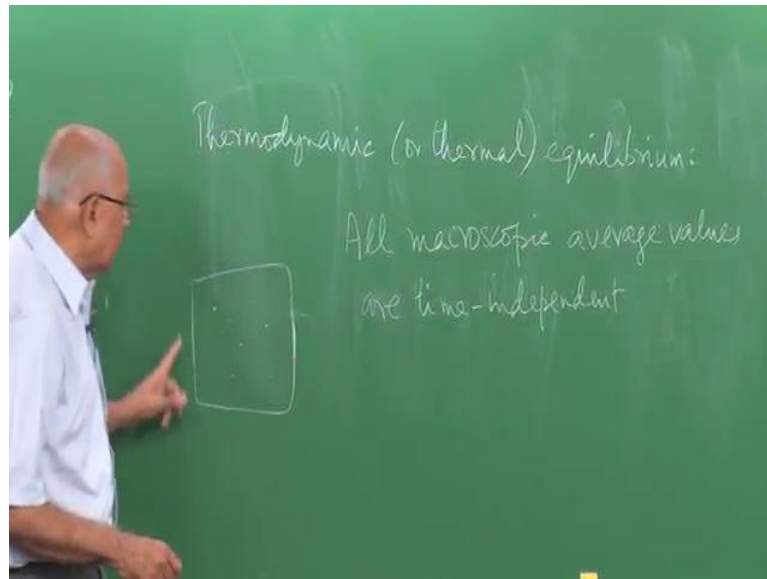
So, thermal thermodynamic, it is called thermal equilibrium; there is a technical way of defining what thermal equilibrium is, but unlike mechanically equilibrium where we understand for instance if you have a particle in a harmonic oscillated potential, the equilibrium point is the minimum of this potential. Similarly, we can talk about the thermodynamic equilibrium, this would be the state which corresponds to the thermodynamic variables being at some minimum, sometimes maximum depending on how you define it.

The minimum of some thermodynamic potential if you like, which is not got the connotation of potential energy, but it can be cost in a language which looks like this, which looks like the minimum of some energy. But, the better way to define thermal equilibrium is to say that it is a state in which of a system, a macroscopic system in which these averages, these thermodynamic variables have values which are time independent.

So, there is no time dependence at all, all macroscopic average values are time independent. As I said, this can be made rigorous, but for our purposes this affixes at the moment, this definition is enough macroscopic average values. Now, of course, this means that if you go back to this analogy of the gas here, this means we are thinking of a situation where the system is static, the macroscopic system in this sense that the

pressure of this gas which is the average force exacted per unit area of the walls of the container is independent of time, it does not change with time at all.

Of course, dynamics is going on inside things r time dependent, because the molecules himself are flying about colliding which each other and so on and there is a lot of dynamics going on. This system is not in mechanical equilibrium in that sense, the elementary constituents need not be in equilibrium at all of course, they are moving, but the averages of the macroscopic quantities are time independent. And of course, should you want to change the state of the system, you must do so in such a way that thermodynamics continuous to apply, which means you always do it sufficiently slowly that the system attains thermodynamic equilibrium always.

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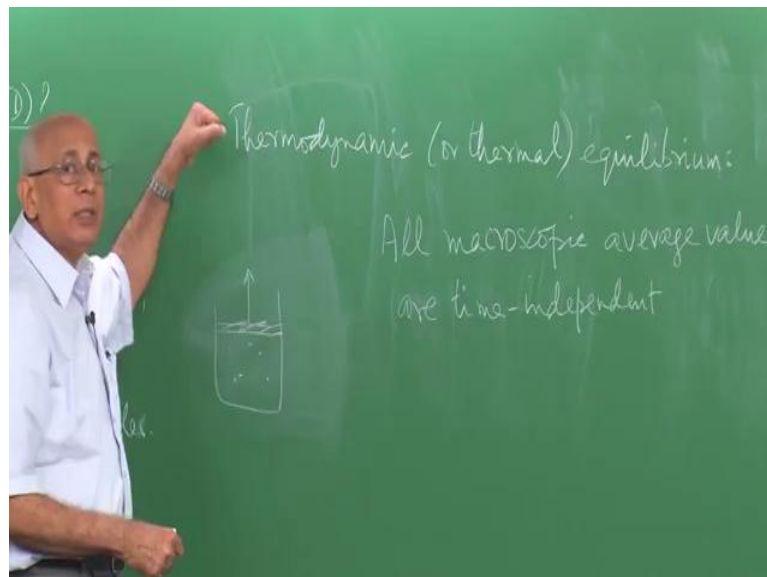
For instance, a very famous example would be to take a piston, gas and put a piston over it and move the piston out very slowly and there is a gas here. So, what you causing is an expansion of this gas here, but it is done so slowly, that at any instant of time compare to the time scale on which the molecules move, the system is essentially static, that the average quantities are time independent and this is called quasi static thermal equilibrium, if you like.

So, the processes are slow enough that you do not have any sudden time dependence coming in. One can extend this and consider cases, where there is time dependence, but

in the most elementary definition I am talking about here, there is no time dependence in these quantities.

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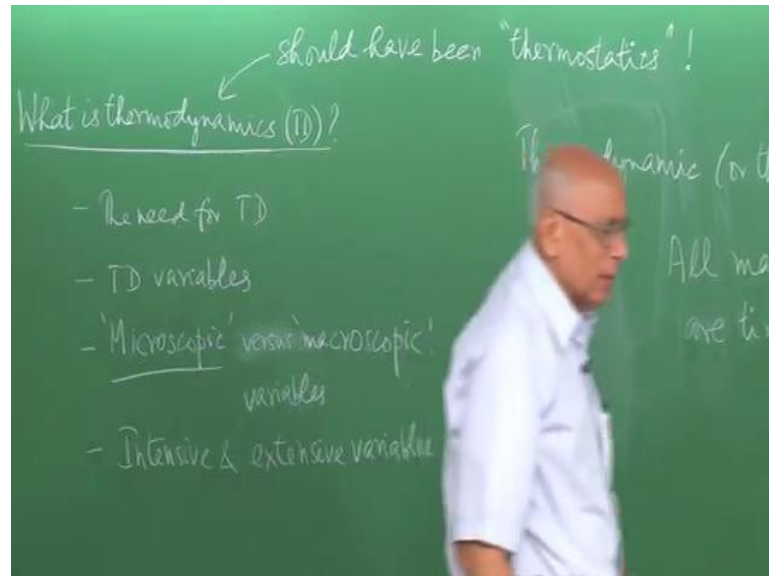
So, the word itself thermodynamics should have been something likes thermo statics, but we are stuck with this term here, so we will leave it as it stands. So, now, we made some statement so far, that we are going to look at cases where you have a large number of elementary constituents, we will not worry about the detailed dynamics or what happens to these constituents, but we will look at average quantities which are averaged over all possible, various possible configurations of the elementary constituents themselves and that should give us some information.

The real miracle, the incredible thing is that even though we are sacrificing detailed information about the microscopic constituents, we can still using just a very small number of loss namely the loss of thermodynamics extracted great deal of information about these average quantities that we are interested in. So, that is the real miracle of thermodynamics here. In the same breath, I should always say that the system itself, by I mean talking about average quantities such as the average energy and so on. What do I mean by that?
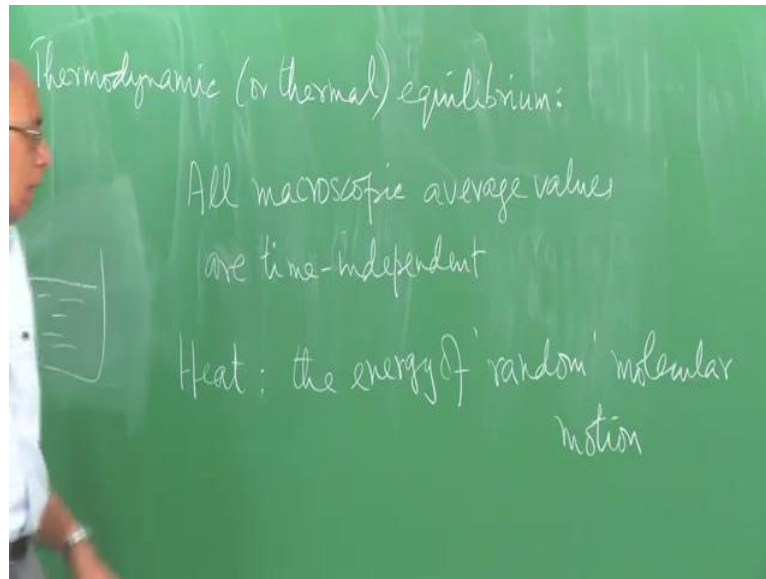
Well, if I take a beaker of water and put it here on this table in contact with the rest of the atmosphere, then as you know if the water is very hot, it is hotter than the atmosphere it losses heat to the atmosphere. The atmosphere gains a certain amount of heat and the whole thing equilibrates at some common temperature, this water is then in thermal equilibrium with the rest of the system, which I would call a heat path or a ((Refer Time: 19:58)), the atmosphere around it.

Now, the molecules of this object is moving around, but the fact that it is at a fixed temperature is a reflection of the fact that the average kinetic energy of each molecule is fixed. It remains unchanged in time at some value, which is determined by the temperature in fact, the temperature is a measure of this average kinetic energy. But, what is interesting is that all the time there are molecules flying out of it and getting back in to it.

There are things going in to the vapor above the liquid and molecules getting back in to the fluid here, there is lot of agitation, thermal agitation here. So, the actual total energy of the molecules of this fluid is not fixed, it is fluctuating, it fluctuates extremely rapidly with time. So, that is the whole point, that an object like this does not have if it is in contact with that atmosphere does not have a fixed energy.

A system at a constant temperature does not have a fixed energy, on the other hand it has a very definite average energy and the symbol E that I have used here is for the average

energy, average over all the fluctuations which arise due to the random thermal motion of the molecules here and of the atmosphere. Now, this realization of what is meant by thermal noise took a long time to occur, it is at the root of what we mean by heat itself.

So, let me write that down heat itself, the energy of random molecule or atomic motion at the atomic or molecular level, the so called molecular motion. It is not random in principle, in principle if you actually know all the forces, all the momentum, all the particles, all the position and so on, then in principle one can compute what these quantities are at later instance of time in principle and then, we randomness.

But, in practice of course, there is randomness, because we do not have that detailed information. So, this random molecular motion, the energy of corresponding to that is what we called heat, it took a long time for this recognition to sink in, it came in the 19th century. Once people like Boltzmann and Gibbs and Maxwell and so on, illustrated what is meant by thermodynamic and statically mechanics.

Then, it was realized that the fluctuations that arise due to random molecular motion is very, very crucial, these fluctuations are important and thermodynamics is a science, which averages over these fluctuations and deals with these average quantities alone. So, in that sense thermodynamics is a science of averages of macroscopic quantities, it is not that the fluctuations are unimportant, they are important, but there is no way of calculating them in general inside the preview, in the preview of thermodynamics itself.

You need to go to a more fundamental subject namely equilibrium statistical mechanics in order to find out, what the effect of the fluctuation says and say little more about this as we go along, because it is important to understand the origin of things like specific heat. Now, having said this about thermodynamics, let us immediately ask what sort of variables have you dealing with now, what are thermodynamic variables really.

We listed a few there, but it is there a better way of writing these variables. Well, since we are going to deal with large system, it is clear that all these variables can be quite large in numerical value. Avogadro's number itself is much, much larger compare to unity and it turns out that you have two kinds of thermodynamic variables.
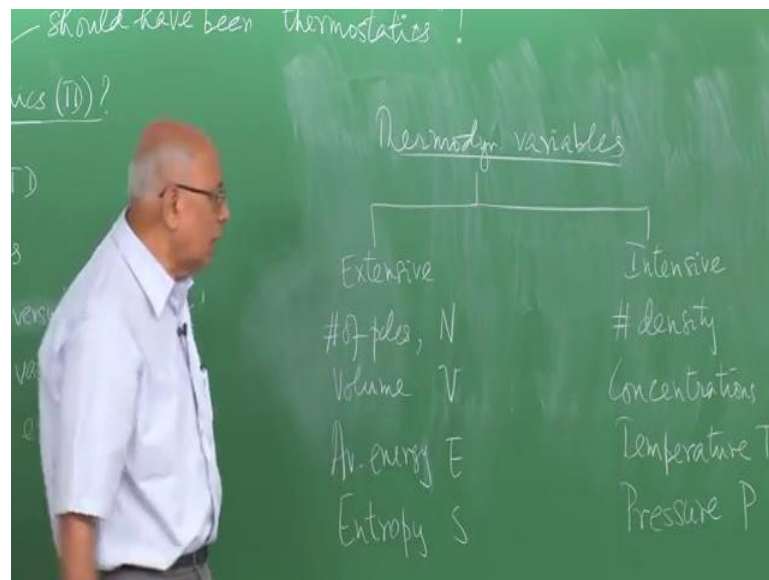
One is the extensive variety and the other is the intensive. What I mean by extensive variables are those which depend on the systems size, in other words if the system size or the number of particles N, that is foremost example of an extensive variable, practically defines what I mean by an extensive variable, the volume of the system. These are extensive variables, they increase with the size of the system in some lose manner, on the other hand corresponding to these two objects, one can think of an intensive variable which does not depend on the actual physical size of the system.

For instance, the number of particles per unit volume, so number density N over V. This clearly does not depend on the size of the system, if I take certain volume and put a volume V and put N particles in it, I double V I double N the density does not change. So, it is an intensive variable here and more similarly whether it is the mass density or number density does not matter. If I have several spacious of a chemical molecular spacious is there, then the concentration of various spacious is certainly an intensive variable, the temperature is an intensive variable.

In fact, the temperature is related as I pointed out to and we will come back to this to the average kinetic energy of each molecule. So, it actually dependent on individual molecules, the property of individual molecules which means you take the total energy divide by the total number of molecules and you get something like the temperature

effectively. So, this again is in intensive quantities here, the pressure is an intensive quantity.

Why do I say this is an intensive quantity? This is the average force per unit area exacted for example, in a fluid or a gas, but what would that in turn depend on. This pressure would again be the force averaged over a large number of particles and you can finally, reduce it to a quantity which is dependent on the density and the temperature. Anytime you write an equation of state, you really saying what the pressure is in terms of other intensive quantities and in case you are not convinced by this, let me point out.

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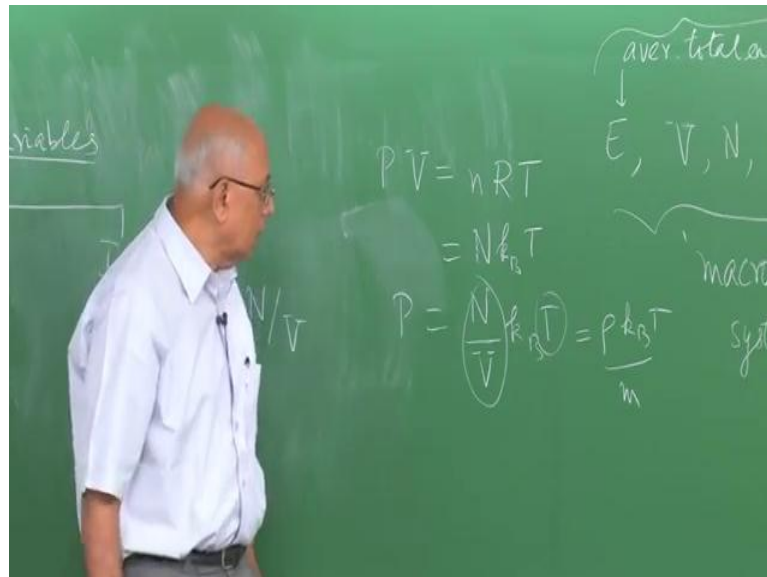
You already know this; we are going to do this again. Remember the ideal gas equation of state was P V is equal to n times R T, this is the form in which you use to the law. Let us not call this n ((Refer Time: 27:39)), n is the number of moles that is what you are used to. This equation can be rewritten as P V equal to the number of particles times Boltzmann constant times T. So, this N and you can rewrite this as P is N over V here Boltzmann T and this quantity is an intensive variable, this is an intensive variable.

Therefore, this is an intensive variable as well; the pressure is definitely an intensive variable. Can we think of anything else here? Well, certainly the average energy of the system, ((Refer Time: 28:19)) so I use the symbol E although it will turn out that very often for a specific kind of energy, you use U here for the internal energy I will talk

about what this U is little while later. Similarly, the measure of the disorder of a system is so called the entropy of the system and so on. These are all extensive variables.

If you increase the system size, these quantities also increase in proportion, on the other hand these quantities do not and they form intensive variables. Now, clearly when you have an equation between two quantities on the left and right, the left cannot be an extensive variable and the right cannot be an intensive variable, they must be of the same kind as we see here. Sometimes, you may want to write things in terms of extensive and intensive quantities, but then the fact is that buried in here, in n R is this number here and therefore, that is an extensive quantity.

This is an extensive quantity and this way of writing it tells you, it is a relation between two intensive quantities. If you bring the mass density into the picture, this is rho k Boltzmann T divided by the mass of the molecule, that is the mass density which is intensive that intensive and this is incentive here.