Mechanics, Heat, Oscillations and Waves
Prof. V. Balakrishnan
Department of Physics
Indian Institute of Technology, Madras

Lecture – 41
Van der Waals Equation

We have been looking at some elementary properties of thermodynamics, the laws of thermodynamics, the classical ideal gas and so on. And today, we turn to a very, very important topic in the study of thermodynamics and statistical physics in general, namely the fact that substances undergo phase transitions, changes of state for instance from solid to liquid or liquid to gas, gas to solid and so on and so forth.

We would like to begin to understand, how this happens and the way to do this is to as a preliminary start with the idea of an ideal gas. And then, ask to what extent does it actually mimic a real substance and what is the basic difference between a real gas and then ideal gas.

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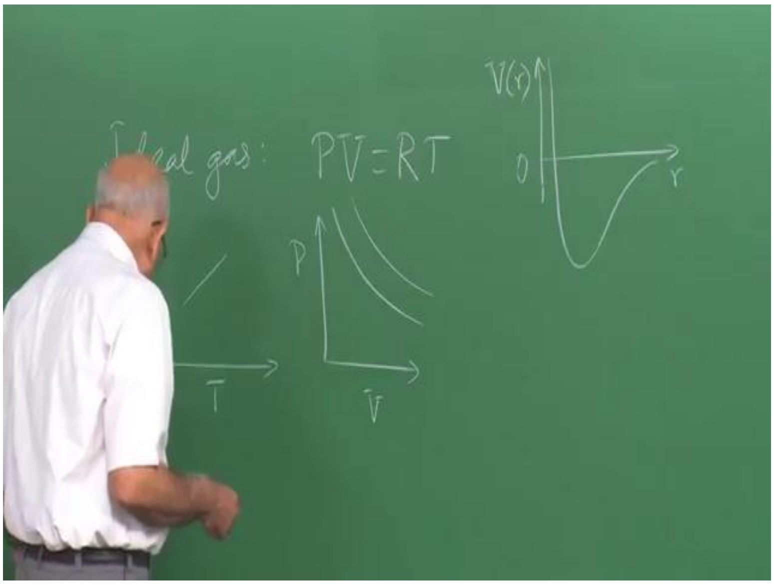

So, let us go back to the ideal gas and notice that in the case of the equation of state was P V is R T for one mole of the substance. And this imply immediately that in thermal equilibrium if you fix the pressure and the volume, the temperature is fixed; if you fix any two of these, the third one is fixed by this equation of state. And we can plot in the so called phase diagrams, we can plot for instance P as a function of T and this is clear that if V is constant and you have a fixed amount of material is some kind of straight line.

On the other hand, you could also plot P versus V here for a fixed value of the temperature and you get a rectangular hyperbola of this kind, you increase the temperature you get a different hyperbola etcetera. There is no way in which this substance, this gas can actually condense to form a liquid. On the other hand, we know that in real life when you take a gas and you increase the pressure on it and decrease the temperature, they comes a stage when the gas condenses in to a liquid.

So, this ideal gas law is clearly inadequate to explain the fact that matter condenses at lower temperatures into the liquid and solid forms. Now, how do we go about trying to fit that in into our formalism? The way to do this is to go back and ask, what did this gas law comes from, remember that it came from the fact that if you plotted the intermolecular potential V of r as a function of the distance.

So, imagine you had one molecule at the origin of coordinates and the another molecule at distance r from it, then the real intermolecular potential for neutral molecule is typically of this form as we have seen several times. Namely below a certain distance the force is repulsive and after a certain distance, there is a long range attraction. We even saw what the form of this potential would be like, it is like 1 over r to the 12 diversions here and 1 over r to the 6 decay to 0 on that side.

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The ideal gas on the other hand is based on the assumption that this inter atomic potential, inter molecular potential is essentially infinite at r equal to 0, hard spheres or hard points colliding elastically with each other. And there is no attractive force at all beyond that, no interaction of any kinds. So, it is not surprising that no matter how much you increase the pressure and decrease the temperature, this model will not display condensation into a liquid phase or any condensed phase.

On the other hand, to rectify this, this is the major problem at the end of the 19 century Vander Waals and several other people proposed modifications to the ideal gas equation of a state. And the modifications proposed took into account the intermolecular potential.

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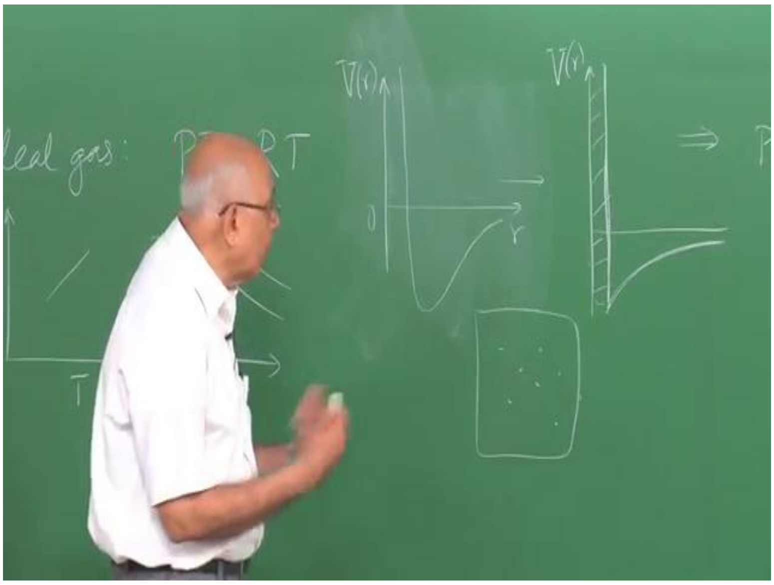

The one that became most famous that we use today as a sort of total typical model of a non ideal gas law is the following. It says instead of intermolecular potential; let us approximate this by the following picture. Let us assume that below a certain distance there is an infinite hardcore repulsion and beyond a certain distance, there is simply an attraction, a long range attraction. So, this is an approximation, this graph is an approximation to this real life graph here, the real physical graph here.

Even that correction suffices actually to produce some features of real gases and this is what the Vander Waals equation of state is. So, this sort of approximation will lead to after lot of calculation will lead to the equation that Vander Waals actually wrote down empirically based on very simple considerations. On the other hand to derive it from first principles using statistical mechanics and this intermolecular potential is a much harder task, but we know where the physics is, in what Vander Waals already wrote down and his idea was the following.

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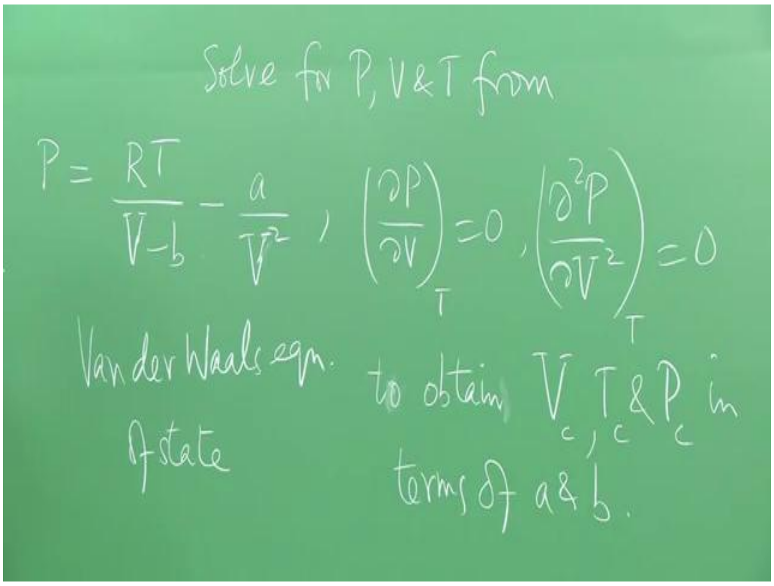

Solve for P, V & T from

$$P = \frac{RT}{V-b} - \frac{a}{V^2}, \quad \left(\frac{\partial P}{\partial V}\right)_T = 0, \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$$

Van der Waals eqn. of state

to obtain $\bar{V}_c$, T_c & P_c in terms of a & b.

He said this implies that the pressure is actually equal to R T divided b v minus b. Because, he allowed for the fact that these two atoms have two molecules cannot get arbitrarily close to each other and sit on top of each other, but there is certain excluded volume due to the finite size of the molecules. Well, today we do not call a finite size for the molecules, because this is a quantum mechanical object and they are fussy objects in some sense.

But, what would we say is that there is a short range repulsive force between them, which cause makes a constant energy too higher for them to actually get in closer than a certain minimum distance from each other. So, that is taken into account by saying the actual available volume to the grass is less than the volume of the container V, so there is a subtraction here.

And then, there is the fact that they attract each other at long distances implies, that if you put them all these molecules inside a container, it implies that due to the attraction they have for each other at long distances from each other, the actual average force and the walls of the container is reduced from what it would have been, if these force have been absent. In other words there is a subtraction to this which is of the form some constant over V square.

There is actually very simple physical argument which tells you why it is 1 over V squared and not V cubed or 1 over V or any other power. But, I do not want to get into that now, what we need to see is that this gas law, this is the Vander Waals the famous Vander Waals equation of state with a and b certain positive constants. And this equation of state is what we would like to work with as a correction to, as an improvement upon the ideal gas equation of state. Well, the first we do is immediately plot what is isotherms look like and instead of these isotherms, you now get a new set of isotherms, which is quite different in shape and it is as follows.

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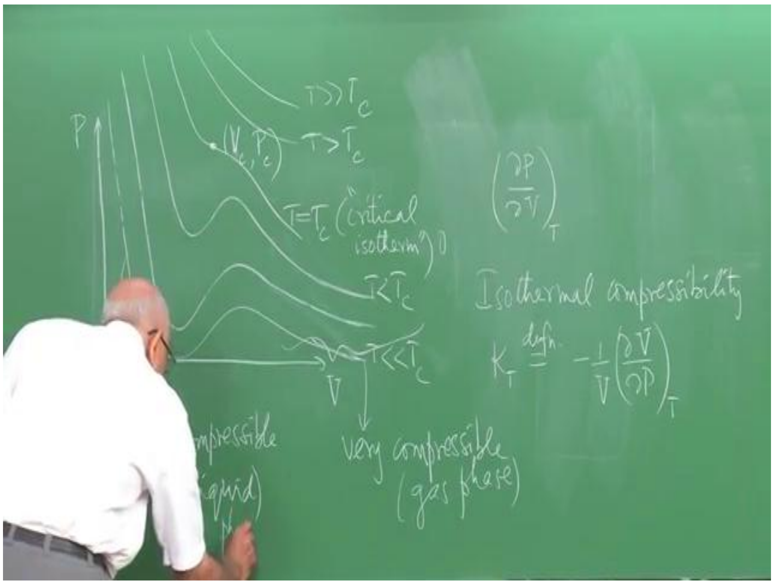

So, we need a larger picture, so let us draw this properly, that is volume and that is pressure and I am going to plot isotherms in other words keep t fixed and ask, ((Refer Time: 07:56)) what this graphs look like when I plot T versus V here. Now, if you rationalize this, move this to the numerator you see immediately that there is a cubic equation, cubic power the third power of V appears. So, the equation the curve is not a very easy curve, not a simple curve, not a hyperbola or anything like that.

On the other hand, if you look at very high temperatures and high enough pressures and volumes, then this correction is negligible and essentially you end up with this R T over V the ideal gas. So, we can a qualitative expect that way out here these curves are going to be like the ideal gas approximately. But, as you come down here depending on the values of the parameters b and a ((Refer Time: 08:37)) remember these are physical dimensions the curve looks very different all together.

And they comes a stage, where you have a curve with a little inflection point and below that the curve starts developing a ne and below that it develops a bigger ne and so on. This is very sketchy, but one could try to fit equation curves of this kind to real gas equations and stack, when the values with the parameters a and b. When we do that, we do not get a curves looks in this, which looks over all in this shape, but it does not look quite like this for easy of convenience of drawing, I have drawn it very schematically.

What really happens is that, with actual values of a and b put in from a real gas data, it turns out that the slope here on the left hand side is much greater than the slope here on this side by a factor of thousands in typical cases. So, it has free serious physical implications, which I will talk about in a minute, but you can see that qualitatively the graph has this shape, so below a certain temperature. So, T greater than a certain critical temperature, this is the isotherm at T equal to T C the so called critical isotherm and you see, what that means and below that the term has a minimum and a maximum.

Mathematically, what happens is, above T C, so here is an isotherm for T less than T C this is much, much less than T C and so on and this curve here T is much, much greater than T C etcetera. Mathematically, what happens, is that there is an inflexion point on the critical isotherm, let me use that critical here. Then, explain, what it means and inflexion point were the slope vanishes p is flat locally as function of V. And the second derivative also vanishes, so the curve which it is also 0 at this point.

And below T C this inflexion point resolves into a minimum and a maximum out here. So, these two separate from each other and go further and further apart as the temperature is lower further and further. What this means now? Is that this gas equation this isotherm this, this equation of state the Vander Waals equation of state is doing the little more than, what will expect of it. It is actually telling us that sufficiently lower temperature and by low I mean lower than this value T C, which by the way can we computed.

So, we can compute this point we get this point has coordinates V c P c and is of course, at temperature T C, we can compute this by solving three simultaneous equations. So, solve for P V and T from this equation delta P over delta V at T equal to 0, this says the slope is 0 on an isotherm. So, constant temperature differentiate this equation are state with respectively you get an algebraic equation put that equal to 0 and then, the curvature is also set equal to 0.

So, solve for this from d 2 P over d V 2 at T equal to 0 you have three equations between three quantities P V and T. And therefore, if there is a solution it is a unique 1 and need it turns out there is a unique solution solve for this P V and T from this to obtain the constant values V c T c and P c in terms of a and b and of course, the gas constant R. Now,. So, that is a simple exercise on algebra, which are I am not to do to save sometime, but in principle they not concerned with that at the moment.

There exists a characteristic V c or P c and a T c functions of these parameters a b and R and uniquely determine such that above T c T greater than T c. The isotherm do not have a king like this are minimum and a maximum and behave more or less like the ideal gas equation of state. But, below it, it is caught a feature that there is minimum and then, maximum and down on this one wing of this curve, which is got a very low slope negative slope, but very small magnitude another, which is negative slope, but very high in magnitude.

And, what does that imply and evolve in mention this is about a 1000 times as biggest that, what is implies is that the slope here has a physical meaning. And, what is the meaning of the slope in this curve delta P over delta V at constant temperature has a physical meaning his says is very large. Now, go back and ask yourself, what the bulk modulus of the gases are the compressibility, which is the inverse of the bulk modulus.

The isothermal compressibility isothermal, because we concerned with constant temperature process these are isotherms here. And, let us give it a name K sub T is define definition compressibility is the reciprocal of the bulk modulus the bulk modulus is stress over volume at a string delta P over the volume at a string this is the inverse of it. So, this is equal to minus 1 over V delta V over delta P at constant temperature.

So, it is the reciprocal apart from this factor it is the reciprocal of the slope here with the minus sign, why minus sign, because it is obvious that if, you increase the pressure on a gas the volume has decrease. So, this would become negative and a minus sign here would give your positive value for the compressibility the compressibility cannot be the negative. That is taken care of by ensuring that the slope of this, this slope here is always negative and that indeed it is out here and out here, but it is not here and will come to that in a minute.

So, this portion seems to be giving as some trouble, but you can immediately see, that if the slope is very large in magnitude, then the reciprocal of the slope is very small. So, the compressibility is very small it is very rigid it the slope is very small this slope it is reciprocal is very large in magnitude and therefore, you have a very compressible 6 system. So, this portion is very compressible this portion on the other hand is very incompressible.

So, it is suggested that, since this is a thousand times as incompressible as this, that perhaps this system is actual this equation is describing not only a real gas, but also the corresponding liquid on the side and indeed this is show. So, this is the liquid phase of the same substance and this is the gas phase, so far, so good. So, it is giving as a bonus it is actually saying that new include the long range attraction between molecules by means of the Vander Waals equation you are actually ensuring that below certain temperature there is the possibility that the same equation of state describes both the gas phase and the liquid phase of the same substance here.

So, this is actually giving as a handle on, how to approach the problem of the time change of phase from one phase to another, this is the very first preliminary step here. But, we have to overcome a certain problem before that, which is the fact that in the region between the maximum and the minimum the slope is positive this slope is positive. But, that is very unphysical it says, if you increase the volume the pressure increases or if you increase the pressure the volume increases.

Whereas, Le Chatelier’s as principle tells us that it should actually decrease for stability it cannot increase and this part of the isotherm cannot be correct it is unphysical. Now, let see, what other consequence it has it for another diagram a simpler diagram and look at just one of these isotherms.

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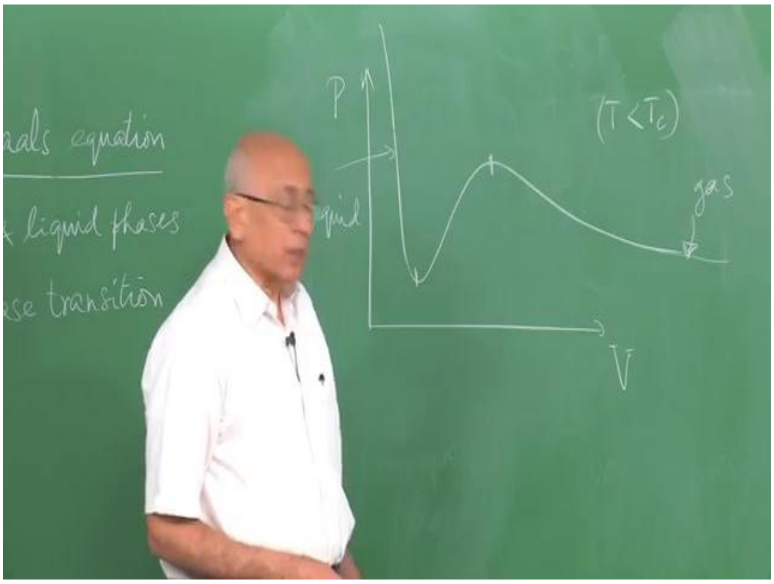

So, once again here is V here is P and if this is your isotherm, then this part is the gas phase and this part is a liquid this kinds the liquid and this is at some temperature T less than T c some fix temperature T less than T C. When this portion of the curve is unphysical it cannot happen the model his wrong the Vander Waals equation of state cannot be complete the correct it is over simplify certain thing. So, that you end up with this unphysical portion of the isotherm it has another consequence if this are correct it would have another consequence.

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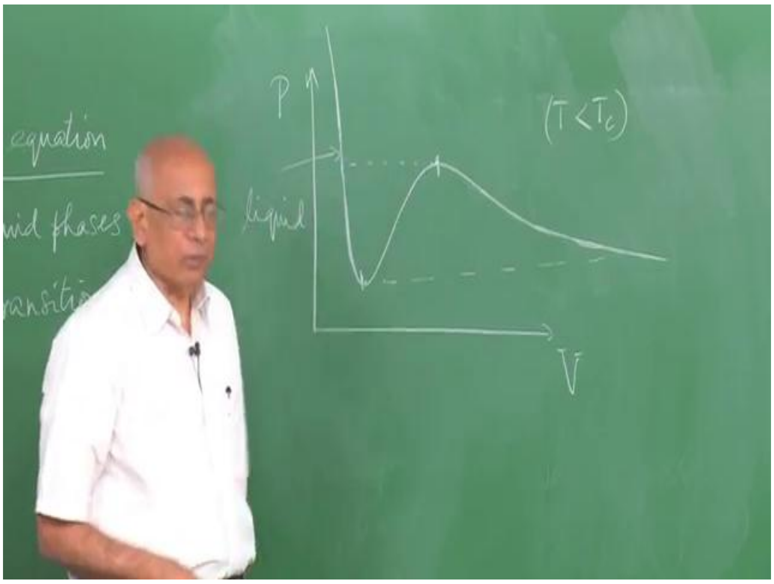

It would have the consequence that as you increase the pressure in the gas phase there should come a stage were the system condenses. And what would happen as you increased, keeping the temperature constant it is ((Refer Time: 19:33)) to jump here and then, move up this isotherm. So, if you took the gas phase and compressed at a constant temperature you increase the pressure at this pressure it would become a liquid and there after remain a liquid as you increase the pressure for there.

On the other hand, if you started with the liquid and decrease the pressure it would have to come down all the way here and then, jump here to the gas phase and go on in this fashion. So, they should be mean that, if you condense and liquefy and condense and evaporate condense and evaporate keeping the temperature constant you end up with the historicist you end up with responses of the transitions at different values of the pressure and that does not happen in practice.

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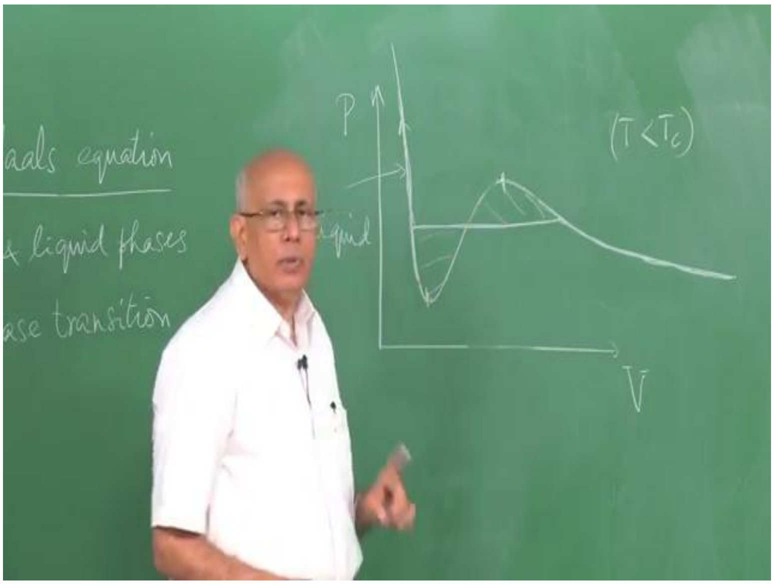

So, what really happens in practice is that, if you took the gas phase and you increase the pressure they comes the stage, when it makes a change in this fashion and goes up and when you decrease the pressure at precisely the same value of the pressure it becomes a gas and goes down here. So, this unphysical part of the isotherm together with the portion, which is in the positive slopes on the correct slopes here.

These two portions are excised or removed in real life and the Vander Waals equation of state has to be modified a little bit in order to take this into account. This construction was actually provide of the Maxwell and I am not going to get into that here, but you could ask at, what point as this happen when does this happen here. And the answer is at happens when this area is equal to that area this is called a Maxwell tie line construction this is called tie line and is an equal area construction here for reasons, which we do not getting to here.

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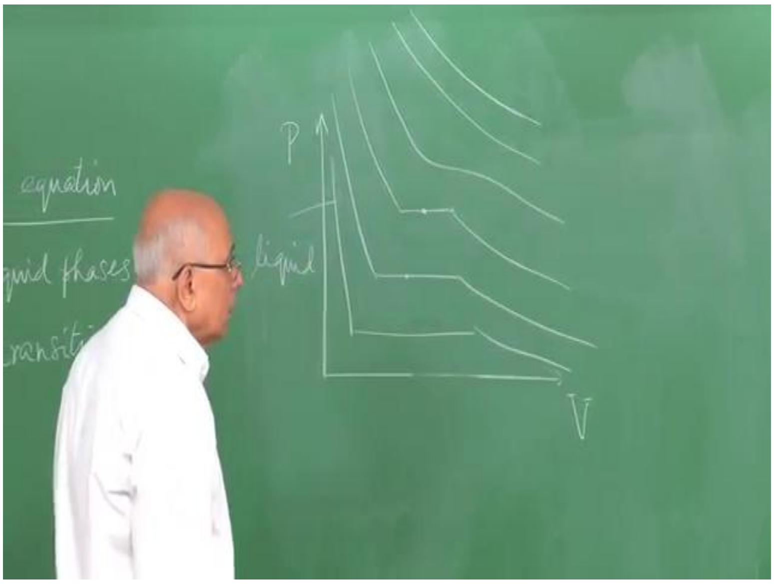

So, the real set of isotherms for real gases for a gas and liquid system is the following. you got these isotherms, which look like ideal gas equations and then, the critical isotherm and below that you have this set of ((Refer Time: 21:41)) in this fashion. So, that is, what a real system looks like and you could ask, what happens, if I took the system and suddenly brought to this point here by would if you, what would it do well it would phase separate.

Then, into a portion that is liquid and a portions that is gas if you brought it here it would phase separate in a specific manner using a rule call the liver rule, which tells you, how much of the liquid and how much of the gas or saturated vapor would be in equilibrium with it. But, this is an extra detail which we will not get into here, but pointer one to make is that this explain. So, rather gives as a handle on, how the liquid phase is a taint.

So, there is actually with the possibility that in the Vander Waals equation of state you can with a modification give to Maxwell actually understand both the gas and the liquid phases. The gas phase has a very low rigidity, very high compressibility; the liquid phase has very high degree of incompressibility or it has high it is bulk modulus is very, very different from that of the gas here, which is highly compressible here, so, so much for the fact that the real gas also allows for the possibility of condensation.

The next thing we have to do is to ask, what is this look like in a plane other than the P V plane? Suppose we did this in the P T plane, what would happen and that brings me to the next topic, which is a change of state the materials and ago.

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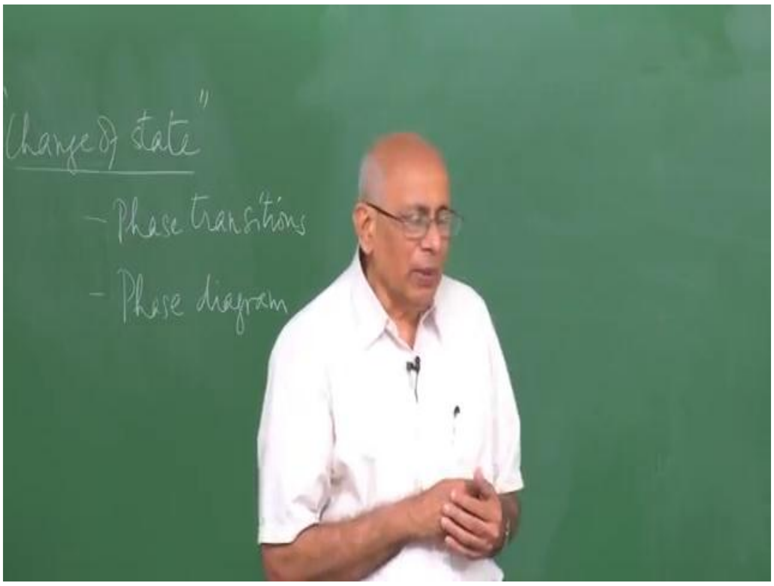

So, let us go on the, so call change of state I put the sing quotation marks it should really we call phase transitions and along with that is the phase diagram. I would like to emphasis before we get on to this that the technical way of saying this the correct way of saying this is change of is a phase transition rather than changes state. Because, I was state is somewhat wag although it says in textbooks elementary textbooks that matter exists in three states there is a liquid state, the gas state, and the solid state, this is the little a emphasize for various reasons, which I will some of, which I will mention here.

For instance, if you say a liquid is different from a solid, because a liquid does not support sphere under sphere it flows where as the solid has a sphere modulus and does not flow. Then, I point out that depending on how rapidly you change the stress on the liquid it may act like a solid. As we know if you take a dive into a swimming pool and you land on a stomach and you land vertically down when you rapidly it you can get hit as if you hitting a solid object.

So, the liquid essentially behave is like a solid object here on the other hand even a very, very solid looking object like pitch or tar will if you allow it to flow and you put a stress on it and allow it to flow it will flow extremely slowly maybe at the rate of a drop a year or a century even. Such an experiment is on by the way the famous experiment where drops of pitch single drops fall eve every several decades later.

So, it flows like a liquid on the other hand it is in a liquid state and since the solid state, but it flows like a liquid. On the other hand the liquid this flowing pool example I gave behaves like a solid depending on the strain rate that you apply on the system. Similarly, if you say liquid flows whereas, the solid does not flow I take a crystal I powdered it becomes micro crystalline and then, becomes a powder and it pouts exactly like a liquid.

So, here is the system, which is apparently in the solid state, but pouts like a liquid and there liquid, which behave like solids as for is a stress response is concern. So, there is really no precise way of saying this except to say that work state is not very precise you could have something in the solid phase, which is a thermodynamically well define statement. and then, in this phase you can have all kinds of physical states you could have a state when it is granule when it is micro crystalline poly crystalline single crystal and so on or even a masses.

You could have for instance various kinds of intermediate states when you take a solid and you powder and you mix it to the liquid you can have a emulsion you can have a gel you can have kinds of objects of this kind, which would all correspond the various physical states. But, as far as the thermodynamic properties are concern you what phase as a very precise meaning and here let us distinguish the simplest tensions is between the gas phase the liquid phase and the crystalline solid phase here. So, if you restrict our self, so that, then we can actually begin to make some precise statements and this is what we will do next.