

Engineering Thermodynamics
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Lecture – 26
Properties of a Pure Substance: Critical state. Compressibility factor

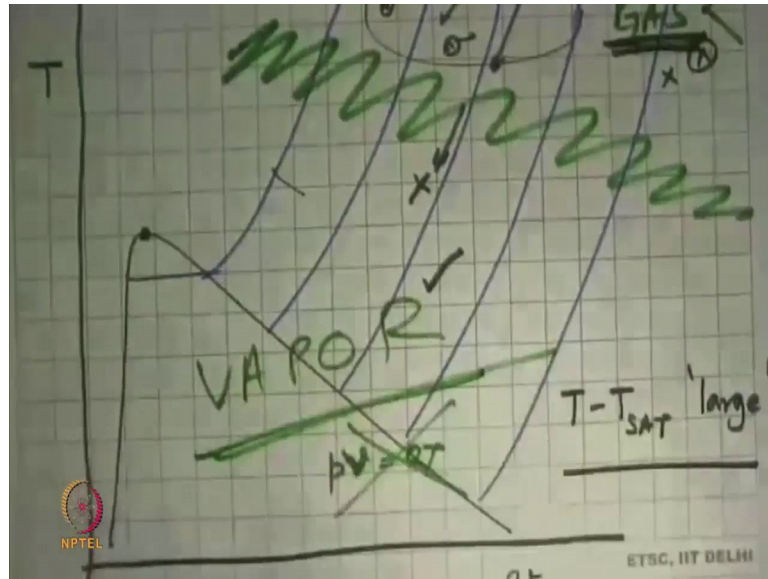
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CRITICAL POINT
Reduced pressure $p_r \equiv \frac{p}{p_{cr}}$
Reduced temperature, $T_r \equiv \frac{T}{T_{cr}}$ $\triangle K$
Ideal gas: $pV = RT$ $R = \frac{pV}{T}$

Which are that at the critical point. We define a new property which we call say reduced pressure, we will call this p_r defined as the actual pressure at that state divided by the critical pressure. And similarly, reduced temperature T_r , this is reduced temperature defined as the actual temperature divided by the critical temperature. Pressures are always absolute, so we do not have a problem. Temperatures be always careful all temperatures must be in Kelvin only for this particular case, we cannot have a negative reduced temperature. So, this is the first thing we define.

And then we say the ideal gas assumption says that the equation of state is $p v$ is equal to RT or if you make a 3-dimensional plot then R this is the constant is equal to $p v$ by T . So, we can pick a p and v which are all what is T and make a plot and we can see that instead of that complex looking 3-dimensional $p v T$ shape, we start now looking at a very nice, well behaved, smooth image. That means, we are in that ideal gas. And our question is why did this is this substance behave like an ideal gas.

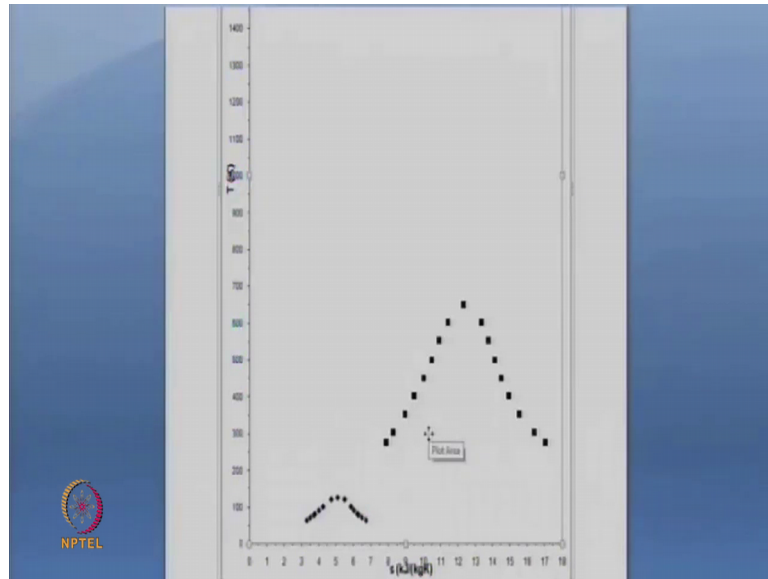
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And it starts, that means, I will start it doing both things which we talked about in the beginning of yesterday's lecture that these molecules are now far away they are behaving like rigid spheres here. There is no other interaction between them, no gravitational attraction, no nuclear repulsion, no electromagnetic forces, they are moving in a random way and they are undergoing perfectly elastic collisions. That is why we said that this is now going to behave like a gas.

This behaviour begins to deviate sharply when they are in this region, at the moment where in a saturated state and liquid state on the supercritical state it completely mixes. There will be some regions of the vapor behaviour where we can still say that ideal gas is approximately valid or at least correction to be made that special state. So, physically this is what happens here. This does not happen in this part of the P-T properties. So, what we do at the first case exactly we say that if we are far away from this way away like in the case of nitrogen. So, we if we make the plot for nitrogen and I will show you a picture.

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See what I have done here is something beyond what you see in the charts. In the sense that I have equalized the reference condition for nitrogen and water and I said, that specific entropy of that both substances at 0 Kelvin is 0. And with respect to that I replotted s_f and s_g on the T s diagram.

So, now, we are looking at a consistent set of specific entropy for two very different substances whereas, according to our tables nitrogen is reference to some temperature, water is reference to 0.01 degree Celsius, we cannot directly plot the two in the same diagram, but this is consistent enough. So, here is what you see. This is nitrogen the T s diagram of nitrogen; this is the T s diagram for water. And what happens now, is that let us take the case of a inlet of a gas turbine. And we are mentioning that temperature there like 1400 Kelvin, 1600 Kelvin are now typical in aircraft engines and also land based power generating units, with that 1400 Kelvin is over here, then for nitrogen we are way far away from this saturation level.

In fact, even if you look at water at that state we are still far away from this thing. So, 1400, 1700, 1900 Kelvin which are now temperature that we are talking of in combustors and burners we are far away from this dome, and we can say that look at away from the critical point anything like this I can quite happily accept that this is ideal gas behaviour. In fact, that what we do for nitrogen critical point of nitrogen is 126 Kelvin, we live in 300 Kelvin plus type of a thing. So, they are above more than 2, two and a half times the

critical temperature of nitrogen. So, reduced temperature the way we just defined a few minutes back for ambient condition for nitrogen it will be about 2 and see we are far away and so we presume that air around us and for all purposes of calculations and analysis we treat air or nitrogen part of the air as ideal gas.

Do the same thing for oxygen curve will be little lower than this slightly, equally good for oxygen to be treated as an ideal gas at certain temperature. And we go actually one step further and we say that look nitrogen oxygen also happen to be very similar molecules at least in the physical sense not the chemical sense, and so we will define air as a new pure substance or pseudo pure substance and assign properties to it and that is what you see in the air property charts.

As the first analysis that is a very good thing to have. But this is what happens that you have one substance at very low temperature; that means, states where water behaves like a saturated state of the same pressure and temperature at which nitrogen behave as an ideal gas and in a combined cycle power plant both are happening in the same system. So, we are going really think twice as to what we are going to do and how we are going to show things in this. So that is what I was trying to show there. And what we do is we make one change to this ideal gas equation by defining Z , the compressibility factor and put the equation $p v$ is equal to $Z RT$.

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CRITICAL POINT
Reduced pressure $\rightarrow p_{r2} \equiv \frac{p}{p_{cr}}$

Reduced temperature, $T_{r2} \equiv \frac{T}{T_{cr}}$ $\triangle K$

Ideal gas: $p v = RT$ $R = \frac{p v}{T}$

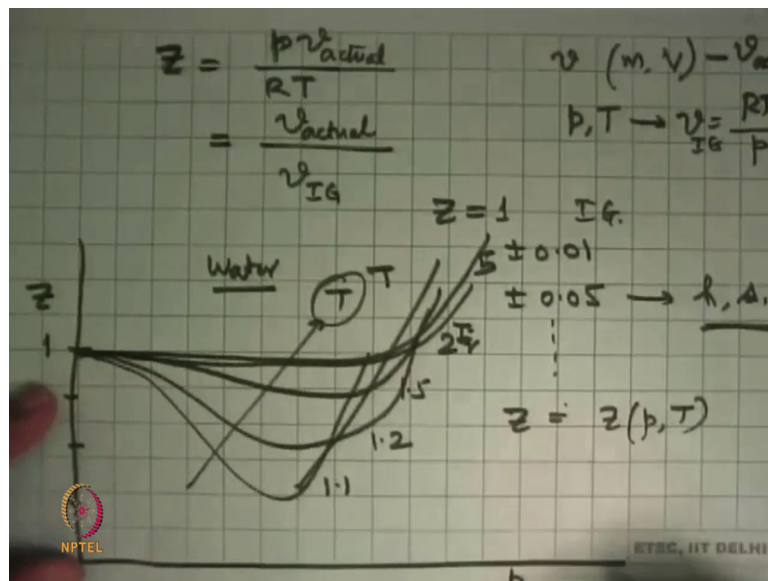
Z : compressibility factor
 $p v = Z RT.$

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So, Z begins to play a factor when that ideal gas behaviour which is the molecular behaviour begins to undergo a change which happens at higher pressures and lower temperatures, ok. So, then we say look I will make some correction and that amount of correction that I need to make this is the function of the pressure and temperature or here we will put reduced pressure and reduced temperature. And once we do that, we get a little better in using a very simple equation of state a little further down.

So, we can say that look now, I do not have to stop here with $p v$ equal to RT if I start using $p v$ equal to $Z RT$ then I can cover this more region also. Z is in this region, Z is one ideal gas behaviour. In this case Z is somewhat of, but I can calculate it and make a correction. And you can continue that logic here also only difference is that the correction that Z will bring $p v$ equal to RT is very big. In fact, here it will be correction of the order of 100. So, it is not 1 percent, 2 percent, 5 percent deviation from ideal gas it is huge deviation from ideal gas. But that forms the basis for a unified set of equations for the entire things are doing, ok.

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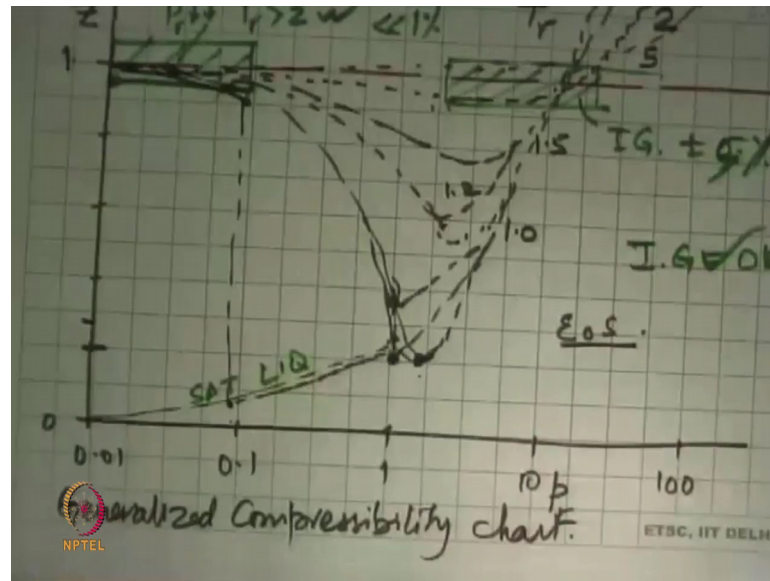
So now, what is Z ? So, thing that happens is we start with, what Z is actually yield $p v$ upon RT , but now, we should be clear that v that we are getting is v actual upon RT . That means, may your medical oxygen cylinder at home it has got a certain specific volume we know pressure and temperature at which it exists, so the actual specific volume we know because the mass and the volume of the cylinder were known independently we

know the pressure and temperature and ideal gas equation was state it tells you that v ideal gas is equal to RT upon p . This is different from this or from this, this is v actual. And the ratio of these two is what we call the compressibility factor. So, this can be written as the actual specific volume divided by the specific volume predicted by the ideal gas equations here, if Z is equal to 1 ideal gas. You know exactly 1 we will get very rarely and it is plus minus 0.1 that is good enough that is an ideal gas.

And then there are some cases I will say look I can tolerate plus minus 0.05 or 5 percent uncertainty in Z we will call the certain uncertainty in h and s and μ and as a first step calculation it is for that, but anything more that will not be right. And what does not get right is when you do this plot Z versus pressure and say we do it for water this is one and below that becomes 0.5, 0.75 something and this is 0. So, I said high temperatures this will become like this and it will go off, whatever the Z values you get. There it will become like that and start going up as the temperature decreases. This is reduced temperature say $2 T R$, reduced temperature is 2 and this reduced temperature is 1.5, reduced temperature is even less it may go here reduced temperature of 5, it will come down 1.2, 1.1 like this this deviation from Z equal to 1 becomes very very low.

Now, we have a problem. And if this was the sort of a plot for water and we could get Z as a function of pressure and temperature then we would have get the similar plot for butane another plot for oxygen another plot for everything else and life would be very very complicated. But nature has its own beauty and instead of plotting p and running parameters as T . So, T here increasing this way we change the coordinates and instead of p we plot the new pressure and instead of T we plot the new temperature then something quite elegant happens.

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This side is reduced pressure and this will be logarithmic state 0.01, somewhere here 0.1, 1, 10, 100 reduced pressure has no units. So, no problem we will put Z over here 1, 0.8, 0.7, 0.6 and up to 0. And now, we will draw lines of constant T_r and what Z they give. So, the first thing we will do is we mark something which we would like to see Z equal to 1. And we start saying that if we reduced temperature is say 2 it will be something like this, this is 2 here. If you are going to 5, it may go on to slightly up here and then take off. So, this might be 1.5 it will start there come down and then start going up, this is 1.5 here, 1 it will come there. And so, 1 will actually be at the critical point, so its actually will comes from the known 0.2. And then go up we can consider this to be like 1.2, this to be 1 and below that we will not draw.

So, this will happen when it is 1 sorry, this line should be like this 1 and 2, so something. So, reduced pressure is 1, reduced temperature is 1 and that Z critical something like 0.27 or something. And below that we start getting a curve like this. And at even lower reduced temperatures you actually start getting up to this point, and then you have a saturated state and then again it is from here it is starts critical. That is the type of behaviour that emerges and we get the numbers little later, but let us see what does it tell as to which are the conditions under which we can safely assume on a period to be an ideal gas, ok.

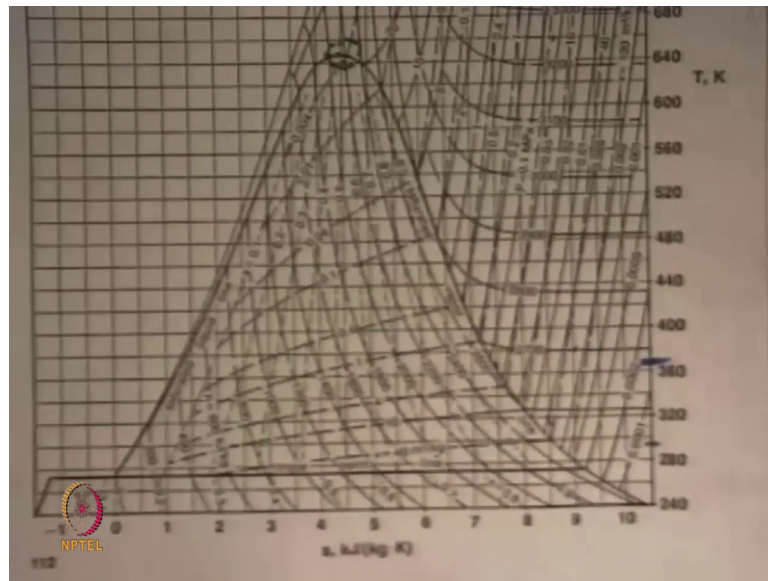
So, the question is under in which part of this chart can I say that ideal gas is and. So, we look at the case where Z is equal to 1 and we say wherever Z is in a band ideal gas is ok and so, one of the region that emerges is right here. So, if reduced pressure is very small and reduced temperature you say greater than 2, then we can safely assume ideal gas to be and that present the state under which the atmosphere falls. So, we are quite happy that whatever we do with air $p v$ equal to RT is the reasonably nice this thing to do for most things that we are looking at unless we are not going to that state.

Then we see another region here that even if you go in to reduced temperatures to a lower value and reduced pressures at below 10 bar, 10 then also we can say that in ideal gas behaviour, but no variation will be about plus minus 5. Here we can be sure that as you go further away here this side variation is well below 1 percent, its quite nice. Here it is not shown us, but it is ok. And at higher pressures is more because these curves are very steep they would go up we cannot assume anything beyond reduced pressure of 10 to be an ideal gas.

And then again even if we say that this reduced pressure reduced temperature is 2, even if it has saturated state then also it is not ok. So, we can only look at this part there some saturated states will also come as ideal gas behaviour, but the saturated liquid state which is this line this has got very large due to Z a very small cannot be considered to be an ideal gas. So, that is what we have introduced now, the chart which is known as the generalized compressibility chart. And people have done lot of curve fitting on this and come up with various different types of equations of state.

The summary of that is given in the notes, and you can look up that that as you start getting away and away from ideal gas behaviour you can use better and better equations of state as long as you are in the gas out of this phase, after which that equation of state is not valid at all. So, we will stop here and take up questions now, and question that we have here is, this is please explain the critical pressure and critical temperature, ok. So, let me put this once again. Now, I will use any of this chart there instead of my own picture, ok.

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So, here we have a T s diagram for water and what we are seeing here is that at this is critical point. At the critical point the difference between vapor and liquid behaviour has disappeared. There is only one state and that we call the critical state or the critical zone, and any state above this to the left of this to the right of this is also a simple homogeneous state.

Second thing, if you heat it or you cool it there is no clear physical difference between two regions two phases with drastically different densities, that does not happen. So, that is what the critical first instant where that does not happen in the critical state. Below the critical state they have any pressure or temperature below the critical state and you heat it or cool it we are likely to get a mixture of I mean saturated liquid (Refer Time: 20:16). So, that is one way to look at critical state.

The second thing you can talk of the critical state is that above the critical temperature and critical pressure which I need properties of living substance, we cannot get a saturated state. A saturated state is possible only at pressures and temperatures below the critical point, that is another thing you can come across. And since there is no big no quantum change in physical properties from liquid to vapor we only see a continuum happening there. So, it means that properties can be described by reasonably nice equations without discontinuities which is what was happening in the saturation states.

So, mathematically and formulation wise that is the other thing to do; I should also mention though that equations of state and the plots that we have they are pretty good in most places, but right near the critical point we have a similarity to the mathematics and it is difficult to do the programming. So now, gradually people are saying that, let us not get too tired up by forcing the critical state conditions to be there, but it is that in this region the substance is a homogeneous thing and we do not see this exchange right, below that pressure, ok. So, that is something more about the critical point. It is the property of heavy substance a unique property and that unique property means you have a p critical a t critical or v critical, s critical, h critical they are all fixed they cannot change and for other substance they are already there.

So, there have many practical means equations where we have to worry about the critical point large power stations anyways the new ones that are there in the country the last 5-6 years they are all have water which has been pumped to pressures above 220 bar, 280 bar, 300 bar pressures they are all be in nice in that whole beyond this the heating is going to be there, and it means that the physical properties are not changing. So, the heat transfer properties will not change very drastically. So, the engineering of that boiler is very different from the engineering of this level right, practically this is equation of a (Refer Time: 22:42), ok. So, that was little more explanation of the critical pressure and critical temperature.

How to calculate the maximum vibration energy of molecule at superheated state? ok. This is a question it says how to calculate the maximum vibrational energy of a molecule at superheated state. Why? If you want to look at molecule to molecule thing it is very difficult, if you want the averages of that to be done you have to go to statistical mechanics use the Boltzmann equation use the partition functions and from there you will get all of them. Most cases that we look at in classical thermodynamics we do not need to go into that.

Then the question which says, please explain the significance of reduced pressure and reduced temperature, ok. The significance is that we are able to move away from specific variabilities that are there from substance to substance. Like I showed in this picture for nitrogen and water, see here this is nitrogen you saturate critical point is over here, water the critical point is here or by my mathematical strength point it will be nice if all of

these could be made into one equation, and there are many instances where something these things can happen there are some cases where this does not happen.

The one case where it does happened is what I have just explained is that the actual pressure we normalize it on the critical pressure, and fortunately what that does for us is that you get a very nice single compressibility chart for all these materials, ok. It is not that everything is lying exactly on this line, there is a variability around this from substance to substance and you are looking at plus minus 2 percent type of a variability in making the generalized compressibility chart in the first (Refer Time: 24:38), ok. So, that is what the reduced pressure and temperature actually helps us. In that we get a common set of pressures and temperatures for which we can compare materials various different types of materials.

Just by looking at their absolute properties we get very funny looking pictures which is very difficult to generalize. So, that is why we do this. The second thing is also that means, when we write the property charts, it is always nice to move away from absolute values into normalized values and then you get an equation which is quite much larger applicability when that equation which are properties for that particular substance. So, we are looking at little more versatility in the same equation we use for many substances that is what that is where this p_r, t_r coming, ok.

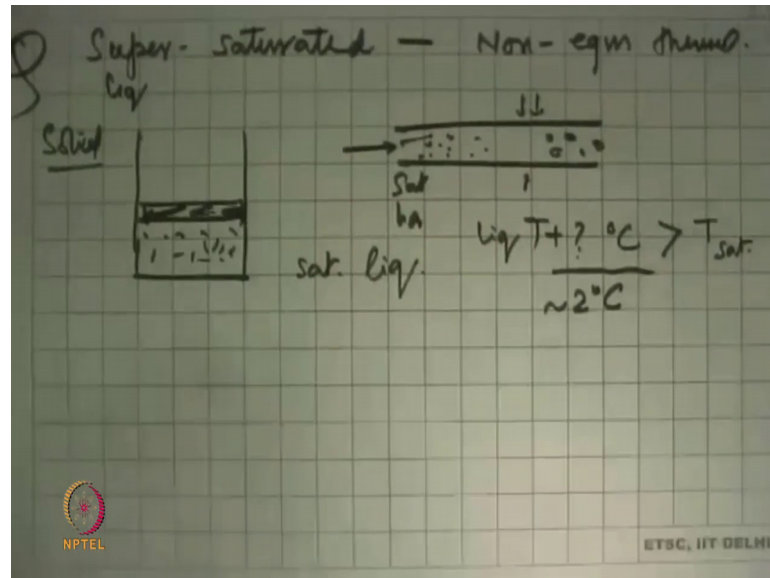
Then there is a question: what are the modern techniques that we use to analyse gases and vapours thermodynamically. Anyways, the good old thing is still the best that we make as a closed system and any new substance that we develop with hoping into it, heat it up with different pressures and temperatures and measure its properties, and then make a curve fit to the $p-v-t$ diagram and get properties from there.

What has changed in the last 50-60 years ago? These are the quality of instruments has improved, the mathematical techniques that we have they have improved a lot and so we think that we can do lot better, but still some of the property diagram say for especially for water which is the first one to be studied which came from way back 70-80 years ago some of the experiments done at that time are still among the best experiment that people have done.

So, doing a good experiment is not about what how many more modern techniques we have, but how well they are able to design scientifically rigorous experiment, ok. Modern

techniques help us to do some things better, but we have to understand the basics very well, ok. Then, there is a question what do you mean by super saturated solid state, ok. I have not such this business of super saturated condition, ok.

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So, we have not done it simply because this goes into non-equilibrium thermodynamics and that is not in the scope of this course. But what you are given example where this issue comes in. What we say that if we take a cylinder piston arrangement, and we have a substance there which is say saturated liquid; throughout the discussion we have said that as soon as we give some energy to this at constant pressure it moves up and immediately some vapor is formed. In reality what happens?

This, or its counterpart in a flow that you are pumping in saturated liquid and you are heating it now and you expect that vapor bubbles will be formed. What has practically been observed is that instead of exactly happening at the saturation temperature the liquid remains in a saturated in as a liquid for a few degrees greater than the saturation temperature and then it changes things. Same thing with the solid. So, if this could be a super saturated liquid or super saturated solid.

So, what it is telling us is that what we learnt in equilibrium classical thermodynamics in reality is the strength deviation from that, and this deviation could be of order of about 2 degree Celsius. Why it happens and how it happens, we cannot explain it from classical

thermodynamics, we have to get back to first non-equilibrium thermodynamics and then go back and look at all the aspects from statistical thermodynamics to explain this.

So, we are not going to go in to this part into a beginning course in thermodynamics and once portion is there you will be worried about that.