Advanced Materials and Processes
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Lecture – 07
Bulk Metallic Glass, Glassy and Amorphous Materials (Contd.)

Hello, welcome to NPTEL. I am Dr. Jayanta Das, from Department of Metallurgical and Materials Engineering, IIT Kharagpur. I will be teaching you advanced materials and processes.

In the last class we have discussed about what one should understand a glass means, means what is really a glass and definitely we understood that glass has an amorphous structure and it should show a glass transition event. And today, we will try to continue the discussion and we will go into little bit deeper.

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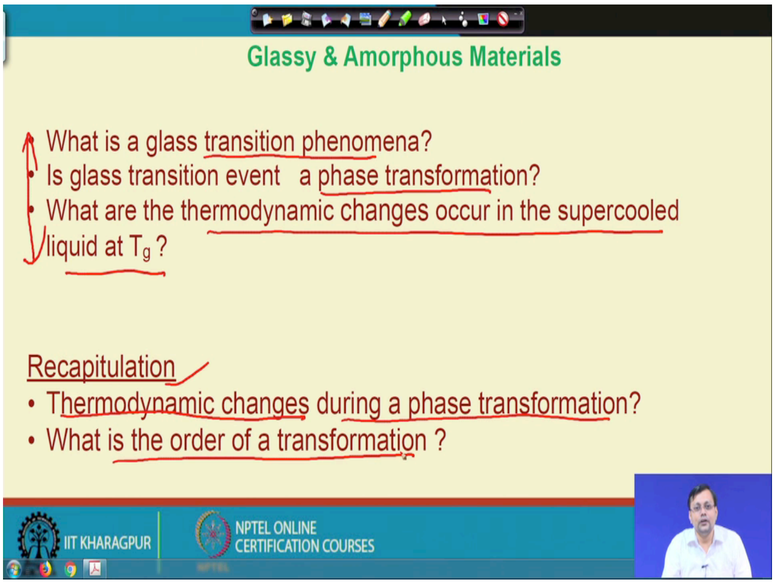

So, basic question always rise in our mind that what one should understand and what we really mean by a glass transition phenomena and whether this glass transition what we are talking about, is it really a phase transformation or something else?

On the other hand, what are the Thermodynamic changes that occur in the supercooled liquid at Tg? Because, we already understood that glass transition is manifested during cooling of a supercooled liquid.

However, before going to this discussion matter, we must recapitulate some of our basic understanding. Means, what are the usual Thermodynamics changes that occurred during a phase transformation? Or let us say what is the meaning of an order of a phase transformation and so on?

So, today, we will be going to the little bit deeper in all these discussion matter.

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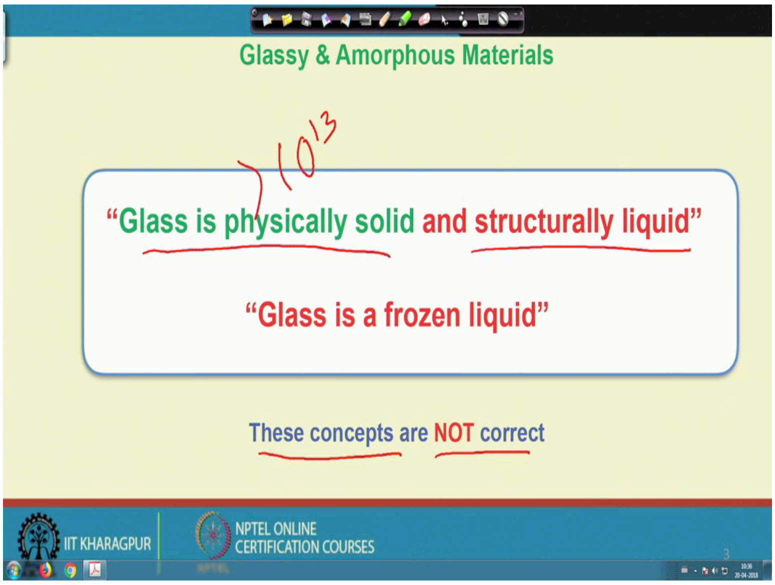

Now, most of the time if you try to think, there are very general concept people talk about. So, one of these very general concept like "Glass is physically solid and it is structurally liquid". Definitely, glass is physically solid because it has a viscosity which is greater than 10^{13} poise. So, it is definitely solid. Whether, but the question comes whether they are structurally liquid or not?

On the other hand, people think that when we start cooling a liquid and we freeze the liquid. So, glass basically forms. So, this glass basically means that it is a frozen liquid. However, I feel that these usual concepts are not really correct. So, today through our discussion, we will try to see that what is the real things happen during glass transition.

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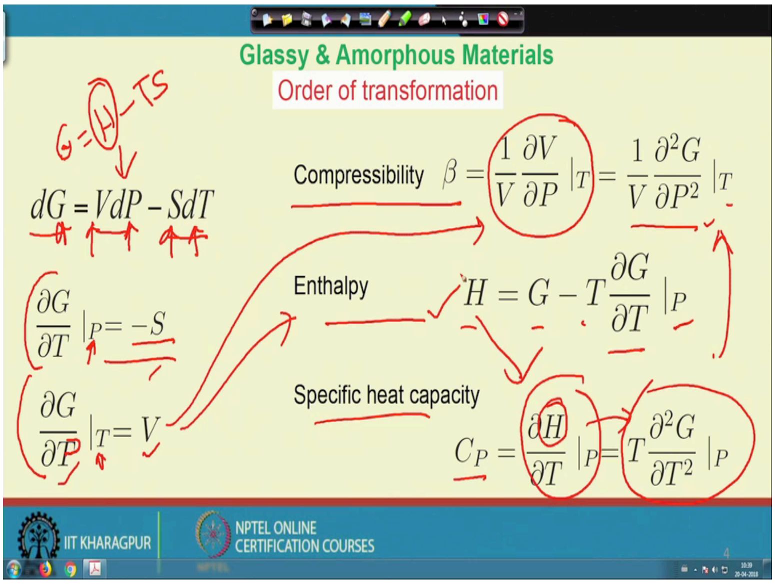

Now, let us try to recalculate some of the basic understanding what we had regarding thermodynamics. So, in thermodynamics, we already know that G = H –TS and from there we come to such a partial equation that $dG = VdP\text{-}SdT$. Here, V is the volume; P is the pressure; G is the free energy; S is the entropy and T is the temperature ok.

And now, if we make the first derivative of dG/dT partial at constant pressure, then we will get this term that is minus S.

$$\frac{\partial G}{\partial T}|P = -S$$

S is stands for the entropy. Now, if we take the same equation and make a partial an equation from dG by dP at constant temperature which is basically V, V is the volume ok.

$$\frac{\partial G}{\partial P}|T = -V$$

And now, I take let us say one of the parameter that is called Compressibility β

$$\beta=\frac{1}{V}\frac{\partial V}{\partial P}|T=\frac{1}{V}\frac{d^2V}{\partial P^2}|T$$

and I simply take the same and put it here, then I will get a second order derivative ok. So, this is the first order derivative and this is the second order derivative at constant temperature.

Now, what is really Enthalpy means? So, here Enthalpy is basically so this is the enthalpy term. So,

$$H = G - T\frac{\partial G}{\partial T}|P$$

So, I basically put it here. So, now, you see that we understood how we can estimate the enthalpy or let us say the specific heat capacity which is also means that if we make a derivative of del H by del T at constant pressure, then we will get C p which is the specific heat capacity at constant pressure.

$C_p = \frac{\partial H}{\partial T}|P = T\frac{d^2 G}{\partial T^2}|P$ We take let us say the same H and simply in terms of free energy we will get a second order derivative again. So, these two terms are somewhat linked with the second order whereas, the S is a first order one or enthalpy. So, during phase transformation process definitely some of this thermodynamic parameters must change. So, let us have a look to how really with temperature these thermodynamic parameter changes.

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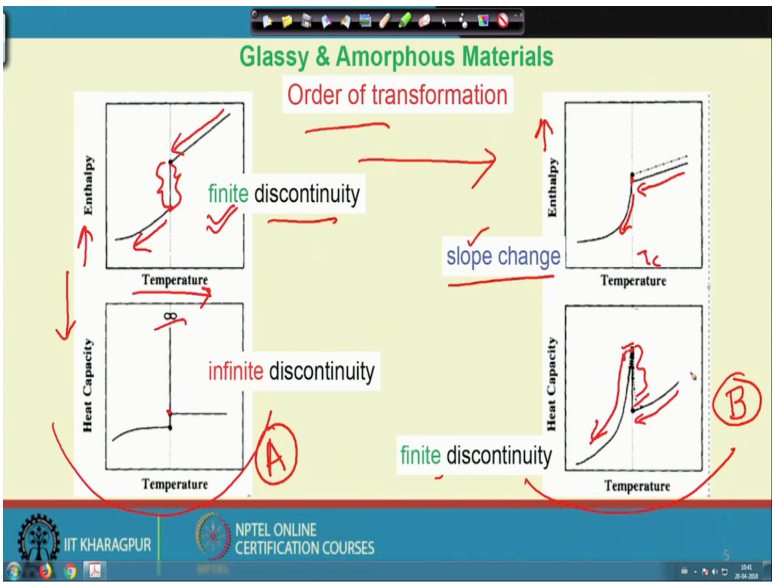

So, here you see, the I try to understand the order of phase transformation and I plot here with enthalpy versus temperature plot and here, if you have looked let us say, during cooling, there is a enthalpy change and here there is a discontinuity. However, this discontinuity is a finite discontinuity because it is a measurable quantity and then, after phase transformation again the enthalpy decreases, but there is no further discontinuity ok.

But in the second case, if you go to the second case here, when we cool it down there is only a slope change ok; there is only a slope change. Now, for the same phase transition if we see the heat capacity change, then there is a infinite discontinuity here ok. So, this particular phase transformation process appears to be different than this one because here there is finite change; here there is slope change where there is no net value change of the enthalpy ok. There is no change in the value of the enthalpy at the phase transition temperature, let us say this is the phase transition temperature.

Whereas, here in the heat capacity if we make basically the derivative of $\frac{\partial H}{\partial T}|P$, then we will get a finite value of the change ok. So, this is a discontinuity definitely; however, there is the finite discontinuity. Because, if we cool it down then again here the specific heat capacity keep on changes ok. So, this two cases let us say are quite different and now, can you please suggest what is the order of this transformation in this two cases case and case b? Let us have a look. Yes.

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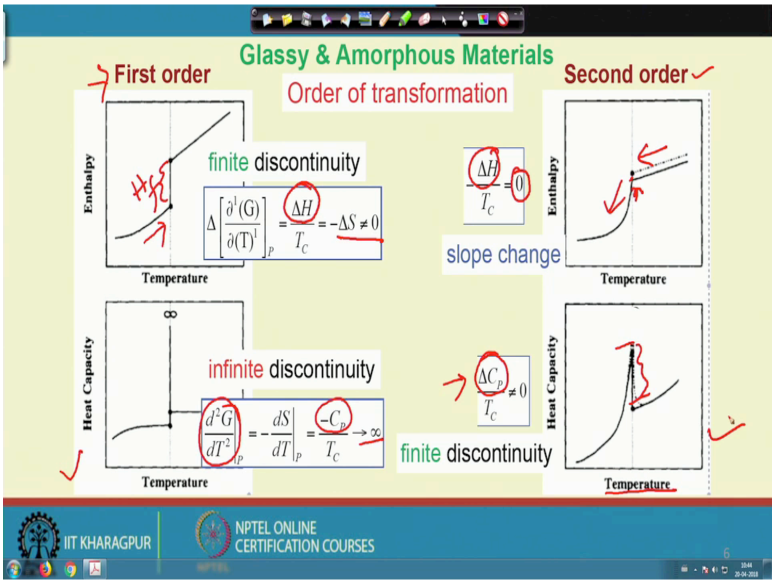

So, here we basically see that this one is a first order, where there will be a finite discontinuity of enthalpy change and here there will be only a slope change ok; whereas, the derivative of the heat capacity or the second order of G term which is the C p here, they are the infinite discontinuity. But in case of the first order transformation, the delta H change is the is a finite value it has and therefore, the delta S is not equals to 0 and we must have a look at what are the such transformation occurred, yes solidification ok.

Solidification is a first order phase transformation. Why? Because definitely during solidification itself, there is a enthalpy change and we know it is called as heat of fusion ok. So, that evolve in the liquid and you need or may be during melting you need to provide some extra heat to the solid so that it melts and that is the heat of fusion we call it heat of solidification or heat of fusion.

And in case of the change for the same phase transition in the heat capacity, so this goes to infinite or infinite discontinuity. In case of second order this there is the ΔH change is is basically 0 ok. So, there is no net change in this ΔH at this phase transition and therefore, you only see there is a slope change during phase transformation of a second order phase transformation; whereas, if you have a look of the second order derivative of these of a enthalpy which is basically gives you the value of C p ok. So, here you will get a finite value which is a finite discontinuity.

So, if you take any of the solid and try to learn the phase transformation process in a dsc and if you try to look at the C p changes or enthalpy changes and then, we can simply have look that that whether it is a first order transformation or a second order transformation ok.

And now if it we simply take these basic understanding what we had in case of a first order or in case of second order and try to compare these with a glass transition phenomena, then we will really understand that what a glass transition whether it is really a phase transformation or not or which order of phase transformation is involved during glass transition.

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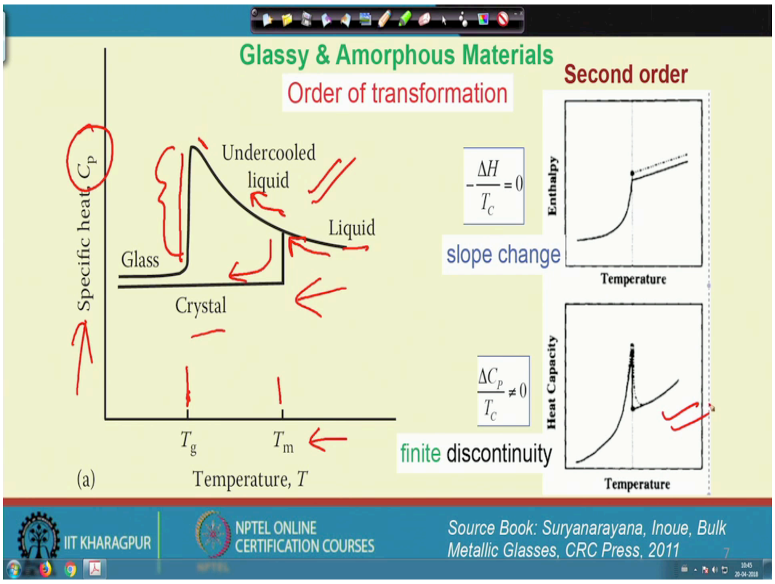

So, I show you here a plot with the specific heat capacity that is C p with the temperature and here if we cool it down from a liquid, we know that liquid cools down and we can we can go to and cool the liquid more and more and we can get a under cooled liquid ok.

And in the under cooled liquid after reaching to a certain temperature level, then glass basically forms. So, here this is a finite discontinuity ok. So, the finite discontinuity of the C p whereas, in case of Crystal formation the path is like that. So, here this is the melting temperature and this is the glass transition temperature ok. So, this particular plot a really matches with such kind of C p change during glass transition.

So, now we understood definitely glass transition is a phase transition and there is no doubt or there is no confusion about it.

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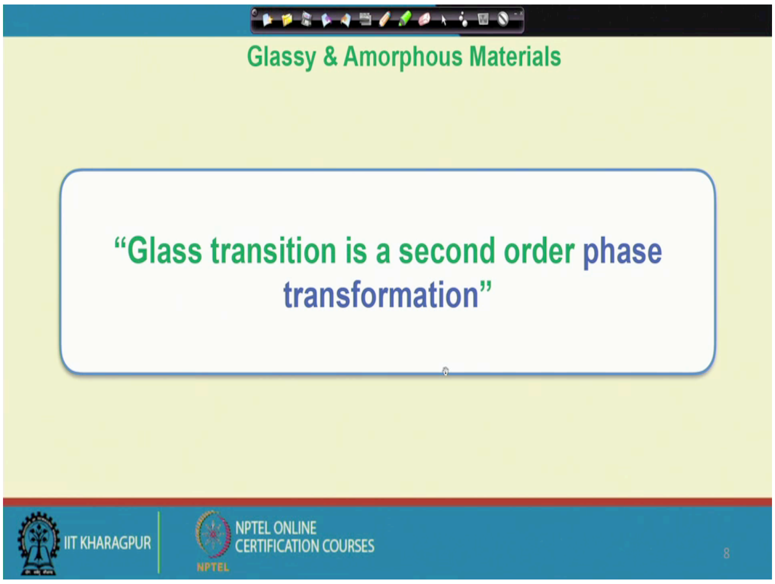

So, we learnt that a Glass transition phenomena itself is a second order phase transformation process and now, let us have a look or try to understand what are the other thermodynamic changes involved during glass transition phenomena ok.

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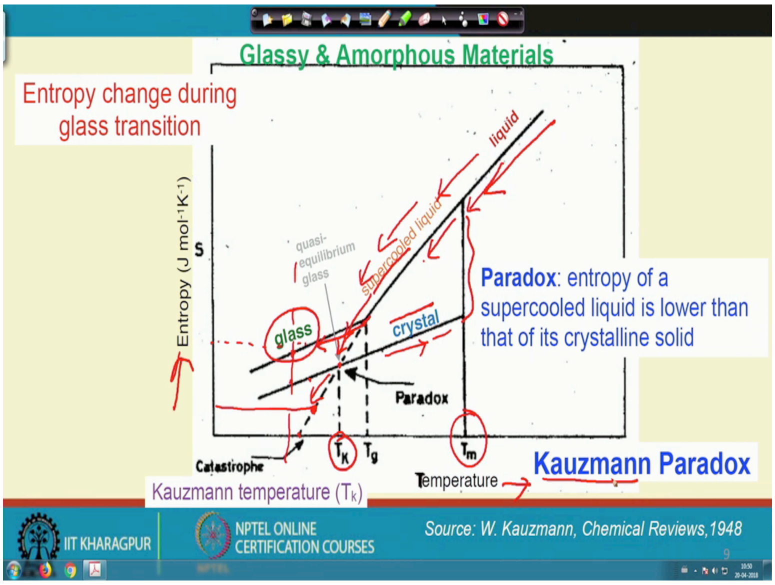

So, I show you here a plot of entropy which is one of the very important aspect or important thermodynamic parameters during phase transition process and here this is the temperature. So, please have a look here, how the entropy of liquid changes? So, when we cool a liquid and then if we bypass crystallization process, we get a supercooled liquid and definitely the entropy continuously decreases ok.

So, the liquid entropy is much higher than the entropy of the super cooled liquid because the randomness in the liquid is much higher than the supercooled liquid. As the temperature is higher, the randomness is also higher which is also valid for any crystalline state.

So, entropy of a crystal also increases if you increase the temperature ok. Now again once again try to have a look that what really does happen when liquid cools down. Now if the liquid undergo solidification into a crystalline phase then definitely there will be a finite discontinuity because $T\Delta S = H$ ok.

So, this gives you the heat of fusion actually and then, we can get a crystal. However, if we can avoid crystallization process and cool down a liquid below melting temperature, then we get a supercooled liquid and then let us assume that we are keep on cooling a supercooled liquid more and more, then what is going to happen in the liquid.

So, if we keep on cooling, then definitely the entropy should come down. Entropy should come down and you will see there is a very very interesting point here. At this point, you see the entropy of a crystal is equals to the entropy of a supercooled liquid ok. Entropy of a crystal is equals to the entropy of a supercooled liquid. This is called a Quasi equilibrium condition or isoentropic condition.

Where, entropy of a supercooled liquid is equals to the entropy of a crystal and you know that crystal is a definitely ordered phase and which is much ordered than a liquid phase or supercooled liquid phase. But, yes. Let us proceed with the further discussion and see.

Now, if I further cool it down, then definitely now you see that the entropy of a supercooled liquid is much lower than the crystalline phase. How it is possible? Because supercooled liquid is a much more random structure. The atoms are organized in a random way and the entropy cannot be lower than a crystalline phase and that basically becomes a paradox and if we cool it down, then entropy catastrophe will occur ok. And therefore, the system does not prefer this path and it find out an alternative path. How?

So, at a transition temperature, at this temperature a transition will occur or phase transformation will occur and the under cooled liquid transformed into a glassy phase ok. And you can see that the glass has much higher entropy level at any given temperature let say at any given temperature than the crystalline phase. And the temperature at which we get the entropy of a supercooled liquid and a crystal equal we call it as T k.

So, this was a proposed and told by a scientist named as Kauzmann and this is a Paradox that I have explained you and it is a known as a Kauzmann Paradox. And therefore, we learnt that definitely the entropy of a glass is at any given temperature is higher than the crystal because the atoms are organized randomly.

At the same time if the supercooled liquid is frozen as a solid and and we call it as a glass, then simply the entropy of that supercooled liquid will be lower than a crystal which cannot be possible and the system always choose a different path so that the supercooled liquid transform into a new phase. So, a new phase will evolve in the supercooled liquid which is known as a glass.

And again, if we heat up this glass or increase the temperature of the glass, then definitely at glass transition temperature, it will show a event in a differential scanning calorimeter ok. And this is a very important observation or thermodynamic explanation of glass transition.

So, what really a glass means because at T_k people assume that at this T_k Kauzmann temperature we get an isoentropic glass which has a same entropy isoentropic supercooled liquid sorry the glass the which cannot stable and liquid cannot be stable after such a lower temperature which has a same entropy level as the entropy of a crystal.

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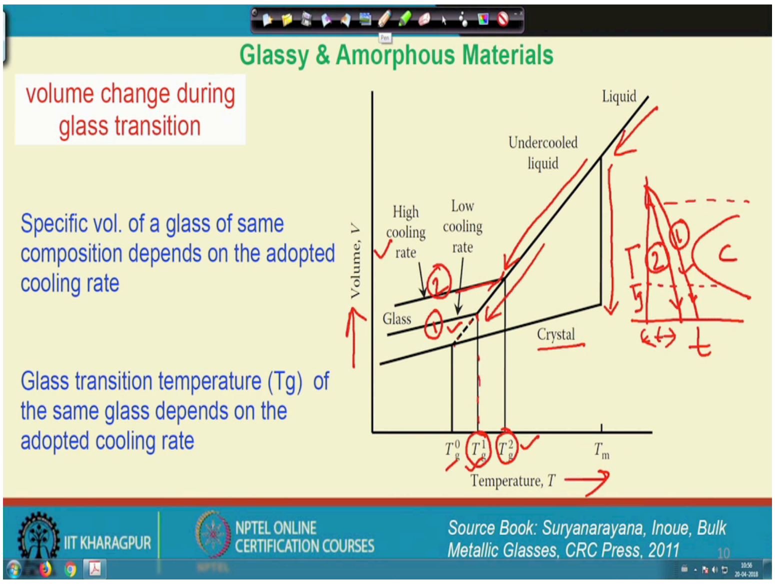

Now, let us proceed further and try to see that what are the other changes may occur. So, so far we have discussed about the specific heat capacity, we have discussed about the entropy.

Again going back to the volume change or specific volume change during glass transition phenomena and here you see once again, the same cooling curve that I showed you in terms of a volume change of specific volume change with temperature axis. So, here again there is a large volume contraction during crystal nucleation and growth and if solidification occurred through the crystallization process.

However, if we if we bypass this crystallization, then definitely the specific volume decreases; however, at a transition temperature that is called glass transition temperature the slope of the curve changes or the slope of the curve changes and further again decreases.

Now, if I take, let us say a composition of a of a known composition and cool a liquid or metallic liquid and cool it differently it means that I cool it fast or I can cool it little bit slow, but in both cases let us say the glass will form. What I want to mean, you can have a look here I just show you a TTT diagram, where here is the temperature and here is the time.

So, this is for crystal I have discussed in the last class and from such a temperature I cool it down. So, here I will get a glass because T g is here and I bypass the crystallization process and I again cool it down in this. So, this is case one and case two. Definitely the cooling rate in case one is lower than the cooling rate in case 2. So, in both the cases, do you think that the glass transition temperature should be the same? Yes, unfortunately it is not.

You can have a look here that when we cool it down and if we cool it much slowly like let us say here case one, then glass transition will occur at a much lower temperature. So, glass transition will occur at much lower temperature than that the case two. Where, case two is a faster cooling rate because we need less time less time to cool it down ok. And in this particular case, the glass transition temperatures will be different. How will be different?

In case of a higher cooling rate, the glass transition temperature will be higher; whereas, in case of a slow cooling rate the glass transition temperature will be slower ok. And we already told that if we extrapolate this plot then we will get a quasi equilibrium glass, where isoentropic situation will occur. But anyway at this moment let us stick to here only the specific volume change.

So, in these two cases, we can see that the glass transition temperature of the same composition are different and it depends on the adapted cooling rate. However, in any thermodynamic phase transformation process, the thermodynamic parameter change or the transformation temperature is fixed and there should not be such kind of transformation temperature change depending on the cooling rate, which is an external variable ok. So, that should not occur.

However, in glass transition process this phase transformation process, we have seen that such thing will occur and so this must be must be a little bit different than what we really know as a second order transformation that we have discussed so far. So, so far we basically talked about that specific volume of a glass of the same composition depends on the adapted cooling rate and the glass transition temperature of a same glass depends on the adapted cooling rate. And therefore, let us try to see what is the conclusion out of this discussion.

And therefore, we really do not call it as a second order transformation we call it as a Pseudo second order transformation because the cooling rate influences an external variable processing condition influences the second order transformation temperature.

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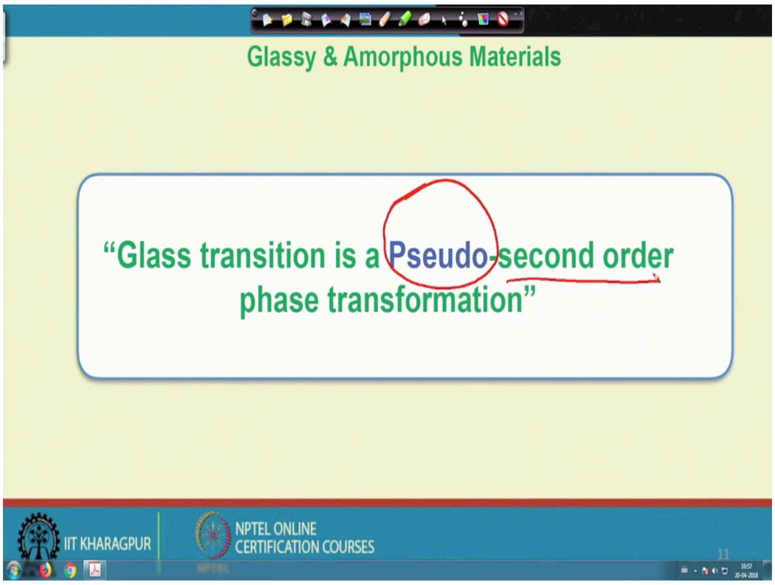

So, we understood so far that glass transition is definitely a phase transition process and it is not at all a frozen liquid or it is simply an amorphous structure that arises due to frozen liquid structure or the structure of a liquid is same as a structure of a glass. So, this concept are completely wrong.

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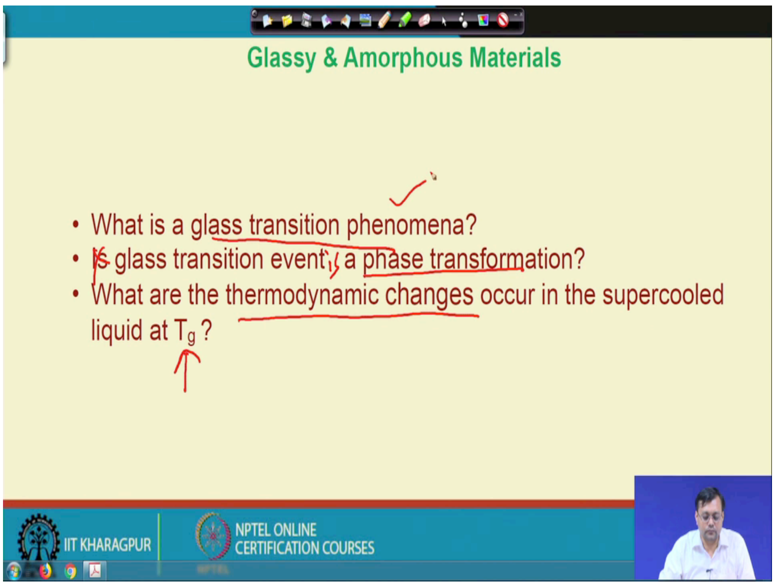

So, so far we understood that glass transition phenomena is definitely a phase transformation process and glass transition event is really in this phase transformation, there are several thermodynamics changes that occur in the supercooled liquid at T_g. T_g is the glass transition temperature and the phenomena is a very characteristic of a second order phase transition process and these local transformation of a glass or the configuration of the liquid is not at all similar as it is in case of a glass.

So, the liquid configuration keep on freezes and keep on keep on come closer and closer and definitely the entropy decreases and the thermal entropy and the configurational entropy, the configurational changes in a glass during a in a supercooled liquid will occur during glass transition. So, configuration of a glass is different than the configuration in the liquid.

Thank you.