Heat Transfer And Combustion in Multiphase Systems
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Lecture 05
Interfacial phenomena key concepts-I

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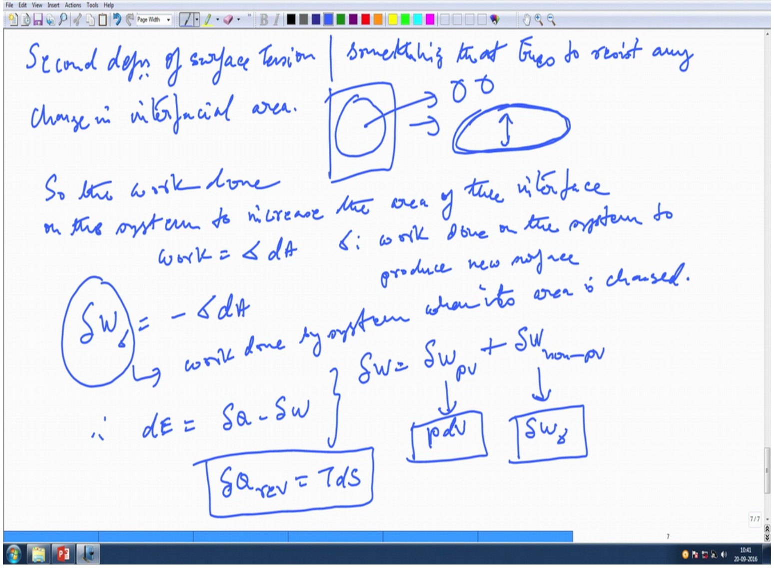

Second defn. of surface Tension | something that tries to resist any change in interfacial area.

So the work done on the system to increase the area of the interface

work = σdA $\quad \sigma$: work done on the system to produce new surface

$\boxed{\delta W_\sigma} = -\sigma dA$

↳ work done by system when its area is changed.

$\therefore dE = \delta Q - \delta W$

$\delta W = \delta W_{pv} + \delta W_{non-pv}$

$\boxed{pdV}$ $\quad \boxed{\delta W_\sigma}$

$\boxed{\delta Q_{rev} = TdS}$

So, in the previous lecture we have seen that how the surface tension is actually defined. Here we are going to look at a second definition of surface tension that is important definition of surface tension okay. Now if you consider it like this that the surface tension is the interfacial tension that tries to resist any increase in interfacial area right.

So this is like kind of a force equivalent definition right so far suspension is something okay which tries to resist any increase in interfacial area something that try to resist right any change in interfacial area correct. That is what it is like, if we have a droplet and you want to squeeze it right. So, far extension is something that tries to prevent this squeezing right always the droplet example comes in handy.

So, you apply some kind of a force on it you try to squeeze it in this particular shape okay. You would not be able to squeeze it spontaneously right. There will be resistance that will be offered right because otherwise this is a stable shape. If you think about it this is a stable shape in which droplets exists right.

You do not see elliptical shape droplets right in your common life right raindrops are spherical right. When water comes out of a faucet and breaks up it is spherical right. So, there are many instances where the shapes are normally spherical okay because of the reason that spherical shapes are the most stable and you know that the elliptical shape okay.

They do not exist naturally. So, there must be some kind of a, if you apply a force for example you can squeeze a droplet right but at the same time you have to realize that there is something that tries to prevent the increase of this interfacial area. So, surface tension can be defined in that light also okay.

So, the work that is done on the system not by the system remember on the system to increase the area of the interface okay is given by some kind of a work term right and that is Sigma into dA right. So, Sigma is basically the work that is done on the system right to produce a new surface. When you flatten this particular thing or when you split this droplet into two droplets.

You are basically creating more interfacial area right. So, new surfaces are created right for that Sigma is basically that the work that is needed for doing that effort right. So, this is like an alternative definition of surface tension. So, in that light we can write the work due to surface tension as - Sigma dA correct okay.

So, this is the work that is done by the system when it is area is changed okay work done by system. That is why the negative sign comes when area is changed okay. So, the decrease in area corresponds to work done by the system therefore dA is basically negative okay. So, that is the reason, is the other way around right. So, that is the definition.

Similarly recall that this is the basic first law definition I am sorry right. Now this work term that we have over here is basically composed of two works called the pv work plus the non pv work right. So, the pv work is basically given by pdv and this work is given by basically this surface tension related right.

So, this is the work that you are most familiar with this pdv mechanical work okay and like a piston moves okay. So, that kind of a work this is the work non pv related work and that it surface tension is one of them okay. We also know that dQ reversible okay is basically equal to Tds right lateral also know okay from the second law essentially.

So, what we have learnt in this particular slide in this particular page is that surface tensions alternative definition is that something that tries to change or resist any change in interfacial area okay. Now this work that is done to create new area is given by Sigma dA. Now this work is done by the system when this area is changed and since the area dA is negative okay.

Because the work is done by the system we are taking it to be a negative sign okay to accommodate to make it positive essentially okay. So, that is the definition that we have.

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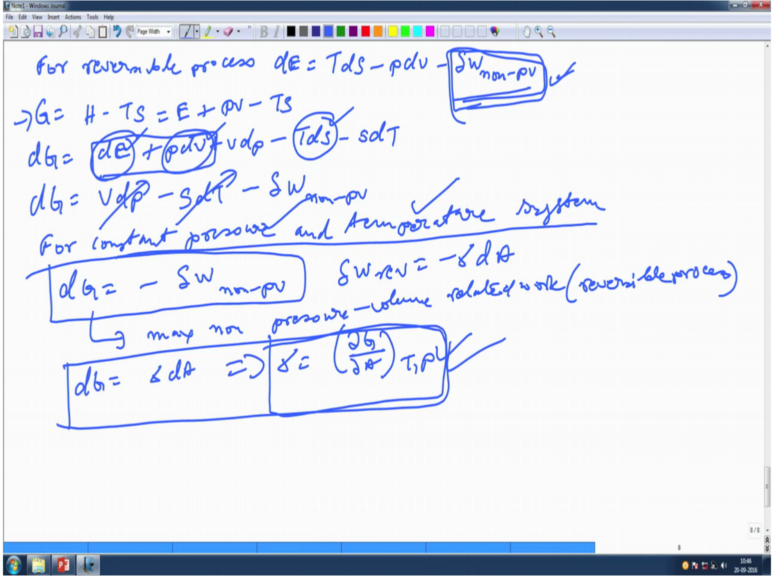

For reversible process $dE = Tds - pdv - \boxed{\delta W_{non-pv}}$ ✓

$\rightarrow G = H - TS = E + pv - TS$

$dG = \boxed{dE + pdv} + vdp - Tds - sdT$

$dG = Vdp - SdT - \delta W_{non-pv}$

For constant pressure and temperature system

$$\boxed{dG = -\delta W_{non-pv}}$$

$\delta W_{rev} = -\gamma dA$

→ max non pressure-volume related work (reversible process)

$$\boxed{dG = \gamma dA \Rightarrow \boxed{\gamma = \left(\frac{\partial G}{\partial A}\right)_{T,P}}}$$

Now let us look at for reversible process okay dE = Tds – pdv minus any non pv related work okay. G which is a Gibb's free energy is H - TS = E + pv - TS dG therefore is basically given as dE + pdv + vdp - Tds - SdT right okay. So dG vdp - Tds - non pv related work that we have over here.

Coming from the definition that we have already cast over there right okay, so, you can see from this expression that we have already know that these terms these two terms over here can be cast in that particular form right. So, you have taken into account that thing okay. So, but that is the expression that you have okay that sorry I made a mistake over here just one second okay.

It is basically SdT okay, so, has to be SdT okay. So, you know that, this term Tds this and this they are all given by this non pv work right okay, the energy because it is - Tds + pdv. So, you can see all these three terms are basically accounted for by this. So, that is what the substitution we have done we have substituted that into this expression okay.

So, that is the expression that we have now for constant pressure and temperature okay system. What do we have? Constant pressure constant temperature means this and this will go of right. So your dG will be nothing but this w non pv work okay. Now, so, this essentially means that dG for a constant pressure, constant temperature system is the maximum non pressure volume related work right.

So, this means is the maximum non pressure volume related work of course this is in a reversible process right okay, is that clear. So, this dG therefore is nothing but Sigma dA because you remember that was - Sigma dA okay. So, this gives us that Sigma is nothing but dG by dA at constant T constant P right.

So, it is a change in Gibb's free energy with respect to the area at constant temperature and constant pressure correct okay. So, this is the second definition of work. So, what we have done over here, we have gone from the basic Gibb's free energy equation substituted a few terms has shown that a change in Gibbs free energy for a constant temperature and constant pressure system is given by the non pv work right.

And the non pv work is nothing but as we already know this was - Sigma dA correct. So, this has been substituted over here and we have got this particular definition right okay. So, this actually shows that this is the alternative definition of the work correct. So, let us now look at before we go to the next thing. Let us look at a couple of other stuff as well.

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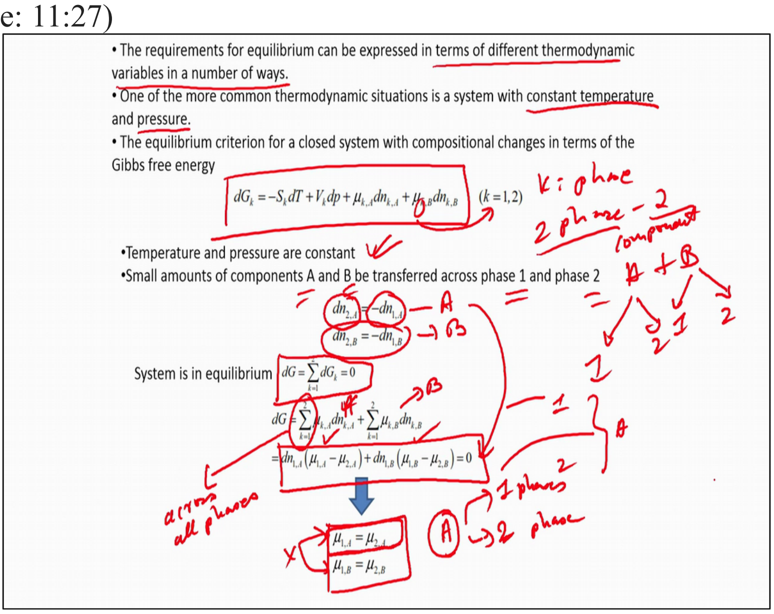

- The requirements for equilibrium can be expressed in terms of different thermodynamic variables in a number of ways.
- One of the more common thermodynamic situations is a system with constant temperature and pressure.
- The equilibrium criterion for a closed system with compositional changes in terms of the Gibbs free energy

$$dG_k = -S_k dT + V_k dp + \mu_{k,A} dn_{k,A} + \mu_{k,B} dn_{k,B} \quad (k = 1, 2)$$

- Temperature and pressure are constant
- Small amounts of components A and B be transferred across phase 1 and phase 2

$$dn_{2,A} = -dn_{1,A}$$
$$dn_{2,B} = -dn_{1,B}$$

System is in equilibrium $dG = \sum_{k=1}^{2} dG_k = 0$

$$dG = \sum_{k=1}^{2} \mu_{k,A} dn_{k,A} + \sum_{k=1}^{2} \mu_{k,B} dn_{k,B}$$
$$= dn_{1,A}(\mu_{1,A} - \mu_{2,A}) + dn_{1,B}(\mu_{1,B} - \mu_{2,B}) = 0$$

$$\mu_{1,A} = \mu_{2,A}$$
$$\mu_{1,B} = \mu_{2,B}$$

We have seen all these things now. Now let us just come this particular section before we go on and see how surface tension and other things are applicable and let us look at the for a multi component systems okay or a system which has got compositional changes okay, what are the requirements right. So, for the requirements of equilibrium can be expressed in terms of different thermodynamic variables that we already know right for such system.

Now let us assume it is a constant temperature and a constant pressure scenario okay. So, the Gibbs free energy for a compositional system in terms of that Gibbs free energy is given by this particular parameter where this K that you see over here is basically nothing but it can be 1, 2, 3, whatever it is right and temperature and pressure are constant.

Now if we assume that small amounts of component A and B can be transferred across phase 1 and phase 2. So, there are two phases right. So, what will happen is that this is this is phase. So, k is basically nothing but the phase. So, it is basically 2 phase, 2 component system right, where the components are A and B right. Each A and B has brought phase 1, phase 2 this has also got the phase 1 phase 2 right okay. So, that is the situation.

We have so far done 2 phase we have done 2 components. Let us look at 2 phase 2 component kind of a scenario. So, assuming that there has been a transfer of components that means some part across the two phases, so, for example there is an interface, you can assume. So, there is phase 1 and phase 2 and both of these accounts under component A.

So, the number of moles change in the second phase is equal to the corresponding loss on both of the first phase okay for component A, this is for A only. Similar thing happens in the case of component B right, so, there has been a change in phase. Now since the system is in equilibrium the Gibbs free energy right has to be equal to zero across all the phases.

Therefore the Gibbs free energy here has to be written across two components and for two phase's right. So, if you look at the thing over here, this is for component A, this is for component B. And this summation that you see over here is nothing but across all phase's correct, okay. So, it is summed over two phases and it is summed over two components also right, okay.

So, if you expand this particular thing out for using this particular these two relationships over here right that there are small changes across the phases, you get this particular relationship okay. Because the change in Gibbs free energy has to be equal to zero. So, therefore what we get out of this is basically the chemical potential of each individual component across the individual phases has to be the same right okay.

So, if component A is present in two phases, phase 1 and phase 2 right, two phases okay. That means the chemical potential okay of phase 1 has to be the same as a chemical potential of phase 2 so long as the component is A. Similarly for component B, the same thing holds. Now it can be a multi-component system also does not really matter.

What it means is that the chemical potential across all the phases A, B, C across all the components A, B, C, D right, has to be the same across all the phases okay. It does not mean that these two are the same just clear the just this is not necessarily the same right okay. What it essentially means that across the phase the chemical potential does not change so long the component is kept constant, got it.

So, this is an important thing that will come because we have done two phases we have done two components. We have now seen what surface tension is. Now we have looked into that what this means in terms of the phase space okay. So, these are the two things that we see over here, so, let us moving to the next slide.

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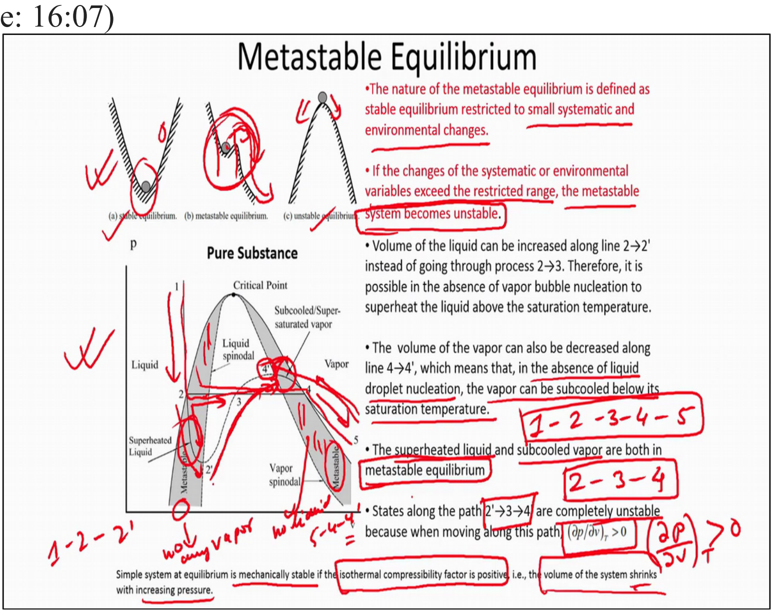

Metastable Equilibrium

- The nature of the metastable equilibrium is defined as stable equilibrium restricted to small systematic and environmental changes.
- If the changes of the systematic or environmental variables exceed the restricted range, the metastable system becomes unstable.
- Volume of the liquid can be increased along line 2→2' instead of going through process 2→3. Therefore, it is possible in the absence of vapor bubble nucleation to superheat the liquid above the saturation temperature.
- The volume of the vapor can also be decreased along line 4→4', which means that, in the absence of liquid droplet nucleation, the vapor can be subcooled below its saturation temperature.
- The superheated liquid and subcooled vapor are both in metastable equilibrium
- States along the path 2'→3→4' are completely unstable because when moving along this path $(\partial p/\partial v)_T > 0$

Simple system at equilibrium is mechanically stable if the isothermal compressibility factor is positive, i.e., the volume of the system shrinks with increasing pressure.

Before we go back to the judge to our notes okay, let us clear up a few other things also because this will come in handy in the thing that we are going to cover next. Now when we say that a system is in equilibrium okay, it means several things right. Equilibrium and having an unstable equilibrium there are several ways to define it okay.

So, for example if you look at this particular picture over here you see that from the parlance of mechanics if you remember your old UG mechanics courses you find that this is called, so, this is called a stable equilibrium okay. Stable equilibrium means that even if you make large changes okay in the large displacements the system will come back to its, a stable state right.

You cannot make the system unstable whereas a system can be an unstable inner in a metastable equilibrium. What does metastable equilibrium means? That it is stable over this range only right, if the displacement is large this will topple and go like that right. So, it is defined as a stable equilibrium restricted to small systemic environmental changes only it is not for large changes.

That means if this model that is there if you take it to a large displacement okay. It will just fall down the hill right whereas in this case it is never going to happen. You can take it here and relieve it; it will come back to its equilibrium position. An unstable equilibrium means with any small displacement, no matter how small it is it will just go into an unstable state.

So, metastable equilibrium is something which is not completely stable not completely unstable either. It is somewhere in between and it is actually stable small displacements not stable for very large displacement right. This is the mechanical equivalent right. So, if the changes in the systemic or environmental variables exceed a certain restricted range. The metastable system becomes unstable right.

So, if there is a large change right not small anymore as you can see if it is more than this okay. The system becomes unstable okay. So, that is very important because of the thing that we are going to look next. Let us look at this particular plot this is a very standard liquid vapour evaporation dome.

Now what happens in this particular case okay what you see is that this is a typical vaporisation path what you are aware from one end to it comes right. Then it enters the two phase zone right and then it enters into the vapour phase correct. As you can see the liquid is first expanded right.

Then it passes through the two phase zone and then it is superheated right. So, that volume correspond to specific volume correspondingly increases. This is the traditional thing that we have all seen over here okay. So, the volume of the liquid can be naturally follows this particular part right okay.

But however it is possible basically that the volume of the liquid can be increased via this particular path as well, this part that you see at the bottom right okay. So, it is for what happens to the liquid it is basically compressed right, it is basically compressed. But there is no vapour that is available okay. There is no vapour nucleation that has happened.

Because the two-phase do not normally at this particular position if you extrapolate at it up to here you will find that it is a two-phase zone right. But what we have done is that the volume of the liquid has increased right across the path not compressed actually increased the volume instead of going through the process 2 and 3 it has followed this particular path instead of going through that particular part okay.

So, therefore it is possible in the absence of vapour nucleation to basically super heat the liquid above the saturation temperature that is what has happened okay. So, what we have done is that we have basically superheated the liquid above its saturation temperature without actually having any bubble formation or any vapour formation essentially, vapour duo creation right okay.

So, I am sorry I made a mistake when I said that it is basically compressed. It is basically expanded right in this particular zone. Now similarly a similar path can be followed, if we follow this particular trajectory right. So what it happens here is that the volume of the vapour is decrease now? It is decreased along this particular path 5 and 4.

But instead of following 4 and 2 that particular path where it enters into the saturated regime, it can be actual actually made to follow the path 4 to 4 prime okay which means that is the absence of liquid droplet nucleation is a reverse thing. The vapour can be sub cooled below its saturation temperature right. So, what we have done is that it is like a compression we have compressed it okay and we have made the vapour sub cooled okay below its saturation temperature right.

But there is no evidence of liquid formation right. At the saturation point you are supposed to enter the two-phase zone which is basically 2, 3, 4 right. This is the two-phase zone correct, 2, 3, 4 is two phase zone. So, normally you follow the path 1-2-3-4-5 right that is the path that you normally follow.

What you have done over here is that you have followed 1, 2 and 2 prime on the liquid side and you have done 5, 4, 4 prime on the vapour side right. But here you do not have any vapour, no vapour. Here you do not have, no have any liquid, so no liquid, got it, okay. So, this superheated liquid which is this particular section and sub cooled vapour which is this particular section are both in metastable equilibrium.

A typical example of a metastable equilibrium however the interesting question that you might ask is that what happens to 2, 3, 4 prime can the can that path be followed right. But 2 or rather 2 prime 3, 4 prime whether that path can be followed or not. This part is completely unstable because if you recall your UG thermodynamics okay.

A simple system is that mechanically stable equilibrium if only the isothermal compressibility factor is positive. That means the volume of the system should shrink with increase in pressure right. So, isothermal compressibility factor has to be positive for a system to be in mechanically stable state at equilibrium right.

So, if you look at this path 2, 3, 4 prime right that is the path 2, 3, 4 prime what you see over here it is completely unstable because the isothermal compressibility factor which is basically dV dT at constant T because this isotherm all right, this is greater than zero correct. So, we can clearly see that the path is completely unstable.

Because as you move along this path you get the reverse of this as a volume of the system okay, actually increases okay with increasing pressure right. So, that is the problem that we have over here it should actually shrink with increasing in pressure right. So, but however 2-2, 2 prime is possible, 4, 2, 4 prime is possible that means it is physically speaking you can actually have super cooled liquid superheated liquid and sub cooled vapour.

Those two paths are possible right but you cannot have the migration from 2 prime, 3, 4 prime because that would be like unstable right. So, this particular shaded region on the left this is called the this is the superheated liquid state okay and the other part here which is the super cooled a sub cooled vapour state or supersaturated vapour whatever you call it okay.

So, that is also another metastable state this is called the liquid spinodal this is called the vapour spinodal okay. So, normally in a way we activity boiling later on, you will find and in fact in the next slide I will show when you do actually boiling these two zones becomes very important right. Because you can actually have a situation where you actually have superheated liquid which is undergo which has not shown any bubble formation.

And superheated and vapour right which; or sub cooled vapour which has not shown any okay.

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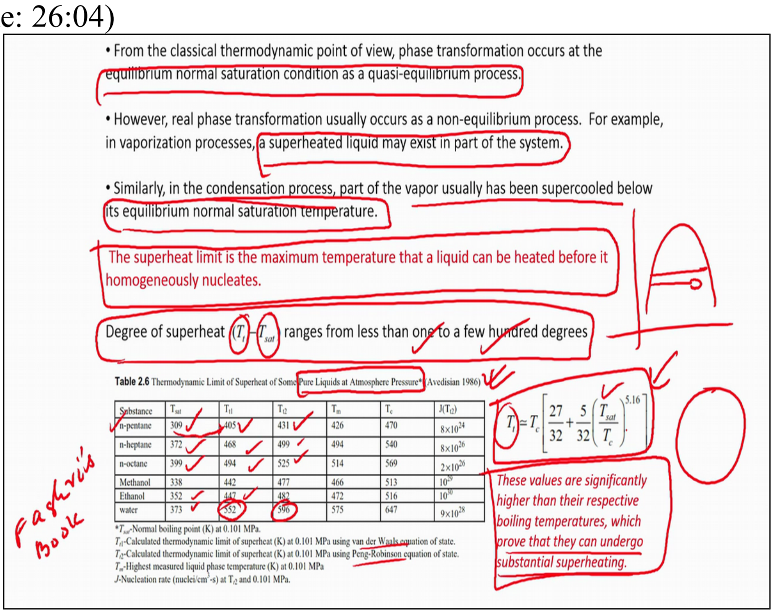

- From the classical thermodynamic point of view, phase transformation occurs at the equilibrium normal saturation condition as a quasi-equilibrium process.
- However, real phase transformation usually occurs as a non-equilibrium process. For example, in vaporization processes, a superheated liquid may exist in part of the system.
- Similarly, in the condensation process, part of the vapor usually has been supercooled below its equilibrium normal saturation temperature.

The superheat limit is the maximum temperature that a liquid can be heated before it homogeneously nucleates.

Degree of superheat $(T_t - T_{sat})$ ranges from less than one to a few hundred degrees

Table 2.6 Thermodynamic Limit of Superheat of Some Pure Liquids at Atmosphere Pressure* (Avedisian 1986)

Substance	T_{sat}	T_{t1}	T_{t2}	T_m	T_c	$J(T_{t2})$
n-pentane	309	405	431	426	470	8×10^{24}
n-heptane	372	468	499	494	540	8×10^{26}
n-octane	399	494	525	514	569	2×10^{26}
Methanol	338	442	477	466	513	10^{29}
Ethanol	352	447	482	472	516	10^{30}
water	373	552	596	575	647	9×10^{28}

*T_{sat}-Normal boiling point (K) at 0.101 MPa.
T_{t1}-Calculated thermodynamic limit of superheat (K) at 0.101 MPa using van der Waals equation of state.
T_{t2}-Calculated thermodynamic limit of superheat (K) at 0.101 MPa using Peng-Robinson equation of state.
T_m-Highest measured liquid phase temperature (K) at 0.101 MPa
J-Nucleation rate (nuclei/cm^3-s) at T_{t2} and 0.101 MPa.

$$T_t \simeq T_c\left[\frac{27}{32}+\frac{5}{32}\left(\frac{T_{sat}}{T_c}\right)^{5.16}\right]$$

These values are significantly higher than their respective boiling temperatures, which prove that they can undergo substantial superheating.

Faghri's Book

So now we just look at some of the details over here okay usually from classical thermodynamics point of view right. The phase transformation occurs at equilibrium normal conditions like it is a quasi equilibrium process right. So, that is what you get in that particular colours right. So, you have that straight section right. So, if you just recall that is what we did right this is the portion which is nice and steady in equilibrium right.

However the real phase transformation like for example boiling another things okay. A superheated liquid may exist that means that liquid spinodal that we showed okay is not a fiction of imagination it actually happens right. In real phase transformation system that is an indeed a mandatory thing.

Similarly in condensation process that is the other way around right the vapour is usually sub cooled right or super cool whatever you call it either way. Below the equilibrium normal temperature it is a sub cooled, this is a very cold vapour right even though it has not undergone the condensation right okay.

But and we will come to that later the superheat limit is the maximum temperature that a liquid can be heated before it homogeneously nucleates. So, there is a threshold also right, beyond this threshold if you do the liquid after that; will homogeneously nucleate start showing vapour pockets right.

So, that is that there is a maximum temperature up to which you can heat it right, beyond the saturation point okay. So, as I said we already established that though we say that liquid vapour transition right the phase change is a quasi equilibrium process it happens along that straight line and things like that. In reality we saw that the vapour is the liquid is actually super heated okay.

And it can be super heated to a certain temperature before you actually start to see the new creation mean bubble formation or vapour formation right. So, people have calculated it okay the degree of superheat actually is not a small quantity it can be from less than a 1 to a few hundred degrees right. So, that means this is the level of superheat and this is the saturation temperature.

So, basically you can heat a liquid okay to a point much above you know its saturation temperature right without having any bubbles. So, if you look at this table once again this is from Fagri's, Amir Fagri book okay which is a prescribed textbook for this particular course okay. You can see that there are for example different pure liquids at atmospheric pressure data compiled by professor Tom Avedisian okay in from a 1986 work.

So, if you look at n-pentane for example its saturation temperature is 309 okay. Now the degree of superheat and these superheat are calculated using Van Der Waals and different other equations of state. We are going to go into those details later. But assuming that whatever it is there is a super heat level.

So, one is 405 one is 431 right, so, that means there is almost a 100 to close to 120 degree Celsius okay that you can heat a liquid before it starts to boil okay. Similarly for n-heptane you see a similar thing n-octane you see a several thing methanol for example also shows a similar thing, ethanol also shows a similar thing and water, water is really high if you look at it is almost close to 200 degrees okay.

552 and 596 right so, it is very, very high okay. So, these values are significantly higher than their respective boiling point. If you look at a boiling point of water under atmospheric pressure is 100 degree Celsius right. But here you are getting high 52 Kelvin okay 552 Kelvin is almost 300 degree Celsius or close to that give or take okay.

So, they can undergo which proved that they can undergo substantial superheating okay even beyond their normal boiling point and in fact in the case of multi-component droplets okay

When you actually have boiling inside a droplet you we actually do see such things okay. So, this can be all encompass in a kind of a correlation which is given by this particular form okay.

So, this is like a correlation which says that how to calculate the degree of superheat basically when you know what is your saturation temperature and other things okay clear. So, once we know so, we know a few things now that there is something called a liquid spinodal there is something called a vapour screen spinodal.

Liquid can be superheated, vapour can be sub cooled. So, there is a degree of superheat that is involved before you see paper or bubbles appearing in the system. This is very important for the boiling community right and this degree of superheat is not just one or two degrees it can be hundreds of degrees essentially it can be very small it can be very large as has been proved by proven by this particular table over here like the work of Avedisian at all.

So, I think this is a very important part that you get which you do not get in your previous thermodynamics book. You always thought that the phase transformation happens across a straight line correct. So, it is a nice like this essentially right so it happens across this particular line.

So, but he phase transformation does not necessarily happen in that particular way okay. You have a system which is quite a bit deviated from its equilibrium where it is in a metastable equilibrium state right. Before it starts to show any vapour formation or if you look at the reverse process which is condensation well whether it shows any condensation process or not okay.

So, just looking at this previous slide okay you can see that we have put a lot of markers over here only the path represented by 2 prime 3, 4 prime is unstable. 2, 2, 2 prime, 4, 2, 4 prime these are stable or metastable path that is something that you should keep in mind because the next thing that we are going to do is a little bit of a boiling I mean little bit of a vapour formation.

How that has actually happens okay. So, let us look at this I mean let us go back to you our journal once again and so before we go so we end lecture 5 over here okay under this note. The next lecture that we are going to start will be on micro scale vapour bubbles and liquid droplets. How they form. Now that we know a little bit about this boiling curve will know a little bit about the interface.

We know a little bit about surfaced and tension right, we know how surface tension can have multiple definitions. So, in the next lecture we are going to look at this particular problem okay. So, meet you in the next lecture.