Multiphase Flow

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Lecture No. # 31
Different Types of Nucleation

Good morning everybody. So, today we will see different mechanisms of vapour formation and in that connection, we will also learn, different types of nucleation. Now vapour formation;

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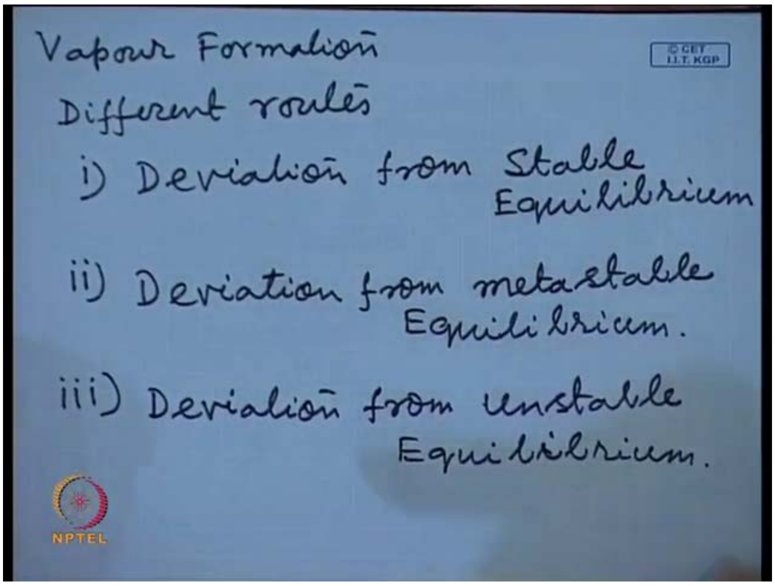

Vapour Formation
Different routes
i) Deviation from Stable Equilibrium
ii) Deviation from metastable Equilibrium.
iii) Deviation from unstable Equilibrium.

So, vapour formation, it has different routes. Basically, for vapour formation what is needed is that that, there is a deviation from the equilibrium. So, vapour formation takes place from the liquid phase vapour forms, if there is a deviation from the equilibrium. And one can think of three types of deviation; deviation from stable equilibrium, deviation from meta stable equilibrium, and finally, deviation from unstable equilibrium.

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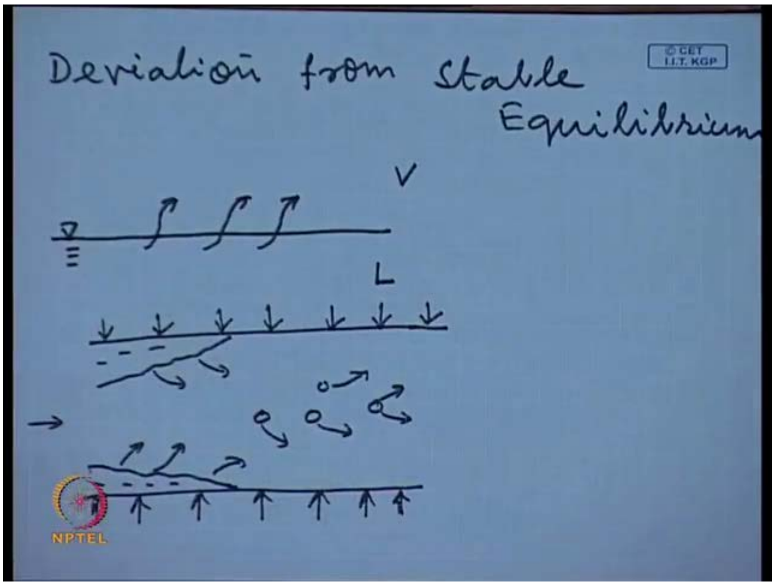

So, let us examine case by case all these three different routes of vapour formation. Now, you see, first let us see deviation from stable equilibrium. So, suppose there is a planar interface; planar liquid interface, this is a planar liquid vapour interface and from the liquid we know that vapour can form, so that means, this is your liquid and this is vapour and from the liquid the vapour is forming. So, basically this transition from the liquid phase to vapour phase is due to a deviation in the stable equilibrium condition. Vapour and liquid, they are co existing together under stable equilibrium and here only there is transition from the liquid to vapour.

Now, one can think of another situation, let us say there is a large pipe; inside the large pipe, there is flow of fluid and this pipe is heated, at the periphery of this pipe - there is heat input, so, what will be; what one can observe under certain operating condition that, that there will be a liquid film adjacent to the pipe wall and from the liquid film, there will be evaporation. So, probably there could be a few droplets also from there; there could be evaporation.

Here also, it is like this that it is a deviation from stable equilibrium. Though exactly it is not a planar surface, the second example exactly it is not a planar surface, but if the pipe line; I mean, pipe diameter is quite large, so compared to that the film curvature that can be minimal and here also, the situation is quite similar as we have seen in the top diagram, where vaporization is taking plane; taking place from a plane liquid surface.

Now, in both these cases what happens? The condition for vaporization is that, the surface temperature of the liquid should be only marginally higher compared to the saturation temperature, corresponding to the pressure, so at that condition only, we will have the vaporization. And here, the vaporization or evaporation process, basically it is called evaporation. So this process the mass exchange and again what will be; the heat transfer that is associated or that is related to the mass exchange, that can be obtained from the molecular flask which goes from one phase to another phase. So, we will not discuss much regarding it, but let us know that, there is one type of vapour formation where there is deviation from the stable equilibrium.

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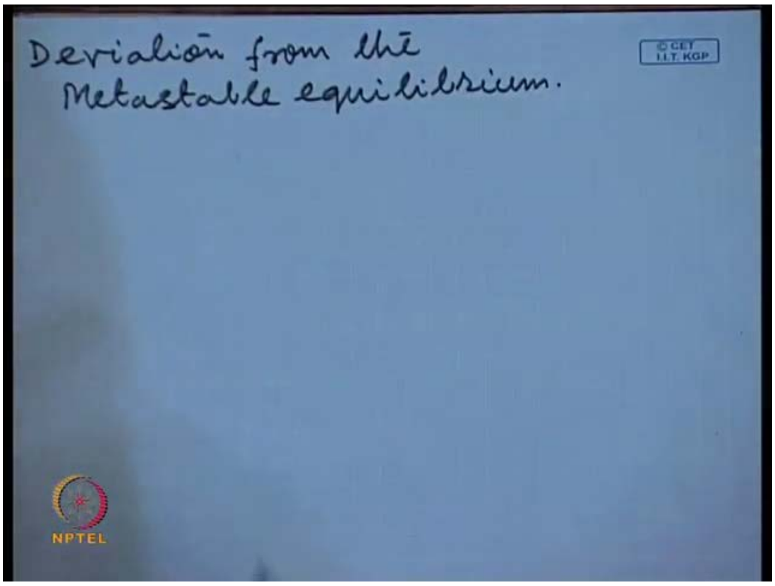

Deviation from the
Metastable equilibrium.

Now, let us go to the second case, deviation from the meta stable equilibrium. Now, it is a very common experience that; it is a very common experience that, though the liquid temperature is above the saturation temperature, immediately vapour formation does not take place. In many situation, one can find that though the liquid temperature is above the saturation temperature, the evaporation or the vapour formation will not take place.

Now, why it is so? If we had to explain it why it is so, then we have to go little bit into the mathematics part of it. You see, similar kind of equation we have derived earlier, but when we are forming the vapour, see if there is a nucleus; vapour nucleus and we have got some sort of a vapour embryo in the bulk of the liquid, then there is a pressure difference in the vapour phase and In the liquid phase.

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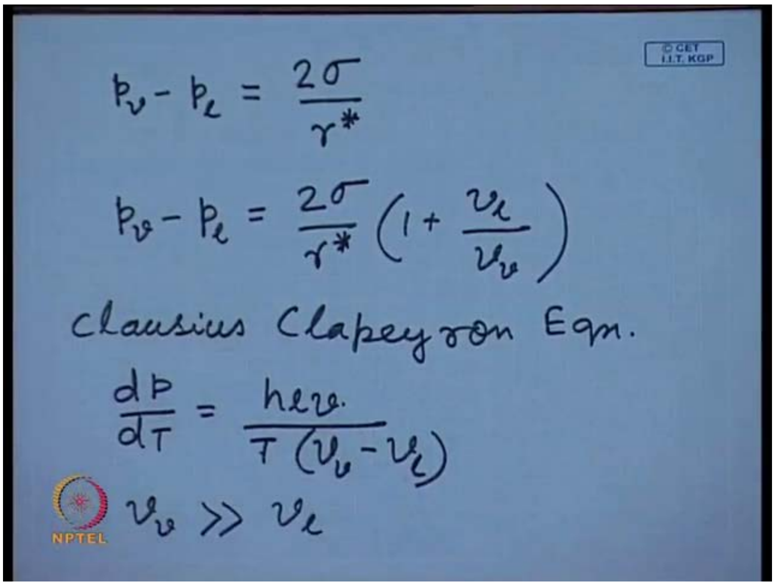

$$p_v - p_l = \frac{2\sigma}{r^*}$$

$$p_v - p_l = \frac{2\sigma}{r^*}\left(1 + \frac{v_l}{v_v}\right)$$

Clausius Clapeyron Eqn.

$$\frac{dp}{dT} = \frac{h_{lv}}{T(v_v - v_l)}$$

$$v_v >> v_l$$

And this, we have already derived for a spherical vapour bubble or vapour embryo, it will be p v minus p l, this subscript they have got their usual meaning, that is 2 sigma by r star, this is our classical young Laplace equation, p v is the pressure in the vapour phase; p l is the pressure in the liquid phase; sigma is the surface tension and r star is the radius of the vapour embryo.

Now, you see it is not a plane surface, so if there is a curvature effect, some people have suggested some correction to this, so this can be corrected something like this, p v minus p l is equal to 2 sigma by r star, one plus v l by v v. So, v l represents the specific volume in the liquid phase and v v that represents the specific volume in the vapour phase.

So, if there is a curved surface approximately one can have, the difference of pressure between the two phases given by this particular formula. Now you see; so, one has to appreciate, that the liquid and vapour at least near the interface, they are very close to the saturation condition and we can use Clausius Clapeyron equation for this particular situation. So, if we use Clausius Clapeyron equation… if we use Clausius Clapeyron equation for this particular situation, so then what we get? … So, this is our Clausius Clapeyron equation, in some form we can write it, h l v is the latent heat of vaporization.

Now here, one can make certain assumptions; one assumption is that, specific volume of vapour that is much much higher compared to the specific volume of liquid and also we can assume that the vapour, that approximately behaves like an ideal gas.

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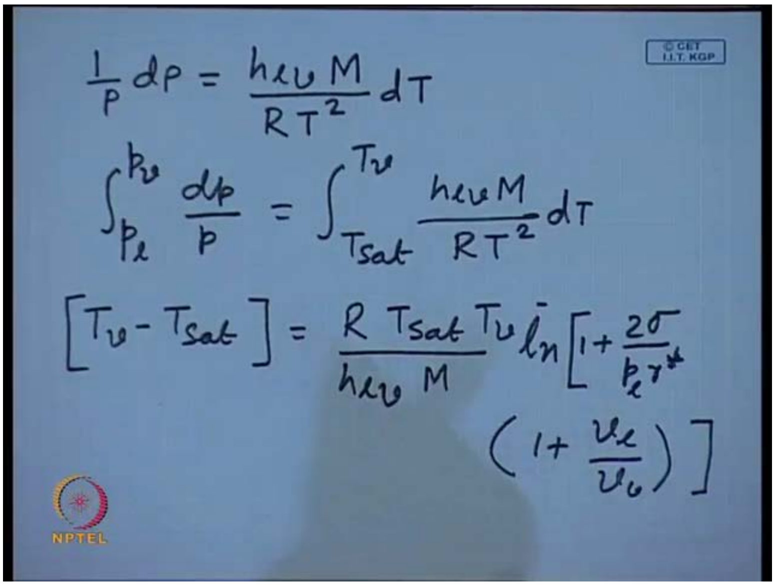

$$\frac{1}{p}\,dp = \frac{h_{lv}M}{RT^2}\,dT$$

$$\int_{p_l}^{p_v}\frac{dp}{p} = \int_{T_{sat}}^{T_v}\frac{h_{lv}M}{RT^2}\,dT$$

$$\left[T_v - T_{sat}\right] = \frac{R\,T_{sat}\,T_v}{h_{lv}\,M}\ln\left[1+\frac{2\sigma}{p_l r^*}\left(1+\frac{v_l}{v_v}\right)\right]$$

So, if we make these two assumptions, then then the equation, that can be simplified and probably that can be integrated also. So one can have, one by p dp, that is equal to h l v M; M is the, M is the molecular weight of the particular fluid; R gas constant; R T squared, divided by R T squared into dT and then this can be integrated. So, if we integrate it from p l to p v, inside the vapour embryo pressure is higher, so we can integrate it from p l to p v, dp by p that is equal to, again at the interface and at the liquid phase near the interface; the temperature is the saturation temperature, where as inside the vapour embryo is higher. So, we will get this particular thing.

And one can do little bit of simplification, with simplification one can write,

Normal log of one plus 2 sigma p l r star, this should be multiplied by one plus v l by v v. You see, this last term is the addition; this last term is the addition, for or to take care of the curvature effect of the bubble.

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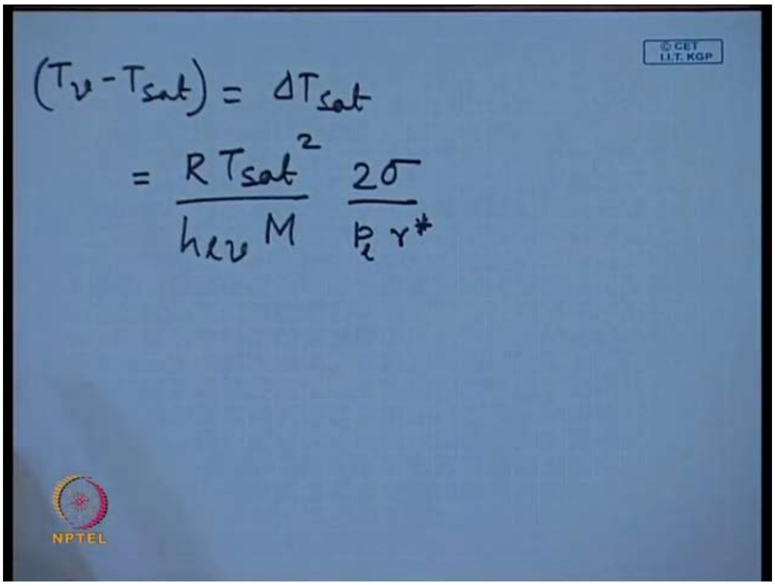

$$(T_v - T_{sat}) = \Delta T_{sat}$$

$$= \frac{R T_{sat}^2}{h_{lv} M} \frac{2\sigma}{\rho_l r^*}$$

Now, generally this can be neglected also, this particular term can be neglected also. As v l is much lower compared to v v, so this is approximately equal to one. Now, with all this approximation and one can write T v minus T saturated, that is equal to delta T saturated, that is again equal to… So, this is after making some approximation, one can write this equation.

So, what does this equation convey? This equation convey that, if I had to make a vapour embryo of r star radius, then I need certain amount of super heat, that is given by T v minus T sat. And of course, this fluid properties; it will depend on the fluid properties, whatever fluid properties I have given, the saturation temperature I have given, so it will depend on that. So, I am getting a relationship, that I need certain amount of degree of super heat for evaporating or for vapour formation, if a vapour embryo of radius r star is to be produced.

Now, what is the relationship between delta T sat and r star? The lower the value of R star, the higher will be the value of delta T saturated; that means, suppose I have to make a small vapour emb; embryo, I need to have a very large degree of super heat.

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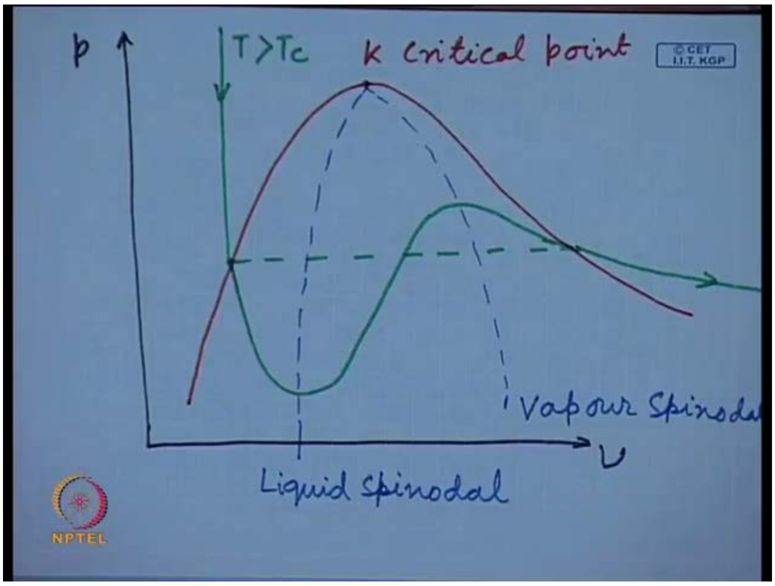

Now, let us go back to some thermodynamics. I think, let me draw this diagram, it will be easier for you to draw it with me, while I will explain. So, this is the conventional p v diagram and we are interested in the two phase dome; we are interested in the two phase dome. So, basically in the p v plane or many common fluids, the two phase dome looks like this, so here we are having critical point.… Now, in normal isotherm in most of the text book is represented like this, this is an isotherm. And here, this isotherm temperature is constant, this is below the critical isotherm. So, this is the normal isotherm which is represented in most of the text book.

What are the different parts or different important, important features of this diagram? So, this line up to k; this is the saturated liquid line and this is the saturated vapour line; on this side, we have got sub cool liquid; on the other side, we have got your super heated vapour; in between we are having a two phase mixture. Now it shows that, if we follow a isotherm then, as as soon as it approaches the saturated liquid line, there is an abrupt change in the slope of this line.

And again as soon as, it approaches the saturated vapour line; vapour curve, then there is an abrupt change in its slope. Now, in many of the natural system or most of the natural system, this kind of abrupt changes are not very common. So, if this situation is conducive, then what happen; this curve will be a continuous curve with continuous slope; continuous change in slope and the nature of the curve will be something like this.

My drawing is little bit exaggerated, but this will be something like this. Now, what we can see that, there are two extreme points in this curve. Now, the blue line which I have drawn towards the left side, this is called… and the other blue line; broken line that is called vapour spinodal.

So, the idea is, suppose I am; what I am doing, I am basically basically reducing the pressure here and I am following this curve, so if I reduce the pressure, the curve will follow in this direction and there will be a change in the slope and after that, it will follow the way I have shown it.

Up to this portion, if there is minimum amount of disturbance, then it will continue to stay only in the liquid state. So, this is a meta stable liquid state, on the other hand; on the right hand side of the curve, we will have the meta stable vapour state. So, it will try to remain in the liquid state only, though the temperature here is the saturation temperature corresponding to the pressure.

Now, what we can see, the temperature is remaining constant and pressure is reducing along this curve up to liquid spinodal. So, what does it mean, that here it is gaining certain amount of degree of super heat. Because, corresponding to this pressure the saturation temperature is lower, but it is remaining at a higher temperature, so it is gaining certain amount of degree of super heat. Now, this degree of super heat is again related as I have shown to the radius of vapour embryo, as the degree of super heat is reducing, so corresponding radius of vapour embryo, that is also reducing. So, at some point, it may come to the molecular dimension.

Now, this is some sort of thermal agitation is always there in the meta stable state of the liquid. Now, what will happen, there is a small but finite, this comes from the statistical thermodynamics, that there is a small but a finite probability that, suddenly at this condition, there will be a large number of vapour embryo in the bulk of the liquid and evaporation will take place or some kind of nucleation; vapour nucleation will take place and process of vaporization will take place. So, this is called homogenous nucleation. So, this particular phenomenon is known as homogenous nucleation, it is not very common, it needs a large amount of degree of super heat, but it is possible and it is possible only, if the liquid stays at meta stable state. So, then it indicates a deviation from the meta stable equilibrium.

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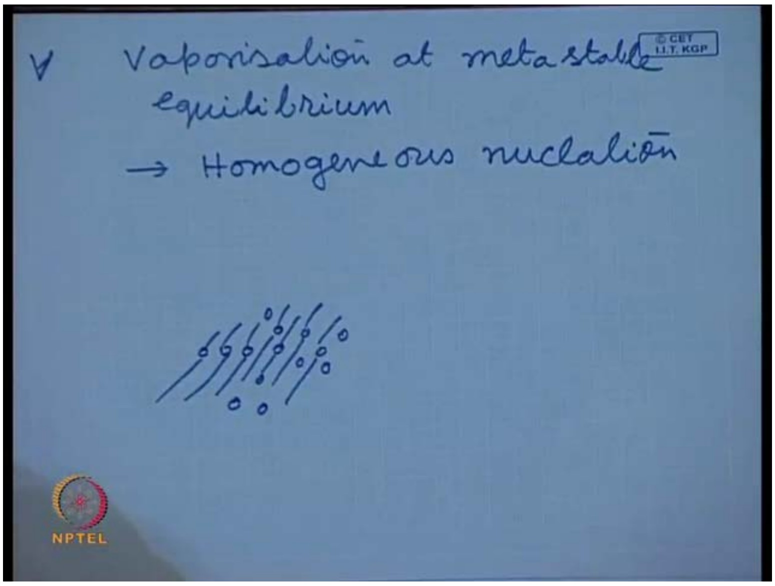

✓ Vaporisation at metastable equilibrium

→ Homogeneous nucleation

So, we have got in the;

This is homogenous nucleation.… Now, homogenous nucleation that can occur only in a very clean system, liquid is very clean and let us say, it is depressurized to a very high value; very suddenly it is depressurized, then we can think of; or one can come across a situation, which is close to homogenous nucleation.

Actually, by if you if you make the calculation, you will find that, homogenous nucleation needs tremendous amount of energy. See, from the liquid when vapour is forming, certain amount of energy is required, because an interface is to be created. And here, small nucleuses are there, so as the as the radius of sphere that reduces, then the surface area increases. So, very large number of small nucleuses are there; so very large number of energy is required. So, for homogenous nucleation, a very large number of energy; large amount of energy is needed; that means, that can come from the degree of super heat, so large degree of super heat is needed. So, it is not very easy to create this situation, but in some situation, we can have this type of a phenomena.

So, if I try to point out the difference between the; if I try to point out the difference between the earlier process and this process, what is the difference? So, in the earlier process of evaporation, what we have seen that, it is taking place place from the plane surface of the liquid, then there is no nucleation process. So, interface that is instable equilibrium; for the two phases, it is instable equilibrium, no nucleus is formed.

In case of homogenous nucleation, we have got a bulk of liquid and in the bulk of liquid, very large number of; this is bulk of the liquid and in the bulk of the liquid, very large number of nucleuses are formed. So here, one need to form certain nucleus, for the vaporization process to proceed. So, that is the difference between these two processes what I have described that, homogenous nucleation and your previous evaporation process. Now, as I have told that homogenous nucleation is not very common commonly we cannot day to day phenomena or let us say, in industrial practice we rarely come across homogenous nucleation.

Then of course, I mean, this is a process of vapour to; liquid to vapour change, there could be a reverse process from vapour to liquid formation. So, there also situation close to homogenous nucleation is possible; not always, again in some unusual or special situation like, you have the formation of fog, so there also something close to; not exactly homogenous nucleation, but something close to homogenous nucleation, because very large number of liquid droplets, very small droplets are formed. Of course, there the system is not very clean, in atmosphere there could be a large number of dust particle etc., But, close to the phenomena which I am describing here is also present; their, that very large number of nucleuses or nuclei are formed.…

Then, most of the system, they are not very clean the way I have described and most of the system are also not homogenous, in the sense, when I am describing homogenous nucleation, it is in the bulk of the liquid, but let us, say the bulk of the fluid that has to be contained in something, so there is a wall; solid wall. So obviously, solid wall that breaks the homogeneity, the condition at the solid wall are different from that, of the bulk of the fluid. So, homogenous nucleation as I have told, that it is difficult to get, because of this reason that, we cannot also make it; make the system totally homogenous. So, then there is another kind of nucleation, that is called heterogeneous nucleation.

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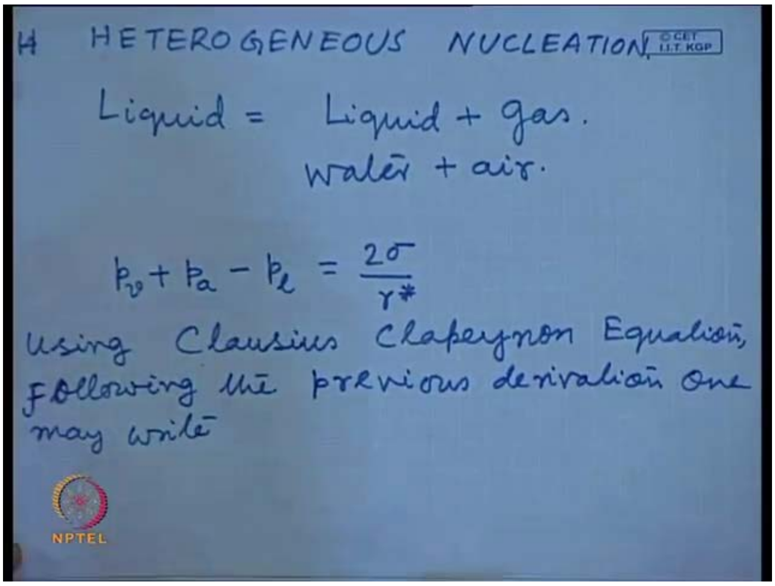

H HETEROGENEOUS NUCLEATION

Liquid = Liquid + gas.

water + air.

$$p_v + p_a - p_l = \frac{2\sigma}{r^*}$$

Using Clausius Clapeyron Equation, following the previous derivation one may write

So, heterogeneous nucleation; how heterogeneous nucleation will be there? Heterogeneous nucleation will be there, because the bulk of the fluid, let us say water; water will have dissolved gas, so it is having some sort of foreign material in it. There could be contaminant in the form of suspended material; suspended solid material and there also will be discontinuity at the wall. So, all these things, they gives rise to nucleus formation. And obviously, these impurities or the surface irregularities, whatever I have described; they are not homogenously distributed. So, the nucleuses; now, the nuclei will be not homogenously distributed and we can call this particular process, as heterogeneous nucleation.

And what has been seen from our day to day experience, as I have told that, if you calculate, the energy requirement for homogenous nucleation, it is tremendously high. But in case of heterogeneous nucleation, you will find that, it is not that high, it is quite low, why it is so.

Now, what we can see in heterogeneous nucleation, as I have told, the liquid is not that pure liquid. So, we can have; in case of heterogeneously nucleation, the liquid is a mixture of liquid plus gas. So, a very common example will be your water plus air; this is a very common example, that we will have a mixture of water and air in case of your day to day experience or in any industrial system. So, if it is air and water mixture, then our all the equations we; which we have used earlier, those equations are to be modified.

How they have to be modified? See the; the equation will be now, p v plus p a minus p l, that is equal to twice sigma by r star.

So, the partial pressure of air or any other dissolved gas in the liquid, that has to be considered also also; that means, total pressure inside the vapour embryo minus the liquid pressure, that is balanced by your capillary force and comes from the basic young Laplace equation.

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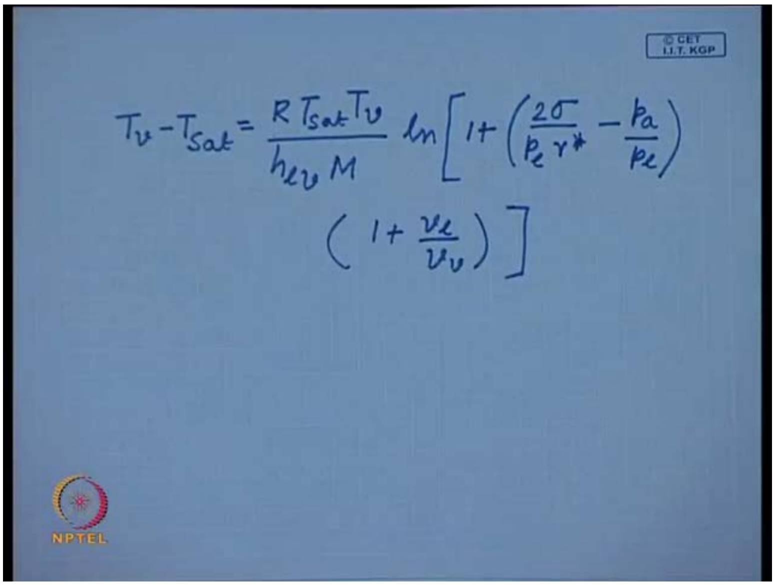

$$T_v - T_{sat} = \frac{R T_{sat} T_v}{h_{lv} M} \ln\left[1 + \left(\frac{2\sigma}{p_l r^*} - \frac{p_a}{p_l}\right)\left(1 + \frac{v_l}{v_v}\right)\right]$$

And again, what we can write is this, using Clausius Clapeyron equation and following the previous derivation … one may write, we can write the following relationship, T v minus T sat, that is equal to R T sat T v. Actually T v is close to T sat, so in some expression, one can have T sat squared also, h l v M l n 1 plus, within … this multiplied by again one plus v l by v v.

So, this could be the relationship for the degree of super heat, which is needed to create vapour embryo. Now here, one can again make certain simplification like v l by v v, that is very small, so one can neglect it and again one can neglect, suppose the quantity of dissolved gas is not much in the liquid, so one can also neglect this quantity.

Then, one will laid to it; logarithmic, I mean logarithmic, natural logarithm of 1 plus 2 sigma by p l r star, again out of these two terms, this is much less than one, so one can expand this in logarithmic series, retain the first term, so some simplification can be done. Now, what is the effect of the dissolved gas in the liquid? What is the effect of dissolved gas in the liquid? Can you identify the effect of dissolved gas in the liquid. If you simplify this, then probably it will be clear, that the dissolved gas in the liquid, that reduces the requirement of degree of super heat.

So, when there are, I mean there is a dissolved gas in the liquid. So, you need lesser amount of or lesser value of degree of super heat, to create the vapour embryo. So that means, the evap evaporation process that becomes more, I mean that, that that is, dissolved gas make that process of evaporation more convenient.

Even then, if you calculate, what is the degree of super heat needed for evaporation to take place, when there is certain amount of dissolved gas. You will be surprised to find that; that is a steel very high value. And our normal experience is that, at a very small super heat; small degree of super heat, we are able to boil the liquid

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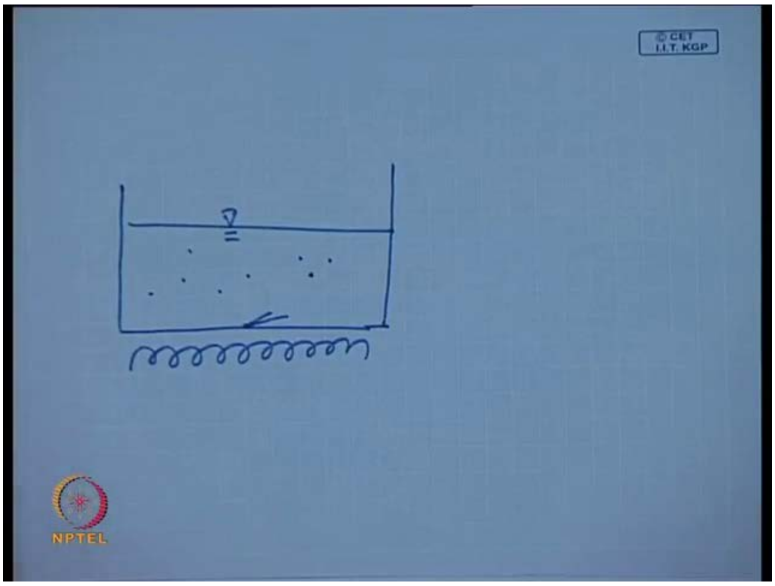

Particularly, if you take the example of water and if you have some sort of a measurement device. Let us say, we have got a pan and the pan is over a heater, so the pan is having liquid liquid water and we have got some method of measuring the surface temperature from where evaporation is taking place. So mainly, at the initial stage evaporation will take place from the surface, you will find the surface temperature at which the evaporation takes place. At which we can identify that the boiling process is has started, the temperature is not very very much different from the saturation temperature; that means, at atmospheric pressure, the saturation temperature will be 100 degree Celsius and probably at hundred – two, three, four degree Celsius, we will have the boiling from the surface.

Whereas, the formula which I have given to you; you will find that, with that if you try to calculate delta T sat, that is much higher. Now where is the (( )), the (( )) lie in the fact, that dissolved gases or for that matter, the suspended particles; small suspended particles in the bulk of the liquid. Though they help reducing the degree of super heat needed for boiling, they are not the, they do not play the main role for the boiling, when we are considering a system like this. Here, the main role is played by the surface of the container. And if I see the surface of the container, the surface of the container, whatever machining process I may adopt; whatever polishing process I may adopt, the surface is not regular surface.

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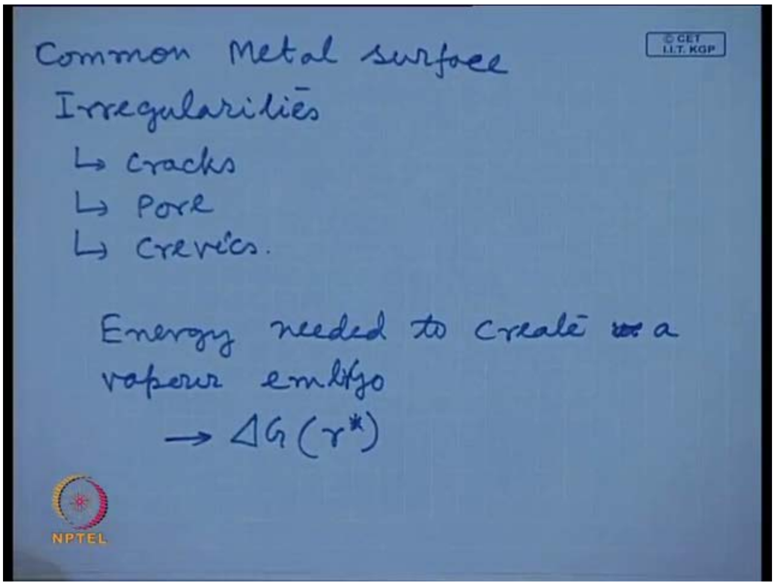

Common Metal surface
Irregularities
↳ cracks
↳ Pore
↳ Crevics.

Energy needed to create a vapour embryo
$\rightarrow \Delta G(r^*)$

So, on the surface, there will be surface irregularities. So, common metal surface, we have irregularities, this we have discussed, but let us look into it in a big detail. So, this irregularities are cracks, pores, crevics etc., and they they play a very major role in reducing degree of super heat needed for boiling.

How? We will not go into very detail kind of mathematics, but we will try to give some sort of logic from the fundamental physics. Now you see, as I have told that, we are;

during the boiling process, we are creating a new surface; we are creating a new surface, so that is why, some amount of energy is needed.

Now that energy, if we can express that energy, energy needed to create a vapour embryo; let us call it delta G, which is also a function of the radius of; which is also a function of the embryo radius. So, energy needed to create a vapour embryo given by delta G, which is a function of r star.

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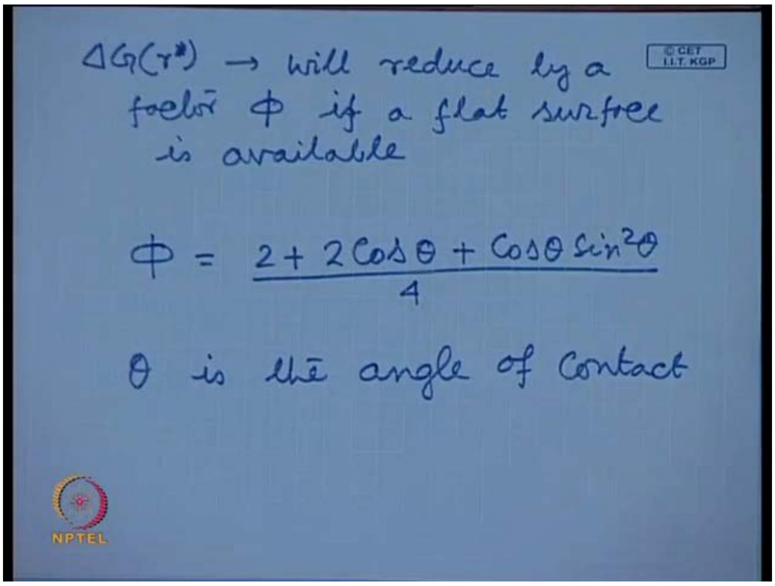

$\Delta G(r^*)$ → will reduce by a factor ϕ if a flat surface is available

$$\phi = \frac{2 + 2\cos\theta + \cos\theta \sin^2\theta}{4}$$

θ is the angle of contact

Now, this vapour embryo, we are assuming that, this vapour embryo is formed in the bulk of the liquid. But let us say that, there is a surface available on which this vapour embryo is formed, then what will happen. So, if there is a plane surface or flat surface available for the formation of vapour embryo, then this delta G r will reduce by a factor phi, if a flat surface is available. If a flat surface is available, then this will reduce by a factor phi.

Now, people have done, again some sort of approximate analysis and this phi can be calculated. This phi is given by 2 plus 2 cos theta plus cos theta sin squared theta divided by 4, where theta is the angle of contact between the between the I mean, it is the vaporization is taking place. So, on this particular solid surface, this, there is a triple line or a triple point, where there is liquid, vapour and solid contact. So at that point, the contact angle, that is given by theta. So, depending on the theta, we will have different values of phi.

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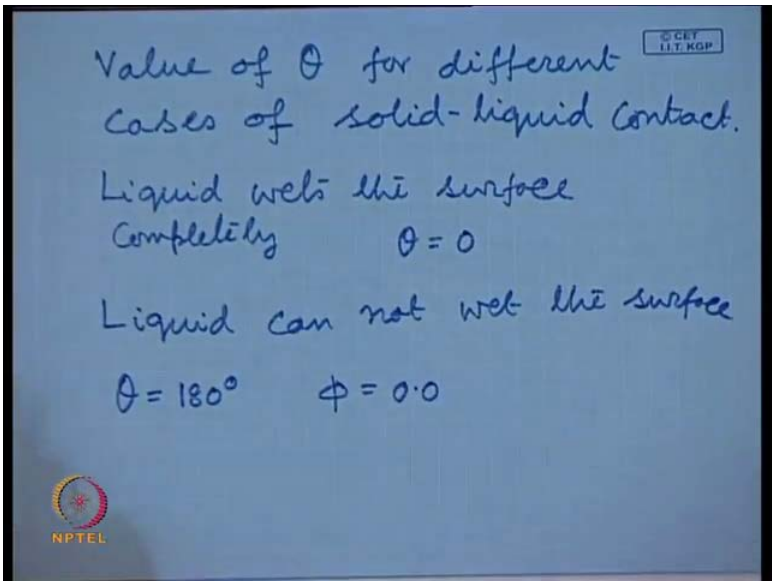

Value of θ for different cases of solid-liquid contact.

Liquid wets the surface completely $\theta = 0$

Liquid can not wet the surface

$\theta = 180^\circ$ $\phi = 0.0$

Now, let us consider different cases, value of theta for different cases of solid-liquid contact. Suppose, the liquid completely; the liquid completely wets the surface; liquid wets the surface completely. So, what do you get, you get theta is equal to zero. So, if theta is equal to zero from your equation, what is the value of phi, phi is equal to one. So, the factor which could reduce the energy needed for the formation of vapour emb embryo that factor is equal to one, so there is no reduction.

So, delta G are, what I will calculate from the thermodynamics, this is your; gives energy. So, the same amount of energy will be retained. So, presence of flat surface is not helping. Now, let us say the other situation, liquid cannot wet the surface; liquid cannot wet the surface. So, theta is equal to, how much? Theta is equal to 180 degree and phi is equal to; so, if phi is equal to 0, then it is making the energy requirement zero and it is also making the requirement of degree of super heat equal to zero, that can be shown, that it will make the requirement of degree of super heat equal to zero.

So, as soon as the saturation temperature is reached, we will have vaporization. So, in this case, as soon as the saturation temperature is reached, we will have vaporization. In the first case, what we will find, that I mean, just like your homogenous nucleation, whatever energy was needed for vapour embryo formation, the same amount of energy will be needed.

In the second case that, we do not require any extra energy, we do not require in our; this one, any degree of super heat as soon as the saturation temperature is reached, our vapour embryo will be formed. Now, practical situation is in between these two

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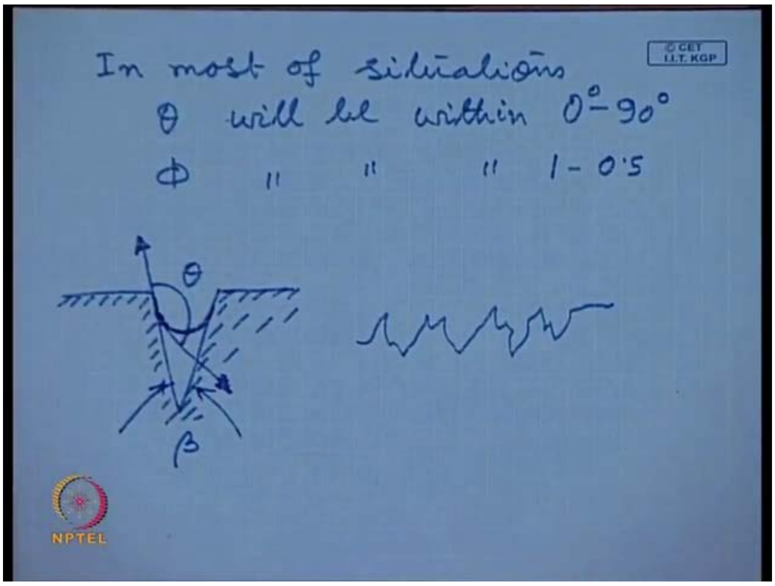

In most of situations
θ will be within $0^\circ - 90^\circ$
ϕ " " " $1 - 0.5$

So, in practical situation what will happen; in practical situation, theta theta value that will be from, in most of the situations. So, theta will lie from, theta will be within 0 to 90 degree. Generally, see, this will be the range, then what will be the phi value, phi will be within 1 to 0.5; 1 to 0.5. So, you can see that normally, in normal case itself, for solid liquid contact, we will have certain reduction in the energy needed for vaporization; certain reduction in the degree of super heat, that we will get.

Now, a drastic thing will happen, because of the irregularities of the surfaces, if there are irregularities, this irregularities, I mean a common way of describing these irregularities, that as if they are some conical pores inside the surface, I mean on the surface.

See, basically the surface will look like this, under a microscope. Now, if I want to idealize in this irregularities in a magnified manner, so it is like that, that you have got some sort of a conical aperture; so, you have got the conical aperture. This is the surface, inside the surface, you have got the conical aperture. And the … in this aperture, you have got, this is the meniscus and this is the solid surface. So, the angle is something like this; this is your theta angle. So, this angle is now having a large value; this theta is no having a large value.

So, for this large value, what we will have? The factor phi will have a small value and we will reduce the degree of super heat. So, if there is a large value of theta, the way I have shown, then with a small degree of super heat vaporization will take place from this spot. And this plot; this spot will now, it will be called as a nucleation site and we will call it, as an activated nucleation site. So, there will be a large number of sites like this (( )) are different; sets are different; included angle; this angle, if we call it; this angle if I call it beta, this included angles are different.

So, at a particular degree of super heat, this site will be activated. If I increase the degree of super heat, another site will get activated. So that is why, when I start boiling, this I have explained the other day also. When I have started boiling, I will see from the pan, vapour bubble is rising only from a limited sites, to start with it.

Then, as the temperature is increasing, I will find, that from more places the vapour bubbles are coming. So, more and more number of nucleus and sites I am activating by increasing the temperature of the surface. So, that is what I am doing in in day to day boiling; day to day phenomenon of boiling, that is what we are experiencing. And also in industrial situation, when on a tube or inside a tube boiling is taking place, the same phenomena is occurring there. So, we have got number of fields and those are actually nucleation sites. Depending on the temperature, number of sites will get activated and we will have nucleation from there.

So, this nucleation is called heterogeneous nucleation. So, you can understand, why it is called heterogeneous nucleation. So, basically you see, we have discussed three process of vapour formation, first process: there is no nucleation and it is a surface phenomena, the second process: that is homogenous nucleation, that is in the bulk of the liquid, heterogeneous nucleation could be in the bulk of the liquid or it could be not on the free surface of the liquid, but on the solid surface, because solid surface contains large number of nucleation sites. And as nucleation sites are necessary or rather formation of nucleation is necessary, so degree of super heat should be higher, in case of homogenous and heterogeneous nucleation.

Whereas, almost at the saturation temperature, evaporation can take place. So, that is the difference between these three processes. Then I will, I mean now we can understand evaporation is important, but in in this course, we are not going to discuss evaporation, because that is not exactly to two phase flow; one can separately discuss the two phases: The fluid mechanics and heat transfer, aspect one can deal in a separate manner. Homogenous nucleation, as I have told that, it is not very important, because it occurs really, it is important; in case of accident scenario etc., in case of, very high pressurization; heat pressurization of liquid, it is important.

But, we are not going to discuss that, but most of the boiling process are due to heterogeneous nucleation, so we will start from here and next day we will see, how does a bubble grow? How does a bubble detach from the surface and then nucleate boiling.

Thank you.