# Heat Transfer And Combustion in Multiphase Systems
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## Lecture 06
## Interfacial phenomena key concepts-II

So, welcome to lecture 6 okay and so, let me show you the book also that you are going to follow:

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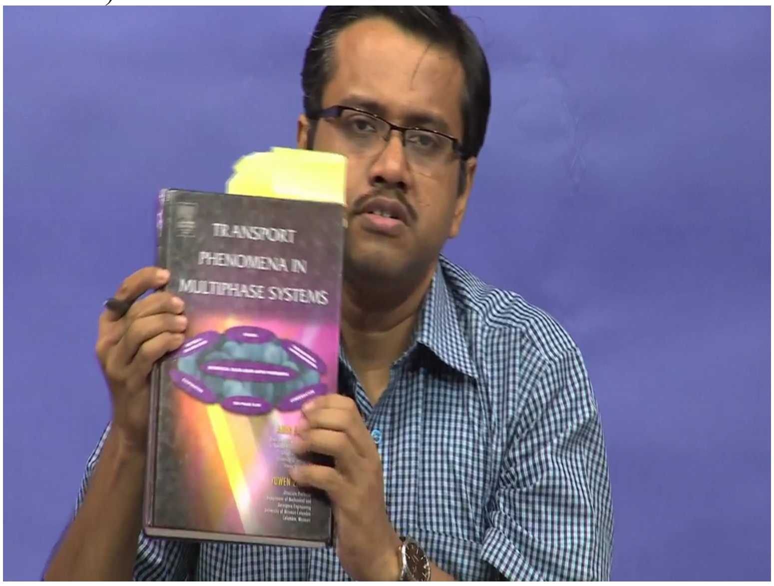

So, this is the book by Transport Phenomena in Multiphase Systems by Amir Faghri and Yuwen Zhang and the other book will be when we go to the droplet combustion and evaporation part we will use Will Sirignano's book. I will show that in due course but this is the book which you should normally follow okay.

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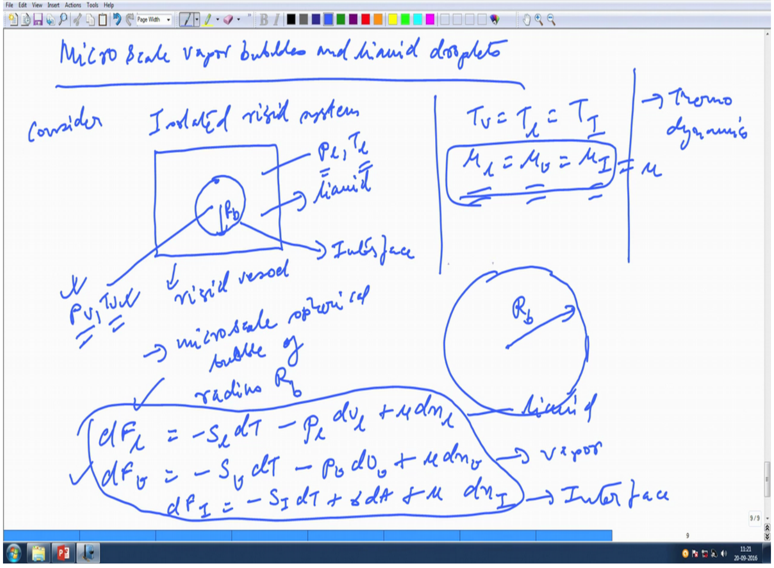

Micro scale vapor bubbles and liquid droplets

Consider Isolated rigid system

→ microscale spherical bubble of radius $R_b$

$T_v = T_l = T_I$

$\boxed{\mu_l = \mu_v = \mu_I} = \mu$ → Thermo dynamics

$dF_l = -S_l\,dT - p_l\,dV_l + \mu\,dn_l$ → liquid

$dF_v = -S_v\,dT - p_v\,dV_v + \mu\,dn_v$ → vapor

$dF_I = -S_I\,dT + \sigma\,dA + \mu\,dn_I$ → Interface

So, let us look at now in this particular lecture Micro Scale Vapour bubbles and liquid droplets. The full fledge a study of vapour bubbles and liquid droplets will be done later on in during the course. But this is just the initial definition, idea of what it is right. So, let us consider us, in this situation that you have an isolated rigid system.

Rigid system is the means of volume on change, right; it is like a rigid vessel okay. And inside this vessel you have this vapour bubble okay. So, there is liquid here this container is filled with liquid the liquid has got a pressure of Pl temperature Tl, this is the interface and we covered a lot about interface just a few in this last few lectures.

This is Pv and Tv okay. These are the corresponding pressure and temperature within the vapour bubble right okay. Now, so, this is the situation right. So, you have an isolated it is like is an enclosed cavity in which you have filled it with water. This vapour bubble due to whatever reasons, it could be due to boiling due to extra heat.

But we have this vapour bubble which is at a temperature of Tv pressure of Pv. We have the liquid temperature of Tl and pressure of Pl and then there is a interface okay. Now from the calculations or the things that we showed earlier this Tv = Tl = TI right. That we did just a few lectures back is not that so.

And we also say mu l = mu v = mu I right, what it means is that the temperature across all the phases of the same right Tv, Tl and TI, they are the same. There is the interface temperature is the same, as the vapour temperature same, as the liquid temperature also, we have also said that the chemical potential is the same across the two phases.

And that chemical potential is the same, as they interface as well okay. So, this is a vapour bubble, this is the condition that we got from our thermodynamics that we did in the last few lecture’s okay. So, the vapour at temperature Tv and pressure Pv is a micro scale spherical bubble with a radius of Rb.

Let us put this radius as Rb, so, if you take the bubble out this is the radius Rb of the bubble right. So, it is basically, what it is a micro scale spherical bubble of radius Rb correct right, okay. The liquid temperature is also at a constant temperature of Tl around the bubble right. So, this part is quite clear.

Now let us apply the Helmholtz free energy function on this okay. So, what is that for the liquid let us write, we are just retaining mu over here because of this particular relation right, let mu is the same okay. So, you can put it as mu for example okay. Similarly dFv that is the one is for the liquid, one is for the vapour right.

So, now that is given as sorry got it that is what the vapour phase. Similarly we can write the same equation for the interface also. Though it is the same right got it. So, these are the three relationships that we can write from the three expressions like one for the liquid, one for the vapour, one for the interface.

And all of these equations we have done like previously. So, now we are applying it to this micro scale vapour bubble in a liquid pool right, where the liquid temperature is kept constant at Tl right okay. Now let us go to the next slide okay.

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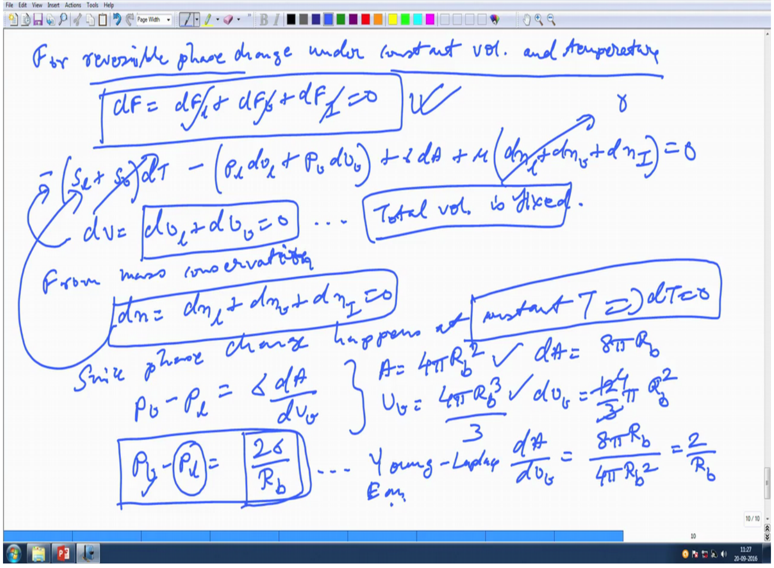

For reversible phase change under constant vol. and temperature

$$\boxed{dF = dF_l + dF_v + dF_I = 0}$$

$\gamma$

$$-(S_l + S_v)dT - (P_l dv_l + P_v dv_v) + \gamma dA + \mu(dn_l + dn_v + dn_I) = 0$$

$dv = \boxed{dv_l + dv_v = 0}$ … Total vol. is fixed.

From mass conservation

$$\boxed{dn = dn_l + dn_v + dn_I = 0}$$

Since phase change happens at $\boxed{\text{constant } T \Rightarrow dT = 0}$

$$P_v - P_l = \gamma \frac{dA}{dv_v}$$

$A = 4\pi R_b^2$ ✓ $dA = 8\pi R_b$

$v_v = \frac{4\pi R_b^3}{3}$ ✓ $dv_v = \frac{\cancel{12}4}{\cancel{3}}\pi R_b^2$

$$\boxed{P_v - P_l = \frac{2\gamma}{R_b}}$$ … Young-Laplace Eqn. $\frac{dA}{dv_v} = \frac{8\pi R_b}{4\pi R_b^2} = \frac{2}{R_b}$

For reversible process phase change under constant volume and temperature okay is dF = dFl + dFv + dFI = 0 right. As the change of Helmholtz free energy is actually equal to 0 in such a consideration in such a case right. Now, so, now let us now we already know if you go to the previous page.

We already saw the individual relations right okay. Now let us add all of these things together right. So, when we add all these things together it Sl + Sv dT - Pl dvl sorry dvl + Pv dv Sigma dA + mu dnl + dnv + dnI = 0 right. Now the total volume is fixed that is what we said right. It is a rigid vessel right. The total volume is fixed.

So, dv = dvl + dvb has to be equal to 0 right because total volume is fixed right. From mass conservation what we can say is that dn that is the rate of change of more; the change in moles dnl + dnv + dni = 0 right. So, what we can do is that we can take and substitute it here. We can take this and substitute it there right.

Because this part will become equal to 0 that we can readily see right, dv part also okay we can substitute, now that you know the relationship between the two. We can substitute them in this equation and try to see what we get out of it okay. And also since phase change happens at constant T right okay. So, therefore this implies that your dT has to be equal to 0.

So, this term also goes to 0 essentially after substituting all of that u become Pv - Pl = Sigma dA by dvv right, okay. Now we already know if it since it is a spherical bubble area is nothing but 4 Pi Rb square, the volume of the bubble is basically 4 Pi Rb cube divided by three, right, okay. If you substitute them back that mean dA will be equal to 8 Pi Rb right, got it.

So, dvv will be equal to, so four third will be 12 by 3 Pi Rb square correct okay. So, this is becoming basically 4. So, now dA by dvv will be equal to 8 Pi Rb divided by sorry it is like this one hand 8Pi Rb divided by 4Pi Rb square right. So, this basically gives us 2 divided by Rb right. So, therefore Pv - Pl becomes 2 Sigma by Rb which is basically also called the Young-Laplace equation right, so clear.

What we did is for reversible phase change occurring under constant volume and temperature. The sum total of the Helmholtz, change of Helmholtz free energy has to be equal to 0. This we know from the previous cases when we were studying equilibrium of the systems okay.

Similarly using this if you sum total all the Helmholtz free energy quantities that means these, these and these, we get term like this. We apply additional constraint like the total volume is fixed. We apply the mass conservation that means there is no net change in the number of moles. And phase change we have also said that it as assume, it happens at a constant T using all that and using the definition of the volume and the area of the bubble right.

We have calculated that the pressure inside the bubble that is Pv okay and the pressure outside the bubble which is the pressure of the liquid okay is basically given by this particular quantity okay. So, that means the pressure inside the bubble is actually more than the pressure outside the bubble that means the liquid pressure right.

Because it maintains the convex shape okay, so Rb and everything is positive basically. So, we can say that the pressure inside the vapour pressure inside the bubble has to be more than the pressure inside the liquid right. And this is what happens when a bubble is actually stable inside a pool of liquid right.

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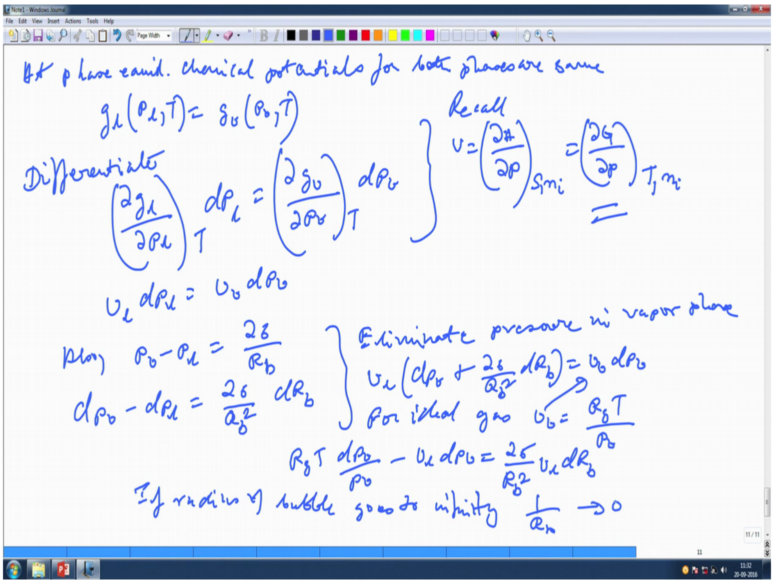

At phase equil. chemical potentials for both phases are same

$g_l(P_l, T) = g_v(P_v, T)$

Differentiate

$$\left(\frac{\partial g_l}{\partial P_l}\right)_T dP_l = \left(\frac{\partial g_v}{\partial P_v}\right)_T dP_v$$

Recall

$$v = \left(\frac{\partial H}{\partial p}\right)_{S, n_i} = \left(\frac{\partial G}{\partial p}\right)_{T, n_i}$$

$v_l \, dP_l = v_v \, dP_v$

Also $P_v - P_l = \frac{2\sigma}{R_b}$

$dP_v - dP_l = \frac{2\sigma}{R_b^2} dR_b$

Eliminate pressure in vapor phase

$v_l\left(dP_v + \frac{2\sigma}{R_b^2} dR_b\right) = v_b \, dP_v$

For ideal gas $v_b = \frac{R_g T}{P_v}$

$$R_g T \frac{dP_v}{P_v} - v_l \, dP_v = \frac{2\sigma}{R_b^2} v_l \, dR_b$$

If radius of bubble goes to infinity $\frac{1}{R_b} \to 0$

So, let us look at now that we have done that. Let us look at a few more alternative types of definitions. So, at phase equilibrium the chemical potentials are the same that we already established right for both phases are same right okay. So, we can say is the Gibbs free energy they are the same right okay, for pressure and temperature whatever I will the Gibbs free energy has to be specified.

If we differentiate, we get dgl by dPl  dPv okay, now if you recall a little bit of your earlier work your volume or s, ni, this is same as your dG dpv T rather not dpv but just put it as okay right. So, that is the definition okay, from the Maxwell relationships you can work out that okay.

Now using this you have Vl dPl = Vb dPv also we just now saw Pv - Pl = 2 Sigma by Rb right that we just now proved. So dPv -dPl = 2 Sigma by Rb square dRb okay. So, if we eliminate the pressure in the  vapour phase, this become Vl or if we try to eliminate is not yet eliminated 2 Sigma by Rb square dRb = Vb dPv.

Now for an ideal gas, vapours in most cases can be taken as ideal gas, ideal gas RgT divided by Pv okay. So, you put that expression for Vb over here. We get RgT dPv by Pv – Vl dPv = 2 Sigma is a Sigma by Rb square Vl dRb. Now if the radius of the bubble goes to infinity very, very large bubble okay. So, the radius of the bubble goes to infinity that means 1 by Rb should approach basically zero right.

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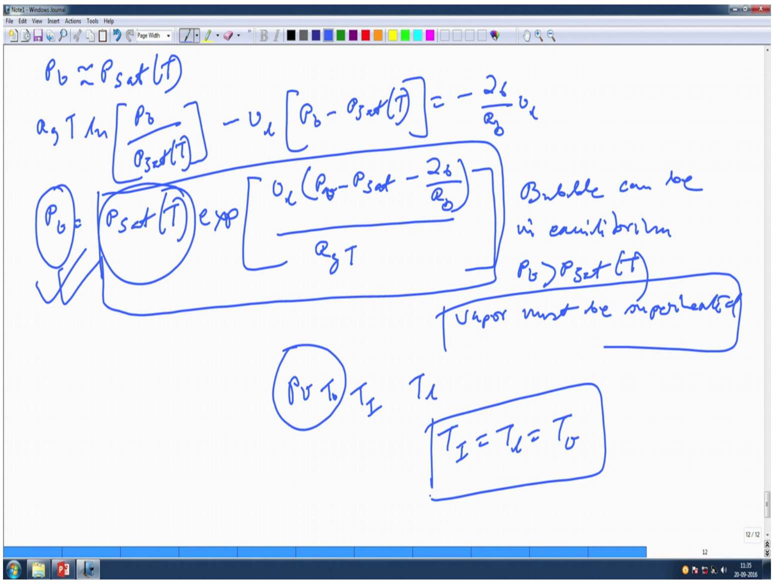

$P_b \simeq P_{sat}(T)$

$$R_g T \ln\left[\frac{P_b}{P_{sat}(T)}\right] - v_l\left[P_b - P_{sat}(T)\right] = -\frac{2\sigma}{R_b} v_l$$

$$P_v = P_{sat}(T) \exp\left[\frac{v_l\left(P_v - P_{sat} - \frac{2\sigma}{R_b}\right)}{R_g T}\right]$$

Bubble can be in equilibrium

$P_v > P_{sat}(T)$

Vapor must be superheated

$P_v$ $T_v$ $T_I$ $T_l$

$T_I = T_l = T_v$

And Pv the same as a saturation pressure right because we have taken it is an equilibrium process there is no super heating or the sub coding or anything like that. So, this equation that we have over here, if you look at this particular equation can be integrated okay can be integrated and we can get RgT ln Pv by P sat - Vl Pb - Psat must be equal to - 2 Sigma by Rb Vl.

That is what you can get. Now if you cast it to take out all these things. So, that Pv would be equal to Psat into exponential Vl Pv - Psat - 2 Sigma by Rb divided by RgT close the bracket. It shows that this bubble is in equilibrium, a bubble can be in equilibrium if and only if Pv is greater than Psat right. So, the vapour pressure that is inside the bubble right has to be more than the saturation pressure.

In other words the vapour should be kind of superheated right must be super heated got it. So, that it comes from the thermodynamics got it. So, the vapour must be superheated because this expression shows that it has to be greater than the P saturation pressure okay. So, this is an important for a bubble to be stable this Pv has to be more than whatever is a saturation pressure because of this temperature is Pv, TI, Tl right okay.

So, it has to be in that same particular form got it okay. So, what we have learnt over here is that we have taken the surface tension analogy right. We have taken the surface tension and we have found out what interfacial behaviour is. We have applied the same over here and we have been able to show two key relationships.

One is the Young Laplace equation which shows that the vapour pressure inside the bubble is more than the liquid pressure right that is the first thing. And second thing that we have shown just by following similar type of thermodynamic analysis. We are shown that this vapour pressure has to be more than the saturation pressure okay at that temperature whatever at which this phenomena is happening.

Because the temperatures are all TI = Tl = Tv right that we know already from a thermodynamic equilibrium relationship right okay. So, this actually shows that this actually shows this almost completes the thermodynamic section. Let us look at the presentation once again.

So, what we will do in the next class is basically go and solve for the generalized governing equations in the multi-phase flow. So far what we have done is that we have looked into the individual thermodynamic relationships that connect multiphases, multi-component. We have looked at the surface tension behaviour which is the most important thing.

We have looked at interfacial when there is an interface present what happens to the chemical potential, to the temperature. We also shown a little bit that the liquid and the vapour can be superheated, sub cooled etc and that need not be that is not a deal breaker per say, okay. So, now that we have covered the thermodynamics aspect of it.

In the subsequent lecture that we are going to give okay we are going to cover the generalized governing equations in the multi-phase flow right. Because the generalized governing equations are the equations which basically tells you that how transport happens.

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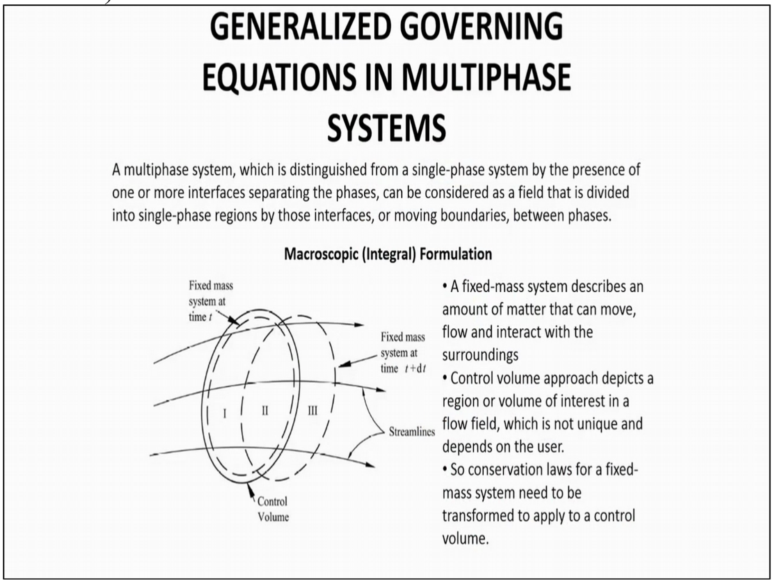

GENERALIZED GOVERNING EQUATIONS IN MULTIPHASE SYSTEMS

A multiphase system, which is distinguished from a single-phase system by the presence of one or more interfaces separating the phases, can be considered as a field that is divided into single-phase regions by those interfaces, or moving boundaries, between phases.

Macroscopic (Integral) Formulation

- A fixed-mass system describes an amount of matter that can move, flow and interact with the surroundings
- Control volume approach depicts a region or volume of interest in a flow field, which is not unique and depends on the user.
- So conservation laws for a fixed-mass system need to be transformed to apply to a control volume.

So far we have not taken into account any transport over here we have just looked at the thermodynamic principles okay that what is non Pv work, what is Pv work and things like that right. So, just to close this lecture, so, let me give you just a brief recap what we have done, is that we have looked into, we have looked into the first one the second law of thermodynamics essentially for a closed system okay.

Then we have gone through Gibbs phase rule right because Gibbs phase rule is something that gives you that what is the degree of freedom of the system okay. We have also looked into the equilibrium and the stability of single phase flow systems and this is where you get that the different principles that the change in Helmholtz energy has to be less than equal to 0 and things like that okay.

Then we have looked into the Maxwell's relationships which is one of the most important parts of the thing okay. You are also suggested to study about the thermo mechanical stability and chemical stability. There are three types of stabilities okay but that you can read from undergraduate book which actually shows that what are the three stabilities and what are the requirements to full fill those things okay.

We have also looked into system with compositional changes but having a single phase okay. So, that means it is a multi-component system we have looked into systems which has got two phases and what are the criteria and we have seen that temperature pressure and the chemical potential has to be the same okay.

We have also looked into the Clausius-Clapeyron equation and their Clapeyron equation only. Then we have looked into the thermodynamics of the interfaces that means what will happen when you actually have an interface into the picture. And then subsequently we have looked into the definition of surface tension.

And we have given as many as three definitions of surface tension okay with respect to energy, with respect to Gibbs free energy, with respect to a Helmholtz free energy okay. And we have shown that what surface tension is all about. Then we have studied the liquid vapour spinodal curve that means basically the metastable equilibrium conditions okay.

We have also looked into the multi-phase multi-component system that means when there are two components and two phases present what are the equilibrium conditions okay. And we have also looked into the superheat limit that means we have already established that liquid and vapour spinodal’s actually do exist.

So, I not look at the superheat limit for the thing for the same. So, apart from that we have done this Micro Scale Bubble and Liquid Droplet Analysis to show that what is the stability criteria, how, what will be the pressure inside a vapour bubble okay. And the same can be done for the liquid also.

So, it is not a big thing okay. So, that is what we have done through the course of these few lectures. So, in the next lecture we are going to start with the Generalized Governing Equations In Multiphase Systems okay. So that will be next.