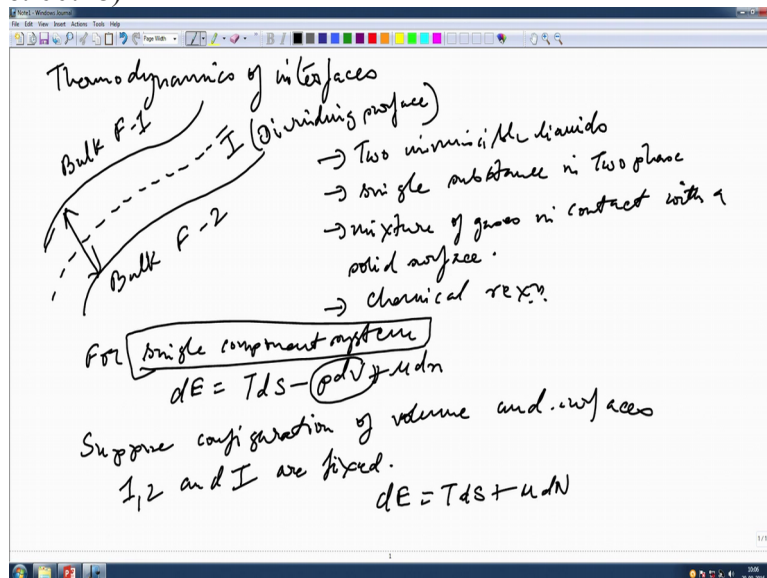


Heat Transfer And Combustion in Multiphase Systems
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Lecture 04
Thermodynamics of Interface-II

Welcome to lecture 4, in the last lecture we said that we are going to do a little bit of the thermodynamics of the interfaces.
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So, in this lecture thermodynamics of interfaces okay. So, let us consider a situation like this. This is bulk fluid 1, this is bulk to fluid 2, this is basically the interface and this is basically the dividing surface also between bulk fluid 1 and bulk fluid 2. So, the two bulk fluids are basically separated by an interfacial region okay.

So, what can happen these; there are several situations that can take place one is that the two fluids may not actually mix with each other in mixable liquid, it could be a situation like that okay. It is also can be taken that is a single substance and it is present in two phases. So, basically bulk fluid 1 and bulk fluid 2 are the same substance. But they exist in two different phases.

So, it could be just water, liquid water and water vapour for example okay. It could be also a mixture of gases say for example mixture of gases in contact with a solid surface. It could be something like that also. It could be a chemical reacting interface that means the two this could be this bulk fluid 1 could be the oxidizer, bulk fluid 2 could be the products. So, it could be something like that.

It is so, in that particular case this interfacial region therefore becomes what we call the reaction zone okay. So, there are multiple such possibilities that can happen right. Now for single component system what we have seen let us just do a small recall from the last class or last classes. Basically we saw that this happened; this we did in the last class correct okay. This is valid for a single component system right.

Now suppose the configuration of the volume and the surfaces 1, 2 and I as it has been marked over here are fixed okay. So, let us put that assumption in suppose configuration of volume and surfaces okay 1, 2 and I are fixed okay, are fixed. So, in that particular case if the volume is fixed this term basically goes to zero. So, that means this dE will now become $T ds + \mu dN$ okay. So, let us go to the next page okay.
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Now consider a scenario where some mass and energy exchange occurs between bulk fluid 2 and interface I. There is no exchange between bulk fluid 1 and interface I.

Total energy of the system remains unchanged

$$E_{\text{Total}} = E_I + E_1 + E_2 \quad \left. \begin{array}{l} dE_1 = 0 \\ dE_{\text{Total}} = dE_2 + dE_I = 0 \end{array} \right\}$$

$$T_I ds_I + \mu_I dm_I + T_2 ds_2 + \mu_2 dm_2 = 0$$

$n_{\text{Total}} = \text{constant} \quad dn_{\text{Total}} = 0 = dn_I + dn_2$
 $dn_I = -dn_2$

Now, so, that is the configuration. Now let us consider a scenario where some mass okay an energy exchange basically in exchange okay occurs between bulk fluid 2 and the interface I got it. However there is no exchange between bulk fluid 1 and interface okay. So, that is I think the typical scenario that we are considering over here.

So, some mass and energy exchange occurs between the bulk fluid and the interface I, but there is no exchange that is occurring between the bulk fluid one and the interface I okay. Now the total energy now as we know that the total energy of the system should be constant basically remains unchanged right, pick a different marker.

So, that E_{Total} the total energy is basically given by the interface energy + $E_1 + E_2$ right okay. Now, because of this exchange that has happened between the bulk fluid 2 and the interface I, the energy in the region between 2 and I, with the energy at one is held constant.

So, therefore any change in the total energy which is of course equal to zero is basically brought about by a change in the energy of 2 + the corresponding energy of EI okay and that is basically equal to 0, right. So, the concept here is nothing in very simple the energy there is an energy exchange that is occurring between this and this essentially well this is basically kept constant.

So, there is a reduction or increase whatever it may be of energy of E2. There is an equivalent increase or decrease of energy of course of the opposite sign of EI. But the total energy of the system is constant so therefore the sum total of these two energies has to be equal to 0, right. Individually of course dE_1 is of course equal to 0 because we are not having any exchange between the bulk fluid 1 and the interface I.

So, hope this part is actually clear okay. Now what this means is that if we substitute expression for E for each of these E2 and EI, what it will give $dI + \mu_I dn_I + T_2 ds_2 + \mu_2 dm_2$ this is equal to 0. This part should be quite clear right what we have done is that basically we are substituted the same relationship right. So that is the expression that we get out of this.

Now since mass and energy both are exchanged so there will be a change in the number of moles also. Though the total number of moles in the system remains constant right n_{Total} is basically a constant is not that so okay because the total number of moles cannot change right. It is like a mass conservation.

So, here of course if we do this dn_{Total} okay this is of course equal to 0 and this 0 is brought about by this $dn_I + dn_2$ once again the number of moles of n_1 has been kept constant because there has not been any mass or energy exchange right. So, that is a simplified kind of a process. So $dn_I = -dn_2$ is a very similar kind of a statement like this energy equation okay up to this point should be clear.
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Entropy balance

$$S_{\text{total}} = S_I + S_1 + S_2 = \text{constant}$$

$$ds_{\text{total}} = 0 = ds_I + ds_2 = 0 \Rightarrow ds_I = -ds_2$$

$$(T_2 - T_I) ds_2 + (\mu_2 - \mu_I) dn_2 = 0$$

\Rightarrow valid for any ds_2 and dn_2

$$\left. \begin{array}{l} T_2 = T_I \\ \mu_2 = \mu_I \end{array} \right\}$$

$$\left. \begin{array}{l} T_1 = T_2 = T_I \\ \mu_1 = \mu_2 = \mu_I \end{array} \right\}$$

Exchange occurs betw. 1 and I, 2 held constant

$$\left. \begin{array}{l} T_1 = T_I \\ \mu_1 = \mu_I \end{array} \right\}$$

So, now we look at the corresponding entropy balance. Let us look at the entropy balance okay. Now s_{Total} okay it is basically given as $s_I + s_1 + s_2$ this is equal to a constant right. So, $ds_{\text{Total}} = 0$ which is basically brought about once again by the change of entropy of the two interfaces because ds_1 was already equal to 0.

So from here we can infer $ds_I = -ds_2$ okay. So, if we rewrite now the expression that we saw in the previous slide let us just look at it just in the previous slide if you look at this expression now. What we can do is that we can cast them in terms of one variable only right. We can because we have ds_2 we have ds_I we have dn_I and dn_2 okay. So, we can try to cast them in one particular form.

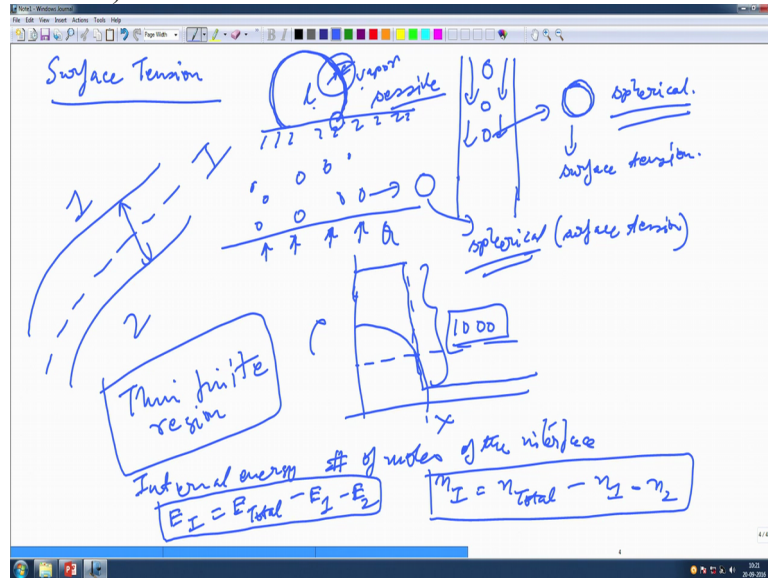
So, by using these relationships like this okay, so, if we do that then this become $ds_2 + \mu_2 - \mu_I dn_2 = 0$ okay. This is valid for any ds_2 and dn_2 got it okay. Since this is valid for any ds_2 and dn_2 individually these two terms must be equal to 0 individually right. So this leads to the statement that T_2 must be equal to T_I because this is valid for any ds_2 and dn_2 right and similarly your μ_2 must be equal to μ_I right.

Now similarly here we have held bulk fluid 1 as constant. Let us do this if we extrapolate and do this between bulk fluid 1 and the interface. You will get an equivalent relationship which will be like sorry which will be like if you want to go for that. It will be T_1 must be equal to T_I and μ_1 must be equal to μ_I right.

If we just assume exchange occurs between 1 and I right and two is held constant correct. So, explicitly what this gives you $T_1 = T_2 = T_I$, $\mu_1 = \mu_2 = \mu_I$ okay. So, this is the key expression for that interface that means the temperature of the interface should be the same as the temperature of the two phase's right.

Which are with which it is in contact similarly the chemical potential of the interface is the same as a chemical potential of the other two phases that are present, right. So, this is an interesting observation okay or an interesting inference that we have drawn out of this particular work okay.

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Now let us look at while we are at interface. Let us look at an important feature of an interface which is called surface tension okay. So, surface tension is a thing that you will encounter not just in it is a quantity or it is a parameter that comes in handy in any type of multiphase flows like with droplet, bubbles whatever it is right.

For example we already saw a few features like for example if you have a droplet sitting on a solid surface right there is surface tension between this. That means that this is liquid and increases the vapour a for example right. So, there is surface tension between the liquid and the vapour okay. There is also surface tension between the liquid and the solid and the vapour and the solid right.

And this is what in common parlance people call that the three phase contact line. So, surface tension is the one which allows this droplet to maintain its shape okay. So, it is not that the liquid vapour surface tension it is the liquid solid surface tension or the vapour solid surface tension okay that allows it to form this kind of a shape.

So, when you actually inject for example say you assume that this is like a tower in which there is a flow and you inject a droplet into this tower right. So, if you look at the droplet and if this flow rate is small, this droplet will be nice and spherical right. So, that spherical shape of the droplet comes precisely due to the surface tension okay.

So of course I have assumed a low speed flow, so that there is no distortion of the shape okay. So, normally and not if the droplet is not under any external stimuli like for example aerodynamic stress and other things it will remain nice and spherical, so this shape is due to surface tension right okay.

So, there are similar such things when you actually have pool boiling that means the surface is heated, you supply heat to a surface. All these bubbles you have seen bubbles right when you actually warm water in a pan right. When you boil the water in a pan you see all these bubbles coming up right.

So, these bubbles are also spherical in shape okay to the best of the; so once again if these bubbles will be spherical in shape, so long there are no external stimuli doing otherwise. So, these are also spherical and these are also due to surface tension right. So, surface tension as we can see is one of the most important parameter it works not just for free droplets and bubbles it also works for droplets on substrates okay.

These are called sessile droplet will spend a few lectures on this kind of droplet as well. So, the sessile droplets are extremely important okay. Now for analyzing the surface tension we basically use the same form that we had earlier that means this is 1 this is 2 and this is basically the interface okay.

So, surface tension is not just what is spherical droplet, it can happen for any types of structures also okay liquid structures also okay. So, here we have taken of course an arbitrary kind of an interface okay. So, it is a liquid vapour interface and it is often marked with a level of high discontinuity that means across for example if we take this droplet into consideration okay.

This is liquid, this is vapour, the density, there is a density jump across this interface. So, there are many of the properties undergo a sharp jump. So, if you want to just plot the density for example this is the bubble. If this is the droplet, so if we have something like this the density will be very high.

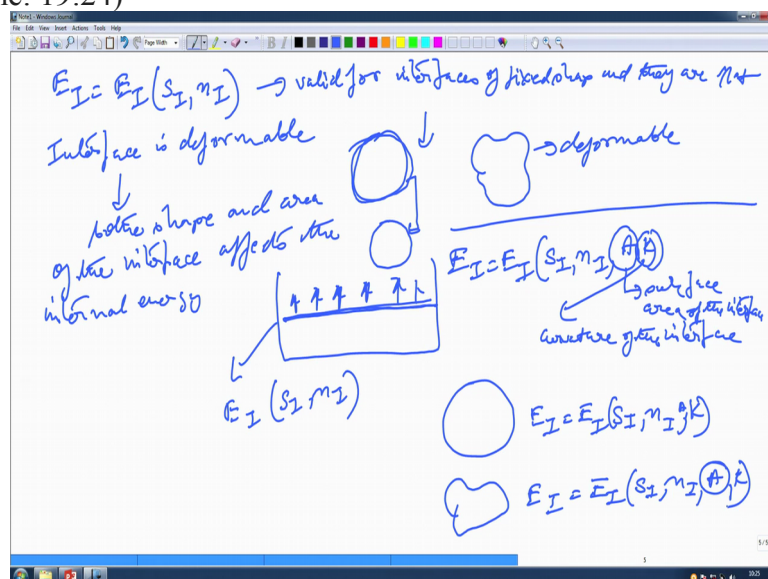
And this is a ρ and this is for example some this cut section, let us term it as x . What will happen is that the density will be very high right up to the interface okay. Then it will attain a sharp drop right. And it will come to a value over here and this drop in the case of liquid and vapour is of the order of thousand, right.

So, similarly many of the properties actually change because of this okay. So, it is a region of sharp discontinuity the properties changes okay. The property between the different phases actually occurs over a thin. But it is it can be considered to be a finite region, so, thin finite region okay. So, the analysis that we are going to do over here is that it is very similar to the analysis that we did just a moment ago.

So, the number of moles if we consider a situation like this, the number of moles of the interface basically is n_I , is basically $n_{Total} - n_1 - n_2$ right. There is a total number of moles that are present at the interface right. Similarly internal energy we can take it as E_I that is the internal energy of the interface that is $E_{Total} - E_1 - E_2$ okay right.

So, this is this should be quite apparent this we just did a few moments ago. So, the interfacial energy and the number of moles that are present at the interface is readily visible okay. Now let us go to the next slide.

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And E_I therefore is a function of both S_I that is entropy and the number of moles of the interface okay which is valid when the shape and location of the interfaces is flat, valid for interfaces okay of fixed shape and they are flat there can be more complicated interfaces if the interface is deformable okay.

If it is a deformable; so you understand the interface is fixed. So, it is as if whatever exchange that is happening between the two phases okay. The interface is remaining kind of a fixed in space. So, it is almost like a hard, rigid, kind of a wall kind of a thing okay. But if interface is deformable which is in most cases the interface is deformable right.

The droplet surface can actually, if you take a droplet like this if you apply some kind of a force on it, the droplet surface can actually corrugate or do something like that. So, this interface is becoming a deformable interface right okay. On the other hand if you just allow this droplet to sit nice and easy okay.

This interface is like a fixed interface okay, the interface is deformable both the shape and the area of the interface affects the internal energy. Both shape and area of the interface affects the internal energy. In that particular case what happens is that we can say that EI is basically not just a function of two parameters with sI , nI , A and K also what are A and K .

A is the surface area and K is basically the curvature and this is the surface area of the interface okay. So, what we can see over here is that if the interface is not deformable there can be situations like that also okay. It is only given by a function of two parameters however when the interface is actually deformable okay.

Then the surface area and the corresponding curvature comes into the picture of course here in this case the interface have got a curvature. So, it does depend on the K the curvature but if it is like a flat interface like this okay this curvature parts does not come into the picture, flat can be for example when you are evaporating, you have a flask okay.

You have a pan and there is evaporation that is happening from the surface correct right. So, this interface is flat and it is not deforming per se it might translate up and down. So, in that particular case in this kind of an interface it is given as EI , sI , nI right whereas in the case of a droplet which is not deforming but still it have that curvature.

So, here EI will be EI , sI , nI and probably K okay and of course you have the surface area of the interface also coming into the picture in this case. But if it deforms okay this area change it is of course a function of area also when it deforms then this area change becomes an important parameter that is this area change then becomes an important parameter okay.

So, the interface is like that so, whether it is deformable or non deformable determines a lot of things okay. So, let us go to the next one.
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So, the change in the EI that is what we are interested in that is the change in the energy of the interface is basically given as dE once again we can write it like this right n , A , K , K here is a curvature. And this is of the interface only recall. So, s , A , K then you have this with respect to A , s , n , K dA + okay fine right.

So, what does it tell you the change in energy of the interface T_i basically depends on which parameters? It depends on the change of the interfacial energy with respect to the entropy and we will see what that term exactly means change with respect to the number of moles at the interface right. It also depends on what we call the change in surface area and the change in curvature right.

So, once you coming back to that droplet example once you deform the droplet to a pancake say for example right by whatever means. So, what you change? You change two things basically you change both the area this is area A_1 this is A_2 . So, A_2 is obviously greater than A_1 right also the curvature changes here it has got one curvature here. It has got two curvatures essentially right.

So, the curvature also changes, so both A changes and K changes also correct okay even though the number of moles and the entropy may not change in the process. So, this deformation part is extremely important when we later do for example a little bit on sprays okay that is how spray atomization and break up and things like that also happens.

Those are multi-phase processes as well as you have correctly guessed by now. So, this dE I am just dropping the I for the time being so that for the ease of writing. So this is Tds of course this you know it is temperature + μdn this you know is the chemical potential + $dE_{A,s,n,K} = dE_{K,s,n,A} + dK$ okay.

Now if the variation in the curvature is negligible right variation in curvature is negligible means when the droplet remains of the droplet right. So, there is no change in curvature per se correct. So, situations like that for example when a bubble actually forms that curvature may actually remain the same.

So, if this is negligible K variation is negligible we are just doing us a special case is negligible it can be negligible okay. What will happen to this particular equation this will actually go to 0, correct, okay. So, we can define this particular term $dE_{A,s,n,K}$ right, this term that we have over here, this can be defined as a quantity called Σ okay.

So, that dE now becomes $Tds + \mu dn + \Sigma dA$ right. So, this Σ is nothing but the surface tension got it. So, surface tension is a rate of change of internal energy with respect to area or change of internal energy with respect to area where the curvature, the number of moles and the entropies are constant okay.

So, that is what we call the surface tension over here okay. So, surface tension can be also represented okay in terms of the Helmholtz free energy equation. See there can be equivalent representations right. So, F for example is $E - TS$ right that we know that is by Helmholtz basic equation right.

So, similarly dF can be written as $dE - Tds - SdT$ right. So, dF can be written as $-SdT + \mu dn + \sigma dA$ where σ this time will be represented as the change of Helmholtz free energy with respect to its area for constant temperature in it okay. Curvature also comes into the picture I am just dropping it for the time being.

Because curvature we have assumed that the curvature is actually small, got it. So, this particular thing proves that this is an alternative definition of surface tension. This is one definition that we saw over here, this is the other definition that we have over here okay. So, we end lecture 1 with the surface tension that what is surface tension over here.

We in the next lecture what we will do is that consider the other alternative definitions of surface tension.