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Lecture – 58 Droplet evaporation – Sessile I

So, right now that since we have finished turbulence and we have finished the laminar flow part forced and natural internal and external and turbulence also we saw how things can be handled what are the definite problems of turbulence, ok. Let us now go into a alight field I mean more advanced topic so to say.

So, here we would not spend a lot of time in going into the details this is just to give you a synopsis that what are the different types of problems that one can encounter ok. So, one of the major problems in which many people work is the area of you know multi phase flows and one of the key multi phase flows is basically all multi phase flows involve droplets, ok. So, droplets are basically drops of fluid which is which is present in many applications for example, if you take gas turbines if you take surface pattering if you take biomedical applications in all applications you will find that droplets is kind of central to all those applications, right.

So, droplet forms one of the fundamental building block, right of any application so to say.

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So, if you so, our lecture will be termed as droplet evaporation, ok. So, we will look at some of the, this is also in the heat transfer domain this also uses convection and also like conduction driven problem and this is a slightly more involved problem. So, it is recommended that for a full fledged understanding you do the companion NPTEL course which is on the heat transfer and come and combustion and fluid flow in basically multi phase systems, right. So, that is a specialized course which is basically tailored to that, ok, here we are just going to give you a synopsis.

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So, first and foremost one of the big areas in which droplets can be important and if you look at the presentation it will be that the most important part of the droplet is in many applications is what we call the sessile droplet, right. In the sessile droplet let is pivotal to a plethora of natural industrial processes like food processing, fire suppression, drug delivery, functional coatings, combustion of nano fuels everywhere, right. So, if you have seen normally that if you spill a drop of coffee on the table, right after some time you see that this is the kind of pattern that it actually forms, very distinctive patterns where all the coffee particles basically goes and gets agglomerated at the edge, right that is what you have seen, right.

Similar things you see in a drop of blood from individuals and of course, there are different markers if the blood is if the individual is suffering from something like anemia or some other things, then the pattern that forms right is very different right. So, how

does it happen it happens because of certain reasons, and these are all uses hydrophilic substrate. Hydrophilic substrate means where if you place a droplet the contact angle that it makes is actually less than 90 degrees. While on the other hand if you do hydrophobic droplets, ok, so, you see different types of things for example, this is a typical cheese right you see different types of patterns that actually forms when you actually evaporate droplets of such kind, ok.

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So, just to give you an idea that when you are dealing with a droplet or a sessile droplet in this particular case and we will do the contact free droplets in the next class when you do sessile droplets, the droplet if you look at it over here how can a droplet evaporate, right. So, evaporation as you know is basically a heat and mass transfer process in which the solvent from the droplet actually evaporates this is the same thing if you keep a pot of water out in the open what happens to the water the water level just starts to come down correct the water level starts to decrease. Why does this happen? This is because through evaporation there is solvent loss, right.

So, similarly when you place a droplet on a platform; that means, on a substrate like this it will undergo evaporation that is quite natural, right. Now, it can undergo evaporation in a varieties of ways. So, you can lose the same mass, but in a varieties of ways. So, one of the way first way is basically what we call a constant contact radius or CCR mode. So,

what happens in a CCR mode is that that two contact lines of the droplets are basically pinned.

So, if you look at it from the top you will always see that the droplet is pinned ok, that means, that contact line does not move right it remains the same. So, if the droplet loses mass in this configuration the only way it can do so, if its height will come down, right; that means, it will become flatter and flatter, right and it is contact angle is going to come down correct it has to because you have to conserve mass and mass can be. So, you are fixing the radius. So, naturally your height of the droplet and the contact angle of the droplet has to come down in this particular configuration. So, this is one way by which a droplet can lose mass.

There is there is a second way by which it can lose mass. So, this is called a constant contact radius mode, then there is a second mode in which the droplet can lose mass and that is called the constant contact angle mode. So, what happens in a constant contact angle mode? Initially you place the droplet like this, right with time the droplet actually slips, so that means, from the top you will see concentric circles right that the droplet is basically slipping, right.

So, the next stage will be this next will be this ok. So, in this particular configuration you can preserve the contact angle. So, you can see that the contact angle is the same because these are like the same droplet, but what will happen is that it is contact radius is now going to come down that is because once again here to conserve mass if your contact angle remains the same then your contact radius has to come down, right. So, it can lose mass in either this way or this way or it can lose mass in a combination of both, that means, sometime some part it can lose mass like this and in some situations it can lose mass by this that is what we call the mixed mode.

So, any sessile droplet which undergoes evaporation, undergoes either through a contact radius mode or a constant contact angle mode or what we call other than that a mixed one, ok. So, if you plot say for example, the contact angle and the contact radius normalized by their initial values you will find that this is the region where it is more or less in a constant contact radius mode, this is the region where it is more or less in a constant contact angle mode and this is the region where it actually shows a mixed mode, ok.

So, you can see that majority of the region it is either in CCR or CCA, but there can be as portion of mixed mode as well. Now, this depends highly on the substrate on the droplet type, right, ok. So, it is very dependent on a few other parameters, ok.

So, why this is important because now if you look at so, these are the different ways by which it can lose mass now, let us look at one fundamental definition which will come in handy when we do the analysis, or we look at the whole thing is a concept of surface tension.

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Now, surface tension why is it important because as I said most of the convective heat transfer problems that you will see will involve droplets, and there will be flow around a droplet the droplet will try to retain it is shape, ok. In sessile droplets is also the same. So, there is a so, what makes the droplet hold it is shape is something called it is it is attributed to surface tension. So, let us look at the surface tension part that how the surface tension is useful over here.

So, if you look at this particular picture you will find that say that there is a liquid and then there is a vapor and this is an interface, right of liquid vapor it is a it is like a hard discontinuity from a macroscale thermodynamics and heat transfer point of view, ok. So, surface tension is basically something which tries to resist an increase in this interfacial area. So, if you try to change this interfacial area to something like this surface tension tries to prevent that effect, right. Now, let us remove all these things and let us try to see that what is the origin of surface tension.

So, basically it is a intermolecular attractive force in the liquid phase holds the molecule in the liquid close to each other and they are balanced in all directions. So, if this is a molecule within the liquid, it has got a force field which is basically isotropic around it, right. However, for molecules at the solid liquid interface, or liquid sorry liquid air interface or liquid vapor interface, ok, the attractive force in the liquid phase is much stronger, right compared to the vapor, right. Because vapors are loosely bound that we already know right is greater.

So, therefore, the molecules at the interface are pulled towards the liquid phase ok. So, this are has a pull towards the liquid phase right which actually prevents any increase in interfacial surface area. So, it tries to keep the area minimum this is the same reason why any blob of fluid if you this is a blob of fluid it ultimately goes into a spherical shape, right. It tries to minimize the area right. So, classical thermodynamics is usually used to establish the relationship between surface tension and other variables. So, for example, you do not have to go through all the motions is basically the interface energy is given as a function of what we call the curvature the area and two other parameters, ok.

So, if you write a change in this energy then the energy it is given by the change in entropy, the change in the in the number of moles and there are two other changes which happens due to the area and the curvature effect. So, if the variation of curvature is negligible, ok, you have a relationship like this where it shows that the surface tension is nothing, but the rate of change where the change of internal energy with respect to area given entropy and the corresponding number of moles are given constant.

So, this is one of the definition you can have multiple other definition in terms of the Gibbs free energy, in terms of the Helmholtz free energy etcetera or the essential concept of surface tension is it tries to minimize the surface area, ok. This tries to minimize that is why you get droplets that is why the sessile droplet that I showed in the previous application holds its shape it does not become.

So, for example, in this particular problem it does not evaporate like this, this is not possible. So, technically you can have the same mass loss in this and this right. So, from here say it becomes this form and from here it becomes this form say the total mass lost

is the same in both the cases, but this is not permissible, right. Though technically conservation of mass allows both configurations to happen not permissible because of the reason that we established here because surface tension tries to minimize the area, the surface area minimization and it is given in this particular form there are alternative definitions as well, coming from a macroscopic equilibrium point of view ok.

So, this is a very important concept which puts a limit then how a droplet should actually evaporate in any field it can be a pure conduction or a diffusion driven problem, it can also be any other type of problem as well ok, it can be a convective flux for example, if the droplet is vaporizing like this if there is a convective flow and if the flow is not too hard right; that means, the flow is not too fast this droplet will evaporate and it will evaporate in a certain way. So, and those ways can be given by these, right all this mode.

So, it is not that this droplet is vaporizing naturally; that means, by more like a diffusion driven problem it can be a convectively driven problem as well, and surface tension tries to change resist any change in the surface area, but if the flow is too strong you can have phenomena's like atomization and things like that which is also quite obvious because the forces because you are applying an external force and the surface tension cannot fight with that external force.

So, you are trying to deform the droplet by using some force right. So, for example, if this is a droplet sitting you are punching you are just poking the droplet right with something. Obviously, your surface tension will try to resist it, but at one point of time it would not be, so, in that case the drop that shape might change, but that is not a naturally occurring event, ok.

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Similarly, usin	g other fundamental relati	ons we get $\sigma =$	$= \left(\frac{\partial F}{\partial A}\right)_{T,n} \qquad \qquad$	$\mathbf{r} = \left(\frac{\partial G}{\partial A}\right)_{r,p}$ Obtained thermodyn energy, we energy	by using first law of a <u>mics involving</u> internal <u>ork done</u> and thermal
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Surface tens due to specif • Surface ten nonpolar f • For a hydr forces and The surfac forces and	ion can be considered a fic forces, like metallic nsion force in a nonpole luid is very low ogen-bonded liquid, sun hydrogen bonding te tension for a liquid m metallic bonding and	s the summation o or hydrogen bondi r liquid is due only face tension is slig tetal is highest beca metallic bonding is	f two parts: one part ng (Fowkes, 1965) y to the dispersion for ghtly higher because ause the surface tens	is due to dispersion force, pree; therefore, the surface the surface tension is due ion is due to a combination the bydrogen bonding	and the other part is tension for a toboth dispersion n of dispersion

So, similarly as I say the other relationships of surface tension is given in terms of Helmholtz free energy and Gibbs free energy this is solved by using the first law of thermodynamics we are not going to go into the details you can work it out of yourself that is it is not a major deal, ok. So, surface tension of different liquids at liquid vapor, interfaces are given over here. So, surface tension is basically considered the summation of two parts; one part is due to the dispersion force, once again you do not have to know the details, one part is the dispersion force and the other part is due to specific forces like metallic or hydrogen bonding, all right.

So, for a nonpolar liquid the surface tension is only due to dispersion force therefore, the surface tension is very very low, like for example, helium nitrogen right their surface tensions are negligible, right very very low several orders low and that is because there is no metallic or hydrogen bonding. For a hydrogen-bonded liquid the surface tension is slightly higher because it is both due to dispersion and hydrogen bonding. So, say for example, water ammonia this has got reasonably high surface tensions, right.

So, that is why when you put a water on a surface you see it attain a particular shape, right, whereas, if you put nitrogen and other things we just go flat right it will just wet the surface completely, right. So, when you actually have your glass you will see that water is sitting on the glass in that particular form right that is because it is surface strain is reasonably high, ok.

Surface tension of liquid metal ; however, is the highest it is a combination of dispersion and metallic forces and metallic bonding is much much stronger than hydrogen bonding, right. So, for example, silver mercury if you have seen a blob of mercury you will find that it is almost like this right, that is because of the simple reason it is surface tension is very very high, ok.

So, because the surface tension is very very high the liquid metals actually form this you know that is why mercury almost slides over any surface any given surface it will slide. Of course, whether a droplet will weight a surface or not that depends on several parameters like what is it is interaction with the surface right, but if you have a very high surface tension it is likely that you will form this kind of a bead kind of a structure, ok. So, this is surface tension is important and we gave this idea.

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Now, let us look at droplets on hydrophilic substrates, and see how convection comes into effect here ok. So, if you look at the droplet on a hydrophilic surface which is evaporating with a with a pinned contact line; that means, the contact radius it is evaporating in what we call the CCR mode now, right.

So, the evaporation is maximum you can show, the contact radius remains constant throughout the droplet evaporation lifetime. So, that is all; that means, if you plot it will show something like this the contact radius that is R by R naught will show something like this with time maybe towards the end you might have a little bit of a drop, ok. So,

that being said near this three phase this is called the three phase contact line the evaporation is highest there and it progressively reduces as you go to the top, ok. So, evaporation is maximum at the edge and least at the apex which is at the center of the droplet and the contact radius remains constant throughout the droplet evaporation right, ok.

So, what happens is that is as follows. So, there is a differential evaporation that you have created even if it is natural; that means, there is no flow outside, ok, there is no fluid flow; that means, no air flow which is augmenting it right it is just that the evaporation flux here is more than here, ok. So, naturally what happens is that here the solvent loss is more than the solvent lost there, right. So, it automatically you know what it does it creates what we call a capillary flow in which fluid from this part actually rushes to the three phase contact line basically to dip to make up for the depleted solvent because it is a constant the edge is actually pinned right. So, the liquid rushes to that edge to make up for the solvent that is lost, ok.

So, automatically it creates what we call a convective flow or a capillary flow in this case are radially outward capillary flow towards the edge which is responsible basically for the coffee ring effect that we said earlier; that means, if this droplet actually has particulate matter then all the particulate matter will be transferred from the droplet bulk to the droplet edge just because the contact line is pinned in order to make up for the depleted solvent right and so, you naturally create a convective environment inside the droplet, right. Even though the droplet is vaporizing you know you know diffusion based way right; that means, it is a diffusion based phenomena; that means, there is no external flow.

So, it is like akin to conduction problem right it is like a conduction problem, but it is a variable conduction problem; that means, the droplet is not evaporating in the same way along its surface, right. So, therefore, this creates this differential diffusion or the mass loss actually creates this directed flow towards the droplet edge.



So, Deegan was the first person to basically solve this particular problem and let us see that how he actually solved it. We are not going to go into their details the absolute details. So, let us take that this is the droplet right this is the droplet correct, ok so, now, if you see the rate of change of fluid in an infinitesimal annular element of the droplet, at a radius r. So, at some radius r you have this thin strip that Deegan constructed through the thin strip there is an evaporation which is given by J s, right.

So, there is a fluid which is entering and leaving this particular control volume correct. So, the rate of change of this fluid can be cast in this particular equation, where v is basically called the vertically average radial flow. So, this v has been averaged in the vertical direction right though it varies in the radial direction, ok. So, if you have this kind of a situation you are basically you are averaging v over the section ok, but you are not averaging it in the radial direction. So, radially the v is allowed to vary, ok. So, this is the equation that you actually get that is a rate of change of height is given by this right and this is basically the axis of symmetry this is the plane of symmetry.

So, the v that you get; that means, the vertically average to radial velocity right is given by this complicated form, because we want to know the velocity right the nonzero velocity arises when there is a mismatch between the local evaporation rate and the rate of change of the interface. So, specifically you can see that that this velocity would have gone to 0, if the interface and the evaporation fluxes would have matched exactly, right, but it is not the case. So, therefore, you create naturally a flow field inside the droplet.

So, to compute v we need to specify h and J right; that means, h and J right, these are the two parameters which are basically unknown. So, h is easy to calculate because assuming that the droplet is like a spherical cap that is called a Spherical cap. You can calculate h in this following manner once again we are not going through the math you can work it out in your spare time this is just to give gator. So, this gives you h.

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The evaporation flux J s depends on whether the rate limiting step is transfer of mass or the diffusive relaxation of the saturated vapor in the vicinity of the interface. So, this big is a question that how our droplet actually evaporates, right. So, if you take a droplet like the one that we have shown over here you know what the evaporation phenomena for a diffusion driven problem is that initially, the droplet evaporates and forms a layer right of saturated vapor in it is vicinity right mean. So, this vapor that exists is under saturated condition right saturated at the temperature of the droplet surface. So, if the droplet surface temperature is T s, so, the saturation vapor pressure for corresponding to that T s is there on near this area right.

So, if this would have persisted the droplet would have stopped evaporating, because the relative humidity of this particular layer is 100 percent. This is exactly what happens during the monsoon seasons that your wet cloths do not dry; that is simple reason is that

the entire atmosphere is at a relative humidity of close to 100 percent. So, it would not dry right or the drying rate will be very minuscule. Similar thing happens over here the temperature of the surface is T s, right. So, the vapor that exists in that thin strip around the droplet is actually given as c s all right.

Now, in order for the droplet to continuously evaporate this layer has to relax; that means, it has to decay and make way for more. So, that happens due to the concentration gradient usually between the ambient; ambient is c infinity, this is c s. So, you have a driver like c s minus c infinity, right over some length scale L, right. So, that actually relaxes the vapor which is around the droplet surface, right. So, the rate limiting is means which one basically throttles the process one is the transfer of mass and the other one is this diffusive relaxation; that means, how fast it can actually relax. So, that you can have the mass actually go so, for a steady state diffusion problem it is basically a Laplace operator right that is because it is like a conduction problem is essentially like a conduction problem, ok.

The assumption is good for times which are longer than D by R squared because D by R square D is basically being the diffusion coefficient, ok. So, that is basically the time scale that it takes for the diffusion to happen. So, along the surface of the droplet the boundary conditions are the air is saturated with ca c equal to c s. Normal to the substrate the vapor gradient is obviously 0 and c converges to the free stream vapor concentration which is basically c infinity far away from the droplet far away in this case essentially means that the droplet is I mean it is not far away means at infinity it is like several diameters away.

So, the Deegan said that the boundary value problem is similar to a charged conductor if we equate c with the electrostatic potential and J, which is the flux term with the electric field ok, but the evaporation current actually diverges near the contact line ok. So, that is still an unsolved problem in the droplet evaporation parody.

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So, now what you get is that you get your J s these are the solutions you get your J s vary like this, ok. Once again it kicks up as you can see when r is equal to when small r becomes equal to capital R right you get a discontinuity and this is your lambda, lambda is given in terms of the contact angle, there is a significant you can cast J in terms of the evaporation rate. So, J from the surface is given as J naught multiplied by this factor where J r and t can be determined from the rate time dependence of h and basically h. So, the change of droplet volume you can cast it in this kind of an equation like this.

So, the velocity now can be computed by combining this equation and the equation that we showed earlier this particular equation you combine these two and use that the Laplace of the velocity is equal to 0. So, you can solve for this for this equation and get the final answer.



So, if you measure these values experimentally you find this is delta is basically equal to R minus capital R minus small r you see that the velocity and delta are given in this particular way. Of course, very close to the interface, they very close when r is equal to capital R the entire thing basically starts to blow up. So, you have to use some factor to basically scale it down, right.

So, you stop here in the next class we are going to look at some more insights of these sessile droplets and we are also going to look into some of the important parameters in a in a contact free droplet as well.

Thank you.