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Lecture 30 Heat transfer and transport processes in sessile droplets

So, welcome to today's lecture, last class what we did was that we look into spherical droplet and we looked into the different evaporation and the condensation type of models. The evaporation models and the how the flow field inside the droplet actually behaves and what will be the equations, the relevant equations.

But there is one other class of applications in which droplet on a substrate becomes very important. So, in this particular lecture what we are going to do is that we are going to look into the sessile droplet evaporation aspect. By sessile droplet I mean the droplet which is sitting on a substrate remember in the in the very first few lectures we did that a droplet on a substrate can be hydrophobic it can be hydrophilic.

It can exhibit different contact angles different rates of spreading, what is the apparent contact angle, what is the real contact and we covered all these things with details, in the last few classes. Now in this particular class we are going to look into how the evaporation of those sessile droplets that actually take place and that is very, very important in the current situation.

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If you look at the slide, so, this is the file droplet evaporation sessile droplet evaporation. I, so; it is like any droplet which is sitting on a platform. So, this is for example a hydrophobic

droplet because if you look at that is the kind of contact angle that you have or actually this one is a contact angle. So, it is more than 90 degrees okay.

And then you have the sessile, the hydrophilic case where you have the contact angle which is much, much less than 90 degrees. So, these droplets actually sit on substrates as we know that this contact angle is normally a function of many things including the substrates, type of liquids that you are using etcetera.

So, this is not something that water can be hydrophobic on a particular substrate it with some other thing in a different substrate. So, there is no hard and fast rule right that which one it depends with a combination of the substrate and the liquids that you are actually dealing with. Now this is very different from the spherical droplets that we did so far.

In a spherical droplet what we did we saw that there was some recirculating flows right, inside right, if you recall. So, this was called the Hill Spherical Vortex right and mostly this flows, there was some flow field outside. This is a gas phase flow field and we devised equations that how the evaporation from the droplet surface actually happened right.

If you recall the last few lectures that is all that we did and we found that there are different types of models like type one is like the d square law, type 2, type 3, type 4 right. So, there was no contact with the substrate as such this is like a contact free droplet so to say right, contact free. So, the interface is wholly between liquid and a gas right.

Here of course you have that three phase contact line right if you look at that that is the threephase contact line. It is like a line because it just extends throughout the whole thing right. So, there is gas, there is liquid and then there is a substrate and we all know that there is like three types of surface tensions are there right between gas and liquid between solid and liquid and between solid and gas right.

We already discussed it in more details that these were the types of contact I mean the types of surface tension and this is called a three-phase contact light right. So, if you look at it, it is like a line right and we also say that there is some small layer that is absorbed okay on the surface okay which actually alters the contact line dynamics.

So, we spend some time earlier looking at the contact line motion and we also said that these droplets can actually operate in a different types of ways okay and if you recall they were called CCA CCR right and mixed different types of modes and we will cover some of those things in details in a next few slides right.

So, that is a droplet if it evaporates like this, this is like a CCR kind of a mode, if it evaporates this is a droplet and evaporate like that, that is like a CCA mode right CCA CCR correct, okay. So, this we already covered in some details and this depends on what kind of a substrate you have. So, it is highly dependent on the intermolecular phenomena also.

We are not going to go into that kind of a detail but we are going to establish that how this droplet actually is evaporates. So, it evaporates along the boundary right okay is this isotropic, is it uniform if somebody asks you for example in the case of a uniformly vaporizing drop that we saw that it was more or less isotropic right.

The vaporization pattern as far as the assumptions went, of course in cases where there are wakes that are formed behind the contact free droplets this could be other things as well right. But we assume that it was more or less isotropic evaporation, if you recall that what we did earlier right.

Here of course here of course we need to know whether this evaporation pattern right, this evaporation pattern is it isotropic, is it uniform spatially right. These are the questions that we are trying to answer over here is it different in hydrophobic than compared to a hydrophilic say for example, is the pattern different right.

What are the kinds of flow fields that are created within such droplets? We know that this is Hill Spherical Vortex. What about this? What about this what kind of flow fields are created inside. Because of this diffusion it is a completely diffusion problem, so, there is no flow around the droplet. So, that is the premise of our assumption.

So, this is like you put a drop of water on a platform and you let it evaporate. We are trying to understand that dynamics assume that there is no flow around the droplet there is no convective flow field around the droplet let us see what happens. (Refer Slide Time: 06:51)



So, why is it important, that is because the droplet evaporation is pivotal to a plethora of natural and industrial processes like food processing, fire suppression, formation of microcapsules, drug delivery, functional coatings and even combustion of what we call the new generation of fuels which is like nano's fuels.

This also we covered a little bit in our very early lectures right. So, it is pivotal for example drug delivery it is very important we mostly deal with sessile drop listen in such scenarios. It can be also droplets, it can be also contact free droplets, it can be also used for creating a pattern on a surface.

So, you have a plate you want to create all kinds of patterns on it right, you mostly useful droplets for that right. So, it actually cuts across multiple domains it is just not mechanical engineering, it is just not pharmaceutics, it is there everywhere right. Now when a droplet was actually spilled and this experiment you guys can do at your home right that if you have a cup of coffee.

You take a cup of coffee and you spill a small drop of that coffee on a substrate right. And assume that the contact line remains spinned that means you spill the coffee, it actually on an hydrophilic substrate. The contact line kind of remains pinned and this is how the surface of the drop that actually regresses, got it.

So, this is at different here actually time increases right. So, you find something very interesting happens you get what we call a coffee ring pattern do you see that pattern around there on the outskirt of this line, so this thing's. These are called what we call the coffee ring pattern, you see that there is a lot of intense deposits, the particle's the coffee particles basically they have got deposited on the perimeter.

But not in the interior, no deposits here right, amazing right, normally what we do you expect that you spill a coffee everywhere in that particular spillage there will be deposits everywhere right. Instead what you have is deposit along a boundary right. It is like a boundary right there is no practically no deposits in the interior, very, very interesting right.

And this happens when this is contact line is spinned okay. So, that is that is very, very good right, okay. So, why is this coffee ring formation happens and we are going to spend a little bit of time on this, this work is dedicated to actually Deegan is the one who actually found a complete solution for this.

This is very intriguing kind of a phenomenal right that you spill a coffee, drop of coffee why should the particles all go towards the edge. Why not there should be any deposits in the center all right. Similarly when you actually drop if you look at these are the different blood drops from different persons like for example right.

So, A for example the blood drop you can see they are cracking and slacking of the blood drop. This is from a healthy person, this is a person with anaemia this is a person once again in good health okay. And this is once again from a person who is suffering from height hyperlipidaemia. So, it you can see this is also can act just by watching the evaporative pattern and the deposit pattern one can use that as a diagnostic tool also right.

So, just by looking at patterns at dried pattern basically that means dried patterns is only form due to evaporation right, there is no other mechanism. So, when you have a dried pattern like this right you can actually just by looking at the dried pattern you can make medical diagnostics got it.

That is interesting right so you can make medical diagnostics based on that right. So, we have shown like several interesting kind of phenomenon however when you actually go to the Hydraphilic are all hydrophilic substrate examples right. When you go to hydrophobic substrates say for example okay.

You see a whole lot of other types of phenomenas also like you see this particular type of structures that form if you look at them right. You can see sometimes these are like highly buckles kind of shape okay. These are very interesting shapes that you get with all kinds of morphologies. If you look at the morphologies over here this is a perfect candidate for producing nano particles, right.

It can be also used to produce this patterns the surface patterns you can see because of their shapes okay. And all of these happen due to the drying of droplets on hydrophobic substance, right. So, this is all due to evaporation. So, this is important right. So, therefore I am trying to emphasize the point that this is very important right to have; to know all kinds of things.

So, from food, pharmacy, nutrition it can be other industries like surface patterning, nano particle production and there is a whole gamut of applications for this kind of work okay. So, that provides the motivation. (Refer Slide Time: 12:29)



Now a brief recap of what the modes of evaporation are. We covered that in a little bit earlier. It can be constant contact radius mode in which the contact angle decreases with the contact radius remains constant right, okay. So, let us take these two examples from here to here if you look at the state, what you say, this is the initial state of the droplet.

This is the final state right as you can see the contact radius this R remains constant for the droplet volume has gone from there to there, right. So, the contact angle has to change, previously that was the contact angle. Now that this is the content right, So, this is like a constant contact radius mode of evaporation.

In which the contact line basically remains spinned okay. Then there is also the provision for constant contact angle in which the contact radius decreases but the contact angle remains constant. So, for example in this case as you can see the contact radius have gone from that to this, right. But the contact angle if you find they are more or less the same right.

So, this is theta is constant but R is not constant okay and then there can be the mixed mode in which both the contact radius as well as the contact angle changes like for example there is thing that you see over here okay, both have changed okay, mixed mode. So, we cannot attribute it either to the constant contact angle or to the constant contact radius.

If you transfer this to a plot then it is much easier and it is not like that a droplet through its entire life history only exhibits constant contact radius or a constant contact angle. It can exhibit all three modes right depending on the different phases in its lifetime. Now for example what we have plotted over here, we have plotted the instantaneous contact radius with the initial contact radius right and this we have plotted with time right.

And on this axis what we have plotted is that we have plotted the instantaneous contact angle with the initial contact angle right okay. So, now what you see over here if you if you follow this for example this yellow curve that you see over there right. What we will find is that in this region right, you can see that the contact radius hardly decreases by about 5 percent right.

So, this is like almost like 5 percent decrease in contact radius CR, right. So, this can be taken as like a constant contact radius mode, so to say, right, okay. On the other side if you just look at this red coloured plot over here which plots basically the contact angle you find that in this region, right. The contact angle reduces by about 10 percent not more than that right over a period of 400 seconds.

So, this can be almost taken as a CCA mode or a constant contact angle mode right. But however in the stage three if you look at it okay you will see that the contact angle drops very sharply the contact radius also drops. So, it can be taken as mixed mode right. So, in one life history of the droplet this is a single droplet these results that we are actually showing over here.

Initially it exhibited for the first say 100, 150 seconds which showed a CCR mode a constant contact radius mode. In the next 400 seconds or so it showed the CCA or the constant contact angle mode. And the last 300 seconds or so it showed a mixed mode right, so in the constant contact radius mode the contact radius decreased by only 5 percent.

The constant contact angle reduced by about 10 percent so they are not exactly constant but they are very equal to each other right okay. So, that is what we have got out of this particular figure. So, you can see in this particular case that droplet okay which is a hydrophobic droplet in this case it shows all the contact angle modes right, all the different modes of this operation that is important.

So, do not attribute it just to one particular class of droplets right, a single droplet evaporating on a substrate can exhibit all this modes together okay. (Refer Slide Time: 17:02)



We take a look at the hydrophilic substrates now, so the droplets which are evaporating on hydrophilic substrates we already said has a contact angle of less than 90 degrees. The contact angle contact radius mostly remains constant throughout the droplet evaporation process these are particularly true for pinned droplets.

Like that coffee strain that we showed right and another important interesting thing is that evaporation is maximum at the edges and least at the center of the droplet. So, this is important this is the apex and this is the edge right, so, this is apex and this is the edge. So, what we are trying to say is that if we plot the J which is the evaporation flux term right.

J will be highest near the edge and it will be lowest at the apex right because of this evaporation rate, so to say, right. There is a radially outward flow that is actually created in such hydrophilic droplets right. So, the flow is like this if you look at it the flow goes like this right because this part is evaporating faster.

So, the solvent supply is directed toward that part to meet the evaporation load right to meet the evaporation flux. The enhanced evaporation flux okay the flow is actually directed towards the edge which actually evaporates at a faster rate. This is an experimentally observed fact and if you look at the corresponding streak lines okay.

This is just like a fluorescence imaging that people have done is that you see that up there is experimental evidence where you can see those streaks and you see the edge. So, there is lot

of deposition a lot of transport towards the edge okay from the droplet center. So, the center of the droplet is actually here and this is the edge right.

So, it is; if you look at it, this is the top view. So, from the top view you will see the flow is like that right okay. And from the side view this is a side view the same flow will look something like that right. So, this clearly shows experimentally as well as this is a diagrammatic representation.

That there is a radially outward capillary flow towards the edge resulting in the formation of the coffee ring because particles are preferentially transported from the center of the droplet towards the edge right. So, naturally when we looked at the coffee ring in the previous slide like here right. When we saw that coffee ring it is very clear that why the deposit should form at the edge.

That is because the flow is radially outward right. Why the flow is radially outward that is because there is stronger evaporation from near the edge of the droplet clear, on this part. So, this actually shows that the evaporation is maximum at the edges, this leads to a radially outward capillary flow.

And if there are particulate matter present in the droplet like in the case of a coffee drop, there are coffee bits particles this gets transported and gets preferentially deposited at the edge with the center not showing any particles at all okay. These are also valid for spherical type particles. There are other types of particles which can be very different right. So, we are not going to go into those details immediately okay. (Refer Slide Time: 20:52)



So, the Deegan propose the solution to understand this entire process right. So, this is mathematical solution punched with some experimental data. So, let us look at that in a little bit more details over here okay. So, what you see is that this is a section of that hydrophilic droplet okay. So, this is the axis of symmetry.

So, this is the boundary and this is how he has taken a control volume like this over here which has got a height h okay and we already know that there is a radial flow this is the contact angle theta c. This is the evaporation flux that happens from that particular section, got it, okay. So, what you can first write about this particular problem is what is the mass conservation inside that control volume.

So, this is basically like a control volume right. So, what is the rate of change of the amount of fluid in an annular element which is at a radial distance R from the center line? So, if this is the whole droplet this is the thing we have taken a section over here which is located at a distance R right. And this has got evaporation flux over there.

Some velocity which is actually bringing the flow in, got it, okay. So, the rate of change of amount of fluid infinitesimal annular element at a radial distance R, what it would be given by it will be given by the rate of change of the height okay plus whatever the flow is actually bringing in right. So, that is the convection term and then whatever is the loss that is happening due to evaporation understood.

So, the rate of change of height of this elemental area of this control volume is basically whatever fluid that you are bringing in, into that control volume right, net fluid that is brought in and whatever is a loss that is happening due to the evaporation right, okay. So, normally the second term that you see over there dh by dr okay or partial of h which with respect to the radius.

That is usually and square of that is basically very small so they are usually neglected right, okay. So, there is a vertically average section through which and V is basically the vertically average radial flow. So, the flow velocity might vary along the length of this interface but we are taking one average velocity.

So, it basically has been averaged okay over the height of the droplet right. It has been averaged over the height. So, if you have done your like Paul Howsen type of integral formulations in your boundary layer in your Fluid Mechanics course, it should come very naturally to you okay.

So, from this equation you can actually then write an expression for the air for the height averaged or vertically averaged radial velocity you can write it in this particular form okay and if this term can be neglected if that is the case. The non 0 V or the non zero value of this V happens when there is a mismatch between the local evaporation rate and the rate of change of the interface that is quite apparent.

If this and this where the same right then there would be no flow correct if the is the change of this interface and the evaporation rate they are the same then there would be no flow at all right. But the non-zero velocity arises because these two values are not the same okay. So, that means your rate of change of your height that is the interface height is not the same as the mass loss due to evaporation got it.

So, that is why there is a mismatch between the local evaporation rate and the rate of change of the interface. Local evaporation rate is this Chi Js that you see over here okay. So, to compute V our aim is to compute this velocity V. We need to specify what about that h and what about that Js that is not J that is Js right okay.

So, how do you compute the h because h is the height if you know the height rate of change of height and if you know the local evaporation rate we can calculate what is going to be the velocity. I am talking about from a theoretical perspective; experimentally of course people have computed that velocity.

So, that can be used as a ready validation of this entire thing right. So, h by h that it means the height of the droplet at any particular radius and at any particular time because that is what we have written r,t assuming a spherical cap approximation, spherical cap is this okay. It is like a part of a camp essentially so it is like a spherical cap.

So, you can call, you can finish off a complete circle and that is the part which is basically there okay. You are assuming a spherical cap approximation from geometry and you can work this out you can show that this is the relationship where capital R is basically the total radius that is the contact radius of the droplet, h0, t is basically the apex height that means this height.

This height is 0,t okay because 0 is r = 0, so that is the symmetry line okay and small r is at any radial distance. So, at any radial distance you can find out what will be the height of this particular interface right. So, that is what we want because we want you need to know that instantaneous height and you need to know the instantaneous Js to compute what will be the instantaneous velocity correct.

Up to this it should be clear okay. So, before we go okay, so because the lecture time is actually for this; in the next lecture we will pick it up from here and we will show that what happens due to this okay. So in the next lecture;