Multiphase Microfluidics Dr. Raghvendra Gupta Department of Chemical Engineering Indian Institute of Technology, Guwahati

Lecture – 02 Interfaces, Surface Tension and Wetting

Hello, in this lecture we are going to cover 3 important topic; which are fundamental to any multiphase flows and more so for multiphase microfluidics. The first one is interfaces, then the related edge surface tension and when we have 3 phase contact lines then we talk about wetting. So, interface is in any multiphase system interface is basically a the boundary line between 2 phases.

(Refer Slide Time: 01:05)



Now, if we look at in the framework of continuum mechanics, or under the assumption of continuum, where we assume that each fluid is continuous, all the molecules are we can the Knudsen number edge so small. That we can assume the fluid to be in continue. So, one fluid and another fluid the boundary between them is called an interface.

So, in that sense this can be represented by a geometric surface that can differentiate 2 different fluids for example, gas and liquid. And the boundary between them is what we call interface. Now, from our day to day life, we can conclude that the interface between 2 phases is generally a curve, curve if it is in 2 D and planar surface of 0 or negligible

thickness in 3 dimensions and these interfaces, and the interface is considered to be smooth.

So, there might be certain instances where you have the interface number of a small amplitude waves are present, but if you look at microscopically in under the continuum mechanism the interface is considered to be smooth. But at the molecular level, the separation between 2 fluids at the molecular level it depends on the interactions between the molecules and the brine Brownian diffusion.

(Refer Slide Time: 02:55)



So, if you look at microscopically you can have a picture of an interface. So, let us say this is a droplet on a solid surface. And so, this is liquid phase and this is gas phase, and this one is solid. So, what we have the interface between gas and liquid. This is the interface between gas and liquid.

Now, if we have a molecular view of this, then what we will see is that let us say one fluid is representing by molecules; which are filled and another fluid represented by the molecules which are not fluid.

So, that is a molecular or microscopic view of the interface.



So, when we have a interface separating 2 fluids, 2 different fluids. Generally what happens that the molecules in the bulk, they are attracted by other molecules. So, this molecule for example, at the center is attracted by molecules on all sides of it. And in the bulk they have a certain equilibrium. Now these interactions can be Van der Waal interactions for organic liquids or for polar liquids like water these interactions can be in terms of hydrogen bonds.

Now, when this molecule is at the interface, than it experiences the forces from the neighboring molecule, but on the other side it does not experience any or even if it does, then this the force is not symmetric. So, there is a net surface energy. So, at the interface it has interactions with the same molecules and the interaction off let us say this is liquid and this is gas. So, the interface the molecules which are at the interface, they have interaction with the liquid molecules at the bottom and the gas molecule send the top.

So, there is an no a symmetry or dissymmetry that is caused at the interphase, and to take into account, this a symmetry and the surface energy caused by this we define what is called surface tension. So, this take into account this molecular effect. Now this phenomenon can be for any type of interface, it can be the interface between liquid and gas, it can be interface between liquid liquid to immiscible liquids it can be interface between solid and gas or it can be interface between solid and liquid. But more commonly the surface tension concept or the interface and surface tension concept comes into picture for gas liquid and liquid flows ok.

So, the surface tension is it has the units of energy per unit surface area. So, it can have unit of joule per meter square, or it can have the unit of Newton per meter of force per unit length. Or generally it may be represented by milinewton per meter. It can be represented in the literature; you might see that it will represented by the symbol sigma and another place as it is represented by the symbol gamma.

So, surface tension basically takes into account the surface energy or the force imbalance that is caused because of that interaction of the molecules at the interface is not symmetric. So, that is taken to account in surface tension. Now if we want to make an estimate of surface tension; let us say, if in the fluid the total cohesive energy per molecule is U, then at the interface because it is molecule is able to interact only with has the molecules.

(Refer Slide Time: 08:09)



Then the interest the energy loss is U by 2. And if the molecular dimension is delta, and the corresponding molecular surface area will be proportional to delta square.

So, surface tension is this energy loss, because the fluid or the molecule is at the interface the energy loss per unit area. So, we can say that surface tension is, about U over 2 delta square where delta is the molecular dimension. The surface tension from this one can say

that if U is high than surface tension is going to be high, so the molecules or the fluids or the liquids which has large cohesive energy and small molecular dimensions they are supposed to have higher surface tensions.

For example, the highest surface tension is for liquid metals. So, for example, one of the examples of liquid metal is mercury. And mercury has surface tension of 425 0.4 or about 500 millinewton per meter. And oil and organic liquid, they have a smaller values of surface tension, because ah. So, for example, ethanol has a surface tension value of 22.1 millinewton per meter at room temperature. For water the surface tension is 72.8 milli newton per meter.

Now, it might be taken into account here; that when we talk about the surface tension. The values that we represent, it generally the surface tension value with the liquid and air. the value is generally not different very different for any other gas. So, liquid and gas surface tension value will be like this.

(Refer Slide Time: 10:19).



And for now, the similar arguments what we have discussed for a gas and liquid system, same thing holds true for a liquid liquid system; where the 2 liquids are invisible [vocalized-noise]; however, the surface tension in the liquid liquid system is generally known as or interpreted as well called interfacial tension. When the fluids are miscible; that means, the molecules can diffuse from one fluid to another, and in such case interfacial tension is 0. One example is that you have fresh and saltwater than the salt

molecules can diffuse from one fluid to another and the interfacial tension in this case is 0 for solid liquid case also the interface is the solid surface that is in contact with a liquid that is the interface.

Generally, it is not easy to measure the surface tension for the solids, but many theoretical analysis for example, we will see Young's law later in this lecture. They use the solid surface tension for analysis ok.

(Refer Slide Time: 11:37)



So, the surface tension it depends on or it changes with mainly 2 properties the first one is temperature. So, if the temperature keeps increasing as we know from thermodynamics that at critical point there is no distinction between the 2 phases gas and liquid. So, at the critical point the surface tension becomes 0. And Eotvos found a relationship for surface tension or temperature dependence of surface tension. So, where sigma is surface tension and that is equal to 1 over nu L power 2 by 3 T minus Tc; where Tc is the critical temperature and nu L is the molecular volume.

Later on, Katayama and Guggenheim, the improve the relationship that was given by Eotvos and they given a relationship in the form sigma is equal to sigma star 1 minus T over Tc to the power n; where sigma star is a constant for a liquid. And an is an empirical factor. now this n has a value of about 11 by 9 for organic liquids. Now it has been suggested that it can be the n can be approximately close to 1.

So, the surface tension temperature dependence of surface tension can be represented by a linear expression; where sigma is equal to sigma naught plus 1 plus, sigma naught into 1 plus beta into T minus T naught; where sigma naught each tem the surface tension a temperature T naught. So, this is a major difference value and from that one can calculate the surface tension and different temperatures ok.

(Refer Slide Time: 13:47)



So, the surface tension it decreases always with temperature. So, you might see this beta; that means, is negative. And when surface tension let us say at an interface there is heat transfer. So, because of heat transfer there is a temperature gradient. And the temperature gradient will cause a gradient in surface tension. So, imbalance of these tangential forces, because surface tension causes a normal stress, but then is the surface tension is different at 2 different places at the interface, then it results in an interface a tangential force at the interface. And the fluid from warm region for low sigma to high sigma a motion is established at the interface and this motion is known as Marangoni convection.

So, Marangoni convection is basically the convection of the fluid, near the interface because of the gradient in surface tension. And in this case, this gradient and surface tension is caused by gradient in temperature. The fluid moves from low surface tension value to high surface tension value, and low surface tension means at high temperature. So, fluid from the warm regions, it will move to the colder regions ok and this effect is propagated this effect is at the interface, but because of the viscous effects, the motion or Marangonic convection is propagated to the bulk of the fluid ok.

(Refer Slide Time: 16:08)



Now, another parameter or another thing that affects the value of surface tension for the fluids is the presence of surfactants. So, what is surfactant? Surfactant is it is basically what is called surface active agent. So, these surface-active agents are generally long amphiphilic molecules; which have a hydrophilic head and hydrophobic tail. So, hydro means water or in general terms it can be liquid or so, hydrophilic head; that means, the head is attracted towards the liquid or water and hydrophobic it is not attracted or it is repelled by the water

So, these surfactants are generally added to biological sample to prevent aggregate formation, or the to prevent the addition of target molecules from nearing to the surface, and it has a number of applications where one want to change the value of surface tension or reduce the surface tension. So, the surfactants when it is introduced in the liquid the diffusion they liquid and then reach at the interface and because of their amphiphillic nature they do not move at the interface and they are captured at the interface. So, they lower the value of the surface tension of the liquid.

So, if we plot an interface and the interface, and there will be the surfactant. So, will something like this where the head edge, hydrophilic head. And these are hydrophobic tails. So, with the increase in surface concentration when the surfactant concentration in

the bulk is increased, the surfactant concentration at the interface or at the surface will also increase until it reaches a critical value; which is called CMC or critical micelle concentration.

(Refer Slide Time: 18:56)



So, the surfactant molecules at above this concentration the surfactant molecule is start making groups together in the bulk and formations. At low concentration, the if we plot the surface tension with concentration of surfactant, then it is something like this. So, as we can see, initially it decreases linearly and slowly at initially means at low surfactant concentration the surface tension value decreases slowly. Near CMC or near the critical concentration when the entire interface is occupied by the surfactant molecules, the surface tension value decrease significantly and after that, because no more surfactant molecules can occupy the interface because the interface is already saturated with it.

So, the surface tension value remains constant. So, like when we have temperature gradient a Marangoni convection is observed. Similarly a gradient in surface tent concentration also gives rise to a gradiating surface tension. So, which again gives rise to Marangoni convection and the motion edge from low surface tension value to high surface tension values; so, low surface tension values means high concentration of surfactant, and high sigma is low concentration of surfactant.

(Refer Slide Time: 21:18).



So, what we have learned is about surface tension and the effect of temperature and concentration of surfactant on the value of surface tension. Now another important point is that what is the pressure jump, or what do we call Laplace law that relates the curvature of the surface or curvature of the interface with the pressure drop across the interphase. So, to understand that first we need to understand what is curvature and edge the curvature, edge it can be defined as the inverse of the radius of curvature.

So, curvature can be for it curved for a 2-dimensional case and it can be for a plane or planar surface for a 3-dimensional case. So, looking at the curvature for a curve, it can be generally defined the by the radius of the oscillating circle. So, for example, for this curve, this the curve that I have drawn by a solid line, at this particular point, the oscillating circle the radius of the osculating circle is the radius of curvature. And the curvature which we generally represent my kappa is 1 over radius of curvature. So, the curvature is inverse of radius of curvature if this radius is R then kappa is equal to 1 over R.

Now, osculating circle oscillating circle means the circle that can fit closes to the curve at the contact points. So, the radius of curvature will be different at this point and at this point because the radius of the osculating circle should be different at the each point ok. And the radius of curvature it can be positive it will be positive for convex surfaces, and it will be negative for concave surface.



Now, coming to the curves the curvature in mathematical form it can be defined as in this manner. So, for a curve which is represented by in terms of 2 variables, function of 2 variables say x and y 2 coordinates in 2 d x and y. So, f x y is equal to 0, if it represents a curve. Then the curvature is defined as del dot del f over norm of del f vector. So, this is the divergence of the gradient of f.

It is direction because this is the gradient of f, and it is divided by the norm. So, this is basically the direction vector for the gradient of f. it is divergence each one gives us the curvature. For an explicit function here we can write y is equal to f x, the curvature is defined as d 2 y by dx 2 divided by 1 plus dy by dx square raised to the power 3 by 2. And in many cases it can be approximated by d 2 y by dx 2 ok.

Ah when so, this will be possible when dy by dx is significantly less than 1 than we can do ok.



Now so, we have discussed the curvature for a curve. Now for a plane it becomes a more complicated concept. So, if you have a plane. And a vector normal to the plane, any plane that will have this normal vector will cut the plane. It will intersect this surface along a curve. And this can be there can be number of curves, or they can be number of planes that can contain this vector.

So, each such curve will have it is own vector or it is on it is own curvature. So, the mean curvature of a plane or a for of a surface is defined by the principle curvatures of this we had the principle curvatures are maximum and minimum curvatures; that means, the curves which are formed by the intersection of a plane that contains this vector. The curves which had maximum and minimum curvature containing this vector the sum of those is defined as the mean curvature. So, the principal curvature, and it so happens and these the principle curvatures are located in 2 perpendicular planes.

So, if for example, for a sphere, there are 2 main curvatures, and both of them are 1 over R, and another is also 1 over R. because all mean curvatures or all curvatures are same. So, that is equal to 2 over R is the curvature for a is sphere on the other hand for a cylindrical surface, the maximum radius of curvature and the minimum radius of curvature. So, in one case it will be in finite, and another case it will be R where R is the radius of the cylinder kappa is equal to 1 over infinity plus 1 over R. So, that is equal to 1 over R.



So, what we have learned, but about the curvature that how we can calculate the curvature for a curve and the curvature for a surface. So, Laplace law, it relates the pressure inside a bubble and or a droplet to the curvature. if you have done the excess pressure inside a bubble or droplet is generally given by delta p is equal to 2 sigma over R for a spherical bubble or droplet.

So, let us see how we can find out this expression. now consider a sphere or a spherical droplet, which has a radius R. and the pressure inside this droplet is p 0 outside pressure is p 1, and now we want to extend this spherical droplet by an infinitesimal amount so that the radius become R plus dr. and what we need to do is to calculate the work that is required for this extension from R to R plus d R.

So, in such a process, there are 2 different type of works that are being done. The one that will be equal to; let us say del W for expansion that will be equal to p dV work because there is a change in volume. So, dV and the pressure is p 1 minus p 0 because it is working against this pressure. So, p 1 minus p 0 dV that is the work for this expansion, and then the work due to surface change in surface area.So, that will be equal to sigma where sigma is surface tension into dA.



So, at the thermodynamic equilibrium, this total work is equal to 0; that means p 1 minus p 0 dV plus sigma dA is equal to 0. So, from this we get this expression that, p 0 minus p 1 is equal to sigma dA by dV.

Even though we have done this derivation with respect to a a spherical bubble, but this can also be done for any arbitrary shape of the interface. and dA for a spherical bubble will be for because a is 4 pi R square. So, dA is 8 pi R dR. and v is 4 by 3 pi R cube, and dV is equal to 4 by 3 pi into 3 R square dR. So, 3 3 becomes along that tv is equal to 4 pi R square dR. So that means, that axes pressure is equal to sigma dA is 8 pi R d R divided by 4 pi R square dR.

So, p 0 minus p 1 is equal to 2 sigma over R for a spherical droplet. and in general for a surface we can give sigma as equal to dA over dV. This you can say axe pressure, or the pressure difference or the normal stress jump, that is defined and the interface that delta p is equal to sigma in general it is given by sigma kappa and. So, the kappa edge the curvature was sigma over radius of curvature.

So, this law is known has Laplace law. And this tells us the normal stress jump or pressure jump across the interface for a bubble or a droplet. So, it depends on the curvature kappa.

(Refer Slide Time: 34:46)



So, until now we have been talking about the interface between 2 fluids. Now if we look at the 3 phase, there will be 3 phase contact between the fluid. So, you have a solid surface, and at the solid surface there can be a droplet sitting over it. Now this droplet may be sitting like this, or it may spread like a thin liquid film.

So, this is liquid film, now it depends that when these 2 different phenomena will occur. Sometimes the droplet might be sitting edge a semi is spherical or part of his spherical part of a sphere, or portion of a sphere. And other case it might be a planar liquid film. So, these 2 different situations when it wets it completely and makes a film then it is called complete wetting, wetting and then it is forming a droplet part of a phase sphere and it is called partial wetting. And this depends on that if it is a completely wetted surface or partially wetted surface, it will depend on the properties of the solid surface liquid as well as the gas surrounding it.



So, a liquid spreads if the energy of the system is lowered by the presence of the film. So, that means, that if a the surface energy per unit surface area, let us say for this is sigma this edge solid surface and there is a gas surrounding it. So, this is sigma S G.

Now if we have a liquid film, and it wets it then we have 2 different surface energies here. This is liquid, solid and gas at the top. So, here we will have sigma liquid and solid, plus sigma liquid and gas. So, if the presence of a liquid film lowers the surface energy then complete wetting will occur. So, let us write this. If the presence of a liquid film on the solid surface lowers the total surface energy of the system, complete or total wetting would occur. If that is not the case then only partial wetting will occur.

So, in case of partial wetting sigma SG is less than sigma SL plus sigma LG.

(Refer Slide Time: 39:50)



So, in case of partial wetting, the contact may be hydrophilic or hydrophobic. So, it is called hydrophilic, let us define contact angle first. Say we have a droplet and the angle between the solid surface and this and interface is called theta. And it can take another kind of shape where the angle is more than 90 degree. So, in this case theta is less than 90 degree, and in this case, theta is greater than 90 degree.

So, theta is less than 90 degree or theta is called contact angle. And if the contact angle is less than 90 degree, then it is considered to be a hydrophilic surface, and if it is more than 90 degree, and it is called hydrophobic for water the term hydro is used for any general liquid one can say lyophilic and lyophobic contact ok.

Consider a droplet on a so Use force balance to deter	lid surface mine the contact angle	
y Osy Do Usi	$\frac{\alpha_{s} - \text{direction} :-}{\sigma_{s_{g}} = \sigma_{s_{L}} + \sigma_{L_{g}} \cos \theta}$ $\boxed{C_{ob} \theta = \frac{\sigma_{s_{g}} - \sigma_{s_{L}}}{\sigma_{L_{g}}}}$	0 = Contact ang

Now, Young's law, which gives us the contact angle for the surface turns, and for different surfaces, let us consider a droplet which is placed on a solid surface and the contact angle at this surface is theta and if we defined the surface tension for different interfaces. So, for sigma liquid and gas this is sigma solid and liquid, this is sigma solid and gas. So, as we have seen that surface tension can be considered as force per unit length.

So, using the force balance if this is our, we can have a coordinate system, in the x direction along the surface, and y direction normal to it. So, force balance at in x direction if we balance the forces. then we can see that sigma SG force per unit length sigma S G will be equal to sigma SL, plus sigma LG cos theta, where theta is contact angle. So, if we rewrite it, we will get cos theta is equal to sigma SL over sigma LG.

So, this law is known as Young's law. And this gives us a relationship between the contact angle, and the 3 different surface tension values. So, in summary in today's lecture what we have covered is basics of surface tension. First we talk about what interface stage, and in or we can consider the interface to be surfaces of 0 thickness, and smooth surfaces which delimits or which separates the 2 fleets.

Now, we also discussed that because of the different or a asymmetry or dissymmetry in the molecular attraction set the interface because at one side the fluid, experiences the attraction from one kind of molecules, and on the other side of the interface it experiences attraction from different kind of molecules. So, there is a symmetry or there is surface energy generated. And this is accounted for in surface tension. And this surface tension, there are 2 different 2 2 laws that we have discussed one is Laplace law, or it is also called Young Laplace law. So, this gives us delta p is equal to sigma into kappa in general.

So, delta p is the axes pressure axes pressure means the pressure inside the liquid droplet or gas bubble, minus the place were surrounding it. That pressure difference or the normal a stress difference is sigma kappa; where kappa is the curvature and sigma is surface tension. The surface tension depends on temperature, and surfactant concentration.

So, with increase in temperature surface tension decreases and with increase in surfactant concentration also surface tension decreases and if there is a gradient in surface tension at the interface then we see a convection setting up at the interface, and this convection is known has Marangoni convection. Another law that we have discussed today is Young's law; which relates the surface tension between 3 different phases or surface tension for 3 different phases with the contact angle.