Microscale Transport Processes

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Lecture No. # 19
Electrowetting

We are going to have our first look at specific phenomena, which is gaining importance in everyday research that is electro wetting;and how this has led tonew branch of physics, which is known as digital micro fluidics.Now,the concept is electro wetting was known to us for more than hundred years, but the use of electro wetting in order to specifically move a drop of liquid from one point to another in a precisely controlled path has led to the new branch of engineering, which manipulates fluid motion,and that is digital micro fluidics.

So, we are going to have our first look on the basics of electro wetting,its potential uses the equations that govern the electro wetting process, the physics behind it, and how this electro wetting can be applied in a variety of fields to move liquid from one point to another. Now, whenever there isa need for precisemovement precise movement of very small quantities of liquids, and those liquids could be discrete drops as well. The question comes is what would be the method?How do we move a liquid droplet from one point to another?Theusual methods and machines that we knowwill obviously beof no use to move such a small quantity of let us say discrete drops.

So, one has to think of alternative ways by which the drop can be made to move.One way ofhandling situations likethis could be to alter the surface of the solid surface on which the drop is resting. Whenever the nature of the solid substrate is altered, it is going to give rise toa different surface energy of the system, and this difference in surface energy of the solid substrate in contact with the liquid can give rise to forces, which are commonly known as surface tension forces.

Normally,what we see that the surface tension forces,they are not relevant mostly in micro scalesystems, but as the system dimensions grows smaller and smaller, the effect of body and other forces would progressively diminish, and the surface forces wouldtake over, and they could be the major force available, major force applicable when the system dimension becomesmillimeter level,and even more prominent when it becomes at the micron level.

So, the basic problem boils down to how do we change the surface energy of a surface, and if you can change the surface energy of the surface would that lead to a motion in the droplet. So, we need to apply certain external forces may be or certain operations need to be done on the solid surface to change its surface energy. Soinitially, in the first part of this lecture on electro wetting, we would constituteon the ways to change the surface energy and there by the surface tension of the system.

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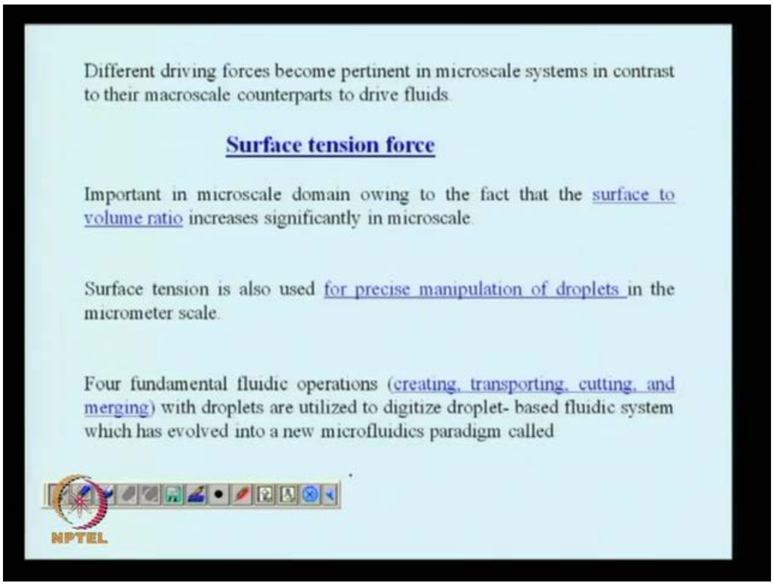

Different driving forces become pertinent in microscale systems in contrast to their macroscale counterparts to drive fluids.

Surface tension force

Important in microscale domain owing to the fact that the surface to volume ratio increases significantly in microscale.

Surface tension is also used for precise manipulation of droplets in the micrometer scale.

Four fundamental fluidic operations (creating, transporting, cutting, and merging) with droplets are utilized to digitize droplet- based fluidic system which has evolved into a new microfluidics paradigm called

So, as I mentioned that,the driving forces become different when we go into the micro scale system, and compare to macro scale, the surface tension becomes starts to dominate as the surface to volumeratio increases and in the micro scale.So, can we use surface tension for the precise manipulation of droplet in the micrometer scale? So, thisis the fundamental question or the fundamental process, which then has led to four distinctly different fluidic operations. Can we use surface tension as a force to create a droplet or to transport a droplet from one point to another? Can we cut a droplet into a number of smaller droplets, and can be merge two droplets together to form a relatively bigger droplet? Because these are going to be fundamental operations tofundamental operation which would be necessary, which would convert the droplet based fluidic systems to digitize them in such a way and this has given rise to a new micro fluidicsparadigm;that is commonlyknown as digital microfluidics.Soin this class,we willgive we willsee what digital micro fluidics is all about and the forces, the science and the engineering applications of digital micro fluidics.

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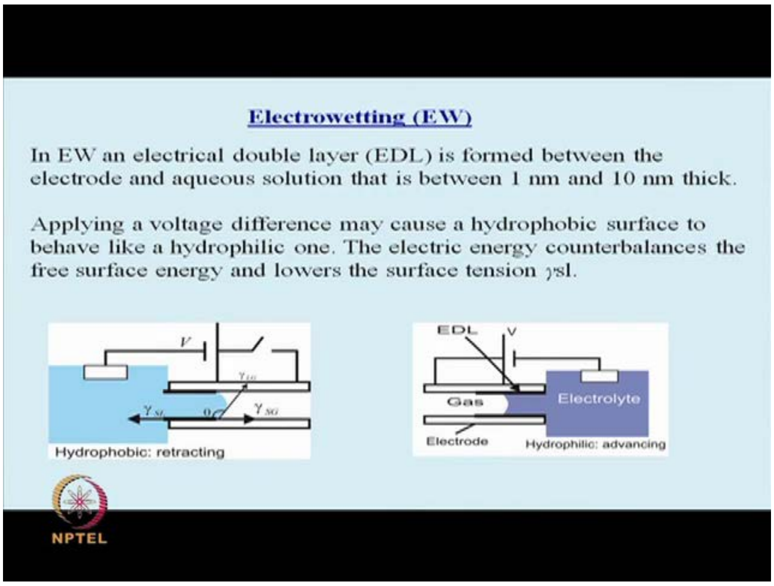

Electrowetting (EW)

In EW an electrical double layer (EDL) is formed between the electrode and aqueous solution that is between 1 nm and 10 nm thick.

Applying a voltage difference may cause a hydrophobic surface to behave like a hydrophilic one. The electric energy counterbalances the free surface energy and lowers the surface tension γsl.

So, this has gone given a rise to the firstthe first thing is, can we can we change the surface energy?Now towards the middle of this lecture, Iwill give you some examples of changing the surface energy of a surface by external means, whicharemay not be reversible,which are difficult to maintain.So, the need to have something which is quote unquote switchable is extremely important. Can we think of a system, in which the nature of the surface changes very quickly to something drastically different; for example, from hydrophobic can we make the surface hydrophilic, and then when that external effect is taken out of the system, it immediately goes back to its previous stepstage state which is hydrophobic.

So, electric field has been shown to alter the surface energy in such a way that, this hydrophobic hydrophilic interaction or interchange is easy to accomplish.The first example of this electric double, the first example of electric field enhanced wettingpresent that can be encountered in a droplet was given by the scientist Lippmann around 1875. This example that I am showing here, the figure that I am showing here is;let ussay this is a liquid which forms a finite contact angle a large contact angle with the solid which is a conductor.

So, this is a conductor and we have an electrolyte in contact in contact with the conductorand as finite large contact angle is formed in between the solid-liquid interface. And then, a potential difference is applied in between the electrode and the electrolyte and when that happens, the electric double layer is formed in which, the charges opposite charges are going to accumulate at the solid side of this solid-liquid interface and on the liquid side.

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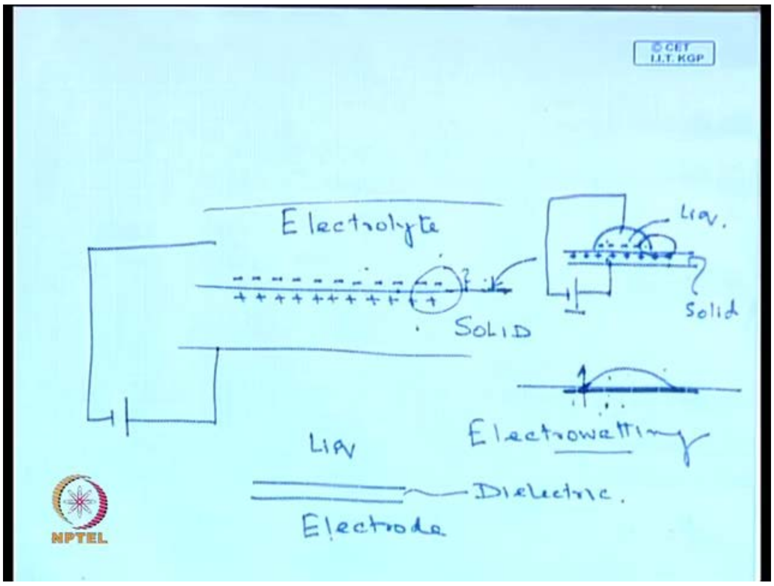

So, if weif we can think the electric double layer can be thought of;let us say this is a solid; this iswhich is the way and we would like to see, how the electric double layer is going to be formed, and this is in contact with a battery and here I have one electrolyte. So, when the circuit is on what weare going to see is that,positive charges are going to accumulate on the solid side of the interface and the negative charges from the electrolyte will form a layer in the electrolyte.

So, this formation of oppositely charges near the solid-liquid interface on application of an electric field is the thickness of this; this is known as the double layer. So, wewould say, there is double layer has formed inside the electroweight electrolyte on very close to the solid liquid interface, and when that happens this accumulation of charges, since it is it is a spontaneous process.It is going to lower the energy of this surface. As the surface energy is lowered, the solid-liquid surface energy is lowered; this will give rise tospreading of the electrolyte on the solid.

So, this phenomena or this concept has been utilized for electro wetting. So, if Ihave a droplet which is sitting on a solid and then, I have an electric field being applied between the between the liquid of the droplet and this being the conductor sowhat would happen is that, the charges are going to form near the interface inside the droplet, and positive charges are going to accumulate on the solid side of the interface. As a result, the surface energy will change and the droplet will spread.

So, this spreading of the dropletliquid present in the droplet on application of an electro electric field is known as electro wetting,which was first observed by the scientistLippmannsomewhere around 1800,1870s or so.So, can we can wenow this is this was known for quite some time, but can we use this for some practicalapplications; that is something which we would like to see. But,if you if you see thisentire process we would see that there is a limitation because, if the potential difference between the solid the electrode and the electrolyte is slightly large. Whenif it is only, if it is very small then, this electro wettingphenomena can be observed, but if you would like to increase the voltage then, this process will breakdown since a current would flow in between from the electrodefrom the electrode to the electrolyte.

So, only few tens ofvoltscan be applied in between the electrolyte and the electrode without passing a current in between them. So, howdo we…So, this limit severely limits the applicability of electro wetting in terms ofin terms of changes in contact angle in terms of appreciable changes in contact angle. So, we can only change the contact angle by a small amount because, any increase in voltage would lead to a current flowing in between the solid and the electrolyte there by rendering the entire electro wettingelectro wettingprocess inoperable.

So, in order to circumvent this specific problem, the concept has come later on is,if we could introduce a dielectric layer in between the electrode and the droplet then, the question of having a current passing through in between the solid and the electrolyteat slightly higher voltages can be eliminated. So, that is the concept which has been shown hereand which is commonly known as the electro wetting on dielectric. Soin electro wettingon dielectric, a dielectric layer is placed in between is placed in between the electrodeandthe liquid.

So, the liquid would be here which is not in contact with the electrode any more, but a dielectric will be layer will be introduced in between the two. So now, I can have appreciably sufficiently higher voltages that can be applied in between the electrode and the liquid. So, electric field is large and as the electric field is large, significant changes in contact angle would be possible, and this is what is shownin this figure,which is taken from publicationby Lee in 2002, which has appeared in sense in the journal sensors and actuators.

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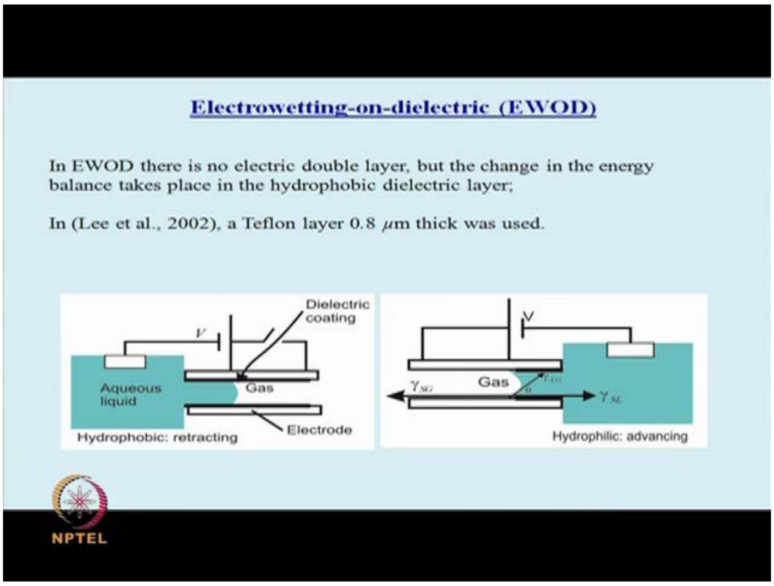

Electrowetting-on-dielectric (EWOD)

In EWOD there is no electric double layer, but the change in the energy balance takes place in the hydrophobic dielectric layer;

In (Lee et al., 2002), a Teflon layer 0.8 μm thick was used.

Here now, I have the solid covered with a dielectric coating. In… it is in contactin contact with an aqueous liquid. So, when this circuit is closed that is not going to be found any electric double layer, but the change in energychange in energy takes place in the hydrophobic dielectric layer. So, the nature of this dielectric layer has to be hydrophobic and since it is an ananan… since it is hydrophobic,the liquid is going to form a convex meniscus over here.Now,when you apply sufficiently high electric field in between this and the liquid then, the dielectric layer acts as an insulator, but sothere is goingnot going to be formation of any electric double layer, but the change in energy surface energy of the dielectric will cause a change in contact angle.

So, we can see that almost from an almost completely non wetting system, it has become partially wetting system with distinct change in the curvature. So, the thethe iflet us say, this is mercury and mercury then, we could see that the convex meniscus has been depressed and it has become a concave meniscus. So, this depression and change in shape of the liquid mercury meniscus can be monitored as a function of applied voltage and you would see that it is going to follow a certain law, certain role which we will see subsequently. But here, you can see that a hydrophobic surface giving rise to a retracting meniscus can be changed to an hydrophilic substance giving rise to an advancing meniscus by simple application of an externally applied electric field, which has anumber of advantages that I will list subsequently.

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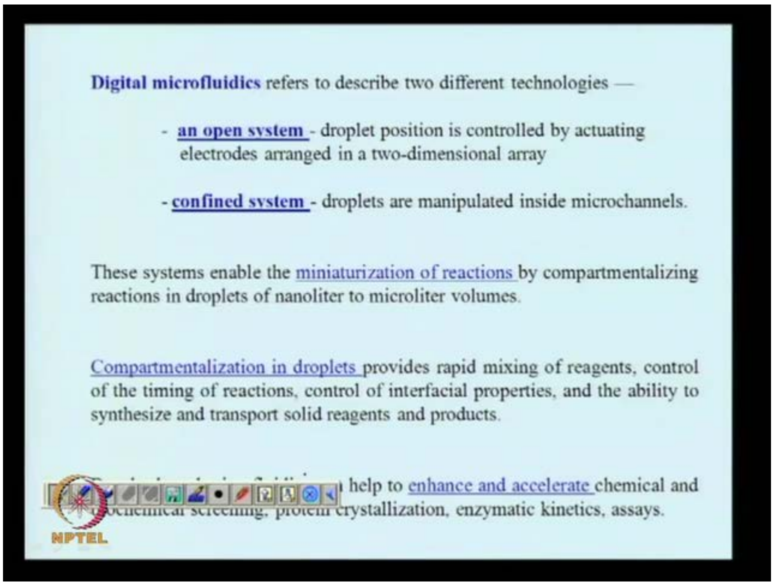

Digital microfluidics refers to describe two different technologies —

- an open system - droplet position is controlled by actuating electrodes arranged in a two-dimensional array
- confined system - droplets are manipulated inside microchannels.

These systems enable the miniaturization of reactions by compartmentalizing reactions in droplets of nanoliter to microliter volumes.

Compartmentalization in droplets provides rapid mixing of reagents, control of the timing of reactions, control of interfacial properties, and the ability to synthesize and transport solid reagents and products.

[illegible] help to enhance and accelerate chemical and [illegible] crystallization, enzymatic kinetics, assays.

Now,a digitalmicro fluidics system can be can be of two different can be a fundamentally two different technologies. One is an open system and the other is in confined system.

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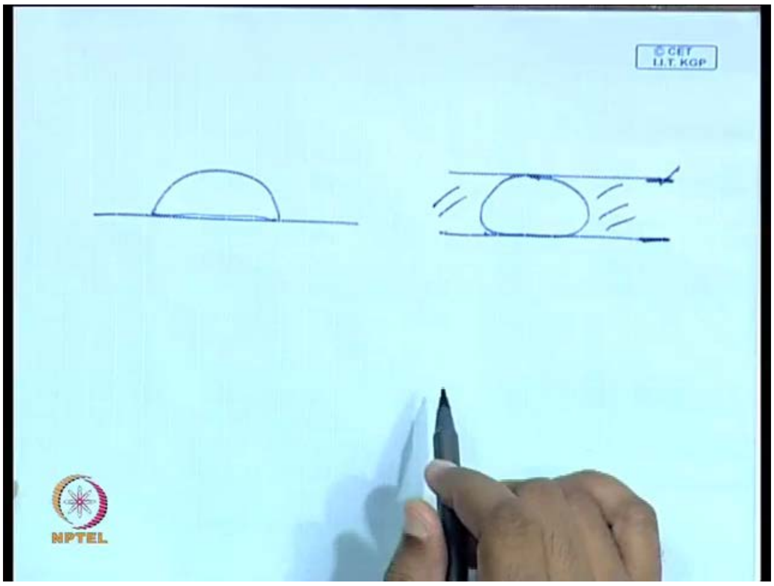

So, when we are dealing with just a drop on a surfaceand this is an example of an open system whereas, if I have a plug of liquid in another medium,and these this is the electrode and this being the dielectric then,it is an example of a closed system. So, in digital micro fluidicsor in the electro wetting, we would see applications of both an open system or an closed system and with fundamental advantages.So, let us try to see, what are the advantages of digital micro fluidics? Now,you…Let us say,youhave a reaction which is taking place insidea droplet. Since the size of the droplet is extremely small, the resistances to mass transfer that diffusion length, the diffusional resistances to mass transfer would be minimized to a large extent inside a droplet.

So, if you have a reactant droplet;reactant one droplet and reactant two droplet, we could bring them close together; you could merge them and you can form a larger droplet. Inside the larger droplet still it is very small in size if it is of micro literdimensions, the resistance to mass transfer would be sosmall that the kinetics of the reaction can be madecan be made faster.So, any reaction which is mass transfer limited would be ideally suited for operation inside a micro droplet,and you couldyou could you could design your system in such a way, that you start with a large droplet.That large droplet could be split into a number of smaller droplets using a specific micro fluidics operation. Then, each of these smaller droplets can be made to move in a path separate from each other.

Now, on the path sits something which is going to react with the droplet which is coming in that path, and when that reaction take takes place suppose, you can monitor the reaction from outside then, a specific let us say chemical present in the micro droplet can be can be monitored or its concentration can be measured. So, in this way depending on how many droplets you are you are dealing with, how many droplets you have broken the initial droplet,you could have several chemicals which can be characterizedwith by reacting them with different chemicals, different reagents.

So, this hasvery important application in many diagnostic devices or lab on a chip diagnostic devices, where one drop of blood could be could be could be split into a large a would be into a significant number of micro droplets, and any specificchemical of interest can be measured into that micro droplet by making it react with some known reagent. So, one droplet could be used for blood sugarmonitoring; the other could be for blood urea monitoring and soon. Sothe compartmentalization of reactions in small droplets giving rise to larger rate is one big advantage of this entire process.

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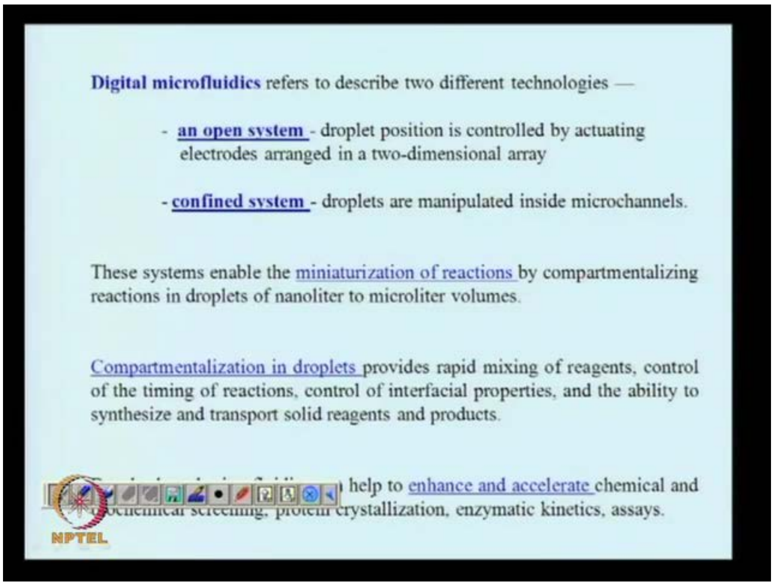

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[illegible] help to enhance and accelerate chemical and [illegible]ochemical screening, protein crystallization, enzymatic kinetics, assays.

So, what you can see thatthis in term would wouldwouldwouldreduce the amount of reagent necessary for such an operation in the this kind of a; this kind of process can also enhance and accelerate chemical and biochemical screening processes, crystallization of certainproteins, the kinetics of enzymes andso on. So, this definitely has significant application.

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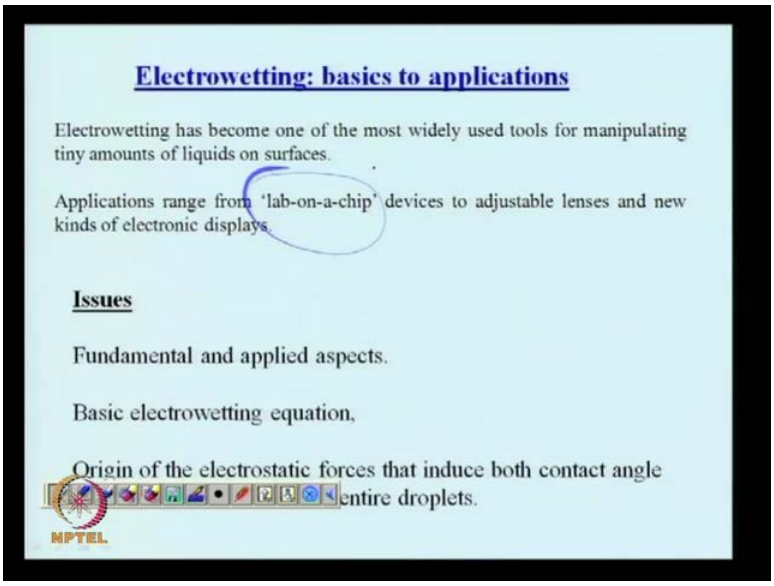

Electrowetting: basics to applications

Electrowetting has become one of the most widely used tools for manipulating tiny amounts of liquids on surfaces.

Applications range from 'lab-on-a-chip' devices to adjustable lenses and new kinds of electronic displays.

Issues

Fundamental and applied aspects.

Basic electrowetting equation,

Origin of the electrostatic forces that induce both contact angle

entire droplets.

And when we think of applying these concept of electro wetting to specific applications for example, lab-on-a-chip,we need to take care of or we need to address certain issues; like, what are the fundamental and applied aspects of electro wetting? What kind of basic equation governing equationcan be used, can be developed for electro wetting?So, what are the origin of electrostatic process that can change that can that canchange contact angle or that can induce bothcontact angle and motion for the entire droplet.

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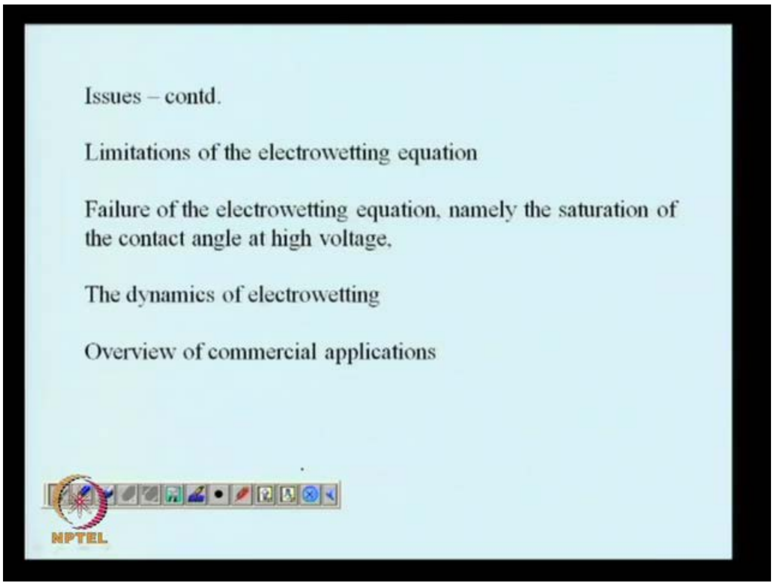

Issues – contd.

Limitations of the electrowetting equation

Failure of the electrowetting equation, namely the saturation of the contact angle at high voltage.

The dynamics of electrowetting

Overview of commercial applications

Is thereany limitation of this electro wetting equation? Soin other words, we would like to address, we would like to identify the failure of the electro wettingequation which is known as saturation of the contact angle at high voltages. Apparently, it seems that as voltage increases as the applied field is increasing, the contact angle will become smaller and smaller, but is there any limit to it? We would see that beyond a certain voltage, the contact angle becomes independent of the applied voltage.

Sono matter even if you increase the voltage beyond that point beyond that value,the contact angle will not decrease anymore. So, your ability to induce a change in contact angle would not follow the basic governing equation or ouror our idea that, by increasing the valueof the contact, value of the applied voltage, we could reduce the contact angleto any value that we desire. In other words, it is it isshown experimentally that you can never make a partially wetting system or a non wetting system convert to a completely wetting system.

So, you would never be able to achieve zero contact angle. So, this saturation of contact angle correspondingwith respect to the applied voltage is one limitation that we have to keep in mind. And then, we have to also think about,what is the dynamics of electro wetting?How do we make a droplet move from one point to another? What are the factors that are going to govern the process? The speed of the process, the response of the electro wetting phenomena as the droplet size is changed, thevelocity with which the droplet would move.

So, what are thedesign parameters that we can change to make the droplet move with a constant velocity with some velocity that we would like to have. And then finally, I would give an overview of the many exciting commercial applications, upcoming commercial applications of the electro wetting concept. So, I would I wouldconcentrate mostly on electro wetting on dielectrics which is which in the short form is commonly known as EWOD.So, we will see…We willwe willgo into the depth of the EWOD in this class and in the next class as well.

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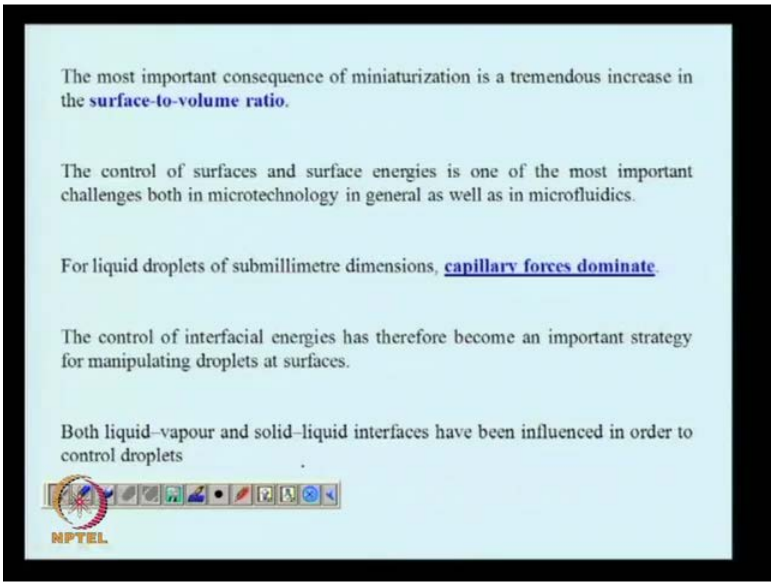

The most important consequence of miniaturization is a tremendous increase in the **surface-to-volume ratio**.

The control of surfaces and surface energies is one of the most important challenges both in microtechnology in general as well as in microfluidics.

For liquid droplets of submillimetre dimensions, **capillary forces dominate**.

The control of interfacial energies has therefore become an important strategy for manipulating droplets at surfaces.

Both liquid–vapour and solid–liquid interfaces have been influenced in order to control droplets

We all know that the important consequence of miniaturization is the increase rapid increase in the ratio of surface to volume ratio. Now, one of the major focus of researchfor a very long time is, how do wecontrol surface energy and the surface forces. When a system size becomes smaller we know that the capillary forces would dominate so,which is the function of this surface tension. So, how do we change the surface tension? So, before the concept of electro wetting was utilized to change the surface energy.

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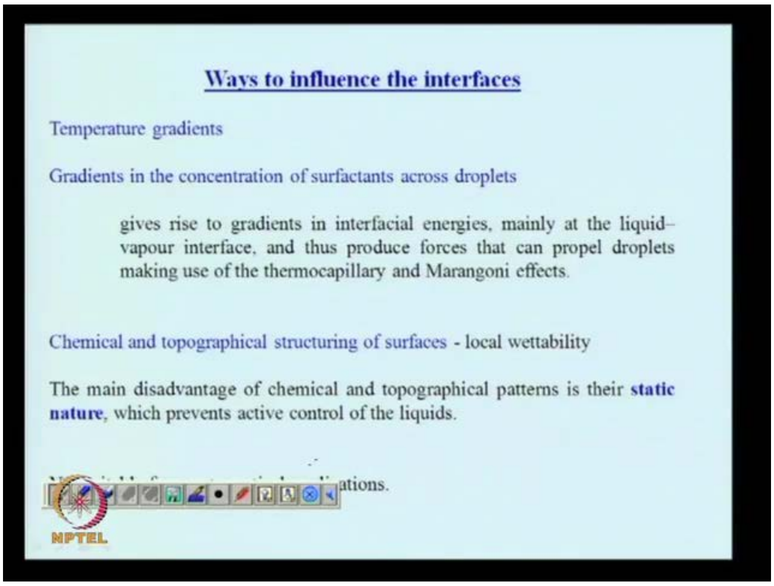

Ways to influence the interfaces

Temperature gradients

Gradients in the concentration of surfactants across droplets

gives rise to gradients in interfacial energies, mainly at the liquid–vapour interface, and thus produce forces that can propel droplets making use of the thermocapillary and Marangoni effects.

Chemical and topographical structuring of surfaces - local wettability

The main disadvantage of chemical and topographical patterns is their **static nature**, which prevents active control of the liquids.

ations.

So, there are there are several items to change the surface tension. So, ways to influence the interfaces, one can use a temperature gradient to make a change in the surface energy. What has beenwhat we know is that surface tension is astrong function of temperature.So, if we can have a difference in temperature in between two points on the surface then, the surface tension values at these two points would be different. Now, we are therefore, creating a surface tension gradient on the surface. Sojust like pressure gradient that is imposed from outside here through a temperature gradient, we are imposing a surface tension gradient that can be used to make liquid flow to make a fluid flow from one point to another.

So, this temperature dependent motion of liquid which is which isdue to surface tension gradient is known as Maranongoni flow. Now, this Maranongoni flow can be affected by surface tension gradient by the imposition of a temperature gradient or by the imposition of concentration gradient as well. So, if we can have a solution containing a solute and if the solute concentration at two points are different, then what would happen is,this would create a surface tension gradient and then this would give rise to flow.

So, we can have Marangoniflow a surface tension gradient driven flow caused by either a temperaturegradient ora concentration gradient. So, this has been shown to become important when the system size becomes smaller as the surface forces start to start to predominate over all other forces. Now, the this this thishas been there has been some effort in order toin order to use this for movement of fluid, but there are certain problems associated with it.In order for a droplet to move on account of induced temperature gradient, the value of induced temperature gradient has to be very large.

So,which is impractical in most of the cases to be used for practical applications;you need several tens of or may be hundreds of degree centigrade per millimeter in order to cause a liquid droplet to move on account of surface tension gradient. Similarly, how do youhow do youpractically create a concentration gradient over such a over a very small distance. So, this has given rise to secondary flows which people have encountered, but these cannot be the primary ways to move liquid.

Now, there has also been efforts to make atopographical structuring of the surface or chemical model chemical modification of this surface which would give rise to local wet ability gradient. So, there has been report in which,you can have alterative, you can have a you can have a gradient of wet abilitywhich is which is thrust upon the surface. You could create a wet ability gradient on a surface by chemical means by the deposition of certain chemicals on a silicon wafer for example, there is a specific chemical which when depositedby a vapor deposition process on the silicon wafersilicon substrate, it would give rise to wet ability gradient, and he could show, it has been shown that a droplet will movein the direction of enhanced hydrophilicityeven against gravity. In other words, if you have an inclined surface and if you put a drop of liquid on the higher hydrophobic side of this substrate then, that droplet will move against gravity along the substrate.

So, which is which is very obviousbecause, the gravity effect of gravity becomes unimportant as the system size becomes smaller. So, the gravity is no longer important. So, even if the substrate is at an angle inclined the droplet due to the hydrophobicity gradient, it will move from the hydrophobic to the hydrophilic side which is which is which is extremelyinterestingto see.It defies the logic and you would see a droplet moving along the inclined moving up the inclined.

Now, that there are certain disadvantages of these chemical and topographical patterns is that they are static in nature. Once you modify the chemical surface chemical nature of the surface,it is going to remain that way. See, there is no way by which you can switch it on and off. So, they are static in nature and therefore, it cannot effectively control or effectively use the same surface we for a different application.Once you make the surface, the surface will remain the way throughout the operation and there are obviously, fabrication of such surfaces will be more complex and mostly this would give rise to secondary flows and not primary flows.

So, people are… We are stilllooking for a switchable method of changing the nature of this surface which is reproducible, which is easy to make and which would give rise to sufficient force for the effective movement of droplets, and this has given a rise to the concept of or to the application of electric field to change the nature of the surface.

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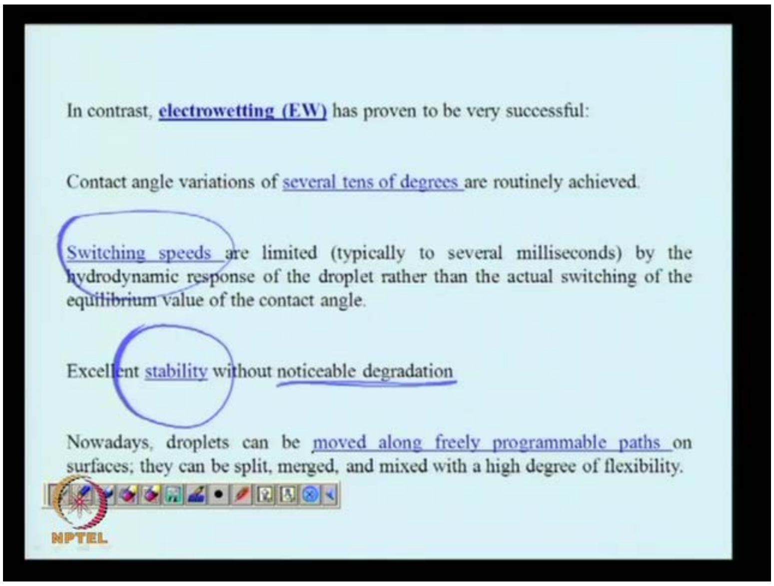

In contrast, **electrowetting (EW)** has proven to be very successful:

Contact angle variations of several tens of degrees are routinely achieved.

Switching speeds are limited (typically to several milliseconds) by the hydrodynamic response of the droplet rather than the actual switching of the equilibrium value of the contact angle.

Excellent stability without noticeable degradation

Nowadays, droplets can be moved along freely programmable paths on surfaces; they can be split, merged, and mixed with a high degree of flexibility.

Now sotherefore, electro wetting has a proven to be extremely successful. You can change contact angles by tens of degrees 20, 30, 50 degree. Change in contact angle is also possible and switching speeds are areare much more than compared to the other cases. Mostly the switching speed is going to be governed or controlled or limited by the hydrodynamics of the droplet. How would the droplet respond to the application of electric field? How fast would be the response?And the response would depend onmostly on the viscous forces;may not be on the inertia, but it is a viscous force which is going to dominate what would be the frequency with which what would be the response frequency of a droplet with change in potential difference across the across the surface, but still the switching speed is much more than that of the other processes we have described so far. And this is extremely important for commercial application, the stability of the surface without any noticeable degradation.

So, as long as we have a very stable surface which is reproducible and when you do not see much degradation over repeated use that, we with a with a with a reasonable switching speed. So, this essentially tells us that,electro wetting will definitely be the method of choice for such operations.And,we see nowadays that droplets are moved freely along the programmable path. So, you are going to have a large number of electrodes in inin a probably in an arraylike this, where on the surface you have several electrodes and depending on,

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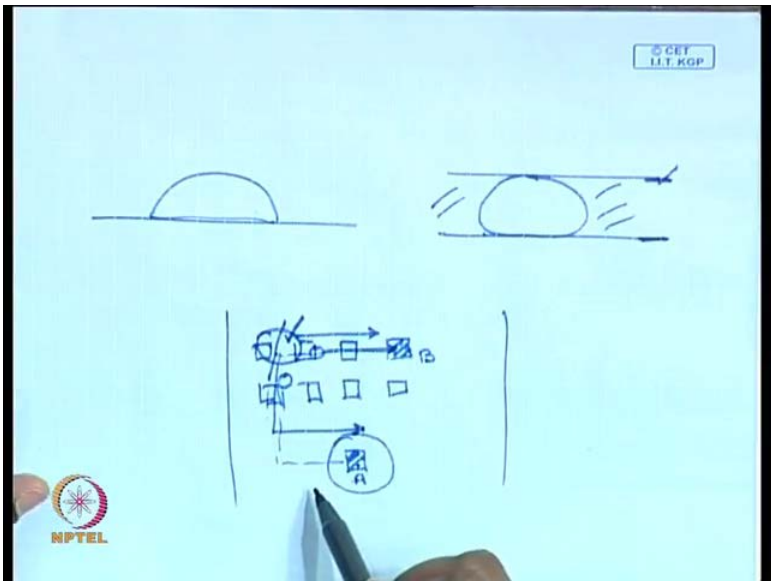

how you switch these off and on?A droplet sitting over here can be made to move either in direction or it can take any path it wants. I mean, you can program the switching on and off these electrodes and thereby, make the droplet move on any prescribed path.Therefore thereby, creating enough flexibility in the entire design of the process such that it can be split and one droplet will move in this direction, and the other droplet will move in another direction.

So, you can have reagents part on one of the electrodes over here, and another electrode over hereand you can monitor the some property. It could be fluorescence;some property of the droplet when droplet when it reacts with the reagent present in this electrode, and present in the other electrode. Thereby, you could monitor may be the concentration of two species present in this droplet. So, the programmability the easy programmability of the entire matrix, electrode matrix, two dimensional electromatrix is enough flexibility of the system which has which has lot of potential for their subsequentcommercial use.

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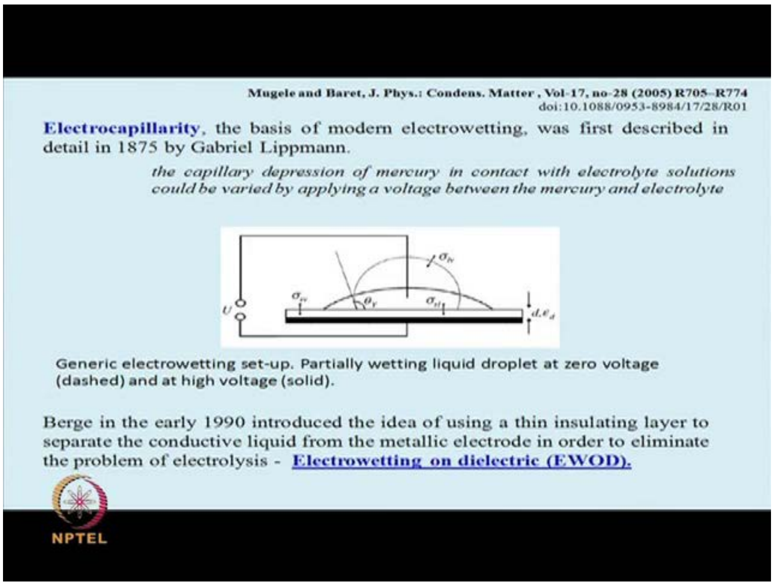

Mugele and Baret, J. Phys.: Condens. Matter , Vol-17, no-28 (2005) R705–R774
doi:10.1088/0953-8984/17/28/R01

Electrocapillarity, the basis of modern electrowetting, was first described in detail in 1875 by Gabriel Lippmann.

the capillary depression of mercury in contact with electrolyte solutions could be varied by applying a voltage between the mercury and electrolyte

Generic electrowetting set-up. Partially wetting liquid droplet at zero voltage (dashed) and at high voltage (solid).

Berge in the early 1990 introduced the idea of using a thin insulating layer to separate the conductive liquid from the metallic electrode in order to eliminate the problem of electrolysis - **Electrowetting on dielectric (EWOD).**

Now, this is classicalsetup figure of a setup wherein 1875Lippmann hasshown that there is sufficient or considerable depression of mercury whenit in contact with an electrolyte solution,and you can you can vary that depression of mercury meniscus by applying a voltage between the mercury and the electrolyte. But,as I said it is limited by the application of a very small amount of very small quantity of voltages.

Soin the early 1990s,Bergehas introduced the idea that a thin insulating layer can be placed in between the conductive liquid and the metallic electrode to eliminate the thethe requirement of a very low voltage to eliminate the possibility of a electrolysis, and this is given rise to electro wetting, the new concept electro wetting on dielectric or in simply EWOD.

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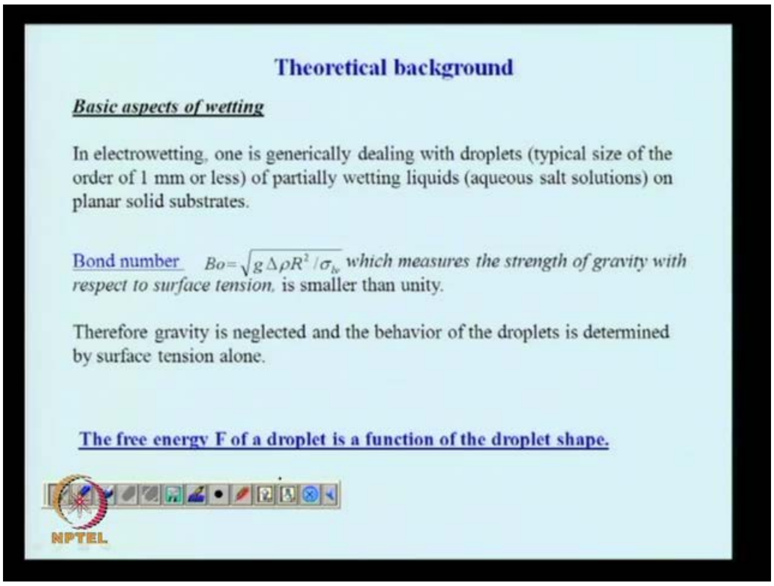

Theoretical background

Basic aspects of wetting

In electrowetting, one is generically dealing with droplets (typical size of the order of 1 mm or less) of partially wetting liquids (aqueous salt solutions) on planar solid substrates.

Bond number $Bo=\sqrt{g\Delta\rho R^2/\sigma_{lv}}$ *which measures the strength of gravity with respect to surface tension,* is smaller than unity.

Therefore gravity is neglected and the behavior of the droplets is determined by surface tension alone.

The free energy F of a droplet is a function of the droplet shape.

So, if you look at the basic aspects of electro wetting,one is we are dealing with droplets the sizes are about a millimeter or it would be less, and they are going to be of partially wetting liquids onsolid substrates. The solid substrates substrate could be a silicon wafer, and the entire process is going to be governed by the bond number which is defined as g, the acceleration due to gravity, the change in density,the difference in density,the radius of the theradius of the droplet and sigma lv is a surface tension.

So, the bond number essentially gives us the relative strength of gravity with respect to surface tension. So, since the effectfor these electro wetting,the effect of surface tension because of the size of the system over shadows the effect of gravity, and the bond numberbond number is smaller than unity. Sosince, the bond number… If the bond number is less than unity then, the effect of gravity can be neglected, and the behavior of the droplet is determined by surface tension alone. So now, we would like to take a look at the different forces which arepresent in a droplet and what would be the governing equation for free energy for energy of a droplet, when it is at equilibrium.

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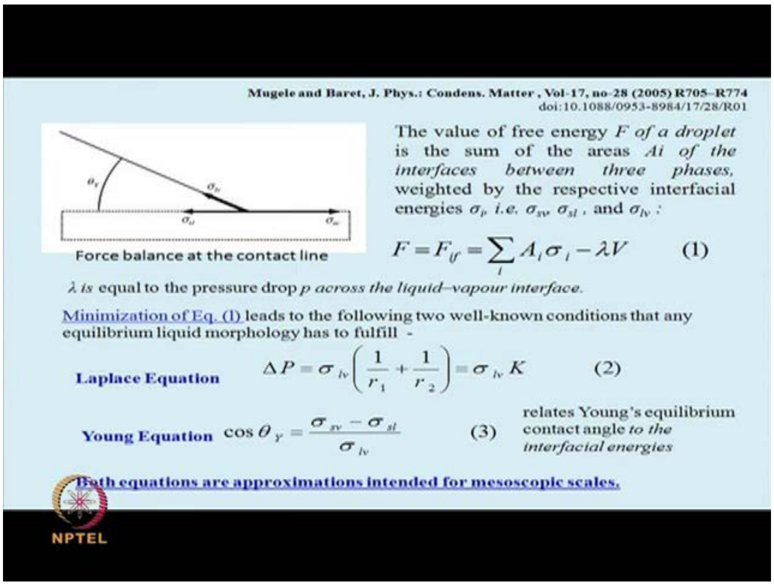

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Force balance at the contact line

The value of free energy *F of a droplet* is the sum of the areas *Ai of the interfaces between three phases,* weighted by the respective interfacial energies σ_i, *i.e.* σ_{sv}, σ_{sl} , and σ_{lv} :

$$F = F_{lf} = \sum_i A_i \sigma_i - \lambda V \qquad (1)$$

λ *is* equal to the pressure drop *p across the liquid–vapour interface.*

Minimization of Eq. (1) leads to the following two well-known conditions that any equilibrium liquid morphology has to fulfill -

Laplace Equation

$$\Delta P = \sigma_{lv}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) = \sigma_{lv} K \qquad (2)$$

Young Equation

$$\cos\theta_Y = \frac{\sigma_{sv} - \sigma_{sl}}{\sigma_{lv}} \qquad (3)$$

relates Young's equilibrium contact angle *to the interfacial energies*

Both equations are approximations intended for mesoscopic scales.

So, the free energy of the droplet is a function is a function of the different interfacial energies of the solid-liquid interface of the solid-vapor interface and the liquid-vapor interface. So, if this is the contact angle, then we know that at atatsteady state, the sum of the free energy of a droplet is going to be the sum of the areas of the interfaces wetted by the respective interfacial energies for example, sigma sv solid-vaporsolid-vapor, solid-liquid and the liquidvapor; soat state thatthe equation that governs the free energy is this, where lambda is equal to the pressure drop across the liquid-vapor interface.

So, if you minimize this equation, this would lead to two very well known equations, well known conditions that the equilibrium morphology of the droplet must fulfill. One is the very famous Laplace equation, which tells us the pressure jump at the across the liquid-vapor interface. So, delta P lv is going to be equal to sigma lv that is the surface tension, liquid-vapor surface tension and K, where K is the curvature of the drop.So, the curvature of the drop is nothing but inverse of these radii of curvatures.And the second equation is young equation which gives us the value of the equilibrium contact angle as a function of the solid-vapor surface tension, the solid-liquid and the liquid-vapor surface tension. Now, one mustemphasize at this point is that both of these equationsor approximations and they are valid only when, the sizes are in macroscopic scale. When the systems size becomes smaller and smaller,this type of equations may not be valid.

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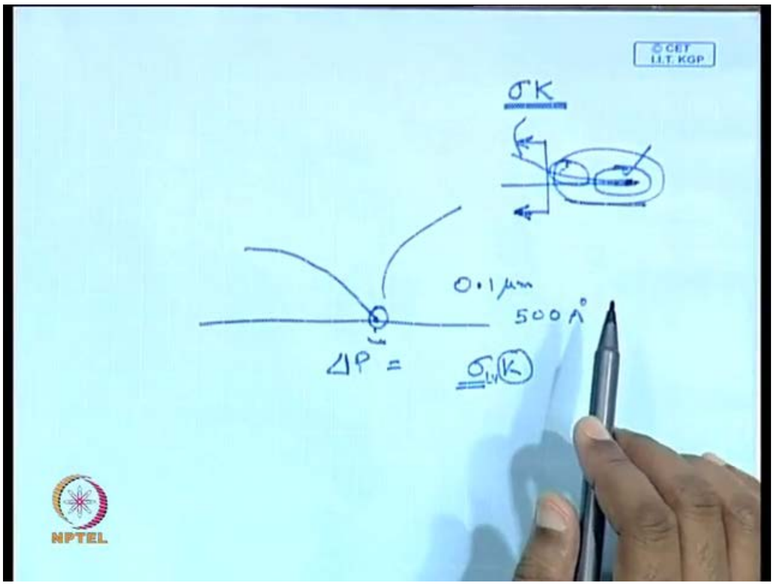

For example, if we if we think of when a liquid meets a solid as the thickness becomes smaller and smaller.Let us say, when the size is less than 0.1 micron or more specifically, when it is of the order of 500 angstrom near the point where the liquid is in close proximity with the solid, additional forces apart from this apart from this sigma K that is delta P is equal to sigma K. This is a surface tension liquid-vapor surface tension and K is the curvature. But beyond this, when the size of the film really becomes very small, additional forcessuch as intermolecular forces of attraction starts to become important in this range. So, if I can… If I magnify this area, we would see for a partially wetting system,it is going to be like this.

So, there would be an adsorbed flat film ahead of the meniscus and a transition region. Soin this region, the intermolecular force would be important. In this region, both intermolecular and surface forces would be important and in this row range is going to be controlled totally by surface forces denoted by sigma K. So, the equations thetwo equations that we have seen sofarwe have seen, the Young’s equation and Laplace equation are valid for the macroscopic scale. We must understand we must understand, we must underline the fact is that these two equations will require presence of additional terms when we aredealing a really thin microscopic label, microscopic contact angles or the contact line in these cases.

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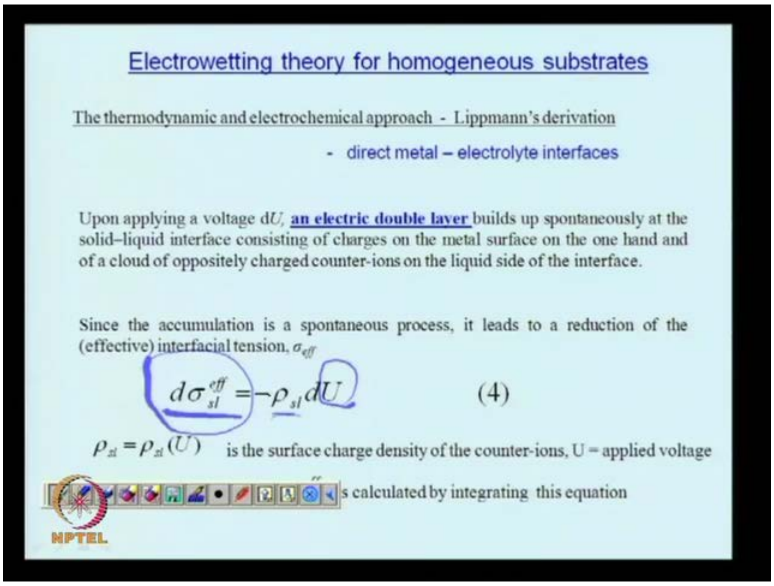

Electrowetting theory for homogeneous substrates

The thermodynamic and electrochemical approach - Lippmann's derivation

- direct metal – electrolyte interfaces

Upon applying a voltage d*U*, **an electric double layer** builds up spontaneously at the solid–liquid interface consisting of charges on the metal surface on the one hand and of a cloud of oppositely charged counter-ions on the liquid side of the interface.

Since the accumulation is a spontaneous process, it leads to a reduction of the (effective) interfacial tension, σ_{eff}

$$d\sigma_{sl}^{eff} = -\rho_{sl} dU \qquad (4)$$

$\rho_{sl} = \rho_{sl}(U)$ is the surface charge density of the counter-ions, U = applied voltage

s calculated by integrating this equation

So, wewe with withthis limitation in mind, now we move tonow our next part which is,how do we how do we express the or what is the electro wetting theory for homogeneous substrates, and we are…we have two different approaches; one is this homodynamic approach and the other is electrochemical approach. And, it is basically between a metal electrolyte interface and when we apply any voltage as we have, as I have mentioned double layer is going to build up spontaneously at these solid-liquid interface. And, it consists of let us say positive charges on the solid side, and negative charges on the liquid side.

Sothis presence of double layer, the formation of double layer is a spontaneous process. Since,it is a spontaneous process;this spontaneous process must give rise to a change, a decrease in the Gibbs free energy of the system. So, the change inchange in free energy is going to manifest itself by a change in the effective interfacial tension which is connected with the surface charge density and U is the applied voltage. So, the change in surface tension, interfacial tension is going to be a function of the applied voltage, and it is also going to depend on this surface charge density of the counter ions.

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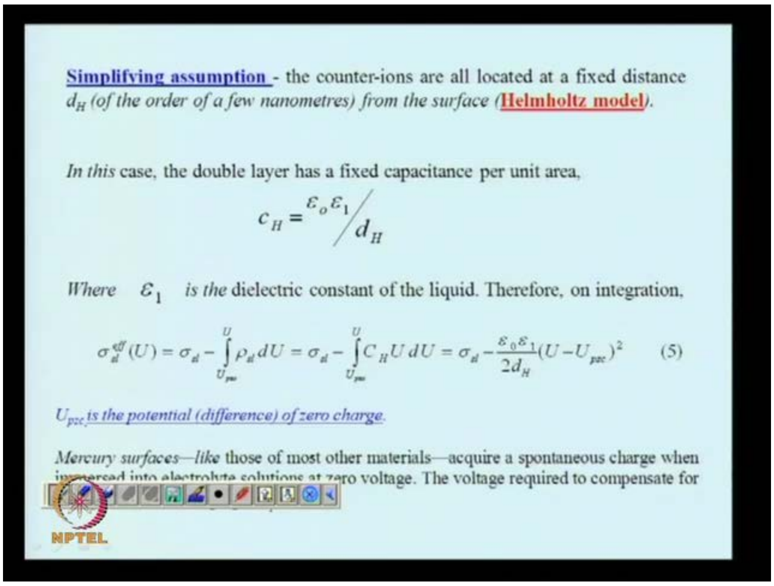

Simplifying assumption - the counter-ions are all located at a fixed distance d_H *(of the order of a few nanometres) from the surface* (**Helmholtz model**).

In this case, the double layer has a fixed capacitance per unit area,

$$c_H = \varepsilon_o \varepsilon_1 / d_H$$

Where ε_1 *is the* dielectric constant of the liquid. Therefore, on integration,

$$\sigma_{sl}^{eff}(U) = \sigma_{sl} - \int_{U_{pzc}}^{U} \rho_{sl}\, dU = \sigma_{sl} - \int_{U_{pzc}}^{U} C_H U\, dU = \sigma_{sl} - \frac{\varepsilon_0 \varepsilon_1}{2d_H}(U - U_{pzc})^2 \qquad (5)$$

U_{pzc} is the potential (difference) of zero charge.

Mercury surfaces—like those of most other materials—acquire a spontaneous charge when immersed into electrolyte solutions at zero voltage. The voltage required to compensate for

Sowith these now, we can move to the next part, next assumption which is like how would the how would the charges are distributed in the liquid.

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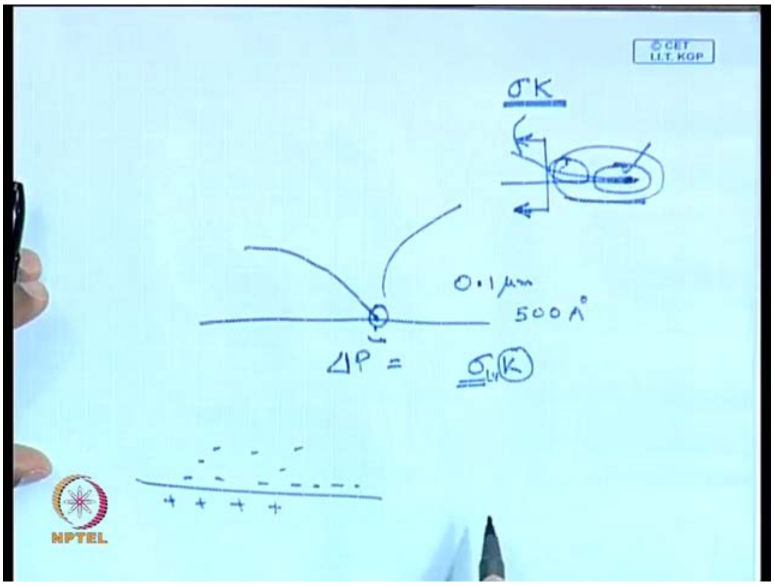

Obviously, the concentration of the charge is very near to the solid surface is going to be more, and as we move away from the surface, the concentration of thecounter ions will reduce progressively. In fact, it would reduce drastically. So, what kind of distribution of counter ions should one take, when one goes from a solid-liquid interface and into the liquid. Now, this is difficult to handlein a compact form.

So, the concept or the proposal of Helmholtz, the model ofthe model proposed by Helmholtz is used which assures that, all the counter ions are going to be situated in a very thin layer of the order of few nano meters, andthisHelmholtz model for the electric double layer has given rise to the concept of a double layer with a fix capacitance per unit area. Sohere, epsilon 1 is a dielectric constant of a liquid and d H is the thickness of thethickness ofthe thickness of the layer as proposed by the Helmholtz model; that is it is a all the charges, all the counter ions are going to be located at a fixed distancefrom the surface.

So, when you youyou use this and integrate this if the previous equation, this is given rise to the change in surface energy as a function of on application of some voltage U; as a function of the surface energy when you do not have any electric field and these are propertiesthese are properties of the solid liquid interface; this is the applied voltage; this is the thickness as predicted by Helmholtz layer and U pzcis the potential difference of zero charge, and this the introduction of U pzc is important because,mercuryand many other surfaces acquire a spontaneous charge when they are immersed into an electric solution even at zero voltage. So, in order to overcome that potential something, someexcess external potential has to be applied in order to make the surface truly zero charged. So, pzc is that charge which has to be applied in order to in order tomake this compensate for thiscompensate for this accumulated potential difference or the generated potential difference even at zero charge.

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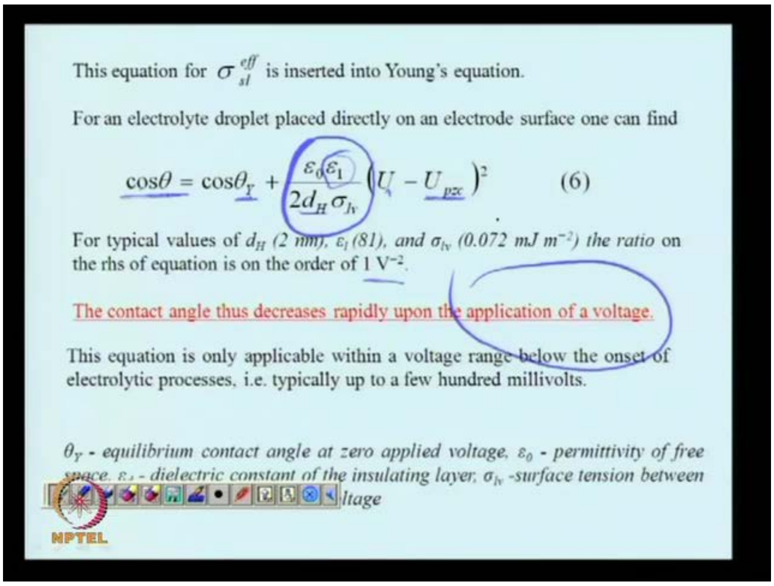


This equation for σ_{sl}^{eff} is inserted into Young's equation.

For an electrolyte droplet placed directly on an electrode surface one can find

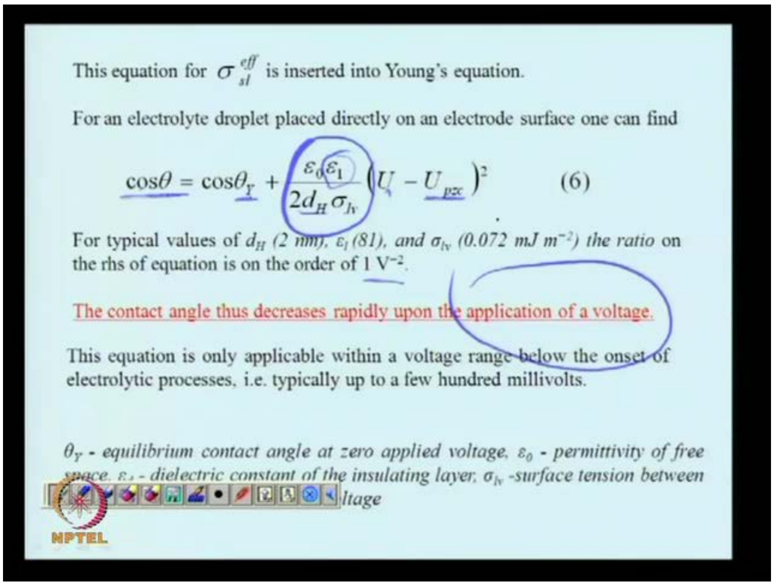
$$\underline{\cos\theta} = \cos\theta_{\underline{Y}} + \frac{\varepsilon_0\varepsilon_1}{2d_H\sigma_{lv}}(U - \underline{U_{pzc}})^2 \qquad (6)$$

For typical values of d_H (2 nm), ε_l (81), and σ_{lv} (0.072 mJ m^{-2}) the ratio on the rhs of equation is on the order of 1 V^{-2}.

The contact angle thus decreases rapidly upon the application of a voltage.

This equation is only applicable within a voltage range below the onset of electrolytic processes, i.e. typically up to a few hundred millivolts.

θ_Y - equilibrium contact angle at zero applied voltage, ε_0 - permittivity of free space, ε_1 - dielectric constant of the insulating layer, σ_{lv} -surface tension between *ltage*



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ltage

So, this equation now can be inserted into Young's equation where the cos theta; theta being the contact angle at any given voltage can be related to a equilibrium contact angle, and in terms of system parameters such as the property epsilon 1 d H; sigma lv is the surfacetension at the liquid vapor interface; U is the applied voltage; and pzc as I mentioned is a potential at zero s.

Sofor typical, if we take typical values of d H, epsilon and sigma lv let us say for a water; this ratio of the right hand side of the equation; this entire ratio isof the order of 1 volt to the power minus 2. Now, you can see thatwith application of voltage,this increases rapidly. So, the contact angle would increase rapidly upon application of a small voltage. So, the… But the limitation is you really have to operate it below the onset of electrolytic electro electrolytic process. So therefore, it can only be operated up to the few up to a fraction of mille volts. So, if yourif your potential difference is beyond that fraction of mill voltthen,your electrolysis process would start and the entire process will be unusable; entire process will break down. So, even though it is a very interesting phenomena to look at a very lowthere the thethethe fact that it can only be used at a very low value of the applied potential; limits is used for any practical applications.

So, simple electro wetting will be difficult to implementfor any practical applications. So, one has to then go to thego to the application or go to the introduction of an dielectric in between the electrolyte and the electrode which would makethe electrolysis impossible at elevated voltages as well.

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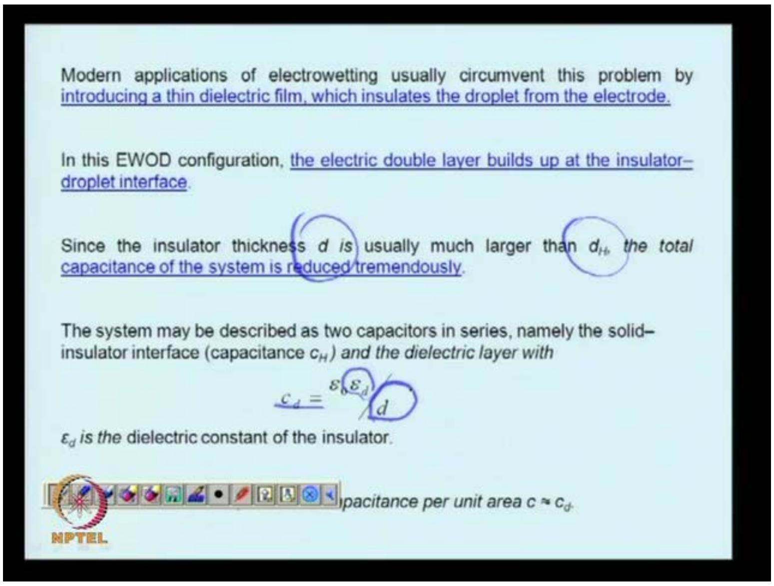

Modern applications of electrowetting usually circumvent this problem by introducing a thin dielectric film, which insulates the droplet from the electrode.

In this EWOD configuration, the electric double layer builds up at the insulator–droplet interface.

Since the insulator thickness *d is* usually much larger than d_H, *the total* capacitance of the system is reduced tremendously.

The system may be described as two capacitors in series, namely the solid–insulator interface (capacitance c_H) *and the dielectric layer with*

$$c_d = \varepsilon_0\varepsilon_d / d$$

ε_d *is the* dielectric constant of the insulator.

pacitance per unit area $c \approx c_d$.

So that is what, we are going tolook at next. So, the thin dielectric film insulates the droplet from the electrode. In the electric double layer builds up at theinsulated droplet interface thereby, causing a change in the surface energy of the dielectric and the capacitance. Since the insulator thickness d ismuch,much larger of the order of microns compared to d H which is of the order of the nano meters then, the capacitors of this system is decreased,reducedto a large extent and this is the capacitance of the insulator where this is thethis is thethis is the…epsilon d stands for the dielectric and one has to see that, this d isthickness of the dielectric and since the capacitance is sodifferent then, the entire capacitance of the system can be approximated as if,it is the capacitance of the dielectric.

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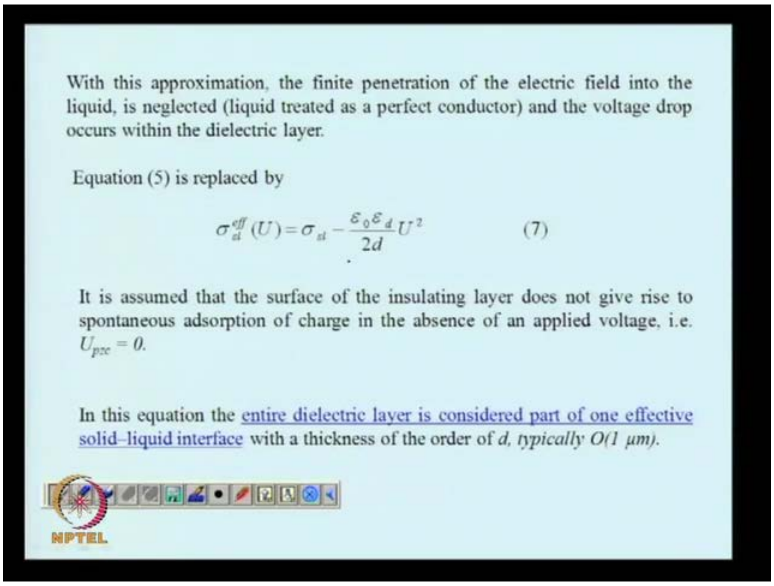

With this approximation, the finite penetration of the electric field into the liquid, is neglected (liquid treated as a perfect conductor) and the voltage drop occurs within the dielectric layer.

Equation (5) is replaced by

$$\sigma_{sl}^{eff}(U) = \sigma_{sl} - \frac{\varepsilon_0 \varepsilon_d}{2d} U^2 \qquad (7)$$

It is assumed that the surface of the insulating layer does not give rise to spontaneous adsorption of charge in the absence of an applied voltage, i.e. $U_{pzc} = 0$.

In this equation the entire dielectric layer is considered part of one effective solid-liquid interface with a thickness of the order of *d, typically O(1 μm).*

So, in the previous expression thereforeis modified by introducing only sigma d in here; d being the thickness of the dielectric,andthe value of U pzc is sosmall that for EWOD cases, where the applied voltages would be in the order of maybe 50, 100,200 and 300 volts; the value of pzc would beunimportant and that is why, it has been dropped from the equation.So, the compact equation for EWOD is the change in the effective surface energy of the system on application of an a potential is going to be equal to whatever be the potential, whatever be the surface energy at zero voltage minus this factor. Andthis…in this equation, the entire dielectric layer is therefore, considered part of one effective solid-liquid interface and withthickness of the order of 1 micron compared to the electric double layer which is of the thickness offew nano meters.

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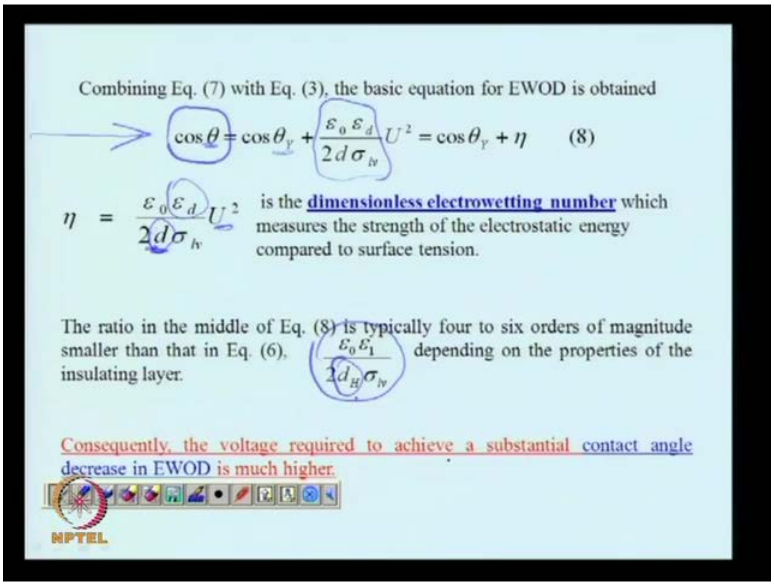

Combining Eq. (7) with Eq. (3), the basic equation for EWOD is obtained

$$\cos\theta = \cos\theta_Y + \frac{\varepsilon_0 \varepsilon_d}{2 d \sigma_{lv}} U^2 = \cos\theta_Y + \eta \qquad (8)$$

$$\eta = \frac{\varepsilon_0 \varepsilon_d}{2 d \sigma_{lv}} U^2$$ is the **dimensionless electrowetting number** which measures the strength of the electrostatic energy compared to surface tension.

The ratio in the middle of Eq. (8) is typically four to six orders of magnitude smaller than that in Eq. (6), $\left(\frac{\varepsilon_0 \varepsilon_1}{2 d_H \sigma_{lv}}\right)$ depending on the properties of the insulating layer.

Consequently, the voltage required to achieve a substantial contact angle decrease in EWOD is much higher.

Now, when you plug that into Young’sequation,this has given rise to the famous equation over here forEWOD. Contact angle equilibriumcontact angle is equal to the equilibrium contact angle plus this term multiplied by U square. This eta is known as the dimensionless electro wetting number which measures the strength of the electrostatic energy compared to the surface tension. So, thisis this is basically something on which you can control, which you can design by changing the thickness of the dielectric layer or by changing the material, and by changing the potential applied potential. You can have a different rate or different value for the new contact angle on application of voltage. Sothis essentially, depends on the properties of the insulating layer and on theon the on the thickness of the insulating layer.

So, this number for EWOD issmaller much smaller than the number corresponding to electro wetting because of this d H over here and d over here. Sothis means that, the voltage required to achieve the substantial contact angle decreasescontact angle decrease in EWODis much higher. That means, if you would like to change the contact angle by let us say 5 degree, the amount of potential difference that you have to apply would be of the order of one-tenth of a mille volt let us say; one tenth of a mille volt in simple electro wetting, but in order to obtain the same 10 degree change inelectro wetting on dielectric, the applied potential would probably be about say 50 degree or may be even more. So, you require higher voltages to actuate contact angle changes in electro wettingon dielectric.

However, the major advantage is that, now you can you are not restricted to few hundred fewmille volts, you can go to 500mille volts. You are only limited by the fact that acts very high elevated voltage. There could be current passing through the dielectrode, which would result in a phenomena known as dielectric breakdown. So, when that dielectric breakdown takes place, the entire surface becomes unusable andthis is some sort of a limitation of the EWOD. But,it still gives us tremendous flexibility in terms of effecting aaa major change in the contact angle which would besubsequently very important for the dynamics of the droplet on a surface.

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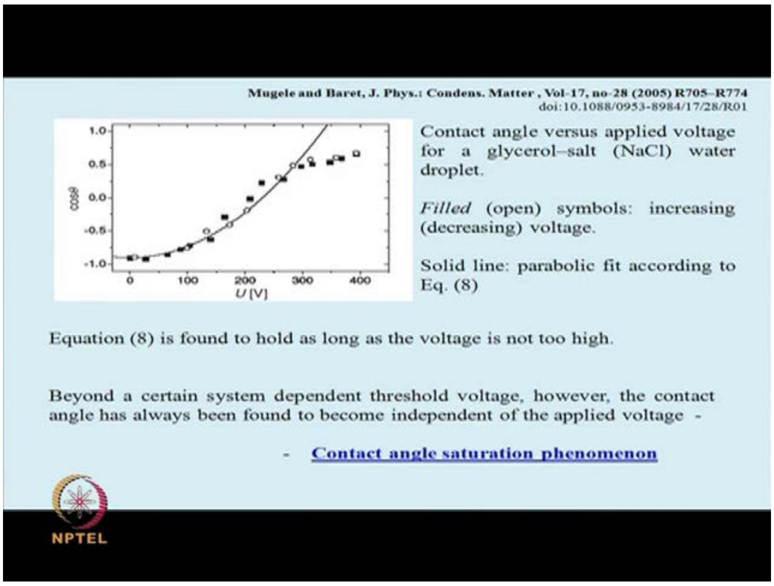

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Contact angle versus applied voltage for a glycerol–salt (NaCl) water droplet.

Filled (open) symbols: increasing (decreasing) voltage.

Solid line: parabolic fit according to Eq. (8)

Equation (8) is found to hold as long as the voltage is not too high.

Beyond a certain system dependent threshold voltage, however, the contact angle has always been found to become independent of the applied voltage -

- **Contact angle saturation phenomenon**

So, EWOD is a preferred methodover EW, and this is then example ofthe contact angle saturation, where you could seethatthe parabolic nature of cos theta variation with the potential is more or less valid up to let us say about 300 volt. But,beyond 200 volt, v will with increase in in in the potential; this is this becomes more or less relatively in (( ))relatively, it is free ofI mean, it is not going to it isit isit is not going to be a function of U anymore. So, this contact angle saturation at somewhere around this value is another limitation of EWOD.

So, if…This is known as the contact angle saturation. Andyou obviously, cannot walk beyond the value and… But even then, this would probably be a change in contact angle by about 30 degree,50 degree that is possible. But,you cannot make a non wetting system completely wetting by simply keepingon keep on increasing the potential difference. So, you are either going to be limited by the dielectric breakdown which is essentially passing of a current through the dielectric at a higher voltages, rendering the process, rendering the surface unusable for subsequent use or you are going to hate the contact angle saturation phenomena, and you would not be able to go beyond that.

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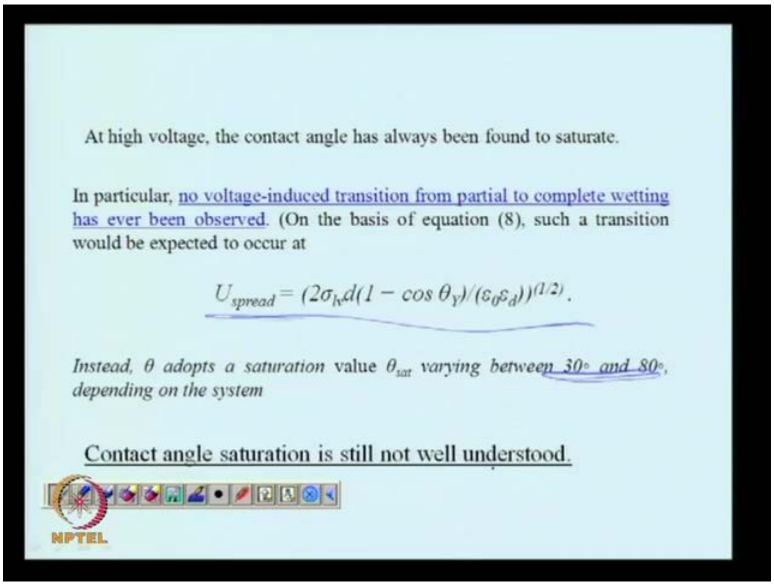

At high voltage, the contact angle has always been found to saturate.

In particular, no voltage-induced transition from partial to complete wetting has ever been observed. (On the basis of equation (8), such a transition would be expected to occur at

$$U_{spread} = (2\sigma_{lv}d(1 - \cos\theta_Y)/(\varepsilon_0\varepsilon_d))^{(1/2)}.$$

Instead, θ adopts a saturation value θ_{sat} *varying between 30° and 80°, depending on the system*

Contact angle saturation is still not well understood.

So, that is what I have already said that,this you areyou get someexpression, but a saturation value between 30 to 80 depending on the surface,depending on the system you are going to…Now, the phenomenon of contact angle saturation isstill not well understood.

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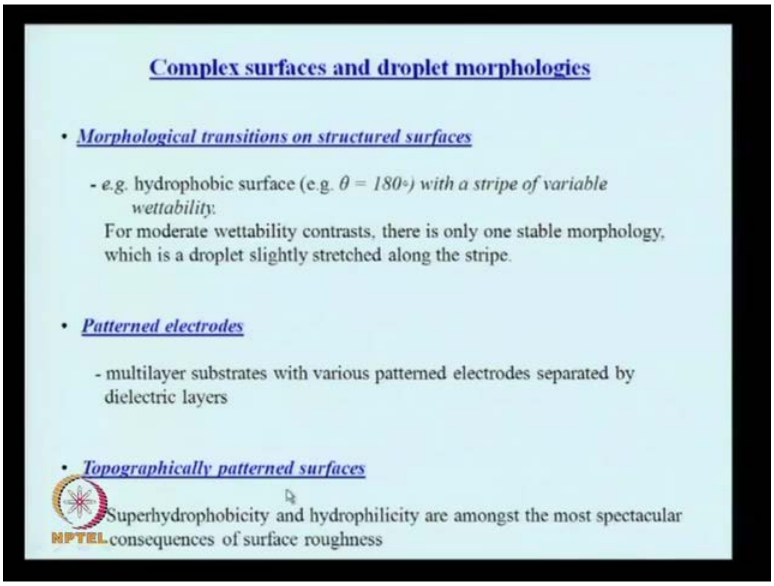

Complex surfaces and droplet morphologies

- *Morphological transitions on structured surfaces*

  - *e.g.* hydrophobic surface (e.g. *$\theta = 180^\circ$) with a stripe of variable wettability.*

    For moderate wettability contrasts, there is only one stable morphology, which is a droplet slightly stretched along the stripe.

- *Patterned electrodes*

  - multilayer substrates with various patterned electrodes separated by dielectric layers

- *Topographically patterned surfaces*

  Superhydrophobicity and hydrophilicity are amongst the most spectacular consequences of surface roughness

Nowin the next class, we are going to talk about more about the complex surface surfaces and droplet morphologies.(( ))How we can change,how we canhow we can make a transition from a hydrophobic surface to a hydrophilic surface by imparting certain structures on the surface; and if you have substructures on the surface microscopic level structures on the surface, how would that change the wetting nature, and how they can be integrated with EWOD to have smoother motion of the droplets for example, over a surface. Andwe would also concentrate on thedynamics of the electro wetting process;the factors on which that on which this electro wetting process would depend, and how or what are the interesting and important applications of EWOD for our everyday use. So, that is all for today thank you.