Microscale Transport Processes

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Module No. # 01

Lecture No. # 40

Interfacial Phenomena in Thin Liquid Films

In this class we are going to talk about something which is very important, but we have not touched upon this subject in the previous lectures. We were talking about micro devices of small channel through which the liquid is flowing. In most of these cases we confined ourselves in close systems though, in electroweting especially in droplet based digital micro fluidics part of this course we spoke about open systems, but we did not consider the case when wetting or a partially wetting thin film comes in close contact with a solid and spreads on the solid and thereby forming an extended film.

Now, you would see towards the end of this lecture is that what happens in that thin film is extremely important in determining what would be the transport properties. For example, heat transfer or mass transfer it is also very important from an technological perspective. So, when a liquid comes in contact with a solid variety of situations may arise and depending on the interaction forces between the liquid and the solid molecules, what happens in the ultrathin part of the film essentially governs the efficiency of many macro processes. So, the motivation for our study in thin films can be classified into the following major points.

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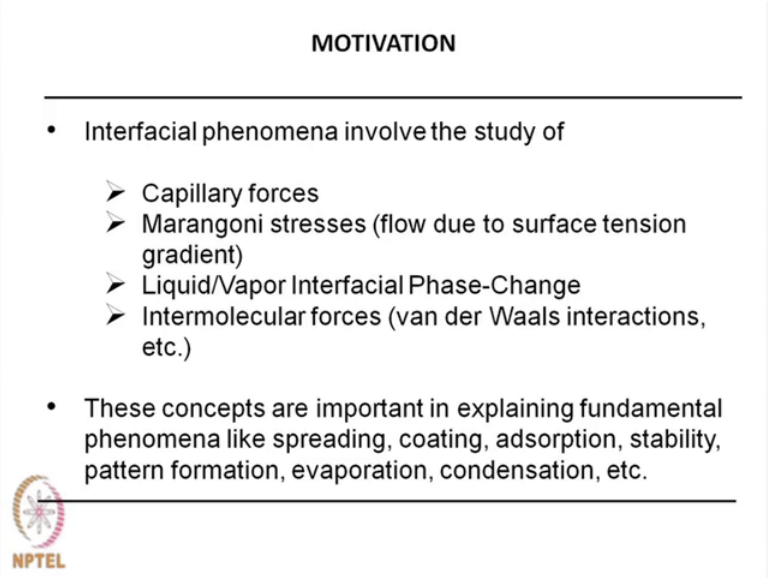

MOTIVATION

- Interfacial phenomena involve the study of
  - Capillary forces
  - Marangoni stresses (flow due to surface tension gradient)
  - Liquid/Vapor Interfacial Phase-Change
  - Intermolecular forces (van der Waals interactions, etc.)
- These concepts are important in explaining fundamental phenomena like spreading, coating, adsorption, stability, pattern formation, evaporation, condensation, etc.

So, what we are going to here is going to show you the different types of forces which are prevalent in the study of the interfacial phenomena of thin films. And they involve capillary forces, where the where the shape of the film governs what would be the pressure at different points in the film. Now, there may be a situation in which there can be temperature difference between two points in the film. So, if there is a temperature difference between two points in the very thin film the surface tensions at those two points could be different. And this difference in surface tension can give rise to flow in the very thin film. So, these type of flows are collectively called as marangoni flows and they are also extremely important when we are thinking about, when we are discussing about flow at the micro or at the nano scale.

We are also interested to know the liquid vapor interfacial phase change, what happens when a liquid and a vapora, when a liquid, when a film separates a solid. A thin liquid film separates a solid from the vapor and how much evaporation we may get from this liquid vapor interface is going to govern is going to decide the heat transfer process. And we will see that how from the ultrathin part of a thin film there can be very high heat and mass flux. So, the that region which is also known as the interline region can be used to design heat exchange equipments at very small scale.

So, the forces which are acting during evaporation from a liquid film to the to it is vapor, we need to quantify that we need to understand the basic physics of the different forces, which are acting in the very thin region and that would have technological implications as well. And finally, we understand that whether a film spreads on the solid or not depends on forces at the molecular level. So, it depends on the vanderwaals interaction forces in between the solid, the liquid and the vapor molecules. So, these physical these the physics of these processes govern not only how the film spreads on the solid. They are important in explaining fundamental phenomena like spreading, coating, adsorption, stability of a drop or of a foam.

So, in pattern formation evaporation, condensation and many other processes.

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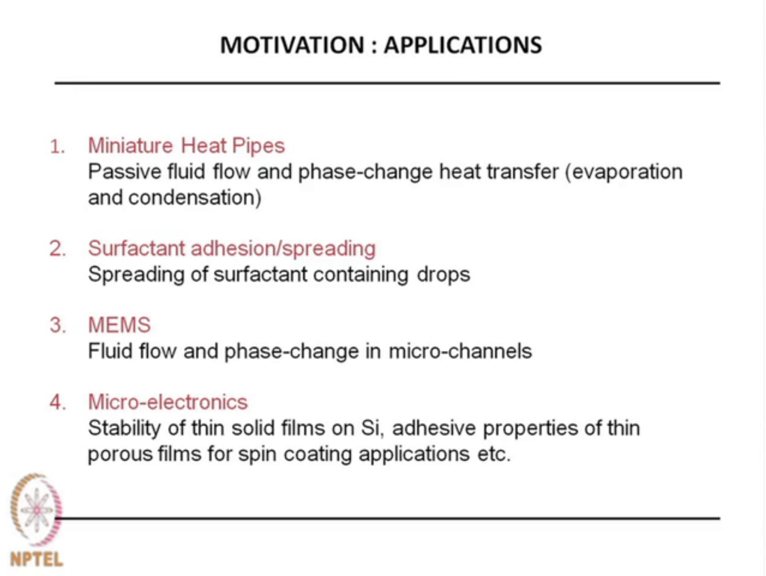

MOTIVATION : APPLICATIONS

1. Miniature Heat Pipes
   Passive fluid flow and phase-change heat transfer (evaporation and condensation)
2. Surfactant adhesion/spreading
   Spreading of surfactant containing drops
3. MEMS
   Fluid flow and phase-change in micro-channels
4. Micro-electronics
   Stability of thin solid films on Si, adhesive properties of thin porous films for spin coating applications etc.

The application of these different processes they essentially motivates us to study deeper into the thin film specially evaporating thin film. So, when we I have given four examples of applications which are a direct result of what happens when we are considering transport phenomena from very thin films. The first one is miniature heat pipes and these are essentially passive fluid flow and phase change heat transfer processes we all know that. The fluid flows in miniature heat pipe are provided by the capillary forces principally by the capillary forces. So, there would be difference in temperature at two points in a miniature heat pipe in the channels of a miniature heat pipe.

And this is going to give rise to a two different shapes of the liquid meniscus at those points. So, when we have a difference in shape at the at two points in the liquid in the liquid meniscus. So, what is going to happen is that the pressure the capillary the pressure at two points should also be different because they are going to be the pressure. Between the pressure jump across a liquid vapor interface is governed by the young laplace equation. So, if we assume that the pressure at the vapor phase is constant is the same at point one and two then the pressure at the liquid phase would be different.

Because p l minus p v pressure at the liquid phase and the pressure at the vapor phase are connected the difference is equal to sigma, which is the surface tension times k which is the curvature. So, if the curvatures are different at two points then the pressure in the liquid is also going to be different and if there is a difference in pressure in the liquid. So, there will be flow from one point from the high pressure to the low pressure. So, this is essentially how a passive miniature heat pipe works. So, whenever we talked about these shape these shape changes in the very thin part of the film we need to know, we have to find out what is the interruption forces that are present in such situations.

So, one of the motivations for studying interfacial phenomena of thin liquid films is the efficient and optimum design of miniature heat pipes. The next application could be in surfactant adhesion and surfactant spreading. So, how would if you would like to wet a surface with a liquid and if it does not do that on it is own the best way the easiest way to do. So, is to add some surfactant in the drop of the liquid on a surface which essentially reduces the surface tension. And forms a film ahead of the drop thereby creating uniform coverage of this surface with the liquid drop of interest. So, how adhesion of surfactant changes the contact angle changes the force field thereby can result in spreading.

Uniform spreading of something over a solid surface is again of importance in many situations especially in lubrication and in coatings. So, that is another example another motivation for study of the phenomena of liquid films of thin liquid films. In mems and in micro fluidics the that is which involve fluid flow and phase change in micro channels or stability of different films on substrate such as silicon. The adhesive properties of thin porous films for spin coating applications all of these are direct applications of the thin of the interfacial phenomena in thin films. So, this has prompted researchers to look deeper into the behavior of a liquid film when it comes in contact with a solid. And this is what the physics of that process is would be the topic of our today’s discussion.

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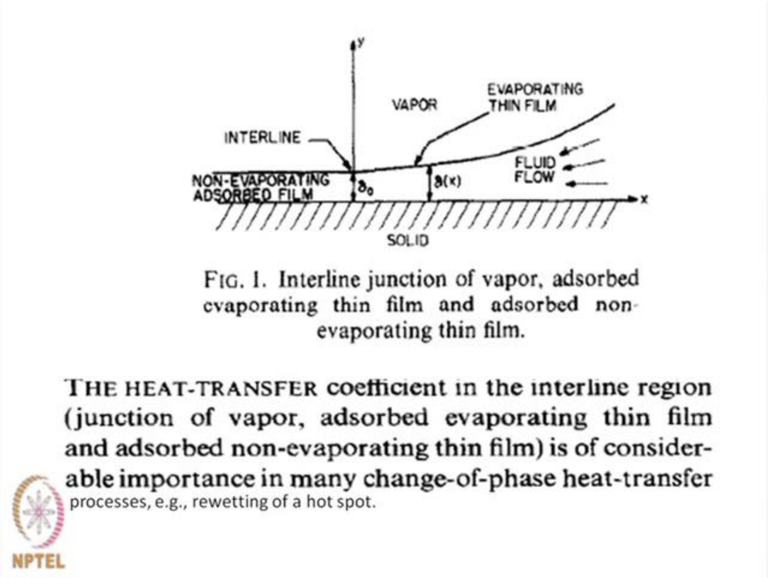

FIG. 1. Interline junction of vapor, adsorbed evaporating thin film and adsorbed non-evaporating thin film.

THE HEAT-TRANSFER coefficient in the interline region (junction of vapor, adsorbed evaporating thin film and adsorbed non-evaporating thin film) is of considerable importance in many change-of-phase heat-transfer processes, e.g., rewetting of a hot spot.

Now, this is a pictorial representation of the different zones in a liquid when we have let us say a solid and a liquid film in contact with it. Now, let us say the solid temperature is more than that of the liquid and then of the vapor. So, what we get is evaporation from the liquid film to the vapor if you carefully we can we can also draw this to describe in more detail what happens to a film.

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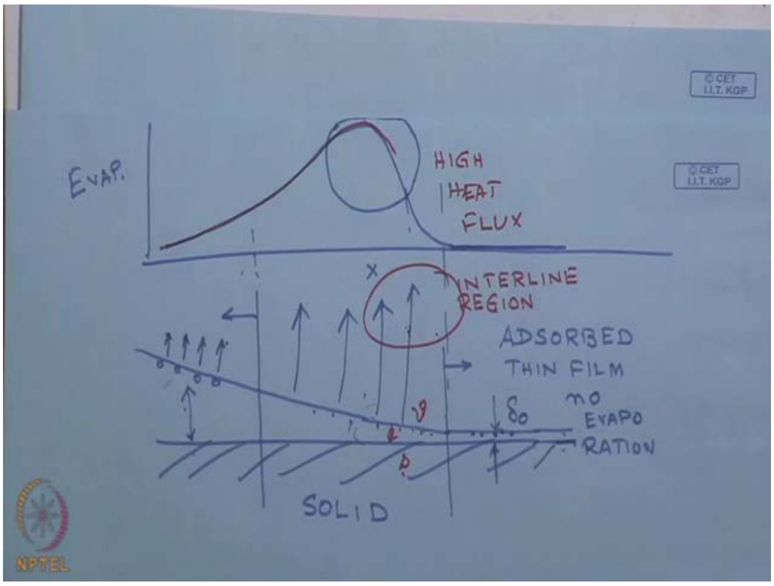

Let us say this is the solid and I have a film which extends and then forms a stable wetting film on that. So, this region of the film is called the adsorbed thin film in here the molecules of the liquid are strongly bound to the solid surface due to intermolecular forces. And therefore, no evaporation can take place from here and the thickness of the film is denoted by delta zero, which is the adsorbed film thickness, which depends on the liquid solid combination. And the temperature of the and the temperature of the solid with respect at temperatures of the solid and the liquid. So, this region where an adsorbed thin film exists there can be no evaporation. In this section of the film is quite thick and the molecules over here they are not bound to the solid so, they are free to evaporate.

So, evaporation is definitely possible from this region, but if you look at the thickness of the film. So, is the thickness of the film is quite large compared to whatever thickness that we have over here then the conduction conductive resistance of the liquid will not allow much evaporation from this region. On the other hand if we come to this region the molecules are not strongly bound to the solid so, therefore, evaporation is possible. At the same time the thickness over here is quite small compared to this so, the thickness is large compared to the adsorbed region. So, the top molecules are allowed to evaporate whereas, the thickness is small compared to this so, the evaporation from this region can be very large.

So, if we could plot the evaporation or the evaporative flux as a function of these locations then what we would what we would get is an evaporation of a zero evaporation then it is going to pass through a maximum and slowly fall as the thickness increases. So, this high heat flux, the high heat flux which is possible from these regions. This can be utilized the high very high heat flux which is possible from a region which is quite thin, but not thin enough such that evaporation is not allowed this region is called the interline region. So, the interline region, this region the interline region is the characterized by the proximity of the liquid, the solid and the vapor phases.

So, these three phases are very close to each other in the interline region and very high value of heat or mass transfer is possible from this interline region. So, this the high heat flux or high heat transfer coefficient of the interline region can be utilized to device and to design heat transfer equipments at very small scales. So, this picture this profile is something which is going to be extremely important. And we will see experimental studies which look at this interline region and see the balance of forces at these regions.

So, if you look at here that this statement which is written in this is that the heat transfer coefficient in the interline region which is the junction of vapor adsorbed evaporating thin film and adsorbed non evaporating thin film. Is of considerable importance in many change of phase heat transfer processes for example, rewetting of a hot spot.

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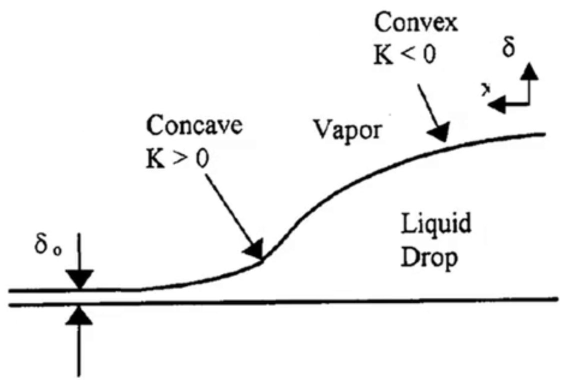

Schematic drawing of the measured interfacial profile of a condensing drop

Now, the situation is slightly different if we look at a partially wetting film. So, in this I have drawn a schematic drawing of interfacial profile of a condensing drop, if you see that the liquid drop it starts as a convex at the at the top convex in nature. So, it is k the curvature is less than 0 and at certain point of time it changes from it is convex shape to a concave shape and asymptotically merges with a thin film in front of it. So, the k value there is going to be greater than 0. So, this change in curvature of a condensing drop from negative to positive and then the curvature will be equal to 0 at the adsorbed film this would be extremely important for spreading, wetting and rewetting studies.

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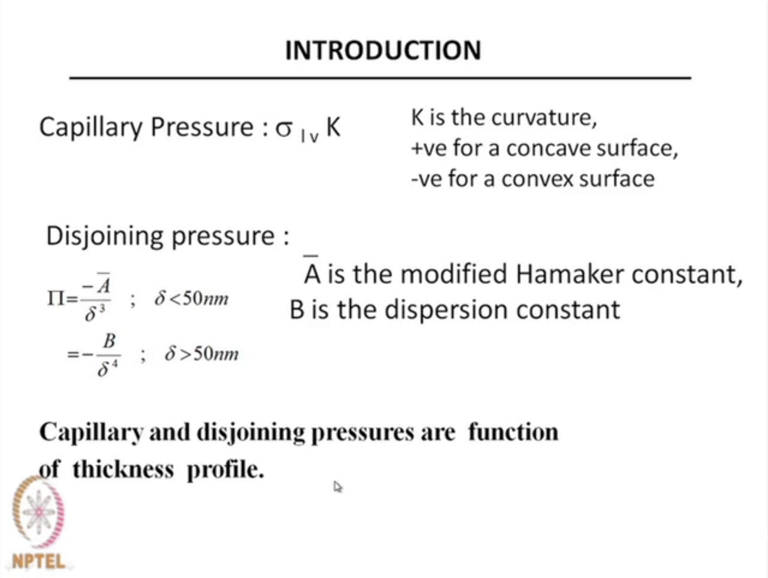

INTRODUCTION

Capillary Pressure : σ_{lv} K

K is the curvature,
+ve for a concave surface,
-ve for a convex surface

Disjoining pressure :

$$\Pi = \frac{-\bar{A}}{\delta^3} \; ; \; \delta < 50nm$$
$$= -\frac{B}{\delta^4} \; ; \; \delta > 50nm$$

$\bar{A}$ is the modified Hamaker constant,
B is the dispersion constant

Capillary and disjoining pressures are function of thickness profile.

Now, we are going to introduce certain specific terms which would help us in characterizing and in understanding the process. The first quantity which is the first factor which we are going to discuss is the capillary pressure. The young laplace equation as I said it is going to be p l minus p v is equal to sigma k and this sigma is sigma l v that is the liquid vapor surface tension and k denotes the curvature the point value of the curvature. So, this sigma k will have unit is of pressure and this is called the capillary pressure. So, the difference between the liquid and the vapor pressure is equal to the capillary pressure.

And the capillary pressure the k the curvature is positive for a concave surface as we have explained in the previous figure and it is going to be negative for a concave sorry convex surface.

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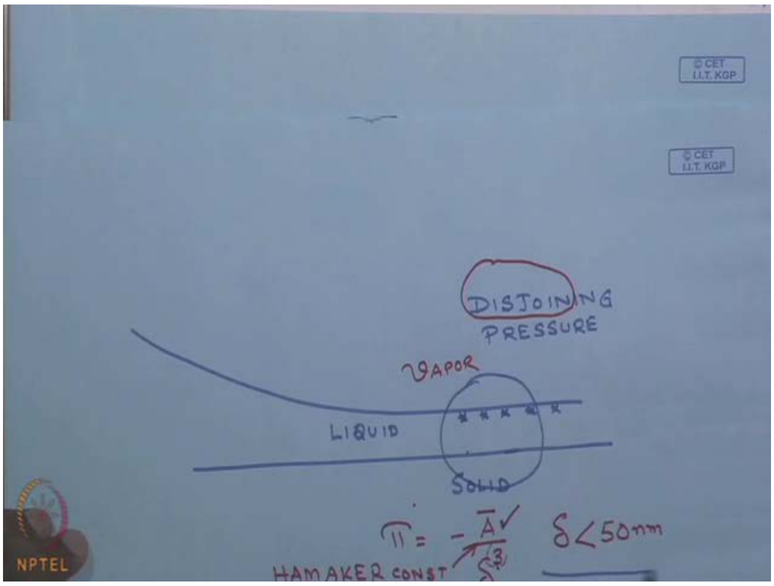

The next quantity of importance is let us think of a very thin film very thin liquid film. In very in a very thin liquid film the top molecules means the molecules which are near the liquid vapor interface are going to fill and attractive a vanderwaals attractive force between the liquid molecule and the solid molecules. So, what would do is that in order to in order to cause evaporation from such a thin film you have to provide an extra superheat. So, the excess pressure of a very thin film so, if I have this very thin portion of the film over here the liquid molecules are going to fill an attractive force towards the solid. This attractive force when expressed in terms of pressure is termed as disjoining pressure.

So, the name disjoining pressure came from the fact that the interactive force disjoins the vapor from the solid by introducing a liquid film in between. So, this is called the disjoining pressure and the disjoining pressure is expressed as a function of the film thickness. So, this index is 3 when the delta the film thickness is less than 50 nanometer and this is going to be to the power this is equal to the power 4 when delta is greater than 50 nanometer. And the quantities A and B are called Hamaker constant or dispersion constant respectively. So, A is called the Hamaker constant and B is called the dispersion constant.

And obviously, they depend on the liquid solid combination and they are ways calculate theoretically calculate the value of Hamaker constant and the values of dispersion constant. Now, these are; obviously, this classification that when it changes from Hamaker this to the power 3 two to the power 4 is slightly arbitrary. But it has been shown experimentally that the measured values of disjoining pressure changes from the delta to the power minus 3 dependence to minus 4 dependence around the value of 50 nanometers.

So, which what it tells is simply is then the capillary at the disjoining pressures are functions of thickness profile. So, if you could measure the thickness of a very thin film accurately then we would be able to obtain the value of the disjoining pressure or the value of the value of the Hamaker constant.

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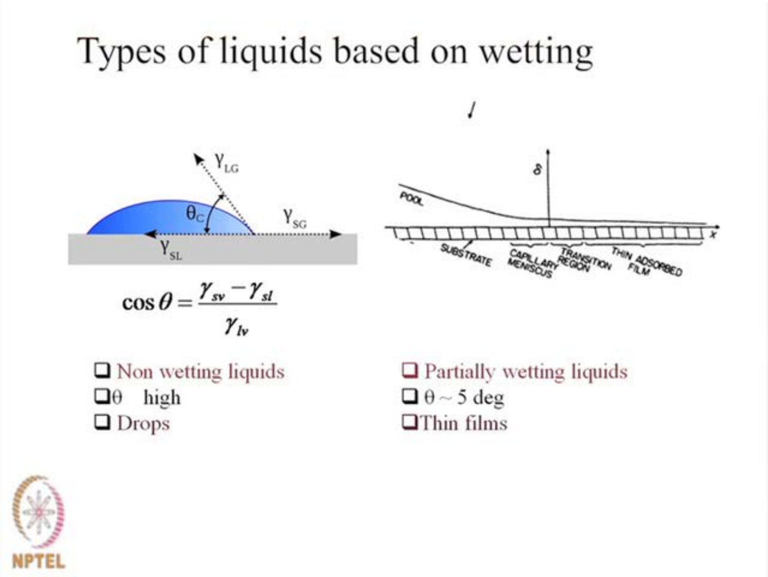

Types of liquids based on wetting

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}$$

☐ Non wetting liquids
☐θ high
☐ Drops

☐ Partially wetting liquids
☐ θ ~ 5 deg
☐Thin films

Now, types of the liquids can be divided based on how the wet a solid surface. So, in this figure you would see that we have a non wetting film on the left and a wetting film on the right. A non wetting film is characterized by the presence of finite contact angle and the contact angle is related to the surface energies as shown over here gamma s v minus gamma s l divided by gamma l v. And the non wetting liquid the value of theta would be would be large and they are quite common in case of drops and so, on. Whereas, on the case of wetting liquid or in partially wetting liquids the value of theta could be quiet small even less than five degrees and or so.

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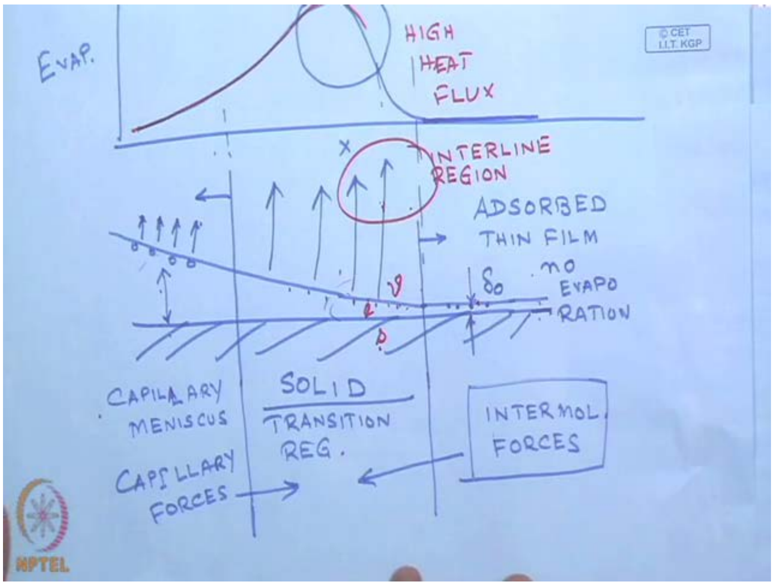

And we have a thin film a head of the thicker film, where thicker film and the division the and the distance and the name of these different regimes as I have said are clear. So, we have an adsorb film over here as I have drawn over here this region in the adsorbed film where intermolecular forces are important. This in this adsorb region it is only intermolecular force which are going to be important in the case of thicker part which is known as the capillary meniscus. It is the capillary forces which are going to be important and in the zone in between the capillary meniscus at the adsorb thin film this is known as the transition film, transition region. And in transition region both capillary force and intermolecular force are going to be important.

So, this is how broadly the different regions of a thin film are quantified.

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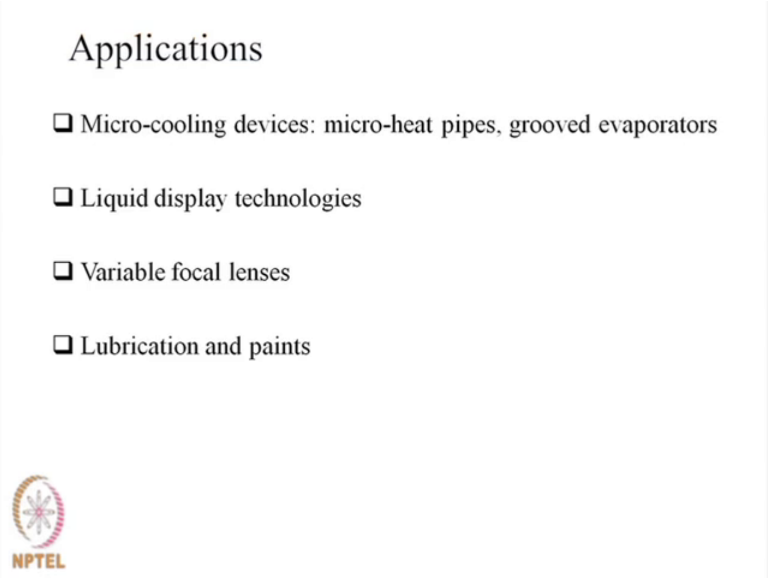

Applications

- ☐ Micro-cooling devices: micro-heat pipes, grooved evaporators
- ☐ Liquid display technologies
- ☐ Variable focal lenses
- ☐ Lubrication and paints

Now, we look at the application once again we look at the applications of thin films they are in micro cooling devices such as in micro heat pipes, in grouped evaporators. They are also prevalent in liquid display technologies, the variable focal lenses, lubrications paints and in many others.

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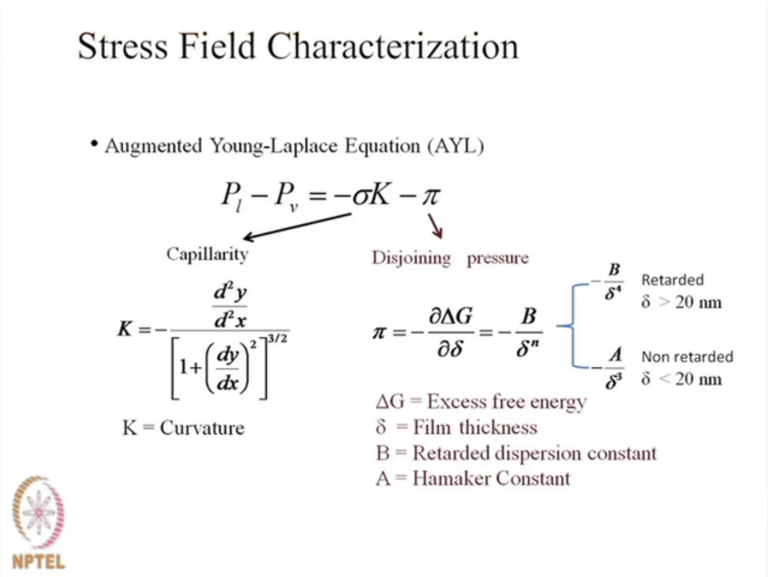

Stress Field Characterization

- Augmented Young-Laplace Equation (AYL)

$$P_l - P_v = -\sigma K - \pi$$

Capillarity

$$K = -\frac{\frac{d^2y}{d^2x}}{\left[1+\left(\frac{dy}{dx}\right)^2\right]^{3/2}}$$

K = Curvature

Disjoining pressure

$$\pi = -\frac{\partial \Delta G}{\partial \delta} = -\frac{B}{\delta^n} \begin{cases} -\frac{B}{\delta^4} & \text{Retarded } \delta > 20 \text{ nm} \\ -\frac{A}{\delta^3} & \text{Non retarded } \delta < 20 \text{ nm} \end{cases}$$

ΔG = Excess free energy
δ = Film thickness
B = Retarded dispersion constant
A = Hamaker Constant

So, if you are going to look at the if you are going to look at the stress field characterization of a thin film the measure governing equation is the augmented young laplace equation. So, if you just have we have young laplace equation then the second term on the right hand side would not be there. The fact that it is a very thin film the fact that intermolecular forces are also important in such films we have to introduce the component of intermolecular forces in this equation. And that is why it is known as the augmented young laplace equation by the presence or by the introduction of the term pi in the in it.

The value of capillary forces which is sigma times K the curvature is can be expressed for a very thin film as a function of the profile where y is the film thickness; x is the distance along the solid. So, d y d x is the slope of the film and so, on. On the other hand the disjoining pressure which tells us the excess free energy of the thin film due to the presence of intermolecular forces can be expressed by the formula minus B by delta to the power n where B is the dispersion constant and A is the Hamaker constant as I have explained before.

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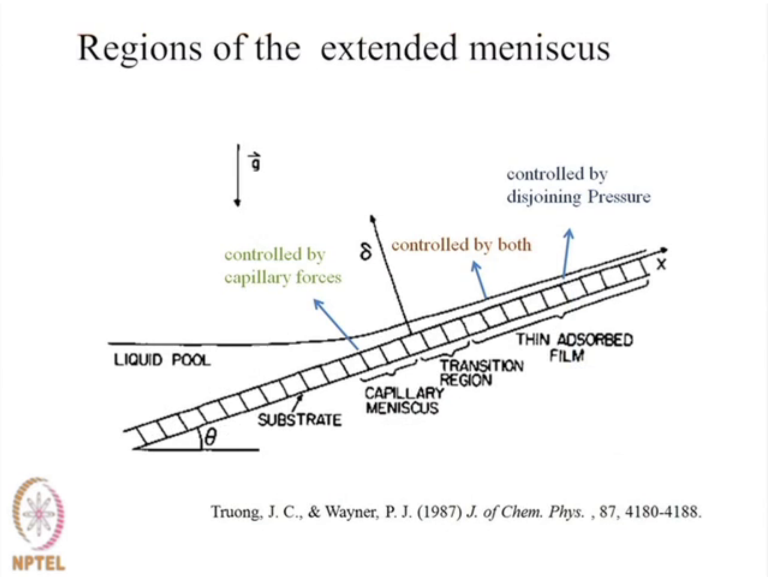

Regions of the extended meniscus

Truong, J. C., & Wayner, P. J. (1987) *J. of Chem. Phys.* , 87, 4180-4188.

So, this is pictorial view of a what we have I have shown you before is the frontal region that is at the very thin part of the film it is controlled by disjoining pressure. In the thicker part of the film it is controlled by capillary forces which is known as the liquid meniscus capillary meniscus. And there is a transition region in between where which is controlled by mostly this disjoining pressure and the capillary forces. So, this picture is about the extension of a liquid film ahead of a liquid pool when an inclined plate is immersed into it. So, the liquid moves ahead of the liquid pool since it is a wetting liquid and forms these three distinct regions.

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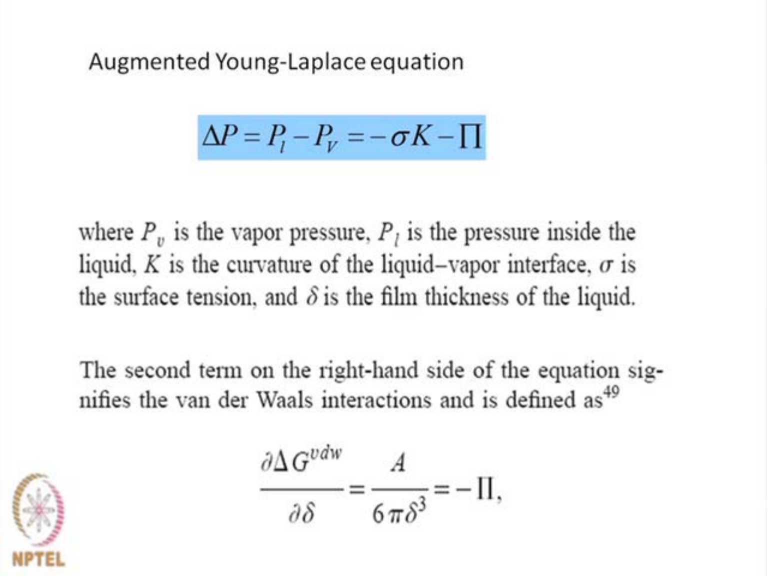

Augmented Young-Laplace equation

$$\Delta P = P_l - P_V = -\sigma K - \prod$$

where P_v is the vapor pressure, P_l is the pressure inside the liquid, K is the curvature of the liquid–vapor interface, σ is the surface tension, and δ is the film thickness of the liquid.

The second term on the right-hand side of the equation signifies the van der Waals interactions and is defined as[49]

$$\frac{\partial \Delta G^{vdw}}{\partial \delta} = \frac{A}{6\pi\delta^3} = -\Pi,$$

So, we have the young laplace equation this P v is the vapor pressure, P l is the pressure inside the liquid, K is the curvature of the liquid vapor interface surface tension, sigma and delta is the film thickness of the liquid. So, we if we look thermodynamically then this interaction this presence of the Vanderwaals interactions is going to change the free energy of the system. And the change in free energy of the system due to Vanderwaals forces is denoted by delta of delta G v d w shows that it is Vanderwaals forces. And it is function of the film thickness, delta G is the excess interfacial free energy per unit area due to Vanderwaals interactions.

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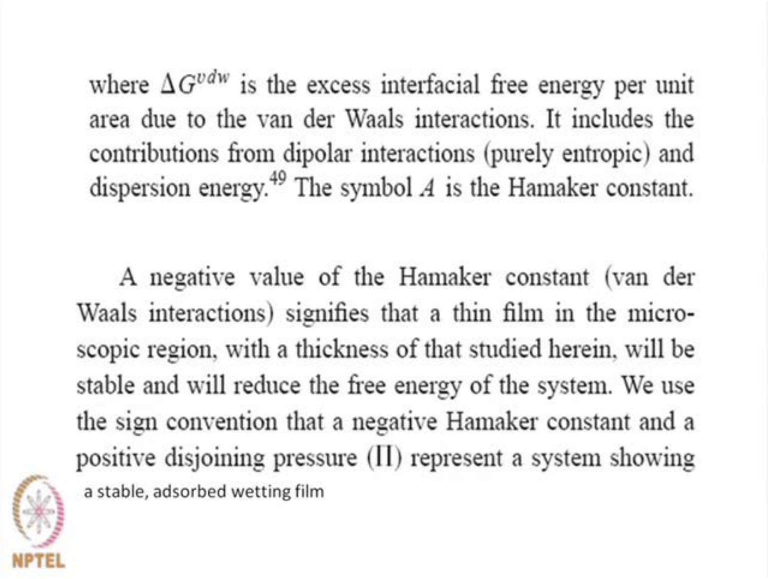

where ΔG^{vdw} is the excess interfacial free energy per unit area due to the van der Waals interactions. It includes the contributions from dipolar interactions (purely entropic) and dispersion energy.[49] The symbol A is the Hamaker constant.

A negative value of the Hamaker constant (van der Waals interactions) signifies that a thin film in the microscopic region, with a thickness of that studied herein, will be stable and will reduce the free energy of the system. We use the sign convention that a negative Hamaker constant and a positive disjoining pressure (Π) represent a system showing a stable, adsorbed wetting film

Now, when the value of Hamaker constant is negative it signifies that a thin film in the in the microscopic region will be stable and will reduce the free energy of the system. So, a negative value of Hamaker constant denotes that it is a wetting system. So, an at stable adsorb wetting film forms if the value of Hamaker constant is negative. And the value of Hamaker constant can be evaluated from this formula for phase one and two which is interacts across the medium three.

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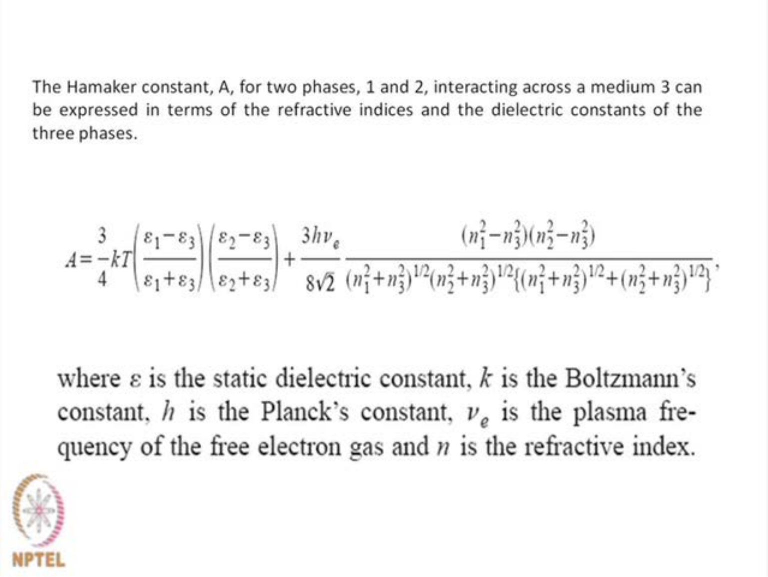

The Hamaker constant, A, for two phases, 1 and 2, interacting across a medium 3 can be expressed in terms of the refractive indices and the dielectric constants of the three phases.

$$A = \frac{3}{4}kT\left(\frac{\varepsilon_1-\varepsilon_3}{\varepsilon_1+\varepsilon_3}\right)\left(\frac{\varepsilon_2-\varepsilon_3}{\varepsilon_2+\varepsilon_3}\right) + \frac{3h\nu_e}{8\sqrt{2}}\,\frac{(n_1^2-n_3^2)(n_2^2-n_3^2)}{(n_1^2+n_3^2)^{1/2}(n_2^2+n_3^2)^{1/2}\{(n_1^2+n_3^2)^{1/2}+(n_2^2+n_3^2)^{1/2}\}},$$

where ε is the static dielectric constant, k is the Boltzmann's constant, h is the Planck's constant, ν_e is the plasma frequency of the free electron gas and n is the refractive index.

So, the two phases one and two are the solid at the vapor and they act across medium three which is the liquid film, that separates phase one solid and phase two which is the vapor. And this interactive forces has it has been shown that their functions of the refractive indices and dielectric constants of the three phases. So, we have epsilon which is the dielectric constant, k is the Boltzmann constant, h is the Planck's constant and n etcetera n one n two n three are the refractive indices of the three phases. So, this formula tells us what is the value of Hamaker constant going to be for a specific liquid solid vapor combination. But it is extremely I must mention that there are people have tried for quite some time to measure the value of Hamaker constant in real systems.

And compared them with that predicted from the previous equation. It is a very difficult task, the main reason it is difficult is that, the surfaces will have to be ultraclean for the values of Hamaker constant. Or the values of the interaction values of the attraction, attractive force to be evaluated and to be comparable with that predicted from the theory. So, small a minute quantities of adsorbed impurities will change the value of Hamaker constant drastically. So, that this formula really tells us the correct result has been proved in some experiments some well controlled experiment, where a surface has been created and immediately the interaction parameters were calculated.

But if leave any surface it is going to adsorbed impurities from the surroundings thereby changing the surface energy drastically. And when that happens the value of Hamaker constant will never be equal to that predicted from the theory. And it is not uncommon to see orders of magnitude difference between the measured value of Hamaker constant and the theoretically predicted value of Hamaker constant. In many experiments in this field if you can come up to an order of magnitudes, if you can make the order of magnitude same between the theoretically predicted value and the experimental predicted value then that is acceptable.

So, this is one reason why in situ characterization of a surface is extremely important to find out the contribution of intermolecular forces on spreading wetting evaporation and so, on. So, no matter what you do you should not use blindly the value of Hamaker constant as predicted from the theory.

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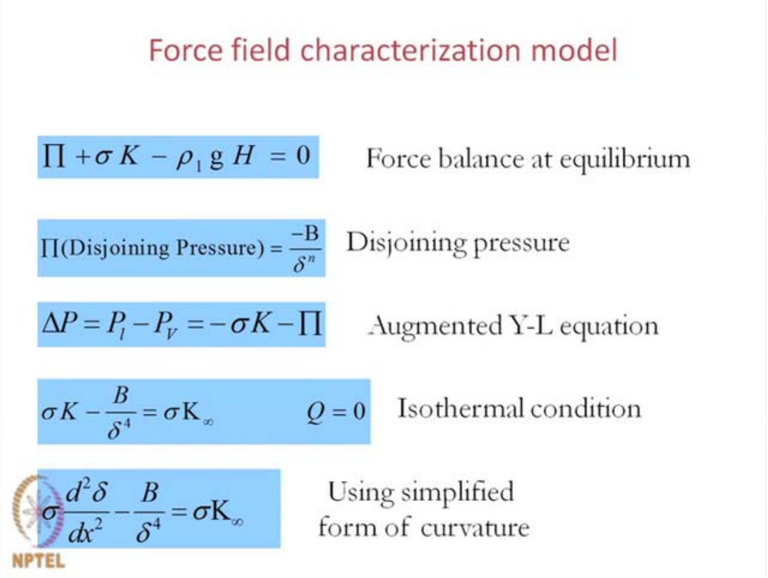

Force field characterization model

$\Pi + \sigma K - \rho_1 g H = 0$ Force balance at equilibrium

$\Pi(\text{Disjoining Pressure}) = \frac{-B}{\delta^n}$ Disjoining pressure

$\Delta P = P_l - P_v = -\sigma K - \Pi$ Augmented Y-L equation

$\sigma K - \frac{B}{\delta^4} = \sigma K_\infty$ $Q = 0$ Isothermal condition

$\sigma \frac{d^2\delta}{dx^2} - \frac{B}{\delta^4} = \sigma K_\infty$ Using simplified form of curvature

So, what I am going to show next is from a research article where we have tried to measure we have tried to characterize the different forces present in a system. Conduct some experiments measure the film thickness profile accurately and try to see what is the value of Hamaker constant. And whether or not they are closed to that predicted from the theory and so, on. So, we will first go into the model the force field characterization model and the experimental say experiment is simple is that we have dipped a surface.

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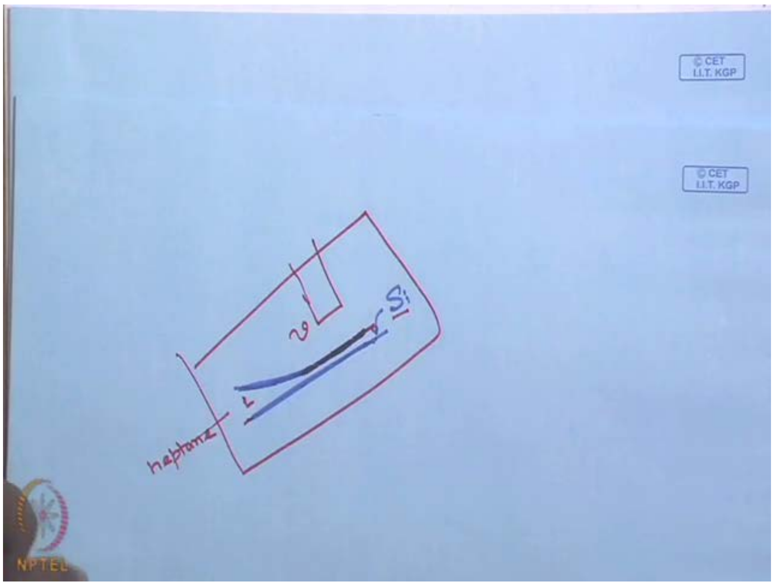

This is a silicon surface the reason that silicon was chosen is because the cleaning techniques of silicon vapors are well documented. And it has evolved over the years as a result of the requirement of the electronics industry. So, I have a liquid pool and a film forms on the silicon vapor and this is a vapor. So, this is enclosed in a chamber and such that the interaction the impurities from the ambient atmosphere cannot come and adsorb one silicon. So, the silicon is carefully cleaned and then liquid and this liquid for this specific experiments the liquid used towards heptanes. Ultrapure heptane and we are looking at the behavior of the liquid film we are measuring the liquid film using optical methods.

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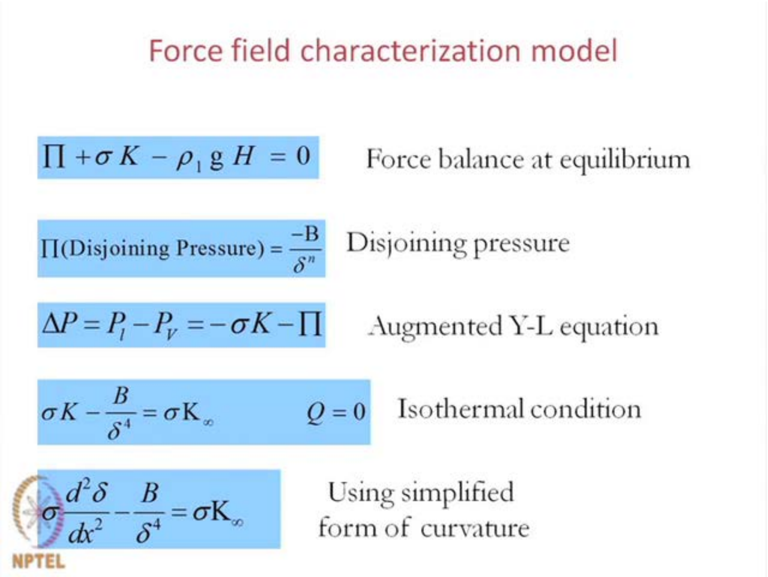

Force field characterization model

$\Pi + \sigma K - \rho_l g H = 0$	Force balance at equilibrium
$\Pi(\text{Disjoining Pressure}) = \frac{-B}{\delta^n}$	Disjoining pressure
$\Delta P = P_l - P_V = -\sigma K - \Pi$	Augmented Y-L equation
$\sigma K - \frac{B}{\delta^4} = \sigma K_\infty \qquad Q = 0$	Isothermal condition
$\sigma \frac{d^2\delta}{dx^2} - \frac{B}{\delta^4} = \sigma K_\infty$	Using simplified form of curvature

So, then we will talk about the optical method later, but if you look at the first equation it is the force balance at equilibrium which simply says that the if everything is at equilibrium; that means, the pressure is same everywhere. So, if the pressure is same then the sum of the disjoining pressure, the capillary pressure and the hydrostatic pressure must be equal to 0. We know how to express disjoining pressure as the function of delta to the power minus n, n being equal to n could be equal to 3 or 4. And a augmented young laplace equation can be used to predict the pressure jump across the liquid vapor interface. And I am going to spend some time on the fourth equation which is for an isothermal condition and which simply tells us which essentially is this, if I have a thin film.

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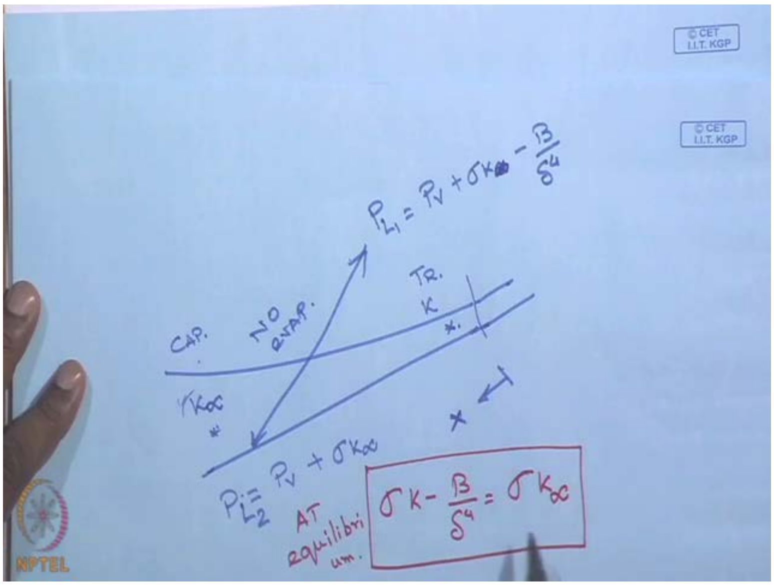

Let us say this is the inclined surface I have a film this from here onwards it is the adsorbed film. So, I am going to pick two points, one in the transition region and one in the capillary region. So, I the let us say the capillary region curvature is K and the transition region I am sorry the capillary transition region curvature is K and the capillary region curvature is called as K infinity. Why it is called K infinity is? That it has been shown experimentally and it is also it can also be shown theoretically is as we move away from the very thin part of the film. The curvature is going to at in a constant value and it is not going to be a function of X so, this value of K infinity is a constant.

So, if I write the young laplace equation then P l would be P v plus sigma K infinity and we do not have any disjoining pressure in this case. But over here this P l 2 and P l 1 is going to be equal to P v plus sigma K infinity and sigma K infinity minus B sorry sigma K minus B by delta to the power 4. Now, this since it is at equilibrium and there is no evaporation, if there no evaporation then there cannot be any flow at study state from point one to point two. So, P l 1 must be equal to P l 2 and what we get essentially then is that sigma K minus B by delta to the power 4 is equal to sigma K infinity. Now, if you look at this equation which is essentially a force balance equation at equilibrium this is extremely important.

At equilibrium when we do not have any evaporation when we do not have any flow then the product of local curvature times sigma minus B which is Hamaker constant delta is the film thickness must be equal to sigma K infinity where K infinity that is the constant curvature.

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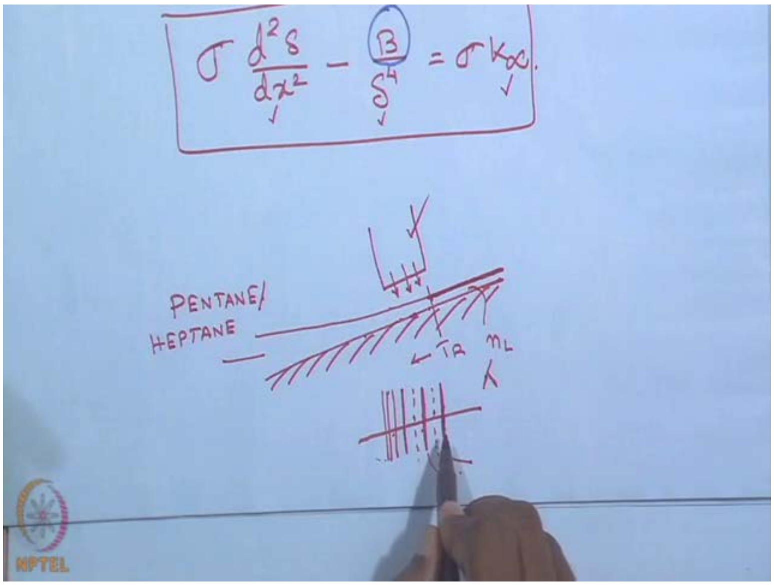

$$\sigma \frac{d^2\delta}{dx^2} - \frac{B}{\delta^4} = \sigma K_\infty$$

So, essentially now we can substitute the value of K the simplified value of K in this equation and what we get is sigma d 2 del by d x square. Neglecting the terms in the denominator since it is the value of the slope would be quite small and therefore, the denominator can be can be approximated by 1 is equal to sigma K infinity. So, this would be the starting point for experimental study. So, if you could measure the value of delta correctly if you can measure the value of delta then, it is possible to find out it is double derivative and we can also measure the value of K infinity. So, it is then possible to find out the unknown B which is the Hamaker constant.

So, this equation is therefore, the method the starting point for finding out the value of Hamaker constant and which has been used in the experiments. So, what we do is we take a silicon surface a thin film and the experiments that I am going to show here. The thin film used is maintained though similar studies with heptane as also we have done with heptane as well. So, it could be pentane, heptanes, octane, and etcetera. And a thin liquid film forms on the solid it moves forward and that equilibrium we have such a surface. Now, when we have such a surface then, we are going to have light or monochromatic light being monochromatic light will be incident on the film.

Now, we have a microscope and through the microscope using filter using a monochromatic filter we can have just a monochromatic light which is being shown on this. Now, when monochromatic light gets reflected from a film covered surface we are going to get alternate constructive fringes and destructive fringes. So, the interference phenomena will provide us with constructive and destructive fringes. So, what we are going to see here is that in the straight portion in the flat portion of the adsorb thin film, there would not be any interference fringes. But the moment the film starts to become curved that is at the junction at the beginning of the transition region onwards, I am going to see alternate dark and bright fringes those are the inter films fringes.

So, over here I am going to see the first dark fringe, then I will see a bright fringe another dark fringe, a bright fringe, dark fringe and so, on. So, as the film becomes thicker so, as I move towards the thicker portion of the film, the fringes will become close to each other. And after some point it is it will not be possible to distinguish between two adjacent bright, two adjacent maxima or minima. So, how far to what distance we can go depends on the magnification of the lens that we are using and the light level of operation. So, we get alternative dark and bright fringes now physics the optics tells us exactly what would be the thickness of the first or the zeroth dark fringe, the first bright fringe, the first dark fringe and so, on.

So, for this and the appearance of the zeroth dark fringe it depends the thick the it depends on whatever be the thickness at this point. Is dependent on n L that is what is refractive index of the liquid lambda which is the wavelength of light that is being used and so, on. So, using standard formulas of optics I know exactly what is the film thickness at this point what is the film thickness at the minima, maxima, minima, maxima and so, on. So, if I could digitize this picture; that means, if I can separate this picture into a number of pixels and do a scan what I would see is that the grey value which is a measure of the the light level at that point. So, after I digitize this I will draw it again clearly over here.

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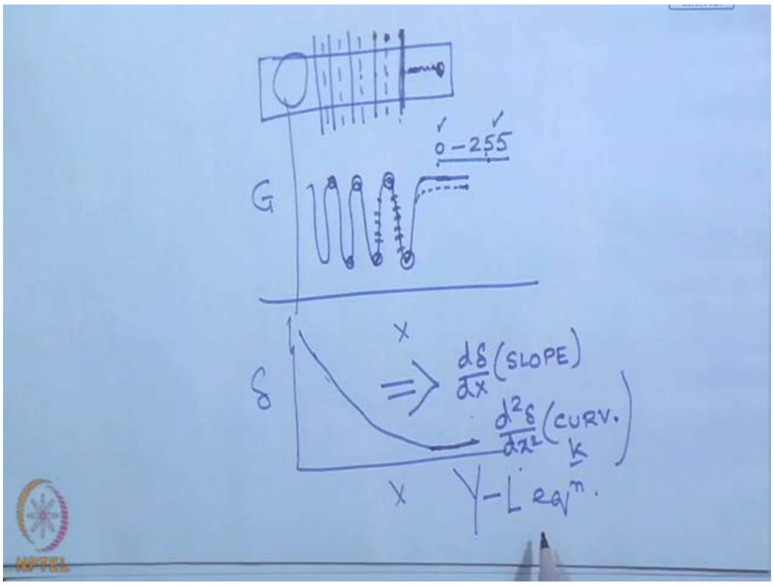

I have fringes the first dark fringe, the second, third, fourth and so, on these are the bright fringes in between. So, at discretely at these discrete points I know what are the thickness, but if I would like to know what is a thickness in between the points also. I need to use a technique called image processing what it does it is it takes the image of the fringes the dark fringe, bright fringe, dark fringe, bright fringe and so, on. And then it digitize this entire image into a number of pixels. So, each pixel can have a value from 0 to 225 depending on the intensity of the film the pixel, can have numerical values from 0 to 225 this being totally dark and this being totally bright. So, each individual pixel acts as a light sensor.

So, we look at the value assigned to the pixel and find out what is the reflectivity of the surface now we understand that as the film cover the solid surface it is reflectivity will increase. So, if I plot the grey values that is 0 to 225 of this of every pixel from here to hear what we see is more or less a constant value of the reflectivity. Since it is a it has adsorbed film then it drops to a minimum corresponding to this and then it moves up corresponding the bright, falls down corresponding to this point moves up and so, on. So, this is how the pixel the grey values of each pixel would look like. So, this is my these are the points at which I know what is the value of the thickness.

But using some other analysis techniques that we have developed it is also possible to find out the thicknesses of in between points as well. And if the adsorbed film thickness is more than it is going to start from here the reflectivity of the film covered surface will be even less. So, finding out the pixel at every point at a finding out the grey values of every pixel points; that means, finding out the reflectivity of every point it is possible now to convert the pixel data into film thickness data. So, delta versus X starts at a value which is the adsorbed thin film thickness and increases till it reaches the capillary part of the meniscus. So, now if I can take the data carefully I have a film thickness profile.

Now, this film thickness profile can now be numerically differentiated to find out d del d X which is essentially the slope of the film or d 2 del d x square which essentially is the curvature or k of the film. So, if we can find out the curvature at every point then I am in a position to use young laplace equation to obtain the unknown value of the Hamaker constant.

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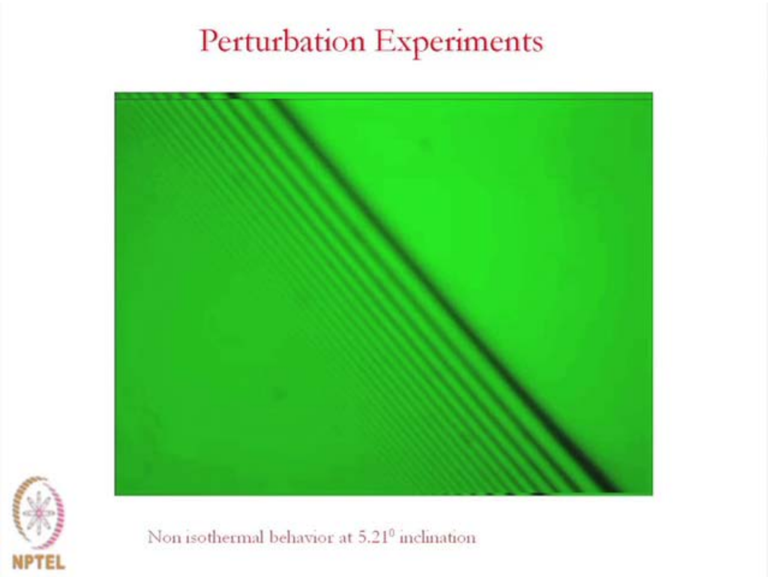

Perturbation Experiments

Non isothermal behavior at 5.21^{0} inclination

So, this is what is done in this and I am showing you the some of the experimental results of our study where you can see the alternate dark and the bright fringes. And what happens is if you perturb the system that if you apply a heat flux to the system what happens is the film starts to move forward and backward. So, the film starts to oscillate when you have a heat source in front of the adsorbed thin film. So, whenever you add heat the film retracts and you can see that the fringes will move back when you switch off the heats of source the film floods forward. So, we can make the film move forward and backward, move we can make the film oscillate and oscillate in between the two points.

Now, the film is extremely sensitive to minutest to the minute changes in temperature of the ambient it can be shown theoretically. That a change of temperature of ten to the power minus three degree centigrade is sufficient to cause departure from the thin from it is equilibrium position. So, we would like to find out the case in which the film is right at equilibrium and how do we do that the way we do that is we perturb the system. We perturb the system by alternatively subjecting it to a very small heat flux and switching it back to zero. So, the film goes from a condensation cycle from an evaporation cycle when the heater is switched on to a condensation cycle when the heater is switched off.

Now, you remember as I have discussed as I have told you before an ideal equilibrium condition is that in which there is no evaporation from the thin film. So, what we were hoping by this successive evaporation and condensation cycle to force the film to go from evaporation to condensation cycle. And back this back and forth motion and taking pictures at a very small time intervals we would be able to capture a condition in which it is at perfect equilibrium. So, I since I it is not possible for me to isolate the system from it is surrounding such that even a small temperature of ten to the power minus three degree centigrade small temperature change can be prevented.

The other option available to me is let it let the film oscillate as a result of a small imposed heat flux and take keep on taking pictures. And you if you are lucky you would be able to capture a point where the two film where the two forces the force which sucks the like liquid towards a thin towards adsorbed film. That is the disjoining pressure which is denoted by B by del delta to the power n, and the capillary pressure which pulls the liquid away this is sigma K. So, there would be a condition in which B by delta to the power n would be exactly counter balanced by sigma K. And when that you think of the thin film as a rubber band it is being pulled in the thinner part by a force which is the disjoining pressure.

And another force pulls it to the thicker part which is the capillary pressure when these two are equal the film is at equilibrium there is no flow and you do not have any evaporation. So, the objective of the experiments was to perturb the film take picture analyze the picture to see what is the value of disjoining pressure and what is the value of capillary pressure can we find a situation in which both of them are very close if not equal. And that value of B so, I have B by delta to the power 4 on one side and sigma K on the other side.

So, at equilibrium what I get then is B by delta to the power 4 is equal to sigma K. So, if these two are equal then I can I can measure K, I can measure delta so, the unknown B can be evaluated directly. So, that was the idea that was the philosophy behind these perturbations experiments and I will show you a move movie how the film oscillates. So, here the film moves forward since the heater is switched off now, the film has started moving backward since we have switched on the heater. And you see there in the frontal part the adsorbed film disappears and the film has moved back and then at another point of time when the film is when they. So, this is when the film has moved back and this must be a large dust particle around which the film has grown.

And then it will when the when this is switched off when the heater over here which is somewhere over here is switched off then the film will move forward again. So, this is how the film will oscillate now this is the summary of the results.

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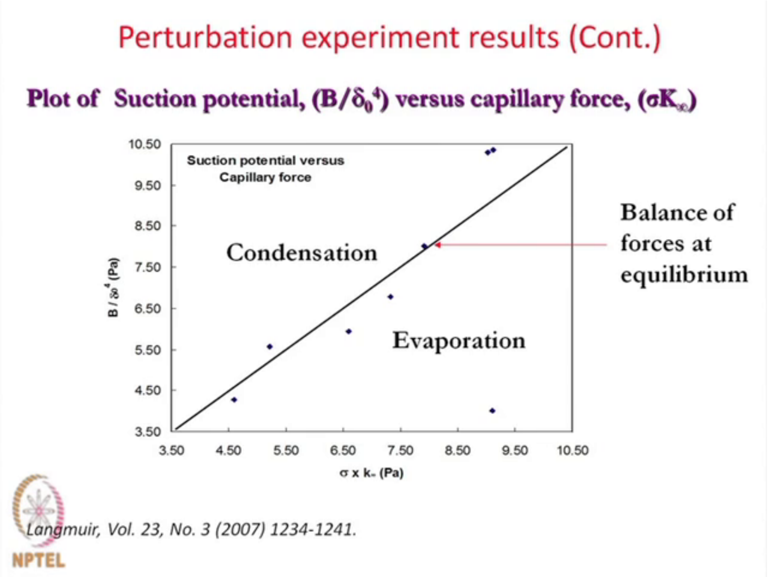

Perturbation experiment results (Cont.)

Plot of Suction potential, (B/δ_0^4) versus capillary force, (σK_∞)

Balance of forces at equilibrium

Langmuir, Vol. 23, No. 3 (2007) 1234-1241.

Where you see that on the left hand side I have B by delta 0 the adsorbed film thickness to the power 4 which has unit is of pressure this is Pascal. And in the in the x axis is sigma K infinity where which is the capillary pressure. So, if the capillary force is more the film retracts and we get evaporation. If B delta 0 to the power 4 is more the film moves towards the thicker film moves towards the adsorbed film and we get condensation. So, B by delta 0 to the power is called the suction potential and sigma K infinity is the capillary force when these two forces are balanced we get an equilibrium situation. And when we get an equilibrium situation then B by delta 0 to the power 4 is equal to sigma K infinity.

So, that is a 45 degree the straight line that you see is the 45 degree line. And you can see that the points even though they are the points are not exactly on the 45 degree line except for one point which is marked by the red arrow. So, that point is denotes a situation in which the two forces are balanced and can this situation can be called an equilibrium situation.

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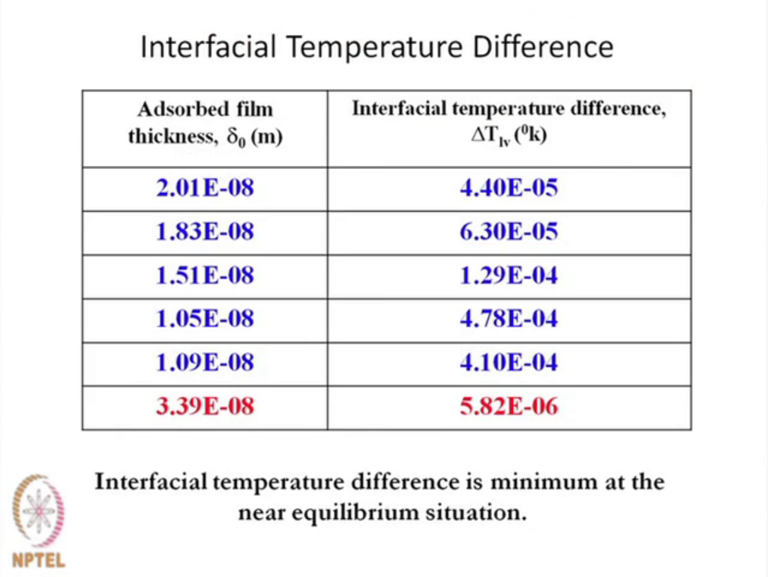

Interfacial Temperature Difference

Adsorbed film thickness, δ_0 (m)	Interfacial temperature difference, ΔT_{lv} (^{0}k)
2.01E-08	4.40E-05
1.83E-08	6.30E-05
1.51E-08	1.29E-04
1.05E-08	4.78E-04
1.09E-08	4.10E-04
3.39E-08	5.82E-06

Interfacial temperature difference is minimum at the near equilibrium situation.

If you look at the interfacial temperature differences there you would see that the difference the red one, the difference the last one, the difference in interfacial temperature, difference as calculated from the experimental data is two orders of magnitude smaller than the other cases. So, interfacial temperature difference is minimum at the near equilibrium situation I call it as near equilibrium situation it is not exactly at equilibrium, but it is a near equilibrium situation. And what we have seen is that this specific point gives us a value of Hamaker constant or dispersion constant which is close to very close to the value that predicted from the d l p theory.

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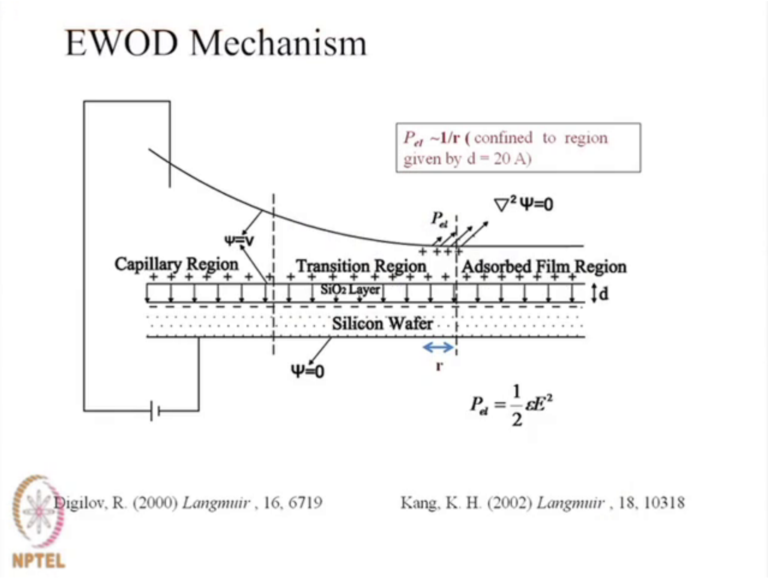

EWOD Mechanism

$$P_{el} = \frac{1}{2}\varepsilon E^2$$

Digilov, R. (2000) *Langmuir* , 16, 6719

Kang, K. H. (2002) *Langmuir* , 18, 10318

And I would quickly draw your attention to another situation in which we have E W O D as we have discussed before E W O D superimposed on a partially wetting film. So, in the sense E W O D application of electric field forms a wetting reduces the contact angle. So, if I can have E W O D on a partially wetting film then the contact angle will decrease and we should be able to have more spreading of the thin film so, this is denoted by this. So, the extra pressure which we denoted as P electric which pulls the liquid towards the adsorbed thin film region.

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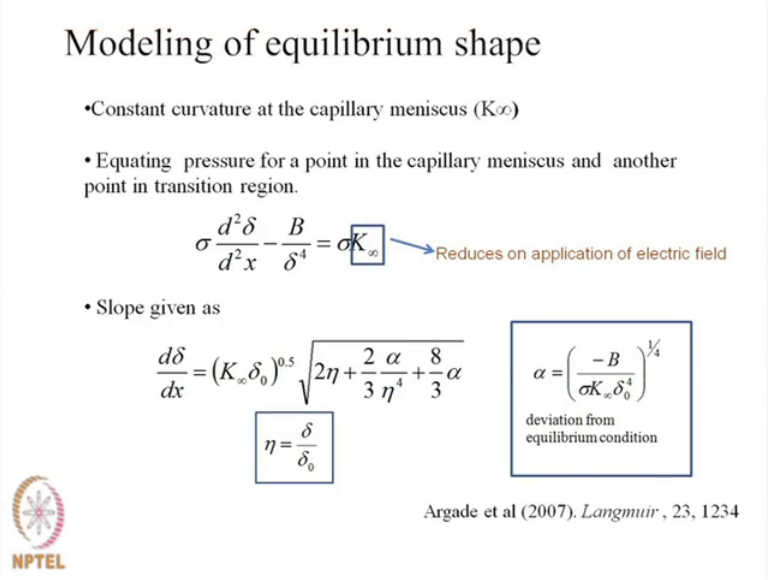

Modeling of equilibrium shape

- Constant curvature at the capillary meniscus (K∞)
- Equating pressure for a point in the capillary meniscus and another point in transition region.

$$\sigma\frac{d^2\delta}{d^2x} - \frac{B}{\delta^4} = \sigma\boxed{K_\infty} \rightarrow \text{Reduces on application of electric field}$$

- Slope given as

$$\frac{d\delta}{dx} = (K_\infty\delta_0)^{0.5}\sqrt{2\eta + \frac{2}{3}\frac{\alpha}{\eta^4} + \frac{8}{3}\alpha}$$

$$\boxed{\eta = \frac{\delta}{\delta_0}}$$

$$\alpha = \left(\frac{-B}{\sigma K_\infty \delta_0^4}\right)^{1/4}$$

deviation from equilibrium condition

Argade et al (2007). *Langmuir* , 23, 1234

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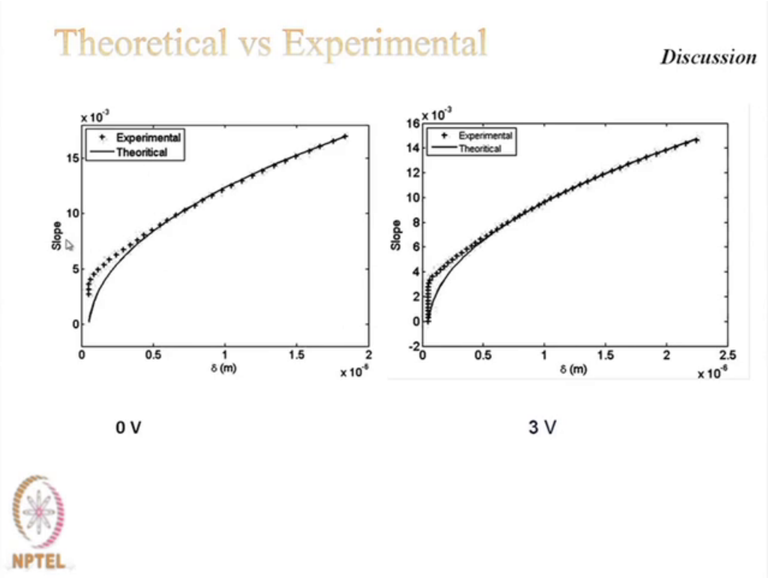

Theoretical vs Experimental

Discussion

0 V

3 V

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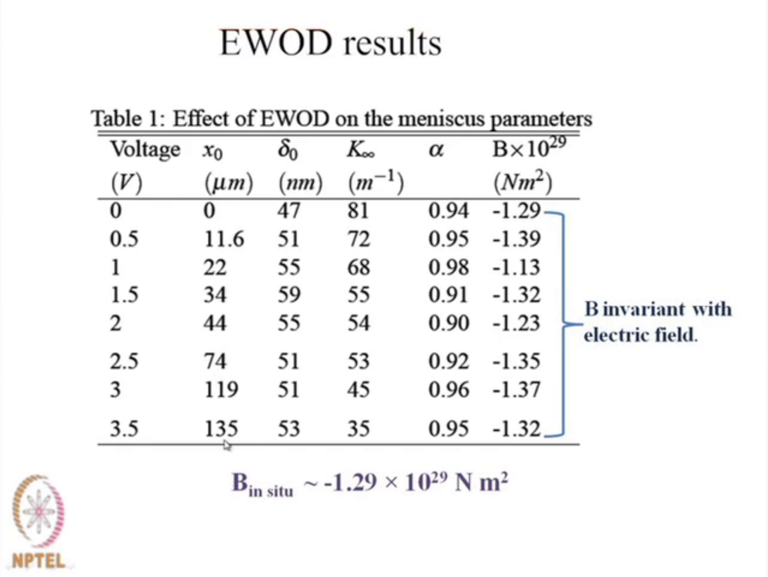

EWOD results

Table 1: Effect of EWOD on the meniscus parameters

Voltage (V)	x_0 (μm)	δ_0 (nm)	K_∞ (m^{-1})	α	$B \times 10^{29}$ (Nm^2)
0	0	47	81	0.94	-1.29
0.5	11.6	51	72	0.95	-1.39
1	22	55	68	0.98	-1.13
1.5	34	59	55	0.91	-1.32
2	44	55	54	0.90	-1.23
2.5	74	51	53	0.92	-1.35
3	119	51	45	0.96	-1.37
3.5	135	53	35	0.95	-1.32

B invariant with electric field.

$B_{in\ situ} \sim -1.29 \times 10^{29}$ N m^2

So, we can we can do similar analysis as we have done before and then they this equation, in this equation the K infinity it reduces on application of electric field. And what we have is the comparison between the theoretical value of slope and the experimental value of slope and the comparison tells gives us the value of the Hamaker constant. So, these are some of the results which I would like to point out this is the voltage. And this is the amount of advancement of the thin film due to the application of voltage and as this increases you can see delta 0 also increases. So, when the film moves forward the value of delta 0 increases. The value of K infinity decreases when the voltage is applied which is understandable because the film becomes more wetting.

If the film becomes more wetting then the value of K infinity has to decrease and the value of dispersion constant it is more or less constant. And it is it shows that the B the dispersion constant is invariant with the electric field which it should be and the value can be calculated in situ the key word here is in situ to be of the same order as that predicted from the d l p theory. So, in this specific lecture I wanted to convey to you is that what happens in the very thin film is extremely important, in many technologically important processes starting from lubrication, starting from heat transfer, film coating and so, many other cases.

And the physics involved is extremely intricate because we have to take into account the intermolecular forces which are present in the system. And the balance of intermolecular capillary forces and electric forces, if present electric field if present tells us what would be the shape of the film. And the shape dependent force at equilibrium tells us about whether the film is going to be a wetting film or a non wetting film. And thereby vastly affecting the property the application of such a film in real life situations. So, small is important ultrathin films are extremely important as far as the micro scale transport processes are concerned. So, that is the message which I would like you to take from this class thank you.