Instability and Patterning of Thin Polymer Films

Prof. R. Mukherjee
Department of Chemical Engineering
Indian Institute of Technology, Kharagpur

Lecture No: # 02

Introduction (Contd.)

Welcome back. I hope you enjoyed the first part of the introduction, as I promised that since it is rather new subject, so we will get going with an extended introduction and I will talk about some more areas, where patterning of polymer films or particularly Meso-scale patterning is important. Then I will start talking today; give you some basic glimpses on what exactly is instability? What exactly instability means? In particularly, in the context of a thin polymer film or a thin film in general, what type of instability we are looking at?

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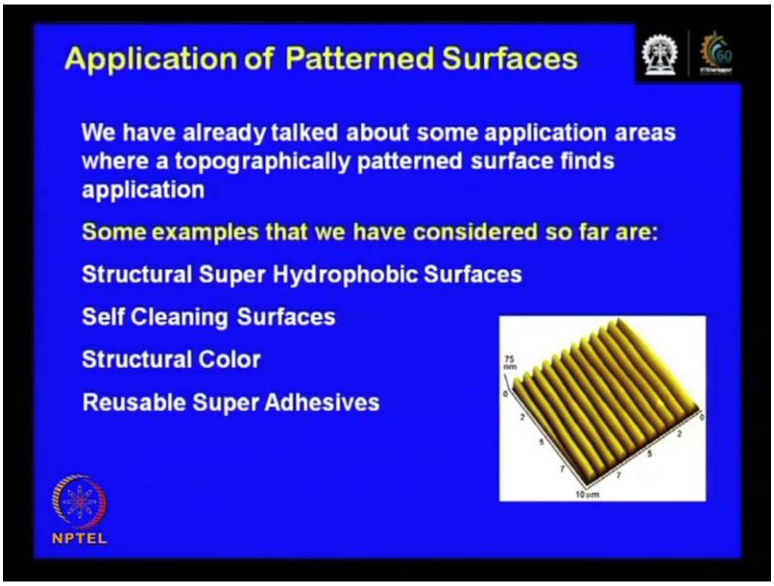

Application of Patterned Surfaces

We have already talked about some application areas where a topographically patterned surface finds application

Some examples that we have considered so far are:

Structural Super Hydrophobic Surfaces

Self Cleaning Surfaces

Structural Color

Reusable Super Adhesives

So, in the previous lecture we have already talked about some application areas where topographically patterned surfaces with meso-scale find application. Some examples that we have considered so far are structural super hydrophobic surfaces, self cleaning surfaces, structural colour and reusable super adhesives etcetera. By topographically patterned surfaces we essentially mean some surfaces like this.

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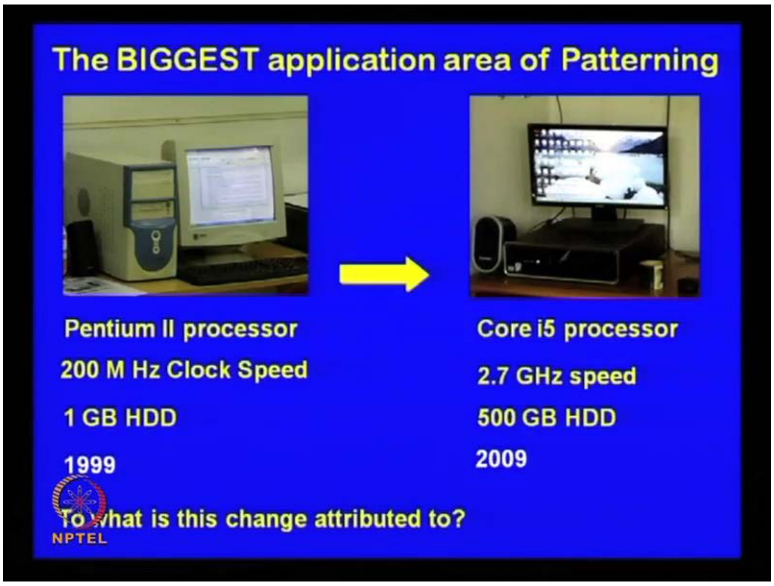

The BIGGEST application area of Patterning

Pentium II processor

200 M Hz Clock Speed

1 GB HDD

1999

Core i5 processor

2.7 GHz speed

500 GB HDD

2009

To what is this change attributed to?

This is all fine. I hope you had some idea about what type of application we talk about. But can you think of at this point of time, the biggest application area of patterning or where topographically patterned surfaces find applications. These areas or these objects or items, we use extremely, intensively and I am sure you are seeing this lecture in one such item. Well, I am referring to microelectronic industry. I do not know how many of you know. Probably, many of you do know that microelectronic industry is the biggest user of a topographically patterned surfaces or patterning techniques.

Now, this is a picture of something not very really and does not come from the prehistoric era. This is a Pentium two processor, a personal computer with a Pentium two processor, which was pretty much the most up to date commodity to possess some 10 years back. Now, it had a clock speed or a processor speed of roughly 200 mega hertz and a hard disk capacity of roughly one gigabyte. This was late 90s or early twenty-first century. Today, the thing shown on the right is pretty common; I core, I 5 processor, I seven processor, clock speed ranging between 2.5 gigahertz to 10, 3 gigahertz it is pretty common, 500 gigabyte hard disk, well terabyte capacity memory. This has also come in.

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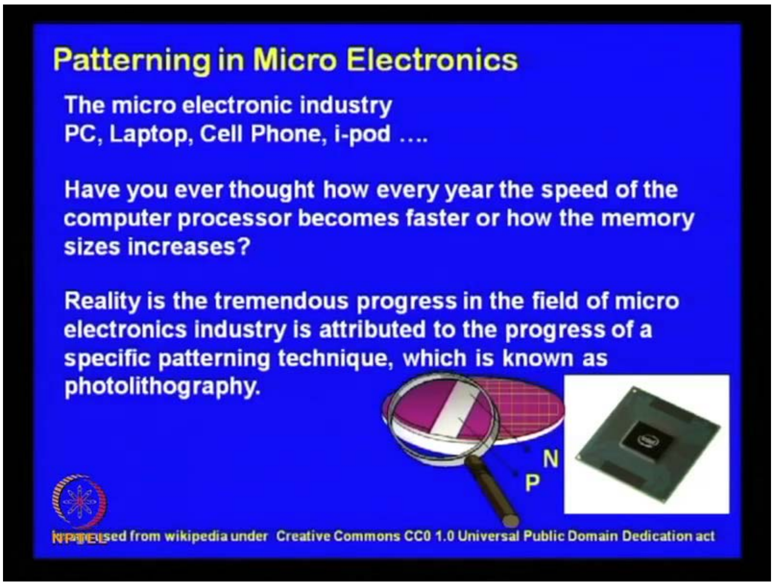

Patterning in Micro Electronics

The micro electronic industry
PC, Laptop, Cell Phone, i-pod ….

Have you ever thought how every year the speed of the computer processor becomes faster or how the memory sizes increases?

Reality is the tremendous progress in the field of micro electronics industry is attributed to the progress of a specific patterning technique, which is known as photolithography.

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Not only these, but a whole lot of things; PC laptops, cell phone, I pod, have you ever considered with every passing year why does your laptop becomes lighter though it becomes faster and its display resolution increases. So, have you ever thought how this is possible or what really is behind this, before you loosely say that well there is a revolution and very fast growth in the area of microelectronics. Well, the reality is the tremendous progress in the field of microelectronic industry, is attributed to progress of a specific patterning technique, which is known as Photolithography. If you remember the contents part of our talk, we have promised that we will discuss this technique in somewhat detail, so that you have an idea about what it is. Just to give you an idea of what, where, exactly this patterning comes into play, you must be knowing that most of the micro, I mean the computer chips or the basic hardware, is essentially semiconductor devices. This is all, till date silicon is the most preferred material. It is one of the reason you have Silicon Valley in California and Bangalore is noted as our own Silicon Valley.

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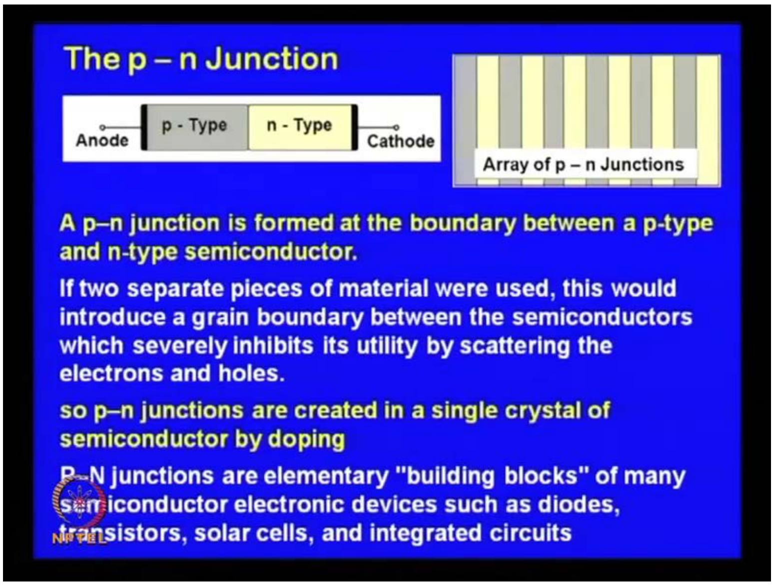

The p – n Junction

A p–n junction is formed at the boundary between a p-type and n-type semiconductor.

If two separate pieces of material were used, this would introduce a grain boundary between the semiconductors which severely inhibits its utility by scattering the electrons and holes.

so p–n junctions are created in a single crystal of semiconductor by doping

P–N junctions are elementary "building blocks" of many semiconductor electronic devices such as diodes, transistors, solar cells, and integrated circuits

Even, if you, I hope you have some idea about what exactly is a semiconductor, a conductor and how it is different between a conductor and an insulator? It can be sort of attributed to the band gap or in terms of forbidden gap. I strongly recommend you to refer to some basic physic text where you can find out why silicon is a very nice semiconducting material. Now, I am sure, you know that in order to construct a semiconductor circuit, the fundamental thing, you need to have is a junction between a p-typeand an n-type semiconductor, which is known by as the p-n junction.

A p-n junction is essentially formed at the boundary between a p-type and an n-type semiconductor. However, if two separate pieces of material are used, it would introduce a grain boundary between the two semiconductors, which severely inhibits its utility, due to scattering of the electron and hole. It sort of hinders the transport electron transport, so p-n junctions are always created in a single crystal or semiconductor.

Typically, the method by which it is done is known as Doping. The details about these processing techniques, is beyond the course of this particular lecture, which we are not going to talk about. You may note that p-n junctions are elementary building blocks of many semiconductor electronic devices such as diode, transistor, solar cells and most importantly integrated circuits. So, essentially what you want to have I mean see one p-n junction is not going to suffice. Not going to do any purpose, so essentially what you want to have is an array of p-n junctions, so every interface between a p-type domain and an n-type domain, acts as a junction.

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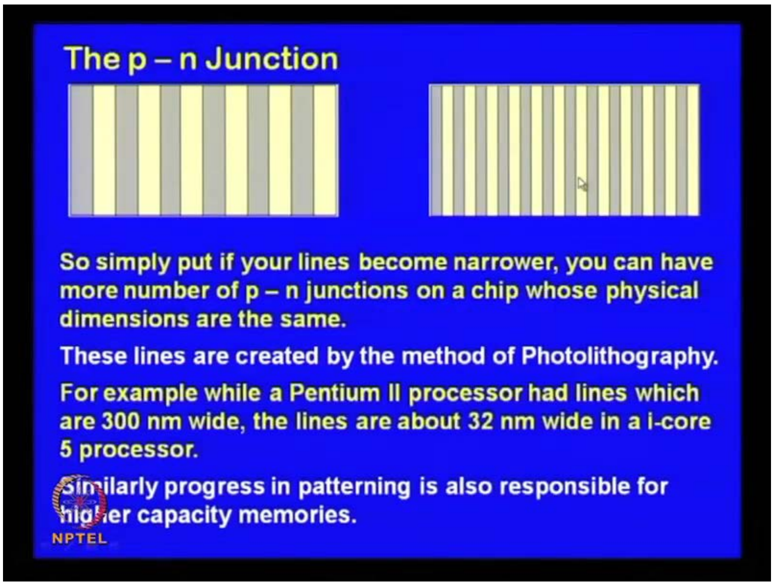

The p – n Junction

So simply put if your lines become narrower, you can have more number of p – n junctions on a chip whose physical dimensions are the same.

These lines are created by the method of Photolithography.

For example while a Pentium II processor had lines which are 300 nm wide, the lines are about 32 nm wide in a i-core 5 processor.

Similarly progress in patterning is also responsible for higher capacity memories.

Now, here comes the trick. Suppose, if you have a physical size of the I C chip or a chip and simply put, if your lines becomes narrower, you can have more number of p-n junctions on a chip whose physical dimensions are the same. Now, here you see the two, we have two chips, which are present. One has wider domains, the other has narrower domains. Therefore, what happens is on the same physical size of the chip, you can plug, you can sort of have more number of p-n junctions. Now, in order to achieve this, what are necessary is your strips or the line with each of the p and n-type domains has to become narrower.

Now, this I mean, how does one create these types of narrow domains? This is what is achieved, eventually what we will discuss subsequently. Now, in one of the lectures is achieved by the technique of photolithography. Of course, doping is done, but the areas where suppose you start off with a p-type semiconductor and you eventually dope it with n-type domains in a preferential manner that is guided by photolithography. Now, for example, when we talk about a Pentium-two processor, which is some 10 years old concept, the lines were around 300 nanometre wide and the lines are now down to around 30 nanometre for an I core 5 processor. Similarly, progress in patterning is also responsible for the higher capacity of memories is what you see.

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Organic Electronics

Flexible Electronics

Lower Cost as compared to Silicon based conventional electronics

Patterning technology

RFID Tag

CD, DVD, Blue Ray Disc

TFT LCD Str.

Now, apart from silicon electronics, there is a lot of recent advancement in the so called organic electronics, which typically rely on polymeric material. One of the biggest application areas is the flexible electronics where you think of or start of thinking of items like flexible display or something like that. Another area where polymer electronics finds extensive application is on the touch pad of your smart phones.

Here also you need extensive patterning techniques to achieve the desired functionalities. Also polymer electronics is thought as a lower cost alternative for silicon electronics for throw away items like RFID tags, also low cost optical storage devices like CD, DVD blue ray disc etcetera are all fabricated on polymer. So, here you see that patterning technique on polymer becomes pretty significant.

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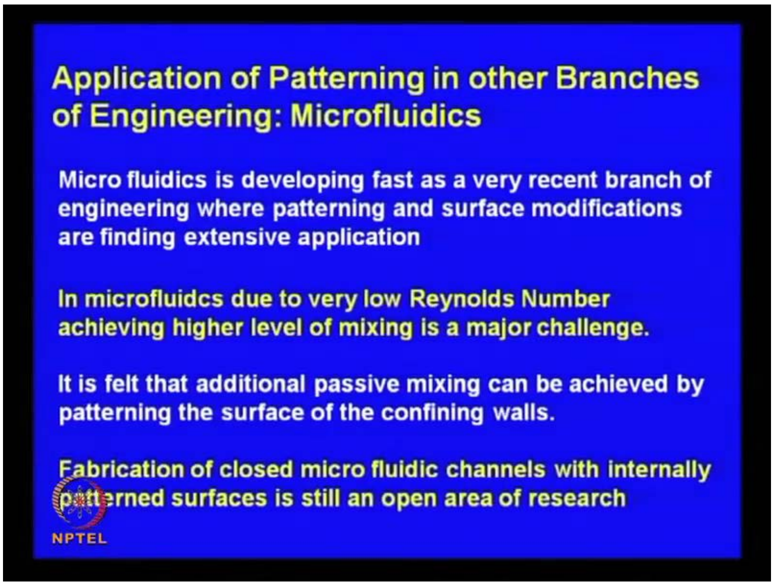

Application of Patterning in other Branches of Engineering: Microfluidics

Micro fluidics is developing fast as a very recent branch of engineering where patterning and surface modifications are finding extensive application

In microfluidcs due to very low Reynolds Number achieving higher level of mixing is a major challenge.

It is felt that additional passive mixing can be achieved by patterning the surface of the confining walls.

Fabrication of closed micro fluidic channels with internally patterned surfaces is still an open area of research

There are other branches of engineering where also patterning has significant roles to play. For example, one such area, which is a very advanced area and itself, is Microfluidics. Microfluidics is evident from the name itself, microfluidics deals with the branch of fluid mechanics which deals with very little volume of fluid. So, essentially its developing fast and as a very recent branch of engineering, where also we find that the patterning and surface modification find or likely to find extensive application. Now, whenever you talk about fluid mechanics the first things that come to your mind is the Reynolds number. That is what actually as an engineer or as a chemical engineer; you know how to distinguish a flow; the expression for which goes as D v rho by mu. Now, the issue is that the moment you talk about a micro scale conduit, for example, where a flow is occurring or something like that.

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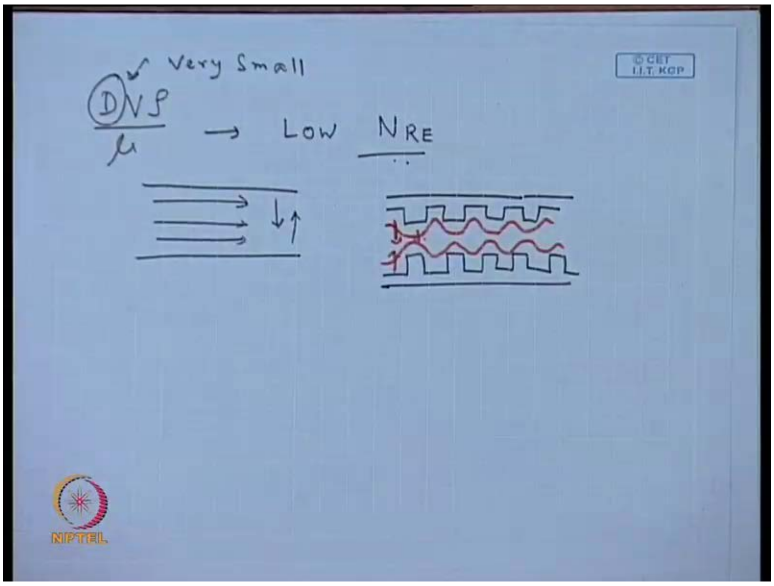

What happens is the parameter out of this D V rho by mu, this D becomes very small. So, this eventually leads to a very low Reynolds number, which implies that achieving certain phenomena in the microelectronic, microfluidic domain becomes extremely difficult and one of them is mixing. So, what is regarded or theoretically predicted and very little experimental evidence is available as of now, is that additional passive mixing can be achieved by patterning the surface of the confining wall. So, essentially you have laminar flow because of low Reynolds number, so that nature of the flow is streamline, so there no literal mixing or transverse mixing.

So, what one can achieve in principle or what can be possible that if you take a conduit whose walls are sort of patterned, then you artificially force your flow to follow the contours of the conduit and eventually they sort of there is some sort of an interaction of the transverse mixing. So, these are some of the concepts where which also rely on patterning.

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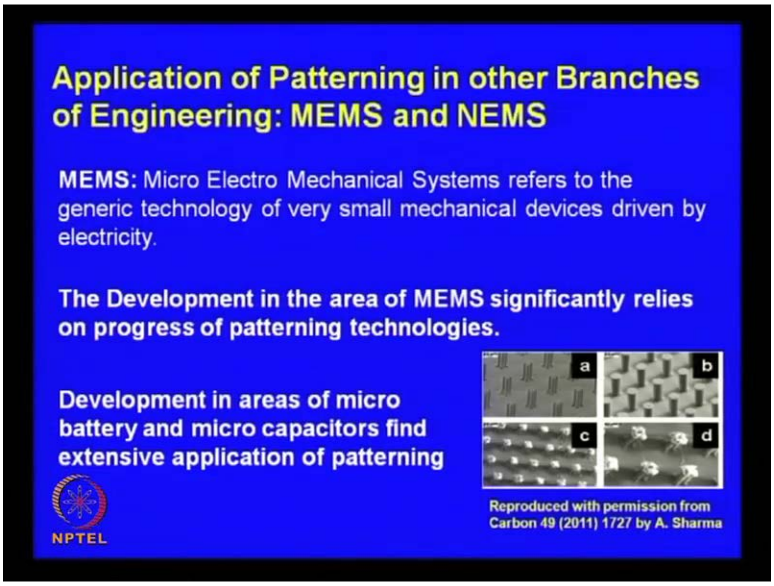

Application of Patterning in other Branches of Engineering: MEMS and NEMS

MEMS: Micro Electro Mechanical Systems refers to the generic technology of very small mechanical devices driven by electricity.

The Development in the area of MEMS significantly relies on progress of patterning technologies.

Development in areas of micro battery and micro capacitors find extensive application of patterning

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Now, to be honest that fabrication of closed microfluidic channels particularly with circular geometry with internally patterned surfaces is still an open area of research and lot of activity is going on and which has distinct potential application areas in future.

There can be other areas like MEMS, which is the acronym for Micro Electro Mechanical System, where one looks at very small components or mechanical devices driven by electricity. Now, of course, one talks about areas like NEMS, which is Nano Electro Mechanical System. The areas of the progress in the areas of MEMS is also a significantly dependent on the progress of patterning technologies, entities or items like micro battery, micro capacitors etcetera, also require robust patterning techniques. What comes out is that for many of the applications other than the microelectronic applications you need topographically patterned surfaces to a large extent.

For many of these areas, which are not exactly microelectronics, the fidelity or the quality requirement may not be as stringent as that is necessary in the microelectronic industry, but one may want to have bulk scale nanostructures, where some amount of defect or might be allowed or some loss of fidelity is acceptable. So, the techniques like photolithography, which are extremely costly, very capital intensive, may not be the optimum or optimal choice for them. So, eventually they are and one comes up with polymer specific techniques for patterning, which we will eventually talk in course of our lecture, which goes by that broader class of techniques known as soft lithography techniques.

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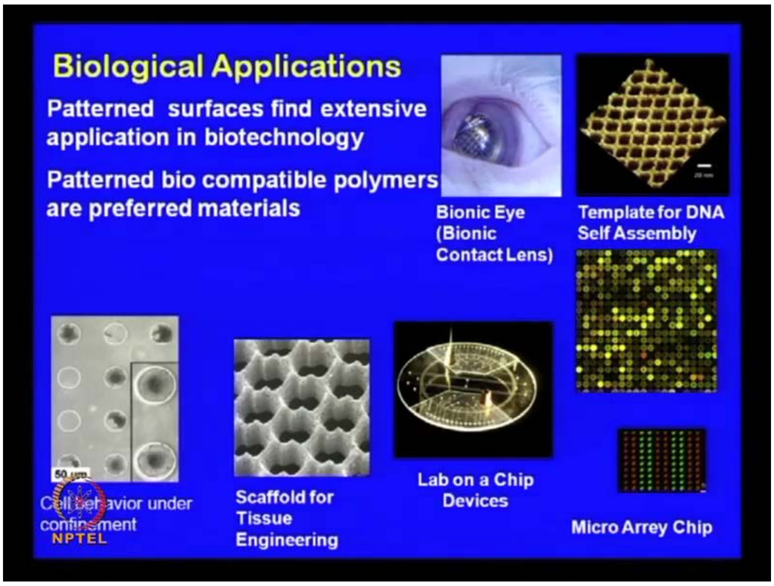

Biological Applications

Patterned surfaces find extensive application in biotechnology

Patterned bio compatible polymers are preferred materials

Bionic Eye (Bionic Contact Lens)

Template for DNA Self Assembly

Cell behavior under confinement

Scaffold for Tissue Engineering

Lab on a Chip Devices

Micro Arrey Chip

Now, before moving on to those aspects, let me also tell you that biological of the pattern topographically or pattern polymer films or pattern surfaces find a whole lot of application in biological areas. For example, bionic eye, which sort of promises bionic contact lens, promises people with a retinal defect to have vision back, template for DNA assembly, lab on a chip devices, which is essentially a combination between biotechnological application and microfluidic application, cell behaviour, scaffold for studying cell behaviour under confinement, scaffolds for tissue engineering and stemcell research, microchip array to investigating (( )) hybridization.

All these application areas require topographically patterned surfaces. One key requirement for biotechnological or biological application would be that the material you take has to be biocompatible. There are biocompatible polymers, so patterning with biocompatible polymers eventually becomes an important area, which can sort of take care or cater to the biological application or biotechnology applications.

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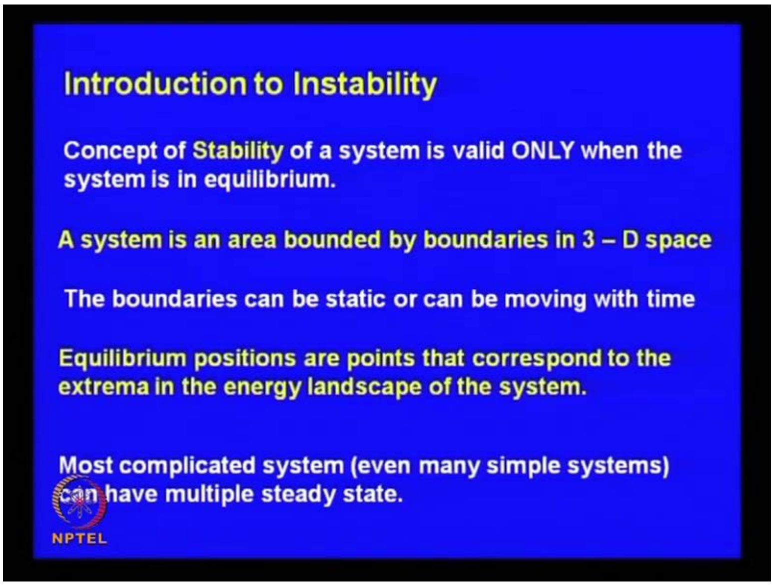

Introduction to Instability

Concept of Stability of a system is valid ONLY when the system is in equilibrium.

A system is an area bounded by boundaries in 3 – D space

The boundaries can be static or can be moving with time

Equilibrium positions are points that correspond to the extrema in the energy landscape of the system.

Most complicated system (even many simple systems) can have multiple steady state.

Now, if you look at the name of the course, we talk about the patterning and instability. As of now, I gave you some bit of basic introduction about patterning which we are going to expand in detail in the subsequent lectures. Now, let me introduce you to the concept to basic concept of instability. What exactly we mean by instability? Now, concept of stability of a system is valid; the first thing to realize that the concept of stability of a system is valid only when the system is in equilibrium. Now, that particular sentence written above contents the word system, so it is important to define what is a system. We can consider in very simple words that a system is a area bounded by boundaries in 3-D space.

Now, there is no restriction that these boundaries have to be static, so these boundaries can be static or can be even moving with time. What exactly is equilibrium? We as an engineer always understand what exactly equilibrium is, we have some gross idea. For example, if you talk in terms of reaction kinetics, you know that when the rates of the forward reaction and the backward reaction matches, probably that is where a kinetic equilibrium is attained. But, typically or generically speaking, equilibrium positions are points that correspond to the extreme in the energy landscape of the system, what I will take up in a minute, and it is also known many of you may appreciate that most complicated real life systems as well as many simple systems also, in day to day life can have multiple steady states.

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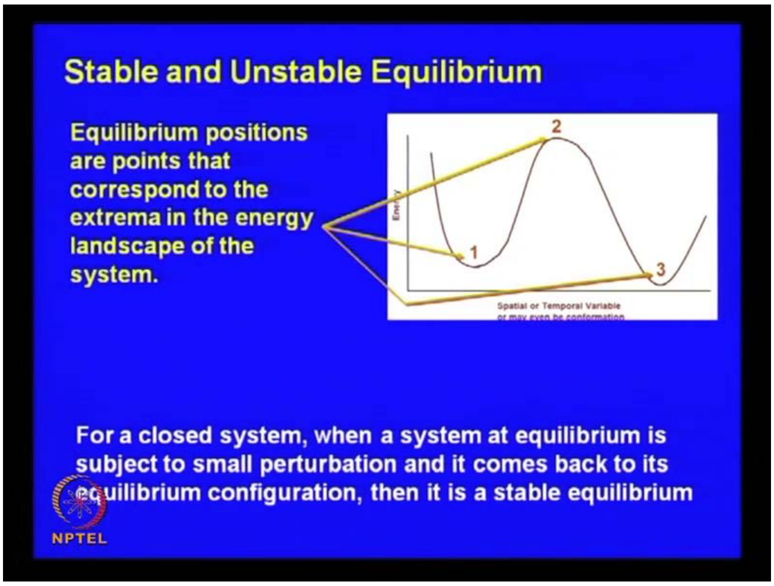

Stable and Unstable Equilibrium

Equilibrium positions are points that correspond to the extrema in the energy landscape of the system.

For a closed system, when a system at equilibrium is subject to small perturbation and it comes back to its equilibrium configuration, then it is a stable equilibrium

So this is what a typical equilibrium curve or energy curve might look like, the y axis is sort of the energy of the system. Of course, in order, to investigate or comment about the equilibrium, you need to define the energy of a system in, as a function of the atoms, which can affect the equilibrium. This energy can be potential energy, it can be combination of potential and kinetic energy or energy in various other forms can also be considered. The x axis can be essentially is the confirmation, so one may want to look at the stability of a system as a function of its confirmation. I will give you a very simple example for that immediately, but it can also be some special or temporal variable.

Now, if you refer to the example, the definition we talked about the equilibrium, which are the extreme on the energy curve. So, going by that way you have three possible equilibrium points in this curve. Those correspond to points are marked as 1, 2 and 3. Now, if you look carefully there is already a difference, some sort of a qualitative difference you can pick up between 1, 2 and 3. While 1 and 3 correspond to the minima in the energy curve, 2 correspond to maxima. So, how do we distinguish it? Reality is that all while all the three of them are equilibrium points, number 2 point, number 2 corresponds to an unstable equilibrium, while points one and three correspond to stable equilibrium. How do we define that or understand that? It is very simple. For a close system, when a system at equilibrium is subjected to a small perturbation and it comes back to its earlier configuration then it is a stable equilibrium.

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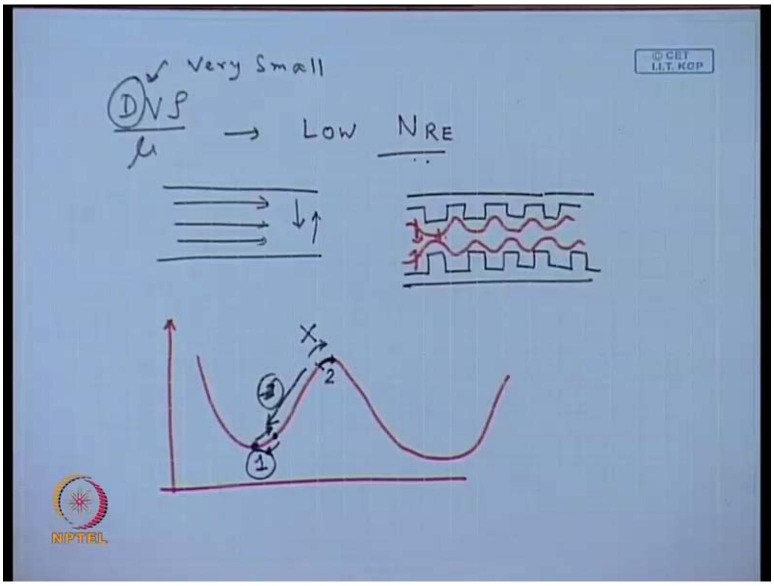

It is something very simple. Suppose, we reproduce this curve qualitatively here, so you have a point here, which is at the equilibrium position. You perturb it little bit, so it is going to follow the energy curve, so you leave, take it up to there and leave it so. Eventually, it comes back to its original configuration. Therefore, the point one indeed refers to a stable equilibrium. in contrast, if you have a point at point 2 and you perturb it a little, well you have actually put it on the slope. So, it is not going to come back to this point, but it is going to go down all the way to the other steady state at one. Therefore, point number 2 is an unstable equilibrium.

Now, continuing with that therefore, we can see that both point 1 and point 3, refer to stable equilibrium configurations. But, is there any difference between the two or the two are identical? Reality is if you look at the graph carefully, you will find that the value of the dependent variable that is energy for point 3 is lower than that of point 1. Now, we know that every natural process eventually tries to attain the minimum energy configuration. So, point 3 corresponds to a lower energy configuration as with respect to point 1. So, point 1 at if you have a system where you have multiple stable equilibriums then all the equilibrium positions which do not correspond to the lowest energy configuration are termed as metastable equilibrium. So, in the in this particular figure point 1 is a metastable equilibrium. It is a stable equilibrium, but it is a metastable one; Point 3 is the stable, most stable equilibrium or it corresponds to the scenario where the minima in the global minima in energy curve is attained.

You may wonder what exactly the difference is. So, before I come to a simple example, the other way you can also look at is that it is possible for one system to hop from one stable equilibrium to the other. So, in principle a system can hop from metastable equilibrium one to stable equilibrium three, but this hopping requires energy penalty, because of the fact that it has to overcome this barrier.

It has to you have to externally supply the necessary amount of energy, so that it can it can overcome the energy difference between e 2 and e 1 and you all know this is the simplest definition of the activation barrier. In other words, if you want to hop from 1 to 3, you want to also hop from three to one, the activation barrier for travelling from a metastable equilibrium to a stable equilibrium will be lower than that for travelling from a most stable equilibrium to the metastable equilibrium. So, naturally under if you are supplying energy to a system hopping from one to three is possible, but once it attains three it is very difficult to the dislodge the system from its stable equilibrium position.

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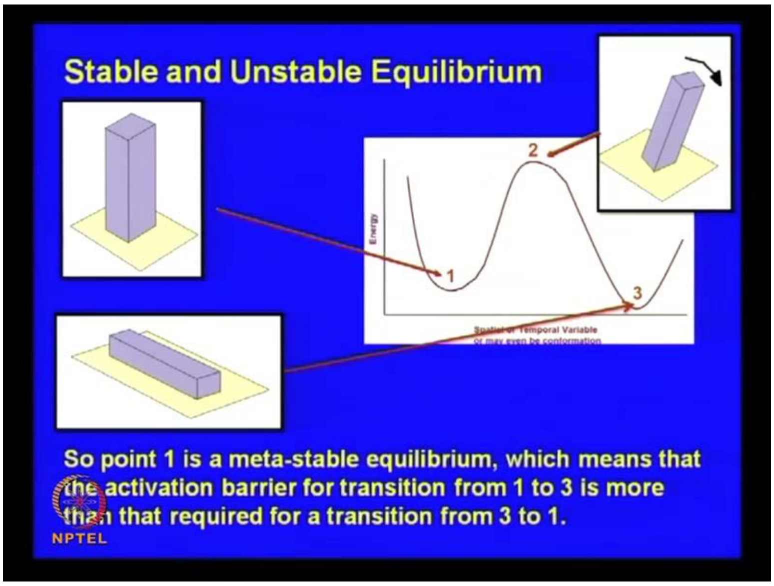

Stable and Unstable Equilibrium

So point 1 is a meta-stable equilibrium, which means that the activation barrier for transition from 1 to 3 is more than that required for a transition from 3 to 1.

Now, want to think of or you may feel that this is a very complicated thing and what is going on and etcetera, but even a system like this, you have a box like thing, which you or a rectangular parallelepiped in shape, you can make it stand like this or you can make it stand like this. So, it is like this. I keep this pen like standing like this or I can have the pen in a horizontal position. Now, if you look carefully, this is also a stable equilibrium and this is also a stable equilibrium, but the chances are if I perturb it more, I perturb it, but, it still remains. But, if I perturb it little more and it falls off going to this configuration.

So, by way of perturbation what I have done is I have actually provided the energy necessary to cross its activation barrier. Well, this equilibrium was metastable indeed, but the activation barrier was not very high. That is why only a little perturbation and it fall. If you look at the jugglers, they can probably make your pen stand like this at a position like this where somehow the energy sort of get balanced and it still stands in a tilted position. So, that will correspond to something that is shown on point number two. I hope this is clear, so that is what I told that even not very complicated system or very simple systems can have multiple equilibrium and this is very clear.

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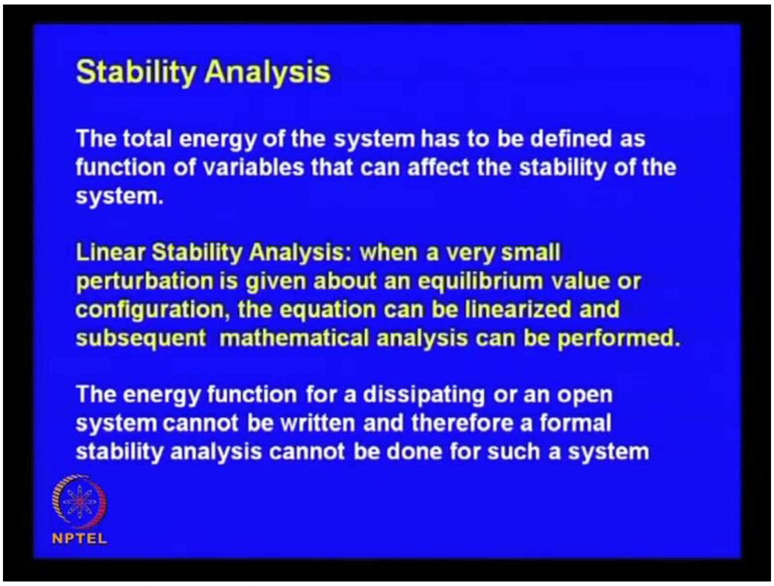

Stability Analysis

The total energy of the system has to be defined as function of variables that can affect the stability of the system.

Linear Stability Analysis: when a very small perturbation is given about an equilibrium value or configuration, the equation can be linearized and subsequent mathematical analysis can be performed.

The energy function for a dissipating or an open system cannot be written and therefore a formal stability analysis cannot be done for such a system

Now, if you want to perform the stability analysis, the total energy of the system has to be defined at first, as a function of variables that can affect the stability of the system. It can be complicated in many ways, because individually finding out the functionalities can be difficult to obtain, so one of the simplest ways to define the or look into the stability of a system is based on the concept of linear stability analysis. When a very small perturbation is given about an equilibrium value or configuration and the equation can be linearized and subsequent mathematical analysis can be performed. The energy of a function for a dissipating or an open system cannot be written and therefore, a formal stability analysis cannot be done for such a system. So, this is important thing to note which we will revisit with an example at a later time.

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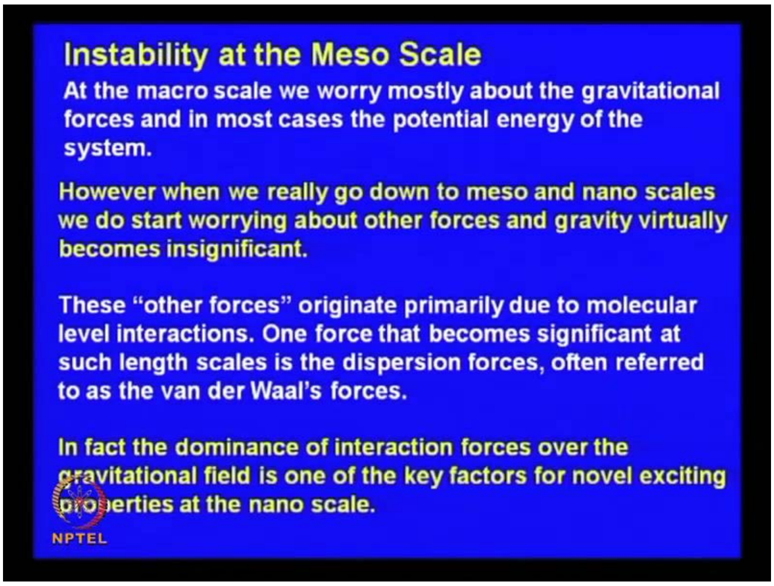

Instability at the Meso Scale

At the macro scale we worry mostly about the gravitational forces and in most cases the potential energy of the system.

However when we really go down to meso and nano scales we do start worrying about other forces and gravity virtually becomes insignificant.

These "other forces" originate primarily due to molecular level interactions. One force that becomes significant at such length scales is the dispersion forces, often referred to as the van der Waal's forces.

In fact the dominance of interaction forces over the gravitational field is one of the key factors for novel exciting properties at the nano scale.

Now, when we talked about instability or stability at a meso scale, we defined or we talked about what exactly is a meso scale. Now, at the meso scale we worry mostly, at the macro scale, I am sorry, we worry mostly about the gravitational forces and most cases the potential energy of the system. However, when we really go down to the meso and nanoscale, we do start worrying about other forces and it can be shown or we you will realize subsequently that at certain length scales, particularly at length scales less than 100 nanometer or even lesser than that, gravity virtually becomes insignificant.

So, there are other type of interaction forces, which dominate at this level and these other forces originate primarily due to the molecular level interaction. One of the forces that become significant in a most general way is as we will see the dispersion forces or which often is loosely referred as the Vander Waals forces. We will talk about it shortly. In fact the dominance of interaction forces over gravitational field is also one of the key factors or key novel factors that often lead to exciting properties at the nanoscale, other than physical confinement effects, where eventually your particles or entities becomes so small that it starts interfering with the structure, internal structure for example, the valence structure band structure of the material leading to some significant changes in property or so called achievement of extraordinary properties.

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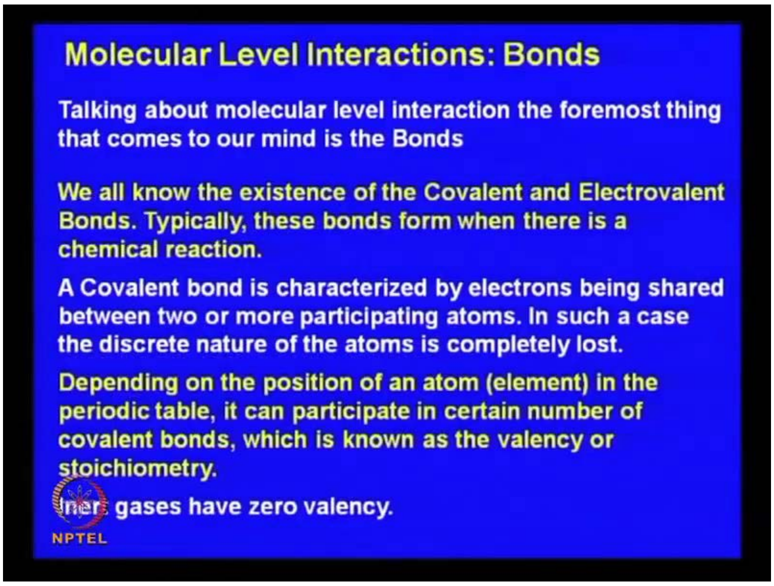

Molecular Level Interactions: Bonds

Talking about molecular level interaction the foremost thing that comes to our mind is the Bonds

We all know the existence of the Covalent and Electrovalent Bonds. Typically, these bonds form when there is a chemical reaction.

A Covalent bond is characterized by electrons being shared between two or more participating atoms. In such a case the discrete nature of the atoms is completely lost.

Depending on the position of an atom (element) in the periodic table, it can participate in certain number of covalent bonds, which is known as the valency or stoichiometry.

Inert gases have zero valency.

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Now, talking about molecular level interaction, the fundamental or the first thing that comes to our mind, which we have all been trained it at our school level is the existence of bonds. Now, we all know the existence of covalent and electrovalent bonds. Typically, these bonds form where there is a chemical reaction; you also know that the most fundamental type of bond we all know is the covalent bond, which is characterised by electrons being shared between two or more participating atoms.

The sharing is in such a fashion that the discrete nature of the atom is almost completely lost. Now, depending on the position of the atom or the element in the periodic table, it can participate in certain number of covalent bonds. I guess, you all know that this is what is known as the valence of that particular element often referred to as stoichiometry. We have also been trained to explain based on this concept that inert gases have zero valence and you know they have a field electrons structure, so they do not have any free electrons to participate in this sort of a sharing and therefore, they remain inert.

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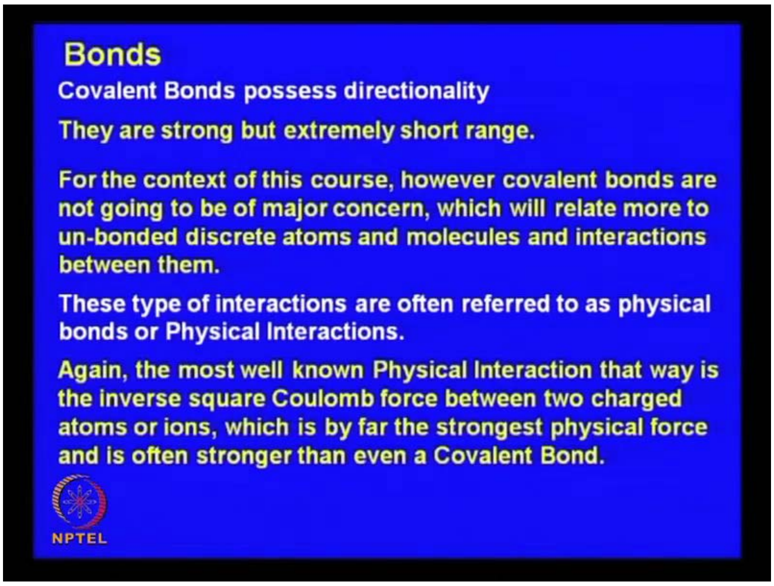

Bonds

Covalent Bonds possess directionality

They are strong but extremely short range.

For the context of this course, however covalent bonds are not going to be of major concern, which will relate more to un-bonded discrete atoms and molecules and interactions between them.

These type of interactions are often referred to as physical bonds or Physical Interactions.

Again, the most well known Physical Interaction that way is the inverse square Coulomb force between two charged atoms or ions, which is by far the strongest physical force and is often stronger than even a Covalent Bond.

The covalent bond poses directionality; they are strong but, extremely short range. So, the interaction or the attraction between atoms, the covalent bond sort of exists between the atoms participating in the molecule formation. For the context of this course, which deals largely with polymers, covalent bonds are not going to be of major concerned. As the course, will relate more to unbounded discrete atoms and molecules and interaction between them. Now, these type of interactions between unbound and discrete entities at the nanoscale or meso scale are often referred to as physical interactions.

Now, it is a little bit surprising that electrovalent bond, which is sort of is governed by inverse square coulomb force between two charged atoms or ions is actually the by far the strongest physical force and is often stronger than a covalent bond. Now, this is exactly what exactly is an electrovalent bond, but reality is that there are arguments or there are scientists who argued that a though these electrovalent bonds are even stronger than the covalent bonds in certain cases, they are actually more of physical interaction and they may not be true chemical bonds. We will not get into all the details, but what you know or what you may know that these type of electrovalent bonds form between molecules, which have ions, which have charge or which can be polarized in presence of a medium for example, and so on and so forth.

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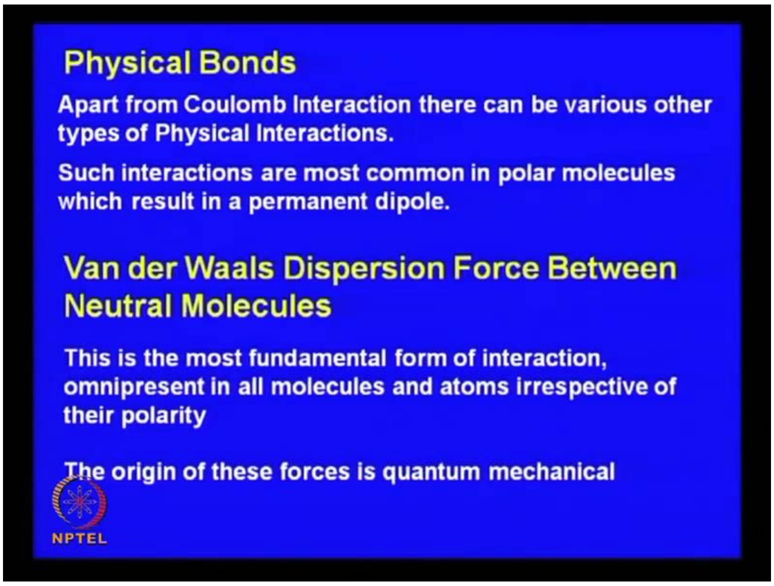

Physical Bonds

Apart from Coulomb Interaction there can be various other types of Physical Interactions.

Such interactions are most common in polar molecules which result in a permanent dipole.

Van der Waals Dispersion Force Between Neutral Molecules

This is the most fundamental form of interaction, omnipresent in all molecules and atoms irrespective of their polarity

The origin of these forces is quantum mechanical

Now, apart from talking about the physical bonds, what is important to realize that apart from coulomb interaction, they can be various other types of or they are even other types of physical interaction. Such interactions are common in polar molecules, which result in a permanent dipole. So, you have a permanent dipole, you can have a permanent dipole permanent dipole type of an interaction, you can have a permanent dipole induced dipole type of an interaction, but the most interesting, most important and the most fundamental type of interaction, is between molecules or atoms irrespective of their polarity, which are known by the dispersion forces. So, it is essentially an induced dipole, induced dipole type of interaction, it even between neutral molecules.

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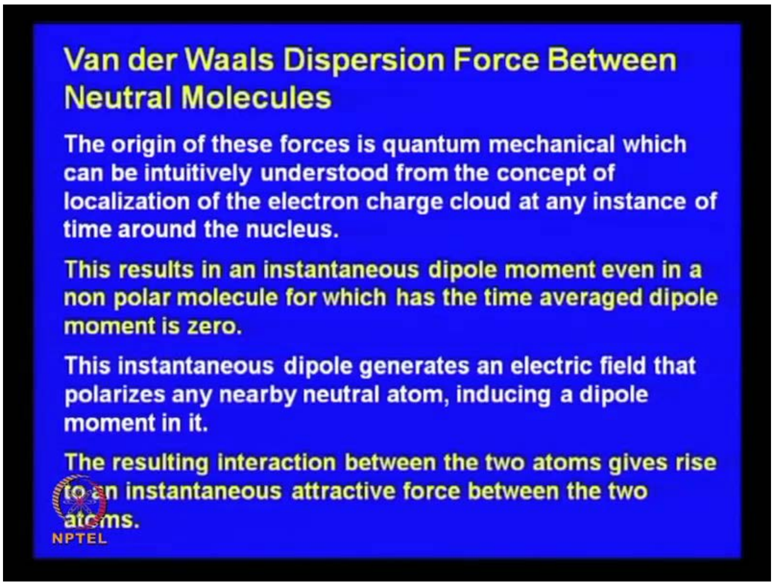

Van der Waals Dispersion Force Between Neutral Molecules

The origin of these forces is quantum mechanical which can be intuitively understood from the concept of localization of the electron charge cloud at any instance of time around the nucleus.

This results in an instantaneous dipole moment even in a non polar molecule for which has the time averaged dipole moment is zero.

This instantaneous dipole generates an electric field that polarizes any nearby neutral atom, inducing a dipole moment in it.

The resulting interaction between the two atoms gives rise to an instantaneous attractive force between the two atoms.

The origin of these forces is quantum mechanical which can be intuitively understood from the concept of localization of electron charge cloud at an instance of time around the nucleus.

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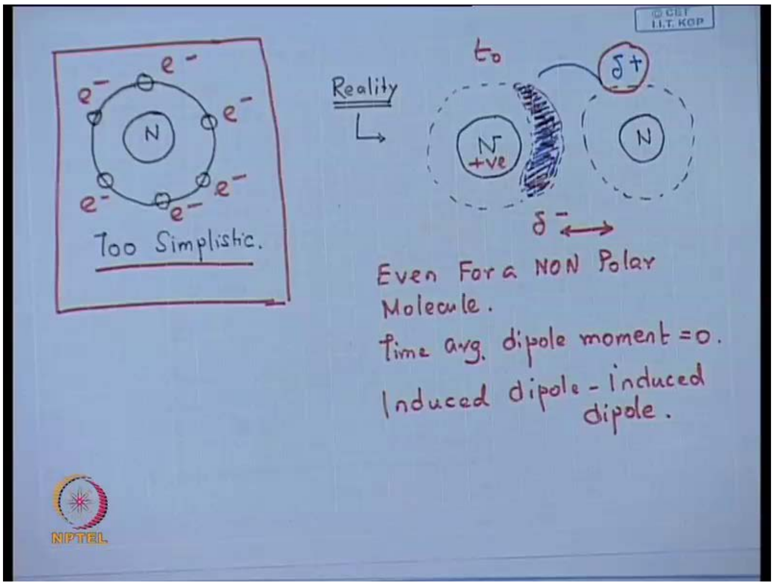

Even For a NON Polar Molecule.

Time avg. dipole moment = 0.

Induced dipole - induced dipole.

So it is something like this. When we talk about the structure of an atom, for example, this is probably the simplest view that comes to our mind. We have a nucleus and electrons are rotating moving around it in some definite paths, probably from your school days, you also remember that we used to look into issues like how it matches with the solar system and how distinct it is. The reality is that the simplest Rutherford model or even certain modifications suggested by Bohr, this is simplest picture, this is too simplistic thing does not happen like this.

What happens is in the very simple form that you have the nucleus, which is the location where all your positive charge or the protons are concentrated, you also have the neutrons. Now, the electrons are encircling this nucleus at very high frequency, so it is more like a very high frequency oscillation around the nucleus. So, even for a nonpolar molecule this is very important. Even for a nonpolar molecule, which can be sort of characterized by a time averaged, by the fact that time averaged dipole moment equal to 0. at any given instance of time, there can be a localization of electron cloud. This results in an instantaneous dipole, localized dipole of delta minus around the area over which the charge localization or electron cloud localization has taken place.

For example, the way the figure has been drawn; let us say at a specific instance of time t 0, this is the area over which there is a localization of the electron cloud. So, what happens is because of this delta minus, which has been localized over this area, it induces a induced dipole delta plus on the neighbouring atom or molecule. Now, since this is delta minus and this is delta plus, so there is going to be an attraction between the two and this attraction is triggered by, is in nature of an induced dipole attraction. But, reality is that nothing physically sort of moves, because of this attraction, because of the fact but, the moment you realize the molecules realize that there is an attraction and it starts moving towards this, you must realize that the localization of the electron clouds shifts from here to some other location and there is.

So, what is important to note is that though the time average dipole moment is 0, at any given instance of time, there exists a nonzero or finite interaction between all the molecules present in the system. So, this results in a instantaneous dipole moment even in a nonpolar molecule for which the time average dipole moment is 0. The instantaneous dipole generates an electric field that polarizes the nearby neutral atom, inducing a dipole moment. We just looked into it with the schematic, the resulting interaction between the two atoms gives rise to an instantaneous attractive force between these two atoms.

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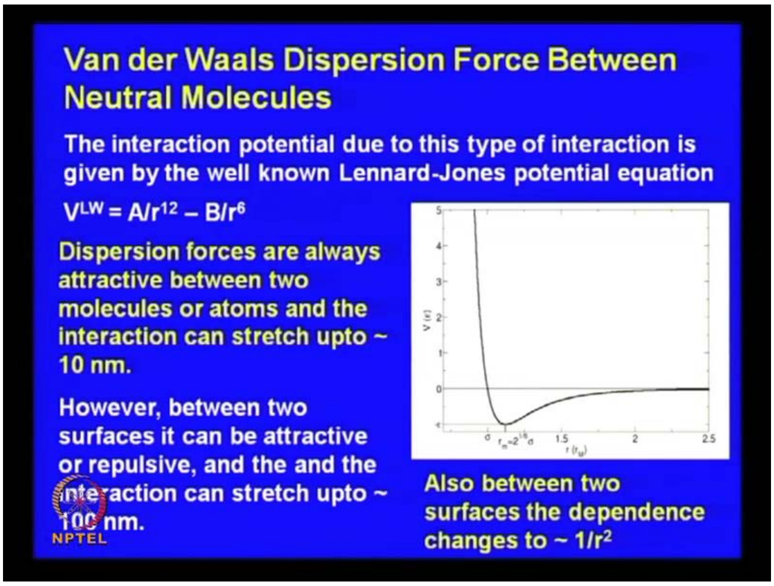

Van der Waals Dispersion Force Between Neutral Molecules

The interaction potential due to this type of interaction is given by the well known Lennard-Jones potential equation

$V^{LW} = A/r^{12} - B/r^6$

Dispersion forces are always attractive between two molecules or atoms and the interaction can stretch upto ~ 10 nm.

However, between two surfaces it can be attractive or repulsive, and the and the interaction can stretch upto ~ 100 nm.

Also between two surfaces the dependence changes to ~ $1/r^2$

Now, many of you probably are aware with this particular curve, which is best known or most well known as the Lennard-Jones potential curve. This interaction potential for this due to these type of induced dipole interaction is probably one of the best ways or the simplest ways for our context to describe it, is based on the Lennard-Jones potential where V L W can be regarded LW refers to the Lifshitz-Van der Waals forces or the London dispersion forces, which also represent these induced dipole type of interaction, which is best represented in the form of A by r to the power 12 minus B by r to the power 6.

Now, it is important to note that what we talked about this induced dipole related is actually taken care by the second term. So, a minus essentially represents attraction simply because of the fact that if you look at the potential curves, as the molecules come or as the molecules or the atoms come closer, their energy. But, what also happens is you have to realize that if you do a thought experiment that you have two atoms or molecules, which are separated infinitely and if you are bringing them gradually closer if they come in very close proximity below a critical separation distance.

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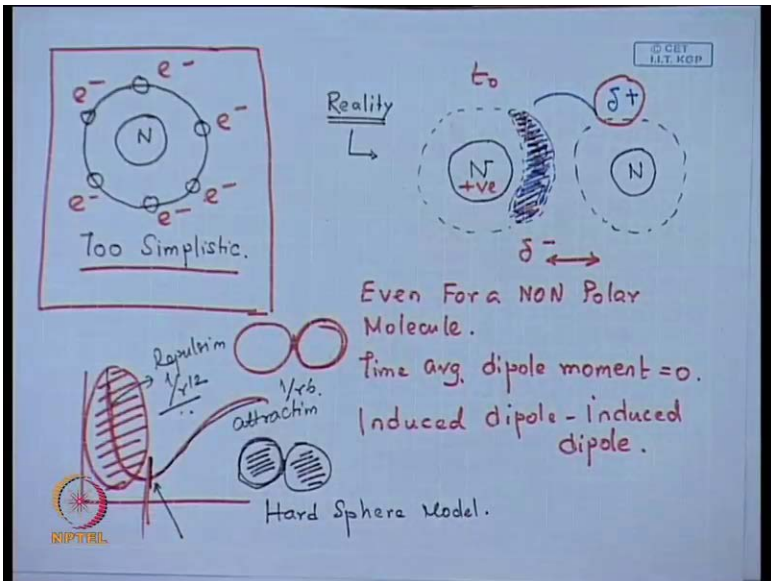

Even For a NON Polar Molecule.

Time avg. dipole moment = 0.

Induced dipole - induced dipole.

There is going to be a physical overlap between their bond between the electron or orbital structures, so that can be this point. So, once the electron or the orbital sort of starts overlapping or impinging with each other, what is going to happen is there is going to be a very short range electrostatic repulsion. So, this part of the curve represents that repulsion that short range electrostatic repulsion and so this particular point, theoretically refers to a point, where the two atoms just touch each other or the outer orbital of the atoms touch each other. Sometimes, we will avoid all the details, because there is no point in going into so many details physics, but this can also be regarded or this is sometime regarded as the Hard Sphere model.

So, what it means that two atoms are regarded as hard spheres, so they cannot impinge upon each other. However, if you may qualitatively understand a Lennard Jones potential to be the this part of the curve refers to the attraction and which is given by 1 by r to the power 6 relation, and this part refers to the repulsion, which is represent by 1 by r to the power 12 type of an interaction. You can see that you have if r is very small then r to the power 12 of course, dominates and therefore, the first term overwhelms the second term in the equation, so you have a effective repulsion. When r is larger, you have something at the denominator, which is raised to the power 12, as compared to raised to the power 6, so the second term becomes larger, so attraction dominates.

Dispersion forces are always attractive between two molecules, we are not talking about the bond repulsion, this is also at times called the bond repulsion, and if you may want to look at what it is you are free to refer to Wikipedia, its bond repulsion. So, dispersion forces are always attractive between two molecules and atoms and stretch up to around ten nanometre. However, this interaction or 1 by r to the power six relation what we talked about is valid between two fundamental particles like atoms or molecules. In reality, there are lots of areas where you see a physical signature of Van der Waals force or this type of dispersion forces, but in most cases this is between two surfaces.

So, for the time being you believe me and we will show it later that be the dispersion forces induced interaction between two surfaces does not scale as 1 by r to the power 6 but, it scales as 1 by r square. Moment the scaling sort of reduces from 1 by r to the power 6 to 1 by r square, what eventually happens is with increase in r the decay becomes sluggish. So, in other words, while for two fundamental particles, let us say the Van der Waals interaction stretches up to roughly around ten nanometre. For two surfaces the dispersion force induced interaction between two surfaces, these type of forces can be presented in about 100 nanometre. This is an important thing, which will be necessary in defining or particularly in classifying what a thin film in our context at subsequently.

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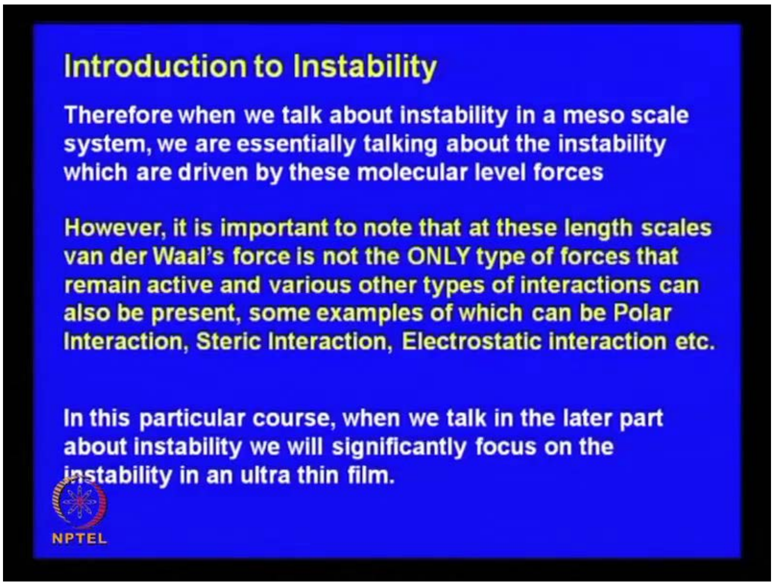

Introduction to Instability

Therefore when we talk about instability in a meso scale system, we are essentially talking about the instability which are driven by these molecular level forces

However, it is important to note that at these length scales van der Waal's force is not the ONLY type of forces that remain active and various other types of interactions can also be present, some examples of which can be Polar Interaction, Steric Interaction, Electrostatic interaction etc.

In this particular course, when we talk in the later part about instability we will significantly focus on the instability in an ultra thin film.

Therefore, when we talked about instability in a meso scale system, we are essentially talking about the instability, which are driven by these molecular forces. It is important to know that at these length scale Van der Waals force or the dispersion force is not the only type of force that remains active and there can be various other types of interaction that can also be present. We already talked that covalent bonding, electrovalent bonding etcetera, the coulomb interactions are important, but for the context of this particular course, where we are mostly going to talk about isolate, discrete and isolated objects, nonpolar molecules most like polymers.

In most cases of nonpolar none of these bonding forces are going to be that significant and we will see that the dispersion forces dominate to a large extent. However, they can be other forces like the steric interaction, which sort of originates due to the steric interaction, means essentially the origin of it is due to the shape of the molecules, which can be dominant for the polymers, which are long chain molecules and which can remain in a entangle stages, as things like that, which are included in steric interactions. We may talk about some of those interactions subsequently. For polymers or nano composites, also the entropic effects become significant. So, you can see that if you want to define the energetic of the system, you have to consider all these interactions forces and that is precisely what I talked about they may not be that simple at all times to define. So, we will see how best we can handle that within the framework an engineering course, so that your physics does not become too complicated. Also while talking about stability in this particular course; we will talk significantly about the stability on an ultra thin film.

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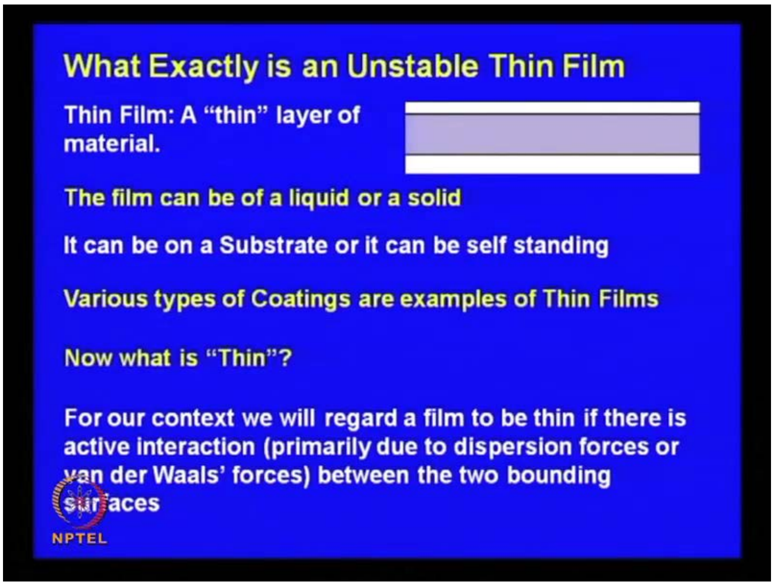

What Exactly is an Unstable Thin Film

Thin Film: A "thin" layer of material.

The film can be of a liquid or a solid

It can be on a Substrate or it can be self standing

Various types of Coatings are examples of Thin Films

Now what is "Thin"?

For our context we will regard a film to be thin if there is active interaction (primarily due to dispersion forces or van der Waals' forces) between the two bounding surfaces

So, you understand a little bit about what stability is by now, we look at the various equilibrium configurations of a system and then we try to figure out, which one of them is the most stable. So, stability essentially means that whether it remains stable with time or not. So, in order to discuss or introduce the concept of the stability of an ultra thin film, which you we will do for a significant part of the course, it is important to note what exactly is a thin film initially. So, a thin film, as you can see from the definition itself is a thin layer of material. This material can be a liquid or it can be a solid, the schematic here shows a sort of a thin film, so you can see that it has two boundaries, the first thing to note. This film can either be so you can have two possible configurations essentially.

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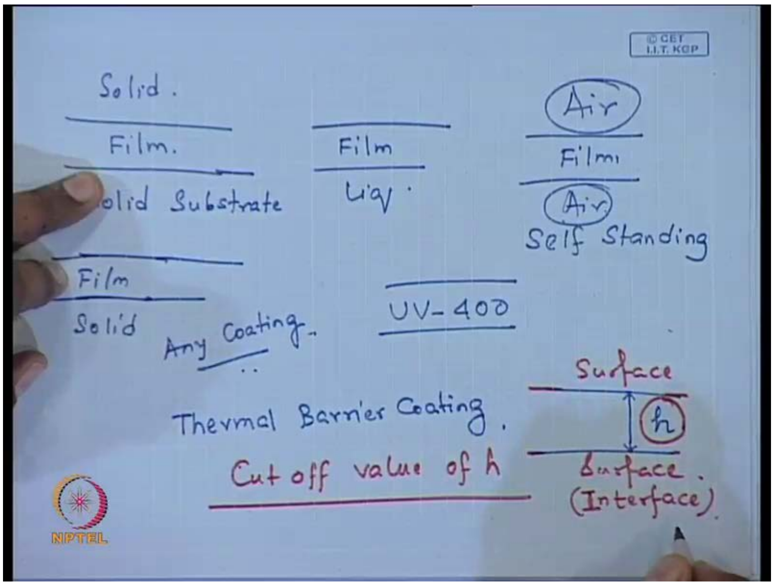

© CET I.I.T. KGP

Solid.

Film.

olid Substrate

Film

Liq.

Air

Film

Air

Self Standing

Film

Solid

Any Coating.

UV-400

Surface

h

Surface.

(Interface)

Thermal Barrier Coating.

Cut off value of h

NPTEL

So, here you have a film. This film can be on a solid, on another solid, which often is referred to as a substrate. This film can also be on another liquid, the film can be sandwiched between two solids or the film can be self standing. You may wonder, so these are a film on a solid is probably the easiest one for you to conceive. Any coating is an example of such a system, what type of coatings we are talking about? The simplest one of course, being the paint you apply on your walls and other items, so it is nothing but a film, which is actually coated on a solid, which is the wall in this particular case.

Talking about hydrophobicity, we talked about the non-stick cookware, which is essentially a layer of teflon thin film is coated on the material. This teflon imparts the hydrophobicity, which we talked about. Many of your modern glasses, if you buy specs, if you buy they come with a anti-scratch coating. So, you have a glass, which sort of has the required curvature to correct your vision and then the cover of that glass or plastic is coated with a fine transparent layer, which prevents scratching of that particular surface or particular lens.

There can be numerous other types of coatings. For example, if you buy a good quality commercial sunglass, you will always find a word like UV-400 written over there. What it means is that it comes with a coating, which sort of filters of the ultraviolet ray. In the previous days class, while talking about diffraction, we talked about the visible wavelength of light to be in the range of 400 to 700 nanometre. So, below 400 nanometre are the ultraviolet rays or ultraviolet light, which is harmful for the eyes. So, any good sunglass, typically we see the visible part of the light, but there is lot of UV light also from the sunrays. If you go out in direct sun so the intention of that coating UV-400 coating is to cut off those unwanted radiations.

Now, you might be surprised that what can be or how can a thin layer of film can be self standing. So, you have air on this side and you have also air on this side, well this is also not rocket science stuff and in many cases you actually know the existence of such a system and well if you can, I can give you a minute to think over what such a system can be. As children, we were fascinated with these particular things and even today, we see if you look at the surface of a bubble, a soap bubble, a self standing bubble or a bubble you generate by sort of blowing a soap solution. The surface of a bubble is actually a thin layer of the soap solution on both sides of which you have air. So, that is an example of a self standing film. As we have talked, so examples of thin films can be various types of coatings.

There can be lots of industrial application, also for coatings, for example, one very important application is the thermal barrier coating, but there can be several other examples as well. Now, we need to worry about one specific term, so this is very simple. You have a thin layer of liquid, which can act as a coating, which can be coated on a substrate, which can be on a liquid or which can be self standing and we term that as a thin film. Critical question to ask yourself at this point of time is what is thin. Do you have a specific number that can define what a thin film is? So, are you talking of a film that is let us say millimetre thick, micron thick, what are you going to term as a thin film.

Well, there are many areas where several micron thick films are termed as thin films, there are many application areas where even a millimetre layer of a material can be regarded as a thin film, but based on the discussion, we had so far, particularly in the last 10 minutes I guess, can we come up with a formalism to define thin films in our context? So, the critical question to ask is, if this is a film what is the restriction on each we are going to impose, so that we can term it to be a thin film. So, what is the value or what is the cut off value of this each and based on what we define our formalism.

if you remember, couple of minutes back, we talked about the existence of the Van der Waals interaction forces between two surfaces or for charge neutral surfaces also that it stretches up to 100 nanometres. So, that way if you see a thin film is nothing but, so in other way of viewing a thin film it is some material, which is separated by two surfaces or interfaces. So, here is a surface, here is also a surface, if the film is self standing so both the surfaces represent the liquid in contact with air. If the film is coated on a solid substrate then it can be the liquid or the mid film material in contact with the solid surface. As we will see in the next talk or next lecture that when a condensed phase is in contact with another condense condensed phase, the general convention is to use the word interface and not a surface. We will take that up later but what you can understand from the discussion we have had so far.

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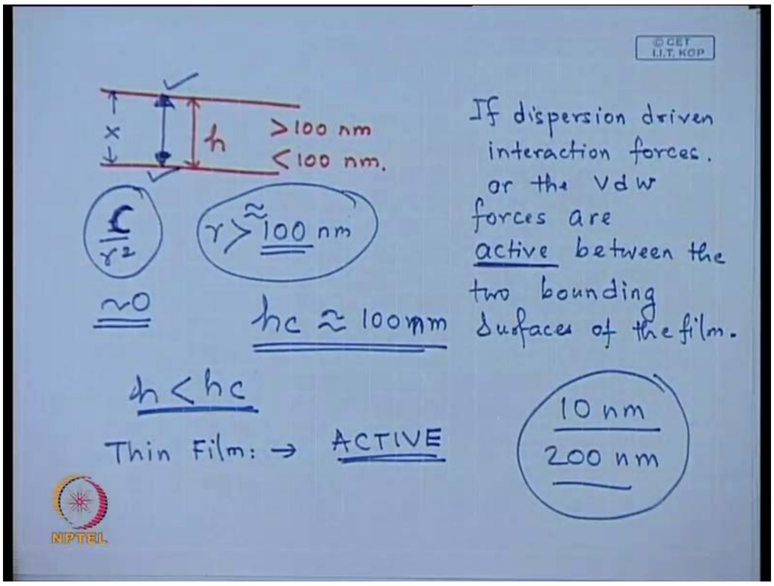

$\frac{C}{r^2}$ ~ 0

$r \gtrsim 100$ nm

$h_c \approx 100$ nm

$h < h_c$

Thin Film: → ACTIVE

If dispersion driven interaction forces. or the VdW forces are active between the two bounding surfaces of the film.

10 nm

200 nm

If you have a film, which is whether its thicker or thinner than roughly 100 nanometer there is going to be a significant difference in that. Well, this number 100 again can vary but, in other way to look at there is going to be a significant difference, if you have dispersion driven interaction forces or loosely speaking the Van der Waals forces are active between the two bounding surfaces of the film. So, what it means is this is the most important thing, whether they are active. We know that we have talked about the this type of induced dipole induced dipole type of interaction is always present between irrespective of the polarity of the molecules, but we did talk about that between two surfaces, they have a scaling of 1 by r square or some constant by r square.

It turns out that if r is greater than 100 nanometre, this term tends to 0, roughly 100 nanometre again, some people talk it about 70 nanometre or 50 whatever. So, if your film is thicker than this critical number or critical thickness then what it means that there is no active interaction due to the dispersion forces between these two interfaces. So, these two interfaces do not interact with each other based on Van der Waals forces or the dispersion forces. In contrast if your film is thinner than that critical thickness, let us say that is hc and we can term that hc in many cases by convention or by experimentally has been shown to be closed to 100 nanometre.

So, if your film thickness h is less than hc, what eventually it means is that there is active Van der Waals interaction or active induced dipole type of interaction between these two interfaces of the film. So, in our context, we will define a thin film to be a system where we have the force to be active and based on that, the cut off typically stretches can be a maximum of 100 nanometre. So, suppose when we talk about a film is let us say, 10 nanometre thick or we say this a film which is let us say 200 nanometre thick.

The key difference is that immediately comes, so it is very difficult to quantify looking only at the numbers whether one is a thick film and one is a thin film, but what you should do based on today’s discussion is be able to quantify is that in case of the first film that is the 10 nanometre film, there is active Van der Waals interaction between the two bounding interfaces, while in the second film the Van der Waals interaction between the two bounding interfaces is probably absent. So, this is what we will see eventually leads to a significant difference in the way the film behaves with time or the energetic of the film as well. So, this is how we will define or we will follow the formalism in defining a thin film for our system.

So, formally for our context, we will regard a film to be thin if there is active interaction primarily due to dispersion forces or Van der Waals forces between the two bounding surfaces, so that is very important. Now, once we understand what we are going to regard as a thin film, so these films can be of liquid, can be of solid, can be of polymer, which can sort of undergo a transition from a liquid state to solid state to a gases state. We will talk about all those things later, but this is the first basic fundamental that I want to make very clear what exactly we are going to define as a thin film for this context of this particular course. Then one of the last slides for the introduction part is what exactly do we want to investigate or want to sort of mean by the stability of a thin film.

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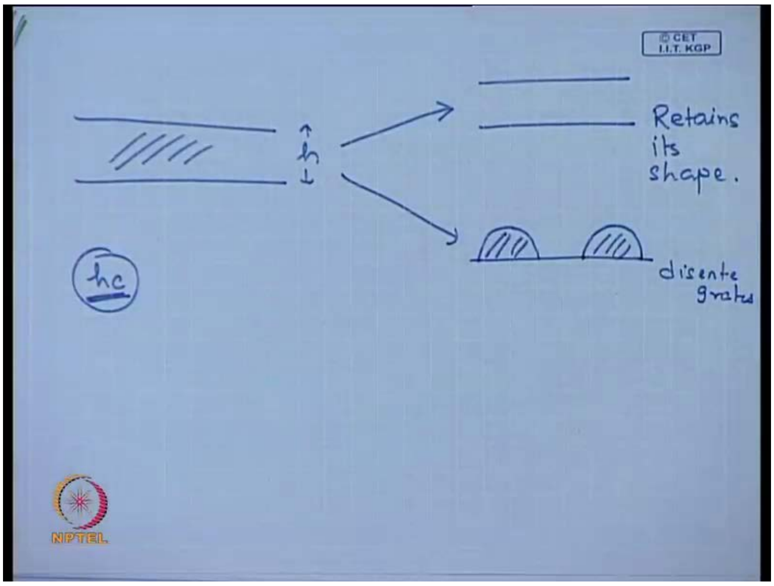

So, essential idea is that you somehow create a thin film, which lets say has a thickness h and if we define the cut off thickness where Van der Waals force can be active or inactive, even if it is less than that particular h, the critical thing to investigate or the thing of our interest will be that with time whether this film remains or retains its shape or it disintegrates. If a film disintegrates, it can form structures like this. So, this was the film material, which disintegrates and forms are isolated patches or something like that.

Now, why it is important is because as we have told that the most important application area of thin film is in coatings. So, in a coating, for any practical application industrial application or even any simple application, you definitely want that your coating remains intact with over a period of time. You do not want your coating to get bad after sometime. If your coating gets bad eventually it loses the functionality. The coating loses its functionality, so in order to have coatings, which are stable, which remains stable overtime, which do not disintegrate. It is extremely important to understand stability of thin films.

The general intention or custom before in coating technology was to go for much thicker coatings. So, this was even when we paint our homes, for example, we all know that we all ask for two coats of paint. So, why this is because the basic idea is that if you coat it or if you give two coats the paint is going to be stable it is not that. It is essentially by giving two coats; you are making your film adequately thick, so that it sort of crosses the h c barrier, so that it does not spontaneously disintegrate. Your painting labour does not know all this but, this was what the basic intention was. Now, the problem is as we have seen, when we talked about development in photolithography and line sizes becoming smaller, devices becoming smaller etcetera etcetera, your feature sizes have become so small that you really cannot have a five micron thick coating, which will sort of automatically grant you the stability on something like a 30 nanometre feature size.

So, with a reduction of feature size, which is attributed to the progress in patterning, your coating thicknesses have also come down, so you have to really worry about now films at an industrial scale, which are very thin, which can be prone to spontaneous disintegration. So, you have to understand the physics of that and then eventually you have to work out strategies, which can suppress or stop this disintegration. Also, we will show that this disintegration process, which is extremely undesirable from the standpoint of coating technology, can also be of viable meso scale patterning technique, which offers lots of flexibility as compared to other conventional techniques, which we are going to discuss. So, this is how based on a combination of patterning as well as the instability, the concepts of instability of an ultrathin film, we will take up our subsequent lectures in days to come.

Thank you very much. We will get started to with our next talk in which we will define some of the basic concepts on surfaces etcetera etcetera. I will stop here.