

Instability and Patterning of Thin Polymer Films

Prof. R. Mukherjee

Department of Chemical Engineering.

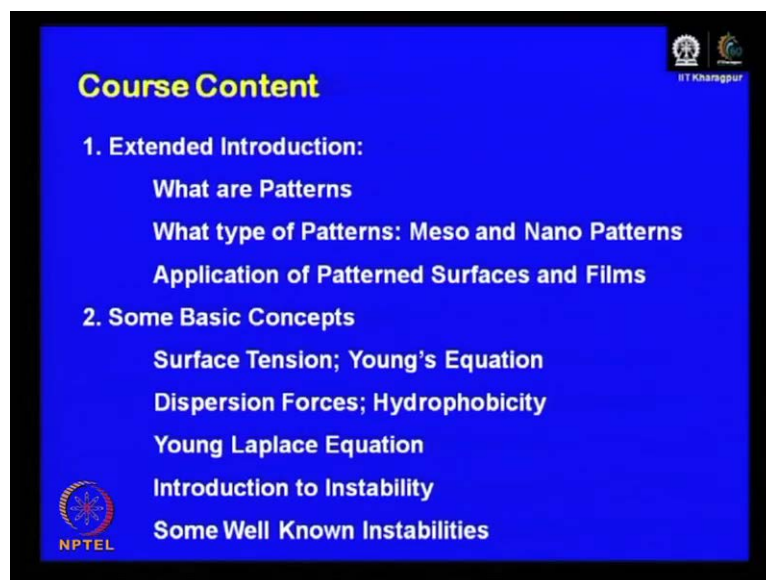
Indian Institute of Technology, Kharagpur

Lecture No. # 01

Introduction

Good morning and warm welcome to this course which goes by the name instability and patterning of thin polymer films. This is a course that we offer at the chemical engineering department at IIT Kharagpur as an **as an** elective for the master students as well as an open elective for the final year under graduate students. You might be slightly surprised with the name because I am sure in your chemical engineering curriculum you have not come across a course that goes by this type of a name. Well do not be scared, it is a course as you will soon find which is extremely or highly interdisciplinary in nature and covers various aspects of chemical engineering, physics, nanotechnology and even some concepts of polymer chemistry and polymer physics.

(Refer Slide Time: 01:07)



The slide is titled "Course Content" and is set against a blue background. It lists two main sections of the course. The first section, "1. Extended Introduction:", includes "What are Patterns", "What type of Patterns: Meso and Nano Patterns", and "Application of Patterned Surfaces and Films". The second section, "2. Some Basic Concepts", includes "Surface Tension; Young's Equation", "Dispersion Forces; Hydrophobicity", "Young Laplace Equation", "Introduction to Instability", and "Some Well Known Instabilities". Logos for IIT Kharagpur and NPTEL are visible in the corners.

Course Content

1. Extended Introduction:
What are Patterns
What type of Patterns: Meso and Nano Patterns
Application of Patterned Surfaces and Films

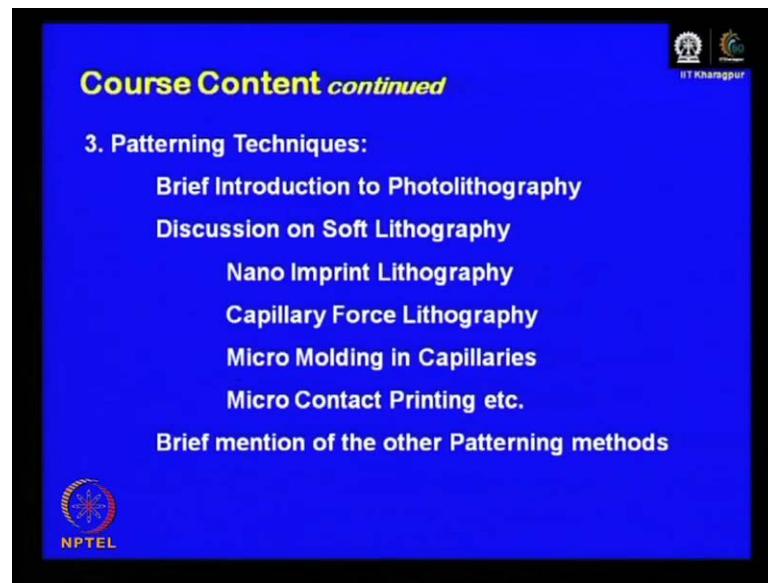
2. Some Basic Concepts
Surface Tension; Young's Equation
Dispersion Forces; Hydrophobicity
Young Laplace Equation
Introduction to Instability
Some Well Known Instabilities

So, let us see how we propose to progress in this course or how we sort of make a may how **how** we plan to unfold the story. Since the area is relatively new to you so we will

go in for an extended introduction so that I can give you some glimpses what patterns are and then we talk about what type of patterns. We are talking about primarily patterns can be at any length scale but we will be in the context of this particular course talking about meso and nano scale patterns.

Ah, then probably what we take up in the first lecture in greater details is the application of such pattern surfaces and films. In order to make progress we need some basic introduction on some basic concepts, some of which will be say surface tension, young's equation, dispersion forces, concepts basic concepts of hydrophobicity and hydrophilicity. Then I will introduce you to the concept of young Laplace equation which essentially is related to the pressure difference or pressure gradient that **exists** exists across a non planner interface. As you have seen from the name of the course itself, there are two apparently distinct aspects one is instability and one **impact** one is patterning. Well, these two are in a way distinct but in a way they are very closely related. Out of the two words probably patterning is something, you are more familiar with so our initial discussion will be on patterning and how to make these patterns. But, we also would eventually introduce at that point at this point of time, the concept of what instability is and what type of instability we are talking about. There are some well known instabilities. For example, the Rayleigh Taylor instability, the saffman instability and things like that. So, some of the **intreupt** concepts we will introduce you will also at this point understand what exactly leads to the so called very well know phenomenon of capillary rise.

(Refer Slide Time: 03:06)



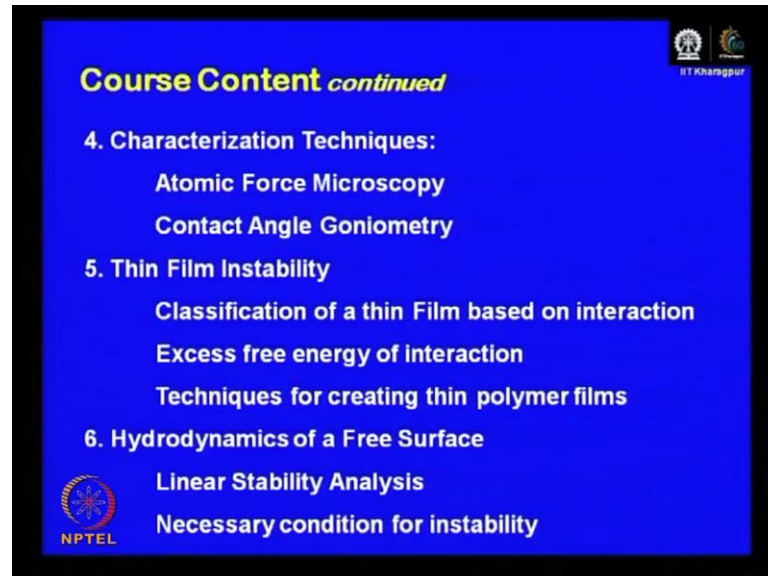
Continuing with our discussion, we will then touch upon the basic patterning techniques at the meso and or the I would say surface patterning techniques. We will talk in very brief details about the basic concepts of photolithography which all the people who were well accustomed with the electronic and **micro electronics** micro electronics industry are extremely well accustomed with.

But then, since this course covers or we will be focusing in greater detail on polymer surfaces and patterns. So, we will I will introduce at that is this point of time the basic concept of soft lithography which is still a very new concept invented sometime in the middle of ninety's by primarily almost parallelly I will say by two groups one at Princeton and one at Harvard. The two biggest names are Stephen Charles at Princeton and white sides at Harvard. And we will talk about some of the soft lithography methods in details some of which include nano imprint lithography which **which** is internationally famous now by the acronym NIL, capillary force lithography CFL, micro molding in capillaries which goes by the acronym mimic, micro contact printing better known as mu c p. There are several other and various variance of all these soft lithography techniques which we will discuss in somewhat detail.

And then we will also show our talk about other patterning methods which allows you to make structures probably, at literal resolution of around ten nanometer. But, some of which are I mean more intense. So, some of the methods can be dip pen nanolithography

which uses an atomic force microscope platform or the **direct** other type of direct write methods

(Refer Slide Time: 04:47)



Now the other thing is we talk about making structures and features which are very very small which are some micron. I mean soon, I will explain what is the exactly is a meso scale but, typically when understand we are planning to make structure which are very very small something like tens of nanometer to a few **few** micron may be. So, one of the critical issue is once you even once you make these structures how really do you see or check for yourself that these structures have been made in the desired fashion. Because, if the first thing that comes to our mind, what one users for seeing very small features this is the optical microscope. But, for these type of structures many cases the optical microscope fails to resolve because of their smallness. So, there are other high end microscopy techniques, scanning electron microscope, transmission electron microscope and a particular microscopy technique again which was invented in the **mid** middle of 80s is the atomic force microscopy. A very very specialized type of a microscope, specifically used for looking at surfaces and features with very small lateral resolution. I guess this course will be a good, I mean to introduce the concept of AFM or the atomic force microscopy at some point in this course will be a good idea.

So, we will look into how the atomic force microscope works. Once, I explain it you will realize, it is a very simple concept and based in which a lot **lot** of things can be done. We

will be extensively talking about surface tension and other related phenomenon, so one of the key instrument that is necessary to determine surface tension of a liquid or that of a substance solid or the interfacial tension is the instrument called goniometer. The method is known as the contact angle goniometry. We will also briefly introduce you to that concept.

Then we will eventually start talking in details about the instability and we will be primarily talking about thin film instability. So, first we will try to classify a thin film based on interaction forces or dispersion forces as it turns out and we will show that essentially for this context. At least, we will regard films which are about thinner than about 100 nanometer to be thin films. Why this classification why this number or from where this magic number 100 nanometer comes up we will try to discuss that because you might have heard the word thin film in various context. So, the first thing that comes to your mind is some sort of a coating.

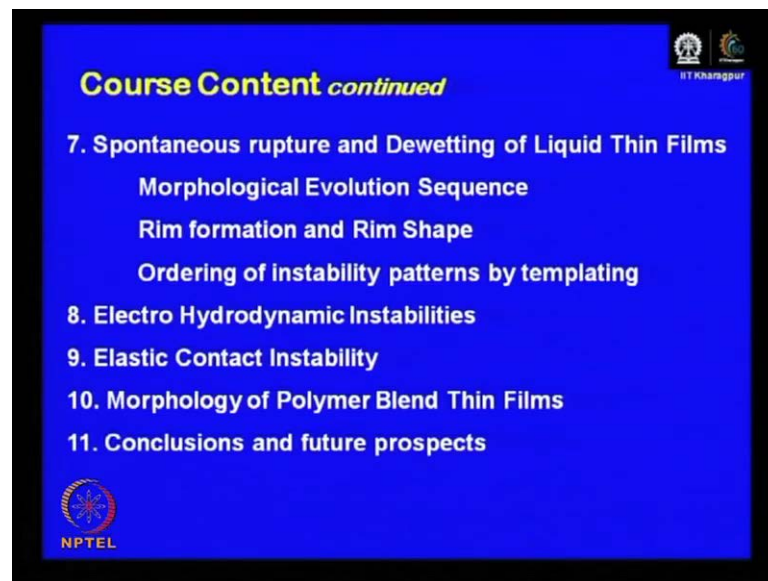
But most of the coating like the paint in the wall or something like that that you see around us are actually much thicker. So, it is rather wagg that way I mean how really you classify a film to be thick or thin. We will try to address this issue and as I said for the context of this particular course at least and many other contexts. We will show that a film that is less than about hundred nanometer possesses some its additional properties or unique properties which are not present in films thicker than that. This is also some sort of a basic bases for various phenomena's or various magical phenomena's which are seen in a very popular area these days which is nanotechnology. I mean you must try to think of or you must wonder what exactly makes nanotechnology so very special. So, we will touch up on some of those fundamental aspects. We will also talk about the concept of excess free energy of interaction present in a thin film and of course, if you talk about thin film and if you really want to make them we need to know how these type of thin films can be made. Primarily, in this method these way, I will touch upon two of the basic techniques which are spin coating and dip coating.

For once we cover these aspects of thin film instability. We will move on to the hydrodynamics of a free surface which eventually will give us the formalism to talk about the thin film in an ultrathin liquids, the instability in an ultrathin liquid film. Where you will see that your chemical engineering concepts of fluid dynamics fluid as a

continuum navier strokes equation ecetera become important .So, all we will do is that or all, we will consider is the navier strokes **equation** equation and under the so called lubrication approximation. I will take that up in greater detail, so then you will realize how your chemical engineering concepts actually bridge rather well with what we are going to talk here. We will also introduce you to the, I will also introduce you to the concept of linear stability analysis, a very well known concept which is again used in various other aspects of chemical engineering.

For example, to understand the stability of a CSTR and based on linear stability analysis. We will show what are the necessary conditions for instability linear stability analysis also give certain **other** other parameters like the dominant wavelength of instability or the initial time scale ecetera which we will take up at that point of time.

(Refer Slide Time: 09:32)



We then talk about in greater detail about the spontaneous rupture and rewetting of thin liquid films which often are often goes by the name the spinodal instability of a thin liquid film. This type of instability understanding, this type of instability is extremely important in various context because these instabilities can be extremely detrimental from the standpoint of a coating.

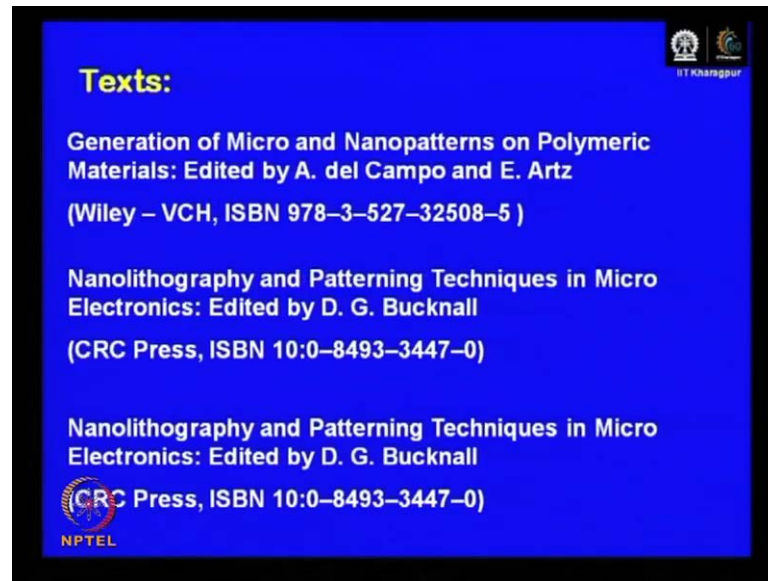
So, from the standpoint of coating one would try to suppress these type of instabilities as much as possible but, these instabilities are also **associated** associated with morphological evolution which can also turn out to be some sort of a viable technique for

patterning. So, we will talk about in details about the morphological evolution sequence. There are some critical issues you might want to remember some of the headers rim formation and rim shape and based on looking at the shape of the rim. One can actually get back or have an idea about the level of this elasticity of the polymer melt or the polymer film or the liquid film we are talking about. And then, we will talk about something very very interesting that is on ordering of the instability patterns by templetting that is this is actually the area where you can see that the two concepts of patterning and instability starts getting merged. And this, I must tell you this is a very advanced area lot of high end research is still going on presently. So, I will introduce you to some of the state of our concepts.

Now, once this spontaneous instability in a liquid thin film is over. We will talk about some more instability settings in polymer films or liquid films. Some of which we includes electro hydrodynamic instabilities in thin polymer films, elastic contact in stability in another type of polymer films which are not liquid but, are **are** of the form of a soft solid elastic film at room temperature or these are the these are films which exhibit room temperature elasticity. To sum up, We will also, I will also introduce you to another very important concept of that is being investigated these days which it is polymer blend thin films, so where you have essentially have two different polymers which are immiscible to each other and you try to cast a film to find out what exactly happens. There are lots of additional physical interaction that comes in and which determines the morphology of the as cast films as well as how the morphology changes or evolves with progress of annealing or heating.

And we will sum it up sum up the course with conclusion and future prospects. But, please do remember that this a **course** this is a pretty open ended course it is not a very classical course. I mean lot of developments are happening even today and I will happy after going through these course contents if some of you decide to go for academics, you will find in various area of high end academics universities or IIT's in India as well as aboard the lot of activity is going on these type of areas. So I hope you **you** will enjoy and you will have a nice time with this particular course. So let us proceed further in the very first slide, I have given my contact details including email so after reading if after at attending these lectures, if you find any difficulty you are free to email me and I will try to clear your doubt as much as possible.

(Refer Slide Time: 12:47)



Texts:

Generation of Micro and Nanopatterns on Polymeric Materials: Edited by A. del Campo and E. Artz
(Wiley – VCH, ISBN 978–3–527–32508–5)

Nanolithography and Patterning Techniques in Micro Electronics: Edited by D. G. Bucknall
(CRC Press, ISBN 10:0–8493–3447–0)

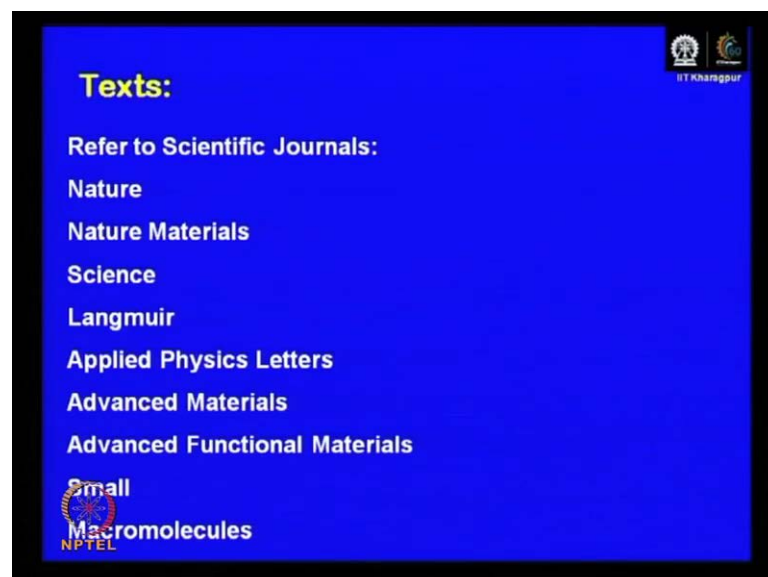
Nanolithography and Patterning Techniques in Micro Electronics: Edited by D. G. Bucknall
(CRC Press, ISBN 10:0–8493–3447–0)

NPTEL

ITKharagpur

Texts well not too many standard text books are available because as I told the course content is pretty recent and it is still evolving. However still few books are available in the market for example, the one generation of micro and nano patterns on polymeric materials. It is a very recent book published in two thousand eleven edited by del campo and arts, it is a Wiley VCH publication nanolithography and patterning techniques. In micro electronics part of it though it talks about micro electronics part of the book covers patterning of polymers as well it is published around 2006 or 7 from CRC press. Nanolithography, it is repeated unfortunately.

(Refer Slide Time: 13:29)



Texts:

Refer to Scientific Journals:

- Nature
- Nature Materials
- Science
- Langmuir
- Applied Physics Letters
- Advanced Materials
- Advanced Functional Materials

Small
Macromolecules

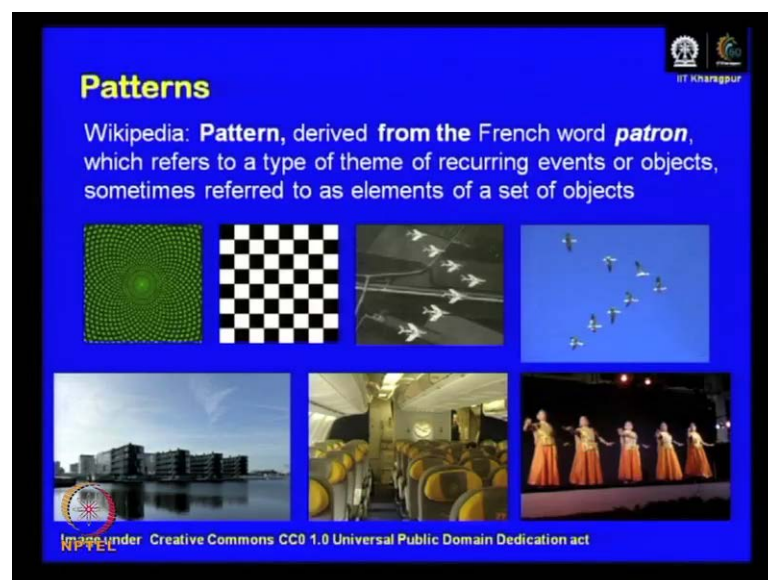
NPTEL

ITKharagpur

I would also strongly request you to make a culture of referring to the top notch journals for example. Lot of these activities are published in **in in** some of the journals because it is it is very new. So, some of the journal you may want to look up would be nature **nature** materials science, Langmuir applied physics letters, advanced materials, advanced functional materials, small macro molecules ecetera. So with these and some of the references available on then you can also refer I mean, this is one thing I must tell you **you** are free to refer Wikipedia at the drop of a hat because that is really one site from which you get lot of basic information and you can augment that with whatever I am talking and teaching here, so that the things become understandable. But, one thing I can tell you that once you attend this course, you will be happy to correlate many of the things you see in and around you happening in nature which apparently with your classical engineering knowledge, you fail to understand or have never thought in detail about what or why exactly it is happening.

So, that is the prime intension I have to show you that many of the phenomenon that you see around us in nature, in the biological world as well **as well** as a in animate world as well as in some of the artificially fabricated materials or commodities we use these days. These type of patterns and features have a very important and key role to play.

(Refer Slide Time: 14:58)



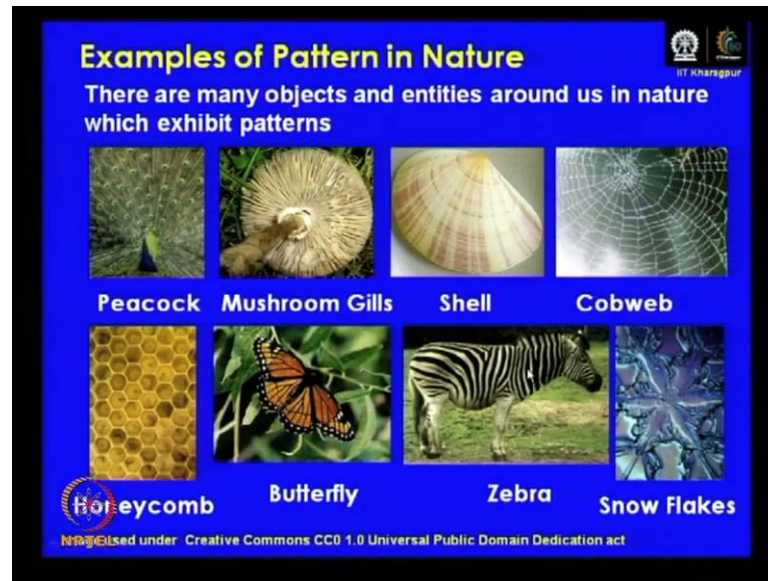
So, now let us get going with a formal introduction of the course. First, try to understand what is patterns. Well, if I define or not really does not matter. We all understand what

patterns are. The some sort of an ordered thing, so you can have patterns you can draw nice patterns or you can have nice patterns on your dress or objects can be made in in a in to form a particular pattern. If you go by the Wikipedia definition well, pattern it is derived from the French word patron which refers to a type of theme of recurring events or objects sometimes referred to as an element of a set of objects.

We probably understand what it means, so these whatever images you see some of them are taken from the Wikipedia, some of them are my own images they are all different patterns so. For example, this is the first one is some sort of a design, the second one we all know it is a simple chess board, third one is a formation of fighter aircrafts that is also some **some** some type of a pattern, fourth one is birds returning home towards the evening they also if you have noticed carefully looked at the sky they come back in some sort of a some sort of a pattern. So, this is also definitely a pattern fifth one is a nice example of a housing complex. Here the architecture is such that it also forms some sort of a nice order.

Even a while entering the interior of an aircraft, if you see that the seats are arranged in some sort of order that is also some sort of a pattern, you see India we come from India, so classical dance form I think this Kuchipudi or Bharathanatiam I am not very sure about it. But, here you see all the ladies are pretty much standing in the same desired style, so that also is some sort of a pattern undoubtedly. So you can see that patterns can be everywhere in and around us try to explore **yourself** explore around you **you** will find patterns. I am very sure many of you the shorts or the dresses, you are wearing has some nice designs and which are a sort of self repeatating so they are also pattern. For example, the one I am wearing of course, has some cross patterns of course.

(Refer Slide Time: 16:57)



Moving on, we can also talk about or find various examples of pattern in nature in and around you. Peacock, our national bird for example, beautiful color we all love to see dancing peacocks. But, have you ever thought what really makes us, so fascinated about peacocks and it is their beautiful design on their on them which **which** makes us makes the peacock so beautiful. Peacocks, mushroom gills, shell even a cobweb net, honeycomb, the beautiful color of a butterfly **outlook** the sort of outlook of a zebra or even a tiger for example, or even snowflakes.

If you look at them many of them have some sort of self repeating feature or patterns. So, it is patterns is not really limited to artificial formation of houses or aircraft add the way aircrafts are flying patterns, you can see are present at all length scale and in and around us in everywhere.

(Refer Slide Time: 18:02)

Patterns *continued*

Patterns can not only be spatial, but it can also be temporal

For example the diurnal motion of the earth itself is a classic example of Temporal Patterns

Patterns can also be partially ordered
For example: a nebula

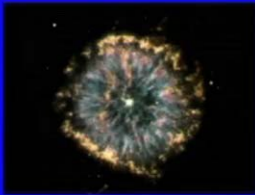
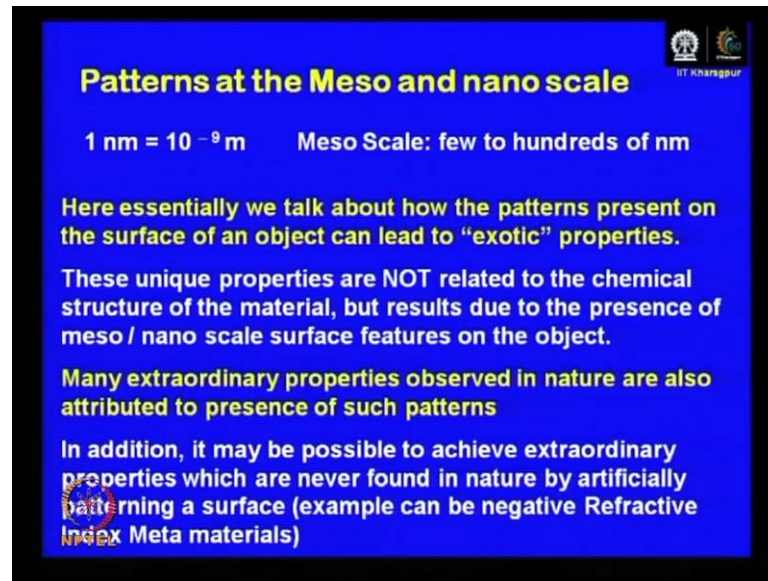


Image under Creative Commons CC0 1.0 Universal Public Domain Dedication act

But, in the context of this particular course we will be interested. Oh, the further **further** you may note that patterns can not only be special but it can also be temporal. So, it may not be the examples we have shown so far are all sorts of spatial patterns where the repetition is in space. But, one can have **repeatating** patterns in time. For example, the diurnal motion of earth itself is a classic example of temporal pattern, every morning the sun rises and every evening it sets, so it is also a regular pattern which is associated to the biological clock of our bodies.

Patterns can also be partially ordered. For example, if you look at this picture of this beautiful nebula, you see there is some sort of a pattern there is something at the center and things are exploding or expanding. But, if you look carefully the it is not exactly a hundred percent symmetrical, you really from your engineering concepts probably cannot draw a central line to locate the symmetry the plane of symmetry. But, still if you have a casual look there are patterns. So, the idea I would like to impress upon you that patterns can be absolutely ordered or they can be partially ordered also.

(Refer Slide Time: 19:04)



Patterns at the Meso and nano scale

1 nm = 10^{-9} m Meso Scale: few to hundreds of nm

Here essentially we talk about how the patterns present on the surface of an object can lead to “exotic” properties.

These unique properties are NOT related to the chemical structure of the material, but results due to the presence of meso / nano scale surface features on the object.

Many extraordinary properties observed in nature are also attributed to presence of such patterns

In addition, it may be possible to achieve extraordinary properties which are never found in nature by artificially patterning a surface (example can be negative Refractive Index Meta materials)

Moving on, however what we would intend to talk in this particular course is patterns at meso and nano scale which are present on the surface. I am sure all of you by now understand what exactly a nanometer means, it is ten to the power minus 9 meter meso scale is sort of a word that is used to sort of define length scales that varies between few to hundreds of nanometer. So, tens of nanometer to couple of micron is what we will regard as meso scale in the context of this particular course. Here essentially we talk about patterns present on the surface of an **object** object that can lead to exotic properties what I mean by exotic these unique properties are not related to the chemical structure or formulation of the material. But, results due to the presence of these surface features on the object. Typically, we know that something is tough for example, metals or something is shining and plastics **plastics** are soft these properties originate from the bulk properties.

But what we are going to talk here is some properties which do not which are not directly related to the bulk properties but, they originate because of the presence of structures or patterns on their surface which are apparently exotic or unique properties. So, many of the **ex excer** extraordinary properties observed in nature are also attributed to presence of such patterns. One of the key research in **the** key intention is in these areas is to somehow mimic those functionalities which are already available in nature and I will give you some examples of that artificially. So, in order to achieve that making these type of patterns become important that is the what we are going to cover in the first part

of our talk. In addition, it may be possible to achieve extraordinary properties which are never found of found in nature by artificially patterning a surface.

For example, I do not know how many of you have already heard but, you are free to do a Wikipedia search. There is this concept meta materials which are also known as the negative refractive index materials which sort of promises that cloaking or invisibility will soon be possible may be in a few years time. Now, these type of materials are not available in nature but, they are artificially being explored and the entire progress in these areas is attributed significantly to the presence of surface patterns or patterning methods.

(Refer Slide Time: 21:38)

Patterns at the Meso and nano scale

Patterns with sub micron and nm resolution find application in host of important areas, some of which are

- Optics
- Micro Electronics including organic electronics
- Structural super hydrophobicity
- Biotechnology

In the initial part of this course we will focus on how some such structures or patterns can be created, with specific emphasis to polymeric materials.

AFM Image
(Atomic Force Microscope)

The slide features a blue background with yellow and white text. In the top right corner, there are logos for IIT Kharagpur and NPTEL. The central text lists application areas, and the bottom right contains an AFM image showing a series of parallel, raised lines on a surface. A scale bar below the image indicates a length of 10 micrometers.

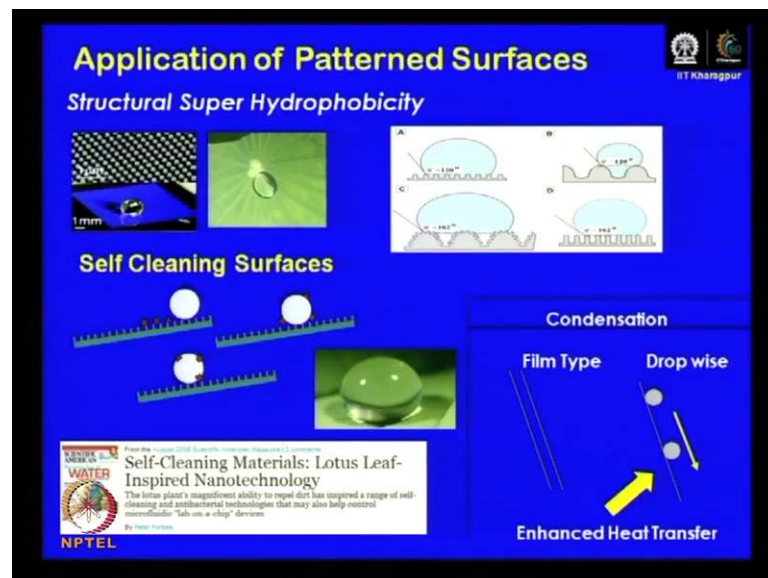
Progressing further patterns with some micron and nanometer resolution, find application in host of important areas some of which are optics microelectronics, one of the key and the most significant users of patterning. I will give you some examples on this, structural super hydrophobicity, lotus leaf effect what is it is also known as many of you probably know. So, when we touch upon this area you will realize what I am talking about lot of application in biology and biotechnology.

So what we are going to talk essentially is some structures like these. So, here you see the scale bar here is 10 micron and you have some 7 8 lines. So, the lines are around 700 or 800 nanometer wide and they are separated by similar sort of a distance. These type of figures you will see a lot in this course. This is an AFM image which is an atomic force

microscope so this type of image you see when you try to investigate a sample under an atomic force microscope. As I have told you in the introduction part that we will cover how an atomic force microscope works or something like that. Just to give you a comparison about the link scale of these lines what you are seeing on your screen a human hair probably one of the thinnest thing or narrowest thing, we know is 50 micron so that is roughly 500 times of these structures **I am sorry**, it is a roughly about 50 times thicker than each of these lines what you are seeing on your screen. So, we are actually planning to talk or we are going to about these type of structures which are very **very** narrow small very small literally. And so, you can imagine making these structures become non trivial at times and also investigating them as to **why** how they have formed and whether they formed accurately also becomes challenging which we I will give you some glimpses how to do that.

So, that is precisely we will do in the initial part of the course we will focus on how some of the structures and patterns can be created and we will specifically emphasize on polymeric materials.

(Refer Slide Time: 23:34)



So, let us talk about some of the applications of pattern surfaces. One of the key application is the concept of structural super hydrophobicity do not be sort of scared with the name or something like that. We all know about the lotus leaf effect. A lotus grows on the surface of a pond and the tree sort of spreads on the pond. However, if you drop a

drop of water on this leaf what happens is the drop simply rolls off rolls off like a metallic ball. I am sure many of you have seen this application or seen this phenomena occurring.

This as it turns out that this ability of a drop of water to roll freely on the surface of a lotus leaf as well as on the surface of many other biological entities or objects some of which include some other leafs and plants including grass, actually as well as bud feather for example, is not attributed due to the specific property of the leaf or the plant. But, is because of the fact that there exists some very tiny structures or humps on the surface of these plants. So, what it makes that instead of the droplet sitting on a flat surface it now sits on corrugated or a patterned surface and as you can see in the schematic here which we will take up in greater detail. Subsequently, once we move a couple we are through for a couple of lectures is the waiting regime changes. I mean these are these are critical concepts, I will talk in greater detail.

So, you can see instead of the drop for example, in figure a schematic figure a instead of the drop sitting in cohesive contact with the surface. There can be isolated air pockets present between the liquid drop and the surface of the substrate. So, these interrupt air pockets sort of aid in this type of a rolling phenomena or really rolling of these drops. Now, this is something what is called the area of super hydrophobicity or structural super hydrophobicity, it is a very important area lot of research advanced research is going on. One of the offshoots of these area is the so called concept of self cleaning surfaces which I will again talk in a little a detail in in in subsequently very soon.

Coming back to your chemical engineering concepts. We all know about condensation in we have all studied about condensation in our heat transfer courses and we know that there exists two types on condensation film: type condensation and drop wise condensation. And I am sure from your heat transfer concepts you also know that from the standpoint of heat transfer film type condensation is preferred over the drop wise condensation. Because in film type condensation, the condensing liquid or condensing vapor which let us say is in this area has does not have a direct access to the cold surface on which its condensing, there is an additional layer of liquid which imparts an additional resistance to the flow path. So, therefore the heat transfer is hindered.

In contrast, in drop wise condensation the condensing vapor **has** sees the **direct** has direct access to the cold wall on which it is condensing so the heat transfer efficiency is higher. The drops formed after condensation which immediately roll off. This you all know and if I also ask you under what condition that there is a transition or what determines a drop wise **condensation** whether you are going to have a drop wise condensation or a film type condensation. Some of you might also say that well if we a rough surface, we will get drop wise condensation. If we have a smooth surface, we will get a film type condensation.

The answer is absolutely correct but, the moment you actually talk about a rough surface, you are essentially talking about the what talked above. It is essentially a combination of the surface energy of the surface on which condensation is occurring along with the roughness or which can be in the form of presence of regular or disordered structures which lead to whether you are going to have a drop wise condensation and film type condensation. So I am sure immediately you realize that these type of patterns what we are going to talk subsequently or what we are talking here has some significance to the engineering knowledge you have already received.

(Refer Slide Time: 27:53)

Application of Patterned Surfaces

C

A silvery stinging air layer encloses the fishing spider (*Ancylopetes bogotensis*, left). Hairs of the fishing spider (right)

fishing spider *Ancylopetes bogotensis*

Hairy structure is plastron

that allows the insect to breathe normally under submerged conditions

D

Water strider *Gerris remigis*

SEM images of a leg showing microsetae and the fine nanoscale grooved structures on a seta

water strider, *Gerris remigis*

Allows the insect to perform gravity defying walk over water.

Simpler examples: Bird Feathers, most plant leaves

From V M NAIK, R MUKHERJEE, A MAJUMDER and A SHARMA, current trends in Science, Platinum Jubilee Special Issue of Indian Academy of Sciences, 2009 Page 129, available online

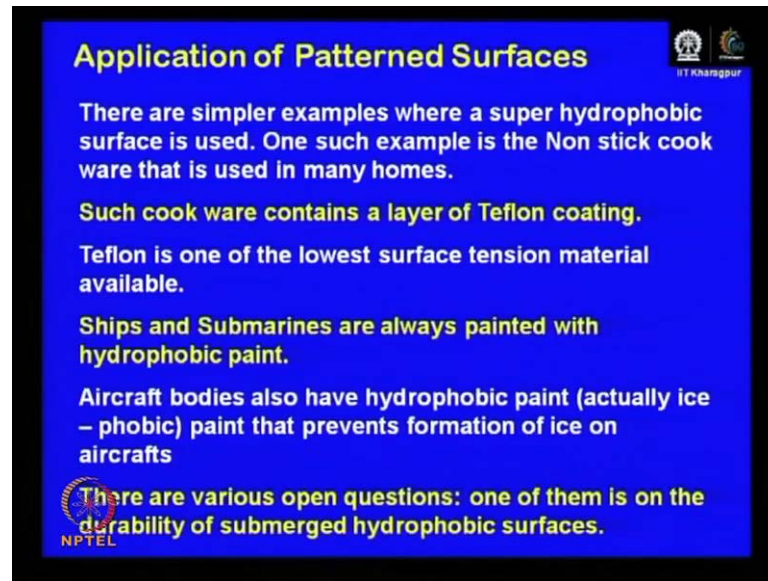
So, we will look into these type of surface related issues in greater detail. Moving on, many of the not only the leafs of plants. But, many of the insects also have extraordinary exhibit extraordinary capabilities which are also attributed to the presence of structures.

For example, there is this fishing spider that its biological name is written there **I am sorry**, I cannot pronounce it properly so what these spiders do that they **they they** go on fishing. So they just dive deep into the water pool so they have something called plastrons which are hairy structures as you can see here in these images along their arms.

So, once they decide to dive in the pool these plastrons sort of form an air pocket around these insects completely. So, what it does it dives but, it is sort of encapsulated in an air chamber so though you know that only a fish can breathe in deep in water, it sort of carries with it an artificial environment of oxygen and it can breathe normally and can spend a long time deep in water similarly, **pro** many of you probably have heard about the insect water strider which sort of can walk over water **water**, it sort of performs a gravity defying walk over water and it turns out that it has some long legs or arms which show that they are some micro textured setae and some nano scale grooved structures on their setae which actually acts as water repellent. So, this forms a very complex contact line with water thereby sort of reducing the effective gravitational influence on the insect so that it does not drown on water and it can sort of walk.

So, in and around us there are various examples in the animal kingdom as well where patterns surfaces or patterns provide some extraordinary properties. You are free to look into this reference which I have put up at the bottom of this slide. It is available free on the internet, so you can just download or you can write to me I will be happy to share it with you.

(Refer Slide Time: 30:14)



Application of Patterned Surfaces

There are simpler examples where a super hydrophobic surface is used. One such example is the Non stick cook ware that is used in many homes.

Such cook ware contains a layer of Teflon coating.

Teflon is one of the lowest surface tension material available.

Ships and Submarines are always painted with hydrophobic paint.

Aircraft bodies also have hydrophobic paint (actually ice – phobic) paint that prevents formation of ice on aircrafts

There are various open questions: one of them is on the durability of submerged hydrophobic surfaces.

NPTEL IIT KHARAGPUR

Moving on there are similar example where super hydrophobic surfaces are used. One such example which all of you, I am sure most of you are aware with is the so called nonstick cook ware which is used in many of our homes. Have you, if you have ever really worried to look into what makes it nonstick as compared to a regular tava or we use.

It is actually turns out that it contains a layer of Teflon **Teflon**. Some of you might be knowing is one of the lowest surface tension materials available to a known to mankind as of today. And **the** it is this particular layer which sort of restricts anything that is that can be oil or any other food stuff to adhere or to stick to the surfaces. Well, so it is sort of comes off easily. You might also see, if you buy a nonstick cookware there is a that a foam that **accompanies** accompanies the cook ware and which says that never scrap this nonstick cook ware with anything other than this foam.

The warning actually is given so that by a way of scrubbing it hard with something else like a brush, you do not spoil the Teflon coating it turns out that these Teflon layer also have some tiny micro structures which sort of aids to the level of the or ease of detachment. We will talk about these things in greater detail in lectures to come. Well, you see that ships submarine aircraft everything is painted but, these paints are completely different than the paint we use for **for** example, painting our walls and buildings ships and submarines are always painted with hydrophobic paint because of the

fact that parts of ship and almost entire part of the submarine remains submerged. So, you really do not want water to sort of really stick onto the surface very preferentially because the because of the simple fact that there might be significant microbial growth or growth of a marine algae and animals on the surfaces of these vehicles.

So, that is a major area aircraft bodies also have a hydrophobic paint. Actually ice phobic paint that is a new term that is being coined by some of the researchers because commercial aircrafts fly at altitudes varying between 35,000 feet to 40,000 feet where the temperatures can be easily between minus 50 to minus 70 degree centigrade. So, there is a significant chance of ice condensing on the surface of water of the aircraft which is dangerous from the stand point of navigation and in order to avoid that these special type of paints are given to aircrafts also. There are various open questions in these area, one of them is on the durability of submerged hydrophobic surfaces that is if a surface, if a hydrophobic surface remains under water for a long time does it remain hydrophobic or it loses part of its hydrophobicity. These are questions which are still open which are extremely relevant to the industry, and **and** there are various industrial market or products which are coming up or are soon going to come up based on these considerations.

(Refer Slide Time: 33:15)



Talking about self leading surface, it is something very similar to a structural super hydrophobic surface. Here, the idea is that you have a patterned or a textured surface, so

when **when** the dust particles which are responsible for dirt or whatever they try to settle on the surface because of the structures present. You can see here that these dust **dust** particles do not adhere to the surfaces well. So, the adhesion itself is restricted the presence of the pattern hinders the addition of any dust particle to the surface and when a water sort of is water drop is flown over such a surface that water drop picks up this loosely adhering dust particles. So, a self cleaning surface sort of combines the two effects of structural hydrophobicity or the so called lotus leaf effect which allows a drop to roll over **roll** freely over a surface, and then it also does not allow dust particles to sort of settle down or on to the surface and have a greater degree of adhesion.

One thing you might be interested to know or it might be in might sound interesting to you that is that a dust typically has a size, a dust particle typically has a size somewhere varying between 4,400 micron. So, eventual idea even, if you look at the schematic one of the key thing is that the features, we have to make are smaller than the dust particles. So, that the particle does not have complete or full contact with the surface. Many of you, I am sure this is a photograph from the city of Chicago, many of you are we us are used ssto seen high rise buildings that come with glass façades which are very **very** shining, almost mirror like which look very beautiful.

Have you ever thought how they remain so shining you really do not see somebody going up every day and wiping it. Well, most of these type of glass blocks that are used for making of these facades actually contain a self cleaning layer. So, that it does not allow the dust to settle preferentially as well as if it is, if some water is sprinkled from the top the water sort of reaches down all the way taking off whatever is present on the surface. So, this is a self cleaning surfaces and super hydrophobicity is indeed, one of the key areas of patterning key application areas of patterning were lot of activity or lot of the patterns we make find a lot of application. And we will soon see that artificially creating such structures are extremely important.

(Refer Slide Time: 35:38)

Structural Color

If you hold the back side of a CD or a DVD, then you see rainbow

The gap between adjacent turns of the spiral is 1.5 microns, which are being separated by a valley 750 nm wide

When visible light falls on such a surface Diffraction of light occurs, resulting in the Rainbow color

Diffraction refers to various phenomena which occur when a wave encounters an obstacle and its effects are generally most pronounced for waves where the wavelength is roughly similar to the dimensions of the diffracting objects

Wave Length of Visible Light: 400 – 700 nm

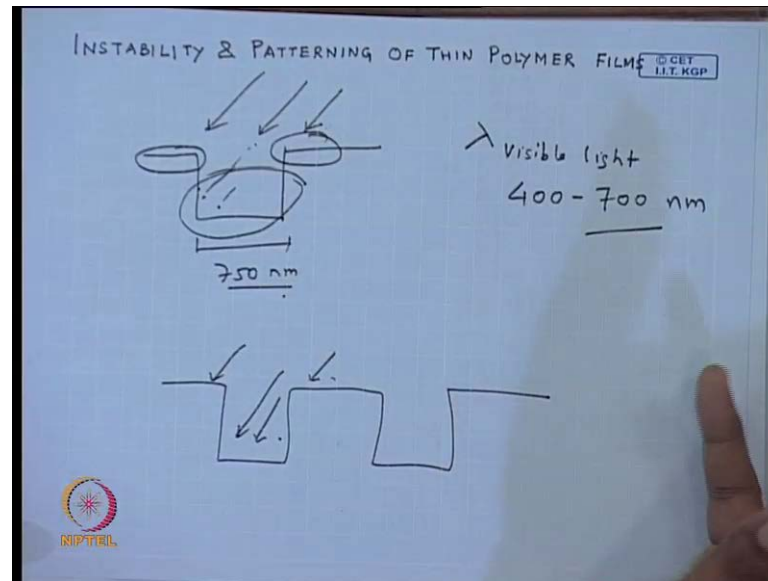
IIT Kanpur
NPTEL

The second aspect, I would like to draw your attention is somewhat related to optics where patterns have play significant role and again. Let us pick up an example what we see every day around us. If you hold a compact disc or a DVD in your hand on the backside of it you see a rainbow color. I am sure all of you have seen it. But, I now want ask you how many have how many of you have thought why this rainbow coloration forms because there is I mean why all of sudden in nature if we see rainbow, it is only after a rainy day under a specific condition and only at one area. But, you hold a CD or a DVD you see all the seven colors that constitute white light. As it turns out which clear from this schematic that CD if you look into the structure of a CD, it actually has a single spiral track that sort of unwinds from the center to the periphery and the gap between two adjacent turns of the spiral is of the order of 1.5 microns and which are separated by a value between them or a **seperation** separation distance between them of roughly 750 nanometer.

So, if you investigate a surface of a **spiece** piece of a CD under a microscope, the gap between two adjacent turns is much much smaller as compared to the radius of curvature of the CD and eventually under a microscope they appear as parallel lines. Now, what happens is when visible light falls on such a surface a specific phenomenon occurs which is known as diffraction. I am sure all of you know what is reflection and what is refraction of light. But, this is the third phenomena which **which** goes by the name diffraction of light which also occurs which actually is the key phenomena that results in

the formation of this rainbow color. Now, if you look at any standard physics **techbook** textbook you will find the diffraction refers to various phenomena which occur when a wave in this case optical wave encounters an obstacle and its effect a generally most pronounced for waves where the wavelength is roughly similar to the **dimension** to the dimension of diffracting objects.

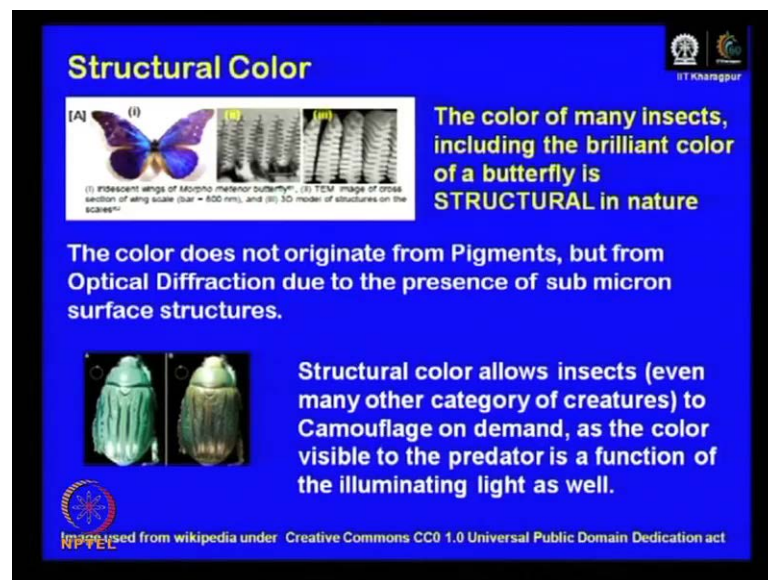
(Refer Slide Time: 37:53)



So, simply put what happens is you have a structure like this onto which light is coming visible light is coming and you may be knowing that the wavelength of visible light is varies between 400-700 nanometer. Now, here we talk about a value which is something of the order of 750 nanometer wide, so if we if the light is falling from an angle what happens is the part of the some of the waves actually get into the light in into the valley some of the waves sort of get blocked off. Because of the confinement effect or the lateral confinement effect or the size, so part of the light gets reflected from these areas while part of the light gets reflected from these areas, this is a very simplistic view. But, you can understand that this structure the presence of the surface structure like this sort of splits up the light in the form that some of the wavelengths are allowed to penetrate all the way up to here and some of the **penetrate** wavelengths are sort of blocked here that is also one of the reason, if you tilt a CD the rainbow coloration or the location of the rainbow color continuously changes.

So, this is something that occurs exclusively due to the presence of the structures or the patterns on the surface and what is important to note that this **structure** this is what is known as structural color. But, what is important to note that this structural color is not limited to CD or DVD.

(Refer Slide Time: 39:20)



But, again in the biological creatures and animal kingdom there is a huge **huge** application or huge, I mean structural colors are seen hugely in a in a big way. For example, the brilliant color you see in the butterfly wings many of you, probably do not know that it is it is to a large extent due to structural color.

So, butterfly peacock these type of things the coloration or the ordered coloration the regular beautiful patterns or the colors you see in many cases. I do not say, it is purely due to structural color but, it is a combination of pigment based color and structural color. For example, the blue color you see behind me is actually a color which is pigment based color it is not **relative**, it is a particular dye that has been given to the cloth or the plastic façade that is up there and that is that is responsible for color. So, essential idea is that when you add a desired pigment and white light falls on to it what happens it absorbs pretty much all the other wavelengths **other** which do not correspond to the blue light. So, the only the wavelength corresponding to the blue light gets reflected from that surface and all other wavelengths are preferentially absorbed giving it the **expression** impression of a blue color.


So, pigment based color you can see is also related to optics. But, it is related to the phenomena of optical absorption in contrast structural color is related to the phenomena of optical diffraction. Now, the color does not structural color, I mean why insects really are insects or animals many of them rely on structural is one of the key advantages that structural color allows insects to do camouflage on demand. Because, in the animal world you must realize the entire dynamics results around the concept of predator and prey. So, when something is trying to catch its food, it would try to sort of remain as much camouflaged as possible from the insect or animal it is targeting to attack.

Similarly, when something feels that it is going to be attacked, it also tries to sort of pick up colors or camouflage it to the maximum possible extent. So, that the other thing that wants to sort of attack it does not feel its presence. You also know that many of the animals have extra sensory powers like dogs for example, have extremely good smelling abilities, snakes can pick up vibration and so on and so forth. But, these are some of the additional instincts animals have and some of the additional instincts are also due to the presence of the structural color which are attributed to the presence of ultrafine features on their surfaces.

(Refer Slide Time: 42:07)

Structural Color

The most well known example of Camouflage on demand is probably seen in Chameleon (a variety of slow lizard that can change color).



Floral Iridescence, Produced by Diffractive Optics, Acts As a Cue for Animal Pollinators

Heather M. Whitney,^{1,2} Mathias Kuhn,^{1,2} Piero Andrei,¹ Leo Chittka,⁴ Ulrich Steiner,^{2,3} & Stanley J. Dyer^{1*}

In a very recent article it was shown by Scientists that insects recognize structural color and NOT pigment based color like us.

2 JANUARY 2009 VOL 323 SCIENCE www.sciencemag.org

In many cases the color is a combined effect of pigmentation and diffraction

Image used from wikipedia under Creative Commons CC0 1.0 Universal Public Domain Dedication act

NPTEL

The classy classic example here is what we all get fascinated as children is about the existence of the **chameleon** chameleons which we know that they can change the color based on the situation.

Well, it is not that that it can change colors to all sorts of colors but, they do have a range over range over which they they do change their colors it can vary between blue to green to brown probably. Chameleons, if you know it is a variety of slow moving lizards that change color and probably, it needs to change the color lies in the fact that it is slow moving. So, it probably cannot move as fast as other reptiles can move. So, in order to sort of not getting eaten up or by getting attacked by other bigger animals, it probably relies on changing its color so that it can match the immediate surrounding. And now, it turns out based on extensive research that there are ultrafine features on the on the skin of these lizards which depending on the stimuli what type of situation, it is subject to they can sort of change the orientation to somewhat extent and it is a combination of pigment based effect as well as the structures present which they allows them to tailor the color. In a very recent work from a group of scientist at Cambridge, they came up with something very very interesting which changed the perception about how animals or particularly the insects visualize.

We all know that the insects have compound eyes is so they have so, it is a multiple number of images that forms in there and so eventually they can have a wider view. It is like a wide view camera wide angle camera but, what was recently shown that the insects in many cases do not recognize pigment based color as we do. So, would term a flower a rose is red because we see that it is red but, it turns out that the insects can recognize the structures associated to that. So, simply put an experiment of something like this was done some set of beetles were trained for a particular red flower and what the scientists did they they replicated the structure of that red flower on some polymer and then these beetles these structured surface was illuminated red and in a in a area where there were various types of flowers and structures and leafs and plants the beetles were allowed to get in. And they could recognize those artificially created surfaces which also have the similar structure as compared as was present in the original red flower onto which they were trained.

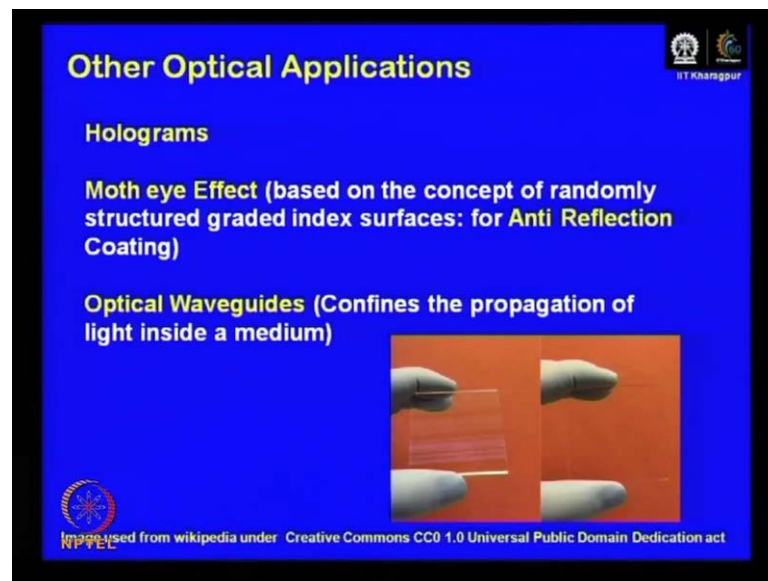
So, that showed that they did recognize the red color but, what it was more interesting is when in a subsequent experiment these artificially created structures which corresponded to the red flower was artificially illuminated in other color. Let us say blue or green, the set of beetles when they were allowed to enter the experimental chamber they were

migrating to the same structure, though now it was appearing to be green or blue. But, which had the structure similar to the red **red** flowers.

So, this is very exciting in the sense that not only, so this shows that structural color is not only due to surface patterns. But, insects probably have their vision or their sense of color based on structural color. So, which was a very significant discovery and it was published in the top notch scientific journal of science very recently in 2009.

So, to sum up on structural color in many cases the color is a combined effect of pigmentation and diffraction. And of course, there is a lot of research that is going on artificial **artificial** structural color where the utility of pattern surfaces or making patterns at desired the length scale become important.

(Refer Slide Time: 46:00)



Of course, there are various other optical applications well, where pattern surfaces find extensive **apps** extensive utilization. For example, holograms some of you, if you care to look at credit card or bank debit card close to the visa or master sign, you will find the there is something is shining that is exactly an hologram what hologram is.

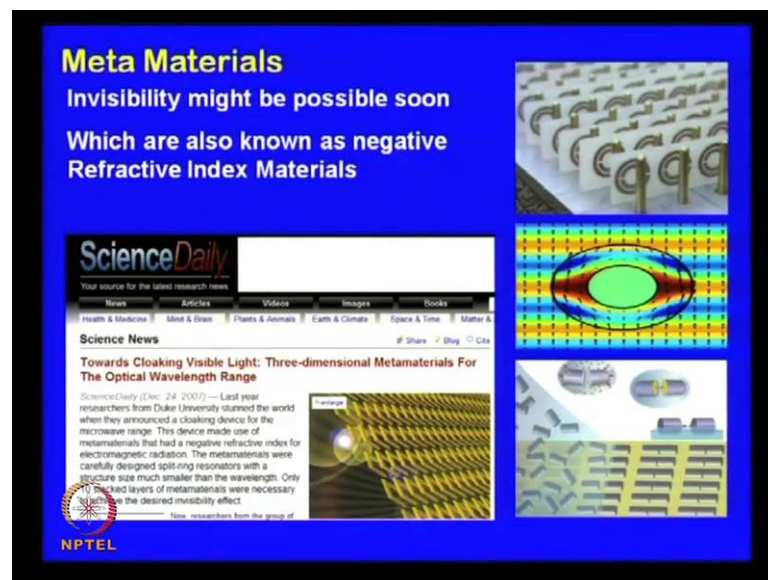
The other important thing very interesting phenomena is the so called moth eye effect which is known as the anti reflection effect because moth eye is a special, if you shine light on them nothing reflects back. So, that that is also very very important and you can

see it in this frame. So, here is a glass slide which the somebody is holding and you can pick up that the lights the lights in the room, some images of that you can see.

So, part of whatever illuminating light is falling on this glass it is getting reflected. But, here again, if you very carefully see a glass slide is being held but, which has a coating of anti reflective coating and so you can see almost nothing gets reflected. So, these type of coatings anti reflective coating, anti glare coating, highly reflective coating. These type of coatings are extremely useful in various optical application. And now, the and more there are research orientation of creating these type of coatings based on patterns.

Another important thing, you can do a Wikipedia search or an internet search is on optical waveguides which also is something very interesting that confines the propagation of light inside a medium and optical waveguides are extremely important in optical communication based on optical signals as well as sensors based on optical properties. So, all these development in all these areas really require artificial patterns with some micron lateral length scale to be fabricated.

(Refer Slide Time: 47:47)



Well, this is something I briefly touched about earlier the probably, the one of the most major thing that is going to come up not in not very distant future is probably, the development in the area of meta materials. I do not know how many of you are aware of this particular area but, it is something really exciting almost similar to science fiction

meta materials promise that they are going to make cloaking possible. So, essential idea is these **these** materials are known as negative reflective index material.

So, essential idea is that he if you look into this particular schematic carefully. What you see that the light waves that are coming can be bent in a desired fashion **oh sorry**, so that it does not pass through this particular area. Now, if I stand in front of you **you** own you will see my or you will recognize my existence because of the fact that you are unable to see what is there behind me. Now, suppose if something can be done so that the light signal that is coming from the back sort of bypasses me completely and then goes to your eyes again you are going to miss me out.

So, suppose if I stand in this particular domain and this is the background you have and you are standing here. So, what is the what the this structure is going to make is its going to bypass me preferentially, and this can be achieved with the with what is being termed as an extremely exotic development or which are termed as meta materials.

Now, the state of art as of now, in the meta materials is that at micro wave frequency cloaking has already been achieved. There are certain scaling issues associated with the property primarily the permittivity and other properties of the material which are being used for meta materials which are still hindering, its development for visual life, for visual way, for the visible wavelength of light. But, I guess significant research is progressing in that particular direction. So, the possible development of meta materials is entirely also entirely attributed to the structured surfaces or patterns.

(Refer Slide Time: 50:01)

Re usable Super Adhesives
Re-usable, Clean, Non Viscous Adhesives

It's a Bio Inspired Concept ... Many of the animals, creatures etc. show surface structures ...

Key here is: **Soft Structures**

body mass →

beetle fly spider gecko

Artificial Gecko Type Structure
Nat. Mater. 2, 461, 2003

NPTEL

The slide features a blue background with white and yellow text. It includes a diagram showing the relative body masses of a beetle, fly, spider, and gecko, with an arrow indicating increasing mass. Below this are four scanning electron microscope (SEM) images of the adhesive structures of each animal. To the right, there are two SEM images of an artificial gecko-type structure, a citation 'Nat. Mater. 2, 461, 2003', and a line graph showing force versus distance for different adhesive structures.

Moving on we come to the third example where again from nature and which again people are trying to artificially replicate is on the concept of usable super adhesives. One of the key example of this, we see everyday around us is the walking gravity define walk of a lizard climbing of a vertical wall, right. So, if you think carefully what is the lizard doing, the first is a lizard has some mechanism that allows it to stick to the wall. So, it does fall due to gravity because if you and I try to the same we will fall off. But, then the lizard moves on, so it is not that it is permanently sticking. So, it moves on, so first it sticks somewhere and then it detaches itself and then moves to the next location.

Now, if you use a cello tape once for example, an adhesive tape. What you can see that may be first time it sticks well, you take it off. Try to stick it at for the second time, it may stick or it may not stick chances are that, it may not stick and third time onwards definitely it will go back. So, what is the problem a cello tape is a reasonably good adhesive but, it is an once use adhesive. Now, suppose the lizard has an extremely good adhesive in **in in** its legs or something like that but, I mean after using four five times, it goes back eventually that would mean that every lizard would essentially can walk five times in its life and then it will perish but, that does not happen.

So, it sort of not only adheres to the surface extremely tightly that allows it to defy gravity but, then again uses its legs again and again and again to sort of perform its walk, it can climb wall vertically it can it can hang on to the ceiling. You all know that, so the

clue is that it is not only super adhesive, it is a reusable adhesive and as it turns out that these are non viscous adhesives as compared to most of the adhesives we use. If you take gum for example, it is a liquid so it is a viscous adhesive and the adhesion is achieved due to what is known as viscous dissipation. So, you just stretch it and then eventually you lose some energy in the form of viscous dissipation and at the cost of which you achieve the adhesion.

Now, this bio inspired concept of artificial adhesives is entirely based on the existence of surface structures or let us say deformable soft surface structures and significant recent work is actually going on in artificially mimicking these structures. So, these are again some examples where textured surfaces can be used and subsequently we will talk of other areas in which pattern surfaces can be used. I will stop here.