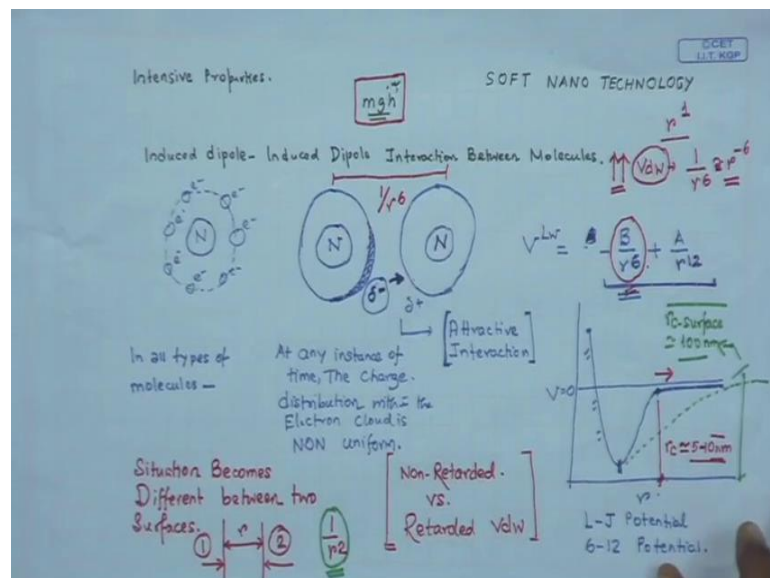


**Soft Nano Technology**  
**Prof. Rabibrata Mukherjee**  
**Department of Chemical Engineering**  
**Indian Institute of Technology, Kharagpur**

**Lecture – 02**  
**Introduction – 2**

Welcome back to the second lecture of this course. We had a short introduction in the first lecture and we will continue with the introduction. 1 of the important things that I highlight at towards the end of the first talk is the existence of Van der Waals source.

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We also discussed, and these are things we will discuss in great a detail that between two molecules the attractive component of Van der Waals source scales as 1 by r to the power 6. From here itself you can get an idea about what is what is happening when the dimensions of the system are very very small, because the gravitational fields sort of scales as m g h or m g r, so it is r to the power 1. In contrast Van der Waals sources scale as 1 by r to the power 6 or it is r to the power minus 6.

Now you all can understand that if r is smaller this term starts to shoot up. And it terms out that at few tend of nanometer length scale gravity is almost nonexistent and the situation is completely dominated by Van der Waals source. There are couples more things we need to understand. If you look at this particular plot, in fact it is there in the PPT also.

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**Van der Waals Dispersion Force Between Neutral Molecules**

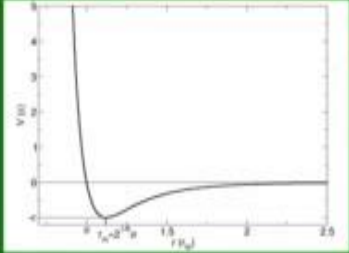
The interaction potential due to this type of interaction is given by the well known Lennard-Jones potential equation

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

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 interaction can stretch upto ~ 100 nm.

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



If you look at this particular plot this is sort of a critical dimension or critical separation distance, why because beyond this or if the separation distance between the 2 molecules is beyond this  $r_c$  there is almost no interaction. And arguably this is of the order of 5 to 10 nanometer maximum. There is a lot of dispute on that. There is one quick search you can do or is on non-retarded versus retarded Van der Waals interaction and find out what it is. This is not in the course, but this is for your own learning.

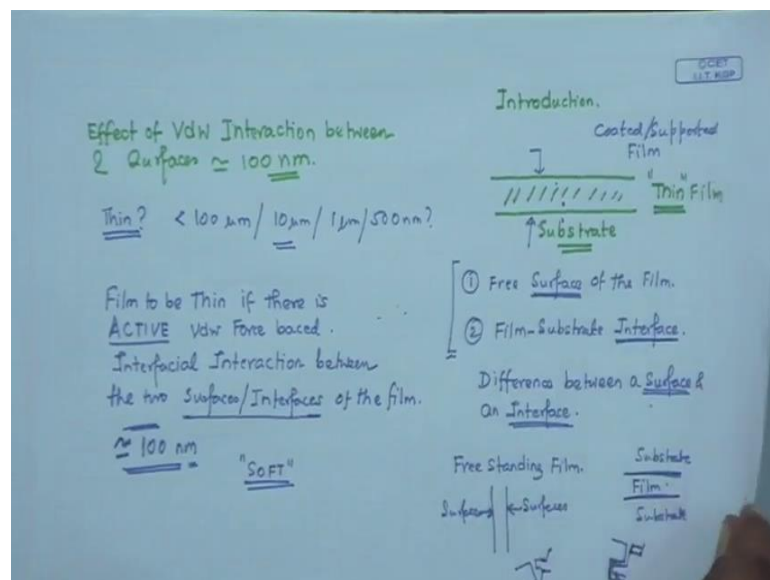
What we understand that between two fundamental particles? The attractions scale as  $1/r^6$  and the interaction stresses between let us say 5 to 10 nanometers. Situation becomes slightly different and this is something you will learn in great detail in the course between two surfaces. And please understand that in a macroscopic system, but even in small systems you really looked at for any engineering application interaction between two molecules. You are more interested in look at the interaction between two surfaces. And therefore, how the Van der Waals source scaled between two surfaces is a very important aspect?

And it turns out that the Van der Waals interaction between two surfaces; let's say surface 1 and surface 2 scales as the scaling does not remain  $1/r^6$  it changes to  $1/r^2$  and as a result if you super pose on the same plot the interaction sort of becomes longer range and this  $r_c$  for surface again  $r_c$  arguably is of the order of 100 nanometer.

Here is something a quick taken message; nano scale dominated by London dispersion forces of the induce dipole induce dipole type Van der Waals forces these are called the dispersion forces. It is dominated by these inter molecular induce dipole Van der Waals sources whose effect between two molecules sort of stress by up to 10 nanometer maximum with a scaling of  $1/r^6$ . However, the same force is responsible for a rather longer range interaction up to 100 nanometers between two surfaces and the scaling sort of changes to  $1/r^2$ .

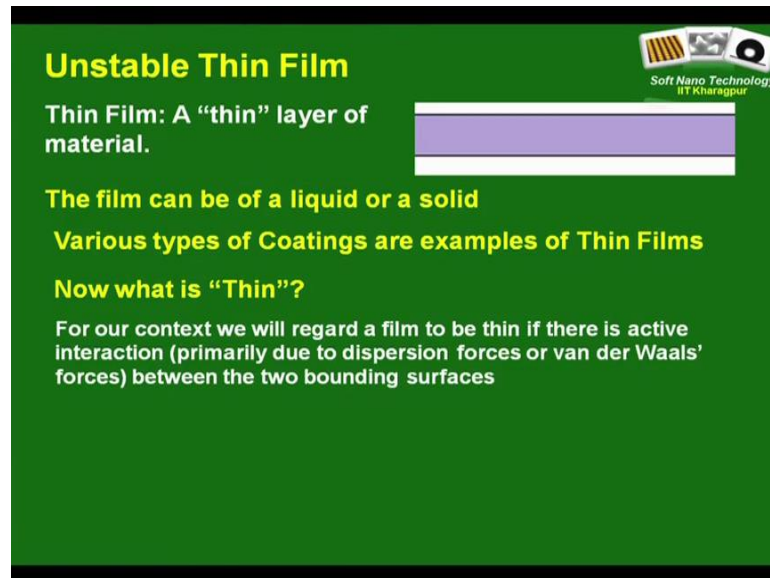
This is something you will learned, but this is I am just giving an introduction. So, these are good concepts to sort of remember.

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What is the consequence? Consequence is we now know the effect of interaction between two surfaces stretches to about 100 nanometer. What is the consequence of this? And do not forget the name of this course it is Soft Nano Technology, where it becomes extremely important is in a thin film.

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**Unstable Thin Film**

Thin Film: A “thin” layer of material.

The film can be of a liquid or a solid

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

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What is the film? It is a layer of material. Let us say it is a film of some material and often films are coated on another layer or a substrate, and that is essentially you all know that these are coatings. Coatings are extremely important in variety of settings, whole lot of functional applications right from your winds to glass wind screen to your non stick cook where to your spectacles these this everything comes with the coating.

What happens in this film? If I now ask you a simple question that. So, the first question that should come to your mind is this what thin. So, what exactly is a thin film, how do define a thin film. So, is it like a number like it is less than 100 micron, do not forget 70 micron is roughly you are here so 100 micron is speedy thin, 10 micron, 1 micron, 500 nanometer what is it. Well, there are different ways to define what are the thin film, and the different context in fact the definition of thin film also changes. But for our context we will considered something to be a thin film not based on any number, but based on something else.

Let us see what a thin film is? In fact, a thin film has two boundaries: one is the free surface of the film, and the second one is the film substrate interface. In fact, the way I have defined the two boundaries also clarifies a pretty important and interesting concepts that concept that is going to come up. And let me highlight it straight away since we are talking about it here. What is the difference between surfaces and interface which going to come up. You can quickly get an idea when two materials both of them on non

condensed, both of them are condensed. That is non condensed is either gas or vacuum they are in contact like here, a film and the substrate material both of them are condensed phases they are in contact they in fact give rise to an interaction.

However, when a condensed phase is in contact with another non-condensed phase which can be gas or which can be vacuum then it is called a surface. So, that is a very important classification. We often tend to sort of use them interchangeably, but in science surface and interface are different things which you need to understand. So, again coming back to the question of what is this. So, see here now we identify that a thin film has boundaries, and in the previous discussion we also found out that when the separation distance between two surfaces is less than about 100 nanometers there is in fact active Van der Waals interaction because beyond this 100 nanometer limit there is no interaction.

That sort of sets the tone for defining what is the thin film in our context, and that is we will consider a film to be thin if there is active; and I emphasize this one Van der Waals force based interfacial interaction between the two surfaces/interfaces. Why I write this surfaces or interfaces? As I am coming in a minute of the film. So, that sort of sets the tone for our setting roughly 100 nanometer as a sort of the limit. So, any film that is about thicker than 100 nanometers we will not consider it to be a thin film, simply because of the fact that based on our concept that there is virtually no interfacial interaction.

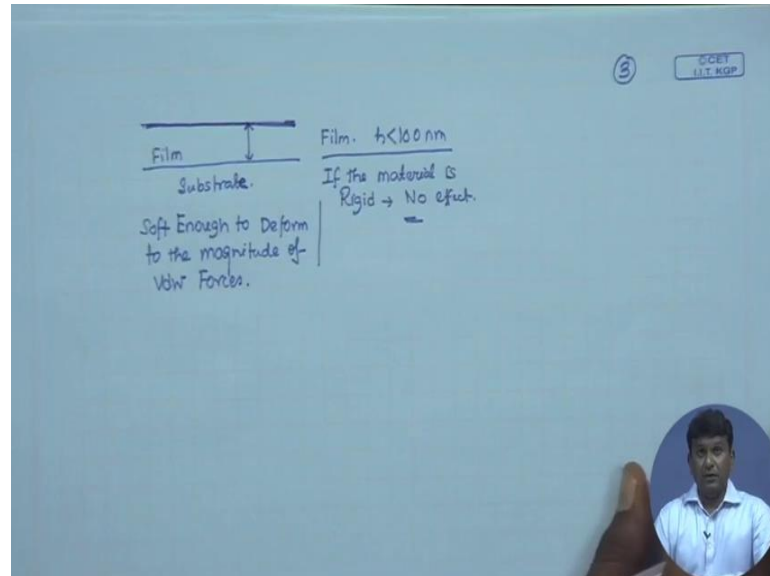
1 quick highlight may be. Why I mentioned between the two surfaces or interfaces because this type of a film which is a coated film, coated or a supported thin film has one surface and one interface we already have discussed about it. But you can in principle have a free standing film. Can anyone think of an example? A very simple example is the, so bubbled doublet periphery of so bubbles, so you can have a free standing film where you have surfaces on both sides. Or you can have a film stand which between let us say two solids it can be a liquid it can be another solid.

In fact, this film has two interfaces and where does one see this type of a film. In fact, lubricating oil in a gear or something like that. In fact, forms films like this so here is the lubricating layer sort is the picture is not that rate may be I can write to draw it later.

Here is 1 gear, the group of a gear and here is another 1, as you can like this. And as you know you have this lubricating film here, so this is a type of a film which is also called

the lubricating film will only have two interfaces. So, this is important, but then why at all we worry about.

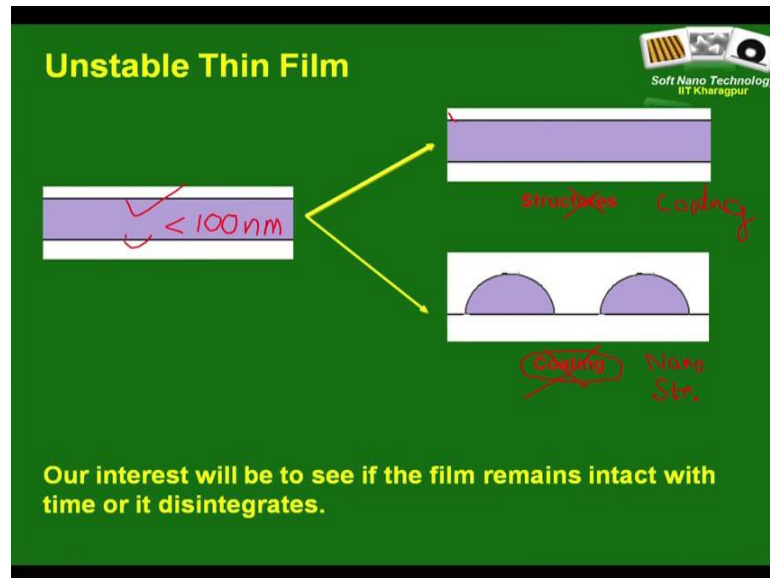
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Now, we worry about it because of something that is amorphous in the title of the course and that is so called soft. Now, you look in to this film or maybe I will just draw it fresh. You have a film which is thinner than let us say 100 nanometers. If it is thinner than 100 nanometers, you now know that there is active interaction Van der Waals interaction between these two interfaces. Here you know found does it matter? If this film is very thin and it is made of a rigid material in fact nothing will happen, if the material is rigid no effect.

However, now consider that you have a film let us say of a liquid or some soft material which is soft enough to deform to the magnitude of this vdw or Van der Waals sources. Then what will happen is depending on the nature of this interaction I have not told I have told that between two molecules of the nature of Van der Waals source is attractive, but we will see in the course of this lecture that a coated film for a coated film or a supported film even the effect of Van der Waals source can be attractive or repulsive based on the nature of the weight ability and surface energy and stuff like that. Those are things you will learn in great detail as a part of this particular course.

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What might happen is you might have a film which is thin enough. As I mentioned that this is thin, so this is about less than 100 nanometers, and there is an active interfacial interaction. So, if the interaction is repulsive between these two interfaces in fact there is absolutely no problem the film will remain stable and sorry, this is a wrong thin I have written. So, this will be the coating this will be a stable film, so this will act as a coating; but if the film if the interaction is attractive then the film might disintegrate and it might evolve into some sort of structures nano structures.

This is what is the so called spontaneous instability in a thin film. You can see it is very difficult to say whether it is good or bad or whatever largely it sort of depends on the application you are looking at, because we have already talk that there are settings where nano structures the something that I am going to come up. Right next where nano structures surfaces are important so you see that this type of a film can be used as a this type of instability or spontaneous instability that has its genesis in Van der Waals sources can be used for nano structuring, but there are certain limitations and we will see how this can be cleverly done.

On the other hand films that are stable act as excellent coatings. Now, give you very very simple example. When the painter is painting any surface you in variable tell him to put two coats. And we all feel that we are doing this in order to sort of if two coats are put up then the painting or the color will look bright. When that is partially correct there is a



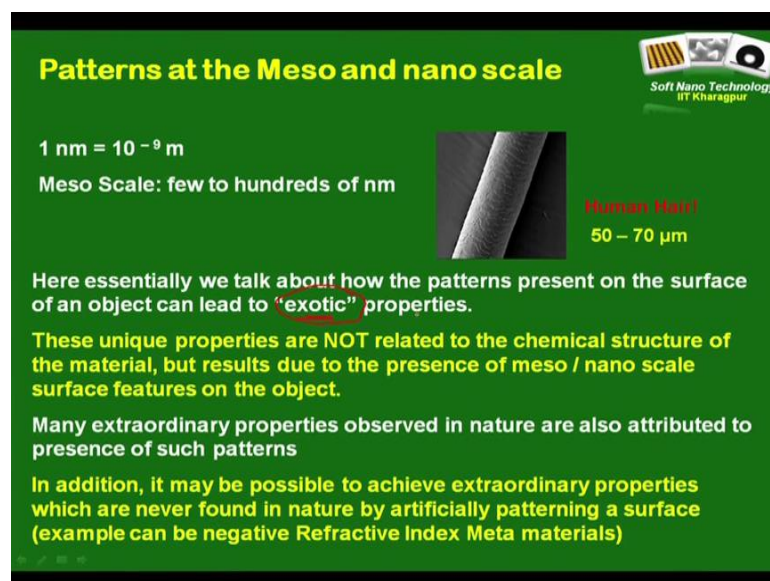
long implicit history behind making two coats is simply by adding two layers you are increasing the thickness of the pain which is also a type of a coating much higher than 100 nanometer.

What are you ensuring by doing this? What you are ensuring is that the films have thick enough and then there is no Van der Waals interaction. And therefore, irrespective of whatever is the interaction between the two surfaces it does not lead to this type of rapture. That is exactly what you do. So, these are the important aspects of Van der Waals sources.

And nano scale or the meso scale, another terminology that I will be using quite frequently that meso scale. It is roughly about 100s of nanometer. And you all know that so called effect of nano is not exactly limited you already have realized because this Van der Waals interaction which is one of the major things which is differences as compared to the macroscopic world a sort of stretches up to 100 nano mater. So, few 100s of nanometer that is where particularly in the in the effect of structuring you will see that there are effects is as length scale that we will talk about the meso scale.

This is again depending on areas of science; people have a tendency of using this. For example, zero light people talk about few nanometers has meso scale, but in our context we will be using few 100s of nanometer has the meso scale.

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**Patterns at the Meso and nano scale**

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1 nm =  $10^{-9}$  m

Meso Scale: few to hundreds of nm

Human Hair!  
50 – 70  $\mu$ m

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 we will now talk about the so called patterns at the nano and meso scale. So, nanometer you all know  $10$  to the power minus  $9$  meter, I just pointed out meso scale is few  $100$ s of nanometer. And this is human hair, so it is  $50$  to  $70$  micron depending on how good the quality of your hair is how much oil you apply or not it will be somewhere between  $50$  to  $70$  micron.

And therefore, we are now talking about definitely things which have some micron and  $100$ s of nanometer often down to few tens of nanometer. So, you should understand that should give your qualitative idea about how small things we are. Talking about what is important about the so called nano scale patterns that we can talk we will be talking about certain exotic properties; certain properties and often there exotic properties which are attributed to the presence of nano structures on the surface.

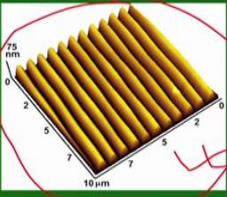
Let us say whether steel is hard or plastic or polymer is soft is attributed to the bulk property of the material. It depends on steel specialized material this is an amorphous material, so since the molecules are arranged especial in order you need much more force to dislodge one molecule or remove it from the lattice. And therefore it is very hard in comparison let us say an amorphous material is much less hard and you can sort of easily break it or things like that.

These are differences in properties which are attributed to the bulk structure of the material. But in the next few slides I will give you examples of situations where you have extraordinary properties. And the properties arise out of surface structures and often the length scales of these structures are micron, or lower than a micron or in maximum in certain cases we microns.

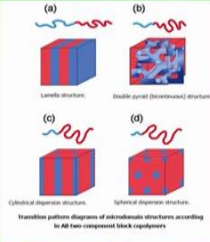
These types of structures are seen nature in biology. And also there is lot of research on replicating these structures artificially which falls into one of the major topics that we are going to cover as I have told in the very first slide are nano patterns. So, let us see what type of things are been talking about.

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**Nano Structured!**  
**What type of structures!**  
Are we talking about some Surface structures? Or internal structures! Or Both!



**Surface Structure**  
If these structures are regular, its referred to as nano patterned surface



**Nano Structured Polymer**  
Example: Blends, Block Co polymers

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The other important thing to really ask is; what type of nano structures are we talking about, because these structures can be on the surface. So, this is an atomic force microscope image of a nano patterned surface or these structures can be internal structures as well.

And this type of structures we will touch upon a little bit of it with polymer blends and may be time permits with block co polymers and things like that. But these types of structures also give rise to extraordinary properties in certain cases. Some examples I will pick up, but most as a part of this course we will devote a lot of time on how to make these a type of nano structures.

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**Patterns at the Meso and nano scale**

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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

**AFM Image**  
(Atomic Force Microscope)

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.

Nano structures have application in whole lot of areas, something I will just highlight optics electronics structural super, hydrophobicity, biotechnology and stuff like that and may be initial part of the course we will focus largely on how to make these types of surface structures or nano patterns.

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**Application of Patterned Surfaces**

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**Structural Super Hydrophobicity**

**Self Cleaning Surfaces**

**Condensation**

Film Type      Drop wise

**Enhanced Heat Transfer**

From the August 2008 Scientific American Magazine | 2 comments  
**Self-Cleaning Materials: Lotus Leaf-Inspired Nanotechnology**  
The lotus plant's magnificent ability to repel dirt has inspired a range of self-cleaning and antibacterial technologies that may also help control microfluidic "lab-on-a-chip" devices.  
By Peter Forbes

Application of patterned surfaces some examples I will quickly launch through. And one of things that you all know is this a drop of water almost rolls down the surface of a

lotus leaf like a drop over like a murder. And this is attributed to presents of surface structures.

In fact, you will soon realize when we talk about Young's equation it is actually a combination of surface structures as well as low surface energy coating that makes this possible. So, these types of surfaces are artificially made.

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**Application of Patterned Surfaces**

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**C**

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

fishing spider *Ancylozetes 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

Even in the animal kingdom there are lots of examples of this type of hydrophobic surfaces again. Many of you probably know the term hydrophilic and hydrophobic, but this is something we will talk in great a detail and we will understand may be in the next lecture itself. So, even in the animal world you see extraordinary features like this fishing spider can stay under water for roughly half an hour or this water strider can work on a water surface.

They are actually attribute to represents of some here is structures in their legs where in this particular case they entrap oxygen which sort of substance the breathing for about half an hour or so. And in this particular case actually this legs are ex ordinarily hydrophobic so there are actually a pockets that needs to some artificial buoyancy effect and they can worked.

There are many similar examples like bird feathers. Birds get weight but they also dry up very free very quickly. I mean if they get weight in drain they do not have the

mechanism to use a hair dryer or a towel most plant leaves. Lotus if it is mandatory it is it is essential for the survival, because the lotus leaf grows on the surface of pond. And now if there is a heavy rain fall what will happen. If water comes on the leaf it does not drain off then the weight of the water is enough to sort of submerge the even the plant will die. In the animal kingdom as well as in the plant kingdom many of the functionalities or attributed to survival, because then not as intelligent as human beings are.

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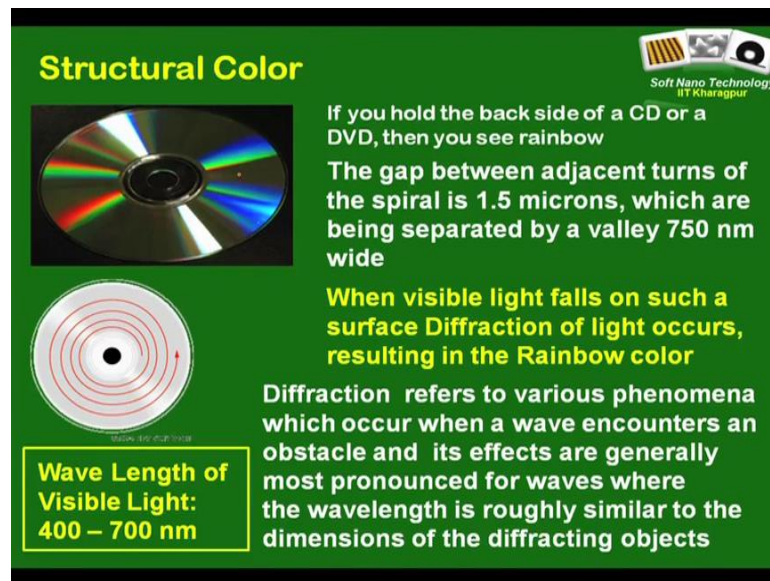


And turns out that many of these extraordinary properties or extraordinary features these sorts of animals or plants have. Have their origin in surface structures and often go down to the nanometer scale. Self cleaning surfaces is again every great example where hydrophobicity has been extensively used and it is widely used now because many of the major cities even in India now if you go you will see tall sky scrapers to all buildings and many of them come with glass facades. And these glasses seem to be always very shiny.

Though the reality is if you leave your bike or cycle or car outside it gathers dust even in within a few days time. So, what is the secret? In fact, it turns out that most of these glasses come with a self cleaning coating so that a drop of water easily rolls down like a lotus leaf. And, as in addition to that as it rolls down it sort of picks up all those particles that are sitting on that. I have shown in a cartoon that this is some sort of structures they are nano pattern surfaces.

This leads to a twofold effect as we will see. One of them is it increases this tendency of rolling or the effective hydrophobicity of the water drop. The other thing is since these structures are seen these surfaces are structured its sort of reduces the addition of the dust particles. So, you can always formally sit on a flat surface, but if the surface has structures you have to you have difficulty in balancing some sort of a similar effect; you will talk about.

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**Structural Color**

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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

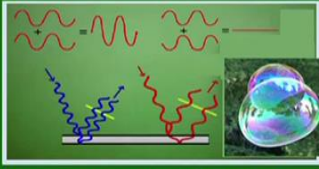
Wave Length of Visible Light: 400 – 700 nm

The second example of this nano patterns is so called structural color. If you take a compact disk CD or a DVD look at the back side of it you have all seen the genesis you see the rainbow colors.



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**Color from white light: Diffraction and Interference**

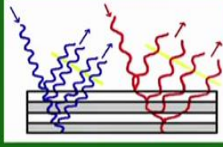


• Two waves interfere constructively if they are '**in phase**' with one another (coinciding hills and valleys), summing strongly.

• But they cancel out if they are '**out of phase**'. This enhances or extinguishes light of different wavelengths, changing the colour of objects built differently.

*constructive interference (left) and destructive interference (right)*

**Structural colour from nanostructures**



- Structural colour doesn't need pigments, and produces brightly colored objects. Combining transparent materials with different refractive index gives constructive interference for a given wavelength.
- It is even better if materials are regular arranged on the nano-scale.
- Stacking layers of two different materials each  $\lambda/4$  thick, gives strong reflection at wavelength  $\lambda$ . Such multilayer objects are a type of 'photonic crystal'.

Now, this color is not attributed to the classical pigment base color we talk about or we know about, but it is attributed to diffraction and interferences which many of you know or you can just try to find it out in little bit detail what it is from the Google. And so two waves interfere constructively in phase with one other the other.

This sort of gives interfere or they can interact in the out of phase and this leads to different wave length, so extinguishing of light of different wave lengths change in the color the object. It is important that if you take a blue disc, just a blue sheet of paper and you turned it, it remains blue from all angles. But you have all seen that if you turned a CD at different angels it exhibits different colors. So, it is due to the so called structural color from nano structures and you can just look into this slide and do some bit of further understanding.

I think this particular talk I will stop here we are running out of time. And I will quickly give you some more examples and move on to context that is some basic issues related to surfaces, interfaces and weighting.

Thank you.