

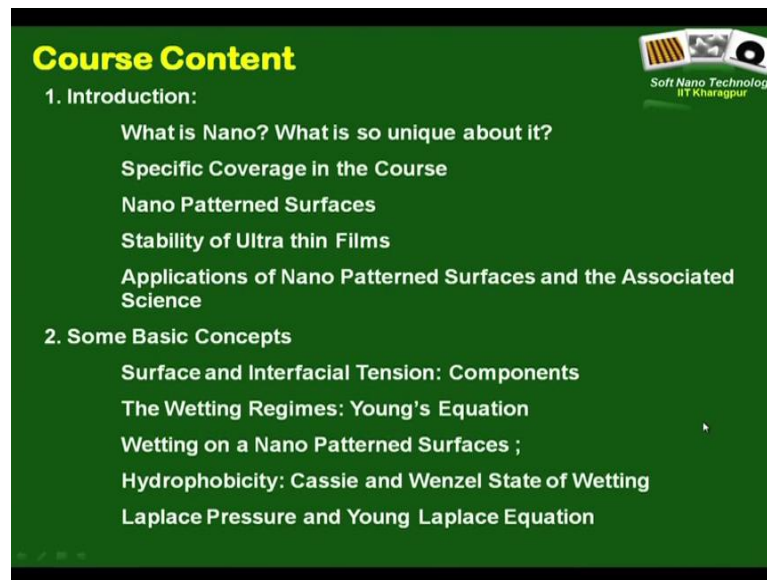
Soft Nano Technology
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Indian Institute of Technology, Kharagpur

Lecture – 01
Introduction – 1

Warm welcome from IIT,+ Kharagpur, and thanks to all of you for choosing the course - the NPTEL online certification course on Soft Nano Technology; you will soon realized that this is a course which is pretty advanced and it is at the inter phase of soft condensed matter physics, lot to do with polymeric materials, nano technology, bit of physical chemistry and surface physics as well. It also has lot of engineering applications and we find full lot of applications and chemical mechanical and other conventional engineering. This is the team, I will be your instructor and you can sort of go to my home page, the home address is a big complicated. I suggest you search in the Google. And the first search Google with my name and the first search result will take you to my home page.

I encourage you to use the online forum that will be offered during the course for your questions and queries, but in any case, you can always get back to me or send me an email. But I will definitely redirect to the online blog or discussion forum because I want any doubt that is particular to any 1 of you should be known to all the participants. This course I will be assisted by 2 of my very bright students, both are outstanding scientist in their own credit, Dr. Nandhini Bhandaru and Ms. Anuja Das.

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Course Content

1. Introduction:

- What is Nano? What is so unique about it?
- Specific Coverage in the Course
 - Nano Patterned Surfaces
 - Stability of Ultra thin Films
 - Applications of Nano Patterned Surfaces and the Associated Science

2. Some Basic Concepts

- Surface and Interfacial Tension: Components
- The Wetting Regimes: Young's Equation
- Wetting on a Nano Patterned Surfaces ;
- Hydrophobicity: Cassie and Wenzel State of Wetting
- Laplace Pressure and Young Laplace Equation

Course content: Well, it is a bit out of box course. So, we will have a bit long introduction on and the things we will cover many of you know what is nano technology, what is so unique about it. Specific coverage of this course, we will talk about nano pattern surfaces and stability of ultra thin films. In fact, these are the two major radius which we will focus, which are also very important from the stand point of nano technology, but often over looked I people are more worried about quantum dots and things like that finite size effect. But these are equally important issues where the effect of nano or the meso scales are prominent. Then we will talk about some of these so called nano pattern surfaces, and talk about the associated science with it.

In order to progress, then we need to clarify some of the basic concepts like surface and inter facial energies components of them. The wetting regimes that is very important concept; we will talk about the Young's equation, which talks about the balance of surface energy when you put a drop of liquid on a solid surface. Then we will talk about wetting on a nano pattern surface, which is very important, it can be it gives raise to the hydrophobicity, the Cassie and Wenzel state and it is responsible for let say rolling of a water drop on a surface of a lotus leaf. And that will also give us the platform to talk a bit about Laplace pressure that is immediate effect of surface tensile, and essentially the young Laplace equation. So, for the first time probably for some view, you will come to know that that a liquid surface in mechanical equilibrium may not have the identical

pressure on both sides if it has curvature and this pressure difference is entirely attributed to surface structure.

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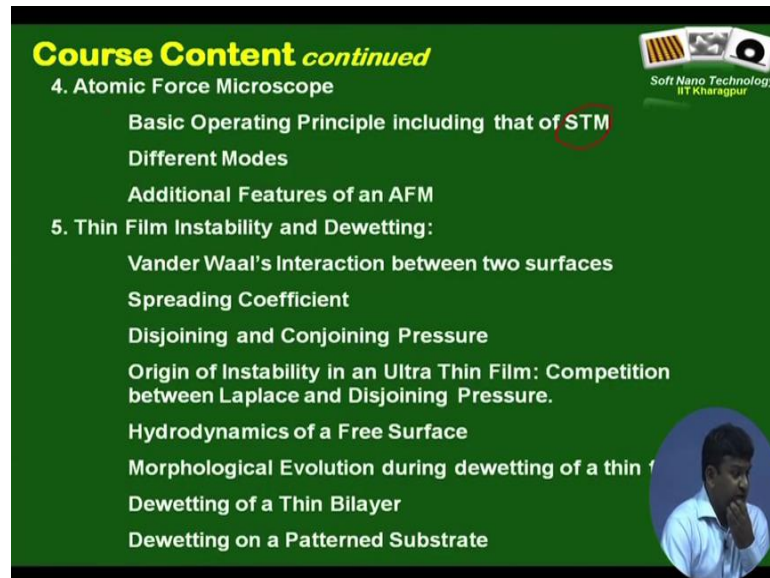


Moving on, we will talk about patterning techniques as I told this nano patterning is one of the key focuses of this particular course. And it is soft because we will be dealing mostly with soft materials, the materials that can be deformed by general forces. This forces can be externally applied mechanical forces or a very, very important thing at the nano scale the Van der Waals forces and that is why we have specifically chose on this soft materials. So, polymers, but it is not limited to polymers, you can even process in organic materials through the soft root or you can also have jells and things like that. But anyway talking about the patterning techniques, we will talk about the nano fabrication methodologies that so called top down, bottom up, self assembly, and I will also give you a quick introduction to surfactants which is a very, very fascinating set of molecules.

We will then go on talking about brief introduction to photolithography. Now photolithography itself can be a same as still long course, but I will just write to give a basic essence of what is photolithography, and what are the major components or major steps associated with photolithography. Then we will move onto the polymers specific a soft materials specific, soft lithography techniques and here are some of the methods that we might be talk, we will be talking about like nano imprint lithography, then capillary

force lithography, micro molding in capillaries, micro contact printing and I assured there will be some more to come.

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Course Content *continued*


4. Atomic Force Microscope

- Basic Operating Principle including that of **STM**
- Different Modes
- Additional Features of an AFM

5. Thin Film Instability and Dewetting:

- Vander Waal's Interaction between two surfaces
- Spreading Coefficient
- Disjoining and Conjoining Pressure
- Origin of Instability in an Ultra Thin Film: Competition between Laplace and Disjoining Pressure.
- Hydrodynamics of a Free Surface
- Morphological Evolution during dewetting of a thin film
- Dewetting of a Thin Bilayer
- Dewetting on a Patterned Substrate

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Then we will talk about; so one of the key issues is that as you fabricate something that is in the nano scale you also need to visualize or see them. And one of the major tools that has in fact significantly enhanced research or contributed in the development of research in nano science area is atomic force microscope. And we will talk bit about the atomic force microscopy, basic operating principles including that of the STM. And we will talk about the different modes, and additional features of an AFM in a very, very condense matter, but this will sort of give you an idea what an atomic force microscopy and do. This will be roughly at the middle of the course, midpoint of the course, and then we will shift gears a little bit and we will move on to instability the spontaneous instability and dewetting of thin films. Particularly, we will be talking about polymer films which on means to sort of take in the liquid form to see or observe these instabilities.

We will talk about details when the context comes. And for that, we need to have a good understanding of Van der Waals interaction between two surfaces that is an important area. Spreading coefficient; we will have to talk or learned what is disjoining and conjoining pressure. Origin of spontaneous instability in an ultra thin film it is essentially competition between Laplace pressure which I already told that its origin and surface

tension and this so called as conjoining pressure. Then we will talk briefly rather qualitatively this one can with look mathematically also, but we will make it look qualitatively in hydrodynamics of a free surface, free liquid surface morphological evolution during dewetting of a thin film. We will then talk about more complex situations like dewetting and instability of a thin bilayer, dewetting on a pattern surface.

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I will also try to give you a bit of introduction and phase segregation and de mixing in a polymer blend film as use spin coating. It is a very interesting area and maybe I will restrict to just one lecture of something like that. Finally, I will give you an introduction or give you an idea about elastic contact instability, another very fascinating set of instability observed in elastomeric polymers - rubbery polymers, rubbery films. And I will give you glimpses of how this technique as recently been used for making nano structures in a very, very controlled way. So, the concepts of we will talk about patterning beyond a negative replica is patterning beyond the maestro a new concept that is coming in patterning, and as you make progress you will understand it in more detail, and then we will rapid up nicely with conclusion and future prospects.

Happy learning, I am sure, I am pretty sure that you going to enjoy this course. This is a pretty open ended course, where developments a taking place even now. So, most of the subjects or topics we are going to cover or sort of this research in this whole area started in early 90s. So, you can now understand that this is indeed very, very recent as

compared to let say classical areas what you study in your text book. For example, the apparently very novel concept of a boundary layer is about more than hundred years old. These are new things. So, the course is still evolving, the topic is still evolving, you find a whole lot of things coming up whole lot of new findings coming up in top level journals even now. So, I might take the liberty of sort of changing the topics a bit to make the course cohesive.

What you need to understand is this is a very compressed course, I will try to make it as lucid as possible, so that you enjoy the essence of the subject and flavor it is more of a non-numerical course. So, do not expect assignments where you have a specific formula, you plug in some numbers get direct calculated values which not going to be like that. Even the assignments are there going to be very easy because I believe that it is important that you enjoy and learn something rather than taking a brain and doing something that is very difficult to do. So, I would request all of you to follow the lectures, follow the text and supplementary materials that I will supply. And please try to participate and all those assignments I am sure it is going to be very easy.

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Resources:

NPTEL **Web** Course on
"Instability and Patterning of Thin Polymer Films"
<http://www.nptel.ac.in/courses/103105065/>

NPTEL **Video** Course on
"Instability and Patterning of Thin Polymer Films"
<http://www.nptel.ac.in/courses/103105066/>

This course is also available in **YouTube**. Just Search with
Rabibrata Mukherjee

All the ppt and hand written text will be uploaded for your reference

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The resource for this course, 1 of the problems of something that is very recent is if you do not have a textbook. Textbooks will be two scattered and things are taken from here and there. So, do not getting search for a textbook. However, you can use NPTEL resources, because I have two courses one is web course where you get all the text, and

you there is also set of video course, which goes by the name instability and patterning of thin polymer films. This is also an elective that I offered at IIT, Kharagpur in the spin semester. So, I would strongly recommend you to either note down these to you are else and use them. So, here this is a web course, here this is a video course. You can also go to this nptel.ac.in website go to chemical engineering and search with the name instability or search with my name and I am sure you will get them.

In addition, this video course the contents are available in the YouTube. So, the best option is just search in YouTube with my name and you will get it. This is a 40-hours course in fact where things have been discussed in much greater details. So, it will act as a very good guide for anything that you need to sort of consult. So, particularly this web course which is return. So, you can use it a sort of text.

What I will also do is all the PPTs that I am using and all the hand written text that sort of the analog was to the black board in this format of a course that we will generate in course of our discussion, I will upload them for your reference. So, all these things will be at your disposal. So, you are free to consult anything that you want to needed any point of time and then just follow the norms of this NOC curriculum or courses.

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Resources:

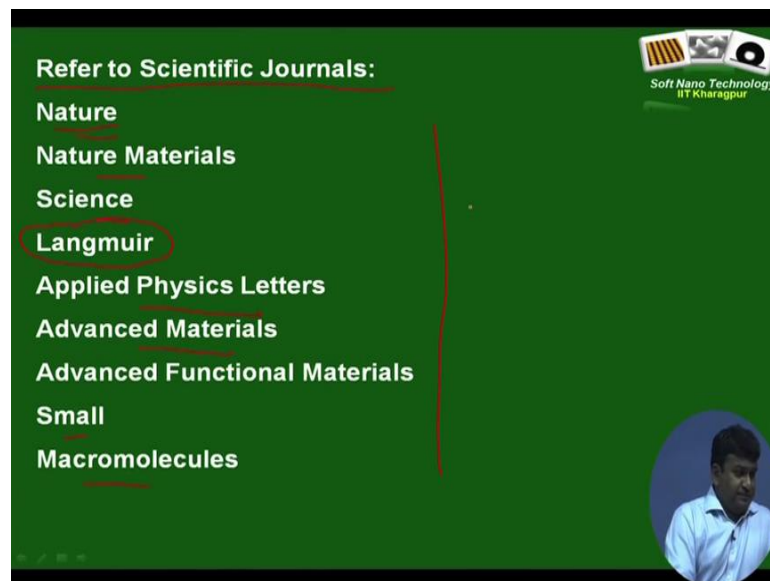
You can also Refer to the following Book Chapters, all of which will be uploaded.

1. Rabibrata Mukherjee (2012), "Soft Lithography and Beyond: Some Recent Developments in Meso Patterning", in *Microfluidics and Micro Scale Transport Process* (ed. Suman Chakraborty), CRC press, ISBN Number: 978-1-4398-9924-3, Chapter 4, pages 111 – 148.
2. Rabibrata Mukherjee (2011), "Liquid Thin Film Hydrodynamics: Dewetting and Pattern Formation", in *Mechanics Over Micro and Nano Scales* (ed. Suman Chakraborty), Springer Science+Business Media, LLC. doi 10.1007/978-1-4419-9601-5_6. chapter 6, pages 193 – 215.
3. Rabibrata Mukherjee and Ashutosh Sharma (2011), "Self Organized Meso Patterning of Thin Polymer Films", in *Encyclopedia of Nanoscience and Nanotechnology* (ed: H. S. Nalwa), Vol 23, pages 1–51, American Scientific Publishers (ISBN 1 – 58883 – 188 – 4).
4. V. M. Naik, R. Mukherjee, A. Majumder and Ashutosh Sharma (2010), "Super Functional Materials: Creation and Control of Wettability, Adhesion and Optical effects by Meso–texturing of Surfaces", in *Current Trends in Science, Platinum Jubilee Special volume of Indian Academy of Sciences, Bangalore*, 129 – 148.

Resources, I will also in addition to those NPTEL resources there are quite of you book chapters or chapters mostly I have written. So, these I will sort have uploaded for your perusal. So, you can use any one of them. And as time comes I will just tell you which

part of the course we need to consult which other book chapters. But you can see it yourself and this roughly covers almost everything, may be other than atomic force microscope you find everything is covered. Atomic force microscope of course is a pretty popular instrument and lots of resources are already available in the net. I would also strongly encourage you to consult Wikipedia as a first learning step Wiki is a great place to learn. So, please feel free find out the key words if you find anything that is new just go and search in the Wikipedia, you will get some idea about it.

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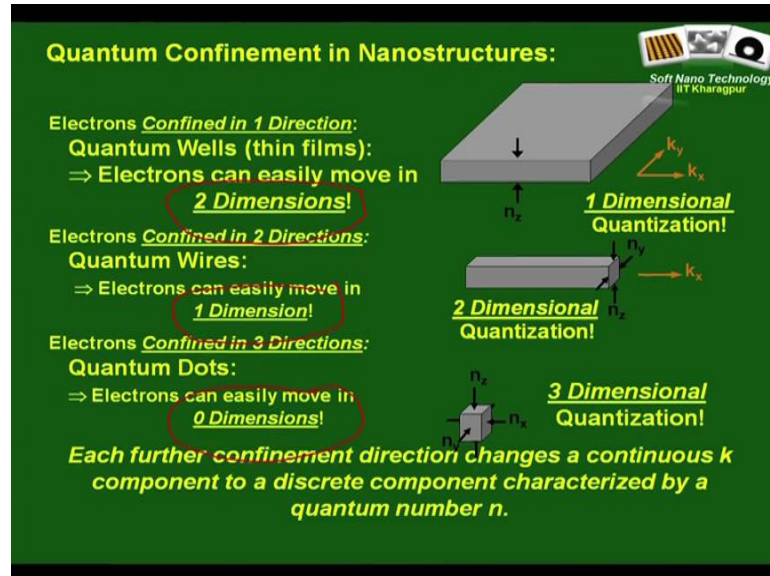


These are the things. Well, as I already told that lot of developments in this area are taking place even now and any scientific discovery or advancement is reported in top scientific journals. So, there are whole lots of journals, where one finds this type of papers coming out. I understand that availability or accessing journal papers might be difficult for many of you, because you need access and which we have in IIT. So, even if you contact us you can always see the abstract you can search or find out this journal home pages and see what type of papers are coming out.

Some of the top journals in the field or even in the field of since are Nature, Nature Materials, Science, and very specific to our topic be journal from American chemical society Langmuir, Applied Physics Letters, Advanced Materials, Small, Macromolecules etcetera. You can find out the home pages some things like that if a particular paper

interest you, you can always mail to any one of us, and we can mail it back to you. So, that is sort of what the course content is.

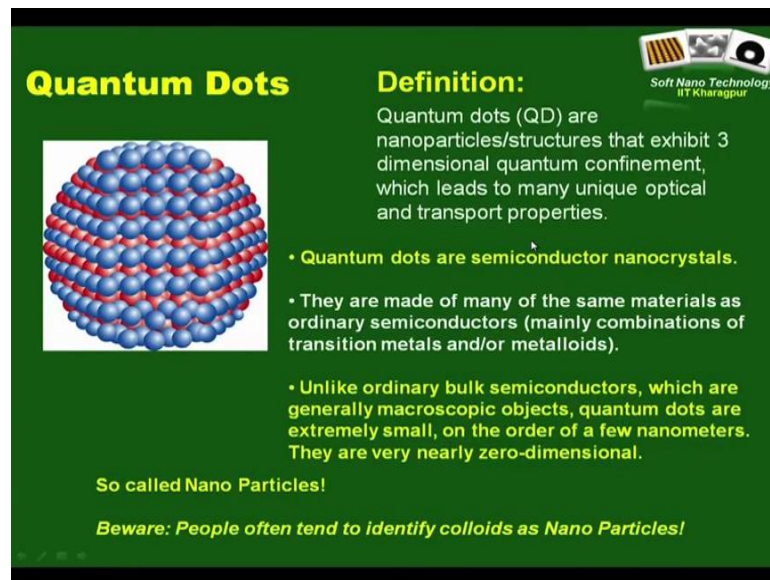
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Let us get started with a very short introduction. So, what is the first thing that comes to your mind, if you talk about nano technology. And the first thing that comes your mind of course, you all know that nano is 10 to the power minus 9 meter compare it with a human here I have a figure somewhere pictures somewhere down the slides which is about 50 to 70 micron. So, now you understand what we are talking about how small we are really talking about.

What is the rather established research area in nano technology is the so called quantum confinement in nano structures. So, either you can have a sheet light material where it is a 2D structure. In fact; the electrons are confined in one direction. You can have wires, where the electrons are confined in two directions or you can have dots and nano particles, where the electrons are confined in all the three directions.

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Quantum Dots

Definition:
Quantum dots (QD) are nanoparticles/structures that exhibit 3 dimensional quantum confinement, which leads to many unique optical and transport properties.

- Quantum dots are semiconductor nanocrystals.
- They are made of many of the same materials as ordinary semiconductors (mainly combinations of transition metals and/or metalloids).
- Unlike ordinary bulk semiconductors, which are generally macroscopic objects, quantum dots are extremely small, on the order of a few nanometers. They are very nearly zero-dimensional.

So called Nano Particles!

Beware: People often tend to identify colloids as Nano Particles!


This in fact the so called quantum dots are one of the basic fundamental building blocks of nano technology. These are essentially made of same material as ordinary semi conductors; mainly combination of transition metal or metalloids. But unlike ordinary bulk semi conductors which are generally macroscopic objects, quantum dots are extremely small on the order of a few nanometers. And they are therefore, considered to be nearly zero dimensional according to this set of definitions. So, this is 0 D object, the where is a 1D object and a sheet is essentially considered to be a 2 D object and here so it is 2D. So, from a 3 D object, you lose in one direction, so it is confined in one of the directions, therefore, it is 2 D.

Here, it is confined in two directions therefore, each 1 D and so on. These are not very important from the standpoint of our course. I just want to show where our course what you are going to learn is different from the classical nano technology what you would typically learned which requires a lot of understanding on quantum mechanics and stuff like that.

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Quantum Confinement

- The reduction in the number of atoms in a material results in the confinement of normally delocalized energy states.
- Electron-hole pairs become spatially confined when the diameter of a particle approaches the de Broglie wavelength of electrons in the conduction band.
- As a result the energy difference between energy bands is **increased** with decreasing particle size.



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What does it lead to, what a leads to is you know that every material has a specific band structure and which is responsible for various properties of the material including optical properties. So, let us say this by gold look so beautiful is because it has certain specific surface Plasmon resonance when visible lights falls on gold. And what happens is if you go on making things smaller and smaller, the band structure due to confinement gets changed. So, this is a very simplified simplistic picture of this quantum confinement effect. And as a result what happens is the intensive property becomes extensive.

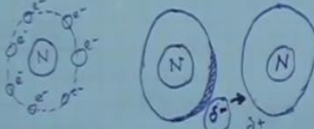
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Intensive Properties.

$\frac{1}{mgh}$

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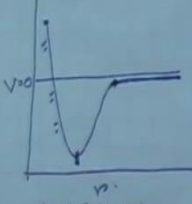
Induced dipole- Induced Dipole Interaction Between Molecules.



In all types of molecules -

At any instance of time, The charge distribution with the Electron cloud is NON uniform.

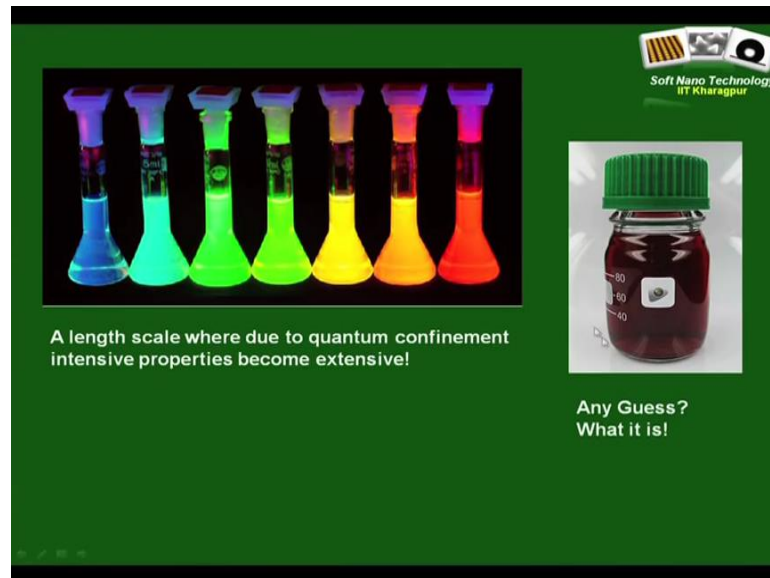
[Attractive Interaction]

$$V_{LJ} = -\frac{B}{r^6} + \frac{A}{r^{12}}$$


L-J Potential
6-12 Potential.

What exactly are intensive properties; intensive property is properties that are independent of the size of a material. So, let us say whether you take 100 grams of gold or 1 gram of gold, it looks the same, but if you go on to smaller and smaller dimensions there is a possibility that things might look or completely different and that is exactly what happens.

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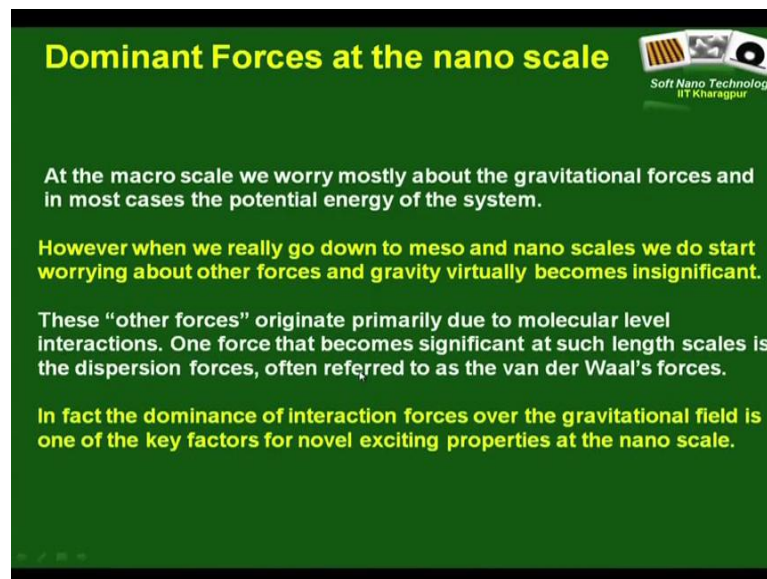



For example, here any guess, what it is, well it turns out to be gold nano particles. So, if you do down to synthesis gold nano particles which are size in the range of 10 nanometer are less because of this confinement effect there is a change in the band structure and you get completely different colors. So, if you look at this particular picture this type of pictures are pretty popular in for people doing researches in quantum dots. These are essentially quantum dots of the same semi conducting crystalline material, but the sizes are different and if you now you illuminate them with let say some light source like uv, they transmit different colors.

This is unique because they are all made of the same material, but the only difference that is there is the sizes are different and that is exactly what I just told you that intensive properties, for example, the appearance of the color of a material is intensive property. It does not depend on its size right, if it does not depend on how much material you have taken its properties start to deviate. So, this is one of the aspects of nano technology is also called quantum dots, quantum confinement of finite size effect to

name it and this was received significant amount of attention. However, this is not what we are going to talk in detail in this course. There are some other aspects of nano technology or there are some other issues that are extremely important in the nano scale which are not that well emphasized in many, many of the settings and that something that we are going to talk about in greater detail.

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Dominant Forces at the nano 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.

Let us try to figure out one particular aspect. What are the dominant forces at the nano scale? In a macroscopic world, we always see that everything is dominated by gravity, but as you go down in size you look into molecules or if you sort of go down much in size in fact, you find that gravity almost becomes negligible. It is because of the fact that gravity sort of the interaction forces scales as $mg h$, h is sort of the height or the separation distance you can say.

And as this h become smaller and smaller this gravitational force becomes tends to become negligible. So, what are the other forces and the other force that really dominates or the nano scale is what is known as the Van der Waal sources this is something we all know in somewhat detail, but I think for as a part of this particular course, we will talk in some sort of a greater detail.

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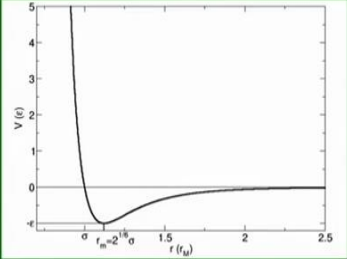
Van der Waals Dispersion Force Between Neutral Molecules

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 $\sim 1/r^2$

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These forces so called Van der Waals force we are talking about is the induced dipole induced dipole interaction between molecules this again has its origin in quantum mechanics. But we will take a very simplistic picture may be will lend some concept from your high school physics or chemistry. How does a molecule look like? So, you have a nucleus and which is surrounded by these electrons. So, this is more of a picture, we are all pretty well conversion with. This also what is called as a Rutherford atom, because Rutherford proposes this picture.

In reality of course, the structure the situation is not so simple it is slightly different in the sense that this electrons actually undergo every high frequency oscillation around the nucleolus. And as a result, at any given instance of time there is in fact, a localization of charge. So, this electron cloud and please do not forget that this is not on one particular plane, this is in the whole 3D space around in the nucleus, the electrons are oscillated there are rotating in a very high frequency.

At any instance of time, what it means is that at any instance of time, the charge distribution within the electron cloud is non uniform. And what does that lead to in fact, that leads to some sort of a localization of a charge of delta minus over a particular location of that particular electron. Now, what does this temporary charge do, it is sort of tries to induce a positive charge on the neighboring molecule. And the moment you have a delta plus and a delta minus between the adjacent molecules, there is now an

interaction and the interaction of course, the nature of interaction is attractive interaction. It is important to note that this so what is the genesis of this interaction it is an induced dipole induce dipole interaction; important to note that, the first induction is due to localization of the electron cloud or non-uniform distribution of the electron cloud around the nucleus. And the second induction is charge induced by this delta minus on the neighboring molecule.

Since what is going to be the net interaction between the two, of course, you have a delta plus and a delta minus and the net interaction is going to be attractive. One can so this is what is known as the induced dipole, induce dipole type interaction and this is represented by some sort of a correlation B/r^6 . Of course, many of you probably have seen this type of a curve. So, this is our separation distance and this is the strength. So, negative is attractive. So, it is in this regime, it is attractive what does it mean that if the two molecules are far away there is no interaction. In fact, this corresponds to $V = 0$, but if they come closer then this charge induction takes place and there is an attraction.

Of course, if the two now physically come closer to each other which actually does not happen, why does not happen the molecules actually do not move because of this Van der Waals interaction. Because by the time the second molecule sort of realizes that there is a net attraction the location of this localized charge in the first molecule changes because of the very high frequency oscillation. This is not a permanent dipole and that is also the most important aspect that this interaction takes place in all types of molecule irrespective of whether they are polar or non polar, independent of whether any dipole is present or not and therefore, it is absolutely universal.

Of course, if these two molecules now physically come closer, we do a thought experiment and they come closer then what is going to happen they are electronic orbitals or outer orbitals of the electrons are going to sort of overlap and that is going to give rise to strong electrostatic repulsion between the two. So, that in fact, represents this part of the curve and it is a shorter range electrostatic repulsion, so that is represented by a $1/r^{12}$ sort of expression. So, this is called the Lennard-Jones potential or the L-J potential, this is also called the 6-12 potential.

Now, we all knew from our school day that Van der Waals force is one of the most fundamental form of forces. But in the macroscopic world we really see its signature. And what I mean or try to emphasize or I will try to emphasize upon you from now onwards that nano scale is also different from the macro scale not only in terms of finite size effect. But it is also a scale where the interaction or the physics are strongly governed by the presents of Van der Waals forces, and that is how why it leads to some very different and extraordinary properties which are attributed to these forces.

The other thing that we will also see I will give you some examples probably in the next lecture. The other thing we will also see that certain material properties are attributed to nano structures that is structures with nano scale or 100s of nanometer dimension which gives raise to some extra (Refer Time: 27:07) properties. That is what we have in these particular introductory lectures for you.

In the next module, we will again continue with an extended discussion on introduction of the topic, so as to impress upon you how the nano scale is different and how some extraordinary properties are attributed to nano patterns or nano scale features.

Thank you.