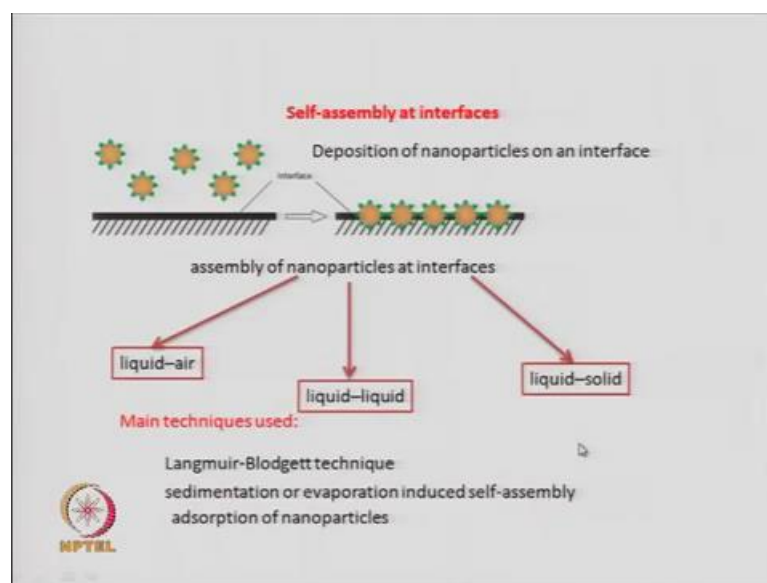


**Nanostructured Materials-Synthesis, Properties, Self Assembly and Applications**  
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**Indian Institute of Technology, Delhi**

**Module - 3**  
**Lecture - 23**  
**Self-Assembly of Nanostructures – III**

Welcome back to this course of nanostructured materials syntheses, properties, self-assembly and applications. We are now in the module 3, and we are trying to understand the concept of self-assembly and the applications that self-assembled nanostructures can be used for. And in self-assembly we have finished two lectures on self-assembly and now, today we will have the third lecture on self-assembly and this is the lecture 9 of module 3.

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So, a self-assembly can be done at interfaces as shown in this figure here. If you have an interface between two different mediums. So, two different media means say you have liquid and solid, so between the liquid and the solid you have an interface. So, can you self-assemble? That means, can you arrange nanoparticles or nanostructures at this interface. So, this interface if you bring around nanoparticles, can you arrange them in a particular fashion like this or in any other fashion maybe, in a square pattern or in a

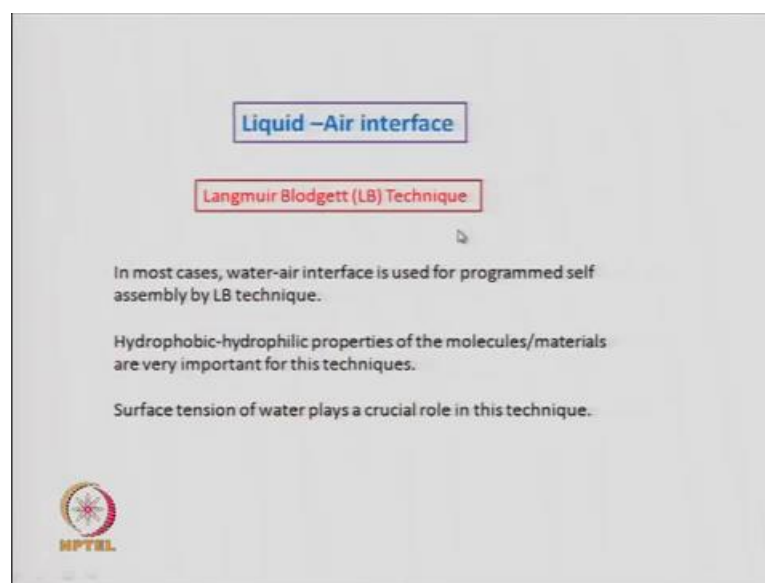
triangular pattern. So, that would be assembly at interfaces. Now based on the how the interface is formed, what are the two different phases.

One of the type of interface you can have is the liquid air interface that means, you have one liquid, on top we have air. So, where the air is meeting the liquid you have that air liquid interface. You can have self-assembled structure made of nanoparticles at this interface. Then, you can have two different liquids and the interface between two different liquids, this is possible when the two liquids coexist with each other. That means, they do not dissolve in each other and it, an example is like water and oil. So, water and oil do not mix, so when you have a layer of water and a layer of oil, you will have an interface and at that liquid-liquid interface you can have assembly of particles.

So, oil generally you can have many types of oil, in the laboratory you are used to a chemicals like toluene, benzene, hexane these are a nonpolar solvents and these are like oil which do not dissolve in water. So, they are nonpolar, water is polar and between the nonpolar liquid and a polar liquid there will be an interface. So, that will give a rise to this liquid-liquid interface. Then, you can have a liquid in contact with a solid and that will give you a liquid solid interface. So, that can be very easy if you have say a silica surface and on top you have a drop of water, then it will create an interface between the liquid and solid.

Now, there are some of the main techniques, which are used today to make these kinds of a nanostructures or the assembly at the interfaces can be due, by the well-known Langmuir Blodgett technique. We will discuss this in detail, then you can have sedimentation or in operation induced self-assembly. Then, you can have absorption of nanoparticles on a surface. So, there are different types of techniques one can use to make ordered assemblies of nanoparticles at interfaces.

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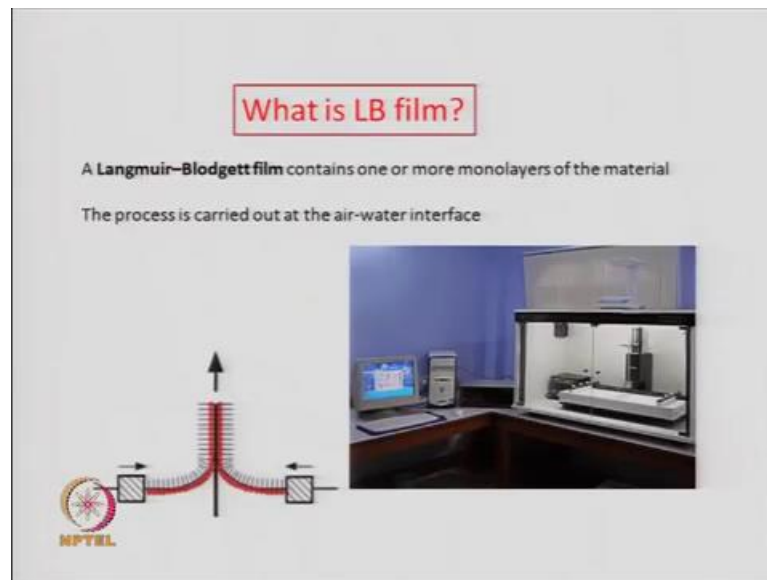


So, first let us discuss the liquid air interface, so by the name you can understand that you have a liquid, on top of which you have air. So, you have an assembly on the surface of the liquid, there is a contact between molecule of air and the molecule of the liquid. Now at that interface, how to make assembled nanostructures, the technique that commonly people use to make nanostructures at the liquid air interface, is using their Langmuir Blodgett technique. And it is, more or less it is called programmed self-assembly, you utilize the solvent or the liquid in most cases is water in the LB technique or the Langmuir Blodgett technique.

So, you are basically looking at the water air interface and there the hydrophobic and hydrophilic properties of the molecules are very important for this kind of technique. So, hydrophobic and hydrophilic for example, you have water so you will have hydrophobic, philic interactions and if you have a surface which is for example, you can have a silica surface, which is a hydrophilic. And you can change the hydrophilic silica surface by using a silane say, alkyl silane and you can make it hydrophobic. So you, these interactions between hydrophobic surfaces with hydrophilic or hydrophobic molecules is important for making a nanostructures using the LB technique.

The surface tension of water plays a crucial role in this technique since water is key the liquid being used in Langmuir Blodgett technique. And hence the surface tension of water will be very important.

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So, let us understand what is this LB film or the Langmuir Blodgett film. So, it contains one or more monolayers of the material. So, a film made at the liquid air interface of some nanoparticles on the liquid, which is water, on the water surface that is basically a Langmuir Blodgett film. And this process as we have discussed has, is a made at the air water interface. So, this is the photograph of a LB trough, so this is called an LB trough, it is made normally of Teflon and you have water inside, on top of which you want to make the film. And on either side of this trough, you see these kind of a Teflon rods, square rods, so they create a pressure on the film.

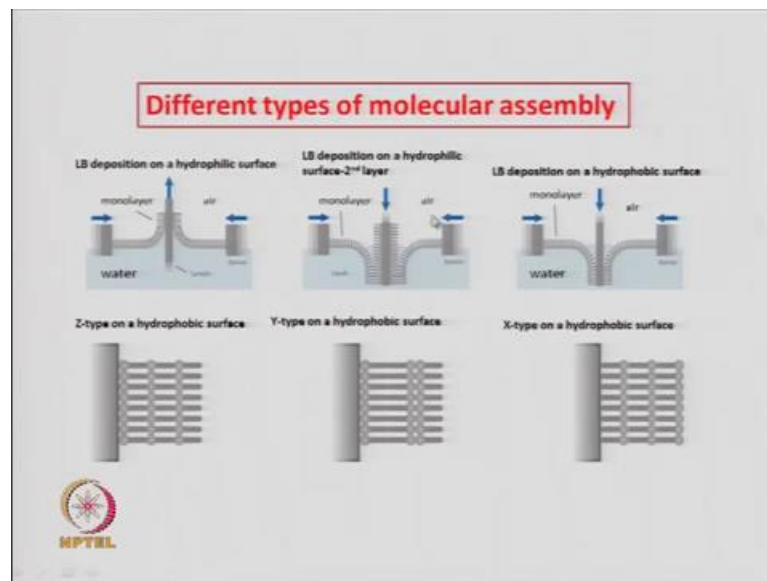
So, they are called barriers and, so this one moves inwards and this also moves inwards, creates a pressure on the surface of the fluid here and the fluid here is water. And if there are molecules on top of water, you can dip a substrate on the, inside the liquid and pull it out and the molecules on top of this water will make a film on the substrate, which can be dipped from the top. So, this can be controlled through a computer the rate at which the barriers move, the rate at which you dip the substrate etcetera can be controlled.

So, this is basically the LB trough it is called and the process which occurs is, that you are moving this barrier which are there 1 and 2 barriers. So, they are here on two extremes and you are pulling this barrier inside, from both directions and the water has got these molecules on top of it. So, when you are creating a pressure and you are dipping the substrate from the top or pulling it out, here the arrow is showing that we are

pulling out the substrate. So, the substrate is here which was dipped in the liquid and is being pulled out. So, when you do that then the molecules on the liquid, on the top of the liquid, the molecules on top of the liquid come on top of the substrate.

So, typically if you have a substrate which is hydrophilic, then the hydrophilic part of this molecule will be adhere towards the substrate or adhered on the substrate. And, so depending on what kind of film you want, whether you want a hydrophobic part sticking out or the hydrophilic back stripping out, you have to take the surface of the substrate accordingly. So, this is the basic process you are pushing from both sides, the barriers which are at these two extremes and creating a pressure on the film of water. And the film of water has got these molecules on top of them, which will get coated onto the substrate and that will form the monolayer. So, one layer of the molecules are now coated on the substrate when you take out the substrate.

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So, this is again showing you now different types of molecular assembly which you can achieve using the LB technique. So, here in the first case you see there is water and you have your substrate and you are pulling out the substrate. The substrate is chosen such that, you want the film to be on a particular substrate and you choose the substrate accordingly. So, you put in pressure from either side so the two barriers are moving in and the one mono layer is forming at the water and air interface. So, on top you have air,

below you have water and you are having a monolayer or an assembly of molecules at the air water interface.

Now instead of pulling it out, you can pull it in. So, this is an LB deposition on a hydrophilic surface. Now you can do LB deposition on a hydrophilic surface for the second layer. So, this is the first layer is formed, now you want to make the second layer. So, after the first layer is formed, so the substrate has come up now you push it back. So, this is showing when you push it back then on top of the first layer a second layer will start forming and you see the two hydrophobic parts are close to each other. So, when you push in the substrate, the second layer of molecules on top of the bottom layer will form the second layer and ultimately you will get a substrate which has got two layers.

So, it is a bilayer on top of the substrate, on a hydrophobic surface if you do the same thing that you did here, here pulled out the substrate it was a hydrophilic surface. When you have a hydrophobic surface, you push in the substrate and you have an LB film with details on top of the hydrophobic surface. So, depends on what kind of substrate you have whether hydrophilic or hydrophobic, then the first monolayer either you have to pull out the substrate, or push in the substrate, depending on what kind of substrate you have whether it is hydrophilic or hydrophobic. Now you can have multiple layers and there are different classifications of these LB films.

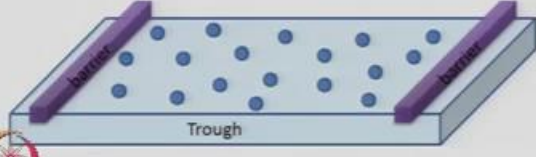
For example, this is showing a three layered LB film and this is called the z type because, all the molecules are pointing in the same direction. So, you have one layer with the head group pointing in towards the surface of the substrate. Then, the second layer is again pointing towards the surface of the substrate. The third layer is also pointing in this direction. This is the opposite type where the tails are close to the substrate and this is on a hydrophobic surface and this is an x type on a hydrophobic surface.

So, if you have alternate that is one pointing in this way, the second pointing that way, that third one again in the reverse direction, then that is called a y type of a molecular assembly a y type of LB film. So, you have different types of LB films and this is precisely the process by which you make the Langmuir Blodgett films on substrates.

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### Intermolecular interactions

- Dipole-dipole forces
- Ion-dipole forces
- Dipole-induced dipole force
- Instantaneous dipole-induced dipole forces or London dispersion forces.

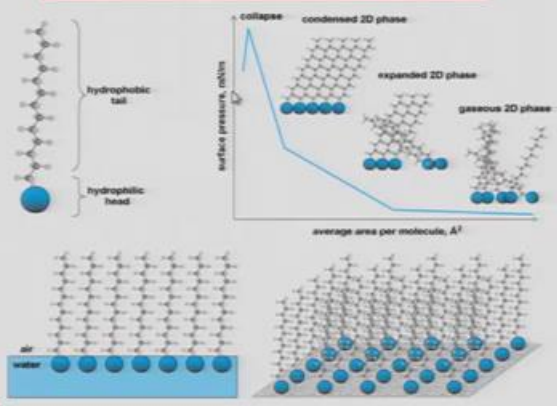


The diagram shows a rectangular trough with two purple barriers on opposite sides. Inside the trough, several blue spheres representing molecules are scattered. The word 'Trough' is written at the bottom center of the trough. The MPTEL logo is in the bottom left corner.

So, what are the interactions when you are making the film. So, this is the trough which we discussed, so this trough contains water and also it contains the molecules which are spread out on the surface of water and you want to make in LB film using these molecules on a substrate. Now the two barriers are shown here, this is one barrier and this is another barrier and you have to push the two barriers close to each other, when you are dipping the substrate to make the film.

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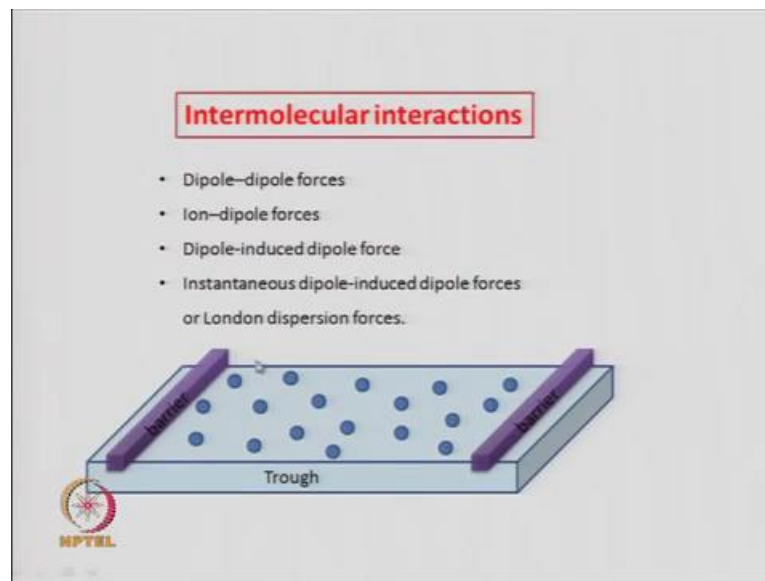
### Different molecular arrangements



The diagram illustrates the transition of amphiphilic molecules from a disordered state to a condensed 2D phase. On the left, a single molecule is shown with a blue 'hydrophilic head' and a grey 'hydrophobic tail'. Below it, a layer of molecules is shown at the interface between 'air' and 'water'. To the right, a graph plots 'surface pressure, mN/m' against 'average area per molecule, Å<sup>2</sup>'. The curve shows a sharp increase as the area per molecule decreases, labeled 'collapse'. Three phases are identified: 'condensed 2D phase' (high pressure, low area), 'expanded 2D phase' (intermediate pressure and area), and 'gaseous 2D phase' (low pressure, high area). Molecular models illustrate the packing in each phase: loose for gaseous, more ordered for expanded, and highly ordered for condensed. The MPTEL logo is in the bottom left corner.

Now you can have different types of molecular arrangements when you are making the film. So, as your bringing the barriers are at a distance, so the average area per molecule is very large, when the two barriers are far off. So, when the two barriers are very far off then the number of molecules per unit area is less. So, the number of molecules per unit area is very less, when the two barriers are very far apart.

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And the surface pressure, the surface pressure when the barriers are very far apart is very less. When you are your bringing the two barriers closer, the number of molecules per the, the average area per molecule you can say is becoming lesser and lesser, as you are bringing their barriers close to each other. So, then the surface pressure rises, so the surface pressure rises and as you bring it farther down it again rises. And this whole plot of the change in surface pressure, with decreasing distance of the barrier layers or you can say decreasing distance decreasing average area available to 1 molecule. If you lower that, the surface area, the surface pressure is increasing and there are certain stages as you can see, the slope of the curve changes at this point and, then again changes at this point and, then there is a further change here.

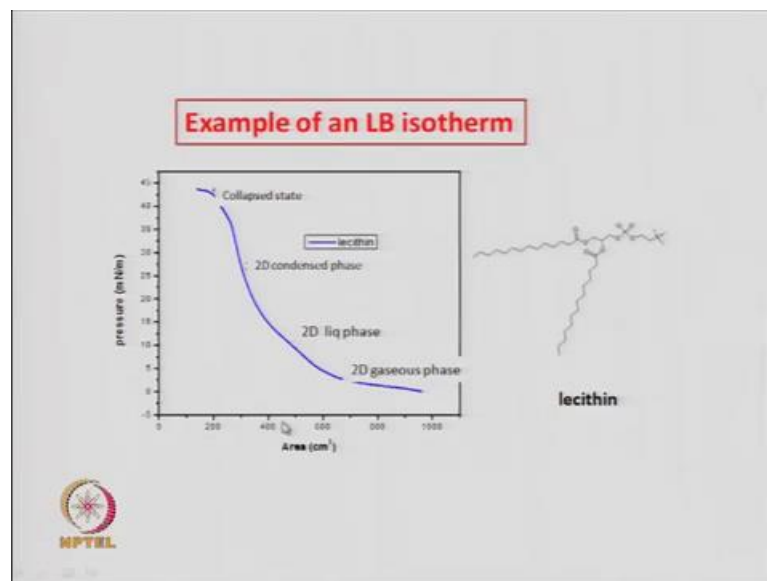
So, this region till you come to the first point is called a gaseous two dimensional phase, when the molecules on the surface of water are totally disordered, that is called the gaseous two dimensional phase. When the area available to the molecule decreases, the molecules start getting arranged in a particular fashion. And that is the expanded two



dimensional phase or it is called the liquid like phase, liquid like two dimensional phase. On further closing down the gap between the two barriers, you are forcing the molecules to arrange in a definite pattern and that is called the solid like two dimensional phase or the condensed two dimensional phase.

If you bring the barriers further close, the pressure will increase drastically and at a particular point, the film, which was very well structured like a solid like regular pattern will collapse and you will have breakdown of the film, Langmuir Blodgett film. So, you have different sections of this plot, the gaseous 2 d phase, the liquid like 2 d phase, the condensed 2 d phase. And then the collapsed film at very high surface pressure, that is when the barrier distance the distance between the two barriers is very low. This is, can be shown on top of the surface it will appear like this, when it is very well ordered. So, the films will look like this where, the blue balls are basically the hydrophilic or the polar head group and these are the carbon chains or the hydrophobic tail, which are pointing outside the aqueous layer.

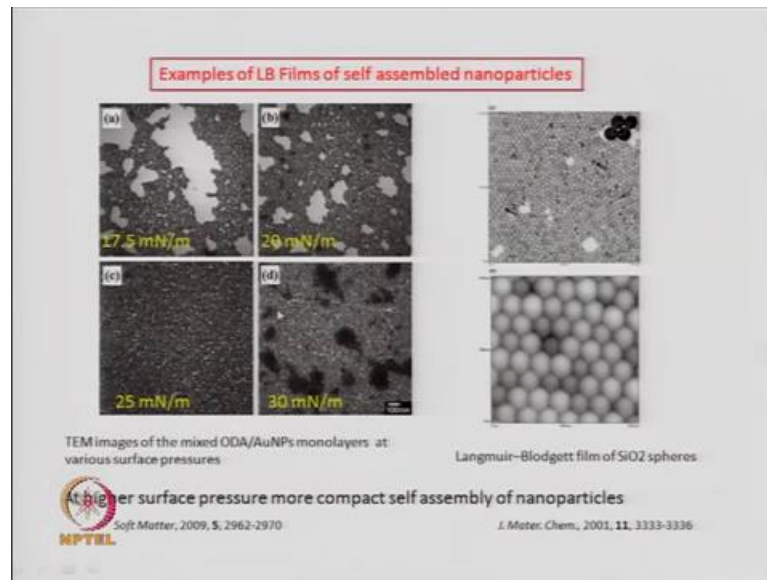
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Now, the same plot which we called a Langmuir Blodgett isotherm where you plot the surface pressure with the area available to each molecule on the surface. So this in a, in a simplified form for lecithin which is a molecule like this, it has a head group which is this trialkyl ammonium head group and, then this hydrophobic chains So, you have the 2 d gaseous phase. So, if you have lecithin molecules on water and you are applying

barrier pressure that means, bringing the barriers close together, then you first go from the 2 d gaseous phase to 2 d liquid like phase, then the 2 d condensed phase. And, then at this point you see there is a breakdown the pressure no more increases, because the order two d phase has collapsed and the Langmuir Blodgett film has broken down.

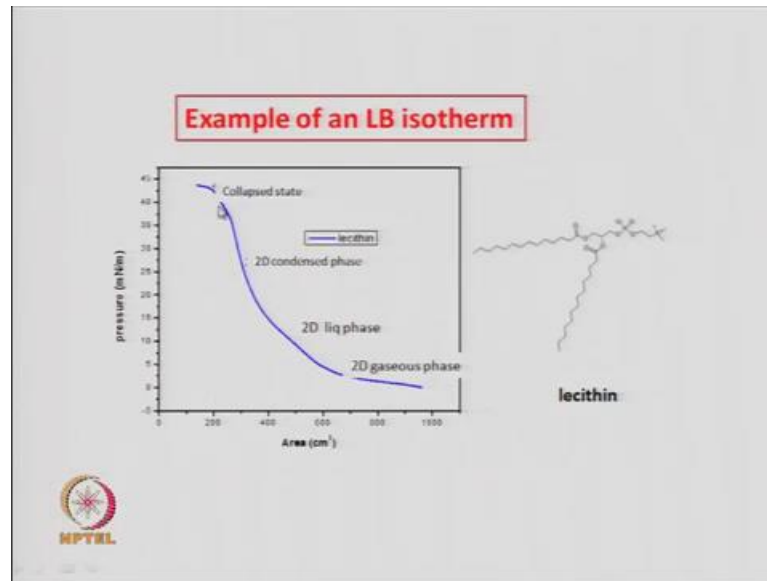
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So, this is an example of an LB isotherm. These are experimental data so these are TEM images of LB films and you can see these are mixed octadecylamine. Octadecylamine will have large this chains, octadecyl chains, this 18 carbon chains and you have gold nanoparticle, they form monolayers at various surface pressures. So, you can see that you have low pressure 17.5 milli newtons per meter applied here and the film is not continuous. As you are increasing the pressure, the film is becoming more homogeneous, more continuous and at 25 nanometers it appears to be exactly a homogeneous.

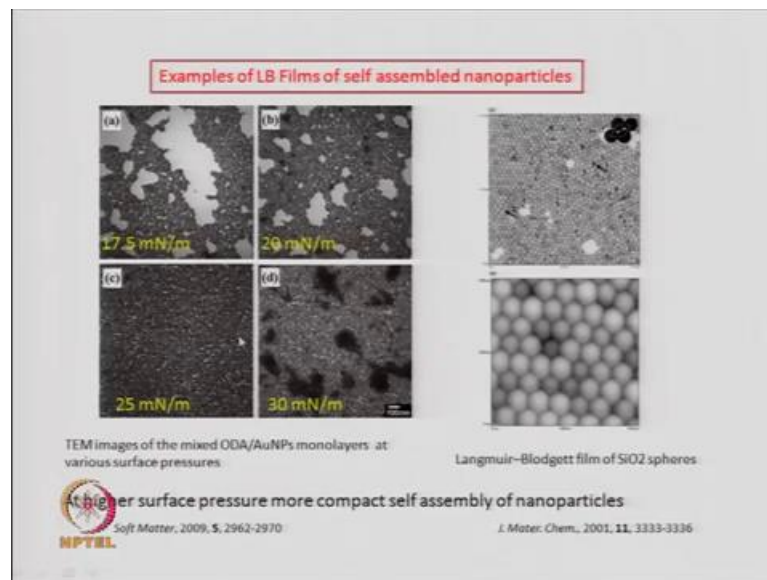
Again, if you overshoot this pressure, in this particular case say you go to 30 millinewtons per meter you start the breakdown of the film and now, you see these holes within the film. So after 25 million newton per meter, you have basically reached the collapsed form a stage of as shown in the LB isotherm.

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So, in this LB isotherm at a particular pressure, for lecithin this is like 200 centimeter square, where the pressure is something like 40, maybe 40 or 40 42 millinewton's per meter. And if you are around that then the Lecithin film breaks down.

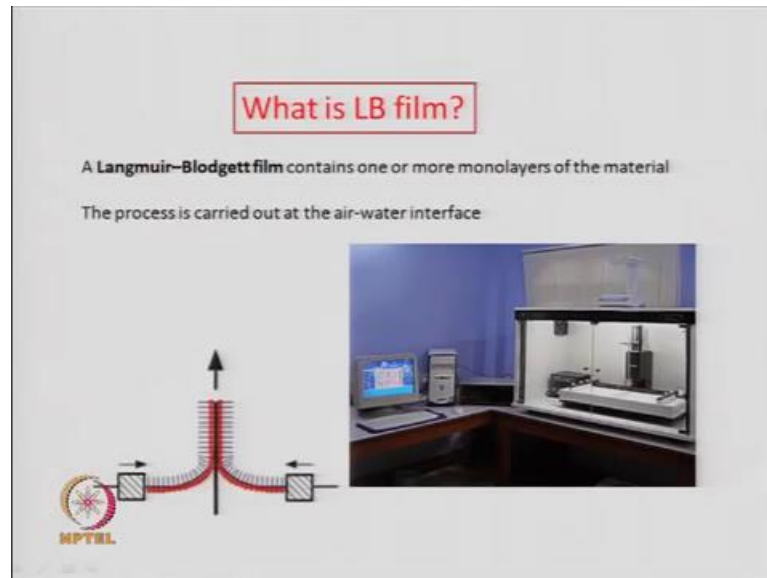
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In this particular case of octadecylamine gold nanoparticle monolayer's, the pressure at which the film breaks down is around 25 to 26 milli Newton per meter. And at in this is another picture of LB films, we can see very nice assembly of a silica spheres made by

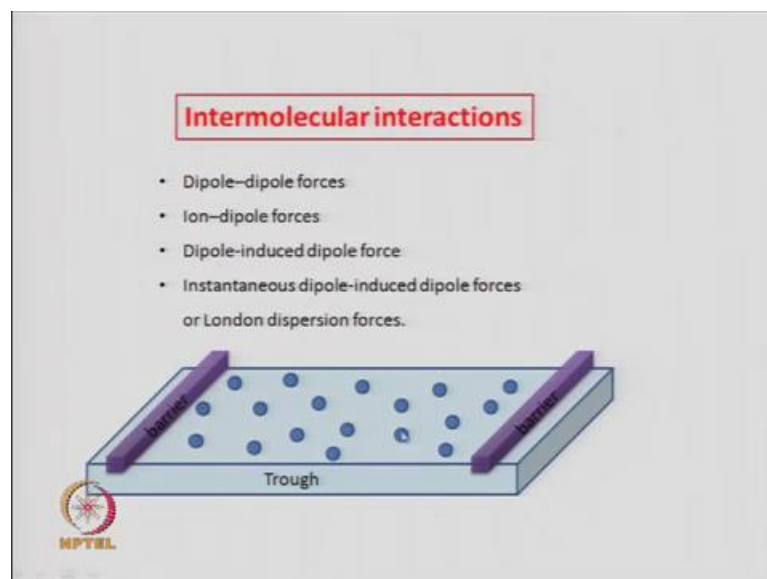
LB method. And you can see a very compact self-assembly of nanoparticles. So, at different a barrier distances.

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So, if you look at the barrier again let me show you the picture, this is the real LB trough, the barriers are here at the two extremes and when you are bringing them together the pressure will increase.

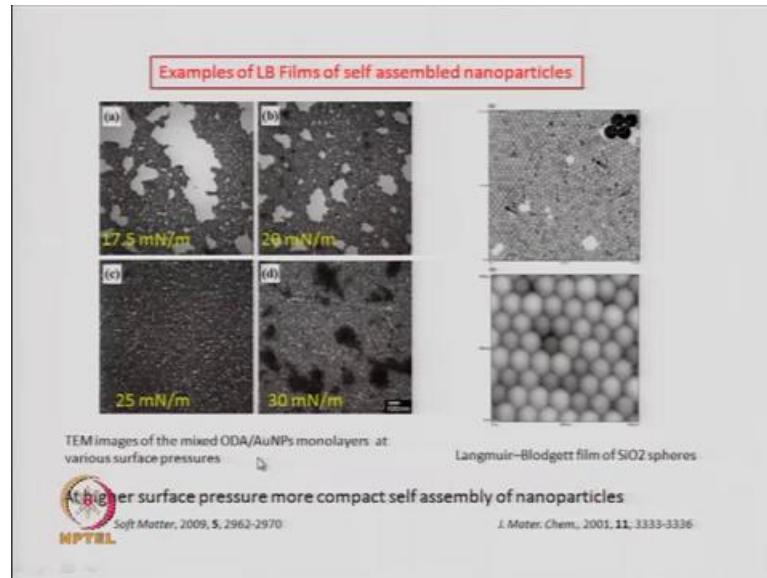
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And this is shown more schematically, the barriers when they move towards each other lower the area available to the molecules on the surface, and then the molecules start

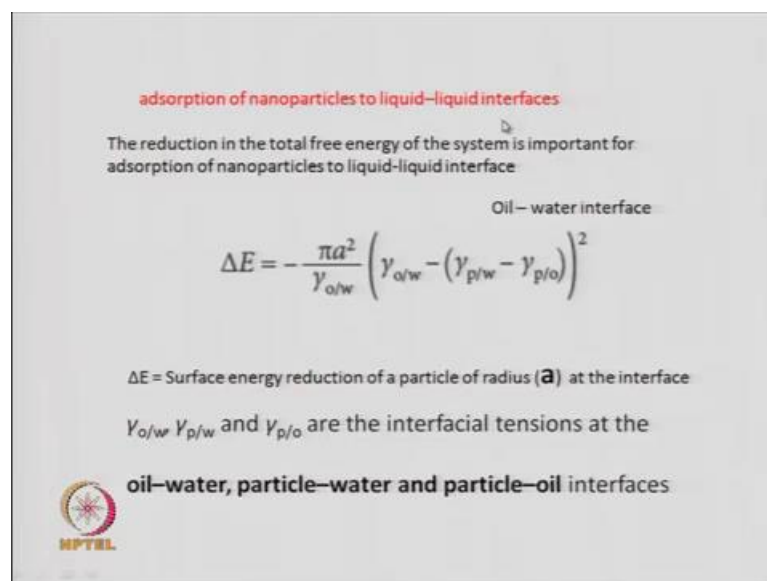
organizing or assembling into regular patterns. Of course, once it forms a complete film, if you put extra pressure that means, if you bring the barriers closer to each other, then the film will disrupt.

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And so that is the example that we did of octadecylamine with gold nanoparticle monolayers, and this was silica spheres making an LB film and forming and assembly of nanoparticles.

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Now, that was air water interface that is liquid and air interface. So, that was one kind of interface how to make self-assembled structures at the air liquid interface. We can also have liquid-liquid interface, so two liquids and then how we can absorb nanoparticles at that interface to form assembly of nanoparticles. So, in this case the, at free energy of the system reduces, the reduction in the total free energy system is important for the absorption. So, whenever adsorption occurs at this interface it should lower the free energy of the system.

So, let us consider an oil water interface and this  $\Delta E$  is the surface energy reduction, which will contribute to the lowering of the free energy. So, this surface energy reduction is given by these terms where, these gammas are basically the surface tension of the oil water interface, the particle water and the particle oil. So, you have different gammas depending on the material you have, which oil you have and which nanoparticle you are using. You will have different numbers for these and you can calculate for a particle of size of radius  $a$ , what would be the reduction in the surface energy based on this equation. And that will give rise to a reduction in the free energy which will lead to the adsorption of the nanoparticles at the liquid-liquid interface.

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$$\Delta E = -\frac{\pi a^2}{\gamma_{o/w}} \left( \gamma_{o/w} - (\gamma_{p/w} - \gamma_{p/o}) \right)^2$$

For example;

$\gamma_{o/w} = 35.7 \text{ mN/m}$   
 $\gamma_{p/o} = 15 \text{ mN/m}$   
 $\gamma_{p/w} = 40 \text{ mN/m}$ ,

$\Delta E$  is about  $-5 \text{ kBT}$  for 2.8-nm-diameter nanoparticles  
 where  $T$  is absolute temperature.

$E$  depends on  $a^2$

The energy gain is smaller and the assembly is less stable for smaller nanoparticles than for larger ones

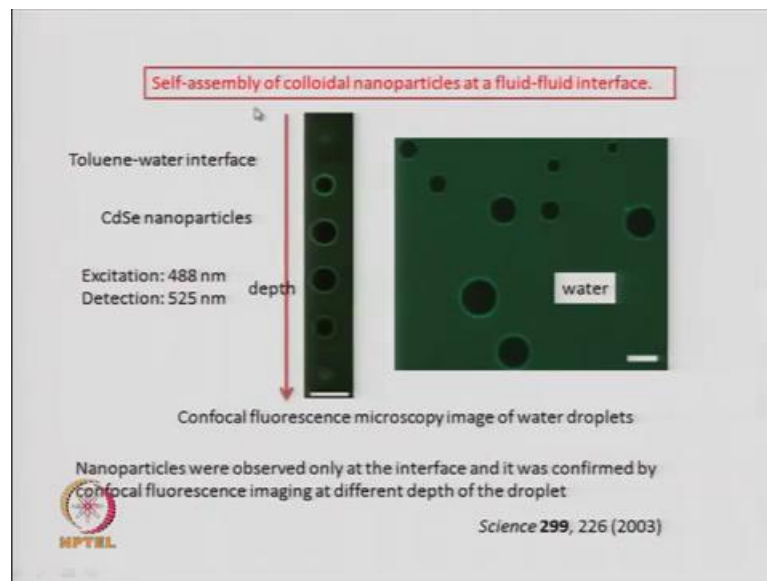
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So, for an example this equation if you take these numbers for example, you take the surface tension between the oil and water to be 35.7 millinewton per meter. And similarly, you take the particle what oil interface you have a surface tension of 15 milli

Newton per meter and the particle water to have 40 milli Newton per meter. Then, that change or the reduction in the surface energy is about minus  $5 k t$ . So, this  $k b$  here is the Boltzmann constant and so it is about minus  $5 k t$ . If the if the diameter, if this diameter of the particle here  $a$  is of course, radius.

So, if the radius is 1.4 nanometer that is for 2.8 nanometer diameter particles, this value comes to around minus  $5 k b t$ . And it is to be noted that,  $e$  here the reduction energy  $\Delta e$  is directly proportional to the square of the radius. So, the energy gain is smaller and the assembly is less stable for smaller nanoparticles, because it depends on the square of the radius and it is negative. So, if it is the particle size is very small, then the monolayer that you get, the LB film you get the self-assembled layer, which you get on the liquid-liquid interface is much less stable than for particles which have a larger radii and that is given by this equation.

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So, this is an example of self-assembly of colloidal nanoparticles at a fluid-fluid or liquid-liquid interface. So, the two liquids here are toluene and water, toluene is an organic solvent, it is nonpolar, water is polar and they do not, they are not miscible and, so when two liquid which are immiscible meet they make an interface. And what happens if you add some cadmium selenide nanoparticles? These cadmium selenide nanoparticles will form an assembly at the toluene water interface. So, if you see these circles, so more clear here if you see these circles, you can see that green emission is a

coming from the 525 nanometer emission from the cadmium selenide nanoparticles, which are at the interface of the toluene and water.

So, the water is outside and toluene is inside and at the interface the cadmium selenide nanoparticles will arrange themselves. So, if you excite them with this 488 nanometer laser, then you can see a green emission which at 525 nanometer, this green emission is coming from only this interface area. If you take a depth profiling that means, this is looking at the same droplet, but in the z direction. So, you are going down in the z direction, you see that when you are going at inside the particles, so it is at the top surface, you see something then your, this is the particle is becoming larger.

Because, you are now at the center of the particle, so the cross section is larger again you are going down further, the cross-section become smaller and smaller and when you go in to the center of the particle, there is no emission. Because, the emission is all at the periphery and, so that suggests, that tells you that the cadmium selenide has not gone inside the liquid particle, but it is at the interface. So, this is a confirmation by confocal fluorescence imaging using studying it, studying the fluorescence coming out from different depths of the same particle, of the same interface and that tells you the self-assembly has taken place at the interface.

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**Liquid-Solid interface**

**Evaporation-mediated methods**

key step : Solvent evaporation

This process can be assisted by

- Electrostatic interactions
- van der Waals forces
- Dipolar interactions

**Importance**

- Highly ordered large-area nanoparticle structures on solid surfaces.
- Single nanoparticle arrays and complex lattices of semiconductor, metal and magnetic nanoparticles can be obtained.

**NPTEL**

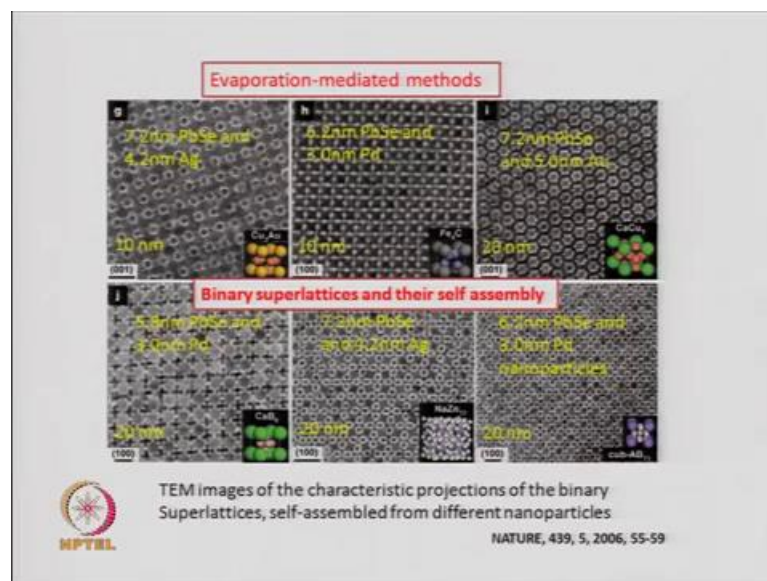
Now, you can come to the example of solid liquid interface. So, we looked at a liquid air interface, we looked at liquid-liquid interface. And then now we want to look at liquid-



solid interface. So, in liquid-solid interface you can repair an assembly of particles by the evaporation mediated method. So, here the key step or the most important step is, how you evaporate the solvent on top of the solid-liquid interface and what is left behind on the solid substrate. So, this process can however be assisted by electrostatic interactions van der Waals forces and dipolar interactions and it is very important because, this methodology of making assembly on a solids is very useful going by the liquid solid interface route.

Because, you can make large area structures, so you can take a large solid surface and you can slowly evaporate the liquid and create a self-assembled and assembled, assembly of nanoparticles on the surface of the solid. And you can use them for applications and examples of semiconductors metal, magnetic nanoparticles have all been demonstrated in the recent past, using evaporation mediated method on the liquid-solid interface.

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So, this is an example of a liquid solid interface, it is a classic paper on, published in nature in 2006, where people have used evaporation mediated method to form patterns. So, you see these are patterns of colloidal particles, lead selenide on silver nanoparticles.