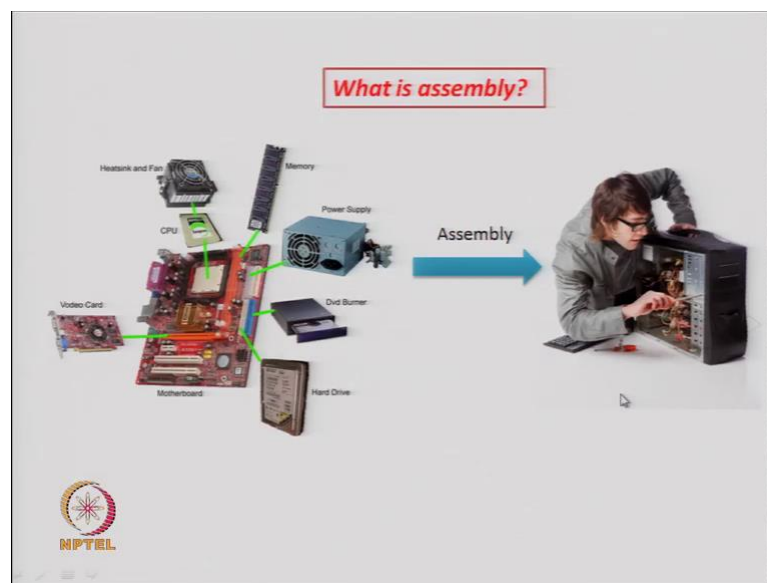


**Nano structured Materials-Synthesis, Properties Self Assembly and Applications**  
**Prof. Ashok. K. Ganguli**  
**Department of Chemistry**  
**Indian Institute of Technology, Delhi**

**Module - 3**  
**Lecture - 21**  
**Self Assembly of Nanostructures – I**

Welcome to this course on nanostructured materials- synthesis, properties and applications. In the previous lecture, we had discussed the concepts of nanowires, their synthesis and applications. Today we are starting the seventh lecture of the module 3, and we start on a new topic, which is self assembly of nanostructures. We will have three lectures on the self assembly of nanostructures. Today, we will discuss the first lecture on the basics of self assembly of nanostructures.

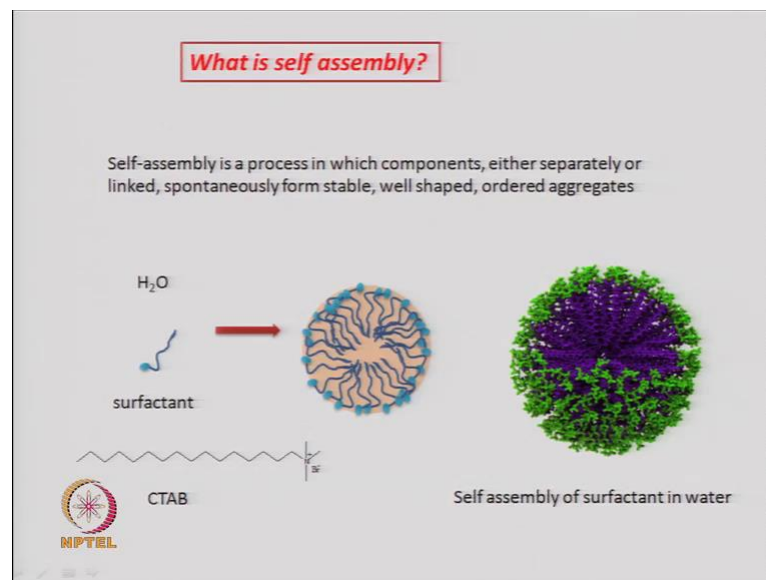
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What is self assembly? If all of you know that when you assemble a computer, there are many parts of a computer. You basically, put together all the different parts and when you assemble all these different parts, it may include a memory, a power supply and so many other things. You are assembling them together to get a final product, which has a particular function. This particular function, which this final product has, depends on all these parts being put together in a particular manner.

If it is not put together in a particular manner then this product will not be able to function, the way it should. Hence, how you assemble the various structures, to give you the final product is very important. This is a normal assembly, which we see in our daily life.

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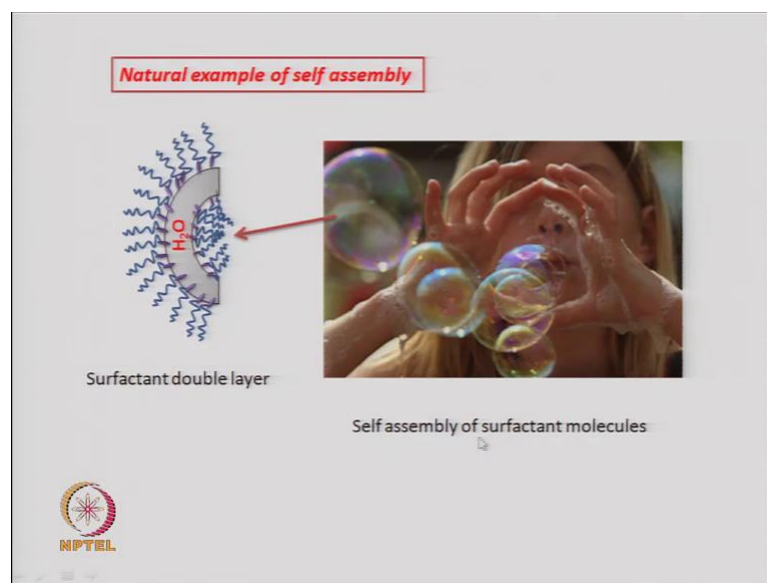
If you want to look at assembly in solutions, then a typical example of self assembly is the case, where you have components, which are either separately or linked spontaneously, form a stable well shaped ordered aggregate. This is shown by this example, where you have a surfactant molecule. A surfactant molecule, as you know, is typically, a long chain hydrocarbon that is made up of carbon-carbon bonds and has a polar head group, which here, is shown as a nitrogen atom with a positive charge. It may be a trim ethyl ammonium ion or a tri ethyl ammonium ion, and this kind of a structure which has a polar head group and a non polar chain is typically called a surfactant. It is shown by this kind of a structure, where you have the head group and the long tail.

When you bring such surfactant molecules, many of such surfactant molecules, if you put them in water then they self assemble; that means, they come together and form some kind of an ordered structure. If you look here, it appears that these surfactant molecules are arranged, such that all of them have their polar head groups on the periphery. Their tails are all pointing inwards. So, they have a particular way of coming

together; of assembling to form this aggregate. This is what we call as a micelle and this is a spherical micelle.

This is an example of self assembly in solution, where you have got an ordered aggregate, from some molecules in a liquid. This can also be seen like, this kind of self assembly in water can assume very large proportions, and you can get many types of very large structures; not only spherical structures; you can get many other types of structures.

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Here is another example from nature, where you can see self assembly. This is an example of a soap bubble. As you know, if you have a soap solution, a soap solution as all of you know, is made up of molecules of soap, which are like the surfactant molecules. They have long chain hydrocarbons with polar head groups. When these large numbers of molecules in water aggregate and you blow some air, then you get these kinds of bubbles. This is an example of a surfactant double layer forming. In the bubble, there is air inside the bubble and there is air outside the bubble.

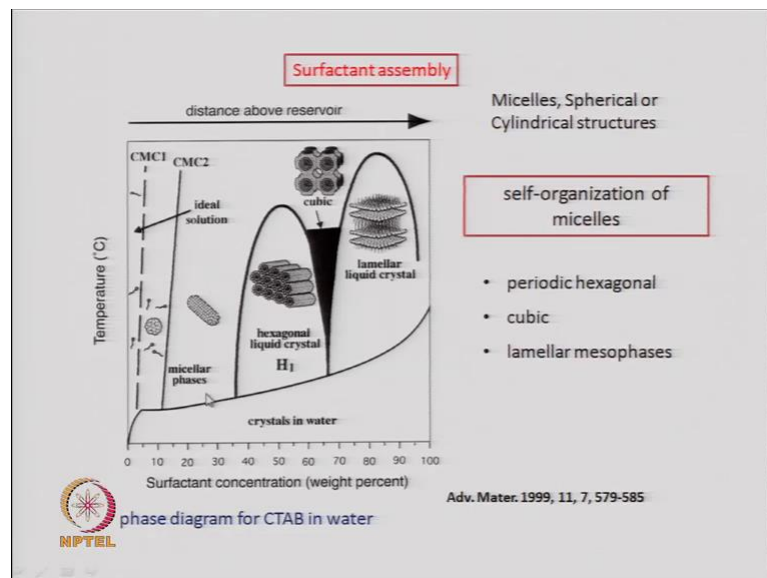
Typically, how you explain the interface between the air, which is inside and the air which is outside is shown here, where you have these polar head groups pointing inwards and the tails point outside. Here outside means, outside the interface. But, actually they are pointing inside the air bubble. Again, you have a thin layer of water and you have more surfactant molecules on the outer periphery of this water. So, you have two layers.

You have an outer surfactant layer aggregated on top of the water molecules, in a fashion, that the polar head groups are close to the water surface.

Similarly, you have an inner interface which is formed by this aggregate of the same surfactant molecules, and again the polar head groups are close to the water surface. So, both ways, if you look away from the water surface; that is either here or here, you have got the tail groups, which are hydrophobic, which are close to the air medium, which is outside or the air medium, which is inside the bubble. This is a natural self assembly and how did you come about; it came about by a natural process. When, you blew air in soap bubbles, in a fashion, which created this structure.

If you put in too much force or too much air, may be, you will not get the bubble. If you put in too less air, you will not get the bubble. So, you know that you try out many times to get the right kind of bubble. That is because, these bubbles will be stabilized for a particular size, for a particular thickness of the film, depending on the type of surfactants, the quantity of surfactants and quantity of water inside. This is an example from nature of self assembly.

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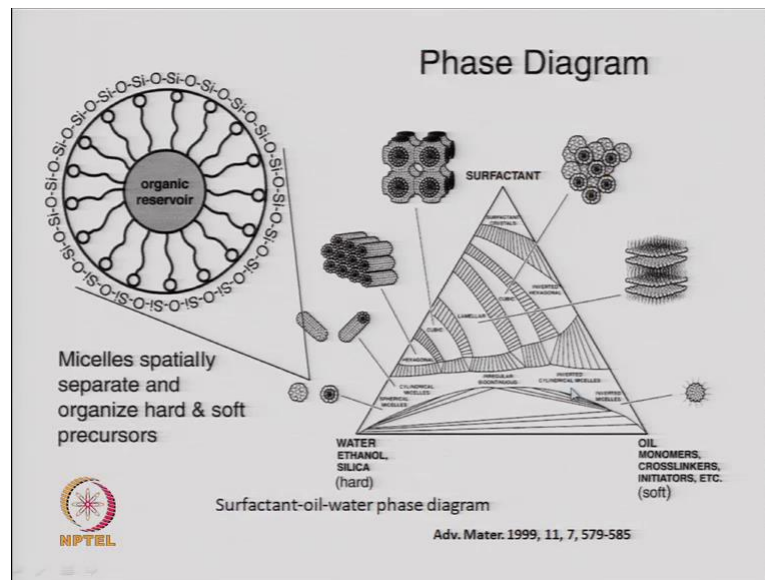
This kind of surfactant self assembly, can be discussed in many types of phase diagrams. This is a particular diagram, where what is being shown to you, that at different surfactant concentration and at different temperature, what kind of aggregates are formed. You can get micelles, which are spherical or cylindrical at particular conditions.

For example, if you see at low surfactant concentration, below 10, you can see that; that means, very small amount of surfactant molecules are here; they are more or less isolated. They do not aggregate to form any structure, till you come to a surfactant concentration which is called CMC1.

Then, these surfactant molecules aggregate to form this kind of micellar structures. If you increase the surfactant concentration further, at a particular temperature, you may get the cylindrical micelles. If you increase the concentration further, you can get these stacked cylinders, which form what we call a hexagonal phase. If you increase the surfactant further, you may get cubic structures of well organized and aggregates of surfactants and very high concentration of surfactant and at somewhat high temperatures, because these are not stable at very low temperature. At low temperature, you will get crystals in water, but at high temperature and high concentration of surfactant, you will get lamellar phases.

This kind of a picture or a diagram shows you, what kind of aggregates, you will get depending on the concentration of surfactant that you have, and the temperature at which you are working. You can have large number of surfactants. This particular diagram is for a surfactant, which is called CTAB, which means cetyl trimethyl ammonium bromide. When you take this CTAB in water and change its concentration, then you can get with isolated surfactants; micellar structures, cylindrical structures, hexagonally arranged cylinders which is called the hexagonal phase, cubic structures and lamellar structures. These kind of periodic structures or aggregates, can be obtained at different concentrations of the surfactant molecules in water. So, you have only taken surfactant and water and changed temperature and you get different structures.

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If you add something more; that means, you look at a fix temperature, but you have three components. One is the surfactant; the other is say, water or polar medium, instead of water, like ethanol or you can have a non polar medium, like oil, is an organic solvent or monomers, or etcetera. Then you can create a ternary phase diagram.

In a ternary phase diagram, you are fixing the temperature and pressure and here, you are varying the concentration of surfactant; water or oil. Depending on their concentration, you will be at certain region, in this triangular phase diagram. For example, for low amount of water and high amount of oil; amount of oil is high and water is very less. So, you are away from water; that means you are somewhere there. You are close to oil and then you will get this kind of inverted micelles, where the polar head groups are inside and water is inside, and oil is outside.

However, if you take very large amount of water and very small amount of oil, with some amount of surfactant, you will be somewhere here. When you are here, you will get these phases. So, very small amount of surfactants and very small amount of oil, but very large quantities of water, will give you spherical micelles. If you expand this; this is a particular type of spherical micelle, where you see, these are the surfactants and the polar head group is outside, and the hydrocarbon chain is inside. You will have the organic solvent here, and outside you will have the aqueous medium.

If you want to make silica surface on that, this silica will be on top because, that is where the polar head groups are. Then you will form silicate on top of it. This kind of phase diagram tells you all the different possible structures, which you can get, taking particular compositions. So, the phase diagram helps you, or guides you to choose the right composition of surfactant, water and oil, to get the kind of structure, which you are looking for.

If you are looking for a cubic structure, then you are here and you know that you have to have less content of oil, and reasonable content of surfactant and quite reasonable amount of water. So, this is the way you have to try to understand phase diagrams, in order to create different structures in surfactant medium or in micellar medium.

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**Importance of self assembly**

The cell contains different complex assemblies such as lipid membranes, folded proteins, structured nucleic acids, protein aggregates, molecular machines, and many others that form by self-assembly.

Self-assembly provides routes to a range of materials with regular structures, such as molecular crystals, liquid crystals, and semicrystalline and phase-separated polymers.

Self-assembly occurs widely in systems of components larger than molecules, and there is great potential for its use in materials (including biomaterials) and condensed matter science.

**Lipid membrane**

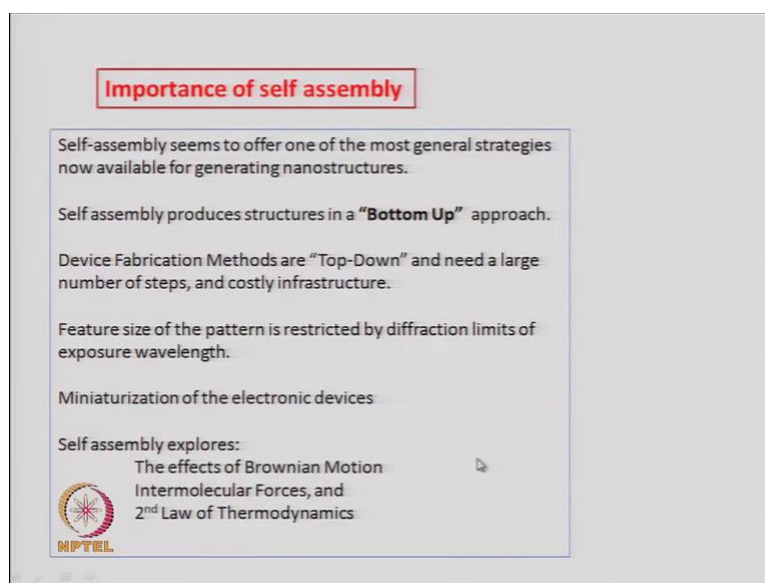
**Protein aggregates**

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Going to the next case, a slide; what is the importance of self assembly? Why do we try to study self assembly? The reason is that we, all the time, see processes especially, in living systems, which are dependent on self assembly. For example, the cell contains different complex assemblies, such as lipid membranes, proteins, nucleic acids and many kinds of molecular entities, which we call them molecular machines. Because, they function like machines, like, they function to pump ions or they can function to pump water across membranes, etcetera. These molecular machines are basically made up of self assembled structures.

So, understanding self assembly is very important in life processes and biological systems. Self assembly also is important, if you want to synthesize inorganic materials like, many nanocrystalline materials, liquid crystals and phase separated polymers. So, it is not only required in understanding biological systems, but also to discover or invent new materials, which depend on self assembly. There are wide number of systems, where self assembly is occurring, and there is great potential for its use in materials, biomaterials and condensed matter science or in the physics and chemistry of materials.

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**Importance of self assembly**

Self-assembly seems to offer one of the most general strategies now available for generating nanostructures.

Self assembly produces structures in a **"Bottom Up"** approach.

Device Fabrication Methods are **"Top-Down"** and need a large number of steps, and costly infrastructure.

Feature size of the pattern is restricted by diffraction limits of exposure wavelength.

Miniaturization of the electronic devices

Self assembly explores:  
The effects of Brownian Motion  
Intermolecular Forces, and  
2<sup>nd</sup> Law of Thermodynamics

**NPTEL**

You can use self assembly to create new structures. That is very important. This method of creating structures, from molecules or small systems to larger systems, is very important in today's world of nanoscience and nanotechnology. This technique of building structures from small to large is called the Bottom Up approach. The Bottom Up approach involves molecules, legants, metalions and builds larger structure, in what we call as the Bottom Up approach.

However, other methods use the Top Down approach, where you start with the large material, and try to remove material, and come down to a smaller structure or a nanostructure. However, top down techniques are very expensive. They require lot of infrastructure and they are not so selective. You lose lot of material, while you are removing atoms and molecules or fragments, from a large worth solid. So, the self assembled process, which nature always uses to build larger structures, uses much less



energy and much less material, is more specific and gives rise to very precisely designed structures.

The feature size of the patterns in the Top-Down methodologies is normally, restricted by the limits of the exposure of the radiation, which you are using to create nanostructures using Top-down method. That is another negative point for the Top-down processes to create nanostructures. Self assembly primarily, uses or explores the effects of brownian motion, that is the motion, that you know; the random motion, which a gaseous molecules have or in a dilute solution, you have the movement of some ions and molecules.

In those effects of brownian motion or the random motion, along with intermolecular forces, there are different types of intermolecular forces. You incorporate them. Their effects, and the second law of thermodynamics which tells you, that entropy has to increase. These are certain concepts, which are important, when self assembly takes place. Because of these factors, self assembled structures are guided towards a particular desired structure, which you want by controlling these factors.

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**What are the driving forces for self assembly ?**


**Weak intermolecular interactions:** thermal energies

**Non covalent interactions:** van der Waals, electrostatic, hydrophobic interactions, hydrogen bonds, and supramolecular assembly etc.

**Weak covalent bonds:** coordination bonds

**Energy of interactions and distance dependence**

Electrostatic energy	:	$1/r$ (long range)
Ion-dipole	:	$1/r^2$
Dipole-dipole	:	$1/r^3$
van der Waals interactions	:	$1/r^6$ (short range)

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What are these forces that we talked about which guide self assembly? These forces can be of different kinds. There can be weak intermolecular interactions like, the thermal energies, of the value of  $k t$ . Then, there can be non covalent interactions which are van der Waals type. They can be electrostatic, hydrophobic interactions. They can be due to

hydrogen bonds and then they can be like, you get in supramolecular assemblies, etcetera. They can be weak covalent bonds like, coordination bonds. These different types of bonds or interactions have some energy associated with them.

It is always better to have an idea of the energy involved with each kind of specific interaction. For example, if you are looking at an electrostatic energy, which comes under non covalent interactions, the electrostatic energy is proportional to  $1/r$ , which is the distance.  $r$  is the distance between two species, which are trying to come together. If  $r$  is the distance between two species, which are trying to come together then the electrostatic energy is proportional to one by  $r$ ; that means, if you change  $r$  by  $r$ ;  $r$  goes to  $2r$ , then the energy will be proportional to one by  $2r$ . So, it is a long range kind of interaction. Ion-dipole interaction goes as one by  $r$  square.

The ion-dipole interactions are weaker than electrostatic interactions. Dipole-dipole interactions go as one by  $r$  cube. So, they are still weaker and van der Waals interactions are really very weak. Hence, they are short range; that means, they can be seen only at very small values of  $r$ . If the  $r$  value is higher, you do not get any van der Waals interaction. So, they are very short range forces since, the energy is proportional to  $1/r^6$ . You must have a feel for the values of these different interactions, when you try to understand the forces, which are interacting between molecules and ions during self assembly.

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Different nonbonding interactions details			KJ/mol
Nonbonding (Intermolecular)			
Ion-dipole		Ion charge—dipole charge	40–600
H bond		Polar bond to H—dipole charge (high EN of N, O, F)	10–40
Dipole-dipole		Dipole charges	5–25
Ion-induced dipole		Ion charge—polarizable e <sup>-</sup> cloud	3–15
Dipole-induced dipole		Dipole charge—polarizable e <sup>-</sup> cloud	2–10
Dispersion (London)		Polarizable e <sup>-</sup> clouds	0.05–40

Chemical structures shown in the table:

- Na<sup>+</sup>·····O(H)<sub>2</sub>
- :O(H)—H·····iO(H)—H
- I—Cl·····I—Cl
- Fe<sup>2+</sup>·····O<sub>2</sub>
- H—Cl·····Cl—Cl
- F—F·····F—F

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What are these different types of bonding interactions, which we discussed? These interactions, which are nonbonding are typically, shown here. This is the ion dipole. This is an ion; positively charged and this is the dipole. The interaction between this, the ion-dipole is basically, between the charge on the ion and the dipolar charge, and the value of the energy is of the order of 40 to 600 kilojoule per mole.

This is an example, where sodium ion is there and in water. A sodium ion in water will see a dipolar interaction with water where, you have a delta negative charge on oxygen and you have a delta positive charge on the hydrogen. This delta negative charge on oxygen, will interact with the positive charge of the sodium ion. Hence, this is a typical case of ion-dipole interaction, with energies in this region; between 40 to 100,200 up till 600 kilojoule per mole. Much weaker interaction is the hydrogen bond. The hydrogen bond is when, you have a hydrogen between two electronegative elements.

For example, A is electronegative and so it will have a delta negative charge. This is say, covalent bond; covalently bonded to hydrogen. When this species is close to another ion, which has a delta negative charge, then this delta negative charge and the delta positive charge on a hydrogen, will interact and this is the hydrogen bond, commonly seen with compounds which have OH groups or have a fluorine attached somewhere to the hydrogen. These kinds of interactions have energy, much smaller than the ion dipole energy. So, the hydrogen bond is weaker than the ion dipole bond.

This is an example of interaction of hydrogen bond between two water molecules. So, you have two water molecules; one in which the hydrogen is covalently bonded, and it is close to another water molecule, which is held by hydrogen bond, due to the delta positive charge on hydrogen and the delta negative charge on oxygen. This is much weaker than the ion-dipole bond. Similarly, you can get dipole-dipole bonds of much lower strength of 5 to 25 kilojoule per mole. Then you can have ion and induced dipole.

For example, oxygen molecule does not have a dipole. So, there is an induced dipole because of the positive charge. The electron cloud, there will be a shift. So, you have an interaction between a ion and the induced dipole on oxygen, and this interaction is much weaker of the order of 3 to 15 kilojoule per mole. You may also have dipole-induced dipole weaker forces and you may also have induced dipole- induced dipole. For example, fluorine molecule; two fluorine molecules are close together, they generate or


polarize each other and generate charges on each other. That induced dipole then gives rise to this bond, which is very weak as you see, can be very weak as 0.05 kilojoule per mole.

So, these are different types of interactions which are possible, and such interactions brings molecule together. In self assembly, that is, what you do; you bring molecules together or ions together and form a larger structure. So, all these different kind of interactions, all or some of them, can bring about self assembly in a particular system.

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**General requirement for self assemblies**

- Pre existing of the components:
- Reversible:
- Control by proper design of components:
- Involving :
  - intermolecular interactions
  - fluid or smooth surfaces
  - weak interactions can be modified
  - equilibrium exists between aggregates and non-aggregates

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The requirements for self assembly- you must have the component; if you want to bring two parts together, you must have those two parts and then when once you bring them together they can join. So, you must have the components with you. The second thing is it should be reversible. Once you form a self assembled structure, it is possible to disassemble the structure, because these interactions which are holding the structure together, is not very strong. Once you put up the parts like, we discussed building a computer from different parts; if we unscrew the whole computer, take out the parts, it should be easy for us to dissemble the parts. Similarly, in molecular systems, in self assembled systems, it should be reversible and it is the structure. The self assembled structure is controlled by properly designing the components which you are starting with.

This assembly brought about, between these components by intermolecular interactions. Then you need fluid or smooth surfaces like, normally, you put the components; they

may be molecules; they are in a solvent or water. In a fluid, where they can rearrange and get adjusted, where their weak interactions can be modified and this aggregate structure, which forms due to self assembly, is always in equilibrium between the non aggregates that is the components, which have not aggregated and the aggregate, basically, there is an equilibrium existing between them.

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The slide is titled "Types of self-assembly" in a blue box at the top. It lists two types:

- Static**: systems that are at global or local equilibrium and do not dissipate energy. An example given is "molecular crystals are formed by static self-assembly".
- Dynamic**: The interactions responsible for the formation of structures or patterns between components only occur if the system is dissipating energy. An example given is "The patterns formed by competition between reaction and diffusion in oscillating chemical reactions".

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The types of self assembly- you can have two major types of self assembly; one in which there is no dissipation of energy. So, that is called a static self assembly. The systems are in a local or a global equilibrium and they do not dissipate energy. The other system is dynamic, where there are interactions only when you have energy dissipation. So, these are two basic differences. Normally, molecular crystals or most of the self assemble structures, that we study are static self assembly.

The dynamic self assembly is commonly seen in nature. We will show you some examples like, a large shoal of fish, which is many fish moving together in the ocean. You can see that, it appears that they are moving together. Thousands and thousands of fishes and there is some energy, which is being dissipated in the movement and that is a dynamic case of self assembly. Similarly, in the atmosphere you have galaxies, which appear to be self assembled from components.

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**Types of self assembly in different systems**

System	Type	Importance
Atomic, ionic, and molecular crystals	S	Materials, optoelectronics
Phase-separated and ionic layered polymers	S	
Self-assembled monolayers (SAMs)	S	Microfabrication, sensors, nanoelectronics
Liquid bilayers and black lipid films	S	Biomembranes, emulsions
Liquid crystals	S	Displays
Colloidal crystals	S	Band gap materials, molecular sieves
Bubble rafts	S	Models of crack propagation
Macro- and mesoscopic structures (MESA)	S or D	Electronic circuits
Fluidic self-assembly	S	Microfabrication
Solar systems	D	
Galaxies	D	<i>Science</i> 295, 2418 (2002)

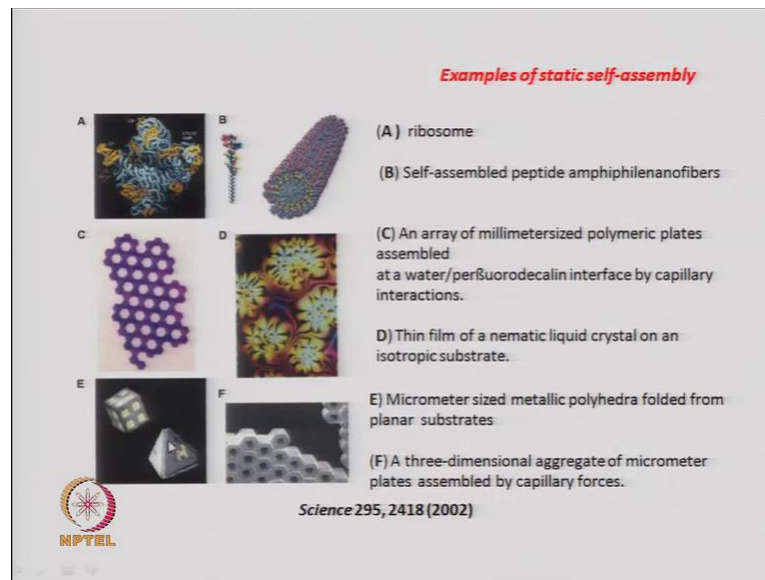


There are these different types of self assembly. You can have molecular crystals like, we discussed self assembly from atoms or molecules. They can be either ionic crystals or atomic also. These materials are all static. The assembly, self assembly static; there is no energy dissipation in this system. These self assembled materials of course, have variety of uses in materials and in optoelectronics. There are many other types of cases.

For example, if you go to self assembled monolayers, which are normally made on a film, on a liquid. You can bake a monolayer of molecules on top of a liquid and may be, we will discuss in future. Some examples, there also it is static self assembly. You are bringing molecules together on a surface of a liquid. Similarly, liquid bilayers; they are also static self assembly like, in biomembranes and emulsions. Liquid crystals used for displays; there also we have static self assembly. Colloidal crystals used for band gap materials, molecular sieves also involves static self assembly.

Dynamic self assembly, as I said, can be seen in the solar system in the galaxies where, you appear to see a particular assembly of planetary material. During this assembly, there is always energy, which is being dissipated, so very large systems. There are chemical reactions also, where you can see the self assembly has dissipation energy. But it is seen especially in solar systems, in galaxies where, this dissipative type of self assembly is present. Most of the systems in chemistry or chemical engineering related to assembly on molecules or a layers or bilayers is all static, and does not involve dissipation of energy.

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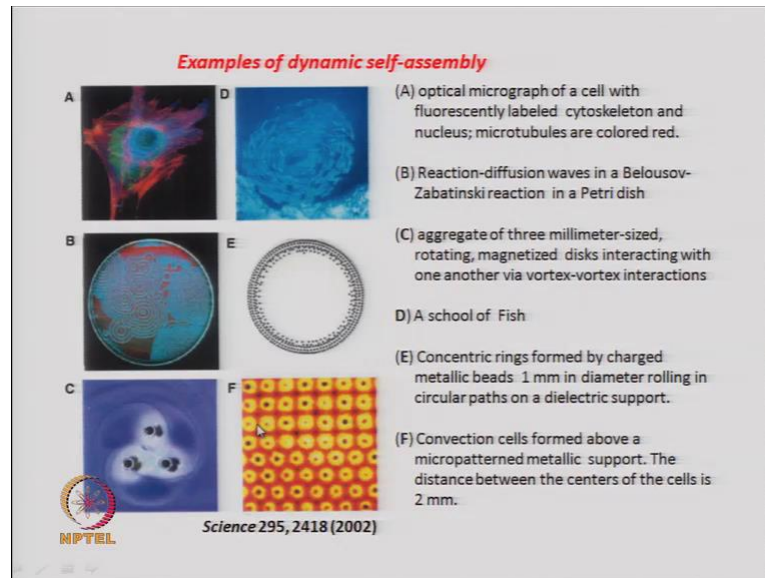


These are some examples of static self assembly. This is in our body, you know ribosome. Ribosome is very important. That is where proteins are synthesized. You can see its self assembled structure and very important function it has, based on this self assembled structure.

This is another polypeptide, which has been self assembled from some nanofibers. This is an example of an array of millimeter sized polymeric plates, which are assembled at a water and perfluorodecalin interface. This is an assembly of a liquid crystal. So, a liquid crystal, where molecules have self assembled, and this has been put on an isotropic substrate. You can have micrometer sized metallic polyhedra. This is in the shape of a cube. This is in the shape of a prism and these have actually been made from planar substrates.

So, you have assembled this cube or this prism from a planar substrate of metal polyhedral. That is another example of a static self assembly. The last one here shown, is a 3-dimensional aggregate of plates, which are in micron size; micrometer sized plates, which are again assembled by capillary forces. These are all examples of static self assembly.

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Examples of dynamic self assembly- For example, here it is shown that a cell with a fluorescently labeled cytoskeleton and nucleus, and the microtubules are colored. These are colored in red, the microtubules. This is an example of a cell, which is in our living cell. This is how this has come about; the cell is by self assembly of several objects which are within the cell.

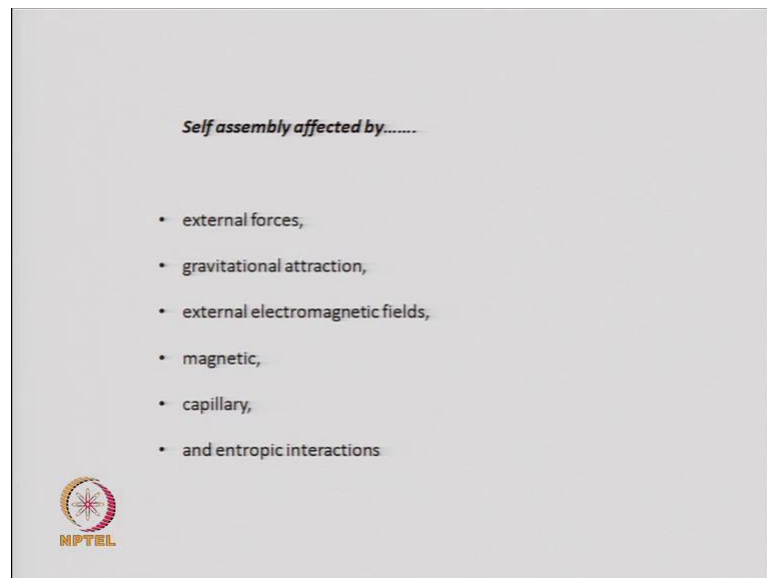
For example, the nucleus and several other bodies which are present inside the cell. This is dynamic. It involves energy dissipation. The second one is a classic case in chemistry. This is found, this kind of a reaction diffusion where, the reaction is occurring. You can see some waves formation, and energy is being dissipated in a particular type of reaction. These reactions are given a name called the Belousov Zhabotinsky reaction. These are particular reactions where, these are also called oscillatory reactions where, you have this dissipation of energy.

The third example is of some aggregate of disks, which are magnetized, and are interacting with each other. They are interacting with each other through, what is called Vortex Vortex interactions. This also involves heat dissipation and so this is a dynamic self assembly. So, these three are self assembled and it is a dynamic self assembly because, there is dissipation of energy. This is an example, which I already mentioned, is a large number of fish in the ocean. You can see that thousands of fish will travel together and it appears, that there is some interaction between them. So, that they know



how to move together within the ocean. This is again, an example of a dynamic self assembly of a school of fish and it involves again, energy dissipation. This is again a man made system of charged metallic beads, which are around 1 millimeter in diameter. They are rolling in circular paths on a dielectric support. So, when they do that it appears that they have self assembled, and there is again, dissipation of energy. This is a micro patterned metallic support. There is a micro patterned metallic support where, the two centers of the cells are at 2 millimeters apart. You can see some kind of a convection cells around these points. This self assembly is again a case of a dynamic self assembly. So, we looked at cases of static self assembly and dynamic self assembly; the two main classes of self assembly.

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Self assembly, if I want to control or how does self assembly gets affected by; they are affected by external forces like gravitational force, electromagnetic fields, magnetic fields, capillary forces and entropic variations. So, all these factors will affect the self assembly.

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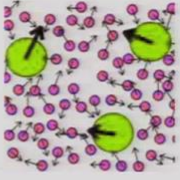
**Factors controlling the Self assembly**

Balance between Brownian motion and intermolecular forces

Brownian motion controls the location of the molecules where intermolecular forces hold the molecules at the particular position.

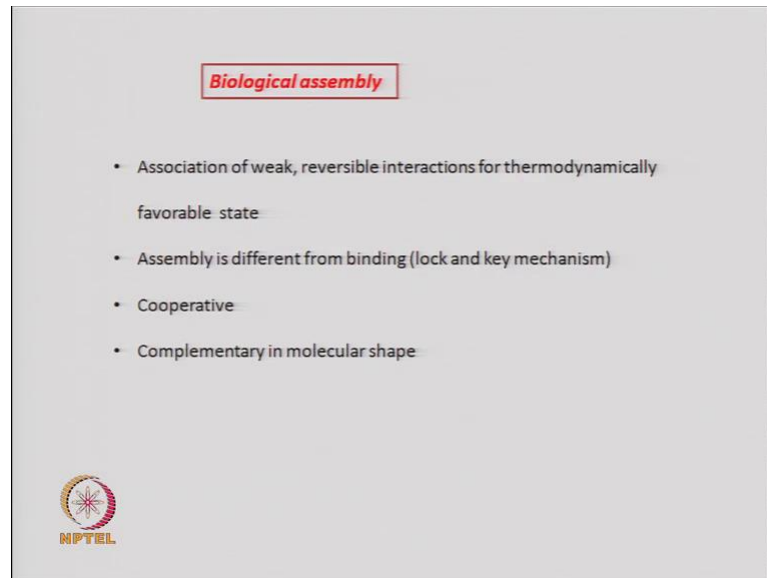
Brownian motion takes care of the incorrect assemblies of the molecules

Brownian motion




Typically, most important two things are Brownian motion and intermolecular forces. Intermolecular forces are of several kinds we discussed, can be due to ion-dipole, induced-dipole, which are the dispersion forces or hydrogen bond. If you can control those intermolecular forces, and somehow balance the Brownian motion with respect to the intermolecular forces, then you can get to a self assembled structure. The Brownian motion controls the location of the molecules. The intermolecular forces hold the molecules at a particular position. Those molecules, which are not in the assembled position, the Brownian motion will help bring it to that location. So, both these things are required. The Brownian motion, which is making the components move towards a self assembled structure and the intermolecular forces holding the components in the self assembled structure.

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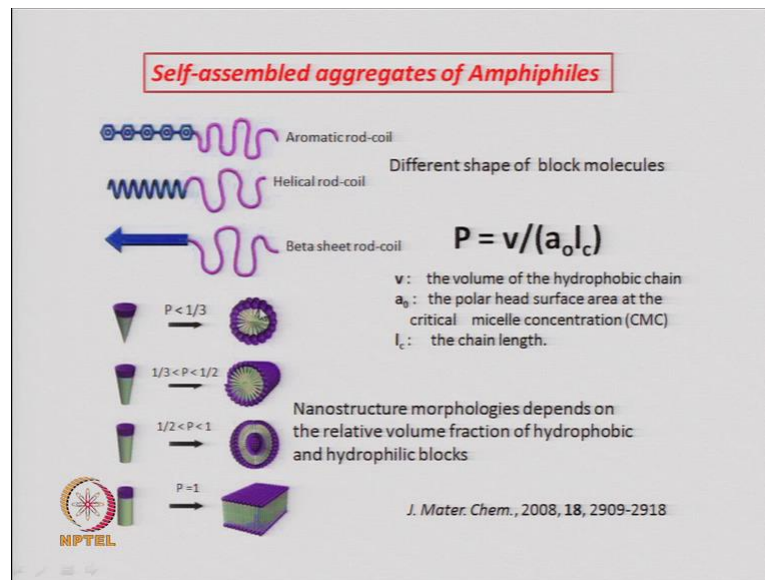
**Biological assembly**

- Association of weak, reversible interactions for thermodynamically favorable state
- Assembly is different from binding (lock and key mechanism)
- Cooperative
- Complementary in molecular shape

 NPTEL

In biology, typically in a biological self assembly, the association of weak and reversible interactions will lead to a thermodynamically favorable state. The assembly is different from binding, which we explain like the enzyme substrate binding in biology, which we say, goes through a lock and key mechanism. This particular biological self assembly is different from binding. Biological self assembly is mostly cooperative and so if you trigger at one place, the effect can be felt over a large space in biological systems. Normally, the self assembly is complementary in biological systems, with respect to molecular shape. So, these are some of the important points one has to be aware of, when discussing biological self assembly.

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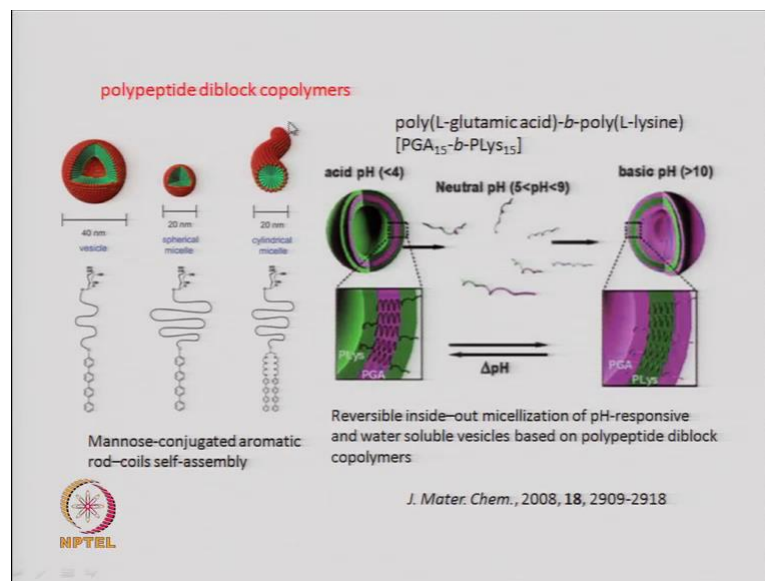
Here, we show you some examples of self assembled aggregates of amphiphiles. Amphiphiles are molecules which can bind, which have interactions with both hydrophilic and hydrophobic group. So, those are amphiphiles. Here, you see, this is an example of an aromatic rod and coil. There is an aromatic rod and a coil. These are helical rods and a coil. This is a beta sheet like, in proteins, you can have the alpha helix, the beta sheet, depending on how the binding is, between the various peptide linkages. So, you can get different kind of aggregates based on these kinds of monomers. These, we can call them, block molecules or these block molecules have different shape.

There is something called packing factor. This packing factor is related to the volume of the hydrophobic chain. You have the hydrophobic chain here. Volume of the hydrophobic chain is given by v divided by the polar head surface area. If you have a polar head group, then what is the surface area of the polar head group is given by a naught, and l c is the chain length of the hydrophobic part. So, if you know these three factors you can calculate P.

Based on the value of P, the aggregate has a different structure. So, if P is less than 1 by 3 then this structure looks like this. This structure will self assemble to form what is called a micelle. However, if P is between 1 by 3 and 1 by 2, that means, the shape is typically like this; not exactly like this. Then, this structure becomes, instead of a spherical micelle, it tends to be like a cylinder. If this value of P is between 0.5 and 1

then it tends to be somewhat, like a vesicle. You can have lamellar structures, when the value of P is nearly equal to 1 and then you have these lamellar types of structures. So, the self assembly leads to different structures, depends on this packing factor, which depends on the volume of the hydrophobic chain, the area of the head group and the length of the hydrophobic chain. So, you can control the morphology of the nanostructure by controlling or varying one or more of these factors.

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This is an example. You start with diblock copolymers. These kind of copolymers, with the mannose; these are sugar group here at the top. You have the aromatic ring with the sugar group, which is mannose in this case. This can give rise depending on the length of this hydrophobic chain; you see, you can vary the length of the chain. You can get a vesicle, which is 40 nanometers wide. You can get a spherical micelle, which is 20 nanometers wide, and you can also get a cylindrical micelle, which has a diameter of 20 nanometers, depending on if you change this group out here. So, you can construct different kind of self assembled structures, if you change the initial component, which is forming the self assembled structure.

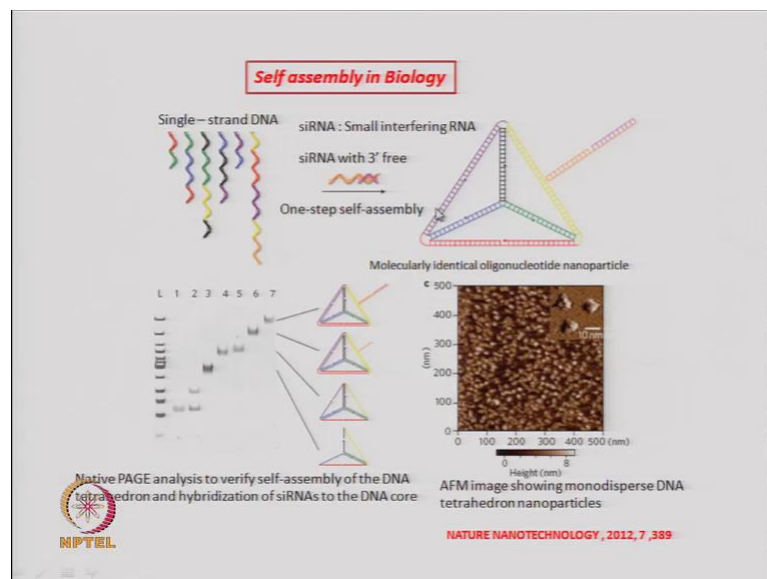
On the right side, we see an example, where you have started with a polymer of L glutamic acid and L lysine, and one of them is, you know, more hydrophilic compared to the other. At low pH; that means, less than 4, you see one kind of a vesicle. So, when the pH is low, this surfactant molecule, which is acting like a surfactant molecule, basically,

a diblock polypeptide of a diblock polymer, that at low pH, gives a structure of vesicle where, the polyglutamic acid is inside and the lysines are outside on the outer periphery.

If you increase the pH; in basic pH, you can see that the glutamic acid comes on the outer part and the lysines is inside, this kind of a reversible reaction where, at low pH, you had this structure and at high pH, you reverse the structure. What was inside has now come outside. This kind of pH responsive systems can be designed and this is just self assembly, which is occurring, depending on the kind of solution that have, the kind of pH you have. You can change the nature or the structure of the self assembled aggregate where, in this case you have lysines on the outside, and in this case you have glutamic acid on the outside.

So, these kinds of direction you can give to the self assemble structure by just changing the pH. However, you have other possibilities. For example, this is an example in biology. In biology, this can be an example where, you can use these vesicles for having, storing some drugs inside and then delivering. In one case, when the drug is inside, you want a particular environment, and when that drug is outside, you can have a different environment, which will bring back the vesicle outside. So, you can control the function of the vesicle by controlling the pH in this example.

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There are many other examples in biology and a lot of work is done in biology using single strand DNA. Normally, DNA as you know, is a double helix. There are two

strands in a DNA. However, you can get single strand DNA. If you use single strand DNA, with the particular sequence of amino acids; different colors here, denote different sequences of amino acids. If you take some combination of amino acids and make a DNA strand of this kind of thing, and then DNA normally, will try to form, it finds its counterpart. So, that it becomes a double helix.

But, if you add the molecule which is called small interfering RNA or siRNA, then this siRNA can bind to the single strand DNA, and then that DNA will not be able to form a double layer. So, what you can do; In this case what has been done is that you mix some of these. Heat it and then cool it. Basically, it will try to find, form a double helix, but in the presence of this small interfering RNA, which particularly has, the three prime position free, like, in the sugar, you have what we call the three prime and the five prime positions.

The three prime positions, if it is free, then it can bind to the five prime position of the strand with which, it is going to combine. So, you can guide the formation of this and then once, this siRNA binds to the DNA, then that DNA can no more form a duplex. So, you can control; from a single strand DNA, you can make a double strand DNA of a particular length, and then stop it by using siRNA. This is called one step self assembly. It was seen that under that conditions, with a particular kind of single strand DNA, it was found that this kind of structure was obtained.

These double lines, basically, show a particular arrangement of the peptide chain. These are different colors; are from these different colors. They have a different peptide linkage. There is a particular order of the polypeptide chain. It forms a structure like this and how did they come to know that they have a structure like this is, that once you do the reaction, and then you do what is called a page analysis, that separates the products based on the molecular weights. You get different such products and that tells you.

For example, this one, by its molecular weight, you can assume because, the higher molecular weights will be here, and the lower molecular weight is here. So, you can find out what structure possibly can be. Using this page analysis, it was found that you can have several of these structures and several of them, were actually experimentally found, using this page analysis. One of them is this structure, which is actually the largest one. This kind of structure where, you can have a particular length of a DNA of a particular

sequence, starting from single strand DNA of a particular sequence, is possible with self assembly.

Here, the self assembly is being done or controlled using this small interfering RNA. You are getting this kind of structure. This can be seen by an AFM image, and these structures have been shown. The monodisperse, this kind of a tetrahedron type of DNA structures have been shown using an AFM picture. So, that will bring us to a close to today's lecture on self assembly, which is the seventh lecture of our module 3. Today was the first lecture on self assembly of nanostructures. We will have subsequently two more lectures on self assembly, in this module itself.

Thank you very much.