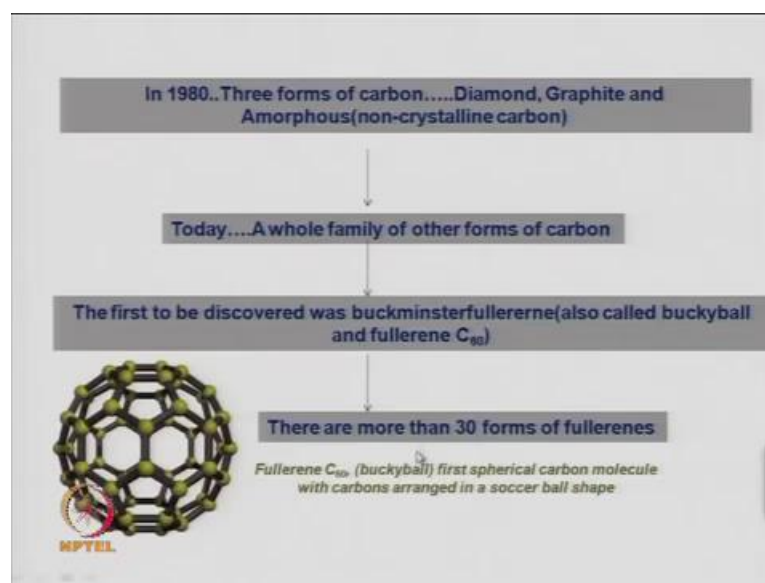


Nano structured Materials-Synthesis, Properties, Self Assembly and Applications
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Indian Institute of Technology, Delhi

Module - 3
Lecture - 15
Fullerenes and Carbon Nanotubes – I

Welcome to the course of nano structured materials synthesis properties, self assembly and applications. We are going to start the first lecture of module 3, we earlier had module one comprising 2 lectures and module 2 comprising 12 lectures. So, totally we have completed 14 lectures and today will be our 15 lecture or for the whole course and is this, is the first lecture of module 3. The first lecture we will start with fullerene and carbon nano tubes and, we will have three lectures on fullerenes and carbon based nano tubes, today we have the first lecture of this.

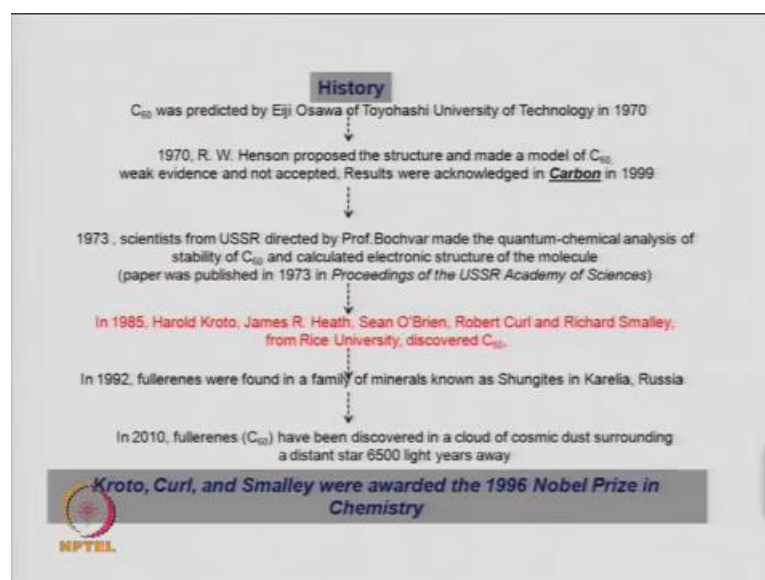
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Now, fullerenes as some of you must have heard was discovered in 1985, but previous to 1985 also there were reports about it. So, we will discuss the historical development of this structure nanostructure called fullerene, you must have all known that normally carbon has 3 allotropic forms. One is diamond, the other is graphite and we have amorphous type of or non crystalline carbon, today we know of many other forms of carbon.

So, among them the first to be discovered among these new forms of carbon is the C 60 molecule which is also called the buckyball and is also called for fullerene. So, today there are many other carbon based molecules which are related to this buckyball with lot number of carbon atoms per molecule. But, there are more than 30 forms of such fullerenes, now why this is called fullerene we will come to that, it basically looks like a soccer ball which has got a 6 membered carbon rings and also 5 membered carbon rings. So, this typical molecule has sixty carbon atoms which is arranged like in a soccer ball or a football, as we know in India, and if you replace the vertices of each other those with carbon. Then this becomes C 60 molecules and this was discovered in 1985 and noble prize was given for this discovery.

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So, historically was this discovery of C 60 in 1985, the first time people thought of this molecule no people have thought about such molecules much earlier. So, for example it was predicted by Osawain 1970 that there can be a molecule like C 60 in 1970 there was another proposal of a model of C 60. But, the experimental evidence was not very strong and hence this structure was not accepted at that time these results have been later acknowledged.

Now, for example in the journal carbon in 1999, much later that Henson propose this structure in 1970, today we know that it is correct and it is known experimentally apart from that in 1973 in U S S R. But, earlier U S S R, it was calculated using quantum

chemical calculations that a molecule like C₆₀ would be stable and the electronic structure of the molecule was calculated. So, the energy level of the molecule, a molecular orbital was calculated for a molecule like a C₆₀ theoretically and a paper was published in proceedings of the U S S R academy of sciences.

So, there were several such studies which were kind of indicating that there can be a molecule like C₆₀, a very symmetrical molecule, a molecule which looks like a football or a soccer ball. So, this molecule was predicted theoretically and some experiments were done, but not flinching evidence was not there. But, in 1985 a team of people from England and USA contributed to the actual discovery of C₆₀, the main players in the discovery of C₆₀ were Harold, Kroto Robert curl and Richard Smalley.

So, James heath was a student at that time and these 4 people work in rice university though Harold Kroto who was visiting a rice university from U K. So, together they discovered C₆₀ in 1985 and the idea behind their discovery was they were looking for molecules on which can be synthesized in the upper atmosphere or in space where plasma exists. So, they were trying to create a plasma are to an electric discharge where such molecules which area probably formed in outer space can be recreated in the laboratory.

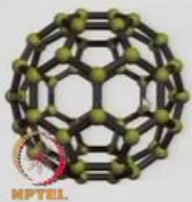
So, during that are discharged of using graphite electrodes, they found a black colored material getting deposited. Then it was analyzed using several techniques including N M R or nuclear magnetic resonance and they conform that it is a C₆₀ molecule and molecule which has 60 atoms of carbon.

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In 1980..Three forms of carbon.....Diamond, Graphite and Amorphous(non-crystalline carbon)

Today....A whole family of other forms of carbon

The first to be discovered was buckminsterfullerene(also called buckyball and fullerene C_{60})



There are more than 30 forms of fullerenes

Fullerene C_{60} (buckyball) first spherical carbon molecule with carbons arranged in a soccer ball shape

MPTEL

And the structure was just like the structure, we showed like a soccer ball.

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History

C_{60} was predicted by Eiji Osawa of Toyohashi University of Technology in 1970

1970, R. W. Henson proposed the structure and made a model of C_{60} , weak evidence and not accepted, Results were acknowledged in Carbon in 1999

1973, scientists from USSR directed by Prof. Bochvar made the quantum-chemical analysis of stability of C_{60} and calculated electronic structure of the molecule (paper was published in 1973 in *Proceedings of the USSR Academy of Sciences*)

In 1985, Harold Kroto, James R. Heath, Sean O'Brien, Robert Curl and Richard Smalley, from Rice University, discovered C_{60} .

In 1992, fullerenes were found in a family of minerals known as Shungites in Karelia, Russia

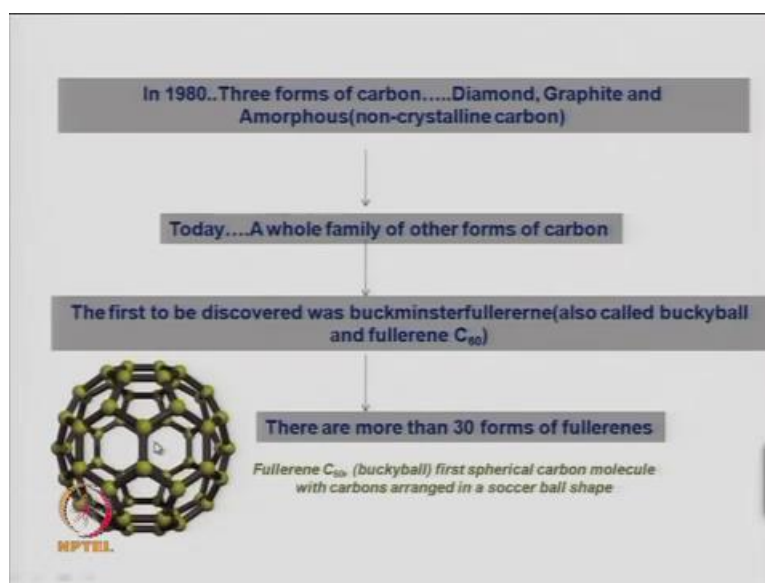
In 2010, fullerenes (C_{60}) have been discovered in a cloud of cosmic dust surrounding a distant star 6500 light years away

Kroto, Curl, and Smalley were awarded the 1996 Nobel Prize in Chemistry

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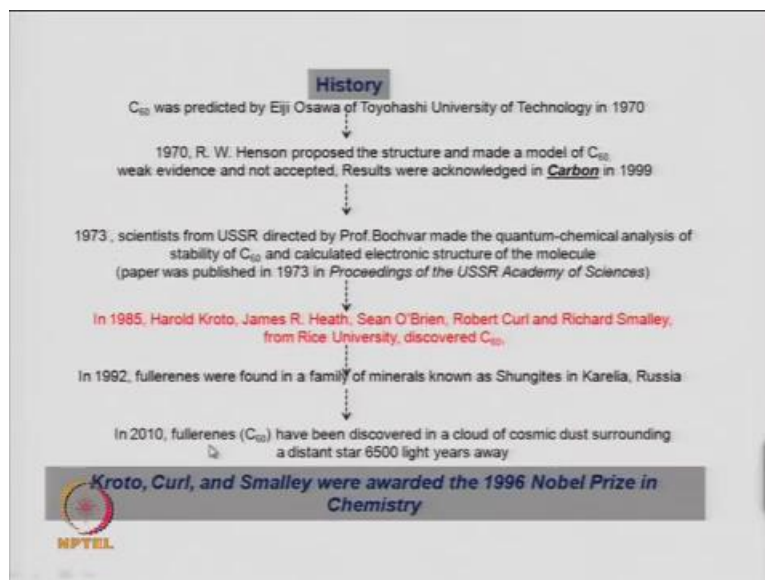
So, this was a the discovery of C 60 by Kroto Curl Smalley and their coworkers at rice university using electric discharge, and then analyzed by several techniques give the structure which was exactly.

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So, which was kind like a soccer ball with 60 carbons having hexagonal rings and pentagonal rings?

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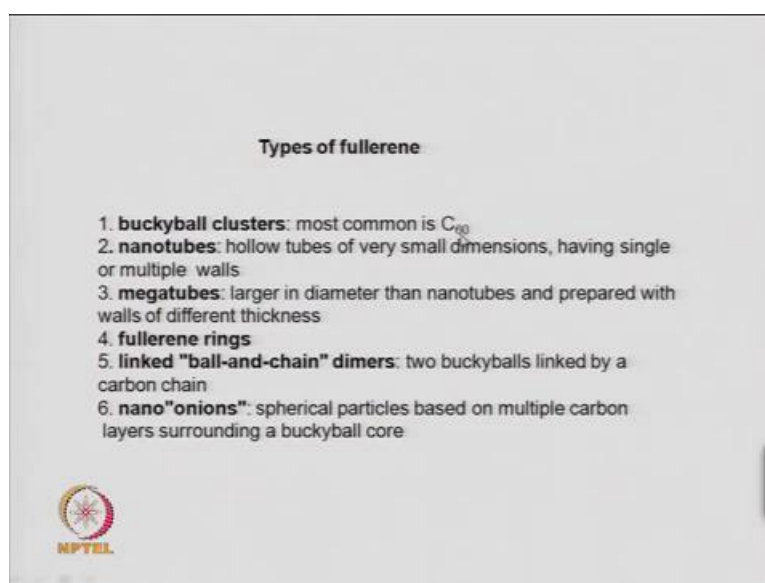


Later, such C_{60} are fullerene kind of materials have been found naturally occurring in Russia and it is also been discovered in cosmic Dustin, a distant star several light years several thousand light years away. So, C_{60} molecule molecules are present in the, in space they are also found in minerals and of course it was made in the laboratory. So, for

their work Harold Kroto Robert and Richard Smalley were awarded the 1996 Nobel prize in chemistry.

Though the discovery they made was in 1985, they were ordered the Nobel prize in chemistry in 1996, it was a great discovery a new allotropic of carbon was discovered. So, it brought about several new molecules related to C 60 like C 70, C 80, C 82 and several large cage like structures ring with cluster like structures were discovered after these fullerene or C 60 was discovered.

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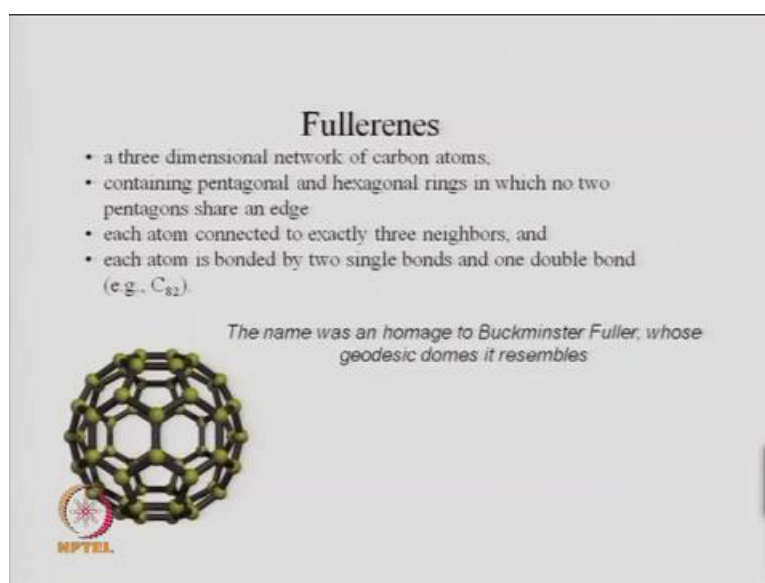


So, the type of fullerenes that we know today are like the common C 60 molecule, we just discussed apart from that we have now made several nano tubes which are made up of carbon. So, these hollow tubes which have a very small dimensions can have single walls or multiple walls based on carbon these nano tubes are very important for several applications as we will discuss in the coming lectures. Then you can have mega tubes much larger in diameter than the nano tubes and can be prepared with walls, which have varying thicknesses. Then you can have full fullerene rings you can also have fullerenes which are linked by carbon chains.

So, those are called ball and chains, so those are called ball and chain kind of dimmers, so 2 buckyball or 260, C 60 molecules which are linked by a carbon chain will then we called a ball and chain dimmer. So, you can have two buckyball which are connected to each other to from fullerene rings then you can have what are called nano onions

spherical particles based on multiple carbon layers surrounding a buckyball core. So, you have a C 60 core and there are layers of carbon surrounding that C 60 molecule, so you may have 5, 6, 7 layers of carbon which is surrounding a C 60 molecules. So, if you take out one layer another layer will be there, so that is why the structure will be like an onion. Hence, it is called nano onion, because the dimension of the C 60 molecule is nanometer in size less than 1 nanometer it is around 0.7 nanometers.

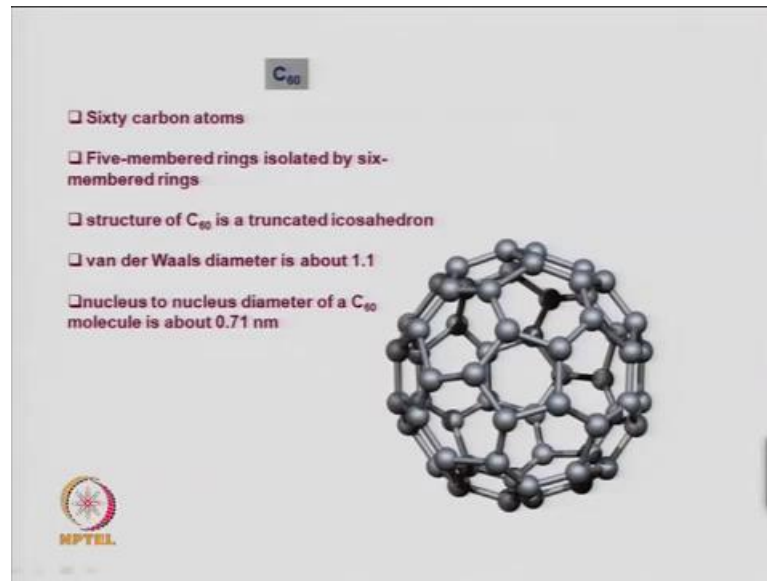
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Now, the name fullerenes come from the name of an architect Buckminster Fuller who first made domes which are like the fuller in structure. So, these geodesic domes as they are called have been made in several places in Canada and many other places which have domes which are in the shape of this kind of the hexagonal rings and pentagonal rings fuse together. So, if you take half of it then it forms a dome which is very similar 2 domes which Buckminster Fuller, an architect made in the 1970s in several countries and, so this molecule is called fullerene after the name of Buckminster Fuller.

So, fullerenes have 3 dimensional networks of carbon atoms, they contain pentagonal and hexagonal rings in which no 2 pentagons share an edge. So, hexagons can share an edge one hexagon can share an edge with one pentagon, but 2 pentagons cannot share an edge. Then each atom is connected to exactly 3 neighbors, 3 other carbon atoms and each atom is bonded to 2 single bonds and 1 double bond example in C 82.

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So, again going through the main characteristics of C₆₀ molecules there are 60 carbon atoms, there are 5 membered rings and there are, so this is a 5 membered ring as you see. Here, there are 5 pentagons and there are 6 membered rings here and this 6 membered ring can be connected to another 6 membered ring in this C₆₀ molecules. But, two 5 membered rings cannot be connected to each other, the van der Waals diameter that means the distance between the electron clouds from one end to another end is about 1.1 nanometers. So, that is like 11 Angstrom, but if you take the nucleus of the carbon here and the nucleus of the carbon then that distance is around 0.7 nanometers which is much less than 1 nanometer.

So, it is on average, you can just say that the fullerene molecule is of the order of nanometer, but of course it depends on what kind of diameter are you defining. So, if you take the van der Waals diameter it is 1.1 nanometer and if you talk about the nucleus to nucleus diameter then it is 0.71 nanometer, which is equal to 7.1 Angstroms.


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Another common fullerene is C_{70} , but fullerenes with 72, 76, 84 and even up to 100 carbon atoms are also known

follows Euler's polyhedron formula, $V - E + F = 2$ (where V , E , F are the numbers of vertices, edges, and faces), that there are exactly 12 pentagons in a fullerene and $V/2 - 10$ hexagons.

Boron Buckyball: A type of buckyball which uses boron atoms, instead of the usual carbon, was predicted and described in 2007

The B_{80} structure, with each atom forming 5 or 6 bonds, is predicted to be more stable than the C_{80} buckyball

 Gonzalez Szwacki, N.; Sadrzadeh, A.; Yakobson, B. "B80 Fullerene: An Ab Initio Prediction of Geometry, Stability, and Electronic Structure". *Physical Review Letters* **98**, 16, 166804. (2007)

Then you can have other than C_{60} , which has 60 carbon atoms, you can have C_{70} which has 70 carbon atoms, you can have C_{72} , C_{76} , C_{84} . So, you can have fullerenes with different number of carbon atoms, but the shape will change slightly. Now, you are number of hexagons and number of pentagonal will change because the number of hexagons and the pentagon's are related. So, always you will have 12 pentagons the hexagons will change and that number will be equal to V by 2 minus 10 where V is the number of vertices.

So, this is given by Euler's polyhedron formula, so if you have C_{82} , if you have 82 vertices then you need to know how many edges are there. So, how many faces and there and you can use this formula V minus E plus F equal to 2 where V , E , F are the vertices edges and faces and you can find out that there will be exactly 12 pentagons and V by 2 minus 10 hexagons. So, if you have C_{84} if you have 12 pentagons, then you, if you, the number of vertices is 84, so 84 by 2 is 42 and 42 minus 10 is 32 hexagons.

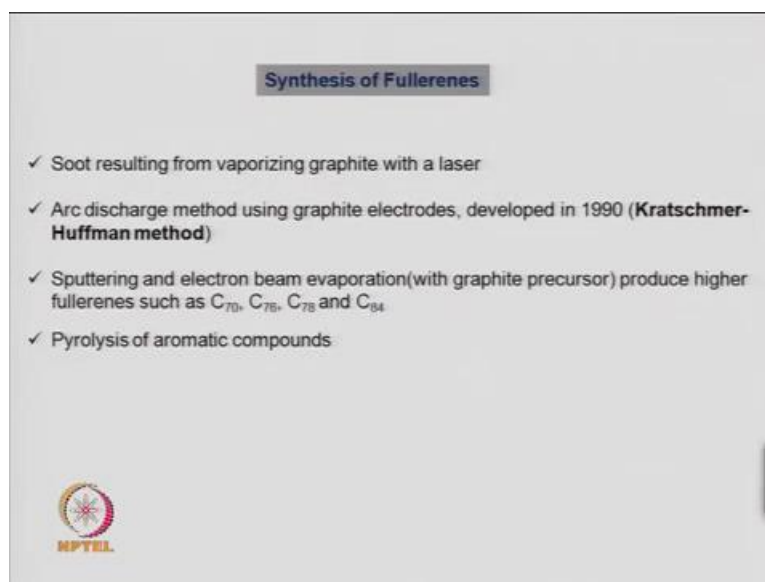
So, you can say that C_{84} that means the cluster or the molecule C_{84} will have 32 hexagons and 12 pentagons. So, in all these fullerenes you will have variable number of hexagons and you will have 12 pentagons and the number of hexagons you can find out if you know the number vertices.

But, the number of vertices you can get from the number of carbon atoms you have on this cluster, so you can have a large variety of these fullerenes all related through

hexagons and pentagonal of carbon. Now, recently in 2007 instead of carbon, boron have at the vertices has also been created to lead to a buckyball kind of structure. However, the formula which has been obtained is be 80 and with each boron forming 5 or 6 bonds and it is predicted that it will be more stable than C 60.

So, this kind of boron buckyball has not been isolated it has been predicted like periodically and described and it is suggested that if it is made. Then this V 80 molecule will be more stable than C 60, so there are lots of new things related to fullerenes which are still under research.

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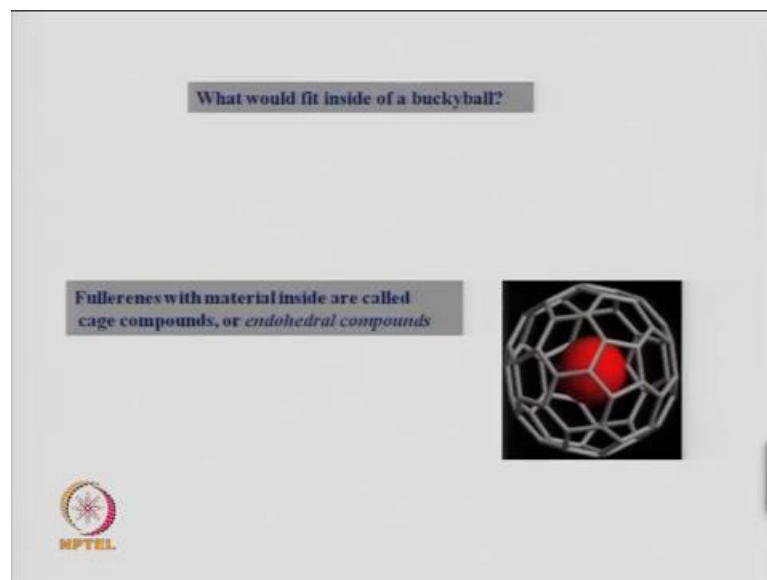
So, how do you synthesize these fullerenes the C 60, C 70 etcetera, so the technique which is used is either you take graphite. So, graphite is basically carbon one allotrope of carbon where which has got sheet like structure or layers of carbon forming hexagonal rings. Now, each layer separated from another layer by Van Der Waals distance of around 3.3 Angstrom and this graphite with if you evaporate by shining laser. Then you can get some soot some carbon material deposited from where you can extract fullerenes another method is what is called the arc discharge method.

So, this is a method where you use 2 graphite electrodes, so again graphite is being used, but you have 2 graphite electrodes. So, you know in the electrodes you apply a potential and you generate a discharge between the 2 electrodes. So, there is a small gap between the two electrodes and between that arc has to be formed, so when you apply a very high

potential on the 2 electrodes then and an arc is created then some soot is deposited in the chamber around these electrodes.

So, this technique was developed in 1990 by Kratschmer and Huffman and this also leads to several fullerenes. So, you can use that technique of shining laser on graphite and collecting the soot or you can use a arc discharge method to or using graphite electrodes by which you can generate soot which collects on the inner walls of the chamber. Now, which you can collect and from that you will get a variety of C₆₀, C₇₀ type of fullerenes and then you have to separate them.

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Then you can use other techniques like where electrons beam evaporation.

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Synthesis of Fullerenes

- ✓ Soot resulting from vaporizing graphite with a laser
- ✓ Arc discharge method using graphite electrodes, developed in 1990 (**Kratschmer-Huffman method**)
- ✓ Sputtering and electron beam evaporation (with graphite precursor) produce higher fullerenes such as C_{70} , C_{76} , C_{78} and C_{84}
- ✓ Pyrolysis of aromatic compounds



Now, where you can produce the higher fullerenes to a larger amount or you can take some aromatic compounds and then heat them, so you take aromatic compounds like normally heat them. So, you can get a shot from that soot also you can get some fullerene type of compound of course the proportion of which fullerene you get depends on the method. Now, to get pure fullerenes by one method is quite a tough job normally you have to separate these fullerenes, so once you get the soot through different chemical processes.

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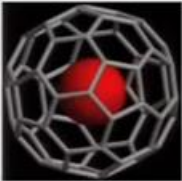
What would fit inside of a buckyball?

An <i>atom</i> of nitrogen	A <i>molecule</i> of hydrogen	A <i>molecule</i> of sulfuric acid
$d = -120$ pm	$d = -150$ pm	$d = -700$ pm
Definitely	Quite possibly	Not likely

Fullerenes with material inside are called **cage compounds, or endohedral compounds**

$M@C_{60}$, where M represents the atom inside of the cage

□ Examples: $N@C_{60}$ and $La@C_{82}$



Now, what would fit inside a buckyball or a C₆₀ molecule, so you see this is a C₆₀ molecule and if can be put something inside that has to be smaller in size. Then this diameter of around 1 nanometer or 0.7 to 1 nanometer depending on how you define the radius the distances, so either you take the Van Der Waals distances. But, you take the distance between the nucleus to the nucleus at the end of these diameter, so what would fit inside a buckyball.

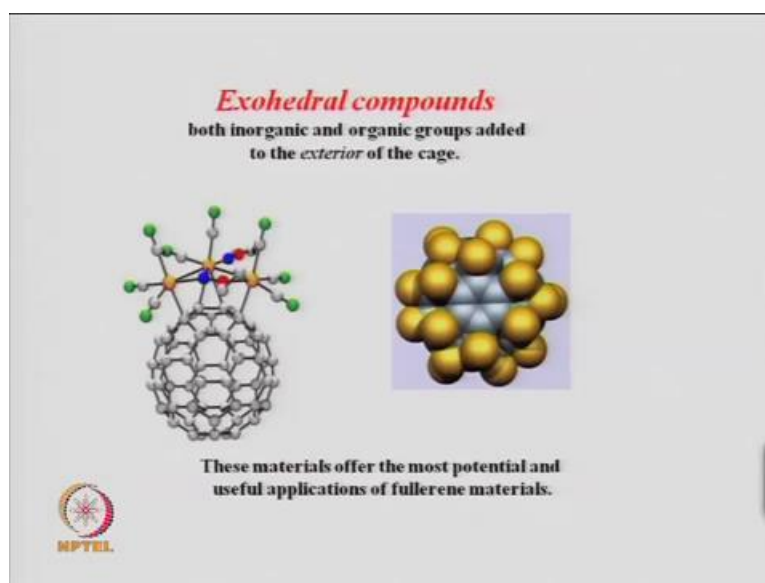
Now, of course it has to be much smaller than 7 Angstrom or much smaller than 0.7 nanometers and such materials where there is something inside the cage are called car and endohedral compounds. So, these are also called cage compounds or endohedral compounds so nitrogen can you put in an atom of nitrogen sure you can put an atom of nitrogen.

But, because what is the diameter of the nitrogen atom it is of the order of 1.2 Angstrom or 0.12 nanometers which is much smaller than 0.7 nanometers is the diameter of the fullerene. So, definitely you can put nitrogen can you put hydrogen, also we can put because it is of the order of 0.5 Angstroms or 0.15 nanometers. So, we can put a molecular of hydrogen in this cage, now can we put a larger molecule say a molecule of sulfuric acid.

So, molecule of sulfuric acid has a diameter of approximately 7 Angstroms which is like 0.7 nanometers and you know this whole thing is of the order of 0.71 nanometers. So, this will be very difficult or more or less impossible to put a molecule of sulfuric acid inside a C₆₀ cage, so not likely, so this is not likely to be the case. Now, such molecules like if you put nitrogen inside this C₆₀ molecule then these are called endohedral compounds and these endohedral compounds are given by this formula where M is whatever you have put inside the cage.

So, if it is nitrogen then you write N at C₆₀ that means N is inside C₆₀, if you put lanthanum a rare earth element and it is known that it goes in inside this cage. But, lanthanum goes into larger fullerenes C₈₂ which has a larger diameter than C₆₀ and lanthanum is a bigger atom than nitrogen. So, lanthanum goes in a C₈₂ kind of a fullerene, but not a C₆₀ fullerene whereas a small atom like nitrogen can go inside C₆₀. So, both of them are endohedral fullerenes because they are in lying inside the cage and the formal is m at C₆₀ where M is inside the cage.

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Now, can we have exohedral, this one was endohedral means inside can we have exohedral, yes we can have, so this is the C 60 molecule and you have got molecule on top of it outside, so this is called an exohedral compound. So, we can have endohedral compound and we can have exohedral compound in the exohedral compound you can have either inorganic groups. So, you may have a metal with some legants, so you can have say platinum or some nickel our gold some metal with some accompanying legants on the surface of the C 60 or 70 molecule and this is another protection.


So, the C 60 or C 70 molecule is inside and you have got these atoms outside so this kind of exohedral compounds have also been made in the laboratory and these gives you lot of applications. So, because you can modify the properties of C 60, C 70 using these molecules which are attached outside on the periphery of the surface of C 60 or C 70 or other fullerene type of compounds.

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Atoms bound to fullerenes outside the ball as salts: structure is $M_x^+C_{60}^{n-}$

M^+ = cation(exohedral)
 X = number to balance the charge on the fullerene

- Electrical resistivity is decreased by many order of magnitude by adding alkali metals as salts.
- As x increases, the resistivity decreases, reaching a minimum for the metallic $x=3$ stoichiometry.
- Further increase in metal stoichiometry, resistivity increases again until a insulator is produced for $x = 6$.
- The metallic $x=3$ state is superconducting, with a superconducting transition temperature of approximately -243°C (30 K) for $M=\text{Rb}$
- Recently, addition of organic compound (like CHBr_3) have shown to increase the conductivity



Now, you can also have atoms bond to fullerenes as salts, for example you can have a salt where you have a positive metal and a negative an ionic 60, so when you have a an ionic C 60 then it is called a fulleride. So, if it is neutral say C 60 molecule then we call it a fullerene when you have a ionic C 60 then we call it a fulleride. So, this metal cation is like a typical cation that you studying chemistry cations are form from elements which donate electrons easily.

So, you have these alkali metals alkaline earth metals like lithium sodium potassium are alkaline metals and you have elements like calcium barium strontium which are alkaline earth materials they like to donate electrons these elements. So, when they donate electrons the electrons go to the C 60 and C 60 can accept those electrons because there are lots of orbitals in C 60 pi orbitals and, you can transfer electrons and then C 60 becomes negatively charged.

So, depending on how many electrons you donate this charge will change from 1 minus 2 minus 2 N minus, so you have a cation which is outside and you have x , the number to balance the charge over here. Now, what happens when you add these electrons when you add these electrons then the electrical conductivity or the resistivity changes because you are now adding electrons to this fullerene moiety. So, which becomes a fulleride and the electrical resistivity decreases by several orders of magnitude, in the case when you are adding alkali metal ions.

So, as X increases you reach a minimum in the metallic resistivity for x equal to 3, so the typical formula that you can generate in these fullerides or something like M_3C_{60} . So, that means three moles of potassium or rubidium or cesium per 1 mole of C_{60} as the maximum it goes, so in that case you will have 3 electrons transfer to C_{60} . So, the charge here will become 3 minus and actually several of these materials like K_3C_{60} or rubidium $3C_{60}$ becomes superconducting at low temperature.

So, a 30 Kelvin which is minus 243 degree Celsius for the metal being rubidium which is an alkali metal down the group this compound rubidium $3C_{60}$ becomes a superconductor at low temperatures of 30 Kelvin. So, that is minus 243 degree centigrade and we have the superconducting properties which mean 0 resistance perfect diamagnetism. But, will show levitation and other properties that any superconductor shows, so in C_{60} and fullerene kind of materials also you can see super conductivity.

Now, you can also recently it has been shown that an organic compound like chloroform it is like bromo form it is called bromo form like you have chloroform for $CSCL_3$ you have bromo form. So, this can be added to C_{60} to increase the conductivity or lower the resistivity, so if you have a metal ions like potassium rubidium etcetera. Also, you can lower the resistivity transferring electrons, similarly it has been recently shown that organic compounds can also be added to C_{60} to show increase in conductivity or decrease in resistivity.

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Combination of endo- and exohedral compounds

$Gd@C_{82}(OH)_n$

The gadolinium (Gd) is inside the cage and the outside is covered with hydroxyl groups.

$Gd@C_{82}(OH)_n$ is a possible enhancement material for magnetic resonance imaging, MRI.

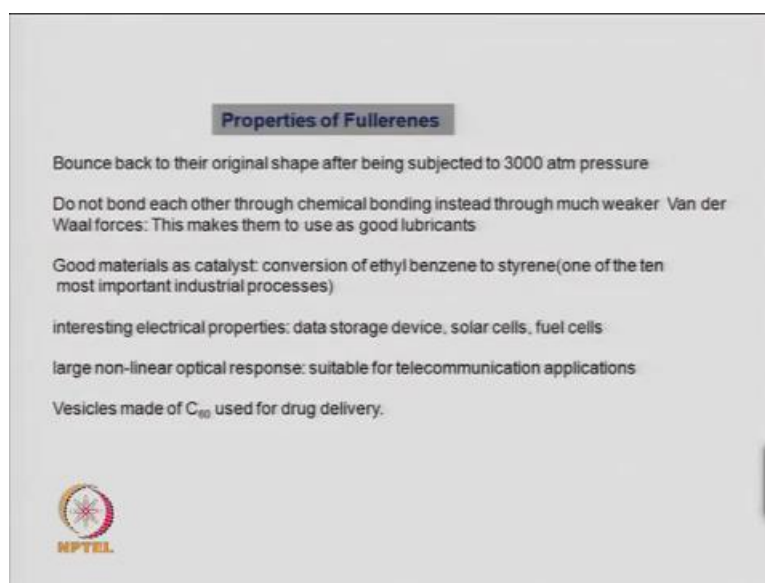
$Gd@C_{82}(OH)_{22}$: Anticancer therapy (*Biomaterials* 30(2009) 3934–3945)



Now, both combination of endo and exohedral compounds that means you have gadolinium Gd it is a lanthanide; that means it belongs to the lanthanide series and gadolinium is inside the C₈₂ moiety. So, this is the formula for an endohedral compound, so gadolinium is inside the cage of C₈₂ and outside C₈₂ you have got hydroxyl groups. So, this is the exohedral part and this is the endohedral part, so you can have a combination of endo and exohedral compounds and this is a classic case.

So, this is what I just mentioned that gadolinium is inside the cage and outside is covered with hydroxyl groups and it is possible material very good material for magnetic resonance amazing that is what their research has shown. So, there is lot of a potential in this material it is also been shown that this material can be used for anti cancer therapy which is very important. So, this kind of material based on gadolinium can be made as a endohedral compound and can also be made as a endo and exohedral compound.

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Now, there are several other properties fullerenes, now fullerenes if you apply pressure so you apply pressure from outside external pressure very high pressure like three thousand atmospheres. So, you we are at one atmosphere, now imagine 3000 times that pressure is falling on an object, so the high pressure the fullerenes get the deform. but as soon as you remove the pressure the fullerenes get back to their original shape.

So, this is a very interesting property of fullerene that after being subjected to very high pressure like 3000 atmospheres, if you release the pressure the fullerene molecule again

comes back to its normal or original shape. So, then the fullerenes do not bond to each other through chemical bonding, so there if you take fullerenes they bond to each other through weak Van Der Waal forces. Now, like in graphite where we have got layers of rings of carbon atoms which do not bond to each other through covalent bonds, but through Van Der Waal bonds.

Hence, graphite is a good lubricant similarly fullerenes also do not bond through covalent bonds to each other and, hence they are also used as good lubricants. But, there are catalytic properties of fullerenes which has been shown. So, for example a very important reaction industrial process which is one of the 10 most important industrial processes in the world is to convert ethyl benzene to styrene.

So, C₆₀ has been shown the fullerenes have been shown to be good catalyst in this conversion of ethyl benzene into styrene there are other properties like electrical conductivity data which can be used in data storage devices in solar cells. Now, in fuel cells these fullerenes also shows large non linear optical response, so non linear optical response means that if you have a frequency ω . Then you can generate a frequency 2ω 3ω that is non linear kind of behavior is observed when you use fullerene type of materials and this is important for telecommunications.

Now, there have been many applications as drugs and also as vesicles for drug delivery, so C₆₀ or other fullerenes and their derivatives have been used as drugs. Now, their C₆₀ has been used to make vesicles; that means channels through which drugs can be delivered inside the body, so there are lots of properties are fullerenes.

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Commercial and Biological applications

Sunscreens	due to photophysical properties
Antibacterials	due to redox and general chemical reactivity
Superconducting materials	due to physical properties

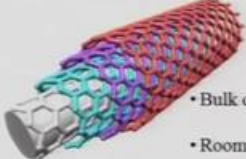


So, these are some commercial and biology applications like sunscreens which is due to the photo physical properties of fullerenes where used as a antibacterial due to their chemical reactivity and red ox properties. Now, superconducting properties like in the alkaline, alkali metal doped fuller rides like K_3C_{60} or rubidium $3C_{60}$, which shows superconducting properties. So, you can have photo physical properties anti bacterial and supper conducting properties in these fullerenes or the derivatives of fullerenes and fuller rides.


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Carbon Nanotube

- Cylindrical fullerene discovered in 1991 (S. Iijima)
- Internal cylinder diameter of 1 to 50 nm
- Length of about 100 nm up to several micrometers and longer
- They can be single walled, called SWNTs, or made up of multiple layers, called MWNTs.



- Bulk or thin films of C_{60} semi-conducting in nature
- Room temperature resistivity of 10^8Wcm

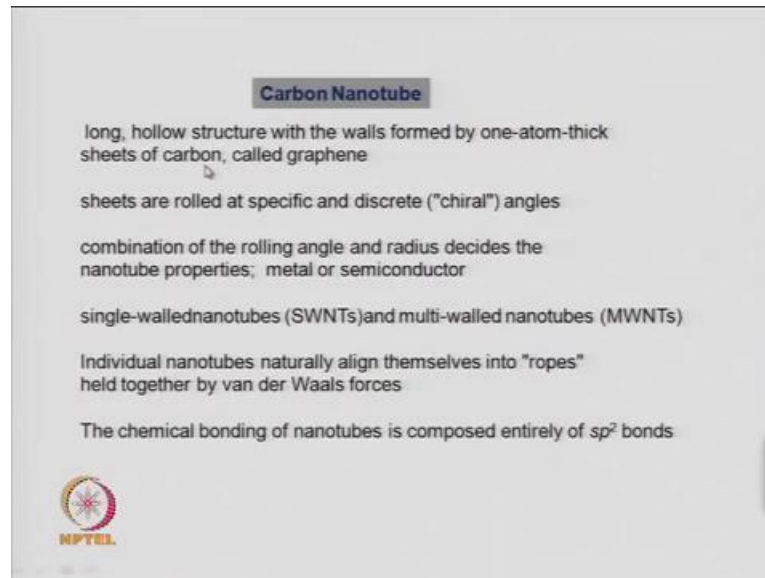


Now, in fullerenes or are 3 a larger congeners like C 82, etcetera, you had a kind of a spherical molecule like a spherical cluster. But if we go towards a cylindrical object then we get what are called carbon nano tubes, so a cylindrical fullerene was discovered in 1991 or was exactly understood in 1991 by Lijima in electron microscopic studies. So, this nanostructure has diameter in the nanometer range like 1 nanometer or so but the lengths can be very large they can be hundred nanometers or they can even be much longer.

So, the internal diameter can be varied from 1 to 15 nanometers and length can be much larger up till several microns, so several thousand of nanometers you can extend and these carbon nano tubes also called C N Ts have tremendous applications. So, they can be made of a single layer of graphene sheet that means only 1 layer of carbon is present and roll together to form to a tube or there are multiple layers. So, if it is made up of only one layer then it is call single wall nano tube if it is made up of multiple layers. Then it is called multi walled nano tube as you see here there are 1, 2, 3 and 4 layers, so this is a 4 layer multi wall nano tube of course all made up of carbon.

But, you can also make single wall nano tubes double wall nano tubes etcetera, they have not lots and lots of properties very interesting properties many of these are semiconducting in nature, but you can also make conducting nano tubes. So, a typical room temperature resistivity is given here it is around 108 ohms, it should be ohm centimeter which is the resistivity of simple carbon nano tubes at room temperature.

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Carbon Nanotube

long, hollow structure with the walls formed by one-atom-thick sheets of carbon, called graphene


sheets are rolled at specific and discrete ("chiral") angles

combination of the rolling angle and radius decides the nanotube properties; metal or semiconductor

single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs)

Individual nanotubes naturally align themselves into "ropes" held together by van der Waals forces

The chemical bonding of nanotubes is composed entirely of sp^2 bonds

 MPTEL

Now, these carbon nano tubes are made of 1 atom thick sheet of carbon, so if you take graphite which has got layers of carbon hexagonal orientated carbons. So, you have got rings of carbon and, if you have one layer of carbon only then it is called graphene. But, if you have several layers of carbon one below the other which is connected through weak Van Der Waal forces then that is graphite. So, graphene is only one layer of graphite, now if you take that one layer of graphite which is called graphene and you roll it up in a cylinder.

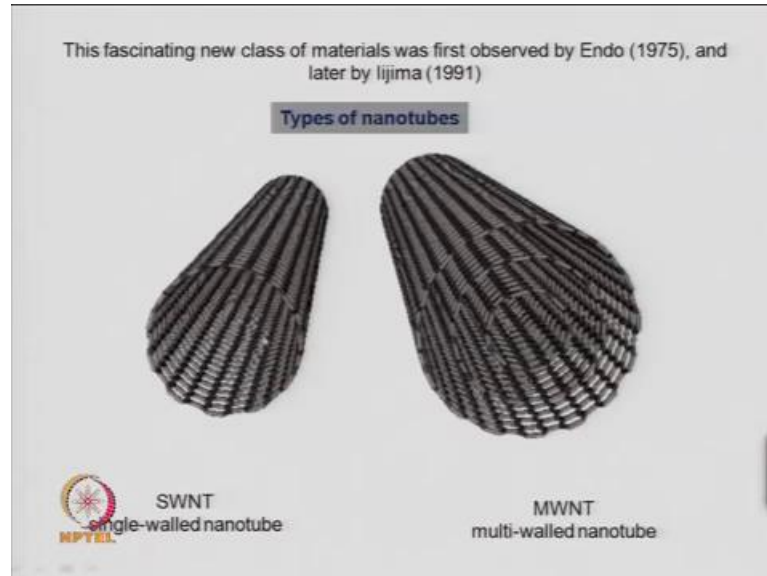
Then you get the carbon nano tube and if you have only one layer then you get single wall carbon nano tube and if you have several layers you will have multi wall carbon nano tube. Now, these sheets if you are rolling the graphene sheet this how are you rolling the graphene sheet will change the nature of the tube, which you will get ultimately.

So, the sheets which are rolled at specific and discrete angles will give rise to different types of nano tubes some of them will become chiral the others will be called zigzag or arm chair as we will discuss. So, you can get single wall nano tube multi wall nano tubes chiral nano tubes and several other kind of nano tubes and individual nano tubes align themselves and are weakly held by Van Der Waal forces.

So, if you have a several nano tubes then you get a bundle of nano tubes and these nano tubes interact with each other through weak van der Waal forces and they have kind of form

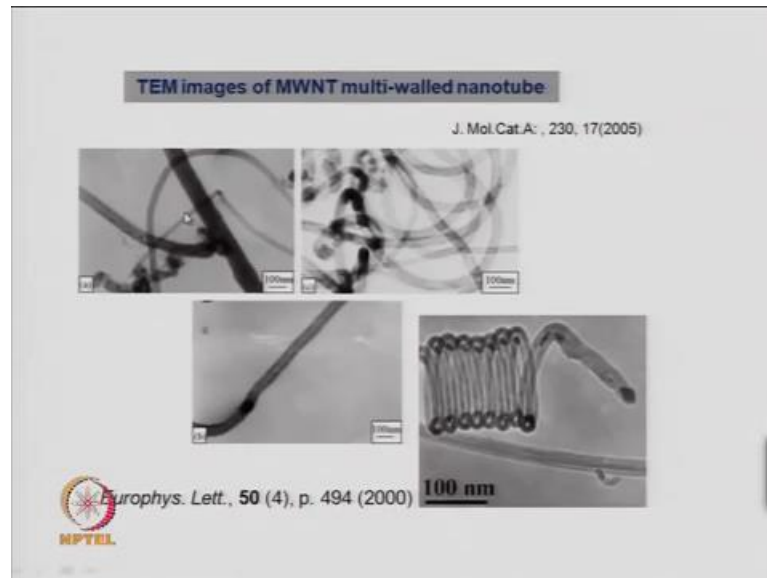
ropes in one direction. Now, the chemical bonding of nano tubes inside the carbons are all S P 2 hybridized carbons, so that is true for all these carbons in these nano tubes.

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So, to have a look at these nano tubes this is a single wall nano tubes and this diameter is of the order of 1 nanometer and this is a multi wall nano tubes. So, you have one nano tube here and then this is the second nano tube and then you have a third nano tube, so this is the multi wall nano tube it was observer first by endo in 1975. But, was really highlighted by Lijima in 1991 and the world came to know about carbon nano tubes through Lijima work in 1991.

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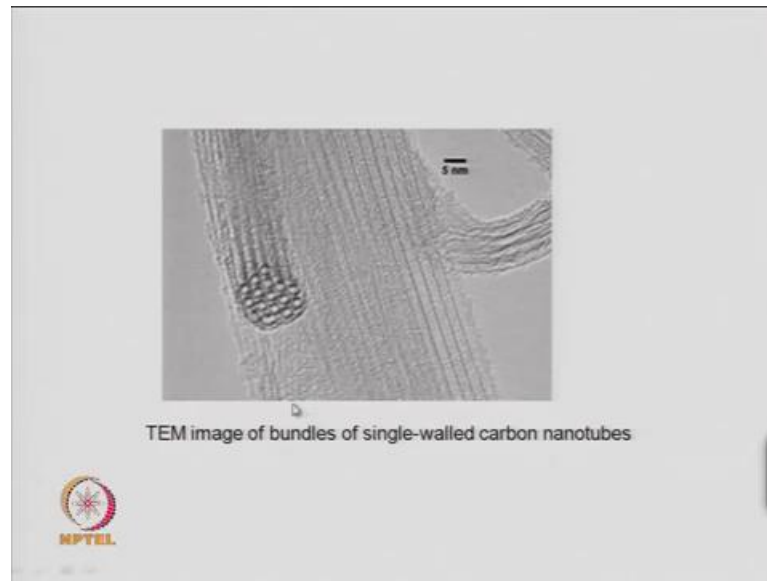


Now, these are some of the real pictures the transmission electron micrographs of multi walled nano tubes and you can see it some of them are broad and wide and this scale is of 100 nanometers. So, this diameter is this is a very thick nano tube these are thin nano tube, so this may be of the order of may be 5 or 10 carbon layers are there in this nano tubes. So, this maybe a 10 nanometer or 5 nanometer tube this is may be a 15 nanometer tube and none of them are single walled nano tube because single walled nano tube, the diameter will be of the order of 1 nanometer in general.

Now, so nano tubes can be straight, they can be spiral and this, they can be of the type of springs they depend how you grow these nano tubes. Then you can control then you need to know how to control the shapes of these nano tube, how to get them straight, how to get there in the spring fashion for certain applications.

So, that depends on the growth conditions how you are doing the discharge or if you are doing using a laser how you are creating these nano tubes. Now, are you using a metal catalyst many times metal catalysts, are use to grow carbon nano tube, so all these things matter to ultimately control the shape of these nano tubes.

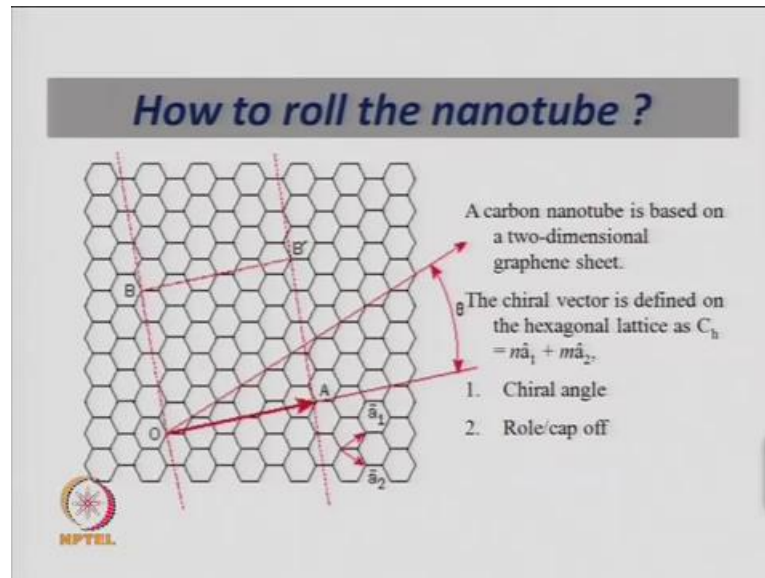
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Now, here you can see a transmission electron micro graph of bundles of single walled carbon nano tubes, so these are a single walled nano tubes. But, there are many such nano tubes, so this is one nano tubes, second nano tubes, is the third nano tube like that there are several nano tubes which are forming a bundle.

So, this ability of these nano tubes to come together is through Van Der Waal forces and these are again a picture of nano tubes this is curd nano tubes and you can see this scale is of five nanometers. So, this diameter is of the order of 1 to 1.5 nanometers typically for single walled nano tubes, so these are all single walled carbon nano tubes.

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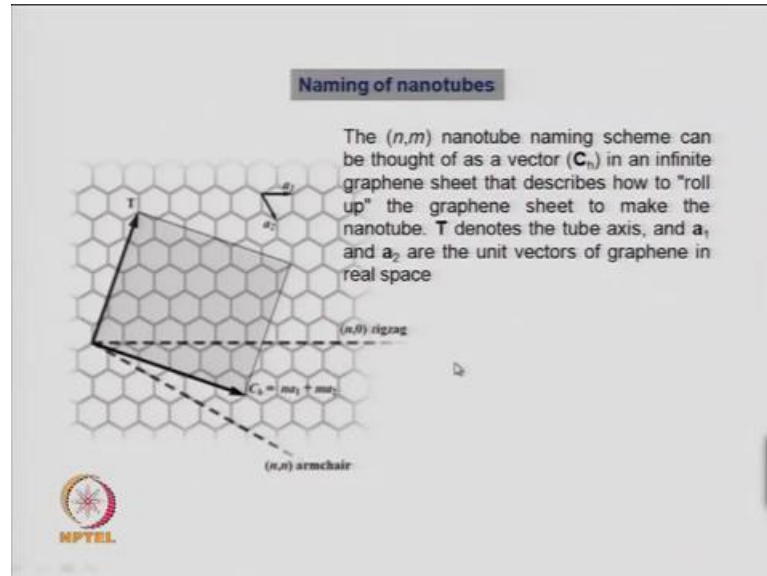
Now, how to roll the nano tube as we were discussing if you have one layer of graphite which is called graphene, so this is a graphene sheet. So, you have all six membered carbons forming the sheet and how do you roll this sheet because if you roll the sheet in one way you get one kind of nano tube. But, if you roll it in another, you get another type of nano tube and other type of nano to you so there are certain definitions, so in this hexagonal lattice you define what is called a chiral vector. So, in this 2 dimensional lattice you define a chiral vector C_n which is dependent on to vectors a_1 and a_2 , so these are the two vectors a_1 and a_2 . So, in any hexagonal lattice you can define these two vectors and what are the numbers or the coefficients of these 2 vectors.

So, if you take a very large a_1 and a very small a_2 , that means n is very large and m is very small you will get one type of ruling. But, if you take n and m both same then it will not result in a chiral it will result in something else if you take n some number and m you make it 0 then you get another kind of nano tube again it will not be chiral. So, the chirality of the tube is dependent on this formula and from this formula you can define the chiral angle θ .

So, these vectors and their coefficients are important the efficient are very important and also what is how do you end the nano tube toward, if you want to close the nano tube at the end and not leave it open then what how do you cap it. So, these are certain things which give flexibility to the various kinds of nano tubes that you can generate using a

simple graphene sheet. But, just based on the angle the chiral angle at which you are rotating this plainer structure or rolling the plainer structure into a cylindrical structure.

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So, that is what I said if you take a vector a one and a two such that the coefficient of a 1 is n and a 2 is 0 that means the vector that you are taking is in this direction because a 2 is 0 and only a 1 exists. So, you are looking at this vector and that means this is the n 0 vector, so this is called the zigzag nano tube the nano tube that you will get if n has a value and m is 0. Then if you roll all the graphene sheet in that manner then you ultimately end up in a nano tube who is a direction.

So, this is, this will be the direction of the nano tube and it is called as zigzag nano tube, so the coefficient m is 0. However, you can choose any other coefficient n and m if you choose n equal to m that means n and m both are same. Then your direction will be in this manner because you have the same magnitude the coefficient of this vector and coefficient of this vector both are same.

So, you will have a resultant like this and that is what it is being shown this is parallel to that the resultant which you get here and you will get the n, n carbon nano tube which is called commonly as the armchair nano tube. So, the zigzag nano tube and the armchair nano tube are two special cases all other nano tube what if you take any other value of n and m you will get chiral nano tubes. But, n 0 and n, n that means the same value for n and m will give you zigzag and arm chair nano tubes.

So, this is the n, m naming scheme it tells you about the vector which you have chosen these coefficients, tell you about that and it will tell you about the chirality of the nano tube which will result. So, if you roll the tube in such a manner that the coefficients which you have chosen are n and m , and this is very important in finding out the property because the properties of the nano tube will depend on this factor.

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The integers n and m denote the number of unit vectors along two directions in the honeycomb crystal lattice of graphene

If $m = 0$, the nanotubes are called zigzag nanotubes


if $n = m$, the nanotubes are called armchair nanotubes

Otherwise, they are called chiral

diameter of an ideal nanotube can be calculated from its (n, m) indices as follows

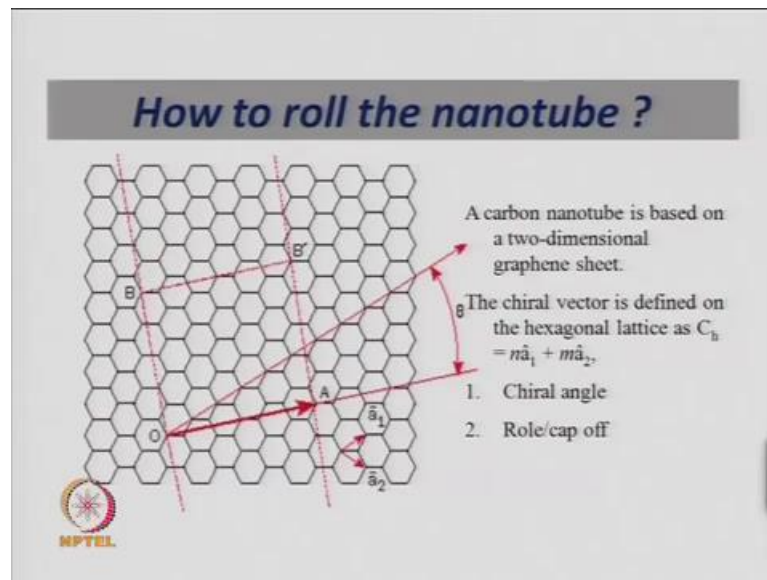
$$d = a/\pi \sqrt{n^2 + nm + m^2}$$

where $a = 0.246 \text{ nm}$.



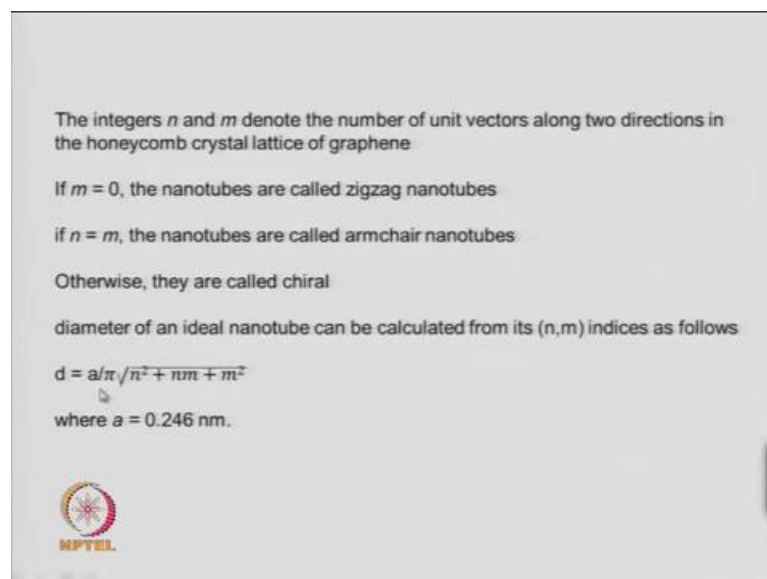
So, the integers n and m as I discussed tell you about the unit vectors along 2 directions in the plainer graphene layer or the carbon layer and if m equal to 0 the nano tubes are zigzag. But, if n and m are same then they are called armchair any other value of n and m they are called chiral nano tubes. So, the diameter of an ideal nano tube can be calculated using n, m and a , where a is this value 0.246 nanometer and actually it comes from this distances.

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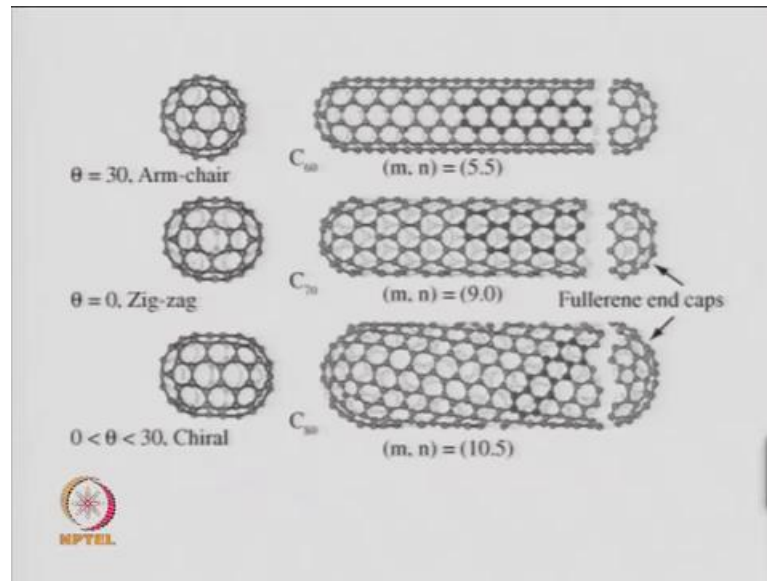
So, it is the distance between this carbon and this carbon the carbon which are 1 and 3 positions, if you measure this distance that is equal to 2.46 Angstrom or 0.246 nanometers.

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So, that is the value of a , if you use that value and you know what is n and what is m you can calculate the diameter of any nano tube.

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Now, when you look at these nano tubes, which result as you roll them in a particular fashion, for example when m is equal to n then you get the armchair type of nano tube and the angle which you have is 30 degrees. So, the chiral angle of course this here 5, 5 means m is 5 and n is 5 and it gives you a nano tube like that and at the end if you want to close it this part we look exactly as half of the C_{60} molecule. So, if you have a arm chair nano tube the cap being part will be C_{60} molecule say exactly like the C_{60} molecule.

However, if you have a zigzag nano tube a zigzag nano tube has a theta value of 0 and if you come to the end of the nano tube you cannot close it with the C_{60} molecule you have to close it with the C_{70} molecule and that is what is shown here. So, you take half of the C_{70} that will exactly fit at this part, so what how to cap the end of a nano tube is also dependent on what kind of nano tube it is nano tube. But, it is if it is armchair nano tube only half of C_{60} can cap it if it is a zigzag nano tube then half of a C_{70} molecule can cap it if it is any other kind.

So, for example this is chiral molecule, it is not zigzag it is not armchair and the angle theta is neither 0 nor 30, it is in between 0 and 30 then that chiral nano tube will have an end which is neither C_{60} nor C_{70} . But, is a half of C_{84} molecule, so a half of C_{84} molecule will cap it that means for different types of a nano tubes you need different types of caps.


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properties of nanotubes change significantly with the (n,m) values

electrical conductivity can show metallic or semiconducting behavior

application of SWNTs

intermolecular field-effect transistors (FET)
intermolecular logic gate using SWCNT FETs was made in 2001
(Martel, R. *et al.* "Ambipolar Electrical Transport in Semiconducting Single-Wall Carbon Nanotubes". *Physical Review Letters* **87** ,2, 256805, 2001




So, the properties of nano tubes change significantly with the n and m values and one like electrical conductivity is a very important property. So, it shows drastic difference you can have metallic nano tubes, semiconducting nano tubes and these properties have been used for applications. Now, one of the first applications was a molecular field effect transistor and this was made in 2001 by I B M who showed that using these carbon nano tubes you can make a molecular field effect transistors. So, which is a great invention, because you are lowering the size of the transistor from a normal transistor of one molecule is being used as a transistor and this was done in 2001.

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Mechanical properties of Engineering fibres

Fiber Material	Specific Density	E (TPa)	Strength (GPa)	Strain at Break (%)
Carbon Nanotube	1.3 - 2	1	10 - 60	10
HS Steel	7.8	0.2	4.1	< 10
Carbon Fiber - PAN	1.7 - 2	0.2 - 0.6	1.7 - 5	0.3 - 2.4
Carbon Fiber - Pitch	2 - 2.2	0.4 - 0.96	2.2 - 3.3	0.27 - 0.6
E/S - glass	2.5	0.07 / 0.08	2.4 / 4.5	4.8
Keylar* 49	1.4	0.13	3.6 - 4.1	2.8



So, there are several other applications of these nano tubes, look at the mechanical properties of these nano tubes. So, carbon nano tube compared to stainless steel, carbon fiber glass and keylar, keylar you know is a polymer and it is used in bullet proof vests if you compare even with keylar. So, most of these numbers you see for carbon nano tube are much higher than these numbers, so look at the strength the strength is 10 to 60 for carbon nano tube where are none of these are of the order of 10.

But they are all less than 5, whether it is steel, whether it is carbon fiber or whether it is this polymer which is used for bulletproof vests. So, today we have discussed several of the features of carbon nano tubes and fullerenes and we will continue our study of carbon based nano structures in the subsequent lectures.

Thank you very much.