Introduction to Materials Science and Engineering
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Lecture – 29
Carbon nanotubes (CNT)

We are discussing carbon structures and we have already discussed by now a structure of grapheme, diamond and graphite.

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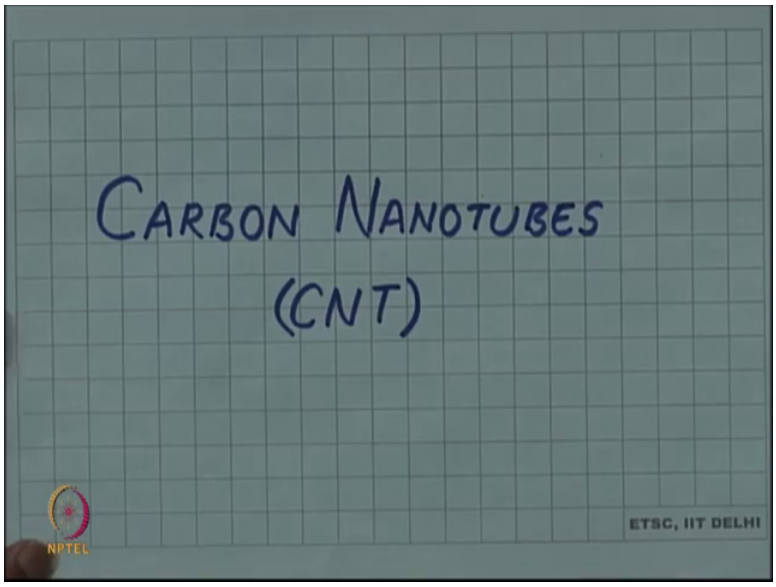

Today, we will discuss our topic is another carbon structure which is very important and is a recently grown much importance in research and development is the carbon nanotube. So, carbon nanotube also sometimes abbreviated as C N T.

So, what is carbon nanotube? The best description of carbon nanotube and a simple description; Comes from relating it to the structure of grapheme, which we are already familiar.

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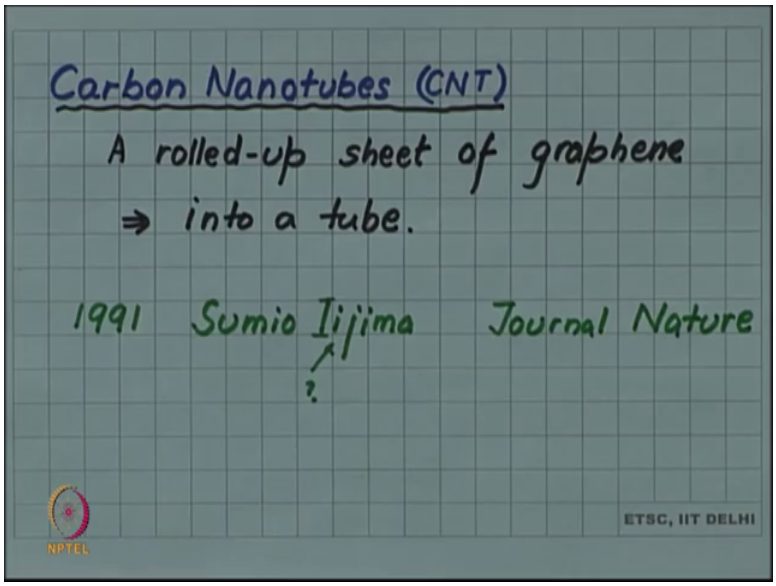

So we have seen that graphene is a hexagonal structure a single sheet two dimensional hexagonal sheet of carbon atoms, just like one layer of graphite. So, carbon nanotube is nothing, but a rolled up it can be considered as a rolled up sheet of grapheme. A tube made by into a tube graphene a rolled up sheet into a tube. This is structure was discovered in1991 by Japanese scientists electron microscopist Sumio Iijima probably only one eye.

So, Sumio Iijima in Japan discovered it in 1991, there is a lot of discussion in literature whether this was the first real first observation of nanotubes or some people have seen it before that, but the fact remains that only after is 1991 paper in a journal called nature a very famous journal; the topic actually caught the attention of the world and a lot of research and development established itself as a field of in its own right. So, that credit does go to Iijima.

So, let us try to relate it to the graphene sheet you will do that soon. So, let us look at some classification of carbon nanotube. One particularly scheme of classification is the so called single walled nanotube or multi walled nanotube.

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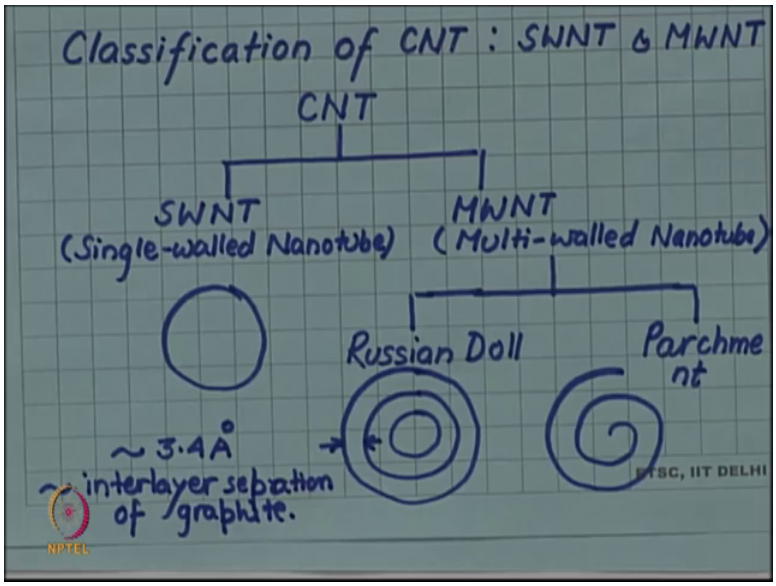

So, let us say CNT we are classifying it into SWNT or single walled single walled nanotube or MWNT which is multi walled nanotube. Name itself is self explanatory in a single walled nanotube a single graphene sheet is rolled into a tube form.

So, you have a single tube and that is called a single walled nanotube. Multi walled nanotube has several walls and again can be classified into two types depending on its structure: one is called interestingly the Russian doll structure and another Parchment structure. The Russian doll structure is several concentrics so instead of just one graphene sheet rolled into a tube you can have several graphene sheet multi walled.

So, several concentric tubes if they are there then this is the Russian doll structure of a multi walled nanotube. In a parchment structure actually there is a single graphene sheet, but that rolls itself like a parchment into a multi walled tube. The distance the inter tube distance in the case of multi walled tube is about 3.4 angstrom which is same as the inter layer separation in graphite. You can think of it is a curved graphite instead of flat graphite. Another classification so that was one classification scheme where we got the single walled and multi walled nanotube.

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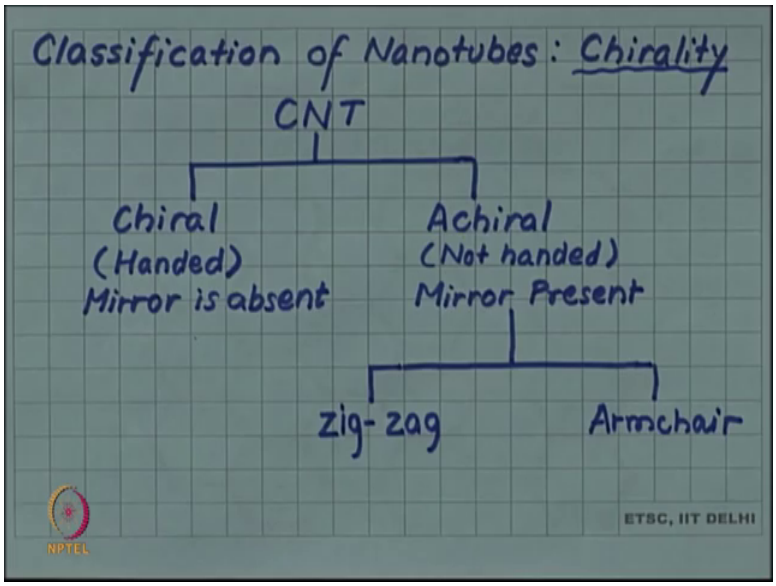

Another classification is based on what is called chirality? So, based on chirality we again classify nanotubes as either chiral or achiral. Well, chiral is just another word for handed. So, when we say chiral we mean that it has a handedness. So, it will come in two varieties a right handed and a left handed version whereas, achiral will not be handed it will not have these two varieties.

So, for example, for example, my hand my a we know that our hands are left handed and right handed I have a left hand and a right hand and these cannot be superimposed although they can be imagined to be mirror image of each other so, but my single hand single hand relax any mirror symmetry. So, that's why when I reflect it into a mirror a different handedness hand is produced

So, for chiral or handed structures it is important that mirror plane is absent mirror is absent only when mirror is absent you can have left handed and right handed version of an object and that is called achiral object whereas, achiral is not handed in this case mirror will be present think of a sphere you don t think of a left handed is sphere or a right handed is sphere and this fact is it related to the fact that is fear has several mirrors a tube doesn't have a left handed or right handed version because tube has mirror. So, any object which will have mirror will not have left handed or right handed version whereas, object where mirror is absent it is possible to have both left handed and right handed.

So, in science or in crystallography if the word chiral and achiral is used for that so, when we say C N T the carbon nanotube is chiral we say that that nanotube will not have any mirror plane whereas, achiral nanotube will have mirror plane present. So, it is more symmetric achiral is more symmetric. Again in achiral two different kinds of tubes have been identified so one is called the zigzag tube and another is called armchair. So, we will look at this soon what is the meaning of zigzag and armchair. So, let us try to make let us try to make a tube out of a graphene sheet.

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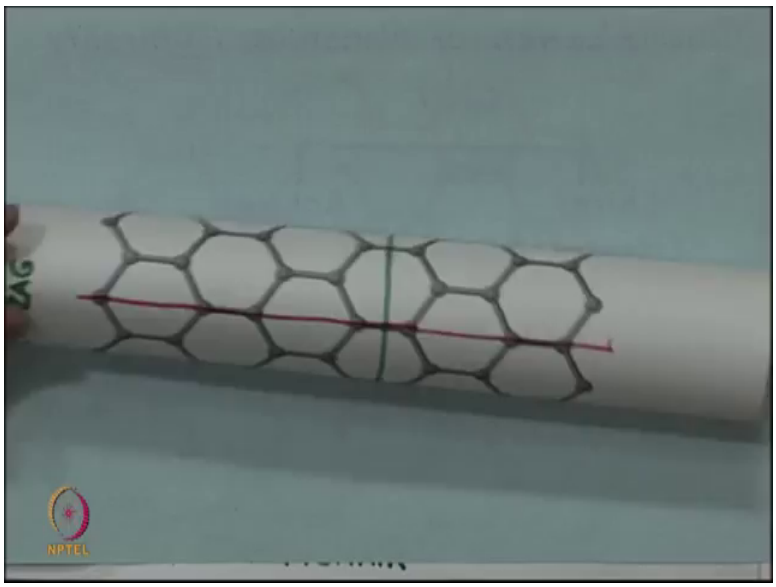

So this is a model of a graphene sheet, just the hexagonal rings are drawn and if I fold it into a tube I will get a nanotube to do this and I want to make a zigzag tube and show it to you.

So, let me try to fold this. So, all I am trying to do is to bring the two edges together such that they meet coherently without leaving any gaps or so. So if I can do that then I have a nice carbon nanotube in this tube if you see; so, let me first try to paste this edge. So, Srikanth can I take your help. So, Srikanth is at a in my course and he will help me to paste it.

So, cello tape is very important in carbon structure as you know from discovery of graphene which was cello tape played an important role, now it is playing an important role in making my model yeah. So, thank you Srikanth he has pasting the tape and I have now a tube form this tube is known as a zigzag tube.

Why it will case is known as zigzag tube? That if you look at the free edge of the tube then you see a zigzag structure. The top free edge it is zigzag structure. Of course, in real nanotubes the there will be a cap a carbon cap of fullerene on the top and bottom to close the ends. So, the nanotubes are closed structure instead of open tubes, but it still the fact remains that there is a zigzag structure on the top and based on this a name zigzag is given, but this is not the only way to fold the tube.

So, another tube I will fold in another structure known as the armchair structure. So, this is again the same same hexagonal tiling with carbon structure shown. So, again I am starting with graphene, but now I want to fold it differently to make it an armchair tube and one thing. So, please see this that in the yeah maybe I can show it here in the zigzag tube along the tube at one set of bonds one set of bonds is parallel to the tube axis and you can see that if you draw a plane passing through these bonds that will act like a mirror plane of the tube.

So, a mirror plane is present in this tube also. So, if I can draw that mirror plane for you maybe I can use a red pen and I am trying to draw a line representing the mirror plane. So, you can see that if you imagine a plane passing through this line and the tube axis the tube the two parts of the tube are mirror symmetric to each other also there is another mirror plane and that is perpendicular to the tube axis.

So, if I draw another line let me use another color pen now. So, perpendicular to the tube axis this plane which will cut the tube a cylindrical tube in a circle. So, this plane also you can see that the top and bottom atom are mirror images of each other and all the atoms will reflect into each other. So, there is it this zigzag tube has two mirrors and; obviously, this will be achiral the zigzag tube cannot be a left handed zigzag tube or a right handed zigzag tube it will just be a zigzag tube it is achiral.

So, now let me try to make armchair for you. So, the same tube this is what is interesting about nanotube structure that although graphene is the same single structure and by folding the graphene or rolling up the graphene we are making the nanotube, but depending on which way we fold we get different structures of the nanotube and these different structures also have different properties.

So, now I am trying to make an armchair for you I will again need help of Srikanth; yeah see I am trying to match the atoms if I do not match the atom then something like this

something like this will come yeah something like this will come. So, your tube is not good or something like this if it happens. So, what I am doing when trying to make the tube is to bring and join the atoms coherently such that there is no such boundary and the tube is continuous along that line.

So, we have synthesized another nanotube now, this is the armchair nanotube.

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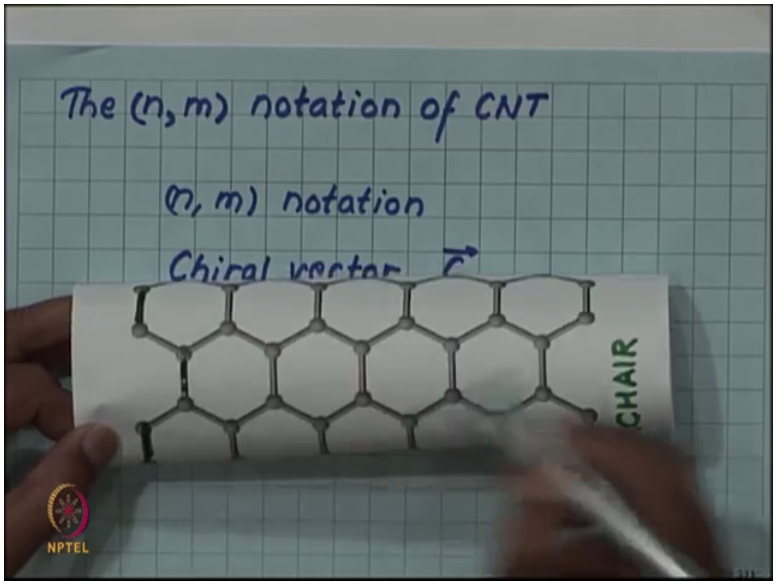

Why it is called armchair? Again if you see; If you see that top edge of the tube now, the last time if you remember in the zigzag tube we saw a zigzag structure, but now you are seeing an interesting structure that you there is a horizontal bond, then there is an inclined bond, another horizontal, then oppositely inclined bond, then horizontal bond. So, it is not going to zigzag it is doing something else and this is what has been imagined by somebody as an armchair. So, these can be thought of these can be thought of as arms of the chair and this is the seat of the chair and somebody can sit comfortably if I can show you here yeah. So, you can see here like this. So, somebody can be sitting comfortably there with his hands on the two side so that's why the name armchair has been given.

So, we will look at these two tubes again in a slightly different and more mathematical way.

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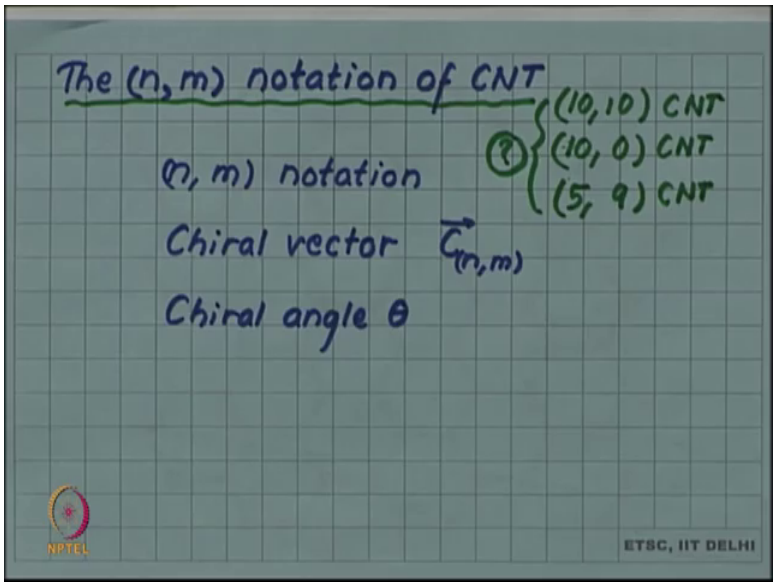

And for that new notation the n, m notation of carbon nanotube is required. So, let us look at the n, m notation; because in literature you will find a 10, 10 carbon nanotube 10, 10 tube 10, 10 C N T or a 10 , 0 C N T or 5, 9 C N T the question is what is the meaning of this notation? So, this is what we want to explain. So, the n, m notation we will explain we will also define two important concepts which are related the chiral vector of the tube and the chiral angle. So, to do this we again begin with our graphene sheet and now I will try to show carefully what I was a telling you that what I do when I was trying to match the atoms along the tube axis.

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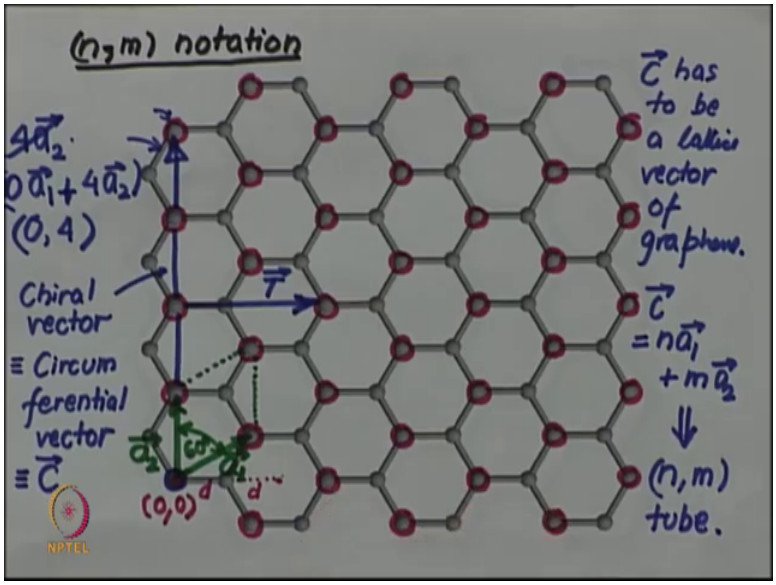

So, let us look at this graphene sheet. We when discussing the graphene structure, we have already talked about that in the graphene structure it is the alternate atoms. So, if I take this atom as in my origin, then the near neighbor is not equivalent. Let me right a brighter color maybe.

So, if this is my origin, then the near neighbor is not lattice equivalent, because it has a different kind of neighborhood you can see this if I take this as my origin o, o, then the origin atom at the origin has a neighbor on its right at a distance equal to the carbon carbon bond distance d, but this atom at the same distance if I travel d we come into the center of the hexagon and there is no atom at the center of the hexagon. So, this we had explained while discussing graphene also. So, I am repeating this here. So, alternate and nearby atoms near neighbors are not equivalent in the lattice sense. it is the next near neighbor which are equivalent.

So, I leave one set of atom and try to mark all the equivalent crystallographically equivalent or lattice equivalent atoms on the sheet. So then I keep taking the alternate ones leaving out the near neighbors. So, all these carbon atoms which I am now mocking are equivalent to each other translational equivalent to each other and equivalent to the atom marked as the origin. And the ones I am leaving out are not equivalent to this set, because there is no lattice translation in the graphene sheet which will bring the marked atom to the unmarked one. So, essentially these a red marked atoms are now forming the lattice of the grapheme. In this lattice we need to find two vectors which are the basis vectors and that is selected.

So, I i for basis vector I have to go from the origin to the nearby equivalent atoms. So, I cannot go to the nearest atom, I go to the next nearest atom and I mark this as one of my basis vectors. Let me call that vector a 1 and then another vector let me call that vector a 2. So, these two green vectors which are at an angle 60 degree to each other define a primitive unit cell of graphene. So, if I complete this; this rhombus will be a two dimensional primitive unit cell of graphene.

So, these two vectors are used to then define all vectors, all lattice vectors in this graphene sheet. We are trying in this exercise we are trying to explain the n, m notation. Now you can see that when I was trying to roll a sheet I was trying to bring the atoms together such that there is a coherence between them and there is no defect along the axis

of the tube. So, the atom should match in terms of lattice that essentially means that I can fold the graphene sheet in a way such that any of the lattice equivalent atom is identified with the origin.

So, if I fold in such a way that a lattice equivalent atom any of these lattice equivalent atom if it overlaps the origin I get a carbon nanotube. So, this brings us to the fact that if I take any vector in the graphene sheet. So, let me take; let me take this particular vector this blue vector. So, this end atom will be identified with the origin. So, that is how I will rap. So, I will rap such that I bring the head of this vector to its tail at the origin.

So, I will get a tube. So, you can see the vector which I have drawn here the blue vector will become the circumference of the rolled up nanotube such vector are known as the chiral vector of the tube; chiral vector. A more transparent name could have been so, let us use that is a circumferential vector, because this is the vector which will become circumference of the tube; obviously, a vector normal to the two circumferential vector for example, a vector like this let me call that t we will form the axis of the tube.

So, this tube will be folded like this; circumferential vector becomes the circumference and the vector along the; and the vector perpendicular to the chiral vector. So, the chiral vector becomes the circumference of the tube and vector perpendicular the chiral vector becomes the axis of the tube. So, that's the definition of the chiral vector and a chiral vector will always be a lattice vector in the graphene sheet. Otherwise you will have defect along the line where you will join as I had shown you in my previous example in trying to when I was folding the nanotube.

So, chiral vector has to be; so chiral vector let us call this c and this chiral vector c has to be a lattice vector of graphene which means it can be expressed as combination linear combination of the two basis vectors a 1and a 2 in particular you can see the chiral vector which I have drawn here this particular chiral vector is 4 a 2 and zero times a one sorry I should write first the a one. So, zero a one plus 4 a 2.

So, I can call this a 04 the nanotube which will form will be given the designation a zero four nanotube which means zero four is the lattice vector of the graphene sheet which will become circumference of the nanotube . So, c has to be a lattice vector of the graphene sheet. So, c can always be expressed as c can be expressed as n times a one plus m times a 2; any lattice vector as you know since we have selected a primitive unit

cell and a 1 and a 2 are the basis of the primitive vector. So, any vector in the sheet will all can always be expressed as n times a 1 plus m times a 2.

So, the resulting tube the resulting tube will be called n, m tube. I hope this designation or this notation is clear. So, we have; so you can see that if one of the one of the components is 0. So, 0 4 tube this time we are getting a zigzag tube because you can see the zigzag structure along the circumference if you want.

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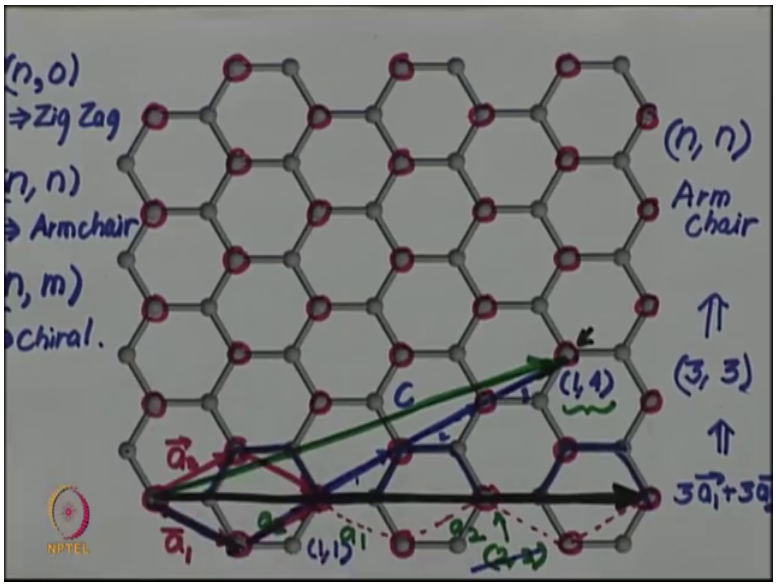

If you want armchair tube you will take a different chiral vector and it will have a different n, m designation. So, let us now try to make a chiral vector for armchair tube. So, I again mark all the alternate atoms as my equivalent sites and in this graphene sheet I will identify a vector which when wrapped up will become circumference of an armchair tubes.

So, remember that armchair had a armchair along its edge had something like this. So, which means that the lattice vector or the chiral vector for the armchair tube will be something like this what I have shown in black here. And if I take my basis vectors again two vectors at 60 degree this time I have changed the orientation from, but that is allowed you can take then any orientation. So, if this is my a 1 this is my a 2 you can see that this chiral vector which I have now marked will be one a 1 plus 1 a 2, then 2 a 1 plus 2 a 2, 3 a 1plus 3 a 2. So, the one which I have drawn out is 3 a 1 plus 3 a 2 in terms of these a 1 a 2 vector.

So, which means the resulting tube will be a 3, 3 tube. Now I will fold like this to bring the head of this vector the chiral vector to its origin and if I join then I will get a tube which will be a 3,3 tube. So, in general any n, m tube will be an armchair tube. So, the two components are equal then you will have an armchair tube finally, I will show you So, both armchair and zigzag as you know were chiral, but of course, since all these atoms are equivalent any of these atoms could have been brought to the origin and a tube could have been created.

So, if you now see. Let us randomly make; let us randomly choose one let us choose this let us choose this atom and let us say that we want to identify this atom with the origin and create a tube which means my circumferential vector will be going from origin to my chosen atom. Now if I try to define this in terms of n and m we see that we have to go remember a 1 and then we took a 2 and another a 1 then another a 2 to come to this point. So, this point was 2, 2 because we had taken 2 a 1s and 2 a 2 to reach here and after that I will I want to reach here. So, sorry this is not parallel to that. So, I should go parallel to this direction. So, which is this one had over short.

So, this is a line which is parallel to my a 2. So, I should come only up to this much. So, not 2, 2, but 2, 1, 1. So, here I have already come to 1, 1 and then I keep going in the two direction by 1, 2 and 3 steps 1, 2 and 3 steps. So, three extra steps in the two direction which means this location is a , 4 location this vector which I have drawn as my chiral vector c is 1 times a 1 and 4 times a 2 we can see now here clearly from this triangle that I i go 1 times a 1 and 4 times a 2 to reach there and so, this becomes my circumferential vector and if I now wrap it up then this will be called a 1 4 nanotube and this will be achiral nanotube arm chair and zigzag by achiral this will be a chiral nanotube.

So, in summary in n, m notation if one of the component is 0 n 0. So, this will be zigzag if both are equal n, n then we have armchair and if neither is 0 nor they are equal we have n m then you have a chiral tube. So, just one more concept which I wanted to show you is the chirality angle or the chiral angle sometimes the tubes are characterized by what are called the chiral angle.

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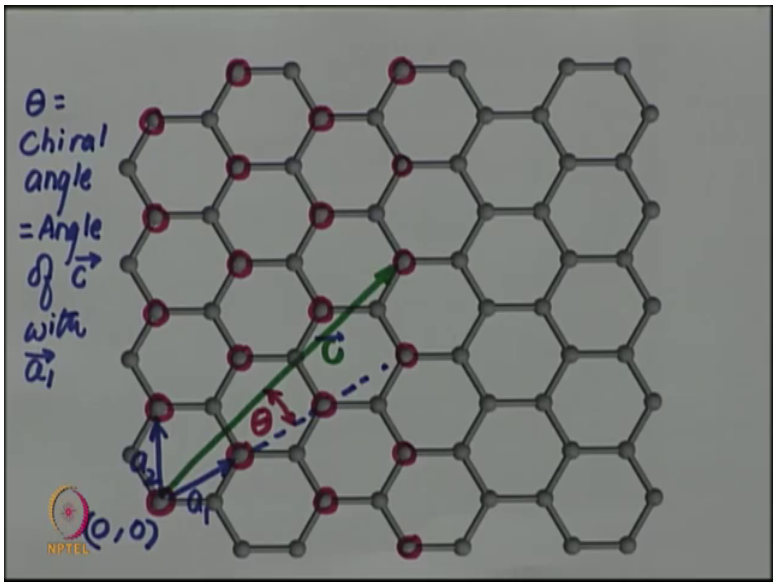

So, that is nothing, but the angle which the chiral vector makes with one of the axis usually taken to be the first axis a 1. So, if we let us say if we have if this is my origin again and these are my basis vectors and let us say that this is the chiral vector c then this chiral vector is making an angle theta with a 1.

So, angle of the chiral vector with a 1 will be known as the chiral angle angle of chiral vector c with a 1, that is the chiral angle and in fact, you can try to derive I leave this I do not do this now in this lecture.

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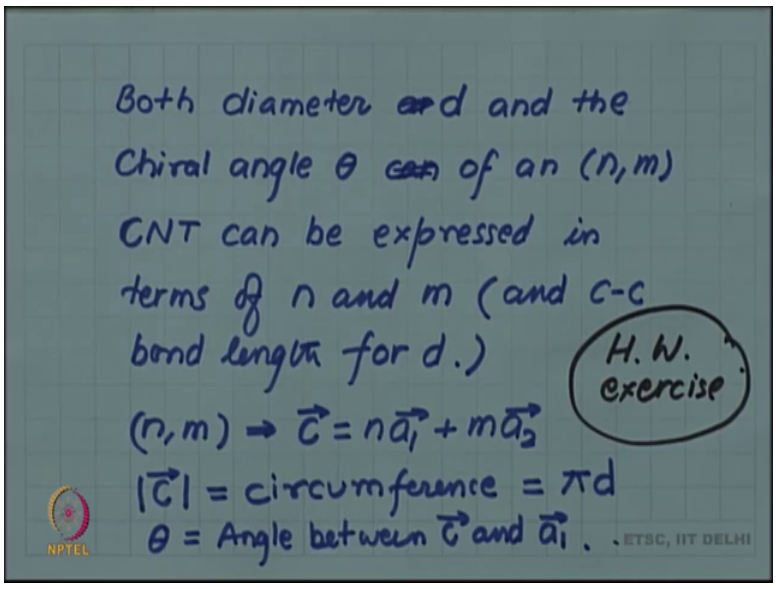

But I leave it as an exercise that both the diameter; both the diameter d and the chiral angle theta of a of an n, m an n, m C N T can be expressed in terms of n and m and of course, for d you also require a length parameter which is the carbon-carbon bond length and for this is an interesting geometrical exercise which I want to leave it as an homework for you because you can see that once the circumferential n, m n, m defines the circumferential vector c because c is nothing, but n times a 1 plus m times a 2.

And of course, once you know the vector c the length we are telling that c becomes the circumferential vector. So, lengths of c is nothing, but circumference. So, this will become pi d. So, with this relationship you can find the diameter in terms of n and m an angle between c theta is by definition angle between c and a 1 there is a nice exercise in vector geometry in non Cartesian frame because your 2 a 1 a 2 are not at 90 degree, but at 60 degree. So, I leave this as an homework exercise for you.

Thank you. With this we finished our discussion on nanotube we are coming close to the end of discussion on carbon structure maybe in the next video we will discuss little bit about fullerene.