Carbon Materials and Manufacturing
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Lecture - 47
Defects in Graphene and the (n,m) Notations

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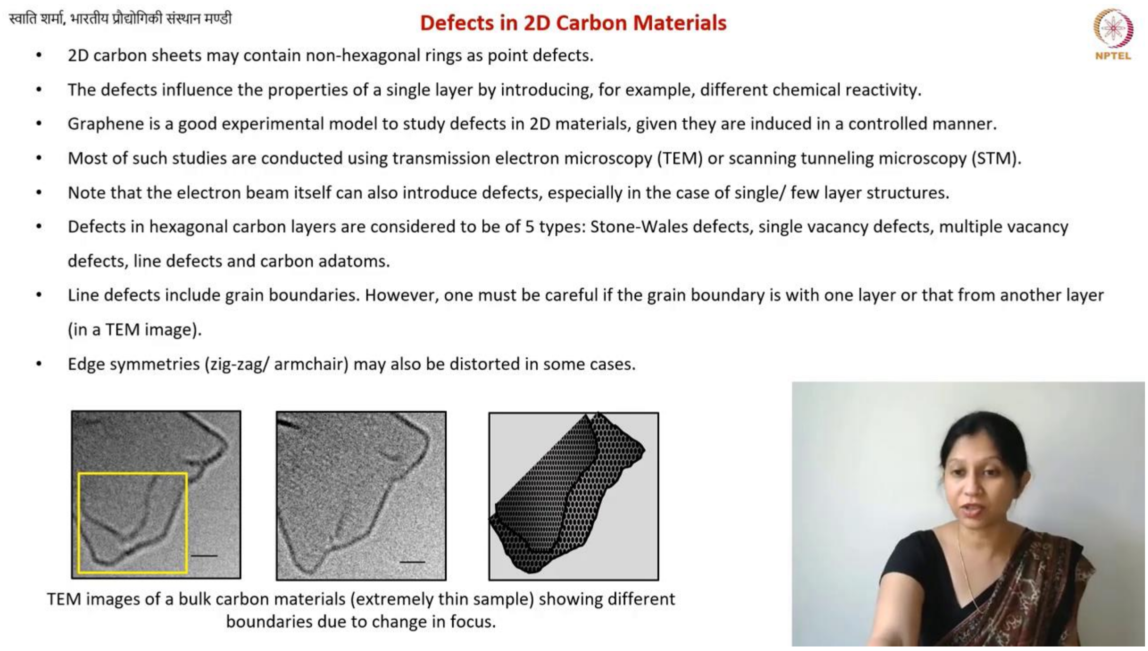

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Defects in 2D Carbon Materials

- 2D carbon sheets may contain non-hexagonal rings as point defects.
- The defects influence the properties of a single layer by introducing, for example, different chemical reactivity.
- Graphene is a good experimental model to study defects in 2D materials, given they are induced in a controlled manner.
- Most of such studies are conducted using transmission electron microscopy (TEM) or scanning tunneling microscopy (STM).
- Note that the electron beam itself can also introduce defects, especially in the case of single/ few layer structures.
- Defects in hexagonal carbon layers are considered to be of 5 types: Stone-Wales defects, single vacancy defects, multiple vacancy defects, line defects and carbon adatoms.
- Line defects include grain boundaries. However, one must be careful if the grain boundary is with one layer or that from another layer (in a TEM image).
- Edge symmetries (zig-zag/ armchair) may also be distorted in some cases.

TEM images of a bulk carbon materials (extremely thin sample) showing different boundaries due to change in focus.

Hello everyone. Now let us talk about what are the possible defects in two-dimensional carbon structures. So, I am not saying defects in graphene because graphene by definition is a defect free single layer of carbon. So, let us say defects in two-dimensional carbon. However, when these graphene-like sheets or graphene layers when they are present in bulk carbon materials; in that case especially, for example, non-graphitizing carbons then, we know that there is a significant number of non six-membered rings. And that is in fact responsible for the curvature, that is why we get these curved carbon structures. And when we have a very high curvature, we also sometimes get completely closed structures, for example, fullerene-like structures which result in the closed porosity of these materials.

So, we know that these kinds of six-membered sheets can also contain the non-six membered rings here and there. Also in the case of graphitizing carbons, it is not like graphitizing carbons do not have any defects otherwise we would not have to anneal them out.

So, we perform the graphitization at very high temperatures; we perform the annealing because we want to get rid of these non-six membered rings and that is how we actually increase the diameter of a crystallite.so, we increase the La.in the bulk carbons as well as, sometimes when you are trying to make graphene, you may get these hexagonal carbon sheets which contain non-hexagonal structures. So, this is when we are talking about 2D carbon sheets.

And often what happens is when you are manufacturing graphene using the CVD technique that we have discussed in detail. In the case of CVD fabrication, often it is already very difficult to control the geometry or the size of your graphene; also the layer thickness maybe you will not get single layers, you will get multi layer graphene, you will get few-layer graphene.

And in that case, the structures that you obtain often contain a lot of defects. So, to say now whether or not you call them graphene; this material in bulk is actually used for a lot of electronic applications, electrical applications, device fabrication nowadays.

So, let us discuss what are the possible geometries of these defects. But also in addition to these geometries, you will find some other geometries as well but there are certain defects which are sort of more stable than the others. So, let us talk about this here.one important thing is also that the defects definitely influence the properties of your graphene.

Sometimes they introduce new chemical reactivity.in principle your graphene should be relatively inert. But if you have a certain let us say unpaired electron, a dangling bond somewhere in the middle, or if you have just nothing but a high energy structure; a structure that has a lot of strain. In that case, you may actually find that your graphene is more reactive compared to the one that does not contain. So, that is the defect-free graphene may not be as reactive. So, people actually introduce defects in order to get certain special types of chemical reactivity.

Also sometimes the grain boundaries in graphene lead to a better electrical conductivity or definitely a different pattern of electrical conductivity along that boundary or dislocation compared to the rest of the structure. So, if you do have some unusual structures in your graphene sheet, you are going to get some unusual properties as well.

Now let us talk about it this way, whether or not the defect-containing structure should be called graphene; one thing we can definitely assume or understand that graphene is a good experimental model to understand these defects. Because defects and the stability of defects and what chemical properties and what new properties will it introduced to your material. These kinds of things can be understood theoretically as well as experimentally.

Now if you can actually get single-layer graphene structures for example, by removing them from HOPG. In that case, you can indeed understand. This is a good experimental model for us to understand what are the kind of defects that can exist in 2D materials? You see I told you in the past it was believed that even 2D materials are not stable. Now, we know that not only they are stable, they also can contain defects and still be stable. But to what extent these defects should be call defects and whether or not we should call it graphene after that and not. This is something debatable, but we are just trying to understand the geometry of defects here.

So, graphene for us is a good experimental model and you can have a look at this graphene under your transmission electron microscope also. There is something known as scanning tunneling microscope it is known as STM.

So, you can see your sample, see the surface; scan your surface of the sample and some of the very advanced TEM and STM are set up. They can actually give you the atomic resolution. So, in that case, you can indeed visualize these defects as well.

One very important thing however, is that when you are performing the TEM experiment, the beam itself can cause defects. So, typically if you are using a beam of more than 80 keV, in that case, you may end up introducing defects while imaging your sample.

This is also something that you need to know. However, there are transmission electron microscopes that can go down to even 30 kilo electron volts. So, in that case you there is a possibility that you can see such defects or you can really get images of them. Here this is some basic descriptions of these kinds of defects in hexagonal graphene-like sheets. They are divided into 5 types and I have mentioned the names here Stone-Wales defects, single vacancy defects and others.

You know the general defects in 3D materials. You have point defects, you have line defects. And you also have some defects of 3D nature like screw dislocation or you can have some sort of slip planes view. Those things are only limited to 3D materials, you are not going to have a stacking fault.

For example, in the case of graphene because it is a single layer, so there is no stacking. There is no question of stacking. Stacking faults of graphite by the way, we discussed in one of the lectures and I think you should also go through that lecture if you are interested in this topic or if you would like to relate the defects in graphene and graphite; I think that is a something that you should see.

The point here is that some sort of dislocations or defects are not possible in a2D material because of the fact that is 2D. However, what is most prominent in this particular case is the point defects. You also have line defects, so your grain boundaries can be considered line defects.

But point defects just by having any non-six-membered rings, so that you would call a point defect. But sometimes also it is not just one ring that is distorted or that is non six-membered, but also it is a set of rings. So, sometimes the defect has a certain geometry that propagates through let say it involves four hexagonal rings in that sheet.

So, you can have these kinds of point defects and then you can have grain boundaries. You can also have carbon adatoms, so on the next couple of slides, I am actually going to showing some of these pictures or at least the illustrations drawings.

So, as I mention the line defects or the grain boundaries, but here there is one very interesting thing again. So, all of these defects, there are two ways of understanding them; one is theoretically as I said that if it is for the crystal structure, if it is even possible to contain such a defect, how much energy it adds to your crystal structure?

So, those are the things that can be understood theoretically. When you want to understand the defects chemically or experimentally then you will often perform these chemical reactivity experiments, but that it is very difficult to perform such experiments with single layers.

So, you will often have this average effect of the entire material. So, also it is not that easy to obtain. Now, what you often end up doing is this TEM STM imaging and I already told you that one problem with that imaging is that you may end up introducing defects. Another problem is that TEM images are the 2D projections of 3D material and the entire material.

Let us see you have 10 layers of your graphene; the 10 sheets of graphene inside your focal plane or within your focal plane, in that case you will not be able to get any depth perception. Here is the image again this was taken when we carbonized phenol-formaldehyde resin. So, this structure you see this yellow box I have drawn here.

This is the point, now you could say that this is a grain boundary or some sort of dislocation or you may try to analyze. But there is also the possibility that these can be two layers stacked on top of each other because all you see in the case of TEM images of graphene is the edges.

This is also very important that you see only the edges and one problem is the lack of depth of perception. But also the fact that you see only edges or at least that those are the edges are brighter than the rest of the structure because graphene is transparent to optical light and also transparent to electrons. If it is a single layer, it is really difficult to image it.

See the second image of the same location just by changing the focus same location. So, in this particular case, you see that there is pretty much nothing visible.it is in the exact same location. And this is just by playing with the focus of your imaging.

So, this can also happen. There is a high probability that you have something like the structure actually is not even just one layer, but it is there are two layers of graphene. So, you need to be very careful when you are performing TEM imaging and when you recognize and say that this is a defect, this is a grain boundary.

Then you need to be very careful because you need to make sure that your interpretation of the TEM images is correct and you need to perform the imaging also in various ways; just by changing the focus, changing the location to ensure that what you are doing is correct.

Other than these potential defects, there is also edge symmetry, sometimes that are broken. So, what do I mean I think I told you that the edges can be either zig zag or armchair type. So, these are the two acceptable configurations for the edges of graphene layers.

But this is one more additional type of defect that you have rough edges, so they do not have any specific type of symmetry, but they have some other type of structure which again makes them more chemically reactive. Already the edges of graphene have dangling box because there is no termination so to say.

So, you have dangling bonds. And sometimes if these structures are not according to these two symmetric arrangements, in that case you can also have higher reactivity along the edges of graphene. So, that can also be considered a defect. now let us see some of these images as I told you.

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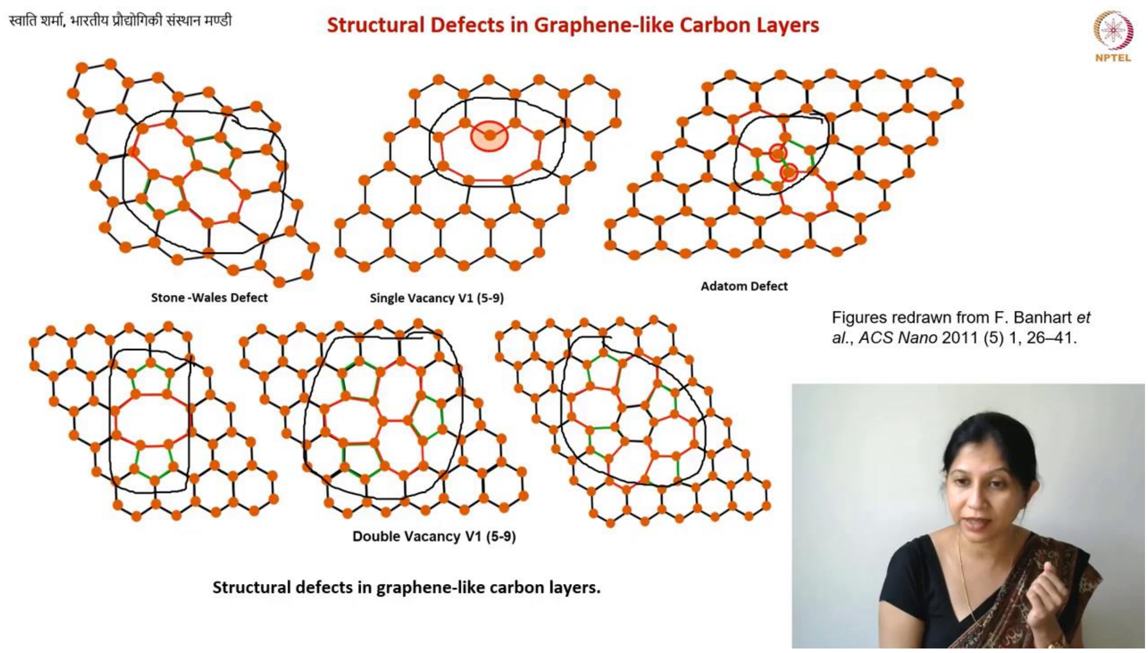
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Structural Defects in Graphene-like Carbon Layers

Structural defects in graphene-like carbon layers.

Figures redrawn from F. Banhart *et al.*, *ACS Nano* 2011 (5) 1, 26–41.

Here on this slide, you can see five types of defects in graphene. All of them are point defects. The first one is the Stone-Wales type of defect and now I do not know how clear it is, but I hope you can see that there are four hexagonal sheets rings that are involved in this defect.

Now, here you see there are two rings that are involved in this defect. In this particular case, this is kind of an interesting structure; there you have an adatoms, you have an additional carbon atom here. So, these kind of defects in the context of 3D materials or when you perform doping and you have a interstitial atoms.

So, something similar, but we have no foreign element. All the defects that we talked about are the defects without the addition of any foreign atom. It is just a carbon atom which has been somehow arranged itself in a certain position during its formation. Afterwards there was not enough energy for it to anneal out or to form a standard the hexagonal type of structure.

So, that particular atom then now stays there; so, this is the adatom vacancy. Here you can see that there are four rings that are involved in this particular type of defect. So, these are call double vacancy defects and they are of different types. So, here you can say even more than four, there are multiple rings that are involved in the formation of these defects. So, these are some of the point defects.

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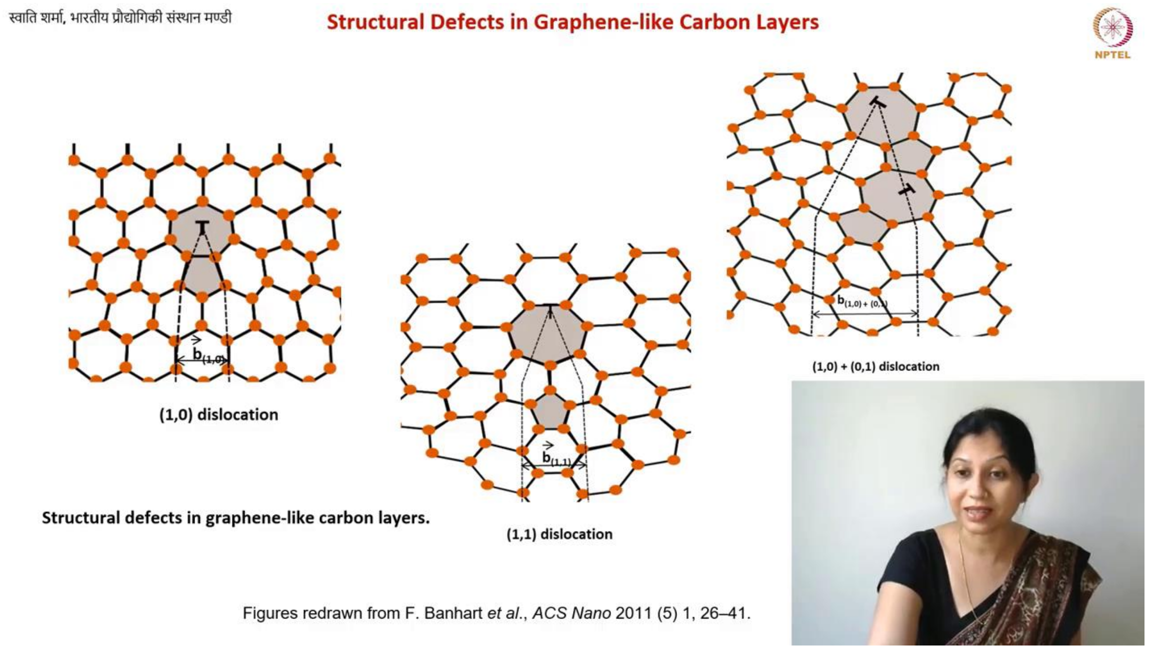

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Structural Defects in Graphene-like Carbon Layers

(1,0) dislocation

(1,1) dislocation

(1,0) + (0,1) dislocation

Structural defects in graphene-like carbon layers.

Figures redrawn from F. Banhart *et al.*, *ACS Nano* 2011 (5) 1, 26–41.

Now, let us talk about the line defects, so you see this T like structure. I have shown the direction of the burgers vector here. So, you can see that you have also certain type of line. The line defects actually propagate or they have a connection of various point defects.

So, if there is one point defect here and then here and then here and then here altogether you can call it a line defect (refer to video at 15:24). Or to gain at least a slightly lower energy state, these point defects will try to connect with each other and form a line defects. That is still slightly lower energy or it is a more preferred configuration.

So, here on this particular slide you can see all these different line defects or dislocations which ultimately lead to the formation of a grain boundary in graphene like structures. So, after discussing all of this now we are moving on to some notations again related to the crystal because this is important for graphene and also for carbon nanotubes and some other things that we are going to learn in our coming classes.

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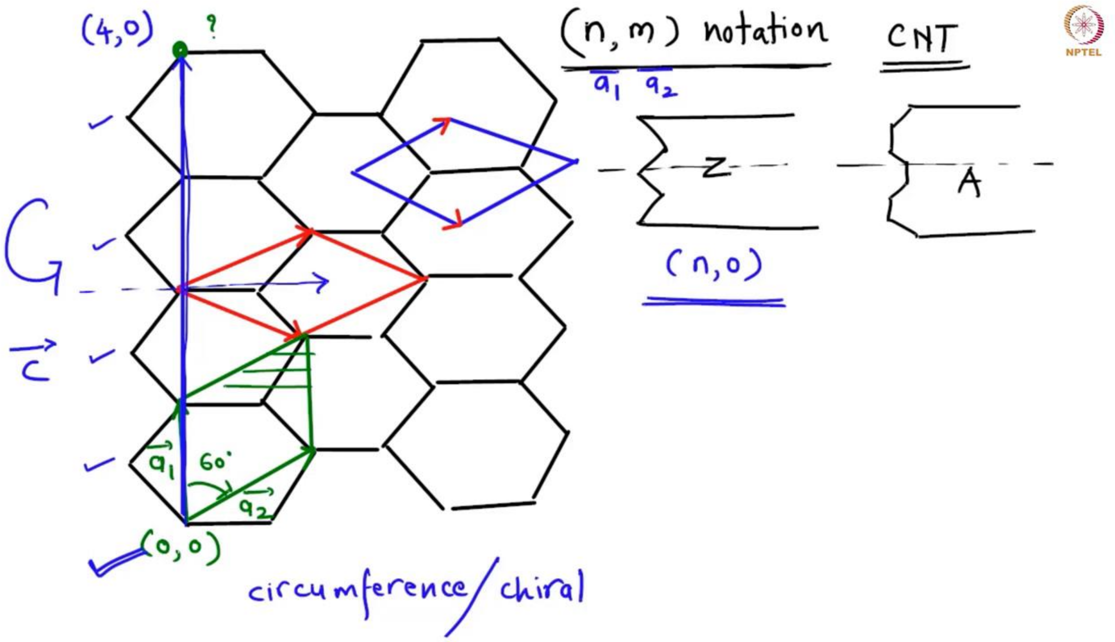

Now what we are going to talk about is known as the (n, m) notations. So, (n, m) notations are very important because this is a method of describing a certain location on a graphene crystal. This becomes even more important when we talk about let us say carbon nanotubes.

If you remember at the beginning of the graphene lecture, I told you that if you fold the graphene sheet then you get carbon nanotubes. That well that is not really chemically true.it is not like this is the method of preparing carbon nanotubes or something.

But why do we say that? We say that because this is the way of describing the crystal structure or a position of any certain atom on a graphene sheet which accordingly will also define the orientation of your carbon nanotube.

You probably also remember that if you had zig zag type of carbon nanotube. If you have something that looks like this then in that case you have this is your zig zag type carbon nanotube.

And if you have some sort of this kind of structure towards the ends then this is your armchair type of carbon nanotube. So, if basically to define the axis of your carbon nanotube and to define the orientation then also you use the (n, m) notations. But I am actually describing it here because (n, m) notations are also occasionally used for understanding the defect in graphene.

So, if you want to tell somebody that this is where the defect is or a non six-membered ring is situated at this location, then you are going to give (n, m) coordinate; that this is the position. So, let us talk about this. This is actually something very simple, if you take your lattice along somewhere on your graphene sheets then whatever you have two lattice vectors right a1 and a2.

So, along a1 whatever distance you need to travel from the origin that is known as n and along a2 whatever distance you travel is known as m. Actually n and m are also exchangeable. So a1 can be associated with m and a2 can be associated with n. There are also few other things in the graphene crystal that are allowed otherwise in many other types of crystals that is not allowed.

So, for example, how do you take your primitive unit cell? So, if you remember what we have discussed previously is something like this - so this is how we take our primitive unit cell. So, we have two atoms a and b, these are not equivalent that. And this is basically the usual method of considering the unit cell of graphene.

But it is also possible to take your unit cell like this because this actually does not change anything, you still have two atoms and even the size of the length of your vectors in the direction does not quite change. So, in that case, this is also one more allowed configuration, what is also allowed interestingly is that you can change the angle.

So, for example, you can also take this particular rhombus as your unit cell. So, why can I choose this as my unit cell? Because if you think about it, your graphene sheet is made of hexagons and these are symmetric hexagons. They all have six-fold symmetry, you can rotate your entire graphene sheet in any way. You can actually also choose any point as your origin. I mean in this particular case when I am going to describe the (n, m) notations I will take this particular point.

But all *a* sides can are can be exchanged with any atom that is of *a* type. When I say exchange; that means I can choose any of my *a* atoms as my origin or any of *b* atoms as my origin. The only thing that I need to keep in mind is that *a* and *b* type atoms are not equivalent and again it has nothing to do with the chemical structure.

But the fact that they do not have the same time types of bonds surrounding them or their neighbors are not the same. So, anyway, *a* and *b* already are the two types of neighbors. So, now, coming again back to the (n, m) notation. Let us say this is the one that I have selected as my crystal lattice now I have this vector.

Let us say a1 and this is my a2 vector are at 60°, they are not at 90°, so this is not a Cartesian system. Well now I take one point, any one point here say on top and this is what I need to define what are the coordinates of this given point?

Now, I am going to see how far I need to travel from my whatever atom I have selected as my origin. So, this is my origin, and this is the vector. Now you can see here that how much distance did you travel? One time a1, two time, three and four times a1.

So, this is my 4 and of course, we have not covered any distance along a2, so that is 0. So, this is as simple as that; this is my (4, 0) point. Now, when I talk about carbon nanotube fabrication using same graphene sheet and I role it up. Then what happens? Now this given (4, 0) point and my (0, 0) point should overlap only then we will get complete tube.

So, if (4, 0) and (0, 0) are overlapping in that case this entire long vector that I have defined here. This vector basically becomes your periphery or your circumference of your tube. So, basically this is the circumference and this vector in fact is often called either circumference or chiral vector.

So, when we talk about the carbon nanotubes then we are going to talk about what is chiral and what is achiral, but the idea here is this is called the chiral vector and this is denoted by C. So, sometimes it is called circumferential and sometimes chiral, but what does it mean; sometimes also you will have another vector that is known as the axis vector.

Because obviously, this is the axis of your carbon nanotube when you are rolling up this graphene sheet. Here you understand is that when you have zig-zag type of carbon nanotubes then the coordinates are going to be (n, 0) type.

Because you are always going to have this kind of configuration n, 0.if the carbon nanotube is (10, 0) that basically means this is a zig zag type of carbon nanotube.

So, now we will talk about the other type - the armchair type of carbon nanotube; actually armchair type of symmetry or how to define that location. This is important for us also on the graphene sheet irrespective of where do we define it fine.

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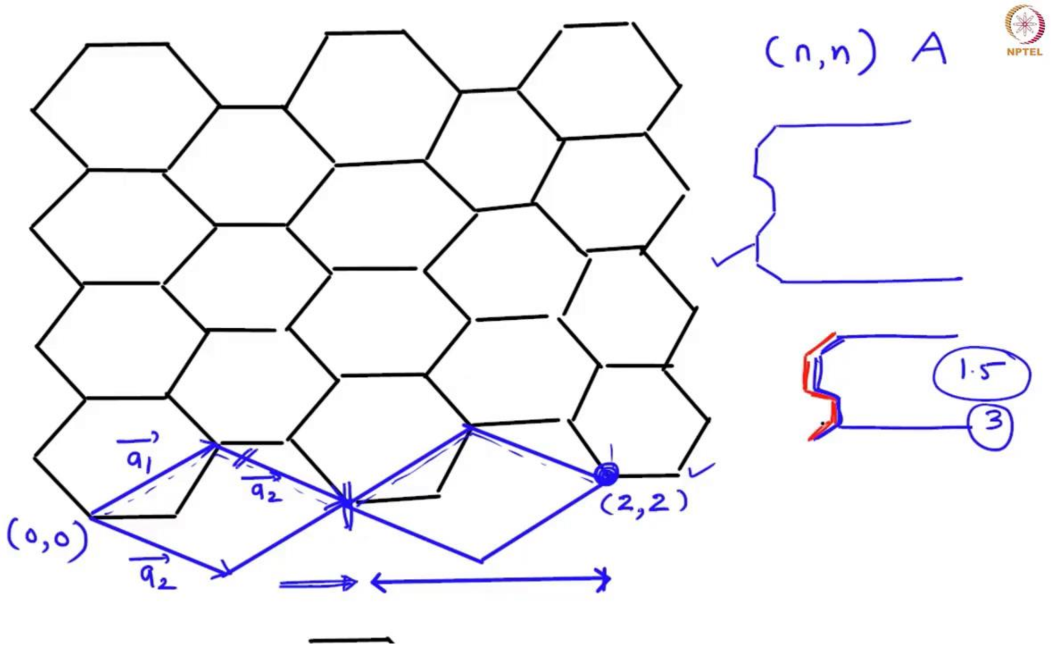

This is again my graphene sheet. I am going to also add one more set of hexagons and the reason for that is that when I talk about armchair symmetry unlike when I was talking about zig-zag. in the case of armchair, it is always good to have even numbers when we are describing the structure.

For example, when I take my lattice now. I will choose this lattice, this here. This is my lattice. And I am selecting this because it is parallel, it is in the direction of the point that I want to describe and this is going to be my point that I am going to describe is this one.

So, the idea is to take the lattice such that it is in the parallel direction. So, in this direction, I take the lattice and then now if you want to redraw the lattice number 1, 2 and 3 and 4. So, you see that in each lattice I am covering sort of two hexagons unlike in the case of zig zag where I was covering only one hexagon.

So, it is then easier to define it for a certain point your (n, m) location where you have even number of hexagons covered. Now, let us see how we do that. So, again this is going to be my origin. So, I have this lattice vector as my a1 and this is a2. How do I get to a1 and a2?

If I want to reach this given point then how much distance I need to travel along a1?that is one times, but how much along a2? Well, this vector here if you see that this is also equivalent to a2 vector, neither the direction nor the magnitude is changing. So, I can also call this is a similar vector.

So, now if you will see I travel one times along a1 and then another one time along a2.similarly over here a1 and then a2. So, the coordinates of this point are going to be 2 times a1 and 2 times a2.

So, I described it like this and I was also taking this point here rather than this point. Because I wanted to describe that if you have this (n, n) type when we talk about tubes. In that case, you are going to get the armchair symmetry in your carbon nanotube.

When you have the armchair symmetry this does not like just end at half. So, you will not have a carbon nanotube which is like this. You will sort of complete this armchair or armchair geometry and that is why rather you don’t take 3 hexagons, but you take 4 because you also want to have this entire thing completed, the armchair competed. This structure is known as armchair because if you will see it actually looks like something like a chair.

So, this is the second type, so now we understand what is the (n, n) or (n, 0) type notation. Now the third one is when you describe a chiral type carbon nanotube and when we talk in the context of graphene. Then we talk about a certain point that cannot be described just by using either armchair or zig-zag type of notation or calculations like how we did it.so this is the third one. This is called the chiral type; when we make two out of it then we call it chiral basically it is neither of these two symmetry.

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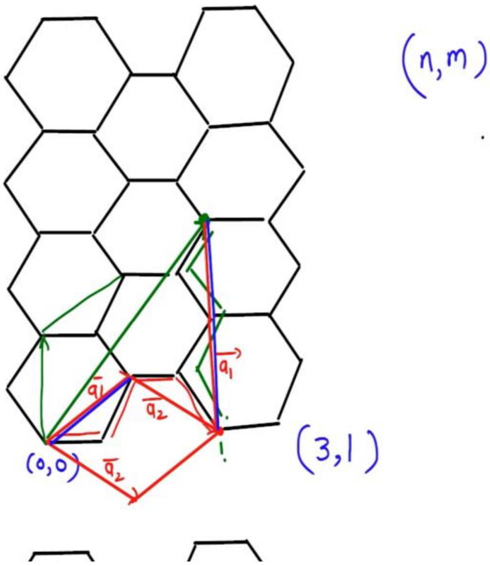

This is our third situation. I have selected some point here. This point, if I try to draw a vector from my origin. Then you will see that it is really difficult to reach this point just by using either zig zag or the armchair type symmetry.

So, how do we calculate? What we basically need to do is we need to see how do we reach this atom. So, what is the possible path? Is this the possible path? In that case you may not be able to you will just reach this point here. But you will not be able to reach the origin, so then we will probably also need to follow some other path.

So, let us again go back to first selecting our lattice here. And then again the same way we have our lattice vectors which are a1 and a2. Now how much do we travel to or how do we reach this point? So, there is one also option that we travel along this, this, this and this here (refer to video at 29:15).

So, basically one time a1 and one time a2 that is simple. So, one time a1 and this vector again is our a2, so one time a1 one time a2 we reach this point. And then from here if we had the other type of unit cell then we could have just walked in this direction, two times. And it is equal to a1, this distance because when we were drawing the n, 0 type of structure; in that case also we saw that if we took the lattice vector lattice somewhere here, then this was also equal to a1.

So, now you know that two times if you travel along a1 and here this was one more time along a1, so in this one here. So, we traveled once along a1, twice along a1 and three times along a1. So, our a1 coordinate becomes 3 and a2 we have traveled once.

Now, you have (3, 1) as the coordinates of this point. What this means is this is something called (n, m). Now, you do not have (n, n) type, also you do not have (n, 0) type of point, now what you have is (n, m) type of point. And if you draw a carbon nanotube then you are going to get neither zig zag nor armchair type symmetry.it is going to be kind of any random mixture of these two types of positions and in that case what you will call it? You will call the chiral type of carbon nanotube.