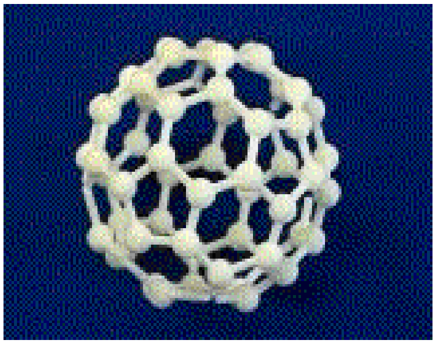
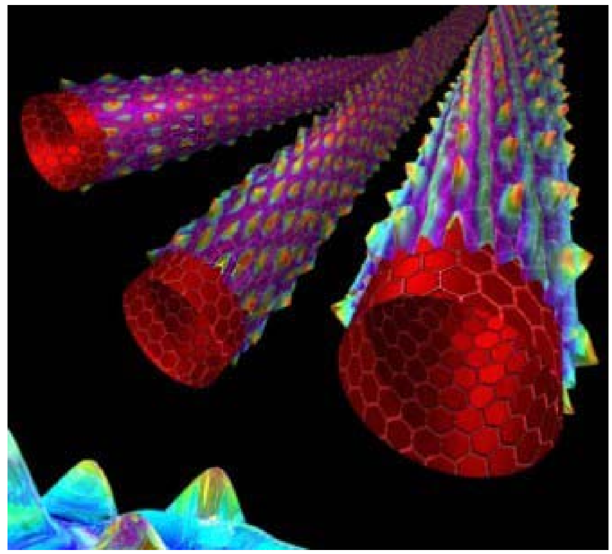
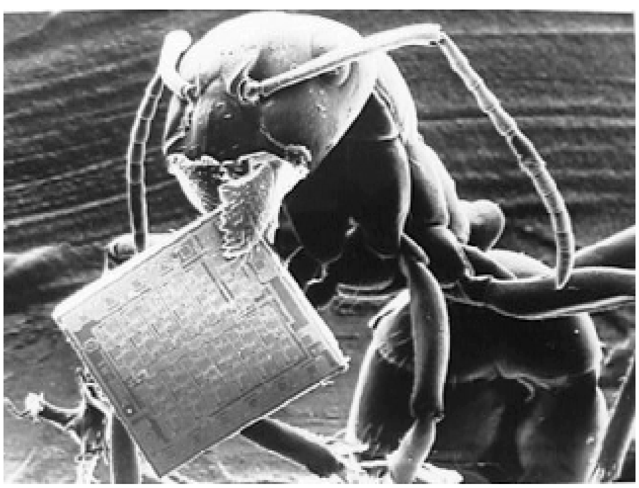
AN INTRODUCTION TO CARBON NANOTUBES







What would be the utility of such machines? Who knows? I cannot exactly see what would happen, but I can hardly doubt about when we have some control o f the arrangement of things on a molecular scale. We will get an enormously greater range of possible that substances can have, and of the different things we can do.

Richard P. Feynman

"There is Plenty of Room at the Bottom" (Dec. 1959)

CPIMA RET Fellow* - s*ummer 2003: Tom Grace; TGrace@slusd.org

Sponsor: Center on Polymer Interfaces and Macromolecular Assemblies, (CPIMA); CPIMA RET Program

Mentor: Professor Hongjie Dai; Department of Chemistry, Stanford University

AN INTRODUCTION TO CARBON NANOTUBES

DESCRIPTION OF LESSON AND INTENDED STUDENT BODY

My goal of writing the educational transfer plan (ETP) on carbon nanotubes was to briefly introduce to the high school chemistry student this growing novel area of organic chemistry in order to enrich their high school chemistry curriculum. Although knowledge of the fullerenes and carbon nanotubes are not currently a California State Standard, I feel it is important to create an awareness of the nanosciences and their potential applications in the future of nanotechnology.

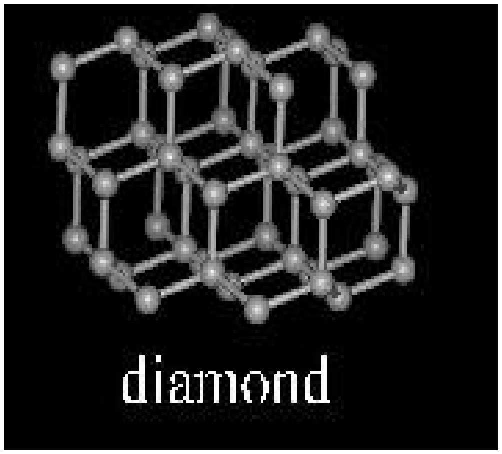
As a high school teacher, all too often my students fail to see the connection between the chemistry they study and its applications in the real world. The typical question of "when are we going to use this stuff," is one that most teachers are asked at one point or another and one in which I actually encourage my students to pose. Furthermore, I also expect if they ask such a question, then they are also responsible for finding answers to satisfy their curiosity. In the case of carbon nanotubes and its underlying chemistry, hopefully this lesson will help them in their quest.

This lesson plan was written with the assumption that the students are enrolled in an introductory chemistry class using a 90 minute block schedule which they attend everyday. I believe this unit can be taught to currently enrolled high school chemistry students in the 10^{th} through 12^{th} grades who have completed courses in the physical sciences and biology. In addition, their computer literacy skills should be at a level where they can complete Internet searches and download information from the World Wide Web.

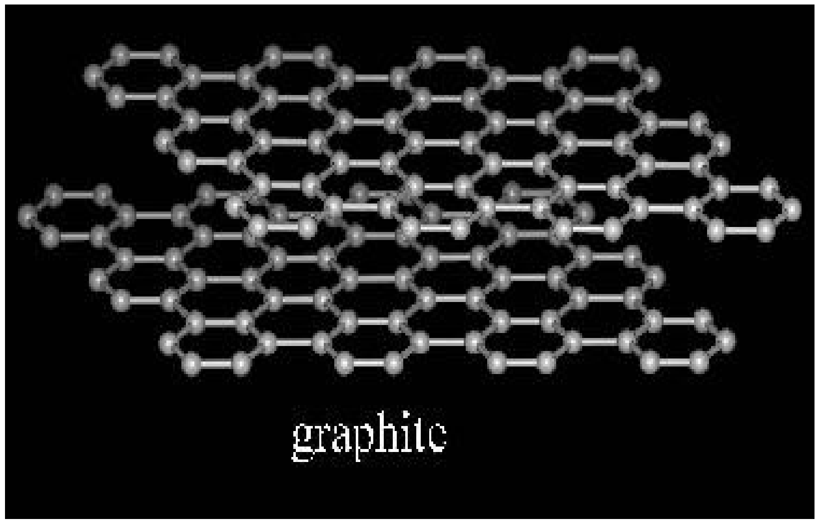
AN INTRODUCTION TO CARBON NANOTUBES

BACKGROUND LEADING UP TO CARBON NANOTUBES:

Until the mid-1980's pure solid carbon was thought to exist in only two physical forms, diamond and graphite. Diamond and graphite have different physical structures and properties however their atoms are both arranged in covalently bonded networks. These two different physical forms of carbon atoms are called allotropes.



Even though diamond and graphite are made of the same carbon atoms, they obviously have different physical properties. Diamond is very hard and graphite is very soft. Use the two pictures to help you explain why this difference occurs.

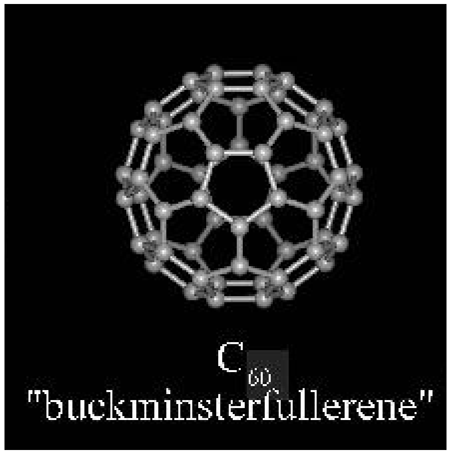


Graphite is composed of graphene sheets of carbon atoms. This is the material that is in our "lead" #2 pencils.

In 1985 a group of researchers led by Richard Smalley and Robert Curl of Rice University in Houston and Harry Kroto of the University of Sussex in England made an interesting discovery. They vaporized a sample of graphite with an intense pulse of laser light and used a stream of helium gas to carry the vaporized carbon into a mass spectrometer. The mass spectrum showed peaks corresponding to clusters of carbon atoms, with a particularly strong peak corresponding to molecules composed of 60 carbon atoms, C_{60}.

The fact that C_{60} clusters were so easily formed led the group to propose that a new form or allotrope of carbon had been discovered. It was spherical in shape and formed a ball with 32 faces. Of the 32 faces, 12 were pentagons and 20 were hexagons exactly like a soccer ball (see picture below)

AN INTRODUCTION TO CARBON NANOTUBES



Each carbon atom in the buckyball is bonded to how many others? Are the pentagons bonded to each other? Did you know that chemists can actually place a metal atom inside the sphere? How cool is that!

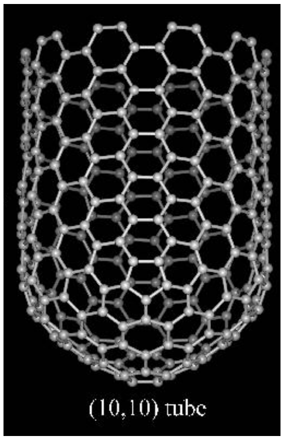
We see this unusual soccer ball-shape expressed in a wide variety of physical objects, for instance soccer balls, new golf balls, architecture, and art. These molecules were named after an architect, Buckminster Fuller, who was responsible for the design of the first geodomes. A geodome that you may be familiar with is "Spaceship Earth" at Epcot Center (Disney World). The soccer ball shaped C_{60} molecule was named "buckerminsterfullerene" or "buckyball" for short.

After this discovery, other related molecules (C_{36}, C_{70}, C_{76} and C_{84}) composed of only carbon atoms were also discovered and they and the buckyball were recognized as a new allotrope of carbon. This new class of carbon molecules is called the fullerenes. Fullerenes consist of hexagons and pentagons that form a spherical shape. Fullerenes have also been proposed as possible HIV inhibitors as well as potential constituents in interstellar space.

DISCOVERY OF CARBON NANOTUBES:

The unique geometric properties of this new allotrope of carbon did not end with soccer shaped molecules, it was also discovered that carbon atoms can form long cylindrical tubes. These tubes were originally called "buckytubes" but now are better known as carbon nanotubes or CNT for short. These molecules are shaped like a tube; imagine a sheet of graphite ("graphene sheet") or chicken wire rolled into a tube.

AN INTRODUCTION TO CARBON NANOTUBES



The carbon nanotube on the left is an allotrope of carbon. It and other carbon molecules now belong to the fullerene family. How is this CNT like the buckyball above? How is it different?

Carbon nanotubes have unique physical and chemical properties that chemists are trying to better understand through laboratory research. One of the physical properties of carbon nanotubes is that it's possible to make them only a single atomic layer thick. This means that they can be about 1/50,000th the thickness of a human hair.

Because of the bonding characteristics of carbon atoms, the physical appearance of carbon nanotubes can often resemble rolled up chicken wire (see pictures above and below). One of the interesting physical properties about carbon nanotubes is that when you have two of them which have slightly different physical structures and they are joined together, the junction (gap or small space) between them can function as an electronic device.

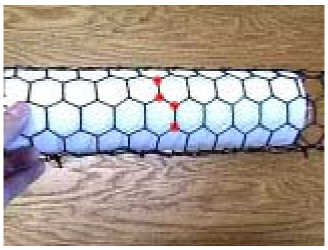
This electronic behavior depends upon the structure of the two tubes. Currently scientists are trying to make carbon nanotubes in large amounts (high yield) with a high degree of purity (little or no material defects), so that the physical structures are all the same. If they have similar physical and chemical properties then it becomes easier to predict their behavior which would ultimately make them more useful for possible nanosensors. These nanosensors could behave like semiconducting materials in microelectronic circuits, or detect small changes in electric current, or register chemical reactivity, or changes in air pressure or temperature.[1, 2] For a more detailed outline of the possible applications of carbon nanotubes see the **FURTHER READING** section of this document.

Since carbon nanotube science is relatively new, scientists from the fields of chemistry, physics and the material sciences are just beginning to unlock its mysteries and hypothesize about its potential applications.

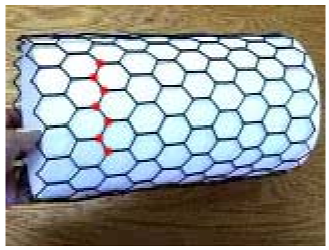
AN INTRODUCTION TO CARBON NANOTUBES

NANOTUBE GEOMETRY:

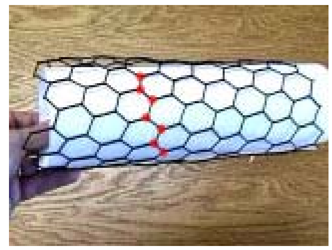
There are three unique geometries of carbon nanotubes. The three different geometries are also referred to as flavors. The three flavors are armchair, zig-zag, and chiral [e.g. zig-zag (n, 0); armchair (n, n); and chiral (n, m)]. These flavors can be classified by how the carbon sheet is wrapped into a tube (see pictures below).



Armchair arrangement of carbon atoms



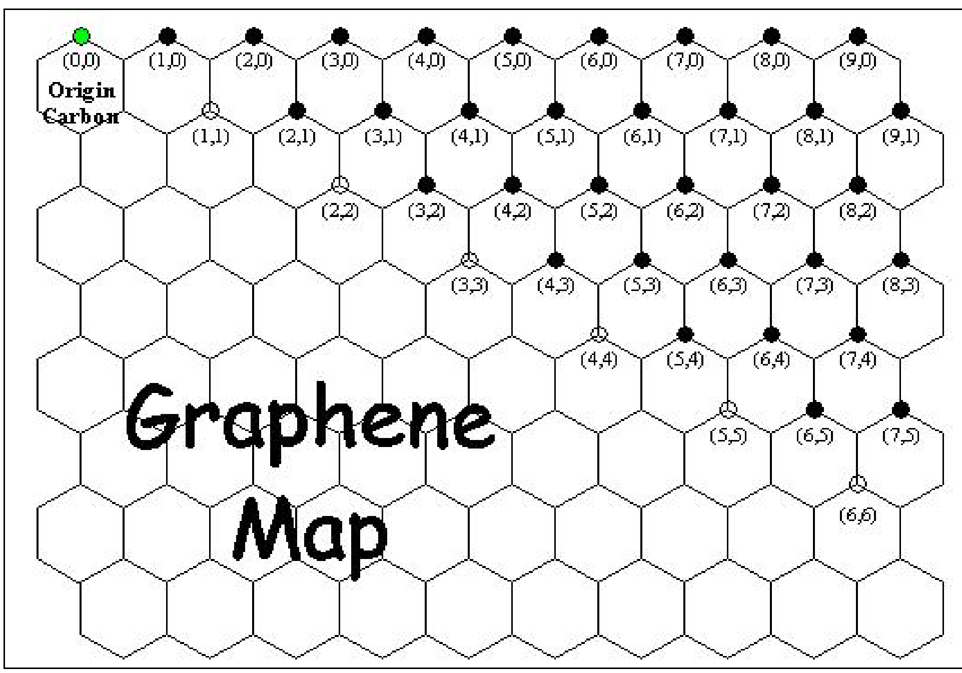
Zig-zag arrangement of carbon atoms



Chiral arrangement of carbon atoms

PAPER MODEL CARBON NANOTUBE ACTIVITY:

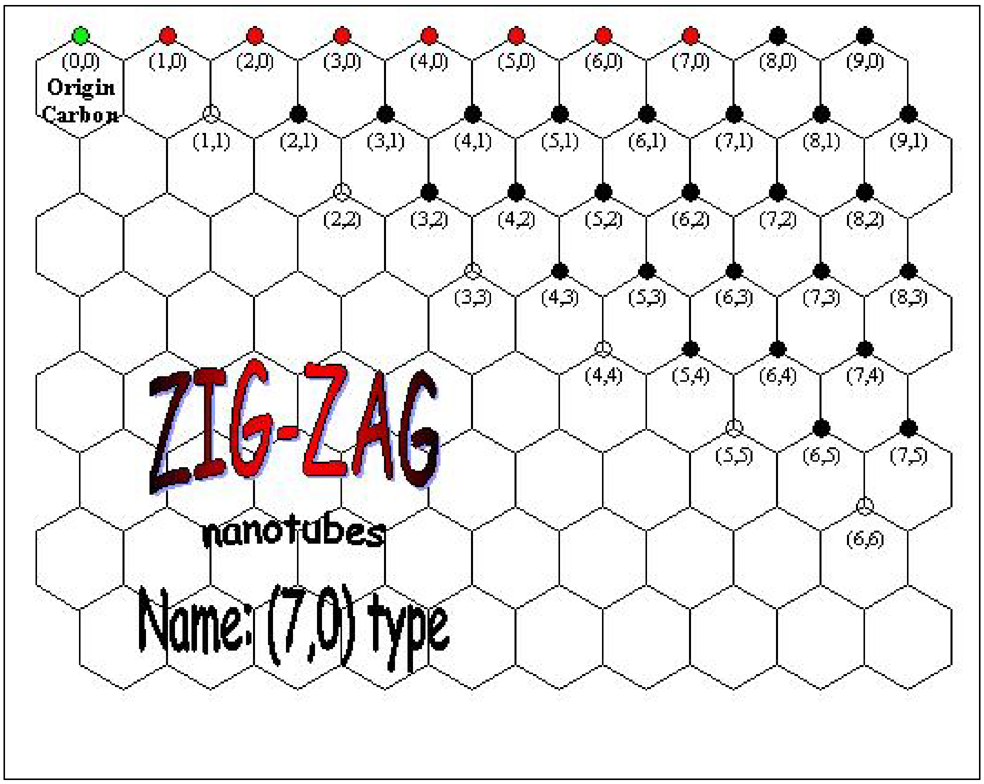
To better understand conceptually how the carbon atoms are arranged geometrically in a real carbon nanotube, you can create a paper model using a printout of a graphene sheet and practice counting a path around it as you roll it up.



To the right is an example of a graphene sheet. Notice how some of the carbon atoms have numbers on them indicating their position within the sheet. A flat piece of chicken wire can also serve as a good model of a graphene sheet.

This exercise can best be done by doing the following: first, download a copy of a blank graphene sheet (one without the numbers you see above) to practice with. To do this, visit http://www.mrsec.wisc.edu/edtec/cineplex/nanotube/index.html to find one. Then using Adobe Acrobat Reader 5.0, print out three copies of the graphene sheet.

Next, take your first sheet and cut along the black line around the edges of the outermost hexagons, so that you end up with a saw tooth edge around the whole outside portion of the paper when you are finished.



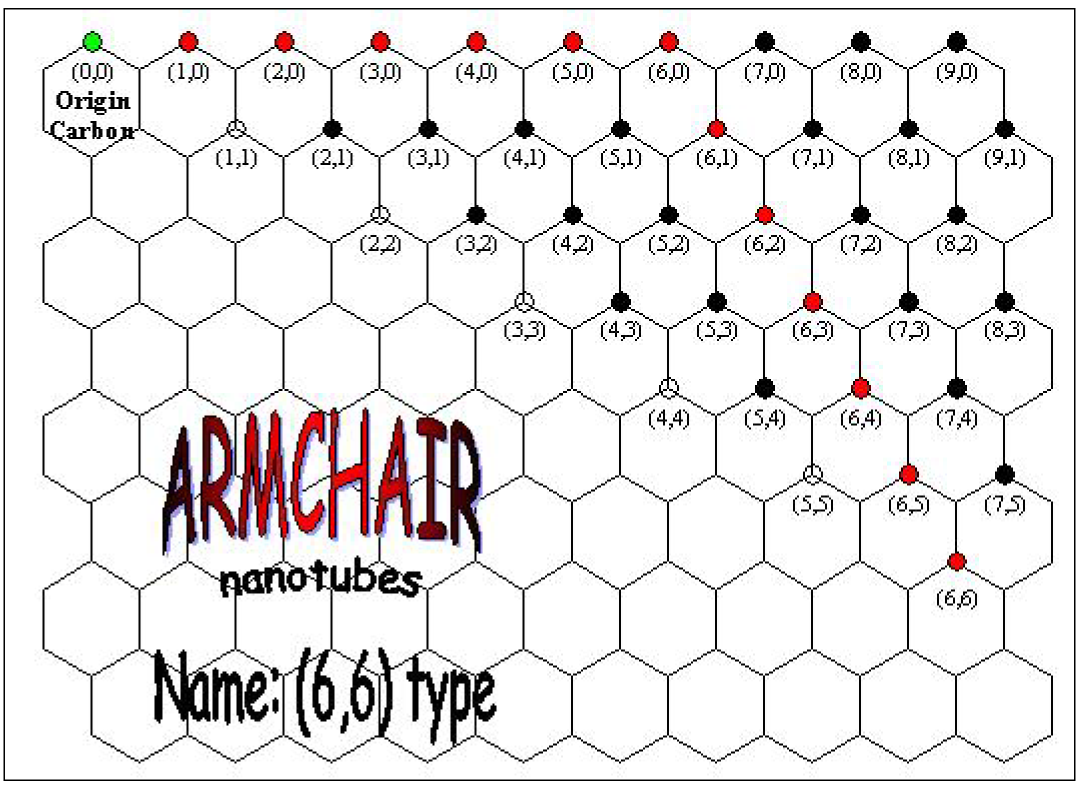
You will need to repeat this step with the two other pieces of graphene sheet paper, so that in the end all three pieces of paper have this same outer saw tooth edge.

Now, let's try and make a paper model of a carbon nanotube. First, we will start with trying to make a zig-zag model which is pictured above.

AN INTRODUCTION TO CARBON NANOTUBES

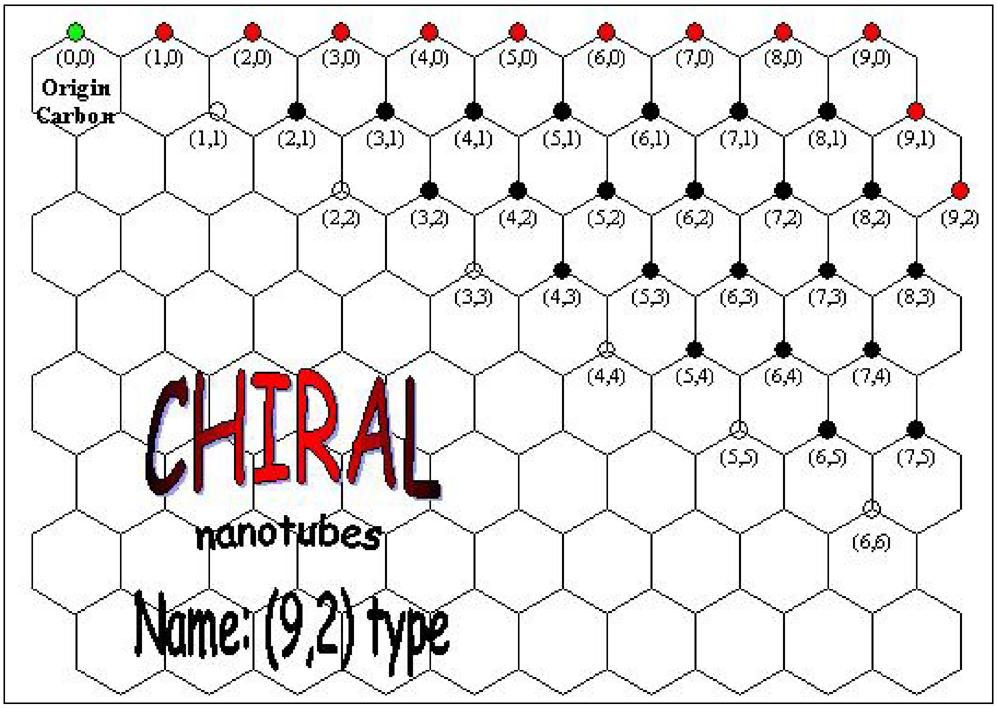
The zig-zag model is the easiest one to count and the best one to try and copy when learning these geometries. Remember, our goal is to start and end at the same point. Hold the starting point between the finger and thumb of one hand (0,0) and use the other hand to count around the rolled up sheet and try to end where you begin. So, count each carbon atom around the tube - (1, 0) (2, 0) (3, 0) (4, 0) (5, 0) etc., until you get back to the starting point. Once you have done this, you have just made a simple carbon nanotube model.

Next, let's try the counting on an armchair model. As you count around the tube, note that you are counting at an angle and it will not be possible to get back to your starting point unless you turn a corner. Note that you have to pick the right place to turn so that you end up at your starting point because you can only turn once. Again, count each carbon atom around the tube - (1, 0) (2, 0) (3, 0) (4, 0) (5, 0) — until you get to a corner; after you turn, the count continues as - (5, 1) (5, 2) (5, 3) (5, 4) etc. - until you get back to the starting point. Practice this one until you get the hang of it. It is a little trickier.

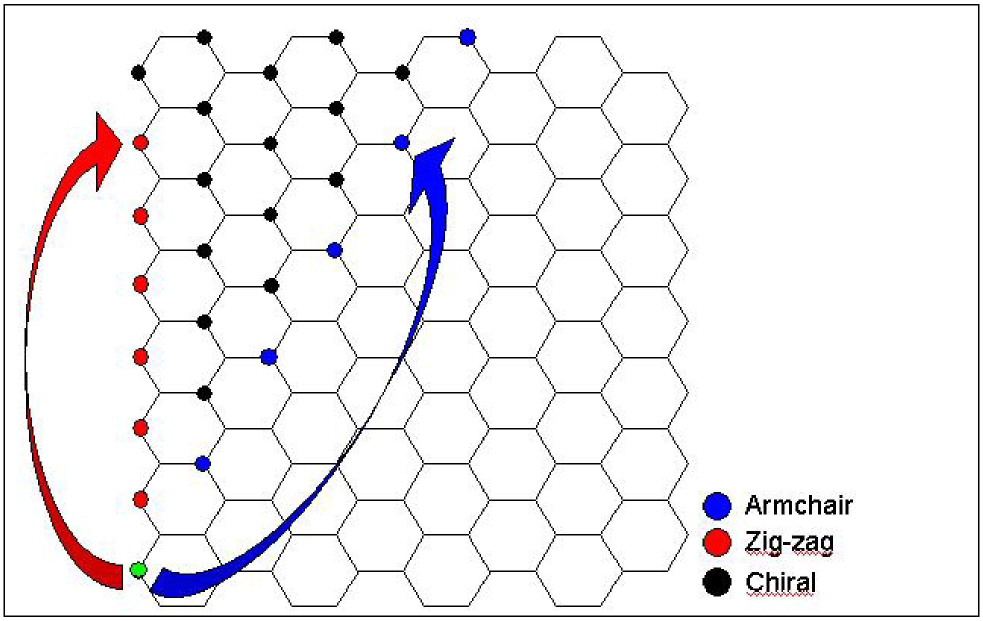


AN INTRODUCTION TO CARBON NANOTUBES

Now let's try to make the last one, which is the chiral model. I think it is the most difficult to copy. It can be counted similarly like the armchair model because it also has a turn it. Remember to try and end up where you start. Again use the sheet below and the one on the next page as a tool to help you.



AN INTRODUCTION TO CARBON NANOTUBES



To further help students in trying to do this activity, I have included the color coded map above which projects all three types of folding onto one graphene sheet.[4]

CARBON NANOTUBE WEBSITE ACTIVITY:

Now that you have practiced creating paper models of the three different carbon nanotube geometries and your hands are tired of folding, let's use the internet to search out examples (pictures, diagrams, cartoons, etc) of each type of nanotube geometry. That is, try and find three examples each of a zigzag, an armchair and a chiral nanotube geometry.

After you find the website where you find that particular carbon nanotube geometry, write the address below under the correct heading, so that your teacher can visit the website and see if it is correct.

ZIG-ZAG
Web addresses for zig-zag geometry
1. ____
2. ____

3. ____
ARMCHAIR
Web addresses for armchair geometry
1.____
2. ____
3. ____
CHIRAL
Web addresses for chiral geometry
1. ____
2. ____
3. ____

FURTHER READING:

Carbon nanotubes are currently being used (·) or considered (Ñ) for a number of significant applications:

- **AFM probe tips.** Single-walled carbon nanotubes have been attached to the tip of an AFM probe to make the tip "sharper". This allows much higher atomic resolution of the surface under investigation. Also, the flexibility of the nanotube prevents damage to the sample surface and the probe tip if the probe tip happens to "crash" into the surface. Piezomax a company started by Max Legally, director of MRSEC's IRG 1, that attaches carbon nanotubes to AFM probes for the purpose of increased resolution as well as decreased wear on sample and probe tip. (see http://www.piezomax.com/index2.html)
- **Flat panel display screens.** When a nanotube is put into an electric field, it will emit electrons from the end of the nanotube like a small cannon. If those electrons are allowed to bombard a phosphor screen then an image can be created. Several companies (SI Diamond, Samsung) are using this technology to replace the bulky electron guns of conventional television sets with these significantly smaller carbon nanotube electron guns. When scientists instead use millions of carbon nanotubes as tiny electron guns, the required dimensions change and the creation of a flat panel display (that can hang on your wall) becomes possible. In fact, some advertising billboards have already been made and are being used. (see http://www.sidiamond.com/) Learn more about how conventional televisions work at www.howstuffworks.com. Learn more about a flat panel display prototype: Wang, Q.H., Yan, M., and Chang. *Appl. Phys. Lett.* **78**, 1294 (2001).
- **Microelectromechanical devices.** Dr. Morinobu Endo at Shinshu University mixed nylon with carbon *fibers* (not nanotubes) 100-200 nm in diameter creating a nanocomposite materials that could be injected into the world’s smallest (as of 2/6/2002) gear mold. The carbon fibers have good thermal conductivity properties that cause the nanocomposite material to cool more slowly and evenly allowing for better molding characteristics of the nanocomposite. The "improved" properties of the nanocomposite allow it more time to fill the tiny micron-sized mold than nylon would by itself. The tiny gears currently are being made in collaboration with Seiko for use in watches. (see http://www.rpi.edu/web/News/NYTNanotubes.htm)
- **Hydrogen storage.** When oxygen and hydrogen react in a fuel cell, electricity is produced and water is formed as a byproduct. If industry wants to make a hydrogen-oxygen fuel cell, scientists and engineers must find a safe way to store hydrogen gas needed for the fuel cell. Carbon nanotubes may be a viable option. Carbon nanotubes are able to store hydrogen and could provide the safe,

efficient, and cost-effective means to achieve this goal. Dillon, A.C. et al. *Science*. **286**, 1127 (1999)

- **Actuators/Artificial muscles.** An actuator is a device that can induce motion. In the case of a carbon nanotube actuator, electrical energy is converted to mechanical energy causing the nanotubes to move. Two small pieces of "buckypaper," paper made from carbon nanotubes, are put on either side of a piece of double-sided tape and attached to either a positive or a negative electrode. When current is applied and electrons are pumped into one piece of buckypaper and the nanotubes on that side expand causing the tape to curl in one direction. This has been called an artificial muscle, and it can produce 50 to 100 times the force of a human muscle the same size. Applications include: robotics, prosthetics. Learn more about carbon nanotube actuators: Baughman, R.H. et al. *Science.* **284**, 1340 (1999).
- **Chemical sensors.** Semiconducting carbon nanotubes display a large change in conductance in the presence of certain gases (e.g., NO_2 and NH_3). When compared to conventional sensors, carbon nanotubes provide the advantages of a smaller size, an increased sensitivity, and a faster response. Wei, Q.-H. et al. *Science*. **287**, 622 (2000).
- **Nanoscale electronics/nanocomputing** Scientists have exploited the mechanical and electrical properties of carbon nanotubes to produce molecular electronic devices. When nanotubes are placed in a grid, the intersections of the nanotubes become bits of information that can be stored non-volatilely. (see more information at Prof. Charles Lieber's website http://cmliris.harvard.edu/html_natalya/research/research.htm) Semiconducting nanotubes also can be used as single molecule transistors.
- **Nanothermometer**. A carbon nanotube can be partially filled with gallium metal. When the temperature is changed, the gallium metal expands or contracts to fill or empty the carbon nanotube. The gallium level in the carbon nanotube varies almost linearly with temperature. This new device may find use in certain microscopies.
- **Flash photography and carbon nanotubes**. Scientists have discovered that as-grown single-walled carbon nanotubes can be ignited by holding a conventional camera flash a few centimeters away and flashing the sample. [3]

AN INTRODUCTION TO CARBON NANOTUBES

ACKNOWLEDGEMENTS:

- Marni Goldman, Ph.D.
- Professor Hongjie Dai
- Professor Bob Waymouth
- Robert Chen
- Hee Cheul Choi, Ph.D.
- Sarunya Bansaruntip

- Dai Research Group; Stanford University Department of Chemistry

Funding Provided By

- NSF-MRSEC (Grant # DMR-0213618) and NSF-REU (Grant # DMR-0243886)
- Center on Polymer Interfaces and Macromolecular Assemblies (CPIMA)

REFERENCE:

[1] T. Brown, H. Lemay, and B. Bursten, ***Chemistry, The Central Science***, Eighth Edition (Prentice Hall, 2002)

[2] H. Dai , ***Accounts of Chemical Research,*** 35, 1035 (2002)

[3] University of Wisconsin Materials Research Science and Engineering Center on Nanostructured Materials and Interfaces and the James Lovell Museum of Science, Economics & Technology in Milwaukee, Wisconsin; Graphene sheets, diagrams and pictures courtesy of ***Carbon Nanotubes Activity Guide***, (2002)

[4] University of Wisconsin Materials Research Science and Engineering Center on Nanostructured Materials and Interfaces and the James Lovell Museum of Science, Economics & Technology in Milwaukee, Wisconsin; ***Carbon Nanotubes Activity Guide***, (2002)