Computer simulation of carbon nanotubes

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1 Visualization, structures, classification

T1 : If it has not already been done for you, start the program by typing Cbond in the terminal window. A small window with some buttons on it should appear.
T2 : First we will look at graphene, which is what a single layer of graphite is called. Nanotubes can be thought of as graphene sheets which have been rolled up (though this is not how they actually are formed). How you do the rolling makes a big difference to the properties of the tube. Click on Structures, then on Graphene in the new box. A third box will appear which allows you to specify some details but just click OK for now.
T3 : Next click Visualize, and in the new box set the "X" and "Y" sliders to 4, leaving the "Z" one at 1. A graphics window should pop up showing part of a sheet of graphene, with the carbon atoms represented by grey spheres. Notice the hexagonal nature of the structure. When you're ready, close the graphics window.
T4 : Now click on Structures, then on Nanotube and OK in the new window that appears. Again click OK to use the default values.
T5 : Now click on Visualize and set the all of the sliders to 1. Now you should see the tube. Use the mouse (by holding down the left button) to rotate the atoms so you can look from different angles.
T6 : Now, you might be thinking, "that doesn't really look much like a tube, it looks more like a ring". This is because you're only seeing one "unit cell" of the tube. You should imagine a real tube as being made from very many of these on top of one another. Actually we can do better than that: Close the graphics window and click Visualize again, but this time move the slider labeled "Z" to 4 or more and click OK. Now when you rotate the structure using the mouse you should see something that looks more like a tube.
T7 : Alternatively, you can choose a different kind of tube, one that has a larger unit cell. Close the graphics window, and click on Structures again. This time, after picking Nanotube, change the second "chirality" index to 4. After clicking OK, click Visualize, and reset the number of unit cells to one. This new tube has a much larger unit cell, so it looks like a tube even with just one unit cell. In fact the unit cell contains 244 carbon atoms.
T8 : Repeat this process, visualizing tubes with different (n, m). Note that m should never be bigger than n (this is a convention, and it is enforced by the program). Nanotubes are usually classified into three types: "armchair", "zig-zag", and "chiral". The word "chiral" can be thought of as meaning "twisted" here. The other words refer to the pattern you see as you look at a circumference. Try to decide what type each tube you visualize belongs to. Then try to see if you can figure out the rule relating n and m to the type.

2 Deformation

T9 : Now we will simulate deformation of a nanotube. First choose a tube whose unit cell is not too short (so (5,5) would be a bad choice) Then click on Computations, then Vertical Strain. We are going to apply strain to the tube along its length–that is, stretch it. In the box that appears the only parameter you need to change at first is the second one ("Scale factor maximum"). Make that 2.0, which means we will stretch the tube to twice its original length. Click OK and then RUN on the main window. It should take no more than a second to run. To see the results click Plot Data, then choose Plot column 2 and OK. The vertical axis of the resulting plot is the energy of the tube per atom. The horizontal axis is the factor by which we stretch it. You will notice an initial quadratic increase (which is the elastic regime, where it's like a spring) followed by a steep increase then a leveling off.
T10 : To see the final state of the nanotube, click Visualize, making sure that all of the sliders are at 1. Also, click on Use stored so that you will see the deformed tube rather than a fresh undeformed one. In the next box which allows you to choose between stored configurations, leave the default, which is the most recent one. You should see that the atoms have been uniformly spread out in the vertical direction. Once atoms got far enough apart from their neighbors above and below the no longer interacted, which is why the energy stopped going up.
T11 : Now, what we've done so far is a uniform stretching. But this doesn't really match what would happen if you actually stretched a tube by holding on to its ends. The main thing missing is allowing the atoms to move while they are being stretched. So we will do that now: In between increasing the overall stretch, we will allow the atoms to move to positions of lower energy using an energy minimization algorithm. Go back to Computations and Vertical Strain, and make two more changes: Set Scale step to 0.01, and set Number of MDMin iterations to 100. Then OK and RUN as before. This time it will take maybe five minutes to run (for a 100-atom CNT).
T12 : Plot the energy again (with Plot Data). Now you should see one or more sharp drops, and the leveling off may or may not happen. Visualize the final structure again, to see what happened(Visualize and Use stored). How would you describe the deformed state? If more than one jump occurred in the energy plot it won't be obvious what exactly happened when. One way to find out would be to estimate from the plot at what stretch factor the first drop happened, then repeat the simulation but only stretching that much. Then you could see exactly what the first "deformation process" was.
T13 : One measure of how strong a tube is is how far it can be stretched before it breaks. Read off the scaling factor where the drop occurred, and convert to strain by subtracting 1. Sometimes this strain is called the "critical strain". A more typical measure of strength would be the actual breaking force or stress (force/cross-sectional area). One can use the data generated by the program (which is saved to a file) to determine the force, but that requires further analysis with a separate program.
T14 : Repeat the process of deformation with minimization for different kinds of nanotubes. See if you notice any patterns in the kind of deformed states you see or in the critical strain, with regard to class (armchair/zig-zag/chiral) or length.

3 Wavefunctions

The program Cbond also includes an interface to our electronic structure code, Dacapo, which can compute the electron wavefunctions for a system and use them to compute accurately the total energy and forces. It takes a while to run (up to 30 minutes for a small nanotube unit cell such as (5,5)) so we won't run it here, but we can look at the output from a previously run calculation.

Click Show wave functions and enter the filename "DCout55.nc". Leave the band number and k-point number at their default values (0) for now and click OK. Two windows will appear (the second might take 10 seconds or so). The first shows a representation of the energy eigenvalues of the system, the chosen one (the band number) highlighted in blue. The Fermi-level is indicated by a green line. The second window is a visualization of the atoms and the wave functions. You can use the mouse to rotate and translate the nanotube and to zoom in and out (play around with the different mouse buttons to figure out which is which).

Now carbon has 6 electrons per atom, but the innermost ("core", 1s) electrons are not relevant for binding or conduction and are not included in the calculation. Since there are 20 atoms in the unit cell of the (5,5) CNT, that makes 80 valence electrons in total, but then because you can put two electrons in an orbital wave function, only 40 orbitals are needed. However for technical reasons another 10 are included in the calculation, and these show up as unoccupied states (states above the Fermi level). For the purposes of plotting, the states (orbitals) are numbered from the bottom up. Try repeating the procedure above but putting in numbers from 0 to 49 for the band number (leave the k-point number at 0).

As you examine different wave functions, see if you can identify the *character* (s, p, d,...) of the atomic orbitals making up the nanotube wave functions. To do that you need the following information: An isolated carbon atom has s and p orbitals, with similar energies. These mix together in different ways to form molecular or band wave functions when carbon atoms are brought close together to make a molecule or solid. In particular in graphene (or graphite) the p_x and p_y orbitals which are oriented in the graphene plane *hybridize* with the s orbital to form three states at 120° angles. These sp^2 states then form covalent σ bonds with corresponding states on neighboring atoms. The remaining p_z orbitals stick out of the plane in both directions. They interact with each other more weakly to form a π-bond, which is really a band spreading over the whole layer.

The key to identifying the different types of bond is *symmetry*, specifically mirror symmetry in the graphene plane. The sp^2 orbitals are symmetric, which means that they do not change sign as you go from one side of the plane to the other (alternatively put, if you flipped them within the plane you would not see any difference). By contrast, the p_z orbitals are anti-symmetric: they do change sign (which is indicated by color in the visualization). The fact that the two sets of orbitals have opposite symmetry properties is why they act completely independently of each other[1]. So to identify the character of the orbitals, you first must identify the symmetry (starting with the question: what does the mirror symmetry correspond to in the nanotube?). The final question is this: what kind of states are involved in transport (conduction) in nanotubes[2]? Hint: Fermi level.

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[1] At least in a graphene layer; in a CNT the symmetry is broken somewhat by the curvature.

[2] The distinction between conducting and semi-conducting CNTs is not important here.