Computer experiments with Carbon bonds

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1 Introduction

In this problem set we will work through several calculations, both using pencil and paper and using the computer, relating to properties of carbon bonding. We will start with the simplest case, two carbon atoms, before considering diamond, graphene and carbon nanotubes. The calculational techniques will develop your understanding of energy and force as well as introduce some basic concepts regarding the mechanical properties of materials.

2 Setting up your Unix environment

When you first sit down in the databar to do this exercise, there are some things that need to be set up in order for certain files and libraries to be found. This only needs to be done once. First, find out what type of shell you are using. Type:

echo $SHELL

If you are running a bash shell[1], include this line in your .bashrc file (note that CASE MATTERS! So make sure it's Software, not software):

source /gbar/erlang/home2/fys/v14322/Software/bin/camposase.sh

If you are running a tcsh or csh shell include this line in your .tcshrc or .cshrc file:

source /gbar/erlang/home2/fys/v14322/Software/bin/camposase.csh

The next time you log in, everything will be ready to go! For this session, you will have to do:

source .bashrc

or source .cshrc or source .tcshrc.

[1] This is the default shell, so this should apply to most people

3 Simulation: Carbon-Carbon Bond

In this section we will explore the properties of a single carbon-carbon bond, using the Brenner potential (force-law) for carbon, implemented as a module of the “Asap” code for classical molecular dynamics. For this exercise, an easy, friendly graphical interface has been developed.

3.1 Cbond

Start the interface by typing Cbond. A small window will appear with several buttons. Click the Structures button to get a list of possible structures to simulate. The first one we will work with is a carbon dimer[2]. Click on Dimer and then on OK. A dialog box will appear asking you to specify two parameters. The first is the distance between the two carbon atoms (in Ångstrom (Å)[3]). You may leave it at the default value or pick a different value. The second allows you to add Hydrogen atoms in order to change the nature of the C-C bond (double, triple, etc). Leave it at zero first, so that we will first actually be studying a quadruple C-C bond. You can display the two atoms using the “RasMol” program by clicking on Visualize (accept the default settings in the visualize dialog box). This will also cause the coordinates of the atoms to be printed in the window where you started Cbond, along with the vectors describing the “box” that the atoms exist in. You can get rid of the RasMol window by simply closing it or choosing “exit” from its “File” menu. The RasMol program also prints a lot of stuff to the terminal window; it is OK to ignore that.

3.2 Calculating a single energy

The first thing we will do is calculate the energy of the system for the C-C separation you have chosen. Click the Computations button and choose Single Energy before clicking on OK. Then click the RUN button. The calculation should take less than a second. The results, namely the total energy, the energy per atom, and the forces on all atoms, will be printed in the terminal window where you started Cbond. If you chose to include Hydrogen atoms in your Dimer, the first two forces belong to the Carbon atoms.

3.3 What do we get?

Question 1 : Do you notice any particular relationship between the two forces? **Question 2** : Do these forces tend to increase or decrease the separation between the atoms? You might want to scroll up (or press Visualize again) to see what the positions of the two atoms were.

Note: In general a single potential energy value has little meaning by itself—you may remember that the zero of potential energy is arbitrary. It happens that in the Brenner potential, zero potential energy corresponds to atoms well-separated from each other (in principle infinitely, but in practice there is a cutoff distance of a few Å), though this is in general not the case for other simulation methods. The energy unit used is the electron volt (1 eV = $1.602 \times 10^{-19} J$). Most of the changes we care about are smaller than 1 eV. We certainly won't care about (or believe!) differences smaller than 1 meV, so there will not be any point in keeping track of more than 3 decimal places in the energy values.

[2] A dimer is a pair of atoms bound together.
[3] $1\text{Å} = 10^{-10}$ m = 0.1 nm

3.4 More data points

Next, repeat this calculation, changing the C-C separation by about ±0.02 Å according to whether the forces "wanted" it to increase or decrease. **Question 3** : Does the energy decrease? A general principle of mechanics is that force points in the direction of decreasing energy[4]. If you are at a minimum of the energy then the force is zero (this is also true of a maximum).

In principle you could repeat the calculation again and again, making smaller and smaller changes to the C-C separation until you "zoom in" on the value that gives the minimum energy. The meaning of this minimum is that it is the equilibrium bond length, what would be measured in an experiment. The value you get should be fairly accurate, since usually force-laws such as the Brenner potential are specifically tuned to reproduce bond lengths correctly.

3.5 Binding energy curve

Instead of having you do this, we can save some time by using a different mode of Cbond. Click on Computations again and this time select Vary Structural Parameter. This will compute several energy calculations in a row; changing one parameter of the given structure each time. We will be varying the C-C bond length of the dimer, which is parameter 0. Choose a range between about 1Å and about 2Å, and set the step size to be 0.01Å. You might want to change the output filename, for example adding a number to it, to be able to keep track of different data sets later on.

To view the data, there are three options: (i) click Plot data (accepting the defaults) for a quick look without analysis (ii) open a new terminal window and "more energyCurve.dat" (or whatever the filename was) to see three columns of numbers—one for the parameter that was being varied, one for total energy, and one for the energy per atom (the total energy is what we care about here) (iii) Also in a new terminal window, use the plotting/analysis program xmgrace (type "xmgrace energyCurve.dat"), which allows you to see the whole curve as well as zoom in on different parts of it. We will call the bond length l and the equilibrium value l_0. The simplest estimate of l_0 is the point in your data set with the lowest energy[5].
Question 4 : What is l_0, according to your data? Include an estimate of the error as half the interval between data points.

3.6 Curvature around the minimum

Apart from the location of the minimum, of particular interest is the curvature (second derivative) there. First make a separate file, copying only the data corresponding to the region about the minimum (where the data looks like a parabola). If you know how to differentiate the data and fit the derivatives using some software (xmgrace for example) then do that. Otherwise you can do it by hand as follows: Take each successive pair of data points, e.g. start with $x1, y1$ and $x2, y2$. The slope over this segment is $s1 = (y2 - y1)/(x2 - x1)$. Since the slope is actually changing this is only an approximation; in particular it is a reasonable approximation for the slope half-way between the two points. So take the x-value for this slope (and let's use z instead of x to avoid confusion)as $z1 = (x1 + x2)/2$. So the new data point is $z1, s1$. Next take $x2, y2$ and $x3, y3$ to make $z2, s2$. In this way construct a list of slopes (there should be one fewer than the original number of data points). If you plot this new data it should be quite close to a straight line which is zero at the minimum. It's OK[6] to remove a couple of points at the ends if they deviate from a straight line; it's only close to the

[4] However, this may appear to be violated if you make changes which are too big and you "overshoot" the minimum.
[5] You can get something more accurate by fitting the data to a parabola, but we won't do that here.
[6] Just this once!

minimum that we expect it to be really straight.
Question 5 : Find the slope k of this line: that is the curvature of the original energy curve.

Now, what is this good for?[7]. Actually, this is easiest to understand as the slope of the second data set you created (which itself consisted of the slopes of the first one). You may know that the slope (derivative) of an energy-versus-distance curve gives the associated force. So the straight line that we got by taking the slopes was just the force-versus-distance curve![8] Now, you may remember that when a force-versus-distance curve is a straight line through the origin, we are basically talking about a spring, and the slope is just the "spring constant". Here you have to take the minimum energy distance as the "zero" of the spring motion, so you can see that for small displacements about the minimum separation, the molecule is basically like a little spring. If you have studied "simple harmonic motion" before, you might know that the frequency of motion for a spring is $\frac{1}{2\pi}\sqrt{k/m}$ where m is the mass of the particle. Here because there are two particles, the mass you should use is actually half the mass of a single atom[9].
Question 6 : Look up the mass of carbon and try plug in the numbers to get the vibrational frequency, but make sure you are consistent with units!
Question 7 : Going back to the energy, write down an expression for the energy near the minimum in terms of k and the variable $x \equiv \Delta l \equiv l - l_0$.

3.7 Binding energy and breaking force

There is more to the energy versus distance curve than the minimum. Look at the full curve again. If it hasn't flattened out on the right then you haven't included enough points, so repeat the calculation with more points.
Question 8 : The "binding energy" of a molecule is the energy needed to break the bond—to remove the atoms to infinite separation, starting from the equilibrium configuration. What is the binding energy of the C_2 molecule?
Question 9 : Calculating the slopes as described above, now for the whole data set, giving the force-versus-distance curve, what force (in eV/Å) would you say is needed to break the C_2 molecule?

3.8 Different carbon bond types

Now, repeat all of the above with each of the different possible numbers of Hydrogen atoms included! (One, two and three hydrogens). The positions of the hydrogens have been hard coded to their experimental values with respect to the carbon atoms, so again all you have to do is play with the C-C separation. By having one, two or three hydrogen atoms per carbon atom you can make the C-C bond to be triple, double or single, respectively. The bond you have been working with is a quadruple bond, which is rarely found in practice.
Question 10 : Make a table showing (1) the equilibrium bond length (2) the spring constant (3) the vibrational frequency (just add the hydrogen mass to the corresponding carbon when determining the reduced mass) (4) the binding energy and (5) the breaking force, for all four types of C-C bond.
Question 11 : Rank the four types of bonds with regard to each of these properties.

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[7] You don't have to answer that.

[8] Strictly speaking I should be more careful to specify which atom's force I'm talking about, and also there's a minus sign I haven't mentioned, but these are not too important for this exercise.

[9] This is called the "reduced mass" for a two-body problem; if the masses are not equal then the reduced mass is $m_1 m_2/(m_1 + m_2)$

4 Quantum accuracy: Dacapo

We will now repeat a very few calculations using the Dacapo program. This program uses quantum-mechanical methods to accurately calculate energies and forces of atoms. It can handle only quite small numbers of atoms at a time[10]. Information about Dacapo can be found at http://www.fysik.dtu.dk/campos/Dacapo/. To pretend that you know how it works, learn the phrase "plane-wave density functional theory code using ultra-soft pseudopotentials". Believe it or not, that actually means something to theoretical physicists! Other useful phrases referring to this kind of simulation include "ab initio", or "first principles".

We will not include hydrogen atoms here (unless you have lots of time). The main difference in procedure is to click the button that says Switch calculator which should change the adjacent text from "asap" to "dacapo". It will take several minutes to calculate a single energy. What is happening during this time is that Dacapo is trying to find the electron wavefunctions that have the lowest energy (the so-called ground-state energy) for the given position of the atoms (nuclei). Calculate 5-10 energies around the minimum (you have an idea of where that is from the earlier work).

While these are running you may start the next section, which does not use the computer.

Question 12 : Once it has finished, determine the vibrational frequency of C_2 from your data.

5 Bulk Properties of Diamond

In this section we will consider the relation between the properties of individual bonds and bulk matter, in particular the diamond form of carbon. Properties such as equilibrium lattice spacing, cohesive energy (also called atomization energy) and elastic constants are closely related to the bond properties we have been investigating. In fact, in the common approximation that only nearest neighbor atoms in the crystal interact, and that the individual pair bonds do not affect each other, there are exact, simple relations between the bond properties and the bulk properties.

5.1 Pencil and paper calculations

First, you need a little information about the crystallography of diamond. A crystal is a solid made up of a group of atoms, called the unit cell, repeated many times (in theoretical work, as well as for most practical purposes, we take it to be infinite). The repetition makes what is called a *lattice*. One unit cell for diamond can be formed as follows. Take a cube of side a (called the lattice spacing or lattice constant), see Fig. 1(a). Next imagine placing atoms in the following four locations: $(0, 0, 0)$, $(0, a/2, a/2)$, $(a/2, 0, a/2)$, $(a/2, a/2, 0)$, see Fig. 1 (b). This is actually the unit cell for the crystal structure known as *face centered cubic*, or fcc.

Question 13 : You might guess, and you would be right, that there should be atoms on the other corners of the cube. Why don't we need to put them there?

Question 14 : Can you see where the name "face centered cubic comes" from?

Finally, to make the diamond lattice, for each of the four atoms you already have, add another atom, displaced by $(a/4, a/4, a/4)$ from the initial atom. This is the diamond unit cell, containing eight atoms (actually you can make a different unit cell for diamond containing only 2 atoms but this one is easier to understand). See Fig. 2.

Question 15 : The displacement mentioned above, $(a/4, a/4, a/4)$ is between two nearest-neighbors of the diamond lattice. What is the nearest-neighbor distance in terms of a?

[10] 50 would be pushing it quite hard, though it depends also on which atoms. Carbon is relatively easy; transition metals are hard.

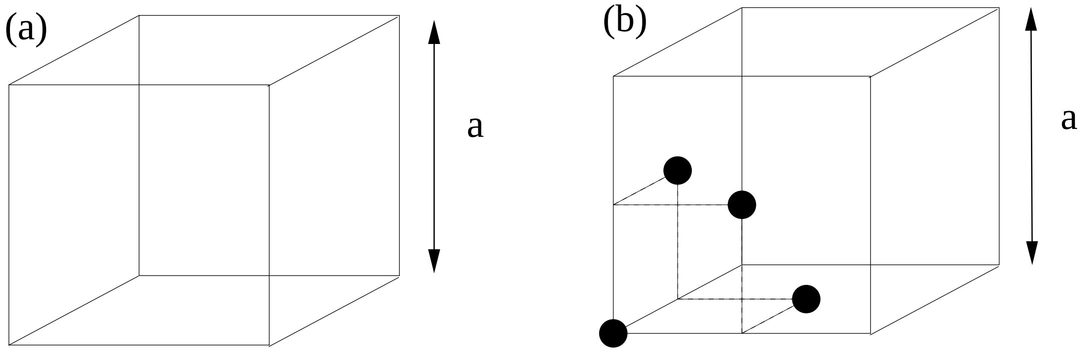

Figure 1: (a) A cube of side a (b) Cubic unit cell for fcc lattice, lattice constant a

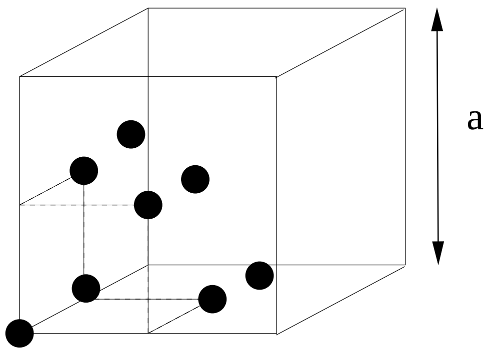

Figure 2: Cubic unit cell for diamond lattice, lattice constant a

Question 16 : How many nearest-neighbor bonds does each atom have?
Question 17 : How many such bonds are there per unit cell?
Question 18 : Which of the dimer bond types from above do you think is most likely to represent the bonds in diamond?
Question 19 : Assuming this bond type, what should the lattice constant of diamond be?
Now we will estimate the *cohesive energy* of diamond. This is the energy, usually expressed in kiloJoules per mole, required to completely separate the atoms from each other.
Question 20 : What is the energy required (for the type of bond you assumed) to break all of the bonds in one unit cell?
Question 21 : What is the cohesive energy in eV per atom?
Question 22 : How many unit cells are there in one mole of diamond? (Recall the one mole contains $N_A = 6.0221367 \times 10^{23}$ atoms)
Question 23 : What is the energy to break all of the bonds in one mole of diamond, in eV?
Question 24 : What is the cohesive energy in kJ/mol?

Next we will consider the *bulk modulus*, B, of diamond. B is related to the bond force-constant (k), the way the cohesive energy is to the bond breaking energy. It is the most basic measure of elasticity, or "springiness", of a bulk material, whereas k is related to the springiness of individual bonds. Again this is about counting bonds and expressing things in appropriate units, although it's a little more involved than the cohesive energy was. To start with we will define B in terms of strain and energy[11]. We have

$$\Delta E = \frac{1}{2} V B \left(\frac{\Delta V}{V} \right)^2 \tag{1}$$

for a piece of crystal with volume V (which we can take to be one unit cell, for convenience, so $V = a^3$). The dimensionless quantity $\Delta V/V$ is called the (volume) strain. In elasticity the strain is always assumed to be small so we can drop any terms that come up with higher powers of strain. This goes for all the "delta" (Δ) quantities too.
Question 25 : What is ΔV in terms of Δa, the change in the lattice spacing? What is it in terms of Δx, the change in the bond lengths?
Question 26 : There is a simple relation between volume strain($\Delta V/V$) and what one might call "linear" strain, $\Delta a/a$. Write this down.
Question 27 : What is the quantity on the left hand side in terms of k and Δx
Question 28 : Now you should be able to solve for B in terms of k and a. Write down the result. What are the SI units of B?
Question 29 : Using the results from the appropriate dimer bond, calculate a value for B, writing down the answer both in eV-Å-type units and in SI units.
Question 30 : Finally, compare your answers to the experimental values for E_{coh} and B which should be displayed on the board in the computer room. Write down the differences between your values and the experimental ones as percentages of the experimental.

5.2 Diamond by simulation

In this section we will see how directly simulating the diamond crystal might improve our calculations of E_{coh} and B. First click Switch Calculator so that we use Asap again, then choose Diamond from the Structures menu and again Vary Structural Parameter from the Computations menu. Choose to vary the

[11] It can also be done in terms of pressure, but energy is the easiest way to make the connection with bonds.

0th parameter, from say 3Å to 6Å. Use a different filename from what you used before! It is a good idea to use Visualize to look at the crystal and see how many atoms are actually being simulated (particularly because it is different when you use dacapo).

Question 31 : How many unit cells are being simulated?

Plot the data, which now is the total energy of the crystal (note the third column in the data file gives the energy per atom)

Question 32 : What is the lattice constant of minimum energy? Is it the same as you predicted based on the bond properties?

Knowing the equilibrium value of a, we can turn other values of a into linear strains. Using the relation you derived above this can then be turned into volume strain. Make a new data file where the x-values (first column) are the volume strains, and y-values are the same energy values as before.

Plot the new data file, energy against volume strain. The data around zero strain should be parabolic. Make a judgment on which data points are within the parabolic region and copy those data to a new file.

Question 33 : Next using xmgrace's fitting procedure, or any other method you know, find the curvature of this parabola. From the definition of B above you should be able to write down its value immediately. How does it now compare to the experimental value?

Optional: Repeat this whole section, but switch to dacapo. This time choose a range of a within the parabolic region about the minimum (of course, dacapo might have a different idea of where the minimum is, but probably not too different), and choosing the step size so that perhaps ten calculations will be done. This is the easiest type of calculation for dacapo, because there is no vacuum needed. Each data point should take maybe 20 seconds. Again either before or after dacapo has run use Visualize to check the number of atoms. How many unit cells are now being simulated? At the end write down your value for B and compare to experiment.

6 Graphene/Graphite: Cohesive energy

The most common form of pure carbon is *graphite*. This consists of layers of atoms, each of which is a hexagonal lattice. A single layer is known as *graphene*. Separate layers interact only weakly with each other, sliding easily over each (making graphite rather soft). To see the structure of a graphene layer, choose Graphene from the Structures menu, and leave the parameters at their default values. Click on Visualize and choose 3 unit cells in the x- and y-directions and 1 in the z-direction. Observe how the layer consists of interlocking hexagons.

Now choose Single Energy from Computations and Run to find the energy of this structure according to Asap/Brenner. The default bond length l has been chosen to be close to the minimum value, but check this by using Vary Structural Parameter to vary the value for l.

Question 34 : Write down the binding energy of graphene (in eV/atom).

Next, select Graphite. This time there are two lattice parameters, a and c; a is the lattice constant within a layer, and is $\sqrt{3}$ times the C-C bond length l, while c is twice the separation between adjacent layers[12]. Again Visualize and rotate the structure with the mouse in order to see the hexagonal structure with the layers.

You might like to try varying c as well, where you will notice something strange: it has no effect on the energy! This is a failure ("limitation" would be a kinder word) of the Brenner potential: in reality all atomic structures have *some* interaction when brought sufficiently close to other structures, even if they are inert

[12] These are the standard lattice parameters for hexagonal crystals in 3D.

(such as Argon or a stable molecule). Because c actually has no effect on the energy, it shouldn't surprise you that graphene and graphite have the same energy (if you take c to infinity in graphite, you get graphene!).
Question 35 : How does the binding energy of graphene/graphite compare to that of diamond? Is there a connection between this comparison and the fact that graphite is more common than diamond?
Optional: Graphite should be reasonably fast (about one minute) to calculate using dacapo. Do a few Single Energy calculations with different values of c. Unlike with Asap/Brenner, you should notice some variation, although if you went ahead with the whole procedure of calculating the binding energy and curvature for this variable, you would get rather low values (meaning that the interaction is quite weak).

7 Nanotubes

Now (finally!) let's look at carbon nanotubes. The first thing to do is just to create the structures and visualize them. Choose Nanotube from the structures menu, and accept the default values for the options. Click on Visualize (default options). Like crystals, carbon nanotubes have unit cells, which repeat along the tube axis (so they are kind of like one-dimensional crystals). The more symmetric tubes, arm-chair and zig-zag, have small unit cells. You should now see one unit cell of a (5,5) nanotube. If you click Visualize again and this time slide the scale for repetitions in the z-direction to 3 or 4, you'll get a better sense of it as a tube. Use the mouse to rotate the tube around to see it from different angles.

7.1 Energies

Note: We have to be a little careful here when using Asap/Brenner. Nanotubes with very short unit cells can cause it to give wrong results because of the periodic boundary conditions interfering with the intrinsic range of the potential[13]. So for all calculations involving symmetric nanotubes, that is armchair ($n = m$) and zig-zag ($m = 0$), and using Asap/Brenner, set the number of unit cells to 2.
Note: We will be looking at the energies of different kinds of nanotubes and comparing them. The only sensible way to do this is to look at the energy **per atom**. In the output files this always appears in the third column (column 2, if you call the first one column zero). If you click on Plot Data you should choose Plot column 2 to get the energy per atom.

If you choose Single Energy from the Computations menu and click Run you will get the energy for the default parameters. This will not necessarily be the minimum energy, since the default C-C bond length is that for an infinite sheet of graphene, which tends not to be the value favored by nanotubes (it tends to expand to reduce the extra energy due to the curvature). What things can we vary to find a lower energy? In the dimer we varied the separation between the two carbon atoms. In diamond and graphite we varied the lattice spacing. What can we do here? In principle the positions of all atoms in the unit cell can be varied. We're going to make the assumption that the nanotube is happy to stay as basically a rolled up graphene sheet, or just a cylinder[14]. A cylinder has two parameters: radius and height. So starting from the default shape, we could squeeze or stretch it along its length, or we could squeeze or expand it radially. However, minimizing with respect to two variables is a little tricky so we will combine them, and vary the overall "scale" of the nanotube (equivalent to uniformly scaling the volume). To do this we will simply vary the C-C bond length (the unit cell size simply scales with this), as we did with the dimer! So choose Vary Structural Parameter in Computations, and choose a small range which includes 1.42, the initial guess

[13] This would be a problem with the other structures too, but the number of unit cells has been selected appropriately to take care of it. With the nanotubes it is important to let the user have control over the number of unit-cells.
[14] and doesn't, for example, want to buckle or deform in some weird way, or turn into a completely different structure.

(note that it is parameter 2 that is being varied). The differences from one nanotube to another will be quite small so make the step size about 0.001 Å.

Question 36 : Run, then either by looking at the output file, or viewing in xmgrace, write down the minimizing bond length, as well as the energy per atom at the minimum.

Question 37 : How does this compare to graphite and diamond?

Question 38 : This nanotube was (5,5). Repeat the procedure for several arm-chair nanotubes, i.e. (n, n) with n ranging from say 3 to 20 (choose say 8 or 9 values). Make a plot, either by hand or using xmgrace, of the minimum energy versus n.

Question 39 : Now do the same for zig-zag tubes, $(n, 0)$, with the same range of n. Add these values to the arm-chair plot. Do the two curves coincide?

The curves shouldn't coincide. What is the main reason that these tubes have different energies (per atom)? It is the curvature. The curvature measures the difference from being flat (obviously) or in other words, the difference from a graphene sheet.

Question 40 : Draw a horizontal line on your plot at the energy of graphene. Do the curves approach this value as n gets bigger?

It may be obvious that n getting bigger implies the diameter getting bigger, and you may also realize that to compare different types of nanotubes we should plot the energies against the diameter, not against n.

Question 41 : Using the formulas $d = a\sqrt{n^2 + m^2 + nm}/\pi$, $a = \sqrt{3}l$, and the values of l (C-C bond length) you determined, write down the diameter of all the tubes you have simulated.

Question 42 : Now make a new plot of energy versus diameter. Both curves should now collapse onto one.

Question 43 : Can you guess the functional form of the dependence on d? A reasonable guess is an inverse power law $E = A + B/d^\alpha$. A quick way to see what α is, is to make a new plot of E against $1/d^\alpha$, starting with $\alpha = 1$, then $\alpha = 2$, etc, and to see which of these gives a straight line. Write down your determination of α.

Optional: Can you give an argument for why α has this value?

Optional: Taking the (5,5) tube again, at the optimal C-C bond length, investigate the tendency to shrink or expand in the radial or vertical directions by choosing Radial Strain and Vertical Strain respectively from the Computations menu. Vary the scale factor from about 0.95 to 1.05 in steps of 0.01 (leave the MDMin iterations at 0). In the resulting output, if the minimum is not at 1.0, then there is a tendency to shrink or expand in the appropriate direction. Actually if it wants to shrink radially it should want to expand vertically and vice versa, because we have already optimized the volume, so further optimization wouldn't change the volume.

7.2 Strength of nanotubes

OK, so now let's get to the real fun. How strong are nanotubes, in fact?[15]. Choose a (5,5) tube (set the C-C bond length to the value you noted had the minimum energy above), and select 4 unit cells. Choose Vertical Strain from Computations, setting the initial scale to 1.0 and the final one to 2.0 (i.e. we will double its length), with steps of 0.05. Leave the MDMin steps at 0 and press RUN. Use Plot Data or xmgrace to look at the total energy (so, "column 1" when you use Plot Data or the second column when you use xmgrace).

Right now we have an energy versus length-scale-factor (how much times the original length). Before we can take the slope we need energy versus length (analogous to energy versus separation in the dimer case). So we need to multiply the x-values by the original length. The easy way to find the original length is to

[15] Or at least maybe not in fact, but according to the Brenner potential.

click Visualize, which will cause the coordinates of the atoms, and more importantly, the vectors describing the 'box' containing the tube, to be printed out under "Unit cell vectors, Angstrom". The number we're interested in is the (3,3) entry of the displayed matrix[16]. This is the height of the periodically repeated cell, and therefore the length of the part of the tube whose total energy you have plotted. Make a new data set (a file, or on paper) with energy versus length and now take the slopes as you did before. This is the force as a function of how long you stretch the tube.

Question 44 : Write down the maximum force. This is a first estimate of the breaking force of the tube. Convert it into Newtons by multiplying by 1.6×10^{-9}. It doesn't sound very big does it? But remember, we're talking about a tiny tube here. We can calculate a more appropriate quantity than the bare force, but first let's do a better calculation.

Choose Vertical Strain again, but now set the scale step to 0.01, and the "Number of MDMin iterations" to 100. Leave the time step at 0.05. MDMin is an algorithm that does further minimization with respect to the atom positions within the unit cell, for a given amount of stretch. The atoms generally won't stay still as you stretch, you know! Press run again. The calculation will take longer now, because now the stretching is broken into 100 steps, and for each of those we're doing 100 steps of minimization.

After again multiplying the x-values by the undeformed length and taking the slopes, you should see something interesting: a sharp drop in the force versus distance curve. What does this mean? You can get an idea by visualizing the deformed nanotube. In the Visualize dialog box, check Use stored, in order to look at the structure that resulted from the calculation, rather than create a fresh undeformed nanotube.

Question 45 : Describe in a few words the final state of the tube.

Depending on what kind of nanotube you simulate, as well as (sometimes) details of how you to the minimization between steps, and how big the steps are exactly[17] different things can happen: you can get a clean break in the tube or defects can be created, such as holes in the hexagonal lattice, or the tube can get drawn out into a wire of atoms. These deformations can occur via several steps, each of which leads to a sudden drop in energy. We will call the "strength" of the tube the force required for the first of these events (materials scientists often talk about "yield stress" and "fracture stress", because typically in materials some kind of severe deformation happens before actual fracture, but we will keep things simple).

Question 46 : Taking the slopes as usual, find the maximum force (before the first drop in energy), i.e. the strength of the tube. It should be somewhat lower than the value you determined without the extra minimization. Write it down in eV/Å(the units it comes out in naturally) and in Newtons.

Question 47 : Now, to make comparisons with other materials, we really need the *stress*, or force per unit area (like pressure, but for pulling). What area should be used? For practical purposes that depends on how you would bundle many tubes together, but let's be simple and take the cross-sectional area of the tube. Using the C-C bond length that you initially specified, and the formulas given above, find the diameter[18], then the area. Write down the stress (force/area) in eV/Å^3. The usual unit for this kind of stress is the GPa (giga-Pascal) or $10^9 Pa = 10^9 N/m^2$. The conversion factor is 1e/Å^3 = 160.2 GPa. Write down the strength of the nanotube (the breaking stress) in GPa.

Question 48 : A high strength steel might have a strength of 0.8GPa. How much stronger is the (5,5) nanotube than this[19], according to the Brenner potential? Are you impressed?

[16] (2,2) if you like counting from zero.

[17] Which is of course is annoying. This business can be as much art as science.

[18] You might question the fact that we divide by the undeformed area when presumably it gets narrower as it's being stretched. This is standard engineering practice, because measuring the deformed area is not always possible.

[19] Our calculation is technically a zero-temperature one. The strength would be lower at room temperature.

8 Write-up

Your report for course 10030: Carbon Nanotubes should include answers to all numbered questions.

9 Possible problems

I get an error when I try to run Cbond Your path has not been set correctly. Did you follow the instructions under "Setting up your Unix environment"?

The calculation is taking for ever You may have switched calculator to "dacapo" instead of asap. Press Ctrl-C to end the program and start again. By default asap is used, otherwise push click on Switch calculator to switch between the two.

The energy per atom is different for different numbers of nanotube unit cells This should only be a problem when the unit cell is very short in the z-direction and when using asap. In that case going to two unit cells is necessary to avoid the Brenner potential having problems with periodic images of atoms.

My output file has not appeared Check first that the calculation has finished running (the Run button should pop back up)