

2

Carbon nanotubes

In this chapter I will describe the basic properties of carbon nanotubes regarding some electronic and mechanical properties. Those properties are the motivation for the study of this carbon structure.

2.1

Carbon

Carbon is an element with atomic number of 6, and a standard mass of 12. It can form a great variety of allotropes such as graphite, diamond, amorphous carbon, fullerenes, carbon nanotubes and the recently discovered graphene (1). The reason for the formation of those many materials and the formation of the huge number of carbon containing molecules, is the presence of four valence electrons on $2s^2 2p^2$ orbitals with almost no interaction with the higher binding energy $1s^2$ core electrons. Because of the low energy difference between the 2s and the 2p orbitals, the wave function of those four external electrons superpose with each other, in what is called Hybridization (3). This process allows a bigger binding energy between the carbon atoms and its surroundings.

Carbon nanotubes can be single wall (SWNT) or multi wall (MWNT). As shown in Fig 2.1, the first one can be viewed as a rolled graphene sheet and the last one can be visualised as multiples SWNTs inside each other. So, it is important to understand the basic properties of graphene in order to understand the basic properties of carbon nanotubes (3).

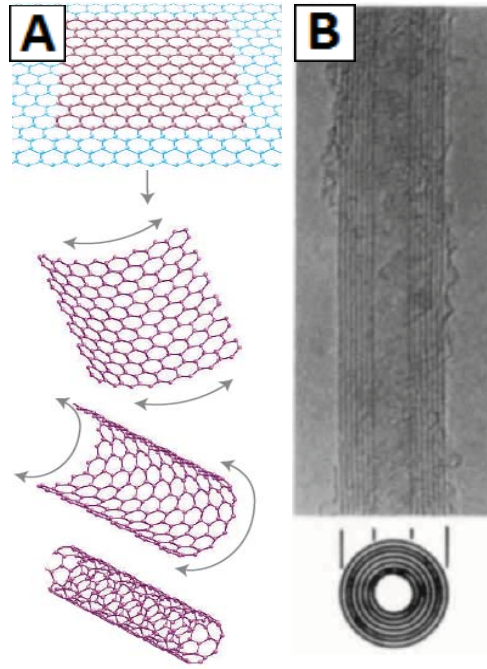


Figure 2.1: A) Shows a graphene sheet being rolled in a SWNT (1) and B) shows a high resolution TEM image of a MWNT (2).

2.2

Basic electronic properties of graphene

Graphene is made of carbon atoms with electrons on a sp^2 hybridization. This electron configuration leads to the planar hexagonal structure observed in Fig 2.1 with a σ bond between the carbon atoms and a π bound perpendicular to the graphene sheet. Eq (1) shows the wave functions of this hybridized orbital.

$$\begin{aligned}
 |sp_a^2\rangle &= \frac{|2s\rangle}{\sqrt{3}} - \sqrt{\frac{2}{3}}|2p_y\rangle \\
 |sp_b^2\rangle &= \frac{|2s\rangle}{\sqrt{3}} + \sqrt{\frac{2}{3}}\left\{\frac{\sqrt{3}}{2}|2p_x\rangle + \frac{1}{2}|2p_y\rangle\right\} \\
 |sp_c^2\rangle &= -\frac{|2s\rangle}{\sqrt{3}} + \sqrt{\frac{2}{3}}\left\{-\frac{\sqrt{3}}{2}|2p_x\rangle + \frac{1}{2}|2p_y\rangle\right\}
 \end{aligned} \tag{2-1}$$

We can perform a simple tight binding calculation on the electrons of the $2p_z$ orbitals of this structure to find the energy dispersion of the π energy bands, which are the most important for the electronic properties of graphene (3).

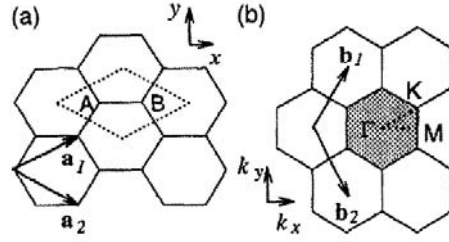


Figure 2.2: (a) Shows the graphene's hexagonal structure, unit cell and lattice vectors. (b) Shows the reciprocal lattice vectors (3).

Selecting the unit cell, the lattice vectors $\vec{a}_1$ and $\vec{a}_2$ and the reciprocal lattice vectors $\vec{k}_1$ and $\vec{k}_2$ of Fig 2.2, we can calculate the energy dispersion eq (2). Where γ_0 is the nearest neighbor transfer integral, s is the overlap integral and $a = \sqrt{\vec{a}_i \cdot \vec{a}_i} = 0.249\text{nm}$ is the graphene's lattice constant. The result of this calculation is plotted on Fig 2.3.

$$E_{\text{Graphene}}(\vec{k}) = \frac{\epsilon_{2p} \pm \gamma_0 \omega(\vec{k})}{1 \pm s \omega(\vec{k})}$$

$$\epsilon_{2p} = \langle \phi_A(\vec{r} - \vec{R}) | \mathbf{H} | \phi_A(\vec{r} - \vec{R}) \rangle$$

$$\gamma_0 = \langle \phi_A(\vec{r} - \vec{R}) | \mathbf{H} | \phi_B(\vec{r} - \vec{R}') \rangle$$

$$s = \langle \phi_A(\vec{r} - \vec{R}) | \phi_B(\vec{r} - \vec{R}') \rangle$$

$$\omega(\vec{k}) = \sqrt{1 + 4 \cos \frac{\sqrt{3} k_x a}{2} \cos \frac{k_y a}{2} + 4 \cos^2 \frac{k_y a}{2}} \quad (2-2)$$

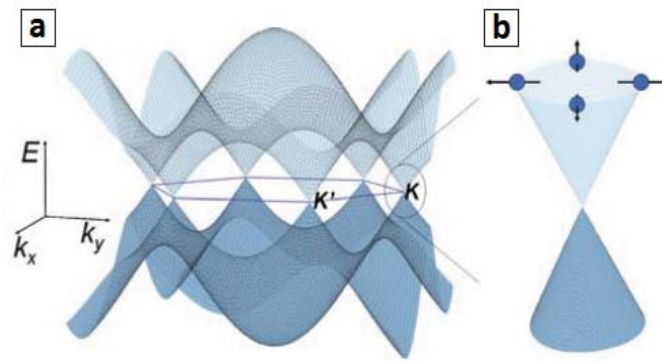


Figure 2.3: a) Shows the energy dispersion of the π band. b) Shows a zero energy gap on the k point (4)

From those relations, we can calculate the density of states of graphene and realize that this material is a zero gap semi conductor at the K point, that is a high symmetry point of the brillouin zone defined at Fig 2.2. This means that any energy value can send an electron from the valence band to the conduction band at this point, and it gives rise to quantum effects on carbon nanotubes (3).

Now we are going to show some basic properties of the structure of carbon nanotubes and then apply the preceding graphene's properties on that structure.

2.3 SWNT structure

Single wall carbon nanotubes can be divided in two categories, depending how the graphene sheet will be rolled to form the tubes. Fig 2.4 shows a graphene sheet with two dashed lines. The angle between them is 30° and the graphene sheet can be rolled in any direction between these two lines in order to form the tubes. This direction will be perpendicular to the nanotube axis. If the chosen direction is 0° or 30° , the SWNT is said to be achiral. More specifically, the 0° direction is said to be zigzag and the 30° direction is said to be armchair. If the sheet is rolled between those angles, the SWNT is said to be chiral. It is important to note that an angle higher than 30° will add no different result from what I have said, since an angle of $(60-\alpha)^\circ$ would just have the same effect of an angle of α° and so on.

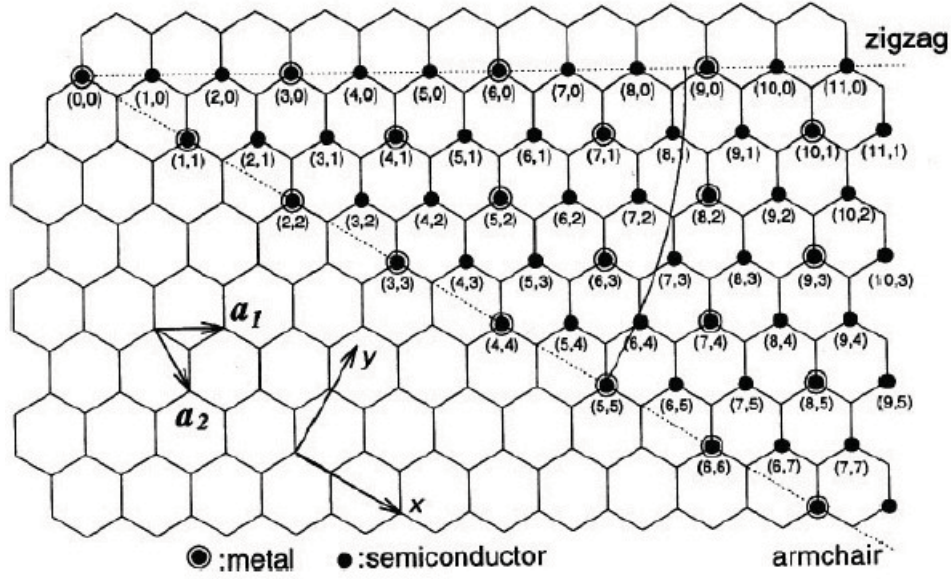


Figure 2.4: The two dashed lines define the limit to the points (n,m) that can form the SWNTs (5).

To form the SWNT structure, the graphene sheet is rolled from the point (0,0) on Fig 2.4 to any point (n,m) given that $0 \leq |m| \leq n$. Considering that the length of the tube is much bigger than the tube's diameter, the pair of numbers (n,m) provides all the SWNT features. The vector linking the point (0,0) to the point (n,m) is called chiral vector and is defined by $\vec{C}_h = n\vec{a}_1 + m\vec{a}_2$, where the vectors $\vec{a}_1$ and $\vec{a}_2$ are the unit vectors of the graphene unit cell found on Fig 2.4 (3).

By this vector, we are able to find the diameter and the translational vector of a (n,m) SWNT, which the last one is the unit vector of the tube (3). The diameter d is related with the chiral vector by:

$$d = |\vec{C}_h|/\pi$$

so,

$$d = a\sqrt{n^2 + m^2 + nm}/\pi \quad (2-3)$$

To find the translational vector $\vec{T}$, we require this vector to be perpendicular to $\vec{C}_h$:

$$\vec{T} = \frac{(2m+n)}{Q}\vec{a}_1 - \frac{(2n+m)}{Q}\vec{a}_2 \quad (2-4)$$

Where Q the greatest common divisor between $2m+n$ and $2n+m$. At last, another basic structural property that the (n,m) numbers can provide is the number of carbon atoms on the unit cell of the SWNT. The portion of the graphene sheet that is used to build the unit cell of the tube is formed by the

chiral and translational vector, and it has an area of $|\vec{C}_h \times \vec{T}|$. And since that area have $|\vec{a}_1 \times \vec{a}_2|$ graphene's unit cell areas, each one with 2 carbon atoms, the number of atoms on the SWNT unit cell is given by (3):

$$\text{Number of atoms} = 2N = \frac{4(n^2 + m^2 + mn)}{Q} \quad (2-5)$$

To find the reciprocal lattice vector of the SWNT, one have to make the following:

$$\begin{aligned} \vec{T} \cdot \vec{K}_1 &= 0 \\ \vec{T} \cdot \vec{K}_2 &= 2\pi \\ \vec{C}_h \cdot \vec{K}_1 &= 2\pi \\ \vec{C}_h \cdot \vec{K}_2 &= 0 \end{aligned} \quad (2-6)$$

Where $\vec{K}_1$ and $\vec{K}_2$ are the reciprocal SWNT vectors along the circumferential direction and nanotube axis respectively. Since we consider an infinitely long SWNT, the $\vec{K}_2$ vector will be continuous. However, the cylindrical structure of the tube will lead to a discrete integer multiples ranging from 0 to $N-1$ of $\vec{K}_1$. This feature can be visualized on Fig 2.5, where it is shown the reciprocal lattice vectors of a (4,2) SWNT as an example (3).

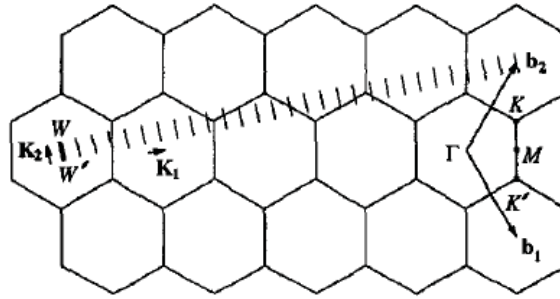


Figure 2.5: This figure shows the reciprocal lattice vectors of a (4,2) SWNT (3).

2.4

Basic electronic properties of SWNTs

One simple way to find the energy dispersion relation of a SWNT is replacing the reciprocal vectors $\vec{K}_1$ and $\vec{K}_2$ of a SWNT into the energy dispersion relation of graphene, in what is called zone folding method. Since the $\vec{K}_1$ vector is quantized due to the cylindrical structure of the tube, the

new energy relations will consist of N cross sections of the graphene's energy relation (3). Eq 7 shows the SWNT energy relations while Fig 2.6 shows those bands for some SWNTs.

$$E_{SWNT,\mu}(k) = E_{Graphene}(\mu\vec{K}_1 + k\vec{K}_2), \mu = 0..N-1 \text{ and } -\frac{\pi}{T} < k < \frac{\pi}{T} \quad (2-7)$$

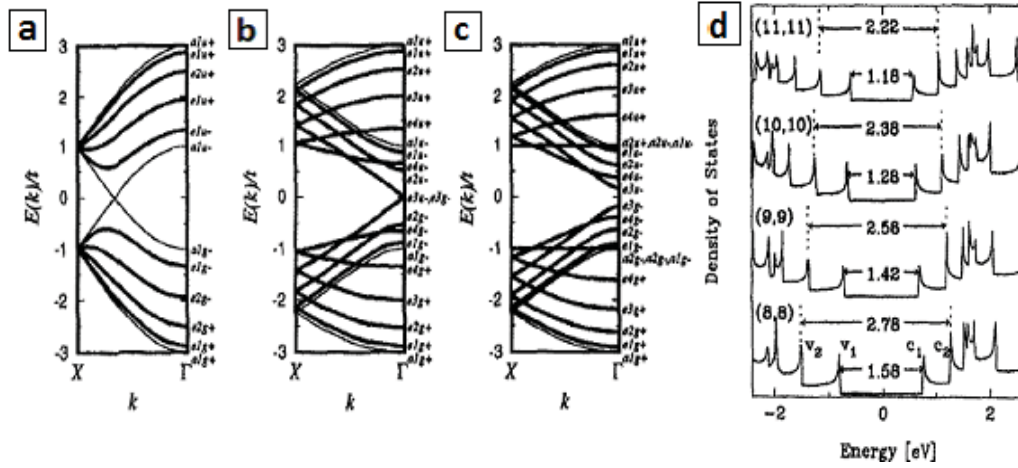


Figure 2.6: This figure shows the energy dispersion for a) (5,5), b) (9,0) and c) (10,0) tubes. d) Shows a plot of the density of states for some tubes (3).

The density of states on Fig 2.6d also shows the presence of peaks that are called Van Hove singularities. Those singularities are due to the cylindrical structure of the SWNTs that quantizes the momentum in the direction perpendicular to the axis and forms energy dispersions with several states with close values of energy. Those singularities are very important to characterization techniques, since electron transitions can occur between those peaks (3).

The SWNT will be a semi conductor if none of those cross sections passes through the K point of graphene. If one of those lines passes through this point, the tube will present a finite density of states at the Fermi level, and will have a metallic behaviour. As a general rule, it can be shown that the SWNT presents a metallic behaviour when the number $n - m$ is divisible by 3. However it is important to keep in mind that the calculation of those energy dispersions are only approximative and the $n - m$ relation can not be applied for SWNTs with diameter less than $\sim 0.5\text{nm}$ (24). Such nanotubes can be found as a central shell of a MWNT, into the channel of a porous crystal or anchored

to the surface of larger nanotubes (24). The metallic SWNTs have a ballistic conduction with a localization length that increase with the tube's diameter. For typical diameters, $\sim 1\text{nm}$, the localization length is over $10\mu\text{m}$, resulting in exceptional ballistic properties (13, 14).

2.5

Basic mechanical properties of SWNTs and MWNTs

Carbon nanotubes are also well known because of its mechanical properties. Min-Feng, Y et al., (6) made a tensile load experiment using MWNTs attached to two AFM tips, as shown in Fig 2.7. They found a Young's modulus on the direction of the tube axis ranging from $\sim 270\text{GPa}$ to $\sim 940\text{GPa}$ for the outer layers of the tested MWNTs (6). Tight binding calculations performed by Hernández, E et al., (15) shows that SWNTs have a Young's modulus on the order of 1.2TPa for the diameters ranging from 0.8nm to 2.0nm . They also performed calculations on other structures such as BC_3 , BN , and BC_2N SWNTs and found that those structures have a lower Young's modulus when compared with pure carbon SWNTs. The obtained values for them are around 0.8TPa to 1.0TPa . This decreasing in this values is due to the less strong interaction between the B-C or the N-C bond in comparison to the C-C bond. They also realized that this values remains approximately constant for diameters greater than 0.8nm for all kinds of SWNTs and have a decreasing value with the decreasing diameter (15).

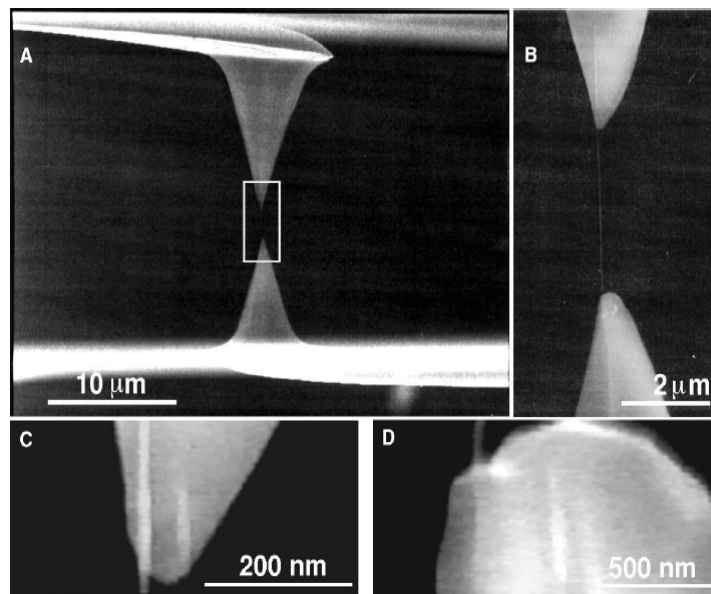


Figure 2.7: Multi Wall carbon nanotube attached to an AFM tip under a tensile load experiment (6).

Carbon nanotubes are quite soft on the direction perpendicular to the wall of the tube (3). More than that, experiments using AFM on the tapping mode had shown that MWNTs have a Young's modulus on the range of 0.3GPa to 4GPa on this direction (25).

2.6

Basic phonon relations of graphene and SWNT

Like the electronic properties, most of the the phonon mode features of the SWNTs can be understood and extracted by the relations of graphene. However, due to the cylindrical structure, the lower frequency modes of graphene will not correspond to the modes of same frequency on SWNTs and some corrections must be made (3). The phonon modes of graphene are described by solving the dynamical matrix equation $\det D(\vec{k}) = 0$ up to the 4th nearest neighbours on the graphene sheet. Fig 2.8 shows dispersions curves calculated by Pedro Venezuela et al., (7).

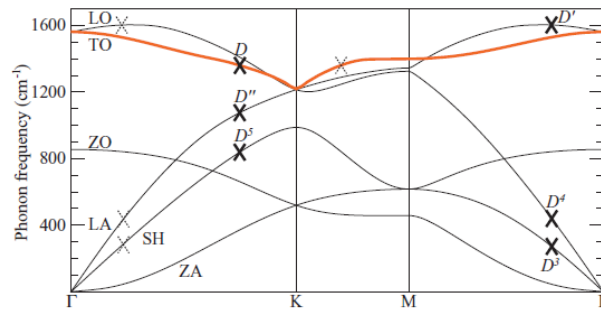


Figure 2.8: This figure shows phonon dispersion curve of a graphene sheet (7).

It is important to note, that due to curvature effects, some of the modes resulting from that equation can not be applied to SWNTs, as shown in Fig 2.9.

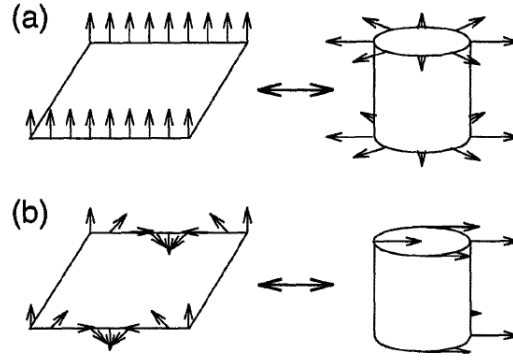


Figure 2.9: This figure shows a) a mode of the of graphene sheet that gives rise to a nonzero mode on a carbon nanotube and b) an acoustic mode of graphene that can not be applied on SWNTs (3).

Taking in account the curvature effects into the dynamical matrix, we get a new dispersion relation for phonons on the SWNT. The plot on the Fig 2.10 shows the dispersion curves.

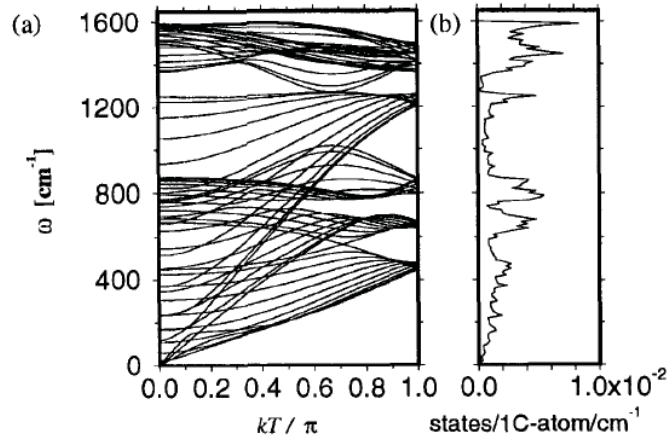


Figure 2.10: This figure shows a) phonon dispersion curve and b) a plot of the density of states of a (10,10) SWNT taking in account the curvature effects into the dynamical matrix (3).