Chapter II

Generalities- Structure of Single-Walled Carbon Nanotubes and Model Potential

2.1 Introduction

Since the discovery of carbon nanotubes in 1991 by Iijima [5], these tubular all carbon-molecules have aroused lot of interest. This is because they show ideal and novel mechanical and electrical properties, which in turn are intimately related to the atomic configuration of the tube structure. Changes in atomic configuration can manifest themselves as local structure deformations in the bond lengths and bond angles. Such structural changes can be induced by various chemical treatments or by mechanical means such as exerting stress, bending strain or when applying pressure on the tube, which can be seen as a very promising way to study the mechanical and electrical properties.

There are numerous ways to roll a graphite sheet to obtain a tube and the resulting structures are most commonly classified by an index pair \((n,m)\) that defines the tube structure in a unique way. The details of this common classification scheme of carbon nanotubes have been given in this chapter. The pair of indices \((n,m)\) defines the chirality, that is, how the hexagons formed by carbon atoms are oriented with respect to the tube axis.

2.2 Crystal structure

A carbon nanotube can be viewed as a sheet of graphite folded into a cylinder (Figure 2.1).

Figure 2.1: Illustration of the structure of a single-walled carbon nanotubes from graphite sheet.
In order to understand the structure of carbon nanotubes, we therefore begin by describing the crystal structure of a graphite sheet.

### 2.2.1 A graphite sheet

Graphite is one of the many forms in which carbon is found in nature. It is built up of weakly coupled layers, separated by 0.34 nm\(^{14,17}\) shown in Figure 2.2(a). Each layer consists of hexagonal (honeycomb) lattice as seen in Figure 2.2(b), where the distance between two neighboring carbon atoms is \(a_{\text{cc}} = 0.142\) nm\(^{16}\) . The layers are ABA on top of each other.

![Diagram of graphite sheet](image)

Figure 2.2: (a) Illustration of the atomic positions in a crystalline graphite. (b) The atomic configuration of a single layer of graphite, known as graphene sheet, showing basis vectors \(\vec{a}_1\) and \(\vec{a}_2\). (c) The unit cell of graphite sheet which contains two carbon atoms and the vector \(\vec{d}\) connect the two carbon atoms in a unit cell. The unit cell is marked by the thick parallelogram.
A single layer of graphite is called a graphene sheet and is shown in Figure 2.2(b) along with the coordinate system chosen to describe the lattice. The hexagonal structure is not a Bravais lattice, and the lattice is described by a two atom basis \([113]\) and two non-orthogonal basis vectors \(\vec{a}_1\) and \(\vec{a}_2\) which, with the chosen coordinate system, are seen to have coordinates:

\[
\vec{a}_1 = \left(\frac{\sqrt{3}}{2}a, \frac{1}{2}a\right) \quad \text{and} \quad \vec{a}_2 = \left(\frac{\sqrt{3}}{2}a, -\frac{1}{2}a\right),
\]

where the graphite lattice constant value can be employed as a first approximation for the length of the basis vector \(a\) and is given by:

\[
a = |\vec{a}_1| = \sqrt{3}a_{\text{cc}} = 2.4612 \ \text{Å},
\]

because the length of the carbon-carbon bond is 1.42 Å and in nanotubes, the curvature induced small chirality dependent variation from graphite bond length. The two atoms in each unit cell are labelled by \(A\) and \(B\) as shown in Figure 2.2(c). Graphene can therefore be described by two equivalent sub lattices with \(A\) and \(B\) atoms at \(\vec{R}_A = n_1\vec{a}_1 + n_2\vec{a}_2\) and \(\vec{R}_B = n_1\vec{a}_1 + n_2\vec{a}_2 + \vec{d}\), respectively, where \(n_1\) and \(n_2\) are integers and the distance \(\vec{d}\) expressed as:

\[
\vec{d} = \frac{1}{2}(\vec{a}_1 + \vec{a}_2),
\]

is equal to \((a_{\text{cc}},0)\) and it connects the two atoms in the unit cell.

### 2.2.2 A Carbon nanotube

The most commonly used notation to differentiate between nanotubes is introduced here. The notation follows that of Saito et al.[17]. The hexagonal network of Figure 2.3 depicts a graphene layer where each of the hexagon corners represents a position of a carbon atom. The graphene layer can be thought of as a tube cut open. Therefore, the figure can be used to visualize the notation and concepts discussed.
To construct the lattice of a single-walled carbon nanotube, a sheet of graphite is folded into a cylinder. Or to put it mathematically: a conformal mapping (i.e. an angle conserving mapping) from a plane of graphene to a cylinder is made. This can be done in many ways.

To distinguish differently folded carbon nanotubes, the chiral vector $\mathbf{C}_h$, that joins two points O and A (or equivalently B and B' as shown in Figure 2.3) on the tube surface, is defined as:

$$\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2,$$  \hspace{1cm} (2.4)

where $n$ and $m$ are integers and each pair of these integers represents a possible tube structure and can be used to classify the structures. The chiral vector $\mathbf{C}_h$ connects the two sides which are folded together and it, thereby, becomes the circumference of the nanotube. Therefore, the crystal structure of a single-walled nanotube is specified by indices $(n,m)$ from equation 2.4. Consider Figure 2.3 and imagine the following operation: for any two lattice points O and A connected by chiral vector $\mathbf{C}_h$, we cut the graphite sheet along the two lines perpendicular to $\mathbf{C}_h$ going through O and A. The strip thus obtain can be rolled into a seamless cylinder by rolling $\mathbf{C}_h$ end to end and thereby the complete crystal structure of the nanotube can be obtained.

![Figure 2.3: Wrapping a graphite sheet to an (n,m) nanotube. The chiral vector $\mathbf{C}_h$ and the strip OABB' can then be rolled into a seamless cylinder by rolling $\mathbf{C}_h$ end to end to construct the completed nanotube.](image)
An alternative way of characterizing the nanotube is by its diameter \( d_t \) and the chiral angle \( \theta \) which is defined as the angle between \( \vec{a}_1 \) and \( \vec{C}_h \). In Figure 2.3, it can be seen that the circumference length of the nanotube is the length of the chiral vector \( |\vec{C}_h| = \sqrt{\vec{C}_h \cdot \vec{C}_h} \) and then the diameter is given by:

\[
d_t = \frac{a}{\pi} \sqrt{n^2 + nm + m^2}.
\]  

(2.5)

The chiral angle \( \theta \) has the values ranging from 0 and \( \frac{\pi}{6} \) because of the hexagonal symmetry of the graphite lattice. The cosine of the chiral angle is expressed with \( n \) and \( m \) as:

\[
\cos \theta = \frac{\vec{C}_h \cdot \vec{a}_1}{|\vec{C}_h| |\vec{a}_1|} = \frac{n + m}{\sqrt{n^2 + nm + m^2}},
\]

or we can put the chiral angle as:

\[
\theta = \tan^{-1}\left(\frac{\sqrt{3}m}{2n + m}\right).
\]  

(2.6)

For each tube with \( \theta \) between 0° and 30°, an equivalent tube with \( \theta \) between 30° and 60° exists, but the helix of graphene lattice points around the tube changes from right-handed to left-handed. The chirality of single-walled nanotubes defined as the ratio \( m \) to \( n \) (i.e., chirality \( = m/n \)). The chirality for achiral tubes: armchair tubes have chirality equal to one while zigzag tubes have zero chirality. For chiral tubes, the chirality is different by different \( m \) and \( n \).

Because of the six-fold rotational symmetry of graphene, to any other chiral vector, an equivalent one exists with \( \theta \geq 60° \). We will hence restrict ourselves to the case \( n \geq m \geq 0 \) (or \( 0° \leq \theta \leq 30° \)). Tubes with indices \((n,n),(\theta = 30°)\) and \((n,0),(\theta = 0°)\) are rolled along symmetry axis of the graphene sheet, and therefore posses special symmetry themselves; they are non-chiral (achiral) single-walled nanotubes, and we denote them armchair and zigzag tubes, respectively. The name derives from the pattern formed when a particular tube is cut perpendicular to tube axis. Zigzag tubes having a zigzag pattern around the circumference and one can see an “armchair” pattern around the
circumference in armchair tubes[114]. Tubes with \((n,m)\), \((n \neq m, 0^\circ < \theta < 30^\circ)\) are called chiral nanotubes. These three patterns are shown in Figure 2.4.

Figure 2.4: Grahite sheet with different values of \(n\) and \(m\) and chiral vector (dot and solid lines). The carbon atoms indicated by colour circles. The blue and red colour atoms show the zigzag and armchair patterns, respectively, while the green colour atoms show chiral arrangement.

From here on, a nanotube structure will be identified by the indices \(n\) and \(m\) and, correspondingly, it will be referred to as an \((n,m)\)-nanotube [14]. Figure 2.5 shows an illustration of the atomic configurations for a section of carbon nanotubes.

Figure 2.5: Structure of single walled carbon nanotube of non-chiral \((10,10)\), \((15,15)\) and chiral \((12,7)\), \((13,7)\) (up). The cross-sectional view of these tubes (down), the width of the dark area is representative of one carbon atom (as in \((15,0)\) or two atoms (as in \((10,10)\).
2.2.3 Translational unit cell

Any nanotube has translational symmetry along the tube axis and therefore it also introduces a large unit cell along the tube axis, which we refer to as the translational unit cell. This unit cell contains a much large number of atoms than two. The translational symmetry can be generated by a lattice vector along the tube axis (commonly called the translational vector [14]) and expressed as:

\[ \vec{T} = t_1 \vec{a}_1 + t_2 \vec{a}_2, \]  

(2.7)

where \( t_1 \) and \( t_2 \) are integers. This translational vector, \( \vec{T} \), is defined as the smallest possible lattice vector (of graphene) perpendicular to \( \vec{C}_h \) and thus parallel to the nanotube axis, as shown in Figure 2.3.

It represent the translation required in the direction of the nanotube axis to reach the nearest equivalent lattice point. By using \( \vec{a}_i \cdot \vec{a}_j = a_i^2 \delta_{ij} + \frac{a_i^2}{2} (1 - \delta_{ij}) \), one has \( \vec{C}_h \cdot \vec{T} = 0 = \frac{a_i^2}{2} \left[ t_1 (2n + m) + t_2 (2m + n) \right] \). Since \( t_1 \) and \( t_2 \) are integers which should be as small (in absolute value) as possible, the expressions for \( t_1 \) and \( t_2 \) in terms of \( n \) and \( m \) are obtained as \( t_1 = -F (2m + n) \) and \( t_2 = +F (2n + m) \). The constant \( F \) is determined by the requirement that \( \vec{T} \) specifies the translation to nearest equivalent lattice point, that is, \( t_1 \) and \( t_2 \) do not have a common divisor except unity. Thus

\[ F = \frac{1}{\gcd(2m + n, 2n + m)} = 1/\gcd_h, \]

Therefore the translation vector is:

\[ \vec{T} = \frac{2m + n}{\gcd_h} \vec{a}_1 - \frac{2n + m}{\gcd_h} \vec{a}_2, \]  

(2.8)

where \( \gcd_h \) is the greatest common divisor of \( (2n + m, 2m + n) \).
The translational period (or the unit cell length) $|\mathbf{T}|$ can be determined in terms of the chiral indices $(n,m)$ as:

$$|\mathbf{T}| = \frac{\sqrt{3}a}{\text{gcd}(n,m)} \sqrt{n^2 + nm + m^2}$$  \hspace{1cm} (2.9)

Thus, the nanotube unit cell is formed by a cylindrical surface with height $|\mathbf{T}|$ and diameter $d_t$. For achiral tubes, equations (2.4) and (2.9) can be simplified to:

$$|\mathbf{T}_z| = \sqrt{3}a, \quad |\mathbf{C}_\alpha| = na \quad \text{(zigzag)} \hspace{1cm} (2.10)$$

$$|\mathbf{T}_t| = a, \quad |\mathbf{C}_\lambda| = \sqrt{3}na \quad \text{(armchair)}$$

### 2.2.4 Unit cell of carbon nanotube

The unit cell of nanotube is defined as the area enclosed by the translational vector $\mathbf{T}$ and chiral vector $\mathbf{C}$, and is in the form of a cylindrical surface with height $|\mathbf{T}|$ and diameter $d_t$. The number of carbon atoms in the unit cell of nanotube $n_c$ can be calculated by dividing the area of the unit cell of nanotube i.e., $A_u = |\mathbf{T}| |\mathbf{C}|$ of the cylindrical surface by the area of one hexagon $A_h$. This ratio of these two areas gives the number of graphene hexagons $q$ in the nanotube unit cell:

$$q = \frac{A_u}{A_h} = \frac{2(n^2 + nm + m^2)}{\text{gcd}(n,m)},$$  \hspace{1cm} (2.11)

where $A_h = |\mathbf{a}_x \times \mathbf{a}_z| = \frac{\sqrt{3}}{2}a^2$ is the area of hexagon.

Since each graphene unit cell contains two carbon atoms, and then the number of atoms in the unit cell of nanotube is:

$$n_c = \frac{4(n^2 + nm + m^2)}{\text{gcd}(n,m)}.$$

\hspace{1cm} (2.12)
In achiral tubes, \( n_c = 4 \gcd \), where \( \gcd \) is the greatest common divisor of integers \( n \) and \( m \). The structural parameters given above are summarized in Table 2.1, assuming the hexagons to be regular, with equal bond lengths \( a_{cc} \). Figure 2.6 shows the unit cells of different structures of single-walled nanotubes.

### Table 2.1: Main information for three types of single-walled carbon nanotubes.

<table>
<thead>
<tr>
<th>SWNT</th>
<th>Tube</th>
<th>( L )</th>
<th>No. of atoms ( n_c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Armchair</td>
<td>( (n,n) )</td>
<td>( 3n^2 )</td>
<td>( 4n )</td>
</tr>
<tr>
<td>Zigzag</td>
<td>( (n,0) )</td>
<td>( n^2 )</td>
<td>( 4n )</td>
</tr>
<tr>
<td>Chiral</td>
<td>( (n,m) )</td>
<td>( n^2 + nm + m^2 )</td>
<td>( 4L/(\gcd_x) )</td>
</tr>
</tbody>
</table>

| Diameter | Translational period \( |\vec{T}| \) | Chiral angle \( \theta \) |
|----------|--------------------------------|-------------------------|
| Armchair | \( \sqrt{3na/\pi} \)             | \( a \)                  | 30°                     |
| Zigzag   | \( na/\pi \)                 | \( \sqrt{3a} \)         | 0°                      |
| Chiral   | \( \sqrt{La/\pi} \)             | \( \sqrt{3La/(\gcd_x)} \) | \( \arccos(n + m/2)/\sqrt{L} \) |

* \( L = n^2 + nm + m^2 \) and \( a = \sqrt{3a_{cc}} \).

Figure 2.6: Structure of armchair (10,10), zigzag (17,0) and chiral (12,8) single-walled nanotubes. The unit cells of the tubes are highlighted; the translational period \( |\vec{T}| \) is indicated by the arrows.
We observe that the armchair single-walled nanotubes have short length unit cells whereas the chiral tubes have long unit cells.

All tubes generated by conformal mapping are translational periodic along the tubule axis. However, even for relatively small-diameter tubes, the minimum number of atoms in a translational unit cell can be large. For example, if \( n = 10 \) and \( m = 9 \) then the radius of tubule is less than \( 0.7\text{nm} \), but the translational unit cell contains 1084 carbon atoms.

Now the unit cell of an arbitrary nanotube and the number of carbon atoms in a unit cell are known. But it still remains to be explained the way the positions of each atom in the unit cell of the tube can be computed. For this aim, we use the helical and rotational symmetries.

### 2.3 Symmetry of single-walled carbon nanotubes

The symmetry of carbon nanotube is described by the so-called line group, which was introduced by different groups [115-123]. Line groups are the full groups of one dimensional systems including translations in addition to the point group symmetries like rotations or reflections. Damnjanovic et al. showed that every nanotube with a particular chirality \((n,m)\) belongs to a different line group [118-123]. Only armchair and zigzag tubes with the same \( n \) belong to the same symmetry group. Moreover, starting from a single carbon atom, the successive applications of all symmetry operations of the group constructs the whole tube. For many applications of symmetry, it is not necessary to work with full line group. Instead, the point group is sufficient. In this section, we explain how use the helical and rotational symmetries to construct the single-walled nanotubes.

#### 2.3.1 Helical and rotational symmetries

In order to generate the atomic coordinates of carbon atoms on the surface of single-walled nanotube, the helical and rotational symmetries are considered [124]. Those which are preserved when the graphene sheet is rolled into a cylinder form the nanotube symmetry. Translations by multiples of the translational period \( |\vec{T}| \) of the graphene sheet parallel to translation vector \( \vec{T} \) remain translations of the nanotube parallel to the tube axis.
Translations parallel to the circumference are perpendicular to translational vector become pure rotations of the nanotube about its axis. Given gcd graphene lattice points on the chiral vector $\hat{C}_h$, the nanotube can be rotated by multiples of $2\pi/\text{gcd}$. Single-walled nanotubes thus have gcd pure rotations in their symmetry group. Translations of the graphene sheet along any other direction are combination of the translations in the translation vector and chiral vector directions. Therefore, when the graphene sheet is rolled up, the result is that we get the translations combined with the rotations about the nanotube axis. The order of these screw axis operations is equal to the number of hexagons of graphene points in the nanotube unit cell. We present here the atomic positions (atomic coordinates in three dimension) of carbon atoms of the tube using helical and rotational symmetries.

We start with an arbitrary carbon atom. This atom is mapped onto the second atom of the graphene unit cell. The gcd-fold rotation about the tube axis then generates all other hexagons with the first atom on the circumference. The screw axis operations (without pure translations) map these atoms on to the circumference, this means map these on to the remaining atoms of the unit cell. Finally, the translation of all the atoms of the unit cell by translational period forms the whole nanotube.

We now consider the primitive (i.e. the minimum) unit cell of carbon nanotube. The nanotube crystal lattice can be seen as built up by two discrete symmetries: helical and rotational symmetries. The point group symmetry of the honeycomb lattice will make many of these equivalents. We show that all graphitic tubules, defined by chiral vector $\hat{C}_h$, can also be defined in terms of their helical and rotational symmetries.

The helical and rotational symmetries of the tubule defined by chiral vector $\hat{C}_h$ can be seen by using the corresponding symmetry operations to generate the tubule. This is done by first introducing a cylinder of radius $C_h/2\pi$. The two carbon atoms in the primitive unit cell of graphite sheet are located at $\vec{d}$ (eq.2.3) and $2\vec{d}$, respectively, in $[0,0]$ unit cell as shown in Figure 2.2(c).
These atoms are then mapped to the surface of this cylinder. The first atom is mapped to an arbitrary point on the cylindrical surface. The atomic position of this atom is \((C, \theta, 0, 0)\), which requires that the position of the second atom be found by rotating this point by angle \(\varphi\) (radian):

\[
\varphi = 2\pi \frac{\mathbf{d} \cdot \mathbf{C}_b}{|\mathbf{C}_b|^2},
\]

(2.13)

about the cylinder axis in conjunction with a translation (unit):

\[
\mathbf{h}_r = \frac{|\mathbf{d} \times \mathbf{C}_b|}{|\mathbf{C}_b|}.
\]

(2.14)

along this axis. In terms of chiral indices \(n\) and \(m\) the, equations 2.13 and 2.14 become:

\[
\phi(n, m) = \pi \frac{n + m}{n^2 + nm + m^2},
\]

(2.15)

and

\[
\mathbf{h}_r = \frac{1}{2} a_{c-c} \frac{(n - m)}{\sqrt{n^2 + nm + m^2}}.
\]

(2.16)

The rotational symmetry operation \(\mathbf{C}_\gcd\) is generated (after the conformal mapping) by the smallest lattice vector proportional to \(\mathbf{C}_b\), which leave the lattice invariant. This is given by:

\[
\mathbf{C}_\gcd = \mathbf{C}_b / \gcd = \frac{n}{\gcd} \mathbf{a}_1 + \frac{m}{\gcd} \mathbf{a}_2,
\]

(2.17)

Next, notice that the cylinder axis must coincide with a \(\mathbf{C}_\gcd\) rotational axis for the tubule. Thus, the position of these first atoms can be used to locate \(2(\gcd - 1)\) additional atoms on the cylindrical surface by \((\gcd - 1)\) successive \(2\pi / \gcd\) rotations about the cylinder axis. Altogether, these \(2\gcd\) atoms complete the specification of the helical motif which corresponds to an area on the cylinder surface:
\[ A_m = \gcd|\bar{a}_1 \times \bar{a}_2| \] \hspace{1cm} (2.18)

This helical motif can then be used to tile the reminder of the tubule by repeated operation of a single screw operation \( S(h, \alpha_h) \) representing a translation \( h \) unit along the cylinder axis and rotation \( \alpha_h \) (radian) about this axis. This makes a spiral of atoms. To find \( h \) and \( \alpha_h \) and hence determine \( S(h, \alpha_h) \), first, there must exist a real lattice vector \( \vec{H} \) in honeycomb lattice as shown in Figure 2.7, which (after the conformal mapping) will generate the helical symmetry. The vector \( \vec{H} \) has the smallest positive component in the direction of the chiral vector \( \vec{C}_h \).

![Figure 2.7: Relation between the hexagonal carbon lattice and chirality of carbon nanotubes. A carbon nanotube is made by folding the graphite sheet into a tube by connecting the two thick dotted lines. The solid vector \( \vec{H} \) is perpendicular to armchair direction and specifies the direction of nearest-neighbour hexagon rows indicated by the black dots. The angle between \( \vec{T} \) and \( \vec{H} \) is the chiral angle \( \theta \). The specific examples shown is a (11,7) tube(left) and (1,3) tube(right).](image)

Let this vector in terms of basis vectors \( \bar{a}_1 \) and \( \bar{a}_2 \), is expressed as:

\[ \vec{H} = p_1 \bar{a}_1 + p_2 \bar{a}_2 \] \hspace{1cm} (2.19)
where $p_1$ and $p_2$ are integers.

The helical variables in terms of the generating vector can then be given as:

$$h = \frac{\left| \hat{H} \times \vec{C}_h \right|}{\vec{C}_h}.$$  \hspace{1cm} (2.20)

and

$$\alpha_s = 2\pi \frac{\left( \hat{H} \times \vec{C}_h \right)}{\vec{C}_h \cdot \hat{C}_h}.$$  \hspace{1cm} (2.21)

In terms of $\hat{H}$ and $\vec{C}_h$, the area of the helical motif on the cylinder surface, $A_m$, is given by $A_m = |\hat{H} \times \vec{C}_h|$ and $|\hat{H} \times \vec{C}_h| = \gcd(\vec{a}_1 \times \vec{a}_2)$ or equivalently:

$$np_1 - mp_2 = \gcd.$$  \hspace{1cm} (2.22)

Putting equations 2.4 and 2.19 in equations 2.20 and 2.21, the helical variables $h$ and $\alpha_s$ in terms of $n$ and $m$ are given as:

$$h(n, m) = \frac{k_1}{2} \frac{\gcd}{\sqrt{n^2 + nm + m^2}},$$  \hspace{1cm} (2.23)

and

$$\alpha_s(n, m) = \frac{\pi \left[ n(2p_1 + p_2) + m(2p_2 + p_1) \right]}{(n^2 + nm + m^2)},$$  \hspace{1cm} (2.24)

where $k_1$ equals to 3.0 for armchair and chiral tubes and 1.0 for zigzag tubes. So $|\hat{H} \times \vec{C}_h| = |np_1 - mp_2|\vec{a}_1 \times \vec{a}_2|$ should be as small as possible but nonzero. Therefore, the integers $p_1$ and $p_2$ should be chosen as the smallest pair of integers (in the sense of minimizing $|\hat{H} = a_1q_1^2 + p_1p_2 + p_2|$, fulfilling the equation 2.19).

We can now identify the helical symmetry for a given nanotube using the equations 2.15, 2.16, 2.23 and 2.24. As an example, consider chiral (1,3) tube for which circumference is
given by the chiral vector $\vec{C}_a = \vec{a}_1 + 3\vec{a}_2$. The translation vector is $\vec{T} = 7\vec{a}_1 - 5\vec{a}_2$ along the tube axis. The vector generating the helical symmetry is $\vec{H} = \vec{a}_2$, which is generating the entire nanotube. Since $\gcd = 1$, so only $2\pi$ rotation leaves the lattice invariant.

If this resultant $S(h, \alpha_a)$ is applied only to the first two atoms mapped to the cylinder surface, then $\frac{1}{\gcd}$ of the tubule is generated. However, if the full helical motif is used, then the entire structure is generated.

The unit cell created by the way explained above can be repeated many times to obtain the resulting tube length. The method presented allows also the use of periodic boundary conditions in the direction of the tube axis, although then only integer multiples of unit cells can be piled on top of each other.

The helical and rotational symmetries described above are a function of one bond length. In the next chapter, we present the modification in the helical and rotational symmetries by taking them as a function of two bond lengths instead of one bond length.

### 2.4 Intra-tube interactions and model potential

There are many problems in physics, chemistry and materials science which require for their solution the knowledge of the total energy of a system of atoms as a function of atomic coordinates. A few examples are determination of surface reconstructions, diffusion paths and barriers, reaction coordinates and barriers, phonon dispersions and interactions, mechanical and thermal properties of materials. One solution to this problem is to construct an empirical interaction potential $V(\{\vec{r}\})$, which gives the total energy, $E$, of a set of particles, as an explicit mathematical function of the set $\{\vec{r}\}$ of particle coordinates. If this function is sufficiently easy to calculate, and if it gives a sufficiently accurate description of the real physical system of interest, then one can perform realistic calculations of the properties of quite large systems, or even of statistical ensembles of such systems. Of course, such an approach will inevitably involve a significant loss of accuracy compared with \textit{ab initio} calculations.
A rigorous calculation of the properties of a system at the atomistic scale is based on solving the many body time dependent Schrödinger equation and obtaining the many-body wave function $\psi(\vec{r}_1, \ldots, \vec{r}_n)$. Unfortunately, exact analytical solutions exist only for a handful of cases such as the hydrogen atom and the harmonic oscillator. Numerically, the problem is intractable for systems containing more than a few particles. The exponentially rising demand of computational resources ensures that exact quantum mechanics is not to be considered as a way to solve condensed matter problems. Researchers have to rely on the approximations of various orders of Schrödinger equation and even on totally classical empirical approaches.

This chapter offers first an overview of the approximations methods. The survey is presented in this section. In this thesis, however, the emphasis is on classical molecular dynamics and empirical carbon modeling by the Tersoff interaction model [125-128].

The methods of modeling the atomic interactions can roughly be divided into three categories: The first principles or *ab initio* methods are the most rigorous ones. Only a few well controlled approximations to justify quantum mechanics are made. Semiempirical methods contain more drastic approximations and may also contain empirically defined parameters. Empirical methods are a group of methods that are tuned to reproduce an empirically defined fitting set. The three categories, their drawbacks and benefits, and the most popular methods of each are briefly described in the various subsections of this section.

(1) **First principle methods**

The most rigorous approach to solve problems in condensed matter physics are the first principle methods. These do not employ any empirical parameters in the calculation. The results are based on quantum mechanics and well controlled approximations. The two most commonly used first principle methods are Hartree-Fock method [129] and the density functional theory [130-131]. The first principles methods are highly accurate but the system size that can be handled is restricted to tens or at most a couple of hundred atoms.
The Hartree approach to the quantum mechanical many-body wave function is to approximate the function by a product of single particle functions. The approximation is refined by adding Fermi-Dirac statistics by replacing the product of the wave functions by the Slater determinant. The method obtained with this inclusion is called the Hartree-Fock approach [129]. Even though the method is not always extremely accurate, it is very much in use. The accuracy can be enhanced but this increases the consumption of CPU-time [132]. In its most rigorous form, the Hartree-Fock method can be used on systems of tens of atoms.

Density Functional Theory (DFT) [130-131] is based on using the electron density $n(\vec{r})$ of the system as the basic variable. The ground state is completely described by the electron density as stated by the Kohn-Sham theorem [130-131]. There are various schemes for determining the energy of the system from the electron density. The simplest form of DFT is local density approximation (LDA), the expressions based on a non-interacting electron gas at the local electron density of the real system. Currently DFT is a very accurate method and its accuracy can be enhanced by the use of methods combining Hartree-Fock and DFT description, e.g., B3LYP functional description (see page 56) [132]. DFT can be used on systems of a few hundred atoms.

(2) Semi empirical methods

Semiempirical methods employ various approximations and may include experimentally fitted parameters. Their advantages as compared to the first principle methods lie in a smaller consumption of CPU-time but they must be employed more carefully to obtain reliable results. Semiempirical methods include interaction schemes like the tight binding method [133] and various molecular orbital methods of computational chemistry [132].

The tight binding method avoids most of the heavy calculation of the *ab initio* methods. There are several methods in this family. The TB-methods have in common a number of simplifications such as minimal basis sets compared to the first principle methods and elimination of difficult integrals that are either made small by mathematical transformation or used as parameters to be fit to experimental data. In principle, every thing that can be calculated by the *ab initio* methods can be calculated by an appropriate tight binding
method and with less CPU-time. The keyword above is the appropriate the generality and the transferability of a tight binding method depend on the approximations. Although valid for thousands of particles, the method used must be assessed case-specifically.

In computational chemistry, the methods similar to tight binding are called the neglect of diatomic differential overlap methods [132]. Also these methods simplify the involved integrals but retain the molecular orbital description. The group involves various methods such as AM1² and PM3³ (see page 56)[132].

(3) Empirical methods

The category of empirical methods contain a wide set of parameterized classical force field that reproduce more or less accurately the fitting set that is determined either from experimental data or from ab initio simulations.

Force-field methods have the benefit of being computationally simple and thus fast. They allow the simulation of large system (up to hundreds of millions of atoms) over a greater time-span (up to microseconds) than the methods presented above. The simplest approximation for the interaction potential takes into account only two-particle interactions. Potentials like this are called pair potentials. The Lennard-Jones potential [134] and the Morse potential [135] are two very well known examples of pair potentials. Although pair potentials are not ideal for the study of mechanical properties of materials, they are very much used because they are simple to implement and algorithms based on pair potentials are kind on computational resources.

There are, however, some severe shortcomings which should be taken into account whenever pair potentials are used. For example, an interaction described by a pair potential model depends only on the distance between the two particles. Thus the potential can not model directional bonding. Pair potentials often predict wrong vacancy formation energies and melting temperatures [132,135].

The construction of an accurate force-field often encounters system and material based difficulties, and often even fundamental limitations. Difficult media are metals, alloys, semiconductors, and oxide-based insulators.
The description of carbon accurately requires a lot of caution and is difficult because the 2s electrons participate in molecular bonding and together with the 2p electron orbitals hybridize to form a wide variety of potential bonding configurations that depend on the environment and on the ambient conditions. Even by itself, carbon form structure as diverse as the isotropic diamond crystal or the anisotropic planar graphite and nanostructures. If the consideration is extended to organic molecules, even only hydrocarbons, the bonding variety and at the same time the complexity of describing it accurately becomes vast.

If covalently bonding materials, like $sp^3$-carbon, are simulated, the modeling of directional bonding is essential in order not to obtain outright wrong results. In general, this means that the interaction potential used must include at least a three-body interaction term. Because carbon is the basis of all organic materials and because diamond and graphite have various applications in materials science, numerous attempts to create accurate classical interaction potentials have been made but only a few of the proposed schemes are widespread. As examples, the interaction potentials for carbon developed by Tersoff [125-128] and Brenner [136] are widely used in the modeling of carbon. Both models are short ranged and cover only the nearest neighbours to speed up the calculations.

In general, the force-field methods can give information on the structure and dynamics of a system, the total energies, entropies, free energies, and diffusive processes in the system. However, these methods are incapable of predicting any properties related to the electronic structure such as electrical conductivity, optical, or magnetic properties. In short, the classical force field methods are structural tools. The general accuracy of results obtained by classical force field methods is far from the level of accuracy obtained by \textit{ab initio} simulations but so are the feasible system size and attainable time scale as well.

In this thesis, the emphasis is on studying the structural parameters of carbon nanotubes through classical means. The choice allows studying structures that have dimensions comparable to the experimentally observed ones. We have used the Tersoff potential for this work.
2.5 Tersoff potential

The interactions between carbon atoms on the surface of the cylindrical tube can be described by a reliable and computational efficient potential, the short-range Tersoff potential which appropriately describes the covalent bonds in diamond and graphite [125-128]. Tersoff potential has already been successfully applied to study many properties of fullerene and carbon nanotubes.

In this section, we describe, in detail, the approach of interaction potential for covalent systems. The central idea is that, in real systems, the bond order (i.e., the strength of each bond) depends upon the local environment [137]. In particular, an atom with many neighbours forms weaker bonds than an atom with few neighbours. For most covalent materials, this dependence is sufficient to stabilize structures with low atomic coordination number (number of neighbours). This dependence also explicitly appears to solve some of the most serious problems of describing covalent systems without introducing any major increase in computational complexity. Because of the crucial role of bond order and its dependence upon local geometry, it seems attractive that this potential should include an environment dependent bond order explicitly into the potential. The total energy $E$ and the interaction potential $V_{ij}$ are taken to have the form [127]:

\[
E = \frac{1}{2} \sum_i E_i = \frac{1}{2} \sum_{i,j} V_{ij}
\]

\[
V_{ij} = f_c(r_{ij})[f_R(r_{ij}) + b_{ij} f_A(r_{ij})].
\]

(2.25)

Here $E$ is the total energy of the system, which is decomposed for convenience into site energy $E_i$ and $V_{ij}$ is the interatomic energy between atoms $i$ and $j$. The indices $i$ and $j$ run over the atoms of the system, and $r_{ij}$ is the distance from atom $i$ to atom $j$. The function $f_R$ represents a repulsive pair potential, which includes the orthogonalization energy when atomic wave functions overlap, and $f_A$ represents an attractive pair potential associated with bonding. The extra term $f_c(r_{ij})$ is merely a smooth cutoff function, to limit the range of the potential, since for many applications short-ranged functions permit a tremendous reduction in computational effort.
The function $b_{ij}$ represents a measure of the bond order and mostly depends upon local environment, and is assumed to be a monotonically decreasing function of the coordination number. Terms which act to limit the range of interaction to the first neighbour shell are included in $b_{ij}$.

The choice of exponential function for $f_{R}$ and $f_{A}$, as in Morse potential:

$$f_{R} (r_{ij}) = Ae^{-\lambda_1 r_{ij}}$$
$$f_{A} (r_{ij}) = -Be^{-\lambda_2 r_{ij}}$$

(2.26)

where $A, B, \lambda_1$ and $\lambda_2$ are all positive definite quantities, characteristic of a given atomic species with $\lambda_1 > \lambda_2$. This choice is based on analytical convenience, but also on the physical grounds that atomic orbitals decay exponentially with distance $r_{ij}$ [125,137]. Here the cutoff function is simply taken as:

$$f_c(r) = \begin{cases} 
1, & r < R - D \\
1 - \frac{1}{2} \sin \left[ \frac{\pi}{2} \left( \frac{r - R}{D} \right) \right], & R - D < r < R + D \\
0, & r > R + D 
\end{cases}$$

(2.27)

which has continuous value and derivative for all $r$, and goes from 1 to 0 in a small range around $R$. $R$ is chosen to include only the first-neighbour shell for most structures of interest. For graphite sheet, the values of $R$ and $D$ are 1.95Å and 0.15Å, respectively. The short range potential is numerically advantageous in many applications and is important for the applicability of simple ideas about the coordination. $b_{ij}$ is taken to have the following form:

$$b_{ij} = (1 + \beta_{ij} \cdot \xi_{\alpha}) - \frac{1}{2} \cdot \frac{c^2}{d_{ij}^2} \cdot \frac{c^2}{\left[ d_{ij}^2 + (h_{ij} - \cos \theta_{ij})^2 \right]^2}$$

(2.28)
where $\theta_{ij}$ is the bond angle between bonds $ij$ and $ik$. For graphite, $\theta_{ij}$ is always 120° (ideal value). In general, for single-walled nanotubes, the bond angles are given by

$$
\theta_{ij} = \cos^{-1}\left(\frac{\hat{r}_{ij} \cdot \hat{r}_{ik}}{|\hat{r}_{ij}| |\hat{r}_{ik}|}\right).
$$

The vectors $\hat{r}_{ij} = (\vec{r}_{ij} - \vec{r}_{i})$ and $\hat{r}_{ik} = (\vec{r}_{ik} - \vec{r}_{i})$ are between atom $i$ and nearest neighbours $j$ and $k$ on the cylindrical surface. The position vectors $\vec{r}_{i}$, $\vec{r}_{j}$, and $\vec{r}_{k}$ and the corresponding bond angles are shown in Figure 2.8.

Figure 2.8: Carbon atoms $i$, $j$ and $k$, the corresponding bonds $i-j$ and $i-k$ and bond angles $\theta_{ij}$.

The parameter $n_{ij}$ has been taken to be very small to ensure short ranged behaviour of the potential and $h_{ij}$ is formally the cosine of the energetically optimal angle. The parameter $d_{ij}$ determines the dependence on angle, and $c$ determines the strength of the angular effect. The bond-angle forces were introduced in the potential $\psi$ so that order bonds $ik$ to atom $i$ weaken the bond $ij$ more or less, depending on the angle between the two bonds. The parameter $\lambda_{ij}$ has been set by Tersoff equal to zero.

The procedure used by Tersoff to calculate the parameters in the potential has been to fit the pair terms and an analytic expression for $b_{ij}$ to a number of properties of the diatomic and solid-state structures (e.g., bond energies and bond lengths, bulk modulus, vacancy formation energies, etc.). In graphite sheet, each atom has local coordination of three (3,
k=1, 3). The reason of taking this local coordination is that at this coordination number, the energy of the graphite sheet is minimized. The nine parameters used in the Tersoff potential are listed in Table 2.2 [126,128].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>A(eV)</td>
<td>1.3036×10³</td>
</tr>
<tr>
<td>B(eV)</td>
<td>3.467×10⁴</td>
</tr>
<tr>
<td>λ₁(Å⁻¹)</td>
<td>3.4879</td>
</tr>
<tr>
<td>λ₂(Å⁻¹)</td>
<td>2.2119</td>
</tr>
<tr>
<td>β_i</td>
<td>1.5724×10⁻⁷</td>
</tr>
</tbody>
</table>

The main important parameters in Tersoff potential are A, B, λ₁, and λ₂. By using the values of two parameters A and B given by Tersoff the bond length and energy of graphite sheet comes out to be 1.46 Å [126], and -7.4 eV/atom, respectively. However, the experimental values are 1.42 Å [16] and -7.3756 eV/atom, respectively. Since these two parameters chosen by Tersoff do not reproduce the graphite bond length accurately, so we have modified two of these parameters A and B so as to get a good agreement of bond length and energy of the graphite with experiments. In the following section, we present in details the modification of these two parameters.

### 2.5.1 Modification of two parameters A and B

The total energy per atom of graphite sheet is:

\[ E(b_1, b_2) = \frac{1}{2} [V(b_2) + V(b_1)] \]

where \( V(b_1) \) and \( V(b_2) \) are the potential energies for one atom in the primitive unit cell which is having three nearest neighbours connected to it by two equal bond lengths \( b_2 \) and one different bond length \( b_1 \) (see Figure 2.9).

In graphite \( |b_2| = |b_1| = b_n = 1.42 Å \), then the total energy per atom of graphite is:
At minimum energy, the first derivative of Tersoff potential should be equal to zero.

\[ \therefore \quad Bb_y = \frac{\lambda_1}{\lambda_2} A e^{(\lambda_2 - \lambda_1) b_y} \]  
\[ (2.31) \]

and

\[ b_y = \left[ \frac{1}{(\lambda_1 - \lambda_2)} \ln \left( \frac{A \lambda_1}{B b_y \lambda_2} \right) \right]. \]  
\[ (2.32) \]

Substituting the equation (2.31) into equation (2.30) we get the final expression of the total energy per atom of graphite sheet as:

\[ E(b_y) = \frac{3}{2} V(b_y). \]  
\[ (2.33) \]
To calculate $A$ and $B$, we have adjusted the equation (2.32) and equation (2.33) to the experimental values of energy and bond length of graphite sheet, respectively. The new values of the parameters $A$ and $B$ come out to be $A(eV) = 1206.709$ and $B(eV) = 315.9646$.

### 2.5.2 Scaling procedure

Scaling procedure is used to choose the optimum values of the parameters $\lambda_1$ and $\lambda_2$ in the potential [137]. The binding energy for a given structure is simply given by equation (2.25) and the equilibrium interatomic separation $b_0$ is determined from $(dE(r)/dr)_{r=b_0} = 0$, which gives:

\[
\exp(-\lambda_1 b_0) = SA \exp(-\lambda_1 b_0) / Bb_0, \quad (2.34)
\]

and

\[
\exp(-\lambda_2 b_0) = B b_0 S^{-1} \exp(-\lambda_2 b_0). \quad (2.35)
\]

Putting equation (2.34) and equation (2.35) in equation (2.25), and let $D_e = -E_e$ where $E_e$ and $D_e$ are the binding and cohesive energy, respectively, we get:

\[
D_e = A(S - 1) \exp(-\lambda_1 b_0), \quad (2.36)
\]

\[
D_e = B b_0 S^{-1} (S - 1) \exp(-\lambda_2 b_0) \quad (2.37)
\]

where $S = \lambda_1 / \lambda_2$.

We need the second derivative of $E(r)$ at equilibrium interatomic separation $b_0$ as:

\[
(d^2E(r)/dr^2)_{r=b_0} = \lambda_1^2 A \exp(-\lambda_1 b_0) - \lambda_2^2 B b_0 \exp(-\lambda_2 b_0) \quad (2.38)
\]

The scaled energy is:
\[ E_\theta = \frac{E(r)}{D_\nu}, \quad (2.39) \]

with
\[ x = \frac{r - b_0}{L_\nu}, \quad (2.40) \]

and
\[ L_\nu^2 = D_\nu \left( \frac{d^2 E(r)}{dr^2} \right)_{r=b_0}. \quad (2.41) \]

Dividing the first term on the right-hand side of equation (2.25) by equation (2.36) and the second term by equation (2.37) we get:

\[ E_\theta^* = \left[ \exp(-\lambda_1 (r - b_0)) - S \exp(-\lambda_2 (r - b_0)) \right]/(S - 1) \quad (2.42) \]

Following the same procedure form equation (2.38) gives via equation (2.41):

\[ L_\nu^2 = (\lambda_1^2 - \lambda_2^2) \frac{S}{(S - 1)}, \quad (2.43) \]

or since \( S = \lambda_1 / \lambda_2 \),

\[ L_\nu = \frac{1}{\sqrt{\lambda_1 \lambda_2}}. \quad (2.44) \]

Combining equations (2.40) and (2.44), we get: \( r - b_0 = x/\sqrt{\lambda_1 \lambda_2} \), which when substituted into equation (2.42), gives us the scaled energy as:

\[ E_\theta^*(x, S) = \frac{1}{(S - 1)} \left[ \exp(-x\sqrt{S}) - S \exp(-x \frac{1}{\sqrt{S}}) \right]. \quad (2.45) \]

This scaling procedure is used to obtain the smooth curve of energy. The value of \( S \) in the potential (not the values of two parameters \( \lambda_1 \) and \( \lambda_2 \)) found to limit the tail of the curve of the energy after the minimum point as shown in Figure 2.10 and the curves are nearly indistinguishable for \( |x| \leq 1 \). If \( S = 2 \) then the potential reduce to the usual Morse
Brenner has discussed and developed the expression of the Tersoff potential for hydrocarbons [136]. He concluded that this potential is suffering from the overbinding. This overbinding occurs when the coordination number becomes four instead of three. He also concluded that the expression of Tersoff potential developed in this way appear to be relatively transferable to other solid-state structures not used in the fitting procedure such as surface reconstructions on silicon [125,127] and interstitial defects in carbon[126]. Tersoff expression also found to be unable to reproduce a number of properties of carbon such as a proper description of radicals and conjugated versus non conjugated double bonds.

When the graphite sheet is rolled up to construct the carbon nanotube, the coordination number remains three and therefore, the overbinding can not occur in carbon nanotubes. Then we think that the Tersoff potential is very suitable to apply on this system.

In the next chapter, we present a numerical procedure which is then applied in this thesis. This procedure is based on modifying the helical and rotational symmetries, using an
empirical potential, Tersoff potential, to calculate the energy of a given nanotube and then
minimizing the energy. We also present the results of our calculations of the tube radius
and tube length effects on the structural parameters for three types of single-walled carbon
nanotubes in addition of studying the chirality effect in chiral nanotubes.

1 B3LYP is short for Becke’s 3-parameter formula, B3, which describes the exchange
functional, and LYP for Lee, Yang, and Parr who developed the correlation
functional.
2 Austin Model 1 is named after the place of its origin, that is, University of Texas,
Austin, USA.
3 Parameterized Model 3 is named so because it was the third parameterized model
released by the person in charge for its development.