Chapter I
Introduction

1.1 History of carbon nanotubes

Carbon materials are found in a variety of different forms, these include graphite, diamond, carbon fibers, and fullerenes. A fullerene by definition is a closed convex cage molecule containing only hexagonal and pentagonal faces, the best known of these is \( C_{60} \) or the bucky ball. Figure 1.1 shows the fullerene structure \( C_{60} \).

![Figure 1.1: A spherical shape of fullerene \( C_{60} \).](image)

Nanotubes too are members of the fullerene structural family, (which also includes bucky balls) (see Figure 1.2). Whereas bucky balls are spherical in shape, a nanotube is cylindrical, with at least one end typically capped with a hemisphere of the bucky ball structure.

![Figure 1.2: A diagram of a single-walled carbon nanotube, a cylindrical shape, capped by hemispheres (bucky balls).](image)

Their name is derived from their size, since the diameter of a nanotube is of the order of a few nanometers (approximately 50,000 times smaller than the width of a human hair), while they can be up to several millimeters in length.
Carbon nanotubes (CNT’s) form a new class of materials that have attracted interest for variety of engineering applications and it is considered to be a type of giant linear fullerene.

In 1952, Radushkevich and Lukyanovich published clear images of 50 nanometer diameter tubes made of carbon in the Russian Journal of Physical Chemistry [1]. This discovery was largely unnoticed, the article was published in the Russian language, and Western scientist’s access to Russian press was limited during the Cold War. It is likely that carbon nanotubes were produced before this date, but the invention of the transmission electron microscope allowed the direct visualization of these structures.


In 1981, a group of Ukrainian scientists published the results of chemical and structural characterization of carbon nanoparticles. Using tunneling electron microscope (TEM) images and x-ray diffraction (XRD) patterns, the authors suggested that their “Carbon multi-layer tubular crystals” were formed by rolling of graphene layers into cylinders. Additionally, they speculated that during rolling graphene layers into a cylinder, many different arrangements of graphene hexagonal nets are possible. They suggested two possibilities of such arrangements: circular arrangement (armchair nanotube) and a spiral, helical arrangement (chiral tube) [3].

In 1987, Howard G. Tennent of Hyperion Catalysis was issued a U.S. patent for the production of "cylindrical discrete carbon fibrils" with a constant diameter between 3.5 nanometers and about 70 nanometers, length 10⁵ times the diameter, and an outer region of multiple essentially continuous layers of ordered carbon atoms and a distinct inner core [4]. Unfortunately this report did not cause a great impact because scientists were more interested in micron-size carbon fibers. It started to have impact when Sumio Iijima in 1991 at NEC Fundamental Research Laboratory in Tsukuba, Japan found CNTs accidentally [5]. He was analyzing a sample of carbon soot received from Yoshinory Ando
of Meijo University. The sample was created by a direct-current arc discharge between carbon electrodes in a noble gas and the structures were examined by Transmission Electron Microscope (TEM). He observed that the sample contained helical carbon microtubules (now called nanotubes) and nanoparticles. Figure 1.3 shows the observation by TEM of multi-walled nanotubes (MWNTs), these are tubes with a number of concentric tubes of carbon nested inside each other, which have different diameters. But not until T. W. Ebbesen and P. M. Ajayan found the right parameters to synthesize carbon nanotubes on large-scale [6]. But still comparison between experimental data and theoretical result could not be made because theoretical models were based on single-walled nanotubes (SWNTs). In 1993, the simplest kind of carbon nanotubes, single-walled carbon nanotubes (SWNTs) was discovered. It was S. Iijima et al. who succeeded to synthesize abundant single-walled nanotubes [7]. Unlike the multi-walled nanotubes which form on the carbon cathode, these single-walled nanotubes grow in the gas phase (a gas mixture of methane and argon). At the same time, an IBM team headed by Bethune et al. used Cobalt as catalysis to grow carbon nanotubes with single-atomic layer walls [8]. These SWNTs can be regarded as a rolled up graphite sheet in cylindrical form.

![Figure 1.3: Transmission Electron Microscope (TEM) images of several multi-walled coaxial nanotubes with various inner and outer diameters and number of cylindrical shells. (a) 5 shells diameter 6.7nm, (b) 2 shells diameter 5.5nm, (c) 7 shells outer diameter 6.5nm, inner diameter 2.3 nm. The pictures show projections of MWNTs perpendicular to their axes, which are running from top to bottom. The separate shells of the tubes are clearly visible [5].](image-url)
Research on the physical properties of nanotubes really took off after 1995, when Richard Smalley et al. at Rice University found a laser ablation technique that could produce single-walled nanotubes at yield of upto 80% instead of the few percent yield of early experiments (see Figure 1.4)[9]. The tubes are formed with a narrow distribution of diameters and generally assemble into “ropes” - bundles of parallel nanotubes so called crystalline ropes and behave like metallic carbon nanotubes. These tightly bundled linear ‘ropes’ are expected to have remarkable mechanical properties as well as superior electronic and magnetic properties.

One of unusual features of nanotubes is that they simultaneously combine widely varying length scales: Their length can be macroscopic, lies between hundreds of nanometers, although the synthesis of even centimeter-long tubes is possible, whereas their diameters are on the nanoscale [10, 11]. Typical diameters for single-walled carbon nanotubes are between 1 nm and 2 nm and for multi-walled carbon nanotubes tens of nanometers. Furthermore, for SWNTs, the physical thickness of the nanotube shell (one carbon atom in thickness) is ill-defined, leading to different definitions of the nanotube parameters by different research groups [12-14].

### 1.2 Hybridization in a carbon atom

Carbon has been studied and used for centuries, and carbon science was long thought to be a mature field. It is the sixth element in the periodic table. It has six electrons and is listed at the top of column IV. Diamond (3D) and graphite (2D) are considered as two natural crystalline forms of pure carbon. So when a whole new class of carbon materials-the
fullerenes, such as $C_{60}$, appeared in the last decade, many scientists were surprised. As a result, we have to change our concepts and understanding of long-known carbon materials.

The six electrons in carbon atom occupy $1s^2$, $2s^2$, and $2p^2$ atomic orbitals. The $1s^2$ orbital contains two strongly bound core electrons and the $2s^22p^2$ orbital contains the more weakly bound valence electrons. These valence electrons form $2s$, $2p_z$, $2p_x$, and $2p_y$ orbitals and play an important role in forming covalent bonds in carbon materials. Now, because the energy difference between the upper $2p$ energy levels and lower $2s$ level is small compared to the binding energy of the chemical bonds, these four electrons can mix with each other leading to an increase in the binding energy of the carbon atom and its neighbours. This mixing of $2s$ and $2p$ orbitals is called Hybridization [15] and the mixing of a single $2s$ level with $n = 1, 2, 3$ of $2p$ electrons is called $sp^n$ hybridization. In diamond, carbon atoms exhibit $sp^3$ hybridization, in which four bonds are directed toward the corners of a regular tetrahedron. The resulting three-dimensional network is extremely rigid, which is one reason for its hardness. The bond length in $sp^3$ carbon is 1.56 Å. Diamond behave as an insulator because all electrons are localized in the bonds within the $sp^3$ network.

In graphite, $sp^2$ hybridization occurs. In this process, one $s$-orbital and two $p$-orbitals combine to form three hybrid $sp^2$ orbitals at $120^\circ$ to each other within a plane (shown in Figure 1.5).

![Figure 1.5: The $sp^2$ hybrid orbitals that form covalent bonds. Each carbon atom uses three of its four available electrons (one $s$ and two $p$ orbitals) to form three $sp^2$ hybrid orbitals that are coplanar and $120^\circ$ apart.](image-url)
This in-plane bond is referred to as a $\sigma$-bond (sigma-bond) as shown in Figure 1.6(a). This is a strong covalent bond that binds the atoms in the plane, and results in the high stiffness and high strength of a carbon nanotube. The remaining $p$-orbital is perpendicular to the plane of the $\sigma$-bonds. It contributes mainly to the interlayer interaction and is called the $\pi$-bond (pi-bond). These out-of-plane, delocalized $\pi$-bonds interact with the $\pi$-bonds on the neighbouring layer. This interlayer interaction of atom pairs on neighbouring layers is much weaker than a $\sigma$-bond. The free electrons in the $p_z$ orbital move within this cloud and are no longer local to a single carbon atom (delocalized). This is the reason why graphite can conduct electricity. The $C-C$ $sp^2$ bond length is 1.42 Å [16] and the spacing between the carbon layers is 3.34 Å [14, 17]. The bond structure of a graphene sheet and the graphite crystalline are shown in Figure 1.6(a) and Figure 1.6(b), respectively.

When dealing with carbon nanotubes the $sp^2$ hybridization is important, here three $\sigma$-bonds per carbon atom are formed and these bonds make a skeleton for a planar structure in two dimensions. This two-dimensional ‘honeycomb’ structure can be seen in Figure 1.6(b) as one layer from graphite crystal, where the atoms would be located on the six points of the hexagon.

Figure 1.6: (a) Basic hexagonal bonding structure for one graphite layer (graphene sheet); Carbon nuclei shown as filled circles, out-of-plane-$\pi$ bonds represented as delocalized (dotted line), and $\sigma$-bonds connect the C nuclei in-plane. (b) Graphite crystalline contains many layers of graphite sheet. The distance between two layers equal to 3.34 Å. The nearest neighbour distance is 1.42 Å.
1.3 Types of carbon nanotubes

There are many types of carbon nanotubes, obtained by rolling up the graphite. The first important type is Single-Walled Nanotubes (SWNTs), Multi-Walled Nanotubes (MWNTs), Fullerite, Torus and Nanoknot.

(1) Single-walled nanotubes (SWNTs)

Most single-walled nanotubes (SWNTs) have a diameter of close to 1 nanometer, with a tube length that can be many thousands of times longer. The structure of a SWNT can be conceptualized by wrapping a one-atom-thick layer of graphite called graphene into a seamless cylinder.

Single-walled nanotubes are a very important variety of carbon nanotube because they exhibit important electric properties that are not shared by the multi-walled carbon nanotube (MWNT). Single-walled nanotubes are the most likely candidate for miniaturizing electronics past the micro electromechanical scale that is currently the basis of modern electronics.

Single-walled nanotubes are still very expensive to produce, around 1500 $ per gram as of 2000, and the development of more affordable synthesis techniques is vital to the future of carbon nanotechnology. If cheaper means of synthesis will not be discovered, it would make it financially impossible to apply this technology to commercial-scale applications [18].

(2) Multi-walled nanotubes (MWNTs)

Multi-walled nanotubes (MWNTs) consist of multiple layers of graphite rolled on themselves to form a tube shape. There are two models which can be used to describe the structures of multi-walled nanotubes. In the Russian Doll model, sheets of graphite are arranged in concentric cylinders, eg., a (0,8) single-walled nanotube (SWNT) within a large (0,10) single-walled nanotube. In the Parchment model, a single sheet of graphite is rolled in around itself, resembling a scroll of parchment or a rolled up newspaper. The interlayer distance in multi-walled nanotubes is close to the distance between graphene layers in graphite, approximately 3.34 Å.
The special place of double-walled Carbon Nanotubes (DWNTs) must be emphasized here because they combine very similar morphology and properties as compared to SWNTs, while improving significantly their resistance to chemicals. This is especially important when functionalisation is required (this means grafting of chemical functions at the surface of the nanotubes) to add new properties to CNTs. In the case of SWNT, covalent functionalisation will break some C=C double bonds, leaving "holes" in the structure on the nanotube and thus modifying both its mechanical and electrical properties. In the case of DWNT, only the outer wall is modified. DWNT synthesis on the gram-scale was first proposed in 2003 by the chemical vapour deposition (CVD) technique, from the selective reduction of oxides solid solutions in methane and hydrogen [19].

(3) Fullerite

Fullerites are the solid-state manifestation of fullerenes and related compounds and materials. Being highly incompressible of nanotube forms, polymerized single-walled nanotubes (P-SWNT) are a class of fullerites and are comparable to diamond in terms of hardness. However, due to the way the nanotubes intertwine, P-SWNTs don't have the corresponding crystal lattice that makes it possible to cut diamonds neatly. The same structure results in a less brittle material, as any impact that the structure sustains spread throughout the material.

(4) Torus

A nanotorus is a theoretically described carbon nanotube bent into a torus (donut shape). Nanotorus has many unique properties, such as magnetic moment 1000 times larger than previously expected for certain specific radii [20]. Properties such as magnetic moment, thermal stability, etc. vary widely depending on radius of the torus and radius of the tube [21].

(5) Nanoknot

Carbon nanotubes are being used to make nanoropes; nanoknots (or nano-knot) have been tied. Scientists published micrograph images of some nanoknots tied in threads made of single-walled carbon nanotube (SWNT).
It is anticipated that nano-knotting will reveal material characteristics that will not be found in unknotted nanothreads. Nano-lashings might use nanoknots to terminate as nano-items are bound together by nanomachines to construct more complex nano-items.

The two-dimensional structure of graphene is simply a single atomic layer of graphite (see Figure 1.7(a)) which is the three-dimensional form of carbon. A single-walled carbon nanotube (SWNT) or multi-walled carbon nanotube (MWNT) also can be seen in Figure 1.7(b) and Figure 1.7(c), respectively.

![Figure 1.7: Carbon nanotubes](image)

In fact, nanotubes come in a variety of flavors: long, short, opened and closed with different types of spiral structure.

After their discovery, scientists from a wide variety of disciplines became fascinated by their properties. The reason for this broad interest can be understood from the fact that nanotubes combine several unique properties which were incompatible in the pre-nanotube age.

### 1.4 Properties of carbon nanotubes

Nanomaterials are expected to be the heart of the next technological revolution in solid-state electronics, to emerge as new structural materials, to serve as systems for controlled
drug delivery and to have a considerable impact in practically all domains of science. Nanostructure based devices taking advantage of their unique functional properties (chemical, optical, magnetic, mechanical, optoelectronics, etc.) are likely to become ubiquitous.

The existence of a characteristic length scale less than ~100 nm is the mark of nanomaterials. This length scale can be for instance a particle diameter, grain size, layer thickness, tube diameter or length. The routes for the synthesis of materials exhibiting such type of length scales are as varied as the imagination of scientists and include membrane-template methods, mechanical attrition, chemical vapour deposition, flame or arc-discharge methods, etc. The results are system which dimensionally can be considered as zero, one or two depending on the number of nano-length Cartesian scales associated with the object. Nanostructuration is not by far confined to human imagination and is also an important choice of Nature, for instance in circumstellar dusts or many biological systems.

Interactions at the nanoscale are usually governed by the fact that the characteristic nanolength becomes comparable with other critical lengths of the system as mean free-paths, scattering or coherence lengths. At the same time, confinement translates in reorganization of the electronic density of state towards more discretized states (Figure 1.8). These two consequences of nanostructuration and their combinations lead to the so-called quantum related effects which determine most of the characteristic properties of nanomaterials. A major consequence of nanoconfinement is the elevated ratio of the number of surface to volume atoms, which becomes another key point for understanding of nanomaterials properties. The ratio of the number of surfaces to the total number of atoms, goes from $10^{-20}$ or less in bulk materials to value close to unity in small nanoclusters, for which it scales as $\sim 1/(\text{Particle diameter})$ and exactly one in nanotubes or fullerenes. Nano-objects can be viewed as intermediate systems between single atoms or molecules and bulk matter. Physical and chemical properties of nanomaterials can then be, in general, totally different from their bulk counterparts, strongly dependent on size and offering new paths for chemistry developments.
Figure 1.8: Scheme of the evolution of the electronic density of states (e-DOS) with nanostructuration. From left to right is shown the progression of the e-DOS from 3-dimensional solid. The reduction of one of the Cartesian dimensions up to nanometric dimension leads to a 2-D solid, reduction of two of the Cartesian dimensions gives a 1-D solid and the reduction of all three Cartesian dimensions generates a 0-D solid.

An additional feature of many nanomaterials that can also play a role in high-pressure studies is porosity. This can be an intrinsic feature as for fullerenes or nanotubes or it can be related or reinforced by the assemblage of nanomaterials as in bundles of nanotubes, fullerites or in assemblages of nanoparticles.

There are three groups of nanomaterials: nanoparticles, nanocage materials and nanotubes.

Carbon nanotubes due to their unique structure, exhibit many extraordinary physical properties, such as high stiffness, tunable electrical conduction between semiconducting and metallic states, one-dimensional quantum wire effect, and electrical field-induced electron emission, etc., with promising technological applications[22].

The greatest advantage of a single-walled nanotube is that it is a macro-molecule and a crystal at the same time. The dimensions correspond to extensions of fullerene molecules and the structure can be reduced to a unit cell picture, as in the case of perfect crystals.

1) Electronic properties of carbon nanotubes

Nanotubes exhibit unique quantum wire properties that are derived from the tube’s nanometer diameter in combination with the special electronic structure of graphite. The electron wavelength around the circumference of a nanotube is quantized due to periodic boundary conditions-only a discrete number of wavelengths can fit around the tube. Along
the tube the electrons are not confined, because of the quantization of circumferential modes, however, the tube’s electronic states do not form one wide electronic energy band but instead split into one-dimensional subbands with bands onsets at different energies. For single-walled nanotubes, these subbands are widely separated in energy. Only two of the one-dimensional subbands cross the Fermi energy in metallic nanotubes; all the current through such tubes is therefore predicted to be carried by only this pair of subbands. Nanotubes are thus predicted to be prototype one-dimensional quantum wires. Due to the quasi-one-dimensional structure, single-walled carbon nanotubes (SWNTs) have been shown to have some unique and interesting physical properties [23].

The conductive properties of nanotubes depend drastically on both diameter and chirality of the hexagonal carbon lattice along the tube [24-26]. A slight change in the winding of hexagon along the tube can transform the tube from a metal into a large-gap semiconductor. It turns out that about two-thirds of tubes are semiconducting and one-third is metallic. The indices \((n,m)\) of single-walled carbon nanotubes are crucially important for the electronic properties of nanotubes. Tubes for which \(n - m = 3i\), with \(i\) an integer, are metallic; all other are semiconducting. Both the semiconducting and metallic types of nanotubes may be of use for nanoscale electronic devices.

**(2) Mechanical properties of carbon nanotubes**

Several theoretical, experimental and computational approaches have been used to find the mechanical properties that include the stiffness and strength. Reported values of the properties vary widely. Calculations of the Young’s modulus of the isolated nanotubes show that it has a value of approximately 1.8 GPa and it decreases somewhat with increasing diameter [27]. The first experimental study of the elastic properties of the single walled carbon nanotubes was carried by Treacy et al. in 1998 [28]. It was found that the Young’s modulus was approximately 1.25 TPa. In 2000, Yu et al. reported Young’s modulus of 1 TPa and maximum tensile strength is of approximately 30 GPa [29]. They can be hundred times stronger than steel while they are one-sixth its weight. A brief comparison of elastic properties (Young’s modulus and the tensile strength) and density of SWNTs, SWNT bundles, MWNTs, graphite (in-plane) and steel is shown in Table 1.1.
Table 1.1: Mechanical properties of CNTs - A comparison [30].

<table>
<thead>
<tr>
<th>Material</th>
<th>Young’s modulus (GPa)</th>
<th>Tensile strength (GPa)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWNT</td>
<td>1200</td>
<td>~150</td>
<td>2.6</td>
</tr>
<tr>
<td>SWNT</td>
<td>1054</td>
<td>75</td>
<td>1.3</td>
</tr>
<tr>
<td>SWNT bundles</td>
<td>563</td>
<td>~150</td>
<td>1.3</td>
</tr>
<tr>
<td>Graphite (in-plane)</td>
<td>350</td>
<td>2.5</td>
<td>2.6</td>
</tr>
<tr>
<td>Steel</td>
<td>208</td>
<td>0.4</td>
<td>7.8</td>
</tr>
</tbody>
</table>

The atomic lattice structure of nanotubes is associated with a high mechanical stiffness as well as great flexibility. Because the nanotubes are highly symmetric molecules linked by many covalent bonds which are in a parallel cylindrical configuration, nanotubes are both very flexible and strong. Regarding the flexibility, nanotubes can be bent strongly without breaking but buckling [31]. Small diameter SWNTs can be elongated by ~30% before breaking [32, 33] and the value for the breaking strength is 55 GPa [29]. Together with their high aspect ratio, this makes them ideal candidates for tips of scanning probe microscope like the Atomic Force Microscope (AFM). If, by bending, the built up strain is increased beyond a critical point, however, the strain localizes in a buckled structure of carbon nanotubes (see Figure 1.9). In the macroscopic world of plumbing and drinking straws, we are used to the fact that buckling of cylindrical structure leads to induced dislocations or even fracture. On that scale, buckling is thus not reversible. By contrast, buckling of carbon nanotubes is reversible. The influence of buckling on the electrical properties has very interesting surprises [34].

Figure 1.9: Model of a single-walled carbon nanotube which is bending at angles as indicated until it buckles [30].
(3) Thermal properties of carbon nanotubes

The behaviour of any material when subjected to a change in temperature (heat) is termed as the thermal property of the material. All nanotubes are expected to be very good thermal conductors along the tube, exhibiting a property known as "ballistic conduction," but they are good insulators laterally to the tube axis. It is predicted that carbon nanotubes will be able to transmit up to 6000 watts per meter per Kelvin at room temperature, comparing this with copper, a metal well-known for its good thermal conductivity, transmits only 385 W/m/K. The temperature stability of carbon nanotubes is estimated to be up to 2800 degrees Celsius in vacuum and about 750 degrees Celsius in air [18].

(4) Defects

As with any material, the existence of the defects affects the material properties. Defects can occur in the form of atomic vacancies. High levels of such defects can lower the tensile strength by up to 85% [35]. Another well-known form of defect that occurs in carbon nanotubes is known as the Stone Wales defect, which creates a pentagon and heptagon pair by rearrangement of the bonds. Because of the very small structure of CNTs, the tensile strength of the tube is dependent on its weakest segment in a similar manner to a chain, where a defect in a single link diminishes the strength of the entire chain [18].

The electrical properties of the tubes are also affected by the presence of defects. A common result is the lowered conductivity through the defective region of the tube. Some defect formation in armchair-type tubes (which can conduct electricity) can cause the region surrounding that defect to become semiconducting. Furthermore, single monoatomic vacancies induce magnetic properties.

The thermal properties of the tubes are heavily affected by defects. Such defects lead to phonon scattering, which in turn increases the relaxation rate of the phonons. This reduces the mean free path, and reduces the thermal conductivity of nanotube structures.

1.5 Potential applications of carbon nanotubes

Carbon nanotubes have attracted the fancy of many scientists worldwide. The small dimension, low density, high stiffness, high strength and the remarkable physical
properties of these structures make them a very unique material. Indeed, NASA is developing materials using nanotubes for space applications, where weight-driven cost is the major concern, by taking advantage of their tremendous stiffness and strength. Composites based on nanotubes could offer strength-to-weight ratios beyond any materials currently available. Companies such as Samsung and NEC have demonstrated product quality devices utilizing carbon nanotubes for field emission display [36-38] and have invested tremendously. Such devices have shown superior qualities such as low turn-on electric field, high emission current density, and high stability. Steady progress has been made in developing single-walled carbon nanotube nanodevices and nanocircuits [39, 42], showing remarkable logic and amplification functions. Single-walled carbon nanotubes are also under intensive study as efficient storage devices, both for alkali ions for nanoscale power sources and for hydrogen for fuel cell applications.

On other fronts, carbon nanotubes also show great potential for biomedical application due to their biocompatibility and high strength. Carbon nanotubes are also being considered for drug delivery: they could be implanted at the sites where a drug is needed without trauma, and slowly release a drug over time. They are also of considerable promise in cellular experiments, where they can be used as nanopipettes for distribution of extremely small volumes of liquid or gas into living cells or onto surface.

In the following sections, we describe several interesting applications of carbon nanotubes based on some of the remarkable materials properties of nanotubes.

(1) Nanotubes as sensors and probes

Carbon nanotubes are very promising for the development of novel technological application, such as tips for scanning probe microscope [41] and sensors [42]. Among the anticipated application of carbon nanotubes is their use as components in biological devices. Most of the research undertaken in this direction has been focused on attaching biological molecules onto these nano-materials.

One of the key issues of biosensor design is the establishment of a fast electron-transfer between the enzyme active site and the electrochemical transducer. The structure dependent metallic character of carbon nanotubes should allow them to promote electron-
transfer reactions at low over potentials. This characteristic, along with their high surface area, provides the ground for unique biochemical sensing systems. The latest advances in production of well-controlled aligned carbon nanotubes array have shown the way for incorporation of nanotechnology in biosensor technology.

The small size and unique properties of carbon nanotubes suggests that they can be used in sensor devices with unprecedented sensitivity. One route to make such sensors is to utilize the electrical properties of carbon nanotubes. Experiment [43] and computation [44-45] have shown that the conductivity of carbon nanotubes can change by several orders of magnitude when deformed by the tip of an atomic force microscope. Carbon nanotube chemical sensors have also been demonstrated: it has been found experimentally that the electrical resistance of a semiconducting single-walled nanotube change dramatically upon adsorption of certain gaseous molecules, such as \( NO_2 \), \( NH_3 \) [46], \( H_2 \) [47], and \( O_2 \) [48]. This phenomenon has been modeled numerically by Peng et al. [49] using Local Density Approximation, LDA, technique.

The high sensitivity of the Raman spectra of carbon nanotubes to their environment also makes them useful as mechanical sensors. Raman spectra are known from experiment to give shifted peaks when carbon nanotubes are under stress or strain [50-52]. This phenomenon has been used to detect phase transitions and to measure stress fields in polymers with embedded nanotubes [53-54].

Carbon nanotube scanning probe tips for atomic probe microscope are now sold by Seiko Instruments and manufactured by Daiken Chemical Company. The mechanical robustness of the nanotubes and the low buckling force dramatically increase probe life and minimize sample damage during repeated hard crashes into substrates. The cylindrical shape and small tube diameter enable imaging in narrow, deep crevices and improve resolution in comparison to conventional nanoprobe-es, especially for high sample feature heights [55-56].

(2) Carbon nanotube-reinforced polymer

The extremely high modulus and tunable electrical and thermal properties of carbon nanotubes offer an appealing mechanism to dramatically improve both strength and
stiffness characteristics, as well as add multifunctionality to polymer based composite systems. Among the encouraging results is work by Qian et al. for a multi-walled carbon nanotube reinforced polymer where good dispersion and matrix bonding was achieved [57]. In this case, using only 0.5 vol % nanotubes reinforcement with no alignment and moderate nanotube waviness, elastic stiffness was improved 40% over that of the neat matrix material and strength values improved nearly 25%. Figure 1.10 shows nanotubes bridging a matrix crack and demonstrates excellent bonding between nanotubes and matrix material. Viscoelastic properties have also been investigated, with some evidence that well dispersed nanotubes impact the mobility of the polymer chains themselves, causing change in glass transition temperature and relaxation characteristics [58-59], a feature not observed in polymer with a micron sized reinforcing phase. Limited work on electrical properties shows that percolation can be reached with nanotube volume fraction of less than 1% [60], leading to dramatic changes in electrical response of the polymer. This enables applications such as polymer coating with electrostatic discharge capability [61].

![Figure 1.10: Carbon nanotubes reinforced materials.](image)

(3) Electrochemical supercapacitors

Supercapacitors have a high capacitance and are potentially applicable in electronic devices. Typically, they are comprised of two electrodes separated by an insulating material that is ionically conducting in electrochemical devices. The capacity of an electrochemical supercapacitor inversely depends on the separation between the charge on
the electrode and the counter charge in the electrolyte. Because this separation is about a nanometer for nanotubes in electrodes, very large capacities results from the high nanotube surface area accessible to the electrolyte. In this way, a large amount of charge injection occurs if only a small voltage is applied. This charge injection is used for energy storage in nanotubes supercapacitors [62].

(4) Carbon nanotubes in interconnect application

Due to the variety of extraordinary properties exhibited by carbon nanotubes which indicate applications in microelectronic interconnect [63] whereas the reasonably large band gap of narrow single-walled nanotube suggests their use as nanoscale transistor elements [64].

If we look at the cross-section of a typical chip like in Figure 1.11(a), we see that nowadays chips have become ‘all wire’. The transistors at bottom make up only a fraction of the total chip, and already today, the speed and performance of such chips is mainly limited by the interconnect, i.e. the copper-bases wiring of the transistors with different metal layers(wires) and the vertical connections between these layers, which are termed via. These vias are prone to electromigration failures as can be seen in Figure 1.11(b). The arrows mark regions, where voids have formed due to the high current densities in these structures. The Information Technology Strategic Research (ITSR) predicts a current density of $3.3 \times 10^6 \text{ A/cm}^2$ in a via, a value which to date, can only be supported by CNTs, where current densities exceeding $10^7 \text{ A/cm}^2$ have been reported in nanotubes without heat sinks [65]. At this ITSR technology node MPU/ASIC half-pitch of 32 nm is predicted. On this scale, traditional interconnect schemes become problematic due to the increase in wire resistances resulting from grain and surface scattering effects and the higher current densities which must be carried [66]. Sufficient heat removal from the chip is already a problem in present day computers. Due to their super thermal conductivity, exceeds that of diamond by a factor of two, nanotubes may also help to remove the heat more efficiently from the chip.
I. Copper Transistors

Figure 1.11: (a) Cross section through a typical chip, which consists mainly of copper-wires and -vias. (b) Copper-via connecting two different metallization levels in chip. The arrows indicate electromigration induced failures. (c) Proposed CNT-via, that should withstand a 1000 times higher current density.

(5) Carbon nanotubes in transistor applications

If a semiconducting SWNT of about 1nm diameter is attached to two separated (metallic) contacts (source and drain), a nearby third gate-electrode can modulate the conductivity of the tube by about 6 orders of magnitude at room temperature. This effect has already been observed in 1998 and has led to a kind of race in the scientific community to achieve the best performing CNT-device [64, 67-68].

(6) Flat panel display

Prototype matrix-addressable diode flat panel displays have been fabricated using carbon nanotubes as the electron emission source [37]. One-demonstration (demo) structure constructed at Northwestern University consists of nanotube-epoxy stripes on the cathode glass plate and phosphor-coated Indium-Tin-Oxide (ITO) stripes on the anode plate. Pixels are formed at the intersection of cathode and anode stripes plate [37], as illustrated in Figure 1.12. At a cathode-anode gap distance of 30 μm, 230 V is required to obtain the emission current density necessary to drive the diode display (~76 μA/mm²). The device is operated using the half-voltage off-pixel scheme. Pulses of ±150 V are switched among anode and cathode stripes, respectively to produce an image.
Recently, a 4-5 inch diode-type field emission display has been fabricated by Samsung (Figure 1.12), with SWNT stripes on the cathode and phosphor-coated ITO stripes on the anode running orthogonally to the cathode stripes [38]. SWNTs synthesized by the arc-discharge method were dispersed in isoroxy alcohol and then mixed with an organic mixture of nitro cellulose. The paste was squeezed into sodalime glasses through a metal mesh, 20 µm in size, and then heat-treated to remove the organic binder. $Y_2O_3:Eu$, $ZnS:Cu, Al$, and $ZnS:Ag, Cl$, phosphor-coated glass is used as the anode.

![Figure 1.12: Left: Schematic of a prototype field emission display using carbon nanotubes. Right: A prototype 4.5 field emission display fabricated by Samsung using carbon nanotubes (image provided by Dr. W. Choi of Samsung Advanced Institute of Technology[38].](image)

(6) Carbon nanotube computer

Researchers at IBM have overcome an important obstacle to building computers based on carbon nanotubes, by developing a way to selectively arrange transistors that were made using carbon nanotubes [70]. The achievement could help make large-scale integrated circuits built out of carbon nanotubes possible, leading to ultrafast, low-power processors. Single-walled carbon nanotubes are one prominent candidate; already researchers have built carbon nanotube transistor that show promising performance. According to estimates, carbon nanotubes have the potential to produce transistors that run 10 times faster than...
even anticipated future generations of silicon-based devices, while at the same time using less power [70].

(7) Ultrastrong carbon nanotube muscles

By spinning carbon nanotubes into yarn a fraction of the width of a human hair, researchers have developed artificial muscles that exert 100 times the force, per area, of natural muscle. This is according to Ray Baughman director of the Nanostructure Institute at the University of Texas at Dallas, who presented the research in Boston at the Materials Research Society Conference. Although the carbon nanotube muscles can outperform muscles on a per-area basis, exerting 100 times the force, natural muscles are much large, making them stronger [70].

(8) Carbon nanotube as a hydrogen store

Everybody known that we have to face two crises related to energy: the exhaustion of fossil fuels and the global warming effects. One possible solution to these problems is to use hydrogen but we’re not there yet. However, physicists from California have found a promising way to store hydrogen inside carbon nanotubes.

Materials with high hydrogen storage capacities are desirable for energy storage applications. Metal hydrides and cryo-adsorption are two commonly used means to store hydrogen, typically at high pressure and/or low temperature. In metal hydrides, hydrogen is reversibly stored in the interstitial sites of the host lattice. The electrical energy is produced by direct electrochemical conversion. Hydrogen can also be stored in the gas phase in the metal hydrides. The relatively low gravimetric energy density has limited the application of the metal hydride batteries. Because of their cylindrical and hollow geometry, and nanometer-scale diameters, it has been predicted that the carbon nanotubes can store liquid and gas in the inner through a capillary effect [71]. A Temperature-Programmed Desorption (TPD) study on SWNT-containing material (0.1-0.2wt% SWNT) estimates a gravimetric storage density of 5-10wt% SWNT when $H_2$ exposures were carried out at 300 torr for 10 min at 277 K followed by 3 min at 133 K [72]. If all the hydrogen molecules are assumed to be inside the nanotubes, the reported density would imply a much higher packing density of $H_2$ inside the tubes than expected from normal
\( H_2 - H_2 \) distance. It was found that no absorption takes place at 300 K. Upon cutting (opening) the nanotubes by an oxidation process, the amount of absorbed \( H_2 \) molecules increased to 4-5 wt\%. A separate study on higher purity materials reported ~8 wt\% of \( H_2 \) adsorption at 80 K, but using a much higher pressure of 100 atm, suggests that nanotubes have the higher storage capacity than any of carbon materials. It is believed that hydrogen in first adsorbed on the outer surface of the crystalline ropes [73].

1.6 Review of work done

It is very difficult to obtain direct experimental information for the structure of single-walled nanotubes, and theoretical information has been given so far [74-79]. The strong similarity of the chemistry of carbon nanotubes to graphite allows theoretical analysis to be done based on empirical methodology imported from studies on graphite.

Raman experiments offer valuable information for the vibration of the ropes of single-walled nanotubes [80]. The Raman spectrum of a SWNT can be broadly divided into two parts: a low-frequency radial mode around 180 cm\(^{-1}\) and a high-frequency tangential mode around 1590 cm\(^{-1}\).

The most important feature in Raman spectrum of CNT’s is the Radial Breathing Mode (RBM), which is often observed between 100 and 250 cm\(^{-1}\). The radial band is sensitive to diameter, irrespective of the chirality of the tube. The frequency of the RBM (\( \omega_r \) in cm\(^{-1}\)) is directly linked to the reciprocal of the nanotube diameter(\( d_t \)). In the case of an isolated SWNT this relation is \( \omega_r = 224/d_t \) [81]. For example, the difference in the breathing mode frequencies of the (10,10) and (11,11) tubes with diameters of 13.4Å and 14.9 Å, respectively, is 17 cm\(^{-1}\) while there is no measurable difference between the breathing mode frequencies of the (10,10) and (17,0) tubes with diameters of 13.4Å and 13.2 Å, respectively[79]. However, non isolated SWNT’s are subject to inter-tube interactions which increase the frequency of the RBM. Resonant Raman scattering has been used to measure the vibrational stemming from tubes of different diameters by looking at the \( A_{1g} \) breathing mode that exhibit a strong dependence on the diameter [82].
This therefore provides a technique to experimentally measure the effect of pressure on the tube. The D mode (the disorder band is well-known in disordered graphite materials and located between 1330 and 1360 cm\(^{-1}\) when excited with a visible laser) is expected to be observed in multi-walled nanotubes. However, when it is observed in SWNT’s, one assumes that it is due to defects in the tubes. The G mode or (TM-Tangential Mode) corresponds to the stretching mode of the carbon-carbon bond in the graphite plane. This mode is located near 1580 cm\(^{-1}\).

Various levels of studies were performed on the properties of the SWNTs, including use of classical molecular mechanics (MM), lattice dynamics (LD), molecular dynamics (MD), tight binding and \textit{ab initio} level quantum mechanical (QM) methods [22,23, 76, 82-89].

Calculations on many properties of single-walled nanotubes like Young’s modulus, bulk and structural properties and thermodynamics have also been reported using one bond length equivalent to graphitic bond length or modified value [90-92]. Cronin et al. have calculated the electronic band structure of semiconducting and metallic nanotubes under uniaxial strain using tight-binding approximations [93]. They used unstrained bond length equal to 1.44 Å for all the nanotubes.

In the tight-binding calculations, to calculate the band structure of carbon nanotubes, the overlap integral assumed has the same value \(-\gamma_0\) for all the three nearest neighbours. This is true for graphene, but for the nanotube the distance to the three nearest neighbours may be changed to a small or a large amount due to the curvature, i.e. one should have three different constant \(\gamma_1, \gamma_2\) and \(\gamma_3\). This will open very small gaps for all metallic nanotubes except for armchair \((n,n)\) nanotubes and the size of the gap depends on the values of \(\gamma_1, \gamma_2\) and \(\gamma_3\) [76,94].

Gao et al. have used extensive molecular mechanics and molecular dynamics and employed an accurate interaction potential derived from quantum mechanics to study the energy, structure, mechanical and vibrational properties of single-walled carbon nanotubes [95]. They investigated the stability domains of circular and collapsed cross section structures of armchair \((n,n)\), zigzag \((n,0)\), and chiral \((2n,n)\) isolated single-walled
carbon nanotubes up to a circular cross section radius of 170 Å. They found that there are three different stability regions based on circular cross section radius. Below 10 Å radii only the circular cross section tubules are stable. Between 10 Å and 30 Å both circular and collapsed form are possible, however, the circular cross section SWNTs are energetically favorable. Beyond 30 Å (crossover radius) the collapsed form becomes favorable for all three types of SWNTs.

Significant effort has been made to calculate the bond lengths in carbon nanotubes using either a model potential or ab initio MD calculations. Robertson et al. carried out first studies on the structure and energetic of isolated small-diameter SWNTs [96]. They have used both empirical potentials and first-principle total energy methods to examine the energetic and elastic properties of all possible graphitic tubules with radii less than 9 Å. They found that the minimum energy structure of (5,5) tubule by direct minimization of the total energy gives a radius of 3.47 Å with both types of carbon-carbon bonds assumed equal with a length of 1.44 Å.

Ab initio calculations on the structural, elastic and vibrational properties of single-walled carbon nanotubes with different radii and chirality have been performed by Sanchez-Portal et al. [97]. They found that different quantities are monitored versus the tube radius and the validity of expectations based on graphite is explored down to small radii, where some deviations appear related to curvature-induced rehybridization of the carbon orbitals. They reported, for armchair and zigzag single-walled nanotubes, two inequivalent bond lengths and three bond lengths in general for chiral tubes. Ab initio molecular dynamics simulations are also performed to investigate the equilibrium carbon-carbon bond lengths and bond angles on small single walled nanotubes [98]. They showed that for both zigzag and armchair nanotubes there are two nonequivalent bond lengths and small variation on the bond angles. They also found that one bond length shrinks while the other bond length stretches.

Gulseren et al. have investigated the curvature effects on geometric parameters, energetics, and electronic structure of zigzag single-walled nanotubes with fully optimized geometries from first-principle calculations [99]. They found that the curvature energies are inversely proportional to the square of radius and both bond lengths and bond angles display a
monotonic variation and approach the graphene values as the radius increases. They also found that one bond length is smaller than that of graphite value while the other one is larger.

A study of the nanotube radius effects on the constitutive model for carbon nanotubes performed by adopting a modified Cauchy-Born rule to incorporate the interatomic potential, Tersoff-Brenner potential, into the continuum analysis [100]. The results showed that the nanotube radius has little effect on the mechanical behaviour of single-walled carbon nanotubes subjected to simple tension or pure torsion, while the nanotube orientation has somewhat large influences. They also reported numerical results of bond lengths, bond angles and carbon nanotube diameter.

Many experimental and theoretical studies have also been done on the bundles as well as isolated single-walled nanotubes under pressure [101-105]. These pressure dependent studies reveal that there exists a transition pressure where either the tubes collapse [101] or the vibrational modes change [102] or loss of reversible deformation [103] takes place. It has been observed that the transition pressure depends on the diameter of nanotubes and not on its chirality [101]. A strongly elliptical cross section of carbon nanotubes under pressure was first proposed by Chesnokov et al. [104]. They proposed this structure and obtained in piston-cylinder experiments.

Zhang et al. have carried out classical molecular dynamics simulations (MDS) using a Tersoff-Brener potential to study the collapse of (10,10) single-walled carbon nanotubes in the 4x4 bundle at pressure of -1.2 GPa [105]. They found that the tubes which are aligned in parallel structure become energetically more favorable than the herringbone structure obtained by Elliott et al. [101].

Wu et al. have investigated the electronic transport properties of single-walled carbon nanotubes under hydrostatic pressure [106]. They used first-principle quantum transport calculations aided by molecular dynamics simulation and continuum mechanics analysis. They demonstrated a pressure induced metal to semiconductor transition of armchair SWNTs. They also found that the first transformation of the cross section from a circle to an ellipse takes place at transition pressure of $P_x \approx 1.55$ GPa for (10,10) nanotube. This first
shape transition is driven by a competition between compression and bending of the tube under pressure, while the second shape transition from ellipse to dumbbell is not physically well defined.

Merlen et al. have performed high pressure resonant Raman experiments on well characterized purified single-walled carbon nanotube bundles (average diameter of SWNT=1.3 nm) study a structural phase transition and electronic properties using argon pressure transmitting medium which is known to enter the tubes[107]. They have not noticed clear sign of phase transformation up to the highest pressure of 40 GPa. They suggested that the progressive disappearance of the radial breathing modes observed while increasing pressure should not be interpreted as the sign of structural phase transition. They have also suggested that it is possible that an extremely progressive evolution of the tube cross section occurs under pressure. Such structural evolution might be extremely difficult to detect by Raman spectroscopy. The vanishing of the RBM does not occur at same pressure range as the Raman spectrum measured using 514.5 nm (5 GPa) and 632.8nm (10 GPa), respectively. Then, the vanishing of the RBM cannot be considered as a sign of a first order structural phase transition.

In a recent x-ray diffraction study, Kawasaki et al. have observed progressive changes in the diffraction pattern of single-walled nanotubes for pressures up to 11.2 GPa[108-109]. Their conclusion is that structural changes might occur but are highly difficult to detect and are extremely sensitive to the quality of the hydrostaticity conditions. In a neutron powder diffraction study performed at pressures up to 5 GPa in nonhydrostatic conditions, Rols et al. have interpreted the strong variation of the (10) Bragg peak as a progressive deformation of the tube section from circular to hexagonal [110].

Nanotubes can also be used as ‘crucibles’ for high pressure chemistry at the nanoscale. We can here consider two different scenarios. The nanotubes can be used as nano-anvils or as nano-pistons. In the first one, the compression of the nanotubes by the pressure transmitting medium act on the systems intercalated inside the nanotubes. In the second one, the penetration of the pressure transmitting medium inside the tube pressurizes the encapsulated system. Many different substances can be introduced in the nanotubes, including hydrogen, halogens, metals or even molecules as fullerenes. We can cite the
recent work of Kawasaki et al. where the nanotube cavity was used to induce the 1-D chain polymerization of $C_{60}$ molecules inserted inside the nanotubes (a system known as a ‘peapod’ for obvious reasons) [111]. Also, electron irradiation of multi-walled nanotubes filled with different materials can lead to similar results [112].

### 1.7 Motivation and importance of present work

Single-walled carbon nanotubes are very important materials. Their properties are dependent on many variables such as tube radius, tube length and the indices (n,m). The radius and length of the tube are a function of the bond length. On the basis of the theoretical and experimental works done up till now, it emerges that various results, thus obtained to investigate the structural properties, are built only on the tube radius. Most of the theoretical studies give large deviation in the value of the bond length in graphite sheet from the experimental value. In addition to, the method of the minimization of the energy done by randomly changing the atomic coordinates of the carbon atoms on the surface of the tubes will produce a symmetry-breaking distortion. To avoid this distortion, we adopt a new theoretical procedure to get a set of the bond lengths associated with the minimized energy of the tubes. With our procedure, the value of the bond length in the graphite sheet comes out to be in good agreement with the experimental value and at the same time, all the atoms remain on the cylindrical surface of the tube and are still in the same chemical environment after minimizing the energy of the tube.

Therefore, we attempt to do a detailed study on the variation of the structural parameters, i.e., bond lengths and bond angles of the single-walled carbon nanotubes as a function of the tube radius and chirality of the tubes. We also study the effect of the tube length on the bond lengths and bond angles. This will help analyse results of Rochefort et al. also have studied theoretically the influence of the finite length on the electronic properties of armchair (6,6) tube[139]. They found that, infinite tube, which is metallic, very short tube has an energy band gap and, therefore, semiconducting.

Furthermore, we also attempt to investigate the behaviour of the structural parameters, bond lengths and bond angles, of the tubes under hydrostatic pressure assuming that the tubes continue to have a circular cross section (i.e., the tubes compress) and also assuming...
them to change to elliptical cross section. The reason of this study is that no detailed studies are available of the behaviour of the structural parameters under a hydrostatic pressure, and at what pressure the transition in shape of the cross section takes place, from circular to oval.

In the next chapter, we present the description of graphite sheet, unit cell of carbon nanotubes with all definitions of the variables of single-walled carbon nanotubes that used in this work. It also contains the theoretical procedure and methodology, such as helical and rotational symmetries as a function of one bond length, model potential, modify of some parameters in Tersoff potential and scaling procedure.