

Chapter 2

Carbon Nanotubes

2.1 Introduction

Carbon nanotubes have attracted significant attention since their discovery, as unique valuable nanostructures, with many outstanding properties, leading them toward being applied in a wide variety of novel and amazing applications. The extraordinary properties of carbon nanotubes stem mostly from their perfect hexagonal structure, as well as their high length to diameter or aspect ratio, which is specific to most of nanostructured materials. In other terms, nanomaterials are all uniquely beneficial in many of today's emerging applications, only as a result of their high aspect ratio. This specific characteristic make them interact with their surrounding environment more efficiently, especially when it comes to adsorption properties and interaction in a gaseous environment. In this chapter, the structure of carbon nanotubes and the methods of fabricating them will be introduced and the defects associated with their structure will be explained in detail.

2.2 Carbon and Carbon-Based Nanomaterials

Carbon, the fourteenth element of the periodic table, with symbol C, is a unique element. This exceptional element tends to bond with various atoms differently and hence, presents a variety of exceptional physical, chemical and biological properties. The atomic number of carbon is six and therefore, it has four electrons in its outer shell. These four electrons, known as valance electrons, are available for participating in different types of chemical bonding. Hence, depending on its covalent bonding type, different allotropes of carbon are formed that exhibit tremendously different properties. For instance, graphite and diamond are both allotropes of carbon, though graphite is soft, black and a very good electrical

conductor, but diamond is very hard, transparent and a very bad conductor! Carbon nanotubes and fullerenes, on the other hand, are the nanoscaled allotropes of carbon with many outstanding properties. Figure 2.1 shows these different allotropes of carbon.

As explained before, the discovery of carbon buckyballs or fullerenes in 1985 was one of the initial stages of the development of nanotechnology. The path of progress was further developed in 1991, when carbon nanotubes were first observed and their remarkable properties were introduced to the world of science and technology. Carbonous nanomaterials had shown to be promising candidates as outstanding engineering materials for their exceptional mechanical, thermal, optical and electrical properties. Having four valance electrons, carbon can get involved in chemical bonding in three different orbital hybridizations, which are the sp , sp^2 and sp^3 hybridizations, happening for instance in alkynes, graphite and diamond, respectively. The hybridization of the atomic orbital of carbons

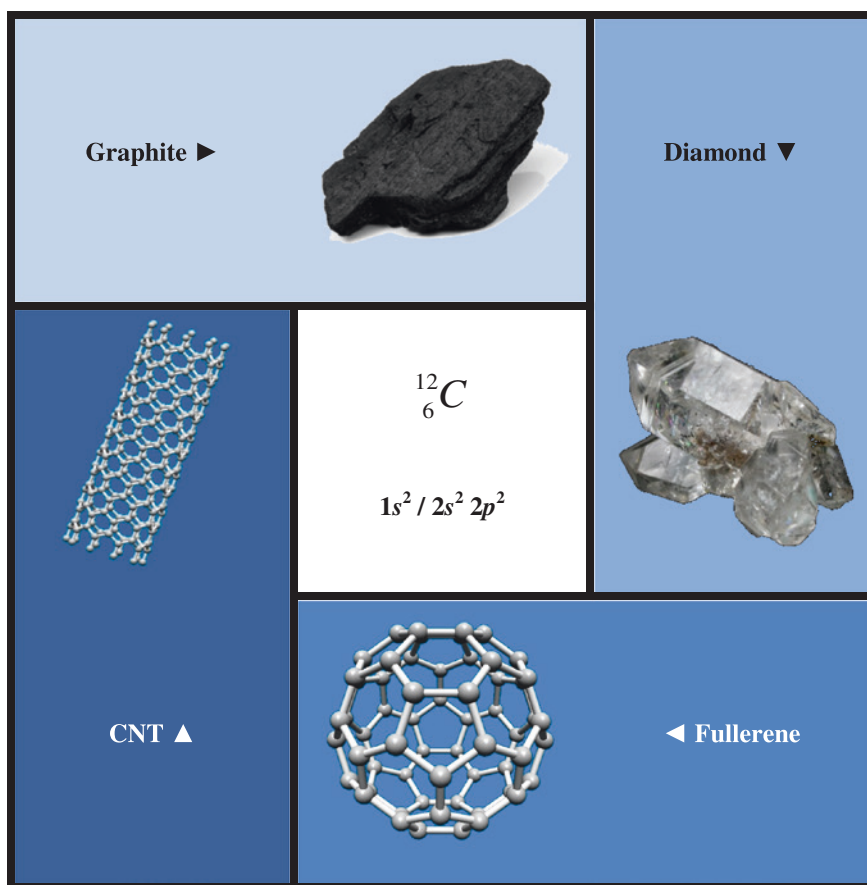


Fig. 2.1 Carbon atom and its allotropes

in carbon nanotubes and fullerenes is of type sp^2 , i.e. similar to that of graphite, making a perfect hexagonal array of atoms (Rahmandoust and Öchsner 2012).

In sp^2 hybridization, three of the valance shell atoms are involved in chemical bonding and hence, there is one free electron, called the π -electron. Materials with extended π -electron clouds, like carbon nanotubes, are called the π -electron materials that exhibit many exceptional thermal and electrical conductivity properties (Ahmadi et al. 2012). The sp^2 C–C bond of CNTs is considered one of the strongest in solid materials; thereby CNTs are expected to yield exceptionally high stiff and strong mechanical properties (Dresselhaus et al. 1995).

2.3 Atomic Structure of Carbon Nanotubes

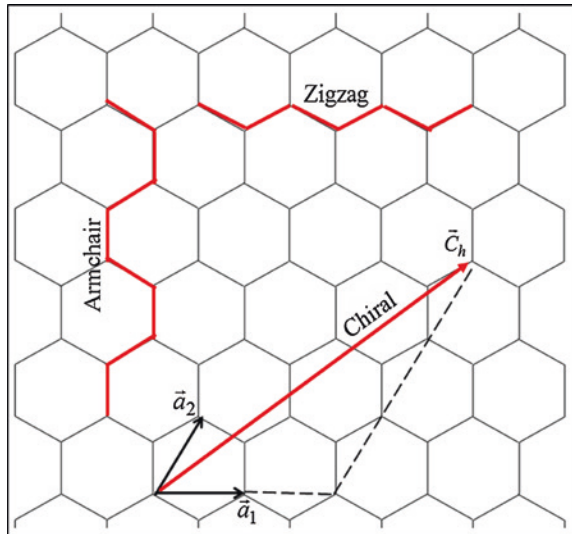
The hexagonal arrangement of atoms in carbon nanotubes and graphene sheets can be described in terms of the tube's chirality or helicity, using the chiral vector, $\vec{C}_h$ or the chiral angle θ . The chiral vector, $\vec{C}_h$, also known as the roll-up vector, is defined by the following equation:

$$\vec{C}_h = m\vec{a}_1 + n\vec{a}_2, \quad (2.1)$$

where the integers n and m are the number of steps along the unit vectors $\vec{a}_1$ and $\vec{a}_2$, as defined in Fig. 2.2. The chiral angle θ determines the amount of *twist* of the carbon nanotube.

Hence, carbon nanotubes are fundamentally classified into three main categories according to their chiral vector, $\vec{C}_h$. A *chiral* (m,n) nanotube in general has unequal, non-zero m and n integers, i.e. $m \neq n \neq 0$ and the chiral angle θ is between its two limits ($0^\circ < \theta < 30^\circ$), whereas for the two limiting cases,

Fig. 2.2 Schematic view of a single-walled zigzag, armchair and chiral carbon nanotubes



i.e. *zigzag* nanotube with chiral angle equal to zero ($\theta = 0^\circ$) and *armchair* nanotube with ($\theta = 30^\circ$), we have $m \neq n$, $n = 0$ and $m = n \neq 0$, respectively. These last two limiting cases are generally known as symmetric carbon nanotubes (Dresselhaus et al. 1995). The chiral, armchair and zigzag carbon nanotubes sometimes exhibit different properties. For instance, chiral, and zigzag nanotubes show semiconducting behavior, whereas armchair carbon nanotubes are categorized as metal and are considered conducting materials (Ahmadi et al. 2012). In addition to chirality, the number of layers is also another factor that is considered for categorizing carbon nanotubes, hence they are categorized as *single-walled carbon nanotube* (SWCNT) and *multi-walled carbon nanotube* (MWCNT) which are explained in detail below.

2.3.1 Single Walled Carbon Nanotubes

A single-walled carbon nanotube can be imagined as a graphene sheet that has been rolled into a tube or cylinder with a diameter in range of 0.4–3 nm. The thickness of the tube's wall is considered equal to that of a graphene sheet, which is about 0.34 nm (To 2006; Tserpes and Papanikos 2005; Li and Chou 2003). For a given (m,n) carbon nanotube, the radius of the tube can be calculated using chiral vector integers, m and n , as follows:

$$R_{\text{CNT}} = \text{Length of } \vec{C}_h / 2\pi = \frac{a_0 \sqrt{m^2 + mn + n^2}}{2\pi}, \quad (2.2)$$

where a_0 is the length of each unit vector. In carbon nanotubes, the sp^2 carbon–carbon bond length is $b = 0.142$ nm and therefore a_0 is equal to $\sqrt{3}b$ (Dresselhaus et al. 1995; Natsuki et al. 2004).

2.3.2 Multi Walled Carbon Nanotubes

A multi-walled carbon nanotube comprises of two to 50 coaxial nanotubes with an inter-layer spacing of 0.34 nm. The diameter of MWCNTs generally ranges from 3–30 nm (Dresselhaus et al. 1995). These nanostructures were discovered and reported first in 1991 by Iijima at the NEC Laboratory in Tsukuba, Japan (Iijima 1991). He observed MWCNTs, using a *high-resolution transmission electron microscope* (HRTEM), 2 years before discovering single-walled carbon nanotubes at the same laboratory (Iijima and Ichihashi 1993). However, approximately at the same time, Russian scientists also reported that they observed carbon nanotubes and nanotube bundles (Gal'Pern et al. 1992; Kosakovskaya et al. 1992). Their discovered structures had generally a much smaller length to diameter ratio compared to what was found in Iijima's laboratory. Bethune also reported

the experimental discovery of single-walled carbon nanotubes in 1993, at the IBM Almaden Laboratory in California, the United States (Bethune et al. 1993).

As explained before, hybridization of carbon atomic orbital in carbon nanotubes is of type sp^2 , in which each atom is joined to three other neighbors in a planar trigonal arrangement forming a hexagonal sheet of covalence bonds. In case of MWCNTs, in addition to the above mentioned strong covalence chemical interactions, individual sheets or cylinders interact with each other by non-covalent interactions that can be adequately described by weak van der Waals force, using the Lennard-Jones potential (Kalamkarov et al. 2006), presented in Eq. (2.3).

$$V_{LJ} = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (2.3)$$

In Eq. (2.3), the terms σ (in nm) and ε (in kJ/mol) are the *Lennard-Jones parameters*. These parameters are material-specific and determine the nature and strength of the interaction. For a carbon–carbon non-covalent interaction, the values of the Lennard-Jones parameters are $\sigma = 0.3851$ nm and $\varepsilon = 0.4396$ kJ/mol. The diagram of the Lennard-Jones potential interacting between two carbon atoms is presented in Fig. 2.3.

As it is shown in the diagram, σ is by definition, the distance at which the potential between the two interacting particles becomes zero and ε is the minimum potential acting on them. As a result of the Lennard-Jones potential, the Lennard-Jones force acts on the particles. The Lennard-Jones force is strongly repulsive when the particles approach too close to each other and is mildly attractive when they are far away. The Lennard-Jones force, given below, is in general considered as a weak force. The critical distance, shown in Fig. 2.4, is the distance at which the force becomes zero is named as r_o and is equal to $r_o = \sqrt[6]{2} \cdot \sigma$

Fig. 2.3 Carbon–carbon Lennard-Jones interaction

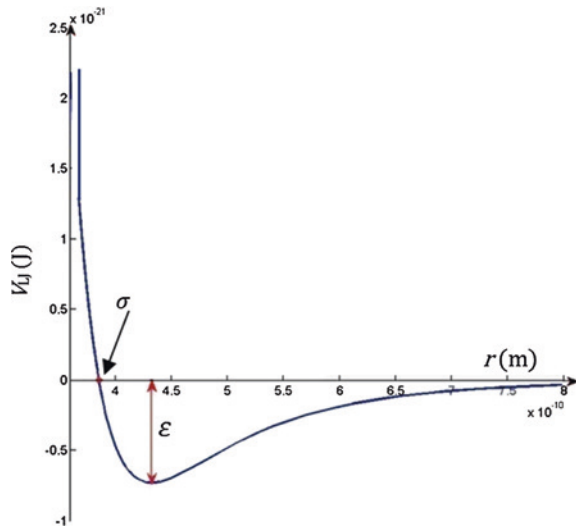
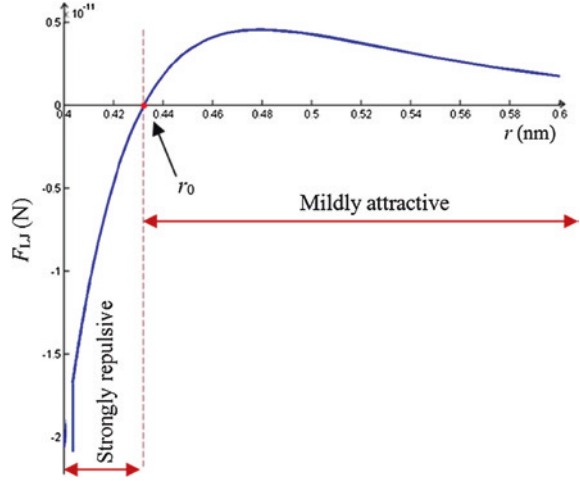


Fig. 2.4 The Lennard-Jones force



$$F_{LJ} = \frac{dV_{LJ}}{dr} = \frac{4\varepsilon}{r} \left[-12 \left(\frac{\sigma}{r} \right)^{12} + 6 \left(\frac{\sigma}{r} \right)^6 \right] \quad (2.4)$$

Although introducing the Lennard-Jones interaction leads to more accurate results with respect to the analytical solution, in modeling multi walled carbon nanotubes, investigations show that obtained results, when this weak interaction was not defined in the model are reliable and the difference is ignorable, especially when longer tubes are modeled and studied (Rahmandoust and Öchsner 2012a, b). However, in many investigations, this type of weak bonding between the layers of carbon nanotubes is defined to achieve more accurate results.

Other than the Lennard-Jones potential, there is another common model for showing two-body interactions, known as the Morse potential function, introduced in the following equations:

$$V(r) = \varepsilon [e^{2\beta(\rho-r)} - 2e^{\beta(\rho-r)}], \quad (2.5)$$

$$F(r) = 2\varepsilon\beta [e^{2\beta(\rho-r)} - 2e^{\beta(\rho-r)}], \quad (2.6)$$

where β is an inverse length-scaling factor, ρ and ε are the equilibrium bond length and displacement energy, respectively. The Morse potential function has been modified for various types of materials and interfaces. In chemistry, physics and engineering, the Lennard-Jones and Morse potentials are commonly used in molecular dynamics simulations, based on the two-body approximation (Ghadyani and Rahmandoust 2015).

2.4 Properties of Carbon Nanotubes

As mentioned earlier, the discovery of carbon nanotubes produced a lot of excitement among scientists, as a result of their remarkable properties and the potential extraordinary application that they could introduce to the world of science and technology. The mechanical strength per volume of carbon nanotubes is much greater than conventional materials. Furthermore, their outstanding electrical properties have made them a suitable option in fabricating flat panel TV and monitor displays, batteries and many other electronic devices. Scientists were correctly dreaming about expanding the borders of their imagination on the new and emerging capabilities that these materials could introduce as a part of many small and smart devices.

2.4.1 Mechanical Properties

It is widely recognized that the elastic modulus of a material is closely related to the chemical bonding of its constituent atoms. The sp^2 carbon–carbon bonding, observed in carbon nanotubes, is considered one of the strongest solid materials; thus, CNTs are expected to yield exceptionally high stiff and strong mechanical properties (Sie 2009). Using different study techniques, Young's modulus of carbon nanotubes, obtained from experimental and numerical investigations, has been reported to be very high, i.e. about 1 TPa.

2.4.1.1 Elastic Modulus

Numerous methods have been employed to study various mechanical properties of CNTs in their perfect and defective forms. Lu posits values of the Young's modulus of CNTs in a range between 0.97 to 1.11 TPa, using empirical force-constant model (Lu 1997), while Krishnan et al. measured Young's modulus for 27 isolated single-walled carbon nanotubes experimentally using transmission electron microscope (TEM) and achieved values between 0.9 to 1.7 TPa, with a mean of $1.25-0.35/+0.45$ TPa (Krishnan et al. 1998). Tight-binding and ab initio quantum mechanical approaches were also applied to investigate Young's modulus of carbon nanotubes in 1999 by Hernández et al. and Sánchez-Portal et al. respectively. Hernández reported a value between 1.22 to 1.25 TPa for different types of CNT chiralities investigated (Hernández et al. 1999a), while Sánchez posits Young's modulus of carbon nanotubes to be almost equal to that of graphene, regardless of the tube's chirality and type (Sánchez-Portal et al. 1999). More recent experimental investigations, using atomic force microscope (AFM), resulted in obtaining Young's modulus value = 1.2 TPa (Tomblér et al. 2000).

Li and Chou obtained values from 0.89 to 1.033 TPa, using continuum structural mechanics (Li and Chou 2003), whereas Natsuki obtained the elastic modulus of CNTs in the range 0.5 TPa to more than 1.1 TPa, depending on the wall thickness, using the same approach (Natsuki et al. 2004). To reported Young's modulus about 1.024 TPa based on continuum mechanics studies (To 2006). Molecular dynamics (MD) was also applied extensively to study the mechanical properties of carbon nanotubes. Chang and Gao used the technique to predict a value of the Young's modulus of 1.06 TPa (Chang and Gao 2003). WenXing et al. considered different chiralities and tube lengths and obtained elastic modulus ranging between 0.904 to 0.939 TPa (WenXing et al. 2004). Molecular mechanics is another very common scientific approach used to investigate the elastic properties of CNTs. In an investigation with the purpose of obtaining the fracture behavior of carbon nanotubes, Duan et al. used this technique to report values between 1.05 and 1.34 TPa for Young's modulus (Duan et al. 2007). Fang et al. observed the influence of different tube diameters on elastic properties of CNTs that ranged from 0.95 to 0.99 TPa for (Fang et al. 2007). First-principles approach led to values around 0.918 TPa for zigzag and about 0.874 TPa for armchair CNTs (Song et al. 2010), whereas by the finite element method (FEM) investigations, Young's modulus of single- and multi-walled CNTs was obtained in the range 1.03–1.05 TPa (Rahmandoust and Öchsner 2012a, b).

Other than single-walled carbon nanotubes, multi-walled carbon nanotubes have also been studied by different scientists. Kalamkarov used FEM to analyze MWCNT and studied their mechanical properties. Young's modulus of the MWCNT, obtained from this research, ranges from 1.32 to 1.58 TPa (Kalamkarov et al. 2006), whereas in a more recent investigation Fan reported Young's modulus to be ranging from 0.99 to 1.03 TPa using the finite element method (Fan et al. 2009). Depending on the approach and the energy potential used, Poisson's ratio of the carbon nanotube was obtained around 0.05–0.28 (Natsuki et al. 2004; Tserpes and Papanikos 2005; Sie 2009; Rahmandoust and Öchsner 2009).

2.4.1.2 Shear Modulus

Shear modulus of carbon nanotubes has also been evaluated by two types of tests, i.e. torsion and tensile tests for both SWCNTs and MWCNTs. The results are generally reported to be in the range of 0.2 and 0.5 TPa, which is considered a high shear modulus. However, the vast reported range is due to the applied method of obtaining the results. According to a recent investigation, the remarkable difference observed between the results from torsion and tensile tests, is due the non-isotropic behavior of carbon nanotubes (Ghavamian et al. 2013).

Jin and Yuan evaluated the mechanical properties of single-walled carbon nanotubes by numerical simulation, using both energy and force approaches. They predicted the shear modulus about 0.546 and 0.492 TPa, respectively (Jin and Yuan

2003). Li and Chou acquired shear modulus of single-walled carbon nanotubes in the range of 0.22–0.48 TPa, by using a structural mechanics approach (Li and Chou 2003). In the case of MWCNTs, Li and Chou obtained the shear modulus value about 0.40 ± 0.05 TPa, which was slightly lower than the results, obtained for SWCNTs, while Yu applied a molecular dynamics method in which single-walled carbon nanotubes were simulated under the torsion test to evaluate their mechanical properties. According to their results, the value of shear modulus changed between 0.37 and 0.5 TPa (Yu et al. 2004). Furthermore, Natsuki developed an analytical method for modeling the elastic properties of single-walled carbon nanotubes. They obtained the shear modulus in the range of 0.32 and 0.37 TPa (Natsuki et al. 2004).

Tserpes and Papanikos obtained the shear modulus of different single-walled carbon nanotubes, varying from 0.283 to 0.504 TPa by defining three-dimensional finite element models (Tserpes and Papanikos 2005). Kalamkarov team used two different continuum-based approaches to model the behavior of CNTs and investigated their mechanical properties. The first approach which was an analytical one, resulted in the shear modulus equal to 0.32 TPa for single-walled CNT and the second approach which was a numerical method, using the finite element method, predicted shear modulus between 0.14 and 0.47 TPa for single-walled and 0.44–0.47 TPa for three- and four-walled carbon nanotubes (Kalamkarov et al. 2006). In addition, To also employed finite element method in which the Poisson's ratio effect was included in the determination of mechanical properties of SWCNTs. This investigation yielded the shear modulus equal to 0.47 TPa (To 2006). A combination of molecular mechanics and continuum mechanics was applied to evaluate the properties of CNTs by Wu. The value of shear modulus obtained by this method was in the range of 0.32–0.41 TPa for SWCNTs (Wu et al. 2006).

The shear modulus of CNTs was also derived by putting the nanostructure under tensile test. Fan and his research team applied the FEM simulation technique to investigate the mechanical properties of MWCNTs. According to their results, the shear modulus of CNTs was calculated in the range of 0.35–0.45 TPa for single-, double- and triple-walled carbon nanotubes (Fan et al. 2009). Rahmandoust and Öchsner applied the same technique based on the substitution of covalent bonds between atoms by beam elements to model multi-walled carbon nanotubes, and by defining non-material links between the layers to introduce the van der Waals force. They finally acquired the value of shear modulus of the multi-walled carbon nanotubes from 0.37 to 0.47 TPa (Rahmandoust and Öchsner 2012a, b), whereas for SWCNTs they reported 0.48 TPa as shear modulus (Rahmandoust and Öchsner 2009). Ghavamian used finite element method to compare the shear modulus obtained from torsion or tensile tests for single and multi walled carbon nanotubes. According to his investigations, increasing the number of CNT walls, leads to a decrease in the value of the shear modulus (Ghavamian et al. 2013).

2.4.1.3 Buckling Behavior and Resonant Frequency

Buckling behavior and natural resonance frequency of single- and multi-walled carbon nanotubes were also investigated by many scholars. Carbon nanotubes are very vulnerable to buckling, as they are long and hollow structures. However, the results show that they are at the same time capable of retaining their buckling capacity and recover their elasticity (Rahmandoust and Öchsner 2012a, b; Ghavamian and Öchsner 2012; Wang et al. 2010; Fan et al. 2009). A brief review on the investigations about the buckling properties of CNTs has been published in 2010 (Wang et al. 2010). Besides, investigations show that adding small portion of CNT's to neat resin, can improve the fundamental frequencies of CNT reinforced composite remarkably, without imposing any striking change in mass density of material (Fereidoon et al. 2013; Formica et al. 2010). Hence, vibrational behavior of CNTs had been investigated accurately as one of the fundamental characteristics of intact/perfect CNT's (Moghadam et al. 2014; Ghavamian and Öchsner 2013a, b). On the other hand, as a result of their small size, carbon nanotubes can make acceptable resonators in signal processing systems as well. The resonant frequency enhances as the size of the resonator decreases and higher resonance frequency is equal to higher sensibility (Santos 1999).

2.4.2 Electrical Properties

The electrical properties of carbon nanotubes were in fact among those first interesting points found about these spectacular structures by scientists. Compared to conventional silicon-based electronics, carbon based nanoelectronics promise greater flexibility and advantages conferred by miniaturization (McEuen 1998). Carbon nanotubes are also considered as potential candidates for molecular-electronics (Vouris 2002) and many remarkable properties of them, peculiarly those that are due to their low dimensionality can be harnessed and gainfully employed in this field (Kelly 1995). However, large scale assembly of CNTs, at a level that would be striking to system designers is still challenging in many applications such as in devices where power savings, radiation hardness, and reduced heat dissipation are in major considerations (DeHon 2002).

In this section, firstly, the classification of CNTs into conductors and semiconductors is discussed and then, the electrical properties of single- and multi-walled CNTs are explained to include significant features of electrical transport, which can affect interpretation of measurements and suitability of them being used in advanced electronics.

2.4.2.1 Conducting and Semiconducting CNT

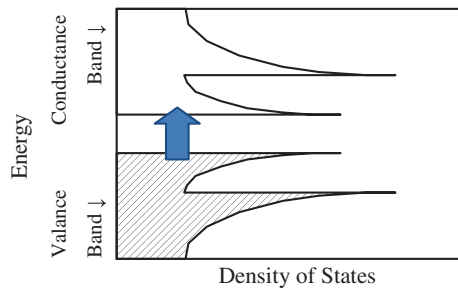
As explained before, carbon nanotubes can be categorized to three various main types according to their helicity, namely zigzag, armchair and chiral tubes. These

different types are described using two integers n and m . According to this method of categorizing, any nanotube can be described by (m,n) for chiral nanotube, $(m,0)$ for zigzag and (m,m) for armchair carbon nanotube, creating variety of diameters and twisting angles. From the electronic properties point of view, carbon nanotubes can behave both as semiconducting and metallic, depending on their twisting angle. In other words, the helicity of the nanotube will influence the band gap of its density of states (DOS), varying from 0 eV to a range between 20 and 2 eV, and hence producing both metallic and semiconducting nanotubes out of the same material, respectively (Ahmadi et al. 2012). Many experimental and theoretical studies have focused on finding the relationship between the CNT's atomic structures and its electronic properties, as well as its electron-electron and electron-phonon interaction effects (Dekker 1999; Tanaka et al. 1997).

According to the available investigations, a given nanotube (m,n) nanotube exhibits metallic conducting properties with zero eV bandgap, if $2m + n = 3N$, where N is an integer equal to 0, 1, 2, etc. and therefore, they have electrons in their conduction bands at room temperature, conduct electricity very well, and are called metallic nanotubes. On the other hand, the tubes are semiconductor if $2m + n \neq 3N$, with a band gap varying inversely with the diameter of the tube. Regardless of the fact that it is necessary to refine the above condition by consideration of bond alternation, experiments on the electrical-conductivity measurement and studies on the other related solid-state properties of CNTs confirm that this rather simple but impressive prediction is capable of giving realistic analysis of the structure's electrical behavior (Ahmadi et al. 2012). Thus, (m,m) armchair and $(3m,0)$ zigzag carbon nanotubes are all metallic and the rest of zigzag CNTs and chiral tubes are semiconducting unless they satisfy the introduced $2m + n = 3N$ rule. In multi-walled Carbon nanotubes, however, modification of the electronic structure, especially in the metallic state, shows that due to symmetry reasons, the electronic structure of the inner tube does not seriously affect the metallic property of the outer-most (Saito et al. 1998).

In an individual carbon nanotube, there are many electrons at different energy levels within the tube's structure. As Fig. 2.5 illustrates schematically, the relative abundance of electrons as a function of the electron energy, which is much higher in the shaded layer, that is the valance band, while the unshaded area includes the energy levels that could be populated by electrons in carbon nanotubes. A photon

Fig. 2.5 Relative abundance of electrons as a function of energy level



whose energy is equal to the difference between a filled and an unfilled state can be easily absorbed, causing an electron transition from the shaded valance band energy state to the unshaded conductance band state. Having such photon absorptions spectrum characteristics, in the ultraviolet to near-infrared wavelength range, one can identify the (m,n) nanotube type by in a sample by analysis of their light absorption spectrum.

Charge carriers such as electrons and holes can move very easily through carbon nanotubes but when dealing with bundles (ropes) of carbon nanotubes, electrons will not only flow down individual tubes, but occasionally they can jump from one tube to another as well. Therefore, carbon nanotube ropes have been known as one of the most electrically conductive fibers ever (Thess et al. 1996). As the electrons within a nanotube are highly polarized, the energy levels of carbon nanotubes depend very much on their environment as well. For instance, application of an external field can shift the relative energies of these states remarkably towards enhancing or lowering their conductivity, making them candidates for printable semiconductor in transistor applications. Likewise, the presence of some types of foreign atoms or impurities can shift these energy levels and affect conductivity and optical behavior of CNTs significantly. In this way, custom functionalization of nanotubes can lead to applications of the nanomaterial as sensors or as probes for detecting cell abnormalities in biomedicine.

2.4.2.2 Ballistic Transport in CNTs

Furthermore, the nanostructure is considered a one-dimensional material and hence it is capable of exhibiting ballistic or quasi-ballistic transport along its main axis (Tans et al. 1998; Wei et al. 2001; Javey et al. 2003; Dürkop et al. 2004). Individual carbon nanotubes have been observed to conduct electrons ballistically, that is, with no scattering, for distances of a few microns (Tans et al. 1998). Ballistic conduction permits substantial current flow with minimal heat generation, which allows nanotubes to carry enormous amounts of current. In fact, carbon nanotubes can carry the highest current density of any known material, with conductivities measured as high as 10^9 A/cm² (Wei et al. 2001), whereas copper fails at current densities of about 10^7 A/cm², so nanotubes can carry current densities about 100 times that of traditional metal conductors. Another advantage of ballistic conduction is that the charge carriers can move very rapidly through nanotubes under the influence of an electric field. The charge carrier mobility in carbon nanotubes can exceed that in traditional electronic materials like silicon by at least an order of magnitude higher (Dürkop et al. 2004), leading to providing the possibility of manufacturing ultra-high-frequency transistors and circuit elements. Finally, as another consequence of ballistic conduction, very low-noise transistors can be fabricated by nanotubes (Javey et al. 2003). Carbon nanotubes are therefore expected to play a central role in many emerging fields of molecular electronics.

2.4.3 Optical Properties

In the late 1990s, theoretical and experimental studies reported the remarkable optical properties of carbon nanotubes after Margulis reported the first theoretical study on the very high third order nonlinearity of CNT and Kataura et al. reported the nonlinear optical properties of single-wall CNT for the first time (Kataura et al. 1999; Margulis 1999). Since then, various potential applications of CNTs have proposed and attracted significant attention in photonics research community. CNTs exhibit an exceptionally high third-order optical nonlinearity and nonlinear saturable absorption with ultrafast recovery time and broad bandwidth operation (Martinez and Yamashita 2011). Thus, they are becoming key components towards the development of fiber lasers, nonlinear photonic devices and several emerging next generation devices, both from an academic and industrial point of view.

2.4.3.1 Saturable Absorption

The optical absorption of CNTs is of saturable, intensity-dependent nature, it is, therefore, a suitable material to employ for specific applications like passively mode-locked laser operation. Saturable absorption is a result of the excitonic absorption in semiconductor nanotubes (Saito et al. 1992). The density of states of a semiconducting CNT can be numerically calculated. In fact, the electronic density of states of CNT, originates from the slicing of the graphene density of states, due to the quasi-1D confinement of the electrons, which leads to the presence of the characteristic Van Hove singularities in their electronic DOS. Semiconducting CNTs absorb photons in the same way an ordinary direct bandgap semiconductor would do when the energy of the photon is equal to the bandgap of the CNT. The CNT's bandgap is inversely proportional to the diameter of the tube. It is particularly fortunate that the diameters of CNTs typically ranges from 1 to 2 nm, which leads to an optical absorption that overlaps the 1550 nm window commonly used for fiber optic technologies.

Current processes for bulk fabrication of CNTs do not provide complete control over the chirality and diameter of the fabricated CNTs and produces a combination of metal and semiconductor SWCNTs and MWCNTs. However, separating the fabricated CNTs according to their chirality is possible through post-fabrication processes. In actual fact, depending on the expected application, a wide or a very narrow distribution of CNT diameters may be beneficial. Hence, the ability to control the mean diameter and diameter distribution in the fabrication, purification and separation processes is very helpful in expanding the application chances of CNTs in photonics science and industry. On the other hand, in terms of absorption for instance, for ultra-short pulse generation, a saturable absorber with a fast recovery time is required, while a slower recovery time could facilitate laser self-starting. Ultrafast recovery times of few hundreds of femtoseconds have been reported making CNTs a suitable material for ultra-short pulse generation.

However, it is worth noting that, the recovery time is not so fast if we consider only isolated semiconducting CNTs, in this case, the recovery time would be in the order of 30 ps (Reich et al. 2004).

The ultrafast response time of CNTs depends on bundle and entanglement of both semiconducting and metallic CNTs. Excited electrons in semiconducting CNTs tunnel and couple to metallic CNTs, resulting in ultrafast recovery time and hence, the combination of the fast and slow processes within the CNT distribution, allows CNT to be a very efficient saturable absorbers. In addition, the inability to fully control the diameter of the CNTs during their growth is advantageous for the implementation of fiber lasers. In fact, the wide distribution of CNT diameters is responsible for the very broadband operation of CNT based saturable absorbers (Kivistö et al. 2009).

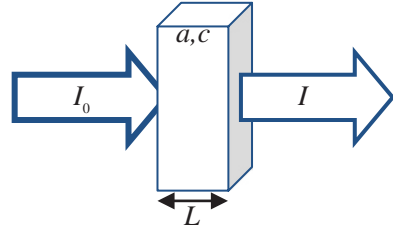
2.4.3.2 Third Order Nonlinearity

The first theoretical studies on the third order nonlinearity of CNTs appeared in 1998 when an estimated nonlinear refractive index coefficient, n_2 , of as high as $2 \times 10^{-12} \text{ m}^2/\text{W}$ was predicted for the nanostructure (Margulis and Sizikova 1998). The theoretical value was several orders of magnitude higher than that of silica glass for instance with n_2 equal to $3 \times 10^{-20} \text{ m}^2/\text{W}$ and chalcogenide glass, with n_2 equal to $2 \times 10^{-18} \text{ m}^2/\text{W}$ which were receiving much attention as a suitable material for the fabrication of highly nonlinear fibers. The optical nonlinearity of CNT comes from the one-dimensional motion of the delocalized π -electrons at a fixed lattice ion configuration. These estimations attracted a great deal of attention since third order nonlinearity is responsible for phenomena such as third harmonic generation, optical Kerr effect, self-focusing and phase conjugation. As a result, third order nonlinear materials can be considered for optical functions such as optical switching, routing and wavelength conversion. The challenging part however, is that for most third order nonlinear optical materials, the third order susceptibility is too low for practical applications and hence the extremely high n_2 of CNT opened a new potential application for CNT (Yamashita 2011). Furthermore, in most cases there is a trade-off between high optical nonlinearity and its recovery. For instance, optical fibers generally exhibit low nonlinearity and a fast response time while semiconductor based devices generally operate with a high nonlinear coefficient and low response time. Remarkably, CNT devices offer a very high nonlinear coefficient combined with a fast response time due to their nanostructures and the Van der Waals induced bundling.

2.4.3.3 Optical Absorption Spectroscopy

When the optical properties of carbon nanotubes are referred, the focus is generally on the σ absorption, photoluminescence, and Raman scattering of the nano-material. Optical absorption spectroscopy (OAS) measures the absorption of

Fig. 2.6 Schematic illustration of Beer-Lambert absorption in a material



electromagnetic radiation which is a function of the frequency (or wavelength) of the incoming ray and its interaction with the sample. When light propagates through an absorbing medium, its intensity decreases exponentially according to the Beer-Lambert law, as

$$I(L) = I_0 e^{-aLc}, \quad (2.7)$$

where I_0 is the intensity of the incident light, a is the absorption coefficient, L is the optical path length, and c is the concentration of absorbing species in the material, as schematically illustrated in Fig. 2.6.

The absorbance for a given wavelength, A is then measured by obtaining the transmitted intensity relative to the incident intensity, given by the following expression,

$$A = -\ln\left(\frac{I}{I_0}\right). \quad (2.8)$$

The optical response of SWCNTs is dominated by transitions between valence and conduction bands. However, momentum conservation only allows transition between those pairs of singularities that are symmetrically placed with respect to the Fermi level. These vertical transitions are labeled as E_{ii} ($i = 1, 2, 3, \dots$), where basically, light will be absorbed when it is in resonance with the E_{ii} values for the (n, m) nanotubes in a sample. Despite the fact that a SWCNT has a sharply peaked density of states, the peaks that are found in OAS are broad due to sample heterogeneity (Tian et al. 2010). A collection of nanotubes however consists of many different types of (n, m) nanotubes mostly, each with a different set of absorption peaks, which add up to production of a broad peak that contains information about the diameter distribution in the sample. Thus, OAS of SWCNTs is often used to evaluate the mean diameter and diameter distribution of nanotubes in a sample, rather than their chiralities.

Although simple one-particle pictures are useful models to interpret some aspects of the experimental results (Liu et al. 2002), it has become increasingly clear that Coulomb interactions also play an important role in determining the optical transition energies of SWCNTs. Both theoretical calculations and experimental measurements show that the exciton binding energies are anomalously large at about 1 eV, in contrast to 10 meV energies that are commonly found in

3D material, which indicates the importance of many-body (MB) effects in the quasi-1D systems (Dresselhaus et al. 2005). The electron-electron Coulomb repulsion upshifts the one-electron energy and the electron-hole Coulomb attraction, on the other hand, downshifts it. Hence, the effects of many-body interactions on the transition energy are worth considering in modeling optical transition energies of SWCNTs.

Aside from the many-body corrections, the curvature effect and the C–C bond length optimization are also missing from the conventional tight-bond (TB) models. It has been shown that the long-range interactions of the π orbitals are not negligible and the curvature of SWCNT walls yields a sp^2 – sp^3 rehybridization (Liu et al. 2002). The curvature effect was included in the TB model by extending the basis set of atomic to orbitals to the orbitals that form the σ and π molecular orbitals, according to the Slater-Koster formalism (Saito et al. 1998). This extended tight-binding (ETB) model, calculated within the frame work of a density functional theory (DFT), which incorporates the TB transfer and overlap integrals as functions of the C–C interatomic distance and is considered as one of the most accurate methods for modeling tight-bond energies (Tian 2012). The method includes long-range interactions and the effects of bond-length variations within the SWCNT sidewall (Samsonidze et al. 2004).

2.4.4 Thermal Properties

Prior to discovery of the properties of carbon nanotubes, diamond was known as the best thermal conductor. The heat flow and thermal conductivity along main axes in carbon nanotubes however is obtained to be of about $3500 \text{ W m}^{-1} \text{ K}^{-1}$ (Pop et al. 2006), whereas values between 900 and $2300 \text{ W m}^{-1} \text{ K}^{-1}$ is reported for the thermal conductivity of diamond. The thermal conductivity is specifically large along the main axis of CNTs, due to the easy propagation of atomic vibrations down the tube. In the direction transverse to its axis, however, the nanotube is much less rigid and the thermal conductivity in that direction is about a factor of 100 smaller (Dresselhaus et al. 2004; Sinha et al. 2005). A SWCNT has a room-temperature thermal conductivity across its axis (in the radial direction) of about $1.52 \text{ W m}^{-1} \text{ K}^{-1}$. As another major different between carbon nanotubes and other carbon materials such as graphite, thermal expansion of conventional CNTs with rather large diameters is known to be essentially isotropic, whereas it is highly anisotropic along the long axis in case of graphite (Ruoff and Lorents 1995). There is however, some disagreement into the exact nature of the thermal conductivity of carbon nanotubes and it is believed that the thermal conductivity of CNTs depends on the temperature and the large phonon mean free paths as well (Berber et al. 2000).

2.5 Manufacturing Techniques

CNTs have probably been around much longer before they were practically discovered, as they may have been produced during various carbon combustion and vapor deposition processes. The electron microscopy however was not advanced enough at that time to distinguish them. Nowadays, there are several methods for producing carbon nanotubes, some of which are more specifically utilized for commercial synthesizing of carbon nanotubes.

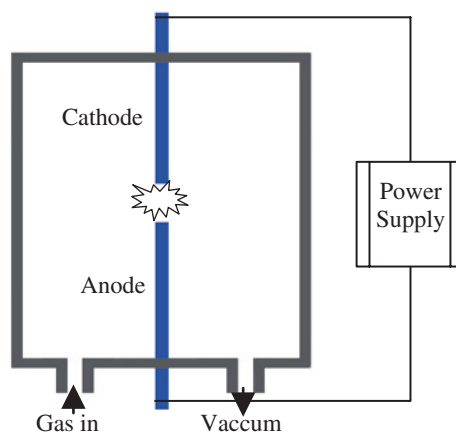
2.5.1 Arc Discharge

Nanotubes were observed in 1991 in the carbon soot of graphite electrodes during an arc discharge that was intended to produce fullerenes. The carbon arc discharge method is actually the most common and perhaps the simplest way to produce CNTs (Wilson et al. 2002). However, the unfavorable point is that it produces a complex mixture of components, and requires further purification to separate the CNTs from the soot and the residual catalytic metals present in the crude product.

As illustrated schematically in Fig. 2.7, this method creates CNTs through arc-vaporization of two vertical carbon rods or electrodes placed end to end, separated by approximately 1 mm, in a chamber that is usually filled with inert gas at low pressure (Wilson et al. 2002). The carbon nanotubes, ranging from 4 to 30 nm in diameter and up to 1 mm in length, are grown on the negative end of the carbon electrode that contains a small piece of iron as a catalyst in a direct current (DC) arc-discharge evaporation of carbon at 20 V (Rafique and Iqbal 2011).

Iijima used this method first in 1991 to produce carbon nanotubes (Iijima, 1991), however the method was employed with some variations to produce different ranges of CNT diameters, types and amounts by different scholars (Ebbesen and Ajayan 1992;

Fig. 2.7 Arch discharge chamber



Bethune et al. 1993; Journet et al. 1997). Investigations that are more recent have shown that it is also possible to create CNTs with the arc method in liquid nitrogen (Jahanshahi and Kiadehi 2013; Hosseini et al. 2012; Wang et al. 2005). As nanotubes were initially discovered using this technique, it has been the most widely used method of both single- and multi-walled nanotube synthesis.

2.5.2 Laser Ablation

Laser ablation process was first developed by Smalley research team in 1995 in Rice University (Guo et al. 1995). In the laser ablation process, as shown in Fig. 2.8, a graphite target is vaporized by being stroke by a pulsed laser in a high temperature reactor while an inert gas is bled into the chamber. The nanotubes are then formed on cool surfaces of the water-cooled Cu collector, as the vaporized carbon condenses (Rafique and Iqbal 2011).

The material produced by this method appears as a mat of “ropes”, 10–20 nm in diameter and up to 100 μm or more in length. Each rope is found to consist primarily of a bundle of single walled nanotubes, aligned along a common axis. By varying the growth temperature, the catalyst composition, and other process parameters, the average nanotube diameter and size distribution can be varied (Rafique and Iqbal 2011). Arc-discharge and laser vaporization are currently known as the major approaches for obtaining small quantities of high quality CNTs. However, both methods are high-energy-consumer and involve with evaporating a limited amount of a carbon source, like graphite. Therefore, scaling up the production I these two techniques to the industrial level has not been achieved. In addition, by vaporization methods, CNTs grow in highly tangled forms, mixed with unwanted forms of carbon and/or metal species. Hence, purifying the produced CNTs, manipulating, and assembling them for building nanotube-device architectures for practical applications would be another major concern in these techniques.

2.5.3 Chemical Vapor Deposition

Chemical vapor deposition (CVD) is a technique that was majorly used in producing thin film semiconductors. However, in 1996 the technique was employed for

Fig. 2.8 Laser ablation reactor

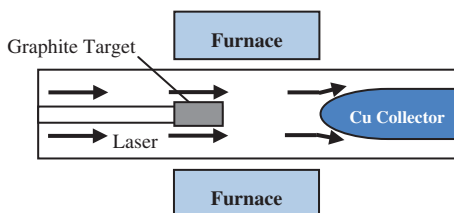
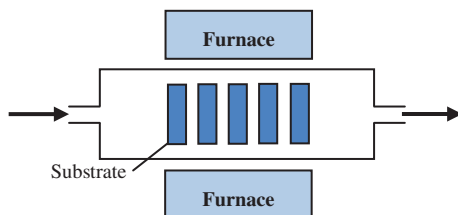


Fig. 2.9 CVD reaction chamber



large-scale production of carbon nanotubes (Li et al. 1996). The priority of this chemical CNT production technique is that the growth direction in large-scale production can be controlled over a substrate. In this method, a mixture of hydrocarbon or source gas and a process gas is made to react in a reaction chamber over a heated metal substrate. The hydrocarbon gas consists of ethylene, methane or acetylene and the process gas includes ammonia, nitrogen, and hydrogen). The temperature of the substrate is normally around 700–1000 °C, at atmospheric pressures. As a result of decomposition of the hydrocarbon gas, the CNTs are formed, deposit and grow on metal catalyst on the substrate. Figure 2.9 shows a thermal CVD

The catalysts particle and the substrate modification can result in production of different types of tubes. For instance, the nanotube diameter depends on the catalyst particle size. The substrate is usually silicon and hence, porous silicon is an ideal substrate for growing self-oriented nanotubes on large surfaces. In addition, glass and alumina are other materials used as the substrate material. The catalysts, on the other hand can be metal nanoparticles, like iron, cobalt, nickel or an alloy of the three catalytic metals. The catalysts are normally deposited on substrates by means of electron beam evaporation, physical sputtering or solution deposition. As the size of the catalyst affects the tube's diameter directly, the catalyst deposition technique should be opted carefully to yield desired results (Rafique and Iqbal 2011).

This method is also known as thermal CVD or catalytic CVD and has been used for decades for producing carbon nanotubes as well as other various carbon materials such as carbon fibers and filaments. However, some other techniques for the carbon nanotubes synthesis with CVD have been developed, such as plasma enhanced CVD, alcohol catalytic CVD, vapor phase growth, aero gel-supported CVD and laser-assisted CVD, some of which will be explained below.

2.5.4 Plasma Enhanced Chemical Vapor Deposition (PECVD)

The plasma enhanced chemical vapor deposition (PECVD) method, is a surface mediated growth technique, intended to generate vertically aligned tubes for commercial manufacturing. In this method, a glow discharge is generated in the reaction chamber by a high frequency voltage applied to its two parallel electrodes.

Fig. 2.10 PECVD reaction chamber

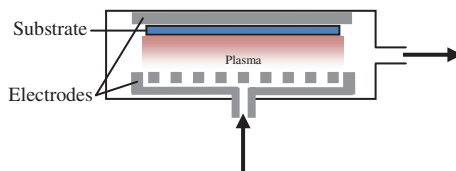


Figure 2.10 shows a schematic diagram of a typical plasma enhanced CVD apparatus with a parallel plate electrode structure.

In this method, substrate is placed on the grounded electrode and the source gas is supplied from the opposite plate. Catalytic metals, such as Fe, Ni and Co are used on for example the substrate to grow carbon nanotubes on them by the glow discharge generated from high frequency power. A carbon source gas, such as C_2H_2 , CH_4 , C_2H_4 , C_2H_6 , CO is supplied to the chamber during the discharge. Similar to Thermal CVD, the catalyst plays an important role in determining the nanotubes' diameter, growth rate, wall thickness, morphology and microstructure (Wilson et al. 2002).

2.5.5 Vapor Phase Growth

Vapor phase growth is another variant of the CVD technique in which the carbon nanotubes are produced directly from supplying reaction gas on the catalytic metal in the chamber without a substrate (Ge and Sattler 1994). In this method, two furnaces are placed in the reaction chamber and ferrocene is used as the catalyst. The first furnace is responsible of vaporization of catalytic carbon at a relatively low temperature and fine catalytic particles are formed. When they reach the second furnace, decomposed carbons are absorbed and diffused to the catalytic metal particles. The diameter of the carbon nanotubes produced by vapor phase growth are in the range of 2 to 4 nm for SWCNTs and between 70 and 100 nm for MWCNTs and the method has been employed successfully for large scale production of carbon nanotubes (Wei 2002; Deck and Vecchio 2005). Furthermore, recent investigations show that by means of this technique, the chirality of the produced CNTs is controllable (Liu et al. 2012).

2.5.6 High Pressure Carbon Monoxide Reaction Method

HIPCO[®] CVD, i.e. high pressure carbon monoxide chemical vapor deposition technique was introduced by Dr. Smalley's research team in 1998 (Nikolaev et al. 1999). The method involves introducing the catalyst in gas phase to the reaction chamber and rapidly mixing a gaseous catalyst precursor (such as iron carbonyl) with a flow of carbon monoxide gas at high pressure and high temperature. The catalyst

precursor decomposes and nanometer-sized metal particles are formed. These tiny metal particles serve as a catalyst. On the catalyst surface, carbon monoxide molecules react to form carbon dioxide and carbon atoms, which bond together to form carbon nanotubes. This process selectively produces 100 % single walled carbon nanotubes. These carbon nanotubes can be used in electronics, biomedical applications and fuel cell electrodes (Unidym-Technology 2008).

As both the catalyst and the hydrocarbon gas are in the gas phase and the nanotubes are free from catalytic supports, the reaction can be operated continuously and hence, the method is suitable for large-scale synthesis of CNTs. Another variant of the technique was also introduced in 2001 in which a mixture of benzene and ferrocene, $\text{Fe}(\text{C}_5\text{H}_5)_2$ reacts in a hydrogen gas flow to form superconductive SWCNTs (Tang et al. 2001). In 2002, the method known as CoMoCAT[®] process was also introduced in University of Oklahoma to modify the process by using Cobalt and Molybdenum catalysts and CO gases. In this method, SWCNT are grown by CO disproportionation at 700–950 °C, at a total pressure that typically ranges from 1 to 10 atm. This process was capable of growing a significant amount of SWCNTs (about 0.25 g-SWCNT/g-catalyst) in a couple of hours (Resasco et al. 2002). However, The CNTs produced by the HiPco process indicate a greater variety of diameters than the material produced by CoMoCAT Process.

2.5.7 Conclusion

In general, chemical CNT fabrication techniques have many advantages compared to arc discharge and laser ablation. In these methods, reaction processes are generally simple and easy to control and manipulate. In addition, raw materials are abundant and in form of gases, therefore, huge amount of energy would not be needed to process. As the methods are capable of producing vertically aligned CNTs on substrate, post refining and purification processes are minimized largely. Finally, large scale industrial manufacturing of CNTs is possible using chemical operations.

Other than the mentioned major methods, some other techniques have also been employed for manufacturing CNTs, namely helium arc discharge method (NASA 2005), electrolysis (Kaptay and Sytchev 2005), and flame synthesis (Wal et al. 2001) that have their own advantages and disadvantages and are only mentioned here to make them available for further studies.

2.6 Defects of Carbon Nanotubes

Carbon nanotubes have shown to be promising candidates as outstanding engineering materials, for their remarkable mechanical, thermal, optical and electrical properties. Therefore, they are expected to contribute in many outstanding

applications in the world of science and industry. Nonetheless, there are several types of imperfections in the structure of carbon nanotubes, which may occur during the process of manufacturing or purposely introduced to the structure for specific applications, making functionalized carbon nanotubes. Defects are an inevitable part of all devices. Although in the macro world, the existence of minor defect does not influence the functionality of devices extensively, in the world of nano, even minor defects can alter the basic properties of the device significantly. Hence, the study of the defects is a major topic that should be investigated very carefully in nanoscience and technology. Therefore, point defects such as vacancies (Rahmandoust and Öchsner, 2009; Ghavamian et al. 2012; Ziaee 2013; Fakhrabadi et al. 2014), improper location of carbon atoms, e.g. perturbed or deformed structures (Rahmandoust and Öchsner, 2009; Ghavamian et al. 2012; Pullen et al. 2005), rearrangement of atoms in a new form, such as the Stone–Wales defect (Stone and Wales 1986; Nardelli et al. 1998); curving and bending of the CNTs (Yengejeh et al. 2014; Ray and Kundalwal 2013; Farsadi et al. 2013) and the presence of doped foreign atoms (Rahmandoust and Öchsner 2009; Ghavamian et al. 2012; Kaw 2006; Hernández et al. 1999b) are some of the defects involved with the structure of carbon nanotubes.

These defects may be majorly categorized into two main groups, i.e. topological defects occurring in the structure of carbon nanotubes, compared to the ideal arrangement of atoms, as well as defects that arise due to the doping of foreign atoms to the structure of carbon nanotubes. Introduction of any defects to the ideal structure of carbon nanotubes will result in a change in physical properties. These changes are in many cases desirable, namely for producing specific enhanced conductivity or semiconductivity or for boosting the sensing ability of the tube, where a controlled introduction of defects is required. On the other hand, the consequences of the existing defects may have undesirable influence on the properties of carbon nanotubes as well, namely decrease of mechanical strength of the structure, or lowered conductivity, that should be considered before the nanostructure is being applied as a functioning part of a device.

2.6.1 Topological Definition and Defects

The first main category of defects happens in the structural arrangement of carbon atoms. In this case, no foreign atoms are introduced to the structure and the defect rises from any imperfection occurring in the perfect hexagonal array of carbon atoms of the nanotube.

2.6.1.1 Atom Vacancies

A vacancy defect is a point defect that occurs naturally in the ideal hexagonal lattice of CNTs, as shown in Fig. 2.11a, in which one or several atoms are missing

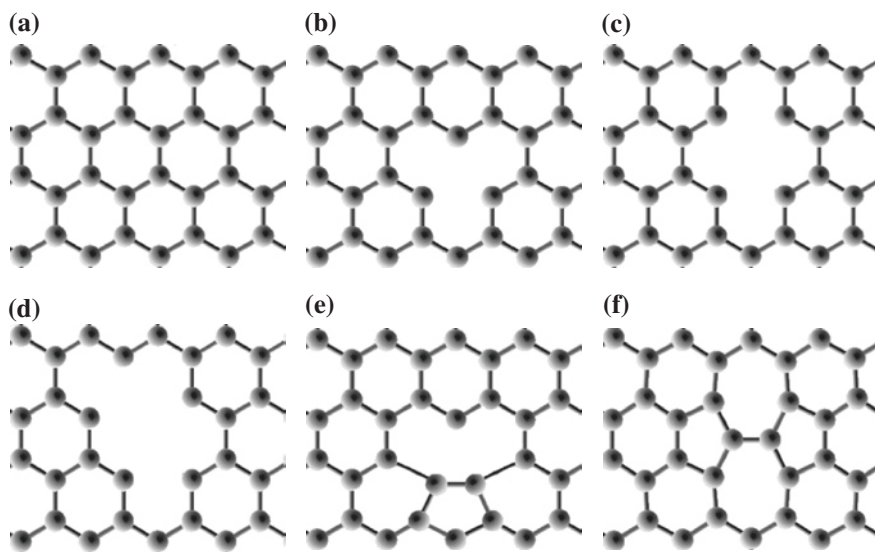


Fig. 2.11 **a** Ideal structure, **b** monovacancy (3DB), **c** double-vacancy, **d** triple-vacancy, **e** reconstructed monovacancy (5-1DB), and **f** Stone–Wales defect

from the structure. Vacancies, as illustrated in Fig. 2.11b through 2.11d, may be formed during solidification process, as a result of the vibrations of atoms, or they may happen due to local rearrangement of atoms after plastic deformation, or by heavy ion bombarding and irradiation of high-energy beams (Collins 2009; Ehrhart 1991). Once that the atom is knocked out its lattice site, the dangling bonds in the vacant site rehybridize to create to some new bonds (Ehrhart 1991) and the atom returns back to the surface of the structure to participate in a new bonding arrangement. Initial reconstruction of the three dangling bonds (sometimes referred to as 3DB defect) is in a way that two of the three free bonds, in a mono vacancy defect, bridge to form a strained 5-membered pentagonal ring, leaving a single dangling bond, hence abbreviated as 5-1DB. The 5-1DB defect is shown in Fig. 2.11e.

The theory of rehybridization which was initially proposed in 1998 by Ajayan et al. (1998) and was later confirmed and by Lu and Pan (2004) will be explained a bit more in detail below. However, the vacancies in the CNT even after initial rehybridization are energetically unfavorable. Hence, in many cases, they split into pentagon-heptagon or 5-7-7-5 defects, as shown in Fig. 2.11f. This type of defect, also known as the Stone–Wales defect, is the most prevalent type of topological defect in the structure of CNTs (Collins 2009).

If single-walled carbon nanotubes are exposed to high-energy beam irradiation, they will continuously loose atoms and try to reconstruct their structure (Ajayan et al. 1998). Uniform irradiation creates vacancies, which could cluster into larger vacancies in the structure, which are as explained before, energetically unstable.

This instability arises from the existence of dangling bonds. However, the structure tries to resolve the vacant sites through atomic rearrangements. Investigations of Ajayan et al. demonstrated that the reconstruction of vacancy defects occur successfully by forming nonhexagonal rings, like pentagon-heptagon pairs defect in the nanotube lattice (Ajayan et al. 1998). Other nonhexagonal rings such as squares, octagons, nonagons, and decagons were also observed at certain stages of the surface reconstruction (Kaw 2006). Though, high-membered rings are found to be unstable and thus, they disappear by the mechanism known as the Stone–Wales mechanism. As a result of the Stone–Wales mechanism, the constituent members of the stable rings in the structure of carbon nanotubes will be confined to a maximum of seven-member rings (Stone and Wales 1986).

2.6.1.2 Stone–Wales Defect

The Stone–Wales defect, in which four adjacent hexagons convert into two pairs of pentagon-heptagons or 5-7-7-5 configuration (Pozrikidis 2009; Stone and Wales 1986) is the final stage in atomic reconstruction of vacant sites. The Stone–Wales defect, also known as the pentagon-heptagon defect, is the most abundantly detected defect in the structure of carbon nanotubes that occurs naturally after initial formation of vacancies. This type of defect is expected to influence the electrical (Azadi et al. 2010), optical (Zhou et al. 2014), thermal (Wei et al. 2012) and mechanical properties (Pozrikidis 2009; Xiao et al. 2010) of carbon nanotubes, to different extents. However, FEM simulation results showed that although the introduction of defects to the body of CNTs weakens their elastic strength, the system is almost capable of restoring its original high elastic modulus by reconstructing its atoms in form of the 5-7-7-5 or Stone–Wales arrangement (Rahmandoust and Öchsner 2015). The Stone–Wales defect can be imagined to be formed by an in-plane $\pi/2$ rotation of a C–C bond (Pozrikidis 2009), as schematically illustrated in Fig. 2.12.

Other than the vacancies that happen naturally and the associated defects that arise from reconstruction of the vacant sites, there are some other defects that perturbates the ideal hexagonal arrangement of atoms in carbon nanotubes. These defects, as explained below, are mostly happening due to intentionally introduced changes in the structure seeking a specific application of CNT as a part of a device.

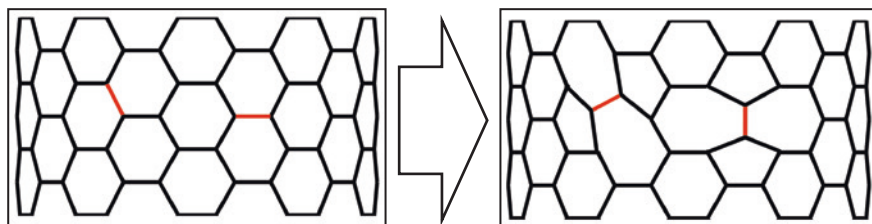


Fig. 2.12 Schematic illustration of the bond rotation in Stone–Wales defect

2.6.1.3 Kink Junctions

In order to produce molecular-size metal-semiconductor, metal-metal, or semiconductor-semiconductor nanojunctions in carbon-based nanoelectronics, some intramolecular connections are formed between two CNTs that have different chiralities (Saito et al. 1996; Chico et al. 1996). The tubes in turn should be connected to each other in a way that the strain energy is minimized and hence one or multiple topologic pentagon or heptagon defects are interposed into the structure to cover the chirality gap, creating a kink junction or a knee connection (Scarselli et al. 2012; Yao et al. 1999), as illustrated in Fig. 2.13. These topological changes create only a small local deformation in the width of the nanotubes (Kaw 2006).

Other than the targeted electrical influence of this type of heterojunction defect, the topological change affects the mechanical properties of the tubes as well. The kink intramolecular junctions tend to influence the stiffness, shear strength and buckling behavior of the carbon nanotubes (Yengejeh et al. 2013; Yengejeh et al. 2014).

2.6.1.4 Welding CNTs

Welding of carbon nanotubes by means of electron beams at elevated temperatures is another technique of merging nanostructures covalently. These molecular junctions are capable of producing various stable geometries similar to X, Y, and T, as shown in Fig. 2.14, that can act as multi terminal electronic devices (Terrones et al. 2002; Ponomareva et al. 2003).

The studies on the density of state in these heterojunctions show that at the region of welding the one-dimensional characteristics of the tube are dramatically affected, which is an important factor in electronic device applications and controlled fabrication of nanotube-based molecular junctions and network architectures that are expected to exhibit exciting electronic and mechanical properties (Kaw 2006).

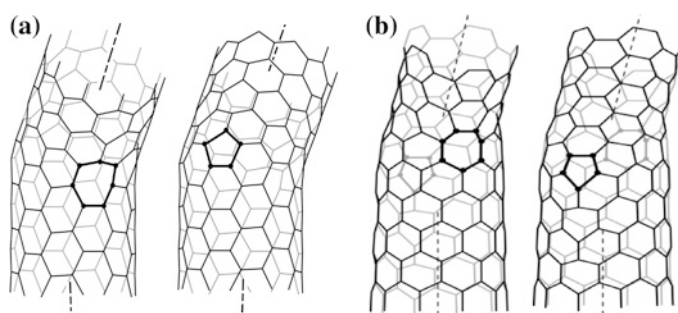


Fig. 2.13 Knee connection between two different CNTs with **a** similar, and **b** different diameters

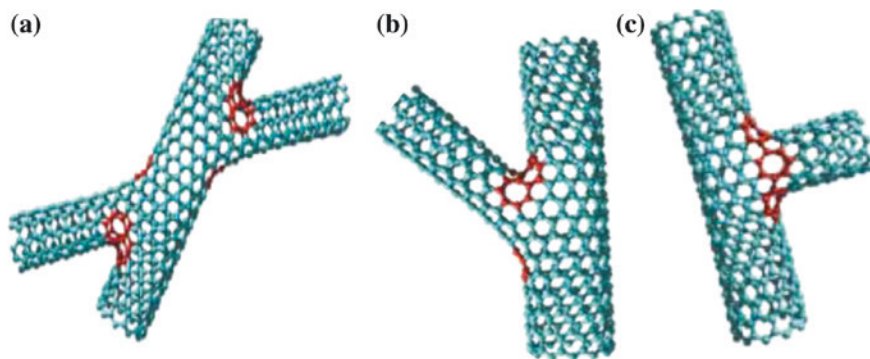


Fig. 2.14 Welded carbon nanotubes with **a** X-, **b** Y-, and **c** T-geometries (adapted from Terrones et al. (2002), with permission; Copyright 2002 by The American Physical Society)

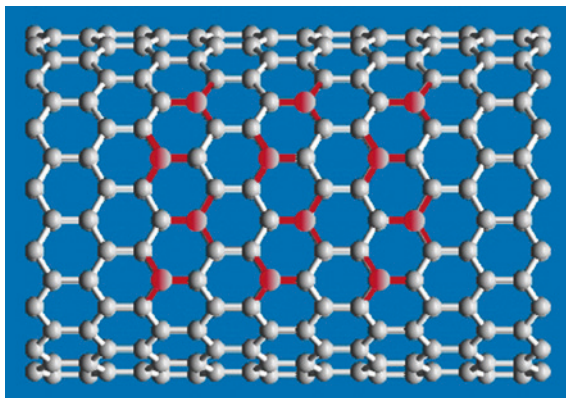
2.6.2 Substitutional Doped Defect

Doping of foreign non-carbon atoms into the structure of sp^2 carbon nanotube systems, provides the opportunity of tailoring the electronic, vibrational, chemical and mechanical properties (Jorio et al. 2008; Terrones et al. 2008). It is in fact an efficient way to modify these nanostructures for different emerging applications. The substitutional heteroatom, like boron, silicon and nitrogen, can reach relatively high doping levels of about 2 % or higher (Wei et al. 2009), which results in altered properties. For instance, regardless of the chirality of the carbon nanotube, both boron- and nitrogen-doped carbon nanotubes show metallic behavior, although the states of acceptors (p-doping) or donors (n-doping) are strongly localized near the Fermi level (valence band) in both cases (Carroll et al. 1998; Czerw et al. 2001). On the other hand, the existence of high percentages of silicon, nitrogen and boron atoms lowers the stiffness of carbon nanotubes remarkably, although the Young's modulus remains above 0.5 TPa (Rahmandoust and Öchsner 2009; Ghavamian et al. 2012). The electron or hole-rich structures that can be obtained by doping group V or III atoms, respectively, can be used to produce n- or p-type nanotubes, which make valuable molecular heterojunction devices (Choi et al. 2000). The structure of doped carbon nanotubes had been studied to observe the pertaining morphological changes compared with the undoped counterparts of each tube (Gai et al. 2004; Villalpando-Páez et al. 2006; McGuire et al. 2005).

2.6.2.1 Group III Atoms; p-Type Nanoconductor

Boron has one electron less than carbon and hence, when it substitutes for C atoms inside the lattice of a single-walled carbon nanotube, a localized state below the Fermi level appears. The absence of an electron in other words, creates a hole in the structure, and the tube converts into a p-type nanoconductor. From the chemical absorption point of view, this structure would be therefore more likely to react

Fig. 2.15 Schematic illustration of boron-carbon islands. Boron atoms and the B–C bonds are marked with *red*



with donor-type molecules, which have electrons to share. Figure 2.15 shows boron-carbon islands in a single walled carbon nanotube.

Boron doped CNTs were produced by growing carbon nanotubes by arc discharge, using a Boron-rich consumable anode (Carroll et al. 1998). Later, the McGuire team produced B-doped single-walled carbon nanotubes with controlled low concentration of dopants (McGuire et al. 2005). Arc Discharge, on the other hand, is mainly used to fabricate B-doped multi-walled carbon nanotubes (Blase et al. 1999). Doping of boron atom during nanotube growth influences the chirality of the produced B-doped CNT. In other words, the introduction of a boron source in the synthesis process will control the tube chirality, toward a preferred zigzag or near zigzag chirality with $\pm 3^\circ$ twist angle (Blase et al. 1999; Hsu et al. 2000).

2.6.2.2 Group IV Atoms; Hillocks

Silicon could also be doped inside SWCNTs (Baierle et al. 2001). Theoretical studies show that substitutional Si atoms induce a strong outward deformation, creating hillocks, making the surface more reactive compared to undoped CNTs (Baierle et al. 2001; Fagan et al. 2003; Rahmandoust and Öchsner 2009). Other than making the nanostructure readier to participate in surface reaction with the surrounding environment, based on finite element studies, the implementation of doped silicon inside the lattice of CNTs results in a linear reduction of the structure's elastic modulus, both in single- and multi-walled carbon nanotubes (Rahmandoust and Öchsner 2009; Ghavamian et al. 2012). Figure 2.16 shows the hillocks created as a result of Si substitution.

2.6.2.3 Group V Atoms; n-Type Nanoconductor

Substitution of group V atoms, like phosphor and nitrogen, with one extra valance electron compared to carbon, induces localized states that may be both below and above the Fermi level. It means that for instance, in case of N doping

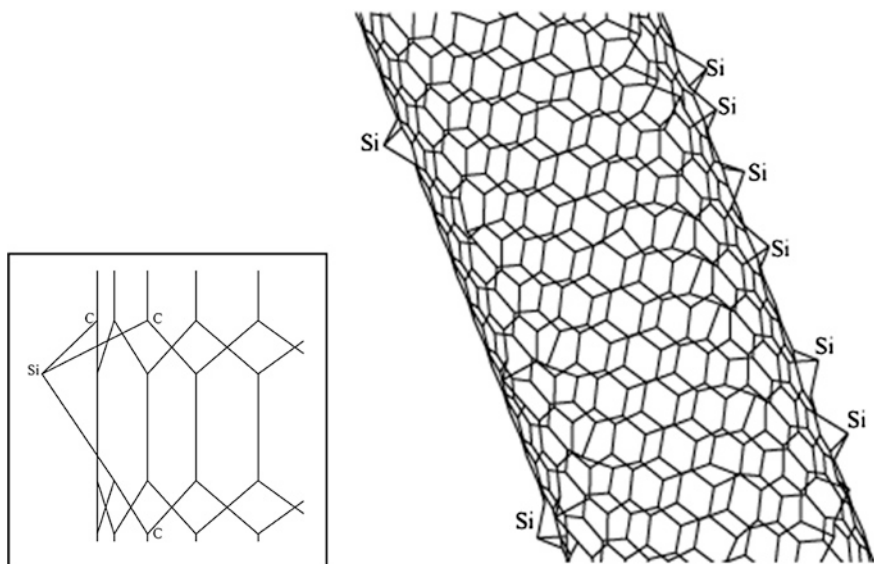


Fig. 2.16 Si-doped SWCNT

in CNTs, also known as CN_x nanotubes, both n- and p-type conducting behavior are expected, depending on the type and the level of doping inside the hexagonal sheet. As shown in Fig. 2.17, there are three different configurations for nitrogen when replacing carbon in an sp^2 lattice (Terrones et al. 2012), namely substitutional graphitic nitrogen, pyridine-like nitrogen, i.e. type1 and type2, respectively, and pyrrole-like nitrogen, type3, from which only the first two are stable in carbon nanotubes, which produce n-type and p-type conductors respectively (Terrones et al. 2008). Furthermore, it has been observed that the number of graphitic nitrogens compared to pyridine-like Ns increases as the overall content of doped nitrogen increases (Terrones et al. 2008).

Nitrogen-doped carbon nanotubes can be fabricated by thermal decomposition of N-containing hydrocarbons over metal particles. The first report on the formation of aligned arrays of N-doped MWCNTs, with concentrations below 2 %, was in 1999 (Terrones et al. 1999). Later in 2001, a similar technique was applied to produce Nitrogen-doped SWCNTs at elevated temperatures (Czerw et al. 2001). More advanced methods were proposed in 2005 and 2006 for fabricating isolated N-doped CNTs and long stranded bundles of defective structures, respectively (Keskar et al. 2005; Villalpando-Páez et al. 2006). However, fabrication of highly ordered structures containing large concentrations of N is hard to achieve (Sen et al. 1997) but on the other hand, low concentrations of doped materials are difficult to detect and hence, the detection of the amount of dopants was only possible using Raman spectroscopy (McGuire et al. 2005).

In case of continuous growth of N-doped single walled carbon nanotubes, only substitutional graphitic nitrogens are observed, in which N is connected to three

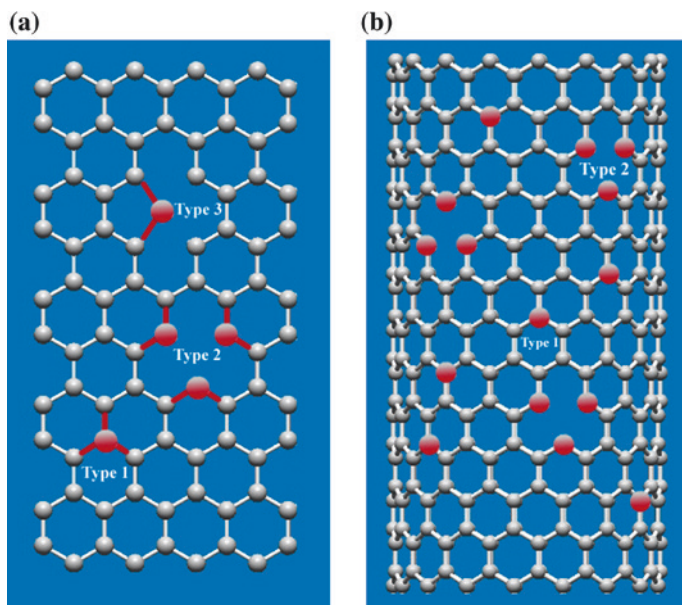


Fig. 2.17 Possible configurations of nitrogen-carbon bonding in **a** Graphene sheet and **b** Carbon nanotube

carbons and has n-type characteristics. Substitutional graphitic nitrogens are more likely to react with acceptor molecules (Villalpando-Páez et al. 2006; Terrones et al. 2008). Pyridine-like N structures, on the other hand, can occur in SWCNTs provided that an additional carbon atom is removed from the lattice. In this type of defect, each N atom is bonded to two carbon atoms, responsible for creating cavities and corrugation in the nanotube structure, which is responsible for the metallic behavior of N-dope CNTs (Czerw et al. 2001).

The mechanical behavior N-doped carbon nanotubes are also studied both experimentally and computationally. The Young's modulus for N-doped MWCNTs is as low as about 30 GPa, due to the relatively high N concentration. The high percentage of defect, i.e. of about up to 5 %, lowers the mechanical strength of CNTs significantly. However, if the low concentration of about 0.5 % nitrogen is doped, the elastic modulus of the structure will not change substantially (Gao et al. 2000).

2.7 Modeling of Carbon Nanotubes

The finite element method has been successfully used as a practicable, powerful, and cost-effective analysis method for the numerical study of a wide range of engineering problems. FEM has many applications from deformation and stress

analysis of automotive, aircraft, building, and bridge structures, to field analysis of heat, fluid flow, magnetic flux, leakage, and other flow problems. In this method, a complex region defining a continuum is divided into simple geometric forms called *finite elements*. The material properties and the governing relationships are considered over these elements and declared in terms of unknown values at element corners. An assembly process, duly considering the loading and constraints, results in a set of equations. Solution of these equations gives us the approximate behavior of the continuum (e.g. Tirupathi and Ashok 1997). Software based tools have been therefore proven to be a very powerful and well-organized tool in characterizing and simulating CNT-based composites.

2.7.1 Nanostructural Simulation

The simulation on the nanoscale explained here, covers the modeling of different types of perfect and imperfect carbon nanotubes, with the purpose of achieving their key mechanical properties. Initially, the method of modeling the structure and properties of zigzag and armchair single-walled carbon nanotubes are introduced and then multi-walled carbon nanotubes are studied. As it is very common to encounter imperfect structures in experiments, modeling of the physical properties of imperfect structures will also be discussed.

The structure of single-walled carbon nanotubes is composed of several carbon-carbon bonds joined together in a hexagonal arrangement. In order to study the mechanical properties of SWCNTs, these bonds were successfully defined in FEM by Euler-Bernoulli linear thin elastic beams, shown in Fig. 2.18 in black color. This element represents the covalent bonding between two adjacent carbon atoms in the nanotube structure (Rahmandoust and Öchsner 2009).

When it comes to MWCNTs, as explained earlier, there are also non-covalent, van der Waals interactions between atoms from any of the two layers of carbon nanotubes. As this type of interaction does not have a material-based nature and hence, it is considered as a weak interaction, *spring* element, with a suitable definition of spring coefficient, was opted to replace it (Rahmandoust and Öchsner 2012a, b). A schematic view of the starting ring of a DWCNT is shown in Fig. 2.18, in which the radial red lines represent the above-explained spring elements and the surrounding black lines are the thin elastic beam elements, representing C-C bonds.

To obtain Young's modulus of the structure, for example, the produced CNTs were fixed from translation and rotation on one end, and a point load was applied to the other end. Furthermore, in order to characterize the properties of carbon nanotubes, using the finite element models, the mechanical properties of each carbon-carbon atomic bond are necessary to be obtained based on its chemical properties. These properties should be then defined as the material properties in the pertinent finite element model.

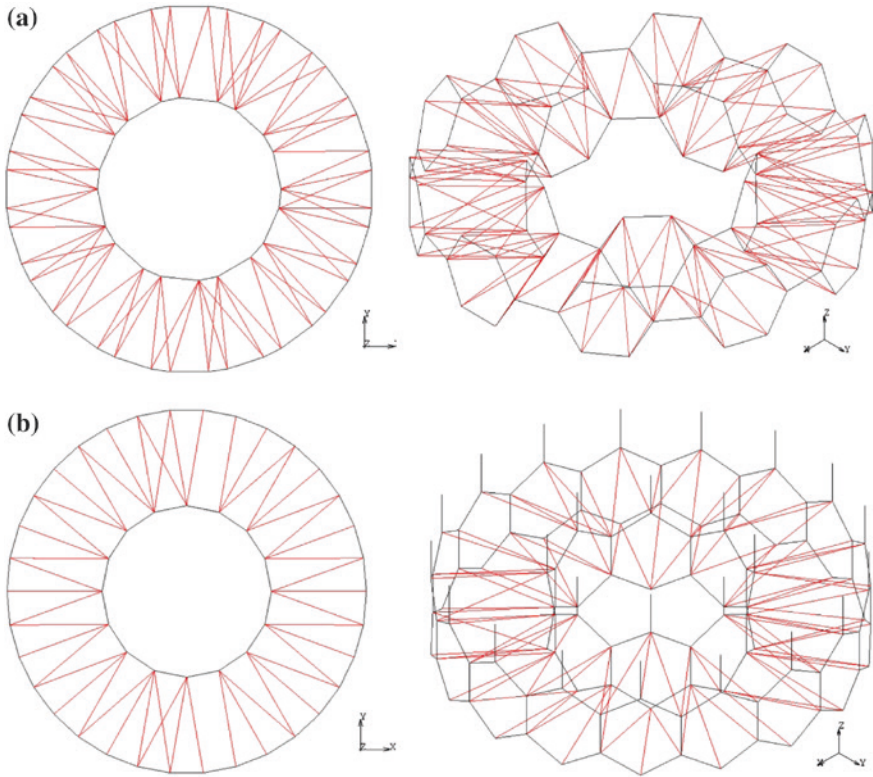


Fig. 2.18 Top- and side-view of first ring for **a** (10,10)-(5,5) armchair DWCNT, and **b** (17,0)-(8,0) zigzag DWCNT

2.7.1.1 Properties of C-C Bonds

Each CNT is considered to be made up of unit blocks that are repeated and rotated around an imaginary circle with a diameter equal to that of the desired CNT. As explained before, the diameter of any specific CNT can be calculated by Eq. (2.2). This is only possible if the CNT unit block is bendable on its bond joints, i.e. on the location of carbon atoms, shown in Fig. 2.19 by dots, to let the structure cover the curvature angle of its tube diameter (Chang and Gao 2003). If we consider having straight non-bending carbon-carbon bonds as FE beam elements, then each unit block of an armchair and a zigzag CNT can be divided into four and two rigid parts, respectively, as shown in Fig. 2.19.

The structure can then be generated by producing the first ring by rotating and repeating the unit blocks around a circle with a diameter equal to that of the desired CNT. Later, after assigning the geometric and the material properties of bonds, these rings are copied and shifted up repeatedly, as shown in Fig. 2.20, to make the whole CNT structure, up to the desired height.

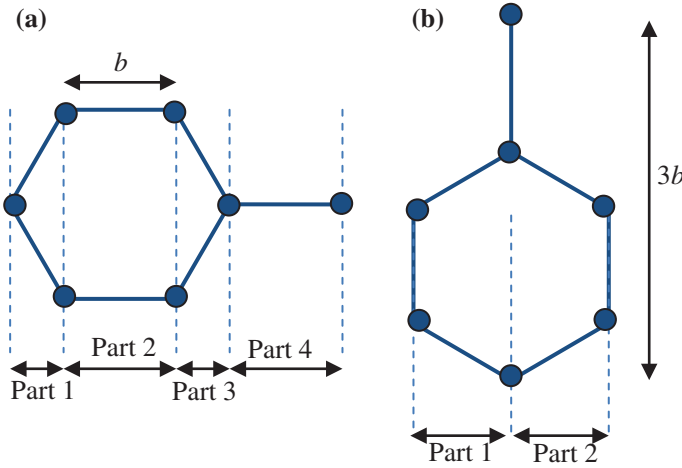


Fig. 2.19 Unit blocks of **a** armchair, and **b** zigzag SWCNTs

The geometric and the material properties of the three-dimensional thin, elastic Euler-Bernoulli beam elements that represent the carbon-carbon covalent chemical bonds can be achieved by studying the atomic interactions. The mechanical properties and elastic modulus of covalently bonded atomic structure depends greatly on the interatomic potential energy acting between the involved atoms. These properties are derived from the bond stretching, bending and torsion behavior. Young's modulus, shear modulus and Poisson's ratio are, for example, values that describe how an isotropic material behaves under different loads in the elastic range. If the Hooke's law is applied in the elastic range, for each generalized beam element, two of these values, i.e. Young's modulus, shear modulus and Poisson's ratio, are enough to be assigned. These quantities can be obtained for a carbon-carbon bond, from the equations given below (Li and Chou 2003; Kalamkarov et al. 2006).

The strain energy under pure axial load P (pure tension) is given by

$$U_P = \int_0^b \frac{P^2}{2EA} db = \frac{EA}{2b} (\Delta b)^2. \quad (2.9)$$

The strain energy of a beam element subjected to a pure bending moment M is

$$U_M = \int_0^b \frac{M^2}{2EI} db = \frac{EI}{2b} (\Delta \alpha)^2. \quad (2.10)$$

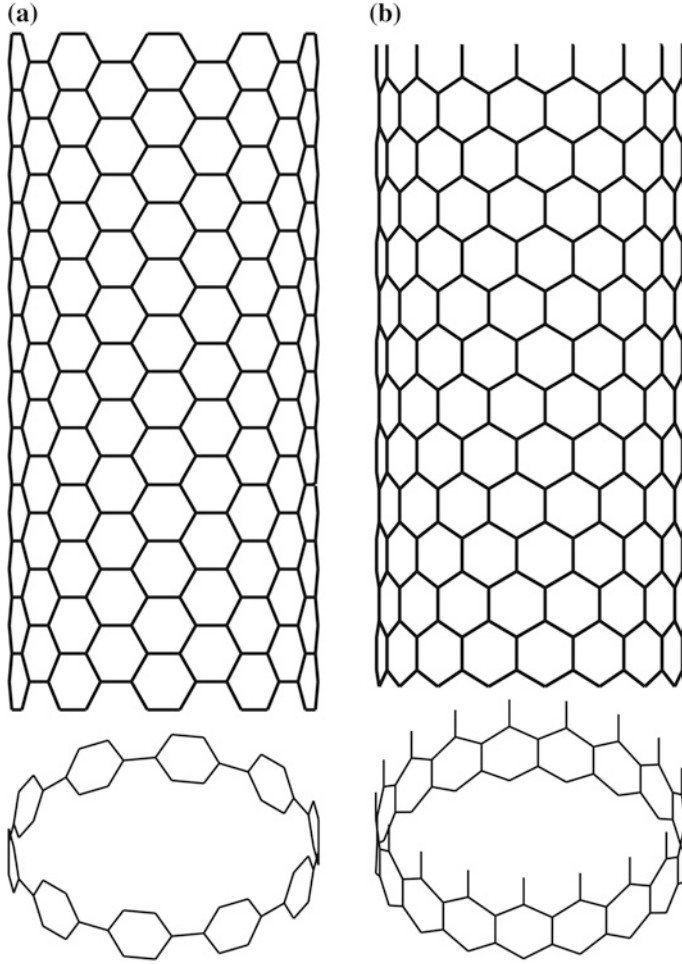


Fig. 2.20 Single ring of FE models of **a** (10, 10), **b** (17, 0) SWCNTs

Similarly, the strain energy of the beam element under a pure twisting moment T is

$$U_T = \int_0^b \frac{T^2}{2GJ} db = \frac{GJ}{2b} (\Delta\beta)^2. \quad (2.11)$$

In the above equations, assuming the terms Δb , $\Delta\alpha$ and $\Delta\beta$ as the axial deformation, bending angle and twist angle respectively, one obtains the tensile stiffness (EA), bending stiffness (EI) and torsion rigidity (GJ) of the structural model in terms of the molecular mechanics force constants k_r , k_θ and k_φ as follows:

$$k_r = \frac{EA}{b}, \quad (2.12)$$

$$k_\theta = \frac{EI}{b}, \quad (2.13)$$

$$k_\varphi = \frac{GJ}{b}. \quad (2.14)$$

In the context of *molecular mechanics*, a force field refers to the functional form and parameter sets used to describe the potential energy of a system of particles or atoms. Force field functions and parameter sets are derived from both experimental studies and high-level quantum mechanical calculations. By means of these constants, the elastic properties of each beam element (assumed to have a diameter d_b and length b) are obtained as:

The bond diameter

$$d_b = 4\sqrt{\frac{k_\theta}{k_r}}, \quad (2.15)$$

Young's modulus

$$E = \frac{k_r^2 b}{4\pi k_\theta}, \quad (2.16)$$

Shear modulus

$$G = \frac{k_r^2 b k_\varphi}{8\pi k_\theta^2}, \quad (2.17)$$

and Poisson's ratio

$$\nu = \frac{k_\theta}{k_\varphi} - 1. \quad (2.18)$$

Based on above equations, for each elastic beam element or in other words for each C–C bond, Young's modulus will be $E = 5.484 \times 10^{-6} \text{ N/nm}^2$ and Poisson's ratio $\nu = 2.15$. The Poisson's ratio obtained here for each carbon–carbon bond, based on molecular mechanics calculations, is equal to 2.15, which does not seem to be an acceptable engineering parameter. This is because molecular mechanics constants were used here to calculate the Poisson's ratio of each bond by Eq. (2.18), which is actually based on classical mechanics and may not be applied at molecular level. Therefore, after encountering the same problem, Natsuki et al. suggested another method for the analytical calculation of Poisson's ratio of a C–C bond.

Table 2.1 Material and geometric properties of a C–C bond

Chemical bond:	Carbon–carbon covalent bond	
Corresponding force field constants	$k_r = 651.97 \text{ nN/nm}$	
	$k_\theta = 0.8758 \text{ nN nm/rad}^2$	
	$k_\varphi = 0.2780 \text{ nN nm/rad}^2$	
Equivalent finite element type:	3-D thin elastic beam	
	Geometric properties	
	Bond radius	$R_b = 0.0733 \text{ nm}$
	Cross section area	$A = 0.0169 \text{ nm}^2$
	Second moments of area	$I_{xx} = I_{yy} = \pi R_b^4/4$ $= 2.26820 \times 10^{-5} \text{ nm}^4$ $I_{zz} = J = \pi R_b^4/2$ $= 4.53456 \times 10^{-5} \text{ nm}^4$

They obtained the value by the following equation equal to 0.27, based on the following equation.

$$\nu = \frac{b^2 k_r - 6k_\theta}{b^2 k_r + 18k_\theta}. \quad (2.19)$$

Table 2.1 provides the material and geometric properties of the finite element corresponding to a covalent carbon–carbon chemical bond.

2.7.1.2 Properties of Non-covalent Interactions

For modeling the CNT structure as a finite element model, covalent bonds are represented by thin elastic beam elements, but when it is about modeling multi-walled carbon nanotubes, it is necessary to define non-covalent forces acting between each two layers of atoms, or in other words, between each two walls of CNTs, as well. This kind of force is defined by the Lennard-Jones force, Eq. (2.4), and it is a function of the distance between the two interacting particles. Although the Lennard-Jones force is a weak force, there is an influencing distance interval considered for the Lennard-Jones force acting between any two layers of MWCNT and that is when the distance between the carbon atoms is between 0.33 to 0.38 nm (Kalamkarov et al. 2006). Thus, it should be considered that by applying an external load on the structure, the locations of atoms with respect to each other change and as a result, the Lennard-Jones force changes. Since there is no material between the interacting particles, it is very important to find the most suitable element to represent this interaction.

Therefore, *spring element* was opted as the best choice, in the sense that it is acting between *two* nodes, it is of non-material nature and it follows a force-displacement equation. The only challenging part of this choice is that spring force

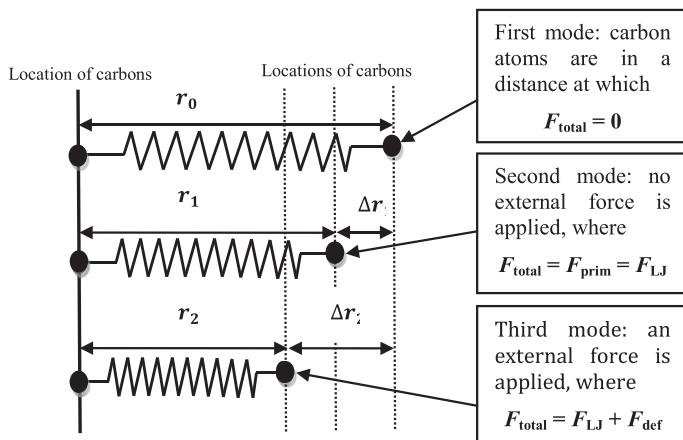


Fig. 2.21 Spring modeling of the Lennard-Jones force

is defined as a function of displacement and not distance, but the Lennard-Jones interaction is a function of distance between two interacting particles. Thus, based on the initial distance between each pair of interacting atoms, a force intersect like a pre-strained spring, has to be defined by a coordinate transformation. Any changes in the distance will later influence the interacting force according to the updated force-displacement equation. Figure 2.21 shows the described situation schematically.

As the Lennard-Jones force equation is a function of the inverse of distance, the software was incapable of processing it in order to derive the pertinent stiffness matrix. Considering that this complex force influences only a very small region of its whole diagram, in the case of MWCTs, two approximations of the force were developed initially to solve the problem. At the specific interval of 0.33–0.38 nm between two layers of coaxial tubes, the Lennard-Jones equation was approximated by a 5th and a 7th degree polynomial with norm of residuals equal to about 10^{-2} and 10^{-4} Joules, respectively. The diagram of the exact equation and its approximations are presented in Fig. 2.22. Although the 7th degree polynomial results in a less norm of residual, the 5th degree shows a better fitting in the critical area of around the initial distance between the two involved atoms, which makes it in general a more desirable choice.

The stiffness of the equivalent spring can also be approximated with a linear polynomial. For this purpose, two cases have to be considered. At first, there is no load applied on MWCNT and the structure is at rest. Thus, no deformation is imposed to the models. In this stage, the Lennard-Jones force between each two carbon atoms of two different walls of the MWCNT, at their initial distance, is referred to as F_{prim} . The second stage is when the model is exposed to an external force which causes the dislocation in the initial position of carbon atoms with

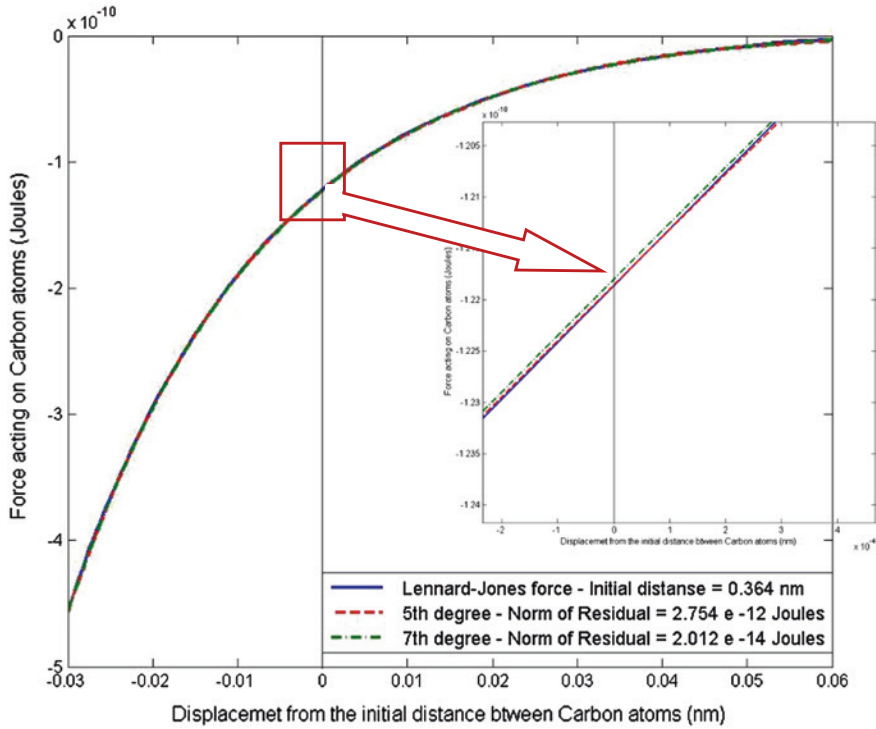


Fig. 2.22 Comparison of the Lennard-Jones force with its approximations

respect to each other and hence a change in the distance between the atoms, which consequently leads to a change in the Lennard-Jones force acting between the two interacting atoms. This force, is defined by $F_{\text{def}} = k \cdot \Delta r$ where k , the stiffness should be calculated approximately for this structure.

The obtained value for stiffness is approximately equal to 0.24245 N/m, calculated by choosing two points from the Lennard-Jones force diagram which is assumed to be linear in the assigned so called Lennard-Jones effective distance for MWCNTs, i.e. $0.33 < r < 0.38$ nm. Considering the discussion brought up before, Eq. (2.18) is obtained to comprehensively define the total force acting between each two carbon atoms, before or after deformation.

$$F_{\text{total}} = F_{\text{prim}} + F_{\text{def}} = \frac{4\epsilon}{r} \left[-12 \left(\frac{\sigma}{r} \right)^{12} + 6 \left(\frac{\sigma}{r} \right)^6 \right] + k \cdot \Delta r \quad (2.20)$$

Figure 2.23 shows an armchair DWCNT unit block, an armchair 5-walled ring and a 5-walled CNT, in which the red lines, connecting the carbon atoms of two walls, represent the Lennard-Jones forces and the black lines are the C–C bonds.

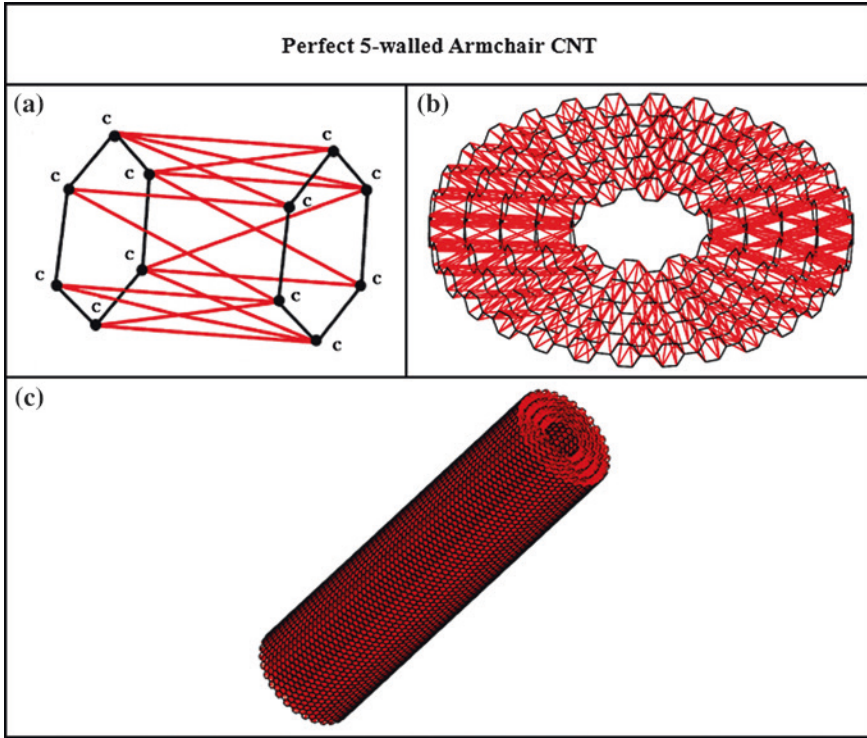


Fig. 2.23 **a** Armchair DWCNT unit block, **b** armchair 5-walled ring, and **c** armchair 5-walled (10, 10)-(15, 15)-(20, 20)-(25, 25)-(30, 30) CNT

2.7.2 Mechanical Properties of SWCNTs

Let us consider in the following a carbon nanotube, fixed on one end from translation and rotation, as it is schematically shown in Fig. 2.24, for two sample armchair and zigzag SWCNTs. In addition, a fixed displacement is applied on the other end along the tube's principal axis (here z -axis). As a result of this displacement boundary condition, a reaction force in z -direction is obtained at each node and the sum of these reaction forces equals the net reaction force P .

2.7.2.1 Young's Modulus

Using the net reaction force P and the deformations, one can find Poisson's ratio ν , Young's modulus E and Shear Modulus G of the structure using the Hooke's law in the elastic range as follows:

$$E = \frac{\sigma}{\varepsilon}, \quad (2.21)$$

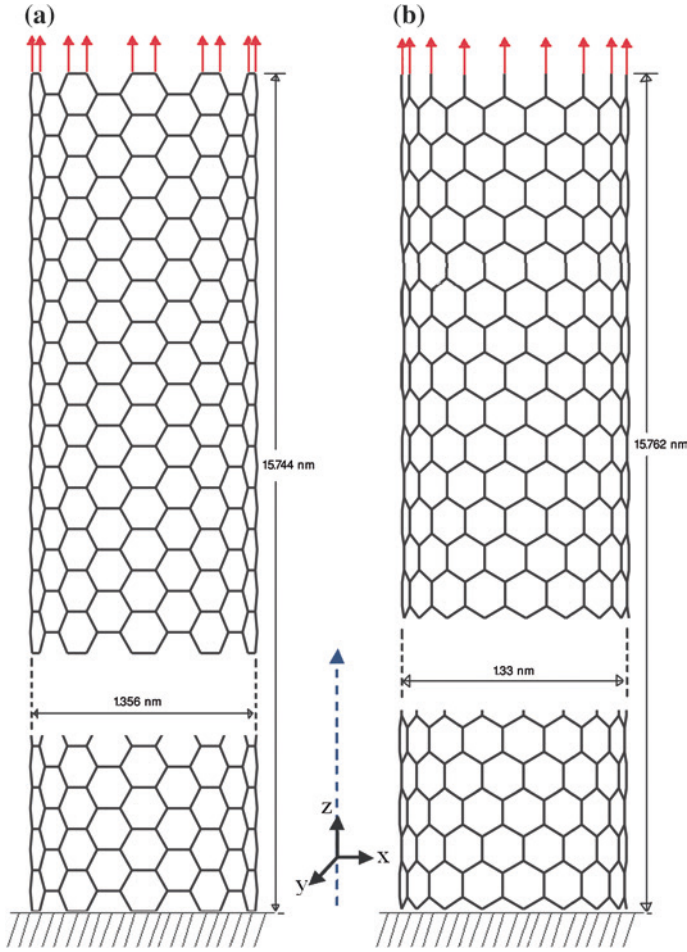


Fig. 2.24 Geometrical dimensions and applied boundary conditions on **a** (10, 10) armchair and **b** (17, 0) zigzag single-walled carbon nanotube

$$\nu = -\varepsilon_{\text{lateral}}/\varepsilon_{\text{axial}} = -\frac{\Delta D}{D} \bigg/ \frac{\Delta L}{L}, \quad (2.22)$$

$$G = \sigma_{\text{lateral}}/\sigma_{\text{axial}} = \frac{E}{2(\nu + 1)}, \quad (2.23)$$

where

$$\sigma = \text{stress} = P/A, \quad (2.24)$$

and

$$\varepsilon = \text{strain} = \Delta L/L. \quad (2.25)$$

In the above equations, A is the area of tube's cross-section, L is the length of the tube and ΔL is the applied displacement boundary condition.

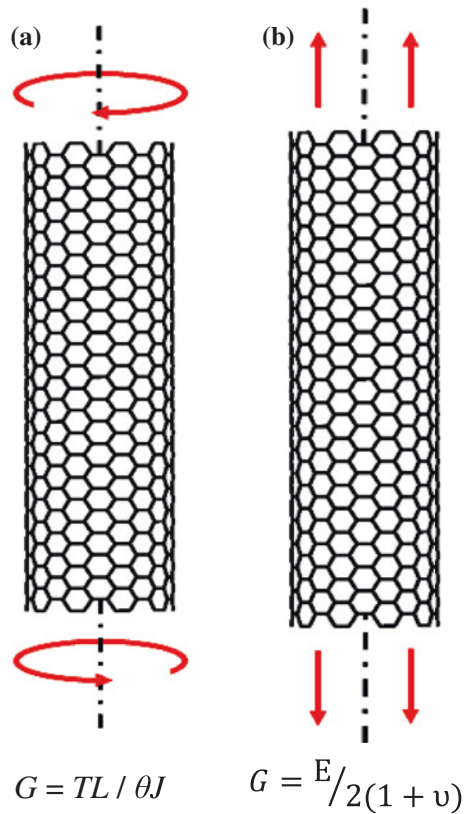
Considering the thickness of the tube's wall to be equal to that of a graphene sheet, $t = 0.34$ nm, the area of the tube, A , will be:

$$A = \pi \left[(R_{CNT} + \frac{t}{2})^2 - (R_{CNT} - \frac{t}{2})^2 \right] = \pi D_{CNT} t. \quad (2.26)$$

2.7.2.2 Shear Modulus

In order to obtain the structure's shear modulus, as illustrated in Fig. 2.25, two approaches can be employed, namely, torsion and tensile tests. In the torsion test, the models are twisted by applying an arbitrary angular displacement around their axis and consequently, the corresponding reaction torque is acquired. Finally, the shear modulus of CNTs is calculated by:

Fig. 2.25 Armchair SWCNT under **a** torsion and **b** tensile test



$$G = TL/\theta J, \quad (2.27)$$

in which θ , T , L and J are the twisting angle, torque, length and polar moment, respectively. As defined below, the polar moment of inertia is:

$$J_n = \sum_{i=1}^n J_i, \quad (2.28)$$

where J_n is the polar moment and J_i is the moment of the i th wall of an n -walled CNT and

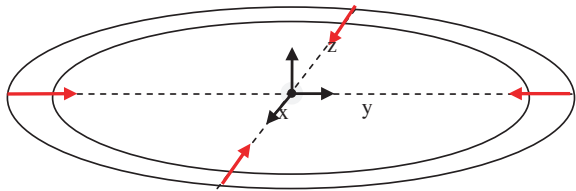
$$J_i = \int r^2 dA = 2\pi \int_{r_{in}}^{r_{out}} r^3 dr = \frac{\pi (r_{out}^4 - r_{in}^4)}{2}. \quad (2.29)$$

For the tensile test, the models are loaded by an arbitrary axial displacement boundary condition and consequently, the reaction force and Poisson's ratio of the models is obtained. Finally, shear modulus of the CNTs is calculated. Comparing the results from tensile and torsion tests and the considerable difference between their results reveals the fact that carbon nanotubes do not behave in an isotropic way and hence, tensile test is not a reliable approach to predict the torsion properties of carbon nanotubes.

2.7.2.3 Poisson's Ratio

Poisson's ratio as stated in Eq. (2.22), is the negative ratio of the circumferential or lateral strain, $\varepsilon_{\text{lateral}}$, to the axial strain, $\varepsilon_{\text{axial}}$. The applied displacement boundary condition results in an elongation of our structures. This elongation causes a reduction in diameter of the whole structure, subsequently. This reaction means that this structure has a positive Poisson's ratio, as it is common for classical engineering materials. Indeed, in some structured materials, mostly polymer foams, Poisson's ratio can be negative which means that by stretching them in one direction, they expand in the perpendicular direction. Therefore, in order to obtain Poisson's ratio, the radial displacement is calculated, as it is shown in Fig. 2.26. However, if Eq. (2.23) of elastic classical mechanics applies, Poisson's ratio can be simply obtained by having Young's modulus and shear modulus values.

Fig. 2.26 Cross-section of a CNT, showing the lateral forces



2.7.2.4 Buckling Behavior

Buckling is a kind of elastic instability in a structure that occurs under a certain compressive load. In the theory of elasticity, the critical buckling load of a structure, as defined in the Euler equation of buckling load, depends on its geometry, as well as its boundary conditions:

$$P_{cr} = \frac{n^2 \pi^2 EI}{(KL)^2}, \quad (2.30)$$

where P_{cr} is the critical buckling load, E is the structure's axial Young's modulus, K is the effective length constant and L is the length of the tube. In the above equation, n defines the buckling mode and I is the structure's second moment of area. As a hollow cylinder is the most similar classical structure to the studied carbon nanotubes, second moment of area defined for a hollow cylinder can be used for obtaining the analytical results, as follows:

$$I = \pi \left[(d+t)^4 - (d-t)^4 \right] / 64 \quad (2.31)$$

in which t is the thickness of the tube and d is the diameter of the pertaining tube.

The applied boundary conditions play an important role in the reaction of the studied structure under load. This influence is described by the concept of the effective length for a classic column structure that is presented as parameter K in Eq. (2.30). There are four different classical modes for buckling and four pertaining effective length parameters for each. The theoretical K values are defined for a column structure. These different modes of boundary condition and different possible buckling behaviors are shown schematically in Fig. 2.27 and the appropriate theoretical value of K for each case is provided (Rahmandoust and Öchsner 2012a, b).

Let us consider the boundary condition of the carbon nanotubes as fixed from translation and rotation on one end and free to move on the other. As explained before, this boundary condition is known as the Cantilever boundary condition and the corresponding K value for this case is ($K = 2$). For this case, the critical buckling load for both armchair and zigzag structures were modeled by the finite element software MSC.Marc and also it was calculated analytically using Eq. (2.30). Table 2.2 shows the accuracy of the obtained values and Fig. 2.28 illustrates the initial buckling of zigzag and armchair SWCNTs.

2.7.2.5 Resonant Frequency

On the other hand, the natural or resonance frequency of a structure depends on its geometry and mass, as well as applied boundary conditions. For a beam element, under the cantilever boundary conditions, the first mode of resonance frequency in Hz, can be calculated by the following equation:

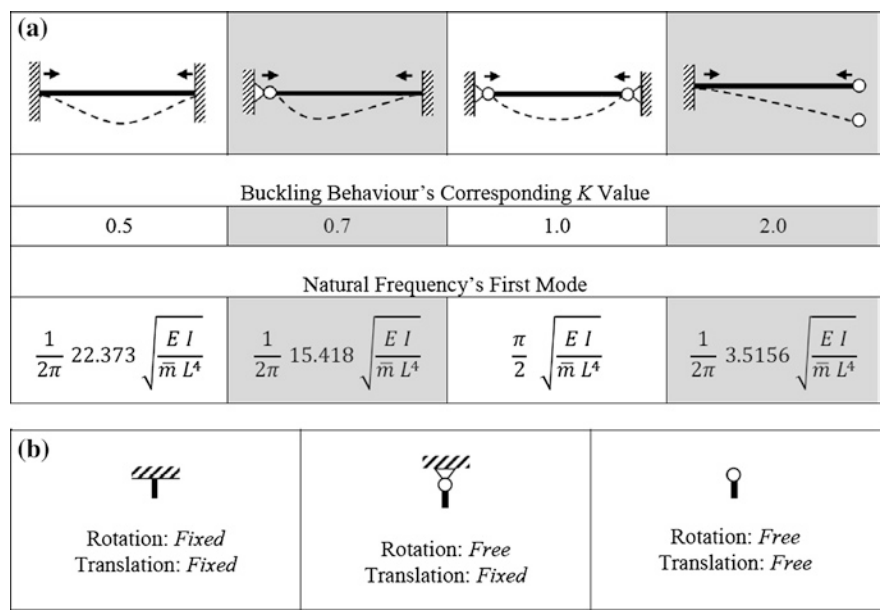


Fig. 2.27 **a** Classical boundary conditions and their corresponding effective length constants for buckling and their first resonance frequency equation, **b** definitions of the symbols of applied boundary conditions

Table 2.2 Comparing the analytical solution of zigzag and armchair SWCNTs critical buckling load, with the optimized finite element results

Carbon nanotube type	Analytical results (nN)	FEM results (nN)	Error (%)
(10, 10) armchair SWCNT	3.668	3.664	0.10
(17, 0) zigzag SWCNT	3.447	3.446	0.03

$$f_1 = \frac{1}{2\pi} 3.5156 \sqrt{\frac{EI}{\bar{m} L^4}}, \tag{2.32}$$

in which $\bar{m}$ is the structure's mass density, i.e. mass per unit length. Second and third modes of frequency are equal to $f_2 = 6.268 \cdot f_1$ and $f_3 = 17.456 \cdot f_1$, respectively (Fan et al. 2009). The FE results for natural frequency of armchair and zigzag SWCNTs were compared to the analytical solution for a hollow cylinder, as shown in Table 2.3.

Like the previous case, the single-walled carbon nanotubes were restricted under a cantilever type boundary condition. By defining the appropriate mass density in the finite element program, the structures' first two modes of natural frequency were simulated. Figure 2.29 shows the different modes of deviation of a (17, 0) single-walled carbon nanotube around its initial straight mode.

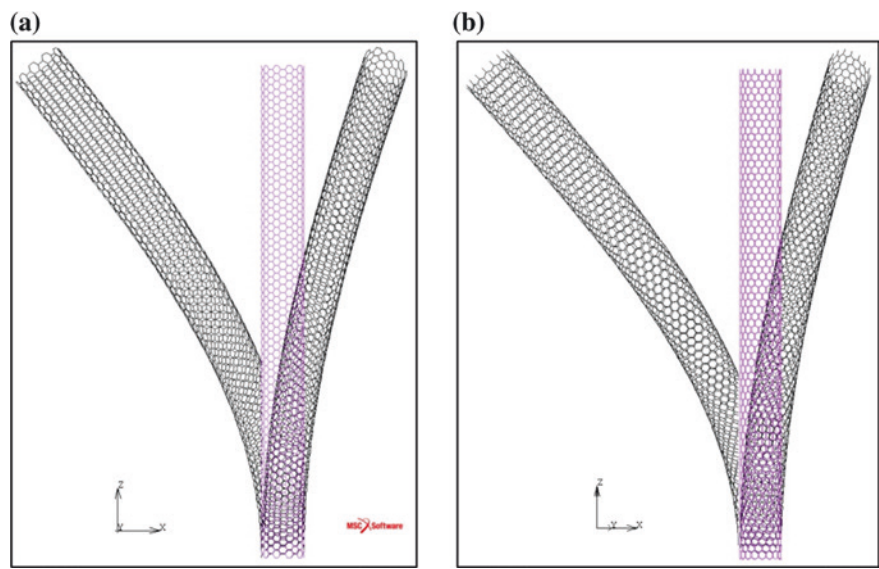


Fig. 2.28 Buckling behavior of **a** armchair and **b** zigzag SWCNTs

Table 2.3 Comparing the analytical solution of zigzag and armchair SWCNTs resonance frequency, with the optimized finite element results

Carbon nanotube type	Results	Frequency mode 1 (GHz)	Frequency mode 2 (GHz)
(10, 10) armchair SWCNT	Analytical	23.97	150.2
	Finite element	23.94	141.1
	Error (%)	0.12	6.05
(17, 0) zigzag SWCNT	Analytical	23.44	146.9
	Finite element	23.43	138.6
	Error (%)	0.04	5.65

2.7.2.6 Single Ring Model

In the modeling of carbon nanotubes, it is necessary to consider a reasonable length for the structure. The length-to-diameter ratio in 1-D nanostructured materials like CNTs is a very important factor. This distinct property is exactly the key of the excellence of nanomaterials compared to other conventional materials. Characterizing the mechanical properties of CNTs by means of numerical simulation, which involves a large number of nodes and elements, is a time consuming process. Hence, being able to obtain valid results by a minimum number of elements will be a valuable advantage in computation-based characterizations of carbon nanotubes.

Hence, the effect of reducing the size of the element from the pristine size down to a single ring was studied. In order to be able to use a single ring of the

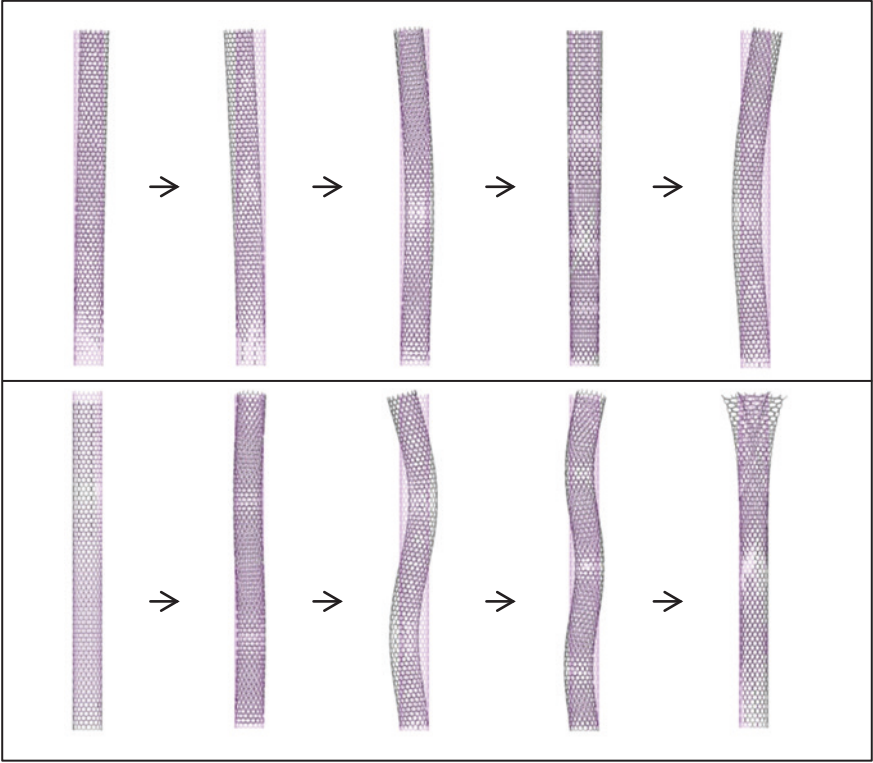


Fig. 2.29 Frequency modes of a zigzag SWCNTs under cantilever boundary condition

SWCNT instead of entire structure, as it is shown schematically in Fig. 2.30, boundary conditions have to be modified in a way that the ring can represent the behavior of the whole structure. For this purpose, the structure was set to be able to move in radial direction but not to rotate tangential to the ring’s wall. In addition, translational movement along the ring’s main axis was disabled at the lower nodes of the ring (Rahmandoust and Öchsner 2012a, b).

Table 2.4 compares the obtained Young’s modulus for a long and a ring SWCNT and gives the error of using a ring instead of the entire tube. As the table shows, the difference between the results, for both zigzag and armchair cases is below half a percent, which proves that the findings are reliable.

2.7.3 Mechanical Properties of MWCNTs

Similar to SWCNTs major mechanical properties of MWCNTs can also be achieved using FE modeling. In case of DWCNTs, different approximations were tested to see how these approaches influences the accuracy of the obtained results. First, the

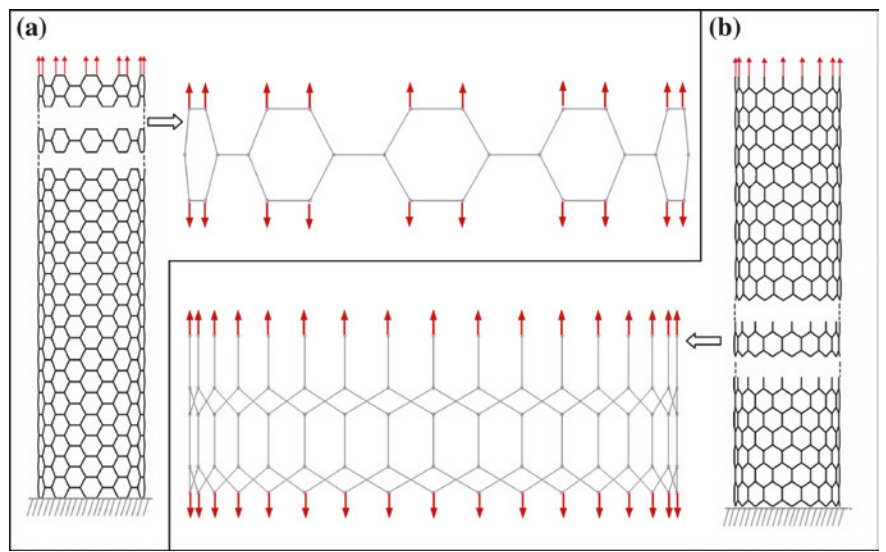


Fig. 2.30 Schematic view of the long and the ring structures for **a** armchair and **b** zigzag SWCNTs

Table 2.4 Young’s modulus of a long and ring SWCNTs

SWCNT type	Perfect form; pristine tube		Modified boundary conditions; single ring		Percentage of error	
	Armchair	Zigzag	Armchair	Zigzag	Armchair	Zigzag
<i>E</i> (TPa)	1.042	1.034	1.047	1.038	0.48 %	0.39 %
Number of nodes	12,280	12,036	70	102	–	–
Length (nm)	50.307	50.268	0.246	0.426	–	–

Lennard-Jones force equation was replaced with a 5th degree polynomial approximation; then, this accurate approximation of the Lennard-Jones force was totally ignored and the obtained results were compared. Finally, as it is going to be explained later, an equivalent spring constant was defined in a way that to approximate the Lennard-Jones force, in its effective distance only, with a linear function of displacement. Furthermore, the DWCNTs were generated as a single ring and a long tube, with and without defining the Lennard-Jones interaction. Tables 2.5 and 2.6 displays the effect of the tested approximations on Young’s modulus and shear modulus of DWCNTs, respectively.

Based on the explained approximations, single- to 5-walled carbon nanotube models were generated and analyzed in the finite element software. These CNTs and their characteristics are presented in Table 2.7. Figure 2.31 shows the Young’s modulus versus the number of walls, in a multi-walled carbon nanotube, where the thickness of the tube’s wall was assumed to be equal to 0.34 nm in all models. The non-linear converging trend of *E* in the diagram implies that by increasing the number of walls, the effect of the inner layers of carbon over the whole

Table 2.5 Young's modulus of DWCNT models in form of a ring and a long tube, with and without the Lennard-Jones force being defined

Type of DWCNT		Young's modulus E (TPa)	
		Long tube; perfect form	Single ring; modified boundary conditions
Armchair	With Lennard-Jones	1.053	1.059
	Without Lennard-Jones	1.051	1.056
Zigzag	With Lennard-Jones	1.033	1.044
	Without Lennard-Jones	1.037	1.045

Table 2.6 Shear modulus of DWCNT models in form of a ring and a long tube, with and without the Lennard-Jones force being defined

Type of DWCNT		Shear modulus G (TPa)	
		Long tube; perfect form	Single ring; modified boundary conditions
Armchair	With Lennard-Jones	0.448	0.514
	Without Lennard-Jones	0.488	0.511
Zigzag	With Lennard-Jones	0.424	0.499
	Without Lennard-Jones	0.470	0.494

Table 2.7 Simulated CNTs and their characteristics

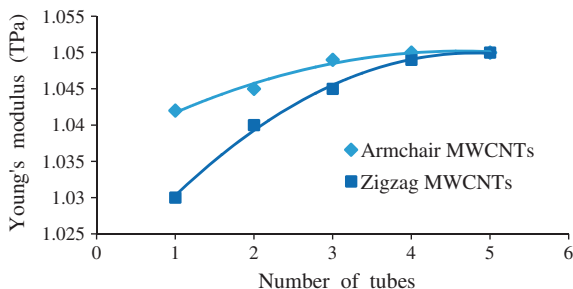
CNT	CNT type	Chirality (m,n)	Length (nm)	Outer radius (nm)
SWCNT	Armchair	(10,10)	15.74	0.6783
	Zigzag	(14,0)	15.62	0.5482
DWCNT	Armchair	(10,10)-(15,15)	15.74	1.0175
	Zigzag	(14,0)-(23,0)	15.62	0.9007
3-WCNT	Armchair	(10,10)-(15,15)-(20,20)	15.74	1.3566
	Zigzag	(14,0)-(23,0)-(32,0)	15.62	1.2532
4-WCNT	Armchair	(10,10)-(15,15)-(20,20)-(25,25)	15.74	1.6958
	Zigzag	(14,0)-(23,0)-(32,0)-(41,0)	15.62	1.6057
5-WCNT	Armchair	(10,10)-(15,15)-(20,20)-(25,25)-(30,30)	15.74	2.0350
	Zigzag	(14,0)-(23,0)-(32,0)-(41,0)-(50,0)	15.62	1.9582

structure reduces toward reaching a rather constant maximum Young's modulus for multi-walled carbon nanotubes.

2.8 Modeling of Defects

Defects are inevitable parts of most of engineering material. In some cases, these defects are purposely introduced to the structure to achieve specifically desired properties and in some other cases, defects occur as a result of the nanostructure's

Fig. 2.31 Young's modulus versus the number of walls in zigzag and armchair MWCNTs



fabrication process. However, either case to be the reason, it is necessary to discover the influence of the defect to the resulted properties of the structure.

2.8.1 Perturbation in Carbon Nanotube's Structure

Studying the effect of misplacement of atoms in carbon nanotube's hexagonal lattice or perturbations, as shown schematically in Fig. 2.32, is very interesting, due to being very likely to happen in experimental studies. When carbon nanotubes are produced experimentally, as a result of local stresses and the effect of environmental pressures, misplacement of atoms are unavoidable. Thus, it is important to control the effect of this defect on the properties of the structure. In order to simulate this type of imperfection, the location of atoms were allowed to change randomly by a specific percent of their distance with respect to each other.

Therefore, the effect of 5–15 % of perturbation in the structure was studied on the mechanical properties, as shown in Fig. 2.33. By introducing perturbation to the structures of both zigzag and armchair single-walled carbon

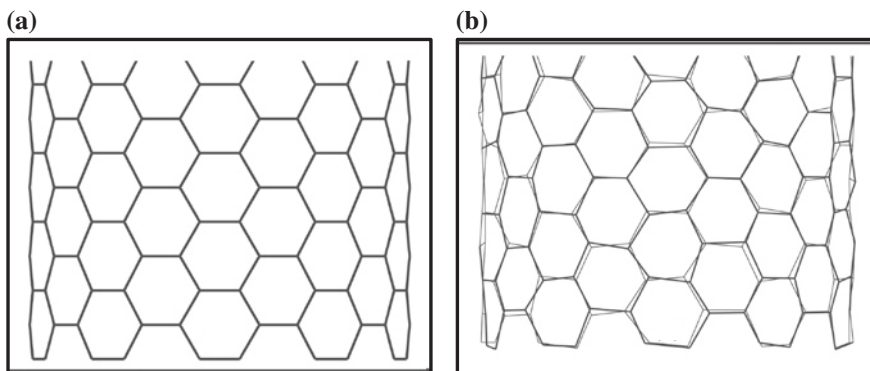


Fig. 2.32 Front view of the **a** perfect and **b** 10 % perturbed SWCNT

Fig. 2.33 Perturbation versus Young's modulus

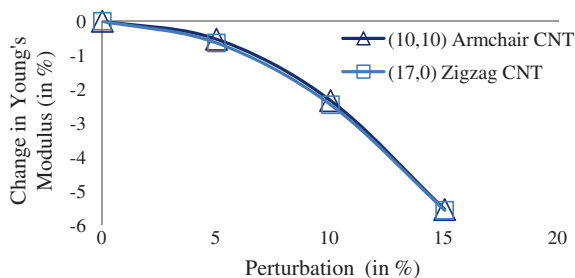
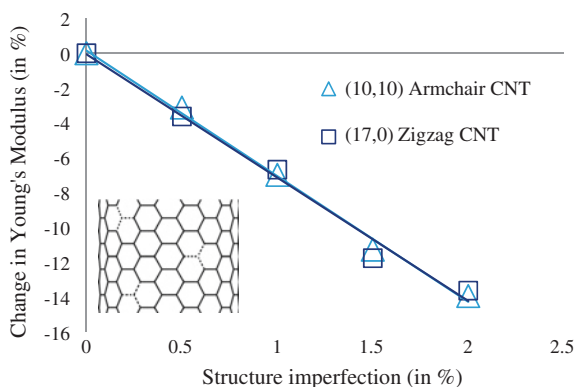


Fig. 2.34 Missing atoms versus Young's modulus

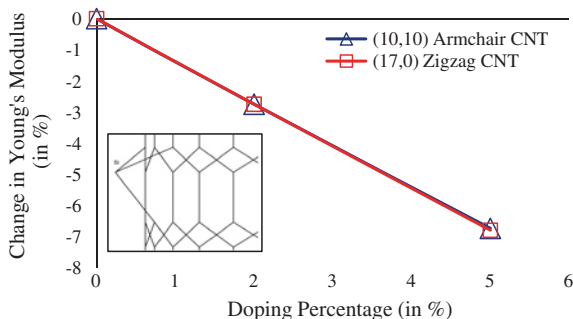


nanotubes, dropdown in Young's modulus was observed. This reduction is not very remarkable in the first 5 % of perturbation but when the structures deviate more from the perfect arrangement, the change in the Young's modulus becomes noticeable (Fig. 2.34).

2.8.2 Atom-Vacancies in CNT Structure

Modeling the effect of some missing atoms on Young's modulus of the two main types of SWCNTs has also been investigated to show that as a result of this defect, by an increase in the number of missing carbons, the structures lose their stiffness rather linearly and very fast, as illustrated in Fig. 2.35. For example, the structure loses 10 % of its Young's modulus when only 1.3 % of the atoms are lost. From the experimental point of view, it is inevitable that the structure changes the arrangement of its constituent carbons from hexagonal to pentagonal or heptagonal forms, in order to minimize its internal potential energy, leading to creation of Stone–Wales defect as explained before. Hence, local strains happen in these locations and the Young's modulus is affected consequently.

Fig. 2.35 Effect Si doping on Young's modulus of SWCNTs



2.8.3 Doped Carbon Nanotubes

This defect is one of the most likely imperfections happening when a definite number of carbon atoms in the perfect structure of the CNT are replaced with other atoms, which causes considerable undesirable changes in the mechanical properties, but perhaps desirable influence on the electrical or chemical properties of the CNT structure. Other than silicon, which is explained here, any other element can also be introduced to the structure to reveal various changes in the mechanical, chemical and electrical properties of the nanostructure, depending on the type of the doped atom and the number of its valence electrons; proper geometrical and material properties should be assigned in the model for the introduced covalent bond. For random dispersion of the imperfections into the structure of CNTs, Matlab programming was performed and results were imposed to the finite element model (Rahmandoust and Öchsner 2009).

The geometric properties for C–C and Si–C bonds are assumed to be nearly the same because the difference in the covalent radius of carbon and silicon is only 28 pm (Cordero et al. 2008) but as a beam element, their material properties are noticeably different. For example $E_{\text{Si-C}} = 7.18327 \times 10^{-6} \text{ N/nm}^2$ (Song et al. 2006), whereas $E_{\text{C-C}} = 5.484 \times 10^{-6} \text{ N/nm}^2$ (Rahmandoust and Öchsner 2009).

For the simulation of Si–C bonds, some percentage of the total number of carbon atoms was randomly chosen in the structure of CNT to be replaced with silicon. Since each carbon atom is encircled by three other neighbor atoms, the centre atom emerges radially out and some hillocks are formed on the structure (Lu 1997), so that the length of the connecting beam elements equal to that of the Si–C bond, as it is schematically shown inside Fig. 2.35. Furthermore, as the diagram implies, although the Young's modulus of Si–C bond itself is greater than C–C bond's E , doping Si atoms into the structure of zigzag and armchair CNTs causes a dramatic reduction in the value of CNT's Young's modulus. The reason is that by increasing the percentage of doped atoms, more hillocks are formed in the structure and Young's modulus of carbon nanotube decreases consequently.

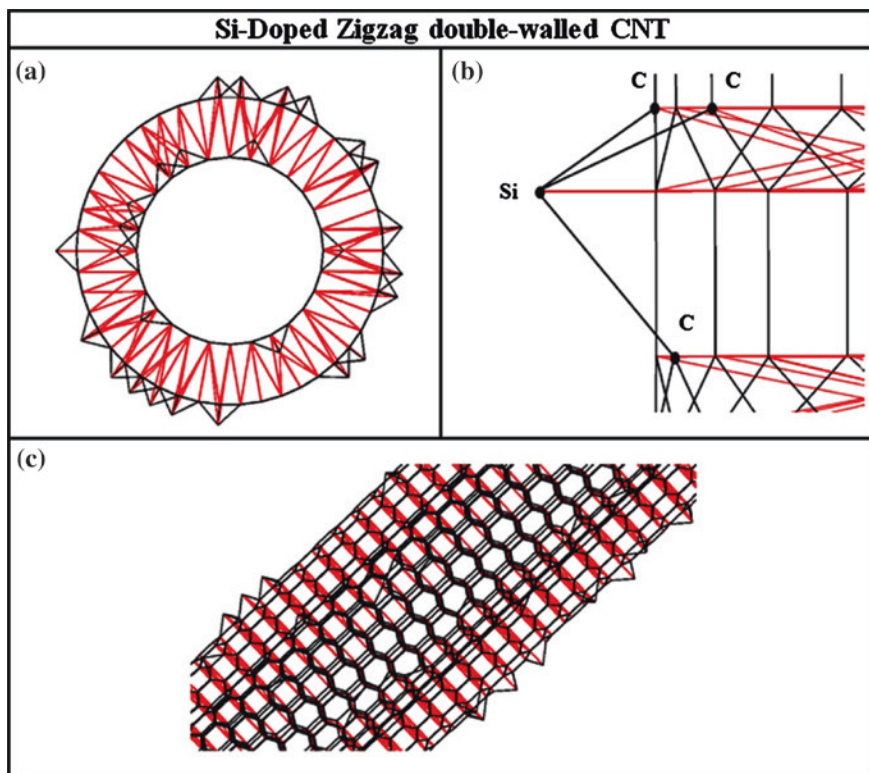


Fig. 2.36 a Top, b zoomed and c global view of a Si-doped DWCNT

Similar to SWCNTs, Si-doped MWCTs show an almost linear decrease in the value of shear modulus by increasing the percentage of Si-doping in CNT models. Figure 2.36 shows a Si-doped DWCNT.

2.8.4 Stone–Wales Defect

The Stone–Wales defect, as introduced earlier in this chapter, is the most abundantly detected defect in the structure of carbon nanotubes that occurs naturally after initial formation of vacancies (Charlier 2002). A Stone–Wales defect can be imagined to be formed by a way of an in-plane $\pi/2$ rotation of a C–C bond (Pozrikidis 2009), as schematically illustrated in Fig. 2.37.

Therefore, for the modeling of the defect, the easiest way was to create the model first in planar form and then to roll it into a tube after rotating the randomly selected bonds for $\pi/2$ degree in-plane. The models with the Stone–Wales defect should be finally optimized by minimizing the Tersoff–Brenner potential.

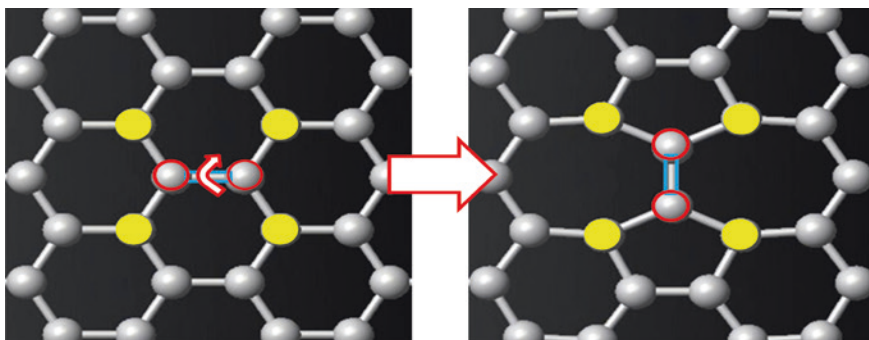


Fig. 2.37 In-plane $\pi/2$ degree rotation of bonds to make pentagon-heptagon defect

Then after assigning proper boundary conditions, an external compression load can be applied to the defected CNT to obtain the Young's modulus, E , of the structure was obtained using Hooke's law in the elastic range and the results were compared with each other and with the ideal mode for each chirality and length.

The results showed that although the introduction of vacancy defects to the body of CNTs weakens their elastic strength, the system is almost capable of restoring its original high elastic modulus by reconstructing its atoms in form of the 5-7-7-5 or Stone–Wales arrangement.

2.8.5 Hetero-Junction CNTs

A local view on the structure of hetero-junction CNTs shows that these nanostructures are made up of the same carbon hexagonal unit blocks, as perfect CNTs. However, the wider view reveals that hetero-junction CNTs are constructed of two CNTs with different chiralities, connected together by a kink, having pentagon-heptagon defect, as shown in Fig. 2.38. These kinks, whose existence and size seem to be noticeably effective on the mechanical properties of hetero-junction

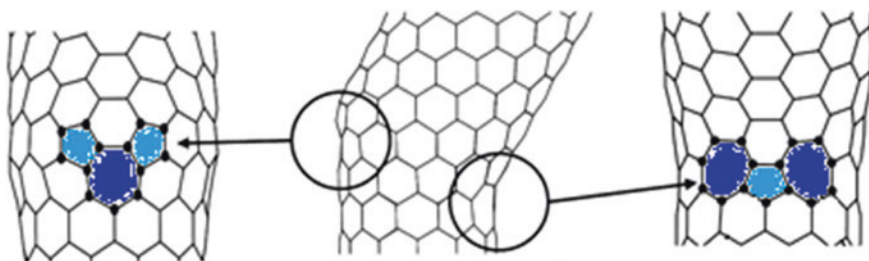


Fig. 2.38 Occurrence of pentagon-heptagon defect on a kink

CNTs, are generally divided into two groups, namely, straight and bent connections (Ghavamian et al. 2015).

For the finite element simulation of the hetero-junction CNTs, CoNTub software can be employed, which is an algorithm for connecting two arbitrary carbon nanotubes. However, since the structure of hetero-junction CNTs comprises of two tubes and a kink part, the structure does not make a homogeneous body. Hence, analytical calculations to determine the moduli and critical buckling loads of hetero-junction CNTs required to be modified with a proper approximation. According to this approximation, each hetero-junction CNT was assumed to be a homogeneous CNT with a constant area, A_{Hetero} and a constant diameter, D_{Hetero} , using the general weight percentage relation, as follows:

$$L_{\text{Hetero}} = L_{\text{Tube1}} + L_{\text{Kink}} + L_{\text{Tube2}}; \quad (2.33)$$

where

$$L_{\text{Kink}} = \frac{\sqrt{3}}{2} \pi (D_d), \quad (2.34)$$

and

$$D_d = d_{\text{wider tube}} - d_{\text{thinner tube}}. \quad (2.35)$$

Hence,

$$A_{\text{Hetero}} = \frac{L_{\text{wider-tube}} \times A_{\text{wider-tube}} + L_{\text{Kink}} \times A_{\text{Kink}} + L_{\text{Thinner-tube}} \times A_{\text{Thinner-tube}}}{L_{\text{Hetero}}} \quad (2.36)$$

$$D_{\text{Hetero}} = \frac{L_{\text{wider-tube}} \times D_{\text{wider-tube}} + L_{\text{Kink}} \times D_{\text{Kink}} + L_{\text{Thinner-tube}} \times D_{\text{Thinner-tube}}}{L_{\text{Hetero}}} \quad (2.37)$$

and

$$A_{\text{Kink}} = \frac{A_{\text{wider-tube}} + A_{\text{Thinner-tube}}}{2}. \quad (2.38)$$

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2016, XXVIII, 220 p. 126 illus., 87 illus. in color.,
Hardcover

ISBN: 978-3-319-00250-7