Chapter VI

Summary and Conclusion

Graphene has a two dimensions structure which can be investigated by introducing regular hexagons and therefore a theoretical model is based on equal bond lengths and bond angles. In the equilibrium structure, ambient condition, of achiral tubes, armchair and zigzag tubes, there are two different directions of the bond lengths with tube axis and in general, three directions in chiral tubes. This raises the question if we need to define more than one bond length and more bond angles in comparison to graphite, furthermore, what are the values of these bond lengths and bond angles which are suitable to single-walled carbon nanotubes?

The aim of this thesis is to answer these questions from the point of the favourable energy. Furthermore, one expects that the responses of these bond lengths and bond angles to applied hydrostatic pressure may be different without shape transition or with shape transition.

The bond lengths are determined for several radii tubes of various lengths. The procedure that has been adopted consists of mainly three parts: firstly, the generation of atomic coordinates on the surface of the circular seamless cylindrical tube based on the modified helical and rotational symmetries using two different bond lengths, secondly, assuming that the atoms are interacting via an empirical potential, Tersoff potential, to calculate the energy of the tubes and finally, minimization of the energy to obtain best possible set of these bond lengths. We also suggest modified parameters in Tersoff potential to reproduce the carbon-carbon bond length in graphite sheet in good agreement with the experimental value. We have also examined the shape of the cross section at ambient condition for single-walled carbon nanotubes. The circular cross section is found the favourable shape at ambient condition for all single-walled carbon nanotubes.

First, we examined the energetically favourable shape of the cross section at ambient condition for tubes. We found that a circular shape of the cross section is the favourable shape in all the tubes. We also investigated the variation of the bond lengths and bond
angles in the equilibrium structure, ambient condition, including the tube radius and length effects for three types of carbon nanotubes, armchair, zigzag and chiral SWNTs. We also studied the effect of the chirality on the bond lengths and bond angles for chiral tubes. Results for achiral SWNTs, armchair and zigzag tubes, show that there are two unequal bond lengths and three bond angles in the tube structure. Two equivalent bond angles are found to be equal and smaller than the third one in armchair SWNTs while in zigzag SWNTs, these two equivalent bond angles are found to be larger than the third one. For armchair SWNTs, one bond length comes out to be larger than that of the graphite value while the other bond length has a smaller value than this. In the structure of zigzag tubes, the results indicated that one bond length has a constant value equal to that of the graphite value whereas the other bond length larger than this. The bond lengths and bond angles are found to be very sensitive to the tube radius in achiral tubes. As the tube radius increases the bond lengths approach the bond length in the graphite and the bond angles move toward the ideal value (120°). We also found that the length of the tube has a significant effect on the bond lengths and bond angles in armchair tubes. In case of zigzag tubes, only the larger bond length changed with the tube length. At tube length larger than the some value, depending on the tube radius and chirality of tubes, these bond lengths and bond angles become constant.

For the structure of chiral SWNTs, we found equal bond lengths and three unequal bond angles to describe completely these structures. The values of the bond length and bond angles are found to depend on the chirality and vary slightly with the change in tube radius. The large deviation of these bond length occurs in the mid region between the chiral angle of zigzag ($\theta = 0^\circ$) and armchair ($\theta = 30^\circ$). We did not obtain any effect of the tube length on the values of the bond length and bond angles in chiral tubes. The reason of the fixed bond length and bond angles with increase in the tube length in chiral tubes is that the length of the unit cell has enough length to cancel any effect of the tube length on the carbon-carbon bonds in the chiral tubes.

The variation of the curvature energy with tube radius and chirality has also been investigated for all tubes. We have found that the curvature effect was depended on the tube radius and chirality. In achiral tubes, as the tube radius increases the curvature effect
decreases. While in chiral tubes the curvature effect was found not dependent on the tube radius. It depends on the chirality. High curvature energy was found at critical chiral angles in the middle region between the chiral angle of armchair and zigzag tubes.

The bond lengths and bond angles were recalculated under hydrostatic pressure. We assumed that the tubes remain have a circular cross section under pressure. In case of armchair SWNTs, we found that the larger bond length decreases faster with pressure in comparison to the smaller one. Indeed, as a result, at some critical pressure, depending upon the tube radius, these bond lengths become equal and then reverse their behaviour above this critical pressure. Two equivalent bond angles are found to decrease with pressure while the third one increases. For zigzag tubes, out of the two bond lengths, only the larger bond length responded to the pressure. Actually it only compresses under pressure. As a result, at some critical pressure, depending upon the tube radius, the larger bond length becomes equal to the constant bond length. In chiral tubes, the bond length compresses under pressure whereas the bond angles correlated with the behaviour of the bond angles in zigzag tubes remain to have the same value at ambient pressure. We also found that the single-walled carbon nanotubes are extremely rigid along the tube axis rather than in circumferential direction.

Furthermore, we recalculated the structure under pressure by relaxing the condition of circular cross section assumed in chapter IV. An analysis regarding the cross-sectional shape transition under pressure at which transition from circular to oval cross section takes place has investigated in this work for armchair(n,n), zigzag (n,0) and chiral (n,m) nanotubes. We found that at some particular transition pressure the shape transition, from circular cross section to oval shape, takes place. There is a different value of the elliptical aspect ratio, the ratio of the shorter to the longer axes in elliptical cross section, for armchair, zigzag and chiral tubes. The transition pressure is found to depend on the tube radius and chirality. As the tube radius increases the transition pressure decreases. This transition pressure also increases with decreasing in the elliptical aspect ratio.

The behaviour of the bond lengths at transition pressure was quite peculiar. For achiral tubes, the larger bond length expanded at transition pressure to take value closer to the value at zero pressure. The other bond length continues to decrease under pressure. This of
course did lead to compress volume; it was the way shape change had to occur. The value of the larger bond length was found to depend on the tube radius while the other bond length on the elliptical aspect ratio and vary slightly with the tube radius. For chiral tubes, the bond length at transition pressure has approximately the same value for all tubes with different radii and different chirality.

The results of the variation of the bond lengths under pressure in the shape transition resulted in a new behaviour of the macroscopic parameters such as tube radius in the circular cross section of SWNTs. At transition pressure, the tube radius in the circular cross section split into two unequal axes, the longer axis and the shorter axis. The longer axis at transition pressure strongly expanded. The new value of the longer axis was very closer to that value at zero pressure. The behaviour of the shorter axis at transition pressure is found to be uncorrelated with the longer axis. It continues to decrease under pressure. The tube resists any increase in the applied pressure by bending the cross section toward a new direction that’s the direction of the shorter axis.

These present interesting results, leading us to conclude that at some critical pressure; firstly, the bond lengths become equal in the circular cross section and then at some increased transition pressure, the cross section of tubes transform to elliptical shape.

We also calculated the bulk modulus for achiral and chiral nanotubes under pressure. Firstly, when the tubes only compress under pressure, the tubes remain having a circular cross section. Our results indicated that the bulk modulus increased with pressure and there is a radius dependence of the bulk modulus. Increase in the tube radius tends to decrease the bulk modulus. Secondly, at shape transition occurs, the value of bulk modulus is found to be smaller than that at zero pressure. We have also found that the tubes have a higher value of bulk modulus at pressure equal to transition pressure but with a circular cross section.

From this work, we can conclude that the structure of isolated achiral single-walled nanotubes has unequal bond lengths while one bond length can completely define the structure of chiral tubes. The structure of single-walled carbon nanotubes is also defined by three bond angles. The circular cross section under ambient condition and at some region
of the pressure is favourable for achiral and chiral tubes. However, there are differences in the behaviour of the bond lengths and bond angles to the applied pressure. Above some particular pressure the cross section of achiral and chiral tubes transforms from circular to oval shape. At transition pressure, the behaviour of these bond lengths also is different in response. Therefore, any study on the electronic, mechanical and thermal properties, under applied pressure of carbon nanotubes should also take into account these different behaviours of the structural parameters and not treat them as equal or equal to that in graphite value.

We believe that the results of this thesis regarding the behaviour of two bond lengths are important. Furthermore, the critical pressure at which these two bond lengths become equal is much more important. The observations made here in this thesis regarding differences in bond lengths behaviour for different chirality variety, specially under hydrostatic pressure should be exploited for characterizing the type of the tube by experimentally correlating possible observable critical pressure and critical bond length or bond lengths at transition pressure in (n,m) tubes in Raman data or any other experiment which reflects this behaviour of the structural parameters. The phonon modes in Raman experiments could broaden depending upon difference in the bond lengths. There could also be shift in mode frequencies. A careful observation near the critical as well as transition pressure may be interesting. The experiments may pay attention to possible masking effect in the Raman modes due to the medium used in their set up used for pressure transmitting. We believe that our results in this work add new modification to main expected features in the high pressure evolution of single-walled carbon nanotubes. It is hoped that these results provide enough motivation for experiments activity aimed to explore the finding presented here.