Ab Initio Study of Chirality Effects Onphonon Spectra, Mechanical and Thermal Properties of Nearly Samediameter Single Wall Carbon Nanotubes

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Abstract:
In this paper, we have used density functional perturbation theory (DFPT) and Pseudo-potential method to calculate the phonon spectrum, phonon density of states (DOS), specific heat capacity and mechanical properties of (5,5) armchair and (9,0) zigzag Single Wall Carbon Nanotubes (SWCNTs). Our calculations show that Young's modulusfor (5,5) and (9,0) nanotubesare higher than 1TPa. We have also shown that the value of compressive Young's modulus for (5,5) nanotube isgreater thanthat for (9,0) nanotube while thevalue of tensile Young's modulus for (9,0) nanotubeisgreater than that for(5,5) nanotube. The result of our calculations shows that thespecific heat capacity of (5,5) and (9,0) nanotubes coincides, therefore we may conclude that thespecific heat capacity of nanotubes is independent of their chirality. Furthermore we have found that the atoms in the armchair nanotubes are positioned as close as possible in the direction of the nanotube axis, therefore they could have more resistant against compressive pressure.
Keywords: *Single-walled carbon nanotubes, Mechanical properties, Young's modulus.*

1. INTRODUCTION

During the last decades, carbon nanotubes, due to the ability of understanding the size importance in physical properties and also their applications in nanostructure materials, have received much attentions [1-5].
Carbon nanotubes are carbon based structures which have been largely used in new technologies because of their specific electronic and mechanical properties. The physical properties of carbon nanotubes will change depending on the geometry. Varying the geometry of carbon nanotubes makes it possible to fabricate low dimensional physical systems in order to achieve higher advantages in technology [6-8].
Numerous studies have been performed to determine the mechanical properties of this nano-structured material [9–13]. Theoretical and experimental investigation indicated an average Young's modulus of around 1 TPa and Poisson's ratio of 0.25–0.28 for single-walled carbon nanotubes (SWNTs), depending on the CNTs' length, diameter, chirality, sample synthesis, type of defect, measurement techniques, and computational theory and parameters.

The vibration behavior of carbon nanotubes (CNTs) has been extensively investigated due to their importance in nano-electro-mechanical systems (NEMS) and nanosensor application.

Various numerical and experimental investigations have been reported on the RBM vibrations of CNTs. S. Basirjafari et al have analytically studied the radial breathing modes of multi-walled carbon nanotubes [14]. A theoretical analysis of the radial breathing mode (RBM) of carbon nanotubes (CNTs) subjected to axial pressure has been presented based on an elastic continuum model by Xiao-Wen Lei et al [15]. They have investigated the effects of axial pressure, wave numbers and nanotube diameter on the RBM frequency.

Carbon nanotubes have the highest tensile strength among the known materials therefore they may be considered as the strangest material ever known. There are covalent bonds between carbon atoms. A tensile strength of 63Gpa was found for multi-walled carbon nanotube in 2000 [16] (about a thousand times tires).

The high thermal conductivity in the direction of the nanotube axis, which is one of the most important properties of carbon nanotubes is in the focus of many researches. Carbon nanotubes will also become insulators in the directions perpendicular to the nanotube axis.

The specific heat capacity of carbon nanotubes is an important quantity in industrial applications and also experimental research. The specific heat capacity can be determined based on statistical mechanics calculations.

Coefficient of thermal expansion of carbon single-walled nanotubes has been investigated analytically and numerically by Askari et al [17]. They have shown that the coefficient of thermal expansion of carbon single-walled nanotubes is independent of their chirality.

In this paper we have theoretically studied mechanical and thermal properties of infinite single wall (5,5) and (9,0) nanotubes. We have calculated the phonon dispersion, phonon density of states and specific heat capacity of these nanotubes. Our calculations indicate that the Youngs's modulus of CNTs is different in tension and compression. Also the results of our calculations show that the specific heat capacity of CNTs is independent of their chirality.

2. CALCULATION METHODS

As is well known in harmonic approximation a solid consists of a periodic array of atoms or ions that will oscillate around their equilibrium positions. The energy needed for dynamical motion is provided by the solid temperature. By calculating the total energy of solid at zero temperature, we may obtain structural properties of carbon nanotubes such as lattice equilibrium constants and bulk modulus.

The vibrational energy of atoms or ions in a dynamical crystal at non-zero temperature will have significant effects on the mechanical and thermal properties of crystal such as heat capacity and thermal expansion.

In this paper Quantum ESPRESSO package has been employed for the DFPT calculations while the DFT part of the calculations were done under local density approximation (LDA) [18]. The effect of the internal electrons on valence electronic states is taken into account by using ultra soft pseudo-potentials [19].

The chosen super-cell was a hexagonal with 14 Å sides so any coupling between neighbor SWCNTs has been eliminated. In addition, the BZ integration was carried out via the Monkhorst– Pack scheme [20, 21] with 1×1×12 k-points. The convergence test with 0.1 μeV tolerance has been done for total energy according to the plane wave's cut off energy up to 544 eV. Moreover, optimization of the ionic positions, lattice parameters and cell volume were achieved after the relaxation when all forces and stresses became less than 0.25meV/Å and 0.05GPa respectively.

3. PHONON PROPERTIES

Figures 1-2 show the phonon dispersions along the tube's axis (z direction) and their DOSs for an armchair (5,5) and an zigzag (9,0) SWCNTs. Considering the lowest energy) acoustic (dispersion curves ,it is deduced that near the Γ) k=0) point the transverse-acoustic (T_A) mode branches are doubly

degenerated and the second branches are belong to the longitudinal-acoustic (LA) mode.

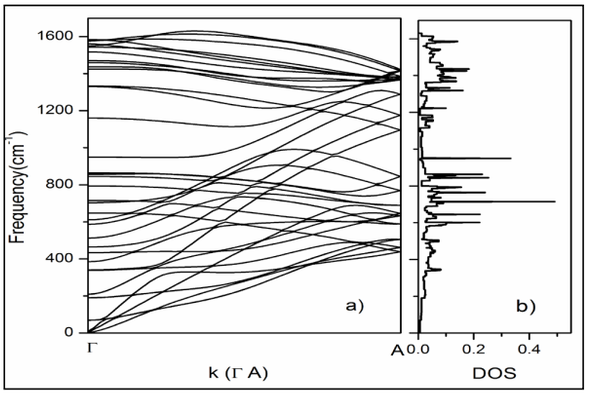

Figure 1: (a) The calculated phonon dispersion relations of an armchair carbon nanotube (5,5) plotted in axial q-vector. (b) Phonon density of states of (5,5) nanotube.

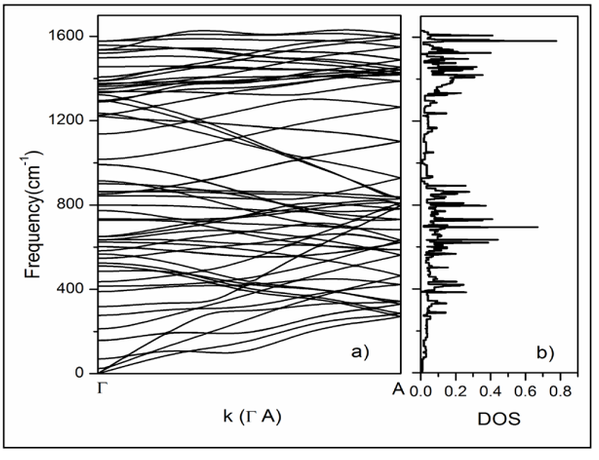

Figure 2: (a) The calculated phonon dispersion relations of an zigzag carbon nanotube (9,0) plotted in axial q-vector. (b) Phonon density of states of (9,0) nanotube.

Moreover, there is a fourth acoustic mode for CNTs, twisting mode (TW), which shows an ionic rotational wave propagation along the tubes [22] and the lowest third branch shows this mode, respectively. Slopes of the acoustic branches around the Γ point $(d\omega/dk)_{k=0}$ give their relevant sound velocities. The sound velocities of the TA and LA phonons for (5,5) carbon nanotube are estimated as V_{TA}=5.51 km/s and V_{LA}=*15.127* km/s, respectively. In addition, the velocity of the twisting acoustic wave is V_{TW}=*14.925* km/s for (5,5) nanotube. The sound velocities of the TA and LA phonons for (9,0) carbon nanotube are estimated as V_{TA}=*10.0649* km/s and V_{LA}=*22.7716* km/s, respectively. The velocity of the twisting acoustic wave is V_{TW}=*15.428* km/s for (9,0) nanotube. The acoustic velocities are reported in Table 1.

Table 1: *The calculated acoustic velocities of (5,5) and (9,0) carbon nanotubes.*

Nanotube	$V_{TA}\left(\frac{km}{s}\right)$	$V_{LA}\left(\frac{km}{s}\right)$	$V_{TW}\left(\frac{km}{s}\right)$
(5,5)	5.51	15.127	**14.925**
(9,0)	10.0649	22.7716	**15.428**

The velocity of LA mode can be used to calculate the elastic constant along the axis of nanotube C_{33} via the relation:

$$V_{LA} = \sqrt{\frac{C_{33}}{r}} \qquad (1)$$

where r is the density of nanotube.
Although the density is an ill-defined concept in the case of CNTs ,[24 ,23] here a nanotube is assumed to be a rolled graphene with3.4 Å thickness) the separation between Carbon layers in graphite .(Table 2shows the longitudinal elastic constants and also the number of ions per unit-cell of the considered SWCNTs.

Table 2: *Radius, number of C atoms per unit-cell and elastic constant (C33) for (5,5) and (9,0) SWCNTs.*

SWCNT	**Radius (Å)**	**N/unit-cell**	C_{33} **(GPa)**
(5,5)	3.4017	20	**515.9**
(9,0)	3.5302	36	**1168.6**

$$\nu_{RBM}(\mathrm{cm}^{-1}) = \frac{2243}{D} - \frac{665}{D^3} \qquad (2)$$

The other vibrational characteristic feature of the SWCNTs is their radial breathing mode (RBM) frequencies (the most important low-frequency

Table 3: *The radial breathing mode (RBM) of (5,5) and (9,0) carbon nanotubes. Number of C atoms in unit cell (N). Radius of the nanotube (R).*

Nanotube	N	R(Å)	$n_{RBM}(\text{cm}^{-1})$ empirical Eq.(2)	$n_{RBM}(\text{cm}^{-1})$ Calculated	Other calculation
(5,5)	20	3.4017	327.58	340.88	332.881 [25]
(9,0)	36	3.5301	315.81	317.21	-

Raman active mode). It involves a collective movement of atoms towards and away from the central axis and its value is different for each tube. The RBM frequency dependence on diameter of SWCNTs is commonly accepted via an empirical formula [23]:

D is the diameter of the nanotube (Å).

Radial breathing modes calculated and radial breathing modes obtained from the empirical equation (2) are compared in table 3.

4. MECHANICAL PROPERTIES

The main mechanical characteristics of the SWCNTs are Young modulus, Y, and Poisson ratio. The Y value direction is defined as:

$$Y = \frac{1}{V_{eq}}\left(\frac{\partial^2 E}{\partial \varepsilon^2}\right)_{\varepsilon=0} \tag{3}$$

where E is the formation energy, V_{eq} and ε are the equilibrium volume and the subjected strain respectively. Here we have used two methods to determine the Y values; i- using the DFT approach for minimizing the formation energy versus the subjected strain along the tube's axis (Murnaghan method [26]), ii- using linear elastic approximation:

$$Y = \frac{\sigma}{\varepsilon} = \frac{F/A_0}{\Delta L/L_0} = \frac{FL_0}{A_0 \Delta L} \Rightarrow F = \kappa \Delta L, \quad \kappa = \frac{YA_0}{L_0} \tag{4}$$

Where e is the inserted strain, L_0 is the equilibrium length, A_0 is the cross-section and κ is the equivalent elastic constant for longitudinal expansion or contraction of nanotube. To find the κ value, we plot the energy variations vs $S = (\Delta L)^2/2$ where ΔL is the length variation of tubes. The κ value can be calculated via the relation: $\Delta E = \kappa S$ (elastic approximation)

Figures 3 and 4 show the energy variation of CNT (5,5) and (9,0) versus S in tension and compression. As it can be seen from these figures the energy linearly increases by increasing S. By calculating the slope of the curve we can obtain the value of Young's modulus of CNTs in tension and compression. However we can find the value of Young's modulus Murnaghan method. Table. 4 indicates the results of our calculations.

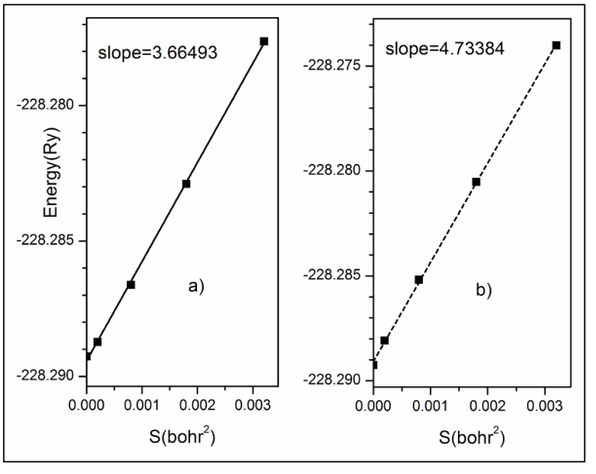

Figure 3: *Energy variation versus $S = (\Delta L)^2/2$ for (5,5) SWCNT: a-tensile state, b-compressive state*

The Y values in third column of table 4 have been obtained via the Murnaghan method; whereas, for determining the compressive and tensile Y values (fourth and fifth columns of the table) we have used the elastic approximation (Figures 3-4). It must

be pointed out that there is a very good agreement between average values of the 4th and 5th columns and the values of the third column. As it is expected, the compressive modulus values are bigger than the tensile ones and the 6th column of the table shows their differences.

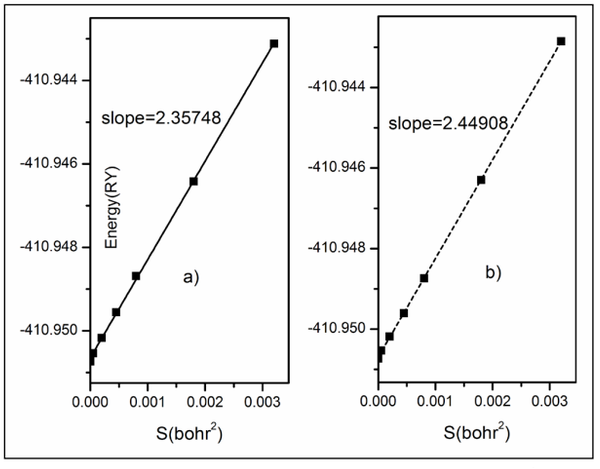

Figure 4: *Energy variation versus* $S = (\Delta L)^2/2$ *for (9,0) SWCNT: a-tensile state, b-compressive state*

Another important mechanical property of a material in the linear regime is the Poisson ratio, which has been defined in a macroscopic context as the negative ratio of the relative change in radius over the relative elongation:

$$\nu = -\frac{\Delta R / R_0}{\Delta L / L_0} \tag{5}$$

Where, R_0 and L_0 are relevant unperturbed radius and length of the sample.

In this regard, by consideration of an isolated tube and finding out the slope of its radius variation versus its perturbing unit- cell elongation (Figure 5) and multiply it by $(-L_0/R_0)$, it would be possible to calculate the Poisson ratio. The results of calculation for the narrow SWCNTs are shown in table 5. As this table shows the Poisson ratios for the zigzag (9,0) nanotube is higher than that for armchair (5,5) nanotube.

Table 4: *Young modulus, Y, for (5,5) and (9,0) SWCNTs. The last column shows* $\Delta Y = Y_{comperessive} - Y_{tensile}$

nanotube	R(Å)	Y(TPa)	Y(compressive) (TPa)	Y(Tensile)(TPa)	ΔY(GPa)
(5,5)	3.4017	1.0885	1.2344	0.9557	278.7
(9,0)	3.5302	1.0458	1.0679	1.0280	39.9

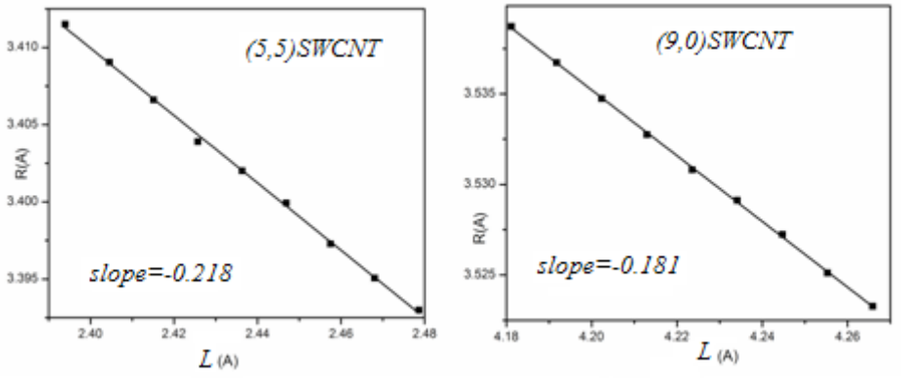

Figure 5: *Least square fitting for variation of the narrow (5,5) and (9,0) SWCNTs versus their unit-cell elongation*

Table 5: *The poisson is calculated for carbon nanotubes*

nanotube	R(Å)	Poisson
(5,5)	3.4017	0.156303735
(9,0)	3.5302	0.217132276

4. SPECIFIC HEAT

In principle, *except in very low temperature region the* phonon contribution to the specific heat, *Cv(T) of materials is significant.* After calculating the phonon DOS for the narrow SWCNTs, we can find out the temperature dependence of their specific heat according to the following expression [27]:

$$C_v(T) = \int_0^{\nu_{\max}} g(\nu)\left(\frac{h\nu}{k_B T}\right)^2 \frac{e^{\frac{h\nu}{k_B T}}}{\left(e^{\frac{h\nu}{k_B T}} - 1\right)^2} d\nu \qquad (6)$$

Where ν is phonon's frequency, $g(n)$ is phonon DOS and $n_{\max}$ is the highest phonon frequency of the material and is related to the Debye temperature, Q_D ($k_B Q_D = h n_{\max}$).

The temperature dependence of specific heat for (5,5) (armchair) and (9,0) (zigzag) SWCNT is shown in figure 6. It is observed that specific heat exhibits almost the same behavior with temperature for both tube types.

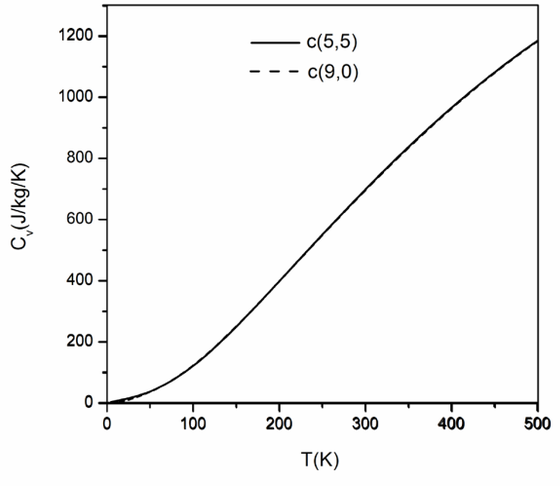

Figure 6: *Temperature dependence of specific heat of (5,5) and (9,0) carbon nanotube.*

5. CONCLUSION

Our results for radial breathing modes (RBM) are in good consistent with the experimental ones. In equation (2), nanotubes radii are the parameters considered to calculate the RBM while the chirality dependence of these modes is ignored in this equation. Our theoretical results predict that the RBM depends on the chirality. The most important application of RBM is in nanotubes purification.

The Young's modulusfor (5,5) and (9,0) nanotubes are greater than 1Tpa, based on our calculations. The value of compressive Young's modulus for (5,5) nanotube is greater than that for (9,0) nanotube while the value of tensile Young's modulus for (9,0) nanotube is greater than that for (5,5) nanotube.

We have also found that the atoms in armchair nanotubes are positioned as close as possible in the direction of the nanotube axis, therefore they could have more resistant against compressive pressure. Furthermore we have shown that the atoms in zigzag nanotubes are positioned as far as possible in the direction of the nanotube axis, therefore they could have more resistant against tensile pressure.

The value of elastic constant coefficient for (5,5) nanotubes in the direction of nanotube axis (C33) is completely different in comparison with the value of Young's modulus. Due to the concentration of atoms in the direction of nanotube axis, the elastic coefficient perpendicular to nanotube axis becomes important while this cannot be observed in (9,0) nanotubes. Finally we have found that the Poisson ratios for the zigzag (9,0) nanotube is higher than that for the armchair (5,5) nanotube.

In room temperature (300 K), the specific heat capacity per mole is equal to 1R (universal constant) which is due to the assumption of quasi one dimensionality of nanotubes.

The outcome of our calculations shows that the specific heat capacity of two (5,5) nanotube and (9,0) nanotube coincides, therefore we may conclude that the specific heat capacity of nanotubes is independent of their chirality. This result is in agreement with the result of analytical and numerical calculations in Ref. [17]

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