Predicting the Phonon Dispersion in Different Carbon Nanotubes using Tight Binding Method

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Abstract - The phonon dispersion relations of four armchair and four zigzag carbon nanotubes have been calculated using tight binding method. First of all, the electronic structure of carbon nanotubes is derived by a simple Tight-binding calculation for the π-electrons of carbon atoms. The calculated electronic structure of a carbon nanotube tells the carbon nanotubes will be either metallic or semiconducting, depending on its diameter and chirality. Then the zone-folding technique is discussed that is the same as that used in treating the electronic structure of carbon nanotubes. Finally the three-dimensional dynamical matrix of different carbon nanotubes are taken into account for curvature of the nanotubes that gives the phonon dispersion relations results of different carbon nanotubes.

Keywords - Armchair carbon nanotube, Zigzag carbon nanotubes, Tight-binding calculation, Chirality and Phonon dispersion

I. INTRODUCTION

Carbon nanotubes (CNTs) become a significant technology because of their marvelous presentation in wide engineering use. It has been described the surprise material of the 21st century, the building blocks for the future of electronics and the substitute for silicon circuits [1, 2]. These materials have been hailed for their material properties and the applications that these properties promise. Carbon nanotubes (CNTs) have high electrical and thermal conductivity, remarkable strength, elasticity and anisotropic shape. This recommends numerous possibilities of nanoscale biological probes and structural elements in many electronic devices [3-5].

A carbon nanotubes form simply honeycomb lattice of a graphene sheet that rolled into a cylinder. Graphene is also the name commonly associated with a single layer of graphite in two dimensions. By itself, the graphene sheet lattice structure is not a Bravais lattice but can be regarded as an underlying square Bravais lattice with a two-atom basis. There are typical covalent bonds between a carbon atom in a graphene and its neighboring atoms. Each carbon atom has three neighboring atoms to which it is connected in the graphene sheet model.

The rule explored in the present work is based on vibration of the nearest neighbor atoms which would yield a coverage final state of deformation under given loads or displacements at specific sites. In fact the idea is based on orthogonalized plane wave and tight binding methods which are placed in the force constant model [6]. We could thus modify the phonon dispersion relation and show that the second nearest neighboring atoms vibrate with the different amplitude, direction and phase from those for the nearest neighboring atoms.

II. MODEL AND NUMERICAL METHOD

As earlier mentioned, graphene is a two dimensional sheet consisting of connected carbon atoms in hexagons like the benzene molecule. The electronic structure of a carbon nanotube (CNT) can be acquired from that of graphene. The wave vector related with the chiral vector \( \mathbf{C}_h \), in the circumferential direction gets quantized. On the other wave-vector associated the direction of the translation vector \( \mathbf{T} \) along the CNT axis remains continuous for an infinite carbon nanotube. These are the boundary conditions of the carbon nanotube. This sets the energy bands in one-dimensional dispersion relationship cross sections of those of graphene. The reciprocal lattice vectors along the carbon nanotube axis \( C_h.K_2 = 0, T.K_2 = 2\pi \), and \( K_1 \) in the circumferential direction, ( \( C_h.K_2 = 0, T.K_2 = 2\pi \) ) expression are given by

\[ K_1 = \frac{1}{N} \left( -t_2.b_1 + t_1.b_2 \right) \]

\[ K_2 = \frac{1}{N} (mb_1 - nb_2) \]

The one-dimensional energy dispersion relations of a carbon nanotube can be written as

\[ E_{CNT}^\nu (k) = E_{g-2D} \left( \frac{k}{K_2} \frac{K_2}{|K_2|} + \nu K_1 \right) \]

(1)

\(-\pi/T < k < \pi/T\) is a one-dimensional wave-vector along the carbon nanotube axis and \( \nu = 1, \ldots, N \).
The periodic boundary condition for a carbon nanotube provides \( N \) discrete \( k \) values in the circumferential direction. These \( N \) pairs of energy dispersion curves correspond to the cross sections of the two-dimensional energy dispersion surface of graphene which is given by (1). Several lines cut near one of the \( K \) points are shown in Figure 1. The separations between two adjacent lines with the length of the cutting lines are given by

\[
|K_1| = \frac{2}{d_{CNT}} \quad \text{and} \quad |K_1| = \frac{2\pi}{T},
\]

respectively. The carbon nanotube gets a zero energy gap if the cutting line passes through a \( K \) point of the two-dimensional brillouin zone (Figure. 1), where the \( \pi \) and \( \pi^* \) energy bands of graphene are degenerate by symmetry. If the \( K \)-point is situated between two cutting lines, such that \( K \) always located in a position one-third of the distance between two adjacent \( K_1 \) lines Figure. 2 then a semiconducting carbon nanotube with a finite energy gap is formed. Thus for a \((n, m)\) carbon nanotube, \( n-m \) is exactly divisible by 3 then the carbon nanotube is metallic where as carbon nanotubes with residuals 1 and 2 of the division \( n-m \) by 3 are semiconducting.

The one-dimensional wave-vectors \( K \) are shown in the BRILLOUIN zone of graphene as bold lines for (a) metallic and (b) semiconducting CNTs.

Here we are giving eight carbon nanotubes in which four carbon nanotubes are armchair and four are zigzag carbon nanotubes as shown in figures 3-10.
The phonon dispersion relations for carbon nanotubes can be determined by folding that of a graphene layer. In general (n, n) armchair carbon nanotubes yield 4n energy subbands by means of 2n conduction and 2n valence bands. Out of these 2n bands, two are non-degenerate and n-1 is doubly degenerate. The degeneracy comes from the two subbands with the same energy dispersion, but different ν-values. In all zigzag carbon nanotubes have the lowest conduction and the highest valence bands are doubly degenerate where as all armchair carbon nanotubes have band degeneracy between the highest valence and the lowest conduction band. Both armchair as well as zigzag carbon nanotubes bands are symmetric with respect to k=0. An armchair carbon nanotubes bands have two valleys at around k = ±2π/3a points and the zigzag and chiral carbon nanotubes can have at most one valley. The bands in armchair cross the Fermi level at k = ±2π/3a thus they are considered to exhibit metallic nanotube [2]. There is no energy gap for few carbon nanotubes. It is valuable to build up an approximate relation that describes the dispersion relations in the regions around the Fermi energy E_F = 0 as electrical conduction is decided by states around the Fermi energy. The expression around the point (0, ±4π/3a) where the energy gap is zero and f(k) is given by

\[ f(k) = 0 \]

is straightforward to show that

\[ f(k) \approx -i \left( 1 + 2e^{\beta_x} \cos(k_x a / 2) \right)^2 \]

with

\[ \beta_x = k_x \mp (4\pi / 3a) \]

The matching up energy dispersion relation can be written as [3]

\[ E_{g \rightarrow 2D}(k) = \pm f(k) \]

\[ = \pm \frac{\sqrt{2}}{2} \sqrt{k_x^2 + \beta_x^2} \]

The energy bands for (n, 0) zigzag carbon nanotubes can be achieved by enforcing the periodic boundary conditions. This define the quantity of allowed wave-vectors k_x in the circumferential direction as nk_x = 2πν, (ν =1.. 2n). This gives the one-dimensional dispersion relations for the 4n states of the (n, 0) zigzag carbon nanotubes

\[ \mp \pi / \sqrt{3}a < k_x < \pi / \sqrt{3}a \]

\[ E_v(k_x) = \pm \frac{\sqrt{2}}{2} \sqrt{k_x^2 + \left[ \frac{4\pi}{3a} \left( \frac{3\nu}{2n} - 1 \right) \right]^2} \] (2)

So, the energy gap for subband v can be written as difference between the energies of the + and -branches at k_x=0.

\[ E_s = \sqrt{22} \frac{2\pi}{na} \left( \nu - \frac{2n}{3} \right) \] (3)

The energy gap has a minimum value of zero corresponding to ν = 2n/3. If n is not a multiple of three then the minimum value of ν - 2n/3is equal to 1/3. This suggests that the minimum energy gap is then given by

\[ E_s = \sqrt{\frac{2\pi}{3a}} \frac{2\pi}{na} = \frac{2a_{c-c}}{d_{CNT}} \approx \frac{0.8eV nm}{d_{CNT}} \]

Where d_{CNT} = na/π is the diameter of the carbon nanotubes in nano-meters. The DOS for semiconducting zigzag carbon nanotubes based on (2) and (3) is given by

\[ g(E) = \sum_{\nu} \frac{8}{3\pi a_{c-c} t} \frac{E}{\sqrt{E - E_s^2 / 2}} \]

Which is an approximately valid only if (E-E_s) << t [4].

For all metallic carbon nanotubes, independent of their diameter as well as chirality, because of the nearly linear dispersion relations around the Fermi energy the density of states (DOS) per unit length along the carbon nanotube axis is a constant given by 8/3πa_{c-c} t [2].
The force constant-phonon dispersion calculations in graphene are valid on carbon nanotubes. The basis of a graphene sheet consists of two atoms named “a” and “b”. Assuming only nearest neighbor interaction between examples the “a” atom and the nearest neighbors, which are three “b” atoms, the angle between each “b” atom is equally spaced with 120°. When folding the graphene sheet into a single walled carbon nanotube (SWCNT) then it is possible to employ the concepts and calculations from graphene sheets [5]. Surely, the calculations are performed on graphene sheets, which is a good approximation if the radius of the carbon nanotube is much greater than the distance between two neighboring nuclei of the carbon atoms in the carbon nanotube. From the literature, we know the diameter of most carbon nanotube is between 0.7 nm and 2 nm, while the distance between the nuclei of the atoms is 1.42 Å [3, 6, 7].

The nearest neighbor interaction among pure π orbitals of the carbon atoms in the graphene sheet is dominating with respect to σ orbitals. For this purpose, we pick out one particular atom to study and consider all of the other nearest neighbor’s atoms on this atom. This arbitrary carbon atom of graphene can vibrate (move) freely while its nearest neighbor atoms are located at their positions without any displacement and movement. In this case, we assume that the tube cut open along the direction of its axis and the atoms lay out as a planer sheet. This yielded a 2D automat grid with only x-y coordinates required to define the system state. Let us keep in mind that the most stable location of our arbitrary atom can be found by minimizing the total bonding energy. Although there are both bonding and antibonding potentials in the graphene sheet [5], we neglect antibonding potential in the present work.

As there are 2N carbon atoms in the unit cell of a carbon nanotube so 6N phonon dispersion branches for the three-dimensional vibrations of atoms are got. The corresponding one-dimensional phonon energy dispersion relation for the carbon nanotube is given by

$$\omega_{\text{CNT}}^{\mu\nu}(q) = \omega_{g-2D}^\lambda \left( q \frac{K_2}{K_1} + \mu K_1 \right)$$

Where $\lambda = 1, \ldots, 6$ denotes the polarization, $\mu = 0, \ldots, N-1$ is the azimuthal quantum number, and $-\pi / T < q \leq \pi / T$ is the wave-vector of phonons. Though, the zone-folding method does not always provide the correct dispersion relation for a carbon nanotube, particularly in the low frequency region. For example when rolled into a carbon nanotube, the out-of-plane tangential acoustic (ZA) modes of a graphene sheet do not give zero energy at the q = 0.

All the carbon atoms of the CNT move radially in and out of plane radial acoustic vibration at q = 0 which is corresponds to a breathing mode (RBM) with a non-zero frequency [8]. To avoid these difficulties, one can directly diagonalize the dynamical matrix.

The electron-phonon interaction Hamiltonian for carbon nanotubes can be written as [9].

$$\overline{H}_{el-ph} = \sum_{k',\nu',k,k,\lambda} M_{k',\nu',k,k,\lambda} c_{k',\nu'}^\dagger c_{k,\nu} (b_{q,\mu,\lambda} + b_{q,-\mu,\lambda}^\dagger)$$

Where $c_{k',\nu'}^\dagger$ and $c_{k,\nu}$ are the electron creation and annihilation operators, respectively. Here $b_{q,\mu,\lambda}^\dagger$ and $b_{q,-\mu,\lambda}$ are the phonon creation and annihilation operators, respectively, and $M_{k',\nu',k,k,\lambda}$ is the electron-phonon matrix element

$$M_{k',\nu',k,k,\lambda} = \frac{\hbar}{2 \rho_{\text{CNT}} L \omega_{q,\mu,\lambda}} \overline{M}_{k',\nu',k,k,\lambda}$$

Where $\rho_{\text{CNT}}$ is the mass density of the carbon nanotube, L is the normalization length and $\overline{M}_{k',\nu',k,k,\lambda}$ is the reduced electron-phonon matrix element of the transition from the initial electronic state $k,\nu$ to the final state $k',\nu'$. Here $k'$ is the wave-vector and $\nu$ is the azimuthal quantum number of electrons.

Because of energy conservation for a scattering event it holds $E_{k',\nu'} - E_{k,\nu} = \pm \hbar \omega_{q,\mu,\lambda}$, where $q$ is the wave-vector, $\mu$ is the azimuthal quantum number, and $\lambda$ is the polarization of the phonon. The matrix element obeys selection rules arising from wave vector and azimuthal quantum number conservation, $q = k' - k$ and $\mu = \nu - \nu'$.

Carbon nanotube has only two degrees of freedom are confined, so an electron can only be scattered forward or backward in the axial direction thus preserving or changing the sign of the band velocity, respectively.

Overall the scattering processes invoke either intra-subband or inter-subband transitions. These intra-subband processes are significant for the electrical and the heat transport in carbon nanotube while for the relaxation of an excited electron or hole in the same subband.
The inter-subband processes give to the radiation less relaxation of electrons (holes) from a given subband to a subband with a lower (higher) energy [9]. The scattering of electrons can take place either in a given valley or between two valleys. These two possibilities of scattering are termed as intra-valley and inter-valley scattering processes. The phonon DOS of all carbon nanotubes have been calculated as shown [10].

Figure 12 represents 6x0 and 6x6 carbon nanotube phonon spectra respectively

Figure 13 represents 6x0 and 6x6 carbon nanotube phonon density of state respectively
Figure 14 represents 8x0 and 8x8 carbon nanotube phonon spectra respectively.

Figure 15 represents 8x0 and 8x8 carbon nanotube phonon density of state respectively.
Figure 16 represents 10x0 and 10x10 carbon nanotube phonon spectra respectively.

Figure 17 represents 10x0 and 10x10 carbon nanotube phonon density of state respectively.

Figure 18 represents 12x0 and 12x12 carbon nanotube phonon spectra respectively.
III. RESULT AND DISCUSSION

It is interesting to note that the energy dependence of the nanotube density of states as shown in Figure 22 and 23 where the density of states for metallic and semiconducting zigzag nanotubes are compared. It is observed that although the number of carbon atoms in these pairs (6x0 and 6x6), (8x0 and 8x8), (10x0 and 10x10) and (12x0 and 12x12) are equal yet the energies each n x n carbon nanotubes show higher energies levels with large number of modes in their respective band than n x 0. It is interesting that the upper frequency slightly increases with increasing in diameter, whereas the lower frequency decreases with decrease in diameter within each phonon spectrum.

So the high energy spectra of carbon nanotubes can be explained by simple splitting of the graphene degenerate optical mode into the non degenerate mode. In each energy spectrum have radial, longitudinal and transversal optical phonon. Besides the longitudinal and transversal acoustic modes there is a radial breathing mode in all spectra. This is obvious that we not expect other effect like again hybridization and dependence of the force constants on the inter-atomic distance to further increase the splitting between the $A_T$ modes.

IV. CONCLUSION

Here the phonon dispersion relations of armchair and zigzag tubes have been calculated within symmetry based tight binding approach.

It is observed that the phonon dispersion in the higher energy levels is more in armchair than zigzag carbon nanotube in the given parameter. The phonon mode density increases with increases in the number (n) in each carbon nanotube. So the highest energy phonons exist in the biggest number (n) of carbon nanotube in both armchair and zigzag carbon nanotubes. When compared in both, the higher energy phonon existed more in the armchair than the zigzag carbon nanotubes respectively.

REFERENCES