ORIGINAL RESEARCH PAPER

The Molecular Mechanics Model of Carbon Allotropes

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ABSTRACT
Carbon can form numerous allotropes because of its valency. Graphene, carbon nanotubes, capped carbon nanotubes, buckyballs, and nanocones are well-known polymorphs of carbon. Remarkable mechanical properties of these carbon atoms have made them the subject of intense research. Several studies have been conducted on carbon nanotubes or graphene. In the present study, the molecular mechanics method was applied to model five polymorphs of carbon with a uniform approach and compare the allotropes of carbon in detail. Also, we obtained Young's modulus and natural frequencies for every form of carbon, which can be useful for researchers. We found that an increase in the diameter of the carbon nanotube would accompany with a drop in its strength and Young's modulus. Moreover, our results show that the capped carbon nanotube has a higher strength compared to that of the non-capped nanotube, which might be due to the end bonds of the carbon nanotube. Finally, we identified extraordinary properties of Buckyball including its strength, which is three times more than that of the carbon nanotube with the same diameter.

Keywords: *Graphene, Carbon Nanotubes, Buckyballs, Young's Modulus, Natural Frequencies.*

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INTRODUCTION

Carbon can form numerous allotropes because of its valency. Graphene, carbon nanotubes, capped carbon nanotubes, buckyballs, and nanocones are well-known polymorphs of carbon. Larger-scale structures of carbon are nanotubes, nanobuds, and nanocones. Other unusual forms of carbon exist at very high temperatures or extreme pressures.

Single-walled carbon nanotubes (SWCNTs) are special polymorphs of carbon with a diameter of 4-5 A° [1-3]. The ideal characteristics of SWCNTs originate from their long macro-morphology (high aspect ratio, length/diameter), remarkable mechanical properties (Young's modulus=1-1.8 TPa), transport conductivity, and thermal conductivity (3000W/m K) [3]. SWCNTs are considered as the building blocks of various nanoscale electronic and mechanical devices because of their significant structural and mechanical properties [4-6].

Ideally, graphite comprises of infinite layers of sp2-hybridized carbon atoms. Within a layer (sheet) of graphene, each carbon atom bonds to three other carbon atoms, forming a planar array of fused hexagons. Graphite is also a good electrical and thermal conductor in the plane directions. The thermal conductivity values of this molecule are ~

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15-20 W and ~0.05-0.1 W [7-10], depending on the sample's history and temperature.

Buckyballs and fullerenes (including C60 and C70) [11-12] form when the dangling bonds at the edges of a real (finite) graphene layer are connected to each other. The chemistry and physical properties of fullerenes have received much attention in this decade, with several functionalized derivatives being reported [12,13,14]. Solar cells [15] and biological applications [16,17] and their derivatives have been recently reviewed owing to their interesting physical properties [18,19].

Several studies have been conducted on the mechanical properties of the allotropes of carbon. In the experimental works, Blakeslee et al. [20] reported a Young's modulus of 1.06 ± 0.02 TPa for graphite. Frank et al. [21] measured Young's modulus of five layers of graphene sheets to be about 0.5 TPa. Gomez-Navarro et al. [22] applied the tip-induced deformation method and estimated Young's modulus of a graphene (with 1 nm thickness) at 0.25 ± 0.15 TPa. Lee et al. [23] employed nanoindentation in the center of a monolayer graphene sheet with the atomic force microscopy (AFM) technique. In addition, they measured Young's modulus at 1 ±0.1 TPa by assuming that the thickness of graphene to be 0.335 nm. Various ab initio (molecular dynamic) calculations on graphene found that Young's modulus values of graphene were 1.11 TPa [24] or 1.24 ±0.01 TPa [25] by assuming that the thickness of graphene was 0.34 nm. MD simulation has also been utilized to gain the mechanical properties of graphene. For example, Young's modulus of graphene was 1.272 TPa [26] with the modified Brenner potential. Also, Memarian et al. [27] obtained a Young's modulus of graphene by molecular mechanics method about 1078.86 and 982.01 GPa in zigzag and armchair directions, respectively.

Many investigations have been done on CNTs. The results show that CNTs have wide ranges of 270-5,500 GPa for Young's modulus and 240-2,300 GPa for shear modulus [28-37, 39]. Nevertheless, the majority of the results show a Young's modulus of 1,000 GPa or 1 TPa and a shear modulus of 400 GPa.

In the present study, we applied the molecular mechanics model in order to model graphene, carbon nanotube (CNT), buckyballs, and nanocones to obtain the mechanical properties and vibrational properties of these allotropes of carbon. It is for the first time that all the carbon's allotropes are simulated by the same method to obtain their mechanical properties. Also, the properties of buckyballs and nanocones were obtained for the first time using the molecular mechanic method.

Modeling

An SWNT can be visualized as a hollow cylinder and formed by rolling over a graphite sheet. It can be uniquely characterized by a vector C in terms of a set of two integers (n, m) corresponding to graphite vectors a_1 and a_2 (Fig. 1) [38].

$$c = na_1 + ma_2 \quad (1)$$

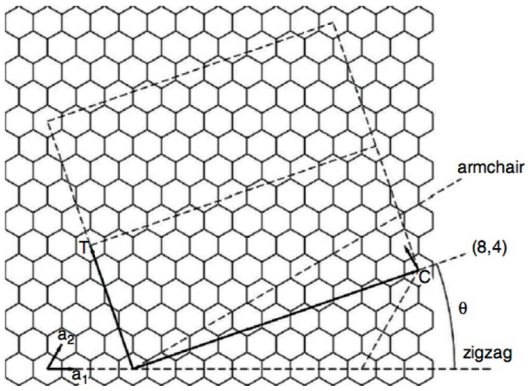

Fig. 1. A nanotube (n,m) is formed by rolling a graphite sheet [38].

Thus, the SWNT is constructed by rolling up the sheet in such a way that the two end-points of the vector are superimposed. This tube is denoted as the (n, m) tube with the diameter given by

$$D = \frac{|c|}{\pi} = a(n^2 + nm + m^2)^{1/2}/\pi \quad (2)$$

Molecular mechanic method

CNTs are a frame-like structure that their bonds can be treated like as the beam members and carbon atoms as the joints. If the electrostatic interactions are neglected, the total potential energy (U_{total}) characterizing the force field can be obtained as the sum of energies due to valence (or bonded) and non-bonded interactions [39]:

$$U_{total} = \sum U_r + \sum U_\theta + \sum U_\emptyset + \sum U_{vdw} \quad (3)$$

where U_r, U_θ, U_ϕ, and U_{vdw} correspond with the energy associated with bond stretch interactions, bond angle bending, torsion, and van der Waals forces (non-covalent). Fig. 2 [39] illustrates various inter-atomic interactions at the molecular level.

Force fields can describe the interaction between individual carbon atoms. Kalamkarov et al. [39] used simple harmonic functions to represent covalent interactions between carbon atoms. The energies associated with each covalent component of Eq. (4) can be mathematically described as [40]:

$$U_r = \frac{1}{2}k_r(\Delta r)^2 \tag{4}$$

$$U_\theta = \frac{1}{2}k_\theta(\Delta\theta)^2$$

$$U_\tau = \frac{1}{2}k_\tau(\Delta\tau)^2$$

Table 1 was employed to establish the linkage between the force constants in molecular mechanics and the beam element stiffness in structural mechanics [41].

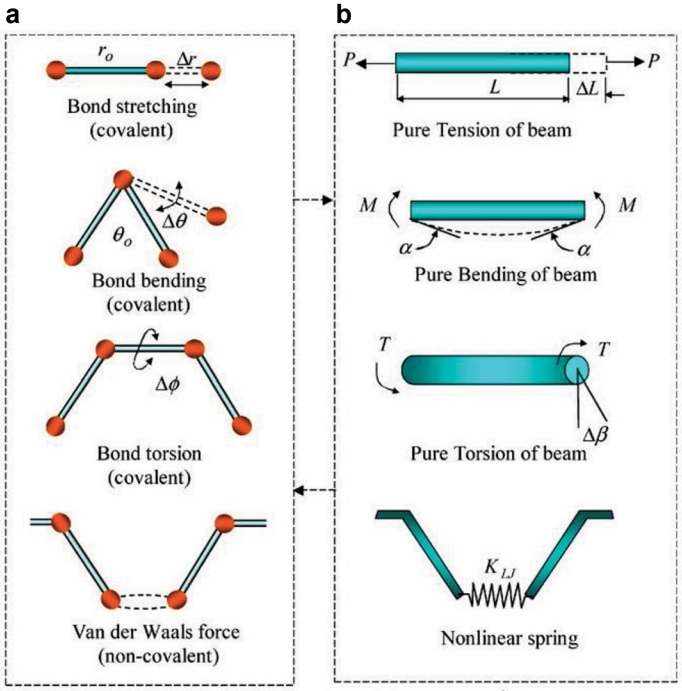

Fig. 2. Equivalence of molecular mechanics and structural mechanics for covalent and non-covalent interactions between carbon atoms: (a) Molecular mechanics model and (b) structural mechanics model [39].

Table 1. Beam element properties

Energy form	Molecular mechanics	Structure mechanics
Stretching energy	$U_r = \frac{1}{2}k_r(\Delta r)^2$	$U_A = \frac{1}{2}\frac{EA}{L}(\Delta L)^2$
Bending energy	$U_\theta = \frac{1}{2}k_\theta(\Delta\theta)^2$	$U_M = \frac{1}{2}\frac{E}{L}(2\alpha)^2$
Torsional energy	$U_\tau = \frac{1}{2}k_\tau(\Delta\phi)^2$	$U_T = \frac{1}{2}\frac{GJ}{L}(\Delta\beta)^2$

In this reference, the parameters are bond stretching increment (Δr), axial stretching deformation (ΔL), bond angle change ($\Delta\theta$), the total rotation angle (2α), the angle of bond twisting ($\Delta\phi$), and torsion angle ($\Delta\beta$).

Therefore, the force constants $k_r, k_\theta \text{ and } k_\tau$ can be represented by:

$$\frac{EA}{L} = k_r, \frac{EI}{L} = k_\theta, \frac{GJ}{L} = k_\tau \quad (5)$$

The values of the force constants k_r, k_θ, k_τ, based on the experience of dealing with graphite sheets, are selected as follows:

$k_r = 938\, kcal.mol^{-1}.\overset{o}{A}^{-2} = 6.53\times10^{-7}\, N/nm$,

$k_\theta = 126\, kcal.mol^{-1}/rad^2 = 8.79\times10^{-10}\, N.nm/rad^2$

$k_\tau = 40\, kcal.mol^{-1}/rad^2 = 2.79\times10^{-10}\, N.nm/rad^2$

[41].

In this study, the BEAM element was selected to simulate the carbon bonds using ABAQUS package. Fig. 3 shows how the hexagonal lattice of the CNT can be simulated as the structure of a space frame.

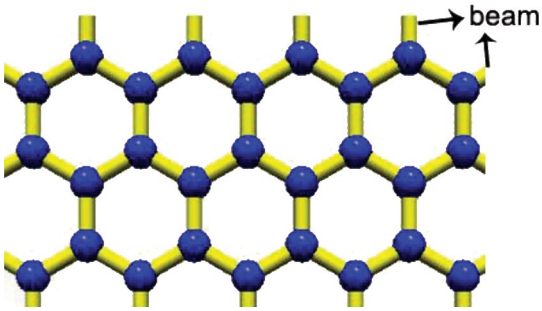

Fig. 3. BEAM element to simulate carbon bonds.

RESULTS AND DISCUSSION

Carbon nanotubes

Carbon nanotubes (CNTs) are tube-like nanostructures with unusual properties. These tubes are useful for nanotechnology, electronics, optics, and other fields of material science.

To estimate Young's modulus of nanoparticles in this research, the following relationships from Beer [49] were utilized:

$$\delta = \frac{FL}{AE} \quad , \quad \sigma = E\varepsilon \quad (6)$$

where F is the load applied to the beam, L is the initial length of CNT, A is the cross-sectional area of the beam, and δ is the calculated displacement of the beam.

Studying the vibrational behavior of carbon-based nanoparticles is critical for various industrial applications such as oscillators and nanocomposites [42]. To investigate the vibrational behavior of carbon nanotubes (CNTs), three major boundary conditions were considered; the cantilevered beam, the bridged CNT, and the one without any boundary conditions. Tables 2 and 3 present the results for nanotubes with chiral (5,0). Figs. 4 and 5 show vibrational behavior and displacement behavior of CNTs.

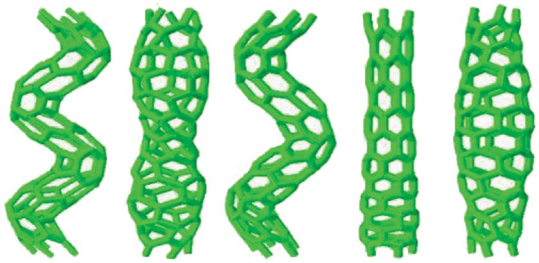

Fig. 4. The vibrational behavior of zigzag nanotubes (5,0).

Fig. 5. Displacement of zigzag (5,0) CNT due to the applied load.

The Young's modulus of CNTs with chiral (10,0) and (5,0) was 965 GPa and 1393 GPa, respectively (Table 2). In a previous work on nanotubes, the results show that CNTs have a wide range of 27 -5500 GPa for Young's modulus [28-37, 39]. Nevertheless, the majority of the results are around a Young's modulus of 1000±200 GPa, which are in good agreement with our results.

Table 2. Young's modulus of Carbon's allotropes

	Diameter[nm]	Length[nm]	Young's Modulus[GPa]
SWCNT (5,0)	3.887	25	1393
SWCNT (10,0)	7.774	25	965
Capped SWCNT (10,0)	7.774	25	1173
Graphene sheet	-	25*24.422	1091
Buckyball	7.11294	-	3628
Nano cone	-	20	3590

Table 3. Natural frequencies (GHz) for SWCNT with different structure and boundary conditions

Mode ID	Zigzag (5,0)			Zigzag (10,0)			Bucky ball
	cantilevered	bridged	free	cantilevered	bridged	none	free
1	127	3350	130	604	7849	266	476
2	127.1	3351	163	604.1	7850	525	764
3	3125	12320	184	4423	17450	1360	1090
4	3543	17140	4209	9393	21840	1740	1440
5	3544	17150	4211	9400	21890	1939	10580
6	8149	32550	12610	12330	31880	3590	10590
7	19630	47250	22360	16950	31890	14750	10595

Capped tube

To be able to investigate the vibration behavior of the capped tube, three major boundary conditions were considered. The first boundary condition was the cantilevered beam. The second one was the bridged CNT, and the third one was without any boundary conditions. The natural frequencies of capped CNTs were obtained using the mode shapes shown in Fig. 6. Also, Table 3 presents the results of the capped tube.

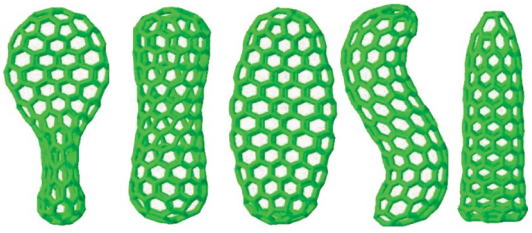

Fig. 6. The vibrational behavior of capped tube.

The Young's modulus of the capped tube with chiral (10,0) was 1173 GPa (Table 2). Schematic of stretched capped CNT is shown in Fig. 7. Comparing these results with those of other studies shows good agreements. Lu [43] reported a Young's modulus of ~1 TPa and a shear modulus of ~0.5 TPa for nanotubes. A molecular dynamics model was used by Yao et al. [44] who obtained a Young's modulus of 1 TPa.

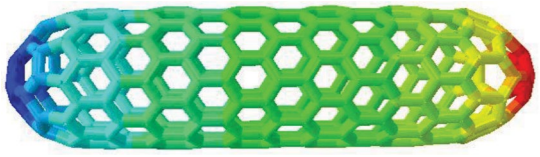

Fig. 7. Displacement contour due to an applied load to the capped tube.

Graphene

Graphene is an allotrope of carbon in the form of two-dimensional and hexagonal lattice sheet.

To investigate the vibration behavior of the graphene sheet, three major boundary conditions were considered. The first boundary condition was the cantilevered condition. The second one was the bridged condition, and the third one was without any boundary conditions. Table 4 demonstrates the obtained results and Fig. 8 shows the mode shapes of graphene.

To estimate Young's modulus of the graphene sheet in this study, the graphene was pulled (Fig. 9) and was employed, where is the measured stress and is the calculated strain of graphene sheet.

Young's modulus of a graphene sheet with 24.422 nm width and 25 nm length was 1091 GPa (Table 2). In this regard, Young's modulus has been reported in experimentally to be between 0.5 and 2 TPa [45]; however, most studies have reported a Young's modulus around 1 TPa [46]. Thus, these results are in good agreement with the previous works.

Table 4. Natural frequencies (GHz) for other carbon's allotropes

Mode ID	Graphene sheet			Nanocone		Capped tube		
	cantilevered	bridged	free	cantilevered	free	cantilevered	bridged	free
1	146	5494	381	6311	127	485	1853	70.2
2	1035	8355	464	6324	429	492	1862	73.2
3	5590	22860	772	8019	1330	1236	3178	658
4	9278	39840	951	8023	5350	3063	8237	1045
5	12180	49640	1010	15470	5360	3457	12590	1285
6	13170	73770	2737	15480	5855	3468	12660	1286
7	36390	84520	5818	16980	8023	12380	12910	2066

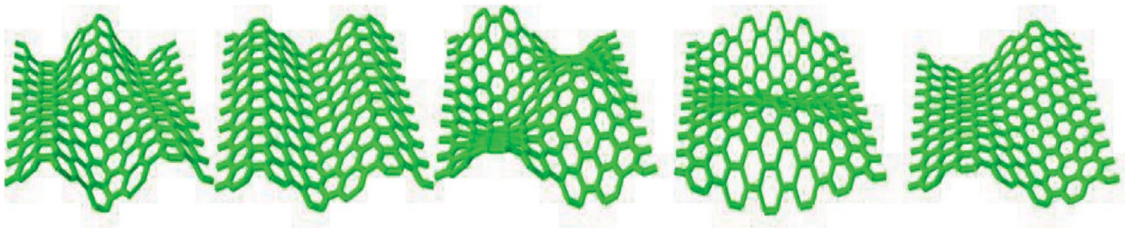

Fig. 8. Vibrational behavior modes of the graphene sheet.

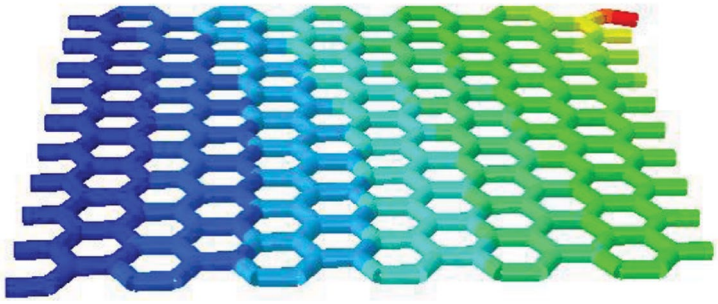

Fig. 9. Displacement due to an applied load to the graphene sheet.

Buckyballs

Buckyball is a spherical shape of carbon allotropes (fullerene molecule C_{60}). This structure is made of 20 hexagons and 12 pentagons (such as a soccer ball).

The vibrational behavior and natural frequency of Buckyball were investigated with no boundary conditions. The mode shapes of buckyball are shown in Fig. 10. It is of note that there is not any report for buckyballs natural frequencies.

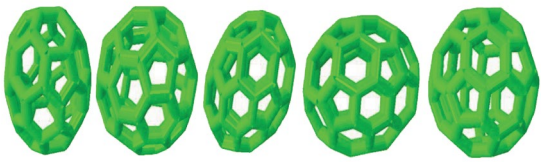

Fig. 10. The modes shapes of the buckyball.

To estimate Young's modulus of buckyball in this work, the relationship was used, where is the measured stress and is the calculated strain of buckyball (Fig. 11).

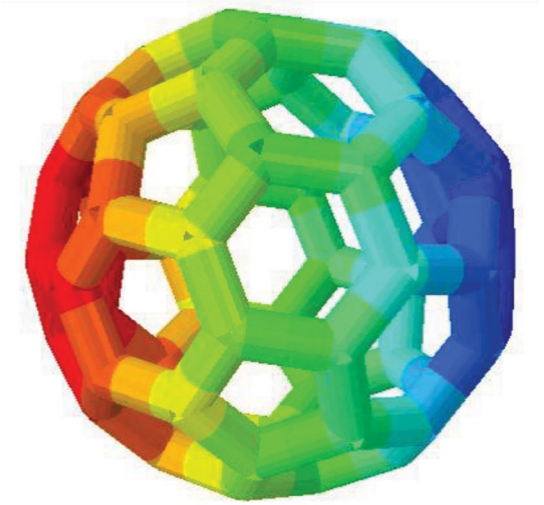

Fig. 11. Displacement due to an applied load to buckyball.

The Young's modulus of the buckyball with 60 atoms was 3628 GPa (Table 2).

There is little work on mechanical properties of buckyballs. Tomoharu [47] indicated that the application of a large amount of stress, almost 2.5 GPa, did not damage the fullerene structures. Moreover, Jeremy et al. [48] studied the hardness of C70 and showed that its hardness was more than that of graphite. So, it can be concluded that the obtained Young's modulus of buckyball is in good agreement with those reported in mentioned works.

Nanocone

Carbon nanocones are conical structures made of carbon and have at least one dimension of the order one micrometer or smaller.

To investigate the vibration behavior of the nanocone, two major boundary conditions were considered. The first boundary condition was the cantilevered condition, and the second one was with no boundary conditions. The natural frequencies of nanocones are shown in Table 4 and the mode shapes are depicted in Fig. 12. In this regard, Narjabadifam et al. [50] found the natural frequency of nanocones using molecular dynamics method, which is around those reported in the present work. Also, Ansari et al. [51] found vibration properties of nanocones using molecular mechanics method and compared their results with those of the molecular dynamics method.

Young's modulus of the nanocone with 20 nm height (Fig. 13) was 3,590 GPa (Table 2). It is noteworthy that there was found no simulation or experimental study on nanocones in literature. However, because of the shape of nanocones, it can be concluded that its strength is more than that of the graphene sheet.

Based on Table 2, it can be concluded that:
Increasing the diameter of the carbon nanotube will decrease its strength (decreases Young's modulus), which can be inferred from the formula as well. From this formula, we can find that increasing the area (A) leads to decreasing the Young's modulus (E). The nanotube with a higher diameter has a higher section area (A) and, thus, a lower Young's modulus.

The capped carbon nanotube is stronger than the non-capped nanotube; because of the end bonds of the carbon nanotube.

Buckyball has extraordinary properties. Its strength is three times more than that of carbon nanotube with the same diameter.

Based on Table 3 and Table 4, it can be concluded that:

For carbon nanotubes, the highest frequency accrues at the bridged boundary condition. According to the Euler Bernoulli theory, the fundamental frequency can be expressed by [52]:

$$f_n = \frac{1}{2\pi}\sqrt{\frac{k_{eq}}{m_{eq}}}$$

where k represents the stiffness, and m is the mass of the structure. The bridged boundary condition leads to an increase in the stiffness of the structure and subsequently an increase in the frequency.

For this reason, the cantilevered carbon nanotubes have a higher frequency than the free-carbon nanotubes.

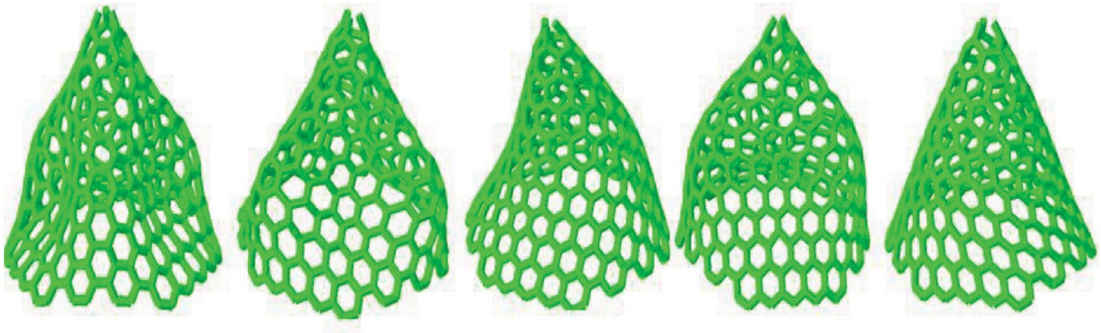

Fig. 12. Vibrational bihavior for nanocone.

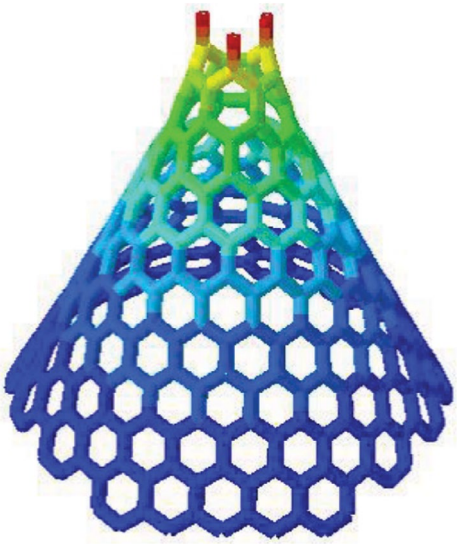

Fig. 13. Displacement due to the applied load on the nanocone.

CONCLUSION

The interesting mechanical properties of allotropes of carbon have attracted researchers thus far. Although many studies have been conducted on carbon nanotube or graphene, in the present study we applied the molecular mechanics method to model five forms of carbon allotropes in order to draw a detailed comparison between the allotropes of carbon. Young's modulus and natural frequencies were obtained for every form of carbon, which

can be useful for researchers. We indicated that the capped carbon nanotube is stronger than the non-capped one. Furthermore, we found that the strength of buckyball is three times more than that of the carbon nanotube with the same diameter.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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