Materials Today Communications 25 (2020) 101404

Contents lists available at ScienceDirect

Materials Today Communications

journal homepage: www.elsevier.com/locate/mtcomm

A reduced form for fundamental transverse modal frequency of carbon nanotubes

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ARTICLE INFO

Keywords:
Modal analysis
Single-walled carbon nanotubes
Carbon nanotubes
Natural frequencies
Transverse mode

ABSTRACT

Carbon nanotube (CNT) has become popular nanomaterial in manufacture of nano-mechanical devices and nanocomposites due to its remarkable mechanical, electrical, and thermal properties. Accurate information of vibrational modes of CNT is important for efficient operation of such nano-devices and nanocomposites. Vibrational modes of CNT are difficult to determine experimentally. Additionally, there is no theoretical or analytical expression for these modes. This paper studies the effect of length, diameter and chirality on the transverse modal frequencies of single-walled CNT (SWCNT) by modelling SWCNTs using molecular-structural-mechanics-approach and conducting finite element simulations. From simulation results, a first-ever reduced form for fundamental transverse modal frequency of SWCNT is developed using non-linear regression. The form predicts our simulation results at 4% mean absolute percentage error, and it predicts results from previous literature at 10 % mean absolute percentage error. The fundamental transverse modal frequency of SWCNT is found to be directly proportional to its diameter, inversely proportional to square of its length, and is unaffected by chirality. This relationship is comparable to Bernoulli-Euler beam frequency equation. Thus, transverse modes can be thought as beam like modes. The developed form can help in designing SWCNTs for nano-devices with desired resonance frequency and for more vibration resilient nanocomposites by tuning SWCNT diameter and SWCNT length.

1. Introduction

Since their finding in 1991 by Iijima and Ichihashi [1], carbon nanotube (CNT) has become increasingly popular nanomaterial due to their extremely high mechanical strength, high electrical conductivity and high thermal conductivity. The Young's modulus of CNTs along their axial direction can be as high as 1 TPa (approximately five times higher than steel) [2] and their tensile strength can be up to 150 GPa (approximately 50 times higher than steel) [2]. In addition, their density is approximately 2267 kg/m^3 [3–6]. Thus, CNTs have extremely high strength to weight ratio due to which they have huge potential for diverse applications. They are being widely used in the matrix of nanocomposites [7–10]. Here, CNTs are used as nano-scale fillers to improve the mechanical, thermal, and electrical properties of fiber-reinforced composites whilst damping its vibrational characteristics [10]. Research shows that CNTs make the original fiber-reinforced composites more vibration resistant [9,10]. Such nanocomposites are being increasingly used in various structural applications in automotive, aerospace, aeronautical, public transportation, and nuclear industries [5]. The knowledge of vibrational modal frequencies of CNT is required for manufacturing CNT-based nanocomposites to ensure no resonance occurs within the operational range. A model that accurately represents the vibrational modes of CNT could be of great help to designers so that they can build vibration resilient CNT-based nanocomposites. CNTs are also used as high frequency resonators in nano-mechanical devices such as nano-sensors, nano-oscillators, charge detectors, field emission devices, and nano-actuators [2,11–14]. In order to push the limits of measurement sensitivities and quality, it would be best if such oscillators and resonators could operate at resonance frequencies, i.e., the modal frequencies of CNT. Therefore, knowledge of vibrational modal frequencies of CNT is important for the efficient operation of these nano-devices. Due to the above reasons, it is highly important to obtain accurate information of the vibrational modal frequencies of CNTs.

Research has been conducted within the last decade to find this information by modal analysis of CNTs using either experimental or numerical techniques. Mehar et al. have experimentally found that modal frequencies of single-walled CNT (SWCNT) reinforced composite panels under free vibration condition increase with the aspect ratio of the panels and the volume fraction of SWCNT [7]. Farrash et al. have experimentally measured damped natural frequency of glass epoxy and

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https://doi.org/10.1016/j.mtcomm.2020.101404
Received 24 February 2020; Received in revised form 26 June 2020; Accepted 26 June 2020
Available online 03 July 2020
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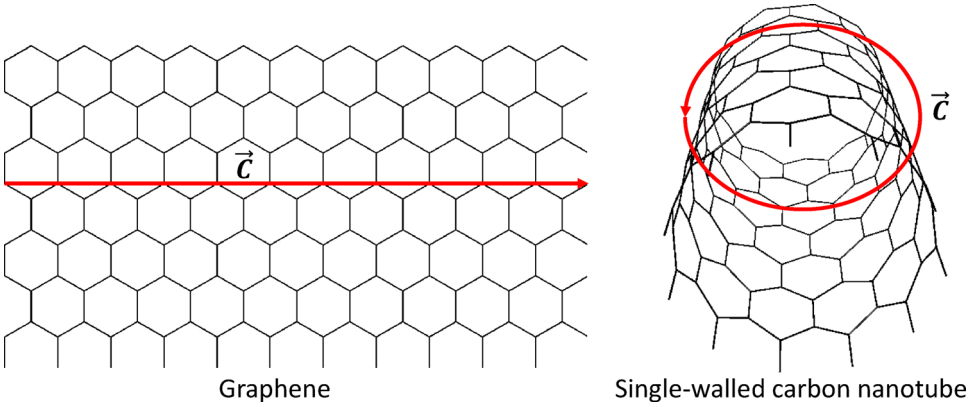

Fig. 1. Rolling up of graphene sheet to form single-walled carbon nanotube.

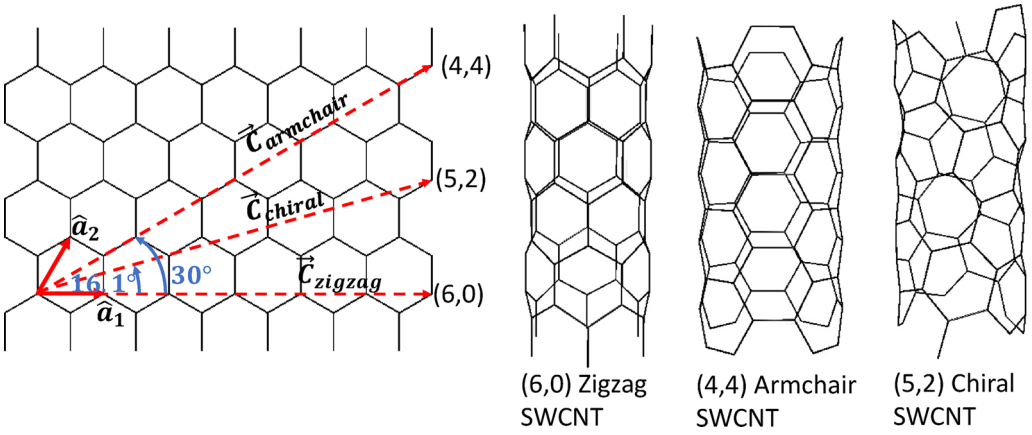

Fig. 2. Structures of different chirality type SWCNT.

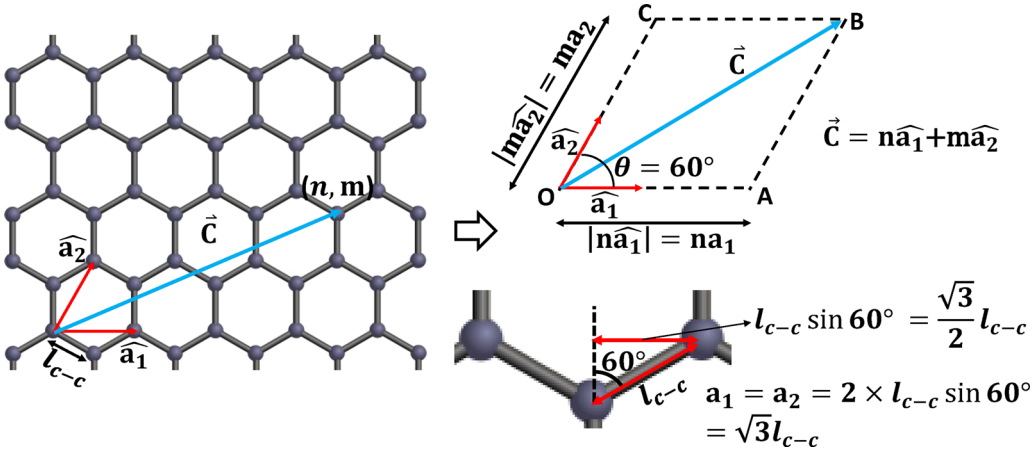

Fig. 3. Geometrical relations in a graphene sheet.

carbon epoxy composite plates with multi-walled CNT (MWCNT) and microfibers as reinforcement [8]. MWCNT addition was found to increase the natural frequencies of the composite plates. Similarly, DeValve and Pitchumani have experimentally found that the first transverse modes in a MWCNT-epoxy carbon fiber composite and a SWCNT-epoxy carbon fiber composite increase with addition of 2% weight fraction of CNT [10]. However, such experimental studies have only been able to test different configurations of composite samples but not the different configurations of the CNT itself. This is because testing the effect of CNT geometry on its vibrational modes requires high resolution electron microscopy to visualize at nanoscale, which is difficult with state-of-the-art equipment capability.

Therefore, numerical techniques are being used instead to test the above using CNT modal analysis. The numerical techniques involve modelling the CNT as a simplified structure and then using numerical tools such as finite element method to calculate its mechanical, buckling, vibrational and thermal properties. The standard techniques for modelling CNT fall under the broad category of: (i) atomistic modelling; (ii) continuum modelling; and (iii) hybrid atomistic-continuum modelling. Atomistic modeling treats the CNT as a combination of atoms and bonds, and predicts the positions of atoms based on interactive forces and boundary conditions (see details in [15–17]) using molecular dynamics (MD) simulation (see details in [15–17]). MD simulation has been used to investigate the vibrational characteristics of CNT. In 2009,

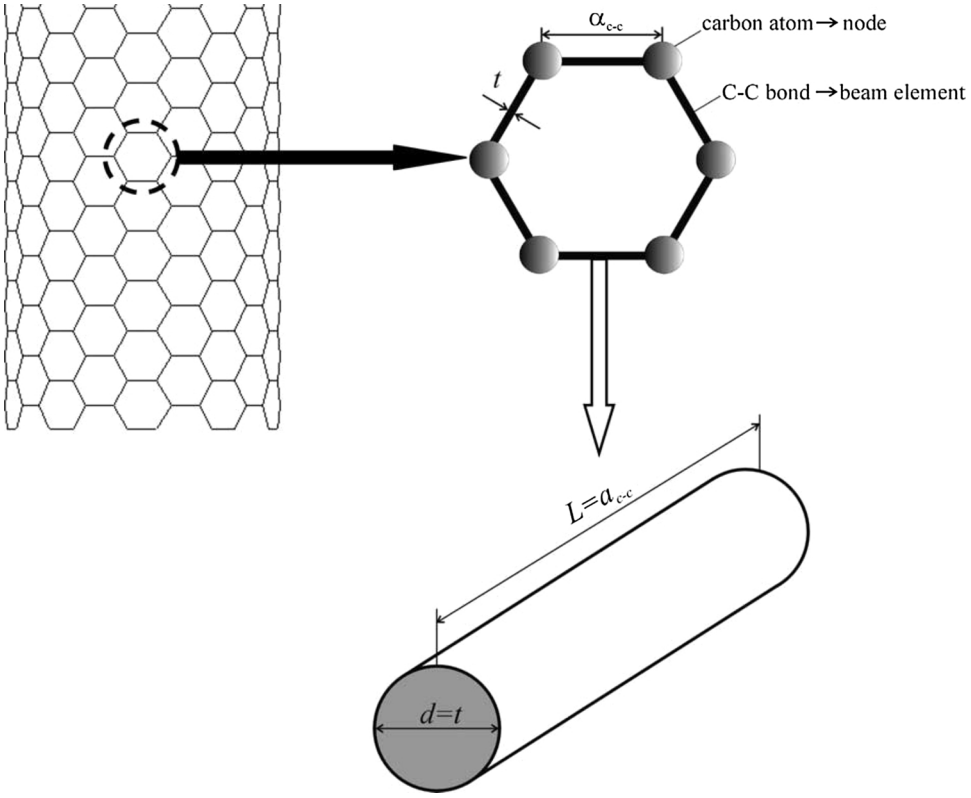

Fig. 4. Simulation of SWCNT as space frame structure [21].

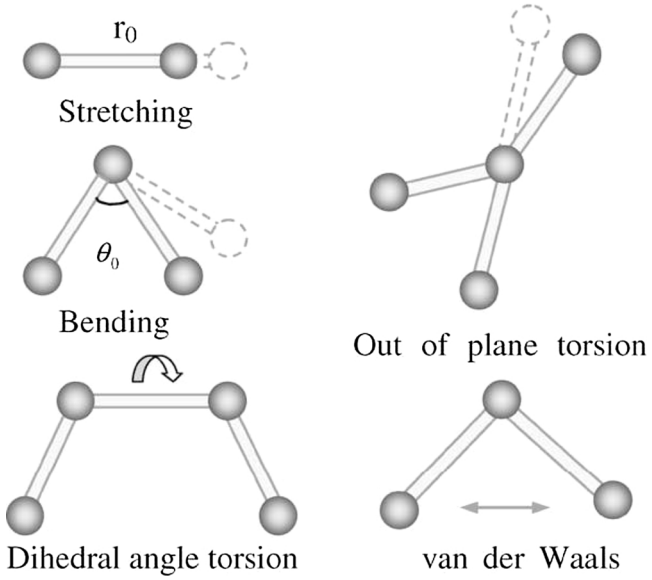

Fig. 5. Interatomic interactions in molecular mechanics [20].

Wu et al. have calculated the first modes of a SWCNT using this technique but their results have not been validated as yet [6]. In 2013, Chang performed MD simulations to find resonance behavior of small-sized sample of armchair CNT models [17], and found that the modal frequencies were comparable to those found from continuum mechanics approach. Atomistic techniques are less popular because they require heavy computation time and are not practical for CNTs with large size. Moreover, they are not able to capture non-linear effects [5].

Continuum modeling is utilized by many engineers to investigate properties of CNTs. The basic assumption in these theories is that a CNT can be modeled as a continuum structure that has continuous distributions of mass, stiffness, etc. So, the lattice structure of CNT is neglected in continuum modeling and it is replaced with a continuum medium. The continuum methods are mostly based on two kinds of theories to simulate CNT properties: the classic beam theory, and shell theory. The classic beam theory models the SWCNT as a continuous hollow elastic beam. The transverse modal frequencies of SWCNT is then given by the following well-known Bernoulli-Euler hollow beam frequency equation [4,18].

$$f_n = \frac{\beta_n^2}{8\pi L^2}\sqrt{\frac{E(D_o^2 + D_i^2)}{\rho}} \tag{1}$$

Here, f_n is the resonance frequency of nth transverse mode of SWCNT; D_o and D_i are the outer diameter and inner diameter of SWCNT respectively; L is the length of SWCNT, E and ρ are the elastic modulus and density of SWCNT respectively; β_n is a constant that is determined from boundary conditions of the SWCNT. For cantilever SWCNT, i.e. for fixed-free end support conditions, $\beta_n = 1.875$; thus the transverse modal frequency of SWCNT from Bernoulli-Euler beam theory is given by the following equation [4,18].

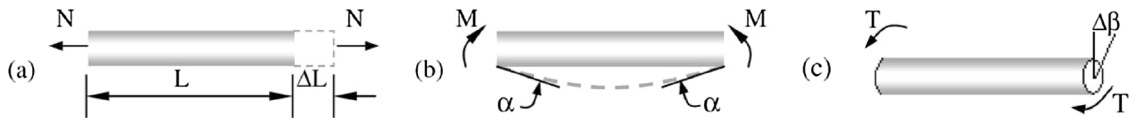

Fig. 6. Pure tension, bending and torsion of a beam element [20].

Table 1
SWCNT models studied.

Model no.	SWCNT type	Chiral angle	(n, m)	SWCNT length (in nm)	SWCNT diameter (in nm)
1	Armchair	30°	(3,3)	20	.4071
2			(5,5)		.6785
3			(7,7)		.9499
4			(9,9)		1.2213
5			(12,12)		1.6283
6			(15, 15)		2.0354
7			(18,18)		2.4425
8			(21,21)		2.8496
9	Zigzag	0°	(3,0)		.235
10			(5,0)		.3917
11			(7,0)		.5484
12			(9,0)		.7051
13			(12,0)		.9401
14			(15, 0)		1.1752
15			(18,0)		1.4102
16			(21,0)		1.6452
17	Chiral	13.9°	(3,1)		.2825
18			(6,2)		.5649
19			(9,3)		.8474
20			(12,4)		1.1299
21			(15,5)		1.4124
22			(18, 6)		1.6948
23			(21,7)		1.9773
24			(24,8)		2.2598
25	Armchair	30°	(9,9)	16	1.2213
26			(9,9)	24	
27			(9,9)	28	
28			(9,9)	32	
29			(9,9)	36	
30			(9,9)	40	
31			(9,9)	44	
32			(9,9)	48	
33	Zigzag	0°	(15,0)	16	1.1752
34			(15,0)	24	
35			(15,0)	28	
36			(15,0)	32	
37			(15,0)	36	
38			(15,0)	40	
39			(15,0)	44	
40			(15,0)	48	
41	Chiral	13.9°	(12,4)	16	1.1299
42			(12,4)	24	
43			(12,4)	28	
44			(12,4)	32	
45			(12,4)	36	
46			(12,4)	40	
47			(12,4)	44	
48			(12,4)	48	

$$f_n = \frac{3.516}{8\pi L^2}\sqrt{\frac{E(D_o^2 + D_i^2)}{\rho}} \quad (2)$$

However, the above equation is not accurate because it assumes SWCNT as a continuous beam, so it neglects any interatomic interactions within SWCNT. Moreover, to use this equation the exact value of elastic properties of SWCNT need to be known. These property values are difficult to determine experimentally as they depend on many environmental factors and current technology doesn't allow accurate measurements in nano-scale. The shell theory models the CNT as a thin hollow cylindrical shell/tube (see details in [5,11]), and it has been used to find the radial breathing modes of SWCNT [5,11]. It suffers from all the limitations as the beam theory. Among the less popular theories is the linear mass-spring model for a both-ends clamped SWCNT (see details in [19]). However, this theory is erroneous compared to beam theory.

To bridge the gaps between atomistic modelling and continuum modelling approaches, hybrid atomistic-continuum modelling approaches have been developed that replace the C—C bond with a continuum element. This approach serves to link computational chemistry of molecular properties with solid mechanics of the representative macroscopic mechanical behavior by equating the molecular potential energy of the nanostructure with the mechanical strain energy of the representative continuum element. "Molecular structural mechanics approach" (MSMA) is the most extensively used hybrid modelling technique to predict elastic and vibrational properties of CNT with good accuracy. MSMA was proposed by Li and Chou in 2003 [20], and it was then combined with finite element method by Tserpes and Papanikos in 2005 [21]. In MSMA, SWCNT is represented as a 3D space frame structure where every C—C bond is taken as a uniform beam with

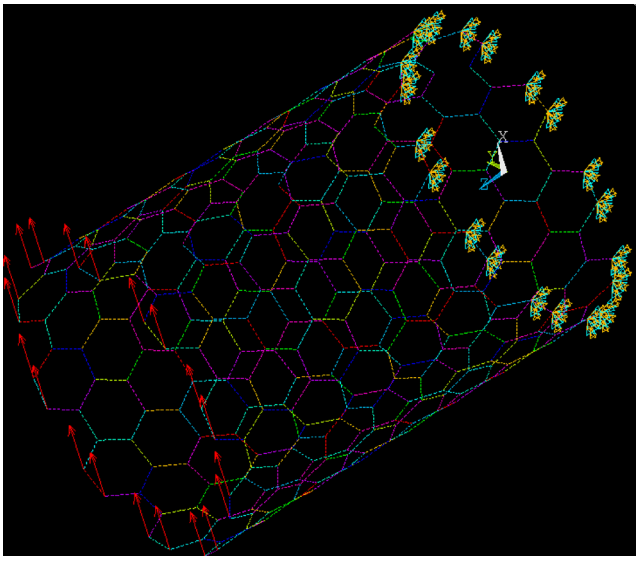

Fig. 7. Boundary conditions for modal analysis of SWCNT.

Table 2
Elastic properties of the beam element in ANSYS APDL.

Property name	Property value (in SI units)	Property value (in Angstrom)
Young's modulus (E)	5487.5×10^9 Pa	548.75 kgÅ^{-1}s^{-2}
Shear modulus (G)	870.7×10^9 Pa	87.07 kgÅ^{-1}s^{-2}
Poisson's ratio (ν)	0.3	0.3
Density (ρ)	2267 kg/m^3	2.267 E-27 kgÅ^{-3}
Cross-sectional radius (r)	733×10^{-13} m	0.7331 Å

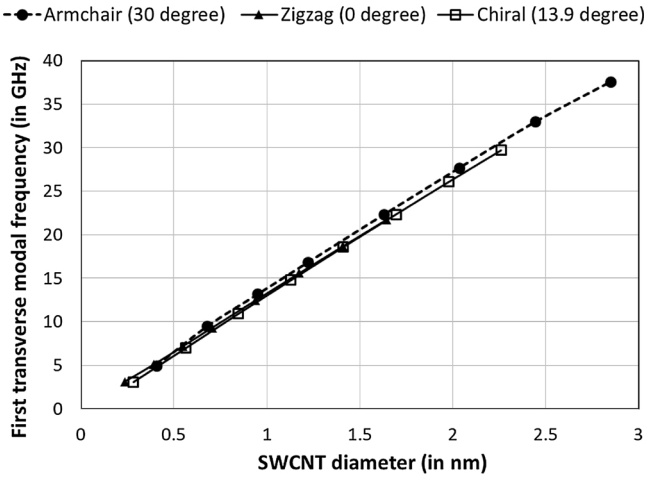

Fig. 8. Variation of fundamental transverse modal frequency with SWCNT diameter and chirality.

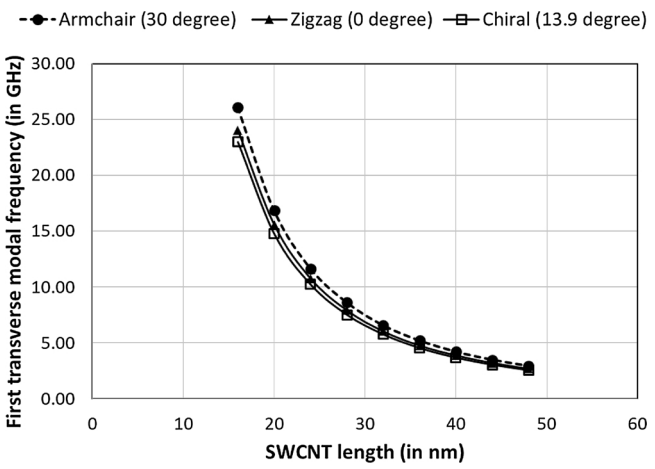

Fig. 9. Variation of fundamental transverse modal frequency with SWCNT length and chirality.

Table 3
Result of linear regression analysis.

Independent variable:	Dependent variable:	
	First mode	
	(1)	(2)
Length (x 10^8)	**−5.7737*****	**−5.7746*****
	(0.3419)	(0.3493)
Diameter (x 10^{10})	**1.3401*****	**1.3349*****
	(0.0665)	(0.0708)
Type Chiral (x 10^8)		−2.5420
		(8.4436)
Type Zigzag (x 10^8)		−2.2440
		(8.7048)
Constant (x 10^{10})	**1.1503*****	**1.1727*****
	(0.1279)	(0.1495)
Observations	48	48
R^2	0.941	0.941
Adjusted R^2	0.938	0.936
F Statistic	358.094*** (df = 2; 45)	171.533*** (df = 4; 43)

Note: *p < 0.1; **p < 0.05; ***p < 0.01.

Table 4
Result of non-linear regression analysis.

Independent variable:	Dependent variable:	
	ln(First mode)	
	(1)	(2)
ln(Length)	**−1.988*****	**−1.987*****
	(0.015)	(0.012)
ln(Diameter)	**1.038*****	**1.033*****
	(0.011)	(0.009)
Type Chiral		−0.052**
		(0.010)
Type Zigzag		−0.023**
		(0.010)
Constant	**29.256*****	**29.279*****
	(0.050)	(0.041)
Observations	48	48
R^2	0.998	0.999
Adjusted R^2	0.998	0.999
F Statistic	11,805.200*** (df = 2; 45)	9,129.074*** (df = 4; 43)

Note: *p < 0.1; **p < 0.05; ***p < 0.01.

circular cross-section, and every carbon atom is taken as a node or the connecting pin between the beams. Thus, the deformation of the structure of CNT can be viewed as deformation of a space frame structure that is composed of connecting beams. The molecular steric energies of CNT as obtained from molecular mechanics research are compared with the strain energies due to structural deformations in the equivalent space frame structure as obtained from structural mechanics theory (see details of this method in section 2.2). This comparison gives the elastic properties namely, Young's modulus, Shear modulus, diameter, and Poisson's ratio of the beam element that represents covalent bonds in a SWCNT.

Hashemnia et al. have used MSMA to study the natural frequencies of SWCNT by computing the mass and stiffness matrix in terms of the elastic properties of SWCNT using finite element method [2]. They have investigated the variation of natural frequencies with respect to the aspect ratio of two zigzag and two armchair CNTs. In 2012, Lee and Lee have performed modal analysis of two armchair and two zigzag SWCNT using MSMA with FEM in ANSYS at fixed beam and cantilever conditions [3]. They found the natural frequencies of first 10 modes of the SWCNTs. Eltaher et al. have done modal analysis using MSMA with ANSYS and found the first nine modes of SWCNT at four different length and 3 different chirality [22]. Moghadam et al. have used finite element MSMA in ANSYS to find that SWCNT fundamental frequency changed with change in boundary conditions, SWCNT length and chirality [23]. These results were derived for CNT with Stone-Thrower-Wales defect. They found out the variation of the first mode of the CNT with variation in position of the defect for armchair and zigzag type CNT. Some works have also been done in comparing results of CNT modal analysis using different modelling techniques. Cheng et al. have calculated the first modes of a SWCNT using MSMA and MD simulation, and found the results using the two methods to have 5% variance [16]. Harrar and Gibson [4] studied the variation in fundamental mode of CNT with the variation in waviness and aspect ratio. They compared the results of CNT natural frequencies using finite element MSMA, finite element shell model and the Bernoulli-Euler classic beam theory. Similarly, in 2012, Fakhrabadi et al. have done modal analysis for 2 and 3-junctioned carbon nanotubes using MSMA [24].

The existing modelling approaches require computation of CNT vibrational modes by first modelling the CNT elastic properties and then conducting modal analysis using a secondary numerical tool. This is a cumbersome approach to finding vibrational modes. None of the existing modelling approaches give a direct analytical model for vibrational modes of CNTs. Moreover, the discussed research work on CNT modal analysis have only studied a couple of CNT models and were not able to establish a relationship between modal frequencies of CNTs and the tube geometrical parameters. In 2011, Fakhrabadi et al. performed the first extensive modal analysis study of 64 SWCNT models using MSMA [14]. They have used SWCNT diameter, SWCNT length and SWCNT chirality as inputs to predict natural frequencies using an Artificial Neural Network [14]. However, they have not found the form of relationship between SWCNT modal frequencies and the geometrical parameters namely, SWCNT diameter, SWCNT length and SWCNT chirality. In 2012, Kim et al. studied the variation of SWCNT modal frequencies and its geometrical features [25] namely, the chirality and length by using normal mode analysis based elastic network model, but were unable to derive the relationship.

From the above discussions it can be concluded that the knowledge of vibrational modal frequencies of CNT is extremely important, but it is difficult to determine experimentally. Additionally, there is no theoretical or analytical expression for these vibrational modal frequencies. In particular, the nature of relationship between CNT geometrical structure and the modal frequencies is unknown. This needs to be established as it can help in developing an analytical expression for CNT modal frequencies and also enable engineers to manufacture CNTs with desired vibrational modes. There needs to be a detailed parametric study to establish this relationship, and hence formulate a reduced form for CNT vibrational modal frequencies. It is the fundamental (first) vibrational mode that is most important as this determines the operational range of structures and also the successive modes. Therefore this

Table 5
Prediction of fundamental transverse modal frequency for our simulated models.

Model no.	Chirality type	SWCNT Length (in nm)	SWCNT Diameter (in nm)	Fundamental transverse mode (in Hz)		
				From simulations	From our reduced form	Absolute % error
1	30° (Armchair)	20	0.4071	4.99E+09	4.99E+09	0.0
2			0.6785	9.50E+09	8.48E+09	10.7
3			0.9499	1.32E+10	1.20E+10	8.7
4			1.2213	1.69E+10	1.56E+10	7.3
5			1.6283	2.23E+10	2.11E+10	5.6
6			2.0354	2.77E+10	2.66E+10	4.1
7			2.4425	3.30E+10	3.21E+10	2.6
8			2.8496	3.76E+10	3.77E+10	0.3
9	0° (Zigzag)	20	0.235	3.13E+09	2.82E+09	10.1
10			0.3917	5.09E+09	4.79E+09	5.9
11			0.5484	7.20E+09	6.80E+09	5.6
12			0.7051	9.32E+09	8.83E+09	5.2
13			0.9401	1.25E+10	1.19E+10	4.5
14			1.1752	1.56E+10	1.50E+10	3.7
15			1.4102	1.87E+10	1.82E+10	2.8
16			1.6452	2.17E+10	2.13E+10	2.0
17	13.9° (Chiral)	20	0.2825	3.08E+09	3.41E+09	10.6
18			0.5649	7.00E+09	7.01E+09	0.2
19			0.8474	1.09E+10	1.07E+10	2.2
20			1.1299	1.48E+10	1.44E+10	2.4
21			1.4124	1.86E+10	1.82E+10	2.2
22			1.6948	2.23E+10	2.20E+10	1.6
23			1.9773	2.61E+10	2.58E+10	1.0
24			2.2598	2.97E+10	2.96E+10	0.2
25	30° (Armchair)	16	1.2213	2.61E+10	2.44E+10	6.4
26		24		1.17E+10	1.09E+10	6.9
27		28		8.62E+09	7.97E+09	7.4
28		32		6.57E+09	6.11E+09	7.1
29		36		5.21E+09	4.82E+09	7.5
30		40		4.21E+09	3.91E+09	7.2
31		44		3.49E+09	3.23E+09	7.5
32		48		2.92E+09	2.71E+09	7.2
33	0° (Zigzag)	16	1.1752	2.4E+10	2.35E+10	2.4
34		24		1.08E+10	1.04E+10	3.2
35		28		7.91E+09	7.66E+09	3.2
36		32		6.04E+09	5.87E+09	2.9
37		36		4.76E+09	4.63E+09	2.6
38		40		3.88E+09	3.75E+09	3.2
39		44		3.20E+09	3.10E+09	3.1
40		48		2.69E+09	2.61E+09	2.9
41	13.9° (Chiral)	16	1.1299	2.30E+10	2.25E+10	2.0
42		24		1.02E+10	1.00E+10	2.3
43		28		7.52E+09	7.35E+09	2.2
44		32		5.77E+09	5.63E+09	2.4
45		36		4.55E+09	4.45E+09	2.3
46		40		3.69E+09	3.60E+09	2.2
47		44		3.05E+09	2.98E+09	2.3
48		48		2.56E+09	2.50E+09	2.2

paper studies the effect of SWCNT's geometrical parameters namely, length, diameter and chirality on the fundamental transverse modal frequencies of SWCNT. An exact relationship between SWCNT geometrical parameters and fundamental transverse modal frequency is derived for the first time. Based on this, the first-ever reduced form for fundamental transverse modal frequency of SWCNT is developed.

2. Theory

2.1. Structure of carbon nanotubes

CNTs are allotropes of carbon and derived from rolled-up sheet of graphene into hollow cylinders with diameters ranging from 1 nm to 50 nm and length from 1 nm to over 10 μm. In a CNT, each atom is bonded covalently with three nearest neighbor and thus hexagonal rings are formed with carbon atom at each corner. Depending on the number of tubes, CNT are of two types namely, SWCNT and MWCNT. This research paper focuses only on SWCNTs, therefore MWCNTs are not discussed further. SWCNT is a special class of allotropes of carbon that consist of a sheet of graphene rolled up to form hollow tube with walls one atom thick. Fig. 1 shows the schematic of obtaining a SWCNT from a typical graphene sheet.

SWCNT are further classified as "Zigzag" type, "Armchair" type and "Chiral" type based on the direction in which a graphene sheet is rolled. Zigzag and armchair are symmetrical structures, i.e., here the carbon hexagonal rings are arranged symmetrically about the tube axis. On the other hand, chiral configuration have structures in which the hexagons are arranged helically around the tube axis. Fig. 2 shows the structures of these types of CNT along with the schematic of their formation from graphene sheets. The direction in which a graphene sheet is rolled is called the chiral vector, $\vec{C}$, which in turn is represented by the set of chirality indices (n, m) and the fixed principal lattice vectors (a_1, a_2) as follows:

$$\vec{C} = \mathbf{n}\hat{\mathbf{a}}_1 + \mathrm{m}\hat{\mathbf{a}}_2 \quad (3)$$

For armchair SWCNT, n = m; for zigzag SWCNT, m = 0; and for chiral SWCNT, n≠ m≠ 0. The chiral vector is an important geometrical

Table 6
Prediction of fundamental transverse modal frequency from published literature using MSMA.

Type	SWCNT Diameter (in nm)	SWCNT Length (in nm)	Published result [14] (in GHz)	Our result (in GHz)	Absolute % error
Zigzag	0.4701	10	27.00	23.16	14.22
		15	12.00	10.29	14.22
		20	6.00	5.79	3.49
		25	4.00	3.71	7.36
		30	3.00	2.57	14.22
		35	2.00	1.89	5.46
		40	1.50	1.45	3.49
Armchair	0.5428	10	29.00	26.90	7.25
		15	13.00	11.95	8.04
		20	7.00	6.72	3.93
		25	4.00	4.30	7.59
		30	3.00	2.99	0.38
		35	2.50	2.20	12.17
		40	2.00	1.68	15.94
	0.9499	10	47.00	48.14	2.42
		15	21.00	21.39	1.88
		20	10.00	12.03	20.35
		25	7.00	7.70	10.03
		30	5.00	5.35	6.97
		35	4.00	3.93	1.76
		40	3.00	3.01	0.29
Zigzag	1.0185	10	47.00	51.76	10.13
		15	21.00	23.00	9.54
		20	12.00	12.94	7.83
		25	6.00	8.28	38.02
		30	5.00	5.75	15.02
		35	4.00	4.23	5.63
		40	3.00	3.23	7.83
	1.4885	15	30.00	34.14	13.78
		20	16.00	19.20	20.01
		25	9.00	12.29	36.54
		30	7.00	8.53	21.91
		35	6.00	6.27	4.50
		40	4.00	4.80	20.01

feature as its direction represents the direction along which graphene sheet is rolled to obtain a SWCNT and its magnitude represents the circumference of the cross-section of the SWCNT. In a typical graphene roll-up defined by indices (n, m) as shown in Fig. 3, $\vec{C}$ is the resultant of the vector OA and OC, therefore the tube cross-sectional circumference is given by:

$$\pi D = |\vec{C}| = \sqrt{n^2a_1^2 + m^2a_2^2 + 2nma_1a_2\cos\theta} = \sqrt{3}l_{c-c}\sqrt{n^2 + m^2 + 2nm\cos 60^\circ} \quad (4)$$

$$\pi D = \sqrt{3}l_{c-c}\sqrt{n^2 + m^2 + 2nm\cos 60^\circ} = \sqrt{3}l_{c-c}\sqrt{n^2 + m^2 + nm} \quad (5)$$

Here, l_{c-c} is C—C bond length in a graphene sheet. Therefore, the SWCNT diameter D is given by following equation:

$$D = \sqrt{3}\frac{l_{c-c}\sqrt{n^2 + m^2 + nm}}{\pi} \quad (6)$$

2.2. Modelling of mechanical properties of CNT

MSMA is a successfully tested and most widely used approach to model the elastic properties of SWCNT [20,21]. Thus, in the presented study, this approach was used to model different types of SWCNT for modal analysis. MSMA is derived from the observation that SWCNT with carbon atoms interconnected via covalent bonds are geometrically similar to 3D space frame structures. Hence, in this approach, SWCNT is represented as a 3D space frame structure where every C—C bond is taken as a uniform beam with circular cross-section, and every carbon atom is taken as a node or the connecting pin between the beams. When a CNT is subjected to external forces, the positional changes of atomic nuclei is constrained by the covalent bonds. Thus, the deformation of the structure of CNT can be viewed as deformation of a space frame structure that is composed of connecting beams. The molecular steric energies of CNT as obtained from molecular mechanics research are compared with the strain energies due to structural deformations in the equivalent space frame structure as obtained from structural mechanics theory. Figs. 4–6 show the schematic of MSMA [21].

From molecular mechanics approach, the total potential energy of a carbon atom is the sum of energies due to bonded interactions and non-bonded interactions as shown by following set of equations [20,21].

$$U_{tot} = U_r + U_\theta + U_\tau \quad (7)$$

$$U_r = \frac{1}{2}k_r(\Delta r)^2;\ U_\theta = \frac{1}{2}k_\theta(\Delta\theta)^2 \quad (8)$$

$$U_\tau = U_\omega + U_\phi = \frac{1}{2}k_\tau(\Delta\phi)^2 \quad (9)$$

Where; U_r, U_θ, and U_τ are molecular energies due to bond stretch, bond angle variation, and bond twist (torsion). Here, energy due to Van der waals interaction has been neglected as its magnitude is negligible compared to other energies. k_r, k_θ and k_τ are the associated force field constants in molecular mechanics, while Δ r, $\Delta\theta$, and $\Delta\phi$ are the bond stretching increment, the bond angle change, and the angle of bond twisting, respectively. From structural mechanics approach, the total strain energy of a beam element due to its structural deformation is given by following set of equations [20,21]:

$$U_{tot} = U_{Axial} + U_{Bending} + U_{Torsion} \quad (10)$$

Table 7
Prediction of fundamental transverse modal frequency from published literature with other modelling techniques.

Paper reference	Method	Type	SWCNT Diameter (in nm)	SWCNT Length (in nm)	Fundamental transverse mode in GHz		
					Published result	Our result	Absolute % error
Strozzi et al. 2014 [11]	Sanders Koiter thin shell theory	Zigzag	0.7834	1.56	1715.00	1618.96	5.60
Chang 2013 [17]	MD simulation	Armchair	0.6785	4.919	122.10	140.20	14.83
			0.6785	7.379	48.90	62.30	27.41
			0.6785	9.838	36.60	35.05	4.23
Georgant-zinos et al. 2009 [19]	Linear spring based model	Armchair	0.4071	10.95	15.98	16.63	4.09
			0.5428	10.95	21.37	22.43	4.98
			0.6785	10.95	26.70	28.29	5.97
			1.0856	10.95	42.31	46.13	9.03
			1.6283	10.95	62.01	70.32	13.41
		Zigzag	0.3917	10.95	13.40	15.98	19.26
			0.5484	10.95	20.18	22.68	12.37
			0.7051	10.95	26.34	29.45	11.80
			1.0968	10.95	41.72	46.63	11.76

$$U_{Axial} = \frac{EA}{2L}(\Delta L)^2;\ U_{Bending} = \frac{EI}{2L}(2\alpha)^2;\ U_{Torsion} = \frac{GJ}{2L}(\Delta\beta)^2 \quad (11)$$

where L and A are the beam length and cross-sectional area, I and J are the moment of inertia and polar moment of inertia of the cross section, E and G are the Young's modulus and shear modulus, and ΔL, 2α, and Δβ are the axial stretching deformation, the total relative rotation angle, and the relative torsion angle, respectively. In MSMA, U_r is equivalent to U_{Axial} and ΔL is equivalent to Δ r (bond stretch is equivalent to beam stretch). Similarly, U_θ is equivalent to $U_{Bending}$ and 2α is equivalent to Δθ (bond angle variation is equivalent to beam bending). U_τ is equivalent $U_{Torsion}$ and Δβ is equivalent to Δϕ (bond twist is equivalent to beam torsion). Thus, the relationship between the molecular mechanics parameters k_r, k_θ and k_τ and the structural mechanics parameters EA, EI, and GJ is deduced to the following relation via the concept of energy equivalence [20,21].

$$\frac{EA}{L} = k_r;\ \frac{EI}{L} = k_\theta;\ \frac{GJ}{L} = k_\tau;\ A = \frac{\pi d^2}{4} \quad (12)$$

Thus, the elastic properties of the beam element (with circular cross-section) representing the C—C bond of SWCNT can be derived as follows:

$$d = 4\sqrt{k_\theta/k_r};\ E = \frac{k_r^2 L}{4\pi k_\theta};\ G = \frac{k_r^2 k_\tau L}{8\pi k_\theta^2} \quad (13)$$

In the presented study, the beam length was set equal to the covalent bond distance of the carbon atoms in the hexagonal lattice, i.e. 1.421 Å. The values of k_r, k_θ and k_τ as found from the experiments in the field of molecular mechanics were set to $k_r = 6.52 \times 10^{-7}$ N– nm^{-1}, $k_\theta = 8.76 \times 10^{-10}$ N– nm– rad^{-2}, and $k_\tau = 2.78 \times 10^{-10}$ N– nm– rad^{-2} [20,21]. After introducing these values into Eq. (13), the elastic properties of the beam element representing the C—C bond in SWCNT are given by:

$$d = 1.466\ Å;\ E = 5487.5 \times 10^9\ Pa;\ \text{and}\ \ G = 870.7 \times 10^9\ Pa \quad (14)$$

The Poisson's ratio, ν is given by the following equation.

$$G = \frac{E}{2(1+\nu)} \Longrightarrow \nu = \frac{E}{2G} - 1 = \frac{5.4875 \times 10^{-8}}{1.7402 \times 10^{-8}} - 1 = 2.15 \quad (15)$$

However, using these values of E and G (see Eq. (15)) we get ν= 2.15, which is greater than 1 therefore has no meaning. It has been numerically proven by Li and Chou [20] that Poisson's ratio has little effect on the computation of the CNT's moduli, and that, theoretically, the Poisson's ratio does not exist in the stiffness formulation of the standard beam elements. Therefore, in this study a typical value of ν= 0.3 was used in modelling SWCNTs.

3. Numerical study

3.1. Aims and objectives

This study had two aims. Firstly, it was aimed at "identifying the geometrical parameters that affect the fundamental transverse modal frequency of SWCNT". Secondly the study aimed at "developing an expression for the fundamental transverse modal frequency of SWCNT". Following research objectives were set to meet the above aims:

i To study the effect of SWCNT diameter on fundamental transverse modal frequency of SWCNT
ii To study the effect of SWCNT length on fundamental transverse modal frequency of SWCNT
iii To study the effect of SWCNT chirality on fundamental transverse modal frequency of SWCNT
iv To develop a reduced form for fundamental transverse modal frequency of SWCNT

3.2. Sample

SWCNT diameter, SWCNT chirality and SWCNT length were taken as independent variables and the first transverse resonance frequency to be obtained upon modal analysis of SWCNT was taken as dependent variable. Based on the principles of design of experiments, following SWCNT models were studied as shown in Table 1.

3.3. Computation tool

ANSYS APDL 17.0 was used to conduct modal analysis. Statistical analysis were performed on the results using the software R.

3.4. Loading conditions

Modes are not affected by the direction and magnitude of applied load/ excitation, but they change on changing the end support conditions. This study tested the cantilever beam configuration, i.e., fixed – free end conditions. So the loading conditions used for modal analysis of SWCNT was 100 N Force applied in transverse direction at the nodes on one end, while applying zero displacement and zero rotation condition to the nodes on the other end (see Fig. 7).

3.5. Procedure

In this study, modal analysis of SWCNT was performed in ANSYS APDL after modelling the SWCNT as a space frame structure using MSMA. SWCNT samples were modelled as space frame elements, where every C—C covalent bond was represented as a 2-node beam element with circular cross-section. The elastic properties of this beam element were calculated using MSMA as obtained from Eqs. (7)–(14). SWCNT geometry was created in the units of Angstrom. Therefore, the SI values of the elastic properties of the beam element were converted into the values in Angstrom, which were entered as input for the beam element in the ANSYS APDL modelling (see right most column of Table 2).

3.6. Results

From modal analysis, modal frequencies and mode shapes were obtained. Figs. 8 and 9 show the plot of the fundamental transverse modal frequencies against the SWCNT diameter and SWCNT length respectively. These frequencies also happened to be the overall first modal frequencies. The modal frequencies have been reported separately in Table 5 (see Section 4). From Figs. 8 and 9, it is observed that these frequencies increase linearly with SWCNT diameter when keeping all other parameters constant; whereas they decrease exponentially with SWCNT length when keeping all other parameters constant. There is no effect of chirality on the fundamental transverse modal frequencies as the plots for different chirality overlap with each other. This observation was confirmed by conducting regression analysis. Since, the nature of relationship between fundamental transverse mode and tube geometrical parameters is not known, both linear and non-linear regression was conducted. Tables 3 and 4 show the result of linear regression analysis and non-linear regression analysis respectively.

4. Discussions

Our regression results show that a non-linear relationship fits better with the results (it has a higher R^2 statistic) than linear regression, and explains 99.9 % variance in the fundamental transverse mode. Moreover, the existing approximation for transverse modes of SWCNT, i.e., the Bernoulli-Euler beam theory also states that the relationship between transverse modal frequencies and SWCNT diameter and length is non-linear [4,18]. Thus, the results of non-linear regression were selected for developing a reduced form of the fundamental transverse modal frequency. Non-linear regression analysis shows that SWCNT

diameter and SWCNT length alone explains 99.8 % variance and SWCNT chirality effect is negligible, therefore only these two geometrical parameters were used for developing the reduced form. Following set of equations show the development of the reduced form.

$$-1.988 \times \ln L^{'} + 1.038 \times \ln D^{'} + 29.256 = \ln f_0 \tag{16}$$

$$f_0 = \frac{e^{29.256} \times D^{'1.038}}{L^{'1.988}} \sim \sim f_0 = \frac{e^{29.256} \times D^{'1.04}}{L^{'2}} \tag{17}$$

Here, $L^{'}$ and $D^{'}$ are length and diameter of the SWCNT in nanometers. In terms of SI units, taking L and D as the length and diameter of SWCNT in meters, the fundamental transverse modal frequency of an SWCNT is given by following equation:

$$f_0 = \frac{e^{29.256} \times (D \times 10^9)^{1.04}}{(L \times 10^9)^2} = \frac{e^{29.256} \times 10^{-8.64} \times D^{1.04}}{L^2} \tag{18}$$

$$\mathbf{f_0} = \frac{11633.74 \times \mathbf{D}^{1.04}}{\mathbf{L}^2} \tag{19}$$

Eq. (19) is the expression for our proposed reduced form for fundamental transverse modal frequency of SWCNT. The accuracy of the developed reduced form is evaluated in-sample by using the standard statistic namely, mean absolute percentage error (MAPE) that is calculated using Eq. (20).

$$APE_i = \frac{f_{modeli} - f_{formi}}{f_{modeli}} \times 100\,;\ MAPE = \frac{\sum_{i=1}^{N} APE_i}{N} \tag{20}$$

Here, APE_i is the absolute percentage error in predicting fundamental transverse modal frequency of i^{th} SWCNT sample. f_{modeli} is the fundamental transverse modal frequency of i^{th} SWCNT sample as obtained from a particular modeling technique (in our case the technique is MSMA in FEM). f_{formi} is the fundamental transverse modal frequency of i^{th} SWCNT sample as obtained from our developed reduced form.

Table 5 shows the fundamental transverse modal frequencies predicted by our proposed form and the same frequencies found from our simulations, along with absolute percentage errors. Our reduced form predicts the fundamental transverse modal frequency of SWCNTs with 4% mean absolute percentage error. Tables 6 and 7 show the fundamental transverse modal frequencies predicted by our proposed form and the same frequencies published by previous authors that have used various different modelling techniques. The mean absolute percentage error in our prediction of the published result is 10 %. The increase in error in predicting other authors' results could be because the reduced form is developed using regression analysis, and any statistical predictive algorithm such as regression has higher predictive accuracy on the sample it was trained than on unseen datasets. Another reason could be the differences in the accuracies amongst different modelling techniques as already self-reported by the authors of the published literature. As discussed in Section 1, the hybrid modelling approach of MSMA is considered more accurate for representing SWCNT compared with continuum techniques like thin shell theory and spring based model [18,26]. Moreover, MSMA is considered to have less computational error compared to atomistic technique of MD simulation [18,26]. Overall, we can say that our developed reduced form has high accuracy in predicting fundamental transverse modal frequency of SWCNTs.

From non-linear regression results, it is found that the fundamental transverse modal frequency is directly proportional to SWCNT diameter, is inversely proportional to square of SWCNT length, and is unaffected by chirality. This relationship is comparable to the Bernoulli-Euler beam frequency equation (see Eq. (2)). Thus, transverse modes can be thought as beam like modes. In our presented study, all first modes were transverse modes (beam like modes). However, this may not always be the case. Previous research shows that the first few modes of SWCNT are either transverse (i.e. bending) or radial (i.e. breathing) [25]. The nanotube need to have a length greater than the diameter by a certain amount for the first mode to be transverse mode [25]. Since, there is no analytical expression for the radial breathing modes of SWCNT, in this paper we would not like to comment on the critical aspect ratio required to ensure the first mode is the transverse mode. This could be investigated as part of the future study. The proposed form can help designers and engineers in manufacturing SWCNTs with desired resonance frequency as needed for operation of nano-devices such as resonators and sensors more accurately. Similarly, a more vibration resilient CNT-based nanocomposite would require increase in SWCNT diameter and decrease in SWCNT length, provided that the length is sufficiently greater than the diameter so that the first mode is transverse mode.

5. Conclusions

A detailed parametric study of SWCNT vibrational modes using SWCNT geometrical parameters namely, its length, its diameter and its chirality was carried out by modelling SWCNTs using MSMA and conducting finite element simulations. From simulation results, a first-ever reduced form for fundamental transverse modal frequency of SWCNT is developed using non-linear regression. Our developed form successfully predicts the fundamental transverse modal frequencies obtained by our MSMA and FEM simulations at a 4% mean absolute percentage error. The form predicts the fundamental transverse modal frequencies of SWCNTs, published in previous literature using different modelling techniques, at 10 % mean absolute percentage error. Thus, the proposed reduced form is successfully tested and validated. It is found that the fundamental transverse modal frequency of SWCNT is directly proportional to its diameter, inversely proportional to square of its length, and is unaffected by its chirality. This relationship is comparable to the Bernoulli-Euler beam frequency equation. Thus, transverse modes can be thought as beam like modes. The proposed reduced form can help designers and engineers in manufacturing SWCNTs with desired resonance frequency for efficient operation of nano-devices. Similarly, the form could help in designing more vibration resilient CNT-based nanocomposites by tuning SWCNT diameter and SWCNT length to get high first transverse mode.

Data availability

The raw data required to reproduce these findings are available in Table 5 of this paper.

CRediT authorship contribution statement

Sneha Singh: Conceptualization, Methodology, Writing - original draft, Writing - review & editing, Validation, Formal analysis, Visualization, Supervision, Resources. **Vikram Dutt:** Software, Data curation, Investigation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mtcomm.2020.101404.

References

[1] S. Iijima, T. Ichihashi, Single-shell carbon nanotubes of 1-nm diameter, Nature 363 (1993) 603–605.
[2] K. Hashemnia, M. Farid, R. Vatankhah, Vibrational analysis of carbon nanotubes

and graphene sheets using molecular structural mechanics approach, Comput. Mater. Sci. 47 (2009) 79–85, https://doi.org/10.1016/j.commatsci.2009.06.016.
[3] J.H. Lee, B.S. Lee, Modal analysis of carbon nanotubes and nanocones using FEM, Comput. Mater. Sci. 51 (2012) 30–42, https://doi.org/10.1016/j.commatsci.2011.06.041.
[4] M.S. Harrar, R.F. Gibson, Numerical simulation of modal vibration response of wavy carbon nanotubes, J. Compos. Mater. 43 (2009) 501–515, https://doi.org/10.1177/0021998308097676.
[5] J.A. Palacios, R. Ganesan, Dynamic response of single-walled carbon nanotubes based on various shell theories, J. Reinf. Plast. Compos. 38 (2019) 413–425, https://doi.org/10.1177/0731684418824997.
[6] C.J. Wu, C.Y. Chou, C.N. Han, K.N. Chiang, Estimation and validation of elastic modulus of carbon nanotubes using nano-scale tensile and vibrational analysis, C. - Comput. Model. Eng. Sci. 41 (2009) 49–67, https://doi.org/10.3970/cmes.2009.041.049.
[7] K. Mehar, S.K. Panda, T.R. Mahapatra, Theoretical and experimental investigation of vibration characteristic of carbon nanotube reinforced polymer composite structure, Int. J. Mech. Sci. 133 (2017) 319–329, https://doi.org/10.1016/j.ijmecsci.2017.08.057.
[8] S.M. Hosseini Farrash, M. Shariati, J. Rezaeepazhand, The effect of carbon nanotube dispersion on the dynamic characteristics of unidirectional hybrid composites: an experimental approach, Compos. Part B Eng. 122 (2017) 1–8, https://doi.org/10.1016/j.compositesb.2017.04.003.
[9] P.S. Samuel Ratna Kumar, D.S. Robinson Smart, S. John Alexis, N. Sangeetha, S. Ramanathan, Modal analysis of mwcnt reinforced aa5083 composite material, Int. J. Civ. Eng. Technol. 8 (2017) 167–177.
[10] C. Devalve, R. Pitchumani, Experimental investigation of the damping enhancement in fiber-reinforced composites with carbon nanotubes, Carbon N. Y. 63 (2013) 71–83, https://doi.org/10.1016/j.carbon.2013.06.041.
[11] M. Strozzi, L.I. Manevitch, F. Pellicano, V.V. Smirnov, D.S. Shepelev, Low-frequency linear vibrations of single-walled carbon nanotubes: analytical and numerical models, J. Sound Vib. 333 (2014) 2936–2957, https://doi.org/10.1016/j.jsv.2014.01.016.
[12] F. Ubertini, A.L. Materazzi, A. D'Alessandro, S. Laflamme, Natural frequencies identification of a reinforced concrete beam using carbon nanotube cement-based sensors, Eng. Struct. 60 (2014) 265–275, https://doi.org/10.1016/j.engstruct.2013.12.036.
[13] C. Li, T.W. Chou, Single-walled carbon nanotubes as ultrahigh frequency nanomechanical resonators, Phys. Rev. B - Condens. Matter Mater. Phys. 68 (2003) 1–3, https://doi.org/10.1103/PhysRevB.68.073405.
[14] M.M.S. Fakhrabadi, M. Samadzadeh, A. Rastgoo, M.H. Yazdi, M. Mosavi Mashadi, Vibrational analysis of carbon nanotubes using molecular mechanics and artificial neural network, Phys. E Low-Dimensional Syst. Nanostruct. 44 (2011) 565–578, https://doi.org/10.1016/j.physe.2011.10.004.
[15] K.M. Liew, X.Q. He, C.H. Wong, On the study of elastic and plastic properties of multi-walled carbon nanotubes under axial tension using molecular dynamics simulation, Acta Mater. 52 (2004) 2521–2527.
[16] H.C. Cheng, Y.L. Liu, Y.C. Hsu, W.H. Chen, Atomistic-continuum modeling for mechanical properties of single-walled carbon nanotubes, Int. J. Solids Struct. 46 (2009) 1695–1704, https://doi.org/10.1016/j.ijsolstr.2008.12.013.
[17] I.L. Chang, Molecular dynamics investigation of carbon nanotube resonance, Model. Simul. Mater. Sci. Eng. 21 (2013), https://doi.org/10.1088/0965-0393/21/4/045011.
[18] R.F. Gibson, E.O. Ayorinde, Y.-F. Wen, Vibrations of carbon nanotubes and their composites: a review, Compos. Sci. Technol. 67 (2007) 1–28, https://doi.org/10.1016/j.compscitech.2006.03.031.
[19] S.K. Georgantzinos, G.I. Giannopoulos, N.K. Anifantis, An efficient numerical model for vibration analysis of single-walled carbon nanotubes, Comput. Mech. 43 (2009) 731–741, https://doi.org/10.1007/s00466-008-0341-8.
[20] C. Li, T.W. Chou, A structural mechanics approach for the analysis of carbon nanotubes, Int. J. Solids Struct. 40 (2003) 2487–2499, https://doi.org/10.1016/S0020-7683(03)00056-8.
[21] K.I. Tserpes, P. Papanikos, Finite element modeling of single-walled carbon nanotubes, Compos. Part B Eng. 36 (2005) 468–477, https://doi.org/10.1016/j.compositesb.2004.10.003.
[22] M.A. Eltaher, T.A. Almalki, K.I.E. Ahmed, K.H. Almitani, Characterization and behaviors of single walled carbon nanotube by equivalent-continuum mechanics approach, Adv. Nano Res. 7 (2019) 39–49, https://doi.org/10.12989/anr.2019.7.1.039.
[23] R. Maleki Moghadam, S.A. Hosseini, M. Salehi, The influence of Stone-Thrower-Wales defect on vibrational characteristics of single-walled carbon nanotubes incorporating Timoshenko beam element, Phys. E Low-Dimensional Syst. Nanostruct. 62 (2014) 80–89, https://doi.org/10.1016/j.physe.2014.04.008.
[24] M.M.S. Fakhrabadi, A. Amini, A. Rastgoo, Vibrational properties of two and three junctioned carbon nanotubes, Comput. Mater. Sci. 65 (2012) 411–425, https://doi.org/10.1016/j.commatsci.2012.08.002.
[25] M.H. Kim, S. Seo, W.K. Liu, B.S. Lim, J.B. Choi, M.K. Kim, A modal analysis of carbon nanotube using elastic network model, J. Mech. Sci. Technol. 26 (2012) 3433–3438, https://doi.org/10.1007/s12206-012-0862-0.
[26] R. Rafiee, R.M. Moghadam, On the modeling of carbon nanotubes: a critical review, Compos. Part B Eng. 56 (2014) 435–449, https://doi.org/10.1016/j.compositesb.2013.08.037.