Int. J. Nanosci. Nanotechnol., Vol. 7, No. 3, Sep. 2011, pp. 137-142

Radial Breathing Mode Frequency of Multi-Walled Carbon Nanotube Via Multiple-Elastic Thin Shell Theory

S. Basir Jafari[1], R. Malekfar[1*] and S. E. Khadem[2]

1- Department of Physics, Tarbiat Modares University, P.O. Box 14115-175, Tehran, I. R. Iran.
2- Department of Mechanical and Aerospace Engineering, Tarbiat Modares University, P.O. Box 14115-177, Tehran, I. R. Iran.

(*) Corresponding author: malekfar@modares.ac.ir
(Received: 10 May 2011 and Accepted: 19 Aug. 2011)

Abstract:
In this paper, the radial breathing mode (RBM) frequencies of multi-walled carbon nanotubes (MWCNTs) are obtained based on the multiple-elastic thin shell model. For this purpose, MWCNT is considered as a multiple concentric elastic thin cylindrical shells, which are coupled through van der Waals (vdW) forces between two adjacent tubes. Lennard-Jones potential is used to calculate the vdW forces between adjacent tubes. The RBM frequencies of MWCNTs predicted by the present shell model are in excellent agreement with the available experimental and atomistic results with relative errors less than 2.5%. The results emphasize the utility of multiple-elastic thin shell theory for modelling the RBM vibrational behaviour of MWCNTs.
Keywords: *Lennard-Jones potential, Multi-walled carbon nanotube, Multiple-elastic thin shell model, Radial breathing mode, van der Waals forces.*

1. INTRODUCTION

Many of carbon nanotube (CNT) properties have been studied experimentally [1-3], and theoretically [4-10]. Raman spectroscopy has provided an extremely powerful tool for the characterization of CNT. The radial breathing mode (RBM) frequency is usually the strongest feature in CNT Raman spectra that plays a crucial role in the experimental determination of the geometrical properties of CNTs. In the RBM, all carbon atoms move coherently in the radial direction creating a breathing-like vibration of the entire tube. This feature is specific to CNTs and is not present in graphite [1]. Therefore, RBM frequencies are very useful for identifying whether a given material contains CNTs, through the presence of RBM modes, and for characterizing the CNT diameter distribution in the sample through the RBM frequency inverse proportionality to the tube diameter [1]. Similar conclusion has also been drawn for multi-walled carbon nanotubes (MWCNTs) of small innermost diameter less than 2 nm [2, 3].

CNTs unique stiffness, strength and low density could influentially affect some of the physical properties of composites filled with CNTs for sound wave absorption [11, 12] or being used as sensors and actuators [13], and nano-devices such as advanced miniaturized switchers [14]. As the MWCNTs could be synthesized simpler than the single-walled carbon nanotubes (SWCNTs), MWCNTs are cheaper than SWCNTs. So, MWCNTs are being used as fillers in the mentioned nanocomposites. It is clear that the effective properties of nanocomposites depend on properties of individual components. So, the study on vibrational characteristics of individual CNTs with appropriate model is very important.

Raman spectroscopy usually shows only the highest RBM frequency of each MWCNT in a sample of MWCNTs. Because the highest RBM frequencies could be used for identifying the innermost diameter of MWCNTs in CNT-based nanocomposites, the aim of this paper is only the prediction of the highest RBM frequencies of MWCNTs, theoretically.

A MWCNT can be described as multiple layers of graphite crystal that are rolled up into a multiple concentric seamless circular cylinder. Due to the nanometeric dimensions of CNTs, it is difficult to set up controlled experiments to measure the properties of an individual CNT [1-3]. Furthermore, Molecular-Dynamics methods [15] are costly and difficult, particularly for large-scale systems. So, continuum elastic mechanical models such as elastic beam models [4-6] and elastic shell models [7-10] have been widely used to study the vibrations of CNTs.

These investigations are very important to predict the accurate vibrational characteristics of MWCNTs. For this purpose, MWCNT is modeled as a multiple concentric elastic thin cylindrical shells, which are coupled through van der Waals (vdW) forces between two adjacent tubes. Lennard-Jones potential is used to calculate the vdW forces between adjacent layers. Afterwards, the coupled dynamic equations of motion have been derived according to the first approximation thin shell theory. Finally, the highest RBM frequency of different MWCNTs has been compared with the available experimental [2] and atomistic [3] results which indicated an excellent agreement with relative errors less than 2.5%. The results emphasize the utility of multiple-elastic thin shell theory for modelling the RBM vibrational behaviour of MWCNTs.

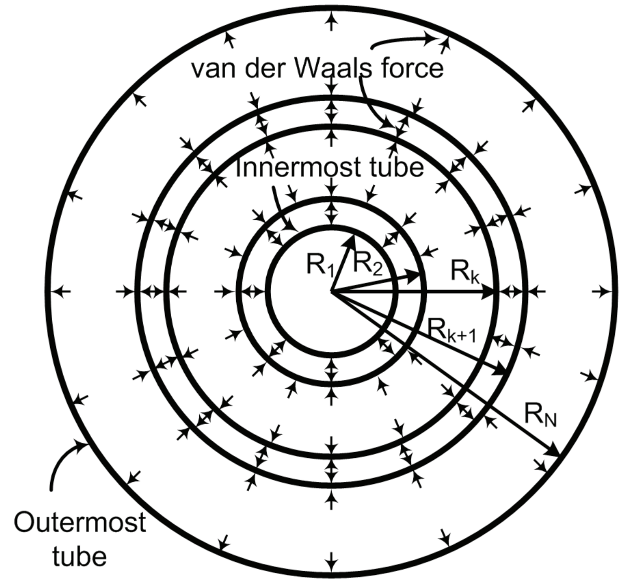

Figure 1: *Illustration of vdW forces between two adjacent tubes of a multiple shell cross section of a MWCNT*

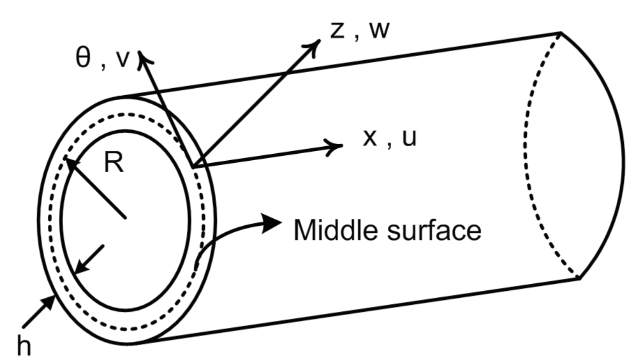

Figure 2: *Modelling of each tube of MWCNT as a thin cylindrical shell in cylindrical coordinates system*

2. MODELLING OF A MWCNT

In this study, MWCNTs are modeled as a multiple concentric elastic thin cylindrical shells, which are coupled through vdW forces between two adjacent tubes (see Figure 1).

Each tube is modeled as an elastic thin circular cylindrical shell with radius R, thickness h, and mass density ρ in cylindrical coordinates (z, θ, x), see Figure 2.

Where x, θ and z are the axial, circumferential and radial coordinates of the cylindrical shell, respectively. In the above figure, u, v and w are the shell displacements along the axial, circumferential and radial directions, respectively.

According to the first approximation in thin shell theory [16], the dynamic equations of motion for a cylindrical shell that are called "Love's equations" are as:

$$\frac{\partial N_{\mathrm{x}}}{\partial x}+\frac{1}{R}\frac{\partial N_{\theta\mathrm{x}}}{\partial\theta}=\rho h\frac{\partial^2 u}{\partial t^2}, \tag{1}$$

$$\frac{\partial N_{\mathrm{x}\theta}}{\partial x}+\frac{1}{R}\left(\frac{\partial N_{\theta}}{\partial\theta}+\frac{\partial M_{\mathrm{x}\theta}}{\partial x}\right)+\frac{1}{R^2}\frac{\partial M_{\theta}}{\partial\theta}=\rho h\frac{\partial^2 v}{\partial t^2}, \tag{2}$$

$$\frac{\partial^2 M_{\mathrm{x}}}{\partial x^2}+\frac{1}{R}\left(\frac{\partial^2 M_{\theta\mathrm{x}}}{\partial x\,\partial\theta}+\frac{\partial^2 M_{\mathrm{x}\theta}}{\partial\theta\partial x}-N_{\theta}\right)+\frac{1}{R^2}\frac{\partial^2 M_{\theta}}{\partial\theta^2}+p=\rho h\frac{\partial^2 w}{\partial t^2}, \tag{3}$$

where N_x, N_θ, $N_{x\theta}$, and $N_{\theta x}$ are the resultant forces of the middle surface of the shell; M_x, M_θ, $M_{x\theta}$ and $M_{\theta x}$ are resultant moments exerted on the middle surface of the shell. In above equation, p is the radial distributed load acted on the shell.

In the RBM, all carbon atoms move in phase in the radial direction creating a breathing-like vibration of the entire tube. Therefore, the RBM vibration is axi-symmetric in the entire tube (e. g. $\partial/\partial\theta=0$ and $\partial/\partial x=0$). So, Love's equations reduce to

$$-\frac{N_\theta}{R}+p=\rho h\frac{\partial^2 w}{\partial t^2}, \tag{4}$$

where N_θ obtains by integrating the stress-strain relation $\sigma_\theta=Ew/(1-\mu^2)R$ across the thickness h of the shell as

$$N_\theta=\frac{E}{(1-\mu^2)}\frac{w}{R}\int_{-h/2}^{h/2}\mathrm{d}z=\frac{Eh}{(1-\mu^2)}\frac{w}{R}, \tag{5}$$

in which E and μ are the elastic modulus and Poisson's ratio of CNT, respectively.

Substituting equation (5) into equation (4) gives the governing equation for the RBM vibration of the kth tube (k=1, 2, …, N) of the MWCNT as

$$-\frac{A}{R_k^2}w_k+p_k=\rho h\frac{\partial^2 w_k}{\partial t^2}, \tag{6}$$

where $A=Eh/(1-\mu^2)$ is the stiffness coefficient of each layer of the MWCNT, and p_k is the vdW pressure acted on the kth tube of MWCNT.

The vdW interaction potential can be estimated as a function of the interlayer spacing between two adjacent tubes via $p_{k(k+1)}=c_{k(k+1)}[w_{k+1}-w_k]$ (k=1, 2, ..., N-1) in which the vdW interaction coefficient between two adjacent tubes is given as

$$c=200\left(\mathrm{erg}/\mathrm{cm}^2\right)\Big/0.16\eta^2,\ (\eta=0.142\ \mathrm{nm})\quad [10]$$

where erg is the CGS unit of energy and 1 erg = 10^{-7} joules. So, the vdW interaction coefficient between two adjacent tubes in this work is considered as c=6.199E+19 (Pa/m).

If the vdW interaction pressure (per unit area) acted on the kth tube by the (k+1)th tube is indicated by $p_{k(k+1)}$, the relation between two pressure is as $p_{(k+1)k}=-(R_k/R_{k+1})p_{k(k+1)}$. Assuming p_k as the total pressure acted on the kth tube of MWCNT, we have

$$\begin{aligned}
&p_1=p_{12}=c_{12}[w_2-w_1],\\
&p_2=p_{23}+p_{21}=c_{23}[w_3-w_2]-c_{12}\left(R_1/R_2\right)[w_2-w_1],\\
&\qquad\ldots\\
&p_{N-1}=p_{(N-1)N}+p_{(N-1)(N-2)}=c_{(N-1)N}[w_N-w_{N-1}]-c_{(N-1)(N-2)}\left(R_{N-2}/R_{N-1}\right)[w_{N-1}-w_{N-2}],\\
&p_N=p_{N(N-1)}=-c_{N(N-1)}\left(R_{N-1}/R_N\right)[w_N-w_{N-1}].
\end{aligned} \tag{7}$$

So, the following N-coupled dynamic equations govern the RBM vibration deflections of the N-walled CNT:

$$-\frac{A}{R_1^2}w_1 + c_{12}[w_2 - w_1] = \rho h \frac{\partial^2 w_1}{\partial t^2}, \tag{8}$$

$$-\frac{A}{R_2^2}w_2 + c_{23}[w_3 - w_2] - c_{12}\left(R_1/R_2\right)[w_2 - w_1] = \rho h \frac{\partial^2 w_2}{\partial t^2},$$

$$\ldots$$

$$-\frac{A}{R_{N-1}^2}w_{N-1} + c_{(N-1)N}[w_N - w_{N-1}] - c_{(N-1)(N-2)}\left(R_{N-2}/R_{N-1}\right)[w_{N-1} - w_{N-2}] = \rho h \frac{\partial^2 w_{N-1}}{\partial t^2},$$

$$-\frac{A}{R_N^2}w_N - c_{(N-1)N}\left(R_{N-1}/R_N\right)[w_N - w_{N-1}] = \rho h \frac{\partial^2 w_N}{\partial t^2}.$$

The vdW interaction coefficient between any two adjacent tubes in this work is considered as c=6.199E+19 (Pa/m). The RBM displacements of the kth tube of MWCNT are of the form

$$w_k = W_k \exp\left(-i\omega t\right), \qquad (k = 1,\ 2,\ \ldots,\ N) \tag{9}$$

where W_k is the radial displacement amplitude of the kth tube of MWCNT, and ω is the angular frequency of the RBM. Substituting the above equation as the MWCNT displacements into equation (8), gives the N-coupled polynomial equations in terms of ω. Equating the characteristic determinant of coefficients matrix constructed from the N-coupled polynomial equations to zero for the non-trivial solution of W_k, gives a characteristic polynomial equation of the order $2N$. Solving the characteristic polynomial equation yields N positive and N negative roots correspond to N RBM frequencies of the N-walled CNT. Following other researchers [7, 8], the highest RBM frequency is referred to as mode 1, the second highest RBM frequency as mode 2 and so on; and finally the lowest RBM frequency is considered as mode N.

3. RESULTS AND DISCUSSIONS

Throughout the paper, the material parameters of MWCNT have been considered as: in-plane stiffness Eh=360 J/m^2, mass density ρ=2270 kg/m^3, Poisson's ratio μ=0.2 [8]. In experimental units, the RBM frequency is related to ω via $f_{\mathrm{RBM}} = \omega/2\pi C$ in cm^{-1} where $C = 2.99792458\times10^8$ m/s [17] is the velocity of light. Because, usually, only the highest RBM frequency of MWCNTs has a considerable Raman intensity and can be easily observed in Raman spectra, we shall focus on the highest RBM frequencies of MWCNTs with innermost diameter ranging from 0.41 to 1.7 nm. The equilibrium interlayer spacing between two adjacent tubes is considered 0.34 nm.

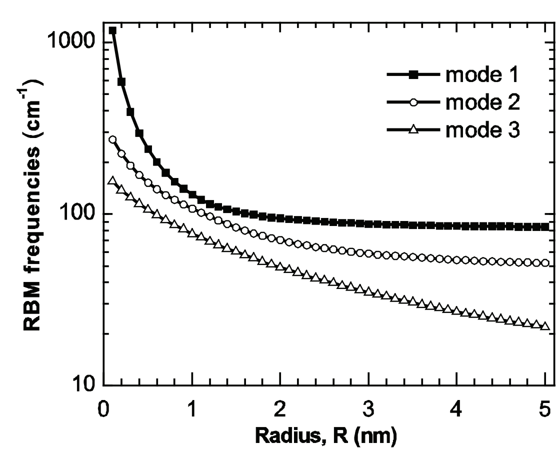

Figure 3. *Influence of changing the MWCNT radius on its three highest RBM frequencies*

Table 1: *Comparison between the results obtained in this work and the available experimental* [*2*]*, and atomistic model* [*3*] *results, and the other researchers' results based on the multiple-elastic thin shell model* [*7, 8*]*. All error percentages have been computed relative to the second column results*

Innermost diameter d_1 (nm)	Atomistic model [3] or experimental [2]		The multiple-elastic thin shell model									
			Considering the vdW interaction between any two tubes			Only considering the vdW interaction between two adjacent tubes						
			c_{Max}=1.52664E+20 (Pa/m)			c=9.918E+19 (Pa/m)				c=6.199E+19 (Pa/m)		
			X. Y. Wang, *et al.* [7]			X. Y. Wang, *et al.* [7]		C. Y. Wang, *et al.* [8]		This work		
	N	f_{RBM} (cm^{-1})	N	f_{RBM} (cm^{-1})	error (%)	f_{RBM} (cm^{-1})	error (%)	f_{RBM} (cm^{-1})	error (%)	N	f_{RBM} (cm^{-1})	error (%)
0.41	5-15	570 [2]	5-50	575.9	1.0	573.6	0.6	576.0	1.1	2-50	572.8	0.5
0.6	5-15	392 [2]	5-50	397.1	1.3	394.5	0.6	395.0	0.8	2-50	393.0	0.3
0.84	5-15	279 [2]	5-50	288.1	3.3	285.1	2.2	286.0	2.5	2-50	282.7	1.3
1.08	20	217 [3]	5-50	228.9	5.5	225.4	3.9	226.0	4.2	2-50	222.1	2.4
1.2	20	199 [3]	5-50	208.8	4.9	205.0	3.0	205.0	3.0	2-50	201.1	1.1
1.36	20	180 [3]	5-50	188.3	7.3	183.9	2.2	184.0	2.2	2-50	179.2	0.4
1.54	20	162 [3]	5-50	171.4	8.0	166.2	2.6	166.0	2.5	3-50	160.3	1.1
1.7	20	149 [3]	5-50	160.7	4.6	154.5	3.7	154.0	3.4	3-50	147.3	1.1

Figure 3 shows the influence of changing the radius of MWCNT on its three highest RBM frequencies. As it is shown in Figure 3, the RBM frequencies are very sensitive to the radius, R, of MWCNT when this geometrical property is extremely small. The frequency of mode 1 monotonically decreases with increasing the innermost diameter of MWCNTs. As it is shown in Table 1, this frequency-diameter relation is consistent with the experimental results [2], and the results obtained by the atomistic model [3] for the same MWCNTs. Figure 3 shows that the sensitivity of the mode 2 and 3 to the changing of the MWCNT diameter is less than mode 1.

Table 1 shows the highest RBM frequencies of MWCNTs with innermost diameter ranging from 0.41 to 1.7 nm with the available experimental and atomic results. The first column shows the MWCNT diameter; the second and third ones are the number of layers of the MWCNT and the highest RBM frequencies from the experimental and atomistic model results, respectively. The forth column shows the number of layers of the MWCNT in the other researchers' theoretical results; the next two columns show the highest RBM frequencies obtained by considering the vdW interaction between any two tubes based on the multiple-elastic thin shell model and their error percentages in comparison with the results of the experimental and atomistic results (the third column), respectively. The next four columns show the highest RBM frequencies obtained only by considering the vdW interaction between two adjacent tubes based on the multiple-elastic thin shell model and the corresponding error percentages in comparison with the results of the experimental and atomistic results. The next column shows the number of layers that are considered for MWCNTs in this study. The last two columns show the results obtained based on thin shell theory in the present paper, and the corresponding error percentages in comparison with the results of the experimental and atomistic results. In this paper, the results obtained just by considering the vdW interaction between two adjacent tubes.

As it is shown in Table 1, the error percentages of the results obtained by considering the vdW interaction between any two tubes are more than the results obtained only by considering the vdW interaction between two adjacent tubes. Also, with decreasing the vdW interaction coefficient, the highest RBM frequencies predicted based on multiple-elastic thin shell theory only by considering the vdW interaction between two adjacent tubes are in more agreement with the experimental results. Therefore, it can be concluded that the results which are obtained in the present paper by considering the vdW interaction *c*=6.199E+19 (Pa/m) only between two adjacent tubes are in more agreement with the experimental and atomistic model results than the other researchers' theoretical results.

4. CONCLUSION

This paper reported a detailed investigation on the highest RBM frequency of the MWCNT based on the multiple-elastic thin shell theory. The following points can be concluded:

- The highest obtained RBM frequencies of MWCNTs with innermost diameter ranging from 0.41 to 1.7 nm are in excellent agreement with the available experimental and atomistic model results with relative errors less than 2.5%.
- The error percentages of the results obtained by considering the vdW interaction between any two tubes are more than the results obtained by considering the vdW interaction only between two adjacent tubes.
- With decreasing the vdW interaction coefficient, the highest RBM frequencies predicted based on multiple-elastic thin shell theory by considering the vdW interaction only between two adjacent tubes are in more agreement with the experimental and atomistic model results.
- The results emphasize the utility of multiple-elastic thin shell theory by considering the vdW interaction only between two adjacent tubes for modelling the RBM vibrational behaviour of MWCNTs, precisely.

REFERENCES

1. M. S. Dresselhaus, G. Dresselhaus, R. Saito, A. Jorio, Phys. Rep. 409 (2005): 47-99.
2. X. Zhao, Y. Ando, L. C. Qin, H. Kataura, Y. Maniwa, R. Saito, Chem. Phys. Lett. 361 (2002): 169-174.
3. J. M. Benoit, J. P. Buisson, O. Chauvet, C. Godon, S. Lefrant, Phys. Rev. B. 66 (2002): 073417-1 (4pp).
4. Y. Yan, X. Q. He, L. X. Zhang, C. M. Wang, J. Sound Vib. 319 (2009): 1003-18.
5. I. Elishakoft, D. Pentares, J. Sound Vib. 322 (2009): 652-664.
6. C. M. Wang, V. B. C. Tan, Y. Y. Zhang, J. Sound Vib. 294 (2006): 1060-72.
7. X. Y. Wang, C. L. Xu, X. Wang, Modelling Simul. Mater. Sci. Eng. 14 (2006): 759-773.
8. C. Y. Wang, C. Q. Ru, A. Mioduchowski, J. Appl. Phys. 97 (2005): 024310-1 (10pp).
9. M. S. Hoseinzadeh, S. E. Khadem, Physica E 43 (2011): 1146-54.
10. K. Dong, B. Y. Liu, X. Wang, Comput. Mater. Sci. 42 (2008): 139-148.
11. R. Verdejo, R. Stampfli, M. Alvarez-Lainez, S. Mourad, A. R. Rodriguez-Perez, P. A. Bruhwiler, M. Shaffer, Compos. Sci. Technol. 69 (2009): 1564-69.
12. Z. Bian, R. J. Wang, D. Q. Zhao, M. X. Pan, W. H. Wang, Appl. Phys. Lett. 82 (17) (2003): 2790-92.
13. C. Li, E. T. Thostenson, T. W. Chou, Compos. Sci. Technol. 68 (6) (2008): 1227-49.
14. M. Rasekh, S. E. Khadem, M. Tatari, J. Phys. D: Appl. Phys. 43 (2010): 315301-1 (10pp).
15. A. R. Leach, Molecular Modelling: Principles and Applications, 2nd ed., Pearson Education Limited, England, 2001, p. 6.
16. W. Soedel, Vibrations of Shells and Plates, 3rd ed., Marcel Dekker, New York, 2005, pp. 7-35.
17. J. Daintith, R. Rennie (Eds.), The Facts on File Dictionary of Physics, 4th ed., Facts On File, Inc., New York, 2005, p. 232.