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A modal analysis of carbon nanotube using elastic network model †

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Abstract

Although it is widely known that both size and chirality play significant roles in vibration behaviors of single-walled carbon nanotubes (SWCNTs), there haven't been yet enough studies specifying the relationship between structure and vibration mode shape of SWCNTs. We have analyzed the chirality and length dependence of SWCNT by using normal mode analysis based elastic network model in which all interatomic interactions of the given SWCNTs structure are represented by a network of linear spring connections. As this method requires relatively short computation time compared to molecular dynamics simulation, we can efficiently analyze vibration behavior of SWCNTs. To ensure the relationship between SWCNT structure and its vibration mode shapes, we simulated more than one hundred SWCNTs having different types of chirality and length. Results indicated that the first two major mode shapes are bending and breathing. The minimum length of nanotube for maintaining the bending mode does not depend on chirality but on its diameter. Our simulations pointed out that there is a critical aspect ratio between diameter and length to determine vibration mode shapes, and it can be empirically formulated as a function of nanotube length and diameter. Therefore, uniformity control is the most important premise in order to utilize vibration features of SWCNTs. It is also expected that the obtained vibration aspect will play an important role in designing nanotube based devices such as resonators and sensors more accurately.

Keywords: Carbon nanotubes; Elastic network model; Normal mode analysis; Vibration characteristics

1. Introduction

Since their discovery in 1991, carbon nanotubes (CNTs) have received attention in many research fields because of their unique and extraordinary properties [1]. Especially, the high strength, stiffness and large aspect ratio between diameter and length of single-walled carbon nanotubes (SWCNTs) make them an ideal candidate for vibration based devices such as resonators and oscillators [2-5]. To examine the feasibility of these devices, it is necessary to understand the vibration behaviors of nanotubes.

Among the various methods, continuum models and molecular mechanics models have been widely used to understand the theoretical vibration characteristic of nanotubes. Sohlberg and co-workers studied vibration behavior of SWCNT by applying continuum mechanics, which assumes the nanotube as an elastic solid rod and shows the possibility of exact predictions of vibrational behavior with the continuum mechanics [3]. Mahan has used thin-walled hollow isotropic cylinders to compute the low-frequency vibration modes of an SWCNT [4]. He obtained the simple formulas which match well the experimental results. In recently recent study, Lee et al. performed vibrational analysis of SWCNTs and single-walled carbon nanocones (SWCNCs) under the difference boundary condition by using the finite element method (FEM) with ANSYS [5]. Chang et al. [6] employed analytical molecular mechanics model to investigate chirality- and size-dependent elastic properties of SWCNTs. They found that Young's modulus increases as the tube diameter and chiral angle increase, whereas Poisson's ratio shows the countertrend. Li and Chou studied the vibration feature of SWCNTs using an atomistic modeling technique called molecular structural mechanics, which was used for predicting static and dynamic properties of a nanotube [7, 8]. Subsequently, they achieved the theoretical resonance frequency of nanotubes. Georgantzionos and co-workers also proposed a linear spring-based model to describe nanotube structures using a harmonic potential with respect to internal coordinates such as bond angles and torsion angles and found that the aspect ratio between diameter and length plays a significant

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role in determining vibration frequencies of SWCNTs [9].

Although there are several attempts to understand the effect of nanotube size and structure on their vibration features using the abovementioned continuum models and molecular mechanics, there has not been yet a quantitative report exhibiting the dependency of vibration mode shapes on nanotube size and chirality because substantial amount of computation time is needed to simulate many different types of SWCNTs in terms of chirality and aspect ratio.

In this paper, the vibration behaviors of armchair, zigzag and chiral forms of SWCNTs are studied and the specific formula representing chirality- and size-dependent vibration mode shapes is introduced. This theoretical study has been performed by the normal mode analysis based on the elastic network model (ENM) in which all interatomic interactions are simply represented as a linear spring network.

2. Method

Even though the conventional continuum approaches are good enough to accurately estimate theoretical resonance frequencies of carbon nanotubes, they have paid less attention to understanding the effect of different atomic structures of nanotubes on their vibration mode shapes [3, 4]. Alternatively, hybrid atomistic/continuum approaches, called molecular structural mechanics [7, 8], and molecular dynamics simulation [6, 9, 10] were employed to investigate dynamic features of SWCNTs in atomic detail. However, these atomistic methods require substantial amount of computation time so that there is a limitation of system size to be handled in real practice [11].

As an alternative but still reliable method, we suggest the normal mode analysis (NMA) based on ENM in which a system is represented as a network of virtual springs connecting spatially proximal atoms [12-19]. NMA is a conventional harmonic analysis to calculate vibration and thermal behaviors of macromolecules around an equilibrium state [15]. Therefore, we can study the vibration characteristic of nanotubes by using the NMA, after building the ENM. Mathematically, we derive the equation of motion of this mass-spring system from Lagrange's equation such that

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\delta}_i}\right)-\frac{\partial L}{\partial \delta_i}=0 \tag{1}$$

where $L = T - V$. T and V is the kinetic energy and potential energy of a given elastic network. If we build the elastic network model with N numbers of atoms, δ_i is the i^{th} component of displacement vector $\delta \in \mathbb{R}^{3N}$. The total kinetic energy is simply defined by the sum of the kinetic energy of all representative points.

$$T=\frac{1}{2}\sum_{i=1}^{n} m_i \left\|\dot{x}_i(t)\right\|^2 \tag{2}$$

Instead of using sophisticated empirical potential functions conventionally adopted in molecular dynamics simulation, we apply a simplified Hookean potential energy function.

$$V=\frac{1}{2}\sum_{i=1}^{n-1}\sum_{j=i+1}^{n} k_{i,j}\left\{\left\|x_i(t)-x_j(t)\right\|-\left\|x_i(0)-x_i(0)\right\|\right\}^2 \tag{3}$$

where $x_i(0)$ is the initial position of the i^{th} atom and $x_i(t)=x_i(0)+\delta_i(t)$. Here, we define $\delta_i(t)$ as a small fluctuation. $k_{i,j}$ is a spring constant between the i^{th} and j^{th} atom, based on the types of chemical interactions such as covalent bond and van der Waals interaction. The following connection rules are applied in this study.

$$k_{i,j}^{connection}=\begin{cases} k_{\text{cov}} & if \ \left\|x_i-x_j\right\|\le R_{vdw} \\ k_{vdw} & if \ R_c<\left\|x_i-x_j\right\|\le R_{vdw} \\ 0 & if \ \left\|x_i-x_j\right\|>R_{vdw} \end{cases} \tag{4}$$

where k_{cov} and k_{vdw} are the ratios of covalent and van der Waals interaction, which are set to be 100 and 1, respectively. They are determined by considering the order of magnitude of chemical bonding energy [20]. R_c and R_{vdw} are also set to be 1.5Å and 4Å, respectively, to distinguish the effective range of covalent bond from that of van der Waals interaction [21]. Although ENM uses a simple Hookean potential energy, it is a very useful tool for studying vibration modes and dynamic features of various SWCNT structures because of its inexpensive computation cost without loss of generality [22]. Substitution of this simplified potential into Equation 1 yields the following equation and its full derivation is available elsewhere [14, 23, 24].

$$M\ddot{\delta}+K\delta=0 \tag{5}$$

M is the global inertia matrix consisting of sub-diagonal matrices $M_{i,i}$ representing the specific mass value. Since the SWCNTs are composed of only carbon atoms and this identical value is not able to affect the vibration mode shape, M is easily constructed as a unit matrix. K is the global stiffness matrix having sub-stiffness matrices $K_{i,j}$ defined by the following equations.

$$\begin{cases} K_{i,j}=-G_{i,j} & ,if \ i\ne j \\ K_{i,i}=\sum_{k=1}^{i-1} G_{k,j}+\sum_{k=i+1}^{n} G_{i,k} & ,if \ i=j \end{cases} \\ , G_{i,j}=k_{i,j}\frac{(x_i(0)-x_j(0))(x_i(0)-x_j(0))^T}{\left\|x_i(0)-x_j(0)\right\|^2} \tag{6}$$

Fig. 1 is a simple ENM schematic of an SWCNT. The elastic network system here is composed of point masses in black

Table 1. Specification of the test nanotubes.

Nanotube type		Diameter (Å)	Length (Å)	Number of tested structures
Armchair	(3,3) ~ (10,10)	4.1 ~ 13.6	10 ~ 160	32
Zigzag	(5,0) ~ (16,0)	3.9 ~ 12.5	9 ~ 108	38
Chiral	(4,2) ~ (12,6)	4.1 ~ 12.4	11 ~ 120	19

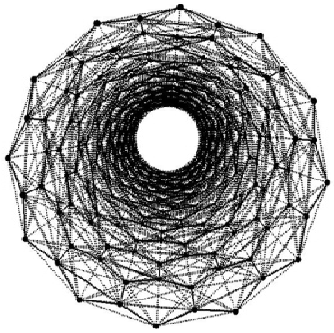

Fig. 1. A schematic of ENM of a part of (12,0) SWCNT. Black dots represent carbon atoms. Solid lines and dotted lines indicate the sp^2 covalent bonds and the van der Waals interactions, respectively.

dots and binary spring connections, which describe the carbon atoms and their chemical interactions, respectively. Two types of lines (solid and dotted) graphically distinguish the covalent bonds from the van der Waals interaction within a cutoff distance of 4Å. After building an ENM with M and K, one can calculate the eigenvalue problem in Eq. (5). As this generalized eigen problem results in both eigenvalues and eigenvectors of the system representing, respectively, vibration frequencies and corresponding mode shapes, magnification of the initial coordinates along the direction to a specific eigenvector render the corresponding mode shape [21, 23, 26]. In addition, statistical mechanics has explained that only a few lowest normal modes can dominantly contribute to the global and collective motions of the system [16, 27-31]. Therefore, we can understand vibration features of a specific system by defining a simple Hookean potential energy from its ENM and then solving the generalized eigen problem.

3. Simulation results and discussion

We have taken a variety of coordinates of SWCNTs from visual molecular dynamics (VMD) and performed all simulations using the Matlab programming [31]. Static pictures have been created and sequentially converted into AVI format to represent vibration mode shapes of SWCNTs by PyMOL [32]. Table 1. lists up all the simulation conditions tested in this study.

As examples, Fig. 2 demonstrates the first five lowest vibration mode shapes of a (7,7) SWCNT in a length of 70Å. Both first and the second (cases (a) and (b)) vibration modes are in the shape of a half sine wave though its vibration directions alter 90 degrees in each case. However, the other modes

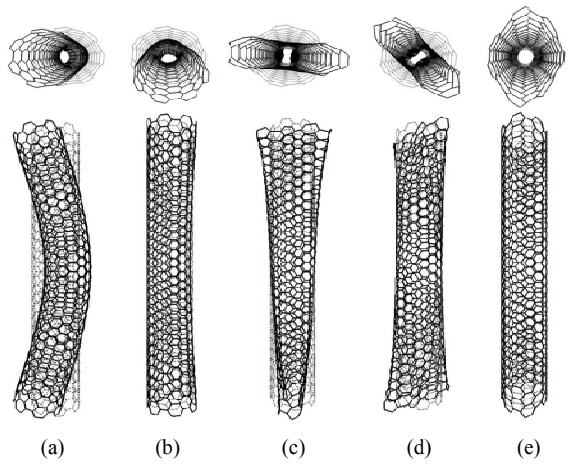

Fig. 2. The first five vibration modes of a (7,7) SWCNT in a length of 70Å.

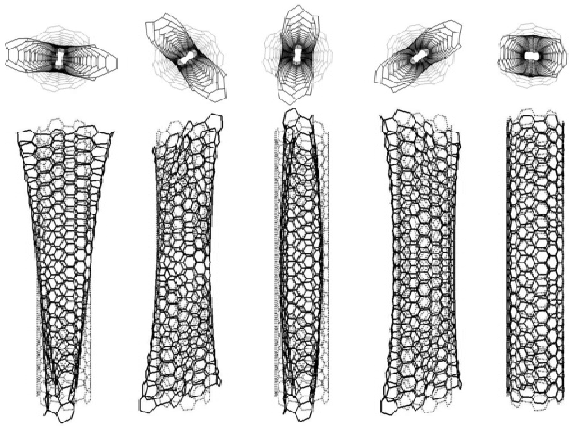

Fig. 3. The first five vibration modes of a (7,7) SWCNT in a length of 50Å.

(cases (c), (d) and (e)) are in the shape of various breathing waves. Although both half sine and breathing modes can be classified through vibration direction in details, we only focused on the types of vibration mode shape in this context [33].

Fig. 3 shows the first five vibration modes of a (7,7) SWCNT in a length of 50Å. There is no different simulation condition except the length of SWCNT compared to the case in Fig. 2. However, the shorter SWCNT shows totally different vibration features. Especially, the third and the fourth modes of the longer SWCNT (cases (c) and (d) in Fig. 2) appear at the first and the second modes of the shorter SWCNT (cases (a) and (b) in Fig. 3). Moreover, new breathing mode shapes are observed at the higher modes in Fig. 3. These two simulation results imply that as the length of SWCNT increases, various breathing modes are weakened. Instead, new bending modes become dominant. User-interactive animations for SWCNTs are available at http://bioengineering.skku.ac.kr/cnt. One can retrieve different mode shapes of SWCNTs shown in Fig. 2 through 4 in a 3D environment.

Next, we tested how much the chirality of SWCNT struc-

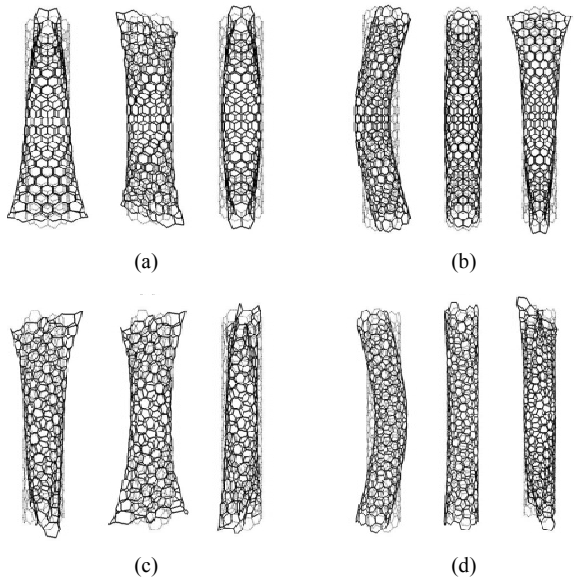

Fig. 4. The first three vibration modes of SWCNTs having different chirality: (a) (11,0) SWCNT in a length of 45Å; (b) (11,0) SWCNT in a length of 55Å; (c) (8,4) SWCNT in a length of 40Å; (d) (8,4) SWCNT in a length of 50Å.

ture influences these vibration features. Fig. 4 displays the first three lowest vibration mode shapes of zigzag and chiral SWCNTs. We can easily find similar results to the case of armchair shown in Figs. 2 and 3. The first and the second vibration modes in both zigzag and chiral forms are exchanged from breathing to bending depending on the length. This result indicates that vibration mode shapes are not sensitive to nanotube types such as armchair, zigzag and chiral, but very sensitive to the aspect ratio. Therefore, each SWCNT is expected to have its own critical aspect ratio between diameter and length at which the two major vibration mode shapes such as breathing and bending are exchanged. If one can formulate this relationship between structure and vibration mode of SWCNTs, it would be a highly effective guideline for designing relevant CNT based devices.

Since the first two modes intrinsically show complementary vibration features owing to its axisymmetric structure, we only take account into the first mode shape in order to keep consistency when finding the critical aspect ratio. All kinds of SWCNTs simulated here have shown almost the same critical aspect ratio unless their length is shorter than 12.3Å. In contrast, the dominant variable which determines vibration characteristics for shorter SWCNTs is not the aspect ratio but the length itself. Therefore, finding each offset value in both length and diameter is needed to determine the exact aspect ratio. These critical values are 12.3Å in length and 5.7Å in diameter, respectively.

Fig. 5 plots a critical or trend line to distinguish different mode shapes. As presented in Table 2, all types of SWCNTs show a similar tendency. Moreover, any SWCNT over the critical line has a bending motion as the first mode shape. By specifying Fig. 5, the bending mode conditions are empirically

Table 2. The critical aspect ratio between length (L) and diameter (D).

Nanotube type		L (Å)	D (Å)	(L-12.3)/(D-5.7)
Armchair	(3,3)	14	4.1	N/A*
	(5,5)	28	6.8	14.588
	(7,7)	63	9.5	13.383
	(9,9)	105	12.2	14.261
Zigzag	(5,0)	12	3.9	N/A*
	(9,0)	30	7.0	13.184
	(12,0)	55	9.4	11.566
	(16,0)	104	12.5	13.441
Chiral	(6,3)	11	4.1	N/A*
	(8,4)	45	8.3	12.667
	(10,5)	67	10.4	11.754
	(12,6)	105	12.4	13.786

* If D < 5.7Å, then the critical length becomes constantly 12.3Å. Therefore, the aspect ratio calculation is meaningless in this range.

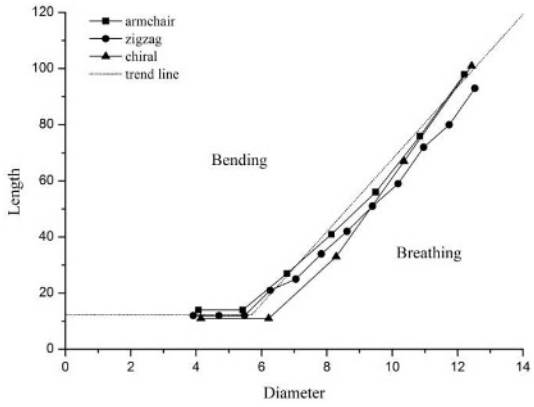

Fig. 5. The critical aspect ratio plot. The green, red and blue lines with specific symbols represent critical aspect ratios for armchair, zigzag and chiral nanotubes, respectively, to differentiate bending mode from breathing mode. The overall trend line is depicted by a black-dotted line.

formulated as

$$\begin{matrix} (a)\ \dfrac{l-12.3}{d-5.7} > 12.9 & (d>5.7) \\ (b)\ l > 12.3 & (d<5.7) \end{matrix}, \tag{7}$$

where l and d are the length and diameter of SWCNTs, respectively. Consequently, depending on the size of the diameter, there are two ways to get a bending mode shape. If $d < 5.7$ Å, SWCNTs should be, at least, longer than 12.3Å as described in Eq. 7(b). If not, they have to satisfy the condition in Eq. 7(a).

4. Conclusions

This paper presented how vibration mode shapes of nanotubes changed depending on their type and size. An ENM

based NMA was applied to reveal the size and chirality dependency of SWCNT vibration. The results indicated that the chirality of SWCNTs (armchair, zigzag, and chiral) does not affect their vibration features, which is in good agreement with the existing data in the literature [34, 35]. However, the aspect ratio between diameter and length of SWCNTs plays an important role in determining either breathing or bending motion of the given SWCNT. Fig. 5 displays the reference plots to necessitate the aspect ratio for being a bending mode shape and Eq. (4) was also proposed as an empirical formula to design a SWCNT structure naturally favorable to a bending motion. On the other hand, it can be a good reasoning why uniformity control in nanotube synthesis is so important in terms of vibration mode shapes. This theoretical result will serve as a practical design factor for nanotube based devices such as resonators and vibration sensors.

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