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PARAMETER STUDY OF DYNAMICAL BEHAVIOR OF CARBON NANOTUBES CONVEYING WATER CONSIDERING CARBON-WATER BOND

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ABSTRACT

In this research, free vibration analysis of Single Walled Carbon Nanotubes (SWCNTs) conveying water is studied. The effects of water flow velocity, CNT's chirality, CNT's diameter, elastic foundation stiffness, various end conditions and CNT's aspect ratio on the fundamental frequencies are studied. The main difference between the present work and previous works done by others is consideration of carbon-water bond potential energy to model the interaction between carbon atoms and water molecules. In spite of the previous works, in this work, water is considered as a discrete medium. Consequently, new interesting results are achieved which indicate that continuum assumption for water media leads to different results.
Results show that the fundamental frequency decreases by increasing the water flow velocity and decreasing the stiffness of the elastic foundation. It also decreases with increasing nanotube aspect ratio as the beam theories predict. Furthermore, the fundamental frequency is smaller for those SWCNTs with larger diameter.

INTRODUCTION

Nanomechanics is one of the fast growing fields of research in recent years. One of the major applications of nanomaterials is their usage in cancer research and neurobiology. Nanoscale sensors are being developed for the purpose of detecting illegal and harmful airborne chemicals. Protective coating is another area that has greatly benefited from nanotechnology. Nanoceramic-type coatings are used to reduce friction and wear in automotive industries. Another key area in nanotechnology is in electronics, micro electromechanical systems (MEMS) and nanoelectromechanical systems (NEMS) [1].

Many researches have been done on the carbon nanostructures after discovery of Carbon Nanotubes (CNTs) in1991 [2]. CNTs have excellent mechanical, electronic, magnetic, thermal and optical properties. For example, their Young modulus is 1 Tpa which is five times more than that of structural steels [3]. CNTs have many industrial applications such as hydrogen storage containers, micromechanical resonators and sensors [4-10]. CNTs are used as hydraulic actuators, sensors and nanopipes for conveying fluids due to their excellent mechanical properties and hollow cylindrical geometry.

CNTs have broad applications in fabricating nanofluidic devices [11]. For instance, they are used as devices for conveying aqueous fluids or micropipes conveying liquids for resonance sensing [11, 12]. They can also be used in nanobiology devices for delivering drugs to a specific organ or blood flow gradually [4]. The first application of CNTs as nanofluidic devices was using them as syringe needles for interrogation of cells [13]. This application can be seen in Fig.1.

Another main application of CNTs is related to the translocation and analysis of DNA and nanotube-based membranes [13].

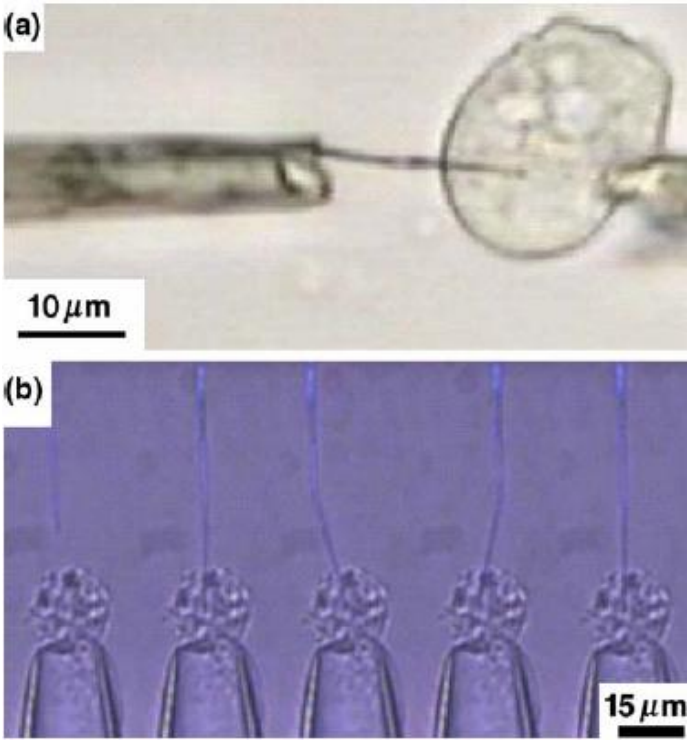

Figure 1: Optical micrographs of: (a) magnetically assembled CNT-tipped pipette poking a MDCK cell (Freedman et al. 2007); (b) carbon nanopipette poking a SMC cell (Schrlau et al. 2008) [13]

Since the fluid conveying properties are highly sensitive to the vibrational characteristics, investigation of CNTs' dynamical properties is very important. In all previous works, it was assumed that both CNT and the liquid conveyed were continuum [5-10, 14]. For instance Yoon et al. [5, 6] investigated the vibrational characteristics and instability of SWCNTs embedded in elastic foundation in 2005, 2006. Another work was done by Khosravian and Raffitabar [7] on determining natural frequencies of SWCNTs considering viscosity of fluid flow in 2007. Dynamical behavior of MWCNTs (Multi Walled Carbon Nanotubes) was investigated in 2009 by Yan et.al. [8]. Dynamics of microsclae pipes containing internal fluid flow and damping, frequency shift and stability phenomena occurred through this interaction were studied by S. Rinaldi et al. [12] in 2010. Some other works were done on the vibrational characteristics of SWCNTs and MWCNTs conveying fluid considering nonlocal beam theories to model CNTs [11, 14-16]. For example, Lee and Chang [14] worked on vibration of SWCNTs conveying viscous fluid using nonlocal Euler-Bernoulli beam theory to model SWCNTs in 2009. In nonlocal elasticity, stress tensor at each point is a functional of strain tensors at every point of the problem domain [17, 18].

Actually, each of the above mentioned works is a kind of generalization of macro mechanics laws and assumptions to nano scales studies. They were deviated from real situations even in density determination of fluid conveyed in a nano channel like a CNT. Due to small scales and large Knudson number of fluid media, the assumption of being continuum may not be valid.

Researchers have studied structure of water molecules arrangements within CNTs and between graphene sheets in many papers [19-22].

In the present work it is assumed that fluid media is not continuum. The results are compared with those of previous works. The differences are described and some conclusions are drawn. Also, the effects of flow velocity, CNT's chirality, CNT's diameter, elastic foundation stiffness, various end conditions and CNT's aspect ratio on the fundamental frequencies of SWCNT's vibration are studied. Nonlocal effects aren't considered in the present investigation.

THEORY

In the present research a SWCNT conveying fluid is embedded in an elastic foundation. The SWCNT is modeled as a beam with fixed-fixed end condition and the elastic foundation is considered as a distributed linear spring. A linear partial differential equation was obtained in the previous studies using Euler-Bernoulli beam vibration equation and Navier-Stokes equation considering water as a continuum media with its conventional density and viscosity. This equation which can be seen in previous articles [7, 14] is:

$$EI\frac{\partial^4 y}{\partial x^4}+2m_f V\frac{\partial^2 y}{\partial t\partial x}+m_f V^2\frac{\partial^2 y}{\partial x^2}-\mu A_f\left(V\frac{\partial^3 y}{\partial x^3}+\frac{\partial^3 y}{\partial t\partial x^3}\right)+(m_f+m_c)\frac{\partial^2 y}{\partial t^2}+Ky=0 \quad (1)$$

y is the lateral displacement of the SWCNT, and x is the axial coordinate. t indicates time. E , I , A_f and m_c are the equivalent young modulus, the area moment of inertia of cross section, the inner area and the mass per unit length for the SWCNT, respectively. V is the water flow velocity. m_f and μ are the water mass per unit length of the SWCNT and water viscosity, respectively. K is the Winkler constant of elastic foundation. I can be calculated by equation:

$$I=\frac{\pi}{64}(d_o^{\,4}-d_i^{\,4}) \quad (2)$$

where d_o and d_i are the outer and inner diameter of the SWCNT, respectively.

The first term in Eq. (1) is due to the SWCNT's elasticity. The second term is the force due to coriolis acceleration

resulting from the movement of the water as a continuum inside the SWCNT as a rotating frame. The third term is the centrifugal force and the forth term is resistance shear force due to water viscosity. The fifth term is the inertial force due to linear acceleration and the last term is related to the elastic foundation effect. This equation can be solved analytically as can be seen in references [7, 14].

New modeling

Water and SWCNT's interaction tangent to the CNT's wall can be calculated using the bond potential between carbon atoms and water molecules by considering Van der Waals bond between them. Van der Waals bond potential usually calculated using Lennard-Jones (L-J) potential function [1]. This potential function is:

$$PE = 4\varepsilon[(\frac{\sigma}{R})^6 - (\frac{\sigma}{R})^{12}] \tag{3}$$

where PE is the bond potential energy between two atoms and ε and σ are two constants depending on two atoms bond strength and equilibrium bond length. R is the distance between centers of atoms interacting with each other. This kind of interaction is defined as a short range interaction because the potential energy declines sharply to zero as the R increases.

Since carbon-hydrogen interactions are much weaker than those of carbon-oxygen, Van der Waals bonds are considered as connections between carbon atoms and oxygen ones, only. Therefore, L-J potential function can be written as:

$$PE_{co} = 4\varepsilon_{co}[(\frac{\sigma_{co}}{R})^6 - (\frac{\sigma_{co}}{R})^{12}] \tag{4}$$

where $PE_{co}, \varepsilon_{co}, \sigma_{co}$ are the corresponding parameters for carbon- oxygen bond interaction. These coefficients can be seen in Table (1) given by reference [23]:

Table1: Constants for L-J potential function obtained with different methods [23]

Study	Water Model	σ_{CO} (Å)	ε_{CO} (kJ/mol)	ΔE (kJ/mol)	θ (°)
Markovic 1999	SPC	3.190	.3910	-12.64	0.0
Gordillo and Marti 2000	SPC-FLX[b]	3.280	.3890	-9.91	55.9
Walther 2001	SPC-FLX	3.190	.3135	-5.19	111.3
Hummer 2001	TIP4P	3.275	.4785	-8.33	48.0
Koga 2001	TIP4P	3.262	.3876	-6.70	
Noon 2002	TIP3P	3.296	.5781	-16.72	0.0
Present Study	SPC/E	3.190	.4389	-7.26	85.5

a. The Markovic, Gordillo and Noon models also included pairwise Lennard-Jones potential terms between carbon atoms and the water hydrogen atoms.
b. SPC-FLX is a flexible water model that allows OH stretch and HOH bending motions.

In this article the last series of coefficients are used.

Therefore, one can add the potential energies of carbon-water bonds and then differentiate the attained summation with respect to the axial direction x to calculate the tangential force and finally project it in the transverse direction to the SWCNT. This force is named wall shear force in this article. Therefore, the following equation can be derived using Euler-Bernoulli beam vibration equation considering water molecules flow inside it and the wall shear force calculation.

$$EI\frac{\partial^4 y}{\partial x^4} + 2m_f V\frac{\partial^2 y}{\partial t \partial x} + m_f V^2\frac{\partial^2 y}{\partial x^2} - F(x)\frac{\partial y}{\partial x} + (m_f + m_c)\frac{\partial^2 y}{\partial t^2} + Ky = 0 \tag{5}$$

where $F(x)$ is the wall shear force calculated from the stated procedure. The forth term is the projection of this force in transverse direction. m_f in Eq. (5) is water molecules mass per unit length of carbon nanotube. It will be calculated by Eq. (13). This linear equation can't be solved by analytical methods because of the forth term. Finite Element Method (FEM) is used to solve the partial differential equation (PDE) (5). Using weak formulation of the above PDE, stiffness, damping and mass matrices can be derived as:

$$K_{ij}^e = \int_0^{he} [EI\psi_i'' \psi_j'' - m_f V^2 \psi_i' \psi_j' + F\psi_i\psi_j' + K\psi_i\psi_j]dx$$
$$i, j = 1,...,4 \tag{6}$$

$$C_{ij}^e = \int_0^{he} 2m_f \psi_i \psi_j' dx$$
$$i, j = 1,...,4 \tag{7}$$

$$M_{ij}^e = \int_0^{he} (m_c + m_f)\psi_i \psi_j dx$$
$$i, j = 1,...,4 \tag{8}$$

K^e, C^e, M^e are the element stiffness matrix, the element damping matrix, and the element mass matrix, respectively. h_e is the element length. As it can be seen these stiffness and damping matrices are asymmetric. ψ_i is the cubic Hermite shape functions used for the beam (SWCNT) discretization. Therefore, a system of linear algebraic equations can be obtained after the assemblage process of elements. Then, the resulting system of equations can be solved as an eigenvalue problem:

$$\left[K^G + i\omega C^G - \omega^2 M^G\right]\{U\} = \{0\} \tag{9}$$

where K^G, C^G, M^G are the global stiffness matrix, the global damping matrix and the global mass matrix, respectively. $\{U\}$

is the vector of all degrees of freedom of finite element model and ω is the complex frequency of vibration. $i = \sqrt{-1}$.

This eigenvalue problem has nontrivial solution if and only if:

$$\left| K^G + i\omega C^G - \omega^2 M^G \right| = 0 \tag{10}$$

The imaginary part of each calculated eigenvalue can be considered as the natural frequency of vibration.

The position of carbon atoms constructing nanotubes and the arrangement of water molecules in the nanotubes should be known. Having information about a SWCNT's index (n, m), one can obtain the arrangement of carbon atoms. We use two equations to calculate an armchair or a zigzag SWCNT's diameter [24]:

$$d = \frac{3a}{\sin(\frac{180}{n})} \tag{11}$$

$$d = a\frac{\cos 30}{\sin(\frac{90}{n})} \tag{12}$$

Equations (11) and (12) represent armchair (n,n) and zigzag (n,0) nanotubes' diameter, d, respectively. In these equations, parameter *a* represents each element length (carbon-carbon bond length). But, for determining the positions of water molecules, we used reference [19].

For SWCNTs with diameters less than 1nm water molecules arrange in a string structure, but in larger SWCNTs they arrange in a cluster like structure as can be seen in Fig. 2.

In article [19] water molecules structures were determined using Monte Carlo Simulations. Figure 2. illustrates water molecules structure in armchair (10, 10) SWCNT in 123K [19].

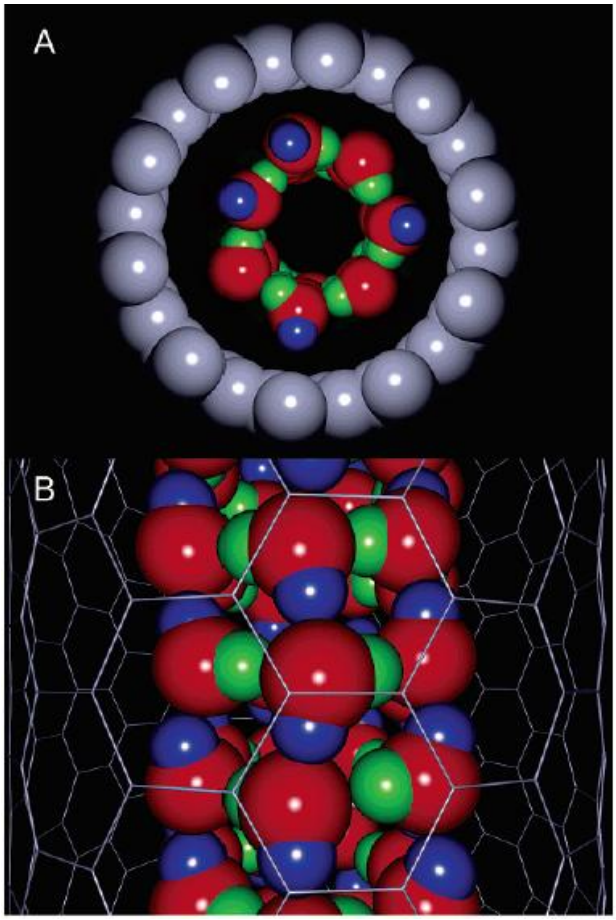

Fig. 2: Snapshot from a molecular simulation of water absorbed in side a (10, 10) SWCNT at 123K forming heptagon rings: (A) end view and (B) side view. Red spheres represent oxygen, blue spheres are hydrogens that are hydrogen-bonded to adjacent rings (inter- rings) and green spheres are hydrogens involved in intra-ring hydrogen bonds. The lines represent the carbon-carbon of the SWCNT [19].

In the reference [19] there was a diagram indicating the behavior of the average energy of various water molecules structures in armchair nanotubes in different temperatures. As it can be seen in Fig. 3., armchair(8,8) SWCNT with 5-ring and 4-ring water molecules structure and armchair(9,9) SWCNT with 6-ring water molecules structure keep their water structure up to room temperature while water molecules structure in the rest become disordered.

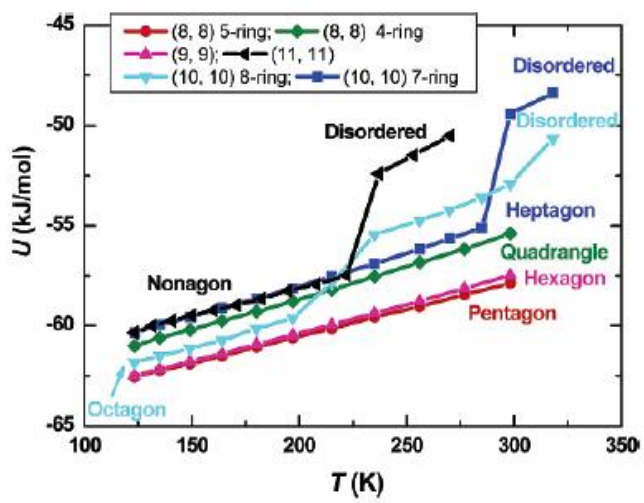

Figure. 3: Average energy for water confined in (8,8), (9,9), (10,10) and (11,11) SWCNTs at temperature ranging from 123 to 318 K from parallel tempering Monte Carlo Simulations[19].

We can see a heptagonal structure (7-ring) for water molecules in this armchair SWCNT. In all types of SWCNTs the distance between inter-ring and intra-ring oxygen atoms is 0.28nm [19]. Therefore, in an armchair (8,8) SWCNT there are 5 water molecules in 0.28nm length. One mole (6.022*10^23) water molecules weight 18 grams. Therefore, m_f can be calculated by dividing mass of 5 water molecules to distance between two water molecules locating in axial direction.

$$m_f = \frac{\left[(5\times 18\times 10^{-3})/(6.022\times 10^{23})\right]}{2.8\times 10^{-10}} = 5.34\times 10^{-16}\, Kg/m \quad (13)$$

If we calculate m_f using water density of $1000\, Kg/m^3$ which is water density when we assume water media as a continuum, it deviates from that calculated with discrete media assumption.

$$m_f = \rho\times \pi d_i^2/4 = 9.73\times 10^{-16}\, Kg/m \quad (14)$$

It is expected that this new m_f is less than that calculated considering conventional water density because the media becomes discrete as a result of confinement in such a small scale. We use the information and diagrams existing in paper [19] and construct our structures using MATLAB. In this work, magnitudes of E and a are considered to be 1000Gpa [14] and 1.42 nm, respectively. The SWCNT's thickness is assumed to be 0.34 nm [3] and carbon density is 2300 Kg/m^3.

RESULTS AND DISCUSSION

We analyzed the effects of flow velocity, stiffness of elastic foundation, CNT's chirality, CNT's diameter, various end conditions and CNT's aspect ratio on the fundamental frequencies of different kinds of SWCNTs. Here, only the results derived for armchair (8,8), armchair (9,9) and zigzag (14,0) SWCNTs are presented. Aspect ratio is defined as the length to diameter ratio of SWCNTs. Diameters of armchair (8,8), armchair (9,9) and zigzag (14,0) SWCNTs are 1.113 nm, 1.246 nm and 1.098 nm, respectively. Their diameters are larger than 1 nm; then water molecules structures are cluster like within these SWCNTs.

Flow velocity effect on the first and second frequencies of clamped-clamped armchair (8,8) SWCNTs is illustrated in Fig. 4. It's interesting that natural frequencies are of order of Tera Hertz. It can be seen that natural frequencies decrease as flow velocity increases. These curves are drawn for flow velocity up to 16000 m/s.

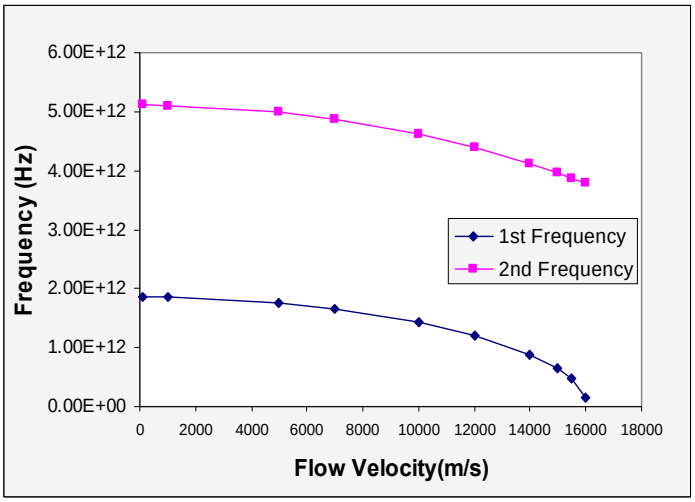

Figure 4: Variation of first and second frequencies with respect to flow velocity for clamped-clamped armchair (8,8) SWCNT with aspect ratio 10

Figure 5. demonstrates the effect of the elastic foundation stiffness on the fundamental frequency of armchair (8,8) SWCNT with aspect ratio 10 clamped in both ends. Fundamental frequency increases by increasing the elastic foundation stiffness as it can be observed in Fig. 5. It becomes zero at a certain velocity named critical velocity in which system doesn't oscillate any more. This critical velocity increases with increase in foundation stiffness. The unit of the stiffness is Newton per squared meters (N/m^2). It's worth noting that foundation stiffness is in the order of Giga Pascal.

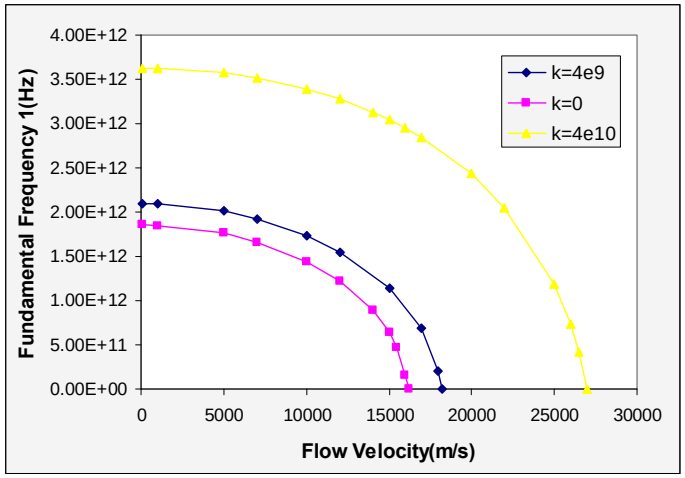

Figure 5: Fundamental frequency variation with respect to flow velocity for clamped-clamped armchair (8,8) SWCNT with aspect ratio 10 and various elastic foundations stiffness

CNT's aspect ratio effect on the fundamental frequency of armchair (8,8) SWCNTs with clamped ends is shown in Fig. 6. for two aspect ratios; 5 and 10. Fundamental frequency decreases as aspect ratio increases at each flow velocity as it is predicted by beam theories.

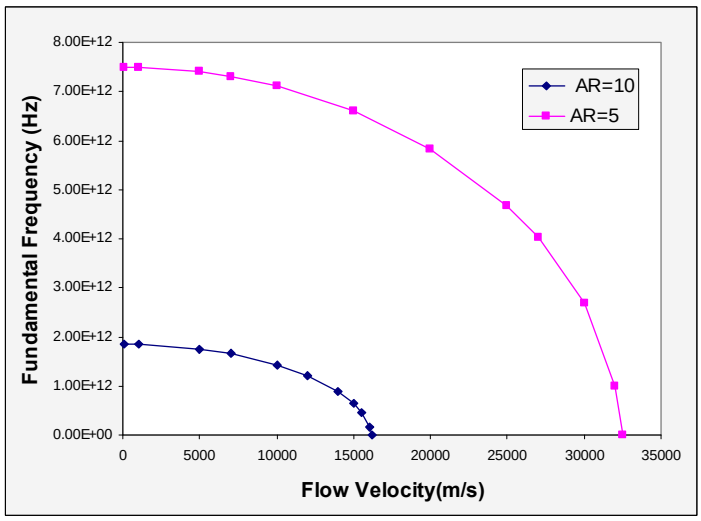

Figure 6: Comparison of fundamental frequency variation with respect to flow velocity for clamped-clamped armchair (8,8) SWCNT with aspect ratios 5 and 10

Effect of CNTs' diameter on the fundamental frequency of CNTs' vibration is presented in Fig. 7. SWCNTs with larger diameters have smaller fundamental frequencies as it is shown in this Figure. It can be concluded that mass increase due to diameter increase is more effective than cross section stiffness increase.

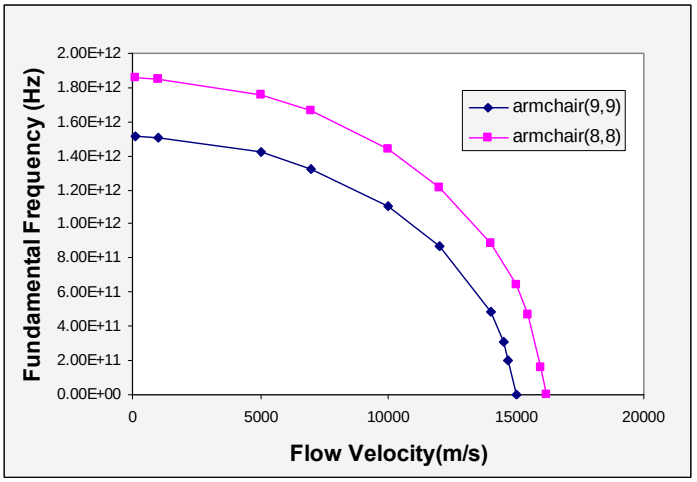

Figure7: Comparison of variation of fundamental frequency with respect to flow velocity between clamped-clamped armchair (8,8) and armchair (9,9) SWCNTs with aspect ratios 10

Figure 8. depicts the effect of end conditions on the fundamental frequency of armchair (8,8) SWCNTs with aspect ratio 10 when water flows through them at a speed of 5000 m/s. It is shown that the fundamental frequency decreases as the end conditions become weaker as it is expected from beam theories.

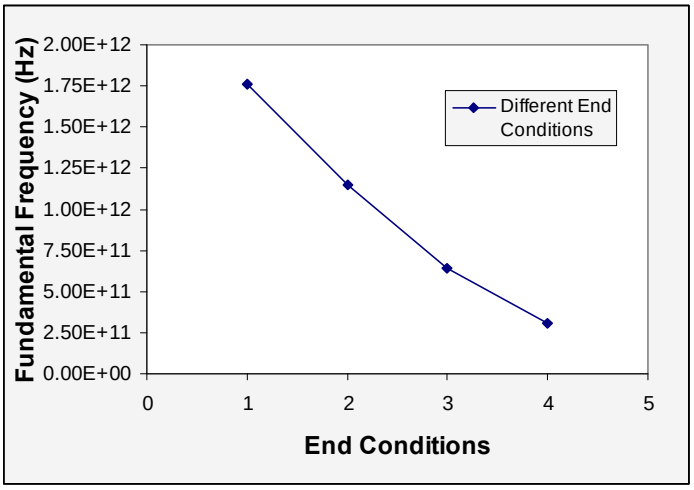

Figure 8: Fundamental frequency variation with respect to flow velocity for armchair (8,8) SWCNT with aspect ratio 10 and various end conditions- (1)clamped-clamped (2)clamped-pin (3)pin-pin (4)clamped-free

CNTs' chirality effect on the fundamental frequency of SWCNTs conveying water vibration is shown in Fig. 9. Fundamental frequencies of clamped-clamped armchair (8,8) and zigzag (14,0) SWCNTs with approximately same aspect ratio are compared in this figure. These two SWCNTs have almost same diameters. Fundamental frequency for zigzag (14,0) is more than that of armchair (8,8) as it is depicted in

Fig. 9. But, because of only little difference between their aspect ratios and diameters, this comparison is not so reliable.

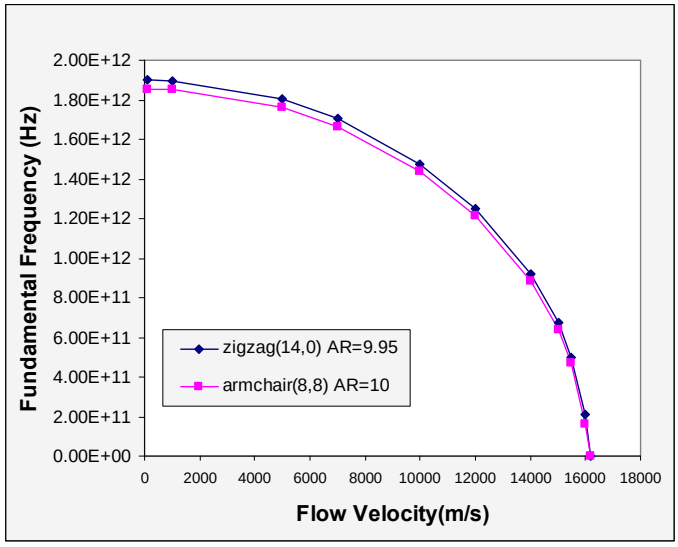

Figure 9: Comparison of variation of fundamental frequency with respect to flow velocity between clamped-clamped armchair (8,8) and zigzag (14,0) SWCNTs with almost same aspect ratios 10

A comparison between present results and those obtained in previous researches is presented in Fig. 10. As it can bed seen, the fundamental frequencies regarding each flow velocity and also critical velocity obtained in the present work are larger than those of Lee et al. [14]. This is due to m_f value in the present work is less than that used by Lee et al. [14].There is a curve in this figure which is coincided on the curve obtained in the present investigation. This curve is obtained using Lee et al. [14] method with m_f calculated based on the assumption of discrete medium in the present work. Therefore, it can be concluded that the difference between results is due to different water mass per unit length of SWCNT calculated in these two different studies. Different m_f s calculations are due to two different assumptions of continuum and discrete water media. However, these different assumptions have no significant effect on the calculation of the wall shear force.

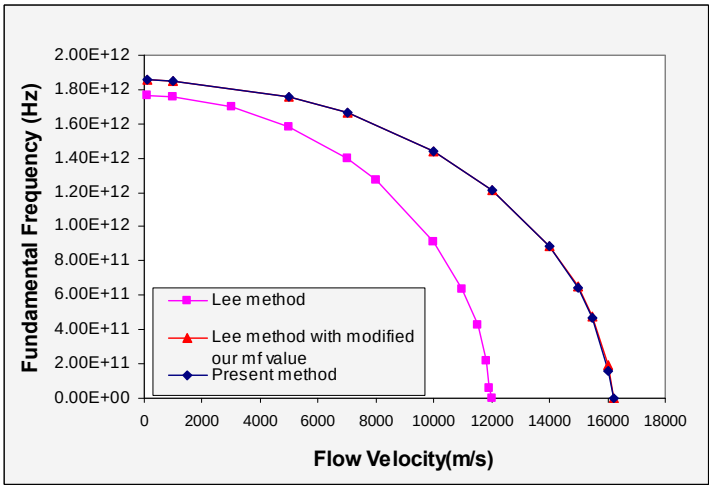

Figure 10: A comparison between present results and Chang results [14] for a clamped-clamped armchair (8,8) with aspect ratio 10

CONCLUSION

It is shown that by increasing the flow velocity, the natural frequencies are decreased. By comparing our results with previous ones it is concluded that the molecular based water density assumption predicts much larger natural frequencies than those predicted by continuum based water density assumption. Also, it is concluded that wall shear force calculation using continuum or molecular model results in similar fundamental frequencies.

Furthermore, it can be concluded that the fundamental frequency increases by increasing the elastic foundation stiffness. It decreases as aspect ratio increases at each flow velocity as it is predicted by beam theories. It is shown that SWCNTs with larger diameters have smaller fundamental frequencies. Another point is that fundamental frequency increases as the end conditions become stiffer as it is expected from beam theories. CNTs' chirality effect on fundamental frequency is also investigated.

The present method can be generalized to model MWCNTs and to consider the interactions in more complex and reliable manner.

NOMENCLATURE

E	equivalent young modulus of SWCNT
F	wall shear force
I	area moment of inertia of cross section of SWCNT
K	Winkler constant of elastic foundation
R	distance between centers of atoms interacting with each other
V	water flow velocity

PE	bond potential energy between two atoms
a	each element length (carbon-carbon bond length)
d	nanotubes' diameter
n, m	SWCNT's indices
t	Time
x	axial coordinate
y	lateral displacement of the SWCNT
μ	water viscosity
ω	complex frequency of vibration
ε, σ	Lennard-Jones constants
A_f	Inner area of SWCNT
PE_{co}	bond potential energy of carbon- oxygen bond interaction
d_i	inner diameter of the SWCNT
d_o	outer diameter of the SWCNT
h_e	element length
m_c	mass per unit length for the SWCNT
m_f	water mass per unit length of the SWCNT
C^G	global damping matrix
K^G	global stiffness matrix
M^G	glabal mass matrix
C^e	element damping matrix
K^e	element stiffness matrix
M^e	element mass matrix
ψ_i	cubic hermit shape functions used for the beam (SWCNT) discretization
$\varepsilon_{co}, \sigma_{co}$	Lennard-Jones constants for carbon- oxygen bond interaction
$\{U\}$	vector of all degrees of freedom of finite element model

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