Available online at www.sciencedirect.com

SCIENCE DIRECT®

Applied Surface Science 246 (2005) 149–158

applied surface science

www.elsevier.com/locate/apsusc

Suitability of boron-nitride single-walled nanotubes as fluid-flow conduits in nano-valve applications

M. Grujicic[a,*], G. Cao[a], W.N. Roy[b]

[a]*Department of Mechanical Engineering, Program in Materials Science and Engineering, Clemson University, 241 Fluor Daniel, Engineering Innovation Building, Clemson, SC 29634-0921, USA*
[b]*Army Research Laboratory, Processing and Properties Branch, Aberdeen, Proving Ground, MD 21005-5069, USA*

Received 16 October 2004; received in revised form 2 November 2004; accepted 2 November 2004
Available online 8 December 2004

Abstract

Molecular-level simulations are used to examine the suitability of boron-nitride single-walled nanotubes (SWNTs) as fluid-flow conduits in the nano-valve applications based on a molecular-mono-layer functionalized silicon cantilever. The interaction between the constituent atoms in the nanotubes is modeled using the Universal Force Field inter-atomic potential. Key functional requirements (a large range of nanotube radii with a stable circular cross section, a low level of strain energy in the nanotube at the onset of bending-induced buckling, relatively high compliance with respect to the radial breathing mode and a low value of nanotube/fluid-molecule binding energy) have been identified for nanotube fluid-flow conduits. The results obtained suggest that boron-nitride SWNTs do not offer any significant functional advantage over their carbon-based counterparts when used in fluid-flow conduit applications. The results also suggests that several of the nanotube properties obtained through the use of the Universal Force Field are quite comparable to their counterparts based on the first-principles quantum-mechanical calculations.

PACS: 81.05.Tp

Keywords: Single-walled carbon nanotubes; Boron-nitride nanotubes; Nano-devices; Nano-technology

---

1. Introduction

Functionalized (typically silicon-based) cantilever nano-beam devices have been extensively studied in the last several years, e.g. [1,2]. Such nano-beam devices often have one face covered (functionalized) with a self-assembled or chemically bonded mono-layer of molecules of the various types and can deflect by themselves (in the presence of a pH change in the surrounding environment) due to differences in the surface stresses between the parallel functionalized and non-functionalized faces. In a recent paper, Solares et al. [3] proposed the design of a fluid-flow

---

* Corresponding author. Tel.: +1 864 656 5639; fax: +1 864 656 4435.

E-mail addresses: mica.grujicic@ces.clemson.edu, mica@ces.clemson.edu (M. Grujicic).

0169-4332/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2004.11.007

Report Documentation Page	*Form Approved* *OMB No. 0704-0188*

1. REPORT DATE **2005**	2. REPORT TYPE	3. DATES COVERED **00-00-2005 to 00-00-2005**

4. TITLE AND SUBTITLE **Suitability of boron-nitride single-walled nanotubes as fluid-flow conduits in nano-valve applications**	5a. CONTRACT NUMBER
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Celmson University,Department of Mechanical Engineering,Clemson,SC,29634**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR’S ACRONYM(S)
	11. SPONSOR/MONITOR’S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT

Molecular-level simulations are used to examine the suitability of boron-nitride single-walled nanotubes (SWNTs) as fluidflow conduits in the nano-valve applications based on a molecular-mono-layer functionalized silicon cantilever. The interaction between the constituent atoms in the nanotubes is modeled using the Universal Force Field inter-atomic potential. Key functional requirements (a large range of nanotube radii with a stable circular cross section, a low level of strain energy in the nanotube at the onset of bending-induced buckling, relatively high compliance with respect to the radial breathing mode and a low value of nanotube/fluid-molecule binding energy) have been identified for nanotube fluid-flow conduits. The results obtained suggest that boron-nitride SWNTs do not offer any significant functional advantage over their carbon-based counterparts when used in fluidflow conduit applications. The results also suggests that several of the nanotube properties obtained through the use of the Universal Force Field are quite comparable to their counterparts based on the first-principles quantum-mechanical calculations.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**10**	

control nano-valve based on a silicon nano-beam actuator functionalized with a covalently bonded monolayer of acrylic-acid molecules which can permit or stop the flow through a fluid-flow conduit, a carbon single-walled nanotube (SWNT). The "*on/off*" switching of the nano-valve is controlled by the changes in pH of its environment. That is, changes in the pH affect the charges of the molecules in the functionalizing monolayer and, thus, control the magnitude of the inter-molecular electrostatic forces and, in turn, the magnitude of the surface stresses at the functionalized face of the nano-valve.

Solares et al. [3] argued that as molecular modeling is transforming from being primarily a tool for studying materials properties to an alternative approach for analyzing the performance of nanosize devices, it is becoming computationally more and more demanding and, often, impractical. This is caused by the fact that the size of the computational problem generally increases as N^2, where N is the number of particles in the system being studied. This problem is particularly agg-ravated by the presence of electrostatic interactions between the charged molecules used for nano-beam functionalization because of the following two main reasons: (a) the geometry of nano-devices is generally not periodic so that efficient electrostatic lattice-summation methods (e.g. the Ewald summation method) cannot be used without introducing spurious effects due to imposition of the non-physical periodic boundary conditions; (b) the use of radial cut-off radii or splines to handle the long-range interactions can underestimate the electrostatic energy by as much as an order of magnitude for the nanosize devices. There is an additional problem associated with the use of molecular modeling methods for simulation of the nanosize devices. Average forces and strain energies used to judge the attainment of equilibrium may not be very reliable in a computational system containing a large number of particles since they may allow large residual forces to be present in a small region while the average force is quite small implying an equilibrium state of the system.

Nevertheless, to obtain a more accurate design of a nano-device, it is critical to include as much molecular-level details as possible. On the other hand, as pointed out above, it is often impractical or even impossible to carry out all the design and analysis steps at the molecular-level. To achieve a compromise, Solares et al. [3] proposed a hybrid method which combines molecular simulations with the classical engineering design. Specifically, molecular simulations are used to determine elastic and electrostatic properties of the individual components of a nano-device which are then used, within a classical engineering design framework, to carry out an analysis of the functionality, design, and optimization of the nano-device.

In a recent work, Grujicic et al. [4] extended the hybrid method proposed by Solares et al. [3] and applied it to the design of the same fluid-control nano-valve described above. Specifically, the method of Solares et al. [3] was extended to include the interactions between different device components (primarily the interactions between the cantilever nano-beam and the carbon SWNT) during the closing operation of such a nano-valve. Toward that end, rather than analyzing the performances of the cantilever nano-beam and the carbon SWNT fluid conduit separately and using the resulting information to judge the functionality of the nano-device and to determine its optimal geometry and dimensions, a finite element method is utilized to analyze the performance of the entire nano-valve. The results obtained are then used as a guide during optimization of the nano-device design. The outcome of this approach was that the optimal designs of the entire nano-valve and its components are quite comparable to those predicted by Solares et al. [3]. Therefore, the work presented in this paper utilizes the approach originally proposed by Solares et al. [3] but extends the work to include boron-nitride SWNTs and to determine if these nanotubes are more suitable as fluid-flow conduits in the nano-device applications.

The organization of the paper is as follows: a brief formulation to the problem being studied is given in Section 2.1. The use of molecular-level modeling to analyze the performance of SWNTs as the fluid-flow conduits in nano-valve applications is presented in Section 2.2. The main results obtained in the present work are presented and discussed in Section 3 while the key resulting conclusions are summarized in Section 4.

2. Computational procedure

2.1. Problem definition

Atomistic configurations of the nano-valve in the open and closed positions are displayed in Fig. 1(a)

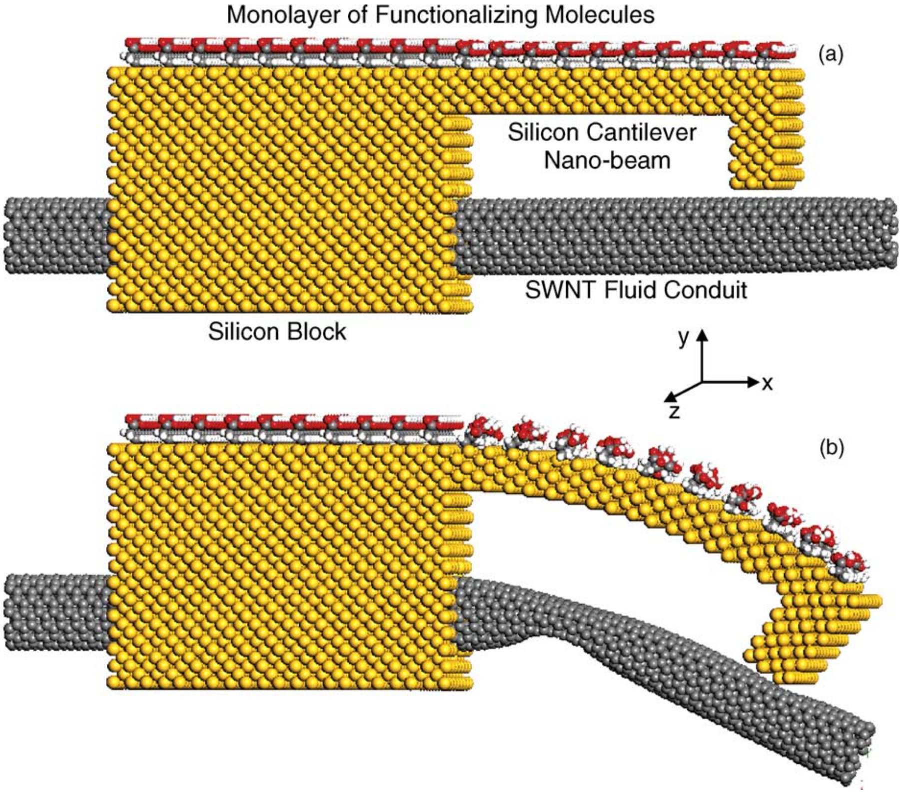

Fig. 1. Atomistic structure of the fluid-flow control nano-valve analyzed in the present work in the: (a) open and (b) closed positions.

and (b), respectively. The nano-valve consists of a silicon block with a cantilever nano-beam, where both are functionalized on their top surface with a single layer of molecules. The silicon block is perforated on its lower part and a SWNT inserted through the perforation. The SWNT acts as a fluid-flow conduit. When the pH in the environment surrounding the nano-valve changes, the functionalizing molecules may acquire a larger charge. This, in turn, gives rise to a larger electrostatic repulsion between the molecules and, subsequently, causes the cantilever to bend downward. If the action of the cantilever causes the SWNT to deflect past the point of bucking, the fluid flow through the SWNT ceased and the nano-valve is in the ‘‘*off*’’ position, Fig. 1(b).

For the nano-valve to function as described above, the reduction in the electrostatic energy associated with an increase in the inter-molecular separation during cantilever bending has to be sufficiently large to compensate for the elastic energies stored in the cantilever nano-beam and in the nanotube (up to and past the point of buckling of the SWNT). For a given charge level of the functionalizing molecules, the electrostatic energy reduction is governed by the molecular surface coverage (surface density) and the surface area of the top face of the block and the cantilever. For a fixed molecular surface density and a fixed value of the combined lengths of the silicon block and the cantilever, the nano-valve width becomes the sole design parameter controlling the functionality of the nano-valve.

It is generally desirable to have a nano-valve width as small as possible since that ensures that the overall size of the nano-valve is minimal, and may also be beneficial to the reliability of the ‘‘*on/off*’’ switching operations of the nano-valve. In the work of Solares et al. [3], it was shown that the minimal required width of the nano-valve could be determined by requiring that the electrostatic energy stored in the functionalizing molecular monolayer is at least equal to the sum of the strain energies stored in the silicon cantilever and in the nanotube at the point of buckling. If the width of the nano-valve is lower than its critical minimal value, the nano-valve will not be fully operational since it would not be able to reach a complete ‘‘*off*’’ position. As explained earlier, the approach of Solares et al. [3] within which each component (functionalized monolayer, silicon cantilever, and nanotube conduit) is considered separately, is employed in the present work. The objective of the present work is, however, to explore the suitability of boron-nitride SWNTs as the fluid-flow conduits in nano-valve applications. Since the functionalizing monolayer and the silicon cantilever beam will not generally need to be redesigned when a carbon SWNT conduit is replaced with a boron-nitride SWNT conduit, only the nanotube conduit will be analyzed in the present work. The question which we will try to answer is: ‘‘Do boron-nitride SWNTs offer any advantage over their carbon-based counterparts when used as the fluid-flow conduits in nano-valve applications?’’

2.2. Molecular modeling procedure

2.2.1. Computational domain

As will be explained in more details in the next section, arm-chair type of single-walled carbon and boron-nitride nanotubes are investigated in the present work. This family of SWNTs is characterized by the chirality (n, $m = n$). To generate carbon and boron-nitride arm-chair SWNTs of a given length and with a given value of the chirality index n, a computer program is written in MATLAB, a general purpose computational and visualization software [5]. MATLAB provides a unique opportunity to visually examine the atomistic configuration associated with each of the SWNTs for correctness, before such configuration is subject to a molecular modeling procedure. All the molecular simulations carried out in the present work involve isolated SWNTs, and hence, the size of the periodic boundary lengths in each case is set at least 10 times as large as the corresponding van der Waals inter-atomic distance. This ensures that no interactions take place between the periodic SWNT images. Examples of the atomic structures of small sections of the carbon and boron-nitride nanotubes are shown respectively in Fig. 2(a) and (b).

2.2.2. Computational method

All the molecular modeling simulations carried out in the present work involved a Molecular Statics method within which the potential energy of the SWNT is minimized with respect to the positions of the constituent atoms. Since the approach was intended to determine the optimized atomic configuration in isolated SWNTs, the periodic-cell lengths were not altered during the energy minimization procedure. All the Molecular Statics simulations carried out in the present work were done using the Accelrys’ Forcite molecular modeling program [6].

2.2.3. Force fields

While the accurate simulation of a system of interacting particles generally entails the application of quantum-mechanical techniques, such techniques are computationally quite expensive and are usually feasible only in systems containing up to few hundreds of interacting particles. In addition, the main goal of simulations of the systems containing a large number of particles is generally to obtain the systems’ bulk properties which are primarily controlled by the location of atomic nuclei and the knowledge of the electronic structure, provided by the quantum mechanic techniques, is not critical. Under these circumstances, a good insight into the behavior of a system can be obtained if a reasonable, physically based approximation of the potential (force field) in which atomic nuclei move is available. Such a force field can be used to generate a set of system configurations which are statistically consistent with a fully quantum-mechanical description.

As stated above, a crucial point in the atomistic simulations of multi-particle systems is the choice of the force fields which describe, in an approximate manner, the potential energy hypersurface on which the atomic nuclei move. In other words, the knowledge of force fields enables determination of the potential energy of a system in a given configuration. In the present work, the Universal Force Field [7] is used within which, the total potential energy of a system of interacting particles, E_{total}, can be expressed as a sum of the following energy terms:

$$E_{\mathrm{total}} = E_{\mathrm{R}} + E_{\theta} + E_{\phi} + E_{\omega} + E_{\mathrm{vdw}} + E_{\mathrm{el}} \tag{1}$$

The Universal Force Field is a purely diagonal, harmonic force field. The bond stretching energy, E_{R}, is

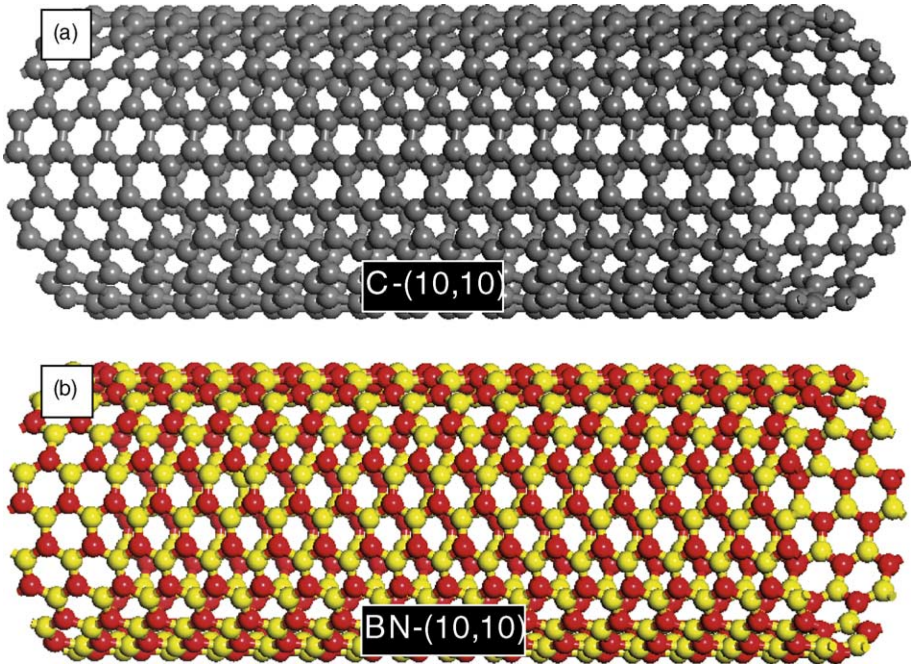

Fig. 2. Optimized atomic configurations in: (a) a carbon and (b) a boron-nitride (10, 10) arm-chair single-walled nanotube.

described by a harmonic term, the three-atom bond-angle bending term, E_θ, by a three-term Fourier cosine expansion, and the four-atom bond-torsion term, E_ϕ, and the inversion term, E_ω, by cosine-Fourier expansion terms. The van der Waals interaction term, E_{vdw}, is described by the Lennard–Jones potential, while the electrostatic interaction term is described by atomic monopoles and a screened Columbic term with a distance-dependent dielectric constant. In other words, the dielectric constant which is the relative permittivity of a medium increase with an increase in the distance between two atomic monopoles. Consequently, while electrostatic interactions between all monopoles are considered, the contributions arising from those separated by a large distance may be insignificant.

Within Forcite [7], the Universal Force Field are available for the entire periodic table of elements. The Universal Force Field potential is generally found to be moderately accurate for predicting geometries and conformational energy differences of organic molecules, main-group inorganics, and metal complexes. It is recommended for organometallic systems and other systems for which other force fields do not have parameters. Within Forcite, the Universal Force Field includes a parameter generator that calculates force field parameters in multi-component systems by combining parameters of the constituent elements. Thus, the force field parameters can be generated for any combination of atom types in the system.

3. Results and discussion

3.1. Selection of the radius of the SWNT fluid-flow conduits

The selection of the radius for a SWNT fluid-flow conduit will be generally based on the desired level of the fluid-flow rate and on the size and shape of the molecules of the fluid flowing through the SWNT conduit. In general, one would like to have at his/her disposal a large range of available radii of the SWNTs in order to match a variety of the fluid-flow/fluid-type requirements for the nano-valve. However, previous molecular mechanics studies, e.g. [8] have shown that carbon SWNTs can maintain a stable circular cross section only up to a radius of approximately 3 nm. In the (*n*, *n*) arm-chair family of carbon SWNTs, the carbon nanotube with the largest radius capable of retaining a stable circular cross section is found to be a (15, 15) SWNT. In the arm-chair carbon SWNTs with a larger radius, the circular cross section subjected to compression (in a direction normal to the nanotube axis) may collapse to a shape consisting of a central region in which the opposite walls of the nanotube are nearly parallel to each other and at a distance comparable to the basal plane spacing in graphite. The side portions of the cross section consist of nearly circular regions with a radius of approximately 0.75 nm which appears independent of the value of the chiral number $n > 15$ in the arm-chair SWNTs. In the arm-chair family of SWNTs between (16, 16) and (45, 45), either the circular or the collapsed cross sections may be stable depending on the magnitude of the compression applied to the SWNT with an initial circular cross section. At low levels of the compression, the circular cross section is stable while at large levels of the compression, the collapsed cross section is more stable. In the arm-chair family of SWNTs, nanotubes with the chirality index $n > 45$, only the collapsed cross section becomes stable.

To examine if boron-nitride SWNTs can offer a larger range of stable circular nanotube cross sections than the carbon SWNTs, a parallel molecular-level analysis is carried out of the stability of circular cross section in arm-chair family of both carbon and boron-nitride SWNTs when the initial circular cross section is compressed until the distance between the atoms of the opposite faces of the SWNT is at most twice the corresponding van der Waals interaction spacing. The results of this analysis are displayed in Fig. 3(a) and (b). The results displayed in Fig. 3(a) and (b) show that, at least within the family of arm-chair (*n*, *n*) nanotubes, both carbon and boron-nitride SWNTs may loose their circular cross section (if subjected to a sufficiently large compression) at an approximately equal maximum value of the nanotube radius of ca. 2.0 nm. This radius corresponds to the arm-chair nanotube chirality of (15, 15). This finding suggests that boron-nitride SWNTs do not extend the required range of nanotube radii with a stable circular cross section as needed in the nano-valve applications.

One may suggest that in place of SWNTs, double-walled nanotubes (DWNTs) can be used to stabilize the circular cross section. We carried out a simple analysis of the stability of carbon and boron-nitride DWNTs, and found that in both cases, a DWNT with the inner nanotube corresponding to a (21, 21) chirality can retain its circular cross section if the outerwall corresponding to a (24, 24) SWNT is used. While using DWNTs may be a promising way for increasing the range of nanotubes with a stable circular cross section, other aspects (e.g. the ability of the nanotube to recover its shape after bending-induced nanotube buckling, the magnitude of the strain energy at the onset of buckling, etc.) must be considered. A detailed analysis of the performance of DWNTs as fluid-flow conduits is beyond the scope of the present work.

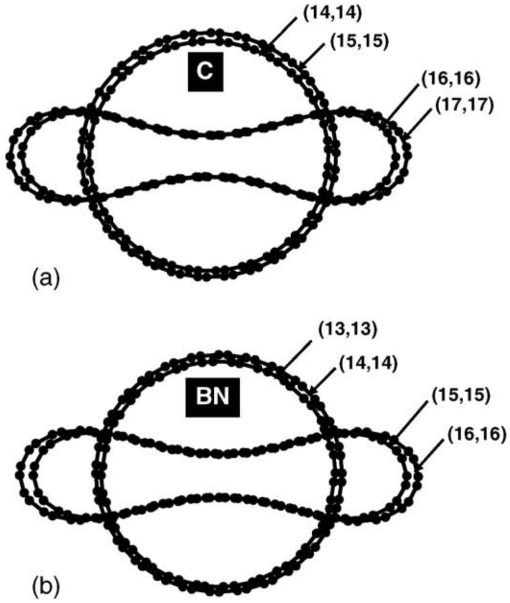

Fig. 3. Effect of the arm-chair nanotube radius on its stable cross section shape in the case of: (a) carbon and (b) boron-nitride SWNTs.

3.2. Strain energy in SWNTs at the point of buckling

As originally shown by Solares et al. [3] and recently confirmed by our combined molecular modeling/continuum finite element work [4], the strain energy in the SWNT conduit at the moment of buckling is a critical design parameter for the nano-valves controlling the minimum required width of the silicon cantilever nano-beam. That is, for a given length of the nano-valve, given length and height of its cantilever portion, a given radius of the SWNT, and a given surface concentration of the functionalizing monolayer molecules, the total energy available for the "*on/off*" operation of the nano-valve depends on the width of the silicon cantilever nano-beam. During the closing step of the nano-valve, the available energy is used to bend the silicon cantilever nano-beam and to bend the nanotube conduit (at least up to the point of buckling of the nanotube). If the strain energy stored in the SWNT at the point of buckling is reduced, one can use a silicon cantilever with a smaller width. This is advantageous, because it leads to a smaller overall size of the nano-valve and, in addition, can result in a higher reliability of the nano-valve operation.

To test if boron-nitride SWNTs are associated with a lower strain energy at the point of buckling, a parallel study of simple bending of a (17, 17) carbon and (17, 17) boron-nitride SWNTs is carried out using a Molecular Statics procedure. It should be noted that (17, 17) arm-chair SWNTs have the radius which falls in the ranges of nanotube radii within which both the circular and the collapsed cross sections of the nanotube may be stable depending on the level of compression. However, our nanotube bending analysis, described in more details in the later portion of this section, showed that both carbon and boron-nitride arm-chair SWNTs up to the chirality (24, 24) are capable of recovering their initial circular cross section ("*on*" position) from a locally buckled cross section ("*off*" position of the nano-valve). That is the reason that (17, 17) SWNT nanotubes in which $n = 17 > 15$ are used in the present work.

The SWNT bending is carried out by constraining the atoms at one end of the SWNT in all three directions and displacing the remaining atoms in the SWNT in accordance with a selected value of the bend curvature. Before the energy of the resulting configuration is minimized using the Molecular Statics procedure, the atoms at the other end of the SWNT are fixed at their displaced positions. Upon completion of the energy minimization procedure, the SWNT bend curvature and the strain energy (defined as a difference between the current potential energy and that in the initial straight SWNT) are recorded. The magnitude of the bend curvature is next increased and the aforementioned procedure repeated starting again from a straight SWNT. The results of this procedure for carbon and boron-nitride (17, 17) arm-chair SWNTs are shown in Fig. 4(a) and (b), respectively. In each case, the point of SWNT buckling is denoted as "*Buckling*". A comparison of the results shown in Fig. 4(a) and (b), suggest that the strain energy in the carbon and boron-nitride (17, 17) SWNTs at the point of buckling are quite comparable to each other, although the carbon SWNTs are associated with an approximately 10% lower level of such buckling strain energy.

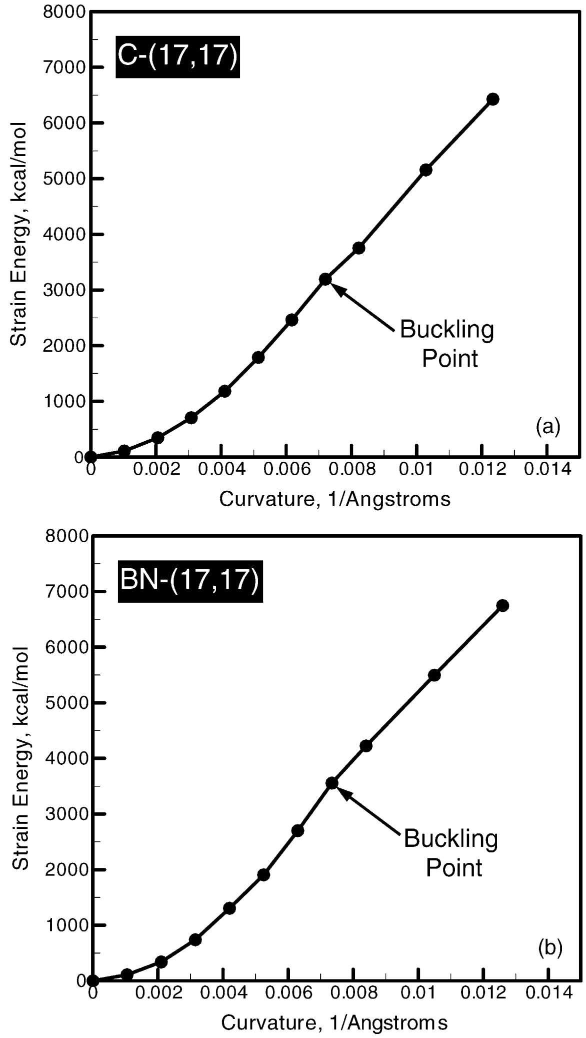

Fig. 4. Variations of the: (a) carbon and (b) boron-nitride (17, 17) arm-chair SWNT strain energies with the bending curvature.

This finding suggests that boron-nitride nanotubes, even from the standpoint of reducing the strain energy in the nanotube at the point of buckling, do not offer any advantage over their carbon-base counterparts. In fact, the boron-nitride SWNTs tend to perform not as well as the carbon SWNTs.

The results displayed in Fig. 4(a) and (b) enable determination of the classical Young's modulus of the carbon and boron-nitride SWNTs. Toward that end, the SWNT is treated as a hollow pipe with a wall thickness equal to the basal-plane spacing (0.337 nm) in graphite [9] (in the case of carbon SWNTs) and to the basal-plane spacing (0.333 nm) in hexagonal BN [9] (in the case of boron-nitride SWNTs). To determine the Young's modulus, E_Y, of carbon and boron-nitride SWNTs, the strain energy curves, E_{str}, displayed in Fig. 4(a) and (b) up to the point of buckling are next fitted to the following fractional relation:

$$E_{str} = \pi E_Y L \frac{r_0^4 - r_1^4}{8R^2} \tag{2}$$

where r_0 and r_1 are the outer and inner radii of the nanotube, L the nanotube length, while R is the bend radius of the nanotube.

This procedure yielded $E_Y = 1.49$ GPa for the carbon and $E_Y = 1.41$ GPa for the boron-nitride (17, 17) SWNTs. These results are very comparable to their counterparts (1.45 and 1.35 GPa, respectively) obtained through the first-principles quantum-mechanical calculations [10] suggesting that the Universal Force Field inter-atomic potentials used give a reasonably good description of the atomic interactions in the two types of nanotubes studied in the present work.

3.3. Radial breathing mode

Periodic oscillations of the SWNTs' radius (commonly referred to as the radial breathing mode) can be important for at least two practical aspects of SWNTs utilization: (a) the radial breading mode frequency is a function of the nanotube radius and chirality and since this frequency can be experimentally determined using Raman spectroscope, it can be used to identify the chirality of the nanotubes; (b) when used as fluid-flow conduits in the nano-valve applications, the compliance of SWNTs relative to the radial breathing mode is a measure of the ease at which the nanotube allows the passage of molecules whose size is comparable to the internal diameter of the nanotube. In other words, if the nanotube is more compliant, it may facilitate the flow of molecules through it.

To determine the relative compliance of carbon and boron-nitride SWNTs, the atomic configuration of an infinitely long SWNT with a given chirality is first optimized and the resulting equilibrium potential energy determined. Then the radius of the nanotube is increased/decreased in increments of 0.03–0.04 Å so that the total change in the nanotube radius does not exceed 1%. This procedure ensures that the energy of a SWNT, analyzed as a radial oscillator, is still within the harmonic region. For each non-equilibrium configuration of the SWNT, the potential energy is computed and subtracted from the equilibrium potential energy to obtain the resulting radial breathing mode potential energy increase. The results of this procedure for the carbon and boron-nitride (17, 17) arm-chair SWNTs are shown as solid circles in Fig. 5(a) and (b), respectively. These results are next fitted using a relationship $\Delta E^{RBM} = k_{RBM}\Delta R^2$, where ΔE_{str} is the potential energy change, RMB is used to denote the radial breathing mode, k_{RMB} is the corresponding harmonic force constant and ΔR a change in the SWNT radius relative to its equilibrium value. The k_{RMB} parameter is a measure of the nanotube stiffness with respect to the radial breathing mode. Since the values of this parameter (per one unit cell of the SWNT) 296.7 and 297.8 J/m^2 for carbon and boron-nitride arm-chair (17, 17) SWNTs are practically identical, one can conclude that boron-nitride SWNTs are not expected to be significantly more efficient than their carbon-base counterparts in facilitating the flow of molecules through it.

The results displayed in Fig. 5(a) and (b) are next used within the frozen-phonon formalism [10] to compute the frequency of the radial breathing mode in the carbon and boron-nitride arm-chair (17, 17) SWNTs. The values obtained (111.4 and 111.2 cm^{-1}), are in a reasonable good agreement with their first-principles quantum-mechanical counterparts (110.0 and 103.7 cm^{-1}) reported recently by Akdim and Pachter [10]. This finding suggests that the Universal Force Field used gives a realistic representation for the inter-atomic interactions within the carbon and boron-nitride SWNTs.

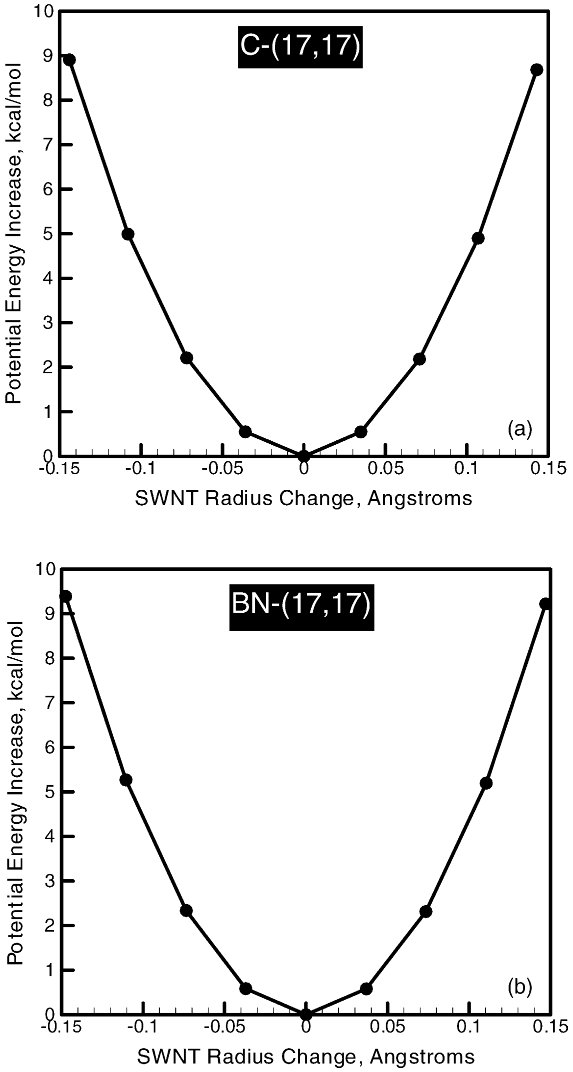

Fig. 5. Variation of the potential energy with a change in the nanotube radius in: (a) carbon and (b) boron-nitride arm-chair (17, 17) SWNTs.

3.4. Fluid-flow internal drag

For a nanotube of a given radius and chirality, a given choice of the fluid flowing through the nanotube conduit, given pressure/concentration differences across the length of the nanotube, the flow rate of the fluid through the nanotube will be affected by the extent of fluid-molecule/nanotube internal wall interactions. If such interactions are significant and of an attractive nature, the fluid molecules would experience a drag resistance which would decrease its rate of their flow through the SWNT conduit. In principle, one would prefer strong repulsive interactions between the fluid molecules and the internal wall of the nanotubes conduit. While in principle the character (repulsive/attractive) of the interaction may vary from one type of molecule to the other, we tried to see if in the case of the most common fluid (water), the two types of SWNTs, carbon and boron-nitride nanotubes, show any significant differences. Toward that end, a single molecule of water is placed inside a (17, 17) carbon and boron-nitride SWNT of length approximately 2.45 nm. The corresponding optimized atomic configurations are displayed in Fig. 6(a) and (b). The binding energy between the H_2O molecule and the SWNT is computed by subtracting the energy of the SWNT containing a H_2O molecule from the sum of energies of the isolated SWNT and an isolated H_2O molecule. The results of this procedure yielded the binding energies of 3.57 and 3.49 kcal/mol for the carbon and boron-nitride SWNTs, respectively. This finding suggests that, at least in the case of water, the molecular-level drag may be lower in the case of boron-nitride SWNTs. However, this level of drag reduction is quite small (by approximately 2%) judging by the values of the nanotube/molecule binding energy obtained.

The same procedure was repeated but considering the flow of ammonia (CH_3) and methane (CH_4) molecules through a (17, 17) carbon and boron-nitride SWNTs. The results obtained show that the binding energy for these molecules to the (17, 17) carbon SWNTs differ only by about 0.5% from their binding energies to the (17, 17) boron-nitride SWNTs. All these results further suggest that the level of drag experience by these molecules during their flow through carbon and boron-nitride nanotubes are quite comparable.

3.5. Overall comparison of boron-nitride and carbon SWNTs

The results obtained in the present work indicate that boron-nitride SWNTs most likely do not offer any significant functional advantage when used in the nano-valve applications. It must be noted, however, that the present findings are based on the use of molecular-level simulations and the Universal Force Field inter-atomic potential. While the agreement between the current results for the Young's modulus and for the radial

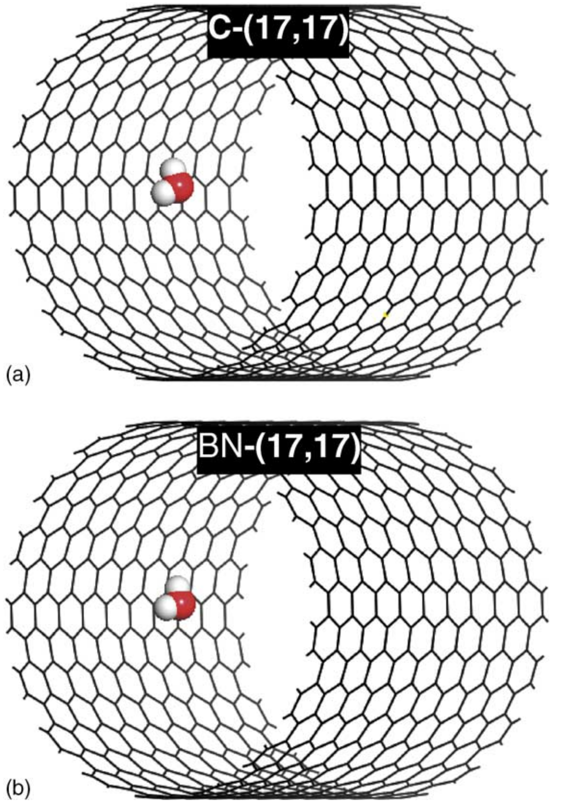

Fig. 6. Optimized atomic configurations in: (a) carbon and (b) boron-nitride arm-chair (17, 17) SWNTs contain a single H_2O molecule.

breathing mode frequency and their first-principles quantum-mechanical counterparts is quite good, the quantum-mechanical calculations are inherently more accurate and will be used in our future work to validate some of the key results obtained in the present work.

4. Conclusions

Based on the results obtained in the present work, the following main conclusions can be drawn:

1. Based on the molecular-level calculations, boron-nitride single-walled nanotubes do not seem to offer any significant functional advantage over their carbon-based counterparts for use as the fluid-flow conduits in nano-valve applications.
2. Double-walled (carbon or boron-nitride) nanotubes appear to offer a possibility for expanding the range of nanotube radii within which the nanotubes are able to retain the circular cross section. Since the existence of a wide range of nanotube radii with a stable circular cross section is an important design requirement for the nanotube conduits, double-walled nanotube should be further studied.
3. The Universal Force Field inter-atomic potential used appear to describe quite realistically the atomic interactions within carbon and boron-nitride nanotubes since some of the structural properties of the nanotube predicted using this potential are in fairly good agreement with their first-principles quantum-mechanical counterparts.

Acknowledgements

The material presented in this paper is based on work supported by the U.S. Army Grant Number DAAD19-01-1-0661. The authors are indebted to Drs. Bonnie Gersten, Fred Stanton and William DeRosset of ARL for the support and a continuing interest in the present work.

References

[1] R. Berger, E. Delamarche, H.P. Lang, Ch. Gerber, J.K. Gimzewski, E. Meyer, H.-J. Güntherodt, Surface stress in the self-assembly of alkanethiols on gold, Science 276 (1997) 2021–2024.

[2] R. Berger, E. Delamarche, H.P. Lang, Ch. Gerber, J.K. Gimzewski, E. Meyer, H.-J. Güntherodt, Surface stress in the self-assembly of alkanethiols on gold probed by a force microscopy technique, Appl. Phys. A 66 (1998) S55–S59.

[3] S. Solares, M. Blanco, W.A. Goddard III, Design of a nano-mechanical fluid control valve based on functionalized silicon cantilevers: coupling molecular mechanics and classical engineering design. http://www.wag.caltech.edu/nanovalve/.

[4] M. Grujicic, G. Cao, W.N. Roy, Finite element analysis based design of a fluid-flow control nano-valve, J. Mater. Sci., submitted for publication.

[5] MATLAB, The Language of Technical Computing, 6th ed. The MathWorks Inc., Natick, MA, 2002, pp. 17–22.

[6] http://www.accelrys.com/mstudio/msmodeling/forcite.html.

[7] A.K. Rappe, C.J. Casewit, K.S. Colwell, W.A. Goddard III, W.M. Skiff, UFF, a full periodic table force field for molecular mechanics and molecular dynamics simulations, J. Am. Chem. Soc. 114 (1992) 10024–10035.

[8] G. Gao, T. Cagin, W.A. Goddard III, Energetics, structure, mechanical and vibrational properties of single-walled carbon nanotubes, Nanotechnology 9 (1998) 184–191.

[9] C. Oshima, A. Nagashima, J. Phys. Condens. Matter 9 (1997) 1.

[10] B. Akdim, R. Pachter, Phys. Rev. B 67 (2003) 245404.