Piezoelectric and elastic properties of multiwall boron-nitride nanotubes and their fibers: A molecular dynamics study

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ABSTRACT

Piezoelectric and elastic properties of multiwall boron-nitride nanotubes are studied using a classical molecular dynamics model with an incorporated strain-dependent dipole potential energy term. The results are applied to predict the piezoelectric and elastic properties of a boron-nitride nanotubes fiber with experimentally obtained diameter and wall number distribution of the nanotubes synthesized by high-temperature pressure methods. Nanotubes of $(m, 0)$-type (zig-zag nanotubes) of up to 10 wall layers and up to 7 nm in diameter are simulated in tension along the tube axis. While the tensile stiffness of all of the simulated nanotubes increases linearly with their radius and the number of wall layers, a substantial difference in the piezoelectric response is found between nanotubes of even and odd number of wall layers due to the particular stacking sequence of the boron-nitride layers. The piezoelectric polarization per unit length of odd-layer boron-nitride nanotubes *increases* linearly with the tube radius, but *decreases* with the number of layers. By contrast, the piezoelectric polarization of even-layer nanotubes is *independent* of the radius, but *increases* linearly with the number of layers. Analytical expressions for the multiwall boron-nitride nanotubes stiffness and piezoelectric coefficients are provided for use in continuum mechanics finite-element models.

1. Introduction

One attractive feature of boron nitride nanotubes (BNNTs) [1,2], which differentiates them from their pure carbon structural counterpart, carbon nanotubes (CNTs), is their intrinsic piezoelectricity [3–7]. This is due to the partially ionic characteristic of the boron (B)–nitrogen (N) bond, compared to the purely covalent C—C bond in CNTs. BNNTs were also shown to possess strong electrostrictive [8] and flexoelectric [9] properties. In combination with their high mechanical modulus and strength matching those of CNT [10–19], superior high-temperature oxidation resistance [2], and enhanced radiation shielding against neutrons [8,9,20], BNNTs are very attractive materials for multifunctional applications in extreme environments.

Analytical and simulation studies of the piezoelectric behavior of BNNTs have been mostly focused on single-wall BNNTs (SW-BNNTs) [3–7,21–24], while synthesized BNNTs are predominantly

multi-wall BNNTs (MW-BNNTs)[1] [1,8,25]. A comparison between single- and double-wall BNNTs was performed in a series of molecular dynamics (MD) simulations to study their vibrational behavior [26,27], and their structural stability [28]. It is argued [1] that the partially ionic characteristic of the B—N bond in the hexagonal boron nitride (hBN) structure of BNNT tends to stabilize the formation of double-wall (DW-) and MW-BNNTs by favoring an alternating B-over-N and N-over-B placement of atoms between two adjacent hBN layers (known as AA'-stacking) [29,30]. The alternate stacking of the hBN layers reverses the dipole direction in each consecutive layer. As a result, as noted in a recent MD study [31], consecutive hBN layers polarize in opposite directions and partially cancel each other to decrease the overall piezoelectric effect in MW-BNNTs. This cancellation effect is more pronounced in BNNTs with even number of layers than with odd number of layers, and is a very interesting feature unique only for MW-BNNTs.

The goal of this work is to investigate in detail the elastic and piezoelectric properties of MW-BNNTs utilizing a recently

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[1] In addition to SW-, DW-, and MW-BNNT for a single-, double-, and multi-wall BNNT, the general abbreviation LW-BNNTs will be used throughout the paper, where L = 1, 2, 3, … indicates the number of layers in the BNNT wall.

proposed method [21] for incorporating piezoelectric behavior into an empirical interatomic potential of Tersoff type for modeling hBN structures by MD simulations. The method was shown to accurately represent the piezoelectric properties of SW-BNNTs as calculated by first-principle calculations [4]. At the same time, the much lower computational cost of the MD technique allows the simulation of large structures, such as MW-BNNTs containing several tens of thousands of atoms. MW-BNNTs of (m, 0)-crystallographic indices [32] (zig-zag nanotubes) are chosen for this study. The (m, 0)-type nanotubes exhibit piezoelectric polarization along their axis when stretched, which is the simplest mode of deformation to simulate, and provides the most accurate results. Analytical representation of the simulation results is also given, based on the analytical expressions for the tensile stiffness of MW-BNNTs, derived by Song et al. [33], and on the extension of the piezoelectric model for SW-BNNTs presented earlier [21]. This analytical representation allows the prediction of the piezoelectric behavior of MW-BNNTs of arbitrary number of layers and of any given radius. While the study is focused on the zig-zag type of nanotubes, which exhibits highest piezoelectric polarization along their axis when stretched among all chiral types [4], the results can be extended in a straightforward way to include BNNTs of general chirality.

The analytical expressions derived from the MD model were applied to predict the stiffness and the piezoelectric coefficients of a fiber consisting of 1000 BNNTs with experimentally obtained diameter and wall number distribution. The BNNTs were synthesized by high-temperature pressure (HTP) methods [25,34] and their structural characterization was performed using high resolution transmission electron microscopy (HRTEM) in combination with atomic force microscopy (AFM).

This paper is constructed as follows. The simulation model for a piezoelectric MW-BNNT is described in Section 2. Section 3 presents the results, first, for the elastic properties of MW-BNNTs, and then for the direct and converse piezoelectric effect in MW-BNNTs. The properties of individual BNNT fibers are considered in Section 4. A conclusion is given in Section 5.

2. Molecular dynamics model for piezoelectric multi-wall BNNTs

2.1. Piezoelectric energy upgrade of the Tersoff potential for a hexagonal BN layer structure

The empirical atomistic piezoelectric model for reproducing the elasto-mechanical properties of hBN layer structures in this study implements a Tersoff type of interatomic potential parameterized by Sevik et al. [35]. The potential is targeted to reproduce closely the structural, mechanical, and vibrational properties of hBN by fitting to first-principle *ab initio* calculations [35]. The thermomechanical properties of this potential are studied in detail by Singh et al. [36].

The piezoelectric behavior of the hBN lattice is simulated [21] by introducing a dipole moment, p_{BN}, to each individual B—N bond. The electrostatic potential created by the dipole moment is added to the Tersoff potential. The direction of the dipole vector follows the direction of the B—N bond polarity (from N to B), and the dipole magnitude is defined as [21]

$$p_{BN} = p_0 \left[\frac{r_{BN} - r_0}{r_0} + t_\theta \sum_{i=1}^{4} \left(\frac{1}{2} + \cos\theta_i \right) \right], \tag{1}$$

where p_0 and t_θ are fitting parameters, r_{BN} and r_0 are the current and the equilibrium length of the B—N bond, and $\theta_{i=1,\ldots4}$ are the bond angles between the B—N bond and the four neighboring bonds in the hBN arrangement. The suggested constitutive relation in Eq.

(1) consists of two terms that counteract each other to produce a polarization proportional to the deviation of the crystal lattice from the hexagonal symmetry. The rationale behind this form comes from theoretical [3] and *ab initio* [5] studies, which explains the piezoelectric effect in BNNTs as a counteraction between electronic and ionic spontaneous polarizations that cancel exactly unless the symmetry of the hBN lattice is broken by inter-tube interactions or elastic distortions. It was shown [21] that Eq. (1) leads to a piezoelectric tensor that satisfies the 3m symmetry of the hBN lattice with coefficients expressed as

$$e_{xxx} = -e_{xyy} = -e_{yxy} = -e_{yyx} = \frac{p_0}{2\sqrt{3}r_0^2}[(1+A) - 3t_\theta(1-A)] \tag{2}$$

where the values of r_0 and A are defined through the interatomic potential and its first and second spatial derivatives at equilibrium [33]. The constant A relates to the magnitude of a shift vector, δ, between the B and N sub-lattices of an hBN plane under strain ε, which was introduced in Ref. [33] and expressed as

$$\delta_\lambda = \frac{2}{3} A \varepsilon_{\alpha\beta} \sum_{i=1}^{3} n_\alpha^{(i)} n_\beta^{(i)} n_\lambda^{(i)}, \tag{3}$$

where the summation is over the three neighboring (i) atoms of bond directions $\boldsymbol{n}^{(i)}$. The subscripts, α, β, and λ, express the Cartesian components of the vector quantities in Eq. (3).

Using Eq. (2) [21], the piezoelectric coefficients per unit cell area can be expressed in electron charges per nanometer (e/nm) if p_0 is in (e × nm), and r_0 is in units of nm. To convert to the standard piezoelectric coefficients per unit volume, one has to divide Eq. (2) by the interlayer spacing h.

The tube polarization per unit cell is given as

$$p_{cell} = e_{11}\varepsilon_s + e_{14}\varepsilon_t \tag{4a}$$

where ε_s and ε_t are the strain in stretch along, and in torsion around the tube axis, respectively. The coefficients, e_{11} and e_{14}, are the nanotube piezoelectric coefficients in stretch and torsion, respectively, and are related to the hBN coefficients in Eq. (2), and to the chiral angle, φ, as

$$\begin{vmatrix} e_{11} = e_{xxx}(1+v)\cos 3\varphi \\ e_{14} = e_{yxy}\sin 3\varphi \end{vmatrix}. \tag{4b}$$

Eq. (2) can be used to adjust the fitting parameters p_0 and t_θ to reproduce the piezoelectric constants of a flat hBN sheet as calculated from first-principles for any given 3-body interatomic potential (not necessarily of Tersoff type). Eq. (2) alone is not enough to define both of the fitting parameters. Additional condition for their determination is to reproduce the increase of the piezoelectric coefficient of a SW-BNNT with the decrease of the nanotube radius due to curvature effects, as calculated from first principles [4]. A fitting method such as the least-square fit, could be used for this purpose. The fit, together with the values of r_0 and A in Eq. (2), depends on the choice of the interatomic potential for a neutral BNNT. In Ref. [21], p_0 and t_θ were given for the case of two previously reported and widely used potentials: by Albe et al. [37], and by Sekkal et al. [38]. The fitted values of p_0 and t_θ for the Sevik et al. potential [35] used in this work are presented in Table 1, together with r_0, A, Poisson's ratio, v, and the Young's modulus, Y. The fit reproduces the e_{xxx} coefficient in Eq. (2) as calculated by Sai and Mele [4].

2.2. Lennard-Jones potential for inter-wall interactions

An essential part of the MW-BNNT model is the interwall interaction between the nanotube layers. This work uses a Lennard-Jones (L-J) type of potential to model this interaction, where the potential energy $U_{\alpha\beta}(r)$ between two atoms of chemical type α or