Interwall interaction and elastic properties of carbon nanotubes

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The physical properties of a wide range of nonchiral single-walled carbon nanotubes (SWNT) and double-walled carbon nanotubes (DWNT) with nonchiral commensurate walls are studied. Equilibrium structures of SWNT and DWNT, as well as the interwall interaction energies of DWNT, are computed using a local density approximation within density functional theory with periodic boundary conditions and Gaussian-type orbitals. Based on *ab initio* structural characteristics, elastic properties of SWNT and DWNT are calculated. Relative motion of the walls of DWNT with different radii and chiralities is explored using *ab initio* results for the interwall interaction energies. Relative positions of nonchiral commensurate walls of DWNT which correspond to extrema of the interwall interaction energy are derived. For DWNT with incompatible rotational symmetries of the walls, the possibility of orientational melting is predicted. *Ab initio* values of barriers to relative rotation and sliding of the walls of DWNT are used to calculate threshold forces. For nonreversible telescopic extension of the walls, maximum overlap of the walls for which threshold forces are greater than capillary forces is estimated. A method for selecting pairs of nonchiral commensurate walls in multiwalled carbon nanotubes (MWNT) is proposed.

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I. INTRODUCTION

Carbon nanotubes are promising material for potential components of future nanoelectronic and nanomechanical devices.[1–4] Weak interwall interactions within MWNT provide perfect bearing for possible novel nanodevices based on relative sliding, rotation, or screwlike motion of the walls.[5–10] Theoretical study of the interwall interaction and relative motion of the walls in carbon nanotubes holds the key to success of these applications.

Neglecting their structure at the ends, which can be either open or closed, carbon nanotubes are single or multiple layers of a cylinder rolled up from graphene sheets. Only one parameter is needed to fully determine the structure of the middle section of a SWNT: the chirality index (n, m) which corresponds to a two-dimensional lattice vector $\mathbf{c}=n\mathbf{a}_1+m\mathbf{a}_2$, where $\mathbf{a}_1$ and $\mathbf{a}_2$ are equivalent lattice vectors of graphene.[11] A segment defined by the vector $\mathbf{c}$ becomes the circumference of cylindrical surface of a nanotube wall which can be well modeled by an infinite tube, where periodic boundary conditions are applicable.[12] Two types of SWNT characterized by the chirality index of (n, n) and $(n, 0)$ have a simple translational symmetry, and these are referred to as armchair and zigzag nanotubes forming different pattern of hexagons in circumference. DWNT consist of two coaxially arranged SWNT with the interwall distance close to the graphite interlayer distance of 3.335 Å.[13]

The walls of DWNT are commensurate if the ratio of the lengths of their unit cells is a rational fraction. In this case, a DWNT is a quasi-one-dimensional crystal with the length of unit cell equal to the lowest common factor of the lengths of unit cells of constituent SWNT. Lack of commensurability between the neighboring nested SWNT implies a dramatic weakening of the corrugation in the interwall interaction potential.[14] Barriers to the relative motion of the commensurate walls of sufficiently long DWNT are proportional to the nanotube length: $\Delta U=\Delta U_c N_c$, where ΔU_c is the barrier per unit cell and N_c is the number of unit cells in the nanotube. Conceivably, there is a possibility of fabrication of DWNT with commensurate walls with a custom-ordered value of barriers to relative motion of the walls. Therefore, these DWNT can be considered as potential components in nanodevices for which a precise control of motion of the walls is required. In contrast to the commensurate case, barriers to relative motion of incommensurate walls of DWNT do not increase with the nanotube length, but fluctuate near the average value.[5,6,15] Such incommensurate systems, even if they contain thousands of carbon atoms, have barriers to the relative motion of the walls comparable to those of a single unit cell. These systems hold promise for application in mechanical elements, providing perfect bearings for possible nanodevices.[7–9,16]

The most commonly used convention employs the term "commensurate walls" for the walls which are commensurate with their structures obtained by graphene plane mapping on a cylindrical surface with the bond lengths kept constant (see, for example, Refs. 14, 15, and 17–20). Otherwise, the walls are defined as incommensurate. However, the bond lengths of the walls of nanotubes slightly differ from those in graphite, and for this reason the lengths of unit cells of isolated commensurate walls are also slightly different. Interwall interactions in DWNT lead to the contraction (or expan-

sion) of the walls and consequent change in the lengths of their unit cells. The lengths of unit cells of constituent commensurate walls may become equal as a result of the interwall interaction (commensurate phase of DWNT) or the walls of DWNT may have a periodic structure of alternating near commensurate regions and incommensurability defects (incommensurate phase of DWNT).

The majority of DWNT with commensurate walls have been studied with semiempirical pairwise potentials for the interaction between atoms of neighboring walls.[14–18] These studies detect the qualitative difference between the relative motion of chiral and nonchiral commensurate walls of DWNT. The motion of the walls of DWNT is determined by a potential surface of the interwall interaction energy as a function of relative displacement of the walls along the DWNT axis and angle of their relative rotation. For DWNT with chiral commensurate walls, the interwall interaction energy surface is extremely flat and corrugations of the surface are smaller than the accuracy of calculations.[17,18] The density functional theory (DFT) calculations of Ref. 21 confirm this qualitative result using the (8,2)@(16,4) DWNT as an example. In this case, the reason for the nearly perfect flatness of the interwall interaction energy surface is a very high density of equivalent minima on the surface attributed to the incompatibility of helical symmetries of the chiral walls.[15] For DWNT with nonchiral commensurate walls, semiempirical calculations show that there always exists an experimentally observable barrier to relative sliding of the walls along the DWNT axis. Only few such DWNT also have the experimentally observable barrier to relative rotation of the walls. These DWNT have compatible rotational symmetries of the inner and outer walls.[17,18] For this reason, DWNT with nonchiral commensurate walls and incompatible rotational symmetries of the walls were proposed as possible rotational nanobearings.[18]

It has been shown in Ref. 21 that the use of semiempirical interatomic potentials fitted to graphite properties is insufficient for quantitative estimations of barriers to the relative motion of the walls for nanotubes with small radii. Barriers to the relative rotation and sliding of the walls calculated for the (5,5)@(10,10) DWNT with the Lennard-Jones interatomic potential[16,18] underestimate the *ab initio* results[21,22] by about an order of magnitude. Barriers obtained using the Kolmogorov-Crespi semiempirical potential[17] are significantly higher than *ab initio* results. The positions of the minima of the interwall interaction energy surface of the (5,5)@(10,10) DWNT calculated using the Lennard-Jones potential[19] are shifted in both sliding displacement and rotation angle by half a period in comparison to the *ab initio* results.[21,22] The presence of two equivalent extrema per unit cell in the interaction energy surface of the (5,5)@(10,10) DWNT found by the tight-binding method[23] contradicts the anticipated topological theorem.[19] For the (5,5)@(10,10) DWNT, the results of Ref. 21 obtained using the local density approximation (LDA) within DFT give correct positions of extrema in the interaction energy surface.

The standard DFT, based on (LDA) or semilocal generalized-gradient approximations (GGA) of electron correlations, cannot capture the key long-range van der Waals or dispersion interactions, which are extremely important in graphitic systems. As a result, neither of the standard density functionals can provide consistent and accurate results for such systems. A successful DFT approach has to account for both the strong local intralayer bonds between the atoms and weak nonlocal van der Waals interlayer interactions. Much progress has been recently made to finding solution to this nontrivial problem. New modified density functionals which encompass nonlocal correlations between the electrons have been proposed[24–28] and thus should successfully capture the nonlocal nature of van der Waals interactions and test the adequacy of LDA approach. .

Another well-established local density functional (LDF) approach is based on the fitting-function technique of Boettger, which employs the all-electron full-potential liner combinations of Gaussian-type orbitals (GTO).[29] The underlying GTO fitting-function technique in LDF calculations is successfully used in the solid-state community to calculate the energetics,[30] electronic structure,[31] equations of state, and elastic constants[32] for crystalline graphite, fullerenes, and carbon nanotubes. For example, the all-electron LDF calculations of Ref. 30 give the following values for basal-plane binding energy of graphite: 80 meV/atom for the Perdew-Zunger LDF exchange-correlation functional and 90 meV/atom for the Heden-Lundqvist LDF functional. However, these values remain roughly a factor of 2 larger than the experimental values of 43 meV/atom (Ref. 33) and 35 ± 10 meV/atom (Ref. 34).

In present study, we use the standard Perdew-Wang exchange-correlation functional[35] together with the Gaussian basis set for carbon which has been optimised for graphite. Such a LDA-DFT-based approach has been used in Ref. 36 and reproduced very well experimental values for the basal-plane binding energy of graphite. The LDA-DFT binding energy of 35 meV/atom reported in Ref. 36 is in excellent agreement with the experimental value of Ref. 34. The applicability of this approach is further endorsed by recent quantitative studies of properties highly sensitive to the interlayer interaction, such as the elastic and electronic properties of graphite. For example, the LDA-DFT C_{44} elastic constant for basal shear is computed to be 4.20 GPa,[36] whereas experiment[37] gives 5.05 ± 0.35 GPa.

In order to explore the experimental range of the interwall distances in DWNT varying from 3.3 to 4.5 Å, the LDA-DFT study has been extended to a set of DWNT with nonchiral zigzag $(n,0)$ and armchair (n,n) commensurate walls of compatible and incompatible rotational symmetries and with different interwall distances. *Ab initio* equilibrium structures and elastic properties of DWNT have been obtained taking into account compression and expansion of the walls due to their interaction. These were subsequently used to derive analytically properties of DWNT which characterize relative motion of their walls. Possible relative positions of the nonchiral commensurate walls of DWNT which correspond to extrema of the interwall interaction energy have been derived. A method for selecting pairs of nonchiral commensurate walls in MWNT, based on measuring the maximum overlap of the walls for which threshold forces are greater than capillary forces, has been proposed. For DWNT with incompatible rotational symmetries of the walls, the possibility of orientational melting—i.e., rotation of the walls caused

by an increase of temperature—has been predicted. This prediction is based on *ab initio* results, which give extremely small barriers to the relative rotation of the walls of such DWNT.

The paper is organized as follows. Sections II–IV present *ab initio* calculations of the physical properties of a wide range of nonchiral SWNT and DWNT with nonchiral commensurate walls. Equilibrium structures of SWNT and elastic properties of SWNT and DWNT are given in Sec. II. Interwall interaction energies, relative positions of the walls corresponding to the energy minimum (equilibrium structure), and barriers to relative sliding and rotation of the walls are evaluated in Sec. III. Section IV gives the results of calculations of the threshold forces for the relative sliding and rotation of the walls and maximum overlap of the inner and outer walls for which the controlled reversible telescoping can be achieved (the pulled-out wall could be completely pushed back by capillary forces restoring a DWNT to its original retracted condition). Our conclusions are summarized in Sec. V.

II. EQUILIBRIUM STRUCTURE AND ELASTIC BEHAVIOR

The properties of nonchiral SWNT and DWNT have been studied using the AIMPRO *ab initio* code.[38] Within the AIMPRO code, the localized orbitals are taken to be Cartesian Gaussian functions. Basis sets are labeled by the orbital symbols. Each symbol stands for a radial Gaussian of a given exponent giving rise to basis functions which are a product of this radial Gaussian with spherical harmonics which have angular momenta from 0 (*s* orbitals) to the value given by the letter (1 for *p*, 2 for *d*, etc.). In this work, the *pdddp* (in order of increasing value of exponents) basis set is used as it gives the lowest total energies for both SWNT and DWNT. Integration over the Brillouin zone is approximated using the Monkhorst-Pack method[39] with 18 *k*-point sampling for DWNT with armchair walls and 15 *k*-point sampling for DWNT with zigzag walls.

In calculations of the equilibrium structure of SWNT's, the lattice parameter t (translational length of the unit cell) is optimized to obtain the value t_s which corresponds to the equilibrium structure. Total energy U_{tot} and structural characteristics are computed *ab initio* for 10–15 fixed values of the lattice parameter t (different values of t correspond to different "quasiequilibrium" bond lengths). The dependence of the total energy on the length of the unit cell is then interpolated using Hooke's law

$$U_{tot}(t) = U_s(t_s) + \frac{\mu(t-t_s)^2}{2}, \tag{1}$$

where U_s is the total energy of the equilibrium structure and μ is the elastic constant of SWNT with length of the unit cell equal to t_s. The values of U_s, t_s, and μ are calculated using the least-squares technique. The total energies U_s of the equilibrium structure calculated using elastic theory are in excellent quantitative agreement with the *ab initio* LDA-DFT total energies obtained with the AIMPRO code. For example, elastic theory gives $U_s = 114.1435$ a.u. for the (5,5) SWNT, $U_s = 228.4791$ a.u. for the (10,10) SWNT, and $U_s = 456.9884$ a.u. for the (20,0) SWNT, whereas the corresponding AIMPRO values are 114.1463 a.u., 228.4793 a.u., and 456.9887 a.u.

Young's modulus of a SWNT is obtained as follows:

$$E_s = \frac{\mu t_s}{2\pi R w}, \tag{2}$$

where R is the radius of a SWNT which corresponds to the equilibrium structure and $w = 3.4$ Å is the effective thickness of the wall.[40–45] The characteristics describing the equilibrium structure of SWNT and their elastic properties are given in Table I.

The following conclusions can be reached on the radial dependence of the structural parameters of the nonchiral SWNT.

(1) For both armchair and zigzag SWNT, the length of the unit cell increases as the radius is decreased. This result differs from the DFT calculations of Refs. 46 and 47 which show significant fluctuations of the length of the unit cell as a function of the radius.

(2) For both armchair and zigzag SWNT, two nonequivalent bond lengths are identified: those which are oriented around the belt of the tube (referred to as b_1) and those parallel to the tube axis (referred to as b_2). For the armchair (n, n) SWNT with $n=4-7$, both b_1 and b_2 bond lengths increase as the radius is reduced, in agreement with results reported in Refs. 41,46,47; similarly to Refs. 46,47, the dependence of the nonequivalent bond lengths on the radius is not monotonic if $n=10-12$. For $n=4-7$, the difference $\Delta b = b_1 - b_2$ is several times higher than that predicted for $n = 10-12$. This result agrees qualitatively with Refs. 46,47; however, we obtain considerably smaller values of Δb. For zigzag SWNT, the b_2 bond length increases as the radius is reduced remaining greater in magnitude than the b_1. The difference Δb also grows with decreasing radius, and it is several times greater for the zigzag SWNT than the armchair SWNT with similar radius. These trends are in agreement with Refs. 46–48.

The values of Young's modulus of SWNT are tabulated in Table I and compared with the literature data. The results obtained using formula (2) coincide within 10% with the best values of Young's moduli calculated by the Hartree-Fock method,[40] plane-wave LDA (Ref. 49) and GGA (Ref. 42) DFT, and tight-binding method.[43,49] The calculated values of the equilibrium translational length t_s of the unit cell differ in third decimal places both for the armchair and zigzag SWNT of different radii. Evidently, two armchair or two zigzag walls with slightly different lengths of the unit cell cannot be commensurate. However, if such walls comprise a DWNT, they can become commensurate after compression or expansion due to interactions.

For DWNT, we derive the common equilibrium translational length t_d of the unit cell as

$$t_d = \frac{t_s^1 \mu_1 + t_s^2 \mu_2}{\mu_1 + \mu_2}, \tag{3}$$

where t_s^1, μ_1 and t_s^2, μ_2 are translational length of the unit cell and elastic constant of the inner and outer walls of DWNT.

TABLE I. Structural characteristics and elastic properties of the walls of SWNT: R (in Å) is the radius of the wall, t_s (in Å) is the translational length of the unit cell, b_1 and b_2 (in Å) are two nonequivalent bond lengths of the nonchiral walls, and E_s (in TPa) is Young's modulus.

Wall	R	t_s	b_1	b_2	E_s	E_s
(4,4)	2.737	2.4498	1.4182±0.0001	1.4163±0.0001	1.038±0.001	0.97[a]
(5,5)	3.408	2.4434	1.4135±0.0001	1.4161±0.0001	1.030±0.006	0.95[a],0.96[b],1.06[c]
(6,6)	4.071	2.4424	1.4123±0.0001	1.4137±0.0001	1.093±0.003	0.98[a],1.09[d],1.22[d]
(7,7)	4.738	2.4423	1.4118±0.0002	1.4124±0.0001	1.099±0.002	
(10,10)	6.748	2.4420	1.4105±0.0002	1.4103±0.0002	1.100±0.003	0.92[a],0.98[e],1.24[d]
(11,11)	7.421	2.4420	1.4108±0.0001	1.4100±0.0002	1.100±0.003	
(12,12)	8.091	2.4419	1.4109±0.0001	1.4109±0.0001	1.098±0.004	
(9,0)	3.532	4.2350	1.4173±0.0002	1.4080±0.0001	1.036±0.001	1.14[c]
(10,0)	3.916	4.2331	1.4149±0.0001	1.4087±0.0001	1.081±0.002	0.94[b],1.05[a],1.22[d]
(18,0)	7.011	4.2301	1.4113±0.0001	1.4091±0.0001	1.074±0.003	
(20,0)	7.790	4.2293	1.4112±0.0001	1.4088±0.0001	1.088±0.002	1.26[d]

[a]Reference 41.
[b]Reference 42.
[c]Reference 40.
[d]Reference 49.
[e]Reference 43.

Translational length t_d corresponds to any region of commensurate DWNT and to the commensurate region of DWNT in the incommensurate phase. The possibility of the commensurate-incommensurate phase transition in DWNT was first predicted in Ref. 50. In the case of the incommensurate phase of DWNT near the phase transition, the walls of DWNT have a periodic structure of alternating commensurate regions and incommensurability defects. A recent high-resolution transmission electron microscopy (HRTEM) study of DWNT (Ref. 51) supports the theory of Ref. 50 and shows that the walls of a nanotube can elastically deform to provide short commensurate segments between the defects of atomic structure (not incommensurability defects in this case).

The effective thickness of DWNT is taken to be a sum of the interwall distance d and the effective thickness w of SWNT. Young's modulus of DWNT is then calculated as

$$E_d = \frac{(\mu_1 + \mu_2)t_d}{\pi(w+d)(R_1+R_2)}, \tag{4}$$

where R_1 and R_2 are radii of the inner and outer walls of a DWNT.

The interwall distances d, translational lengths t_d of the unit cell, the relative differences $t_\delta = (t_s^2 - t_s^1)/t_d$, and Young's moduli E_d of DWNT are presented in Table II. For the armchair $(n, n)@(n+5, n+5)$ and zigzag (9, 0)@(18, 0) DWNT, the interwall distance is close to the interlayer separation in graphite and the calculated values of the energy U_{int} are comparable with the interwall interaction energy of 35–40 meV/atom obtained with the Lennard-Jones potential[16,18] and experimental value of the interlayer interaction in graphite.[34]

TABLE II. Structural characteristics, elastic properties, and interwall interaction of DWNT: d (in Å) is the interwall distance, t_d (in Å) and E_d (in TPa) are the translational length of the unit cell and Young's modulus, the parameter t_δ determines the difference in translational lengths of DWNT and constituent SWNT and is described in the text, and U_{int} (in meV/atom) is the interwall interaction energy (per one atom of the outer wall) of DWNT.

Nanotube	d	t_d	t_δ	E_d	U_{int}
(4,4)@(10,10)	4.011	2.4444	0.00317	0.992±0.002	13.29
(5,5)@(11,11)	4.017	2.4424	0.00061	0.989±0.003	13.36
(6,6)@(12,12)	4.021	2.4421	0.00020	1.005±0.003	13.67
(5,5)@(10,10)	3.344	2.4425	0.00058	1.085±0.004	23.83
(6,6)@(11,11)	3.350	2.4421	0.00019	1.106±0.003	24.09
(7,7)@(12,12)	3.353	2.4421	0.00013	1.106±0.003	24.60
(9,0)@(18,0)	3.478	4.2315	0.00116	1.049±0.003	24.16
(10,0)@(20,0)	3.875	4.2305	0.00091	1.016±0.002	16.76

The calculated Young's moduli of SWNT and DWNT are in good agreement with experimental measurements which all give the value of the Young's modulus in the neighborhood of 1 TPa: the measurements of a force required to bend (stretch) a nanotube give 1.28 ± 0.59 TPa (Ref. 52) [0.27–0.95 TPa (Ref. 53)] for MWNT and 1.2 TPa (Ref. 54) [0.32–1.47 TPa (Ref. 55)] for SWNT, the analysis of thermal vibrations of cantilevered nanotubes gives 1.8 ± 1.4 TPa for MWNT (Ref. 56) and 0.4–1.3 TPa for ropes of SWNT (Ref. 57).

The coordinates of the fully optimized equilibrium structures of the armchair (4,4), (5,5), (6,6), (7,7), (10,10), (11,11), and (12,12) SWNT, (4,4)@(10,10), (5,5)@(10,10), (5,5)@(11,11), (6,6)@(11,11), (6,6)@(12,12), and (7,7)@(12,12) DWNT, zigzag (9,0), (10,0), (18,0), and (20,0) SWNT, and (9,0)@(18,0) and (10,0)@(20,0) DWNT can be obtained from the corresponding author.

III. *Ab initio* CHARACTERISTICS OF THE INTERWALL INTERACTION

Potential relief of the interwall interaction energy $U(\phi,z)$ depends on relative position of the walls. This can be described by ϕ, the angle of relative rotation of the walls about the longitudinal axis of DWNT, and z, the relative displacement of the walls along this axis. The symmetry of the interwall interaction energy surface $U(\phi,z)$, as well as relative positions of the walls corresponding to extrema of the surface, are uniquely determined by the symmetry of DWNT.[17,20] For the $(n, n)@(m, m)$ armchair and $(n, 0)@(m, 0)$ zigzag DWNT, the Fourier expansion of interwall interaction energy surface was given in Ref. 20 as

$$U(\phi,z)=\sum_{M,K(odd)=1}^{\infty}\alpha_K^M\cos\left(\frac{2\pi}{t_d}Kz\right)\cos\left(\frac{nm}{N}M\phi\right)\sin^2\left(\frac{\pi nm}{2N^2}\right)+\sum_{M,K(even)=0}^{\infty}\beta_K^M\cos\left(\frac{2\pi}{t_d}Kz\right)\cos\left(\frac{nm}{N}M\phi\right),\quad(5)$$

where N is the greatest common factor of n and m. There exist two possibilities: namely, the odd case if both n/N and m/N are odd and the even case if either n/N or m/N is even. The even terms are always present in Eq. (5), and the odd terms only occur in the odd case.

According to the anticipated topological theorem,[19] extrema in the interaction energy surface correspond to the relative position of the walls for which a DWNT has the highest symmetry—i.e., when the second-order axes U_2 of the inner and outer walls are in line. The second-order U_2 axis is perpendicular to the principal axis of the wall and passes through the midpoint of the carbon bond or the center of the hexagons. For the armchair $(n, n)@(m, m)$ and zigzag $(n, 0)@(m, 0)$ DWNT, the elementary cell of the interwall interaction energy surface $U(\phi,z)$ contains four different types of critical points (ϕ_c, z_c) (points for which the second-order axes U_2 of the inner and outer walls are in line). If one of the critical points is selected as the origin $(\phi_c,z_c)=(0,0)$, then the remaining three types of critical points can be described as $(t_d/4,0)$, $(0,\pi N/2nm)$, and $(t_d/4,\pi N/2nm)$. The elementary cell of the interwall interaction energy surface contains one critical point of each type in the even case and two critical points of each type in the odd case. All possible relative positions of the inner and outer walls of a DWNT with coincident U_2 axes are listed in Table III.

The amplitude of harmonics in expansion (5) drops rapidly with an increase in M and K.[15,17,19] The LDA-DFT results[21] on the interwall interaction energy surface $U(\phi,z)$ for the (5,5)@(10,10) DWNT show that within the accuracy of calculations (about 5% of the size of the energy barrier), the interaction energy can be interpolated using the first two harmonics of expansion (5):

$$U(\phi,z)=U_0-\frac{\Delta U_\phi}{2}\cos\left(\frac{2\pi}{\delta_\phi}\phi\right)-\frac{\Delta U_z}{2}\cos\left(\frac{2\pi}{\delta_z}z\right),\quad(6)$$

where U_0 is the average interwall interaction energy and ΔU_ϕ and ΔU_z are the energy barriers to relative rotation and sliding of the walls. Comparing expansions(5) and (6), we find that for the armchair $(n, n)@(m, m)$ and zigzag $(n, 0)@(m, 0)$ DWNT, $\delta_\phi=\pi N/nm$ and $\delta_z=t_d/2$. In the even case, δ_ϕ and δ_z are the periods of the relative rotation and sliding of the walls between the equivalent positions. In the odd case, such periods are determined by the $\alpha_1^1\cos(2\pi z/t_d)\cos(nm\phi/N)$ harmonic and are equal to $2\delta_\phi$ and $2\delta_z$, respectively. Semiclassical results[18] with the use of the Lennard-Jones potential confirm that for all considered armchair $(n, n)@(n+5, n+5)$ DWNT with $n=5-15$ and zigzag $(n, 0)@(n+9, 0)$ DWNT with $n=9-18$, the interwall interaction energy can be successfully interpolated using expansion (6) within an accuracy of about 1% of the size of the energy barrier. This shows that the interwall interaction energy surface of DWNT with nonchiral commensurate walls is defined by the first two harmonics in expansion (6). In this case, the four types of the critical points on the surface are the global minimum, global maximum, and two saddle points.

The values of interwall interaction energies calculated in these four critical points fully determine the energetics and energy barriers of DWNT. The interaction energies which correspond to the minimum of the interwall interaction energy surface are shown in Table II. The energy barriers $\Delta U_{m\phi}$ and ΔU_{mz} to the relative rotation and sliding of the walls in DWNT when passing through the minimum of the interwall interaction energy surface are presented in Table IV (only the barriers which exceed the accuracy of calculations, 10^{-5} a.u., are included). These values correspond to the energies per carbon atom of the movable outer wall. The size of basis set has a significant effect on the calculated energies and barriers. In Ref. 21, the interwall interaction energy surface, as a function of the relative rotation and sliding of the walls, has been calculated for the (5,5)@(10,10) DWNT with a smaller basis set, *pdpp*, in the AIMPRO notation. These calculations overestimate the energy barriers, giving the following values: $\Delta U_{m\phi}=0.516$ meV/atom and $\Delta U_{mz}=0.249$ meV/atom.

Extremely small barriers to the relative rotation of the walls of DWNT with incompatible rotational symmetries allow us to predict the possibility of the orientational melting in such DWNT—i.e., the rotation of the walls caused by an

TABLE III. Relative positions of nonchiral commensurate walls of DWNT with coincident symmetry axes U_2. Φ and Z define the relative position of the walls in fractions of a period of the interwall interaction energy surface. If both n/N and m/N are odd (N is greatest common divisor of n and m), the translational period of the interwall interaction energy surface equals the length a of the unit cell of DWNT and the rotational period is $T=2\pi N/mn$. In the even case, these periods are $a/2$ and $T/2$. Symmetry axes U_2 which pass through the center of hexagons are denoted as C1 (the inner wall) and C2 (the outer wall), through the midpoint of the carbon bonds parallel to the principal axis (for zigzag walls) and perpendicular to the principal axis (for armchair walls) as H1 and H2, and through the midpoint of the oblique carbon bonds as O1 and O2.

Φ, Z	Even n/N, odd m/N		Odd n/N, even m/N		Odd n/N, odd m/N	
	ϕ,z	Coincident axes U_2	ϕ,z	Coincident axes U_2	ϕ,z	Coincident axes U_2
0,0	0,0	(H1,H2),(C1,C2), (H1,C2),(C1,H2)	0,0	(H1,H2),(C1,C2), (H1,C2),(C1,H2)	0,0	(H1,H2),(C1,C2), (O1,O2)
0,1/2	0,$a/4$	(H1,O2),(C1,O2)	0,$a/4$	(O1,H2),(O1,C2)	0,$a/2$	(H1,O2),(C1,O2) (O1,O2)
1/2,0	$T/4$,0	(O1,O2)	$T/4$,0	(O1,O2)	$T/2$,0	(H1,O2),(C1,O2), (O1,O2)
1/2,1/2	$T/4$,$a/4$	(O1,H2),(O1,C2)	$T/4$,$a/4$	(H1,O2),(C1,O2)	$T/2$,$a/2$	(H1,H2),(C1,C2), (O1,O2)
1/4,1/4					$T/4$,$a/4$	(H1,O2),(C1,O2),
3/4,1/4					$3T/4$,$a/4$	(O1,H2),(O1,C2)
1/4,3/4					$T/4$,$3a/4$	
3/4,3/4					$3T/4$,$3a/4$	

increase of temperature. Further interesting conclusions can be extracted from the results presented in Table IV on the energy barriers.

(1) Barriers to the relative rotation of the walls in excess of the accuracy of calculations can only be found for the DWNT with a compatible rotational symmetry of the walls.

(2) For the armchair $(n, n)@(n+5, n+5)$ and $(n, n)@(n+6, n+6)$ DWNT, the barrier to the relative sliding of the walls per carbon atom increases as the radius of the DWNT grows.

(3) For the zigzag (9,0)@(18,0) DWNT, the barrier to the relative sliding of the walls is an order of magnitude higher than for the armchair (5,5)@(10,10) DWNT. Note that the radii and interwall distances are very close in value for these DWNT.

Related results were reported using semiempirical interatomic potentials of Kolmogorov and Crespi[14] and Lennard-Jones.[18] Thus, quantitatively accurate *ab initio* results confirm the qualitative conclusions obtained with the use of semiempirical potentials.

For the armchair (5,5)@(10,10) and zigzag (9,0)@(18,0), (10,0)@(20,0) DWNT, we find a discrepancy between the values of barriers to the relative sliding of the walls calculated for the relative positions of the walls at $\phi=0$ and $\phi=\pi N/2nm$. The contribution from the higher harmonic $\beta_2^2\cos(4\pi z/t_d)\cos(2nm\phi/N)$ may be responsible for this dis-

TABLE IV. Characteristics of rigid motion of the walls in DWNT's. ΔU_{mz} (in meV/atom), $\Delta U_{m\phi}$ (in meV/atom), and F_z (in nN) and F_ϕ (in nN) are the energy barriers (per one atom of movable outer wall) and threshold forces for sliding and rotation of the walls; l_{max} (in nm) is the maximum overlap of the walls for which threshold forces are greater than capillary forces. Threshold forces F_z and F_ϕ are calculated for the overlap of the walls $l=100$ nm.

Nanotube	ΔU_{mz}	$\Delta U_{m\phi}$	F_z	F_ϕ	l_{max}
(4,4)@(10,10)	0.018±0.007	<0.007	1.20±0.5		28.4±12.4
(5,5)@(11,11)	0.025±0.006	<0.006	1.80±0.5		21.0±5.3
(6,6)@(12,12)	0.031±0.006	0.010±0.006	2.50±0.5	0.9±0.5	17.2±3.2
(5,5)@(10,10)	0.143±0.007	0.407±0.007	9.70±0.5	32.6±0.5	6.43±0.3
(6,6)@(11,11)	0.178±0.006	<0.006	13.20±0.5		5.25±0.18
(7,7)@(12,12)	0.220±0.006	<0.006	17.80±0.5		4.24±0.1
(9,0)@(18,0)	1.760±0.004	0.029±0.004	71.24±0.15	4.0±0.5	0.9
(10,0)@(20,0)	0.543±0.004	0.028±0.004	24.44±0.15	4.3±0.5	2.08±0.02

crepancy. However, the revealed discrepancy is fairly small and comprises about 7.8% of the barrier to the relative sliding for the (5,5)@(10,10) DWNT, 1.4% for the (9,0)@(18,0) DWNT, and 6.9% for the (10,0)@(20,0) DWNT. As a result, we use expansion (6) to estimating the characteristics of the relative sliding of the walls for all considered DWNT. For the armchair (5,5)@(10,10) and (6,6)@(12,12) DWNT, the discrepancy between the values of the barriers to relative rotation of the walls calculated for the relative positions of the walls at $z=0$ and $z=t_d/4$ is negligible. In this case, expansion (6) is also used to estimate the characteristics of the relative rotation of the walls.

We next study the interaction of nonchiral commensurate walls in DWNT which corresponds to the odd case when both n/N and m/N are odd [the (5,5)@(11,11) DWNT]. Our estimates reveal that in this case, amplitude of the $\alpha_1^1\cos(2\pi z/t_d)\cos(nm\phi/N)$ harmonic which determines the periods of the interwall interaction energy surface is small due to incompatibility of rotational symmetries of the walls, and only the $\beta_2^0\cos(4\pi z/t_d)$ harmonic with half a period has an amplitude which exceeds the accuracy of calculations. The same harmonics have a maximum amplitude for another members of the $(n, n)@(n+6, n+6)$ family; these are the (4,4)@(10,10) or (6,6)@(12,12) DWNT. Therefore, we can conclude that the difference between the interwall interaction energy surfaces corresponding to the odd and even cases is insignificant.

For DWNT with compatible rotational symmetries of the walls, the relative positions of the walls which correspond to the minima of the interwall interaction energy surface can be identified using Table III. These are defined by $(\phi,z)=(0,0)$ for the (5,5)@(10,10) and (6,6)@(12,12) DWNT and by $(\phi,z)=(T/4,a/4)$ for the (9,0)@(18,0) and (10,0)@(20,0) DWNT, where T and a are rotational and translational periods of the interwall interaction energy surface. The positions of the minima of the interwall interaction energy surface of the (9,0)@(18,0) DWNT are shifted in sliding displacement by half a period in comparison to the results obtained using the Lennard-Jones potential.[19]

IV. THRESHOLD FORCES AND CAPILLARY FORCES DETERMINING THE RELATIVE MOTION OF THE WALLS IN DWNT'S

We use expansion (6) of the interwall interaction energy surface to estimate the threshold forces F_z and F_ϕ for the relative sliding and rotation of the walls of DWNT. The threshold forces are expressed as

$$F_z=\frac{\pi\Delta U_{mz}N_m l}{\delta_z t_d},\quad F_\phi=\frac{\pi\Delta U_{m\phi}N_m l}{\delta_\phi R_m t_d},\tag{7}$$

where N_m is a number of atoms in the unit cell of the movable wall, R_m is the radius of the movable wall, and l is the overlap of the walls. Estimations of the threshold forces have been done for the overlap of the walls, $l=100$ nm, which corresponds to the experimental conditions,[2] and the results are presented in Table IV. It can be seen from Table IV that the threshold forces F_z and F_ϕ for the relative sliding and rotation of the walls in nonchiral DWNT lie within the range of forces obtained by atomic force microscopy.[58] This enables the controlled relative motion of the walls of carbon nanotubes to be used in mechanical nanodevices. As shown by Eqs. (7), these forces are proportional to the barriers to relative motion of the walls. For the (5,5)@(10,10) DWNT, *ab initio* values of the threshold forces are several times larger than the semiempirical results of Ref. 18; however, they agree well with the experimentally observed forces.[53] Here, we consider only the case when the barriers are traversed in an adiabatic manner without a local expansion or contraction of walls, and we neglect the contribution from the edges of the walls into the barrier; i.e., we assume that this contribution is small for a sufficiently large overlap l.

Experimental study of relative motion of the walls in MWNT (Ref. 2) shows that the inner core, telescopically pulled out from the outer-shell structure of the MWNT, can be completely pushed back into the outer shell by capillary forces restoring the MWNT to its original condition. Such a telescopic process of extending and retracting the core can only take place if the capillary force F_{cap} is greater than the threshold force F_z. The capillary force F_{cap} does not depend on the overlap l of the walls and can be derived as

$$F_{cap}=\frac{dU}{dl}=\frac{U_{int}N_m}{t_d},\tag{8}$$

whereas the threshold force F_z given by Eqs. (7) is proportional to this overlap. The maximum overlap l_{max} of the walls for which the threshold forces do not hinder the retraction of the core can be determined from the balance of the forces $F_{cap}=F_z$:

$$l_{max}=\frac{\delta_z U_{int}}{\pi\Delta U_{mz}}.\tag{9}$$

Estimations of the maximum overlap l_{max} are given in Table IV. It can be seen that within the same family of DWNT, $(n, n)@(n+5, n+5)$ or $(n, n)@(n+6, n+6)$, the maximum overlap l_{max} goes down with an increase of the radius of the wall. Results tabulated in Table IV also suggest that if the outer wall of the telescopically pulled-out core and the inner wall of the remaining outer-shell structure of the MWNT comprise a nonchiral commensurate pair, the core cannot be pushed back by the capillary forces and the experiment of Cumings and Zettl[2] cannot be successfully performed for this pair of neighboring walls.

Other possible pairs of neighboring walls are chiral commensurate and incommensurate walls. The maximum overlap l_{max} is next estimated for the (8,2)@(16,4) DWNT with chiral commensurate walls. The interwall interaction energy and barrier to the relative sliding of the walls have been computed for this DWNT in Ref. 21 and the reported estimates are $U_{int}=17.5$ meV/atom and ΔU_{mz} is less than 0.001 meV/atom (per atom of the outer wall). Using method described elsewhere,[15] the period of the relative sliding of the walls can be readily calculated as $\delta_z=0.46$ Å. Finally, using Eq. (9) the maximum overlap l_{max} of the inner and outer walls of the (8,2)@(16,4) DWNT for which the controlled reversible telescoping can be achieved is estimated to

be greater than 250 nm. This is the lowest estimate of the l_{max}, and in principle this value can be orders of magnitude greater. In the case of incommensurate walls, the barrier to relative sliding does not increase with the length of the overlap, but fluctuates near some average value.[5,6,14,15] As a result, the threshold force F_z also does not increase with the length of the overlap and therefore does not prevent retraction of the incommensurate inner wall by capillary forces.

Thus, the experiment of Cumings and Zettl cannot be successfully performed only for a pair of nonchiral commensurate walls and the effect of reversible telescopic extension of MWNT can be used for selecting pairs of nonchiral commensurate walls. A range of uses has been suggested for the relative motion of nonchiral commensurate walls in electromechanical nanodevices. The relative rotation of such walls has potential applications in nanobearings[18] and their relative sliding can be used in devices operating in the accelerating mode.[5,6,9]

V. CONCLUSIVE REMARKS

In this paper, we apply the DFT approach to calculate the structural characteristics and elastic properties of armchair and zigzag SWNT which are used to construct a set of DWNT with two armchair or two zigzag walls. We study the interwall interaction and relative motion of the walls of DWNT and calculate the barriers to the relative rotation and sliding of the walls. We show that the first two harmonics of the Fourier expansion of the interwall interaction energy define the shape of the energy surface.

The extremely small barrier to the relative rotation of the nonchiral commensurate walls of DWNT with incompatible rotational symmetries indicates that orientational melting can occur in such DWNT.

Ab initio values of the barriers are used to estimate experimentally measurable quantities. First, we calculate the threshold forces required to initiate the relative sliding of the walls along the axis of a DWNT. This has also led to our attempt to identify the walls in the experiment[2] on the reversible telescoping of the walls of MWNT by capillary forces. Our calculations show that such an experiment cannot be successfully carried out for nonchiral commensurate walls of a MWNT. We propose to use the effect of controlled and reversible telescopic extension of MWNT for selecting pairs of nonchiral commensurate walls.

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[1] R. H. Baughman, A. A. Zakhidov, and W. A. der Heer, Science **297**, 787 (2002).
[2] J. Cumings and A. Zettl, Science **289**, 602 (2000).
[3] L. Forro, Science **289**, 5479 (2000).
[4] Q. Zheng and Q. Jiang, Phys. Rev. Lett. **88**, 045503 (2002).
[5] Y. E. Lozovik, A. V. Minogin, and A. M. Popov, Phys. Lett. A **313**, 112 (2003).
[6] Y. E. Lozovik, A. V. Minogin, and A. M. Popov, JETP Lett. **77**, 631 (2003).
[7] R. E. Tuzun, D. W. Noid, and B. G. Sumpter, Nanotechnology **6**, 52 (1995).
[8] D. W. Srivastava, Nanotechnology **8**, 186 (1997).
[9] Y. E. Lozovik and A. M. Popov, Fullerenes, Nanotubes and Carbon Nanostructures **12**, 485 (2004).
[10] S. Zhang, W. Liu, and R. S. Ruoff, Nano Lett. **4**, 293 (2004).
[11] N. Hamada, S. I. Sawada, and A. Oshiyama, Phys. Rev. Lett. **68**, 1579 (1992).
[12] R. Saito, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, Phys. Rev. B **46**, 1804 (1992).
[13] J. C. Charlier, J. P. Michenaud, and X. Gonze, Phys. Rev. B **46**, 4531 (1992).
[14] A. N. Kolmogorov and V. H. Crespi, Phys. Rev. Lett. **85**, 4727 (2000).
[15] M. Damnjanović, T. Vuković, and I. Milošević, Eur. Phys. J. B **25**, 131 (2002).
[16] R. Saito, R. Matsuo, T. Kimura, G. Dresselhaus, and M. S. Dresselhaus, Chem. Phys. Lett. **348**, 187 (2001).
[17] T. Vuković, M. Damnjanović, and I. Milošević, Physica E (Amsterdam) **16**, 259 (2003).
[18] A. V. Belikov, Y. E. Lozovik, A. G. Nikolaev, and A. M. Popov, Chem. Phys. Lett. **385**, 72 (2004).
[19] M. Damnjanović, E. Dobardzić, I. Milošević, T. Vuković, and B. Nikolić, New J. Phys. **5**, 148.1 (2003).
[20] M. Damnjanović, I. Milošević, T. Vuković, and R. Sredanović, Phys. Rev. B **60**, 2728 (1999).
[21] E. Bichoutskaia, A. M. Popov, A. El-Barbary, M. I. Heggie, and Y. E. Lozovik, Phys. Rev. B **71**, 113403 (2005).
[22] J. C. Charlier and J. P. Michenaud, Phys. Rev. Lett. **70**, 1858 (1993).
[23] A. H. R. Palser, Phys. Chem. Chem. Phys. **1**, 4459 (1999).
[24] H. Rydberg, B. I. Lundqvist, D. C. Langreth, and M. Dion, Phys. Rev. B **62**, 6997 (2000).
[25] E. Hult, Y. Andersson, B. I. Lundqvist, and D. C. Langreth, Phys. Rev. Lett. **77**, 2029 (1996).
[26] E. Hult, H. Rydberg, B. I. Lundqvist, and D. C. Langreth, Phys. Rev. B **59**, 4708 (1998).
[27] W. Kohn, Y. Meir, and D. E. Makarov, Phys. Rev. Lett. **80**, 4153 (1998).
[28] J. F. Dobson and J. Wang, Phys. Rev. Lett. **82**, 2123 (1999).
[29] J. C. Boettger, Int. J. Quantum Chem., Symp. **29**, 197 (1995).
[30] B. I. Dunlap and J. C. Boettger, J. Phys. B **29**, 4907 (1996).
[31] J. W. Mintmire, B. I. Dunlap, and C. T. White, Phys. Rev. Lett. **68**, 631 (1992).
[32] J. C. Boettger, Phys. Rev. B **55**, 11202 (1997).
[33] L. A. Girifalco and R. A. Lad, J. Chem. Phys. **25**, 693 (1956).
[34] L. X. Benedict, N. G. Chopra, M. L. Cohen, A. Zettl, S. G. Lonie, and V. H. Crespi, Chem. Phys. Lett. **286**, 490 (1998).
[35] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).

[36] R. H. Telling and M. I. Heggie, Philos. Mag. Lett. **83**, 411 (2003).
[37] C. S. G. Cousins and M. I. Heggie, Phys. Rev. B **67**, 024109 (2003).
[38] P. R. Briddon and R. Jones, Phys. Status Solidi B **217**, 131 (2000).
[39] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[40] G. Van Lier, G. Van Alsenoy, V. Van Doren, and P. Geerlings, Chem. Phys. Lett. **326**, 181 (2000).
[41] D. Sanchez-Portal, E. Artacho, J. M. Soler, A. Rubio, and P. Ordejon, Phys. Rev. B **59**, 12678 (1999).
[42] S. L. Mielke, D. Troya, S. Zhang, J. L. Li, S. Xia, R. Car, R. S. Ruoff, G. C. Schatz, and T. Belytschko, Chem. Phys. Lett. **390**, 413 (2004).
[43] T. Ozaki, Y. Iwasa, and T. Mitani, Phys. Rev. Lett. **84**, 1712 (2000).
[44] V. N. Popov, V. E. Van Doren, and M. Balkanski, Phys. Rev. B **61**, 3078 (2000).
[45] C. Li and T.-W. Choi, Int. J. Solids Struct. **40**, 2487 (2003).
[46] G. Sun, J. Kürti, M. Kertesz, and R. H. Baughman, J. Phys. Chem. B **107**, 6924 (2003).
[47] J. Kürti, V. Zólyomi, M. Kertesz, and G. Sun, New J. Phys. **5**, 125.1 (2003).
[48] O. Gülseren, T. Yildirim, and S. Ciraci, Phys. Rev. B **65**, 153405 (2002).
[49] E. Hernandez, C. Goze, P. Bernier, and A. Rubio, Phys. Rev. Lett. **80**, 4502 (1998).
[50] E. Bichoutskaia, M. I. Heggie, Y. E. Lozovik, and A. M. Popov, Fullerenes, Nanotubes and Carbon Nanostructures 14, number 1–2 (2006).
[51] A. Hashimoto, K. Suenaga, K. Urita, T. Shimada, T. Sugai, S. Bandow, H. Shinohara, and S. Iijima, Phys. Rev. Lett. **94**, 045504 (2005).
[52] E. W. Wong, P. E. Sheenan, and C. M. Lieber, Science **277**, 1971 (1997).
[53] M. F. Yu, O. Lourie, M. J. Dyer, K. Moloni, T. F. Kelly, and R. S. Ruoff, Science **287**, 637 (2000).
[54] T. W. Tombler, C. Zhou, L. Alexseyev, J. Kong, H. Dai, L. Liu, C. S. Jayanthi, M. Tang, and S.-Y. Wu, Nature (London) **405**, 769 (2000).
[55] M. F. Yu, B. S. Files, S. Arepalli, and R. S. Ruoff, Phys. Rev. Lett. **84**, 5552 (2000).
[56] M. M. J. Treacy, T. W. Ebbesen, and J. M. Gibson, Nature (London) **381**, 678 (1996).
[57] A. Krishnan, E. Dujardin, T. W. Ebbesen, P. N. Yianilos, and M. M. J. Treacy, Phys. Rev. B **58**, 14013 (1998).
[58] F. J. Giessibl, Rev. Mod. Phys. **75**, 949 (2003).