Ab initio study of relative motion of walls in carbon nanotubes

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We study the interwall interaction and relative motion of walls in carbon nanotubes using density functional theory. The interwall interaction energy surface as a function of relative rotation and sliding of walls is calculated for the (5,5)@(10,10) nanotube. The barriers to relative rotation and sliding are estimated *ab initio* for the chiral walls of the (8,2)@(16,4) nanotube. These results are used to extract information on experimentally measurable quantities, such as threshold forces, diffusion coefficients, and mobilities of walls. Possible applications of these nanotubes in mechanical nanodevices are discussed. Two distinct regimes of the wall movement exist: athermal, forced movement (accelerating mode) and movement controlled by thermal diffusion (Fokker-Planck mode). We calculate the limits of these regimes from first principles.

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The discovery of carbon nanotubes[1] is regarded as one of the most important advances in materials in the latter part of the 20th century. A wide range of applications in nanoscale electronic, optical, and magnetic devices can be envisaged, ranging from logic elements to single-molecule sensing devices. The weak interwall interaction within multiwalled carbon nanotubes (MWNTs) gives an extremely smooth solid-solid interface which can provide perfect bearings for possible nanodevices, such as free sliding telescopic arms,[2] nanogears driven by a laser electric field,[3] or ultrasmall switching devices.[4,5] A big family of nano-objects based on relative sliding, rotation or screwlike motion of walls of MWNTs has been proposed recently.[6–9] Theoretical modeling of the orientation and relative motion of walls holds the key to the success of these applications. The first experimental studies of relative motion of walls in nanotubes[2,10,11] and considerable advances in syntheses of double-walled carbon nanotubes (DWNTs),[12–15] yield a firm experimental background for the present theoretical study.

The majority of DWNTs have been studied with semiempirical pairwise potentials for the interaction between the atoms of neighboring walls,[5,7,16–20] or with simple tight-binding techniques.[21,22] The interaction between walls in the (5,5)@(10,10) DWNT (in Hamada index notation) has been particularly well investigated with a variety of methods.[16,18,19,21–24] However, the use of semiempirical interatomic potentials *fitted to graphite properties* is insufficient for quantitative estimations of barriers to relative rotation of walls for nanotubes with small radii. The barriers to relative rotation and sliding of walls calculated for the (5,5)@(10,10) DWNT with the Lennard-Jones interatomic potential[16,19] underestimate the *ab initio* results of Ref. 23 by about an order of magnitude, whereas the barriers obtained using the Crespi semiempirical potential[18] are significantly higher than the *ab initio*. In addition, positions of minima in the interaction energy surface of the (5,5)@(10,10) DWNT calculated using the Lennard-Jones potential[24] are shifted both in sliding displacement and rotation angle by half a period in comparison to the *ab initio* results of Ref. 23 and this work.

Periods of relative rotation and sliding of walls in DWNT between the equivalent configurations, as well as the relative positions of walls corresponding to extrema in the interwall interaction energy surface, are uniquely determined by the symmetry of the system.[18,19] According to the anticipated topological theorem,[24] extrema in the interaction energy surface correspond to the relative positions of walls, wherein the symmetry of a DWNT is maximum (some of the second-order axes U_2 of the inner and outer walls are in line). This statement has been used in Ref. 24 to obtain the relative positions of walls corresponding to minima of the surface for various DWNTs. For the (5,5)@(10,10) DWNT, minima in the interaction energy surface form a rectangular lattice with periods $\delta_\phi = \pi/10 = 18^\circ$ along the direction of relative rotation of walls, ϕ, and $\delta_z = T/2 = 1.23$ Å along the direction of their relative displacement, z, [$T = T(5,5) = T(10,10)$ is the length of translational unit cell]. Previously published local-density approximation (LDA)-density functional theory (DFT) results[23] have been the most accurate estimates for the barriers to relative motion of the (5,5)@(10,10) DWNT, although the value of the rotation barrier has been calculated for the rotation of walls by $2\pi/120 = 3^\circ$. The presence of two equivalent extrema per one elementary cell in the interaction energy surface of the (5,5)@(10,10) DWNT found by the tight-binding method[22] contradicts the anticipated topological theorem.[24] To settle these issues, we calculate the interwall interaction energy surface for the (5,5)@(10,10) DWNT from first principles.

We then address the more demanding problem of the relative motion of chiral commensurate walls in DWNTs and present the first *ab initio* results on the interwall interaction in the (8,2)@(16,4) DWNT. The (8,2)@(16,4) DWNT has a unit cell consisting of 168 carbon atoms, this is the smallest unit cell of commensurate chiral walls. We use the *ab initio* results to estimate experimentally measurable quantities, such as diffusion coefficients, mobilities, and threshold forces for relative rotation and sliding and compare with recently measured threshold forces.[10] We find that the relative motion of walls in DWNTs with chiral and nonchiral commensurate walls are fundamentally different in nature. Dependence of the relative motion of walls on chirality of DWNTs has been previously suggested qualitatively using

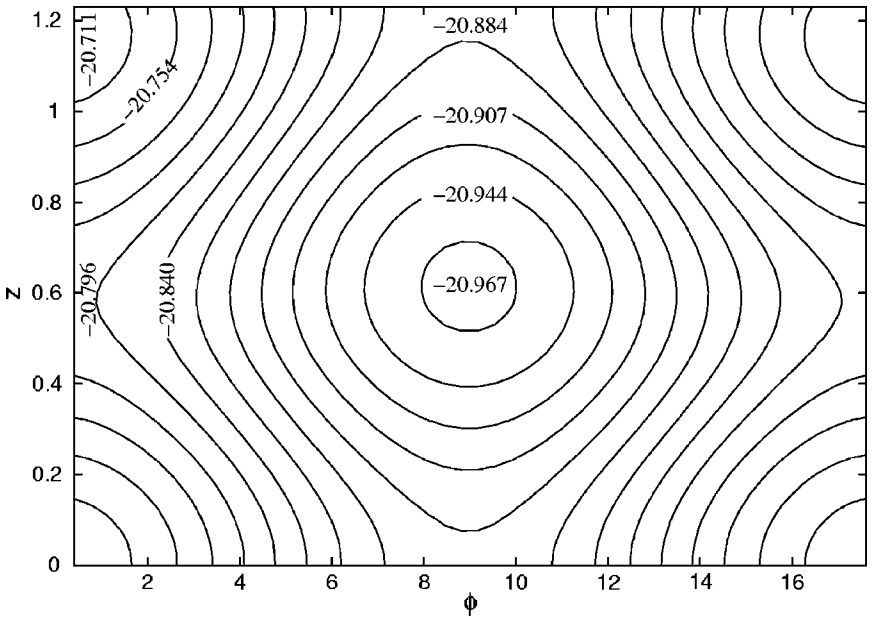

FIG. 1. Interwall interaction energy U (in meV/atom) of the (5,5)@(10,10) DWNT as a function of relative displacement z (in angstroms) of walls along the nanotube axis and angle ϕ (in degrees) of their relative rotation.

semiempirical models.[17–20] We confirm that two distinct regimes of wall movement exist: athermal, forced movement (accelerating mode) and thermal diffusion of walls (Fokker-Planck mode). We estimate the limits of these regimes from first principles.

Interwall interaction energies have been obtained with the AIMPRO supercell code, within the LDA-DFT approach.[25] The pseudowave functions are described by four atom-centered Gaussian functions per atom, expanded in spherical harmonics up to $l=1$, with the second smallest exponent expanded to $l=2$. For the (5,5)@(10,10) DWNT, the supercell consists of 60 carbon atoms and the Brillouin Zone (BZ) sampling has been performed using 12 special k points (in the direction of the nanotube axis). For the (8,2)@(16,4) DWNT, unlike in the electronic structure calculations, two special k points in the BZ is sufficient to achieve the required accuracy of the interwall interaction energies. Nonlocal, norm-conserving pseudopotential[26] and the Perdew-Wang exchange-correlation functional[27] have been used.

Minima in the total energy are found using a conjugate gradient scheme to an accuracy of 1 μeV/atom. Positions of all atoms in the isolated SWNTs are optimized initially, and the interwall interaction energy is then calculated as the difference between the total energy of the DWNT and separate SWNTs without correcting for basis set superposition error. If the full counterpoise procedure of Boys and Bernardi[28] applied, the absolute value of barriers may change within 5% depending on the size of basis set. The basal plane binding energy of graphite[29] and elastic properties of graphite,[30] which are highly sensitive to the interlayer interaction, are both reproduced very well by these LDA-DFT calculations.

The calculated *ab initio* interwall interaction energy surface for the (5,5)@(10,10) DWNT is shown in Fig. 1. Within the accuracy of calculations, the interaction energy can be interpolated as

$$U(z,\phi) = U_0 - \frac{\Delta U_z}{2}\cos\left(\frac{2\pi}{\delta_z}z\right) - \frac{\Delta U_\phi}{2}\cos\left(\frac{2\pi}{\delta_\phi}\phi\right), \quad (1)$$

where U_0 is an average interwall interaction energy, ΔU_z and ΔU_ϕ are the energy barriers to sliding and rotation of walls, respectively. Estimates for the energy barriers obtained from the surface (Fig. 1) are given in Table I.

For the chiral (8,2)@(16,4) DWNT, the barriers are lower than those for the (5,5)@(10,10) DWNT by about two orders of magnitude, because of the incompatibility of symmetries of the chiral walls which results in a high density of equivalent minima on the energy surface.[18,20] Extremely small barriers were previously reported for the (8,2)@(16,4) DWNT ($\Delta U_\phi \simeq 5\times10^{-12}$ meV per atom, Ref. 19) and for several other DWNTs (Refs. 17–20) using semiempirical potentials,

TABLE I. Characteristics of diffusion along a nanotube axis and rotational diffusion of the inner walls in the (5,5)@(10,10) and (8,2)@(16,4) DWNTs. Threshold forces F_x are calculated for a wall 100 nm in length. For the (8,2)@(16,4) DWNT, we estimate the upper limits of the barriers and associated parameters. The details of the calculations are described in the text.

Characteristic	Units	(5,5)@(10,10)	(8,2)@(16,4)
ΔU_{az}	meV/atom	0.249	<0.002
$\Delta U_{a\phi}$	meV/atom	0.519	<0.003
a_z	m^2/s	1.2×10^{-8}	$<0.4\times10^{-9}$
b_z	K/nm	224	<2
a_ϕ	rad^2/s	1.4×10^{11}	$<4\times10^{9}$
b_ϕ	K/nm	465	<3
l_z	nm	52.8	>5500
l_ϕ	nm	25.0	>3000
F_z	nN	8.4	<0.2
F_ϕ	nN	20.0	<0.3

however these efforts were based on the assumption of rigid unrelaxed walls. Absolute value of the minimum of the interwall interaction energy in the (8,2)@(16,4) DWNT is found to be $E_{\min}=-17.5$ meV/atom.

Given the high Young modulus of nanotubes and the very weak interwall interaction, we consider the case of rigid concerted diffusion of walls in DWNTs, i.e., we suggest that all barriers to relative motion of walls in DWNTs are traversed in a commensurate way. We use the Frenkel-Kontorova model,[31] which represents a prototype of modulated incommensurate system, with parameters extracted from our first principles results to assess the possibility of formation of an "incommensurability defect" (ID) on walls of a DWNT. Simple estimates show that the length of an ID is $l_{\mathrm{ID}}=50$ nm with formation energy, $E_{\mathrm{ID}}=1.00$ eV, for the (5,5)@(10,10) DWNT, and $l_{\mathrm{ID}}=170$ nm with formation energy, $E_{\mathrm{ID}}=0.04$ eV, for the (8,2)@(16,4) DWNT. In case of the (5,5)@(10,10) DWNT, energy of the ID formation is too large for the defect to form at room temperature, and for the chiral (8,2)@(16,4) DWNT, we give the lowest estimation of the ID length which can be, in principle, far greater than the estimated value. Therefore, rigid diffusion of walls takes place at room temperature for short movable walls (conditions at which formation of the ID is highly unlikely) and can be considered as a valid process in nanomechanical devices.

Now we turn to the problem of diffusion and drift over these barriers. Recently,[5,7] the Fokker-Planck equation was obtained for the diffusion and drift of DWNT walls at temperatures $\Delta U \ll kT$ along the helical line, where the diffusion coefficient D and mobility B of a movable wall relative to the fixed one were defined as

$$D=\frac{\Omega\delta^2}{2}\exp\left(-\frac{\Delta U}{kT}\right), \tag{2}$$

$$B=\frac{\Omega\delta^2}{2kT}\exp\left(-\frac{\Delta U}{kT}\right), \tag{3}$$

where Ω is the preexponential multiplier in the Arrhenius formula for the transition frequency of the system between the two neighboring minima, δ is a distance between the two neighboring minima of the interaction energy surface $U(z,\phi R)$ in the direction of motion of the wall, R is the radius of the movable wall. In this work, we consider the specific case of rotational diffusion, $\delta=\delta_\phi R$, and diffusion along the nanotube axis, $\delta=\delta_z$.

The factor Ω is often assumed to be the same order of magnitude as the oscillation frequency ω_0 of the system near the minimum. The value of the frequency multiplier was estimated in Ref. 32 as $\Omega=650\pm350$ GHz for the rotational diffusion of shells of the carbon nanoparticle $C_{60}@C_{240}$. For the same system, the averaged frequency of rotational oscillations of the shells is $\omega_0=350$ GHz, giving the ratio Ω/ω_0 close to 1. Since the weak interaction in nanotubes is similar to that between graphitelike layers, we take the value of $\Omega/\omega_0\sim1$.

To estimate the frequency ω_0 of small-amplitude oscillations of a wall near the minimum of the potential relief, we use the expansion of potential (1) near the minimum $U(x)=U_0+\alpha/2x^2+\cdots$. With a simple manipulation, formula (2) can be developed into the expressions below for diffusion coefficients corresponding to diffusion along and about the nanotube axis

$$D_x=a_x\exp\left(-\frac{b_x l}{T}\right),\quad x=z,\phi, \tag{4}$$

$$a_z=\pi\delta_z\sqrt{\frac{\Delta U_{az}}{2m}},\quad a_\phi=\frac{\pi\delta_\phi}{R}\sqrt{\frac{\Delta U_{a\phi}}{2m}}, \tag{5}$$

$$b_x=\frac{\Delta U_{ax}N_a}{l_c k},\quad x=z,\phi, \tag{6}$$

where ΔU_{ax} are the barriers per atom of the movable wall, m is the mass of carbon atom, N_a is the number of atoms in the elementary cell of the movable wall, l_c is the length of the elementary cell, and l is the length of the movable wall. The mobility for sliding along the axis B_z can be easily obtained from the diffusion coefficients D_z using the Einstein ratio $D=kTB$. To characterize the rotational drift we introduce the rotational mobility as

$$B_\phi=\frac{w}{F}=\frac{D_\phi R}{kT}, \tag{7}$$

where w is the angular velocity of the movable wall and F is the sum of tangential components of forces acting on atoms of the movable wall.

To estimate the threshold forces F_z and F_ϕ for the relative sliding and rotation of the walls, we use the expansion (1) of the potential relief. Then the threshold forces can be expressed as

$$F_z=\frac{\pi\Delta U_{az}N_a l}{\delta_z l_c},\quad F_\phi=\frac{\pi\Delta U_{a\phi}N_a l}{\delta_\phi R l_c}. \tag{8}$$

The results of the estimations are tabulated in Table I and they correspond to the range of forces obtained by atomic force microscopy.[33] As the threshold forces are proportional to the barrier to relative motion of walls, their *ab initio* values for the (5,5)@(10,10) DWNT are several times larger than semiempirical ones of Ref. 19, but they agree well with the experimentally observed forces.[10]

In experiment,[2] controlled and reversible motion of walls has been realized experimentally using nanotubes which were hundreds of nanometers in length. Therefore, we first calculate the lengths l_x (see Table I) characterized by one displacement of the wall between the two neighboring minima of the interwall interaction energy surface, on the average, say, during 24 h at room temperature. For the (8,2)@(16,4) DWNT, the length of the inner movable wall exceeds 100 nm both for sliding and rotation (see Table I). For these experimentally feasible cases, we estimate diffusion coefficients and mobilities for diffusion and drift of the inner wall. For the (8,2) wall 100 nm in length, the estimated diffusion coefficient for sliding along the nanotube axis is $D_z>2\times10^{-10}$ m^2/s and the rotational diffusion coefficient is $D_\phi>2\times10^9$ rad^2/s. Corresponding estimations for mobilities are $B_z>5\times10^{10}$ s/kg and $B_\phi>2\times10^{20}$ s/kg m.

Using the (5,5)@(10,10) and (8,2)@(16,4) DWNTs as examples, we consider two different operation modes which can be used in mechanical nanodevices based on the relative motion of walls of carbon nanotubes under the action of external forces, which do not cause their deformation. The motion of walls is controlled by diffusion if $kT \ll \Delta U$, and drift if $F_x \delta/2 \ll \Delta U$ (F_x is the projection of the force causing drift in the direction of motion) and the time-average acceleration is zero. In the case of the (8,2)@(16,4) DWNT, the diffusion of walls is significant and the motion of walls can be described by the Fokker-Planck equation (for forces $F_x \delta/2 \ll kT$).[5,7] In this case, nanodevices, such as the mechanical nanoswitch[4] or nanodrill[5,7,8] can operate in the Fokker-Planck mode based on relative drift. Unfortunately, the Fokker-Planck operation mode does not allow the precise control of relative position. The second type of possible operation mode is the accelerating mode ($F_x \delta/2 \gg kT$). In this mode controlled relative displacement of walls within distances less than δ is possible, and this mode can be used if the barriers to relative motion of walls are high enough to prevent the diffusion. A variety of nanoresistors and electrical nanoswitches operating under accelerating mode can be envisaged.[5,7,8] For the (5,5)@(10,10) DWNT, the diffusion of walls is possible only for a very short length of the inner wall, and this DWNT can be thus only used in nanodevices which operate in accelerating mode, as there is no risk of diffusion of walls to hinder the operation of a nanodevice. The (8,2)@(16,4) DWNT can be used in nanodevices in either mode depending on the temperature.

In summary, we have derived from first principles experimentally measurable characteristics, such as threshold forces, diffusion coefficients and mobilities of walls, for the (5,5)@(10,10) and the chiral (8,2)@(16,4) DWNTs, which are compatible both with symmetry theory and recent experiments. Our approach can be applied to a wide range of pristine and defected DWNTs with different chiralities and strength of interwall interaction.

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