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PAPER

Coaxial carbon nanotubes: from springs to ratchet wheels and nanobearings

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Abstract

Quantum mechanical calculations are performed for double-walled and triple-walled carbon nanotubes (DWCNTs, TWCNTs). We show how the DWCNTs may be modelled by mechanical analogues with interactions mediated by spring forces with weakening elastic constants in addition to a weak van der Waals -like interaction. This enables us to predict the natural frequency of longitudinal oscillations of the DWCNTs, their elastic spring constant and the corresponding interaction between the CNTs. Results of the interaction energy ΔE for the DWCNT system obtained from the mechanical model are in remarkable agreement with those obtained from our quantum mechanical calculations, and we obtain functional dependencies of ΔE on axial elongation and inter-wall separation of the DWCNTs. Our density functional theory calculations reveal that the armchair-armchair systems are significantly more stable than both the corresponding armchair-chiral configurations, as well as the corresponding stacked graphene sheets. The results obtained for translational and rotational motion (slide / roll) of the CNTs indicate a potential use of DWCNTs as springs, ratchet wheels, nanogears and bearings in miniaturized devices. Our work enables us to predict the behavior of DWCNTs of different dimensions and would be of practical importance in the actual construction of nanoscale mechanical parts.

1. Introduction

The physics and chemistry of materials at small scales are of both academic and practical value. They give us an understanding of how natural materials and structures form and behave, and allow us to fabricate structures that may have exceptional mechanical and material properties. At the sub-micrometre and nanometre regimes, as we approach molecular length scales, properties like friction between surfaces, elastic modulii or electrical properties have to be considered anew, since these may vary from classical, macroscopic predictions. Local geometry and curvature effects too become extremely important and may also no longer be neglected when considering point forces and deformations [1, 2]. The manipulation of atomically thin membranes and sheets, and their use in construction of nanotubes, have now become of practical importance technologically. The behavior of materials too changes when confined in nanotubes, and can give rise to interesting electronic and configurational properties [3, 4]. In biological systems too, down to the micron scale where we have vesicles with phospholipid membrane walls, mechanical pulling of these structures at constant velocity yields nanotubes of uniform cross-section; these are employed in fabricating nanofluid devices and drug-delivery systems [5]. Such nanotubes also show interesting, non-trivial, dynamical behavior [6, 7]. Extensive interest has been evinced in the structural and functional properties of carbon nanotubes in the last two decades, although much work had followed the first appearance of filamental carbon structures in transmission electron microscope (TEM) images

in the early 1950s [8, 9]. Some years later with revived interest in the formation of hollow carbon nanotubes (CNTs), work motivated by a desire to understand buckminsterfullerene growth-mechanisms led to the discovery of multi-walled and single-walled CNTs using high-resolution TEM [10, 11].

The discovery of CNTs has revolutionized research in nanoscience and nanotechnology, given their exceptional electronic, mechanical, thermal, and transport properties. Single-walled carbon nanotubes (SWCNTs), for example, can behave as quantum wires, with the molecular wave-functions extending throughout the tube [12]. They have also been used as light-sensitive field effect transistors, motivated by potential applications for use in artificial photosynthesis [13]. With tensile strength of the order of 10^2 GPa and Young's modulus exceeding 1 TPa, CNTs are ideal candidates for use as tethers, cables and machinery in high stress environments like a space elevator [14–16].

While research on SWCNTs has been an active area both experimentally and theoretically in the last two decades, coaxial double-walled carbon nanotubes (DWCNTs), triple-walled carbon nanotubes (TWCNTs) and multi-walled carbon nanotubes (MWCNTs) have gained attention only recently [17]. A DWCNT consists of two concentric single-walled nanotubes (SWCNTs) stabilized principally by weak van der Waals forces, with spacing between the walls ranging from 3.3 to 4.2 Å. The practical advantages of DWCNTs and MWCNTs over SWCNTs lie in the fact that while SWCNTs remain in direct contact with the environment that can modify their properties (for example via chemical functionalization), the presence of outer tube(s) in DWCNTs and MWCNTs protects the inner tubes from any influence of the environment. Moreover, since nanotubes in a DWCNT / MWCNT are held by weak forces between the tubes, they have the ability to mutually roll, rotate and slide. This unique property has been exploited in the field of nanomotors, nanogears, nanobearings, nano-oscillators and actuators [18–23]. For example, Takagi *et al* performed classical molecular dynamics (MD) simulations and proposed a nanomotor consisting of a SWCNT and a DWCNT; they showed that the translational motion of the SWCNT controls the rotational motion of the DWCNT [24].

Comprehensive descriptions of CNT structures and properties can be found in the literature [25]. These nanostructures have come into focus due to recent developments in synthesis and separation of high quality samples [26]. Hirschmann *et al* reported a detailed characterisation of bundled and individual TWCNTs by resonant Raman spectroscopy [27]. Recent studies based on TEM and Raman scattering techniques revealed a mechanical coupling between the concentric walls of a DWCNT [28, 29]. Endo *et al* fabricated a paper-like material consisting of bundles of DWCNTs using chemical vapour deposition [30]. CNTs can be formed by rolling of graphene sheets. The chiral vector $\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2 = (n, m)$, uniquely defines a CNT, with $\mathbf{a}_1$ and $\mathbf{a}_2$ being primitive lattice vectors for graphene; n and m are integers, $0 \leqslant m \leqslant n$. $\mathbf{C}_h$ joins two lattice points of the sheet which on rolling into a nanotube, become indistinguishable [31]. Depending upon how a graphene sheet is rolled, an SWCNT can be one of several types—armchair (n, n), chiral (n, m) or zigzag $(n, 0)$. $\mathbf{C}_h$ provides information about the angle of twist, as well as the diameter D of the tube which is given by

$$D = \frac{\sqrt{3}\, a_{C-C}}{\pi} \sqrt{m^2 + n^2 + mn},$$

(1)

where a_{C-C} is the $C-C$ bond length which can be taken to be 1.42 Å. In this study we have focused on carbon nanotubes of armchair (n, n) type. Thus we denote the DWCNT, which is made of an inner SWCNT type (m, m) (inner tube) and an outer SWCNT (n, n), as $(n, n)@(m, m)$. For example, the $(3, 3)@(8, 8)$ combination corresponds to the DWCNT with inner and outer diameters 4.06 Å and 10.85 Å, respectively.
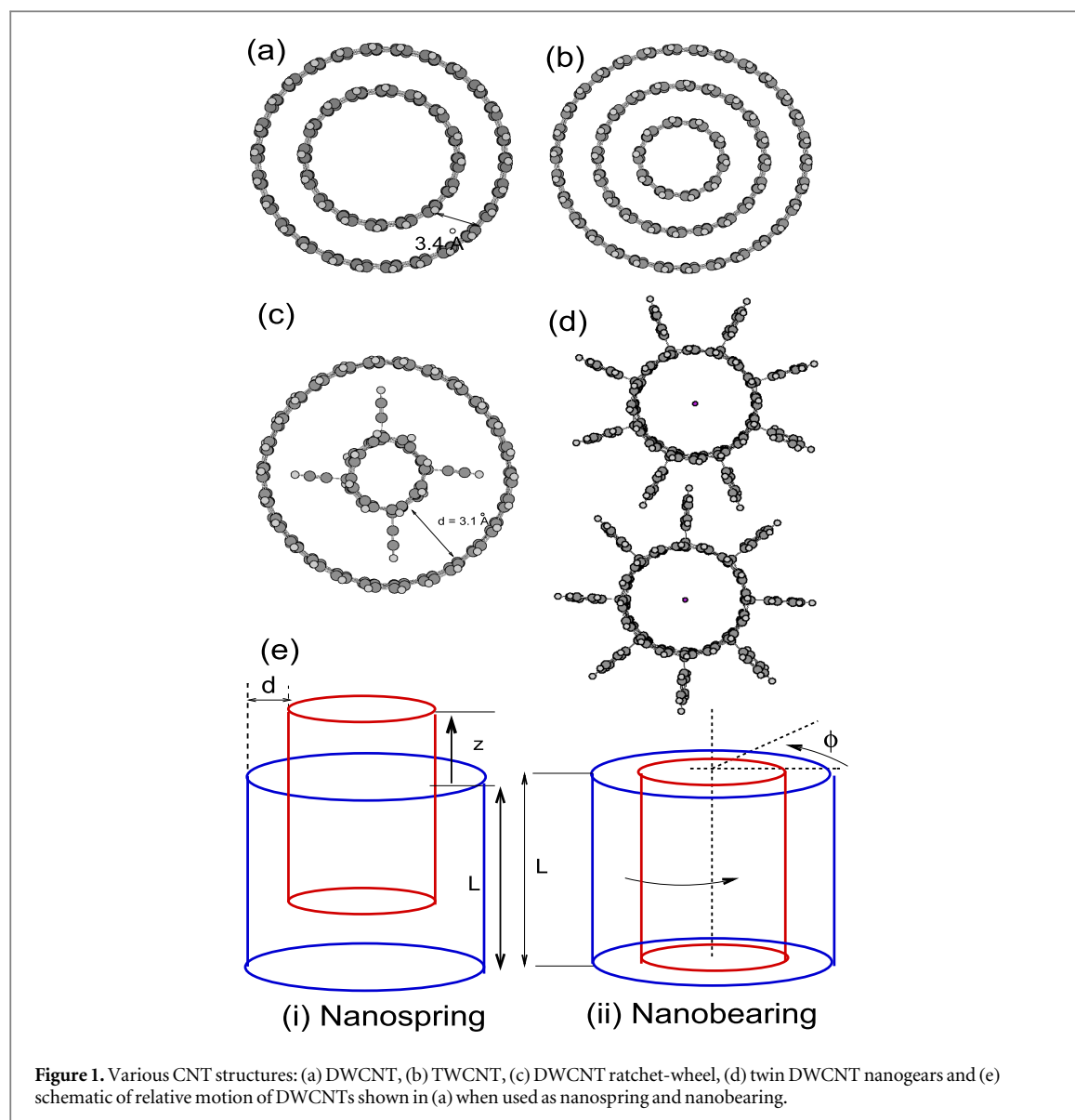
All our calculations were performed using DWCNTs of length 6 Å, except two cases, where DWCNTs of length 12 Å were considered. In the following sections, we study the stability of DWCNTs and show how they may be used as distinct components of nanoelectromechanical systems (NEMs), ranging from nanosprings and nanobearings, to ratchet-wheels and nanogears. These are illustrated in figure 1: (a) DWCNT, (b) TWCNT, (c) ratchet wheel, (d) nanogear and (e) a schematic of the relative motions of the DWCNTs.

The DWCNT has become of practical importance because of the extremely low friction between the two CNTs [18], and its oscillatory behavior has been the subject of study by many authors [20, 21, 32]. We propose a mechanical model analogous to a nanospring that yields results in excellent agreement with behavior seen from DFT calculations and with the values reported in the literature. Our model is distinct from that of others and uses a nonlinear spring interaction, as has been explained in the sections below.

2. Results and discussion

2.1. DWCNT, TWCNT and graphene sheets: a comparison

Calculations were performed for DWCNTs with inter-wall separation (d) ranging from 2.7 Å to 6.9 Å, using density functional theory. We see that as the inter-wall separation increases, the interaction energy decreases drastically. The DWCNTs, on the other hand, become unstable for combinations $(n, n)@(n + 4, n + 4)$.

Figure 1. Various CNT structures: (a) DWCNT, (b) TWCNT, (c) DWCNT ratchet-wheel, (d) twin DWCNT nanogears and (e) schematic of relative motion of DWCNTs shown in (a) when used as nanospring and nanobearing.

Details may be found in table S1 available online at stacks.iop.org/MRX/5/075023/mmedia, provided as supporting information[†]. We found $(n, n)@(n + 5, n + 5)$ DWCNTs to be favoured energetically and the most stable for our purpose, and we used these as the typical DWCNTs for further calculations. DWCNTs with various diameters $((3, 3)@(8, 8)$ to $(7, 7)@(12, 12))$ were considered while keeping the inter-wall separation constant at $d = 3.4$ Å. It was observed that the interaction energy ΔE increased with increase in nanotube diameter. Details may be found in table 1. as might be expected, ΔE has a linear dependence on the total number of carbon atoms, N_C, in the DWCNT system, as shown in figure 2. A linear regression model yielded an expression of the form

$$\Delta E \approx -1.500 - 0.527 N_C, \tag{2}$$

and was tested for a large DWCNT system $(11, 11)@(16, 16)$ containing 324 atoms. This fit to the calculated data, when extrapolated for $N_C = 324$, predicted an interaction energy of -172.48 kcal/mol, while the actual interaction energy was found to be -173.89 kcal/mol, an error of only 1.5 kcal/mol. It may be safely deduced that the interaction energy for much larger DWCNT systems can be predicted using this linear regression model to a very good degree of accuracy, within about 1%–2%. We also compared ΔE for the DWCNT system with that of stacked graphene of similar size (with the same number of carbon atoms) with an identical inter-planar separation of 3.4 Å. Interestingly, the DWCNT system is found to be significantly more stable than the corresponding stacked graphene by at least 25 kcal/mol (see table 1(a)). This is not surprising, considering the fact that the interaction energy of tubular structures (in comparison to sheets) include therein an extra stabilizing contribution from the curvature energy that scales as (κ/r^2) (κ being the curvature modulus and r the radius of curvature of the tube), that further reduces the interaction energy of nanotubes in comparison to that of graphene sheets.

Table 1. Table showing the interaction energy ΔE for: **1a.** DWCNT and stacked graphene, for same inter-wall separation d, and **1b.** TWCNT configurations, showing how sum of the interaction energies for the constituent DWCNTs correspond approximately to that of the TWCNT.

1a. DWCNT, stacked graphene

DWCNT ((n, n)@ (n + 5, n + 5)) ((n + 1, n)@ (n + 5, n + 5))	d (Å)	ΔE (kcal/mol)	$\Delta E_{graphene}$ (kcal/mol)
(3, 3)@(8, 8)	3.4	−71.27	−43.62
(4, 3)@(8, 8)	3.1	−40.27	
(4, 4)@(9, 9)	3.4	−86.16	−58.88
(5, 4)@(9, 9)	3.1	−47.62	
(5, 5)@(10, 10)	3.4	−94.89	−69.64
(6, 5)@(10, 10)	3.1	−53.92	
(6, 6)@(11, 11)	3.4	−108.40	−85.73
(7, 6)@(11, 11)	3.1	−57.42	
(7, 7)@(12, 12)	3.4	−121.73	−99.97

1b. Triple-wall CNT configurations.

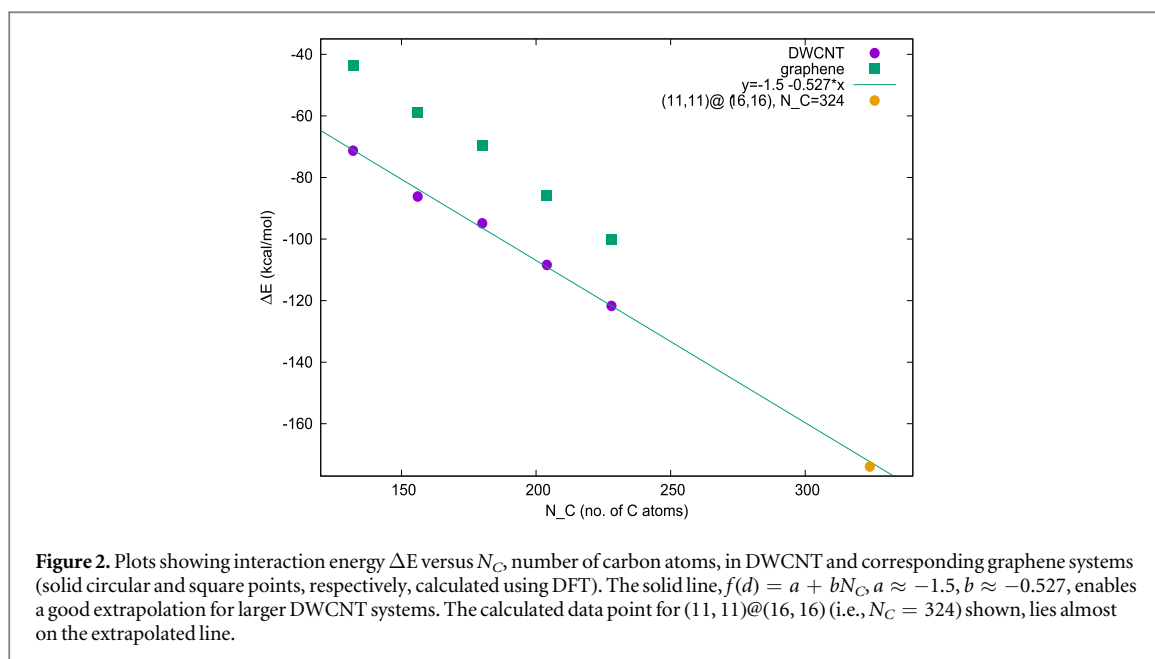| DWCNT$_{1-2}$, DWCNT$_{2-3}$ $\Delta E_1, \Delta E_2$ (kcal/mol)	DWCNT$_{1-3}$ ΔE_3 (kcal/mol)	$\sum \Delta E$ (DWCNTs) $= \sum_{i=1}^{3} \Delta E_i$ (kcal/mol)	TWCNT$_{123}$ ΔE_{TWCNT} (kcal/mol)
(3, 3)@(8, 8), (8, 8)@(13, 13) −71.27, −134.87	(3, 3)@ (13, 13) −4.76	−210.90	−211.10
(4, 4)@(9, 9), (9, 9)@(14, 14) −86.16, −148.12	(4, 4)@ (14, 14) −5.6	−239.88	−240.17
(5, 5)@(10, 10), (10, 10)@ (15, 15) −94.89, −160.98	(5, 5)@ (15, 15) −6.37	−262.24	−262.28

We also find that the interaction energy of nanotubes of the armchair-armchair combinations (n, n)@(n + 5, n + 5) is roughly twice as large as that of the chiral-armchair combinations (n + 1, n)@(n + 5, n + 5). It is worth mentioning that the chiral-armchair systems have an inter-wall separation of 3.1 Å, which is sub-optimal, as compared to the 3.4 Å separation for the armchair-armchair configurations. It is also to be noted that our value of 3.4 Å is in excellent agreement with the experimental findings of 3.23–3.37 Å reported in the literature [27].

Table 1(b) tabulates interaction energies of triple walled CNTs of the form (n, n)@(n + 5, n + 5)@ (n + 10, n + 10). This is a comparison of ΔE for the TWCNT, to ΔE for each of the two constituent DWCNTs in it (the innermost CNT and the middle CNT, the middle CNT and the outermost CNT, and the innermost CNT and the outermost CNT). As might not seem unreasonable, we find that the interaction energy for the TWCNT is comparable to the sum of the constituent DWCNT interaction energies, as shown in table 1. Therefore, the stability of TWCNTs may be estimated from the stability of the constituent DWCNTs.

2.2. The DWCNT as a nanospring

Supplementing the experimental work on comparative sliding motion of the CNTs in DWCNTs [18], several authors have modelled DWCNTs using frictional and van der Waal interactions, using both analytical methods and molecular dynamics simulations [20, 21, 32]. An elaborate model has also been constructed by Cox *et al* [33] for nanotube oscillation in nanotube bundles. Our work is distinct from these. Our simple mechanical model considers a nonlinear spring with additional van der Waals interaction, and interaction energies obtained are

Figure 2. Plots showing interaction energy ΔE versus N_C, number of carbon atoms, in DWCNT and corresponding graphene systems (solid circular and square points, respectively, calculated using DFT). The solid line, $f(d) = a + bN_C$, $a \approx -1.5$, $b \approx -0.527$, enables a good extrapolation for larger DWCNT systems. The calculated data point for $(11, 11)@(16, 16)$ (i.e., $N_C = 324$) shown, lies almost on the extrapolated line.

matched with quantum mechanical calculations performed using density functional theory, as detailed below. These have not been done earlier and we obtain excellent agreement. Recent work points to evidence of mechanical coupling between the layers of a DWCNT, indicating the merit of this approach [28, 29].

2.2.1. DFT calculations

We surmised that the DWCNT system could be considered as a nanoscale analogue of a spring or damper, with the inner nanotube free to move out telescopically along the axis. Our DFT calculations support this premise— plots of the interaction energy as a function of axial displacement z are shown in figure 3(a). The data points correspond to the $(3, 3)@(8, 8)$, $(4, 4)@(9, 9)$, $(5, 5)@(10, 10)$ and $(6, 6)@(11, 11)$ systems. We have performed calculations for 6 Å long DWCNTs as well as 12 Å long systems. The results reveal that doubling the length does not alter the general behavior of the interaction energy shown by the system. The plots we show here are for the 6 Å CNTs (data for the 12 Å DWCNTs are shown in the plots in figure S1 as Supporting Information†). While considering the translational motion of the inner tube with respect to the outer tube, we find that DWCNTs can behave as elastic nanosprings, but with a behavior that is not quite Hookean, since the data points clearly do not fall on parallel parabolic contours as would be expected from Hookean springs.

2.2.2. A mechanical model

In order to capture the behavior of the DWCNT 'nanospring', we consider a very simple mechanical analogue.

We imagine a pair of concentric cylinders, each with a certain number of molecular units of length L_m, one stacked on top of the other, to a total length L. These can be visualized as pairs of concentric rings, where each outer ring has M atoms and each inner ring has N atoms. We approximate the interaction between these rings by means of N identical springs (with the same elastic spring constant k). As the inner CNT moves out, extending out along the axis by a distance z, in our model there is an elastic restoring force acting on the system due to the stretched springs between the two tubes. We assume softening of the effective spring constant to occur as the inner tube projects out, and limit the influence of each elastic unit to an axial distance of approximately L/L_m. The spring is no longer Hookean, but nonlinear. Assuming a symmetric distribution of springs around the inner CNT so that only the component of the restoring force parallel to the axis remains while the radial components mutually cancel out (i.e., $F_{eff} = -Nk' \sin\theta (\sqrt{d^2 + z^2} - d)$, with $\sin\theta = z/\sqrt{d^2 + z^2}$ and $k' \equiv k(1 - z/L)$). k' is the effective spring constant that weakens as the inner CNT moves outwards, with decreasing contribution to the spring force with increasing distance traversed along the axis. The effective restoring force on the inner CNT is then

$$F_{eff} = -Nkz\left(1 - \frac{z}{L}\right) + \frac{Nkzd}{(d^2 + z^2)^{1/2}}\left(1 - \frac{z}{L}\right).\qquad(3)$$

Additionally, a short-range interaction between the two CNTs separated by a spacing of d is also included in the form of a $1/d^6$ van der Waals interaction. Another interaction term, which acts as a harmonic, stabilizing potential acting radially between the two CNTs and does not influence that part of the CNT that has moved out, is also included. This latter term reduces monotonically as the inner tube moves out of the outer DWCNT tube
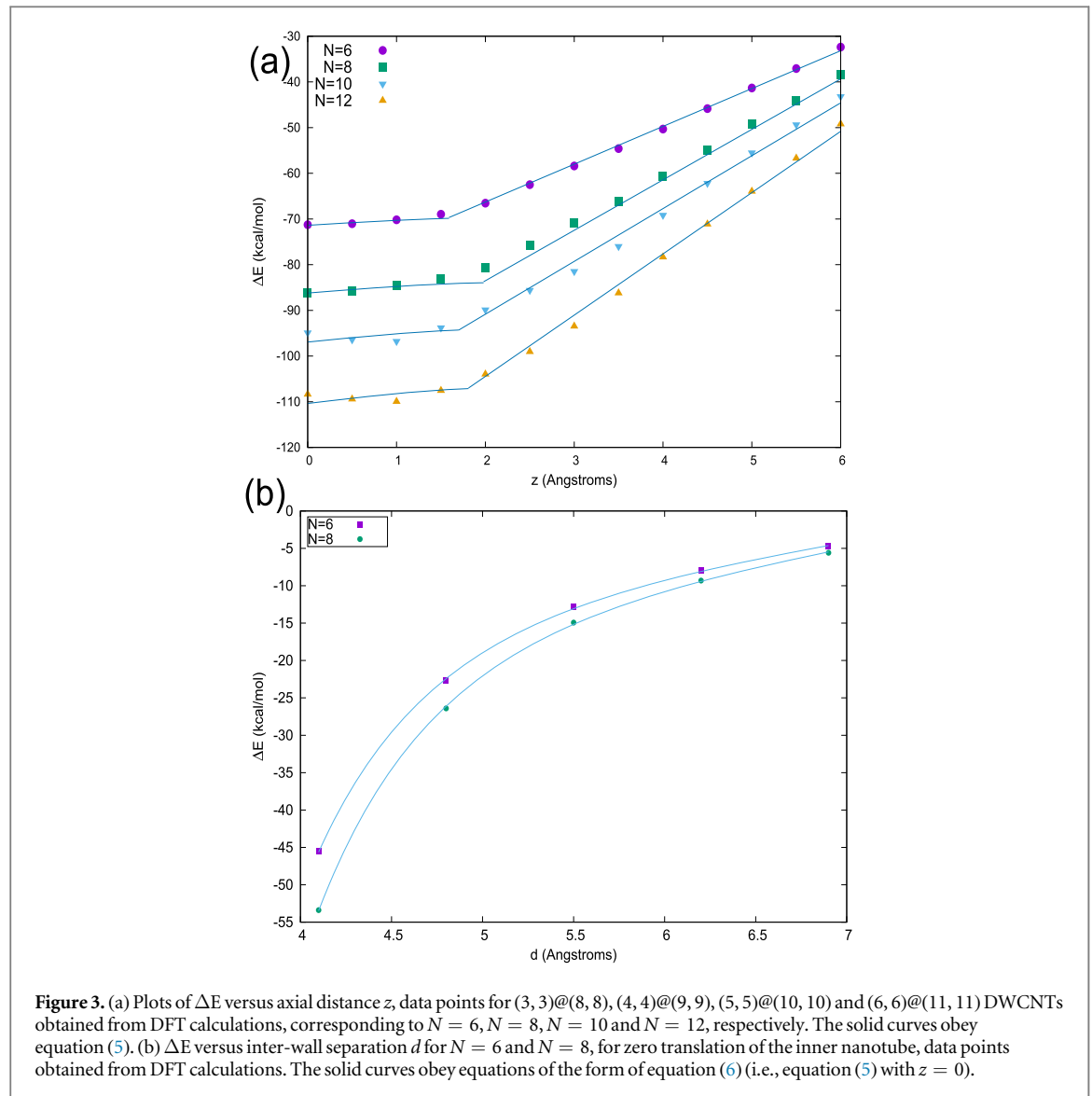
Figure 3. (a) Plots of ΔE versus axial distance *z*, data points for (3, 3)@(8, 8), (4, 4)@(9, 9), (5, 5)@(10, 10) and (6, 6)@(11, 11) DWCNTs obtained from DFT calculations, corresponding to $N = 6$, $N = 8$, $N = 10$ and $N = 12$, respectively. The solid curves obey equation (5). (b) ΔE versus inter-wall separation *d* for $N = 6$ and $N = 8$, for zero translation of the inner nanotube, data points obtained from DFT calculations. The solid curves obey equations of the form of equation (6) (i.e., equation (5) with $z = 0$).

and vanishes when it exits completely. With this quasi-mechanical model, the expression for the interaction energy of the coaxial CNTs may then be obtained (by integrating the restoring force over the length extended) as:

$$E_I = E_0 + \frac{Nkz^2}{2} - \frac{Nkz^3}{3L} - \frac{Nkd^3}{L}\tan^{-1}\left(\frac{z}{d}\right)$$
$$- Nkd^2(\sec(\tan^{-1}(z/d)) - 1) + \frac{c}{d^6}$$
$$+ \frac{(pNkd^2)}{2}\frac{L - z}{L}, \tag{4}$$

$$E_{II} = E_0' - \frac{Nkz^3}{3L} + \frac{c}{d^6} + \frac{(pNkd^2)}{2}\frac{L - z}{L}, \tag{5}$$

where E_I and E_{II} correspond, respectively, to the interaction energies of the system when the inner tube has moved but a short distance along the axis (approximately a little more than the length of a molecular unit L_m, or about 1–1.5 Å), and second, when the displacement of the inner nanotube is significantly larger than L_m. E_0 and E_0' are constants of integration. The variable *p* is a tuning parameter that adjusts the magnitude of the radial harmonic interaction term (the last term in equation (4)). When the inner CNT remains completely inside the outer one, with zero *z* displacement, equation (5) reduces to

$$E = E_0 + \frac{c}{d^6} + p\frac{Nk}{2}d^2. \tag{6}$$

A comparison with DFT calculations immediately validates our model as a reasonable one. It will be appreciated that the spring constant *k* and the van der Waals coefficient *c* are not expected to change for different CNTs of the

same length, even for different N. We therefore retain the same value of k and c for all the DWCNTs of length 6 Å, after obtaining these by a best fit of the (3, 3)@(8, 8) DWCNT data. The only fitting parameters for the other data are the constants E_0 and E_0', and the harmonic potential parameter p. Incidentally, we find, on inspecting the values obtained for p, that $p \sim N^{-0.32}$, so that the magnitude of this term for a given L, d and z increases as $\sim N^{0.68}$. As can be seen from figure 3(a), remarkable agreement is obtained between the data points from our DFT calculations, and the curves obtained from our mechanical model. The model predicts accurate results for the 12 Å DWCNTs as well (see figure in Supplementary Information[†]). Figure 3(b) is a plot of the interaction energy as a function of the inter-wall separation d for the case where the inner nanotube is completely within the outer nanotube, with no translation. The solid curves obey equation (6). As can be seen, there is again excellent agreement between the two.

2.2.3. A question of timing: natural oscillations

The above agreement between an intuitive toy model and DFT calculations emboldens us to venture into estimating what the natural oscillation frequencies of these nanosprings would be. For very small displacements of the inner CNT, that are even smaller in magnitude than the inter-wall separation d, we can reasonably assume that the nonlinear behavior of the spring would be negligible and the spring would be Hookean. Our model gives a value for the elastic spring constant k to be in the range of approximately 0.344 N/m (for the 6 Å long DWCNTs) to 0.415 N/m (for the 12 Å DWCNTs), corresponding to a force that is of $O(10^{-2}\text{nN})$. Taking into account the number of atoms in the inner CNT, we can approximate the natural frequency of oscillation ν of this nanospring, using $\omega \equiv 2\pi\nu = \sqrt{k/m}$, m being the oscillator mass. For our system, we find $\nu \approx 78\text{--}109$ GHz for the 6 Å -long DWCNTs and $\nu \approx 60\text{--}85$ GHz for the 12 Å -long DWCNTs. These are similar to the expected frequencies of oscillations (50–80 GHz) for DWCNTs [33] (and with results reported by other authors [21, 34] and justify our use of a mechanical spring model to extract additional useful information from the data generated by DFT calculations. At room temperature, DWCNT systems would be expected to oscillate with such frequencies due to thermal energy.

2.3. Nanobearings

We now investigate the effect that a mutual rotation of the CNTs would have on the interaction energies of the DWCNT. We find that these DWCNTs could be used as near-ideal nanobearings in the construction of NEMs. With change in angular position, the interaction energy change is almost negligible, in the range of approximately 0.2–0.4 kcal/mol (for most configurations) to about 1 kcal/mol, as can be seen from figure 4. We also note that it might be possible to incorporate very fine control into NEMs by appropriate use of DWCNTs of required size. The (6, 6)@(11, 11) DWCNT, for instance, has a fascinatingly regular ramp-like energy profile, but with an extremely low, almost flat amplitude. One could postulate that these could be used as metronomes for measuring two very-near phase-differences. This is because sawtooth-like, ramp profiles with respect to time are signatures of stick-slip behavior in a system, with two or more time-scales present [7], while here we see a similar behavior with respect to angular rotation. For most practical purposes, these small energy ranges are practically negligible, and we would expect the DWCNTs to exhibit smooth, frictionless rotation, an ideal property of nanobearings.

2.4. Ratchet wheels and nanogears

2.4.1. Ratchet wheels

The ratchet-wheel is constructed using the combination of (4, 4) and (13, 13) SWCNTs. The (4, 4) CNT was modified by adding four acetylide groups (H–C≡C–) in a symmetrical manner. The fully optimized geometry is depicted in figure 1(c). We know that the hydrogen atoms present in the acetylide groups are acidic in nature and have $\delta+$ positive charge. Thus, the four hydrogen atoms would interact with the electron cloud of the outer (13, 13) nanotube and form CH-π bonds. Figure 5(a) shows the potential energy profile when the inner (4, 4) nanotube is rotated along its axis. In order to rotate the inner (4, 4) CNT, the four CH-π bonds have to be broken, which requires an energy of $\sim$16–18 kcal/mol. We can see that the ratchet-wheel structure is stable at $0°$, $90°$ and $180°$ when the four CH-π bonds are intact. On the other hand, the structure is most unstable at $45°$ and $135°$ (maxima) when the CH-π bonds are broken. One question that would immediately come to mind is why, in the presence of apparent rotational symmetry of the outer tube, should this distinctive behavior at these four points be seen. This can be attributed to the directionality of the CH-π interaction. The acetylide group may or may not point directly towards the centre of the hexagons in the outer CNT; it may instead be directed at the C–C bonds between two hexagons. This therefore leaves a non-uniform energy profile, as seen in figure 5. This property may constructively be used in the design of nanoscale ratchet wheels, requiring the supply of a finite energy to turn a certain angle. Thus, by adding an appropriate number of substituents and/or by adjusting the diameter of the DWCNT used, one can tune the energy profiles as desired.
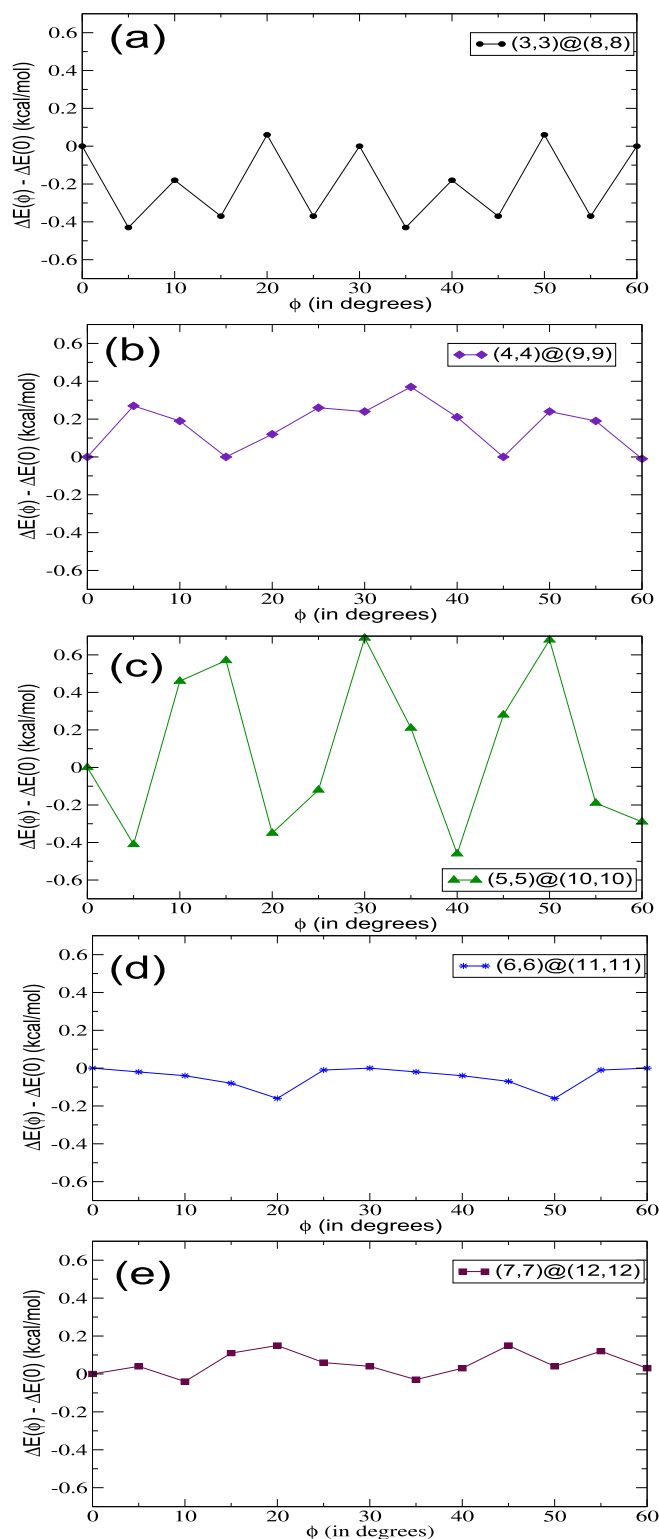
Figure 4. ΔE versus rotation angle ϕ for different DWCNTs: (a)(3, 3)@(8, 8);(b)(4, 4)@(9, 9);(c)(5, 5)@(10, 10);(d)(6, 6)@(11, 11);(e) (7, 7)@(12, 12). ΔE at $\phi = 0$ is the reference for plotting different $\Delta E(\phi)$. Small ΔE ranges makes these ideal nanobearings.

2.4.2. Nanogears

Nanogears can be constructed by attaching suitable chemical groups to SWCNTs. We have chosen phenyl groups as substituents which would act as teeth of the gears. Figure 1 (d) shows nanogears comprised of two (8, 8) SWCNTs, each having 8 phenyl groups directed outward. The two centres of mass are kept at a separation of ≈ 20.12 Å. Two sodium ions are placed at each CNT-gear's centre of mass. While the individual gears can be stabilised by strong cation-π interactions between the sodium atom and the π-electrons of the nanotube, the dimer system could be stabilised by the weak $\pi - \pi$ interactions between those phenyl groups which are in close
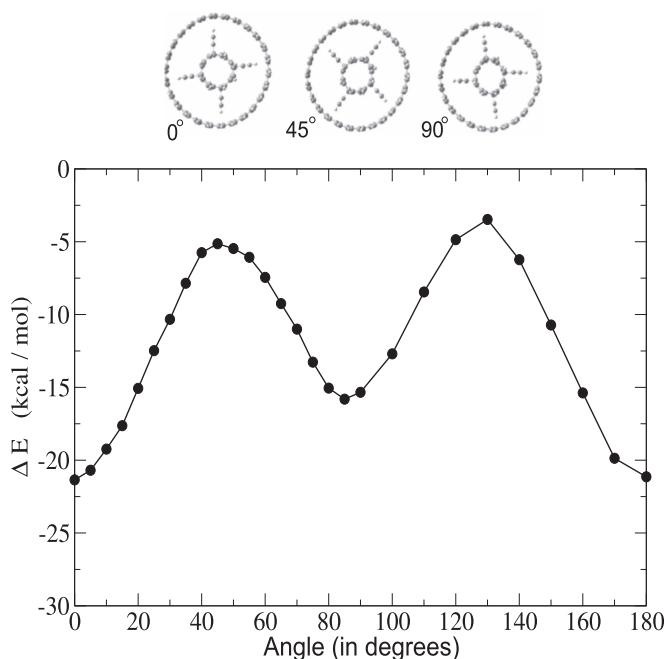
Figure 5. Ratchet wheel: Interaction energy ΔE as a function of different angular positions ϕ of the inner tube with its 4 arms bearing acetylide groups. The ratchet wheel is also shown at three representative angles corresponding to two local minima and a maximum of ΔE. $\Delta E(\phi = 0)$ is taken as the reference zero energy.
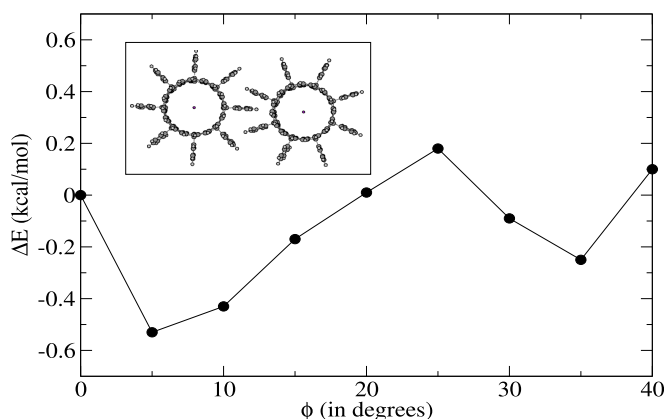

Figure 6. Nanogear: ΔE as a function of rotational angle ϕ, for twin $(8, 8)$ nanogears. $\Delta E(\phi = 0)$ is taken as the reference zero energy. A representative twin nanogear system is shown in the inset.

proximity of 3.2–3.6 Å. The π-π interaction between the two benzene molecules was reported to be -2.7 kcal/mol [35]. Here, we have four such interactions (though not in optimal positions/directions). We would expect the dimer to be stabilised by $\sim$6–8 kcal/mol with respect to the individual units. This nanogear system is rotated around the axis passing through the sodium atoms.

The change in the interaction energies at various rotation angles is depicted in figure 6. The energy barrier for the rotation is computed to be less than 1 kcal/mol. Therefore, it can be inferred that due to rotation the existing π-π interactions would be broken and new π-π interactions would be formed simultaneously between the neighbouring phenyl groups; thus the loss in energy would be minimal. We propose a 'no-friction' gear, which would rotate due to the thermal energy at room temperature in the absence of an external source.

3. Conclusions

We find that DWCNTs (armchair-armchair configurations) are excellent candidates for making nano-scale devices, where they can be used as springs, bearings, ratchet wheels and gears.

When considering the telescopic extension (along the central axis) of the inner CNT with respect to the outer CNT in a DWCNT, we obtain the interaction energy of the system as a function of axial extension, through DFT calculations.

A simple, mechanical model that we construct for the system, as two cylinders interacting through a nonlinear spring force (with weakening elastic constants) and a van der Waals potential, successfully replicates the quantum mechanical DFT results, as shown in section 1.2 (and in the Supplementary material† for longer, 12 Å long DWCNTs). Interestingly, the dependence of ΔE on inter-wall separation that is obtained from our DFT calculations, is also exactly replicated by our model. Our mechanical model also enables us to calculate the force between the two CNTs in the DWCNT, and the natural frequency of oscillation of the system, which we find to be approximately in the range of 60–100 GHz for the DWCNTs considered.

It will be observed that our results of oscillation frequencies of 78–109 GHz (for 6 Å long DWCNTs) and 60–85 GHz (for 12 Å long DWCNTs) are in good agreement with the results in the literature of 75 ± 8 GHz [21], reported frequencies in the range 50–80 GHz [33], and that of 62 GHz for telescopic oscillations of DWCNTs that has also been reported [34].

We can therefore confidently predict the values of the natural oscillating frequency and the elastic constant of DWCNTs, which are of practical significance in the actual construction and use of DWCNTs as nanosprings. We concluded that double-walled carbon nanotubes may also be used as smooth, frictionless nanobearings, due to the almost negligible change in the interaction energy of the system for a rotation of the inner CNT with respect to the outer, for most configurations. We tentatively propose that it might also be able to introduce very fine control in NEMs through these DWCNT nanobearings, as regular, ramp-like behavior was seen in the interaction energy plot of one DWCNT structure, a signature of stick-slip behavior. Due to the very small range in values of interaction energy, this would be possible only in systems which are very well shielded from thermal fluctuations.

By introducing additional chemical groups as spokes radiating outwards from the inner CNT, we are able to theoretically construct and investigate a DWCNT ratchet-wheel and obtain its energy profile. An appropriate choice of tube diameter and chemical substituents would tune the behavior of these ratchet-wheels as required. We also investigated the feasibility of using CNTs as nanogears, by addition of suitable chemical groups to the outer surface of SWCNTs that would act as spokes. We find that two twin, spoked SWCNTs act as almost frictionless nanogears. These revalidate the findings in [36].

Our investigation of the interaction energies ΔE of DWCNTs yields a linear dependence of ΔE on the total number of carbon atoms in the system. DWCNTs are also more energetically favourable as compared to graphene sheets; for a given radius of curvature, there is a uniform difference between ΔE for the DWCNTs and the corresponding graphene sheet, implying a contribution to the stability that could be attributed to the curvature energy.

The results of our calculations reported in this paper assume perfect nanotubes, free of any imperfections. The presence of defects is expected to enhance inter-wall frictional effects [37]. Defects that are very relevant to CNTs include vacancy and Stone-Wales defects. While defects may be expected to reduce the load carrying capacity of CNTs [38], it is anticipated from the stress-strain curves of nanotubes with and without defects (see [38]) that for smaller values of strains, this would essentially just change the value of the slopes, without changing their qualitative behaviour. Under such conditions, we do not anticipate the need for any revision in our approach to the problem. A more systematic study of DWCNTs that are not ideal, and with defects in their structure, is the subject of our study currently underway and will be reported elsewhere, being outside the scope of this paper.

The stability of the DWCNT structures fall in an energy range of approximately 40 to 120 kcal/mole. They are therefore expected to be stable even under thermal fluctuations.

Fennimore *et al* [19] constructed rotational actuators based on carbon nanotubes, with the outer diameter of the MWCNTs used being found to vary from 10 to 40 nm. Characterization studies reported in the literature [27, 39] indicate that catalytically-grown DWCNTs of the dimensions commensurate to those in the structures theoretically studied by us may be formed in the laboratory. Fennimore *et al* [19] have also fabricated a motor with the bearing being 10 nm in diameter.

Bourlon, *et al* [40] constructed a nanoelectromechanical system consisting of a plate rotating around a multiwalled nanotube bearing. The outer layers of the MWCNT were removed through electrical breakdown and the rotating plate attached to the inner CNT that turned inside the (fixed) outer shells. Telescopic motion of MWCNTs have been experimentally studied by Zettl and collaborators [41] using a transmission electron microscope (TEM) using the core layers of the MWCNTs, the outer layers having again been removed through electrical breakdown. The shortest possible segment of armchair carbon nanotubes, a cycloparaphenylene 'carbon nanohoop' structure has also been synthesized in the laboratory [42].

We believe therefore that constructing such structures as the rotors, nanosprings and gears that we have discussed in our paper, would be feasible in the laboratory, once technical difficulties for device construction at these small scales are mastered.

To summarize, CNT systems in the form of DWCNTs and SWCNTs clearly show a wealth of mechanical and dynamical properties that can be controlled, predicted and put to practical use in devising machinery in the nanoscale. We hope this work would encourage experimentalists to fabricate these systems and verify our predictions.

Acknowledgments

Appendix

All the Density Functional Theory (DFT) calculations were performed using the Turbomole package [43, 44]. The geometries of the nanotubes were optimised using the dispersion-corrected density functional theory (BLYP-D3 functional) and the double-zeta (def2-SVP) quality basis set [45]. The interaction energies for the co-axial nanotubes were calculated using the BLYP-D3 method with triple-zeta valence polarized (def2-TZVP) basis set. Popov and co-workers [46] showed that the DFT-D3 method gives accurate interaction energies for stacked graphene systems. All the scan calculations for slide / roll motion were performed using fixed coordinates. Hydrogen atoms were added manually to satisfy the valency of the carbon atoms at the periphery. The geometry of the nanogears could not be optimized due to limited computational resources. The coordinates of the atoms were fixed during calculations. It is to be noted that resolution of identity (RI) approximation was used to speed up the calculations [47]. For larger systems, multipole accelerated RI-J (MARI-J) approximation was also used [48]. The interaction energies (ΔE) for the DWCNTs were computed using the super-molecule approach

$$\Delta E = E(nn@mm) - (E(nn) + E(mm)) \tag{7}$$

where, $E(nn)$ and $E(mm)$ are the energy values for the two single-walled carbon nanotubes and $E(nn@mm)$ is the energy value for the double-walled carbon nanotube. Similarly, the interaction energy for the triple-walled carbon nanotube was calculated using:

$$\Delta E = E(nn@mm@kk) - (E(nn) + E(mm) + E(kk)) \tag{8}$$

The data obtained for the DWCNTs and TWCNTs using the above two equations are listed in table 1.

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References

[1] Lu Q and Huang R 2009 *Int. J. Appl. Mech.* **1** 44
[2] Lu Q, Arroyo M and Huang R 2009 *J. Phys. D: Appl. Phys.* **42** 102002
[3] Ghosh S, Sood A K and Kumar N 2003 *Science* **299** 1042
[4] Kumar P, Ramachandran C N, Mishra B K and Satyamurthy N 2014 *Chem. Phys. Lett.* **618** 42
[5] Jesorka A, Stepanyants N, Zhang H, Ortmen B, Hakonen B and Orwar O 2011 *Nat. Prot.* **6** 791
[6] Cuvelier D, Chiaruttini N, Bassereau P and Nassoy P 2005 *Europhys. Lett.* **71** 1015
[7] Ashok B and Ananthakrishna G 2014 *J. Chem. Phys.* **141** 174905
[8] Radushkevich L V and Lukyanovich V M 1952 *Zh. Fiz. Khim. (Russ. J. Phys. Chem.)* **26** 88
[9] Davis W R, Slawson R J and Rigby G R 1953 *Nature* **171** 756
[10] Ijima S 1991 *Nature* **354** 56
[11] Ijima S and Ichihashi H 1993 *Nature* **363** 603
[12] Tans S J, Devoret M H, Dai H, Thess A, Smalley R, Geerligs L J and Dekker C 1997 *Nature* **386** 474
[13] Hecht D S, Ramirez R J A, Briman M, Artukovic E, Chichak K S, Stoddart J F and Gruner G 2006 *Nano Lett.* **6** 2031
[14] Artsutanov Y 1967 Komsomolskaya Pravda (July, 1960); an English description appears in V. Lvov *Science* **158** 946
[15] Isaacs J D, Vine A C, Bradner H and Bachus G E 1966 *Science* **151** 682
[16] Pearson J 1975 *Acta Astronaut.* **2** 785
[17] Shen C, Brozena A H and Wang Y 2011 *Nanoscale* **3** 503
[18] Cumings J and Zettl A 2000 *Science* **289** 602
[19] Fennimore A M, Yuzvinsky T D, Han W-Q, Fuhrer M S, Cumings J and Zettl A 2003 *Nature* **424** 408
[20] Rivera J L, McCabe C and Cummings P T 2003 *Nano Lett.* **3** 1001

[21] Rivera J L, McCabe C and Cummings P T 2005 *Nanotechnology* **16** 186

[22] Popescu A, Woods L M and Bondarev I V 2008 *Nanotechnology* **19** 435702

[23] Huang Z 2008 *Nanotechnology* **19** 045701

[24] Takagi Y, Uda T and Ohno T 2008 *J. Chem. Phys.* **128** 194704

[25] Dresselhaus M S, Dresselhaus G and Eklund P C 1996 *Science of Fullerenes and Carbon Nanotubes* (San Diego: Academic Publishers)

[26] Green A A and Hersam M C 2011 *ACS Nano* **5** 1459

[27] Hirschmann T C, Araujo P T, Muramatsu H, Zhang X, Nielsch C, Kim Y A and Dresselhaus M S 2013 *ACS Nano* **7** 2381

[28] Levshov D *et al* 2011 *Nano Lett.* **11** 4800

[29] Ghedjatti A, Magnin Y, Fossard F, Wang G, Amara H, Flahaut E, Lauret J-S and Loiseau A 2017 *ACS Nano* **11** 4840

[30] Endo M, Muramatsu H, Hayashi T, Kim Y A, Terrones M and Dresselhaus M S 2005 *Nature* **433** 476

[31] Philip Wong H-S and Akinwande D 2011 *Carbon Nanotube and Graphene Device Physics* (New York: Cambridge University Press)

[32] Zheng Q and Jiang Q 2002 *Phys. Rev. Lett.* **88** 045503

[33] Cox B J, Thamwattana N and Hill J M 2008 *Proc. R. Soc.* A **464** 691

[34] Zavalniuk V and Marchenko S 2011 *Low Temp. Phys.* **37** 336

[35] Sinnokrot M O, Valeev E F and Sherrill C D 2002 *J. Am. Chem. Soc.* **124** 10887

[36] Srivastava D 1997 *Nanotechnology* **8** 186

[37] Servantie J and Gaspard P 2006 *Phys. Rev. Lett.* **97** 186106

[38] Chandra N, Namilae S and Shet C 2004 *Phys. Rev. B* **69** 094101

[39] Kim Y A, Muramatsu H, Hayashi T, Endo M, Terrones M and Dresselhaus M S 2006 *Chem. Vap. Deposition* **12** 327

[40] Bourlon B, Christian Glattli D, Miko C, Forr L and Bachtold A 2004 *Nano Lett.* **4** 709

[41] Kis A, Jensen K, Aloni S, Mickelson W and Zettl A 2006 *Phys. Rev. Lett.* **97** 025501

[42] Jasti R, Bhattacharjee J, Neaton J B and Bertozzi C R 2008 *J. Am. Chem. Soc.* **130** 17646

[43] TURBOMOLE V6.2 2010 *University of Karlsruhe and Forschungszentrum* (Germany: Karlsruhe GmbH)

[44] Arnim M v and Ahlrichs R 1998 *J. Comp. Chem.* **19** 1746

[45] Grimme S, Antony J, Ehrlich S and Krieg H 2010 *J. Chem. Phys.* **132** 154104

[46] Lebedeva I V, Lebedev A V, Popov A M and Knizhnik A A 2017 *Comput. Mater. Sci.* **128** 45

[47] Eichkorn K, Treutler O, Ohm H, Häser M and Ahlrichs R 1995 *Chem. Phys. Lett.* **240** 283

[48] Sierka M, Hogekamp A and Ahlrichs R 2003 *J. Chem. Phys.* **118** 9136