Oscillation induced worm-like locomotion of carbon nanotubes†

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Harmonic oscillation of a doubly clamped single-walled carbon nanotube rope is significantly damped by the resistive force of friction at intertube contacts and the energy transmission rate has been estimated to be lower than that on a metal wire excited at similar frequency and vibrating length by one order of magnitude.

Introduction

The assembly of carbon nanotubes (CNTs) into microscope fibers has drawn much attention in recent years and various fabrication techniques have been developed, including mechanical extrusion, roller spinning and acid assisted injection.1–3 Compared with individual tubes the tensile strength of CNT fibers is lower by one order of magnitude and the structural weakness has been verified including increased defect density, finite tube length and intertube sliding.4 CNTs made by catalytic pyrolysis are essentially defective and the tube length mostly distributes at 5–10 μm.5 Therefore, the CNT fiber strength is mainly controlled by intertube binding, i.e. the stronger the intertube strength the greater the effective tensile load transfer to on-tube covalent bonds.6–8 A recent study has revealed that a CNT suspended between metal islands behaves as an excellent harmonic oscillator and resonance frequency (fn) can be electrostatically tuned via a gate voltage (Vg); the relationship between fn and Vg being fn ∝ Vg, fn ∝ Vg and fn ∝ Vg2/3 at low, intermediate and high Vg, respectively.9 So far, little is known about harmonic oscillation of CNT ropes, particularly the bonding character at intertube junctions upon elastic wave propagation remains to be established. In this work, a doubly clamped single-walled CNT (SWCNT) rope is excited at a broad frequency domain and harmonics of resonance frequency are recorded and analyzed according to the classical model. We find that rope oscillation induces a longitudinal stress triggering nanotube migration and elastic wave propagation is therefore dragged by the resistive force of friction at intertube junctions. This outcome explains the observed low energy transmission rate, significant resonance energy (Ere) dissipation and high damping factor. Tube movement via creeping and buckling mode is also discussed.

Experimental

SWCNTs made by ferrocene pyrolysis are spun into microscope fibers through a spin-nozzle device and three as-made fibers are merged and again twisted into a rope (10 μm in diameter). This yields regular twists along the rope axis and the winding angle revealed by scan electron microscopy (SEM) is ca. 60–70°, corresponding to 20–25 turns mm−1 (Fig. 1a).4 Unwinding is prevented by forming networked SWCNTs on the rope surface (Fig. 1a) and fabrication is briefed as follows.

Fig. 1 (a) Twisted SWCNT rope coated networked nanotubes, (b) experimental set up, (c) structure of rope fixed by silver paste (left-end), (d) top view of a fixed-end, (e) structure of SWCNT rope fixed by silver paste (left-end), (f) the laser beam spotted rope, (g) the suspended SWCNT rope. (h) The φ vs. frequency at L = 1 mm (dark), 3 mm (red) and 5 mm (green).

† Electronic supplementary information (ESI) available: SWCNT rope with less winding; SEM image of PZT treated rope and oscillation induced structural changes present at the rope surfaces. See DOI: 10.1039/b925210j

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As-made twisted rope is immersed into SWCNTs dispersed in acetone for 5 s and subsequently extracted. This procedure allows transfer of the dispersed SWCNTs onto the rope surfaces and is repeated until the deposited nanotubes are networked. The rope has a linear density ($\rho$) of $1.76 \times 10^{-3}$ kg m$^{-1}$ and weight ratio between the coating net and the rope is very low ($1 \times 10^{-3}$). The SWCNT rope is stretched and fixed onto a silicon wafer attached to an ultrasonic PZT transducer (Fig. 1b–g) and a low power micro-laser beam (0.1 mW) is employed to measure the rope displacement upon vibration at different string lengths ($L = 1, 3$ and 5 mm) (Fig. 1f). The stretched rope is excited with a constant power (5 mW) in ambient conditions and the frequency is scanned at 0–100 KHz.

Results and discussion

A doubly clamped string displaces significantly only at resonance frequency and the phenomenon can be well described by the equation below

$$f_n = \frac{n}{2} \sqrt{\frac{T}{\rho L^3}}$$

where $n$ and $T$ are integer (mode number) and string tension. In the current study, $T$ is produced when a nanotube rope is attached to the substrate and can be determined by inserting the obtained $f_n$ into the equation. Fig. 1h shows vibration amplitudes ($\Phi$) vs. frequency at $L = 1$ mm (dark), 3 mm (red) and 5 mm (green), and the $n \propto L$ is owing to the fact that more resonances are excited when $L$ increases. At $L = 1$ mm, the fundamental resonance ($n = 1$) emerges at 20 KHz and other harmonics of resonance frequency ($n$ multiples) are detected at 44 KHz ($n = 2$), 58 KHz ($n = 3$) and 78 KHz ($n = 4$), slightly deviating from the calculated data (i.e. 40 KHz, 60 KHz and 80 KHz). The fundamental resonance shifts to a lower frequency domain when $L$ increases and the measurement gives 13 KHz for $L = 3$ mm and 7 KHz for $L = 5$ mm, consistent with the prediction by eqn (1). It is noteworthy in the current study that the rope is excited with a constant power consistent with the prediction by eqn (1). It is noteworthy in the previous experiment carried out on a single suspended SWCNT chamber pressure and $n$ lies on 100–150 m s$^{-1}$, a value which decreases with air adsorption and is attributable to $\rho$ increase. In our study, the $\nu$ reduction by air intercalation between the tubes is unlikely, first, the vibrating main mass comes from the SWCNT rope, and second, the chemisorbed air content is only 0.1 wt%.$^{10}$ Accordingly, the lower $\nu$ in SWCNT rope relative to the value observed in a single SWCNT possibly arises from large damping and is supported as follows. For SWCNT ropes the structure is held by intertube cohesion and on-tube covalent bonds so $f_n$ detected here is a result of $E_{tn}$ transfer between bonding characters (coupling). Accordingly, the $E_{tn}$ is expected to dissipate at on-tube and intertube oscillators.

We have calculated the damping factor ($\zeta_n$) according to the equation $\zeta_n = \Delta F(f_n)$ and the bandwidth ($\Delta F$) is determined by the half-power points of $f_n$(Fig. 1b). Table 1 shows $\zeta_n$ at $n = 1$ and 2, and the average value of various $L$ has been estimated to be $1 \times 10^{-2}$, greater than the value observed for a single nanotube by one order of magnitude.$^{11}$ The question however remains as to what causes a large $\zeta$ in the SWCNT rope. For an oscillating SWCNT the elastic wave is primarily transmitted via covalent medium and the vibration resonance is controlled by the effective spring constant, i.e. $\omega_n = 2\pi f_n = p_o^2/2L^2[\gamma(a_0 + b_0)/\rho]^{1/2}$, where $a_0$ and $b_0$ are the inner and outer tube diameters, $\omega_n$ is the undamped frequency, $Y$ is Young’s modulus (100 GPa) and $p_o$ for eigenvalues (1.875). Substitution of the above numbers into the equation yields $\omega_n = 10^6$ Hz, exceeding the current study ($0–10^5$ Hz) by one order of magnitude. In other words, the on-tube covalent bonds do not damp the rope oscillation below $10^6$ Hz and the $\nu$ is truly reduced by intertube junctions.

The large $\zeta$ found in the SWCNT rope also implies a low energy transmission rate ($dK/dt$) and equation is expressed as

$$\frac{dK}{dt} = \frac{(\rho \nu \nu^2 \Phi^2) \cos^2(kx - wt)}{2}$$

where $(\rho \nu \nu^2 \Phi^2)/2$ is the transmitted energy ($E_T$), $\nu$ is the angular frequency and $k = 2\pi/j$. Table 2 shows $dK/dt$ obtained at $n = 1$ and 2, and the average $E_T$ is 0.1 mW. For a fixed string the excitation energy ($E_{ex}$) is the sum of dissipated energy ($E_D$) and $E_T$. $E_T$ is the excitation energy corresponding to the PZT power (5 mW) employed in the current study. Substitution of the obtained $E_{ex}$ and $E_T$ into equation gives $E_D = 4.9$ mW, indicative of the significant energy dissipation (i.e. $E_{ex} > E_T$). It is worth mentioning that SWCNT length ($L_{tube}$) is much shorter than the trench width fabricated in this work so the rope structure is primarily held by intertube binding upon stretching. In this respect, the $T$ obtained here is equivalent to the rope cohesive energy $E_{coh} = 0.66[C_0 r^2 - 3] + U_{int}(8\pi r^{2.3}J]$, where $U_{int}$ is the interaction energy per unit length of tube and $C_0 = 1.02$ eV$^{4}$. The equation clearly indicates the $\nu$ increase (or $\zeta$ decrease) with increasing $U_{int}$ and tube winding number. We have excited a SWCNT rope with less winding (15 turns mm$^{-1}$) and the average $\Delta F$ and $\zeta$ are

<table>
<thead>
<tr>
<th>$\zeta_n$ ($\times 10^{-3}$)</th>
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<tbody>
<tr>
<td>$n = 1$</td>
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<tr>
<td>1 mm</td>
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<td>26.1</td>
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Table 1: Damping factors for SWCNT rope at various $L$.

<table>
<thead>
<tr>
<th>$\frac{dK}{dt}$ ($\times 10^{-3}$)</th>
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<tbody>
<tr>
<td>$L = 1$ mm</td>
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<tr>
<td>$n = 1$</td>
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<td>2.62</td>
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Table 2: Rate of the energy transmission for the SWCNT rope at various $L$. 

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found to be twice those in Fig. 1h (ESI). This outcome is also consistent with data previously calculated for SWCNT rope strength, i.e. \( U_0 = 0.4 \) eV for compacted (Fig. 1a) and 0.12 eV for loose ropes (ESI).

CNTs show the moving activities in an electrostatically charged rope and the tubes only migrate when the bundle exhibits a low packing efficiency within the hexagonal lattice. This is because electron correlation is negligible between the non-aligned tubes, thus lowering \( E_{\text{cor}} \) and the static friction force at intertube contacts. Tube migration is also anticipated in our study, first, SWCNTs are winding and hexagonal packing is therefore unlikely, and second, the \( E_{\text{re}} \) dissipation via resistive intertube friction means an axial stress acting on tubes. So far, tube migration in an oscillating rope has not been reported and the observations above seem to suggest that the tube moves as a result of oscillation induced stress formation. For an oscillating system the return of displaced string to equilibrium relies on the structural elasticity and our simulation carried out at \( \Phi \neq 0 \) shows a distinguishable C–C bond extension along the \( a \)-axis. Simulation is carried out as follows, first, a SWCNT bundle (51.12 Å in length, atomic number = 240) is built within a \( 5 \times 5 \) nm window and the central and surrounding spiral tubes (5,0) are spaced by 3.115 Å (top, Fig. 2a), second, the density functional theory is treated with exchange–correlation and Perdew-Ultrasoft pseudopotentials, and the SCF tolerance threshold is set at \( 10^{-6} \) eV/atom for structural convergence and 0.04 Å for the Monkhorst–Pack \( k \)-point grid separation, third, the potential energy of each atom is derived from the COMPASS force field and the cut-off distance between non-bonded atoms is set at 15.5 Å, fourth, the tube is stretched (\( \sigma = 10 \) GPa) simultaneously along [100] and [\( 1 \bar{1} 0 \)] directions so the structure remains unchanged at the center of mass [000]; and fifth, the time-frame for stress relaxation is set at 36 fs. We find that

![Fig. 2](image_url)

(a) (top) Simulated packed SWCNTs before structural optimization (yellow highlights spiral tube). (lower) Simulated packed SWCNTs after structural optimization. (b) Tube axial extension upon stress application for (5,0) (top) and (10,0) tubes (lower). The yellow highlights the relative movement of hexagonal ring at relaxed (top panel) and stressed states (lower panel). (c) A worm-like locomotion mechanism for tube migration (i-iv). Insert: a damped spring model linked with two masses (top left) and optical images of closed loops at rope surface (top right).
packed SWCNTs become loose after structural optimization and the pitch decreases from 0.0125 to 0.009 turns per nm, attributable to tube flexibility (lower, Fig. 2a). The loose bundle structure however facilitates tube sliding within the rope and will be discussed in the text. At a stressed state the C–C bond is lengthened by 5.38% and retracts to 1.42 Å upon stress release (i.e. $\Phi = 0$) (top, Fig. 2b). For a larger tube (10,0) the C–C bond extension decreases to 3.64% and the underlying mechanism is due to the fact that increasing sp$^2$ characters along the tube circumference enhances the resisting force to tensile stress (lower, Fig. 2b). The differentiated elongation ($x$) becomes significant when $L_{\text{tube}}$ increases and we find $x = 17.4$ nm at $L_{\text{tube}} = 1 \mu$m and $x = 34.8$ nm at 3 $\mu$m, exceeding the threshold value for the tube bending (8–12 nm). In practice, the rope consists of finite SWCNTs exceeding the threshold value for the tube bending, thus giving $L_{\text{tube}}/r = 31 \sim 40$ in the current study. The buckled tube is straightened when the rope again displaces and slides to $x = 0$ (iii–iv). If tube buckling however exceeds the critical angle (50–60°) the kinking mode emerges and straightening via elastic creeping would be unlikely. This develops a closed loop upon rope oscillation, consistent with Fig. 2c (top right).

Experiments were also carried out on a PAN-based carbon fiber (CF) with a similar diameter (insert, Fig. 3a), and the average $\zeta$ is found to be much lower compared with the SWCNT rope, i.e. $\zeta_a = 4.6$ ($n = 1$) and 3.6 ($n = 2$) at $L = 1$ mm, 4.4 ($n = 1$) and 3.4 ($n = 2$) at $L = 3$ mm, and 8.7 ($n = 1$) and 3.1 ($n = 2$) at $L = 5$ mm. Note that CF has a comparable $\rho$ and $T$ ($\sim 3 \times 10^{-3}$ N) with SWCNTs so small $\zeta$ is attributable to low $E_{\text{re}}$ dissipation. Fig. 3b plots $E_{\text{re}}$ at $L = 1$ mm based on equation $E_{\text{re}} = k\Phi^2 m/2 (e^{-\zeta o \Phi})$ where $m$ is the string mass and $\zeta$ is obtained from Table 1. At $n = 1$, the $E_{\text{re}}$ storage in oscillating CF is greater by five-fold relative to the SWCNT rope, supporting a low dissipation process. When the mode number increases $E_{\text{re}}$ is carried by a multi-oscillator, thus reducing the $E_{\text{re}}$ magnitude. For the SWCNT rope, the $E_{\text{re}}$ is very small and remains below 20 pJ throughout, again verifying a significant dissipation. Additional evidence in support of low $E_{\text{re}}$ dissipation in CF comes from the fact that the material mainly consists of continuous graphene sheets has previously been detected in CNT-polymer composites and the critical $L_{\text{tube}}/r$ ratio for tube bending upon compression by the surrounding matrix was found to be 10.5. In the current study, $r$ lies on 0.6–0.8 nm and $x$ available for bending is 25 nm, thus giving $L_{\text{tube}}/r = 31 \sim 40$ in the current study. The buckled tube is straightened when the rope again displaces and slides to $x = 0$ (iii–iv). If tube buckling however exceeds the critical angle (50–60°) the kinking mode emerges and straightening via elastic creeping would be unlikely. This develops a closed loop upon rope oscillation, consistent with Fig. 2c (top right).

Fig. 3 (a) $\Phi$ vs. frequency at $L = 1$ mm (dark), 3 mm (red) and 5 mm (green) for CF: insert shows SEM image of CF. (b) $E_{\text{re}}$ storage in the oscillating SWCNT rope (dark) and CF (red).
oriented along the fiber axis so damping via the interlayer sliding known to occur only at high temperature is relatively difficult compared with intertube motion.\textsuperscript{19}

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References