Limits of mechanical energy storage and structural transformations in twisted carbon nanotube ropes

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Supporting on-line material

Calculation details and comments

The equilibrium structure of a twisted nanotube rope may be characterized by the optimum twisting, stretching, bending and compression strains of individual nanotubes and nanotube pairs. These deformations may be determined by optimizing the total energy expression in Eq. (10). This optimization may be performed analytically in view of the fact that the strains $\varepsilon_{\circ}$, $\varepsilon_{||,i}$, $\varepsilon_{\angle,i}$ and $\varepsilon_{\perp,ij}$ are interrelated in a given twisted rope. Analytic expressions presented below allow us to analyze the relative significance of particular deformation modes and suggest ways to optimize energy storage.

In a twisted rope, the twist strain $\varepsilon_{\circ}$ of each individual strain equals that of the entire rope. The axial strain $\varepsilon_{||,i}$ of the coiled strand i of the rope, represented schematically in the bottom panel of

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Fig. (3a), is given by [1,2]

$$\varepsilon_{||,i} = \sqrt{1 + (\varepsilon_\circ \rho_i / d_{(n,m)})^2} - 1 \ , \tag{A1}$$

where ρ_i is the coil radius and $d_{(n,m)}$ the nanotube diameter. Similarly, the bending strain can be expressed as

$$\varepsilon_{\angle,i} = \varepsilon_\circ \frac{\varepsilon_\circ \rho_i / d_{(n,m)}}{\left(\varepsilon_\circ \rho_i / d_{(n,m)}\right)^2 + 1} \ . \tag{A2}$$

When optimizing the rope geometry, we need to consider that the nanotube diameter is related to the inter-tube separation d_{ij}, which determines the coil radius ρ_i and also depends on the compression strain $\varepsilon_{\perp,ij}$. This reduces significantly the number of independent variables for structure optimization. Optimization is easiest for ropes with symmetric cross-sections. Ropes containing $N_s = 2, 3, 4$ nanotube strands do not have a central nanotube, in contrast to ropes with $N_s = 7, 13, 19$ nanotube strands that do have a nanotube in the center.

The maximum energy storage capacity for the individual deformation modes is listed in Table 1. The theoretical maximum energy storage capacity $J = 12.35$ MJ/kg of a twisted rope then corresponds to the sum of storage capacities of all individual modes. This value could only be reached if all deformation modes were to reach the elastic limit simultaneously, which is practically never the case. In general, among the different deformation strains $\varepsilon_\circ$, $\varepsilon_{||,i}$, $\varepsilon_{\angle,i}$ and $\varepsilon_{\perp,ij}$, the maximum reversible energy storage density in a twisted rope is determined by the deformation mode, which reaches the elastic limit first. The other deformation modes provide only a fraction of their maximum energy storage capacity.

To estimate the energy storage amount in a rope twisted to its elastic limit, we first introduce the new variable $x = \varepsilon_\circ \rho_i / d_{(n,m)} = \rho_i \varphi / l_0$ that describes the deformation of nanotube strand i subject to the twist rate φ / l_0 in a coil or radius ρ_i. Then, Eq. (A1) reduces to

$$\varepsilon_{||,i} = \sqrt{1 + x^2} - 1 \tag{A3}$$

and Eq. (A2) to

$$\varepsilon_{\angle} = \varepsilon_{\circ}\frac{x}{x^2+1} \; . \tag{A4}$$

If there were no limit on x, then the maximum bending strain could be estimated using the expression in Eq. (A4). $\varepsilon_{\angle}$ reaches its maximum at $x = 1$, yielding $\varepsilon_{\angle,max} = \varepsilon_{\circ}/2$ for the maximum bending strain. In reality, the allowed value range of x is limited by the elastic limit of the axial strain $\varepsilon_{||,max} = 0.12$ according to Table 1, which translates to $x \lesssim 0.50$ according to Eq. (A3) and thus to $\varepsilon_{\angle} \lesssim 0.40\varepsilon_{\circ}$. At the elastic limit of twisting $\varepsilon_{\circ,max} = 0.52$ according to Table 1, we find $\varepsilon_{\angle}, max = 0.21$ for the maximum bending strain and the optimum coil radius $\rho_i/d_{(n,m)} = x/\varepsilon_{\circ} = 0.97$.

We thus conclude that for specific twisted ropes, we may be able to simultaneously reach the elastic limits $\varepsilon_{\circ,max} = 0.52$, $\varepsilon_{||,max} = 0.12$ and $\varepsilon_{\angle,max} = 0.21$. Neglecting compression, the sum of twisting, stretching and bending deformation energies amounts to $J = 11.96$ MJ/kg if the ideal condition $x = \varepsilon_{\circ}\rho_i/d_{(n,m)} = 0.97$ may be reached by all nanotube strands in a rope.

This condition may be achieved in a simple rope with N_s nanotube strands and no central nanotube. All nanotubes form corners of a polygon with N_s corners in cross-section and share the same coiling radius ρ. Ignoring the difference between 0.97 and unity for the optimum value of $x/\varepsilon_{\circ} = \rho/d_{(n,m)}$, we may approximate $d_{(n,m)} \approx \rho$. Considering the simple geometry of the polygonal cross-section of the rope, where the nanotubes are separated by the inter-wall distance $d_{iw} \approx 3.0 - 3.5$ Å, we find

$$d_{(n,m)} = \frac{d_{iw}}{2\sin(\pi/N_s) - 1} \; . \tag{A5}$$

Using Eq. (A5) we are able to estimate the optimum nanotube diameter that maximizes energy storage in a rope of N_s nanotubes. With the optimum nanotube diameters as a function of N_s at hand, we are able to present the optimum number of strands $N_{s,opt}$ as a function of given nanotube diameter in Fig. 5. We need to point out the limits of the model ropes discussed here, since Eq. (A5) provides unphysical results for $N_s \geq 6$.

The value $J = 11.96$ MJ/kg achieved in the simplified rope due to twisting, stretching and bending only is a significant fraction of the $J = 12.35$ MJ/kg, given by the sum of all decoupled deformations at their elastic limit according to Table 1. In reality, the maximum storage values shown in Fig. 4 are lower, since the optimum value $x = 0.97$ can not be reached by all nanotubes in a rope simultaneously.

Comparison of maximum achievable gravimetric energy storage densities J in Table 1 reveals that twisting is most important, followed by stretching, bending and compression. The high energy cost of twisting is mostly due to stretching and compression of C-C bonds, and only to a lesser degree to changes in bond angles, often called bond bending. Our structure optimization studies of isolated nanotubes indicate that stretching and bending primarily cause bond bending, which is a softer deformation mechanism. Neglecting the role of bond stretching in these deformations, we can relate the bending force constants to the stretching force constant by $k_\angle = k_{||}/12$. Using the value $k_{||} = 32.5$ eV, given in Table 1, this estimate yields $k_\angle = 2.71$ eV, which is close to the value $k_\angle = 3.94$ eV that is listed in Table 1. We also find the elastic limit of bending to be related to that of stretching by $\varepsilon_{\angle,max} = 2\varepsilon_{||,max}$. Using the value $\varepsilon_{||,max} = 0.12$ from Table 1, we estimate $\varepsilon_{\angle,max} = 0.24$, in good agreement with the value 0.21 listed in Table 1.

According to Table 1, depending on the deformation path, the maximum energy density in a hydrostatically compressed nanotube array ranges from $J = 1.29 - 4.62$ MJ/kg, thus competing in significance with twisting and stretching. These values represent a rope with an infinite number of strands and no surface. Lower values occur in ropes with a finite number of strands, since the compression energy scales with the number of pairs of adjacent nanotubes, which is reduced from 6 in the interior to as few as 3 at the rope periphery. In the extreme case of a 2-rope, the maximum values of J listed in Table 1 are reduced by a factor of 3.

Next we derive a simplified expression for the energy storage per atom $\Delta E/N$ as a useful counterpart of Eq. (10) which uses the deformations $\varepsilon_\circ$, $\varepsilon_{||,i}$, $\varepsilon_{\angle,i}$ and $\varepsilon_{\perp,ij}$ as formally independent quantities. Our objective is to derive an energy expression that depends only on the twist strain $\varepsilon_\circ$ that is externally applied to the entire rope. Using this expression, we intend to study the relative importance of the individual strains as a function of $\varepsilon_\circ$.

In the following derivation, we will limit ourselves to ropes with a peripheral layer containing $N_{s,p}$ nanotube strands at a constant distance $\rho = \rho_p > 0$ from the center. Among these, we will consider ropes with a nanotube at the center, characterized by $\rho_c = 0$, or no central nanotube. Examples are ropes with 2 strands, described by $N_s = N_{s,p} = 2$, and with 7 strands, described by $N_s = 7$ and $N_{s,p} = 6$. The nanotubes at the rope periphery form a regular polygon in cross-section. Rather than specifying all inter-tube separations in terms of the equilibrium value $d_0 = d_{(n,m)} + d_{iw}$, we introduce the parameter λ, defined by $\lambda = \rho/[d_0(1-\varepsilon_\perp)]$, which completely characterizes the geometry of a radially compressed rope. For nanotubes at equilibrium distance $d_0(1-\varepsilon_\perp)$ along the rope periphery, we find $\lambda = (2\sin(\pi/N_{s,p}))^{-1}$. For small values of the rope twist strain $\varepsilon_\circ$, Eqs. (A1) and (A2) may be rewritten as

$$\varepsilon_{||} \approx \frac{1}{2}\left(\frac{\lambda d_0}{d_{(n,m)}}\right)^2 (1-\varepsilon_\perp)^2 \varepsilon_\circ^2 \qquad \text{and} \qquad \varepsilon_\angle \approx \frac{\lambda d_0}{d_{(n,m)}}(1-\varepsilon_\perp)\varepsilon_\circ^2 \,. \tag{A6}$$

These relations simplify Eq. (10) to

$$\frac{\Delta E}{N} \approx \left(\frac{k_{||}}{4}\left(\frac{\lambda d_0}{d_{(n,m)}}\right)^4 (1-\varepsilon_\perp)^4 + k_\angle \left(\frac{\lambda d_0}{d_{(n,m)}}\right)^2 (1-\varepsilon_\perp)^2 \right) \frac{N_{s,p}}{N_s}\varepsilon_\circ^4 + k_\circ \varepsilon_\circ^2 + k_\perp \frac{N_\perp}{N_s}\varepsilon_\perp^2 \,, \tag{A7}$$

where $N_\perp$ is the total number of pairs of adjacent nanotubes in the rope. Examples are a 2-rope with $N_\perp = 1$ and a 7-rope with a central nanotube and $N_\perp = 12$.

At a given twist strain $\varepsilon_\circ$, the optimum value of $\varepsilon_\perp$ that minimizes the energy can be obtained from $\partial(\Delta E/N)/\partial\varepsilon_\perp = 0$. This is equivalent to

$$k_{||}\left(\frac{\lambda d_0}{d_{(n,m)}}\right)^4 (1-\varepsilon_\perp)^3 \varepsilon_\circ^4 + 2k_\angle \left(\frac{\lambda d_0}{d_{(n,m)}}\right)^2 (1-\varepsilon_\perp)\varepsilon_\circ^4 - 2k_\perp \frac{N_\perp}{N_{s,p}}\varepsilon_\perp = 0 \,. \tag{A8}$$

Eq. (A8) suggests that $\varepsilon_\perp$ is a function of $\varepsilon_\circ^4$. For small values we obtain

$$\varepsilon_\perp = \frac{1}{2k_\perp}\frac{N_{s,p}}{N_\perp}\left(k_{||}\left(\frac{\lambda d_0}{d_{(n,m)}}\right)^2 + 2k_\angle \right)\left(\frac{\lambda d_0}{d_{(n,m)}}\right)^2 \varepsilon_\circ^4 + O(\varepsilon_\circ^8) \,. \tag{A9}$$

The approximation is valid for $\varepsilon_\circ \lesssim 0.1$, before the terms of the order $O(\varepsilon_\circ^8)$ become important.

With the above expressions we are now able to roughly estimate the energy dependence of the individual deformation mechanisms on the twist strain of the rope only. The energy contribution of twisting has an $\varepsilon_\circ^2$ dependence. The energy contributions of stretching and bending have an $\varepsilon_\circ^4$ dependence for $\varepsilon \lesssim 0.1$. Correcting terms for these modes share the same $\varepsilon_\circ^8$ dependence with compression. This analysis explains, why twisting energy dominates at low values of $\varepsilon_\circ$ and loses its leading role at higher twist rates.

The simplified energy storage expressions for the individual deformation modes may now be combined to

$$\Delta E/N \approx k_\circ \varepsilon_\circ^2 + k_1 \varepsilon_\circ^4 + k_2 \varepsilon_\circ^8 + O(\varepsilon_\circ^{12}) \,, \tag{A10}$$

where

$$k_1 = \frac{N_{s,p}}{4N_s}\left[k_{||}\left(\frac{\lambda d_0}{d_{(n,m)}}\right)^2 + 4k_\angle\right]\left(\frac{\lambda d_0}{d_{(n,m)}}\right)^2 \tag{A11}$$

and

$$k_2 = -\frac{1}{4k_\perp}\frac{N_{s,p}^2}{N_\perp N_s}\left[k_{||}\left(\frac{\lambda d_0}{d_{(n,m)}}\right)^2 + 2k_\angle\right]^2\left(\frac{\lambda d_0}{d_{(n,m)}}\right)^4 \,. \tag{A12}$$

Equations (A10, A11, A12) correspond to Eqs. (2, 11, 12).

Close inspection of Fig. 3(d) reveals that the functional form in Eq. (A10) reproduces the numerical DFTB results adequately in the range $\varepsilon_\circ \lesssim 0.2$. The values of $k_\circ$, k_1 and k_2 used in the fitted functions of Fig. 3(d) are listed in Table 3.

We found it instructive to compare these fitted values to estimates based on Eqs.(A11) and (A12). These estimates, obtained using $d_0 = d_{(n,m)} + d_{iw}$ with $d_{iw} = 3$ Å, are listed in Table 3 alongside the DFTB fits. For most nanotube ropes, we find the fitted values of $k_\circ$ to agree closely with the value $k_\circ = 3.14$ eV listed in Table 1. With the exception of the 2-rope, the fitted values of k_1 are somewhat smaller than the values estimated using Eq. (A11). This reflects the fact that the elastic response due to stretching, bending, and compression is, to some degree, affected by the degree of torsion especially in ropes with many strands. The value of k_2 gains importance in

Eq. (A10) especially at higher twist rates. All values of k_2 that are listed in Table 3 are negative, since the elastic response to torsion is expected to soften at high twist rates. There are sizeable differences between the values fitted to DFTB calculations and those estimated using Eq. (A12), which is not surprising in view of the fact that energy contributions in Eq. (A10), which have k_2 as pre-factor, are much smaller than those with k_1 as pre-factor at small values of $\varepsilon_\circ$, where this equation is valid. An additional reason for the differences in the listed values of k_2 is that the compression pathways found in the atomistic DFTB calculations of the ropes may differ somewhat from those found in infinite nanotube lattices. In spite of these limitations, we find the simple expression in Eq. (A10) to be surprisingly accurate and capable of semi-quantitatively estimating the total energy storage capacity of a twisted nanotube rope.

Movies

Supporting on-line material contains the following movies:

(10,10)CNT-twist.gif is an animated gif file depicting the twisting of a (10,10) carbon nanotube, obtained using DFTB calculations and described in Figure 1(a) of the main manuscript. Spontaneous flattening of the nanotube is introduced at a critical twist rate.

(10,10)CNT-stretch.gif is an animated gif file depicting the stretching of a (10,10) carbon nanotube, obtained using DFTB calculations and described in Fig. 1(b) of the main manuscript.

A-compress_hydro.gif is an animated gif file depicting the compression of (18,0) nanotubes under hydrostatic pressure along pathway A, obtained using DFT calculations and described in Fig. 2 of the main manuscript.

B-compress_hydro.gif is an animated gif file depicting the compression of (18,0) nanotubes under hydrostatic pressure along pathway B, obtained using DFT calculations and described in Fig. 2 of the main manuscript.

C-compress_hydro.gif is an animated gif file depicting the compression of (18,0) nanotubes under hydrostatic pressure along pathway C, obtained using DFT calculations and described in Fig. 2 of the main manuscript.

D-compress_hydro.gif is an animated gif file depicting the compression of (18,0) nanotubes under hydrostatic pressure along pathway D, obtained using DFT calculations and described in Fig. 2 of the main manuscript.

2rope_10_10.gif is an animated gif file depicting the twisting of the two-strand (10,10) CNT rope, obtained using DFTB calculations and presented in Fig. 4 of the main manuscript. The end-on view represents the cross-section of the rope. Spontaneous flattening of the nanotubes is introduced at a critical twist rate.

6rope_10_10.gif is an animated gif file depicting the twisting of the six-strand (10,10) CNT rope, obtained using DFTB calculations and presented in Fig. 4 of the main manuscript. The end-on view represents the cross-section of the rope. Spontaneous flattening of the nanotubes is introduced at a critical twist rate.

7rope_6_6.gif is an animated gif file depicting the twisting of the seven-strand (6,6) CNT rope, obtained using DFTB calculations and presented in Fig. 4 of the main manuscript. The end-on view represents the cross-section of the rope. Spontaneous flattening of the nanotubes is introduced at a critical twist rate.

7rope_18_0.gif is an animated gif file depicting the twisting of the seven-strand (18,0) CNT rope, obtained using DFTB calculations and presented in Fig. 4 of the main manuscript. The end-on view represents the cross-section of the rope. Spontaneous flattening of the nanotubes is introduced at a critical twist rate.

For the sake of illustration, all animations are presented side-by-side in side view and in end-on view. The range of applied strain for stretching, twisting and compression extends into the inelastic regime.

References

(1) Teich, D.; Fthenakis, Z. G.; Seifert, G.; Tománek, D. *Phys. Rev. Lett.* **2012**, *109*, 255501.

(2) Teich, D.; Seifert, G.; Iijima, S.; Tománek, D. *Phys. Rev. Lett.* **2012**, *108*, 235501.