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ORIGINAL PAPER

Constitutive behavior of pressurized carbon nanoscrolls

Xinghua Shi · Nicola M. Pugno · Huajian Gao

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Abstract Carbon nanoscrolls (CNSs) are a class of graphene-based nanoscale materials with great potential for applications in nanotechnology and bioengineering. Fundamental description, understanding and regulation of these materials may ultimately lead to a new generation of integrated systems that utilize their unique properties. A particularly interesting property of a CNS is that there exists a stable equilibrium core size which can be uniquely determined from the basal graphene length, the interlayer spacing, the interaction energy between layers, the bending stiffness of graphene, as well as the difference between the pressure inside the core of the CNS and that on its outer surface. Here we investigate the strongly nonlinear constitutive behaviour of a CNS under pressure, focusing on its deformation, stability and biaxial modulus in response to its inner and external pressures. Our study suggests pressure sensitive applications of CNSs such as nanopumps and nanofilters.

Keywords Carbon nanoscrolls · Griffith theory · Molecular dynamics · Graphene · Pressure

1 Introduction

Carbon nanoscrolls (CNSs) have attracted significant interests in recent years (Viculis et al. 2003; Xie et al. 2009; Savoskin et al. 2007; Roy et al. 2008; Chuvilin et al. 2009; Shioyama and Akita 2003). Unlike the tubular structure of carbon nanotubes (CNT), a CNS is made of a continuous basal graphene sheet rolled up in a spiral form. CNSs were first discovered in a chemical process when graphite was intercalated with potassium metal, exfoliated with ethanol and then sonicated (Viculis et al. 2003). Recently, a simple and effective way was developed to fabricate CNS on SiO_2/Si substrate, in which a graphene sheet extracted mechanically from graphite was found to spontaneously roll into CNS in isopropyl alcohol solvent (Xie et al. 2009). Due to their unique topology, CNSs have shown unique structural (Chen et al. 2007; Braga et al. 2004, 2007; Coluci et al. 2007; Mpourmpakis et al. 2007), dynamical (Braga et al. 2004) and electronic (Xie et al. 2009; Chen et al. 2007; Pan et al. 2005; Rurali et al. 2006) properties. More specifically, it has been found that a stable formation of CNSs exists with energy lower than that of precursor graphene (Braga et al. 2004).

X. Shi · H. Gao (✉)
Division of Engineering, Brown University,
610 Barus and Holley, 182 Hope Street, Providence,
RI 02912, USA
e-mail: Huajian_Gao@brown.edu

X. Shi
e-mail: xinghua_shi@brown.edu

N. M. Pugno (✉)
Laboratory of Bio-inspired Nanomechanics "Giuseppe
Maria Pugno", Department of Structural Engineering,
Politecnico di Torino, Corso Duca degli Abruzzi 24,
10129 Torino, Italy
e-mail: nicola.pugno@polito.it

The core of CNSs can be significantly changed upon charge injection, which makes it a natural choice for a new class of efficient nanoacutators (Rurali et al. 2006). The flexible core and large surface area also enable the CNSs to be utilized as potential materials for hydrogen storage (Braga et al. 2007; Coluci et al. 2007; Mpourmpakis et al. 2007). Recent experiments on electrical-transport measurements (Xie et al. 2009) show that the resistance of CNSs is weakly gate-dependent but strongly temperature-dependent. In addition, the CNSs can sustain a high current density, making it a good candidate as microcircuit interconnects. These studies indicate that CNSs hold great potential for applications in nanotechnology.

Parallel to experimental and molecular dynamics (MD) simulation studies, theoretical models have also been developed to describe the equilibrium configuration of CNSs (Shi et al. 2010a), as well as their structural and dynamical properties (Shi et al. 2009, 2010b,c). It has been shown that a stable equilibrium core size of CNSs can be uniquely determined from the basal graphene length, the interlayer spacing, the interaction energy between layers of CNS and the bending stiffness of graphene (Shi et al. 2010a). The dynamical breathing and translational motions of CNSs have also been theoretically investigated (Shi et al. 2009, 2010b). In these studies, the surface energy of a CNS is considered to be tuneable by an applied electric field to control or perturb the core size. The present paper is aimed to investigate the constitutive behaviour of a pressurized CNS via theoretical modelling and molecular dynamics simulations, and to show that an externally applied pressure can also be utilized to control the core size of CNS.

Note that the core expansion of a carbon nanoscroll involves a balance between elastic energy (bending energy of the graphene sheet) and surface energy (van der Waals adhesion energy), that is formally identical to the classical Griffith's criterion. Therefore adhesion, which is key in nanosystems, can be treated as a fracture process.

2 Theoretical model

A graphene sheet of length B and width L is rolled up into a CNS with inner core radius r_0, outer radius R and interlayer spacing h (Fig. 1a). The configuration can be described by a radial function as

$$r = r_0 + \frac{h}{2\pi}\vartheta. \tag{1}$$

The total length B of the graphene sheet can be approximately described as

$$Bh = \pi\left(R^2 - r_0^2\right). \tag{2}$$

The pressure applied on the outer surface of the CNS is denoted as p_e whereas the pressure inside its inner core is p_i. The elastic energy per unit area in the graphene is taken as

$$\frac{\mathrm{d}W}{\mathrm{d}A}(r) = \frac{D}{2}\frac{1}{r^2}, \tag{3}$$

where D is the bending stiffness. Note that $\mathrm{d}A \approx Lr\mathrm{d}\vartheta$. The total elastic energy in the CNS is obtained by integrating Eq. (3) as

$$W = \frac{\pi DL}{h}\ln\left(\frac{R}{r_0}\right). \tag{4}$$

Consider an infinitesimal change in the core radius r_0 of the scroll. The change in strain energy would be

$$\mathrm{d}W = \frac{\pi DL}{h}\left(\frac{\mathrm{d}R}{R} - \frac{\mathrm{d}r_0}{r_0}\right) = -\frac{\pi DL}{h}\frac{R^2 - r_0^2}{R^2}\frac{\mathrm{d}r_0}{r_0}, \tag{5}$$

where the relation $r_0\mathrm{d}r_0 = R\mathrm{d}R$ from differentiating Eq. (2) has been used. On the other hand, the change in total surface energy of the CNS is

$$\mathrm{d}\Gamma = 2\pi\gamma L\left(\mathrm{d}r_0 + \mathrm{d}R\right) = 2\pi\gamma L\left(1 + \frac{r_0}{R}\right)\mathrm{d}r_0, \tag{6}$$

where γ is the surface energy per unit area. The virtual work associated with an infinitesimal perturbation in the core size is

$$\mathrm{d}\Phi = -p_i 2\pi Lr_0\mathrm{d}r_0 + p_e 2\pi LR\mathrm{d}R = -2\pi Lr_0\mathrm{d}r_0 p, \tag{7}$$

where $p = p_i - p_e$. Therefore, the change in free energy Eassociated with a "virtual core expansion" is

$$\frac{\mathrm{d}E}{\mathrm{d}r_0} = \frac{\mathrm{d}W}{\mathrm{d}r_0} + \frac{\mathrm{d}\Gamma}{\mathrm{d}r_0} + \frac{\mathrm{d}\Phi}{\mathrm{d}r_0}. \tag{8}$$

The equilibrium core size can be calculated by setting $\mathrm{d}E = 0$, similarly to the classical Griffith's criterion for fracture propagation, which yields

$$2\pi\gamma\left(1 + \frac{r_0}{R}\right) = \frac{\pi D}{h}\frac{R^2 - r_0^2}{R^2}\frac{1}{r_0} + 2\pi r_0 p. \tag{9}$$

This leads to the following equation governing the core size of the CNS,

$$\frac{2\gamma h}{D} = \frac{1}{r_0} - \frac{1}{R} + \frac{2hp}{D\left(1/r_0 + 1/R\right)}, \tag{10}$$

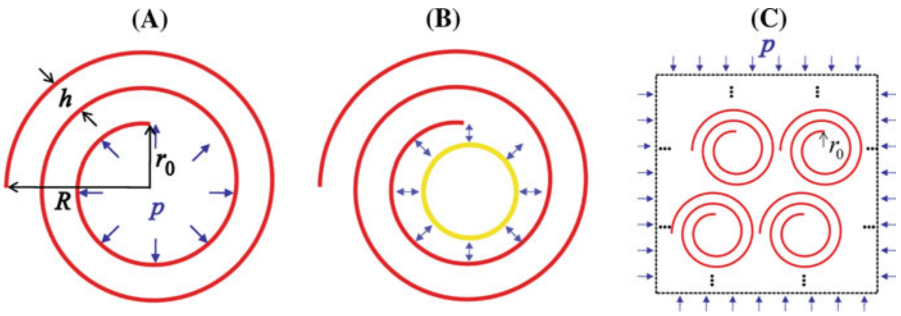

Fig. 1 **a** Schematic illustration of a carbon nanoscroll with inner core radius r_0, outer radius R and interlayer spacing h. **b** An internal pressure is applied by inserting a carbon nanotube inside the core. **c** A CNS crystal under biaxial compression

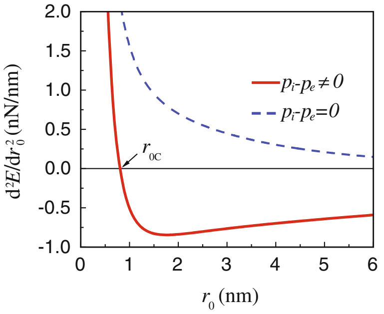

Fig. 2 Second derivative of free energy of a CNS with respect to its core size. The *dash line* is for the case without pressure difference ($p_i - p_e = 0$) and *solid line* for a finite pressure difference ($p_i - p_e \neq 0$)

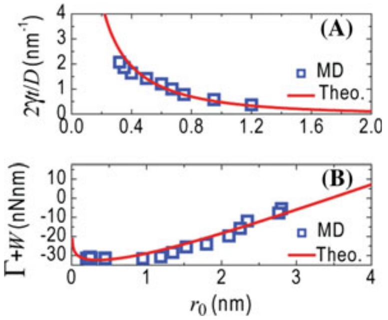

Fig. 3 **a** The ratio between surface energy and bending modulus of graphene as a function of the CNS core size. **b** The potential energy as a function of the core size. All results are obtained in vacuum. Squares are the MD results and *solid line* is the theoretical prediction (taken from Ref. Shi et al. 2010a)

or

$$p_i - p_e = \frac{D}{2h}\left(\frac{2\gamma h}{D} - \frac{1}{r_0} + \frac{1}{R}\right)\left(\frac{1}{r_0} + \frac{1}{R}\right), \qquad (11)$$

where $R = \sqrt{\frac{Bh}{\pi} + r_0^2}$.

The stability of the system requires $\frac{\mathrm{d}^2 E}{\mathrm{d}r_0^2} \geq 0$. Under constant pressure, this condition is reduced to

$$\frac{\mathrm{d}^2 E}{\mathrm{d}r_0^2} = \frac{DBL}{R^2 r_0^2} + \frac{2DBL}{R^4} + 2\pi\gamma L\left(\frac{1}{R} - \frac{r_0^2}{R^3}\right) - 2\pi L\left(p_i - p_e\right) \geq 0. \qquad (12)$$

Taking the parameters as $D = 0.11\,\mathrm{nN}\cdot\mathrm{nm}$, $\gamma = 0.4\,\mathrm{nN/nm}$, $h = 0.34\,\mathrm{nm}$, $B = 200\,\mathrm{nm}$, Fig. 2 shows the second derivative of free energy with respect to the core size. In the absence of a pressure difference ($p = p_i - p_e = 0$), $\frac{\mathrm{d}^2 E}{\mathrm{d}r_0^2}$ is always greater than zero, indicating that the equilibrium configuration of CNS is stable. Figure 3a shows that the above theory is in excellent agreement with molecular dynamics (MD) simulations on how the surface energy, the bending stiffness, the interlayer spacing of graphene and the length of graphene sheet influence the core size of the CNS (Shi et al. 2010a). Figure 3b plots the evolution of potential energy (elastic energy plus surface energy) as a function of the core size. The results shown in Figs. 2 and 3 clearly indicate that there exists a stable configuration of CNS with an equilibrium core size.

Under constant pressure $p = p_i - p_e \neq 0$, however, $\frac{\mathrm{d}^2 E}{\mathrm{d}r_0^2}$ is greater than zero only when the core size is below some critical value r_{0C} (Fig. 2). This indicates that there is a critical pressure, beyond which the CNS becomes unstable under constant pressure. To further investigate the influence of pressure on the core size of CNS, a critical radius $r_0 = r_{0C}$ for unstable expansion under constant pressure is determined from

$$\frac{\mathrm{d}p\left(r_0\right)}{\mathrm{d}r_0} = \gamma\left(-\frac{1}{r_0^2} - \frac{r_0}{R^3}\right) + \frac{D}{h}\left(\frac{1}{r_0^3} - \frac{r_0}{R^4}\right) = 0. \qquad (13)$$

Inserting r_{0C} into Eq. (11) yields the critical pressure as

$$p_C = p\left(r_0 = r_{0C}\right). \qquad (14)$$

Closed form solutions exist in the two asymptotic limits, corresponding to “thin” or “thick” CNSs. For thick CNSs, $R = r_0\sqrt{1+\alpha}$ where $\alpha = \frac{Bh}{\pi r_0^2} \to \infty$ (note that α is the ratio between the cross-sectional area of the CNS and that of its inner core); accordingly, Eq. (11) becomes $p\,(r_0) \approx \frac{\gamma}{r_0} - \frac{D}{2hr_0^2}$. In the absence of pressure, setting $p = 0$ gives the equilibrium core radius $r_{0e} \approx \frac{D}{2\gamma h}$. The critical core radius for unstable expansion under constant pressure can be derived according to Eq. (13) as

$$r_{0C} \approx \frac{D}{\gamma h} = 2r_{0e}. \tag{15}$$

The corresponding critical pressure is

$$p_C \approx \frac{\gamma^2 h}{2D}. \tag{16}$$

For thin CNSs, $R = r_0\sqrt{1+\alpha}$ with $\alpha = \frac{Bh}{\pi r_0^2} \to 0$; Eq. (11) becomes $p\,(r_0) \approx \frac{2\gamma}{r_0} - \frac{BD}{2\pi r_0^4}$. For $p = 0$, the equilibrium core radius is $r_{0e} \approx \left(\frac{BD}{4\pi\gamma}\right)^{1/3}$. The critical core radius for unstable expansion under constant pressure is

$$r_{0C} \approx \left(\frac{BD}{\pi\gamma}\right)^{1/3} = 4^{1/3} r_{0e}. \tag{17}$$

The corresponding critical pressure is

$$p_C \approx \frac{3}{2}\left(\frac{\gamma^4 \pi}{BD}\right)^{1/3}. \tag{18}$$

Figure 4 shows the predicted equilibrium core size as a function of the pressure. As the core of CNS is expanded, the pressure increases first, reaches the peak at a critical core radius, and then drops. The asymptotic results for thick and thin CNSs are indicated as crosses in Fig. 4. It is seen that the pressure used to expand the core of a thick CNS with large graphene length B is generally smaller than that used for a thin CNS, indicating a counterintuitive result that it is easier to expand a thick CNS to a specific core size than a thin CNS.

To investigate the constitutive behaviour of a pressurized CNS, Eq. (11) is rewritten as

$$p_i - p_e = \gamma\left(\sqrt{\frac{\pi L}{V - BhL}} + \sqrt{\frac{\pi L}{V}}\right) - \frac{DB\pi L^2}{2V\,(V - BhL)}, \tag{19}$$

where $V = \pi R^2 L$. Figures 5a, b show the pressure difference as a function of volume, with result showing similar features as Fig. 4. The biaxial modulus of the CNS can be defined as

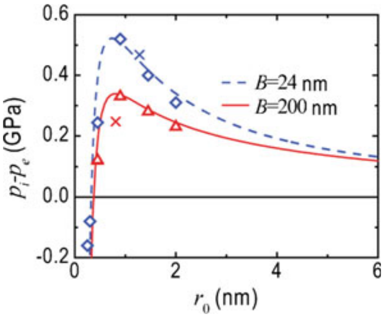

Fig. 4 Pressure difference vs equilibrium core size of CNSs for different graphene lengths calculated from theory (*line*) and MD simulations (*scatters*). The crosses are the asymptotic solutions for *thick* and *thin* CNSs

$$K = -V\frac{\partial p}{\partial V} = \frac{\gamma}{2}\left(\sqrt{\frac{\pi L}{V}} + \sqrt{\frac{\pi L V^2}{(V - BhL)^3}}\right) - \frac{BD\pi L^2}{2\,(V - BhL)^2} - \frac{BD\pi L^2}{2V\,(V - BhL)}. \tag{20}$$

Figures 5c, d show that the biaxial modulus of a CNS varies with its volume. The dash lines indicate the volume when $p_i - p_e = 0$. It is seen that the biaxial modulus increases as the core is compressed and decreases as the core is expanded. When $p_i - p_e = 0$, the biaxial modulus is 20 GPa for $B = 20$ nm and 80 GPa for $B = 200$ nm. We would like to point out that these values are greatly affected by the surface energy of the CNS. In Fig. 5c, the surface energy has been taken as $\gamma = 0.4$ nN/nm, and the biaxial modulus is 20 GPa; decreasing the surface energy to $\gamma = 0.2$ nN/nm reduces the biaxial modulus to 3 GPa.

3 Molecular dynamics simulations

Molecular dynamics (MD) simulations are a suitable tool for investigating the structural and dynamic properties of CNSs. We have performed MD simulations to investigate the influence of pressure ($p_i - p_e > 0$) on the core expansion of CNS. The MD package Gromacs 4 (Hess et al. 2008) was used to simulate the behaviour of CNSs described by a Morse bond, a harmonic cosine term for the bond angle, a cosine term for torsion and a Lennard-Jones (L-J) term for the van der Waals (vdW) interaction. These interactions are expressed as (Walther et al. 2001)

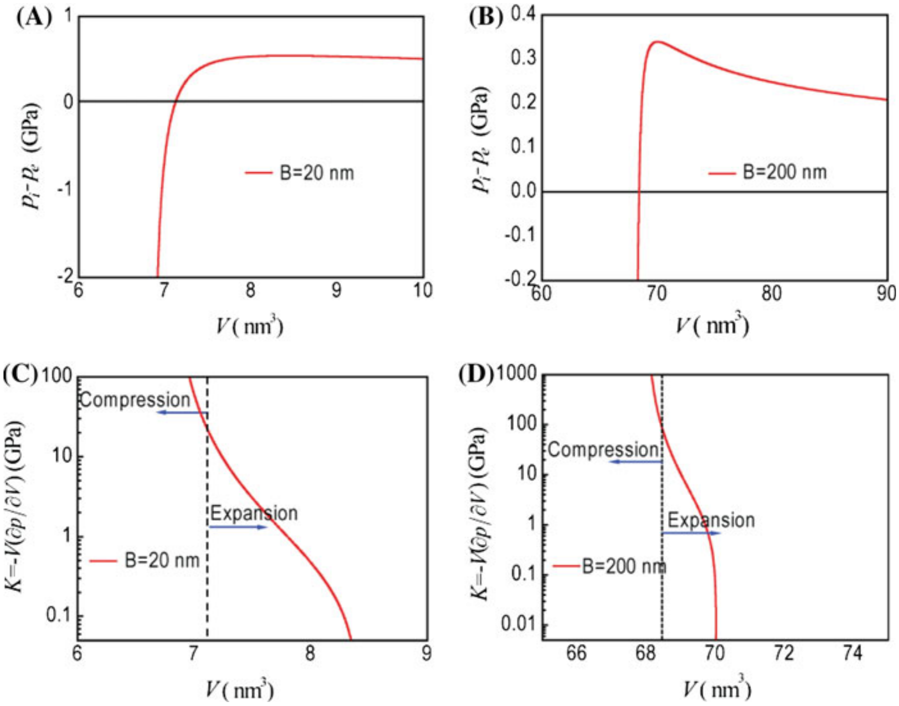

Fig. 5 Pressure difference as a function of volume of a CNS with two different graphene length **a** $B = 20\,\text{nm}$ and **b** $B = 200\,\text{nm}$. The biaxial modulus of the CNS as a function of volume for **c** $B = 20$ nm and (**d**) $B = 200\,\text{nm}$. The *dash lines* indicate the volume when $p_i - p_e = 0$

$$
\begin{aligned}
U\left(r_{ij}, \theta_{ijk}, \phi_{ijkl}\right) = {} & K_{Cr}\left[e^{-k_C\left(r_{ij}-r_C\right)} - 1\right]^2 \\
& + \frac{1}{2}K_{C\theta}\left(\cos\theta_{ijk} - \cos\theta_C\right)^2 \\
& + \frac{1}{2}K_{C\phi}\left(1 - \cos 2\phi_{ijkl}\right) \\
& + 4\varepsilon_{CC}\left[\left(\frac{\sigma_{CC}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{CC}}{r_{ij}}\right)^{6}\right],
\end{aligned}
\tag{21}
$$

where k_C defines the steepness of Morse potential well, r_{ij} denotes distance between two bonded atoms, θ_{ijk} and ϕ_{ijkl} are the bending and torsional angle, r_C, θ_C and ϕ_C are reference geometrical parameters for graphene, K_{Cr}, $K_{C\theta}$ and $K_{C\phi}$ are the force constants of stretching, bending and torsion, respectively, and $\sigma_{CC} = 0.34\,\text{nm}$ and $\varepsilon_{CC} = 0.3601\,\text{kJ/mol}$ are the Lennard-Jones parameters for carbon. Room temperature (300 K) and atmospheric pressure (1 bar) are maintained in all simulations.

The surface energy of the CNS is defined as the excess energy associated with the total exposed surface. According to this definition, the variation of total surface energy associated with changes in core size is $\delta\Gamma = 2\pi\gamma(\delta r_0 + \delta R)L$ (this equation can be integrated as $\Gamma = 2\pi\gamma(r_0 + R)L + constant$). To obtain the value of surface energy per unit area γ, we conduct MD simulations and plot Γ versus $(r_0 + R)$, the slop of which then gives γ (Shi et al. 2010a).

Due to the anti-symmetric spiral form of CNS, it is actually difficult to directly apply force to the inner surface of CNS in MD simulations. As shown in Fig. 1b, one can mimic an applied internal pressure by insertinga carbon nanotube (CNT) into the core of CNS. By calculating the internal force between the CNT and CNS, the inner pressure of CNS can be determined. Following this method, the pressure levels for different core sizes of CNS are obtained by inserting CNTs with different radii.

In studying the contraction of CNS when $p_i - p_e < 0$, we encountered similar difficulty described above. In this case, we constructed a crystal consisting of a closed packed bundle of CNSs (Fig. 1c). The CNS crystal is then subjected to biaxial compression, which can be easily realized in MD simulations. Assuming that the pressure near the center of the CNS crystal is uniformly distributed, we calculate the core size of the CNS as a function of the applied pressure on the CNS crystal. The results listed in Fig. 4 show excellent agreement with the corresponding theoretical predictions.

4 Discussions and conclusions

In the present paper, we have theoretically investigated the equilibrium core size, the stability and the biaxial constitutive behavior of a pressurized CNS. Under externally applied pressure, the CNS undergoes biaxial expansion ($p_i - p_e > 0$) and contraction ($p_i - p_e < 0$). We found there exists a critical core size of CNS for unstable expansion under constant pressure. Also, the biaxial modulus of a CNS is sensitively dependent on the applied pressure, increasing with pressure in biaxial compression and decreasing with pressure in biaxial expansion. The biaxial modulus is further found to depend on the size and the surface energy of CNS. These studies suggest pressure sensitive applications of CNSs in nanotechnology, such as nanopumps (Pugno 2008) and nanofilters.

Although not discussed in detail here, we have also studied deformation of a CNS under uniaxial compression. In this case, instead of core contraction/expansion, the CNS tends to deform along the force direction and collapse, analogous to multiwalled carbon nanotubes under compression. It seems that the highly nonlinear constitutive behavior of CNSs involving its core contraction or expansion is mostly associated with pressure loading.

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