UNDULOID-LIKE EQUILIBRIUM SHAPES OF SINGLE-WALL CARBON NANOTUBES UNDER PRESSURE

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Overview

- The study of the mechanical response of carbon nanotubes subjected to different types of loading has attracted a lot of attention in the last two decades.
- This interest emerged shortly after the experimental discovery of multi wall [Iijima, 1991] and single wall [Iijima and Ichihashi, 1993] [Bethune et al., 1993] carbon nanotubes and the reported progress in their large-scale synthesis [Ebbesen and Ajayan, 1992].
- It is motivated to a large extend by the observed remarkable mechanical and shape-dependent thermal, optical and electrical properties of these carbon allotropes with promising applications in nanotechnology.
- In this work, we use a continuum model to determine in analytic form a class of unduloid-like equilibrium shapes of single-wall carbon nanotubes subjected to uniform hydrostatic pressure. The parametric equations of the profile curves of the foregoing shapes are presented in explicit form by means of elliptic functions and integrals.

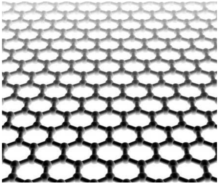
Overview

1. Carbon Nanostructures (CNS')
   - Graphene
   - Fullerenes
   - Carbon Nanotubes (CNT's)
2. Modelling of CNS' Equilibrium Shapes
   - Interatomic Potentials and MD simulations
   - Deformation Energy in Continuum Limit
   - Variational Statement of a Continuum Model
3. Axisymmetric Equilidrium Shapes
   - Shape Equation
   - Exact Solutions of the Shape Equation
   - Parametric Equations of the Unduloid-Like Surfaces
4. References

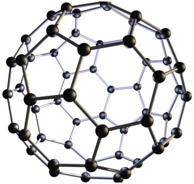
Carbon Nanostructures (CNS')

Graphenes, Fullerenes, Nanotube, Nanotori, Wormholes, Schwartzites, ...

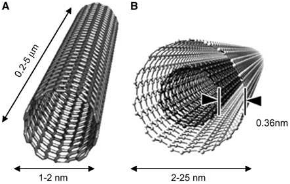
Stable configuration of curved (bent and/or stretched) graphene



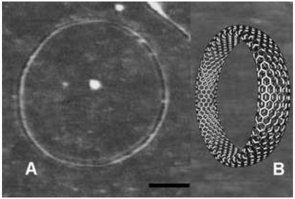
Graphene



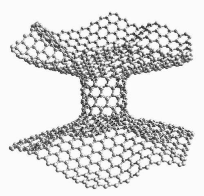
Buckyball



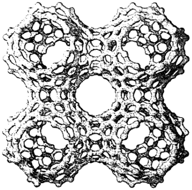
Nanotubes



Nanotorus



Wormhole

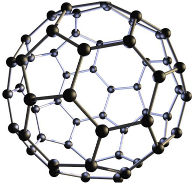


Schwartzite

Carbon Nanostructures (CNS')

Graphenes, Fullerenes, Nanotube, Nanotori, Wormholes, Schwartzites, ...

The Nobel Prize in Chemistry 1996 was awarded to Robert F. Curl Jr., Sir Harold W. Kroto and Richard E. Smalley *for discovery of fullerenes* in 1985. Nowadays, it is a common opinion among the scientists that this discovery is the onset of “carbon nano-research”.



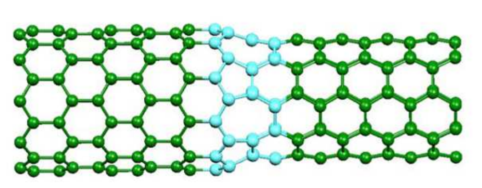
C_{60} fullerene, with remarkable stability and symmetry.

Experimental observations of peculiar CNS' were reported prior to 1985: [Radushkevich & Lukyanovich, 1952], [Oberlin, Endo & Koyama, 1976–1977]

The Nobel Prize in Physics 2010 was awarded to Andre Geim and Konstantin Novoselov *for groundbreaking experiments regarding the two-dimensional material graphene.*

Utilization

- Some of these CNS' (especially CNT's) are utilized as basic ingredients of nano-structured materials such as nano-tube-based nano-composites or functionalized CNT membranes used in water desalination, for instance.
- Others are basic building blocks of nano-electromechanical systems (NEMS), nano-sensors and other nano-devices.
- Materials, devices and technologies based on CNS' are now distributed in a wide variety of human activities.
- Nano-junctions.



Modelling of CNS' Equilibrium Shapes

Interatomic Potentials, MD simulations

- One of the most widely used approaches for determining the mechanical response of CNS's is the molecular dynamic (MD) simulation.
- Within this approach, a CNS is considered as a multibody system in which the interaction of a given atom with the neighbouring ones is regarded. The energy of this interaction is modelled through certain empirical interatomic potentials.
- [Tersoff, 1988] suggested a general approach for derivation of such potentials and applied it to silicon.
- [Brenner,1990] adapted and modified Tersoff's results and suggested an interatomic potential for carbon atomic bonds.
- Another potential of this kind was introduced in [Lenosky et al., 1992].
- Recently, a modification of the Lenosky potential was introduced in [Tu and Ou-Yang, 2008].

According to [Lenosky et al., 1992], the deformation energy of a single layer of curved graphite carbon has the form

$$\mathcal{F} = \epsilon_0 \sum_{(ij)} \frac{1}{2} \left(r_{ij} - r_0\right)^2 + \epsilon_1 \sum_{i} \left(\sum_{(j)} \mathbf{u}_{ij} \right)^2 + \epsilon_2 \sum_{(ij)} \left(1 - \mathbf{n}_i \cdot \mathbf{n}_j\right)^2 + \epsilon_3 \sum_{(ij)} \left(\mathbf{n}_i \cdot \mathbf{u}_{ij}\right)\left(\mathbf{n}_j \cdot \mathbf{u}_{ji}\right),$$

- r_{ij} is the bond length between atoms i and j after the deformation
- r_0 is the initial bond length of planar graphite
- $\mathbf{u}_{ij}$ is a unit vector pointing from carbon atom i to its neighbor j
- $\mathbf{n}_i$ is a unit vector normal to the plane determined by the three neighbors of atom i
- ϵ_0, ϵ_1, ϵ_2, ϵ_3 are the so-called bond-bending parameters

The summation $\sum_{(j)}$ is taken over the three nearest-neighbor atoms j to i atom and $\sum_{(ij)}$ is taken over all nearest-neighbor atoms.

Modelling of CNS' Equilibrium Shapes

Deformation Energy in Continuum Limit

In continuum limit, both [Lenosky et al., 1992] potential and its modification, introduced in [Tu and Ou-Yang, 2008] in order to take into account that the energy costs due to the in-plane and out-of plane bond angle changes are quite different, yield one and the same expression for the deformation energy (see [Tu and Ou-Yang, 2002, Tu and Ou-Yang, 2008]), namely

$$\mathcal{F} = \int_{\mathcal{S}} \left[\frac{k_c}{2}(2H)^2 + k_G K + \frac{k_d}{2}(2J)^2 + \tilde{k} Q \right] \mathrm{d}A \tag{1}$$

- $\mathcal{S}$ surface representing the atomic lattice of the deformed nanotube as a two-dimensional continuum;
- H mean curvature
- K Gaussian curvature
- J "mean" strain
- Q "Gaussian" strain
- $\mathrm{d}A$ the area element on the surface $\mathcal{S}$
- k_c, k_G, k_d, $\tilde{k}$ constants given through the bond-bending parameters used in the respective atomic lattice model

- It is noteworthy that the functional $\mathcal{F}$ is quite similar to the deformation energy of an isotropic thin elastic shell modelled within the framework of the nonlinear Kirchhoff-Love shell theory (cf. [Landau & Lifshitz, 1986]) and coincides with it if $k_G/k_c = \tilde{k}/k_d$ (see [Tu and Ou-Yang, 2006] and [Tu and Ou-Yang, 2008] for more details). This corresponds fairly well to the observed elastic behaviour of CNT's.
- The findings provided by high-resolution transmission electron microscopy demonstrated that these nanostructures can sustain large deformations of their initial circular-cylindrical shape without occurrence of irreversible atomic lattice defects. As noticed in [Iijima, 1996]: "*Thus, within a wide range of bending, the tube retains an all-hexagonal structure and reversibly returns to its initial straight geometry upon removal of the bending force.*"
- Actually, [Yakobson et al., 1996] developed a continuum mechanics approach based on this shell theory for exploration of the mechanical properties and deformed configurations of CNT's, although, they noted: "*its relevance for a covalent-bonded system of only a few atoms in diameter is far from obvious*".

Within the present study:

- The second term in the deformation energy $\mathcal{F}$ accounting for the in-plane deformation is neglected since the contribution of the bond stretching to the deformation energy is less than 1% (see [Lenosky et al., 1992]).
- Instead of this, the carbon nanotube is assumed to be inextensible upon deformation. Moreover, we assume that a uniform hydrostatic pressure p is applied to the deformed surface $\mathcal{S}$.

According to these assumptions, the equilibrium shapes of a CNT are determined by the extremals of the bending part of the deformation energy $\mathcal{F}$ under the constraints of fixed total area A and enclosed volume V:

$$\mathcal{F}_b = \int_{\mathcal{S}} \left[\frac{1}{2} k_c (2H + c_0)^2 + k_G K \right] \mathrm{d}A + \lambda \int_{\mathcal{S}} \mathrm{d}A + p \int \mathrm{d}V \qquad (2)$$

where λ is the Lagrange multiplier corresponding to the constraint of fixed total area, which is interpreted as a tensile stress, the pressure p appears as another Lagrange multiplier corresponding to the constraint of fixed enclosed volume V and the extra constant c_0 is added to take into account the screw dislocation core-like deformation as it was suggested in [Xie et al., 1996].

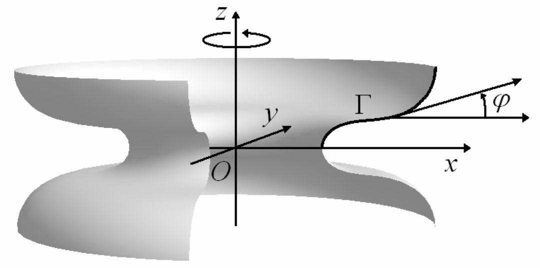
The corresponding Euler-Lagrange equation, further referred to as the shape equation, was derived in [Ou-Yang and Helfrich, 1989] and reads

$$\Delta H + (2H + c_0)\left(H^2 - \frac{c_0}{2}H - K\right) - \frac{\lambda}{k_c}H = -\frac{p}{2k_c}\,. \tag{3}$$

Here Δ is the Laplace-Beltrami operator on the surface $\mathcal{S}$.

Axisymmetric Equilidrium Shapes

Sketch of a Surface of Revolution



Sketch of a surface of revolution obtained by revolving around the z-axis a plane curve Γ laying in the xOz-plane, which is defined by the graph $(x, z(x))$ of a function $z = z(x)$. Here, φ is the (tangent) slope angel.

Suppose that a part of an axisymmetrically deformed SWCNT admits graph parametrization. This means that it may be thought of as a surface of revolution obtained by revolving around the z-axis a plane curve Γ laying in the xOz-plane, which is determined by the graph $(x, z(x))$ of a function $z = z(x)$.

For each such surface the general shape equation (3) reduces to the following nonlinear third-order ordinary differential equation

$$\begin{aligned}\cos^3\varphi\frac{\mathrm{d}^3\varphi}{\mathrm{d}x^3} \quad = \quad & 4\sin\varphi\cos^2\varphi\frac{\mathrm{d}^2\varphi}{\mathrm{d}x^2}\frac{\mathrm{d}\varphi}{\mathrm{d}x} - \cos\varphi\left(\sin^2\varphi - \frac{1}{2}\cos^2\varphi\right)\left(\frac{\mathrm{d}\varphi}{\mathrm{d}x}\right)^3 \\ & + \frac{7\sin\varphi\cos^2\varphi}{2x}\left(\frac{\mathrm{d}\varphi}{\mathrm{d}x}\right)^2 - \frac{2\cos^3\varphi}{x}\frac{\mathrm{d}^2\varphi}{\mathrm{d}x^2} \\ & + \left(\frac{\lambda}{k_c} + \frac{c_0^2}{2} - \frac{2c_0\sin\varphi}{x} - \frac{\sin^2\varphi - 2\cos^2\varphi}{2x^2}\right)\cos\varphi\frac{\mathrm{d}\varphi}{\mathrm{d}x} \\ & + \left(\frac{\lambda}{k_c} + \frac{c_0^2}{2} - \frac{\sin^2\varphi + 2\cos^2\varphi}{2x^2}\right)\frac{\sin\varphi}{x} - \frac{p}{k_c}\end{aligned} \tag{4}$$

(derived in [Hu & Ou-Yang, 1993]) where φ is the angle between the x-axis and the tangent vector to the profile curve Γ, i.e., the tangent (slope) angel, considered as a function of the variable x.

[Naito at al., 1995] discovered that the shape equation (4) has the following class of exact solutions

$$\sin\varphi = ax + b + dx^{-1}, \tag{5}$$

provided that a, b and d are real constants, which meet the conditions

$$\frac{p}{k_c} - 2a^2 c_0 - 2a\left(\frac{c_0^2}{2} + \frac{\lambda}{k_c}\right) = 0, \tag{6}$$

$$b\left(2ac_0 + \frac{c_0^2}{2} + \frac{\lambda}{k_c}\right) = 0, \tag{7}$$

$$b\left(b^2 - 4ad - 4c_0 d - 2\right) = 0, \tag{8}$$

and

$$d\left(b^2 - 4ad - 2c_0 d\right) = 0. \tag{9}$$

Exact Solutions of the Shape Equation

Six types of solutions of form (5) to Eq. (4) can be distinguished on the ground of conditions (6) – (9) depending on the values of c_0, λ and p.

Case A. If $c_0 = 0$, $\lambda = 0$, $p = 0$, then the solutions to Eq. (4) of the form (5) are $\sin\varphi = ax$, $\sin\varphi = ax \pm \sqrt{2}$ and $\sin\varphi = dx^{-1}$, the respective surfaces being spheres, Clifford tori and catenoids.

Case B. If $c_0 = 0$, $\lambda \neq 0$, $p = 0$, then the solutions of the considered type reduces to $\sin\varphi = dx^{-1}$ (catenoids).

Case C. If $c_0 = 0$, $\lambda \neq 0$, $p \neq 0$ and $p = 2a\lambda$, then only one branch of the regarded solutions remains, namely $\sin\varphi = ax$ (spheres).

Case D. If $c_0 \neq 0$, $\lambda = 0$, $p = 0$, then one arrives at the whole family of Delaunay surfaces corresponding to the solutions of the form

$$\sin\varphi = -\frac{1}{2}c_0 x + \frac{d}{x}\,\cdot \tag{10}$$

Case E. If $c_0 \neq 0$, $\lambda \neq 0$, $p = 0$ and

$$\frac{\lambda}{k_c} = -\frac{1}{2}c_0\left(2a + c_0\right),$$

one gets only solutions of the form $\sin\varphi = ax$ (spheres).

Exact Solutions of the Shape Equation

Case F. If $c_0 \neq 0$, $\lambda \neq 0$, $p \neq 0$, then four different types of solutions of form (5) to Eq. (4) are encountered: (a) $\sin\varphi = ax$ (spheres) if

$$\frac{p}{k_c} = 2a\left(\frac{\lambda}{k_c} + ac_0 + \frac{c_0^2}{2}\right); \tag{11}$$

(b) $\sin\varphi = ax \pm \sqrt{2}$ (Clifford tori) if

$$\frac{p}{k_c} = -2a^2c_0, \quad \frac{\lambda}{k_c} = -\frac{1}{2}c_0\left(4a + c_0\right); \tag{12}$$

(c) solutions of the form (10) (Delaunay surfaces) if

$$p + c_0\lambda = 0; \tag{13}$$

(d) solutions of the form

$$\sin\varphi = -\frac{1}{4}c_0\left(b^2 + 2\right)x + b - \frac{1}{c_0 x}, \tag{14}$$

which take place provided that

$$\frac{p}{k_c} = -\frac{1}{8}c_0^3\left(b^2 + 2\right)^2, \qquad \frac{\lambda}{k_c} = \frac{1}{2}c_0^2\left(b^2 + 1\right). \tag{15}$$

Parametric Equations of the Unduloid-Like Surfaces

Below, we derive the parametric equations of the surfaces corresponding to the solutions of form (14) to Eq. (4).
First, it is clear that the variable x must be strictly positive or negative, otherwise the right-hand side of Eq. (5) is both undefined and its absolute value is greater than one, which is in contradiction with the sin-function appearing in the left-hand side of this relation.
Next, according to the meaning of the tangent angle

$$\frac{\mathrm{d}z}{\mathrm{d}x} = \tan\varphi \tag{16}$$

which for the foregoing class of solutions (14) implies

$$\left(\frac{\mathrm{d}z}{\mathrm{d}x}\right)^2 = \frac{\left[b - \frac{1}{c_0 x} - \frac{1}{4}c_0\left(b^2+2\right)x\right]^2}{1 - \left[b - \frac{1}{c_0 x} - \frac{1}{4}c_0\left(b^2+2\right)x\right]^2}\,. \tag{17}$$

Parametric Equations of the Unduloid-Like Surfaces

In terms of an appropriate new variable t, relation (17) may be written in the form

$$\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)^2 = -\frac{1}{u^2} Q_1(x) Q_2(x) \tag{18}$$

$$\left(\frac{\mathrm{d}z}{\mathrm{d}t}\right)^2 = \frac{1}{4u^2} \left(Q_1(x) + Q_2(x)\right)^2 \tag{19}$$

where

$$u = -\frac{4}{c_0 \left(2 + b^2\right)^{3/4}}$$

$$Q_1(x) = x^2 - \frac{4\,(b+1)}{c_0\,(b^2+2)} x + \frac{4}{c_0^2\,(b^2+2)} \tag{20}$$

$$Q_2(x) = x^2 - \frac{4\,(b-1)}{c_0\,(b^2+2)} x + \frac{4}{c_0^2\,(b^2+2)}\,. \tag{21}$$

Parametric Equations of the Unduloid-Like Surfaces

It should be noticed that the roots of the polynomial $Q(x) = Q_1(x)Q_2(x)$ read

$$\alpha = \frac{2\,\mathrm{sign}\,(b)}{c_0\sqrt{b^2+2}}\,\frac{h-1}{h+1}, \qquad \beta = \frac{2\,\mathrm{sign}\,(b)}{c_0\sqrt{b^2+2}}\,\frac{h+1}{h-1} \tag{22}$$

$$\gamma = \frac{4b}{c_0\,(b^2+2)} - \frac{\alpha+\beta}{2} + i\,\frac{2\sqrt{2|b|+1}}{c_0\,(b^2+2)}$$

$$\delta = \frac{4b}{c_0\,(b^2+2)} - \frac{\alpha+\beta}{2} - i\,\frac{2\sqrt{2|b|+1}}{c_0\,(\epsilon^2+2)}$$

where

$$h = \sqrt{\frac{1+|b|+\sqrt{2+b^2}}{1+|b|-\sqrt{2+b^2}}}\,. \tag{23}$$

Hence, Eq. (18) has real-valued solutions if and only if at least tow of these roots are real and different. Evidently, the roots γ and δ can not be real, but α and β are real provided that $|b| > 1/2$ as follows be relations (22) and (23).

Parametric Equations of the Unduloid-Like Surfaces

Now, using the standard procedure for handling elliptic integrals (see [Whittaker and Watson, 1922, 22.7]), one can express the solution $x(t)$ of equation (18) in the form

$$x(t) = \frac{2\,\mathrm{sign}\,(b)}{c_0\sqrt{b^2+2}}\left(1 - \frac{2h}{h + \mathrm{cn}(t,k)}\right) \tag{24}$$

where

$$k = \sqrt{\frac{1}{2} - \frac{3}{4\sqrt{2+b^2}}}\,.$$

Consequently, using expressions (20) and (21), one can write down the solution $z(t)$ of equation (19) in the form

$$z\,(t) = \frac{1}{u}\int\left[x^2(t) - \frac{4\,b\,x(t)}{c_0\,(b^2+2)} + \frac{4}{c_0^2\,(b^2+2)}\right]\mathrm{d}t. \tag{25}$$

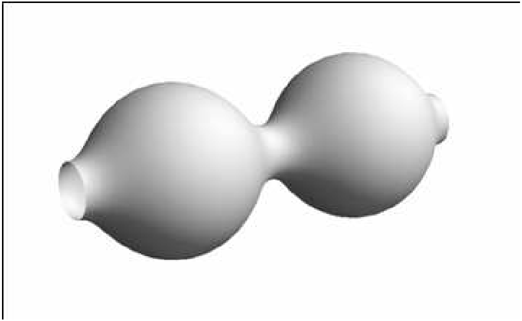
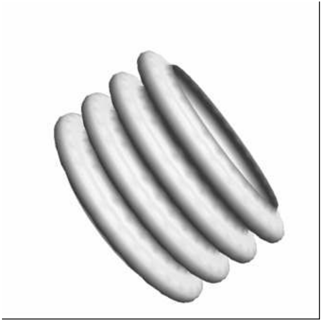
Parametric Equations of the Unduloid-Like Surfaces

Finally, performing the integration in the right-hand-side of Eq. (25), one obtains

$$z(t) = u \left[\mathrm{E}(\mathrm{am}(t,k),k) - \frac{\mathrm{sn}(t,k)\,\mathrm{dn}(t,k)}{h + \mathrm{cn}(t,k)} - \frac{t}{2} \right] . \tag{26}$$

Thus, for each couple of values of the parameters c_0 and b, (24) and (26) are the sought parametric equations of the contour of an axially symmetric unduloid-like surface corresponding to the respective solution of the membrane shape equation (4) of form (14).

Examples

(a)  (b) 

Unduloid-like surfaces obtained using the parametric equations (24) and (26) for: (a) $p/k_c = 1.75$, (b) $p/k_c = 12.1$.

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