Fourteenth International Conference on
Geometry, Integrability and Quantization
June 8–13, 2012, Varna, Bulgaria
Ivaïlo M. Mladenov, Andrei Ludu
and Akira Yoshioka, Editors
Avangard Prima, Sofia 2013, pp 244–252
doi: 10.7546/giq-14-2013-244-252

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

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Abstract. In this work, a continuum model is used 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.

1. Introduction

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 [11] and single-wall [2, 12] carbon nanotubes and the reported progress in their large-scale synthesis [6]. 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 nano technology.

It is observed (see, e.g. [25]) that under different growth conditions, carbon nanotubes take different kinds of stable or metastable shapes (straight, curved, helical).

The aim of the present work is to give an analitic description of a class of axisymmetric equilibrium shapes of single-wall carbon nanotubes (SWCNT's) subjected to uniform hydrostatic pressure. For that purpose we use the continuum model developed by Ou-Yang *et al* [18, 20, 22]. This model is based on the continuum limit of the interatomic interaction potential proposed by Lenosky *et al* [14] to describe the deformation energy of a single layer of curved graphite carbon, which has been modified recently by Tu and Ou-Yang [22] to take into account that the energy costs due to the in-plane and out-of-plane bond angle changes of the carbon-atom lattice upon deformation are different.

2. Deformation Energy and Shape Equation

In continuum limit, both the Lenosky potential [14] and its modification introduced in [22] yield one and the same expression for the deformation energy (see [20,22]), namely

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

where $\mathcal{S}$ is a surface representing the atomic lattice of the deformed nanotube as a two-dimensional continuum, H and K are its mean and Gaussian curvatures, $\mathrm{d}A$ is the area element on the surface $\mathcal{S}$, J and Q are the first and second invariants of the in-plane deformation tensor, which are often referred to as the "mean" and "Gaussian" strains, respectively, and k_c, k_G, k_d and $\tilde{k}$ are constants given through the bond-bending parameters used in the respective atomic lattice model (see [14, 22]).

It should be noted that expression (1) for the deformation energy follows as well from other continuum theories for carbon nanostructures based on the interatomic interaction potentials of Tersoff-Brenner [3, 19] type and developed using kinematic assumption such as the Cauchy-Born rule or its modifications (see [1] and references therein).

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 (see e.g. [13]) and coincides with it if $k_G/k_c = \tilde{k}/k_d$ (see [21, 22] for more details). This corresponds fairly well to the observed elastic behaviour of the carbon nanotubes

and their essentially two-dimensional atomic lattice structure with intrinsic hexagonal symmetry. Actually, Yakobson *et al* [26] developed, apparently motivated by the aforementioned properties of the carbon nanotubes, a continuum mechanics approach based on this shell theory for exploration of their mechanical properties and deformed configurations. It should be acknowledged that this article has had a huge impact on the continuum modelling of the mechanical behaviour of carbon nanostructures.

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 [14]). 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 all these assumptions, the equilibrium shapes of a carbon nanotube 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. This scheme yields the functional

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

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 by Xie *et al* [25].

The energy functional (2) is well-known in the theory of lipid bilayer membranes. In the model proposed by Helfrich [9], its local extrema determine the equilibrium shapes of such a membrane, the constant c_0 (called the **spontaneous curvature**) being introduced to reflect the asymmetry of the membrane or its environment. The corresponding Euler-Lagrange equation, further referred to as the **shape equation**, was derived by Ou-Yang and Helfrich [17] and reads

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

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

An exhaustive analytic description of the cylindrical shapes corresponding to the translationally-invariant solutions of the shape equation (3) is presented in Vassilev *et al* [23] and Djondjorov *et al* [4]. It is worth noting that Zang *et al* [27, 28] have compared recently cross-sections of single-wall carbon nanotubes subjected to uniform hydrostatic pressure obtained by the solutions of equation (3) and by molecular dynamics simulations. As a result, an excellent agreement was observed, see [28, Figure 3]. This observation justifies the applicability of the considered continuum model at least as far as the determination of the cylindrical equilibrium shapes of single-wall carbon nanotubes under hydrostatic pressure is concerned.

3. Axisymmetric Equilidrium Shapes

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 $z = z(x)$, see Fig. 1. For each such surface the general shape equation (3) reduces to the following nonlinear

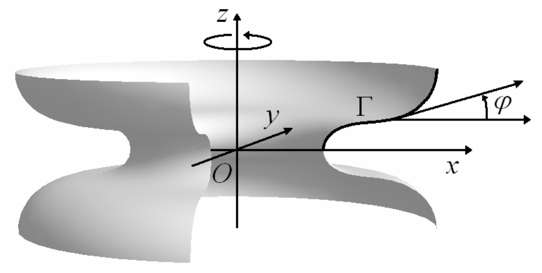


Figure 1. Sketch of a surface of revolution obtained by revolving around the z-axis a plane curve Γ laying in the xOz-plane, which is defined by the graph $(x, z(x))$ of a function $z = z(x)$. Here, φ is the (tangent) slope angle.

third-order ordinary differential equation

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

(derived by Hu and Ou-Yang in [10]) where φ is the angle between the x-axis and the tangent vector to the profile curve Γ, i.e., the tangent (slope) angle, considered as a function of the variable x.

In 1995, Naito *et al* [16] 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

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

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

$$b\left(b^2 - 4ad - 4c_0d - 2\right) = 0 \tag{8}$$

and

$$d\left(b^2 - 4ad - 2c_0d\right) = 0. \tag{9}$$

Three types of solutions of form (5) to equation (4) are distinguished in [16] on the ground of conditions (6) – (9): (*i*) $b = d = 0$, (*ii*) $d = 0$, $b = \pm\sqrt{2}$ and (*iii*) $b = 0$. For the purposes of the present paper, however, it is convenient to classify these solutions, which actually depend on the values of the constants c_0, λ and p, in another way. The following six types of solutions of form (5) to equation (4) can be distinguished on the ground of conditions (6) – (9) depending on the values of the constants c_0, λ and p.

Case A. If $c_0 = 0$, $\lambda = 0$, $p = 0$, then the solutions to equation (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** (see [7, 8, 15]) 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).

Case F. If $c_0 \neq 0$, $\lambda \neq 0$, $p \neq 0$, then four different types of solutions of form (5) to equation (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

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

(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

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

4. Parametric Equations of the Unduloid-Like Surfaces

Below, we derive the parametric equations of the surfaces corresponding to the solutions of form (14) to equation (4).

First, it is clear that the variable x must be strictly positive or negative, otherwise the right-hand side of equation (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

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

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

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

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

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

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

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

$$\gamma = \frac{4b}{c_0\left(b^2+2\right)} - \frac{\alpha+\beta}{2} + \mathrm{i}\frac{2\sqrt{2|b|+1}}{c_0\left(b^2+2\right)} \tag{22}$$

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

where

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

Hence, equation (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).

Now, using the standard procedure for handling elliptic integrals (see [24, §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

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

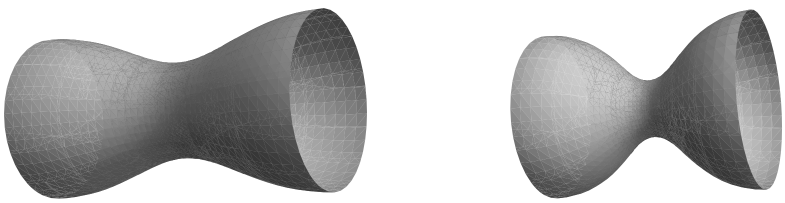
Consequently, using expressions (20) and (21), one can write down the solution $z(t)$ of equation (19) in the form

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

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

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

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).



(a) (b)

Figure 2. Unduloid-like surfaces obtained using the parametric equations (24) and (26) for: (a) $p/k_c=0.6962$, (b) $p/k_c=1.1250$.

Acknowledgements

The author would like to acknowledge the financial support of the Bulgarian Ministry of Education, Youth and Science under the Operational Program "Science and Business" BG051PO001/3.3-05-001 within "Human Resources Development Framework" of the European Social Fund, 2007–2013.

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