



Stable Shapes of Thin Anisotropic Nano-strips

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Abstract: The elastic properties of a thin anisotropic nano-strip are characterized by its intrinsic mean curvature and intrinsic curvature deviator. It is shown that minimization of the elastic energy of the strip including the deviatoric contribution may explain

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the stability of the observed helical and twisted shapes of inorganic nano-strips (helix A and B).

Keywords: Theory and modelling, helical nano-strips, twisted nano-strips, electron microscopy, deviatoric elasticity

INTRODUCTION

Flat, helical and twisted micro and nano-strips (Fig. 1) can be found in different inorganic (1), organic (2–4) and biological systems (5–7). Their equilibrium shapes are usually not flat and therefore in general they cannot always be considered as isotropic (3, 8, 9). The stable shapes of isotropic thin strips (10) and multilayered organic (11) and inorganic (12) closed shells have often been determined by minimization of the Landau-Helfrich bending energy (13)

$$w_b = \frac{k_c}{2}(2H - C_0)^2 + k_G K, \quad (1)$$

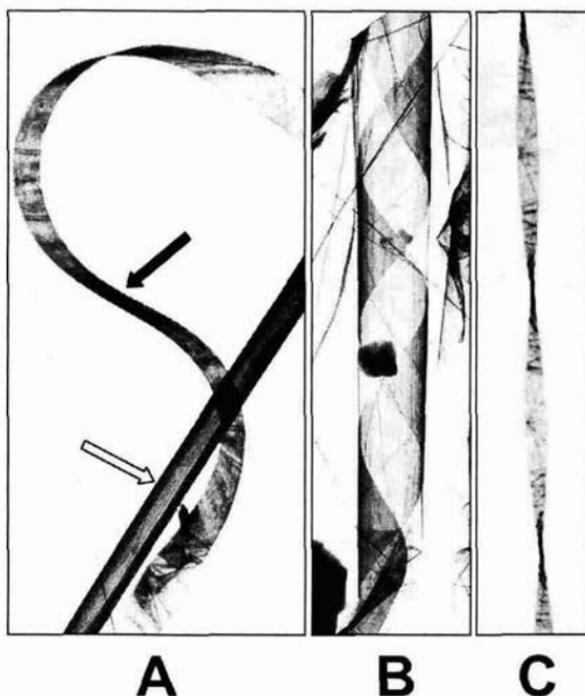


Figure 1. Transmission electron micrograph of a cylindrical MoS_2 nanotube, $2.2 \mu\text{m}$ in diameter (white arrow), and a collapsed nanotube-strip, $3.3 \mu\text{m}$ in width (black arrow) (A); helix A—helically wound WS_2 strip, $2.1 \mu\text{m}$ in width, rolled up around thin-walled microtube, $1.35 \mu\text{m}$ in diameter (B); and helix B—a twisted WS_2 strip, 58 nm in width (C).

where $H = (C_1 + C_2)/2$ is the mean curvature, C_0 is the spontaneous curvature, $K = C_1C_2$ is the Gaussian curvature, while k_c and k_G are the splay and saddle-splay modulus, respectively. The above expression for the isotropic bending was upgraded for the case of anisotropic bending by considering the tilt and chirality (8, 14), or in-plane orientational ordering (3, 6, 9, 15) of the material constituents. In this work we consider the anisotropic bending of inorganic thin strips by taking into account the deviatoric properties of the material (16). In this model we introduce two spontaneous curvatures; the spontaneous mean curvature H_m and the spontaneous curvature deviator D_m . We show that the variation of H_m and D_m may explain the observed differences in topology of inorganic strips (helix A, helix B, flat strip) (Fig. 1). The theory presented may be used to determine the elastic constants of anisotropic micro- and nano-strips.

FREE ENERGY

In our model a strip is treated as the two-dimensional surface of a continuum, taking into account that the strip is in general anisotropic in two dimensions. It is considered that the elastic energy of a given very small element of the strip in the absence of external forces is equal to zero if its principal curvatures C_1 and C_2 are equal to its intrinsic principal curvatures C_{1m} and C_{2m} . If a given shape has such principal curvatures in all its points, the elastic energy of such a shape is zero.

We define the elastic energy per unit area of a very small element of the strip with area dA as the energy of mismatch between the actual curvature of this element and its intrinsic curvature. The shape of both continua are described by the curvature tensors \underline{C} and \underline{C}_m , respectively. The tensor \underline{C} describes the actual curvature while the tensor \underline{C}_m describes the intrinsic curvature, i.e., the curvature which would be energetically the most favourable (Fig. 2). In the respective principal systems the curvature tensors include only diagonal elements:

$$\underline{C} = \begin{bmatrix} C_1 & 0 \\ 0 & C_2 \end{bmatrix}, \quad \underline{C}_m = \begin{bmatrix} C_{1m} & 0 \\ 0 & C_{2m} \end{bmatrix}. \tag{2}$$

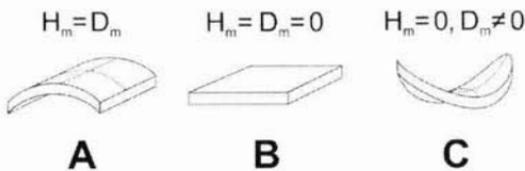


Figure 2. Schematic figure of the most favourable shapes of a small surface element having different values of the spontaneous mean curvature H_m and spontaneous curvature deviator D_m .

The principal systems of these two tensors are in general rotated in the tangential plane of the surface by an angle ω with respect to each other. The mismatch between the actual local continuum curvature of the surface and the intrinsic curvature in the absence of external forces is characterized by the tensor $\underline{M} = \underline{R} \underline{C}_m \underline{R}^{-1} - \underline{C}$, where \underline{R} is the rotation matrix (16).

The small patch of the strip should overcome this mismatch in order to fit into its place in the actual membrane. This is reflected in the energy that is needed for such a deformation. The elastic energy per unit area w is a scalar quantity. Therefore each term in the expansion of w must also be scalar (13), i.e., invariant with respect to all transformations of the local coordinate system. In this work, the elastic energy density w is approximated by an expansion in powers of the invariants of the tensor \underline{M} up to the second order in the components of \underline{M} . The trace and the determinant of the tensor are taken as the set of invariants,

$$w = \frac{K_1}{2} (\text{Tr } \underline{M})^2 + K_2 \text{Det } \underline{M} \quad (3)$$

where K_1 and K_2 are constants. Taking into account Eqs. (2)–(3) and the definition of the tensor \underline{M} , the energy density w can be written as

$$w = (2K_1 + K_2)(H - H_m)^2 - K_2(D^2 - 2DD_m \cos 2\omega + D_m^2) \quad (4)$$

where $D = (C_1 - C_2)/2$ is the curvature deviator (16, 17), $H_m = (C_{1m} + C_{2m})/2$ is the spontaneous mean curvature and $D_m = (C_{1m} - C_{2m})/2$ is the spontaneous curvature deviator. It can be seen from Eq. (4) that the material properties of an anisotropic thin strip can be expressed in a simple way by only two parameters: the spontaneous mean curvature H_m and the spontaneous curvature deviator D_m . Fig. 2 shows schematically cylindrical, flat, and saddle-like intrinsic shapes of the thin strip.

If the element of the surface is isotropic (i.e., $D_m = 0$), Eq. (4) transforms into the Helfrich-Landau expression for the area density of the energy of isotropic bending (Eq. (1)), where $k_c = K_1$, $k_G = K_2$ and $C_0 = (2K_1 + K_2)H_m/K_1$.

EQUILIBRIUM SHAPES OF STRIPS

In this work we shall consider two kinds of helical strips: helix A and helix B (Figs. 1, 3). The surface of the helical strips $\mathbf{r} = (x(u, v), y(u, v), z(u, v))$ is described parametrically by two independent parameters u and v . A simple example of parametric form is adopted where u is equal to z , while x and y are determined by the rotation of the curve $f(v)$ around the longitudinal symmetry axis z in the plane perpendicular to this axis as follows:

$$\begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} \cos kz & -\sin kz \\ \sin kz & \cos kz \end{bmatrix} \begin{bmatrix} v \\ f(v) \end{bmatrix}, \quad (5)$$

Here the parameter v is the radial distance from the symmetry axis, while the constant k determines the pitch. Equation (5) yields

$$\mathbf{r} = (v \cos kz - f(v) \sin kz, v \sin kz + f(v) \cos kz, z). \tag{6}$$

Helix A

First we shall consider a twisted strip in the form of helix A (Fig. 3). In order to describe the helical shape (helix A) the function $f(v) = (\rho^2 - v^2)^{1/2}$, i.e., part of a circle is chosen. The circle arc of length l is determined by the angle $\phi = l/\rho$. Here ρ is the radius of the imaginary cylinder on which the strip of width $2v_0$ is helically wound. The pitch is $P = 2\pi/k$, while the pitch angle is $\psi = (\arctan(1/k\rho))$ (Fig. 3). Using the above definitions, the surface of the wound strip in the form of helix A can be written in the parametric representation as

$$\mathbf{r} = (v \cos kz - (\rho^2 - v^2)^{1/2} \sin kz, v \sin kz + (\rho^2 - v^2)^{1/2} \cos kz, z) \tag{7}$$

where $v \in [-\rho \sin(l/2\rho), +\rho \sin(l/2\rho)]$ and $z \in [0, z]$. The length of the arc (l) can be determined as $l = 2v_0/\sin\psi$.

The mean curvature H and the curvature deviator D are constant over the whole of helix A strip ($H = D = 1/2\rho$). Therefore the energy density w can be written as

$$w_A = K_1 \left(\frac{1}{2\rho} - H_m \right)^2 + K_1 \left(\frac{1}{4\rho^2} - \frac{1}{\rho} D_m \cos 2\omega + D_m^2 \right) \tag{8}$$

where we assumed for the sake of simplicity that $K_2 = -K_1$.

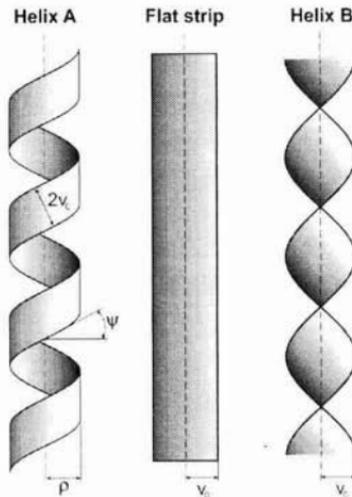


Figure 3. Schematic presentation of helical (A and B) and flat nano-strips.

Let us now consider the special case where $H_m = D_m$, which means that the intrinsic principal curvature C_{2m} is zero (Fig. 2A). If the intrinsic principal axis corresponding to C_{2m} is rotated by an angle β with respect to the longitudinal axis of the flat strip, then for helix A the angle $\omega = 90^\circ - \beta - \psi$. Therefore the energy density w_A and also the corresponding total energy of the strip in the form of helix A is minimal for $\rho = 1/2H_m = 1/2D_m$ and $\omega = 0$. Since in this case the energy density w_A is zero this also means that this is the minimal possible value of w_A (without mechanical stress). From $\omega = 0$ it also follows that the equilibrium value of the pitch angle is $\psi = 90^\circ - \beta$.

Based on the presented results it can therefore be concluded that the A helix configuration of the strip is favoured by equal spontaneous curvatures H_m and D_m , where the pitch angle of the helix A is determined by the orientation of the principal system of the intrinsic curvature tensor \underline{C}_m with respect to the longitudinal axis of the strip in the flat configuration (β).

From the observed shape of the helically wound WS_2 strip with the pitch angle $\psi = 55^\circ$ (Fig. 1B), the rotation of the intrinsic principal axis $\beta = 90^\circ - \psi = 35^\circ$ can be determined assuming $\omega = 0$. Further, by taking into account $\rho = 1.35 \mu\text{m}$ (Fig. 1B), the spontaneous curvature deviator $D_m = 1/2\rho$ of the observed Helix A WS_2 strip was estimated to be $\sim 7 \cdot 10^{-4} \text{ nm}^{-1}$.

As well as in inorganic systems (Fig. 1), stable twisted helical structures can also be found in organic systems such as collagen molecules in which three polypeptide chains (α -chains) are wound together in a triple helix (5) or in binary lipid monolayers (4).

Helix B

In the second step we shall consider a strip twisted in the form of helix B (Fig. 3). For the sake of simplicity we assume that the cross-section of the strip in the $x - y$ plane is always a straight line of length $2v_0$ regardless of the grade of deformation. Therefore the function $f(v)$ in Eq. (6) is identically equal to zero ($f(v) \equiv 0$) yielding

$$\mathbf{r} = (v \cos kz, v \sin kz, z), \quad (9)$$

where $v \in [-v_0, +v_0]$ and $z \in [0, z_0]$. The equations of differential geometry (see for example ([11])) yield the following expressions for H , D , and dA

$$H = 0, \quad (10)$$

$$D = k/\sqrt{1 + k^2v^2}, \quad (11)$$

$$dA = \sqrt{1 + k^2v^2} \, dv \, dz. \quad (12)$$

The result $H = 0$ yields $C_2 = -C_1$ which means that for each point on the strip there exists at least one normal cross-section with a curvature

equal to zero. Using the Euler formula we can write for the curvature of this particular cross-section $C = C_1 \cos^2 \varphi + C_2 \sin^2 \varphi = 0$ where φ is the angle between one of the principal directions and the plane of the normal cross-section having the curvature $C = 0$. From the preceding equations it follows that $\tan \varphi = \pm \sqrt{C_1/C_2} = \pm 1$ or $\varphi = \pm 45^\circ$. This means that the principal directions of the strip are rotated by an angle of 45° with respect to the $C = 0$ normal cross-section plane. For the sake of simplicity we shall assume that the principal directions of the intrinsic continuum curvature of the strip coincide with the principal directions of its actual local continuum curvature at this point so that $\omega = 0$. This means that the principal directions of the intrinsic curvature tensor are rotated by 45° with respect to the transversal axis of the strip.

Let us now derive the energy of the strip. For the sake of simplicity we assume that $K_2 = -K_1$ (see Eq. (4)) and introduce dimensionless quantities where v_0 is taken as the unit of length ($h_m = H_m v_0$, $d_m = D_m v_0$). The area density of elastic energy w (Eq. (4)) is integrated over the area of the strip, divided by K_1 and z_0 to yield the elastic energy of the strip per unit of normalized length of the helix (z_0): $\varepsilon(k) = (\int w dA)/z_0 K_1$

$$\varepsilon(k) = \frac{h_m^2 + d_m^2}{2k} \left(2k\sqrt{1+k^2} + \ln \left(\frac{k + \sqrt{1+k^2}}{-k + \sqrt{1+k^2}} \right) \right) - 4kd_m + k \ln \left(\frac{k + \sqrt{1+k^2}}{-k + \sqrt{1+k^2}} \right), \quad (13)$$

where we assume that $\omega = 0$. The equilibrium shape of the twisted strip is determined by minimization of the energy $\varepsilon(k)$ as a function of k , where the integral in the expression for $\varepsilon(k)$ is calculated numerically. Fig. 4 shows the equilibrium shapes of a B helical strip for different values of d_m at $h_m = 0$. It can be seen that for isotropic strips having $h_m = d_m = 0$ a flat strip is the most favourable shape ($k = 0$), while for $h_m = 0$ and nonzero values of d_m the B helical shape ($k \neq 0$) is energetically more favourable.

From a comparison of the observed shape of the twisted WS_2 strips (Fig. 1C) and the predicted theoretical shapes of the B helical strips with minimal elastic energy (Fig. 4), the normalized spontaneous curvature deviator $d_m \sim 0.015$ was determined. By taking into account $v_0 \sim 30$ nm (Fig. 1C) the spontaneous curvature deviator D_m of the observed twisted WS_2 strips was estimated to be $\sim 5 \cdot 10^{-4} \text{ nm}^{-1}$.

CONCLUSION

Recently, an interesting phenomenon, referred to as the collapse of micro and nanotubes, has been observed (16, 18). Usually, MoS_2 micro and nanotubes are hollow cylinders composed of many S-Mo-S trilayers (Fig. 1A, white

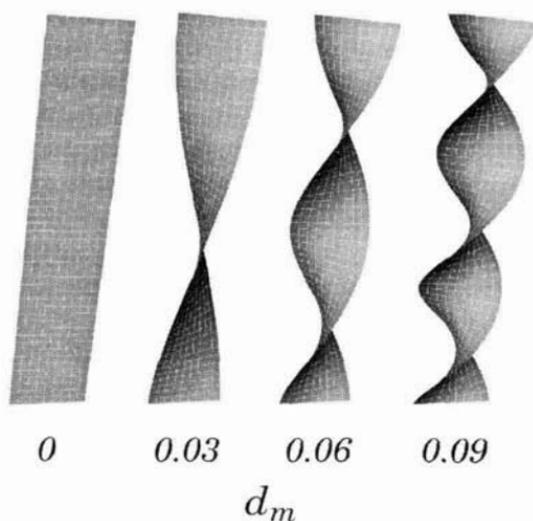


Figure 4. Calculated B helical shapes with minimal energy for different values of d_m and $h_m = 0$.

arrow), but some collapsed (flattened) tubes also appear (Fig. 1A, black arrow), which may be considered as flat strips. It was indicated that deviatoric elasticity may provide an explanation for the observed collapse of multishell inorganic micro and nanotubes (16). It was found that if the tube perimeter exceeds a certain threshold, the collapsed shape corresponds to the absolute minimum of elastic energy (16).

Based on these results we were encouraged to explore the possible role of deviatoric elasticity in the stability of helical and twisted shapes observed in inorganic strips. We assumed that thin inorganic strips are in general not flat when they are in a state of minimal free energy. In the past, the preference of thin isotropic strips and shells for bent states was usually mathematically characterized by a material constant called the spontaneous curvature C_0 . The corresponding elastic free energy per unit area may then be written in the form of Eq. (1) (12, 13). In this work we assumed that the observed inorganic strips are in general anisotropic. Consequently, in the contrast to the case of isotropic strips and shells considered in previous studies, the preference of anisotropic thin strips for bent states are described by two intrinsic parameters, the spontaneous mean curvature H_m and the spontaneous curvature deviator D_m (Eq. (4)). The stable shapes of strips were then determined by minimization of their elastic energy, including the deviatoric contribution.

Based on the results presented we conclude that for an isotropic nano-strip having $H_m = D_m = 0$ flat geometry is the most favourable, while for an anisotropic nano-strip having $H_m = 0$ and nonzero values of D_m , B helical geometry is more favourable. Helix A is favoured by equal spontaneous

curvatures, i.e. $H_m = D_m$, where the pitch angle ψ is determined by the orientation of the principal axes system of the intrinsic curvature tensor.

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