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Deviatoric elasticity as a possible physical mechanism explaining collapse of inorganic micro and nanotubes

V. Kralj-Iglič [a], M. Remškar [b], G. Vidmar [c], M. Fošnarič [c], A. Iglič [c,*]

[a] *Institute of Biophysics, Faculty of Medicine, Lipičeva 2, SI-1000 Ljubljana, Slovenia*
[b] *Jožef Stefan Institute, Jamova 39, SI-1111 Ljubljana, Slovenia*
[c] *Laboratory of Applied Physics, Faculty of Electrical Engineering, Tržaška 2, SI-1000 Ljubljana, Slovenia*

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Abstract

A mechanism is proposed that explains collapse of the multishell inorganic micro and nanotubes. A single shell is considered as a thin elastic plate with anisotropic properties. The derived elastic energy is expressed by the mean curvature and the curvature deviator. If the tube perimeter exceeds a certain threshold, the collapsed shape corresponds to the absolute minimum of the elastic energy.

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In the last years, the interest in inorganic micro and nanotubes has been increasing. The carbon nanotubes [1] are being extensively studied [2]. Also, the nanotubes composed of other materials have been synthesized and explored [3–5]. In synthesizing MoS_2 micro and nanotubes, an interesting phenomenon, that we refer to as a collapse, was noted [6]; usually, MoS_2 micro and nanotubes are hollow cylinders composed of many S–Mo–S trilayers (Fig. 1A), however some stable flattened (i.e., collapsed) multitrilayer structures also appear (Fig. 1B). Although the MoS_2 tubes are very soft against radial forces, it seems that the collapse is not caused by mechanical manipulation during the sample preparation [6]. The collapse could rather be triggered by an obstacle that would affect the tube growth [6] so that the tube becomes thicker due to increasing number of trilayers. In this Letter we propose that deviatoric elasticity that originates in the anisotropic properties of the layered structure is a possible physical mechanism that can explain the collapse of cylindrical MoS_2 micro and nanotubes and the stability of the collapsed tubes (Fig. 1).

As we are interested in the general principles of the phenomenon we consider a single S–Mo–S trilayer closed into a tube. We take that the tube is very long so that the end effects can be neglected. A single trilayer is treated as a thin elastic plate. Its shape is described by the equations of differential geometry of a two-

* Corresponding author.
E-mail address: ales.iglic@fe.uni-lj.si (A. Iglič).

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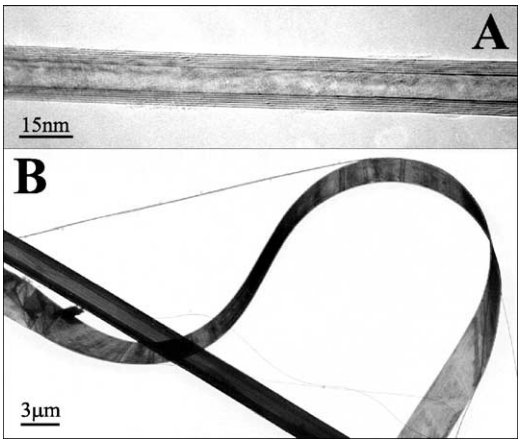

Fig. 1. A: High-resolution transmission electron micrograph of the MoS_2 nanotube. Dark fringes correspond to molybdenum atomic layers. The nanotube consists of seven MoS_2 layers. B: Transmission electron micrograph of the collapsed MoS_2 microtube. The thickness of the tube estimated from the ribbon turn is approximately 70 nm.

dimensional surface. However, the three-dimensional structure of the trilayer as well as its interaction with the adjacent trilayers is taken into account by the appropriate choice of energy. The continuum approach is used where it is taken into account that the trilayer is in general anisotropic within the trilayer plane.

It is considered that the elastic energy of a chosen very small element of the trilayer is in the absence of the external forces equal to zero at the characteristic principal curvatures $C_{1\mathrm{m}}$ and $C_{2\mathrm{m}}$. We call these principal curvatures the intrinsic principal curvatures. If a given shape had such principal curvatures in all its points, the elastic energy of such shape would be zero.

We define the elastic energy per unit area of a very small element of the thin plate with area dA as the energy of mismatch between the actual local continuum curvature of this element and the intrinsic continuum curvature. The shape of both continuums are described by the curvature tensors $\underline{C}$ and $\underline{C}_{\mathrm{m}}$, respectively. The tensor $\underline{C}$ describes the actual curvature while the tensor $\underline{C}_{\mathrm{m}}$ describes the intrinsic curvature, i.e., the curvature which would be energetically the most favorable. In the respective principal systems the curvature tensors include only the diagonal elements

$$\underline{C} = \begin{bmatrix} C_1 & 0 \\ 0 & C_2 \end{bmatrix}, \tag{1}$$

and

$$\underline{C}_{\mathrm{m}} = \begin{bmatrix} C_{1\mathrm{m}} & 0 \\ 0 & C_{2\mathrm{m}} \end{bmatrix}. \tag{2}$$

The principal systems of these two tensors are in general rotated for an angle ω with respect to each other. The mismatch between the actual local continuum curvature and the intrinsic continuum curvature in the absence of the external forces is characterized by the tensor $\underline{M}$:

$$\underline{M} = \underline{R}\,\underline{C}_{\mathrm{m}}\underline{R}^{-1} - \underline{C}, \tag{3}$$

where $\underline{R}$ is the rotation matrix,

$$\underline{R} = \begin{bmatrix} \cos\omega & -\sin\omega \\ \sin\omega & \cos\omega \end{bmatrix}. \tag{4}$$

The small patch of the membrane 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 deformation. The elastic energy per unit area dE/dA is a scalar quantity. Therefore each term in the expansion of dE/dA must also be a scalar [7], i.e., an invariant with respect to the rotation of the local coordinate system. In this Letter, the elastic energy density dE/dA 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,

$$\frac{dE}{dA} = K_1(\mathrm{Tr}\,\underline{M})^2 + K_2\,\mathrm{Det}\,\underline{M}, \tag{5}$$

where K_1 and K_2 are constants. Taking into account Eqs. (1)–(4), the energy density dE/dA can be written as

$$\frac{dE}{dA} = \frac{\xi}{2}(H - H_{\mathrm{m}})^2 + \frac{\xi + \xi^{\star}}{4}\big(\hat{C}^2 - 2\hat{C}\hat{C}_{\mathrm{m}}\cos(2\omega) + \hat{C}_{\mathrm{m}}^2\big), \tag{6}$$

where

$$H = \frac{1}{2}(C_1 + C_2), \tag{7}$$

is the mean curvature,

$$\hat{C} = \frac{1}{2}(C_1 - C_2), \tag{8}$$

is the curvature deviator,

$$H_{\mathrm{m}} = \frac{1}{2}(C_{1\mathrm{m}} + C_{2\mathrm{m}}), \tag{9}$$

is the mean curvature of the intrinsic shape,

$$\hat{C}_{\mathrm{m}} = \frac{1}{2}(C_{1\mathrm{m}} - C_{2\mathrm{m}}), \tag{10}$$

is the curvature deviator of the intrinsic shape, $\xi = 8K_1 + 2K_2$ and $\xi^\star = -8K_1 - 6K_2$. It can be seen from Eq. (6) that the area density of the energy of the tube is characterized by two constants ξ and $\xi^\star$ and three parameters ω, H_{m} and $\hat{C}_{\mathrm{m}}$. The energy density (6) can be obtained also by integrating the square of the difference between the curvatures of the normal cuts of the intrinsic shape and the actual shape over all possible normal cuts through the selected point [8].

If the trilayer were isotropic ($\hat{C}_{\mathrm{m}} = 0$) Eq. (6) can be written in the form of the area density of the energy of isotropic bending [7,9]

$$\frac{dE_{\mathrm{b}}}{dA} = \frac{k_{\mathrm{c}}}{2}(2H - C_0)^2 + k_{\mathrm{G}}K, \tag{11}$$

where C_0 is the spontaneous curvature,

$$K = C_1C_2 = H^2 - \hat{C}^2, \tag{12}$$

is the Gaussian curvature, while k_{c} and k_{G} are the splay modulus and the saddle-splay modulus, respectively. The microscopic constants ξ, $\xi^\star$, H_{m} and $\hat{C}_{\mathrm{m}}$ are connected to the elastic constants k_{c}, k_{G} and C_0. By comparing the expressions (6) and (11) we get the relations $k_{\mathrm{c}} = (3\xi + \xi^\star)/8$, $k_{\mathrm{G}} = -(\xi + \xi^\star)/4$ and $C_0 = 4\xi H_{\mathrm{m}}/(3\xi + \xi^\star)$.

It can be seen from Eq. (6) that the area density of the energy of an anisotropic thin plate can be expressed in a simple way by two invariants of the curvature tensor: the mean curvature and the curvature deviator. For the trilayer with intrinsically anisotropic properties this set of invariants is favored over a set composed of the mean curvature and the Gaussian curvature that are usually considered as the fundamental invariants for description of the two-dimensional surfaces. The main difference between the expressions (6) and (11) derives from the choice of the reference state of the system. For isotropic material, however, the use of both sets of invariants is equivalent.

The equilibrium shape is the shape with the minimal elastic energy. As we are interested in the general behavior of the system and not in the details of the shape we describe the contour by a variational ansatz with a sufficient number of parameters. We consider only the shapes with a constant cross-section along the longitudinal (ζ) axis. This cross-section lies in the (χ, ψ) plane and is given by the variational ansatz

$$\psi(\chi) = \pm\left(a + \frac{(c\chi)^2}{1 + (c\chi)^2}\right)\sqrt{b^2 - \chi^2}, \tag{13}$$

where a, b and c are parameters and $\chi \in [-b, +b]$. The sign $+$ pertains to the contour above the χ axis and the sign $-$ pertains to the contour below the χ axis. By taking into account the definition of the principal curvatures C_1 and C_2 [10], the mean curvature H and the curvature deviator $\hat{C}$ can be expressed as

$$H = -\frac{\psi''}{2(1 + \psi'^2)^{3/2}}, \tag{14}$$

and

$$\hat{C} = |H|, \tag{15}$$

where $\psi' = d\psi/d\chi$ and $\psi'' = d^2\psi/d\chi^2$. The infinitesimal area element is $dA = \sqrt{1 + \psi'^2}\, d\chi\, d\zeta$. The mean curvature defined by Eq. (14) is positive for the convex regions (such as parts of sphere or cylinder) and automatically negative for the concave regions. The normal direction to the surface is outwards for all points. The curvature deviator (Eq. (15)) is always positive.

In the following, dimensionless quantities are used. The elastic energy of the tube is divided by $\xi/2$ and calculated per unit of the normalized length L to yield a dimensionless quantity $dE/d\zeta$,

$$\frac{dE}{d\zeta} = \frac{2}{\xi L}\int \frac{dE}{dA}\, dA. \tag{16}$$

The minimum of the elastic energy is sought at constant dimensionless contour perimeter

$$2\pi \int \sqrt{1 + \psi'^2}\, d\chi = 2\pi R_0, \tag{17}$$

where R_0 is the dimensionless radius of the cylindrical tube with the circular contour.

In the minimization procedure the parameter c as the function of the parameters a and b is determined numerically from the constraint (17). The parameters a and b are then determined by the minimization of $dE/d\zeta$. The integrals in Eqs. (16) and (17)

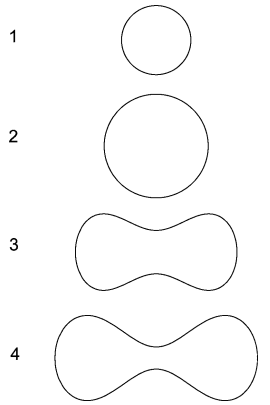

Fig. 2. The calculated cross-sections of the equilibrium shapes for increasing relative perimeter of the tube; R_0: 1.0 (1), 1.5 (2), 2.0 (3) and 2.5 (4) at $H_m = \hat{C}_m = 1$ and $\omega = 0$. The cross-section of the tube is circular for $R_0 < 1.87$ while the tube is in the collapsed state for larger R_0.

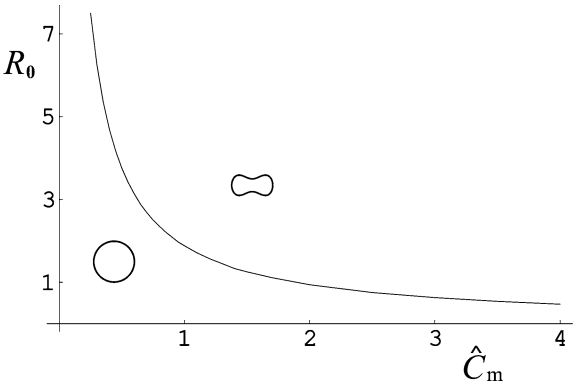

Fig. 3. A $(\hat{C}_m, R_0)$ phase diagram of equilibrium shapes of the tube with constant cross-section along the longitudinal axis; $H_m = \hat{C}_m$, $\omega = 0$.

are calculated numerically. The material properties of the tube are described by the intrinsic mean curvature H_m and intrinsic curvature deviator $\hat{C}_m$. As the tube at the beginning grows into a cylindrical shape, from a cylindrical shape of the S–Mo–S we assume that the intrinsic shape is a cylinder with $H_m = \hat{C}_m > 0$. For simplicity, it is taken that $\omega = 0$.

In general, for anisotropic thin closed plates (i.e., for $\hat{C}_m \neq 0$) the energy per unit of normalized length $dE/d\zeta$ has two minima with respect to a and b. One minimum corresponds to the cylindrical tube with the circular contour, while the second minimum corresponds to the collapsed tube. At smaller values of R_0 the minimum of $dE/d\zeta$ corresponding to the cylindrical tube is the global minimum of $dE/d\zeta$. However, with increasing R_0, at a certain threshold, the minimum of $dE/d\zeta$ corresponding to the collapsed tube, becomes the global minimum of $dE/d\zeta$.

Fig. 2 shows the cross section of the calculated equilibrium shapes of the material with anisotropic properties ($H_m = \hat{C}_m = 1$). For simplicity, it is taken that $\xi = \xi^\star$. The contour length R_0 is increased from the top to the bottom. The tube cross-section is circular at smaller values of R_0 while it is in the collapsed state above some threshold value of R_0. In contrast, for isotropic thin plates ($\hat{C}_m = 0$ and $H_m \geqslant 0$) the calculated equilibrium state of the tube is cylindrical for all values of R_0. A nonzero intrinsic curvature deviator is therefore prerequisite for the initiation of the collapse of the cylindrical tube with a large contour length. Based on these theoretical results we suggest that the observed collapse of the cylindrical MoS_2 micro and nanotubes that occurs during growth of the tube into a multitrilayer structure [6] is spontaneous, in order to keep the elastic energy of the tube as low as possible. Namely, during the growth of the tube into the multilayer structure the perimeter of the layers increases. For the outer layers the collapsed state becomes energetically more favourable. When this effect becomes large enough to render the collapsed state of the whole tube energetically the most favourable, the collapsed state becomes the stable state of the tube. These suggestions are in accordance with observations [6].

Fig. 3 shows the $(\hat{C}_m, R_0)$ phase diagram exhibiting the regions corresponding to the stable shapes of the single-trilayer tube with constant closed cross-section along its longitudinal axis. The phase diagram shows two different regions of shapes: the region of cylindrical tubes with circular cross-section and the region of collapsed tubes. The critical value of R_0 where the collapse of the tube occurs, decreases with increasing intrinsics curvature deviator $\hat{C}_m$ (Fig. 3).

The variational problem regarding the shape with minimal energy can be expressed by the differential equation [13]. In this Letter we have used a variational ansatz as we were interested in general behavior of the system and not in the details of the shape. However, the model can be in the future upgraded also in this direction.

The collapsed shapes were observed also in carbon nanotubes [11]. It was suggested that the collapse of the carbon nanotube is initiated by some external

mechanical force while the collapsed structure is kept stable by the van der Waals attractive forces between the nanotube walls [11].

We think that the van der Waals forces are important also in stabilizing the collapsed shapes of MoS_2 micro and nanotubes, however, based on the results presented in this Letter we argue that some other mechanism such as the intrinsic anisotropy of the trilayer (described by the parameters H_m and $\hat{C}_m$) is necessary to trigger the collapse. The intrinsic anisotropy of the trilayer may be a consequence of the interaction between the trilayers. A perfect match of the two adjacent trilayers cannot be obtained as the curvature of the adjacent layers is different. While in the direction of the tube axis the distance between the atoms may stay the same, the differences in the interatomic distances between individual layers are necessarily present along the tube circumference. In order to yield the most favorable match, defects in the structure may appear [12]. We may say that in this Letter the trilayer is described as a thin elastic plate with uniformly distributed anisotropic defects.

In this Letter we start with the assumption that the initial equilibrium shape of the S–Mo–S trilayer is a cylinder ($H_m = \hat{C}_m > 0$) with certain orientation of the atomic lattice with respect to the geometrical axes of the cylinder ($\omega = 0$) and propose an explanation for the collapse of this structure. At the present stage of the knowledge on the process of the formation of the MoS_2 nano and microtubes we cannot say why the S–Mo–S trilayer initially attains the cylindrical shape.

Stable nano and microtubes have been found also in organic systems such as in surfactant systems [14], protein systems [15], in phospholipid membranes [16, 17] and in cell membranes [18]. The deviatoric elasticity provides an explanation for the stability of the cylindrical phospholipid nano and microtubes [17] and of the tethers connecting a vesicle and a mother cell [18]. In these systems the anisotropic properties of the membrane were explained by orientational ordering of the membrane constituents [8,17–19].

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