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Energy of Formation of Chrysotile Nanotubes

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Abstract—An energy model for the formation of nanotubes and nanoscrolls from thin sheets was constructed. Two major factors responsible for rolling up were identified: size misfit of the crystal lattices forming the sheet and different surface energies on its opposite sides. An optimal cross-sectional geometry was calculated for chrysotile nanotubes. The influence of major physical parameters (Young's modulus and difference in surface energies) on the nanotube radius was considered.

Keywords: nanotubes, nanoscrolls, chrysotile, surface energy, rolling up

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Over the past decade, nanotubes have attracted increased attention due to their unique mechanical, electrophysical, magnetic, sorption, and catalytic properties [1–20]. To understand the mechanism of formation of nanotubes and their growth kinetics and structural features is of importance for preparing nanotubular structures with desired characteristics.

A large class of nanotubular structures is represented by cylindrical nanotubes and nanoscrolls, formed by rolling up of thin sheets like quasi-2D crystal lattices comprising one or several polyhedral networks of different atoms. Nanotubes from vanadium oxide and molybdenum and tungsten sulfides, as well as hydrosilicate nanoscrolls with the imogolite, chrysotile, and other structures are typical examples of such structures [21–33]. This sheets lack a symmetry axis, due to which two major rolling up factors arise: difference in the surface energies on the opposite sides of the sheet and size misfit of polyhedral networks [13, 34]. The same driving forces are responsible for the formation of nanoscrolls with a more intricately organized structures fabricated by the Prinz technology [35] and formed under the action of surface tension and other interfacial factors [36, 37].

Even though much effort has been made to understand the influence of the above-mentioned energy factors on the geometry of cylindrical nanotubes [34, 38–42], there still remained a lot of questions to be answered. In the works on the energy of rolling up of cylindrical nanotubulenes no attention has been given either to a possibly nonzero value of the curvature of an unstressed sheet or to the difference in the surface energies on the opposite sides of the sheet.

Experimental calorimetric studies revealed no significant differences between the heats of formation of lamellar and tubular hydrosilicates [43, 44]. At the same time, the very fact that nanoscrolls are formed from compounds of the same composition but with a lamellar morphology suggests that nanotubes are preferable by the energy. The insufficient accuracy of the calorimetric experiment can be compensated by a theoretical study into the energy of sheet rolling up.

Thus, the main goal of the present work is a theoretical analysis of the influence of energy, mechanical, and structural parameters on the formation of cylindrical nanotubulenes.

Energy model of the formation of cylindrical nanotubes. In a general case, the rolling up of a planar sheet into a cylindrical nanotube can be accompanied by chemical and structural transformations [45]. Here we restrict ourselves by the processes that are accompanied by morphological transformations, and, therewith, such transformations are analyzed exclusively in terms of energy changes. Since we consider here exclusively the energy aspects of nanotube formation, the rolling up mechanism is of no concern which can

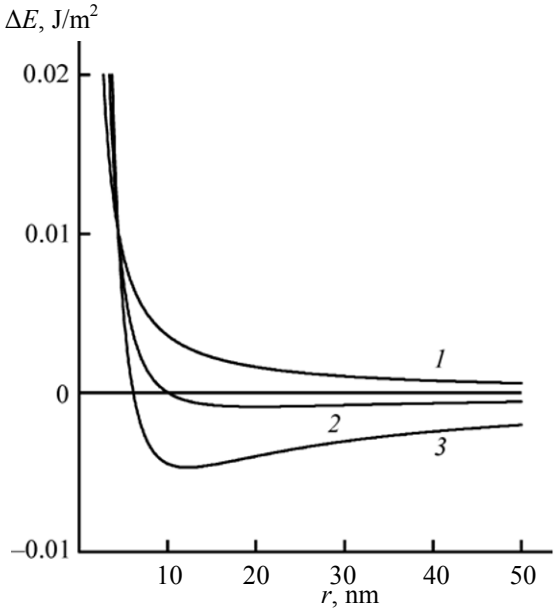

Fig. 1. Change of the total energy on rolling up into a tube with the radius r at $\Delta\sigma$ 0.3 J/m^2 and Y (*1*) 60, (*2*) 300, and (*3*) 600 GPa.

vary depending on the conditions of formation and the initial state of the reaction system.

Another assumption relates to mechanical characteristics of the nanosheets being rolled up. Even though, according to Krivtsov and Morozov [46], elastic moduli depend on sheet thickness and the Young's modulus of nanotubes depends on their diameter [47], in our elastic energy calculations the Young's modulus is assumed to be constant. This assumption is based on the fact that the sheet thickness before and after rolling up is almost the same.

The surface energy of a particle 3–5 nm in diameter is a function of its curvature [48, 49]. In this work we neglect this dependence. Such assumption is by no means always correct. For example, it is too rough in the case of nanoscrolls with the imgolite structure in view of the small diameter of imogolite nanotubes [24].

Further assumption is associated with the fact that the aspect ratios (the ratio of the tube length to its external diameter) of nanotubular structures are generally several hundreds. Under such assumption, nanoscrolls can be considered indefinitely long.

In the present work we focus on the energy of the rolling up of a planar sheet to form single-wall nanotubes. The energy of rolling up to form multiwall nanotubes will be the subject of our next publication.

Taking into account that, unlike what is stated in [41], the curvature of an unstressed thin sheet can be different from zero, the equation for elastic energy related to unit surface can take the following form.

$$E_d = 0.5D(c - c_0)^2. \quad (1)$$

Here $D = Yh^3/[12(1 - \nu^2)]$ is the flexural rigidity; Y, the Young's modulus; h, sheet thickness; c, sheet curvature, c_0, curvature of a mechanically unstressed sheet; and ν, the Poisson's ratio.

It should be noted that with certain nanotubes, for example, carbon and boron–nitrogen, we can suppose that c_0 is equal to 0, as has been done in the calculation of the rolling up energy of nanotubes in [45, 50, 51]. However, in the case of nanotubes with the chrysotile structure, c_0 takes a nonzero value. This is explained by the size misfit of interconjugated quasi-2D networks of silicon oxide tetrahedra and metal oxide octahedra [13, 27, 34, 52]. To form a mechanically unstressed structure, these conjugated networks bend with the curvature c_0 to compensate for their size misfit. A hypothetical planar sheet having a similar structure will have an elastic energy which can be calculated by Eq. (2).

$$E_{d,f} = \lim_{c\to 0} E_d = 0.5Dc_0^2. \quad (2)$$

The rolling up of a thin sheet is also affected by the difference in the surface energies on its opposite sides. In a general case, such situation is characteristic of all sheets with different compositions and structures of their opposite surfaces. The contribution of this factor for a finite-curvature sheet is given by Eq. (3).

$$E_s = (1/r)[\sigma_o(r + h/2) + \sigma_i(r - h/2)]. \quad (3)$$

Here $r = 1/c$ is the sheet radius at half thickness and σ_o, σ_i, specific surface energies on the outer and inner sides of the sheet, respectively. For a planar sheet, $E_{s,f} = \sigma_o + \sigma_i$.

The change of the total energy for the rolling of a planar sheet is given by Eq. (4).

$$\Delta E = (E_d + E_s) - (E_{d,f} + E_{s,f}). \quad (4)$$

After substitution and transformation we obtain Eq. (5).

$$\Delta E = [Yh^3/24(1 - \nu^2)][(1/r - 1/r_0)^2 - 1/r_0^2] + \Delta\sigma h/2r. \quad (5)$$

Here $\Delta\sigma = \sigma_o - \sigma_i$.

It should be noted that the rolling up to form a scroll is also possible. Its cross-section can be described by the Archimedean spiral. The change of

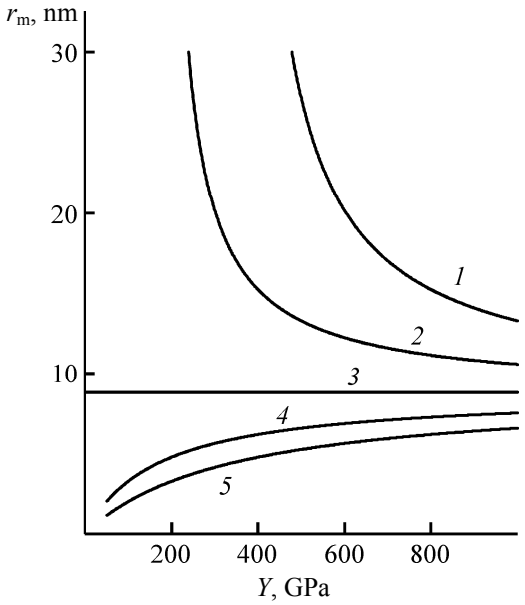

Fig. 2. Dependence of the nanotube radius at the total energy minimum r_m on the Young's modulus at $\Delta\sigma$ (*1*) 0.6, (*2*) 0.3, (*3*, *4*) –0.3, and (*5*) –0.6 J/m^2.

the scroll radius along the length will depend on the torsion angle φ expressed in polar coordinates.

$$r_{scl} = r + f\varphi = r + \varphi/2\pi(h + t). \quad (6)$$

Here t is the interlayer spacing. The spiral constant f is calculated under the condition that over one full turn the radius should change by $(h + t)$.

The elastic energy of the scroll is an integral by the length of the spiral in polar coordinates [Eq. (7)].

$$E_{d,scl} = 1/2\pi\int_0^{2\pi}[Yh^3/24(1 - \nu^2)](1/r_{scl} - 1/r_0)^2 d\varphi. \quad (7)$$

The surface energy of the scroll is given by Eq. (8).

$$E_{s,scl} = 1/2\pi\int_0^{2\pi}1/r_{scl}[\sigma_0(r_{scl} + h/2) + \sigma_i(r_{scl} - h/2)]d\varphi. \quad (8)$$

Substitution of Eqs. (8) and (7) into Eq. (4) gives the change of the total energy for the rolling up of a thin sheet to form a scroll.

Modeling of chrysotile nanotubes. To calculate the energy gain associated with chrysotile sheet rolling up we should estimate the physical constants. The possible values of the Young's modulus (Y) were chosen based on the experimental data in [6, 19, 39]. According to these data, the Young's modulus of chrysotile can vary over a wide range (from 60 to 600 GPa and higher), depending, apparently, on structural defects in nanotubes. As a certain intermediate value we chose the Y value of 300 GPa predicted by calculations. The Poisson's ratio was set at 0.2. According to [53], the radius r_0 of a mechanically unstressed scroll with the chrysotile structure was set at 8.8 nm. The bilayer thickness (h 0.4 nm) and interlayer spacing (t 0.3 nm) were taken from the TEM data in [13].

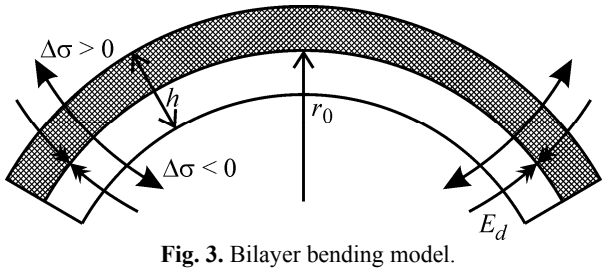

Fig. 3. Bilayer bending model.

Figure 1 shows the $\Delta E(r)$ dependences calculated by Eq. (5) for $\Delta\sigma = 0.3$ J/m^2. All the dependences have an unsymmetrical minimum, whose shape and position depend on the Young's modulus. The sharp rise of ΔE at decreasing r suggests that there is a limiting nanotube curvature radius. After rolling up into a scroll, the $\Delta E_{scl}(r)$ dependence repeats in many respects those in Fig. 1. One distinctive feature of the $\Delta E_{scl}(r)$ dependence is that the scroll radius at an energy minimum ($r_{m,scl}$) is always smaller that the tube radius at an energy minimum (r_m), by about 0.4 nm, i.e. by a value of the order of h and t. Most likely, this feature is associated with the fact that the scroll ends move apart by $-h/2$ and $+h/2$ from the tube radius to form an interlayer space. The energy difference between tubes and scrolls is about 10^{-4} J/m^2.

Figure 2 shows the behavior of r_m at different $\Delta\sigma$ and Y. In the absence of any $\Delta\sigma$ contribution (Fig. 2, curve *3*), the sheet bends with the equilibrium radius $r_m = r_0$. At $\Delta\sigma > 0$, the factors of size misfit and surface energy difference act in opposite directions (Fig. 3). As a result, the bilayer will unbend so that the side with a higher surface energy occupied a smaller (inner) surface. The unbending degree is the higher the lower is the Young's modulus of the bilayer. By contrast, at $\Delta\sigma < 0$ the rolling up effect is enhanced, and the enhancement is, too, the stronger the lower is the Young's modulus. The elastic forces arising due to size misfit in any case tend to return the bilayer to the state with a zero curvature radius r_0.

Thus, the proposed energy model for nanotube rolling up allows a prediction of the effect of size

misfit of spatially conjugated crystalline networks forming the bilayer, as well as its mechanical characteristics and surface energies on the morphology of the resulting nanotubes. Calculations by the suggested model for nanotubes with the chrysotile structure are qualitatively consistent with the real geometric parameters of the nanotubes. It should be noted that the proposed model is also appropriate for the morphologic analysis of multiwall cylindrical tubes and scrolls, provided the energy of interlayer interaction energy is taken into account.

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