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Unduloid-like equilibrium shapes of carbon nanotubes subjected to hydrostatic pressure

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Carbon nanotubes

Carbon nanotubes are carbon molecules in the shape of hollow cylindrical ¯bers of nanometer-size diameter and length-to-diameter ratio of up to $10^7 : 1$.

Carbon nanotubes exhibit extraordinary strength, unique electrical properties, and are e±cient conductors of heat. For this reason, carbon nanotubes have many practical applications in electronics, optics and other ¯elds of material science.

If the tube wall is composed by one layer of graphite atoms, then the tube is referred to as a single-walled one (SWNT). Otherwise, the tube is called multi-walled (MWNT).

Discovery

The predominating opinion among the scientists working in this ¯eld is that they are discovered by Sumio Iijima in 1991. However, carbon nanotubes have been produced and observed prior to 1991.

In 1952 appeared a paper in the Soviet Journal of Physical Chemistry (in Russian) by Radushkevich and Lukyanovich where images of 50 nanometer diameter tubes made of carbon are presented.

In 1976{1977 Oberlin, Endo and Koyama published three papers (Carbon 14(2), 133{135; Journal of Crystal Growth 32(3), 335{349; Japanese Journal of Applied Physics 16(9), 1519{1523) where hollow carbon ¯bers (SWNT) with nanometer-scale diameters are shown.

In 1987, Howard G. Tennent of Hyperion Catalysis was issued a U.S. patent for the production of cylindrical discrete carbon ¯brils with a constant diameter between about 3.5 and about 70 nanometers..., length 10^2 times the diameter ...

Discovery

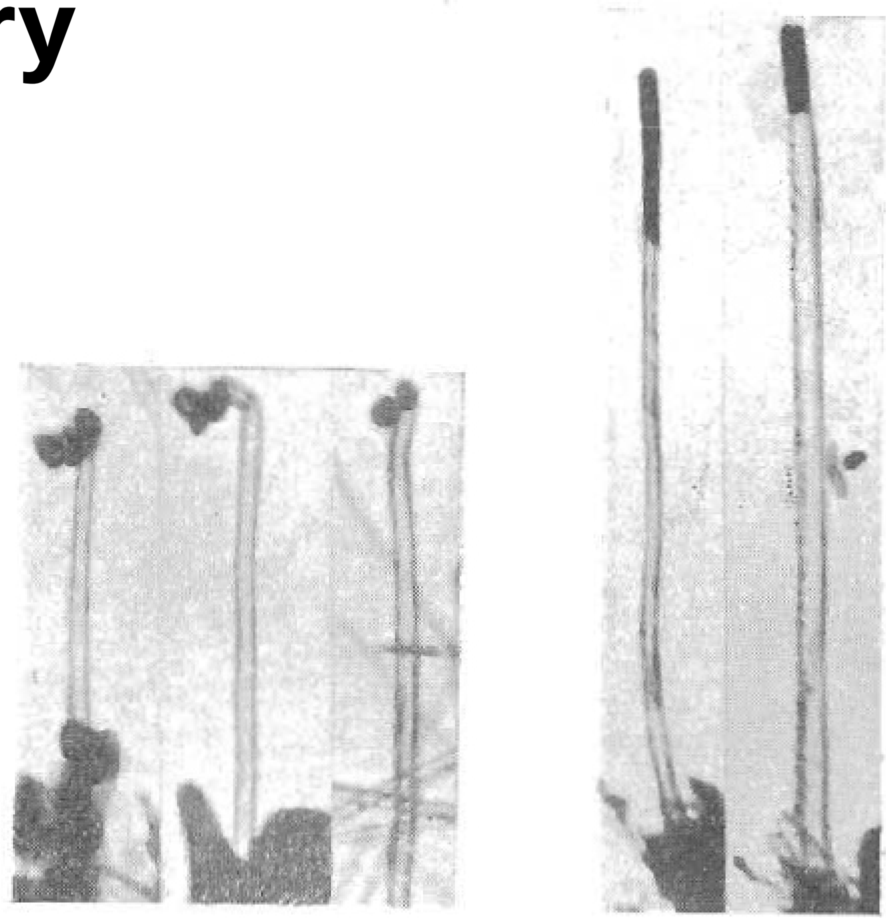


Рис. 7
× 20.000

Modelling

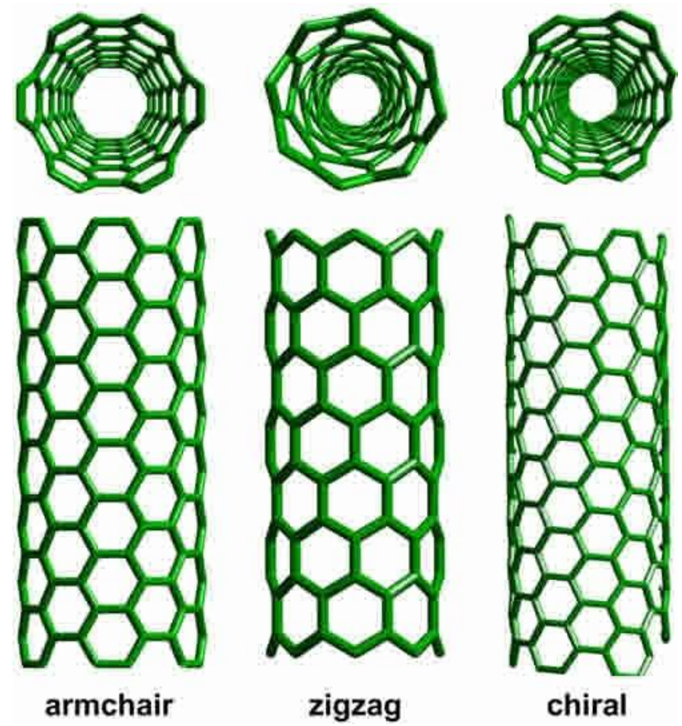
Discrete approach

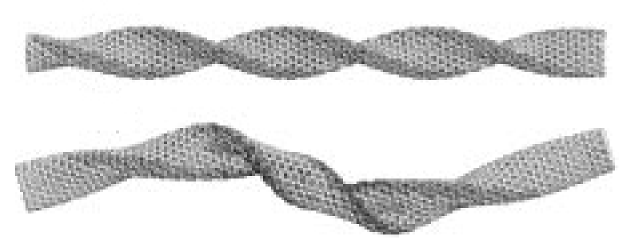
The tube is considered as a multibody system whose behaviour is described by empirical interatomic potentials, one of which is named after Terso® (1988) and Brenner (1990) and another one, named after Lenosky et al. (1992). MD simulations.

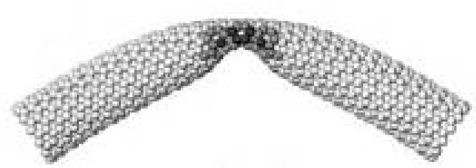
Results:

{ Large elastic deformations of the carbon nanotubes.

{ Bending rigidity of the tubes is much less than streching rigidity.







Continuum approach

Yakobson et al. (1996) suggested carbon nanotube models from classical elastic rod and shell theories. Large scattering of the computed elastic moduli.

Tu and Ou-Yang (2008) { continuum limit of the Lenosky potential. In this approach, the tube is regarded as a two-dimensional surface S embedded in the three-dimensional Euclidean space R^3 and assumed to exhibit purely elastic bending described by its mean H and Gaussian K curvatures. Its equilibrium shapes are determined by the extremals of the curvature energy functional

$$F_c = 2k_c \int_S H^2 dA - k_G \int_S K dA + \text{stretching energy},$$

where, k_c and k_G are two material constants associated with the bending rigidity of this surface.

Approximation: Neglect the streching energy and substitute it with an inextensibility constraint.

Shape equation

Final expression for the functional

$$F_c = 2k_c \int_S H^2 \mathbf{d}A - k_G \int_S K\,\mathbf{d}A + \lambda \int_S \mathbf{d}A + p \int_V \mathbf{d}V;$$

where λ is a Lagrangian multiplier corresponding to the constraint of fixed area of the surface S, and the last term is the work done by the pressure p over the deformation of the volume V whose boundary is S.

Helfrich theory of the lipid bilayer membranes.

Shape equation (Euler-Lagrange equation for the foregoing potential)

$$\Delta H + (H^2 - K)H - \sigma H + q = 0; \quad \sigma = \frac{\lambda}{k_c}; \quad q = \frac{p}{k_c}$$

where Δ is the Laplace-Beltrami operator of the surface S.

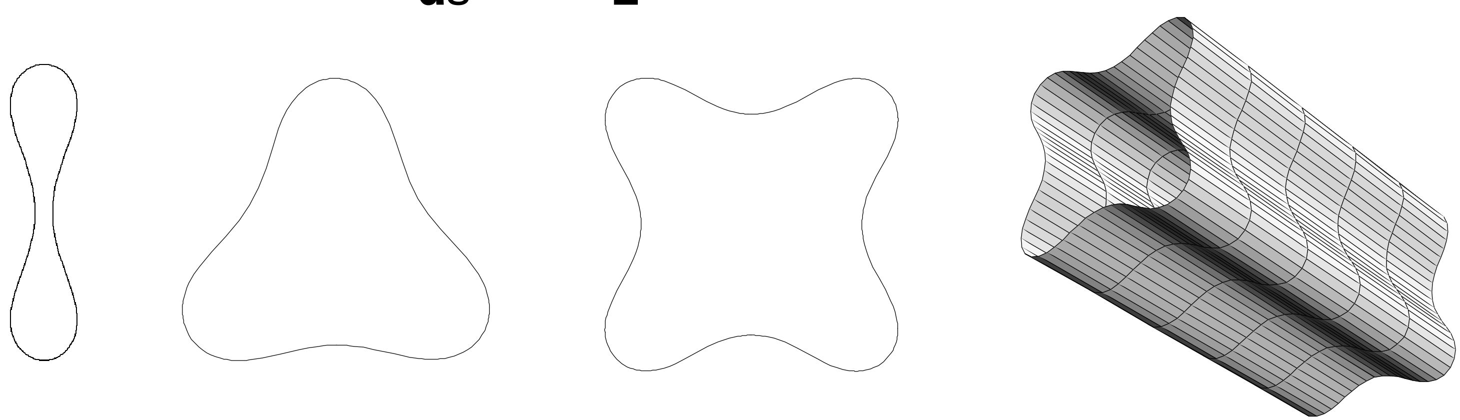
Cylindrical equilibrium shapes

In the case of cylindrical surfaces in $\mathbb{R}^3$ whose directrices are plane curves of curvature $\cdot(s)$ parametrized by their arclength s we have

$$H = \frac{1}{2}\cdot(s); \quad K = 0;$$

and the shape equation simpli¯es to

$$\frac{d^2\cdot(s)}{ds^2} + \frac{1}{2}\cdot^3(s) \;¡\; ¾\cdot(s) + q = 0:$$



Comparison of MD simulations and continuum approach for cylindrical equilibrium shapes

Zang J., O. Aldr§s-Palacios and F. Liu (2007) Commun. Comp. Phys. 2(3) 451{465

(1) Comparison and excellent agreement between the results of MD simulations and continuum approach using the theory of elastic rings under pressure.

(2) It is established, that for $q < q_c = 3$ only the circular shape exists.

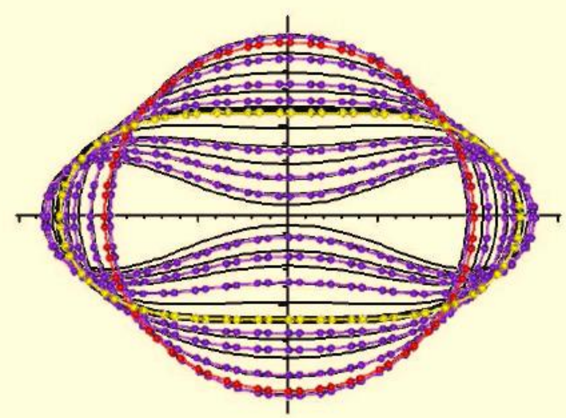


Figure 8: Evolution of cross-sections of SWNTs under hydrostatic pressure, illustrating the perfect agreement between the solutions of variational geometry analysis (black lines) and atomistic simulations of a (18,18) tube. The color dots are atoms with the red marks the first shape transition and the yellow the second.

Axisymmetric equilibrium shapes

If a surface S is axisymmetric, it is completely determined by its profile curve (contour). Therefore, we seek plane curves which, being rotated about a line, form surfaces whose mean curvatures satisfy the shape equation.

Let $x = x(s)$, $z = z(s)$ be the parametric equations of the contour in the Cartesian frame $(x; z)$, where s denotes the contour archlength. Let ψ denotes the angle between the tangent vector of the contour and the x-axis.

In the axisymmetric case, the shape equation reads

$$\frac{d^3\psi}{ds^3} = -\frac{2\cos\psi}{x}\frac{d^2\psi}{ds^2} - \frac{1}{2}\left(\frac{d\psi}{ds}\right)^3 + \frac{3\sin\psi}{2x}\left(\frac{d\psi}{ds}\right)^2 + \frac{2\sigma x^2 + 2 - 3\sin^2\psi}{2x^2}\frac{d\psi}{ds} + \frac{2\sigma x^2 - 2 + \sin^2\psi}{2x^3}\sin\psi + 2q.$$

Boundary conditions

Three boundary conditions hold at a free edge (a curve C corresponding to $s = s_0$) of a carbon nanotube

$$\left[\frac{d\psi}{ds} + \left(1 - \frac{k_G}{k_c}\right)\frac{\sin\psi(s)}{x(s)}\right] = 0;$$

$$\left[\left(\pm\left(\frac{k_G}{k_c}\right)^2 \frac{\cos\psi(s)}{x(s)} + \frac{\gamma}{k_c}\right)\frac{\sin\psi(s)}{x(s)}\right]_C = 0;$$

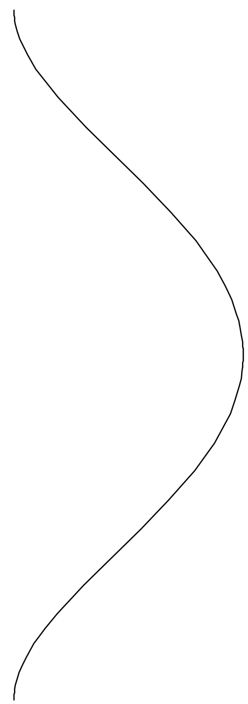
$$\left[\frac{1}{2}\frac{k_G}{k_c}\left(2 - \frac{k_G}{k_c}\right)\left(\frac{\sin\psi(s)}{x(s)}\right)^2 + \sigma - \frac{\gamma}{k_c}\frac{\cos\psi(s)}{x(s)}\right]_C = 0;$$

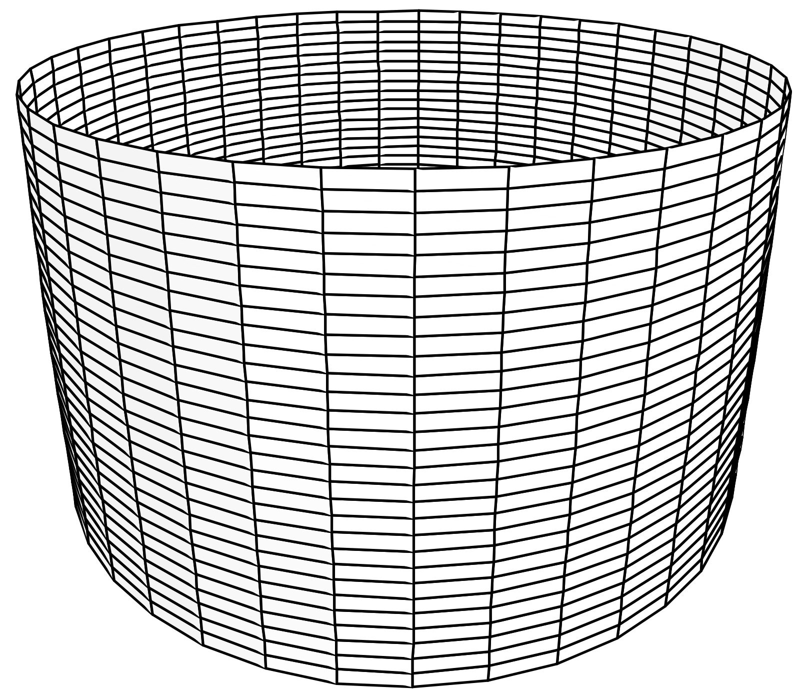
where γ is a line tension in the curve C.

Suppose $\psi(s_0) = \pm\pi/2$. Then, the boundary conditions simplify to

$$\left.\frac{d\psi}{ds}\right|_{s=s_0} \pm \left(1 - \frac{k_G}{k_c}\right)\frac{1}{x(s_0)} = 0; \quad \gamma = 0; \quad \frac{k_G}{2k_c}\left(2 - \frac{k_G}{k_c}\right)\frac{1}{x^2(s_0)} + \sigma = 0:$$

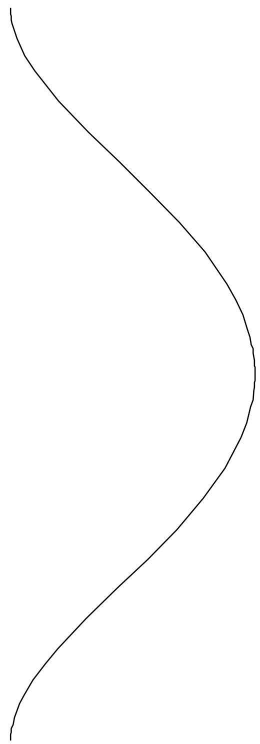
Case $q < q_c$

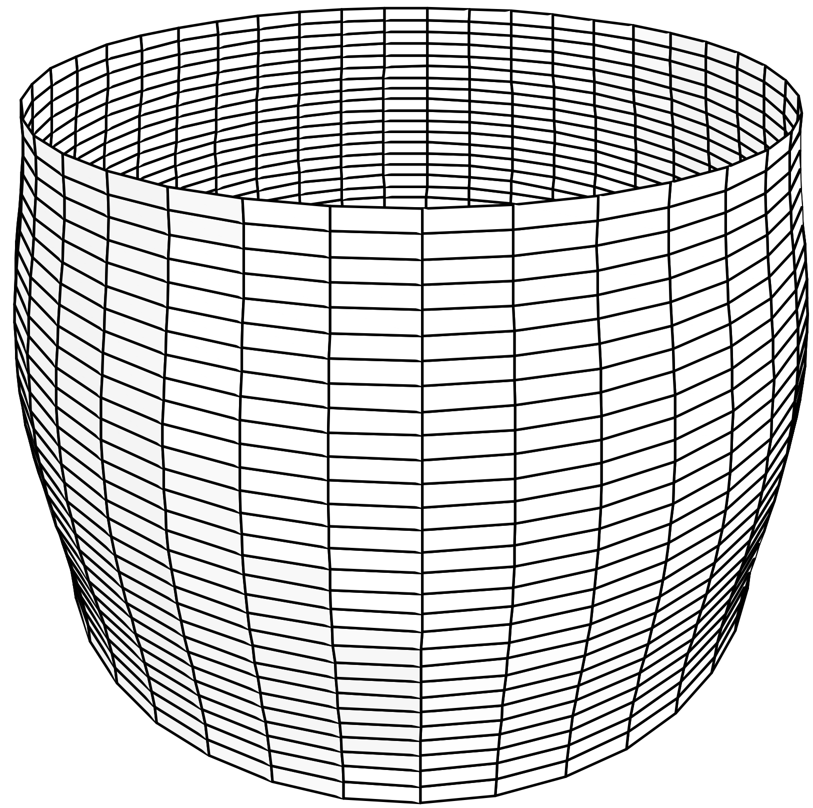




$q = 1.2$, $\delta = 0.7\%$

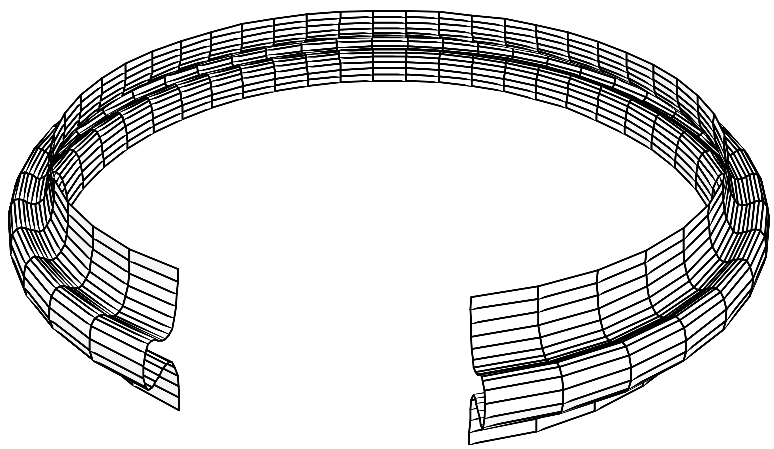
Case $q \geq q_c$



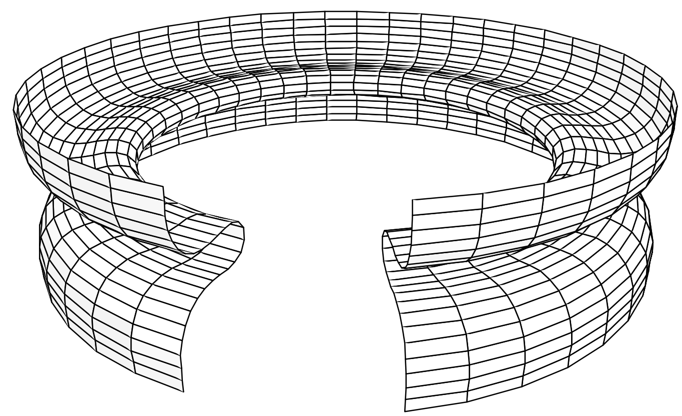


q = 30.88, δ = 7%

Large q

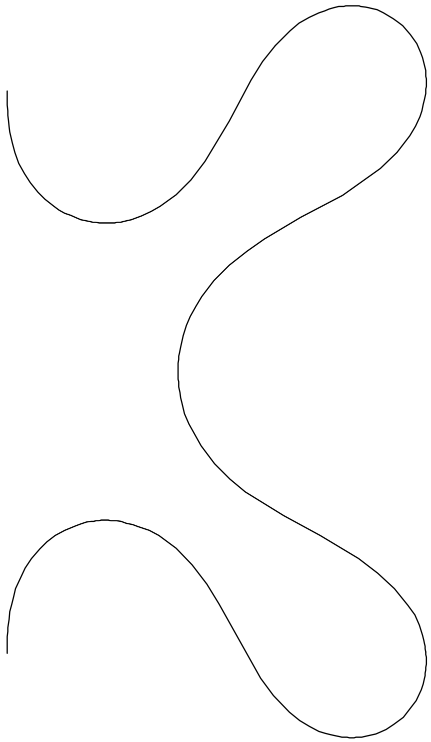


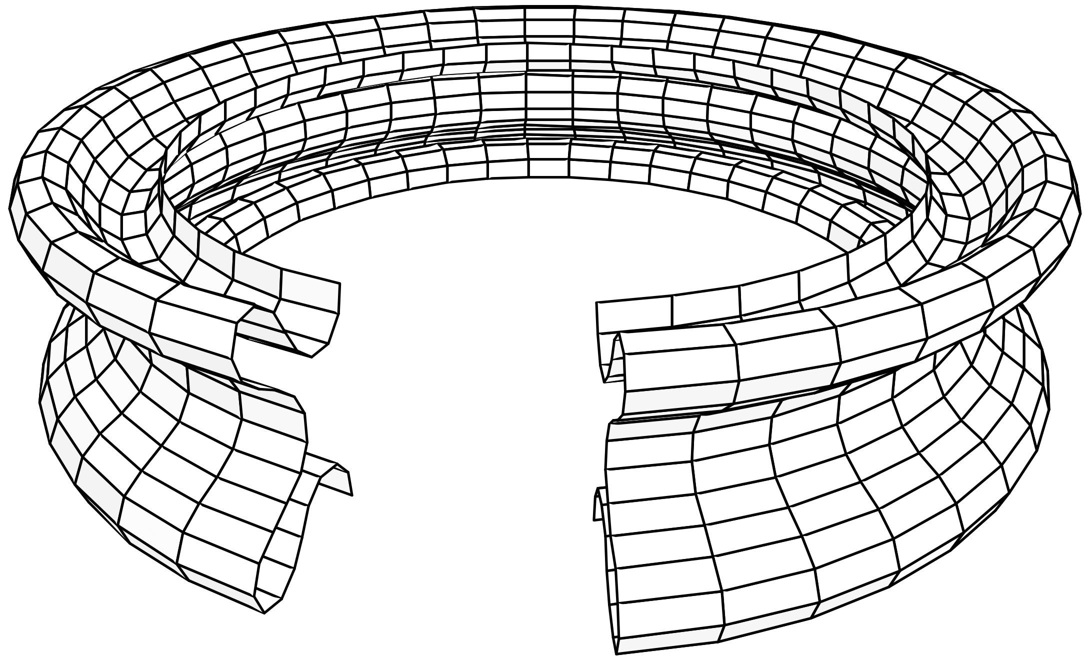
$q = 525$



$q = 529$

Negative q





$q = -345$

Acknowledgments

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Thanks for your attention