Mechanical Properties of Nanosprings

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Nanostructures (nanotubes, nanowires, etc.) have been the object of intense theoretical and experimental investigations in recent years. Among these structures, helical nanosprings or nanocoils have attracted particular interest due to their special mechanical properties. In this work, we investigated structural properties of nanosprings in the Kirchhoff rod model. We derived expressions that can be used experimentally to obtain nanospring Young's modulus and Poisson's ratio values. Our results also might explain why the presence of catalytic particles is so important in nanostructure growth.

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The development of structures as nanotubes and, more recently, nanowires has attracted great attention from the scientific community to the field of nanoscience due to the large range of possible applications and new physical phenomena [1,2]. The great variety of electrical and mechanical properties presented by *nanostructures* can be exploited for the development of new technological applications [2–6].

Among the members of the family of these nanostructures, helical nanosprings or nanocoils, in particular, have special mechanical properties for potential applications in nanoengineering.

It is known [7] that the synthesis of nanowires and nanosprings requires the presence of a metallic catalyst. Following the vapor-liquid-solid (VLS) growth model, known since 1964 [7], a liquid droplet of a metal absorbs the building block material for the growth of the nanowire from the surrounding vapor and, after supersaturation of the absorbed material within the droplet, the excess material precipitates at the liquid/solid interface forming the wire beneath the metallic droplet.

In the case of helical structures, mechanisms for helical growth have been recently proposed. Amelinckx *et al.* [8] introduced the concept of a spatial-velocity hodograph to describe the helical growth of nanotubes of carbon, where the asymmetry arises from variations in the velocity of the growth in the perimeter of the carbon nanotube. McIlroy *et al.* [9] developed a modified VLS growth model to explain the formation of helical nanosprings based on the interactions between the metallic catalyst and the nanowire. The interesting feature in this case is that the structure of the nanospring is amorphous [9]. The modified VLS growth model can, therefore, be applied to nanosprings of different materials [9–11].

Besides the initial success of the proposed growth models for the helical structures, the experimental control of the synthesis of nanosprings is still in development. Also, there are few proposed approaches for the physical characterization of these structures. Volodin *et al.* [12] have studied the elastic properties of helix-shaped nanotubes using atomic force microscopy (AFM). They used a circular beam approximation to model the elastic response of a single winding of coiled nanotube. Recently, Chen *et al.* [13] measured the spring constant of carbon nanocoils and used a classical approach which relates the spring constant to the shear modulus of the composite material.

In this Letter, we propose the application of the Kirchhoff rod model [14] to the analysis of the elastic properties of the helical nanosprings. This approach provides a more complete framework to study both statics and dynamics of the nanosprings. Also, we can obtain a set of expressions that permits us to measure the elastic parameters of the material that composes the nanospring and to directly compare them with the values for the bulk case.

The Kirchhoff model has been extensively used to study the statics and the dynamics of continuous rods. Examples of applications of this model are the study of the structure and elasticity of DNA [15–21], the tendril perversion of climbing plants [22,23], and slender cables subject to thrust, torsion, and gravity [24]. Since some of the helical nanostructures are amorphous, a continuous mechanical model, as the Kirchhoff one, is perfectly appropriated to investigate their elastic properties. In fact, in the case of nanotubes, the literature presents examples of modeling them as solid cylinders [25,26], or as solid hollow cylinders [27].

In Kirchhoff's theory, the rod is seen as an assembly of short segments. Each segment is loaded by contact forces from the adjacent ones. The classical equations for the conservation laws of linear and angular momentum are applied to each segment in order to obtain a one-dimensional set of differential equations for the statics and dynamics of the rod in the approximation of the small curvature of the rod as compared to the radius of the local cross section [28]. These equations contain the forces and torques, plus a triad of vectors describing the deformations of the rod. In this Letter, we shall be concerned only with static solutions and, therefore, only the static Kirchhoff equations will be presented:

$$\mathbf{F}' = 0, \quad (1)$$

$$\mathbf{M}' + \mathbf{d}_3 \times \mathbf{F} = 0, \quad (2)$$

where $\mathbf{F}$ and $\mathbf{M}$ are the total force and torque across the cross sections of the rod, respectively. $\mathbf{d}_3$ is the vector tangent to the centerline or the axis of the rod. The prime denotes the derivative with respect to the arclength s of the rod. In order to solve the equations, we introduce the constitutive relationship from linear elasticity theory [28] for a rod with a circular cross section:

$$\begin{aligned}\mathbf{M} &= EI(k_1 - k_1^{(0)})\mathbf{d}_1 + EI(k_2 - k_2^{(0)})\mathbf{d}_2 \\ &\quad + EI\Gamma(k_3 - k_3^{(0)})\mathbf{d}_3, \end{aligned} \quad (3)$$

where $\mathbf{d}_1$ and $\mathbf{d}_2$ lie in the plane normal to $\mathbf{d}_3$, for example, along the principal axes of the cross section. $\Gamma = 2\mu/E$ is related to Poisson's ratio σ through

$$\Gamma = (1 + \sigma)^{-1}. \quad (4)$$

E and μ are the Young's and shear moduli, respectively. I is the moment of inertia of the circular rod given by $I = (\pi r^4)/4$, with r being the cross-section radius. k_i, $i = 1, 2, 3$, are the components of the so-called *twist vector*, $\mathbf{k}$, which defines the variation of the director basis $(\mathbf{d}_1, \mathbf{d}_2, \mathbf{d}_3)$ with the arclength s through the expression: $\mathbf{d}_i' = \mathbf{k} \times \mathbf{d}_i$, $i = 1, 2, 3$. $k_i^{(0)}$, $i = 1, 2, 3$, are the curvature and torsion of the rod in its unstressed shape. They are also known as the *intrinsic curvature* and *intrinsic torsion* of the rod.

A helical solution of the Kirchhoff Eqs. (1)–(3) is given by the following expressions:

$$\mathbf{k} = \kappa\mathbf{d}_1 + \tau\mathbf{d}_3, \quad (5)$$

$$\mathbf{F} = \gamma\tau\mathbf{k}, \quad (6)$$

where κ and τ are the geometric parameters *curvature* and *torsion* of a helix, respectively, and $\gamma = (\kappa_0/\kappa) - 1 - \Gamma[(\tau_0/\tau) - 1]$. κ_0 and τ_0 are the *intrinsic* curvature and torsion of the helix ($\mathbf{k}^{(0)} = \kappa_0\mathbf{d}_1 + \tau_0\mathbf{d}_3$), respectively.

The spatial solution for the axis of a helix with curvature κ and torsion τ can be written as

$$\mathbf{x}(s) = \frac{\kappa}{\lambda^2}\cos(\lambda s)\mathbf{e}_1 + \frac{\kappa}{\lambda^2}\sin(\lambda s)\mathbf{e}_2 + \frac{\tau}{\lambda}s\mathbf{e}_3, \quad (7)$$

where $\lambda = \sqrt{\kappa^2 + \tau^2}$. $(\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3)$ is a fixed Cartesian basis. The radius R and pitch P of the helix are related to the curvature and torsion through

$$\kappa = R\lambda^2, \qquad \tau = \frac{P}{2\pi}\lambda^2. \quad (8)$$

It is possible to show that λ is also given by

$$\lambda = \frac{1}{\sqrt{R^2 + \frac{P^2}{4\pi^2}}}. \quad (9)$$

McMillen and Goriely [23] have obtained a direct expression for Hooke's constant h of a helix with intrinsic curvature $\mathbf{k}^{(0)} = \kappa_0\mathbf{d}_1 + \tau_0\mathbf{d}_3$, in terms of the properties of the material from which the rod is made, the Young's modulus, and the moment of inertia of the cross section. It is given by

$$h = \frac{EI\lambda_0^3}{2\pi N}\left(1 + \frac{\tau_0^2}{\kappa_0^2}\right), \quad (10)$$

where $\lambda_0 = \sqrt{\kappa_0^2 + \tau_0^2}$ and N is the number of coils.

Following McMillen and Goriely's paper, we derived a simple expression for the component of the torque in the $\mathbf{e}_3$ direction, M_z:

$$M_z = EI(\kappa - \kappa_0)\frac{\kappa}{\lambda} + \Gamma EI(\tau - \tau_0)\frac{\tau}{\lambda}. \quad (11)$$

From Eqs. (10) and (11) we can verify, experimentally, two properties of the material from which the nanospring is made: the Young's modulus E and the Poisson's ratio σ.

We can test Eq. (10) using the parameters for a unit nanocoil considered by Chen *et al.* [13]: the diameter of the nanowire $d = 120$ nm, the radius of the helix $R = 420$ nm, and the pitch of the helix $P = 2000$ nm. The material has a Poisson's ratio $\sigma = 0.27$ and a shear modulus $\mu = 2.5$ GPa. From Eq. (4) and the relation $\Gamma = 2\mu/E$, we obtain $E = 6.35$ GPa. Using Eqs. (8) and (9) and the measured Hooke's constant of the nanocoil, $h = 0.12$ N/m [13], we obtain, with Eq. (10), $E \simeq 6.88$ GPa for $N = 1$ (unit nanocoil).

We could not test Eq. (11) because of the lack of experimental measuring of the torque of the nanosprings.

Figure 1 shows a scheme to obtain Young's modulus by measuring the force $\mathbf{T}$ along the axis of the nanospring and its elongation d due to this force. It is an analog scheme to one that Chen *et al.* used to measure the spring constant of carbon nanocoils [13]. Equation (10) can be

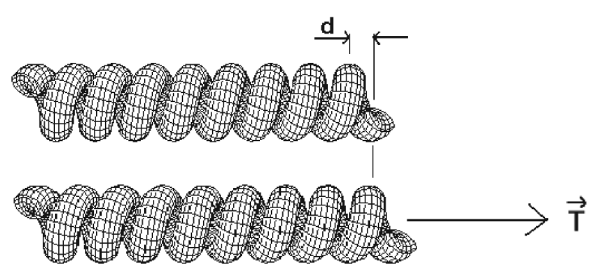

FIG. 1. Outline of the experiment to measure Young's modulus E. The extremities of the nanospring must be held fixed. The helix shown in this figure is proportional to the nanospring of radius $R = 51$ nm and $P = 85$ nm. See the text for the details.

used to obtain the Young's modulus. It requires the knowledge of the moment of inertia of the cross-section radius, I, and the values of the curvature, κ_0, and the torsion, τ_0, of the unstressed helix that can be obtained by measuring the radius, R, and the pitch, P, of the nanospring, before applying the force [R_1 and P_1 of Fig. 2, and using the Eqs. (8) and (9)].

Figure 2 shows a scheme to obtain Poisson's ratio. By measuring the applied torque, in the direction of the axis of the helix, and measuring the resultant curvature, κ, and the resultant torsion, τ [by measuring the radius R_2 and the pitch P_2 of the stressed helix and using the Eqs. (8) and (9) to obtain κ and τ], we can use Eq. (11) to obtain the parameter Γ. Here, the values of κ_0, τ_0, I, and the measured Young's modulus E in the first scheme, are needed. Poisson's ratio, σ, can, therefore, be obtained using Eq. (4).

In both schemes, the extremities of the nanospring must be held fixed in order to avoid relaxation. The helices seen in Figs. 1 and 2 are in scale with a nanospring of radius $R = 51$ nm and pitch $P = 85$ nm.

It is interesting to investigate if the measured values of the Young's modulus and the Poisson's ratio are the same as the bulk elastic modulus of the material from which the nanospring is made. The motivation is the recent measurement of the Young's modulus of gold thin films, deposited in AFM cantilevers [29]. It was found that the Young's modulus of gold thin films is about 12% smaller than its bulk elastic modulus [29].

The existence of nonuniform helical nanosprings have been reported in Ref. [10]. The tridimensional structures of these nanosprings could be investigated with the Kirchhoff rod model. Variations in the rod diameter can be considered in the Kirchhoff equations and the possible tridimensional structures can be numerically integrated [30].

Recently, Goriely and Tabor developed a dynamical method to test the stability of the equilibrium solutions of the Kirchhoff equations [31]. They showed [32] that helices with intrinsic curvature ($\kappa_0 \neq 0$ and $\tau_0 \neq 0$) do not admit unstable modes being, therefore, dynamically stable. McMillen and Goriely [23] also studied how differential growth can affect the intrinsic curvature of biological materials as the climbing plants. Our results show that the same conclusions are valid for nanosprings. This is a very important result that could explain why the presence of metallic catalyst is so important to the growth of nanostructures such as nanotubes and nanowires. It was proposed that one of the functions of the metallic catalyst is to promote differential growth in the nanostructures [3]. Our results suggest that the physical mechanism behind this differentiated growth is that the catalytic particles by their intrinsic asymmetric geometric features induce intrinsic curvature that gives dynamical stability to the nanosprings. Particles that would favor higher curvatures (up to a certain limit) would be catalytically more efficient.

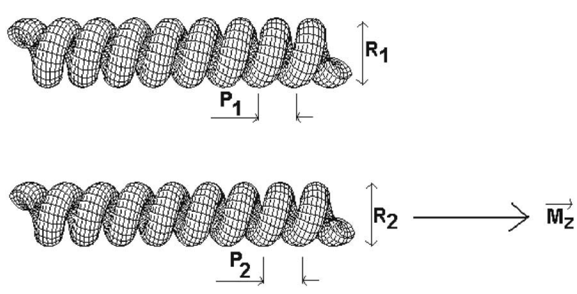

FIG. 2. Outline of the experiment to measure Poisson's ratio σ. The extremities of the nanospring must be held fixed. See the text for the details.

The importance of the dynamical stability is that it permits the process of asymmetric growth to evolve uniformly. At the same time, the asymmetric growth generates the intrinsic curvature necessary for the stability. Thus, the asymmetric growth provided by the asymmetric geometric features of the metallic catalyst is a self-sustained process, from the mechanical point of view. From the thermodynamic point of view, the asymmetric growth depends on the asymmetry of the work of adhesion, i.e., the work required to shear the metallic catalyst from the nanowire [9], and the energy needed to break the droplet-nanowire bond is thermodynamically proportional to the work of adhesion.

It is interesting to mention the recent report on spontaneous polarization-induced growing of nanosprings and nanorings of piezoelectric zinc oxide (ZnO) by Kong and Wang [33] produced without using catalyst particles. They found that the mechanism for the helical growth is the consequence of minimizing the total energy contributed by spontaneous polarization and elasticity. The electrostatic forces play a rule of the external forces holding the rod in the helical shape. In contrast with structures grown with the presence of catalyst particles, their structures do not present intrinsic helical curvatures. They are also not very uniform. This is an indirect evidence that the catalyst particles can drive the asymmetric growth, providing the necessary dynamical stability for the uniform growing. This example highlights the importance of the relationship between the metallic catalyst and the dynamical stability of the nanosprings.

In summary, we have demonstrated that the Kirchhoff rod model is an efficient tool to study both statics and dynamics of a great range of different types of filaments, especially to nanosprings. We derived expressions for Hooke's constant and an applied torque for the nanospring, and we proposed two schemes for the measurement of the two elastic constants of the material from which the nanospring is made: the Young's modulus and the Poisson's ratio. The Kirchhoff model can also be applied to the study of nanowires since these structures are also amorphous. This physical characterization of the nanosprings is an important step for the development of applications in nanoengineering. Another important result from our model is that intrinsic curvature increases the dynamical stability of the nanostructures and can explain why the presence of catalytic particles (that induce intrinsic curvature) is so important to grow nanostructures. We hope the present study can stimulate further experimental investigations on the relationship between the catalytic particles and the nanostructure stability.

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