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Bending of multilayer nanomembranes

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ABSTRACT

Governing equations are developed for bending of an elastic circular membrane under in-plane tension (prestress) and out-of-plane uniform pressure or concentrated force. These relations are applied to fitting observations on nanomembranes made of CVD-grown and mechanically exfoliated graphene, graphene oxides with various concentrations of defects, molybdenum disulfide, bismuth selenite, and tungsten diselenide. Good agreement is demonstrated between the experimental data and results of simulation. It is shown that the elastic modulus per layer of a multilayer membrane is independent of the number of layers *n*, whereas the prestress grows exponentially with *n*. Simple equations are suggested to describe the effect of defects in the crystalline structure of a nanomembrane on its mechanical properties. These equations and validated by comparison of the model predictions with observations of graphene oxide.

1. Introduction

A novel family of 2D crystalline materials, including graphene [1], boron nitride [2], transitional metal oxides and dihalcogenides [3,4], silicene and germanane [5] have attracted substantial attention in the past decade due to their fascinating physical properties, as well as a wide range of potential applications as functional materials for fuel cells, solar cells, batteries, supercapacitors, flexible displays, field-effect transistors, photovoltaic, photodetection, and photocatalysis devices, nanoelectronic and nanoelectromechanical systems, and membranes with nanometer-sized pores for filtration, ion retention, and gas separation [6,7]. A characteristic feature of the 2D materials is that their electronic structure, as well as magnetic, electrical, and light-emission properties are strongly affected by deformation [8,9], which opens a way for precise, fast, and reversible modulation of these properties by external forces (strain engineering [10]).

To study mechanical properties of a 2D material, a membrane formed by an atomic monolayer or a few layers bridged by adhesion forces is suspended over a cylindrical cavity in a substrate. Radius a of the cavity exceeds thickness h of the membrane by several orders of magnitude. Bending of the membrane occurs under the action of a uniform pressure q or a concentrated force P applied at its center. Under the assumptions that (i) the response of the 2D material is isotropic and linear elastic with in-plane Young's modulus E and Poisson's ratio ν, and (ii) the maximum deflection W exceeds strongly thickness h, deformation of a membrane is described by the Foppl–von Karman model in the membrane regime. According to this concept, the external load (q or P) is connected with the maximum deflection W by the semi-empirical equations [11,12]

$$q = 4\frac{\sigma^0}{a}\left(\frac{W}{a}\right) + \frac{8E_{2D}}{3(1-\nu)a}\left(\frac{W}{a}\right)^3, \tag{1}$$

$$P = \pi\sigma^0 a\left(\frac{W}{a}\right) + E_{2D}a\left(\varphi\frac{W}{a}\right)^3, \tag{2}$$

where σ^0 stands for the prestress (in-plane tension with dimension N/m) induced by interaction between the membrane and the substrate, $E_{2D} = Eh$ denotes the 2D elastic modulus (with dimension N/m), and $\varphi = (1.049-0.146\nu-0.158\nu^2)^{-1}$.

The applicability of the Foppl–von Karman model requires the following conditions [13]: (i) the energy of out-of-plane bending is small compared with the energy of in-plane stretching, and (ii) the prestress is small compared with the external load. For a circular membrane under uniform pressure these restrictions read $Eh^3 \ll qa^4$ and $\sigma^0 \ll (Eq^2a^2)^{\frac{1}{3}}$. Although these inequalities are fulfilled in experiments, treatment of observations reveals large deviations between the measured elastic moduli and their theoretical predictions [14,15]. A number of simplifications used in derivation of Eqs. (1), (2) may be a reason for these discrepancies. To check this hypothesis, governing equations for bending of a circular membrane are developed without additional assumptions, and adjustable parameters in these relations are found by matching observations. We intend to demonstrate that our estimates of the Young's modulus (i) differ substantially from those grounded on Eqs. (1), (2) and (ii) are close to predictions based on the first principles calculations.

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The other objective of this study is to examine how elastic modulus E and prestress σ^0 evolve with number of layers n in a multilayer membrane. Eqs. (1) and (2) do not provide an indisputable answer to this question, see [16] and the references therein. It has been revealed that E is independent of n [17], grows with n [18], decreases with n [19], or does not show a clear dependence on thickness of a multilayer structure [20]. The same ambiguity is demonstrated for the prestress σ^0, for which different trends have been reported. This uncertainty may be explained by two reasons: (i) an unavoidable inaccuracy of measurements in bending tests on nanostructures, and (ii) the presence of (at least, hypothetical) mechanisms for the growth (driven by reduction of wrinkles in individual nanosheets due to van der Waals interactions between layers) and decay (induced by interlayer sliding and formation of defects in nanosheets under layer-by-layer assembly) in E with number of layers. Our aim is to show that E remains independent of n, while σ^0 grows exponentially with number of layers (this tendency is revealed for nanomembranes whose thickness h is small compared with maximum deflection W, and it cannot be extrapolated to bulk materials).

Our third objective is to assess the influence of defects in the crystalline structure of a nanomembrane on its mechanical properties. These defects are developed due to chemical treatment of graphene-like materials at the stage of exfoliation of bulk materials (preparation of graphene oxide and reduced graphene oxide from graphite), as well as under etching of sacrificial supports employed in (i) preparation of CVD (chemical vapor deposition)-grown membranes and (ii) transfer of nanosheets to a substrate for testing.

The exposition is organized as follows. Governing equations for bending of a thin circular membrane are formulated in Section 2. Deformation of prestressed membranes under the action of a uniform pressure and a concentrated force is described in Sections 3 and 4, respectively. Analysis of observations on bending of multilayer membranes is conducted in Section 5. The effect of defects on the mechanical properties of graphene oxide membranes is discussed in Section 6. Concluding remarks are formulated in Section 7.

2. Bending of a circular membrane

We consider a circular membrane with radius a and constant thickness h. An arbitrary point of the membrane is described by Cartesian coordinates x_k with unit vectors $\boldsymbol{i}_k$ $(k = 1,2,3)$ and cylindrical coordinates $r,\theta,z = x_3$ with unit vectors $\boldsymbol{i}_r, \boldsymbol{i}_\theta, \boldsymbol{i}_3$. The 2D strain tensor in the membrane is denoted by $\epsilon = \epsilon_{jk}\, \boldsymbol{i}_j \boldsymbol{i}_k$, and the 2D stress tensor reads $\boldsymbol{\sigma} = \sigma_{jk} \boldsymbol{i}_j \boldsymbol{i}_k$, where summation over repeated indexes $j,k = 1,2$ is presumed. We suppose that the initial state of the membrane does not coincide with its reference (stress-free) state and denote by $\epsilon^0 = \epsilon^0_{jk}\, \boldsymbol{i}_j \boldsymbol{i}_k$ the tensor of residual strains. The 2D elastic strain tensor reads

$$\epsilon_e = \epsilon - \epsilon^0, \tag{3}$$

and its first and second invariants are given by

$$J_{e1} = \epsilon_e : \boldsymbol{I}, \quad J_{e2} = \epsilon_e : \epsilon_e,$$

where $\boldsymbol{I}$ stands for the 2D unit tensor, and the colon denotes convolution. The specific mechanical energy of the membrane per unit area in the plane (x_1,x_2) reads

$$U = \frac{Eh}{2(1+\nu)}\left(J_{e2} + \frac{\nu}{1-\nu} J_{e1}^2\right), \tag{4}$$

where E denotes the Young's modulus (with the dimension N/m^2), and ν stands for Poisson's ratio (these parameters are treated as constants). The 2D stress tensor $\boldsymbol{\sigma}$ is expressed in terms of the 2D strain tensor ϵ by the formula

$$\boldsymbol{\sigma} = \frac{\partial U}{\partial \epsilon}. \tag{5}$$

Combination of Eqs. (4) and (5) implies that

$$\epsilon_{11} = \epsilon^0_{11} + \frac{1}{Eh}(\sigma_{11} - \nu\sigma_{22}), \quad \epsilon_{22} = \epsilon^0_{22} + \frac{1}{Eh}(\sigma_{22} - \nu\sigma_{11}), \quad \epsilon_{12} = \epsilon^0_{12} + \frac{1+\nu}{Eh}\sigma_{12}. \tag{6}$$

Deformation of the membrane is described by the displacement vector $\boldsymbol{u} = u_k \boldsymbol{i}_k$ with $u_k = u_k(x_1,x_2)$. Presuming ϵ to coincide with the Lagrange strain tensor, we calculate its components by means of the conventional relations

$$\epsilon_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i} + u_{k,i} u_{k,j}), \tag{7}$$

where $u_{i,j} = \partial u_i / \partial x_j$. In what follows, we focus on deformations with small gradients of in-plane displacements,

$$|u_{1,1}| \ll 1, \quad |u_{1,2}| \ll 1, \quad |u_{2,1}| \ll 1, \quad |u_{2,2}| \ll 1,$$

and moderate rotations around the axes $\boldsymbol{i}_1$ and $\boldsymbol{i}_2$,

$$|u_{3,1}|^2 \ll 1, \quad |u_{3,2}|^2 \ll 1.$$

Under these conditions, Eqs. (7) read

$$\epsilon_{11} = u_{1,1} + \frac{1}{2} w_{,1}^2, \quad \epsilon_{22} = u_{2,2} + \frac{1}{2} w_{,2}^2, \quad \epsilon_{12} = \frac{1}{2}(u_{1,2} + u_{2,1}) + \frac{1}{2} w_{,1} w_{,2}, \tag{8}$$

where $w = u_3$ denotes deflection of the membrane, and $\bar{\boldsymbol{u}} = u_1 \boldsymbol{i}_1 + u_2 \boldsymbol{i}_2$ stands for the in-plane displacement vector.

To develop equilibrium equations for bending of the membrane under the action of pressure $q = q(x_1,x_2)$ directed along the vector $\boldsymbol{i}_3$, we introduce the functional

$$\Psi = \int_\Omega U\,\mathrm{d}a - \int_\Omega q w\,\mathrm{d}a, \tag{9}$$

where $\mathrm{d}a = \mathrm{d}x_1 \mathrm{d}x_2$ is the elementary area of the domain Ω occupied by the membrane in the (x_1,x_2) plane, the first term stands for the mechanical energy stored in the membrane, and the other term equals the work on external forces. For definiteness, we consider deformation of a membrane with a clamped edge,

$$w|_{\partial\Omega} = 0, \quad \bar{\boldsymbol{u}}|_{\partial\Omega} = \boldsymbol{0}, \tag{10}$$

where $\partial\Omega$ stands for the boundary of Ω. Calculating variation of Ψ and equating it to zero, we arrive at the equilibrium equations

$$\nabla \cdot \boldsymbol{\sigma} = \boldsymbol{0}, \quad \boldsymbol{\sigma} : \nabla\nabla w + q = 0, \tag{11}$$

where ∇ is the 2D gradient operator, the dot stands for inner product, and the colon denotes convolution.

We now focus on axisymmetric deformation of a circular membrane under the action of pressure q (that depends on radius r only) and equi-biaxial prestress,

$$\epsilon^0_{11} = \epsilon^0_{22} = -\epsilon^0, \quad \epsilon^0_{12} = 0. \tag{12}$$

Here ϵ^0 is a constant, and the sign "−" means that the membrane is under pretension before loading. Under these conditions, the displacement vector is determined by $\boldsymbol{u} = u_r(r)\boldsymbol{i}_r + w(r)\boldsymbol{i}_3$, where u_r denotes radial displacement, and the in-plane stress tensor is given by $\boldsymbol{\sigma} = \sigma_{rr}(r)\boldsymbol{i}_r \boldsymbol{i}_r + \sigma_{\theta\theta}(r)\boldsymbol{i}_\theta \boldsymbol{i}_\theta$, where $\sigma_{rr}, \sigma_{\theta\theta}$ stand for the radial and tangential stresses. A set of two differential equations for the unknown functions σ_{rr} and w is derived in Appendix A. The first equation reads

$$\sigma_{rr} \frac{\mathrm{d}w}{\mathrm{d}r} = -Q, \quad Q(r) = \frac{1}{r}\int_0^r q(s) s\,\mathrm{d}s. \tag{13}$$

The other equation can be presented in two equivalent forms

$$\frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^3 \frac{\mathrm{d}\sigma_{rr}}{\mathrm{d}r}\right) + \frac{Eh}{2}\left(\frac{\mathrm{d}w}{\mathrm{d}r}\right)^2 = 0, \tag{14}$$

$$r\frac{\mathrm{d}}{\mathrm{d}r}\left[\frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r}(r^2\sigma_{rr})\right] + \frac{Eh}{2}\left(\frac{\mathrm{d}w}{\mathrm{d}r}\right)^2 = 0. \tag{15}$$

The boundary conditions for Eqs. (13) and (14), (15) are given by