Edge-stress induced warping of graphene sheets and nanoribbons

Ashwin Ramasubramaniam, University of Massachusetts - Amherst
Y. W Zhang
C. D Reddy
V. B Shenoy

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Edge-Stress-Induced Warping of Graphene Sheets and Nanoribbons

V. B. Shenoy, C. D. Reddy, A. Ramasubramaniam, and Y. W. Zhang

1 Division of Engineering, Brown University, Providence, Rhode Island 02912, USA
2 Institute of High Performance Computing, Singapore 138632
3 Program in Applied and Computational Mathematics, Princeton University, Princeton, New Jersey 08544, USA
4 Department of Materials Science and Engineering, National University of Singapore, Singapore 119260

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We show that edge stresses introduce intrinsic ripples in freestanding graphene sheets even in the absence of any thermal effects. Compressive edge stresses along zigzag and armchair edges of the sheet cause out-of-plane warping to attain several degenerate mode shapes. Based on elastic plate theory, we identify scaling laws for the amplitude and penetration depth of edge ripples as a function of wavelength. We also demonstrate that edge stresses can lead to twisting and scrolling of nanoribbons as seen in experiments. Our results underscore the importance of accounting for edge stresses in thermal theories and electronic structure calculations for freestanding graphene sheets.

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Graphene, an atomic layer of carbon atoms arranged in a honeycomb lattice, is actively being pursued as a material for next-generation electronics because of the high mobility of charge carriers and the potential to control their density by applying a gate voltage [1–3]. In addition, the ability to alter the electronic properties of finite size graphene sheets by varying their size, shape, and the orientation of their edges can enable circuit design and miniaturization using standard patterning and lithography techniques. The edges in such nanometer sized graphene based device structures strongly influence their electronic properties. Among the two primary edge structures, armchair and zigzag, the latter is known to possess localized edge states with energies close to the Fermi level [3]. These states lead to intriguing phenomena such as zero-conductance Fano resonances, vacancy configuration dependent transport, valley filtering, half-metallic conduction, and spin Hall effect [2,3].

Depending on the type of edge termination, the bonding configuration of atoms located at the edges of graphene sheets can be considerably different from an atom in the periodic honeycomb lattice. If the atomic bonds at the edge are shorter (longer) than the typical bonds in graphene, then the edge will be under a state of compressive (tensile) stress. Indeed, recent experiments have reported scrolled and staggered edges in freestanding graphene [4]. In this Letter, we show that intrinsic “edge” stresses can have a significant influence on the morphology of graphene sheets. We find that edge stresses can lead to warping and rippling of graphene sheets, which allows for the reduction of the edge energy at the cost of deforming the “bulk” sheet. Our atomistic simulations and analytical calculations show that morphology of the warped sheets depends strongly on both their sizes and shapes and the magnitude of the edge stresses. Since the electronic structure of graphene is strongly altered by both strain and curvature [3], these results should have important implications for graphene based devices.

The mechanical deformation of a freestanding graphene sheet can be understood by considering the effect of edge stresses. The edge can be modeled as an elastic string that is either stretched or compressed and glued to the sheet. The tensile forces exerted on the sheet by a compressed elastic string, for example, are shown schematically in Fig. 1(b). When the unbalanced forces on the sheet are compressive, the sheet can lower its energy by buckling out of plane. However, when the forces are tensile [Fig. 1(b)], intuition would suggest that this will only lead to in-plane stretching of the sheet.

In this Letter, we show that counter to what is expected from intuitive reasoning, the total energy of sheets with compressive edge stresses can be lowered by stretching of the atomic bonds brought about by out-of-plane movement.
of the atoms. We call this mode of deformation warping, to distinguish it from the buckling that primarily involves bending of the sheet without stretching. In what follows, we show that depending on the size and shape of the sheets, warping may only be localized to the boundaries or can influence the overall morphology of the sheets. We study warping in sheets with zigzag and armchair edges using an interatomic bond-order potential and show that the warped shapes observed in these simulations can be reproduced using finite element simulations that account for edge stresses.

The edge stress of a 2D sheet can be defined in a manner similar to the well-known concept of surface stress of a 3D crystal [5]. Following this analogy, we write the energy per unit (reference) length of an infinitely long planar 2D sheet of width \( w \) as

\[
\mathcal{E}(\epsilon, w) = \frac{1}{2} E_b \epsilon^2 w + 2\tau \epsilon + 2\frac{1}{2} E_e \epsilon^2 + C, \tag{1}
\]

where we have retained terms up to quadratic order in axial strain \( \epsilon \); \( \tau \) denotes the edge stress, \( E_b \) and \( E_e \) are the elastic moduli of the sheet and the edges, respectively, and \( C \) is a constant that does not depend on strain. Note that the factors of 2 in the second and third terms in Eq. (1) account for the contributions from the two edges of the sheet. In this work, we use the reactive bond order (AIREBO) potential as implemented in the software package LAMMPS [6, 7] to obtain the edge stresses and moduli for different edge terminations. This potential allows for covalent bond breaking and creation with associated changes in atomic hybridization within a classical potential, thus enabling simulations of micron-size sheets.

The edge stresses and moduli for the armchair and zigzag terminations were determined by computing the energies for strained graphene ribbons as a function of their width and fitting them to Eq. (1). We find that the edge stresses of armchair and zigzag terminations are compressive and of magnitude 10.5 and 20.5 eV/nm, respectively, while the edge moduli for these terminations are 112.6 and 147.2 eV/nm, respectively. We also note that elastic moduli for sheets oriented along armchair and zigzag were found to be nearly equal to \( E_b = 2000 \) eV/nm\(^2\). This result is in excellent agreement with the value 2120 eV/nm\(^2\), obtained from recent experiments [8].

In order to study the stability of flat freestanding sheets to warping or buckling, we first perturb them by allowing random out-of-plane displacement to the atoms. The amplitudes of the applied perturbations range from 0.1–0.5 Å. The atoms in the perturbed sheet are then allowed to relax using a conjugate gradient algorithm [6] until the relative change in energy is less than \( 10^{-10} \) eV. We studied the stability of nearly square sheets (Fig. 2) and nanoribbons (Figs. 4 and 5) terminated by zigzag and armchair edges. Upon relaxing the square sheets from their perturbed configurations, we find that they develop ripples of different wavelengths primarily confined to the edges. The amplitudes of the ripples and the distances through which they propagate into the sheets are found to decrease with their wavelength (Fig. 2). Why do ripples form on the edge and how are their amplitudes and wavelengths related to the elastic properties of the sheet? We answer these questions next, using both finite element simulations and an analytical model.

In our finite element model [Figs. 2(c) and 2(d)], graphene is modeled as an elastic plate, whose Young’s modulus \( E_p \) and thickness \( t \) are computed by equating the effective 2D modulus, \( E_p t = E_b = 2000 \) eV/nm\(^2\) and flexural rigidity to the bending modulus of graphene, \( E_p t^3/12(1-\nu^2) = B = 1.5 \) eV [9]. Residual stresses corresponding to the edge stresses for armchair and zigzag orientations are assigned to the finite elements at the appropriate edges of the sheet. The elastic properties of these elements are also calibrated to the edge moduli of the two terminations. As in the atomistic simulations, we apply an initial perturbation to a nominally flat sheet and allow it to relax. All simulations are carried out in a finite deor-
strain components arising from this perturbation are scale over which the ripples penetrate into the sheet. The form \( \zeta(x_1, x_2) = A \sin(kx_1) e^{-x_2/l} \) to the sheet, as shown in Fig. 3, where \( k \) is the wave number and \( l \) gives the length scale over which the ripples penetrate into the sheet. The strain components arising from this perturbation are \( \epsilon_{ij} = \frac{1}{2} \frac{\partial^2 \zeta}{\partial x_i \partial x_j} \), from which strain energy density associated with stretching the sheet can be written as

\[
U_s = \frac{M}{8} \left[ \left( \frac{\partial \zeta}{\partial x_1} \right)^2 + \left( \frac{\partial \zeta}{\partial x_2} \right)^2 \right]^2, \tag{2}
\]

where \( M = E_b/(1 - \nu^2) \). The edge energy per unit length is

\[
U_e = \frac{1}{2} \tau_e \left( \frac{\partial \zeta(x_1, 0)}{\partial x_1} \right)^2 + E_e \left( \frac{\partial \zeta(x_1, 0)}{\partial x_1} \right)^4. \tag{3}
\]

The total energy per period \( \lambda = 2\pi/k \) [12] is then

\[
U = \int_{x_1=0}^{2\pi/k} U_s \, dx_1 + \int_{x_1=0}^{2\pi/k} \int_{x_2=0}^{\infty} U_e \, dx_1 \, dx_2 = \frac{\pi \tau_e A^2 k^2}{2} + \frac{3\pi E_e A^4 k^3}{32} + \frac{\pi M A^4}{8} + \frac{3k^4 l^4 + 2k^2 l^2 + 3}{16kl^3}. \tag{4}
\]

When edge stresses are compressive \( (\tau_e < 0) \), the first term will always lead to lowering of the total energy through stretching of the edges. Thus, the flat sheet becomes unstable to formation of waves on its edges. The penetration depth of the waves can be determined by setting \( \partial U/\partial l = 0 \), which yields the relation

\[
l = \sqrt{\frac{1 + 2\sqrt{7}}{12\pi}} \lambda = 0.23 \lambda. \tag{5}
\]

Using this result in the Eq. (5), the optimum amplitude of the ripple is found to be

\[
A = \sqrt{-\frac{\lambda \tau_e}{(\pi \sqrt{20 + \sqrt{7}}/18)M + (3\pi^2/2\lambda)E_e}}. \tag{6}
\]

For typical parameters, \( M = 2000 \) eV/nm\(^2\) and \( E_e = 100 \) eV/nm and \( \lambda \sim 10 \) nm, the second term in the denominator of Eq. (6) is about 2 orders of magnitude smaller than the first term. Therefore, the penetration depth and amplitude of the ripples scale linearly and with the square root of the wavelength, respectively. For the square sheets in Figs. 2(a) and 2(b), the amplitudes of waves along the zigzag edges (2.8 and 2.2 Å, respectively) are close to the amplitudes obtained from Eq. (6) (2.6 and 2.1 Å, respectively). Similarly, the penetration depths are found to be close to 25% of the wavelength and obey the linear scaling

![FIG. 3 (color online). Out-of-plane perturbation \( \zeta = A \sin(kx_1)e^{-x_2/l} \) applied to a semi-infinite planar sheet.](image)

![FIG. 4 (color online). (a)–(f) Relaxed shapes of 7.62 nm × 2.37 nm nanoribbons. The longer and shorter sides are terminated by zigzag and armchair edges, respectively. (g)–(m) Finite element simulations of edge-stress-driven warping in 7.62 nm × 2.37 nm nanoribbons.](image)
predicted by the analytical model. Further, the amplitude of the modulations on the armchair edges are always found to be smaller compared to the zigzag edges since the edge stress in the former case is only half of the edge stress in the latter case.

In sheets in Fig. 2, the penetration depths of the ripples were significantly smaller than the dimensions of the sheet, so that warping is localized near the edges of the sheet. However, if the length or the width of a sheet becomes comparable to the penetration depth, warping can span over the entire sheet leading to dramatic changes in its shape. This is particularly true for nanoribbons considered in Figs. 4 and 5. When the wavelength of the edge waves is comparable to the length of the nanoribbons, we see large arching or twisting. Shorter wavelengths lead to sinusoidal modulations that are in or out of phase on the two sides of the ribbons.

While the final shapes of the warped sheets appear quite different from each other and are in general dependent upon the initial perturbation, they are nearly degenerate in energy. For the sheets in Figs. 2 and 5, all the warped shapes are energetically favored over the planar sheet by 2.5 and 1 eV, respectively. Although we have not computed the energy barriers for transitions between the different shapes, preliminary molecular dynamics calculations at room temperature indicate that the sheets readily develop traveling waves along the edges that enable facile transitions between various modes. It is worth noting that the typical amplitudes and wavelengths of the edge waves for the square sheets are comparable to the approximate values of 4 Å and 5 nm observed in the room temperature experiments of Meyer et al. [1]. In contrast, room temperature Monte Carlo calculations by Fasolino et al. [13] on fully periodic sheets suggest typical amplitudes of 0.7 Å and wavelengths of 8 nm. Our results therefore underscore the importance of accounting for edge stresses within thermal theories for freestanding graphene sheets.

In conclusion, we have shown that compressive edge stresses along the armchair and zigzag terminated edges lead to warping of graphene sheets and nanoribbons. The influence of edge stresses is found to be more dramatic in the latter case, leading to large-scale distortions in the shapes of the ribbons. We have demonstrated that finite element simulations can predict the warped shapes of graphene sheets if the edge elastic properties are included in the analysis. Therefore, if these properties can be accurately determined for any given edge termination or structure (for example, using first principles calculations), the morphology of large sheets can be studied using the finite element method obviating the need for expensive atomistic simulations. Recent experiments [4] have reported scrolled edges (with amplitudes of 0.4 nm, comparable to the amplitudes of ripples predicted in our work) in freestanding graphene sheets. However, the nature of the edge terminations and presence of adsorbed molecules at the edges of the sheet are difficult to determine experimentally. If high-resolution images of the atomic structures of the edges can be available, rippling and scrolling can be quantitatively studied using the methods developed here. Finally, because of the close connection between strain, curvature, and electronic structure [3], our work suggests means to control morphology and hence the electrical and magnetic properties of graphene sheets and nanoribbons by engineering the edge stresses, for example, by doping or functionalizing the edges.

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*Vivek_Shenoy@brown.edu

[9] The bending modulus computed with the AIREBO potential was found to be nearly equal for sheets bent along the armchair and zigzag edges. We take $v = 0.25$.
[11] We have not considered the contribution to strain from sinusoidal in-plane displacements as they do not contribute to overall stretching of the edge and therefore do not alter the total edge energy, in agreement with finite element simulations.
[12] For the perturbation in Fig. 3, stretching and bending energies scale as $E_s \sim MA^4 k^2$ and $E_b \sim BA^3 k^2$, respectively, which gives $E_s/E_b \sim MA^2/B$. For $M = 2000$ eV/nm$^2$, $A = 0.5$ nm, and $B = 1.5$ eV, $E_s/E_b \sim 300$. Bending energy can therefore be neglected.