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Mechanical properties of graphene nanoribbons with disordered edges

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ABSTRACT

Using density functional theory (DFT), we investigate mechanical properties and failure characteristics of chiral and achiral graphene nanoribbons. Specifically, we study the dependence of maximum strength, Young's modulus and failure pattern of nanoribbons on their widths, edge chirality and passivation. Besides investigating nanoribbons with perfect edges, nanoribbons with defective edges are considered and the impacts of the presence of Klein or edge pentagonal defects on the properties of nanoribbons are studied. Our DFT results show that as the width of achiral ribbons are reduced, their strength increases. Moreover, significant size effects on the Poisson's ratio of armchair ribbons and Young's modulus of zigzag ribbons are observed. The DFT modeling predicts that the presence of defects reduce the strength of chiral nanoribbons while defects might counter intuitively increase the Young's modulus of chiral nanoribbons. The first-principle simulations show that achiral nanoribbons always fail along a zigzag surface, however the failure pattern of chiral nanoribbons can be more complicated and be accompanied by the nucleation of other kind of defects such as pentagonal–heptagonal rings prior to failure.

1. Introduction

Graphene high mechanical strength [1], sophisticated electronic properties [2] and excellent thermal conductivity [3] have inspired intensive investigations of its applications in nanoelectronic and nanocomposite devices such as graphene transistors [4], sensitive sensors [5] and ultracapacitors [6]. In addition to bulk graphene sheets, quasi-one-dimensional graphene nanoribbons (GNRs), generated by using lithographic patterning of bulk graphene [7,8], chemical synthesis [9,10] and unzipping of carbon nanotubes [11], display even more outstanding electronics and physical properties. In GNRs, the confinement of the electronic wave functions and the effects of the edges open a band gap which can be tuned by changing the nanoribbons widths and crystallographic orientations [7]. The creation of gap, which does not exist in bulk graphene sheets, is an important feature which can be exploited in the usage of GNRs in field effect transistors and other integrated nanoelectronic devices.

Reliable usage of graphene nanoribbons in nanodevices necessitates a fundamental understanding of their mechanical properties. This is due to the fact that mechanical failure or undesirable deformation of graphene nanoribbons can lead to the whole device failure. Furthermore, very often mechanical properties of graphene nanoribbons determine essential properties of nanodevices. Specific examples are resonators and nanoswitches which will include a graphene cantilever beam as their main building block [12,13]. In these devices, the essential properties of the nanodevice, such as the sensitivity of resonators or the pull-in voltage of nanoswitches, directly depend on the stiffness of the graphene cantilever beam [14]. Since the stiffness is a function of Young's modulus, the design of such devices needs the knowledge of the mechanical properties of graphene nanoribbons. Hence, understanding the mechanical properties of GNRs expedites the design and fabrication of graphene based nanodevices by reducing the number of the required experiments.

When nanoribbons are cut from a bulk graphene sheet, their edges generally consist of a combination of zigzag and armchair configurations. However, if a ribbon terminates exclusively by armchair or zigzag edges on both sides, the ribbon is respectively classified as armchair or zigzag nanoribbon. So far, most of the studies on the properties of GNRs have been focused on nanoribbons with pure zigzag and armchair edges [15–18], and mechanical properties of nanoribbons with mixed armchair and zigzag edges have not yet been thoroughly studied. Sub-10-nm GNRs posses chirality independent semiconducting properties [19,20] which allows their usage in nanoelectronic devices without concerning about controlling their chirality during synthesize process. Thus, besides zigzag and armchair nanoribbons, it is important to understand the mechanical behavior of nanoribbons with arbitrary

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edges. On the other hand, even for the zigzag and armchair ribbons, the mechanical properties reported by different studies are not consistent. Some researchers report increasing Young's modulus and mechanical strength by reducing GNRs characteristic size [17,18], while others report an opposite trend [15,16]. The source of discrepancies between different studies can be attributed to the different nature of the methods and the level of approximations in the simulations. Therefore; in this paper, we use first principle calculations based on density functional theory to minimize the empiricism effects on the numerical results.

Defects can also be present in graphene edges. Experimental characterizations [21–25] have provided direct evidence of edge defects with different topologies; among them are vacancy defects [26,27] which are generated if a carbon atom is missing from the edge and Klein defects [21,22,28] consisting of an extra carbon atom linked to a single atom of the edge. The presence of such edge defects can drastically influence important characteristics such as transport properties [29] or conduction gap [30] of nanoribbons. Edge defects can also impact the mechanical properties of nanoribbons. In this perspective, besides considering nanoribbons with perfect edges, we employ DFT simulations to study nanoribbons with disordered edges.

In this paper, after introducing our computational methodology in Section 2, the properties of armchair and zigzag nanoribbons are studied in Section 3. The main focus is to understand how widths of nanoribbons affect important mechanical properties of armchair and zigzag nanoribbons. The chiral nanoribbons with and without defects are investigated in Section 4 where the impact of chiral angle, edge defect and edge passivations on their strength, stiffness, Poisson's ratio and failure pattern are studied.

2. Computational methodology

The simulations of this paper are performed using the density functional theory (DFT) code SIESTA [31,32]. In our simulations we have used the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) [33] with doulbe-ζ polarization (DZP) orbital basis set. The ionic cores are represented using Troullier and Martins pseudopotentials [34] factorized with Kleinman–Bylander nonlocal projector [35]. An energy mesh cutoff of 300 Ryd for real space integrations is considered and the atomic positions are optimized by employing a conjugate gradient algorithm until the forces on atoms are less than 0.01 eV/Å.

To validate the modeling approach and the pseudo-potentials used, we first compute the mechanical properties of bulk graphene using the four-atom unit cell shown in Fig. 1. By relaxing the atomic positions, the equilibrium carbon–carbon bond distance in bulk graphene is computed as 1.43 Å. Using the four-atom unit cell, we obtain the stress–strain relations of bulk graphene. Uniaxial tensile load is applied by incrementing the unit cell length in the loading direction and relaxing the other stress components to zero. The stress–strain curves obtained from uniaxial loading in the zigzag and armchair directions are shown in Fig. 2. Using the stress–strain relationship, graphene Young's modulus is calculated as 1.05 TPa. The calculated stress–strain curves and Young's modulus are in good agreements with those reported in the literature [1,36,37].

3. Zigzag and armchair nanoribbons

The geometrical structure of zigzag graphene nanoribbons (ZGNRs) and armchair graphene nanoribbons (AGNRs) are shown in Fig. 3a and b, respectively. In our computations, nanoribbons axes lie along the $x-$direction, and the $z-$direction is normal to the ribbon plane. We classify the armchair graphene nanoribbons by the number of dimers N in the unit cell which are parallel to the ribbon axis (N-AGNR), whereas zigzag graphene nanoribbons are characterized by the number of zigzag dimers N across the nanoribbon width (N-ZGNR). The classifications of armchair and zigzag graphene nanoribbons are shown schematically in Fig. 3.

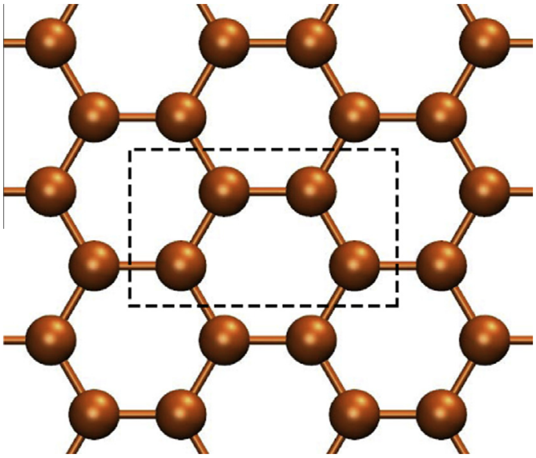

Fig. 1. Four-atom bulk graphene unit cell (dashed rectangle) used for stress–strain calculations of bulk graphene.

The unit cells used in the DFT calculations of armchair and zigzag nanoribbons are shown in Fig. 3. Since nanoribbons are periodic only along their longitudinal axis, the spurious interaction between images in the directions perpendicular to the nanoribbon axis is prevented by setting a vacuum space of at least 15 Å in the $y-$ and z-directions. To ensure that all the carbon atoms are sp^2 bonded, the carbon atoms on the nonperiodic edges are passivated with hydrogen atoms. We ignore spin–orbital interactions in our DFT calculations on armchair ribbons. However, our DFT simulations indicate that spin–orbital interactions might be important for wide zigzag nanoribbons (N > 10) under high strains. Therefore, spin–orbital interactions are considered in all the simulations of zigzag nanoribbons. A Monkhorst–Pack grid of $30 \times 1 \times 1$ k-points are taken for reciprocal integrations of graphene nanoribbons.

3.1. Results and discussions

The unrelaxed lattice constants of armchair and zigzag nanoribbons along the $x-$axis are $a_A^{unrel} = \sqrt{3}a$ and $a_Z^{unrel} = a$ where a is graphene lattice constant (see Fig. 3). Due to the edge effects, the actual (relaxed) lattice constant of nanoribbons which minimizes

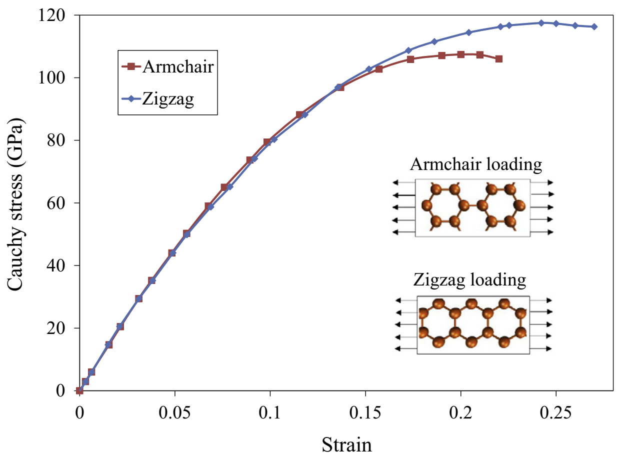

Fig. 2. Stress–strain curves of bulk graphene in the armchair and zigzag directions.