

Surface-adsorption-induced bending behaviors of graphene nanoribbons

Zuoqi Zhang,¹ Bin Liu,^{2,a)} Keh-Chih Hwang,² and Huajian Gao³

¹Department of Engineering Mechanics, Institute of High Performance Computing, Singapore 138632

²Department of Engineering Mechanics, AML, Tsinghua University, Beijing 100084, China and Center for Nano and Micro Mechanics, Tsinghua University, Beijing 100084, China

³School of Engineering, Brown University, Providence, Rhode Island 02912, USA

(Received 3 January 2011; accepted 26 February 2011; published online 22 March 2011)

We investigate bending behaviors of graphene nanoribbons (GNRs) induced by surface adsorption of hydrogen atoms or molecules. At low adsorption coverage, it is shown that the chemical adsorption of hydrogen atoms causes a GNR to bend away from the adsorbed atoms while the physical adsorption of hydrogen molecules causes it to bend toward the adsorbed molecules. Interestingly, these trends are reversed at high adsorption coverage. There exists a range of linear responses for both chemical and physical adsorptions, which points to promising applications of GNRs as sensitive chemical-/biosensors. © 2011 American Institute of Physics.

[doi:10.1063/1.3569589]

Graphene, a single layer of carbon atoms in a honeycomb lattice, has attracted much recent attention for its unique two-dimensional structure and physicochemical properties,¹⁻³ as well as its wide potential applications in electronics,^{4,5} photonics, and optoelectronics,⁶ energy storage and conversion,⁷ and chemical-/biosensing.⁸⁻¹¹ The extraordinary electronic properties of graphene could be attributed to its unusual two-dimensional Dirac-like electronic excitations that can be effectively controlled by applying external electric and magnetic fields, or by altering sample geometry or topology.² These properties offer distinct advantages for controlled design and fabrication of devices but they also cause concerns that disorders due to intrinsic and extrinsic sources can adversely affect the electronic properties of graphene nanoribbons (GNRs), and consequently the quality of GNR-based electronic devices. While intrinsic sources such as edge effects can lead to warping and rippling of free-standing or suspended GNRs,¹²⁻¹⁴ extrinsic sources including adatoms and adsorbed molecules could also exert considerable influences on the geometrical configurations of GNRs due to their small out-of-plane stiffness. The latter has not been thoroughly investigated so far. Sensitive chemical and biological nanoscale sensors are essential for nanoelectromechanical systems (NEMS). Recently, carbon or boron nitride nanotubes have been used to construct biosensors via their mechanical responses to attached mass.¹⁵⁻¹⁸ From a mechanical point of view, GNRs should be one of the ideal candidates for highly sensitive sensors since its two-dimensional crystal structure has very small bending stiffness. The present letter is concerned with the influence of surface adsorption on the bending behaviors of GNR via an atomic-scale finite element method (AFEM).¹⁹ We find that surface adsorption can cause GNRs to deform to various degrees depending on the type (chemical or physical) and coverage of adatoms or molecules. Our results could have important implications on the potential applications of GNRs as sensitive chemical-/biosensors, as well as new-generation electronic elements since the electronic properties of

graphene can be strongly altered by both strain and curvature.²

The simulations were carried out using the AFEM (Ref. 19) and the second-generation Brenner interatomic potential for hydrocarbons.²⁰ AFEM is an order-N atomistic simulation method that takes advantage of the computational algorithms of finite element method, e.g., in employing a stiffness matrix associated with atomic displacements. The total energy of the system is expressed as a sum of the energy in all C-C and C-H covalent bonds as well as the van der Waals nonbond energy. The van der Waals interaction is represented by the 6-12 Lennard-Jones potential, $U(r) = -A/r^6 + B/r^{12}$, with $A = 1.142 \times 10^{-5}$ eV nm⁶ and $B = 1.194 \times 10^{-8}$ eV nm¹² for the interaction between carbon atoms and hydrogen molecules, and $A = 8.333 \times 10^{-6}$ eV nm⁶ and $B = 5.582 \times 10^{-9}$ eV nm¹² for the interaction between hydrogen molecules. Minimization of the total energy then gives the atomic positions at equilibrium.

To understand the deformation of the GNR due to surface adsorption, it is instructive to first consider the interaction between a single hydrogen atom/molecule and a GNR. Figure 1(a) shows the contour of the out-of-plane displacement of a GNR bonded by an overhang hydrogen atom. The atomic displacement of the GNR is seen to be upward everywhere with all carbon atoms moving toward the hydrogen atom. The displacement reaches a maximum of 0.05 nm at the carbon atom in direct bond with the hydrogen atom, which is in good agreement with prior result 0.046 nm.²¹ The adsorbed hydrogen atom attracts its bonded carbon atom while repels the other neighbor atoms, resulting in a pair of force couples that drive the GNR to bend locally downward; see Fig. 1(b). Figure 1(c) shows the contour of the out-of-plane displacement of a GNR interacting with an overhang hydrogen molecule via van der Waals interaction. Contrary to Fig. 1(a), the atomic displacement is seen to be downward everywhere with all carbon atoms moving away from the hydrogen molecule. This is because van der Waals interaction is attractive for atoms far away while becoming repulsive for atoms nearby, resulting in a pair of force couples that causes the GNR to bend locally upward. It is interesting to note that the pair of force couples induced by a physically adsorbed hydrogen molecule is opposite to that by a chemi-

^{a)}Electronic mail: liubin@tsinghua.edu.cn. Tel.: +86-10-62786194. FAX: +86-10-62781824.

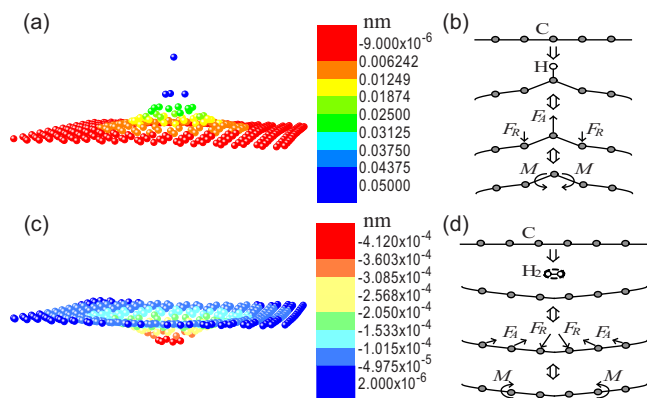


FIG. 1. (Color online) The interaction between a single overhang hydrogen atom/molecule and a GNR: (a) the out-plane displacement contour of the GNR due to a single chemisorbed hydrogen atom; (b) schematic of an equivalent pair of force couples on the graphene due to the chemisorbed hydrogen atom; (c) the out-plane displacement contour of a GNR due to a physically adsorbed hydrogen molecule; (d) schematic of an equivalent pair of force couples on the graphene by the physically adsorbed hydrogen molecule.

cally adsorbed hydrogen atom; see Fig. 1(d). Since van der Waals interaction is usually much weaker than covalent bonds, the out-of-plane displacement in Fig. 1(c) is much smaller than that in Fig. 1(a).

Cantilever or cantilever-like devices are being widely used in microelectromechanical system (MEMS) and NEMS. The present work is concerned with GNR-based cantilevers. To study a chemisorbed GNR, a cantilever of 10.5 nm in width (along the fixed edge) and 1.8 nm in length (free extension) was considered, with a total of 800 carbon atoms. Note that a GNR with a long clamped edge is not a typical cantilever, and the word “cantilever” in the present letter should be understood in a loose sense. The GNR is in the armchair configuration along the left edge where atoms colored in black are fixed [see the initial figure in Fig. 2(a)]. We note in passing that atoms or ionic groups in the environment could be chemically adsorbed to the GNR surface under high speed impact or in the presence of some defects

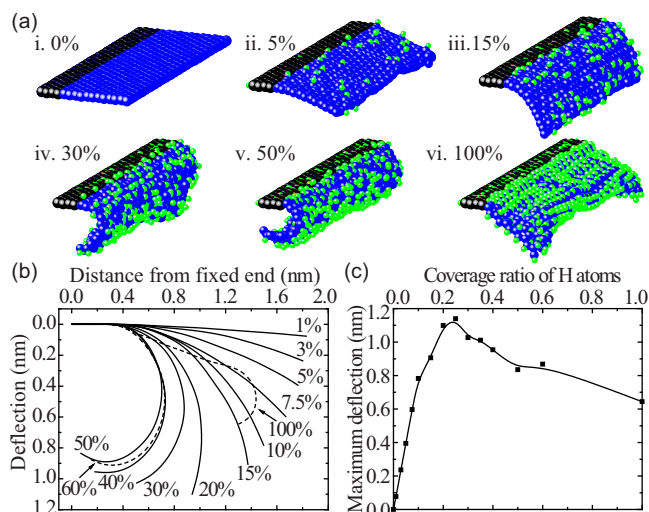


FIG. 2. (Color online) Simulation results of chemisorbed GNR. (a) Equilibrium configurations: dark gray balls represent carbon atoms, black balls the fixed carbon atoms, and light gray balls the hydrogen atoms; (b) deflection curves; and (c) the maximum deflection of GNR under different coverage ratios of chemisorbed H atoms.

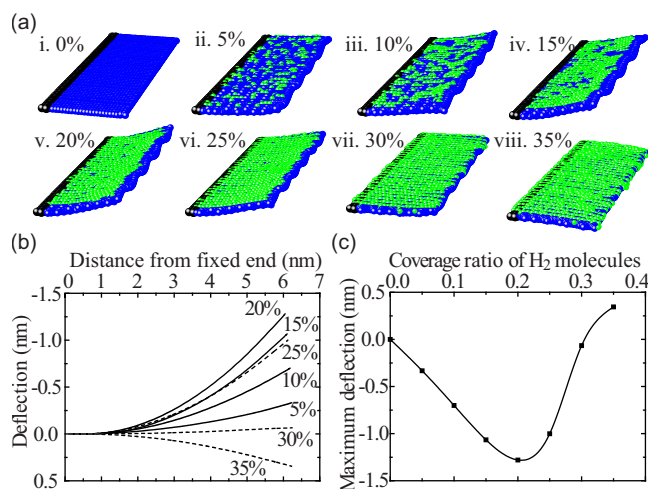


FIG. 3. (Color online) Simulation results of physisorbed GNR. (a) Equilibrium configurations: dark gray balls represent carbon atoms, black balls the fixed carbon atoms, and light gray balls the hydrogen molecules; (b) deflection curves; and (c) the maximum deflection of GNR cantilever under different H₂ coverage ratios.

(e.g., vacancies). In our simulations, different numbers of hydrogen atoms were chemically bonded at random sites on the upper side of the GNR, and the corresponding equilibrium configurations were calculated subsequently. Defining the coverage ratio as the ratio of the number of adsorbed atoms/molecules over that of all carbon atoms in the GNR, Figs. 2(a)ii–vi show deformed configurations of the GNR for H coverage ratios ranging from 5% to 100%. In the absence of adsorbed hydrogen, slight ripples can be seen along the free edges of the GNR, but no substantial warping, bending, or torsion¹⁴ were observed as the edge effects have been heavily constrained by the fixed boundary condition. The average deflection curves are plotted in Fig. 2(b). The deformed configurations in Fig. 2(a) combined with deflection curves in Fig. 2(b) suggest that chemisorbed H atoms can induce significant structural deformation of the GNR, and that the deformation increases with increasing H coverage when the coverage ratio is less than 50%. This trend can be understood as follows. The effect of each H atom can be represented as a pair of force couples, and the effect of multiple pairs of force couples usually results in larger bending deformation. However, as the H coverage ratio exceeds 50%, the equivalent force couples start to overlap and the combined effect begins to decrease. It is worth noting that, in a real adsorption process, H atom flux increases the coverage ratio gradually, and the upper limit of the coverage found in experiments is 50%.^{22,23} The deflections of the free end, i.e., the maximum deflection of the GNR, are shown in Fig. 2(c) for different H coverage ratios. It is found that the maximum deflection is linearly proportional to the coverage of H atoms in a considerable range (<20%), which indeed suggests potential applications of GNRs as chemical-/biosensors based on their adsorption-deformation relationship or the adsorption-deformation-electrochemistry relationship.

Compared to chemical adsorption, various molecules or atomic groups can also be physically adsorbed on the GNR surface via van der Waals interaction. Considering that the van der Waals force is relatively weak, the physisorbed GNR is taken to be larger in size compared to the chemisorption case. As shown in Fig. 3(a)i, the GNR is in the armchair

configuration along the left edge, and the black atoms on the left edge are fixed. The GNR is 9.7 nm in width and 6.3 nm in length with a total of 2296 carbon atoms. H₂ molecules were randomly placed on the upper side of the GNR cantilever with van der Waals interactions between H₂ molecules and between carbon atoms and H₂ molecules. Figures 3(a)ii–viii show the equilibrium configurations of the GNR cantilever at different coverage ratios of H₂ molecules, with obvious upward bending and ripples along the free edges. The deflection curves under different coverage of H₂ molecules are plotted in Fig. 3(b). Figure 3(a) together with Fig. 3(b) suggests that the upward bending first increases with the increasing H₂ coverage until a critical coverage ratio of 20%, and then gradually decreases and almost vanishes at 30% coverage. Above 30% coverage, the GNR cantilever starts to bend in the reverse direction, i.e., bending downward. At small H₂ coverage ratios, there is little van der Waals interaction between H₂ molecules and the total effect of H₂ adsorption can be regarded as simple superposition of many equivalent upward couples; hence, the GNR cantilever bends upward. However, at large H₂ coverage ratios, the simple superposition is no longer valid since the van der Waals interaction between H₂ molecules cannot be neglected. The transition between upward and downward bending occurs at 30% coverage. This can be roughly understood and predicted by a simple model as follows. We first regard the H₂ adsorbed GNR cantilever as a bilayer cantilever, with adsorbed H₂ forming the upper layer contributing to the surface stress of the system. When the coverage ratio is less than the critical value, H₂ molecules are far away from each other with attractive van der Waals force, and the resulting surface stress due to the H₂ layer is tensile, causing the GNR cantilever to bend upward. When the H₂ coverage ratio exceeds the critical value of 30%, the H₂ molecules become highly compacted with compressive surface stress, causing the GNR cantilever to bend downward. If all H₂ molecules are assumed to be arranged as a triangular lattice on the upper surface of the GNR and the equilibrium distance between H₂ and the length of C–C bond is roughly taken to be 0.332 nm and 0.145 nm, respectively, the critical coverage ratio of zero surface stress is estimated to be about 28%, in close agreement with the simulation result of 30%. The maximum deflection, defined as the deflection at the free end of the GNR, is plotted against the H₂ coverage ratio in Fig. 3(c). It can be seen that the maximum deflection of the GNR cantilever responds linearly to the H₂ coverage ratio when the coverage ratio is less than 20%. This feature again indicates that GNR cantilevers may have great potential applications as chemical-/biosensors in MEMS or NEMS.

In summary, the bending behaviors of GNR cantilevers due to chemical and physical surface adsorption have been systematically studied via atomic simulations. The results show that both chemical and physical adsorption could induce substantial bending of GNR cantilevers. Chemical adsorption causes the GNR cantilever to bend away from the adsorbed atoms while physical adsorption causes it to bend toward the adsorbed molecules. This can be understood from the point of view that the pair of equivalent force couples due to C–H covalent bond (chemical adsorption) is completely different from that due to van der Waals interaction (physical adsorption). As the van der Waals interaction between H₂ molecules changes from attraction at small H₂ cov-

erage (<30%) to repulsion at large H₂ coverage (>30%), the deformation of GNR cantilever due to physical adsorption undergoes a transition from upward bending to downward bending. Since the electronic properties of graphene can be strongly altered by both strain and curvature,² these results indicate that surface adsorptions could have significant affect on the performance of GNR-based devices, and further studies should be carried out to isolate GNR-based electronics from unexpected atoms or molecules. The linear response function between the bending deformation of GNR cantilevers and the coverage ratio for both chemical and physical adsorptions point to potential applications of GNRs as sensitive chemical-/biosensors based on their bending behaviors under surface adsorption.

The authors give many thanks to Professor Yonggang Huang for valuable discussions. Z.Z. and H.G. acknowledge financial support under the A*Star VIP program “Size Effects in Small Scale Materials” hosted at IHPC in Singapore. B.L. acknowledges the support from National Natural Science Foundation of China (Grant Nos. 10702034, 10732050, 90816006, and 10820101048) and National Basic Research Program of China (973 Program) Grant Nos. 2007CB936803 and 2010CB832701.

- ¹K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, and A. A. Firsov, *Nature (London)* **438**, 197 (2005).
- ²A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, *Rev. Mod. Phys.* **81**, 109 (2009).
- ³M. Terrones, A. R. Botello-Mendez, J. Campos-Delgado, F. Lopez-Urias, Y. I. Vega-Cantu, F. J. Rodriguez-Macias, A. L. Elias, E. Munoz-Sandoval, A. G. Cano-Marquez, J. C. Charlier, and H. Terrones, *Nanotoday* **5**, 351 (2010).
- ⁴Z. H. Chen, Y. M. Lin, M. J. Rooks, and P. Avouris, *Physica E (Amsterdam)* **40**, 228 (2007).
- ⁵A. K. Geim and K. S. Novoselov, *Nature Mater.* **6**, 183 (2007).
- ⁶F. Bonaccorso, Z. Sun, T. Hasan, and A. C. Ferrari, *Nat. Photonics* **4**, 611 (2010).
- ⁷Y. H. Hu, H. Wang, and B. Hu, *ChemSusChem* **3**, 782 (2010).
- ⁸M. Zhou, Y. M. Zhai, and S. J. Dong, *Anal. Chem.* **81**, 5603 (2009).
- ⁹M. Pumera, A. Ambrosi, A. Bonanni, E. L. K. Chng, and H. L. Poh, *TrAC, Trends Anal. Chem.* **29**, 954 (2010).
- ¹⁰Y. Y. Shao, J. Wang, H. Wu, J. Liu, I. A. Aksay, and Y. H. Lin, *Electroanalysis* **22**, 1027 (2010).
- ¹¹R. Chowdhury, S. Adhikari, P. Rees, S. P. Wilks, and F. Scarpa, *Phys. Rev. B* **83**, 045401 (2011).
- ¹²J. C. Meyer, A. K. Geim, M. I. Katsnelson, K. S. Novoselov, T. J. Booth, and S. Roth, *Nature (London)* **446**, 60 (2007).
- ¹³M. H. Gass, U. Bangert, A. L. Bleloch, P. Wang, R. R. Nair, and A. K. Geim, *Nat. Nanotechnol.* **3**, 676 (2008).
- ¹⁴V. B. Shenoy, C. D. Reddy, A. Ramasubramaniam, and Y. W. Zhang, *Phys. Rev. Lett.* **101**, 245501 (2008).
- ¹⁵R. Chowdhury, S. Adhikari, and J. Mitchell, *Physica E (Amsterdam)* **42**, 104 (2009).
- ¹⁶S. Adhikari and R. Chowdhury, *J. Appl. Phys.* **107**, 124322 (2010).
- ¹⁷H. L. Lee, J. C. Hsu, and W. J. Chang, *Nanoscale Res. Lett.* **5**, 1774 (2010).
- ¹⁸R. Chowdhury and S. Adhikari, “Boron nitride nanotubes as zeptogram-scale bio-nano sensors: Theoretical investigations,” *IEEE Trans. Nanotechnol.* (to be published).
- ¹⁹B. Liu, Y. Huang, H. Jiang, S. Qu, and K. C. Hwang, *Comput. Methods Appl. Mech. Eng.* **193**, 1849 (2004).
- ²⁰D. W. Brenner, O. A. Shenderova, J. A. Harrison, S. J. Stuart, B. Ni, and S. B. Sinnott, *J. Phys.: Condens. Matter* **14**, 783 (2002).
- ²¹M. Volpe and F. Cleri, *Surf. Sci.* **544**, 24 (2003).
- ²²T. Zecho, A. Guttler, X. W. Sha, B. Jackson, and J. Kupperts, *J. Chem. Phys.* **117**, 8486 (2002).
- ²³D. Yu and F. Liu, *Nano Lett.* **7**, 3046 (2007).