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Effect of Curvature on the Mechanical Properties of Graphene: A Density Functional Tight-binding Approach

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ABSTRACT

Due to the high cost of experimental analyses, researchers used atomistic modeling methods for predicting the mechanical behavior of the materials in the fields of nanotechnology. In the present study the Self-Consistent Charge Density Functional Tight-Binding (SCC-DFTB) was used to calculate Young's moduli and average potential energy of the straight and curved graphenes with different curvature widths under axial strain. Also, this method was used to determine the magnitude of the curvature on the aforementioned mechanical properties. From the results it can be concluded that Young's moduli of straight graphene is equal to 1.3 TPa and this mechanical property decreases slowly by decreasing the curvature width of graphenes. Also, the average potential energy and Young's modulus of graphenes decrease with increasing the number of curvature. In next section the Young's moduli of one-atom vacancy and two-atom vacancy defect were calculated and it was found that this mechanical property decreased with increasing the number of atom vacancy in the curved graphene.

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1. Introduction

Graphene is one of the exquisite materials that have stimulated researchers due to its particular properties and applications so as to carry out novel investigations [1]. It is a generally acknowledged fact that three sorts of graphene can be characterized: mono-layer graphene, double-layer graphene and few-layer graphene containing several layers lower than ten [2]. The monolayer graphene as a two-dimensional matter is constituted of carbon which is bonded together with sp²-bonded atoms in the form of hexagonal structure [3, 4]. Beyond that, there are multilayer graphene sheets structured with multiple monolayer ones [2]. Compared with Carbon NanoTubes (CNTs) and fullerenes, scientists have turned their eyes onto graphene sheets as a result of their exceptional mechanical and thermal attributes and outstanding electrical conductivity [5, 6]. The significant elite properties of graphene are: ballistic electron carrier [7], bioadaptability and thermal stability [1], quantum Hall effect [8, 9], extremely great Young's modulus [10], high elasticity

[11], superior fracture strength [12], thermal conductivity [13], and particular surface area [14]. Because of these properties, graphene is favorable for a large number of applications in nanoelectronic [7] such as super-capacitors [15], batteries [16], sensors [17] as well as the fact that the fabrication of electronic device can be eased using some kind of graphene sheets prepared from graphite [18]. Furthermore, slim graphene films can be used as electrodes in the solar cells [19]. Coupled with this, due to scant density and great aspect ratio, graphene is one of the eligible entrants for enlarging graphene-reinforced composite [4], e.g. it can be scattered throughout the inorganic [20] or polymeric matrix [21] and ceramics [20] to make an ideal composite.

Needless to say, trimming and evolving numerical instruments so as to simulate the mechanical traits could lower the expenses of projects [3]. Despite the fact that multitude theoretical computational investigations have been carried out by researchers to identify the mechanical traits of graphene sheets, the results of them are various due to

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different theoretical methods they are based upon [22-25].

Totally, the mechanical traits of graphene are described utilizing two principal simulation procedures which can be divided into the following classifications: analytical continuum mechanics and atomistic modeling methods. Regarding this fact, it should be added that the analytical continuum modeling is formed utilizing the expanded theories in elasticity [26, 27].

However, in the atomistic modeling methods, the nanomaterial is modeled in nanoscale including various details such as the position of atoms, the interactive forces and the boundary conditions. In contrast, the atomistic modeling is challenged and led to some disadvantages in some circumstances, for instance, it is not performed logically in the models involving a large quantity of atoms, complex formulation, and etc. [28]. It is necessary to point out that the atomistic modeling can be categorized into three principal approaches: (a) extremely classical actuarial mechanics methods like Molecular Dynamic (MD), (b) Monte Carlo (MC), that both of them use the second Newton's law for nanoscale construction with several thousands atoms [23], and (c) quantum mechanical methods as an ab-initio investigation methods for nanoscale system, contain several hundreds atoms. Beyond that, some well-suited and mixed methods as ab-initio techniques exist such as Local Density (LD), Tight Binding Molecular Dynamics (TBMD) and Density Functional Theory (DFT) [29].

The DFT is a circa fast and low-priced ab-initio investigation method which can be utilized to calculate meticulous electronic and constructional attributes of the molecular systems. In comparison to other ab-initio approaches, the DFT is a far more capable method for modeling the large systems [30]. In addition, the DFT has more accurate and reliable outputs than those of the MD methods [28].

In order to calculate the mechanical attributes and entire energies of nanostructures, latterly, a density functional theory based tight-binding (DFTB) calculation is used as a practicable method which is parameterized directly utilizing the DFT method [31]. It should be added that the DFTB calculation can be utilized in calculations of large systems, besides; it is worth noting that the DFTB calculation is majorly based upon the first-principles rather than other tight-binding models [32]. Although some studies are focused on predicting the mechanical properties of graphene using the DFTB approach, to the best of our knowledge, there is no study on the mechanical properties of the curved graphenes in the previous literatures.

The present study examines the effect of curvature of graphenes on the Young's modulus by SCC-DFTB calculations. Furthermore, we consider two other effects on the Young's modulus of the curved graphenes: the amount of curvature and the type of defect in the curved graphenes.

2. The Computational Method

In this study, the geometry optimization and elastic properties were calculated by the Self-Consistent Charge Density Functional Tight-Binding (SCC-DFTB) calculations, using the DFTB+ program package. The SCC-DFTB approach uses an arranged set of integrals derived from the DFT calculations, which leads to a substantial reduction in the computational time. The SCC-DFTB calculations have recently been shown to successfully describe the potential energy and mechanical properties of the carbon nanostructures, showing a good agreement with experiments and higher-level theoretical methods [15-17]. In this study, the Slater-Koster (S-K) -type parameter [18] was implemented, and the self-consistent convergence criterion was set to be 10^{-6} a.u. For the geometry optimization, the structure was considered fully optimized when the forces on each atom to be converged were less than 10^{-5} a.u.

3. Results and Discussion

In this section, the Young's moduli of straight and curved graphenes with different curvature widths, W , (as shown in Fig. 1) was determined under axial strain based on the aforementioned SCC-DFTB calculation. The axial strains are obtained by simulating axial tension, which is applied by changing the atom-atom distance in small steps (0.01 \AA) and then relaxing the model via the DFTB method. Four different curvature widths for graphenes are applied to obtain the deformation potential energy at different strains to consider the effect of magnitude of the curvature on the Young's moduli of the graphenes. Figure 2 illustrates the optimized schematics of the four different curved graphenes.

The diagrams of changing the potential energy versus the strain for straight and curved graphenes are shown in Fig. 3. As can be seen, the potential energy exactly behaves as the parabola diagrams. The average potential energy is achieved by dividing the potential energy by the total number of atoms in the graphene at the minimum potential energy.

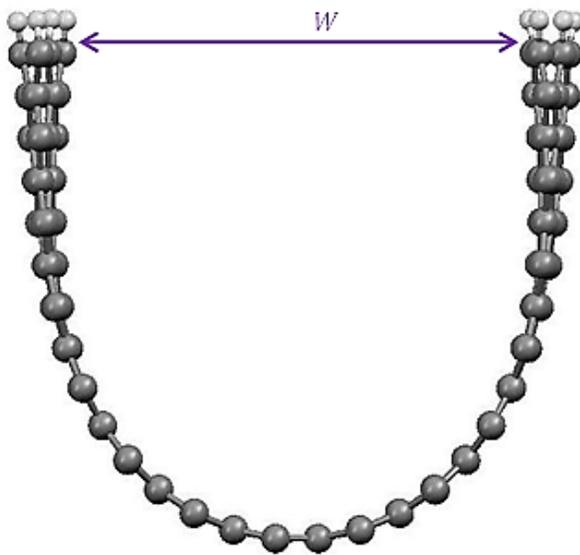


Figure 1: The curved graphene with curvature width W

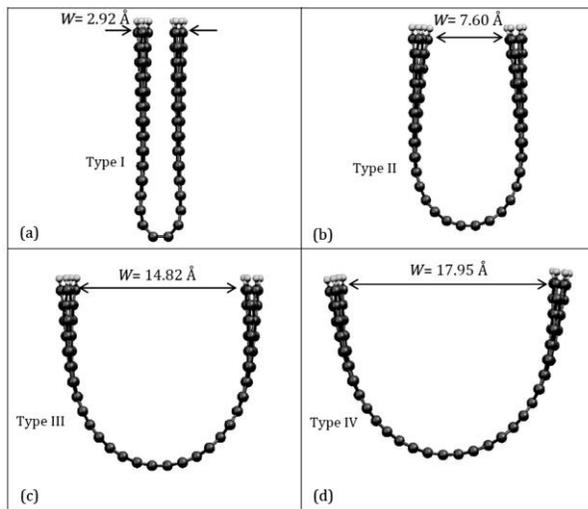


Figure 2: The different curvature width for graphenes

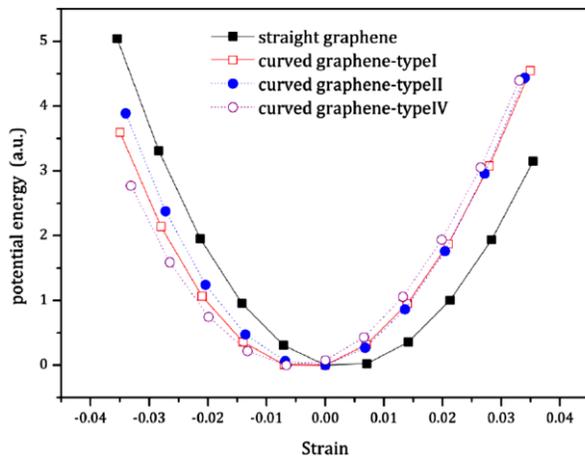


Figure 3: The deformation potential energy versus the strain for straight and curved graphene

From the Table 1, it is obvious that the average potential energy decreases slightly with decreasing the curvature width of graphene. For example, the average potential energy is equal to -44.85 eV for a curved graphene-type IV and -44.77 eV for a curved graphene-type I. Then, we have calculated the Young's modulus, Y , of the graphenes along the axial direction as a function of length to evaluate their hardness. The Young's modulus of the graphenes is calculated by the conventional definition, which involves the second derivative of the deformation potential energy with respect to the strain with the following formula [26]:

$$Y = \frac{1}{V_0} \cdot \frac{\partial^2 E}{\partial \epsilon^2} \quad (1)$$

Where the function E is the deformation potential energy of the system, ϵ is the strain and V_0 is the equilibrium volume. The results obtained from the Young's modulus of graphenes for different curvature widths are listed in Table 1. According to these results, the Young's modulus of straight graphene is equal to 1.31 TPa, which is in a good agreement with the previous studies on graphene with a similar length. For example, Van Lier et al. [14] use ab-initio methods and find that the Young's modulus of graphene is equal to 1.11 TPa. Also, Jing et al. [33] use Molecular Dynamics (MD) to calculate the Young's modulus of graphene. They report that the young's modulus of graphene is equal to 1.03 TPa. Moreover, Ganji et al. [34] in 2015 calculate the Young's modulus of straight graphene by SCC-DFTB and MD calculations and find that this property is equal to 1.42 and 1.41 TPa, respectively.

Table 1. The average potential energy and Young's modulus for graphene for different curvature width

graphene	Average potential energy (eV)	Young's modulus (TPa)
curved graphene-type I	-44.77	1.26
curved graphene-type II	-44.80	1.28
curved graphene-type III	-44.81	1.28
curved graphene-type IV	-44.85	1.29
straight	-45.52	1.31±0.16

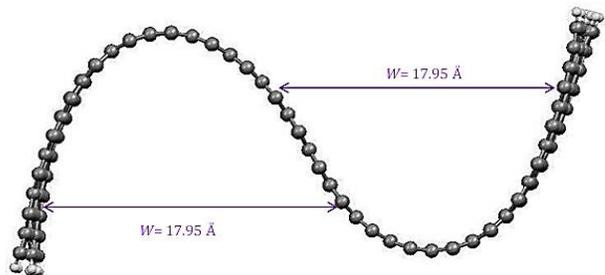


Figure 4: The optimized structure of a two-curved graphene

In addition, we observe that the Young's moduli of curved graphenes are decreased by decreasing the curvature width of graphenes slowly from 1.29 TPa for curved graphene-type I. This decrease in the modulus can be due to a decrease in the average energy of the atoms in the curved graphenes.

Moreover, we have studied the effect of the number of curvature on the average potential energy and Young's modulus of graphenes. The optimized structure of two-curved graphene is illustrated in Fig. 4. It is found that the average potential energy and Young's modulus of two-curved graphene are equal to -44.47 eV and 1.23 TPa, respectively. Thus, according to the previous calculated results, the average potential energy and Young's modulus of graphenes decrease with increasing the number of curvature. In this section, we have considered the effects of the Stone-Wale (S-W), one-atom vacancy (one-vac) and two-atom vacancy (two-vac) defects on the mechanical properties of curved graphenes. The optimized structures of the S-W, one- and two-atom vacancy defect curved graphene systems are depicted in Fig. 5. The value of Young's modulus for the S-W system is 1.26 TPa, which is slightly smaller than that of the curved graphenes-Type IV (1.29 TPa). It is also found that with increasing the number of atom vacancy in the curved graphenes the Young's modulus decreases from 1.25 for one-vac system to 1.21 TPa for two-vac system.

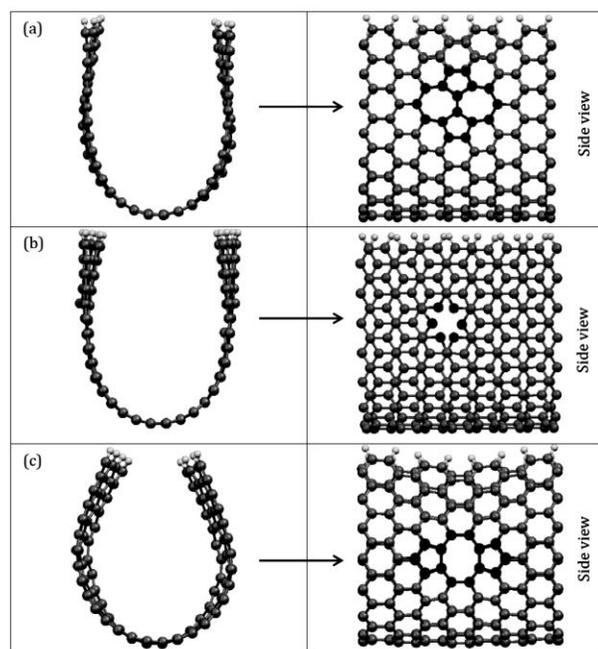


Figure 5: The optimized structure of the S-W, one- and two-atom vacancy defect curved graphene

4. Conclusions

In current study, we used the SCC-DFTB approach to calculate mechanical properties of straight and curved graphenes such as Young's modulus and potential energy with different curvature widths. From the results, it can be calculated that potential energy decreases slightly with decreasing the curvature width of graphene. Also, we found that the Young's modulus of straight graphene was equal to 1.31 TPa and this mechanical property decreased by decreasing the curvature width of graphene and Young's modulus of graphene with minimum of curvature width being equal to 1.26 TPa. Moreover, we studied the number of curvature on mechanical properties and we showed that the graphene with two curvatures had Young's modulus and potential energy about 1.23 TPa and -4.47 eV respectively. Also, we considered the effects of one-atom vacancy and two-atom vacancy defect and found that Young's modulus decreased about 1% and 4% respectively in comparison with straight graphene.

References

- [1] Rajasekaran G, Narayanan P, Parashar A Effect of Point and Line Defects on Mechanical and Thermal Properties of Graphene: A Review. *Crit Rev Solid State Mater Sci* 2016; 41: 47-71.
- [2] Parvez K, Wu ZS, Li R, Liu X, Graf R, Feng X, Müllen K Exfoliation of graphite into graphene in aqueous solutions of inorganic salts. *J Am Chem Soc* 2014; 136: 6083-6091.
- [3] Georgantzinos SK, Giannopoulos GI, Anifantis NK Numerical investigation of elastic mechanical properties of graphene structures. *Mater Des* 2010; 31: 4646-4654.
- [4] Zhao X, Zhang Q, Chen D, Lu P enhanced mechanical properties of graphene-based poly (vinyl alcohol) composites. *Macro-molecules* 2010; 43: 2357-2363.
- [5] Stankovich S, Dmitriy AD, Geoffrey HBD, Kevin MK, Eric JZ, Eric AS, Richard DP, SonBinh TN, Rodney SR graphene-based composite materials. *Nature* 2006; 442: 282-286.
- [6] Li D, Kaner RB graphene-based materials. *Nat Nano-technol* 2008; 3: 101.
- [7] Novoselov KSA, Andre KG, Morozov SV, Jiang D, Zhang Y, Dubonos SV, Grigorieva IV, Firsov AA electric field effect in atomically thin carbon films. *Sci* 2004; 306: 666-669.
- [8] Novoselov KSA, Andre KG, Morozov SV, Jiang D, Katsnelson MI, Grigorieva IV, Dubonos SV, Firsov AA two-dimensional gas of massless Dirac fermions in graphene. *Nature* 2005; 438: 197-200.

- [9] Novoselov KS, Jiang Z, Zhang Y, Morozov SV, Stormer HL, Zeitler U, Maan JC, Boebinger GS, Kim P, Geim AK room-temperature quantum Hall effect in graphene. *Sci* 2007; 315: 1379.
- [10] Meo M, Rossi M prediction of Young's modulus of single wall carbon nanotubes by molecular-mechanics based finite element modelling. *Compos Sci Technol* 2006; 66: 1597-605.
- [11] Gomez-Navarro C, Burghard M, Kern K elastic properties of chemically derived single graphene sheets. *Nano Lett* 2008; 8: 2045-2049.
- [12] Lee C, Wei XD, Kysar JW, Hone J measurement of the elastic properties and intrinsic strength of monolayer graphene. *Sci* 2008; 321: 385-388.
- [13] Balandin AA, Ghosh S, Bao W, Calizo I, Teweldebrhan D, Miao F, Lau CN superior thermal conductivity of single-layer graphene. *Nano Lett* 2008; 8: 902-907.
- [14] Van Lier G, Van Alsenoy C, Van Doren V, Geerlings P ab initio study of the elastic properties of single-walled carbon nanotubes and graphene. *Chem Phys Lett* 2000; 326: 181-185.
- [15] Chen W, Rakhi RB, Alshareef HN Capacitance enhancement of polyaniline coated curved-graphene supercapacitors in a redox-active electrolyte. *Nano-scale* 2013; 5: 4134-4138.
- [16] Zhou X, Wan LJ, Guo YG Binding SnO₂ Nanocrystals in Nitrogen-Doped Graphene Sheets as Anode Materials for Lithium-Ion Batteries. *Adv Mater* 2013; 25: 2152-2157.
- [17] Kulkarni GS, Reddy K, Zhong Z, Fan X Graphene nanoelectronic heterodyne sensor for rapid and sensitive vapour detection. *Nature Commun* 2014; 5: 4376.
- [18] Gilje S, Han S, Wang M, Wang KL, Kaner RB a chemical route to graphene for device applications. *Nano Lett* 2007; 7: 3394-3398.
- [19] Wang X, Zhi L, Müllen K transparent, conductive graphene electrodes for dye-sensitized solar cells. *Nano Lett* 2008; 8: 323-327.
- [20] Watcharotone S, et al. graphene-silica composite thin films as transparent conductors. *Nano Lett* 2007; 7: 1888-1892.
- [21] Yu A, Ramesh P, Itkis ME, Bekyarova E, Haddon RC graphite nanoplatelet-epoxy composite thermal interface materials. *J Phys Chem C* 2007; 111: 7565-7569.
- [22] Lu Q, Arroyo M, Huang R elastic bending modulus of monolayer graphene. *J Phys D Appl Phys* 2009; 42: 102002.
- [23] Gao Y, Hao P mechanical properties of monolayer graphene under tensile and compressive loading. *Physica E* 2009; 41: 1561-1566.
- [24] Xiao J, Staniszewski J, Gillespie J tensile behaviors of graphene sheets and carbon nanotubes with multiple Stone-Wales defects. *Mater Sci Eng A* 2010; 527: 715-723.
- [25] Ertekin E, Daw M, Chrzan D elasticity theory of topological defects in carbon nanotubes and graphene. *Philos Mag Lett* 2008; 88: 159-167.
- [26] Behfar K, Seifi P, Naghdabadi R, Ghanbari J an analytical approach to determination of bending modulus of a multi-layered graphene sheet. *Thin Solid Films* 2006; 496: 475-480.
- [27] Shokrieh MM, Rafiee R prediction of Young's modulus of graphene sheets and carbon nanotubes using nanoscale continuum mechanics approach. *Mater Des* 2010; 31: 790-795.
- [28] Shokrieh MM, Rafiee R a review of the mechanical properties of isolated carbon nanotubes and carbon nanotube composites. *Mech Compos Mater* 2010; 46: 155-172.
- [29] Omata Y, Yamagami Y, Tadano K, Miyake T, Saito S nanotube nanoscience: A molecular-dynamics study. *Physica E* 2005; 29: 454-468.
- [30] Utkov H, Livengood M, Cafiero M using Density Functional Theory Methods for Modeling Induction and Dispersion Interactions in Ligand-Protein Complexes. *Annu Rep Comput Chem* 2010; 6: 96-112.
- [31] Cai J, Wang Y, Wang C effect of ending surface on energy and Young's modulus of single-walled carbon nanotubes studied using linear scaling quantum mechanical method. *Physica B* 2009; 404: 3930-3034.
- [32] Ganji MD, Fereidoon A, Jahanshahi M, Ahangari MG elastic properties of SWCNTs with curved morphology: Density functional tight binding based treatment. *Solid State Commun* 2012; 152: 1526-1530.
- [33] Jing N, Xue Q, Ling C, Shan M, Zhang T, Zhou X, Jiao Z Effect of defects on Young's modulus of graphene sheets: a molecular dynamics simulation. *Rsc Adv* 2012; 2: 9124-9129.
- [34] Memarian F, Fereidoon A, Ganji MD Graphene Young's modulus: Molecular mechanics and DFT treatments. *Super-lattices Microst* 2015; 85: 348-356.