Graphene Young's modulus: Molecular mechanics and DFT treatments

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ABSTRACT

Despite of the numerous theoretical and experimental investigations on the mechanical properties of graphene as a unique nano-structured material, a precious value for this important property has not yet been presented. In the present work, the Young's modulus of single layer graphene sheet has been investigated by using comprehensive classic as well as quantum mechanics (QM) calculations. Molecular mechanics (MM) approach with various well-defined force-fields such as AIREBO, Tresoff and EDIP potentials have been considered. In QM category, several conventional methods (DFTB and DFT-LDA/GGA) have been employed. The results show that EDIP potential method predicts more accurately the graphene Young's modulus value compared to experimental results. Furthermore, despite the various theoretical results reported elsewhere, the EDIP potential calculations result reveals that Young's modulus has the same value at both zigzag and armchair directions. From the results obtained here, we found that among the various MM and QM methods considered here the EDIP method seems to be the most convenient method for evaluation of both structural geometries and mechanical properties of carbon based graphene-like materials. This is because of its less computational costs accompanied with reliable results comparable with the experiments.

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1. Introduction

Graphene, a two dimensional nanostructure with sp^2 bonded carbon atoms, has been attracted tremendous interest in last few years due to their unusual electron transport properties and also their extraordinary mechanical properties [1–5]. High tensile strength of these unique structures is attributed to the strength of covalent bonds between carbon atoms [4]. Since previously it was assumed that the in-plane elastic moduli of a single-layer graphene sheets are identical to hexagonal crystal graphite, little attention has been paid to their mechanical properties [4]. Also in contrast with nanotube or buckyball, graphene atoms are accessible from both sides, so stronger interaction with surrounding molecules is created [3]. On the other hand, sp^2 bonded carbon atoms of graphene sheet which are bonded to only three other atoms, have the ability to interact with forth atom. Great tensile strength and the high surface area to volume ratio combined with this capability, make it extraordinary unique in composite materials [3]. Also they are suitable for many other applications in modern technology such as gas detector [1], mechanical resonator [2]. Because of the importance of this unique material a large amount of experimental and theoretical efforts have been done in order to obtain its mechanical and electrical

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properties [6–13]. One of these mechanical properties is elastic moduli, which has been a subject of intensive research in recent years [1–3,6,7].

Calculations of elastic moduli of single layer graphene sheet range from Quantum Mechanic (QM) calculations to molecular dynamic simulations and continuum models. Many researchers have used experimental methods to obtain Young's modulus. The experimental and theoretical published data for Young's modulus of graphene varies significantly. Experimentally, the Young's modulus of graphene has been measured by using atomic force microscope. The measured value for Young's modulus is 1.0 ± 0.1 TPa in this experiment [14].

Different theoretical values were obtained by using different effective thickness of graphene sheet, and different potential functions (force-constants) with various algorithms. In order to avoid confusion on thickness definition, all the reported articles use 0.34 nm as the thickness of graphene sheet. In available theoretical studies, graphene Young's modulus were reported 0.974 TPa by Lu [15] and 1.238 TPa by Jin and Yuan [16] using molecular dynamics simulation, and 1.24 TPa by Hernandez et al. [17] using tight binding molecular dynamics. Xiao [18], Wu [19], and Natsuki [20] reported the same value of 1.06 TPa for Young's modulus by using respectively an analytical molecular structural mechanics model, combination of molecular and continuum mechanics, and combination of molecular and solid mechanics. *Ab initio* methods have been used by Kudin et al. [6], Van Lier et al. [21], and Liu et al. [22]. Kudin predicted a Young's modulus of 1.02 TPa and Poisson's ratio of 0.149, Van Lier and Liu respectively reported a Young's modulus equal to 1.11 and 1.05 TPa for single layer graphene sheet.

In several literatures Tersoff–Brenner potentials have been used to describe the mechanical properties of single layer graphene sheets, with Young's modulus predictions between 0.694 and 0.714 TPa, and Poisson's ratios from 0.397 to 0.417 [23,24].

Reddy et al. have used Brenner's potential and Cauchy–Born rule [9] to describe the mechanical properties of graphene sheets. Rajendran and Reddy have shown the maximum numerical precision using the above methods to calculate the stiffness of single layer graphene sheets and carbon nanotubes [11]. They found mechanical properties of graphene sheets based on equivalent continuum modeling. The value of Young's modulus that has been reported in their work is 1.095–1.125 TPa for armchair sheets and 1.106–1.201 TPa for zigzag sheets.

Another Brenner's potentials have also been used by Huang et al. [8] to calculate the in-plane Young's moduli, Poisson's ratios and thickness of graphene sheet and single wall carbon nanotubes (SWCNTs), with the Young's modulus of 0.694 TPa. In 2003 Li and Chou [25] for the first time found a relationship between computational chemistry and structural mechanics. In this method each carbon atom play the role of joints and the bonds play the role of mechanical links and replaced with a beam element. They reported 1.033 TPa as the Young's modulus of graphene. Then Shokrieh and Rafiee [26] used this continuum model and the obtained Young's modulus is 1.04 TPa. Also Hemmasizadeh et al. [10] used continuum model and the reported Young's modulus is 0.669 TPa. Gao and Hao [27] in 2009 by quantum molecular dynamics reported the value of 1.1 TPa for armchair graphene Young's modulus and 0.6 TPa for zigzag graphene Young's modulus. Yanovsky et al. [28] used QM and the obtained Young's modulus is 0.737 TPa. Ni et al. [29], Tsai and Tu [30], and Ansari et al. [31] used molecular dynamic simulation and the reported Young's modulus respectively is 1.1, 0.912 and 0.8 TPa. In 2010 Georgantzinos et al. [32] used finite element method and the reported Young's modulus is 1.367 TPa.

F. Scarpa et al. have proposed truss-type analytical models and an approach based on cellular material mechanics theory to describe the in-plane linear elastic properties of the single layer graphene sheets. The reported value is 1.042 TPa for armchair sheets and 1.040 TPa for zigzag sheets [13]. All above mentioned published results are summarized in Table 1. It can be found that different values of the graphene Young's modulus have been obtained by various computational methods. If the Molecular Mechanics (MM) method was used just a specific potential was considered or if the QM method was used, just one of them is considered. The lack of a coherent study with all high precision methods together is obvious. In fact, in this article in order to find the best method among the most known classic and QM methods, it is tried to use all methods on the same system and compare them with each other.

We have used various potentials in MM category and several methods from Density Functional Tight Binding (DFTB) and Density Function Theory (DFT) in QM methods.

In order to reasonably compare the results of present study with other published results, a thickness of 0.34 nm is used in the present study. In terms of bond length the results within the DFT and MM with Adaptive Intermolecular Reactive Bond Order (AIREBO) and Environment-Dependent Interatomic Potential (EDIP) calculations are the most accurate methods and for the Young's modulus, the DFT and MM-EDIP approaches were found to be more reliable methods compared to experimental results.

2. Computational methods

Over the span of three decades, molecular modeling has appeared as an achievable and powerful approach to chemistry, because, the simulation of different processes in solids and biological systems earned more and more importance [33]. Different effective algorithms and powerful processors make this opportunity for users to observe systems with thousands atoms for several microseconds. Finding a reasonable compromise between computational cost and reliable results is a big challenge for researchers. Molecular mechanics calculations and quantum chemical calculations are two important approaches which are able to complement experiment as a means to uncover and explore new chemistry [33].

Molecular Mechanics or force-field methods use classical mechanics to model molecular systems and predict the energy of a molecule as a function of conformation [34].

Table 1
Comparison of Young's modulus results for graphene sheet.

Reference	Method	Young's modulus (TPa)
Lee [12]	Experiment	1.0 ± 0.1
Lu [13]	Molecular dynamics	0.974
Jin and Youn [14]	Molecular dynamics	1.238
Hernandez [15]	Tight binding molecular dynamics	1.24
Xia [16]	An analytical molecular structural mechanics model	1.06
Wu [17]	Combination of molecular and continuum mechanics	1.06
Natsuki [18]	Combination of molecular and solid mechanics	1.06
Kudin [4]	*Ab initio*	1.02
Van Lier [19]	*Ab initio*	1.11
Liu [20]	*Ab initio*	1.05
Brenner [21,22]	Tresoff-Brenner potentials	0.694–0.714
Huang [6]	Brenner potential	0.694
Rajendran [9]	Equivalent continuum model	1.096–1.125 (Armchair)
		1.106–1.201 (Zigzag)
Li and Chou [23]	Continuum model	1.033
Shokrieh [24]	Continuum model	1.04
Hemmasizadeh [8]	Continuum model	0.689
Gao and Hao [25]	Quantum molecular dynamics	1.1 (Armchair)
		0.6 (Zigzag)
Yanovsky [26]	Quantum mechanics	0.737
Ni [27]	Molecular mechanics	1.1
Tsai [28]	Molecular mechanics	0.912
Ansari [29]	Molecular mechanics	0.8
Georgantzinos [30]	Finite element method	1.367
Scarpa [11]	Truss-type analytical models	1.042 (Armchair)
		1.04 (Zigzag)

Table 2
The calculated and experimental values for bond length and Young's modulus of graphene sheet.

Methods	Bond length (Å)	Young's modulus (GPa)
Airebo	1.41	828.9 (Armchair)
		995.14 (Zigzag)
Tresoff	1.464	982.01 (Armchair)
		1078.86 (Zigzag)
EDIP-Mark	1.42	**1023.95** (Armchair)
		1022.01 (Zigzag)
GGA	1.426	1084.84
LDA	1.414	1079.26
SCC-DFTB	1.421	1395.08
nonSCC-DFTB	1.421	1401.01
Experimental results	1.415/1.42	1000 ± 100

The bold values are related to the most accurate method EDIP-Marks.

In the field of MM calculations, EDIP-Marks [35], Tersoff [36] and AIREBO [37] potentials are implemented by using the "General Utility Lattice Program" (GULP) [38] and "Large-scale Atomic/Molecular Massively Parallel Simulator" (LAMMPS) [39] softwares respectively There is prosperity of reliable interatomic potentials implemented in these softwares. It is worth noting that combined with their powerful potential libraries LAMMPS and GULP become a valuable platform to do MM calculations for the solid crystals. Meanwhile, a distinct feature of these potentials is their good performance in describing the formation and breaking of bonds.

The first complex models of interatomic interactions is EDIP potential, wherein two-body terms and angular three body contributions is considered [40]. At first, this potential just used for silicon compounds [41], but some years later extended to carbon by Marks [42]. It is important to know that, closer interactions which considered in EDIP potential have a good agreement with density function theory [43]. Another important features of EDIP is speed of calculations which make a significant improvement in its performance, so study of large systems with this potential is possible [43].

Tersoff potential which is defined by two-body interaction is built on the concept of bond order. In fact this potential is somehow complicated [40]. One of the advantages of Tersoff potential over conventional molecular mechanics force fields is that it can, with the same parameters, describe several different bonding states of an atom, and thus may be able to describe chemical reactions properly [44].

The last MM potential is AIREBO which is applicable for mixture of atoms [40]. In AIREBO potential both the long-range atomic and single bond torsional interactions are considered [37]. Since in AIREBO and Tersoff potentials only the 1st- and 2nd-nearest-neighbour interactions were considered, these are less time-consuming compare to first-principle approaches [45]. This advantage of these potentials is especially helpful for large-scale atomic simulations [45].

The second approach is quantum mechanics which is a fundamental branch of physics and deals with physical phenomena at nanoscopic scales. Quantum mechanics can show behavior of atoms during chemical bonding, so is significantly important in the development of modern technologies [46].

Density functional theory (DFT) is one of the computational quantum mechanical modelling method which can be used in physics, chemistry and materials science in order to investigate their structure at an atomic scale [47]. With this theory, the properties of system can be determined by using their electron functions. Despite of popularity and versatility in computational physics and chemistry, there are still difficulties in describing intermolecular interactions, especially van der Waals forces [47]. Subsequently, DFT can be increasingly applicable for prediction of atomistic behavior of complex systems in the chemical and material science area. Specifically, this method is implemented for the study of systems which synthesizing them has a lot of difficulties. Since experimental studies in such systems, encumbered by incompatible results and non-equilibrium conditions these calculations are really necessary [47]. Also DFT has been admired for calculations in solid-state physics since the 1970s and the results obtained have agreed quite satisfactorily with experimental data [48–51].

The *first-principles* DFT calculations were performed with a Local Combination of Atomic Orbital (LCAO) using the *ab initio* simulation code, Spanish Initiative Electronic Structure for Thousands of Atoms (SIESTA) [52,53]. We adopted both the generalized gradient approximation (GGA) as described by Perdew–Burke–Ernzerhof (PBE) [54] and the Local Density Approximation (LDA) as described by Ceperely–Alder (CA) [55] to treat the electronic exchange and correlation effects.

For all the DFT calculations, a split-valence triple-ζ basis set of atomic orbitals was used, including polarization functions with an energy shift of 50 m eV and a split norm of 0.25 [53,56]. A $7 \times 7 \times 1$ Monkhorst–Pack grid for k-point sampling of the Brillouin zone was set, and the atomic positions were relaxed until the residual forces on each atom were lower than 0.005 eV/Å. An energy cutoff of 125 Ry for the grid integration was considered to represent the charge density [53].

Whereas DFT solve Schrödinger's equation by the calculation of complex integrals, just can be used on small scale. On the other hand, although DFT is very efficient, all properties of a system cannot describe with adequate accuracy because of their empirical nature. Another QM calculations which is called DFTB describes a class of approximative DFT methods [57–59]. Contrasting the usual approximate Hartree–Fock methods, or conventional DFT on a tight-binding basis, the DFTB approach uses a tabulated set of integrals derived from *ab initio* DFT calculations [60] which lead to a significant accelerate of the calculations because explicit integration is not necessary in the method. Also stability of simulations shows similarity of DFTB and DFT method [61]. Another important advantage of DFTB is capability of calculating both molecular and solids systems with the same theory [59].

The Self-Consistent Charge Density Functional Tight Binding (SCC-DFTB) and nonSCC-DFTB calculations were performed using *ab initio* DFTB code, DFTB+ [62] which uses the DFTB method based on a second-order expansion of the Kohn–Sham total energy in DFT with respect to charge density fluctuations. The zeros-order approach is the same as a common standard non-self-consistent tight-binding scheme while, for the second-order approach, a transparent, parameter-free and readily calculable expression for generalized Hamiltonian matrix elements can be derived [62]. In this work, the Slater–Koster (S–K) type parameter set [58] was used. For the C atom, the $2s$ and $2p$ electrons were explicitly included in the calculations. The structure was fully optimized using the conjugate-gradient algorithm until the atomic forces were smaller than 10^{-7} a.u.

In all procedures, a vacuum of 30 Å was used in the direction perpendicular to the graphene sheets, and the sheets were periodic in the X- and Y-directions.

We expect that DFT methods show the most accurate results in comparison with MM and DFTB calculations since the other methods are fit to DFT calculations. However, DFT is recognized to be more expensive computationally compared to both MM and DFTB methods [63]. On the other hand, DFT method has a relatively low computational cost, compared with other QM approaches such as full potential hybrid DFT and MP2 methods, which makes it an ideal method for calculating the electronic structure of rather large systems [64].

All calculations (MM, DFTB and DFT) were performed on a $7 \times 7 \times 1$ graphene sheet, as depicted in Fig. 1(a). We choose a computational cell containing 98 atoms to facilitate a computationally tractable direct comparison between all the above mentioned methods.

3. Results and discussion

The Young's modulus of single layer graphene sheet under uni-axial strain was determined. The optimized structure was used for the mechanical properties investigation. The axial strains were obtained by simulating uni-axial tension and compression, which was applied by changing the atom–atom distance in small steps (±0.01 Å). The corresponding potential energy is computed for a series of loadings. The definition of Young's modulus involves the second derivative of the potential energy versus strain. So the potential energy with respect to strain was plotted for each above mentioned methods. As expected, the potential energy exactly behaves as the parabola diagrams. Young's modulus is given by the following expression:

$$Y = \frac{1}{V_0} \frac{\partial^2 E}{\partial^2 \varepsilon} \tag{1}$$

where V_0 is defined as the volume of graphene sheet: $V_0 = a \times b \times t$ and a, b, and t are respectively length, width and thickness of the graphene sheet. E is potential energy and $\varepsilon = \frac{\Delta L}{L_0}$ is the axial strain of graphene; in which ΔL is changes in bond length with respect to initial bond length.
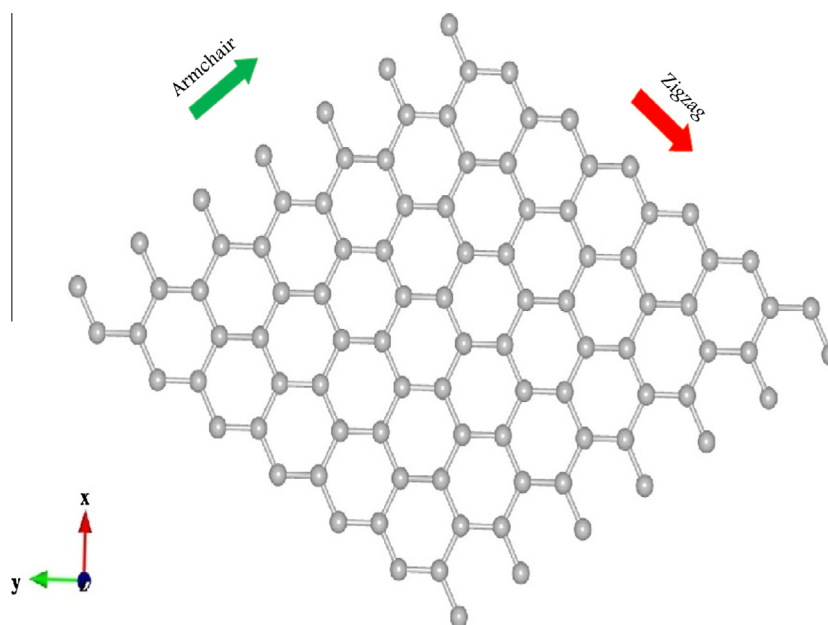
Fig. 1. Models for a 7 × 7 graphene sheet.

The accuracy of used methods is evaluated by comparison of optimized geometries of graphene against the existing experimental data. The experimental value of C–C bond's length in graphene was reported 1.415 [65] and 1.42 Å [66]. The potential energy and bond length were calculated within above mentioned methods, which are divided into two general categories: MM and QM.

In the MM category three well known potential was used: AIREBO, Tresoff, and EDIP-Marks. The results obtained with AIREBO potential show that, bond lengths of C–C bonds in the optimized structure is about 1.41 Å, which is found to be slightly less than the reported experimental values [65,66]. In order to calculate the Young's modulus of graphene sheet, strain energy versus axial strain curves are obtained as shown in Fig. 2(a). Eq. (1) was used to compute the corresponding Young's modulus. The calculated modulus is 995.14 GPa in zigzag direction while in the armchair one, the value was estimated to be about 828.94 GPa. The obtained results reveal that this method underestimates both the C–C bond length and the Young's modulus in comparison with the experimental values.

However, Tersoff potential overestimates the C-C bond lengths of graphene (1.464 Å). In addition, the Young's modulus obtained within this MM approach is estimated to be about 1078.86 and 982.01 GPa in zigzag and armchair directions, respectively. As it is obvious from the results, Tersoff potential overestimates slightly the bond length value while predicts reasonably the Young's modulus in comparison with the experimental value. Fig. 2(b) shows strain energy with respect to strain obtained by Tersoff potential.

The last considered approach in MM category is EDIP-Marks potential. Equilibrium bond lengths calculated by EDIP–Marks potential are about 1.42 Å, which is exactly equal to reported experimental result [66]. Fig. 2(c) shows strain energy with respect to strain with the selected potential. The Young's modulus was determined to be about 1022.01 GPa in zigzag direction and 1023.95 GPa in armchair direction which indicate that this MM approach agrees very well with the experiment. From the results obtained by MM approaches considered here we found that EDIP-Marks potentials seems to be suitable approaches for both structural geometries and mechanical properties investigations for carbon based graphene-like materials.

In QM category, four conventional approaches have been employed; DFTB, DFT within both LDA and GGA methods. In the case of DFTB method both SCC-DFTB and nonSCC-DFTB approaches were used to calculate the bond length and potential energies for the system under study. The optimized bond length obtained from both considered methods is 1.421 Å. This value is close to the experimental value and it tends to overestimate bond length slightly. The Young's modulus for the zigzag and armchair orientations obtained from nonSCC-DFTB are 1203.21 and 1203.15 GPa, respectively. The Young's modulus for the zigzag orientation obtained from SCC-DFTB is 1201.27 GPa. As it is obvious from the results obtained one can conclude that these QM methods overestimate the Young's modulus and deviate from experimental value, remarkably. The potential energy versus strain of these two methods is shown in Fig. 3. In order to calculate Young's modulus of graphene sheet within the *first-principles* DFT method both the LDA and the GGA approaches were employed. Equilibrium bond lengths obtained from the selected methods are 1.414 and 1.426 Å for the LDA and the GGA methods, respectively, which are in agreement with the experimental values. The potential energy against strain of these two methods is shown in Fig. 3(c) and (d).
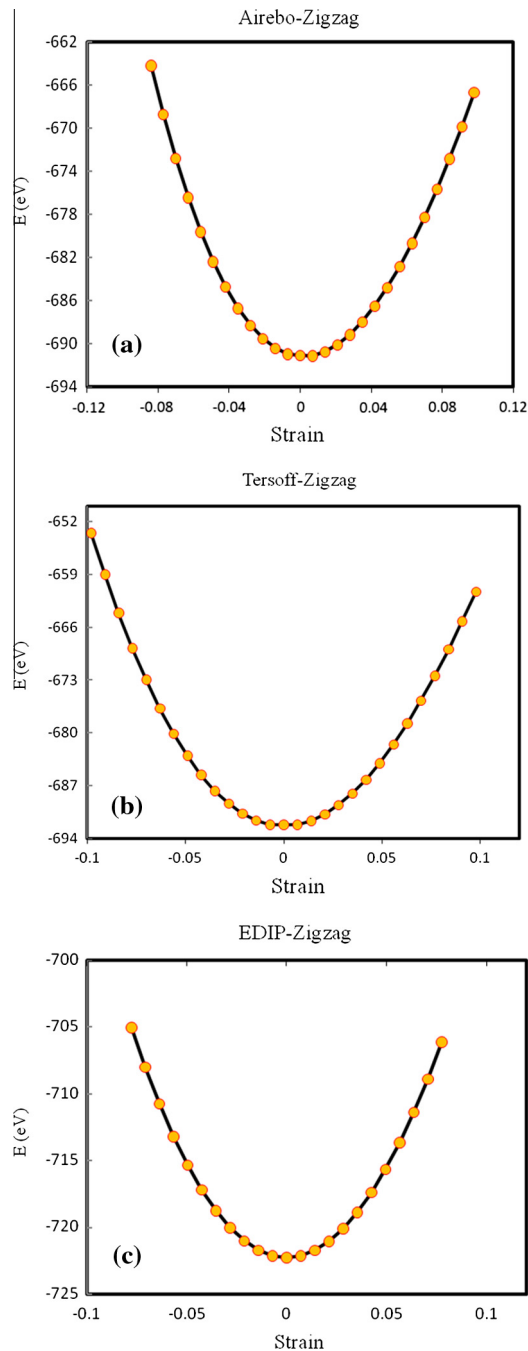
Fig. 2. The potential energy against strain for graphene sheet by using molecular mechanics methods with (a) AIREBO (b) Tersoff, and (c) EDIP force-fields.

The Young's modulus was obtained by second order polynomial fit of these data and the results are respectively 1079.26 and 1084.84 GPa for the GGA and the LDA methods. Our *ab initio* DFT results show that both the LDA and GGA approaches slightly overestimate the Young's modulus in comparison with the experimental data. Compared to the DFTB calculation results however, the results obtained by using the DFT methods are relatively close to the experimental value in both geometries and mechanical properties. Our optimized bond length and calculated Young's modulus are summarized in Table 2.

From the results obtained in this work, one can conclude that all methods which predict different values for graphene Young's modulus in various directions unable to present a reliable result for mechanical properties. As it can be seen from the various computational methods considered here, it was found that MM-EDIP method is a superior method among the various MM and QM approaches for structural geometries as well as mechanical properties evaluation. This is due to its very
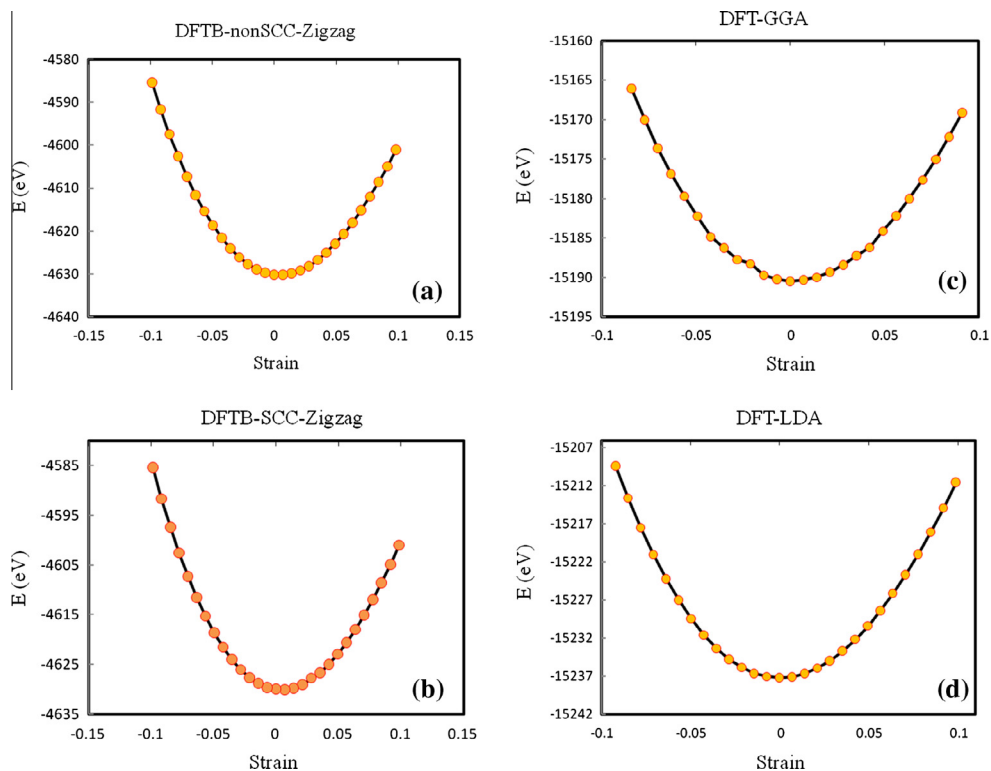
Fig. 3. The potential energy against strain for graphene sheet by using (a) DFTB-non-SCC, (b) DFTB-SCC, (c) DFT-GGA and (d) DFT-LDA methods.

low computational cost accompanied with reliable results comparable with experimental values. The accurate finding against the experiment result can be attributed to the appropriate parameterization of EDIP potential with respect to state-of-the-art full potential DFT level of theory methods. In this parameterization, closer interactions are described appropriately while EDIP and DFT are in good qualitative agreement for the energy barrier between sp^2 and sp^3 hybridizations. This unique parameterization provides EDIP a noteworthy advantage over the Tersoff and Airebo potentials where the use of arbitrary cutoff functions leads to qualitatively wrong barriers for bond-forming and bond-breaking processes [67,68].

4. Conclusion

In order to compare computational methods in terms of computational cost and accuracy of methods, different methods from MM to QM were performed. We have reported the optimized bond length and Young's modulus of single layer graphene sheet with various methods. In MM approach AIREBO, Tersoff and EDIP-Marks potentials have been used. The bond length obtained from EDIP-Marks potential is in very good agreement with experimental data and the calculated results for Young's modulus showed that this method can predict the Young's modulus extremely close to experimental results. So between these MM methods EDIP-Marks seems to be more reliable than other counterparts.

In QM category DFTB and, DFT-LDA/GGA methods have been employed. Between these considered methods the calculated results showed that, computed bond length with DFT-LDA method is equal to the reported experimental value. Comparison of calculated Young's modulus showed that DFT methods (LDA and GGA) approach can predict the Young's modulus with a little deviation.

It is obvious from the results that considered QM methods are reliable in terms of mechanical properties, but these methods are expensive in terms of computational cost and can be used for systems with a finite number of atoms. Because of these limitations and with regard to the accuracy of results, for carbon compounds, EDIP-Marks potential is the most appropriate method compared to other classic and QM methods. In four categories these method are compared with each other; computational cost, computational time, accuracy and number of system's atoms.

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