Simulations of Graphene Sheets based on the Finite Element Method and Density Functional Theory: Geometry Modeling under the Influence of Defects

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Abstract. In the present research, imperfect graphene sheets were generated and their vibrational property was studied via finite element analysis. The effect of vacant sites in the arrangement of these nano-structures was examined. The fundamental frequency of the defect free and imperfect nano-sheets was acquired based on two different approaches. The first approach was a pure finite element simulation. The second approach was a refined finite element simulation at which the vicinity of a defect was first evaluated according to the density functional theory (DFT) and then the refined geometry was implemented into a finite element model. The findings of this research show that the fundamental frequency of graphene sheets decreases by presenting microscopic imperfection to the formation of these nano-materials. In addition, it was pointed out that the geometry based on the more precise DFT simulations gives a higher decrease in the fundamental frequency of the sheets for all considered cases.

Introduction

The applications and characteristics of graphene sheets, carbon nanotubes (CNTs) and their modifications have been a growing research field over the past few years [1-3]. Since their discovery, various methods have been used for the mechanical description of carbon nano-structures which are basically divided into the branches of experimental and theoretical

investigations [4]. The results of some investigations on the vibrational properties of graphene sheets and CNTs are presented in the following. In 2009, Hashemnia et al. [1] studied the vibrational properties of graphene sheets and single-walled CNTs (SWCNTs). They evaluated the natural frequency of these nano-configurations. Based on their findings, it was concluded that the natural frequency declines as aspect ratio rises. After that in 2012, Firouz-Abadi and Hosseinian [3] investigated the free vibration specifications of a SWCNT in the surrounding area of a fully constrained nano-sheet. After that, they obtained the static distortion of the tube by applying a molecular structural model and in view of nonlinear van-der-Waals interactions. They finally linearized the governing equations of motion about the static equilibrium state and obtained the natural frequencies. Muc and Chwal [5] investigated control of defects in CNTs. The control of their approach was based on the examination of the frequencies from the proposed computational system. After that, Ebrahim Zadeh et al. [6] studied the influence of imperfections on the frequency of CNTs. They also investigated the effect of changing the position of one defect in the length of the CNT on its natural frequency. According to their results, it was shown that the presence of vacancy imperfections reduces the natural frequency of the tubes. In 2014, by applying a molecular mechanics approach, Maleki Moghadam et al. [7] studied the effect of Stone-Wales imperfections on the natural frequency of SWCNTs. They finally concluded that the frequencies are reliant on boundary conditions, chirality, defect position, and CNT length. Recently in 2015, Amjadipour et al. [8] studied the vibrational response of defective curved CNTs using the finite element method (FEM). They explored the effect of curvature, aspect ratio, and vacancy defects on the fundamental frequency of SWCNTs. They showed that the critical waviness is dependent upon the aspect ratio and indicated that by growing the length of SWCNTs, the critical waviness ratio rises. The review presented above indicates that researchers apply quite different methods, i.e. FEM or molecular dynamics (MD), to model the mechanical behavior of nanostructures. Modeling defects in graphene-related nanostructures is not a trivial matter. For example, it is known that removing an atom from graphene leads to a distortion of the structure of the remaining graphene atomic positions around the vacancy [9]. A proper treatment of the distortion requires at a minimum careful density functional theory based calculations of the distorted geometry. In this article, the local neighborhood of a defect was modeled based on two different approaches. The first method is just deleting the atoms and not to consider any restructuring. The second approach considers a re-modeling the bonds and considering the reformation of the structure. The advantages and disadvantages on the modeling approach based on the FEM and MD approaches are highlighted in Table 1.

Table 1. Advantages and disadvantages of different modeling approaches of nanostructures

	FEM	MD
computation time	very low	very high
model size	large	small
rearrangement of atoms after removal	no	yes

It should be noted that MD simulations are restricted to smaller models and are very demanding in regards to computer. Nevertheless, the MD approach allows to accurately investigating the geometry in the neighborhood of defects. Our hybrid approach takes advantage of the strengths of both methods (FE: larger models and quick calculations; MD: more precise geometry representation).

Materials and methods

Graphene is an allotrope of carbon in the form of a two-dimensional, microscopic scale, honeycomb lattice. Carbon nano-structures including CNTs, fullerenes, hetero-junction tubes, nano-cones, etc. are imagined by rolling up graphene sheets. The structure of a graphene sheet with dimension of 25 nm times 25 nm was generated and the collected data was transmitted to computer software [10]. Then, the finite element analyses (FEA) were performed and the vibrational response of undamaged and imperfect graphene sheets was investigated. The computational approach was performed in two different ways in regards to the geometry generation. In the first approach, the pure FE approach, elements and nodes were simply deleted to create vacancies of different natures. The second approach started first with DFT simulations to calculate the real geometry in the vicinity of a vacancy defect. This geometry was then implemented into the finite element (FE) model (now called a hybrid FE model) to have a more accurate representation of the defective area. Therefore, our developed local areas around impaired sites lead to refined outcomes [11]. In realistic circumstances, various types of atomic impurities might be present in the nano-sheets inevitably. It has been stated that these defects have a remarkable influence on the behavior of nano-structures [12-14]. In the first approach (the pure FE method), nodes and elements were simply deleted in the case of vacancies. In the second approach (DFT), a refined geometry was obtained for the vicinity of the defect area. This is based on the fact that the DFT simulations considered a restructuring of the C-atom locations. This refined geometry was introduced to the FE model. Vacancy imperfections are classified into numerous types including mono-, di-, tri-, and pinhole vacancies. All these atomic defects in the configuration of graphene sheet are shown in Fig. 1. Figures 1 and 2 illustrate the bond length and geometry of graphene sheets around the atomic imperfections obtained from the FE and DFT simulations. It should be noted that the bond length for a perfect structure is 0.142 nm [15, 16].

Figures 3-7 schematically compare the differences between atomic defects based on two distinguished methods, i.e., FE and DFT. It should be noted that the total area and physical dimensions of graphene sheets are kept the same. As it is noticeable, the geometry of the graphene sheet after introducing the defects may reveal some considerable differences depending on the applied approach.

Figure 3. Comparing the structural differences of mono-vacancy defect based on (a) FE and (b) DFT

Figure 4. Comparing the structural differences of di-vacancy defect based on (a) FE and (b) DFT

Figure 5. Comparing the structural differences of tri-vacancy defect based on (a) FE and (b) DFT

Figure 6. Comparing the structural differences of pinhole vacancy defect based on (a) FE and (b) DFT

Figure 7. Comparing the structural differences of Stone-Wales defect based on (a) FE and (b) DFT

Results and discussion

The fundamental frequency is generally assessed to explore the vibration response of organizational members. In the current study, defect free and imperfect graphene sheets were simulated based on FE and DEF and their natural frequency was calculated. As an example, Fig. 8 indicates the differences between the FE geometry and DFT geometry as an overlay in a combined illustration. Based on Fig. 8, it is obvious that each approach presents different geometries and as a result, different values of natural frequency are expected. It was also calculated that the DFT geometry produces a different bond length for some elements after

announcing microscopic defects to the structure of graphene sheets. For instance, in the case of the double vacancy, one bond length of the nano-sheet was 0.166 nm (more than 10% larger than the perfect bond length in the configuration of defected graphene sheets).

Figure 8. Different geometry of FE (dotted line) and DFT (blue line) tri-vacancy defects as an overlay

For investigating the vibrational response of imperfect nano-sheets, 1, 2 and 3% of C-atoms and their corresponding bonds were randomly selected and eliminated from the structure of the sheet. The results in Figs. 9 to 13 indicate that carbon vacancies noticeably decrease the fundamental frequency of these particular nano-structures under four edges simply supported boundary condition. This is more observable at higher modes of natural frequency. Based on the results for 3% of defects, the difference in percent for the pure FE and the hybrid FE/DFT approach for all cases of imperfection including 5-7 defect, mono-, di-, tri-, and pinhole vacancy is 0.93, 0.29, 0.5, 1.28, and 2.37%, respectively. It was also pointed out that the geometry based on DFT simulations contributes a higher decrease in the natural frequency of the sheets for all considered cases.

Figure 9. Modification in the first natural frequency of nano sheet caused by single carbon vacancy under four edges simply supported boundary condition

Figure 10. Modification in the first natural frequency of nano sheet caused by di-vacancy defect under four edges simply supported boundary condition

Figure 11. Modification in the first natural frequency of nano sheet caused by tri-vacancy defect under four edges simply supported boundary condition

Figure 12. Modification in the first natural frequency of nano sheet caused by pinhole vacancy defect under four edges simply supported boundary condition

Figure 13. Modification in the first natural frequency of nano sheet caused by 5-7 defect under four edges simply supported boundary condition

Conclusions

Defect free and imperfect graphene sheets were generated by FEM and a hybrid FEM/DFT approach and their vibrational response was explored. It was pointed out that presence and growth of any impurity in the construction of graphene sheets result in a major reduction in the steadiness of these particular nano-materials. In addition, it was pointed out that these two approaches (FE and FEM/DFT) present different results and consequently, different vibrational behavior of graphene sheets. It should be noted that DFT-based calculations indicate more realistic results and therefore, the research on the mechanical properties of different carbon nano-materials based on this particular approach could be considered as future works. MD simulations are in general very expensive in regards to computational time and disk space. On the other hands, FE simulations are by several magnitudes faster and less requirement on disk space. Thus, FE allows to consider much larger models if the computer hardware is limited. The research on the mechanical behavior of different carbon nano-materials based on this particular approach could be considered as future works. If simulations are based on the pure FE approach, this work offers an estimate for the expected error due to the simplification of the geometry representation. It is reported that the proposed approach has limitations e.g., the non-bond interactions between C atoms are not modeled and the temperature condition is not reflected which could be studied in future research works.

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