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Studying the Mechanical Properties of Graphynes Using Molecular Dynamics Simulations

Molecular dynamics simulations are used to study the mechanical properties of graphynes. To study the effect of atomic structure and graphyne size on the Young's and bulk modulus, armchair and zigzag nanosheets with different side lengths and aspect ratios are considered. It is shown than the fracture of armchair graphynes occurs at larger strains. Comparing Young's modulus of armchair and zigzag nanosheets with a constant aspect ratio, it is observed that the value of side length have not significant effect on the Young's modulus of graphynes. Besides, the schematic of graphynes axial and biaxial loading at different strains is represented.it is shown that fracture propagates in a linear pattern

Keywords: *Graphynes; Mechanical properties; Molecular dynamics simulations.*

1. Introduction.

Having the various hybridized states including sp, sp², and sp³, in addition to the ability to bind with nearly all elements have caused to existing numerous carbon allotropes such as fullerenes [1], grapheme [2], nanoring [3] and nanotube [4]. Besides, the = C = C = bonds of grapheme sheets can be replaces by acetylene linkages, $-C \equiv C -$, to form some exotic allotropes which consist of mixed sp and sp² states of carbon atoms. This replacements lead to some allotropes which poses quite different optical and electronic properties from common carbon allotropes [5-7]. To this end, recently some carbon allotropes have successfully synthesized [8-9] or predicted [10-11].

Replacing one third of = C = C = bonds of graphene by acetylene linkages, a stable structure, named as graphyne, is obtained [12]. The electronic, optical and mechanical properties of graphynes have been studied by researchers [13-15]. Kang et al. [16] investigated the elastic, electronic, and optical proper ties of the

2D graphyne sheet. Using generalized gradient approximation and hybrid functional, they computed band structure of graphyne. They found that the value of band gap obtained by using the hybrid functional is one half of the values obtained by using the other approach. Moreover, strong anisotropic optical properties were observed. Zhou et al. [17] used density functional theory and generalized gradient approximation to study the electronic structure of graphyne and its boron nitride analog (labeled as BN-yne). They found that both graphyne and BN-yne are direct bandgap semiconductors.

Peng et al. [18] used first-principles calculations based on the Density Functional Theory to study the mechanical properties of graphynes. They found Young's modulus and Poisson ratio of graphynes as 162 N m and 0.429, respectively. They also formulated the elastic response of graphynes by a continuum description. Zhang et al. [19] employed molecular dynamics simulations to study the thermal conductivity (TC) of four different graphynes. They found that the presence of acetylenic linkages leads to significant reduction in the TC. They also observed that the TC of graphynes is strain and temperature dependent. Besides, the graphyne related structures such as graphyne nanotubes [20], a-graphyne-like carbon nanotubes [21], graphyne sheet and its BN analog [17] have been the subject of different studies. Coluci et al [22] used tight-binding and ab initio density functional methods to study the electronic properties of graphyne

initio density functional methods to study the electronic properties of graphyne nanotubes. They studied three graphyne nanotube families, two of which showed metallic behavior for armchair nanotubes and either metallic or semiconducting behavior for zigzag ones. The third one was predicted to have diameter- and chirality-independent band gap. Enyashin et al. [23] used tight-binding band theory to study the BN and BCN nanotubes with a-graphyne-like wall structures. They predicted that similar to ordinary BCN nanotubes, a-graphyne-like BCN form low-density loosely-bound films and molecular solids.

The elastic properties of graphyne sheets under the tensile in-plane loading are studied here by using molecular dynamics (MD) simulations. The effects of side length and aspect ratio on Young's modulus of graphynes are investigated. Besides, Young's moduli of armchair and zigzag graphynes are compared. The bulk moduli of graphynes with different geometries are obtained by simulating the sheets under two-directional tensile in-plane loads.

2. Methodology

All of the MD simulations are used by using LAMMPS MD code [24, 25]. The interactions between carbon atoms of graphynes are modeled by adaptive intermolecular reactive empirical bond-order (AIREBO) potential function [26]. The simulations are considered under the NVT (constant number of molecules, constant volume, and constant temperature) condition. To integrate the equations of motions, the velocity Verlet [27] and Nose-Hoover thermostat [28] algorithms are used. The time step of 1 fs is used.

3. Simulation results and discussion

As it can be seen in Fig. 1. three types of C–C bonds are observed in graphenes which are $C(sp^2)$ - $C(sp^2)$ for the central aromatic rings, $C(sp^2)$ -C(sp) for the bonds between aromatic rings and triple bonds and C(sp)-C(sp) for triple bonds. The lengths of these bonds are considered as 1.49 Å, 1.48 Å and 1.19 Å respectively [29].



Figure 1. Schematic of different bond types in the structure of graphyne.

The armchair and zigzag graphyne sheets are shown in the Fig. 2.a. and b are the side length and width of the graphyne sheet, respectively. The armchair and zigzag graphyene sheets with different side lengths and aspect ratios are selected to study the effects of atomic structure, side length and aspect ratio on the mechanical behavior of the graphynes. The tensile loads are applied on the horizontal edges of the sheets to compute Young's modulus. Moreover, the biaxial loading condition is used to obtain Bulk modulus.

3.1. Young's Modulus

Due to ambiguity of the thickness of nanostructures [30-33], the in-plane Young modulus is used here which can be defined as [34]:

$$Y_{S} = \frac{1}{A_{0}} \left(\frac{\partial^{2} E_{S}}{\partial \varepsilon^{2}} \right)$$
(1)

in which E_s is the strain energy of the system, A_0 initial unit cell area and strain. The strain energies of two samples armchair and zigzag graphyne sheets are represented in Figs. 3 and 4 versus strain.



Figure 2. Schematic of the (a) armchair and (b) zigzag graphyne sheets.



Figure 3. Strain energy of a 40×80 $Å^2$ armchair graphyne sheet versus strain.



Figure 4. Strain energy of a 40×80 Å² zigzag graphyne sheet versus strain.

As it can be seen in these figures, the first drop in the strain energy-strain graphs can be considered as the fracture initiation. Comparing Figs.3 and 4, it can be seen that the fracture initiation of armchair graphyne sheet occurs at 32% strain, while that of armchair graphyne sheet happens at 23% strain. So, one can conclude that armchair graphyne sheets tolerate larger strains than the zigzag graphyen sheets with the same geometries. Due to releasing energy releasing caused by bond breakage at this step, a considerable temperature increase is observed at this step (Figs. 5 and 6). The other picks which can clearly be seen in Fig. 6 relates to other bond breakages.



Figure 5. Temperature of a 40×80 Å² armchair graphyne sheet versus strain.



Figure 6. Temperature of a 40×80 Å² zigzag graphyne sheet versus strain

To study the effect of aspect ratio on the mechanical properties of graphyne sheets, armchair and zigzag graphynes with the side length of a = 40Å and different aspect ratio b/a, form 0.5 to 3, are considered. The computed value of in-plane Young's modulus is represented in Fig. 7. As it can be seen, increasing aspect ratio results in decreasing Young's modulus. However, for aspect ratios larger than 1, the graphs take a flat form for both armchair and zigzag graphynes. So, it can be said that the in-plane Young's modulus for graphenes with sufficiently large aspect ratios can be considered to be independent of side width *b*. Besides, although the modulus of armchair graphyne at the aspect ratio of 0.5 is about 18% larger than that of zigzag sheets, for the aspect ratios larger than 1.5, the graphs converges. So, it can be concluded that for large graphyne sheets, the armchair and zigzag nanosheets have approximately the same in-plane Young's modulus.



Figure 7. In-plane Young's modulus of armchair and zigzag graphyne sheets with the side length of 40 Å versus graphyne aspect ratio

The effect of graphyne side length on Young's modulus is depicted in Fig. 8. The aspect ratio of graphynes is considered as 1.5. As it can be seen, for a constant aspect ratio, the Young's modulus is approximately independent of side length. Comparing Figs. 7 and 8, it can be concluded that the value of 1.5 can be considered as an aspect ratio after which the in-plane Young's modulus is almost constant.



Figure 8. In-plane Young's modulus of armchair and zigzag graphyne sheets with the aspect ratio of 1.5 versus graphyne side length

The schematic of a 40×80 Å² armchair graphyne sheet is given in Fig. 9. As it can be seen until 31.79%, the armchair graphyne sheet experiences no bond breakage. At this step a bond breakage happens and propagates horizontally parallel to side length. The final figure of graphyne after fracture can be seen in this figure.



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Figure 9. Schematic of a 40×80 Å² armchair graphyne sheet at different strains.

3.2. Bulk Modulus

The following equation can be used to obtain the bulk modulus:

$$B = A_0 \left(\frac{\partial^2 E_s}{\partial A^2} \right)$$
(2)

where A is the instant area of unit cell. Square graphynes with different side lengths are considered here. As it was previously the graphynes are considered to

be under the biaxial loading to obtain the bulk modulus. The strain energy of a 90 \times 90 Å² graphyne under biaxial loading has been plotted versus instant area in Fig. 10. As for uniaxial loading, drops relate to bond breaking and it can be seen that the breakage happens in several steps.



Figure 10. Strain energy of a 90×90 Å² zigzag graphyne sheet under biaxial loading versus unit cell area

The bulk moduli of graphyne sheets with different side lengths are given in Fig. 11. As it can be seen, similar to the behavior observed for Young's modulus, increasing side length result in decreasing the bulk modulus. However, t bulk modulus is more sensitive to the side length than Young's modulus. The initial slop of curve is higher. However, this slope decreases for larger graphynes. It can be predicted that continuing this graph results in a flat part after which increasing side length does not have a significant effect on the bulk modulus.



Figure 11. Bulk modulus of graphyne sheets versus side length

The profile of graphyne under biaxial loading at different strains is shown in Fig. 12. As it can be seen the bond breaking starts at the corners of the sheet. Then it propagates in a straight line parallel. As it can be seen, due to the boundary effects, the final fracture occurs near the boundaries.



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Figure 12. Schematic of a 70×70 Å² graphyne sheet at different strains.

4. Conclusions

The mechanical properties of graphynes were studied using molecular dynamics equations. The effect of different parameters including atomic structure, side length and aspect ratio on Young's modulus of graphynes were investigated. It was shown that for small graphynes, Young's modulus of armchair graphynes is larger than that of zigzag graphynes. However, this dependency vanishes for larger graphynes. Besides, although for a constant side length, at smaller side length the Young's modulus decreases with aspect ratio significantly, this dependency reduces with increasing the aspect ratio. A linear patter was found in the fracture propagation of graphynes under both uniaxial and biaxial loadings. Finally the effect of graphyne side length on the bulk modulus was studied. It was seen that bulk modulus is more sensitive to side length than Youn's modulus.

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