

Young's Modulus and Poisson's Ratio of Monolayer Graphyne

R. Ansari^a, M. Mirnezhad^a, H. Rouhi^{a*}, M. Faghihnasiri^b

^aDepartment of Mechanical Engineering, University of Guilan, Rasht, Iran, P.O. Box 3756

^bDepartment of Physics, University of Guilan, Rasht, Iran, P.O. Box 41335-1914

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*Corresponding author:

E-mail address:

rouhi.hessam@gmail.com

Phone: +98 131 6690276

Fax: +98 131 6690276

Abstract

Despite its numerous potential applications, two-dimensional monolayer graphyne, a novel form of carbon allotropes with sp and sp² carbon atoms, has received little attention so far, perhaps as a result of its unknown properties. Especially, determination of the exact values of its elastic properties can pave the way for future studies on this nanostructure. Hence, this article describes a density functional theory (DFT) investigation into elastic properties of graphyne including surface Young's modulus and Poisson's ratio. The DFT analyses are performed within the framework of generalized gradient approximation (GGA), and the Perdew–Burke–Ernzerhof (PBE) exchange correlation is adopted. This study indicates that the elastic modulus of graphyne is approximately half of that of graphene due to its lower number of bonds.

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1. Introduction

The past two decades have witnessed tremendous advances in the synthesis and applications of new carbon allotropes [1], as reflected by considerable research effort directed towards fundamentals and characterization of these materials. Among these new allotropes, fullerenes [2], carbon nanotubes [3], nanorings [4] and graphene sheets [5] have become hot research areas in materials science and condensed matter physics.

Graphyne is another new non-natural allotrope of carbon containing sp and sp² atoms whose

atomic structure was proposed by Baughman et al. [6] in 1987. It is constructed from hexagonal carbon rings which are connected together by carbon triple bonds and similar to graphene, has an in-plane hexagonal symmetry [6]. Up to now, the synthesization of graphyne has not yet been reported. However, there are some research works into methods for synthesis of its substructures [7, 8]. Recently, experimental success has been achieved in the synthesis of graphdiyne which is a substructure of graphyne [9, 10].

A survey of the literature reveals that numerous theoretical studies on different properties of

graphyne and its substructures have been carried out [11-19]. Narita et al. [11] applied a full-potential linear combination of atomic orbitals method within the framework of local density approximation (LDA) to study the optimized geometries and electronic properties of graphyne and its substructures. Kondo et al. [12] calculated the band-gap of graphyne at the extended Hückel level equal to 0.89 eV. The optoelectronic properties of graphyne and graphdiyne were studied by Haley [13]. Based on DFT in conjunction with the Boltzmann transport equation, Long et al. [14] investigated the electronic structure and charge mobility of graphdiyne sheet and nanoribbons. They indicated that the graphdiyne sheet is a semiconductor with a band-gap of 0.46 eV. Zhou and co-workers [15] analyzed the nature of bonding and energy band structure of graphyne and its boron nitride (BN) analog called "BN-yne" using DFT within the framework of GGA. Their work showed that the band-gap can be modulated by changing the size of hexagonal ring and the length of carbon chain. The energetics and dynamics of lithium in graphyne were studied by Zhang et al. [16] using first-principles calculations. They revealed that the high lithium mobility and high storage capacity make graphyne a promising candidate for the anode material in battery applications. Based upon DFT, Pan et al. [17] explored the configurations and electronic properties of graphyne and graphdiyne nanoribbons with armchair and zigzag edges. Recently, Cranford and Buehler [18] published a paper in *Carbon* on the mechanical characteristics of graphyne using the classical molecular dynamics (MD) simulations. Their atomistic simulations were performed for both in-plane and bending deformation including material failure, as well as

intersheet adhesion. It was concluded that unlike graphene, the fracture strain and stress of graphyne significantly depends on the direction of applied strain and the alignment with carbon triple-bond linkages.

The literature review shows that most of previous works have mainly focused on the electronic properties of graphyne. A good understanding of its elastic properties seems to be interesting and necessary due to potential structural applications of graphyne. Hence, the present work reports the exact values of elastic properties of graphyne including surface Young's modulus and Poisson's ratio. The analysis is based on DFT calculations in the context of GGA using the exchange correlation of the Perdew-Burke-Ernzerhof (PBE). Also, all simulations are performed using the Quantum-Espresso code [19].

2. Model and Results

The present calculations are performed based upon DFT within the framework of GGA-PBE via the Quantum-Espresso code. Brillouin zone integration is applied with a Monkhorst-Pack [20] k -point mesh of 20 x 20 x 1 and the cut-off energy for plane wave expansion is selected to be 80 Ry.

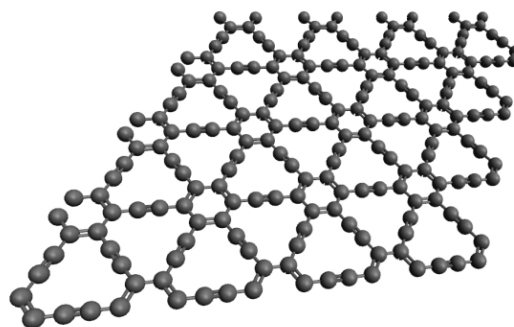


Fig. 1. Schematic view of the geometric structure of monolayer graphyne

As it is shown in Fig. 1, two-dimensional monolayer structure of graphyne is one-atom-thick layer of sp and sp^2 hybridized carbon atoms in which aromatic carbons are connected together by sp hybridized acetylenic linkages. A first-principles study demonstrated that DFT results for the strain energy calculations are insensitive to the increase of unit cell dimension [21]. Therefore, for the sake of simplicity, the unit cell used in the calculations performed herein is assumed be the smallest hexagonal unit cell. The unit cell of a relaxed monolayer graphyne is presented in Fig. 2. The calculated optimized lattice constant is 6.87 \AA , which is in reasonable agreement with those reported in [11,15]. Lattice parameters and atomic positions in various strained graphynes are also tabulated in Table 1.

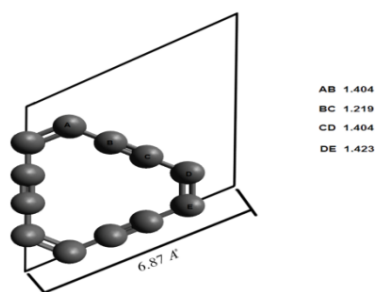


Fig. 2. Unit cell parameters of relaxed graphyne.

Young's modulus is defined as the second derivate of energy with respect to the applied strain [22]. Surface Young's modulus is a more suitable parameter for measuring the strength of graphene-like structures rather than Young's modulus, due to the ambiguity that exists in defining the distance between adjacent layers of these structures. Moreover, for the present DFT calculations, the super-cell approximation is used. The (c) parameters of unit cell must be equal to a large value to avoid the interaction between different

layers. As a result, one of the lattice parameters (c) is unknown.

Table 1. Lattice parameters and atomic positions for strained graphynes

Strain	Lattice Parameters (Angstrom)	Atomic Positions	
		X	Y
-0.02	a = 6.734	1.432	0.006
		2.809	0.018
		4.016	-0.017
		5.393	-0.005
		0.765	-1.234
	b = 6.871	1.472	-2.441
		2.053	-3.509
		2.761	-4.715
		6.094	-1.230
		5.405	-2.435
0	a = 6.871	4.856	-3.515
		4.162	-4.720
		1.422	0.000
		2.826	0.000
		4.045	0.000
	b = 6.871	5.448	0.000
		0.711	-1.232
		1.413	-2.447
		2.022	-3.503
		2.724	-4.718
0.02	a = 7.008	6.159	-1.232
		5.458	-2.447
		4.848	-3.503
		4.146	-4.718
		1.411	-0.004
	b = 6.871	2.843	-0.011
		4.073	0.011
		5.505	0.004
		0.659	-1.230
		1.355	-2.453
	1.988	-3.498	
	2.684	-4.721	
	6.226	-1.234	
	5.507	-2.459	
	4.845	-3.490	
	4.126	-4.715	

Hence, the DFT calculations are carried out with 30 Å distance between adjacent layers to avoid the interaction between them. Motivated by these reasons, surface Young's modulus is reported in this study instead of Young's modulus, which is equal to Young's modulus multiplied by graphene thickness. Surface Young's modulus is defined as [21]

$$Y_s = \left(\frac{1}{A_0} \right) \times \left(\frac{\partial E_s}{\partial \epsilon^2} \right) \quad (1)$$

where A_0 is the equilibrium area of system and E_g is the strain energy. Also, Poisson's ratio is expressed as the ratio of the transverse strain to the axial strain, i.e.

$$\nu = \frac{-\epsilon_{trans}}{\epsilon_{axial}} \quad (2)$$

Fig. 3 represents the strain energy of graphyne versus the applied strain in the harmonic region which can be taken between $-0.02 < \epsilon < 0.02$. After the harmonic region, an anharmonic phase happens where higher order terms can no longer be omitted in the strain energy equation. Using Eq. (1), the calculated value for surface Young's modulus of graphyne is obtained equal to 190 N/m. This value is in good agreement with the one reported in [18]. Moreover, considering the experimental value of 340 ± 50 N/m for surface Young's modulus of graphene [23], one can conclude that the stiffness of graphyne is approximately half of that of graphene. This can be attributed to the lower number of bonds in graphyne as compared to that of graphene. Also, the results show that Poisson's ratio of graphyne is 0.5.

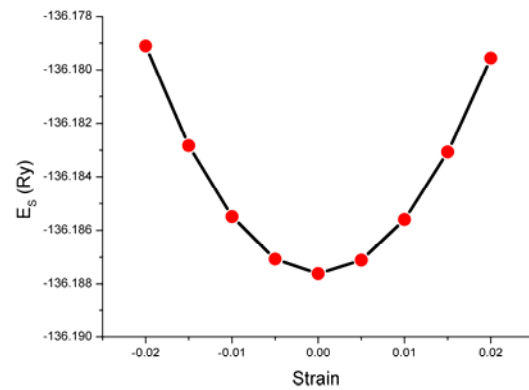


Fig. 3. Variation of the strain energy E_s with the strain of graphyne

3. Conclusion

The elastic properties of graphyne, a class of carbon allotropes with sp and sp^2 atoms, were theoretically predicted in this paper using a first-principles analysis. Based on DFT within the framework of GGA and using the exchange correlation of PBE, surface Young's modulus and Poisson's ratio of graphyne were calculated in the harmonic region equal to 190 N/m and 0.5, respectively. It was shown that graphyne is softer than graphene owing to its lower number of bonds. The present results were indicated to be in good agreement with the existing data from the literature.

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