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Anisotropic elastic modulus, high Poisson's ratio and negative thermal expansion of graphynes and graphdiynes

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ABSTRACT

Graphyne (GY) and graphdiyne (GDY) are two-dimensional one-atom-thick carbon allotropes highly considered to substitute graphene in electronic applications because of the prediction of non-null band-gap. There are multiple configurations of GY structures not yet fully investigated in literature. In this work, by means of classical molecular dynamics simulations, the Young's modulus, Poisson's ratio and linear thermal expansion coefficient (TEC) of all originally proposed seven types of GYs and corresponding GDYs are calculated. The dependence of these properties with the density of the structure is investigated for the first time. Quadratic increasing of the TEC of GY and GDY structures with density was found. The elastic modulus of GYs and GDYs were shown to be more sensitive to their density than general porous materials. In particular, non-symmetric structures are much softer along the armchair direction than along zigzag direction, implying that the elasticity along armchair direction of GY and GDY structures are similar to that of porous gels materials. Values larger than unity were found for the Poisson's ratio of some non-symmetric GYs and GDYs. A simple honeycomb mechanical model is shown to capture the observed values of Poisson's ratio of GYs and GDYs.

1. Introduction

Graphyne (GY) and graphdiyne (GDY) are two-dimensional one-atom-thick carbon allotropes whose structures can be imagined as simply formed by coherently replacing certain carbon-carbon bonds in a graphene hexagonal network by acetylenic (−C≡C−) and diacetylenic (−C≡C−C≡C−) linkages, respectively [1,2]. Although proposed in the 80s by Baughman et al. [3], GYs have got increasing interest in the last few years mainly because of the prediction of non-null band-gap for some types of GYs [1–7]. This indicates the possibility to use them in electronic nanodevices instead of graphene [7]. Generally speaking, GYs can be good electrical conductors or semiconductors [3–10], are predicted to present higher conductivity than graphene [11,12], have smaller in-plane stiffness than graphene, what depends on the number of acetylenic or diacetylenic linkages [13–26], and have much lower thermal conductivity than graphene [9,27–30]. Good electrical and poor thermal conductivity form a good combination for possible applications of GYs in thermoelectrics [27–28]. Besides, the presence of acetylenic and diacetylenic linkages introduces two-dimensional porosity to the GY and GDY structures. Combinations of all these interesting properties have inspired ideas on possible applications of GYs and GDYs such as on manufacturing nanotransistors, anodes in batteries, desalination, hydrogen storage, amongst others [1,2,31–35].

GYs have not been yet synthesized, but subunits of GY and GDY structures have been produced as reported in the literature [36–39]. The synthesis of GDYs has been claimed for a nanoscale film [40], tubes [41], and ordered stripe arrays [42]. Recently, the production of very thin stacks (24 nm thick) of multilayered GDY nanosheets has been reported [43]. It is worth to mention the work of Han et al. [44] which used first-principles methods to derive a chemical potential phase diagram of GYs and graphene in order to suggest the best experimental conditions for the synthesis of GYs.

Graphyne-based structures such as nanoribbons [45,46], nanotubes [47–52], AB stacking of α-graphynes (γ-graphynes) or the so-called "AB-α-graphityne" ("AB-γ-graphityne") [53], as well as functionalized GYs [54–57] have been also subject to study, mostly using first-principles methods.

In the literature, the most studied GY structures are the ones with prefixes called "γ-", "6,6,12-", "β-", and "α-"graphynes. Most of the papers about these structures performed their studies on individual GYs or GDYs, or families of the same type of graphynes having *one*, *two*, *three* or *more* adjacent acetylenic linkages (graphyne, graph*di*yne, graph*tri*yne, or graph"*more*"yne, respectively). However, although more recent studies have presented comparisons of some physical properties of more than one type of GY (see, for example, the Refs. [7,10,16,25]), here we are concerned with a more comprehensive and

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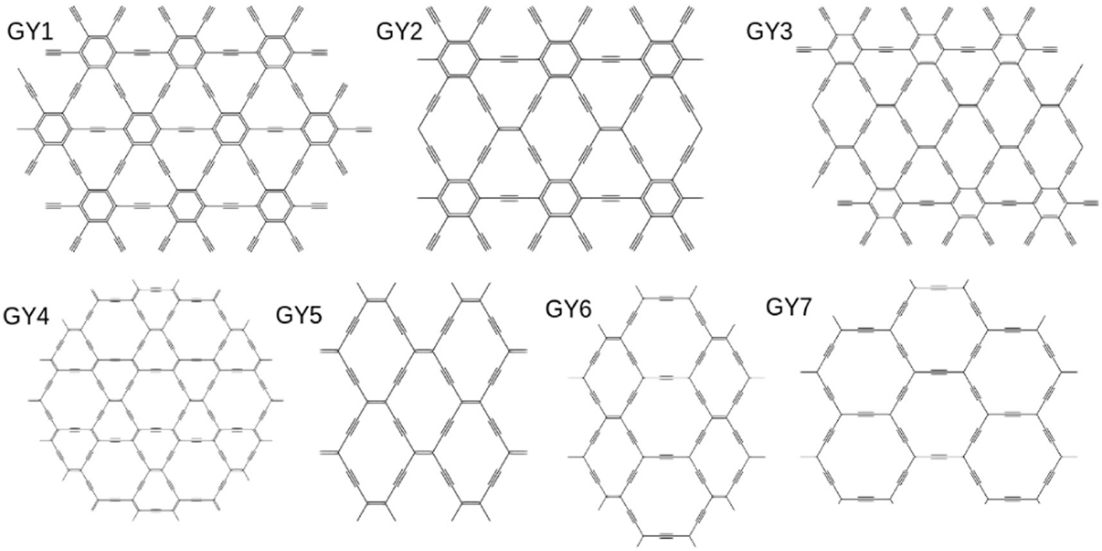

Fig. 1. The seven GY structures proposed by Baughman et al. [3]. Horizontal (x) and vertical (y) axes are called "armchair" and "zigzag", respectively. The numbering notation and sequence are the same as defined by Ivanovskii [1]. In the literature, GY1, GY2, GY4 and GY7 are called "γ-", "6,6,12-", "β-", and "α-"graphynes, respectively. Along the text, we will make use of both notations when comparing our results to those from literature. Corresponding GDYs from GDY1 to GDY7 are similar but with diacetylenic linkages instead of acetylenic ones.

comparative study of the Young's modulus (or in-plane stiffness in units of force per unit length), Poisson's ratio and linear thermal expansion coefficient (TEC) of the original seven types of GYs proposed by Baughman et al. [3], and the corresponding GDYs, as a representative subset of the most commonly researched structures in the literature, which includes more exotic possible configurations [58].

Fig. 1 shows the GY structures with the numbering notation defined by Ivanovskii [1] that will be adopt here for simplicity. The corresponding GDYs can be formed by changing the acetylenic to diacetylenic linkages and will have the same numbering notation.

Regarding the mechanical properties of graphynes, Chen et al. [11], Cranford and Buehler [13], and Zhang et al. [16] were the first to calculate the elastic modulus and/or fracture properties along armchair and zigzag directions of γ-, β- and α-graphynes (our GY1, GY4 and GY7 structures). Additionally, Chen et al. [11] and Zhang et al. [16] observed a strong anisotropy in the mechanical properties of the 6,6,12-graphyne (our GY2 structure). This result agrees with the observation that only 2D structures with square or hexagonal symmetries present symmetric elastic constants along armchair and zigzag directions [59]. This anisotropy was also observed in the electrical properties of 6,6,12-graphyne (or GY2) [7,10]. In speaking of anisotropy, Cranford and Buhler [13] reported about 18% of difference between armchair and zigzag Young's modulus of γ-graphyne. As γ-graphyne has hexagonal symmetry, this difference should not be so high.

Here, we investigate the anisotropy in the mechanical properties of all seven types of GYs and corresponding GDYs. As they are less dense than graphene, we also investigate their elastic modulus-density relationship. Non-symmetric GY and GDY structures will be shown to present an interesting dependence of their mechanical behavior on the direction along which the stress is applied.

Another interesting property of GYs, not fully explored yet, is the thermal expansion. The thermal expansion relates the variation of the dimensions of an object to the variation of temperature. It is known that graphene presents negative in-plane thermal expansion coefficient [60–68]. This thermal contraction has been attributed to large negative Grüneisen parameters related to out-of-plane acoustic modes that are predominantly excited at low temperatures [60]. Acoustic out-of-plane transversal modes are easily excited because of the planarity of graphene [66]. As graphynes are also two-dimensional structures, it is expected that they present negative TEC. To our knowledge, there are only three works reporting the calculation of the linear thermal expansion coefficient of graphynes [10,17,69] and except for the work of Reference [17] the other two [10,69] reported values of graphyne TEC up to one order of magnitude larger, in modulus, than that of graphene, at temperatures below or close to room temperature. All of these works used first-principles methods to calculate the TEC of graphynes. Here, we present the calculations of the linear TEC of all seven types of GYs and corresponding GDYs using classical molecular dynamics (MD) simulations. We show that the thermal contraction of GYs and GDYs are one order of magnitude larger than that of graphene.

We also calculated the Poisson's ratio of GYs and GDYs. Literature reported calculations of Poisson's ratio of α-graphyne [21,25,26], β-graphyne [25], γ-graphyne [18,20,24,25,70], α-graphdiyne [21,26], γ-graphdiyne [14,20,59] and the graphite-like structures AB-α-graphityne and AB-γ-graphityne [53], most of them from first-principles methods. Couto and Silvestre [24] reported a difference of about 7% between the calculated Poisson's ratio along two different directions of γ-graphyne. Here, by employing a methodology that does not assume any symmetry of the structures (as explained ahead), we verify these results, reveal the isotropy or anisotropy in the elastic properties of not yet studied GYs and GDYs, and show that some structures also possess values of Poisson's ratio above unity. A honeycomb mechanical model is considered to interpret these results for the Poisson's ratio of GYs and GDYs. Table 1 presents our results together with the existing literature values of Young's modulus and Poisson's ratio of all GY and GDY structures studied here.

2. Theory and computational methods

2.1. Linear thermal expansion coefficient (TEC)

The linear TEC, α, of a material is defined by:

$$\alpha_L(T) = \frac{1}{L}\left(\frac{dL}{dT}\right)_P, \qquad (1)$$

where $L = L(T)$ is the equilibrium length of the material at the absolute temperature T, under constant pressure P. Here, our calculations are made at zero pressure and we will omit this dependence from now on.

In order to calculate the TEC of the GYs and GDYs, the equilibrium lengths of the structure along x (armchair) and y (zigzag) directions as functions of the temperature T, $L_x(T)$ and $L_y(T)$ respectively (see Fig. 1 for the definition of "x" and "y" directions), must be obtained. Then, we