Nanomaterials for Aeroespace Applications: the Mechanical Behavior of Graphyne

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Abstract: Graphyne is an allotrope of carbon with excellent mechanical, electrical and optical properties, and its vastness of applications is yet to be unveiled. For this reason, the scientific community has been providing a great deal of attention during the last few years, especially in its characterization. Regarding the mechanical characterization, the present work aims to develop a reliable finite element model to simulate graphyne sheets. First, the covalent bonds and interatomic van der Waals forces are simulated through the use of beam and bar finite elements, respectively. The results extracted from two models (with and without van der Waals forces) are then compared to better understand the influence of different kinds of interatomic forces on the mechanical properties of graphyne. Then, the elastic properties of graphyne sheets (Young's moduli, Poisson's ratio, shear moduli and bulk modulus) are evaluated using finite element method for the first time. Finally, this thesis also includes for the first time the finite element simulation of a graphyne sheet under the influence of temperature. The results obtained from all simulations are subjected to comparison with previously obtained results from other works available in the literature, achieved through molecular dynamics and density functional theory simulations. The present model is able to correctly simulate the mechanical behavior of graphyne and successfully obtain its elastic properties.
Keywords: Finite Element Analysis, Graphyne, Mechanical Properties, Temperature.

1 – Introduction

Providing the basis for life on our planet, carbon is found in many known life forms. Its numerous hybridizations (sp, sp^2, sp^3) possessing strong chemical bonds display a rich variety of arrangements allied to the ability to bind to itself as it does to almost all elements. Besides the well-known crystalline forms carbon can take, as diamond and graphite, it also has numerous allotropes, namely, graphene, fullerenes, carbon nanotubes and several structures of graphyne (Katsnelson 2007). These allotropes have shown distinct mechanical (Roman and Cranford 2014), (McCarthy et al. 2014), electronic (Mak et al. 2012), (Lazic and Crljen 2015), chemical properties (Ren et al. 2015) and optical (Bhattachary et al. 2015) over the last years.

Graphene has been found to be one of the strongest materials ever tested while being only a monoatomic layer of carbon atoms in a honeycomb lattice (Lee et al. 2008). This carbon allotrope sheets can be rolled-up to later form fullerenes and carbon nanotubes. Nanotubes can be made with a single wall, thus being named as single-walled nanotubes, or several, being named as multi-walled nanotubes. They have shown evidence of an enormous amount of tensile strength (Lee et al. 2008) and excellent conduction of heat and electricity (Haskins et al. 2011).

After the discovery of graphene, plenty of two-dimensional materials were and still are proposed and simulated, experimentally or computationally. Graphene/boron nitride (Peng and De 2012), graphene oxide (Peng and De 2013), aluminum nitride monolayers (Peng et al. 2013) and hydrogenated graphene are some of the examples.

As for graphyne, it was predicted to exist, but it's quite hard to synthesize currently. However this material has a vastness of possibilities in terms of distinct structures. It's a one atom thick material much like graphene, but unlike graphene, this carbon allotrope can have between 33 and 100% acetylenic linkages in its composition. Among the most known geometries of graphyne are α, β and γ-graphyne. The aforementioned linkages have great influence both on its mechanical properties and heat conduction. In matter of electrical properties, this material displayed a band gap in the semiconductor range and this

band gap can be changed through mechanical strain (Narita et al. 1998), (Kang et al. 2011).

With such discoveries on the abovementioned carbon allotropes, extensive studies have been, are and will be conducted on exploring their properties and future applications. Either by experimental or computational means, until they can be synthesized in larger quantities.

2 – Outline

The efforts in this thesis will be directed towards the calculation of some of such properties using the finite element method (FEM). In resume, the following three objectives are assumed:

1. To develop a consistent finite element model to simulate the mechanical behavior of graphyne.
2. To calibrate this finite element model with results available in literature and obtained from either MD or DFT calculations.
3. To assess the influence of non-bonded forces (van der Waals forces) and temperature on the elastic properties of graphyne.

Regarding that many possible structures of graphyne could be assumed, γ-graphyne will be adopted for the present study. Hereafter, we shall designate γ-graphyne simply as graphyne. Hence, this work seeks to provide a new path to analyze this promising carbon allotrope. To the author's knowledge, this is the first work on the application of FE method to study graphyne mechanical properties.

3 – Methodology

3.1 – Model Description

A squared graphyne sheet is built in order to study its elastic properties. The sheet resembles that investigated by Cranford and Buehler (2011) using MD: each side is approximately 10 nm long – see the sheet geometry studied by Cranford and Buehler (2011) in Figure 1. The software chosen was Ansys Mechanical APDL 14.0 (2013). To simulate the interactions occurring between the carbon atoms, most known by the name of covalent bonds a suitable element was chosen in Ansys 14.0® (2013), hence element Beam4 was used. The base model, which is here designated as *Reference Model*, will account for three different types of covalent bonding, being them (i) aromatic, (ii) single and (iii) triple. Aromatic, single and triple bond length are 1.49, 1.48 and 1.19 Å, respectively. Such bond lengths were assumed to be the same as Cranford and Buehler (2011) applied on their molecular dynamics simulations (Cranford and Buehler 2011).

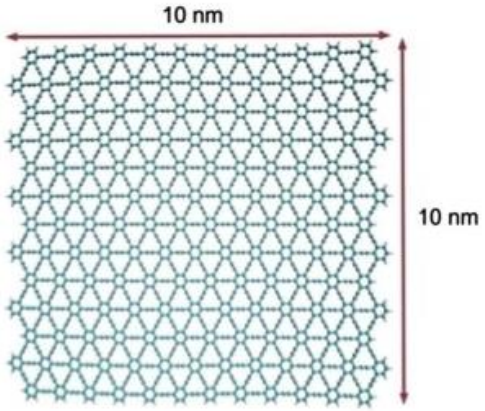


Figure 1 - Geometry of graphyne sheet studied by Cranford and Buehler (2011) using MD

To obtain the covalent forces being exerted by the interatomic bonds the formulation proposed by Odegard et al. (2002a) was followed, which was successfully implemented to evaluate the stiffness of CNTs and graphene. Therefore, to calculate the bond-stretching interaction Young's Modulus, Eq. 1 was used as follows

$$E^{\alpha}A = 2K^{\rho}L \tag{1}$$

which depends on bond length (L), cross-sectional area (A) and the stretching force constant (k^{ρ}). According to Odegard et al. (2002a), this constant has a value of k^{ρ}=469 Kcal/mol/Å^2. Besides the C-C bond-stretching interaction, the bond-angle variation interaction also should be taken into account when calculating the bond-angle interaction Young's Modulus, given by

$$E^{\beta}A = \frac{32K^{\theta}}{L}\left[\sin\frac{\Theta}{2}\right]^2 \tag{2}$$

This equation is applied to calculate bond-angle interaction Young's Modulus for each one of the three covalent bonds. In this equation, and besides the bond length (L) and cross-sectional area (A), it also depends on the undeformed bond angle (Θ) and the angle variation constant (k^{Θ}), which is k^{Θ}=63 Kcal/mol/rad^2, according to Odegard et al.

(2002a). It should be noted that Θ is purely dependent on the angle between two adjacent covalent bonds, acting on the same carbon atom.

It is now important to mention that both equations (1) and (2) give the axial stiffness (EA) of a given C-C bond. Therefore, the calculation of E is dependent on the value of cross-section area while the opposite is also true (the value of A depends on the value of E). In conclusion, what really matters is the axial stiffness value (EA) and not the individual values of E and A. Therefore, we start by assuming that the cross-section area of the beam is equal to A=1 $Å^2$ (note that 1Å=0.1nm). These properties should be inserted on the APDL code to sucessfully generate the model, along with the total Young's modulus of each covalent bond.

It's important to define the direction of the material before providing further information about the model to be simulated, hence Fig. 2 is shown.

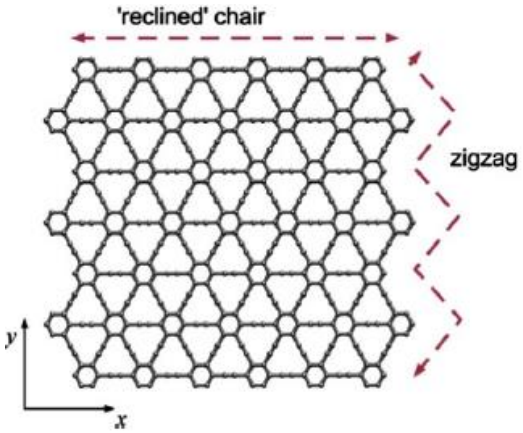


Figure 2 - Definition of the geometry of graphyne edges (Cranford and Buehler 2011)

The finite element model previously described (*Reference Model*) accounted for bonded interactions between carbon atoms. However, it is known that forces exerted between atoms may also be due to non-bonded interactions. These forces are designated as *van der Waals* (vdW) forces and are due to the proximity between atoms, regardless of being bonded or not.

The model we now present accounts not only for bonded interactions but also for non-bonded interactions. Because it will include the effect of *van der Waals* (vdW) forces, it is designated as *vdW Model* (Fig. 4). vdW forces tend to be relatively weak compared to the forces due to the covalent bonds (Granta 2015). With this second model, we'll attest the veracity of this statement applied to the graphyne. The *vdW Model* was built following the same steps as before, but now vdW forces are added to the Reference Model (Fig. 3).

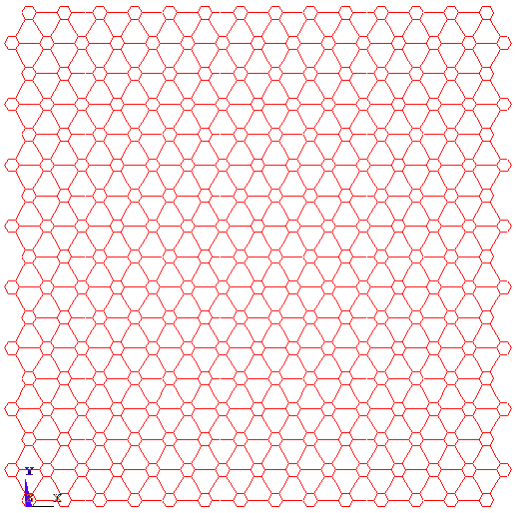


Figure 3 - Reference Model: graphyne sheet with covalent bonds

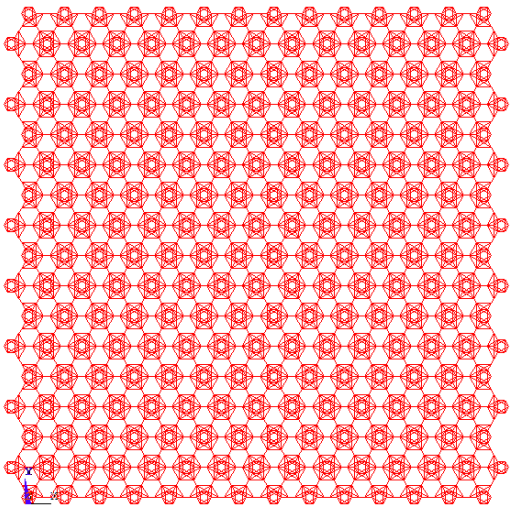


Figure 4 - vdW Model: graphyne sheet with both covalent and vdW bonds

To do so, a new finite element was chosen specifically to simulate the effect of these forces, and how a carbon atom will interact with its neighbor carbon atoms on the presence of such vdW contribution. The finite element chosen in Ansys 14.0® (2013), is designated Link180. Having the element selected, some geometrical properties should be given. They are the cross section area A and Poisson's ratio. As for Poisson's ratio, once again it was assumed a value of zero. Regarding the calculation of mechanical properties, the bar axial stiffness due to vdW interaction is also obtained from the formulation by Odegard et

al. (2002a), following the well-known 12-6 potential of Lennard-Jones,

$$E^w A = \frac{2\rho^{ij} D^{ij}}{\left(\rho - \rho^{ij}\right)^2}\left[\frac{1}{2}\left(\frac{\rho^{ij}}{\rho}\right)^{12} - \left(\frac{\rho^{ij}}{\rho}\right)^{6}\right] \quad (3)$$

$$D^{ij} = \sqrt{D^i D^j} \qquad \rho^{ij} = \sqrt{\rho^i \rho^j} \quad (4)$$

in which (i) the deformed interatomic distance is ρ, (ii) the well depth of interaction between carbon atoms i and j is D^{ij}, and (iii) the vdW equilibrium distance for interaction between carbon atoms i and j is ρ^{ij}. The aforementioned variables (defined via Eqs. 4) are quite useful in case the different interacting atoms. In this case, because only carbon atoms exist, $D^{ij}=D^i=D^j$ and $\rho^{ij}=\rho^i=\rho^j$. In the case of carbon, Odegard et al. (2002a) stipulate D^{ij} = 0.07 Kcal/mol and ρ^{ij} = 3.55 Å.

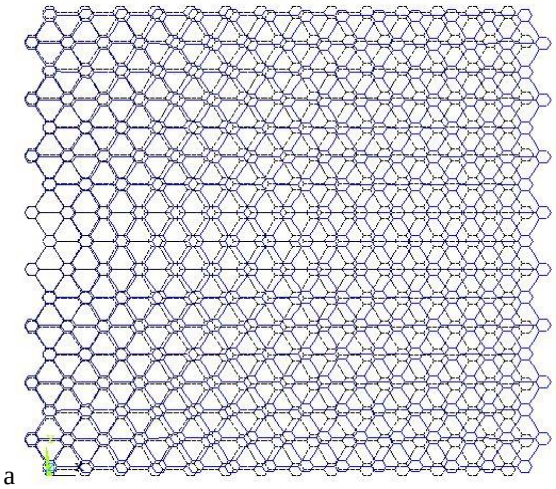
3.2 – Boundary and Loading Conditions

With the graphyne sheet modeled on Ansys 14.0®, boundary conditions should imposed in order to study its mechanical properties. Therefore, four main tests were performed to both models of the graphyne sheet:

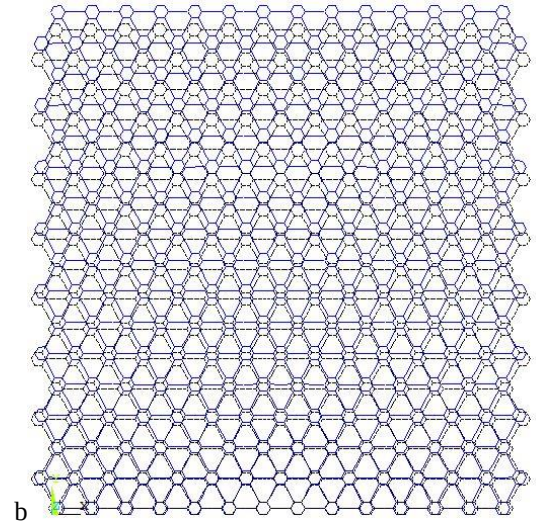
- Uniaxial tensile test in the armchair direction (X-axis) – the graphyne elastic modulus E_x and Poisson's ratio ν_{yx} will be determined from this test.
- Uniaxial tensile test in the zigzag direction (Y-axis) – the graphyne elastic modulus E_y and Poisson's ratio ν_{xy} will be determined from this test.
- Biaxial tensile test (XY-plane) – the graphyne bulk modulus K will be determined from this test.
- Shear test (XY-plane) – the graphyne shear modulus G_{xy} will be determined from this test.
- Such analyses must be done using the graphyne sheet with covalent bonds only (Reference Model, Fig. 3) and the graphyne sheet with both covalent bonds and vdW forces (vdW Model, Fig. 4). In total and after the APDL codes were written to every different case, we should had eight distinct programs.

3.3 – Results and Discussion

Firstly, the best way to confirm if the simulations were running smoothly was to plot the graphyne sheet before and after being stretched/sheared by the applied forces. Such images, are presented in Fig 5 for the four tests (in case of Reference Model).



a



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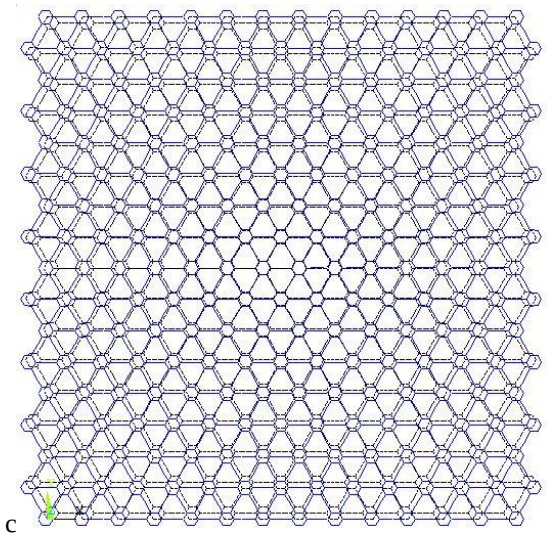

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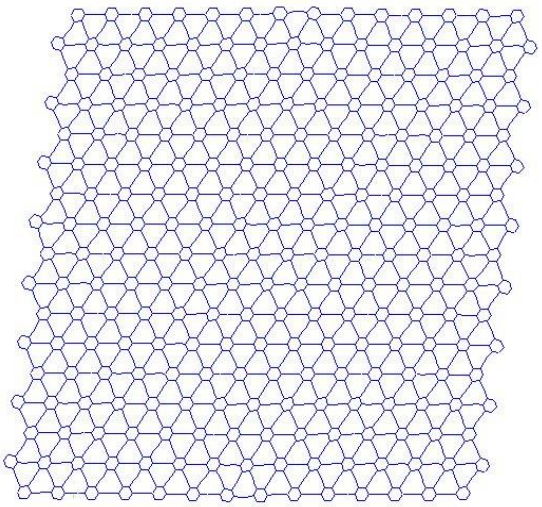

d

Figure 5 - Initial and deformed shapes of graphyne sheet (Reference Model): a) uniaxial tensile test on armchair direction, b) uniaxial tensile test on zigzag direction, c) biaxial tensile test, d) shear test

With all the results regarding deformations adopted by the allotropes sheet during the simulations, we can finally achieve the main objective: to obtain the elastic properties of graphyne. Before that, we know that since graphyne is a discrete atomic structure, it has no real thickness (like continuous plates or shells have). In this case, the values of elastic modulus are given in N/m (Yang and Xu 2012). However, being a 2D material, some similarity with plates and shell exist. In this case, a thickness of 3.2 Å is usually adopted. With this, we are able to calculate the elastic modulus values in GPa (or TPa) and compare with those obtained by Cranford and Buehler (2011) and Zhang et al. (2012). To obtain the results of Young's Modulus in GPa, one must divide the stress σ (obtained in N/m) by the thickness t=3.2 Å. This value comes from adhesion energy results, presented in Cranford and Buehler (2011).

Bear in mind the results shown at Table 1 from other authors were previously obtained by means of molecular dynamics (MD) ot density functional theory (DFT) simulations.

The observation of the results shown in Table 1 shows that we are in the presence of an orthotropic material, as the values of Young's modulus in armchair (X-axis) and zigzag (Y-axis) directions are not equal. Their difference is roughly 20 N/m, which corresponds to 9.5%. Comparing the graphyne Young's modulus with that of graphene which has around 325 N/m in armchair direction and 315 N/m in zigzag direction according to Yang and Xu (2012), we easily conclude that graphyne is a more flexible (less stiff) material than graphene. Bearing in mind that graphene is also slightly orthotropic, the percentage difference is higher for graphyne than for graphene. It should also be highlighted that graphyne is stiffer in the armchair direction than in the zigzag one ($E_x > E_y$).

Regarding the Poisson's ratio, it can be concluded that graphyne exhibits a high transversal contraction in both directions, as the Poisson's ratio varies around 0.40. Because the Poisson's ratio becomes smaller for the zigzag direction of the graphyne sheet than for its armchair direction ($\nu_{yx} > \nu_{xy}$), one can conclude that graphyne has also orthotropic behavior regarding the transversal contraction. In this case, the percentage difference (about 6.5%) is even smaller than for the Young's moduli (about 9.5%).

Table 1 – Mechanical Properties of Graphyne

Property	Reference Model	vdW Model	Cranford and Buehler (2011)	Zhang et al. (2012)	Yang and Xu (2012)	Asadpour et al. (2015)	Units
E_x	228.4 (713.7)	229.9 (718.5)	201.4 (629.4)	(508.0)	~155.0	190.69	N/m (GPa)
ν_{yx}	0.421	0.421				0.410	-
E_y	208.5 (651.6)	209.8 (655.7)	247.0 (772.0)	(505.0)	~150.0	-	N/m (GPa)
ν_{xy}	0.396	0.396	-	-	-	-	-
K	164.5	165.5	-	-	-	122.7	N/m
G_{xy}	70.5	71.0	-	-	-	77.0	N/m

In order to validate our finite element model, we compare our results with those obtained by other researchers. These results comprise MD results using AIREBO potentials (Cranford and Buehler 2011, Zhang et al. 2012, Yang and Xu 2012, Hou et al. 2015), or using generalized gradient approximation (Asadpour et al. 2015). The few results available in the literature are more accurate than ours because these methods take into account many other parameters involved in atomic scale. Our model can be viewed as an approximation to these MD models. Nevertheless, it can be concluded, from the observation of Table 1, that the elastic properties of graphyne derived from our finite element model are fairly comparable to those more rigorous ones.

Furthermore, similarly to the results by Zhang et al. (2012) and Yang and Xu (2012), we also attained a Young's modulus for the zigzag direction slightly smaller than that for armchair direction. Yet, the results by Cranford and Buehler (2011) are in disagreement with ours and those by Zhang et al. (2012) and Yang and Xu (2012): the Young's modulus they obtained for the zigzag direction was higher than the value for the armchair direction. On the other hand, the absolute difference between both Young's moduli (armchair and zigzag) determined by Cranford and Buehler (2011) is higher than ours, but with opposite trend. The absolute difference between both Young's moduli (armchair and zigzag) determined by Zhang et al. (2012) and Yang and Xu (2012) is much lower than ours, but with the same trend. Comparing the resulting in-plane bulk modulus of graphyne, we can observe that although being somewhat different, our value is of the same order of magnitude of that presented by Asadpour et al. (2015). Finally, the obtained shear modulus result is remarkably close to the one obtained by Asadpour et al. (2015). Furthermore, Hou et al. (2015) analyzed the shear behavior of several graphyne sheet configurations and got a value of around 75 N/m for shear modulus, which also agrees very well with the one obtained from our finite element model.

4 – Temperature effect on Graphyne

4.1 – Model Description

To study the graphyne behavior under different temperatures, we use the Reference Model developed in the previous chapter with some adjustments. The number of atoms, covalent bonds and its bond types are exactly the same. This means that the beam elements (Beam4) simulating the forces between atoms are the same, as well the geometrical configuration of the model.

The calculation of the covalent forces acting between each pair of carbon atoms took place on Chapter 3 recurring to the molecular mechanics model proposed by Odegard et al. (2002a). However, the previously studied models confined our study of the mechanical properties to a constant value of temperature. Therefore, we shall develop a finite element model that can take into account the variation of temperature. To fulfill this task, we will apply the equations proposed by Zhang et al. (2007). In their work, they studied the effect temperature variation (from 0 to 600 K) on the mechanical properties of carbon nanotubes. Although their objective was not to study graphyne, their molecular mechanics model enables us to calculate the interatomic bond force constants depending on the temperature. Thus, such equations shall be presented next.

According to Zhang et al. (2007), the bond-stretching force constant can be obtained from

$$K_{ij}^{T} = 2G\frac{Z_i^* Z_j^*}{\left(r_{ij}^{T}\right)^3} \tag{5}$$

where G = 332.06, r_{ij}^{T} is the bond length between atoms i and j, and Z_i^* and Z_j^* are the nuclear effective charges of these atoms. According to Zhang et al. (2007), the bond-bending force constant is taken from

$$K_{ijk}^{T} = 2GZ_i^* Z_k^* r_{ij}^{T} r_{jk}^{T} \frac{\left[2\left(r_{ij}^{T}\right)^2 \cos\theta + r_{ij}^{T} r_{jk}^{T}(\cos 2\theta - 5) + 2\left(r_{jk}^{T}\right)^2 \cos\theta\right]}{2\left[\left(r_{ij}^{T}\right)^2 - r_{ij}^{T} r_{jk}^{T}\cos\theta + \left(r_{jk}^{T}\right)^2\right]^{5/2}}$$

where θ is the angle between C-C bonds and r_{jk}^{T} is the bond length between atoms j and k.

The superscript T means those variables that are dependent on temperature, whereas the others depend only on the position and geometry of the atoms and its inherent connections. The angle θ, depends solely on the position of the carbon atoms, but Z_i^*, Z_j^* and Z_k^* are described by the abovementioned force constant equations solved for environmental temperatures. This happens as a consequence

Table 2 - Mechanical Properties of Graphyne under Temperature Influence

Property	**0**	**300**	**600**	**Units**
E_x	270.550 (807.612)	269.115 (803.328)	268.315 (800.940)	N/m (GPa)
ν_{yx}	0.4339	0.4344	0.4347	
E_y	246.592 (736.096)	245.320 (732.299)	244.609 (730.176)	N/m (GPa)
ν_{xy}	0.4099	0.4103	0.4106	
K	198.032 (594.140)	197.541 (589.675)	196.99 (588.030)	N/m (GPa)
G_{xy}	78.772 (235.140)	78.329 (233.818)	78.087 (233.096)	N/m (GPa)

of the small variation experienced by the nuclear effective charges even when there are large changes on the bond lengths, as said by Badger (1935). As for the values of the bond stretching and bond bending force constants, both were obtained in 1995 by Cornell et al.

Hence, considering environment temperature as 300K, we have $K_{ij}^{300K} = 469\,Kcal/mol/\text{Å}^2$ and $K_{ijk}^{300K} = 63\,Kcal/mol/rad^2$.

To solve the required equations, we now only need the values of bond length and angles. Zhang et al. (2007) in their paper present the much needed values, but only for the aromatic bonds, since they were studying the mechanical properties on nanotubes. To adjust their model to our needs, we had to calculate the bond length of the single and triple bonds beforehand.

To obtain the Young's modulus interaction on every interatomic bond, Eq. 1 and 2 must be adapted to accomodate the environmental change of temperature.

$$E_s^T = \frac{2K_{ij}^T . r_{ij-jk}^T}{A} \quad (7)$$

$$E_b^T = \frac{32K_{ijk}^T}{A.r_{ij-jk}^T}\left[\sin\frac{\Theta}{2}\right]^2 \quad (8)$$

Performing once more the simulations required to obtain the results of elastic properties, now with the influence of temperature, Table 2 was built.

4.2 – Results Discussion

When we first compare the obtained results from Chapter 3 with the ones we just got, we can conclude that even if the method to obtain such results is partially different, namely the equations used to calculate the interatomic bond force constants, the graphyne sheet shows a similar behavior. The armchair Young's modulus is still higher than the one on zigzag direction, now both values differ by ~25 N/m. Thus, graphyne it's an orthotropic material for this range of temperature at least.

Although the graphyne model presented on this chapter is stiffer, according to the results, than the one previously used on Chapter 3 and 4, it shows a bigger Poisson's ratio. On top of that, the shear modulus is only slightly bigger (~10%) than previously for any value of temperature. Which is an indicator of graphyne's elasticity. The reason for such difference in values comes from the assumed bond lengths. For this chapter analysis, we used the same bond lengths as Zhang et al. (2007), while in Chapter 3 the bond lengths were extracted from Cranford and Buehler (2011). Since Eqs. 7 and 8 use the same variables as Eqs. 1 and 2, even if the bond force constants are the same (which happens for room temperature) the resulting bond stiffness will be increased, resulting in higher values of graphyne's elastic properties.

While the sheet Young's modulus experience a steeper decrease between 0 and 300 K, in its values, behavior that is similar on the shear modulus, the Poisson's ratio increases

accordingly. As for the in-plane bulk modulus, there's a faster decrease on its value between 300 and 600 K. However, the differences on every property are rather small and such event is supported by the fact that every bond length was calculated based on carbon nanotubes bond lengths (Zhang et al. 2007). Distinct bonds should have different behaviors within the same range of temperatures, which means the acetylenic linkages ought to have quite different deformations.

Having access to the few results available from other authors, we'll now present their results so we can better compare with what we have. On Fig. 6 we have images regarding DFT calculations effectuated by Shao et al. (Shao et al. 2012). The right image shows the variation on the Young's modulus experienced by their simulation of a graphyne sheet, within a range of temperatures. As for the left image, it shows the elastic constants C_{11} and C_{12}, needed to obtain the values of Poisson's ratio, bulk and shear modulus. Comparing their results in terms of Young's modulus with ours, we're able to find the same pattern of events, with a slight decrease on its values from 0 to 600 K. Quantitatively, we can say that their Young's modulus is lower than ours for all range of temperatures. This fact corroborates the already mentioned distinct effect of temperature on the dilatation of the acetylenic linkages in relation with the aromatic bonds, all composing the graphyne.

From the left image, values of bulk and shear modulus can be extracted, within the range of temperatures we're interested in, as well as Poisson's ratio. Through simple calculations the results were obtained.

This author's results show some disparity, quantitatively speaking compared to ours in terms of Poisson's ratio and bulk modulus, the first value being half of ours, while the last is nearly 35% less. Following the logic of Young's modulus results, the material will become more flexible at higher temperatures. Qualitatively, the bulk modulus follows this logic, hence decreasing its value from 0 to 600 K. The same, however doesn't happen to the shear modulus, as it shows a peak for environment temperature, 300 K. Oddly enough, the Poisson's ratio decrease, unlike ours. Sadly, this is the only source we've found with such results for comparison.

Therefore, we have good agreement on the Young's and bulk modulus behavior with this author, even if the values itself are higher in our case.

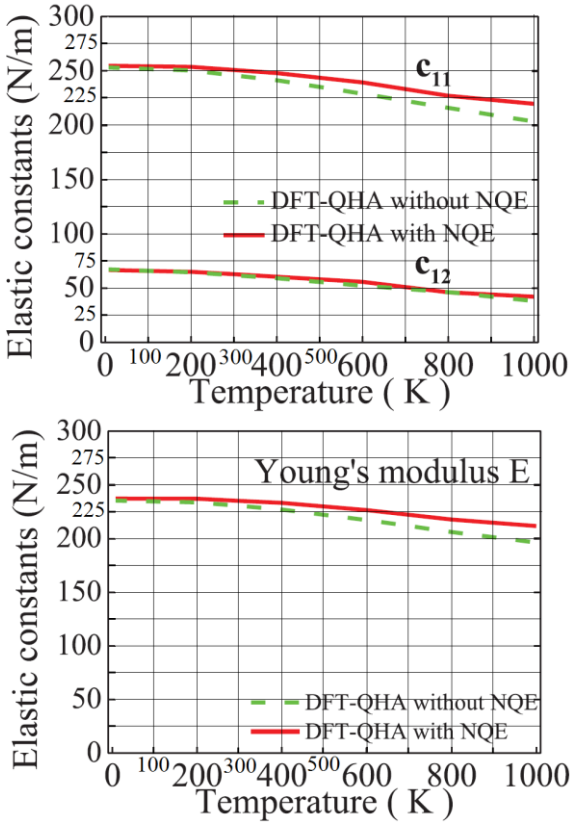

Figure 6: Elastic constants C_{11}, C_{12} and Young's modulus obtained by Shao et al. (Shao et al. 2012).

5 – Conclusions and Future Developments

This thesis explored the mechanical properties of graphyne, through the construction of a suitable FEM model that could study the mentioned properties variation with the imposition of certain forces and later temperatures.

The main findings of this thesis, can be summarized in brief:

- The influence of van der Waals interatomic forces on the elastic properties of graphyne is negligible and can be disregarded unless the covalent bonds undergo large deformations before breaking.
- The finite element models of graphyne developed in this work proved to be simple but fairly accurate. The mechanical properties (Young's modulus, Poisson's ratio, bulk modulus, shear modulus) obtained from the developed models were in agreement with those previously obtained by other authors using much more complex computational models (MD or DFT).

Furthermore, the finite element model showed that graphyne exhibits orthotropic behavior, a fact that agrees with previous conclusions of other researchers.

- The present finite element model showed the temperature influence on the graphyne sheet had little impact on its elastic properties, hence it can be disregarded within the range of temperatures (0K to 600K).
- As for the obtained results, the present work agrees qualitatively well with the results available in the literature, showing a small decrease in graphyne's mechanical properties with a temperature increase. Quantitatively, our results showed to be higher than those found in the literature. The reason for this evidence has to do with the assumed bond lengths that were based on bond lengths acting on carbon nanotubes. As we know, the nanotubes in general, being made of graphene or graphyne, display shorter bond lengths than the plain sheet of the same material, and looking at the equations in Chapter 4, we can easily understand they are highly dependent on the bond length imposed.

After the presentation of this work, it is believed there are still many and interesting improvements to be done in these finite element models, as well as other future developments. These include:

- Incorporation of nonlinear stiffness variation with the interatomic distance in bar elements, so that van der Waals stiffness may vary with the distance between atoms and allow an exact representation of Leonard-Jones 12-6 potential.
- Development of similar models for sheets with increasing size and defining the optimum sheet dimensions, i.e. those that minimize the number of degrees of freedom and guarantee convergence of results.
- Development of similar models for sheets with chiral orientations, i.e. sheets for which the natural directions (armchair and zigzag) are not oriented with the directions of sheet edges.
- Introduction of failure criteria in bond material properties (elasticity limits) and find the strength properties of graphyne.
- Study of graphyne mechanical behavior for a larger range of temperatures.
- Implementation of a model to study the elastic properties of stacking sheets of graphyne, both with the same and different orientations.

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Bibliography

Asadpour M, Malakpour S, Faghihnasiri M, Taghipour B (2015) Mechanical properties of two-dimensional graphyne sheet, analogous system of BN sheet and graphyne-like BN sheet. Solid State Com 212 (2015) 46-52

Aykol M, Hou B, Dhall R, Chang SW, Branham W, Qiu J, Cronin SB (2014) Clamping Instability and van der Waals Forces in Carbon Nanotube Mechanical Resonators. Nano Lett. 14 (2014) 2426-2430

Baimova JA, Liu B, Dmitriev SV, Zhou Kun (2015) Mechanical properties of crumpled graphene under hydrostatic and uniaxial compression. J Phys D: Appl Phys 48 (2015) 095302

Baughman RH, Eckhardt H (1987) Structure-property predictions for new planar forms of carbon: Layered phases containing sp^2 and *sp* atoms. J Chem Phys 87 (11)

Bhattachary B, Singh NB, Sarkar U (2015) Pristine and BN Doped Graphyne Derivatives for UV Light Protection. Int J Quantum Chem 115 (2015) 820-829

Choudhary V, Gupta A (2011). Polymer/Carbon Nanotube Nanocomposites, Carbon Nanotubes - Polymer Nanocomposites, Dr. Siva Yellampalli (Ed.), ISBN: 978-953-307-498-6, InTech, DOI: 10.5772/18423

Cornell WD, Cieplak P, Bayly CI. Gould IR, Merz KM, Jr., Ferguson DM, Spellmeyer DC, Fox T, Caldwell JW, Kollman PA (1995) A Second Generation Force Field for the Simulation of Proteins, Nucleic Acids and Organic Molecules. J Am Chem Soc 1995, 117, 5179-5197

Cranford SW, Buehler MJ (2011) Mechanical properties of graphyne. Carbon 49 (2011) 4111-4121

Gong L, Kinloch IA, Young RJ, Riaz I, Jalil R, Novoselov KS (2010) Interfacial Stress Transfer in a Graphene

Monolayer Nanocomposite. Adv Mater 2010, 22, 2694-2697
Gong T, Lam DV, Liu R, Won S, Hwangbo Y, Kwon S, Kim J, Sun K, Kim JH, Lee SM, Lee C (2015) Thickness Dependence of the Mechanical Properties of Free-Standing Graphene Oxide Papers. Adv Func Mater 2015, 25, 3756-3763
Hou J, Yin Z, Zhang Y, Chang T (2015) An Analytical Molecular Mechanics Model for Elastic Properties of Graphyne-n. J App Mech 82 (2015) 094501-4
Hu M, Jing Y, Zhang X (2015) Low thermal conductivity of graphyne nanotubes from molecular dynamics study. Phys Rev B 91 155408 (2015)
Iijima S (1991) Helical microtubules of graphitic carbon. Nature 1991;354: 56–58
Jing Y, Wu G, Guo L, Sun Y, Shen J (2013) Electronic transport properties of graphyne and its family. Comp Mat Science 78 (0213) 22-28
Kang J, Li J, Wu F, Li SS, Xia JB (2011) Elastic, Electronic and Optical Properties of Two-Dimensional Graphyne Sheet. J Phys Chem C 2011, 115, 20466-20470
Odegard GM, Gates TS, Wise KE, Park C, Siochi EJ (2002) Constitutive modeling of nanotube-reinforced polymer composites. Comp Science Tech 63 (2003) 1671-1687
Odegard GM, Gates TS, Nicholson LM, Wise KE (2002) Equivalent-continuum modeling of nano-structured materials. Comp Science Tech 62 (2002) 1869-1880
Peng Q, Dearden AK, Crean J, Han L, Liu S, Wen X, De S (2014) New materials graphyne, graphdiyne, graphone and graphane: review of properties, synthesis and application in nanotechnology. Nanotech Science and Appl 2014:7 1-29
Seidel GD, Chatzigeorgiou G, Ren X, Lagoudas DC (2014) Multiscale Modeling of Multifunctional Fuzzy Fibers Based on Multi-Walled Carbon Nanotubes. Modeling of Carbon Nanotubes, Graphene and their Composites 135-176
Shao T, Wen B, Melnik R, Yao S, Kawazoe Y, Tian Y (2012) Temperature dependent elastic constants and ultimate strength of graphene and graphyne. J Chem Phys 137, 194901 (2012)
Tserpes and Papanikos (2013) Finite Element Modeling of the Tensile Behavior of Carbon Nanotubes, Graphene and Their Composites. Modeling of Carbon Nanotubes, Graphene and their Composites 303-329
Zhang YY, Pei QX, Wang CM (2012) Mechanical properties of graphynes under tension: A molecular dynamics study. Appl Phys Lett 101, 081909 (2012)
Zhang YC, Chen X, Wang X (2007) Effects of temperature on mechanical properties of multi-walled carbon nanotubes. Comp Sci Tech 68 (2008) 572-581
Zhang YY, Pei QX, Mai YW, Gu YT (2014) Temperature and strain-rate dependent fracture strength of graphynes. J Phys D: Appl Phys 47 (2014) 425301