Elastic modulus of defected graphene sheets

J Bocko and P Lengvarský

Department of Applied Mechanics and Mechanical Engineering, Technical University of Košice, Letná 1/9, 042 00 Košice, Slovakia

E-mail: jozef.bocko@tuke.sk

Abstract. In this paper, the elastic modulus of single-layered graphene sheets (SLGSs) with and without defects is investigated using the finite element method. The SLGSs with two chiralities (armchair and zigzag) are modeled by beam elements. At first, the SLGSs without defects are investigated then the carbon atoms and corresponding beam elements are removed and the elastic modulus of SLGSs is determined. The increasing number of defects apparently decreased the elastic modulus of graphene sheets.

1. Introduction

Graphene sheet is a two-dimensional plate of carbon atoms organized in a honeycomb structure. The carbon atoms are connected by sp2 hybridization. This connection makes graphene sheets with high tensile strength and elastic modulus [1–3]. The basic approach was based on the creation of the connection between the MD and the continuum mechanics. This approach was established by Li and Chou [2] for simulation of graphene sheets and carbon nanotubes. They used a beam element for modelling of interatomic bonds between two adjacent carbon atoms. Simultaneously with these papers [2,4] started the investigation of Young’s modulus and other material properties of graphene sheets [3] and CNTs by FEM. Marenić et al. [5] investigate the quantification of the linear and non-linear elastic mechanical properties of graphene sheets based on the judicious combination of molecular mechanics simulation results and homogenization methods. Hartmann et al. [6] investigated the material properties of graphene sheets by the atomistic simulation approach. They computed Young’s modulus, Poisson’s ratio and thickness of graphene from the finite element computations. The beam elements for modeling nanostructures were used by Tserpes and Papanikos [7]. Wang et al. [8] investigated the effect of Stone-Wales type defects and vacancies to fracture strength of graphene. The stochastic material properties and different types of defect was investigated by Savvas and Stefanou [9]. The categorize defects, emphasize their importance and introduce their new ways was mentioned in review article [10].

In this paper, the elastic modulus of single-layered graphene sheets (SLGSs) with and without defects is investigated using the finite element method. The SLGSs with two basic chiralities (armchair and zigzag) are modeled by beam elements. At first, the SLGSs without defects is investigated then the carbon atoms are removed and the elastic modulus and membrane stiffness of SLGSs is compared.
2. Analysis of the single layer graphene sheet

At first, the connection between molecular mechanics and structural mechanics is defined. The interatomic interactions (figure 1) are replaced by the classic loading states in structural mechanics (figure 2). The analysis of the SLGSs is performed for the two configurations called as armchair \((n,n)\) and zigzag \((n,0)\), with different lengths in nanometers. All configurations of the SLGSs are modeled by the beam elements. These represent covalent bonds in the SLGSs and their nodes represent carbon atoms (figure 3).

At first, the graphene sheet in the molecular mechanics is represented by the total steric potential energy. This energy is sum of all energies due to valence or bonded interactions and non-bonded interactions and is equal

\[
U_{\text{total}} = \sum U_r + \sum U_\theta + \sum U_\phi + \sum U_\omega + \sum U_{\text{vdw}},
\]  

(1)

where \(U_r, U_\theta, U_\phi, U_\omega, U_{\text{vdw}}\) are a bond stretch interaction, a bond angle bending, a dihedral angle torsion, an improper (out of plane) torsion, a non-bonded van der Waals interaction, respectively.

\[ \text{Figure 1. Interatomic interactions in molecular mechanics.} \]

\[ \text{Figure 2. Tension, bending and torsion of an element.} \]
Then, the main contribution for the SLGSs is only from the first four terms of equation (1). From this statement, we can write equations

\[ U_r = \frac{1}{2} k_r (r - r_0)^2 = \frac{1}{2} k_r (\Delta r)^2, \]  
\[ U_\theta = \frac{1}{2} k_\theta (\theta - \theta_0)^2 = \frac{1}{2} k_\theta (\Delta \theta)^2, \]  
\[ U_\tau = U_\theta + U_\alpha = \frac{1}{2} k_\alpha (\Delta \phi)^2, \]  

where \( k_r, k_\theta, k_\alpha, \Delta r, \Delta \theta, \Delta \phi \) are the bond stretching force constant, bond angle bending force constant, torsional resistance, the bond stretching increment, the bond angle change and the angle change of bond twisting, respectively [2,4].

We can conclude that the section of the beams which represent carbon-carbon bonds is circular, identical and moments of inertia are equal. Then we obtain basic stiffness parameters as \( EA, EI \) and \( GJ \) from connection between molecular mechanics and continuum mechanics as

\[ U_A = \int_0^L \frac{1}{2} N^2 dL = \frac{1}{2} \frac{N^2 L}{EA} = \frac{1}{2} \frac{EA}{L} (\Delta L)^2, \]  
\[ U_M = \int_0^L \frac{1}{2} M^2EI d\alpha^2 = \frac{2EI}{L} \alpha^2 = \frac{1}{2} \frac{EI}{L} (2\alpha)^2, \]  
\[ U_T = \int_0^L \frac{1}{2} T^2GJ d\beta^2 = \frac{1}{2} \frac{T^2 L}{GJ} = \frac{1}{2} \frac{GJ}{L} (\Delta \beta)^2, \]  

where \( U_A \) is the strain energy of a uniform beam of length \( L \) subjected to axial force \( N \), \( \Delta L \) is axial elongation, \( U_M \) is the strain energy of a uniform beam under bending moment \( M \), \( \alpha \) is the rotational angle at the ends of the beam, \( U_T \) is the strain energy of a uniform beam under tension \( T \) and \( \Delta \beta \) is the relative rotation between the ends of the beam [2,4].

Finally, the input properties of the beam elements (figure 3) are obtained from this connection. The diameter of the beam element is \( d = 0.1466 \) nm, the length of the beam element is \( L = 0.142 \) nm (the distance between two carbon atoms is \( a_{C-C} = 0.1421 \) nm), the elastic moduli of the beam elements are \( E = 5.4875 \) TPa and \( G = 0.871 \) TPa.

The elastic modulus is computed from the elongation of graphene sheets with one end restrained in axial direction and the other end stretched in axial direction by prescribed displacement. The elastic modulus of SLGSs is obtained from relation

\[ E = \frac{\sigma}{\varepsilon} = \frac{F}{A \Delta L / L}, \]  

where \( F \) is the applied tension force (computed from reaction forces in nodes), \( A \) is the cross-sectional area of graphene sheet and \( L \) is the total length of graphene sheet. The cross-sectional area is expressed as

\[ A = bh, \]  

where \( b \) is the width of graphene sheet and \( h \) is the graphene sheet thickness.
3. Finite element analysis

The computations are performed by the program ANSYS APDL. The graphene is modelled as frame structure using beam elements and nodes. The BEAM4 element is used for the representation of the interatomic interactions. The carbon atoms are replaced by the nodes of these elements. The elastic modulus of the graphene sheet is computed from structural response. The graphene sheet is loaded by the uniaxial load, one side of the graphene sheet is restrained in axial direction with lateral displacements being allowed. The graphene sheet is stretched by applying the axial displacement on the opposite side. The value of this displacement is for all simulations equal to 0.001 nm. The analysis is performed for two different chiralities (table 1) of graphene sheets with length varied from 5 to 50 nm. Every chirality of graphene sheet has own width. From these simulations the elastic modulus $E$ for two different thickness and membrane stiffness $C$ of graphene sheets are computed.

| Chirality (n,m) | Width (nm) |
|----------------|------------|
| 10,0           | 2.4612     |
| 13,0           | 3.0766     |
| 17,0           | 4.1841     |
| 6,6            | 2.4157     |
| 8,8            | 3.683      |
| 10,10          | 4.1209     |

Membrane stiffness $C$ is computed from equation

$$C = Et,$$

where $E$ is the Young’s modulus and $t$ is the thickness of graphene sheet. The Young’s modulus is computed from equation (8).
The defected graphene sheets are modeled by removing random carbon atoms (nodes) and corresponding beam elements attached to these atoms (nodes). The carbon atoms (nodes) removed from SWCNTs are 1 %, 3 %, and 5 % of the total amount. The finite element model of graphene sheets with length equal 5 nm created in ANSYS APDL is shown in figures 4-6.

4. Results and discussion
All computed Young’s moduli of graphene sheets for the same size of the thickness $t$ as diameter $d$ are shown in figure 7. It is clear that Young’s moduli of graphene sheets increase slightly with the size of the sheets and depends on the chirality. Computed Young’s moduli for the thickness $t = 0.34$ nm are shown in figure 8. From these figures is clear that Young’s modulus depends on the thickness of the graphene sheet. For this reason, the membrane stiffness is better tool for evaluation of elastic material properties of graphene sheets (figure 9). The chirality of the graphene sheets also affects the elastic material properties. The graphene sheets with chirality $(n,n)$ have higher values of elastic properties then graphene sheets with chirality $(n,0)$.
Figure 7. Variation Young’s modulus with change length of graphene sheet with thickness $t = 0.1466$ nm.

Figure 8. Variation Young’s modulus with change length of graphene sheet with thickness $t = 0.34$ nm.

Figure 9. Variation of membrane stiffness with change length of graphene sheet.

The computed Young’s moduli for defected graphene sheets with thickness $t = 0.1466$ nm are shown in figures 10-15. The Young’s moduli decrease with increasing number of defects. The small deviations of curves from their regular shapes are caused by the location of defects in places with boundary conditions. It is clear that defects with increasing number of missing carbon atoms affect similarly graphene sheets with different chiralities. There is a significant decrease in the Young’s modulus for graphene sheets with defect exceeding 3%.
Figure 10. Variation Young’s modulus with change length of defected graphene sheet (10,0) with thickness $t = 0.1466$ nm.

Figure 11. Variation Young’s modulus with change length of defected graphene sheet (6,6) with thickness $t = 0.1466$ nm.

Figure 12. Variation Young’s modulus with change length of defected graphene sheet (13,0) with thickness $t = 0.1466$ nm.

Figure 13. Variation Young’s modulus with change length of defected graphene sheet (8,8) with thickness $t = 0.1466$ nm.

Figure 14. Variation Young’s modulus with change length of defected graphene sheet (17,0) with thickness $t = 0.1466$ nm.

Figure 15. Variation Young’s modulus with change length of defected graphene sheet (10,10) with thickness $t = 0.1466$ nm.
References

[1] Iijima S 1991 Helical microtubules of graphitic carbon Nat. 354 56–8
[2] Li C and Chou T-W 2003 A structural mechanics approach for the analysis of carbon nanotubes International Journal of Solids and Structures 40 2487–99
[3] Cao G 2014 Atomistic Studies of Mechanical Properties of Graphene Polymers 6 2404–32
[4] Li C and Chou T-W 2003 Elastic moduli of multi-walled carbon nanotubes and the effect of van der Waals forces Composites Science and Technology 63 1517–24
[5] Marenić E, Ibrahimbegovic A, Sorić J and Guidault P-A 2013 Homogenized Elastic Properties of Graphene for Small Deformations Materials 6 3764–82
[6] Hartmann M A, Todt M, Rammerstorfer F G, Fischer F D and Paris O 2013 Elastic properties of graphene obtained by computational mechanical tests EPL 103 68004
[7] Tserpes K I and Papanikos P 2005 Finite element modeling of single-walled carbon nanotubes Composites Part B: Engineering 36 468–77
[8] Wang M C, Yan C, Ma L, Hu N and Chen M W 2012 Effect of defects on fracture strength of graphene sheets Computational Materials Science 54 236–9
[9] Savvas D and Stefanou G 2018 Determination of random material properties of graphene sheets with different types of defects Composites Part B: Engineering 143 47–54
[10] Terrones H, Lv R, Terrones M and Dresselhaus M S 2012 The role of defects and doping in 2D graphene sheets and 1D nanoribbons Rep. Prog. Phys. 75 062501

Acknowledgments
This paper was supported by the Ministry of Education of Slovakia Foundation under grant project VEGA No. 1/0500/20.