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Modeling of Graphene's Elastic Properties with an Analogy of a Truss Structure

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Abstract

The superlative properties of graphene sheet have arisen great interest to many researchers in recent years, since graphene discovery. So far, there are several mathematical models to calculate these properties in the literature but most of them are too involved to utilized and interpreted and some is physically incorrect. In this paper, a new and meaningful approach for calculating the elastic properties of graphene is developed from a link between computational chemistry and solid mechanics. The representative unit cell element (RUE) of a braced-truss structure model is constructed to study graphene load-deformation relationship. Regarding the two-dimensional configuration of graphene, the equivalent elastic truss or rod members represent only the bond stretching and bond-angle variation. The method of calculation equates the total steric potential energy of nanostructure with the strain energy of the braced-truss model. The model can be used to predict all of the elastic properties of graphene based on the deformation of stretching and hinging. Deformation analysis of graphene up to 20 percent strain shows its large extensibility yet still exhibits linear force-displacement relation with respect to an external load.

Keywords*:* graphene, braced-truss model, stretching, hinging.

1. Introduction

Graphene is an allotrope of carbon in the prefect planar form with only one atom in thickness and each atom is connected by a single or double covalent bonds. Perfect two-dimensional form and covalent bond make graphene to be superlative material because it is the strongest, the thinnest, the most stiff, the most stretchable, and very conductive for both heat and electricity, etc. [1-4]. Due to its outstanding electronic and mechanical properties, the researchers are interested in applying graphene in order to develop and upgrade various devices. Thus, thorough knowing and understanding graphene's properties is a very important issue for many future scientific explorations.

Modeling is one way to evaluate graphene's properties. Several authors have developed mathematical models based on different approaches. Li and Chou [5] considered graphene sheet as a frame-like structure in which primary bonds were treated like load-bearing beam members undergoing bond stretching, bond bending, and bond torsion. Each atom acts as a joint of the related members. The model of Li and Chou employs the link between structural mechanics and molecular mechanics. The same concept of having three modes of deformation was adopted by Tserpes and Papanikos [6] as well as Sakhaee-Pour [7]. The former group utilized a finite element model, whereas the latter one worked on an atomistic simulation to predict graphene properties. In the finite element model, the nodes are carbon atoms and the bonds are three-dimensional elastic beam elements. In the atomistic simulation model, on the other hand, the covalent bonds are substituted by beams to simulate the interaction forces between carbon atoms under external loadings. Scarpa, et.al [8] comprehensively presented many graphene models; i.e. a truss-type analytical model, an equivalent honeycomb model, and finite element models. The truss-type analytical model was derived from Odegard, et.al [9], under the concept of cellular mechanics theory. Truss or rod elements represent only stretching effect of bonds in graphene. The equivalent honeycomb model was adopted from Master and Evan's research [10], from which elastic properties was predicted based on the deformations of the honeycomb cell walls, such are stretching, hinging, bending, and shearing. The graphene deformation was separated into three subcases, namely stretching-hinging mode, stretching-hinging-shearing mode, and mode of all deformations occurring together.

As can be seen in the above literature, the researchers typically used rod and beam structures to represent bond stretching and bond bending or bond shearing of carbon atoms, respectively. However the flexure and shear deformations in the beam are not quite valid because they do not physically happen in the actual chemical bondings. Due to the nature of atomic bondings, the energy mainly involves bond stretching, and angle variation (or so-called hinging in this paper). In addition, the chemical bond is just force-force of attraction and repulsion between two atoms so the interactive force in bond should always be in straight line no matter how atoms are moving. Obviously, these atomic bondings and interactions do not engage with the bending and shearing at all. Therefore, in this work we develop a graphene model based on a truss structure that embraces the only deformation modes of stretching and hinging. The primary covalent bond is treated as a rod of main truss structure having only stretching or contracting

deformation. The secondary atomic interaction is considered as a braced member contributing to hinging or angle variation. Force fields of AMBER (Assisted Model Building for Energy Refinement) for stretching and hinging modes are utilized to create a connection between chemical bonding stiffness and structural stiffness [11]. Elastic properties of graphene i.e. modulus of elastically and Poisson's ratio can be calculated by applying Castigliano's first theorem and two dimensional generalized Hooke's law.

2. Modeling procedure

The proposed method of modeling graphene nano-structure with braced-truss model is outlined below. As stated above, the approach uses the total steric potential energy of molecular models and mechanical strain energy of truss in solid mechanics. Thus, the link between energy of molecular mechanics and continuum mechanics, under specified deformations can be developed. The calculation takes into account only the assumption of planar displacement; out of plane deformation is neglected in this case.

2.1 Molecular mechanics model

In molecular mechanics, the viewpoint of computational chemistry of nano-structure material is the description of the energies between individual atoms. The general form of the total steric potential energy can be described in sum of energies due to bond interactions, non-bonded interactions, and electrostatic interaction:

$$U_{total} = \sum U^{l} + \sum U^{\theta} + \sum U^{\tau} + \sum U^{w} + \sum U^{vdw} + \sum U^{el} \quad (1)$$

where U^{l} is energy from bond stretching interaction, U^{θ} from bond angle variation, U^{τ} from dihedral angle torsion, U^{w} from inversion (out-of-plane torsion), U^{vdw}, and U^{el} from non-bonded interaction such as van der Waals force and electrostatic force. A hexagonal cell of graphene in the x-y plane has undeformed length (l_m) between two atoms and initial angle (θ_m) between two bonds, as shown in Fig. 1.

Due to the nature of graphene and its loading conditions in two dimensional, the energy terms are considered only bond stretching interaction and bond angle variation. Out-of-plane angle and non-bonded interactions are not important and can be negligible.

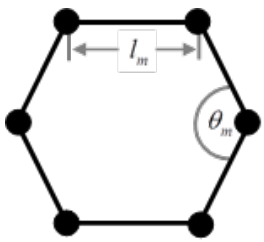

Fig. 1 Hexagonal cell of graphene

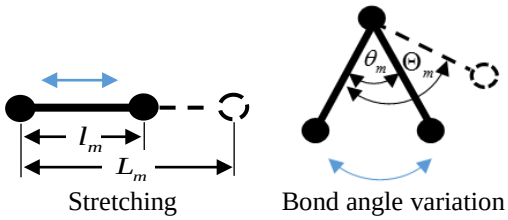

Fig. 2 Interatomic interactions of 2D consideration in molecular mechanics.

Each term of energies can be characterized by force field. Using the AMBER force field [11], the sum of energies is expressed as:

$$U_{total} = \sum_m k_r \left(l_m - L_m\right)^2 + \sum_m k_\theta \left(\theta_m - \Theta_m\right)^2 \quad (2)$$

whereas shown in Fig. 2, L_m is deformed interatomic distances from bond stretching, and Θ_m is deformed interatomic angle from bond angle variation. The terms k_r and k_θ refer to force fields of bond stretching and bond hinging.

2.2 Solid mechanics model

In solid mechanics, a braced-truss model is used to represent the molecular mechanics. The braced-truss model consists of rods between pin-joint to represent interatomic bonding between carbon atoms, having two types of rods a and b for representing the bond stretching (or primary bond) and the bond angle variation (or secondary bond), respectively (Fig. 3). By using the model the truss structure, which can exhibit only stretching degrees of freedom, the strain energy of two types of rod are:

$$U^{t} = \sum_m \frac{1}{2}\frac{A_m^a E_m^a}{l_m^a}\left(l_m^a - L_m^a\right)^2 + \sum_m \frac{1}{2}\frac{A_m^b E_m^b}{l_m^b}\left(l_m^b - L_m^b\right)^2 \quad (3)$$

where A_m is area of rod and E_m is Young's modulus of rod. Comparing the total steric potential energy of molecular mechanics in equation (2) and the strain energy of solid mechanics in equation (3), the relationships between the force fields and Young's moduli of rods are:

$$E^a = \frac{2k_r l^a}{A^a}, \qquad E^b = \frac{24k_\theta}{l^b A^b} \quad (4)$$

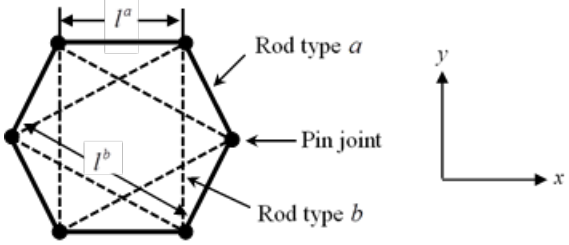

Fig.3 Braced-truss model of a graphene cell

3. Representative unit cell element (RUE) of braced-truss graphene model

RUE consists of the necessary primary and secondary bonds, as shown in Fig.4 (a). The Castigliano's first theorem is applied to determine internal and external forces by specifying displacement at the specific nodes on the braced-truss model, as also illustrated in Fig.4 (a) and (b). Quantities u_1, u_2, and u_3 are horizontal displacements of point D (G), point C (J, H), and point B (A, I), respectively. Quantity v is vertical displacement of point C (D, E). According to these specified displacements, the elongation (or contraction) in each member can be computed and classified into four types of deformations as expressed in equation (5).

$$\begin{aligned} e_{DE} &= 2u_1 \\ e_{DJ} &= \sqrt{\left(l^a \sin\theta - u_1 + u_2\right)^2 + \left(l^a \cos\theta + v\right)^2} - l^a \\ &\approx -\frac{u_1}{2} + \frac{u_2}{2} + \frac{\sqrt{3}v}{2} \\ e_{CH} &= 2v \\ e_{EJ} &= \sqrt{\left(l^b \sin 2\theta + u_3\right)^2 + \left(l^b \cos 2\theta + v\right)^2} - l^b \\ &\approx \frac{\sqrt{3}u_3}{2} + \frac{v}{2} \end{aligned} \tag{5}$$

In the above, e_{DE} is elongation in the horizontal main truss members (e.g. DE and GF members). e_{DJ} is elongation in the oblique main truss member (e.g. DJ and GJ members). e_{CH} is elongation in the vertical braced-truss members (e.g. CH, DG, and EF members). e_{EJ} is elongation in the oblique braced truss members (e.g. EJ and FJ members). Additionally, the horizontal main truss members in the middle, such as AJ member are haft as long as DE member so the elongation of such member is u_1. The elongations of oblique braced members BD and BJ altogether are equal to that of member EJ and hence, they can combine to be that of an oblique braced truss member. θ in equation (5) is equal to 30◦, as shows in Fig. 3. It should be noted that the elongation terms after the first equality sign are the nonlinear kinematics of u_1, u_2, u_3, and v, whereas the right most terms are the linearized version. The linearization is done by using Taylor's expansion and truncating the higher order terms.

Similar to equation (3), the strain energy of RUE of the braced-truss model illustrated in Fig. 4 can be expressed as:

$$U = \sum_i^{24} \frac{1}{2} \frac{E_i^n A_i^n}{l_i^n} \left(e_i\right)^2 \tag{6}$$

when n represents either rod type a or rod type b.

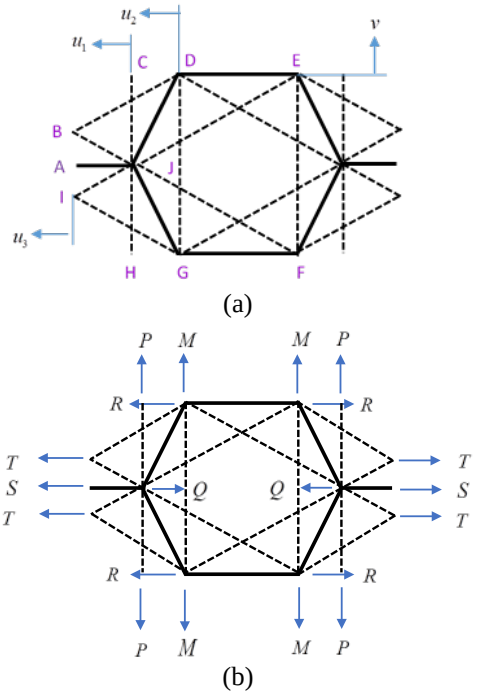

Fig. 4 Schematic of RUE of graphene including primary and secondary bonds (a) deformation at specified nodes; (b) external forces.

By using the Castigliano's first theorem, the external forces M and P can be evaluated in equation (7).

$$2M + 2P = \frac{\partial U}{\partial\left(2v\right)} \tag{7}$$

As also a reaction force in RUE P can be expressed as the internal force in member CH, or

$$P = \frac{E^b A^b}{l^b} e_{CH} = \frac{2E^b A^b v}{l^b} \tag{8}$$

The external force R is resulted from deformation $2u_1$ as shown in equation (9).

$$2R = \frac{\partial U}{\partial\left(2u_1\right)} \tag{9}$$

In addition, the external force Q can be calculated from equation (10).

$$Q = \frac{\partial U}{\partial\left(2u_2\right)} \tag{10}$$

Finally, the external force T and S can be found by using equation (11).

$$2T + S = \frac{\partial U}{\partial\left(2u_3\right)} \tag{11}$$

Similar to equation (8), Reaction force S is equated to the internal force in member AJ as expressed in equation (12).

$$S = \frac{E^a A^a}{l^a} e_{AJ} = \frac{E^a A^a}{l^a} u_1 \tag{12}$$

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The system of four equations (7), (9), (10), and (11) with the aid of equations (8) and (12), can be solved for the four unknown displacement u_1, u_2, u_3 and v. The result leads to the internal force of the braced-truss model:

$$S = \frac{2\left(12A^bE^bl^aR + A^aE^al^b\left(T + 3R + \sqrt{3}M\right)\right)}{3\left(6A^bE^bl^a + A^aE^al^b\right)}$$

$$F_{DE} = \frac{12A^bE^bl^aR + A^aE^al^b\left(T + 3R + \sqrt{3}M\right)}{3\left(6A^bE^bl^a + A^aE^al^b\right)}$$

$$F_{DJ} = \frac{2\left(-6A^bE^bl^aR + A^aE^al^b\left(T + \sqrt{3}M\right)\right)}{3\left(6A^bE^bl^a + A^aE^al^b\right)} \quad (13)$$

$$P = \frac{-2A^aE^al^bT + 6A^bE^bl^a\left(-T + R + \sqrt{3}M\right)}{\sqrt{3}\left(6A^bE^bl^a + A^aE^al^b\right)}$$

$$F_{EJ} = \frac{T}{\sqrt{3}}$$

To calculate Young's modulus in the y-direction (the vertical direction) and the associated Poisson's ratio, there must appears only the applied external load M in the y-direction, the other external forces are set to be zero ($R = Q = T = 0$) as illustrated in Fig 5(a). However, P and S do not vanish because they are reaction forces of the RUE that exist to maintain the structural equilibrium. The force resultants (or force per unit length) and strains are determined by taking into account the remaining forces and displacements of RUE in the x-direction and y-direction as shown in Fig.5 (a) and (b).

Therefore, force resultants and strains of graphene under the external load can be evaluated to be:

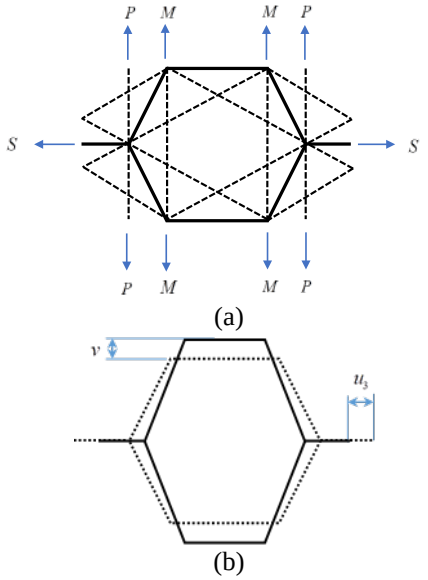

Fig. 5 RUE of graphene (a) under the external load M (b) deformation after applied the external load in the y-direction

$$N_x = \frac{2A^aE^al^bM}{18A^bE^bl^{a^2} + 3A^aE^al^al^b}$$

$$N_y = \frac{2}{3}\left(\frac{1}{l^a} + \frac{6A^bE^b}{6A^bE^bl^a + A^aE^al^b}\right)M \quad (14)$$

$$\varepsilon_x = \frac{-2l^bM}{\sqrt{3}\left(6A^bE^bl^a + A^aE^al^b\right)}$$

$$\varepsilon_y = \frac{2\sqrt{3}l^bM}{6A^bE^bl^a + A^aE^al^b} \quad (15)$$

According to the two dimensional generalized Hooke's law, Young's modulus over one atom thickness or so-called tensile rigidity, and Poisson's ratio can be related to the resultant forces and strains in the two directions as expressed in equation (16). In the equation the assumption of in-plane isotropy is used for the hexagonal structure of graphene. Hence, the tensile rigidity in the x-direction should be the same as that in the y-direction ($E_x = E_y = E$).

$$\begin{bmatrix}\varepsilon_x\\ \varepsilon_y\end{bmatrix} = \begin{bmatrix}\frac{1}{E} & -\frac{\nu}{E}\\ -\frac{\nu}{E} & \frac{1}{E}\end{bmatrix}\begin{bmatrix}N_x\\ N_y\end{bmatrix} \quad (16)$$

Therefore, the tensile rigidity and Poisson's ratio of braced-truss model can be computed to be:

$$E = \frac{2\sqrt{3}\left(6A^{b^2}E^{b^2}l^a + A^aA^bE^aE^bl^b\right)}{l^b\left(9A^bE^bl^a + A^aE^al^b\right)} \quad (17)$$

$$\nu = \frac{3A^bE^bl^a + A^aE^al^b}{9A^bE^bl^a + A^aE^al^b} \quad (18)$$

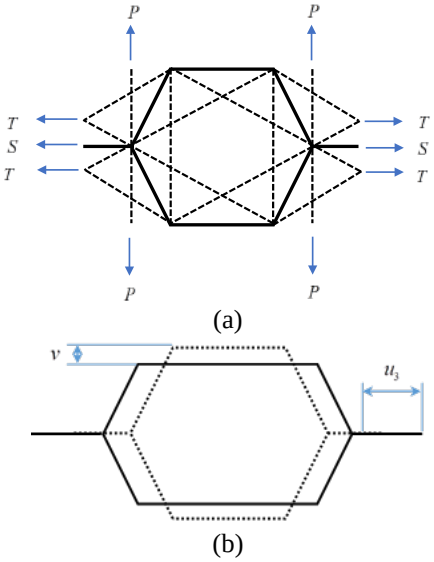

Fig. 6 RUE of graphene (a) under the external load T (b) deformation after applied the external load in the x-direction

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On the other hand, to calculate tensile rigidity and Poisson's ratio by applying external force in the x-direction (the horizontal direction), the undesired forces are equated to zero ($M = R = Q = 0$) as illustrated in Fig.6. Likewise, the reaction forces P and S do not become zero in order to maintain equilibrium. Accordingly, force resultants and strains of graphene under the external load T can be evaluated to be:

$$N_x = \frac{4T\left(9A^aE^al^b + 2A^aE^al^b\right)}{3\sqrt{3}l^a\left(6A^bE^bl^a + 3A^aE^al^b\right)}$$

$$N_y = \frac{-4T\left(3A^bE^bl^a + A^aE^al^b\right)}{3\sqrt{3}l^a\left(6A^bE^bl^a + A^aE^al^b\right)} \quad (19)$$

$$\varepsilon_x = \frac{2Tl^b\left(5A^bE^bl^a + A^aE^al^b\right)}{3A^bE^bl^a\left(6A^bE^bl^a + A^aE^al^b\right)}$$

$$\varepsilon_y = \frac{-2Tl^b\left(3A^bE^bl^a + A^aE^al^b\right)}{3A^bE^bl^a\left(6A^bE^bl^a + A^aE^al^b\right)} \quad (20)$$

Substituting equations (19) and (20) in equation (16) and utilizing the same assumptions, the identical elastic properties to those expressed in equations (17) and (18) can be obtained. This definitely validates the isotropic material behavior of the braced-truss model.

4. Results and discussions

For numerical calculation, the AMBER force field parameters used in this paper are given below [11].

k_r = 3.26×10^{-7} N/nm

k_θ = 0.438×10^{-10} N.nm

The length of primary bond and secondary bond are as follow [28].

l^a = 0.142 nm

l^b = 0.246 nm

An example of force-displacement relations is displayed in Fig. 7. It shows the results in linear and non-linear kinematics. For the small displacement, the results are identical and exhibit linear stiffness behavior. Additionally it the external force M increases much further, the plot indicates that graphene can be stretch upto about 20% in the direction of the applied force without changing in stiffness constant (continuous linear slope). This coincides with the claim from the literature that graphene is the most elastically stretchable crystal. Fig. 8 and 9 show the comparison of the calculated tensile rigidity and Poisson's ratio with those reported in the literature. The results indicate the rational predictions of the graphene elastic properties by the present braced-truss model.

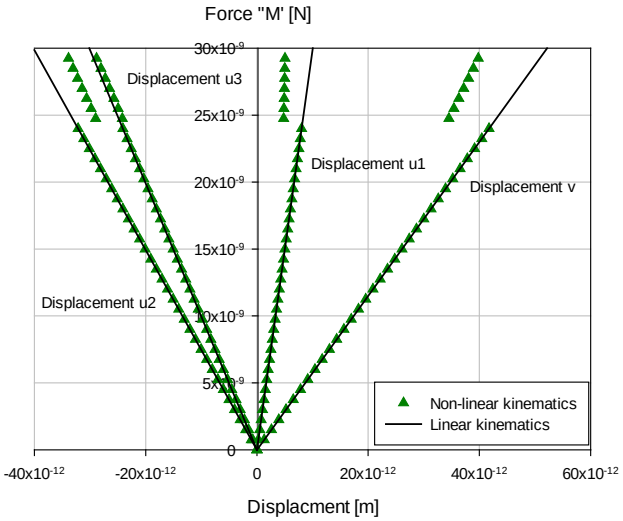

Fig. 7 External force versus displacement relationship for large deformations.

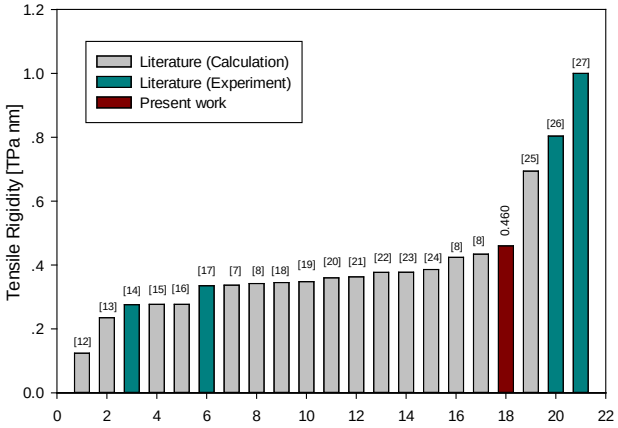

Fig. 8 Tensile rigidity bars of graphene from literature and present work.

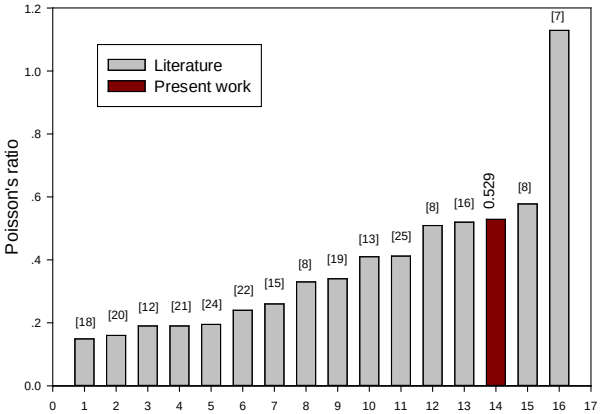

Fig. 9 Poisson's ratio bars of graphene from literature and present work.

5. Conclusions

A mathematical model has been developed and used to investigate the elastic properties of graphene through the link between computational chemistry and solid mechanics. It presents the relation of nanoscale

of graphene to macroscale of structural members. In order to resemble graphene physical and electronic structure, a new braced-truss model is proposed. Rods or truss member are used to represent primary and secondary bonds. The results of tensile rigidity and Poisson's ratio are 0.472 TPa.nm and 0.526, respectively. The prediction provide a reasonable estimation compared to the values from the literature. The method could be applied to model other nanostructures to analyze and evaluate their elastic properties in a tractable manner.

6. Acknowledgement

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