Elastic Moduli of a Single-Layered Graphene Sheet with Finite Element and Geometrical Approaches Using Equivalent Spring Modeling

J. Ghanbari[1], K. Behfar [2], R. Naghdabadi[1]

Summary

The elastic moduli of a single layered graphene sheet in two orientations are studied by two different methods, finite element and geometrical approaches using equivalent spring modeling. The graphene sheet is defect-free and has a regular structure of hexagonal lattices. In equivalent spring modeling, the atomic bonds are modeled using a linear spring with spring constant equal to atomic bond tangent stiffness. A prescribed displacement is applied to the atomic structure, and strain measures are determined geometrically. The graphene sheet behaves like an orthotropic material and has different moduli in x and y orientations.

Introduction

One of the most important material constants in classical continuum mechanics is modulus of elasticity. Variety of methods are used to determine the modulus of elasticity of materials in nanoscale, such as *ab-initio* quantum mechanics, molecular dynamics modeling using inter-atomic potentials, and laboratory practices. However, there are very few continuum studies of carbon nanostructures because at small length scales representative of nano- and micro-engineered material systems, continuum models are not flexible enough to accommodate individual atomic scale processes. Among the limited continuum studies, a carbon nanotube is either modeled as a cylindrical shell, a beam or many truss members. Two critical parameters in the shell model, namely the elastic modulus and shell thickness of a carbon nanotube, are determined by fitting the tensile and bending stiffness obtained from molecular dynamics simulations.

In this paper, we use the finite element and analytical methods to determine the moduli of elasticity in nanoscale. The model which is used to simulate the behavior of a graphene sheet in two methods, involves spring-like segments as an approximation to atomic bonds. Atomic locations are presented as nodal points, and between these nodes, there are spring elements with linear relationship among elongation and resulting force. Spring constant is determined using Taylor series approximation for inter-atomic potential around equilibrium position. The inter-atomic potential which is used in our calculations is well-known Tersoff-

[1] Department of Mechanical Engineering, Sharif University of Technology, Tehran, Iran.
[2] Department of Civil Engineering, Sharif University of Technology, Tehran, Iran.

Brenner potential. Simple tension test simulation is used to determine the elastic moduli of the graphene sheet.

Modeling Atomic Bonds as Linear Springs

Energetics at the atomic-scale is governed by quantum mechanics. Because of complexity of quantum mechanics energy functions, it is convenient to work with simpler potential energy functionals obtained empirically. One of the most popular inter-atomic potentials is so-called Tersoff-Brenner potential. Tersoff [1] and Brenner [2] determined the inter-atomic potential for carbon as:

$$V(r) = V_R(r) - BV_A(r) \tag{1}$$

For atoms i and j, where r_{ij} is the distance between atoms i and j, V_R and V_A are the repulsive and attractive pair terms given as follow:

$$\begin{cases} V_R(r) = \dfrac{D^{(e)}}{S-1}\, e^{-\sqrt{2S}\beta(r-R^{(e)})} f_c(r) \\ V_A(r) = \dfrac{D^{(e)}S}{S-1} e^{-\sqrt{2/S}\beta(r-R^{(e)})} f_c(r) \end{cases} \tag{2}$$

The parameters $D^{(e)}$, S, β, and $R^{(e)}$ are determined from the known physical properties of carbon, graphite and diamond, and are given at the end of this section; the function f_c is merely a smooth cutoff function to limit the range of the potential, and is given as follow:

$$f_c(r) = \begin{cases} 1 & ; \quad r < R^{(1)} \\ 0.5 \times \left\{ 1 + \cos\left[\dfrac{\pi(r - R^{(1)})}{R^{(2)} - R^{(1)}} \right] \right\} & ; \quad R^{(1)} < r < R^{(2)} \\ 0 & ; \quad r > R^{(2)} \end{cases} \tag{3}$$

which is continuous and has a cutoff of $R^{(2)} = 0.2\ nm$ and $R^{(1)} = 0.17\, nm$ to include only the first-neighborhood for carbon. The parameter B_{ij} in Eq. (1) represents a multi-body coupling of the bond between atoms i and j, and the local environment of atom i, which is given by:

$$B_{ij} = \left[1 + \sum_{k(\neq i,j)} G(\theta_{ijk}) f_c(r_{ik}) \right]^{-\delta} \tag{4}$$

where r_{ik} is the distance between atoms i and k. f_c is the cutoff function given

in Eq. (3), θ_{ijk} is the angle between bonds $i-j$, $i-k$. The function G is given by:

$$G(\theta) = a_0\left[1+\frac{c_0^2}{d_0^2}-\frac{c_0^2}{d_0^2+(1+\cos\theta)^2}\right] \tag{5}$$

For atoms i and j having different local environment, Brenner [2] suggested to replace the coefficient B_{ij} given in Eq. (1) for $\overline{B}_{ij}$ given as follows:

$$\overline{B}_{ij} = (B_{ij}+B_{ji})/2 \tag{6}$$

The parameters $D^{(e)}$, S, β and $R^{(e)}$ in Eq. (2), δ in Eq. (4), and a_0, c_0 and d_0 in Eq. (5) have been determined by Brenner [2] to fit the binding energy and lattice constants of graphite and diamond for simple- and face-centered cubic structures. In fact, Brenner [2] gave two sets of parameters for carbon, that we have used second set of these parameters.

$$\begin{aligned} &D^{(e)} = 6.00\,eV,\ S = 1.22,\ \beta = 21\,nm^{-1},\ R^{(e)} = 0.1390\,nm;\\ &\delta = 0.50000;\\ &a_0 = 0.00020813,\ c_0 = 330,\ d_0 = 3.5 \end{aligned} \tag{7}$$

It is worth noting that S, δ, a_0, c_0 and d_0 are dimensionless parameters. Considering Eq. (7), computing B needs the known location of the atoms around the considered atom. As noted previously, structure of atomic bonds in graphene sheet are honeycomb-wise hexagons. Accordingly, each carbon atom is surrounded by three atoms having atomic bonds, which have the angle equal to $2\pi/3$. Obtaining explicit expressions for V_R and V_A as functions of r, we can compute derivatives of the potential function as follow:

$$\frac{dV}{dr} = -894.63e^{-32.8\,r+4.56} + 863.09e^{-26.89\,r+3.74} \tag{8}$$

$$\frac{d^2V}{dr^2} = 29346.55e^{-32.80\,r+4.56} - 23206.46e^{-26.89\,r+3.74} \tag{9}$$

Eq. (8) represents the force acting on the atom due to change in the inter-atomic distance. Differentiating Eq. (8) with respect to r, the second derivative of the potential energy as a function of r is obtained. Since, the spring constant should be determined at the equilibrium position, so we substitute $r = 0.144\ nm$, equal to carbon-carbon bond length of graphite [3] (alternatively, obtained by setting Eq. (8) to zero), into Eq. (9) and compute the spring constant as follows:

$$k = \left.\frac{d^2V}{dr^2}\right|_{r_0} = 4620.026\ \ eV/nm^2 = 755.37\ \ N/m \tag{10}$$

Accordingly, the equivalent spring constant for the bond stiffness in graphite is obtained. Assumptions which we have used for carbon bonds, contain small deformation and small rotation cases. Small rotation assumption was made because, for computing B, we need the angle between bonds, and this angle is assumed to be equal to $2\pi/3$ as the equilibrium bond angle, which is only true for small deviations of equilibrium point. It is noted that even in pure tension, the bond angles may change, and due to this fact, small deformation assumption has been made. For small external forces in pure tension, the bond angle is approximately considered constant and equal to $2\pi/3$, so expression for B is only calculated at the beginning of load step.

Finite Element Modeling

As previously noted, atomic bond structures in graphene sheet are honeycomb-like hexagons. For the purpose of modeling this structure, we put a node on the location of each atom. A spring element is defined between each pair of nodes corresponding to an atomic bond. Spring constant of these elements have been determined in the previous section.

The major purpose of the analyses is to obtain the elastic moduli. To this end, it is sufficient to apply a small prescribed deformation and calculate the developed reaction forces. Boundary conditions of rectangular models are fixed nodes on one side, and applied prescribed displacement on the opposite side. The sides parallel to the direction of tension test simulation are assumed to be fixed in the perpendicular direction.

The forces required to apply a known prescribed displacement are determined by the finite element software (Ansys) for a rectangular grapheme sheet. Dividing the total force to the length of the side which the displacement is applied on and the effective thickness of the graphene sheet, the stress in the sheet is determined. Knowing the value of the prescribed displacement and the length of the other side of the model, the strain developed in the sheet is calculated. Likewise, the simple tension test is simulated in both x and y orientations to study the behavior of the graphene sheet.

Table 1: The elastic moduli by finite element method using equivalent spring modeling

E_1	3.34 *TPa*
E_2	2.237 *TPa*

Geometrical Approach

In order to obtain the elastic modulus of a graphene sheet, we use geometrical deformation measures. In contrast to the finite element section, according to Figure 1, a representative element of the graphene sheet is chose and the element

is assumed to be displaced in δ. Then, the developed forces in the spring elements corresponding to atomic bonds are determined.

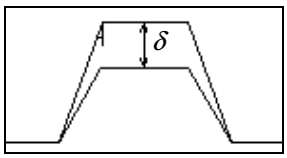

Figure1: illustrates the displacement of a representative element in δ.

The stress and strain corresponding to the representative element of the graphene sheet are obtained as follow:

$$\begin{cases} \sigma_1 = \dfrac{2k\delta\,(\cos 30)^2}{3at_{eff}} \\ \varepsilon_1 = \dfrac{\delta}{a\cos 30} \end{cases} \tag{11}$$

where t_{eff} is the thickness of the graphene sheet, k is the spring constant , a is the bond length in the graphene sheet and δ is the prescribed displacement exerted to the representative element of the graphene sheet. In order to obtain the elastic modulus in the perpendicular direction, another representative element is considered as illustrated in Figure 2 and is displaced δ.

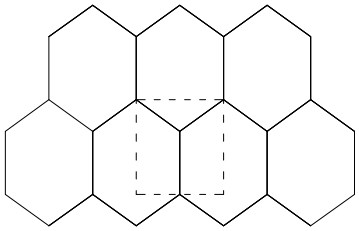

Figure2: illustrates the representative element of the graphene sheet.

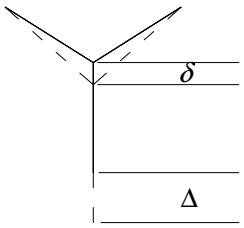

Figure3: illustrates the displacement of a representative element in δ.

By equalizing the forces induced in the bonds of the representative element, a relation between the displacements is obtained $\Delta = 3\delta/2$ .The stress and strain induced by the applied displacement δ on the element are determined as follow:

$$\begin{cases} \sigma_2 = \dfrac{k\Delta/3}{2a\cos 30\ t_{eff}} \\ \varepsilon_2 = \dfrac{\Delta}{3/2\ a} \end{cases} \tag{12}$$

Table 2: The elastic moduli by geometrical method using equivalent spring modeling

E_1	4.95 *TPa*
E_2	3.302 *TPa*

Conclusion

The results obtained in the current study feature different values for the elastic moduli in two orientations. Therefore, the grapheme sheet can be considered as an orthotropic plate. Also, the results achieved by two methods differ from each other, meanwhile the ratio of E_1 / E_2 is about 1.5 and similar in two methods due to the fact that both methods are initiated from equivalent spring modeling.

It should be noted that the values in Tables 1 and 2 are in good agreement with the experimental results reported in the literature [3, 4]. We can assume that a nanotube is constructed by rolling a graphene sheet [4], so we are allowed to compare the results for elastic modulus of nanotube to that of the graphene sheet.

A large variation of Young's moduli was reported from 0.40 to 4.15 TPa with an average of 1.8 TPa in different reports. Krishnan et al. [5], have used TEM to observe the thermal vibration of a SWNT at room temperature and has reported Young's moduli of SWNTs in the range from 0.90 to 1.70 TPa, with an average of 1.25 TPa. Wong et al. [6], have used AFM to bend a MWNT, and a large variation of Young's modulus for MWNTs (0.69–1.87 TPa) have been determined. Yakobson et. al. [7] comparing molecular dynamic simulations and continuum mechanics theories for shells, obtained the elastic modulus equal to 5.5 TPa and the effective thickness of SWNT equal to 0.066 nm.

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