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ALTERNATIVE FINITE ELEMENT BASED MODELING APPORACHES FOR CARBON NANOTUBES

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ABSTRACT

Carbon Nanotubes (CNTs) are rolled sheets of graphene which include carbon atoms only. CNTs have attracted the interest of scientists and engineers because of their superior mechanical properties. To this end, significant amount of work has been done for atomistic modeling of CNTs. However, modeling of CNTs with pure atomistic approaches is computationally expensive. Therefore, continuum based approaches such as finite element method (FEM) have alternatively been proposed. The purpose of this work is to compare alternative FE modeling approaches for graphene and CNTs. FE models are created by using the commercial FE software ANSYS APDL. Elastic constants, such as the Young's modulus, the shear modulus and the Poisson's ratio, of a single CNT are computed by alternative FE approaches and the results are compared with the literature.

INTRODUCTION

In the literature, different approaches have been used to model the mechanical behavior of CNTs. These studies can be divided into two groups (i) Molecular Dynamics (MD) based models, and (ii) Finite Element (FE) based models. In FE-based models, CNTs are modeled as a space-frame structure where every connection point stands for a carbon atom as can be seen in Figure 1.

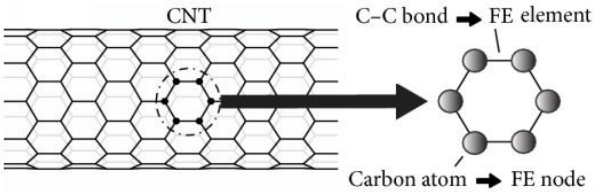

Figure 1: Atomistic-Continuum Approach [Yengejeh, 2009].

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Elastic properties of the elements that are used in FE models can be obtained by equating atomistic force potentials to energy formulations derived from the Castigliano's theorem for different deformation modes like stretching, bending and torsion as given in Figure 2.

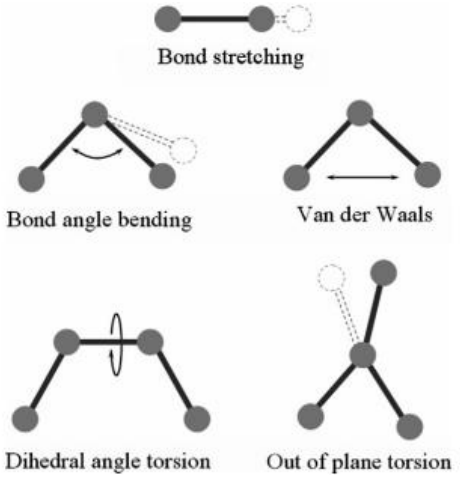

Figure 2: Deformation types of C bonds [Tserpes,2005]

In the present work, the Modified Morse Potential is used. The Modified Morse Potential is the harmonic form of the Morse Potential which can be equated to the strain energy stored in finite elements to obtain required elastic rigidities of finite elements which simulate the C-C bonds in CNTs. As it can be seen in Figure 3, the Modified Morse Potential and the Morse Potential are similar when the inter-nuclear separation is small.

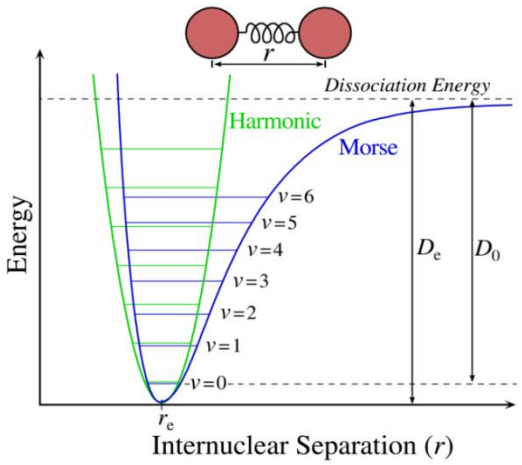

Figure 3: Modified Morse and Morse Potential [Wikipedia,2017]

The modified Morse potential can be expressed as a sum of individual energies due to bonded and non-bonded interaction energy terms as given below,

$$\mathrm{U_{total}} = \mathrm{U_r} + \mathrm{U_\theta} + \mathrm{U_\varphi} + \mathrm{U_w} + \mathrm{U_{vdw}}$$

where $\mathrm{U_r}$, $\mathrm{U_\theta}$, $\mathrm{U_\varphi}$, $\mathrm{U_w}$, $\mathrm{U_{vdw}}$ represent the bond stretching, the bending, the dihedral torsion, the out-of plane torsion and the non-bonded van der Waals energies, respectively.

Generally, non-bonded energies are negligible in covalent systems and the contribution of out-of plane torsion energy is less significant with respect to first three term [Gelin,1994]. Due to these assumptions the first three terms contribute most to total energy and can be expressed simply as following quadratic forms,

$$\mathrm{U_r} = \frac{1}{2} k_r (\Delta \mathrm{r})^2, \quad \mathrm{U_\theta} = \frac{1}{2} k_r (\Delta\theta)^2, \qquad \mathrm{U_r} = \frac{1}{2} k_\tau (\Delta\varphi)^2$$

Elastic strain energies stored in beams can be written as below,

$$U_s = \int_0^L \frac{N^2}{E_b A_b} dl = \frac{1}{2}\frac{N^2 l}{E_b A_b} = \frac{1}{2}\frac{E_b I_b}{l} = \frac{1}{2}\frac{E_b I_b}{l}(\Delta l)^2$$

$$U_b = \frac{1}{2}\int_0^L \frac{M^2}{E_b I_b} dl = \frac{1}{2}\frac{E_b I_b}{l}(2\alpha)^2$$

$$U_t = \frac{1}{2}\int_0^L \frac{T^2}{G_b J_b} dl = \frac{1}{2}\frac{G_b J_b}{l}(\theta)^2$$

where U_s, U_b and U_t correspond to axial, bending and torsion energies, respectively. After equating the strain energies to the bond energies of the modified Morse potential, the following relationships are found for the rigidities

$$\frac{E_b A_b}{l} = k_r, \qquad \frac{E_b I_b}{l} = k_\theta, \qquad \frac{G_b J_b}{l} = k_\tau$$

l is the bond length which is equal to 0.1421 nm, E_b is the Young's modulus, G_b is the shear modulus, A_b is the cross-section area, I_b is the moment of inertia and J_b is the polar moment of inertia of the beam. The C-C bond is assumed to have a circular cross section with a diameter d. A_b, I_b and J_b can be defined in terms of the diameter:

$$A_b = \frac{\pi d^2}{4}, \qquad I_b = \frac{\pi d^4}{64}, \qquad I_b = \frac{\pi d^4}{64}$$

Solving for E_b and d in above mentioned equations and setting l =0.1421 nm give:

$$d = 4\sqrt{\frac{k_\theta}{k_r}}, \qquad E_b = \frac{k_r^2 l}{4\pi k_\theta}, \qquad G_b = \frac{k_r^2 k_\tau l}{8\pi k_\theta^2}$$

Solution of the last three equations gives necessary inputs for finite element modeling of C-C bonds. Following stretching, bending and torsional force constants are used [Cornell,1995][Jorgensen,1990]:

$$k_r = 6.52 \times 10^{-7}\ \mathrm{N/nm}$$

$$k_\theta = 8.76 \times 10^{-10}\ \mathrm{N\,nm/rad^{-2}}$$

$$k_\tau = 2.78 \times 10^{-10}\ \mathrm{N\,nm/rad^{-2}}$$

Substituting these constants into mentioned equations and setting l=0.1421 nm give;

$$d = 0.147\ \mathrm{nm}$$

$$E_b = 5488\ \mathrm{nN/nm^2} = 5488\ \mathrm{GPa}$$

$$G_b = 870.7\ \mathrm{nN/nm^2} = 870.7\ \mathrm{GPa}$$

The geometrical properties like area, moment of inertia and polar moment of inertia of the beam elements are obtained from the diameter.

$$A_b = \frac{\pi d^2}{4} = 0.01688\ nm^2$$

$$I_b = \frac{\pi d^4}{64} = 2.269 \times 10^{-5}\ nm^4$$

$$J_b = \frac{\pi d^4}{64} = 4.537 \times 10^{-5}\ nm^4$$

Finite elements corresponding to C-C bonds such as beams, trusses or springs can be defined by using above given mechanical and geometric properties.

When C-C bonds are modeled with beam elements in finite element method, the bond angle bending energy of the carbon bonds is represented by the bending energy of a single beam. However, bending of a single C-C bond is physically not possible. The bending energy of carbon bonds is indeed related to the energy due to the change of angle between two carbon bonds. Therefore, in this study 3-D truss and spring elements are also used for modeling C-C bonds as an alternative to beam elements. Use of truss-spring elements for the modeling of bending behavior simulates the nature of bond bending more accurately. When compared to a CNT, it is easier to model graphene sheet with truss-spring elements. Therefore, at first a graphene sheet is modeled with both truss-spring elements and beam elements for a comparison.

Linear spring elements are used to model bending behavior of the bonds, see Figure 4. Using torsional spring for modeling is also an alternative option. However, in this work only linear springs are used. Elastic properties of linear springs are found as

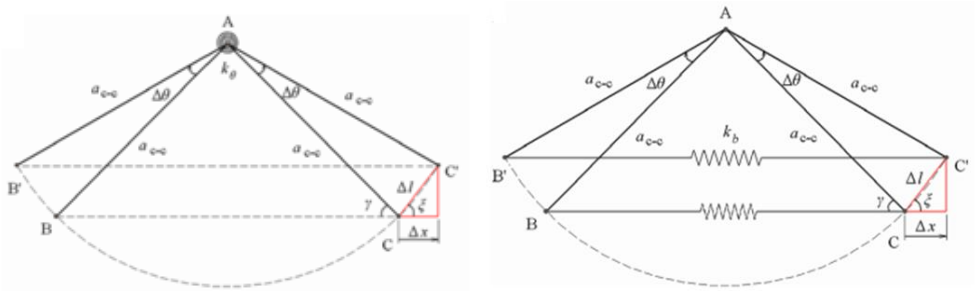

Figure 4: Torsional spring to linear spring stiffness evaluation [Giannopolus,2007]

For small angle changes $\Delta\theta$ the change in position of point C can be expressed as

$$\Delta l = a_{C-C}\,\Delta\theta$$

Where $\mathbf{a_{C-C}}$ is the length of the C-C bond, $\Delta\theta$ is the change in the angle as shown in Figure 4. $\Delta\mathbf{x}$ is the horizontal displacement of point C which is equal to the elongation of the linear spring. It is computed as

$$\Delta x = \Delta l \cos\xi$$

$$\cos\xi = \cos(90° - \gamma) = \frac{\Delta x}{\Delta l}$$

The energy due to bond angle bending is assumed as harmonic (in Molecular Dynamics)

$$E_{MD} = \frac{1}{2}\,k_\theta (2\Delta\theta)^2$$

The equivalent energy due to stretching of a linear spring is

$$E_{Sp} = \frac{1}{2} k_b (2\Delta x)^2$$

Equating the above energy expressions together with horizontal displacement and elongation equations give the relation between k_θ and k_b

$$k_b = \left(\frac{1}{a_{C-C}\cos(90° - \gamma)}\right)^2 k_\theta$$

The Modified Morse Potential is used as in the case of CNT modeling. As given in above, k_θ= 8.76E-10 N nm/rad^{-2} and a_{C-C}= 0.1421 nm. The angle $\gamma = 30°$ for the hexagonal lattice of the graphene. Then the above equation can be solved for k_b. The stiffness of the linear spring is found as,

$$k_b = 1.73 \times 10^{-7} \text{ N nm} = 173.53 \text{ nN nm}$$

FINITE ELEMENT MODELING

Above mentioned finite element modeling approaches are presented below.

CNT Modeling

Coordinates of the exact atomic structure of CNTs are obtained from ConTube 1.0 [Melchor,2007]. DesignModeler and ANSYS APDL are used for the modeling and finite element analyses. In present work, beam elements are used for the CNT modeling.
Equivalent beam approach is based on a continuum beam which provides the same mechanical properties of a CNT under tensile, bending and torsional loading. For a CNT, in order to get mechanical properties, the rigidities have to be obtained first. Then the rigidities are used to find the equivalent beam diameter which is then used to obtain mechanical properties like the Young's modulus, the shear modulus, the Poisson's ratio of a CNT.
In ANSYS, there are two types of elements to model a beam, which are BEAM4 and BEAM188. BEAM188 is the Timoshenko beam which gives good results if the beam is slender. In this study, diameter and length of the single beam, which used for C-C bonds, are 0.147 nm and 0.1421 nm respectively. Therefore, BEAM4 is selected over BEAM188 because of very high diameter to length ratio of the beam.
The CNT is fixed at one end and an axial displacement, a transverse displacement and a twist are applied to the other end separately to simulate these 3 types of loading as boundary conditions for the CNT.

Graphene Modeling

Coordinates of the carbon atoms for the graphene model are obtained according to the chiral vector. The model is created by using ANSYS APDL. Equivalent sheet approach is based on a continuum sheet which provides the same mechanical properties of a graphene under tensile loading.
In order to simulate a simple tension test the graphene sheet placed in XY plane the graphene is fixed at one end in X and Z directions and a displacement in -X direction is applied to the other end. This end is also constrained in Z direction. One of the corner nodes at each end is fixed in Y direction to prevent rigid body motions.

RESULTS

The reaction forces FX, FY and torque T due to applied axial displacement, transverse displacement and twist are computed by finite element analyses. After the computation of the reaction forces, the rigidities $E_{eq}A_{eq}$, $E_{eq}I_{eq}$ and $G_{eq}J_{eq}$ of the CNTs are determined for different chiralities and lengths. The rigidity results are given in Figure 5.

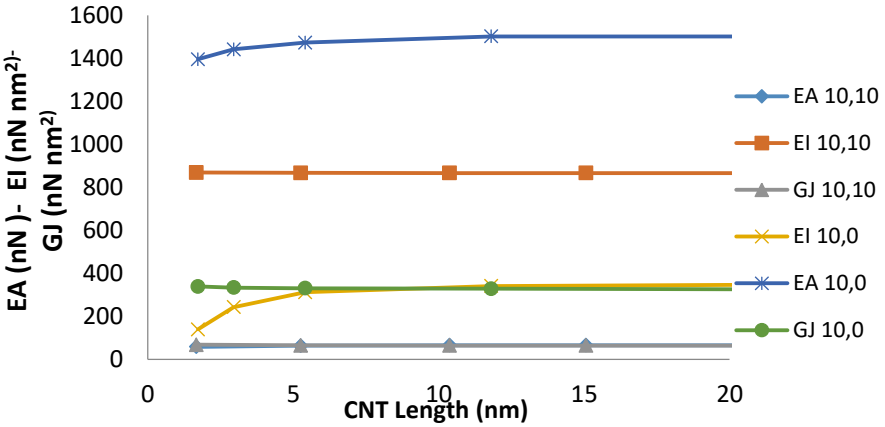

Figure 5: Rigidity results

A further assumption of $t_n = 0.34\ nm$ (wall thickness of hollow beam) allows us to determine the equivalent diameters of the equivalent hollow beams. Mechanical properties can be calculated by using rigidities and equivalent diameters.
As can be seen in Figure 5, the mechanical properties of CNTs become almost length independent if they are longer than 5 nm. D_{eq}, A_{eq} and I_{eq} are calculated from the rigidity results. Finally, by dividing the tensile and the bending rigidities to A_{eq} and $I_{eq}$the Young's modulus can be found. The Young's modulus is found in the range 1.069-1.078 TPa, from the rigidity results of beams having lengths of 10-20 nm interval and different chiralities. It is found that, the equivalent beam approach gives results similar to literature, see Table 1.

Table 1: Results reported in literature for (10,10) CNT

	Present Work	Liew et al. [Liew,2001]	Hernandez et al. [Hernandez,1998]	Meo and Rossi [Meo,2016]	Liu and Hu [Liu,2012]	Mohammadpour and Awang [Mohammadpour,2011]
E [TPa]	1.074	1.043	1.24	0.926	0.927	2.037

It could be found that in [Liu,2012], the modulus of elasticity changes %3 for a graphene sheet having width/length ratio in the range 0.185 to 3.027. The width/length ratio of the graphene sheet in the present work is around 0.3. It could be assumed that modulus of elasticity is independent from the width/length ratio in the mentioned width/length range. Comparisons of present work with literature are also presented in Table **3**.

Table 2: Finite element results of graphene

Model		Dimensions [nm]	Number of elements	Number of Nodes	Reaction Forces [nN]
Truss-Spring	Zigzag	8.67x2.71	4647	8975	14.349
	Armchair	2.84x8.62	4915	9995	15.496
Beam	Zigzag	8.67x2.71	1352	2296	11.013
	Armchair	2.84x8.62	1442	2436	12.225

Table 3: Modulus of elasticity E [TPa] of graphene sheet

Present Truss-Spring Armchair	Present Beam Armchair	Present Truss-Spring Zigzag	Present Beam Zigzag	Meo and Rossi [Meo,2016]	Li and Chou [Li,2003]	Bao et al[5] [Bao,2004]	Liu and Hu [Liu,2012]
1.38 (35.3%)	1.09 (6.9%)	1.35 (32.4%)	1.035 (1.5%)	0.9445 (7.4%)	1.05 (2.9%)	1.02	1.192 (16.9%)

CONCLUSION

An atomistic-continuum approach is used through to finite element method in order to calculate the rigidities of the CNTs. The beam elements are used in modeling of the CNTs. The rigidity results are used to calculate elastic properties by using the equivalent beam approach. In the present work, the calculated Young's modulus values are found to be consistent with the literature.

A more realistic approach is taken into consideration for the bond bending behavior by using truss and spring elements. This approach is used in modeling a graphene sheet. For the modeling of graphene, the approach with the beam elements is also used in order to see effectiveness of the new approach. The graphene model which has truss-spring elements shows stiffer behavior according to model with beam elements. The results of the model with beam elements are found to be more consistent with the literature.

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[5] Experimental value, percentage differences are given in parenthesis with respect to following formula; (value of the model-experimental value)/experimental value.

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