Estonian Journal of Engineering, 2009, **15**, 2, 77–86 doi: 10.3176/eng.2009.2.01

FE modelling of multi-walled carbon nanotubes

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Received 28 August 2008, in revised form 27 January 2009

Abstract. In this paper a theory of multi-walled carbon nanotubes and a suitable way for modelling them using the finite element method is presented. A brief reference to FE modelling of a single-walled carbon nanotube (SWNT) is given as an introduction to modelling of multi-walled carbon nanotubes, consisting of several layers of SWNT. Also, a theory of the connection interface between nanotube layers and its influence on the loading is given. A SWNT finite element model is used to model a multi-walled carbon nanotube (MWNT). A brief theory concerning MWNT is given, as well as a theory of modelling a connecting interface between layers, as a result of van der Waals interactions. Different loading conditions are used as examples of multi-walled carbon nanotubes under specific loads. Results are compared with those given by other authors.

Key words: nanotechnology, multi-walled carbon nanotube, finite element method.

1. INTRODUCTION

In the past twenty years nanotechnology and nano-oriented materials, especially carbon nanotubes, have aroused a major interest among engineers and scientists, owing to works of Iijima [1] and Tersoff [2]. Carbon nanotubes have unique and remarkable mechanical and electrical properties, such as high stiffness, strength and the ability to recover from elastic buckling. The Young and shear moduli of carbon nanotubes obtained by experiments (1 TPa and 0.5 TPa, respectively) and theoretical considerations lead to further research of carbon nanotubes, especially of multi-walled carbon nanotubes. The latter have not been studied as much as single-walled carbon nanotubes, although they were discovered first and their mechanical properties are different from those of single-walled carbon nanotubes.

One of the most interesting applications of carbon nanotubes is nano-composite materials. In order to fully explore their potential for application in composite materials, a knowledge of elastic properties and behaviour of multi-walled carbon nanotubes is necessary. Their extremely small size presents a challenge to researchers, thus computer modelling is one of the logical solutions.

There are two approaches to computer modelling of carbon nanotubes: molecular dynamics and the finite element method. Finite element approach, which is used in this paper, is based on the substitution of covalent bonds between atoms with beam elements, and is described in detail in Section 3.1. Finite element method is used by many authors for the research of mechanical properties of carbon nanotubes under different loads like buckling and bending [3], strength prediction of carbon nanotubes [4] and using a FEM model of a carbon nanotube in composites [5].

There is a special non-bonded interaction between layers of a multi-walled carbon nanotube – the van der Waals interaction. Modelling of this interaction is described in detail in Section 3.2.

2. MULTI-WALLED CARBON NANOTUBES

A carbon nanotube can be considered as a large molecule consisting of carbon atoms, forming a hexagonal mesh. It may also be regarded as a one atom thick sheet of graphite, rolled into a tube with high aspect ratio. Such a tube can be considered as a fundamental structural unit, known as single-walled carbon nanotube. Using that fundamental structural unit, a multi-walled carbon nanotube can be formed. MWNTs are in fact concentrically nested SWNTs, with a distance between the layers or walls equal to 0.34 nm. Each atom in a single layer has three nearest neighbouring atoms and they are bonded by covalent bonds, which have characteristic properties (bond length and bond angle). Atoms on different layers of MWNTs are not connected by covalent bonds and the only interaction between them is through van der Waals forces. Van der Waals forces are rather weak compared to covalent bonds.

A carbon nanotube is characterized by the diameter and chiral angle θ, or by chirality of the tube. Chirality is defined by chiral vector, $\vec{C}_h$

$$\vec{C}_h = n\vec{a}_1 + m\vec{a}_2. \tag{1}$$

Chiral vector is in the direction along which the graphite sheet is rolled up to form a nanotube and it defines a carbon nanotube through three basic patterns: zig-zag, with chiral angle $\theta = 0°$, armchair with chiral angle $\theta = 30°$ and basic chiral nanotube with chiral angle in the range $0° < \theta < 30°$. In Eq. (1), n and m are integers, which represent the number of steps along the carbon bond of the hexagonal lattice, and $\vec{a}_1$ and $\vec{a}_2$ are unit vectors, as shown in Fig. 1.

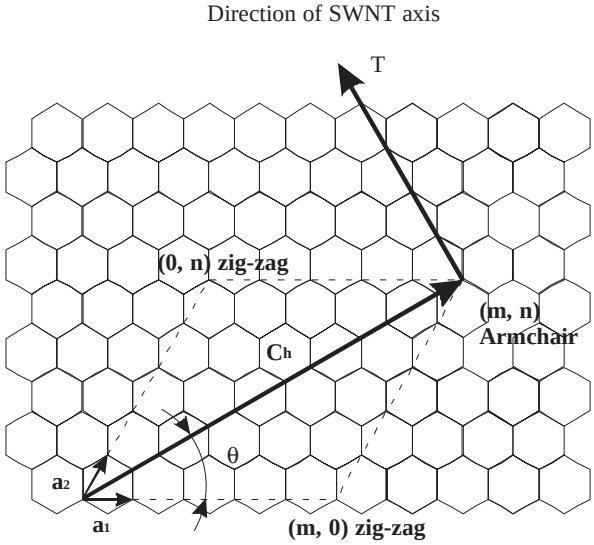

Fig. 1. Chiral vector in the structure of the carbon nanotube [6].

Thus the vectors $(0, n)$ and $(m, 0)$ denote zig-zag nanotubes, the vectors (m, m) or (n, n) denote armchair nanotubes and all other vectors correspond to chiral nanotubes.

Since the layers of MWNT are structurally independent of one another, the chirality of the layers may be different. The distance between neighbouring layers is assumed to be 0.34 nm, that is, the same as the spacing between adjacent graphene sheets in graphite.

3. STRUCTURAL MECHANICS MODEL OF THE MWNT

3.1. Finite element model of the carbon nanotube

A carbon nanotube is a frame-like structure, with characteristic bond length and bond angle. Thus when a nanotube is subjected to external load, the displacements of atoms are constrained by these bonds, and total deformation of the nanotube is the result of bond interactions. Therefore by substitution of these bonds with isotropic beam elements a carbon nanotube can be made to form a frame-like structure consisting of nodes and elements.

In order to do so, a linkage must be found between molecular mechanics and structural mechanics. That linkage can be described using the force field, which is generated between carbon atoms, generated by electron–nucleus and nucleus–nucleus interactions. That force field can be expressed in the form of steric potential energy

$$U = \sum U_r + \sum U_\theta + \sum U_\phi + \sum U_{vdw}, \tag{2}$$

where U_r denotes energy, associated with bond stretch interaction, U_θ is bond angle bending, U_ϕ is torsion (dihedral and out of plane) and U_{vdw} is the non-bonded van der Waals interaction (forces). Terms of Eq. (2) can be expressed as

$$U_r = \frac{1}{2}k_r(r - r_0)^2 = \frac{1}{2}k_r(\Delta r)^2, \tag{3}$$

$$U_\theta = \frac{1}{2}k_\theta(\theta - \theta_0)^2 = \frac{1}{2}k_\theta(\Delta\theta)^2, \tag{4}$$

$$U_\phi = \frac{1}{2}k_\phi(\Delta\phi)^2, \tag{5}$$

where r and θ are the distance and bond angle after deformation, r_0 and θ_0 are the undeformed distance and bond angle, while terms Δr, $\Delta\theta$ and $\Delta\phi$ correspond to the change in bond length, bond angle and angle change of bond twisting, respectively. Constant k_r is the bond stretching force constant, k_θ is the bond angle bending force constant and k_ϕ is the torsional resistance of the chemical bond.

Let us compare these results with strain energies in structural mechanics:

– the strain energy of uniform beam of length L subjected to axial force N:

$$U_A = \frac{1}{2}\int_0^L \frac{N^2}{EA}\mathrm{d}L = \frac{1}{2}\frac{N^2 L}{EA} = \frac{1}{2}\frac{EA}{L}(\Delta L)^2, \tag{6}$$

– the strain energy of a uniform beam under pure bending moment M:

$$U_M = \frac{1}{2}\int_0^L \frac{M^2}{EI}\mathrm{d}L = \frac{2EI}{L}\alpha^2 = \frac{1}{2}\frac{EI}{L}(2\alpha)^2, \tag{7}$$

– the strain energy of a uniform beam under pure torsional moment T:

$$U_T = \frac{1}{2}\int_0^L \frac{T^2}{GJ}\mathrm{d}L = \frac{1}{2}\frac{T^2 L}{GJ} = \frac{1}{2}\frac{GJ}{L}(\Delta\beta)^2, \tag{8}$$

where E is the Young modulus, ΔL denotes axial deformation, α denotes the rotation angle or bend angle, and $\Delta\beta$ is relative rotation between the ends of the beam or twist angle. Since Eqs. (3), (4) and (5) represent the same quantities, only in different systems, a direct relationship between the parameters of molecular mechanics and parameters of structural mechanics can be obtained:

$$\frac{EA}{l} = k_r, \quad \frac{EI}{l} = k_\theta, \quad \frac{GJ}{l} = k_\phi. \tag{9}$$

The parameters in Eq. (9) are sufficient for modelling a single-walled carbon nanotube as a frame-like structure with beam elements.

3.2. Van der Waals forces

Since van der Waals interactions are non-bonded, in comparison with covalent bonds between atoms, van der Waals interactions are very weak. Consequently, they are not considered in this paper. It is of special interest to see influence of these interactions on the Young and shear moduli. Introduction of such bonds leads towards substantial increase in computational costs, thus excluding them from the model is beneficiary.

As said before, atoms on different layers of MWNT are not connected by covalent bonds. The only interaction between them is through van der Waals forces, which can be either an attraction force or a repulsion force. The attraction will appear when atoms approach each other within a certain distance, while repulsion will occur when the distance between atoms becomes less then the sum of their contact radii. Using the general Lennard–Jones "6–12" potential

$$U(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \tag{10}$$

the van der Waals interaction can be modelled. In Eq. (10), r represents the distance between interacting atoms, ε and σ are the Lennard–Jones parameters; for carbon atoms they are $\varepsilon = 3.86\times10^{-13}$ Nnm, $\sigma = 0.34$ nm. Taking a derivative of $U(r)$ relative to r, an expression for the van der Waals force is obtained:

$$F(r) = -\frac{\mathrm{d}U(r)}{\mathrm{d}r} = 24\frac{\varepsilon}{\sigma}\left[2\left(\frac{\sigma}{r}\right)^{13} - \left(\frac{\sigma}{r}\right)^{7}\right]. \tag{11}$$

In MWNT, an atom, situated in one layer, can form an interacting pair with several atoms from the neighbouring layer as long as the distance between the pair of atoms is less then 2.5σ (0.85 nm). Thus the conclusion is that the van der Waals force between two atoms is highly non-linear.

4. DETERMINATION OF MWNT MODULI

4.1. Structural model

FEM modelling of SWNT was described in detail in [7], thus here only a brief review is given. Extension to a model of multi-walled carbon nanotube with two layers, double-walled carbon nanotube (DWNT) is straightforward. Using this model, through different loads the Young and shear moduli of a DWNT can be determined.

Using notations of Eq. (9), in which constant values k_r, k_θ and k_ϕ are taken from [8], based on the experience with graphite sheets, we obtain:

$$k_r = 938\ \text{kcal}/\text{mol}\text{Å}^2 = 651.72\ \text{nN}/\text{mm},$$
$$k_\theta = 126\ \text{kcal}/\text{mol rad}^2 = 0.875\ \text{nNnm}/\text{rad}^2,$$
$$k_\phi = 40\ \text{kcal}/\text{mol Å}^2 = 0.2779\ \text{nNnm}/\text{rad}^2.$$

With arbitrarily selected property of the beam elements ($E = 1\ \text{nN}/\text{nm}^2$), structural mechanics parameters of the beam element, such as cross sectional area A, moments of inertia I_1 and I_2, torsional constant J and shear modulus G are calculated. Values used for modelling covalent bonds between atoms with beam elements, recorded in author's previous paper [7], are given in Table 1.

Next step is modelling of a carbon nanotube as a frame-like structure, using the above mentioned beam model of a covalent bond.

Our DWNT consists of two armchair SWNTs (Fig. 2), of which the inner tube is (10, 10) armchair SWNT, whilst the outer tube is (15, 15) armchair SWNT. Interlayer spacing is 0.34 nm. Some geometrical characteristics are given in Tables 2 and 3.

Table 1. Properties of the beam element

Cross-sectional area, A	92.544 nm^2
Moments of inertia, I_1, I_2	0.1243 nm^4
Torsional constant, J	0.10277 nm^4
Shear modulus, G	0.384 nN/nm^2

Table 2. Inner SWNT geometric and mesh properties

Type	Armchair
Chirality	10, 10
Av. diameter	1.4 nm
Length	17.22 nm
No of nodes	2820
No of elements	4210

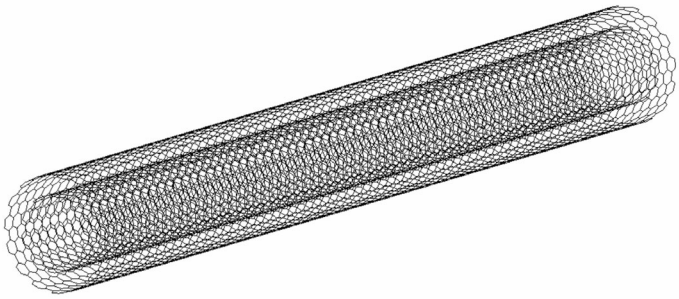

Fig. 2. FEM model of DWNT.

Table 3. Outer SWNT geometric and mesh properties

Type	Armchair
Chirality	15, 15
Av. diameter	2.08 nm
Length	17.22 nm
No of nodes	4230
No of elements	6315

4.2. The Young modulus of DWNT

To obtain the Young modulus, nanotubes were connected with a rigid element, i.e. top nodes of each nanotube were connected with centrally positioned master node, constrained to form a cantilever beam, and axially loaded at their free end with a force of 5 nN, Fig. 3. The Young modulus is calculated using the following equation:

$$E = \frac{FL}{A\Delta L}, \tag{12}$$

where F is axial force, L is double-walled nanotube's length, ΔL is elongation and A is cross-sectional area of DWNT, which is calculated as

$$A = \frac{\pi}{4}[(d_o + 0.34)^2 - (d_i - 0.34)^2]. \tag{13}$$

Here d_o is the outer tube diameter and d_i the inner tube diameter. Using Eqs. (12) and (13) and the elongation, obtained through axial load, $\Delta L =$ 0.0223053 nm, the Young modulus of DWNT is 1.04 TPa. For comparison, Li and Chou [9] obtained the Young modulus of a two layer armchair MWNT of the same diameter, equal to 1.05 ± 0.05 TPa.

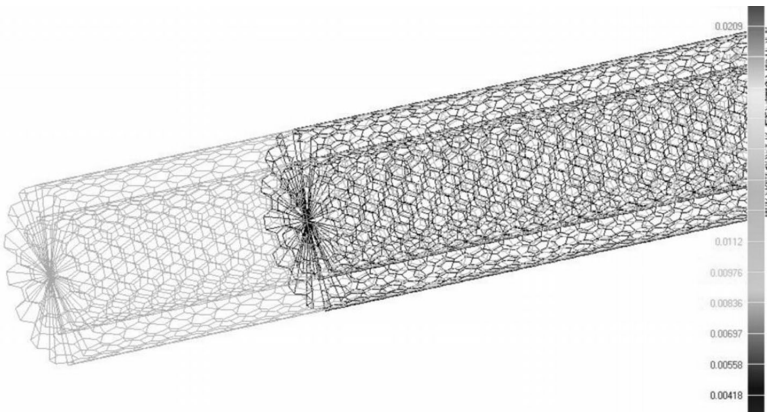

Fig. 3. Axial load of a DWNT.

4.3. The shear modulus of DWNT

In order to determine the shear modulus, the DWNT must be subjected to a torsional load, i.e. the DWNT is constrained in the same manner as in axial loading, forming a cantilever beam and loaded with torsional moment M = 5 nNnm (Fig. 4). The shear modulus G is calculated as

$$G = \frac{ML}{\varphi I_P}, \tag{14}$$

where M is the applied moment (torque), L is the length of the DWNT, φ is the torsional angle at the end of the tube and I_p is the polar moment of inertia, which is calculated as

$$I_p = \frac{\pi}{32}[(d_o + 0.34)^4 - (d_i - 0.34)^4]. \tag{15}$$

The torsional angle, φ obtained through torsional load, was 0.063455 rad. Using it in Eqs. (14) and (15), the shear modulus is obtained: $G = 0.418$ TPa. According to [9], the average shear modulus of a two-layer MWNT is about 0.4 TPa and is lower than that of an SWNT.

Comparing these two shear moduli with the shear modulus of a SWNT, modelled in [7] ($G = 0.419$ TPa), the results may be considered satisfactory.

Figure 5 shows another example of loading of a DWNT by bending.

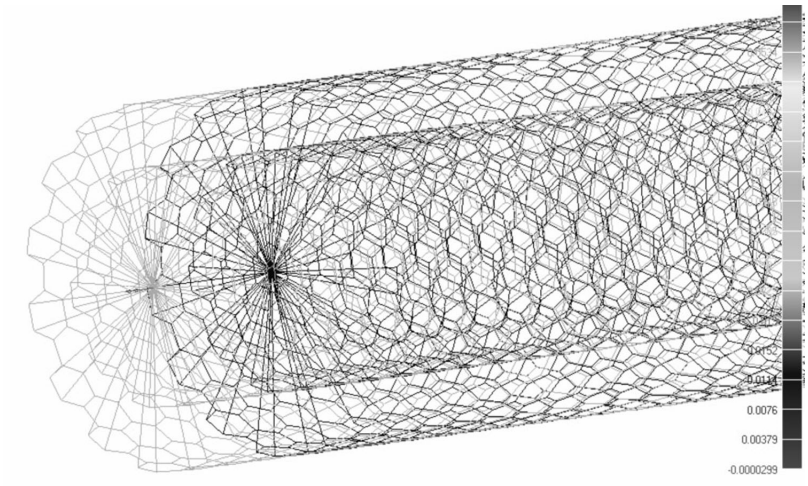

Fig. 4. Torsional loading of a DWNT.

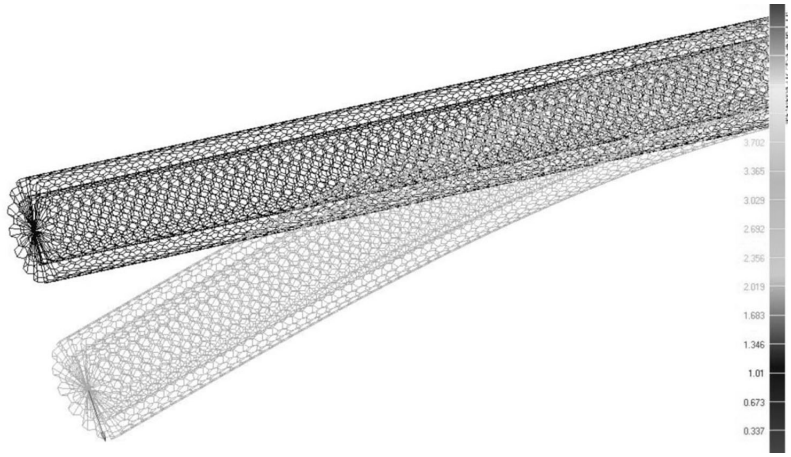

Fig. 5. Bending of a DWNT.

5. CONCLUSIONS

Structural mechanics model of a multi-layered carbon nanotube, using the finite element method, has been presented. This model as well as the method of modelling such molecular structures is in fact an extension of the previous work on SWNT modelling. The results of modelling, expressed through the Young and shear moduli, were compared with the results of other authors.

Next step in CNT research is incorporation or, better said, further investigation of the influence of van der Waals interactions on MWNT properties, i.e. finding a proper and correct way of modelling of such non-bonded interactions. Using these findings, the behaviour of a MWNT in different conditions and with different parameters can be explored. These can be, for example, influence of the diameter and of the number of layers on MWNT properties, influence of the temperature etc. The main goal of these CNT investigations is finding the right way to use the SWNT and MWNT model in modelling a composite material, using multiscale modelling for analysing nanocomposite materials.

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Mitmeseinalise süsiniku nanotoru modelleerimine lõplike elementide meetodil

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On käsitletud mitmeseinaliste süsiniku nanotorude teooriat ja nende modelleerimist lõplike elementide meetodil (LEM). Üheseinalise süsiniku nanotoru (SWNT) LEM-i lühiülevaade on toodud sissejuhatusena mitmeseinalise süsiniku nanotoru (MWNT) modelleerimisele, viimane koosneb mitmetest SWNT kihtidest. Samuti on kirjeldatud nanotoru kihtidevahelise ühenduse teooriat ja selle mõju koormustulemustele. MWNT modelleerimiseks on kasutatud üheseinalise süsiniku nanotoru lõplike elementide mudelit. Esitatud on MWNT teooria lühikirjeldus, samuti van der Waalsi vastasmõjust tingitud kihtidevahelise ühenduse modelleerimise teooria. Mitmeseinaliste süsiniku nanotorude modelleerimisel on kasutatud eri koormustingimusi. Tulemusi on võrreldud teiste autorite vastavate töödega.