Computers and Structures xxx (2013) xxx–xxx

Contents lists available at SciVerse ScienceDirect

Computers and Structures

journal homepage: www.elsevier.com/locate/compstruc

A molecular structural mechanics model applied to the static behavior of single-walled carbon nanotubes: New general formulation

R. Merli [a,*], C. Lázaro [a], S. Monleón [a], A. Domingo [b]

[a] Departamento de Mecánica de los Medios, Continuos y Teoría de Estructuras, Escuela Técnica Superior de Ingenieros, de Caminos, Canales y Puertos. Universidad Politécnica de Valencia, Camino de vera s/n, Valencia, Spain
[b] Departamento de Ingeniería de la Construcción, Escuela Técnica Superior de Ingenieros de Caminos, Canales y Puertos, Universidad Politécnica de Valencia, Camino de vera s/n, Valencia, Spain

ARTICLE INFO

Article history:
Received 23 April 2012
Accepted 30 November 2012
Available online xxxx

Keywords:
Single-walled carbon nanotubes
Molecular structural mechanics
AMBER potential
Morse potential
Prestressed state
Graphene sheet

ABSTRACT

A new general formulation for the mechanical behavior of Single-Walled Carbon Nanotubes is presented. Carbon atoms are located at the nodes of an hexagonal honeycomb lattice wrapped into a cylinder. They are linked by covalent *C–C* bonds represented by a truss or spring element, and the three-body interaction among two neighboring covalent bonds is reproduced by a rotational spring. The main advantage of our approach is to allow general load conditions (and any chirality) with no need of specific formulation for each load case, in contrast with previous works [26,27,31]. Four load configurations are adopted: tension, compression, bending and torsion of cantilevered SWCNTs. Calculations with our own codes for both AMBER and Morse potential functions have been carried out, aimed to compare their final results. Initial positions of the atoms (nodes) into nanotube cylindrical geometry has been reproduced in great detail by means of a conformal mapping from the planar graphene sheet. Therefore, the effect of initial SWCNTs curvature has been introduced explicitly through a system of initial stresses (*prestressed* state) which contribute to maintain their circular cross-section. Numerical results and deformed shapes for nanotubes with several diameters and chiralities under each load case are used to obtain their mechanical parameters with the only objective of checking the present formulation with previous works [28,30,20,24]. Also, the significance of the atomistic discrete simulations at the nano-scale size against other continuum models is underlined.

1. Introduction

Since their discovery [1], carbon nanotubes (CNTs) have attracted great interest of researchers and scientists because of their remarkable physical, mechanical and electrical properties [2]. For instance, CNTs show a singular coupling between mechanical strain and electrical conductivity [3,4], becoming ideal candidates for making nano-sensors and nano electro-mechanical systems (NEMS), with promising applications in robotics and biomechanics.

Regarding Materials Science and Engineering, nanotube reinforced composites and polymers have shown a wide range of potential applications, specially where a high ratio strength to weight is needed (e.g., aircraft industry). The main structural properties are their extreme longitudinal stiffness [5–8] (Young's modulus $\simeq 1$ TPa) and tensile strength [9–11] ($\sigma_y \simeq 50$ GPa).

Single-walled carbon nanotubes (SWCNTs) may be conceptualized as the result of rolling up a graphene sheet into a cylinder, and Multi-walled carbon nanotubes (MWCNTs) can be formed by placing several cylinders each one inside the rest coaxially, with a distance between walls of 0.34 nm as in bulk graphite. Each graphene sheet is formed by carbon atoms arranged in a covalent-bonded honeycomb lattice and the only link among carbon atoms of different sheets is the Van der Waals (VDW) interaction. Attending to the orientation of the hexagonal lattice with respect to the nanotube axis (chirality), three types of SWCNTs can be found:

1. ZigZag $(n,0)$ – One third of the bonds are parallel to the tube axis.
2. Armchair (n,n) – One third of the bonds are perpendicular to the tube axis.
3. Chiral (n,m) – All of the bonds are oblique to the tube axis.

where (n,m) are two integers which geometrically characterize the hexagonal lattice orientation into the cylinder (see [2]). The Zig-Zag and Armchair nanotubes are also called achiral and they are axisymmetric.

Covalent *C–C* bonds can be modeled by using the Tersoff–Brenner potential [37,38], which correctly corresponds with the

* Corresponding author. Tel.: +34 963877677.
E-mail addresses: ramergis@doctor.upv.es (R. Merli), carlafer@mes.upv.es (C. Lázaro), smonleon@mes.upv.es (S. Monleón), adoming@mes.upv.es (A. Domingo).

0045-7949/$ - see front matter © 2012 Civil-Comp Ltd and Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.compstruc.2012.11.023

Morse potential for strains below 10% [9]. On the other hand, VDW interaction has been usually modeled by using the well-known 6–12 Lennard–Jones potential. More details for the potentials adopted in this work will be given in Section 4.

Previously to the practical applicability of nanotubes in manufacturing composites (as in other structural applications), a deep understanding of their mechanical behavior is needed. For this purpose, several experimental studies related to Multi-walled nanotubes [10,12–15] and to SWCNTs ropes [11,16] have been carried out. However, to date, there is no experimental studies about individual SWCNTs due to their extremely small size and the subsequent difficulties in their manipulation. Therefore, theoretical work may be helpful for evaluating the structural response of SWCNTs.

Although many analytical or numerical methods applied to the mechanical behavior of nanotubes have been developed, they roughly fall into two different categories: atomistic scale and continuum scale methods. The atomistic methods (Molecular Dynamics, ab initio, tight-binding) can successfully reproduce physical phenomena as buckling [17,18] and estimate elastic parameters of CNTs [3,7], but they have the disadvantage of being limited at a relatively low number of atoms (about 10^9 according to [19]) because of their high computational cost. Related to MD methods, the motion of a system of N particles is described dynamically by a vector of instantaneous positions and velocities (dimension 6*N*). In addition the time dependence implies using algorithms of time-integration sometimes complicated. Also, a difficult issue in MD is to describe the heat conduction with the surrounding media. Opposite to MD calculations, our MSM model have the following advantages:

1. No heat conduction is required to be accounted for in the formulation. Then, some reliability is sacrificed in order to simplify the model.
2. MSM models are basically static and no time-integration is needed.
3. For the same system size, only 3*N* fundamental variables are involved (nodal displacements). This reduction implies a much higher numerical performance of the algorithm.

On the other hand, continuum methods are computationally cheaper and capable of analyse longer systems, but the choice of some parameters for establishing an equivalence with the atomistic level may be controversial. In fact, the wall thickness range from $t = 0.066$ nm [17] to the usual value of 0.34 nm [20] which corresponds to the inter-planar distance in graphite. Even some authors deem CNTs as solid cylinders [19]. Moreover, continuum methods are insensitive to atomistic defects which have an important influence on the final response of CNTs.

Derived from Molecular Dynamic (MD) methods, a molecular structural mechanics (MSM) model may be adopted, which is reasonable in terms of computational expense whereas atomistic scale is correctly displayed. Some previous works [21,22,24] considered CNTs as a frame system with carbon atoms located at nodes and rigid bars (provided with axial, flexural and torsional stiffnesses) representing covalent bonds. Different layers in MWCNTs were connected by several truss rods between neighboring atoms. Alternatively, Odegard et al. [23] modeled the graphene sheet as a 2D truss model with additional rods trough the unit hexagonal cell.

In the context of materials with granular structure at the microscopic level (microscale), lattice networks composed of Reissner's beam elements have been utilized in order to solve some conceptually related problems, as the dynamic fracture of a brittle material [25]. Hence, in the MSM framework, the use of Reissner beam elements with large rotations could be a promising extension for dealing with high local deformations into the nanotube wall.

Another kind of MSM model was called the 'stick-spiral' model by Chang and Gao [26] where covalent bonds were reproduced by axial springs and the three-body interaction was introduced directly by three spiral springs on each node. In that work (extended later in [27]), the influence of diameter and chirality in the Young's modulus and Poisson's ratio was analyzed for ZigZag and Armchair SWCNTs taking the curvature of the wall into account. The same subject was investigated by Chang and Gao [28] but neglecting the curvature and similar issues were addressed by Wang [29]. Also Natsuki et al. [30] extended their previous work to the tensile and compressive behavior of SWCNTs. All the aforementioned researches related to MSM have taken advantage of the axisymmetry of ZigZag and Armchair nanotubes, limiting their calculations to a small unit cell involving only a few atoms.

Moreover, Chang et al. [31] generalized the work in [26] to Chiral SWCNTs and extended it to the study of shear modulus. In a more general way, Meo and Rossi [20] implemented the 'stick-spiral' model in the commercial code ANSYS® and included Chiral SWCNTs in the study of the longitudinal behavior.

The main contributions of this paper can be outlined as follows:

1. In this paper, the main objective is to analyze the tensile, compressive, flexural and torsional behavior of SWCNTs by means of the 'stick-spiral' model and show the influence of the diameter and chirality in their mechanical response. For this purpose, analytical expressions have been derived through an energy approach and have been numerically implemented. The main advantage of our approach is the ability to reproduce general load conditions (and any chirality) with no need of additional equations, in contrast with previous works which treat specific load situations and chiralities with *ad hoc* equations for each case, and are limited to a small unit cell involving only a few atoms under a particular load case (see [26–31]). This advantage translates into a higher versatility to deal with physically more realistic cases (e.g., the different chiralities and load configurations produced during the SWCNTs growing procedure).
2. A special issue not explicitly included in MSM models (although the wall-curvature was included in the equations) is the *preenergy*, defined as the excess of strain energy from an infinite planar graphene sheet to the nanotube [17,32]. As has been shown [5,33–35], this preenergy is proportional to the curvature of the wall $1/R^2$ (where R is the tube radius) leading to an stabilization effect into its cross-sectional area. In this paper, we introduce the preenergy as a system of initial strains which produces a 'prestressed state' previous to the action of any external loading. Namely, the influence of this initial stresses is not negligible (differences around 5–15% in longitudinal stiffness are obtained), mainly in axial behavior of single-walled carbon nanotubes (SWCNTs) as we can state from our results. Nonetheless, many released references simply ignore this fact.
3. A detailed comparison between the more usual interatomic potential functions (AMBER and Morse) has been performed under several load cases: tension, compression, bending and torsion. Likewise, both force–lengthening and moment-distortion nonlinear relationships have been regarded with Morse potential, generalizing the work of Meo and Rossi [20]. In this way, we keep the straightforward relationship between both interatomic potentials and both kinds of structural elements (bar elements and rotational springs) into the 'stick-spiral' model. However, we have not included any geometrical updating into the iterative procedure.
4. Our numerical results have been compared with those from the standard beam models and we have concluded that the applicability of continuum methods is doubtful because they are unable to reproduce the atomistic detail at that nanoscale

Please cite this article in press as: Merli R et al. A molecular structural mechanics model applied to the static behavior of single-walled carbon nanotubes: New general formulation. Comput Struct (2013), http://dx.doi.org/10.1016/j.compstruc.2012.11.023