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One-dimensional nonlocal elasticity for tensile single-walled carbon nanotubes: A molecular structural mechanics characterization

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ABSTRACT

The parameters required for modeling tensile single-walled carbon nanotubes (SWCNTs) with a nonlocal rod model are estimated. Molecular structural mechanics (MSM) simulations are carried out for the mechanical analysis of SWCNTs with different diameter, length and chirality. Representative axial strain fields are then used in a parameter estimation procedure as reference solutions to tailor a nonlocal rod model. Obtained nonlocal parameters are further validated by comparing the total strain energy of MSM reference solutions and corresponding nonlocal rod solutions. The effect of size and chirality on the optimal value of the estimated parameters is discussed in details. Analytical relations between nonlocal parameters and geometry of the SWCNTs are obtained.

1. Introduction

Fundamental insight into the behavior of carbon nanotubes (CNTs) is customarily obtained with atomistic simulations (Rafiee and Moghadam, 2014). Although accurate, these simulations are usually computationally intensive and not particularly suited for the analysis of long CNTs or more complex systems such as CNT networks or composites. Here, we propose a one-dimensional nonlocal rod model which is kinematically and energetically equivalent to a generic axially loaded single-walled carbon nanotube (SWCNT).

The most used atomistic approaches for the analysis of carbon nanotubes (CNTs) include *ab initio* calculations (Sánchez-Portal et al., 1999), molecular dynamics (Liew et al., 2004), and molecular mechanics (Belytschko et al., 2002). Although accurate, the application of these procedures is limited to small-scale atomistic systems. In an effort to decrease the computational effort of atomistic simulations, Li and Chou (Li and Chou, 2003) proposed a simple and efficient approach, referred to as molecular structural mechanics (MSM), which combines molecular mechanics and classical structural mechanics. In MSM, CNTs are modeled as space frame structures in which beam and spring elements replace covalent bonds between carbon atoms. Based on this concept, Tserpes and Papanikos (Tserpes and Papanikos, 2005) developed a three-dimensional finite element model to investigate the mechanical properties of armchair, zigzag and chiral SWCNTs. The results obtained by these authors are in good agreement with those provided by theoretical and experimental studies (Yakobson et al., 1996; Lu, 1997; Xin et al., 2000). The computational effort of MSM is, however, still considerable for long nanotubes.

An alternative approach to atomistic simulations of CNTs relies on equivalent continuum formulations which are relatively simpler and result in a reduced computational effort. In modeling SWCNTs with a continuum mechanics model, the discrete atomic lattice of the nanotube is replaced by a continuous and homogeneous solid. In general, either isotropic and anisotropic shells (Yakobson et al., 1996; Chang, 2010) or one-dimensional theories such as Euler–Bernoulli and Timoshenko beam models (Poncharal et al., 1999; Yoon et al., 2004) as well as rod models (Yao and Lordi, 1998) are employed.

The use of classical continuum formulations at the nanoscale, however, might be questionable (Chang et al., 2006). Classical theories do not account for small length scale effects induced by the discrete structure of SWCNTs. Promising approaches are those based on nonlocal continuum mechanics which allows the consideration of size effects by introducing small-scale parameters in the constitutive relation. The main advantage of a nonlocal formulation lies on the possibility of accounting for interatomic long range interactions (in Eringen's nonlocal theory (Eringen,

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1983), the strain at a given point is a weighted average of the strain at surrounding points). Applications of nonlocal continuum mechanics to the study of CNTs are reported in several papers (Sudak, 2003; Zhang et al., 2005; Arash and Wang, 2012).

Although several studies on the modeling of SWCNTs with nonlocal formulations have been carried out, only few attempts have been made to determine the value of the nonlocal parameters. Duan et al. (2007) and Hu et al. (2011) calibrated the small-scale parameters for the free vibration problem in SWCNTs by using molecular dynamics simulations. They found that the estimated nonlocal parameters vary with the aspect ratio, mode shapes and boundary conditions of the SWCNTs. A similar approach was used in Khademolhosseini et al. (2012) to capture size effects in the dynamic torsional response of (6, 6) and (10, 10) armchair SWCNTs with a nonlocal shell model. Narendar et al. (2011), by using MSM, derived an expression of the small scale parameters to study the ultrasonic wave propagations in SWCNTs.

In this contribution, we estimate the nonlocal parameters for tensile armchair, zigzag and chiral SWCNTs by comparing the axial strain field calculated with MSM and a nonlocal elastic rod model. First, MSM is used to investigate size and chirality effects on SWCNTs Young's modulus and on the strain field in tensile simulations as discussed in Section 2.3 and 2.4, respectively. Then, a two-component local/nonlocal model (Eringen, 2002; Benvenuti and Simone, 2013), a variant of the classical integro-differential Eringen's formulation, is considered for the modeling of SWCNTs as continuum rods. The corresponding one-dimensional constitutive equation is summarized in Section 3. Instead of the classical Gaussian kernel, the atomistically-based kernel developed by Picu (2002) is adopted. As in atomic pair potentials (Rapaport, 2004), this kernel has a positive value at the origin and becomes negative at some distance. Finally, the identification of the nonlocal parameters is performed by means of an optimization procedure by minimizing the discrepancy between MSM and nonlocal axial strain fields as described in Section 4. To improve the agreement between atomistic and nonlocal results, the quadratic penalty method (Nocedal and Wright, 2006) is used. The effect of diameter and chirality on the value of the calculated parameters is further discussed. Hence, an analytical relation between the nonlocal parameters and the nanotubes diameter and chirality is derived.

To our knowledge, this paper represents a first attempt to estimate nonlocal parameters for the modeling of SWCNTs subjected to static axial load by using an atomistic (MSM) model. The results presented herein ensure the reliability of nonlocal formulations to model tensile carbon nanotubes and, in particular, to predict their axial strain field and strain energy.

2. Molecular structural mechanic simulations of single-walled carbon nanotubes

2.1. Atomic model of single-walled carbon nanotubes

Molecular structural mechanics (MSM) is an atomistic modeling technique to study the mechanical properties of materials at the atomic scale. Similar to molecular mechanics (MM), molecules in MSM are modeled as discrete systems of balls (representing atoms) and springs (representing covalent and non-covalent bonds). Thus, knowing the position of the atoms and the stiffness of the chemical bonds that hold them together allows to predict the mechanical response of an atomic structure.

The constitutive equations for the structural elements depend on the mathematical relations describing the total potential energy Π of a molecule (Lewars, 2010) which is expressed as:

$$\Pi = \sum_{bonds} \Pi_{stretch}(\Delta r) + \sum_{angles} \Pi_{bend}(\Delta\omega) + \sum_{dihedrals} \Pi_{torsion}(\Delta\phi) + \sum_{pairs} \Pi_{nonbond}(\Delta r). \tag{1}$$

Here, $\Pi_{stretch}$, Π_{bend}, $\Pi_{torsion}$ and $\Pi_{nonbond}$ are the energy contributions corresponding to bond stretching, angle bending, torsional motion around a single bond and stretching of non-covalent bonds (van der Waals forces), while Δr, $\Delta\omega$ and $\Delta\phi$ denote variations of covalent or non-covalent bonds length and angles between three atoms and dihedral angles (see Fig. 1 for a representation of these quantities). As observed in Li and Chou (2003) and Ru (2000a), the energy contribution from van der Walls interactions is negligible for covalent systems undergoing small deformations. Therefore, we neglect the contribution of $\Pi_{nonbond}$ in (1) since the small deformation hypothesis is adopted in this work.

Assuming the bond stretching and angle bending terms defined by the modified Morse potential (Belytschko et al., 2002) and the torsional contribution described by a parabolic function (Kalamkarov et al., 2006), the energy contributions in (1) are defined as:

$$\Pi_{stretch}(\Delta r) = D_e\left[\left(1 - e^{-\beta\Delta r}\right)^2 - 1\right], \tag{2}$$

$$\Pi_{bend}(\Delta\omega) = \frac{k_\omega}{2}\Delta\omega^2\left[1 + k_{sextic}\Delta\omega^4\right], \text{ and} \tag{3}$$

$$\Pi_{torsion}(\Delta\phi) = \frac{k_\phi}{2}\Delta\phi^2. \tag{4}$$

According to Belytschko et al. (2002) and Kalamkarov et al. (2006), the constant parameters D_e, β, k_ω, k_{sextic} and k_ϕ are equal to 0.603105 nN nm, 26.25 nm^{-1}, 0.9 nN nm/rad^2, 0.754 rad^{-4}, and 0.278 nN nm/rad^2, respectively.

To study the mechanical properties of SWCNTs with MSM, we consider a frame finite element model geometry computed according to Kołoczek et al. (2001) with the constitutive equations of each structural element derived from (2)–(4). More specifically, the covalent bonds are defined as two-node space frame elements with the relation between axial force and axial stretch expressed as

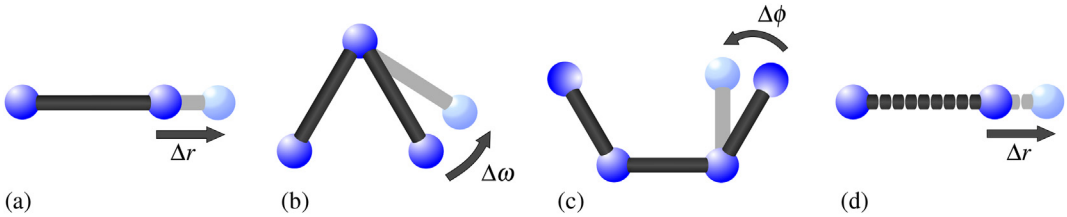

Fig. 1. Interatomic interactions in molecular structural mechanics: (a) bonds stretching, (b) angle bending, (c) torsion and (d) stretching of non-covalent bonds.