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Fracture and progressive failure of defective graphene sheets and carbon nanotubes

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ABSTRACT

An atomistic based finite bond element model for the prediction of fracture and progressive failure of graphene sheets and carbon nanotubes is developed by incorporating the modified Morse potential. The element formulation includes eight degrees of freedom reducing computational cost compared to the 12 degrees of freedom used in other FE type models. The coefficients of the elements are determined based on the analytical molecular structural mechanics model developed by the authors. The model is capable of predicting the mechanical properties (Young's moduli, Poisson's ratios and force–strain relationships) of both defect-free and defective carbon nanotubes under different loading conditions. In particular our approach is shown to more accurately predict Poisson's ratio. The numerical prediction of nonlinear stress–strain relationships for defect-free nanotubes including ultimate strength and strain to failure of nanotubes is identical to our analytical molecular structural mechanics solution. An interaction based mechanics approach is introduced to model the formation of Stone–Wales (5-7-7-5) topological defect. The predicted formation energy is compared with *ab initio* calculations. The progressive failure of defective graphene sheets and nanotubes containing a 5-7-7-5 defect is studied, and the degradation of Young's moduli, ultimate strength and failure strains of defective nanotubes is predicted.

1. Introduction

Carbon nanotubes (CNTs) [1] exhibit exceptional physical properties: small size, low density, high stiffness, high strength and excellent electronic and thermal properties [2–7]. These exceptional mechanical and physical properties along with low weight of CNTs and recent improvements in their synthesis and purification techniques make CNTs excellent candidates for use in tailoring properties of composites [8–10].

There is evidence that defects can appear at the stage of CNT growth and purification [11,12], during device or composite production (e.g. chemical functionalizations) [13,14], or under mechanical strains [15]. Research has indicated that even a small number of defects in the atomic network will result in some degradation [16,17] of their mechanical properties. Such defects also act as scattering centers for phonons propagating along the tube axis, thus reducing intrinsic tube conductivity. The modeling of mechanical properties of these defective CNTs on a microscopic and atomistic level represents a great challenge from both theoretical and experimental points of view.

In general, the theoretical approaches based on quantum/molecular mechanics, including the classical molecular dynamics (MD) and *ab initio* methods, give accurate results, but they are much more computationally expensive and only suitable for small systems containing limited number of atoms. Some recent developments based on continuum mechanics have been reported for estimating elastic properties of nanotubes, such as the representative continuum truss model [18], the continuum structural mechanics model [19], and the analytical molecular mechanics model [20]. These methods only predict elastic constants such as Young's moduli and/or Poisson's ratio of CNTs because the harmonic energy potential functions were used. In order to model the mechanical behavior of CNTs up to or beyond bond breaking, a more complex interatomic potential function is needed. The Brenner potential function [21] is considered more accurate and versatile. It can handle changes in atom hybridization and bonds with atoms other than carbon. A continuum mechanics approach directly incorporating the Brenner potential function has been developed by Huang's group [22,23] to model elastic properties and stress–strain relationships of carbon nanotubes based on a modified Cauchy–Born rule. Recently, another simple analytical molecular structural mechanics model [24] incorporating the modified Morse potential function [25] has been developed by the authors to model defect-free CNTs under tensile and torsion loadings. By incorporating the modified Morse potential the authors are

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able to predict the entire nonlinear stress–strain relationships including the ultimate strength and strain to failure of the nanotubes. The analytical model has been extended to solve mechanical responses of single- and multi-walled CNTs under internal and external pressure loadings [26,27] as well as aligned nanotube-composites [28]. The analytical model not only provides simple closed-form solutions but also presents a better insight of the role of the atomic networks.

Continuum based models have not been well developed for predicting the effects of defects on mechanical properties of CNTs and nanotube composites. The quantum mechanics and molecular dynamics (MD) simulations are still the main tools to look at the effects of defects on mechanical [4,16,17,25,29–32] and thermal properties [33,34] of CNTs. One attempt using a continuum based atomistic model to study defect nucleation in carbon nanotubes under mechanical loadings can be seen in the study by Jiang et al. [35]. Very recently, the effect of defects on fracture of nanotubes has been studied by Tserpes et al. [36,37] using the Finite Element (FE) based model where they assumed that the dimensions of the nanotube structures remain unchanged after the formation of defects, which may not be true in general as atoms redistribute to minimize energy. In this paper, a finite bond element method for the mechanical behavior of defective CNTs has been developed. The developed numerical method is equivalent to the analytical molecular structural mechanics model [24] for defect-free CNTs. An interaction based mechanics approach is proposed to determine the equilibrium geometry configurations of the topological 5-7-7-5 defect [38] in single-walled carbon nanotube and their residual atomic forces. Then, the stress–strain relationship of defective CNTs containing a Stone–Wales defect is predicted by using the present finite bond element method based on the modified Morse potential function. Progressive failure in the post failure region is investigated and a few computational examples are discussed. The predictions compare favorably to the corresponding published results from experiments and numerical calculations (i.e. tight binding or molecular dynamics) for armchair and zigzag carbon nanotubes.

2. An atomistic based finite bond element model

A single-walled carbon nanotube can be viewed as a hollow cylinder rolled from a graphene sheet, composed of carbon hexagons. The diameter of the nanotube can be calculated as $d = \frac{\sqrt{3}a}{\pi}\sqrt{(n_1^2 + n_2^2 + n_1 n_2)}$ where $a = 0.142$ nm is the C–C bond length, and the pair of integers (n_1, n_2) are indices to represent its helicity such as armchair ($n_1 = n_2$) and zigzag ($n_2 = 0$) nanotubes.

There are several different potential functions available [21,39,40] for describing C–C bond interaction other than simple harmonic functions. Among them, the modified Morse potential function [25] is simple and is used in the present study. The modified Morse potential function was correlated to the Brenner potential function for strains below 10%. In this paper, a new term E_{torsion} is added to consider the bond energy due to angle variation of bond twisting $\Delta\phi$ which has been found to be negligible for defect-free tubes [19] and was neglected in earlier studies.[20,24–27] However, this term may play a more important role in defective tubes. The energy potential function is given as follow:

$$E = E_{\text{stretch}} + E_{\text{angle}} + E_{\text{torsion}} \tag{1}$$

where E_{stretch} is the bond energy due to bond stretch Δr and E_{angle} is the bond energy due to bond angle variation $\Delta\theta$, and

$$E_{\text{torsion}} = \frac{1}{2}k_\phi(\Delta\phi)^2 \tag{2}$$

The parameters associated with the terms E_{stretch} and E_{angle} can be seen in Refs. [24,25]. The force constant associated with the term (2) is taken as [19,41,42] $k_\phi = 0.278$ nN nm/rad^2.

The stretch force, the angle-variation moment and the torsional moment can be obtained from differentiations of equation (1) as functions of bond stretch, bond angle variation and torsion angle variation, respectively:

$$F(\Delta r) = 2\beta D_e(1 - e^{-\beta\Delta r})e^{-\beta\Delta r} \tag{3a}$$

$$M(\Delta\theta) = k_\theta|\Delta\theta[1 + 3k_{\text{sextic}}(\Delta\theta)^4] \tag{3b}$$

$$M_\phi(\Delta\phi) = k_\phi\Delta\phi \tag{3c}$$

A constant bond torsional stiffness is implied by Eq. (3c). The stretch stiffness and the angle-variation stiffness can be further obtained from differentiations of equations (3a) and (3b) as functions of bond stretch and bond angle variation, respectively:

$$k_r(\Delta r) = 2\beta D_e^2(1 - 2e^{-\beta\Delta r})e^{-\beta\Delta r} \tag{4}$$

$$k_\theta(\Delta\theta) = k_\theta|\Delta\theta\lfloor 1 + 15k_{\text{sextic}}(\Delta\theta)^4\rfloor \tag{5}$$

Analytical solutions for predicting nonlinear mechanical behaviors of defect-free SWCNTs have been investigated by using an effective "stick-spiral" model based on a unit cell approach [24]. The effective "stick-spiral" model uses a stick with Eq. (3a) to model the force–stretch relationship of the C–C bond and a spiral spring with Eq. (3b) to model the angle bending moment resulting from an angular variation of bond angle. The stick is assumed to have an infinite bending stiffness and finite torsional stiffness. One can include the torsional term by using the stick with Eq. (3c).

For a defective nanotube with loss of local symmetry, the unit cell approach becomes inappropriate, and a generalized molecular mechanics (MM) model [43] or a finite element (FE) type model [19] are needed to include the entire molecular structure system of the defective nanotube in order to consider the effect of defects on its mechanical response. In this paper, we propose a new FE type model for nanotubes based on the effective "stick-spiral" model. Bond elements are developed for simulating deformation modes of the chemical bonds.

Typically the FE type model [19] uses a beam element [44] with sectional stretch stiffness for the force–stretch relationship of the C–C bond, sectional flexural rigidity for the angle bending moment (Eq. (3b)), and sectional torsional stiffness for the torsional moment (Eq. (3c)). Each element has 12 degrees of freedom. The major differences between the FE type model and the effective "stick-spiral" model are the assumptions made with respect to the bending stiffness (flexible vs rigid). The bond element used in the present paper has infinite bending stiffness (the stick) with finite bending stiffness of the two end joints (the spirals) indicated by the square box shown in Fig. 1. Each of the three molecular deformation modes (stretching, angle variation, and angle torsion) are represented by tension, bending and torsion of a bond element with 8 degrees of freedom $u_e = [\,u_{xi}\ \ u_{yi}\ \ u_{zi}\ \ \phi_i\ \ u_{xj}\ \ u_{yj}\ \ u_{zj}\ \ \phi_j\,]$. The element can be stretched (pure tension) and torqued (pure torsion) along its axial direction and bent by relative transverse displacement without angle changes at the two ends. The bond angle variation of the bond element can be associated with the relative transverse displacement (e) between the two ends as $d\theta = e/a$ (Fig. 1c). The present approach, designated the finite bond element model, is expected to give the same solution as the "stick-spiral" model [20,24] for defect-free CNTs. The stick-spiral model with infinite bending stiffness [20,24] represents the true physical deformation modes and is able to predict both in-plane stiffness (Young' modulus) and Poisson's ratio of CNTs accurately.

For the bond element defined in Fig. 1 in a three-dimensional space, the elemental equilibrium equation can be established for every bond element. The final system of equations with appropriate boundary conditions imposed can be solved by the displacement-control Newton–Raphson method. A MATLAB program has