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Nonlinear elastic properties of graphene sheet using MM3 potential under finite deformation

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ABSTRACT

MM3 interatomic potential is combined with Cauchy–Born rule for the first time to predict elastic properties of the graphene sheets at infinitesimal and finite strains. Further, using plane stress condition, basal plane stiffness and Poisson's ratio calculated using MM3 potential are found to be 310.59 nN/nm and 0.28, respectively. The elastic properties calculated using MM3 potential are somewhat better as compared to those of predicted through Tersoff–Brenner and second generation REBO potentials when compared with the experimental results. Elastic properties are also obtained with MM3 potential considering alternative empirical constants for bond stretch energy term. The present results are also compared with those obtained through modified Morse and first/second generation REBO potentials. The present multiscale model in the framework of MM3 potential will also facilitate the further investigations on the large atomistic structures with greater accuracy.

1. Introduction

Nanoscience and nanotechnology have emerged as new areas of research involving various synthesized nanomaterials such as carbon nanotubes (CNTs) discovered by Iijima [1] and graphene sheets (GSs), a single layer of carbon atoms, first separated by Novoselov et al. [2,3] from bulk graphite through micromechanical cleavage. Single walled carbon nanotube (SWCNT) is considered to be the strongest material with strength greater than diamond [4]. Due to the exceptional thermal, mechanical and electrical properties, CNTs and GSs are found quite suitable for engineering applications including sensing/actuation, electronic components, nanoelectromechanical systems, load bearing members, oscillators, manufacturing, medical science (e.g. artificial bones and teeth), atomic force microscope cantilever tips, and molecular transportation etc. For the design of devices involved with CNTs and GSs, one of the requirement is to investigate the mechanical characteristics (stiffness/strength properties, static and dynamic response) of these structures. Limited experimental studies have been carried out on the prediction of elastic properties, static and dynamic behaviour of single/multi walled carbon nanotubes (SWCNTs/MWCNTs) [5,6] and GSs [7–9]. These materials are widely used in structural materials as a reinforcement to improve their elastic response [10,11]. Due to the experimental difficulties at small scale, the mathematical modelling and analysis of CNTs and GSs is explored as an efficient tool to understand their structural behaviour using quantum mechanics simulation, molecular mechanics/dynamics simulation, continuum modelling (beam, plate and shell models), stress and strain gradient nonlocal continuum modelling, and multiscale modelling.

The continuum elastic models (such as beam, plate and shell models) can be employed to study the mechanical behaviour of 2D nanostructures if their length/diameter is several times of the bond length between the carbon atoms [12]. In continuum modelling of such 2D nanostructures, tensile/shear moduli and Poisson's ratio are estimated based on the comparison of mechanical behaviour (natural frequencies, mode shapes, deflection, dynamic response) predicted through experiments/atomistic simulations and continuum models. Treacy et al. [13] experimentally reported the Young's modulus of individual CNTs in 11 walled CNT varying from 0.4 to 4.15 TPa with an average of 1.8 TPa. The elastic properties were estimated by comparing the vibration amplitude of CNT measured using transmission electron microscope to that predicted through the Euler–Bernoulli beam model. The Young's modulus was reported to be ~1.25 TPa by comparing the temperature induced vibration response measured using transmission electron microscopy to that of predicted through Euler–Bernoulli beam model [14]. The Young's modulus was predicted as 1.28 ± 0.59 TPa and 1.0 TPa by comparing the measured deflection of cantilever and fixed CNTs using atomic force microscope with that predicted using Euler–Bernoulli cantilever [15] and fixed Timoshenko beams [16], respectively. However, due to the presence of van der Waals (vdW) interactions, the elastic properties predicted through the single beam

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model were not accurate for the modelling of MWCNTs with smaller length to diameter ratio and a few number of concentric tubes [17,18]. Continuum modelling is computationally efficient way to study the mechanical characteristics of nanostructures but their inability to capture the effect of material nonlinearity due to nonlinear interatomic interactions limits their applications and predictions may alter with the inclusion of material nonlinearity. Further, the equivalent thickness for continuum model is questionable which may predict inaccurate bending modulus as compared to that predicted through atomistic simulations.

The continuum models for CNTs and GSs (discrete structures) cannot capture the small scale effects [19]. The theoretical characterization of CNTs using nanorod/nanobeam model and continuum plate model for GSs was explored in the literature. To capture the small scale effects, different nonlocal continuum stress and strain gradient theories such as: Eringen's nonlocal stress gradient theory [20–23], strain gradient theory [24], modified couple stress theory [25] were employed for analyzing the nanostructures. However, the determination of nonlocal scale parameter is somewhat arbitrary without any theoretical framework. From the different stress and strain gradient elasticity theories, Eringen's nonlocal stress gradient theory is widely employed to characterise the mechanical response of single/multi layered graphene sheet (SLGS/MLGS) [26–28].

In order to capture the mechanical response more accurately including material nonlinearity, atomistic simulation is a powerful tool to characterise materials at atomic scale for predicting the benchmark solutions. These are broadly classified into two categories (i) Quantum mechanics approaches: *ab initio* and tight binding simulation (ii) Molecular mechanics/dynamics (MM/MD) simulations. The *ab initio* and tight binding methods under quantum mechanics simulation produce more accurate results as compared to MM/MD simulations. MM/MD simulation is a powerful and computationally efficient tool for atomistic system with relatively large number of atoms as compared to *ab initio* and tight binding methods. In MD/MM simulation, atoms are considered as point masses and the equations of motion are derived on the basis of the Newtonian mechanics. In MD simulation, effect of temperature is taken into account and equations of motion are solved using time integration techniques. In MM simulation, equilibrium equations derived through the minimization of the potential energy functional are solved. In MM/MD, interactions between the atoms are modelled by interatomic potentials like Lennard–Jones potential [29], first and second generation reactive empirical bond order potentials [30–32], Morse [33] and modified Morse potential [34], molecular mechanics force fields: MM2 [35], MM3 [36], MM4 [37], universal force field (UFF) [38] etc. In the space frame modelling of nanostructures, bonds between the atoms are modelled as beam/truss elements. The cross sectional properties of these beams are obtained by equating the interatomic potential energy with the strain energy of continuum beams/truss. As the number of nodes in computational model based on space frame approach are equal to the number of atoms, it is computationally prohibitive as compared to continuum and multiscale modelling.

To achieve the accuracy of MM simulation and computational efficiency of continuum modelling, the multiscale modelling approach is employed for the atomistic system with large number of atoms. In the multiscale modelling, the constitutive matrix calculated directly from molecular potential functions at atomic scale is used at the continuum scale. The molecular model accounting for the bond interactions is coupled to continuum model through Cauchy–Born rule. The elastic properties of SWCNTs and GSs using multiscale modelling were estimated using the interatomic potentials in conjunction with Cauchy–Born rule [39,40], higher order Cauchy–Born rule [41–43] and exponential Cauchy–Born rule [44]. The variation of extensional and bending tangent stiffness coefficients of GS with strain and curvature was reported using multiscale approach based on first and second generation REBO potentials [45–47]. From the reported studies, it may be noted that the most of the studies in the multiscale framework to model the effect of material nonlinearity are based on Tersoff–Brenner interatomic potential. However, the elastic properties obtained with Tersoff–Brenner potential differ significantly from those of reported in experimental studies [9]. Berinskii and Borodich [48] noted the similar behaviour of REBO potentials and calculated elastic properties with harmonic type improved potentials. However, the quadratic type harmonic interatomic potential considered in Ref. [48] is incapable to model the material nonlinearity due to nonlinear atomic interactions and lack of proper nonlinear models for accurate description of graphene mechanical properties was brought into the conclusion. To the best of the authors' knowledge, nonlinear constitutive model for GSs in the framework of multiscale modelling using more accurate interatomic potential such as MM3 interatomic potential, has not be addressed in the literature. In the present work, nonlinear constitutive behaviour of GSs under finite strains using Cauchy–Born rule in conjunction with the MM3 interatomic potential, along with the modified Morse potential for the purpose of comparison, is reported. The present results are also compared with those of obtained through first and second generation reactive empirical bond order (REBO–I and REBO–II) potentials [47].

2. MM3 and modified Morse potential for carbon

The MM3 interatomic potential contains energy terms with higher order than quadratic in nature and is found to be suitable to study the elastic properties of GSs and CNTs. In MM3 interatomic potential, the total energy of the atomistic system is expressed as:

$$V_T = \sum U_s + \sum U_\theta + \sum U_\varphi + \sum U_{s\theta} + \sum U_{s\varphi} + \sum U_{\theta\bar{\theta}} + \sum U_{vdW} \tag{1}$$

where V_T is total potential energy of the atomistic system in kcal/mole, U_s, $U_\theta$and $U_\varphi$are the energies due to bond stretch, bond angle and dihedral angle, respectively, $U_{s\theta}$, $U_{s\varphi}$ and $U_{\theta\bar{\theta}}$ are the cross interaction energies due to stretch–bend, stretch–torsion and bend–bend interactions, $U_{vdW}$is energy due to non–bonded van der Waals interactions. The mathematical form of these energies as a function bond lengths and angles is expressed as [36]:

Bond stretch energy:

$$U_s = 71.94 k_s (r - r_0)^2 \left[1 - 2.55(r - r_0) + \frac{7}{12} 2.55^2 (r - r_0)^2\right] \tag{2a}$$

In–plane bending energy:

$$U_\theta = 0.021914 k_\theta (\theta - \theta_0)^2 \left[\begin{array}{l} 1 - 0.014(\theta - \theta_0) + 5.6 \times 10^{-5}(\theta - \theta_0)^2 - \\ 7.0 \times 10^{-7}(\theta - \theta_0)^3 + 9.0 \times 10^{-10}(\theta - \theta_0)^4 \end{array}\right] \tag{2b}$$

Torsional energy:

$$U_\varphi = \frac{V_1}{2}(1 + \cos\varphi) + \frac{V_2}{2}(1 - \cos 2\varphi) + \frac{V_3}{2}(1 + \cos 3\varphi) \tag{2c}$$

Stretch–bend interaction energy:

$$U_{s\theta} = 2.51118\, K_{s\theta} [(r - r_0) + (\bar{r} - \bar{r}_0)] (\theta - \theta_0) \tag{2d}$$

Torsion–stretch interaction energy:

$$U_{s\varphi} = -5.9975\, K_{s\varphi} (r - r_0) (1 + \cos 3\varphi) \tag{2e}$$

Bend–bend interaction energy:

$$U_{\theta\bar{\theta}} = -0.021914\, K_{\theta\bar{\theta}}\, (\theta - \theta_0) (\bar{\theta} - \bar{\theta}_0) \tag{2f}$$

van der Waals interaction energy:

$$U_{vdW} = \varepsilon \left[-2.25 \left(\frac{r_v}{r}\right)^6 + 1.84 \times 10^5 \exp\left(\frac{-12r}{r_v}\right)\right] \tag{2g}$$

The values of constant parameters in the energy terms in Eq. (2) are extracted from mm3.prm file of the open source MM simulation