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Letter

Size dependency and potential field influence on deriving mechanical properties of carbon nanotubes using molecular dynamics

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ABSTRACT

A thorough understanding on the mechanical properties of carbon nanotube (CNT) is essential in extending the advanced applications of CNT based systems. However, conducting experiments to estimate mechanical properties at this scale is extremely challenging. Therefore, development of mechanistic models to estimate the mechanical properties of CNTs along with the integration of existing continuum mechanics concepts is critically important. This paper presents a comprehensive molecular dynamics simulation study on the size dependency and potential function influence of mechanical properties of CNT. Commonly used reactive bond order (REBO) and adaptive intermolecular reactive bond order (AIREBO) potential functions were considered in this regard. Young's modulus and shear modulus of CNTs are derived by integrating classical continuum mechanics concepts with molecular dynamics simulations. The results indicate that the potential function has a significant influence on the estimated mechanical properties of CNTs, and the influence of potential field is much higher when studying the torsional behaviour of CNTs than the tensile behaviour.

Since the discovery by Iijima [1], carbon nanotubes (CNTs) have attracted considerable attention due to their remarkable mechanical, electrical and thermal properties. In particular, CNTs have shown a broad range of applications in nanotechnology, especially in the development of nanosensors, nanomechanical resonators and as reinforcement in composite materials [2]. However, in order to further extend the CNT-based applications of nanotechnology, experimental demonstrations of versatility of CNTs have to be supported in parallel by theoretical/computational models of CNT-based systems. In this regard, accurate knowledge on constitutive properties such as Young's modulus (E), shear modulus (G), and Poisson's ratio (ν) of CNT is essential to describe their mechanical behaviour under different loading, boundary and environmental conditions. However, the use of experiments at this scale to measure constitutive properties is extremely challenging and only few studies have been reported [2]. These limitations of experimental investigations can be overcome by developing mechanistic models to estimate the mechanical properties of CNTs along with the integration of CNT mechanics with existing continuum mechanics concepts.

Atomistic systems such as CNT can be accurately modelled by using the first principles methods. However, due to high computational cost, the first principles methods are only applicable to systems with several hundreds of atoms. Continuum modelling is the most computationally efficient method. Those are, however, unable to account for quantum effects of matter at nanoscale, and also the discrete nature of matter at nanoscale [3]. Combination of continuum concepts with properties derived using atomistic analysis provides an attractive method to analyse the systems at the nanoscale [4–6]. In this regard, molecular dynamics (MD) plays an important role in studying the nanoscale systems.

Many researchers have used atomistic modelling approaches to determine tensile strength, elastic modulus, shear modulus, and Poisson's ratio by simulating tension and torsion tests of CNT [7–9]. The general approach involves the determination of potential energy of a CNT using MD for different strain levels and then computation of the stress–strain curve using numerical quadrature methods. However, the properties of CNT reported in the literature indicate different ranges of values depending (0.8–1.2 TPa) on the CNT diameter and methods of analysis [10–14]. The different trends of size dependency of CNT's shear moduli reported in the literature are significant among these. For example, Yu et al. [7] have reported that shear modulus substantially increases with increasing diameter, whereas, experiments and several theoretical models show an opposite trend [15,16]. Some authors have

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estimated the shear modulus of CNT from Young's modulus and Poisson's ratio obtained from MD simulation of tension tests and using the classical isotropic elasticity relationship between E, ν, and G. These results differ from the shear modulus estimated from MD simulation of a pure torsion test of CNT. Therefore, it is important to examine the reasons for the different trends of size-dependency of CNT moduli reported in the literature and differences in shear modulus values reported from different approaches (i.e., tension vs. torsion). In our opinion, advanced modelling of CNT systems has limited value if the reasons for the above disagreements are not well understood. Furthermore, accurate estimation of elastic moduli is critical to the continuum analysis of CNT-based systems and devices.

This paper investigates the size dependency and potential function influence on the mechanical properties of CNT derived from MD simulations. Nanoscale MD simulations of CNTs subjected to direct tension and torsion loading were used in this regard, where the commonly used reactive bond order (REBO) and adaptive intermolecular reactive bond order (AIREBO) potential functions represent the molecular interaction. MD simulations were performed for different chiralities and diameters to understand the influence of potential field on the size dependency of the moduli. In addition, the validity of common isotropic elastic relationship between E, ν, and G was also examined. Also, the size and potential field dependence of torsional strengths was investigated.

REBO potential (also called Tersoff–Brenner potential) was originally developed to simulate chemical vapour deposition of diamond [17], and later was modified to provide more accurate treatment of the energetic, elastic and vibration properties of solid carbon and small hydrocarbons (second generation potential) [18].

In REBO potential, the energy stored in the bond between atom i and atom j (E_{ij}^{REBO}) is given as

$$E_{ij}^{\mathrm{REBO}} = f\left(r_{ij}\right)\left(V_{ij}^{\mathrm{R}} + b_{ij}V_{ij}^{\mathrm{A}}\right), \tag{1}$$

where b_{ij} is the bond order term which modifies the strength of the bond depending on the local bonding environment, $\mathrm{V}_{ij}^{\mathrm{R}}$ and V_{ij}^{A} are repulsive and attractive potentials, respectively, r_{ij} is the distance between atoms i and j, and $f\left(r_{ij}\right)$ is called the cut-off function. The purpose of the cut-off function is to limit the interatomic interactions to the nearest neighbours [18].

Even though REBO potential is successful in describing the intermolecular interactions in carbon and hydrogen materials [17], it is not appropriate for every hydrocarbon system due to its inability to explicitly capture non-bonded interactions and torsional interactions. By addressing these shortcomings of REBO potential, AIREBO potential has been developed [19], which is an extension of the REBO potential

$$E_{ij}^{\mathrm{AIREBO}} = E_{ij}^{\mathrm{REBO}} + E_{ij}^{\mathrm{LJ}} + E_{ijkl}^{\mathrm{TORS}}, \tag{2}$$

where E_{ij}^{AIREBO} is the total potential energy of a bond between atoms i and j, indices k and l also refer to individual atoms, E^{REBO} is the REBO part, which is explained above, E^{LJ} is the Lennard-Jones potential that considers the non-bonded interactions between atoms, and E^{TORS} includes the torsional interactions between atoms into the total energy.

The original cut-off function for the REBO potential is given by

$$f(r) = \begin{cases} 1, & r < R^{(1)}, \\ 1 + \cos\left[\dfrac{\pi\left(r - R^{(1)}\right)}{\left(R^{(2)} - R^{(1)}\right)}\right], & R^{(1)} < r < R^{(2)}, \\ 0, & r > R^{(2)}, \end{cases} \tag{3}$$

where $R^{(1)}$ and $R^{(2)}$ are the cut-off radii, which have the values of 1.7 Å (1 Å = 10^{-10} m) and 2 Å, respectively. The values of cut-off radii are defined based on the first and second nearest neighbouring distances of hydrocarbons.

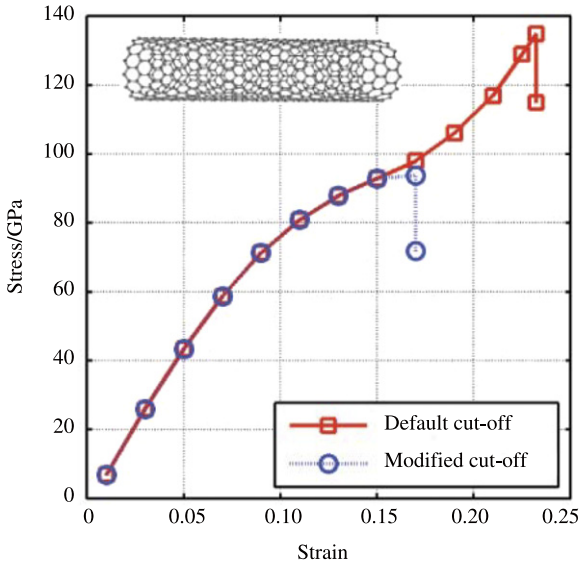

Fig. 1. Stress–strain curves of the (10,10) CNT.

It has been observed that the cut-off function could cause non-physical strain hardening in stress–strain curves of carbon nanostructures [20,21] whereas experiments [22] and *ab-initio* calculations [23] do not show any strain hardening. Therefore, researchers have modified the cut-off radii ranging from 1.9 Å to 2.2 Å [24,25] to eliminate this non-physical strain hardening. However, none of the previous studies have given much insight into the effect of cut-off function on the stress–strain relation, and this non-physical behaviour continues to prevail in recent simulation studies [21,26].

To fully understand the influence of the cut-off function, and also to identify the best cut-off radii, a set of uniaxial tensile test was performed in this study on a 4.8 nm long (10,10) CNT using LAMMPS MD simulator [27]. The stress–strain curve obtained with default cut-off function (given in Eq. (3)) indicates strain hardening at strain value around 0.16 as shown in Fig. 1. In order to remove this non-physical behaviour, various modified cut-off functions were tested [6]. The results show that a modified cut-off function, $f_{\mathrm{m}}(r)$ given in Eq. (4) eliminates the strain hardening when the cut-off radius (R) is 2 Å.

$$f_{\mathrm{m}}(r) = \begin{cases} 1, & r < R, \\ 0, & r > R. \end{cases} \tag{4}$$

Fig. 1 also shows a stress–strain curve based on the modified cut-off function, which qualitatively agrees with the behaviour observed in experiments [20] and *ab-initio* calculations [23]. In order to obtain further insight into the effect of cut-off function on fracture of an individual bond, the force–strain curve of the carbon–carbon (C–C) bond between atoms 1 and 2 in Fig. 2 was studied by increasing the bond length r. The positions of other atoms, relative to atoms 1 and 2, were kept unchanged. As shown in Fig. 2, the strain hardening of the force–strain curve disappears when both cut-off radii are equal to 2 Å, since bond breaking takes place before bond length reaches 2 Å. It should be noted that the modified cut-off function in Eq. (4) is not continuous as opposed to the original cut-off function in Eq. (3). However, this discontinuity does not affect the simulation results since C–C bond length does not reach the cut-off radius of the modified function (i.e., 2 Å). Therefore, the modified cut-off function given in Eq. (4) was used in the ensuing MD simulations.