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Nanomechanics of single walled carbon nanotube with water interactions under axial tension by using molecular dynamics simulation

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ABSTRACT

The mechanical characteristics of single walled carbon nanotube (SWCNT) with surrounding water interactions are studied in this work using molecular dynamics simulation method. The effect of chirality, geometry of the SWCNT and the presence of end caps on water submerged SWCNT is investigated by subjecting the SWCNT to axial tensile loading. The findings show that the presence of surrounding water molecules will reduce the mechanical strength of SWCNT. Our findings also show that the location and concentration of defects will strongly affect the mechanical strength of water submerged SWCNT. Furthermore, the mechanical strength of a nano-fluidic device is investigated by subjecting a free form capped SWCNT filled with varying water concentrations under tensile loading. This study is of paramount importance in the field of nano-biotechnology and we found that the concentration of filled water molecules affect the mechanical properties of SWCNT under tension. Additionally, we also carried out the tensile loading of the water-filled SWCNTs submerged in water for its potential applications in the nano-biotechnology, nano-level drug delivery and nano-level fluid flow. Our findings reveal that although the interaction of surrounding water molecules affects the mechanical properties, the elastic strength and the resistance to mechanical loading is quite exceptional which suggests the SWCNTs to be promising candidates for applications in nano-biological and nano-fluidic devices.

1. Introduction

Research in carbon nanotubes (CNTs) has generated significant interest in materials science and nanotechnology due to its remarkable physical and mechanical properties [1–6]. The unique combination of ultra-light weight and high strength of CNTs makes it a promising candidate for applications in nano-level drug delivery [7], nanoelectromechanical systems (NEMS) [8,9], nano-fluidic devices [10,11] and nano-level filtration systems [12]. These attractive applications of CNTs for its use in nano-level biological devices and NEMS require a critical investigation of the mechanical properties in a biological medium. Extensive studies on the mechanical properties of free standing CNTs determined by theoretical or experimental methods have been widely reported in the literature [13–17]. The elastic and plastic responses of CNTs under axial tension using the second generation REBO potential [18] was investigated by Liew et al. [19]. The studies showed that the effect of geometric size of CNTs on the tensile behavior is relatively insignificant. In addition, for the case of multi-walled CNTs (MWCNTs), the failure under tension is always initiated from the outermost layer. Tang et al. [20] employed molecular dynamics (MD) simulation to study the mechanism of super elongation of CNTs at high temperatures. They found that the defect interaction and generation in CNT leads to multistage necking resulting in subsequent tensile fracture. The structural vibrational analysis of the fluid conveying single walled CNTs (SWCNTs) was analyzed by Reddy et al. [21,22]. The analysis was significant since they were able to quantify the description of mass flow rate inside the SWCNT as a function of the natural frequency of SWCNT. Zhang et al. [23] studied the effect of various types of defects on the torsional responses of defective SWCNT. The studies showed that the torsional strength is strongly dependent on the chirality, type of defects, and temperature. The elastic properties of SWCNTs with bents along the axial direction of tube were conducted by Wong et al. [24,25]. Their studies reported that the presence of bents in the tube axis has little impact on tensile loading while significantly affecting the compressive properties of SWCNTs. The above mentioned literature studies is a clear indicator of the exceptional mechanical properties of CNTs. However, the mechanical property of CNTs in a biological medium (e.g. water) for its potential applications in nano-bio technology is yet to be investigated. The investigation of mechanical properties of CNTs in water is of fundamental importance for its application in nano-scale bio-fluidic devices. Furthermore, the influence of geometrical characteristics and the effect of defects on the elastic properties of a CNT in water medium presents an important design data to the bio-medical engineering community for the application of CNTs in nano-level

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drug delivery and nano-fluidic based NEMS devices. The influence of size, defects and the effect of end caps on the mechanical properties of SWCNTs submerged in water is presented in this paper. In addition, free form capped SWCNTs filled with water molecules were used in this study to resemble a nano-drug carrier. Studies were conducted on these free form water-filled SWCNTs to investigate the effect of the water concentration on the mechanical properties of the SWCNT. Furthermore, the effect of a surrounding biological medium was also investigated by subjecting these water-filled SWCNTs to tensile loading submerged in water. The mechanical properties of SWCNTs under tensile loading under various forms of water interaction have been comprehensively studied and the results are presented in this paper.

2. Computational model

The numerical simulations described in this work is carried out by using the classical molecular dynamics simulation method in which force field equations are used to describe the inter-atomic interactions. These inter-atomic interactions can be divided into the interaction between the carbon atoms of SWCNT, the interaction between the water molecules and the carbon atoms of SWCNT and the interaction between the water molecules. The inter-atomic interactions of carbon atom in SWCNT is described using Brenner's second generation reactive empirical bond order function (REBO) [18]. The REBO potential is able to accurately describe the properties of solid-state and molecular carbon nanostructures [26] while maintaining the accuracies of the *ab initio* and semi-empirical methods in simulating large systems [27]. The REBO function is defined mathematically as,

$$E_{\mathrm{REBO}} = V_R(r_{ij}) - b_{ij}V_A(r_{ij}) \tag{1}$$

where the repulsive and attractive pair terms are given by V_R and V_A respectively. The b_{ij} term is used to include the reactive empirical bond order between the atoms.

The non-bonded interactions between the SWCNTs and the water molecule is typically modeled using a Lennard–Jones (LJ) potential function [28,29]. This is due to the reason that the LJ potential is able to accurately describe the short-range electron repulsion and long-range electron attraction that is sufficient to describe the interactions between the CNT and water molecules [28–30]. The LJ potential is tuned using the parameters obtained from Ref. [31] to accurately describe the experimentally observed water-graphene contact angle. The non-bonded interactions between the carbon atoms and the water molecule is given by [31].

$$E_{non\text{-}bond} = \sum_{i,j} 4\varepsilon \left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6} \right] \tag{2}$$

where $\varepsilon_{CO} = 0.3135$ kJ/mol, $\varepsilon_{CH} = 0.253$ kJ/mol which is the well depth parameter, $\sigma_{CO} = 0.319$ nm, and $\sigma_{CH} = 0.282$ nm denote the collision diameter between carbon to oxygen and carbon to hydrogen respectively [31].

The interaction between the water molecules is described using the flexible fixed-point charge (FPC) water model [32]. The FPC water model is capable of accurately reproducing the properties of water for different ranges of pressure, temperature, integration time steps and system sizes. Additionally, the FPC model is the most accurate 3 site water model that makes it ideal for MD computations of biological systems involving large number of water molecules [33]. The FPC water model is described as:

$$E_{\mathrm{FPC}} = E_{bond} + E_{bend} + E_{vdW} + E_{els} \tag{3}$$

where E_{bond} and E_{bend} are intra-molecular potential function that represents the bond strength energy and bending energy in a water molecule respectively. The terms E_{els} and E_{vdw} denote the electrostatic potential and van der Waals potential between water molecules respectively. The complete details of this potential function is described in the work by Zhang et al. [32].

3. Simulation details

The work described in this paper can be broadly classified into two parts. The first part focuses on the mechanical properties of open ended (uncapped) SWCNT submerged in water. The second part of the study concentrates on the mechanical properties of the free form and water submerged capped SWCNTs with varying concentrations of water molecule filled inside the SWCNT. It should be noted in an open ended SWCNT, the water molecules can freely flow in and out of the tube during equilibration. However, for the case of SWCNTs with end caps, the water molecules are completely prevented from entering inside the tube due to the presence of end caps.

The mechanical properties of the SWCNTs under water interaction is studied by subjecting the SWCNT to uni-axial tensile loading as depicted in Fig. 1. The effect of size on the mechanical properties of the SWCNT is investigated by varying the length and diameter of the SWCNT. We also present the elastic properties of armchair and zigzag SWCNTs in this paper to understand the effect of chirality on the tensile loading properties of water submerged SWCNT. The effect of vacancy defects on the mechanical properties of water submerged SWCNT is studied by introducing vacancy defects in the SWCNT. We first introduced a single vacancy defect in the SWCNT, and the defect is subsequently expanded along the radial or axial direction forming high concentration vacancy defects (Fig. 2). This method of defect reconstruction not only helps us to understand the effects of defects on the mechanical properties of water submerged SWCNTs but also the effect of number and the location of defects on the tensile properties of water submerged SWCNTs.

Before the SWCNT is subjected to tensile loading, it is equilibrated to release any residual stresses by achieving thermal equilibrium in an NVT ensemble. All simulations are carried out by maintaining the system temperature at 300 K and the density of water molecules at 0.9 g/cm^3. The Nose–Hoover thermostat [34,35] is employed to achieve the temperature stability of the system. Following equilibration, the SWCNT is subjected to tensile loading by applying a constant outward displacement (strain rate = 0.001 ps^{-1}) on the atoms at both ends of the SWCNT. This value of strain rate (0.001 ps^{-1}) allows us to adequately describe the tensile elastic properties of SWCNT at 300 K [36] while ensuring faster computation time. The system is allowed to relax after every 1000 time steps such that the atoms attain the favorable minimum

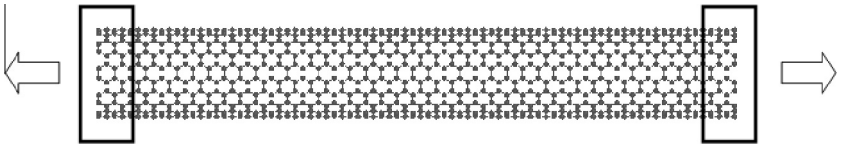

Fig. 1. The procedure of tensile loading of the SWCNT in our study. The end atoms enclosed within the rectangle are subjected to an outward displacement (strain rate = 0.001 ps^{-1}) to effect tension.