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A critical study of the parameters governing molecular dynamics simulations of nanostructured materials

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ABSTRACT

Molecular dynamics (MD) simulations have been used extensively over the past two decades to determine the mechanical and physical properties of nanomaterials. However, the discrepancy between the reported results from these atomistic studies shadows the reliability of this computationally efficient technique. This inconsistency is attributed to the misuse and incorrect application of MD as evidenced by the arbitrary use of interatomic potentials, cut-off function parameters, strain rate, time increment, and domain size in the conducted simulations. In this paper, we highlight erroneous simulations by investigating the influence of these parameters on the elastic and fracture properties of nanostructured materials; including carbon nanotubes, graphene, and boron nitride (BN) sheets subject to direct and contact loads. The effect of interatomic potential type was investigated by comparing the predicted properties from AIREBO, Tersofff, CVFF, and ReaxFF potentials with those obtained with experimental and DFT techniques. The cut-off function parameters were also investigated to determine the optimum inner and outer cut-off radii selected to capture the actual physical behavior and avoid the reported strain hardening phenomena. Furthermore, MD simulations with strain rates spanning several orders of magnitudes and time increments ranging from 0.1 to 20 fs were performed to define the maximum allowable parameters for each material and loading scheme. Additionally, graphene and BN sheets with side length up to 500 Å were modeled to determine the size and edge effects on the mechanical properties. Finally, a set of parameters is recommended in each investigation to help guiding future atomistic studies obtaining reliable results using the available computational resources.

1. Introduction

Molecular dynamics (MD) simulations have been used extensively over the last two decades for modeling nanomaterials [1]. However, several parameters influence the obtained properties from MD simulations including interatomic potential type, cut-off function radii, time step, strain rate, and domain size [2,3]. Determining quantitatively the effect of each parameter on material properties is very critical in achieving reliable results.

Different interatomic potentials and force fields have been used over the past two decades to study CNTs, graphene, and their composites [4–7]. As a result, the reinforcement effect of CNTs and graphene in their nanocomposite might be underestimated or overestimated depending on the interatomic potential used to model the system. Furthermore, all force fields that use harmonic function to model atomic bond such as CVFF force field do not permit bond formation and breakage, which limits the simulation to only small deformation [8–10]. On the other hand, other reactive interatomic potentials such as AIREBO and ReaxFF potentials can be used to model bond breakage and hence allowing studying large deformation and fracture mechanisms [11–14]. Another source of the contradictions in the reported mechanical properties the literature is the selection of the cut-off function parameters in Tersoff and AIREBO potentials [15,16]. For example, the original minimum and maximum radii in the cut-off function for the covalent bonds in AIREBO potential are 1.7 Å and 2.0 Å, respectively. However, these values cause unphysical strain hardening in the structure at high strains. To address this problem, researchers varied the cut-off function parameters to achieve properties that are in good agreement with those obtained with experimental and DFT techniques [17,18].

Selecting the appropriate time step in MD simulations is very critical for obtaining reliable results with a reasonable computational cost, achieving energy conservation, and preventing the MD system from exploding [19]. Different time steps ranging from 0.1 to 15 fs were used in previous MD simulation of CNTs, graphene, and BN structures [20–22]. Budarapu et al. [23] have studied the effect of time step on crack initiation and growth mechanisms in Graphene using MD

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simulations. Their results showed a significant dependence of post yielding behavior of Graphene on time step and a time step of 0.1 fs was required to accurately monitor crack initiation and propagation in the fracturing sheet. However, such a small time step will require an enormous computational cost to model large systems for longer periods.

Conducting MD simulations at very high strain rates means that the molecular structure does not have enough time to respond (equilibrate) to the applied load [24]. The effect of strain rate in MD simulation on the predicted mechanical properties were investigated in the literature to determine a suitable range of loading rates that gives reliable results. However, the reported results of these investigations were contradicting, with some papers indicating a significant effect of the strain rate on all mechanical properties, while others showing slight to no effect [25]. For example, Liu et al. [26] found that the tensile strength of CNTs is strongly affected by the applied strain rate [27]. On the other hand, Wei et al. [28] found that the tensile yield strain of a SWCNT was slightly influenced by the strain rate. Zhang et al. [29] reported that the strain rate used in MD simulations has a negligible impact on the predicted Young's modulus of graphene. Zhao and Aluru [30] showed that the influence of strain rate on the fracture stress of graphene was only significant at elevated temperatures. Han et al. [31] studied the effect of strain rate on the mechanical properties of BN sheets via MD simulations. Their results showed that Young's modulus decreases while fracture stress and strain increase with increasing the strain rate. A contrast relationship between mechanical properties of BN sheets and strain rate was reported by Mortazavi et al. [32]. Their results showed no dependence between Young's modules and the strain rate and a very slight dependence between tensile strength and the loading rate.

The effect of graphene and BN sheet size on the mechanical properties were also investigated by several research groups [33–37]. However, the reported results of these atomistic studies are contradicting, with several studies showing a growing weakening effect with increasing the size [37,38], while other concluding the opposite [39]. The influence of the sheet size originates from the presence of free edges and the associated compressive forces due to dangling bonds in edge atoms [40]. For example, Zhao et al. [39] studied the size effect of the elastic properties of graphene using MD simulations. Their results showed that Young's modulus of graphene increases with the increase of the sheet size. Another MD study concluded that the elastic properties of graphene increase with the sheet size until reaching a stable point (bulk level) at a width of 4 nm [22]. On the other hand, an MD study by Qiang et al. [38] indicated that the elastic and fracture properties of graphene decrease with the increase in the sheet size and the properties reach their bulk level at a sheet width of 6 nm. This discrepancy in the reported results were attributed to the difference in the interatomic potential and temperature in each study [22].

In this paper, a comprehensive MD investigation is carried out to examine the effects of interatomic potential type, cut-off function parameters, time step, strain rate, and domain size on the elastic and fracture properties of CNTs, graphene, and BN sheets. Atomistically, the impact of these parameters on the properties depends on the testing technique adopted. This is due to the distinct behavior and fracture mechanism associated with each loading type. To address this issue, numerical compression and tension tests were performed on SWCNT, while numerical tensile and nanoindentation tests were carried out on graphene and BN sheets. A thorough investigation of the effect of the type of the interatomic potential on the mechanical properties of graphene and CNTs is presented by considering the following interatomic potentials: CVFF, ReaxFF, Tersoff, and AIREBO. A wide range of strain rates ($\dot{\varepsilon} = 2 \times 10^{-4} - 16\,ns^{-1}$) and time steps (t = 0.1–20 fs) have also been investigated to determine the critical values for each material and testing technique; ensuring that we capture the material behavior without altering the physical nature of the process. Graphene and BN sheets with dimensions up to 500 Å × 500 Å have been modeled to study the effect of domain size (i.e. edge effect) on the material strength and fracture mechanism. The predicted properties from the conducted MD simulations were compared with recently obtained numerical and experimental findings [15,39,41–51]. Decidedly, the findings of this work should help in understanding the source of anomalies and inconsistency among the reported data in the literature and also in finding the appropriate parameters for each specific loading and material type in future studies.

This paper is organized as follows. Following this introduction, the methodology and the objectives of this study are outlined in Section 2. The results of the conducted MD simulations for the considered materials are presented and discussed in Section 3. Finally, the main contributions and conclusions are summarized in Section 4.

2. Methodology

Molecular dynamics is a well-established method typically used to compute the time evolution of a system of interacting atoms by calculating the interaction force between them and numerically integrating their kinetics using Newton's law of motion [52]. The interaction forces between the atoms are calculated from the gradient of the interatomic potential. Several parameters influence the ability of MD simulations to accurately predict the material behavior, such as interatomic potential type, cut-off function radii, strain rate, time step, and domain size (edge effect).

We conducted comprehensive MD simulations to study the effect of the aforementioned parameters on the elastic and fracture properties of CNTs, graphene, and BN sheets. Fig. 1(a)–(f) show the MD models and the applied boundary conditions used in our simulations. Both uniaxial tensile and indentation simulations were performed for graphene (Fig. 1(a) and (c)) and BN sheet (Fig. 1(b) and (d)), while uniaxial tension and compression simulations were conducted for SWCNTs (Fig. 1(f)). A pyramid-shaped diamond tip was used for the nanoindentation simulations, as shown in Fig. 1(e). The height and base dimensions of the indenter were selected to be 34 Å and 24 Å × 24 Å, respectively. The indenter tip contained 9 carbon atoms (3 atoms × 3 atoms).

All MD simulations were performed with large-scale atomic/molecular massively parallel simulator LAMMPS [53] using one of the following interatomic potentials: the adaptive intermolecular reactive bond order (AIREBO) potential [34], Tersoff-type empirical interatomic potential [54], the consistent valence force field (CVFF) [55], and the reactive force field (ReaxFF) [13]. A detailed description of each potential function is presented in the Supplementary Material. The cut-off function parameters in AIREBO and Tersoff were varied to investigate their effects on the mechanical properties. The equations of motion was integrated using the velocity–Verlet algorithm [56] with time steps ranging from 0.1 fs to 20 fs. The energy of the initial structure was minimized using the conjugate gradient algorithm to obtain CNTs, graphene, and BN sheets with optimized configurations. The minimized structures were considered to be optimized once the change in the total potential energy (PE) of the system between subsequent steps is less than 1.0×10^{-10} kcal/mol [57,58]. Subsequently, MD simulations were performed in the NVT ensemble for 10^5 time-steps to equilibrate the minimized structures. The tensile simulations were then performed with strain rates ranging from $\dot{\varepsilon}$ ranging from $2 \times 10^{-4} to \sim 16\,ns^{-1}$, while the nanoindentation simulations were performed at different loading rates (indenter speed ranging from 0.001 to 10 Å/ps). The procedures of the uniaxial tensile and nanoindentation simulations are presented in detailed in our previous studies [18,59,60]. Table 1 summarizes the investigated parameters and the conducted MD simulations in the current study. A detailed discussion of each investigation is presented in the following sections.

3. Results and discussion

In this Section, we present and discuss the results of the conducted MD simulations of the effect of the aforementioned parameters on the