Fracture Analysis of Vacancy Defected Nitrogen Doped Graphene Sheets Via MD Simulations

Hassan Shirzadi Jahromi\textsuperscript{a,*, b}, Fatemeh Mehdipour\textsuperscript{b}, Ghasem Firooz\textsuperscript{c}

\textsuperscript{a} Department of Mechanical and Aerospace Engineering, Western Michigan University, Kalamazoo, USA
\textsuperscript{b} Institute for Solid Mechanics, Dresden University of Technology, Dresden, Germany
\textsuperscript{c} Department of Mechanical and Aerospace Engineering, Shiraz University of Technology, Shiraz, Iran

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\textbf{Abstract} & \\
The novel hexagonal monolayer sheet of carbon atoms, graphene, has attracted great attention due to their exceptional electrical and mechanical properties. Their phenomenally high strength and elastic strain, nevertheless, can be altered by structural defects due to stress concentration. In this paper, the fracture behaviour of graphene sheets and nitrogen doped graphene sheets with vacancies were investigated using molecular dynamics (MD) simulations at the different temperatures of 300K, 500K, and 900K. The results reveal a significant strength loss caused by both the defects and vacancies and doped nitrogen in graphene. The deformation process of graphene at various strain rate levels, with regard to the failure behaviour, is discussed. The validity of the proposed MD simulations is verified by comparing the simulation results with the available predictions from the quantized fracture mechanics.
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1. Introduction

The Ilijma’s invention of carbon nanotubes [1] opened a new way to conduct research of nanotechnology’s science. Lots of applications and the outstanding physical, mechanical, and electrical properties of carbon nanotubes and graphene [2-12], make them the subject of intensive studies. Increasing research efforts of graphene has been enticing since its discovery [13]. Graphene possesses many superior properties such as exceptional elastic properties [14], high mechanical strength, and extremely high Young’s modulus (about 1TPa) and fracture strength (130 GPa) [15], chemical inertness, high heat conduction, and piezoelectricity [16, 17]. Chemical vapor deposition (CVD) and mechanical exfoliation [18], chemical reduction of graphene oxide sheets [19], can be led to produce graphene [20]. However, the premier properties of graphene saliently diminish owing to defects generated by both material production processes such as Stone-Wales (S-W) type defects, dislocation like defects, single and multiply vacancies, accessory chemical groups, or carbon adatoms [21]. Therefore, the study of the imperfect graphene sheets will be an important problem. Molecular dynamics (MD) simulations are recognized as one of the most reliable methods in the study of nanostructured materials. The elastic behavior of graphene sheets using molecular dynamics simulations subjected to various static loading conditions such as axial, pressure and torsional [22] has been studied in the literatures. Fracture behavior of nanostructures is important for many engineering and nano-electro-mechanical systems such as sensor devices [23] and clocks. Guo et al. [24] performed MD simulations to study various aspects of energy dissipation in gigahertz oscillators. The mechanisms of energy dissipation in graphene oscillators was studied by Zhao et al. [25]. They understand the differences between oscillators with short graphene sheets and long ones. In this current study, molecular dynamics (MD) simulations based on Tersoff-Brenner many-body potential function is presented to perform a comprehensive investigation into the fracture behavior of graphene sheets with defects and doped nitrogen. To validate the results, the fracture strength predicted from the simulation is compared with the so-called quantized fracture mechanics (QFM) theory [26] and previous atomic models [27].

* Corresponding author: hassan.shirzadijahromi@wmich.edu

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2. Molecular dynamics simulation

Molecular dynamics simulation is a powerful method based on Newtonian equations. It is numerically determining the pathway of atoms. The point to the MD simulations is to select an exact potential energy model. The carbon-carbon interatomic forces are represented by the Tersoff-Brenner potential function implemented in the LAMMPS [28]. Fracture analysis is a significant mechanical response and presents a design constraint on many nano structural systems, particularly in the field of nano materials and graphene. To simulate fracture behavior of a monolayer graphene sheet, the Tersoff-Brenner many-body potential function is chosen. It is expressed as:

\[
E_i = \frac{1}{2} \sum_{i \neq j} V_{ij}. \tag{1}
\]

\[
V_{ij} = f_c(r_{ij})[V_{rep}(r_{ij}) + b_{ij}V_{att}(r_{ij})]. \tag{2}
\]

\[
b_{ij} = b_{ij}(g_{ij}) = \sum_{k} f_c(r_{ik})g(\theta_{ijk})f(r_{ij} - r_{ik}). \tag{3}
\]

where \( r_{ij} \) is the distance between pairs adjoining atoms \( i \) and \( j \), \( V_{ij} \) is the bonding energy, \( b_{ij} \) is an empirical bond-order term, \( V_{att} \) and \( V_{rep} \) are the attractive and repulsive parts of the potential, \( f_c(r_{ij}) \) is cutoff function and \( g_{ij} \) is the coordination [29-31].

The MD simulation model for uniaxial tensile test of graphene with the chirality angle of \( \approx 10^\circ \) is illustrated in Figures 1 and 2. The chirality angles equal to 0° and 30° are called armchair and zigzag, respectively. A model consisting of 800 carbon atoms with geometric dimensions of \( I = 42.6 \) Å and \( J = 49.2 \) Å demonstrated in Figure 2 for MD simulation was created. In order to neglect the size effect based on Zhao and et al. the diagonal length of the model was selected as 6.5nm. Another model with the same number of atoms was built and nitrogen atoms were randomly replaced with carbon to simulate nitrogen doped graphene sheet. Figure 3 illustrates a schematic of nitrogen doped graphene sheet. The modeled graphene structure was left to relax at atmosphere pressure along the periodic directions for boundary conditions at room temperature using constant pressure temperature by means of Nosé–Hoover barostat and thermostat method (i.e. NPT ensemble) [32]. The uniaxial load was applied to the graphene sheet alongside both zigzag and armchair direction by deflection rate of 0.005 ps\(^{-1}\) and timestep of 0.001 ps. Moreover, in order to reduce the intensity of high strain rate effects on the obtained properties, the raised temperature as a result of high loading strain rates must be damped by performing the constant temperature simulations during the loading step.
3. Results and Discussion

To validate the MD model, the fracture strength of a pristine graphene sheet was determined. Figure 4 demonstrates the stress-strain curves of two zigzag and armchair directions. The engineering stress is around 145 GPa and 110 GPa for armchair and zigzag direction, respectively. These values have a great agreement with the experimental determination 130 GPa [26] and previous numerical simulation [27].

In this paper, vacancy defects models were built to evaluate the effects of different numbers of vacancies at a temperature range of 300-900 K under tension along the armchair direction. Figure 5 shows the removed atoms from the middle of the graphene sheet to provide a vacancy defects model for simulations. It can be considered fracture strength decreases with an increasing number of vacancies as well as temperature. For the graphene sheet with two vacancies, the engineering strength loss is 35.62%, 42.53% and 45.12% at the 300K to 900K temperature range. Figure 6 illustrates the evaluated fracture strength at different temperatures for different numbers of vacancies. These results are compared with the available QFM theory results and there is a very good agreement between QFM and MD simulations results.
Figure 5. Schematic view of vacancy defects made in graphene sheet (a) 8 atoms removed - (b) 7 atoms removed – (c) 3 atoms removed – (d) 1 atom removed.

Figure 6. Fracture strength of defected graphene at different temperature range versus number of vacancy defects. QFM [26] and MD simulations.

In this work, the effect of vacancy defects on a nitrogen doped graphene at 300K was evaluated. The simulated model during the tension is shown in figure 7. The results compared with a single layer graphene sheet without nitrogen. Figure 8 shows the Fracture strength of defected nitrogen doped graphene and graphene sheet versus number of vacancy defects in MD simulations. Results show decrease in fracture strength by doping nitrogen in the graphene sheet as well as increasing the number of vacancy defects.

Figure 7. Schematic of single layer nitrogen doped graphene sheet with vacancy defect. Blue (lower radius) represent carbon atoms and yellow (higher radius) are nitrogen atoms. (a) relaxed sheet, (b) initiated fracture (c) fractured.
4. Conclusions

The novel hexagonal monolayer sheet of carbon atoms, graphene, has attracted great attention due to their exceptional electrical and mechanical properties. Their phenomenally high strength and elastic strain, nevertheless, can be altered by structural defects due to stress concentration. In this paper, the fracture behaviour of graphene sheets and nitrogen doped graphene sheets with vacancies were investigated using molecular dynamics (MD) simulations at the different temperatures of 300K, 500K, and 900K. The results reveal a significant strength loss caused by both the defects and vacancies and doped nitrogen in graphene. The deformation process of graphene at various strain rate levels, with regard to the failure behaviour, is discussed. The validity of the proposed MD simulations is verified by comparing the simulation results with the available predictions from the quantized fracture mechanics.

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