Effect of spatial distribution of nanopores on mechanical properties of monolayer graphene

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Abstract: Since the discovery of graphene, it has immense popularity among scientists and researchers due to its superior mechanical and electrical properties. In the present study, the effects of the spatial distribution of nanopore defects on the mechanical properties of the single-layer graphene sheet (SLGS) are investigated. Based on Tersoff potential functions, molecular dynamics (MD) simulations are conducted to perform the uniaxial deformation of defected graphene. The nanopore defects are induced intentionally at various spatial locations on a pristine graphene sheet for studying the variation in its mechanical properties such as fracture strength, Young’s modulus and failure strain.

The results illustrate that the mechanical properties are predominantly dependent on the spatial locations of the defects. It is also observed that the mechanical properties are slightly higher in case of zigzag direction than armchair direction but it decreases with the presence of defects in both the cases. In the consequence, it is suggested to consider spatial locations of defects while fabricating nanodevices with graphene.

Keywords: Graphene, molecular dynamics, nanopore, LAMMPS, iso-strain

1. INTRODUCTION

Graphene, a two-dimensional allotrope of carbon, is one of the most versatile materials known. The astonishing properties of graphene being the lightest and strongest material known and excellent conduction of electricity and heat has led to its wide utilization in the fields of Biosensors [1], Biomedical [2], Nano-composites [3-5]. The exceptional electromechanical [6–8] and magnetic [9] properties of graphene have intrigued attention from researchers from various parts of the world. Graphene-based nanoelectromechanical systems (NEMS) have shown applications in various disciplines from biomedicine to telecommunication [10]. The first-time graphene was produced by Prof. Andre Geim and Prof. Konstantin Novoselov in 2004 in the University of Manchester in the process of examining how efficient graphite is as a transistor, they dissected a piece of graphite, one layer after another until only one single layer remained by a process called as mechanical exfoliation.

With these astonishing properties present in graphene, the high strength observed in pristine graphene [6] is sparking great interest for numerous applications such as in electronic devices and biological membranes [11]. For example, single-layer graphene can have a loading capacity equivalent to a 50-nm-thick film [12]. In 2008 Lee et al. [6] experimentally calculated the intrinsic breaking strength and elastic properties of a free-standing single-layer graphene membrane by performing nanoindentation in an atomic force microscope and figured out Young’s modulus ($E$) to be 1.0 Terapascals (TPa) and fracture strength to be 130 Gigapascals (GPa). This finding proved graphene as one of the stiffest
Graphene can be produced by several methods but are not limited to simple arc discharge, electrochemical synthesis, unrolled carbon nanotubes, chemical vapour deposition (CVD). Large scale fabrication of graphene up to several square centimetres with excellent electrical and optical properties is possible through CVD [13]. But with most of the fabrication techniques, production of pristine graphene is quite impossible due to unavoidable intervening of factors such as chemicals and heat transfers. So, it’s obvious that the graphene produced might be subjected to structural irregularities. An extensive amount of research has been done to characterize the exact mechanical properties of pristine graphene, but due to the methods of producing graphene, it will have a certain percentage of unavoidable defects hampering its mechanical properties. So, it is essential to study graphene with a certain concentration of defects. Till date, several experimental techniques, as well as computational techniques, have proved that defects have a major impact on the mechanical, chemical and electronic properties of graphene. Kim et al. [14] had shown that one-dimensional defects in graphene have a hefty influence on its properties, such as mechanical strength and electrical charge transport. Banhart et al. [15] have studied structural defects in graphene and proved that deflections from pristine graphene can be convenient in some applications.

Molecular dynamics simulations are exhaustively used in the study of mechanical properties of graphene. Jing et al. [16] showed that the presence of defects decreases Young’s modulus of a graphene sheet and it decreases further with increasing concentration of defects. Wei et al. [12] showed how defects interact in two-dimensional crystals, which is essential for using stretchable and high-strength graphene [6] for electronic applications. Wang et al. [17] simulated graphene sheets having Stone–Wales type defects using molecular dynamics simulations at multiple temperatures and indicated that the defects and vacancies can lead to a decrease in strength of graphene. Dewapriya and Rajapakse [10] investigated the strain rate and temperature-dependent variation in the mechanical strength of graphene.

With the concise literature study, it was found that the defects are unavoidable in graphene and also researchers have exhaustively studied the properties of a defected graphene sheet. Most of them have shown that defects reduce the fracture strength, Young’s modulus and failure strain of graphene. However, the study of the variation of these properties with the spatial location of nanopore defects on a SLGS is not adequate. So, the purpose of this study is to show how the locations of nanopore defects largely impact the mechanical properties, when that SLGS with nanopores is loaded at a particular strain-rate in armchair and zigzag directions separately.

In the present study, we intentionally induced the defects in pristine graphene sheet at different spatial locations and implemented the iso-strain approach with the strain rate of 0.001/ps in both armchair and zigzag direction of graphene.

2. MODELLING AND SIMULATION

In the present research work, MD simulations were carried out in Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [18] based on Tersoff potential energy function. The Tersoff style potential is a pair potential which represents the potential energy between three individual atoms. It computes a 3-body Tersoff potential for the energy $E$ of a system of atoms as

$$E = \frac{1}{2} \sum_i \sum_{j\neq i} V_{ij}$$

where,

$$V_{ij} = f_c(r_{ij})[f_R(r_{ij}) + b_{ij} f_A(r_{ij})]$$
Here, $V_{ij}$ represents the potential energy of the system. $f_R$ is a two-body term representing repulsive pair potential and $f_A$ includes three-body interaction representing attractive pair potential, whereas $f_C$ is a cut off function. $r_{ij}$ represents the distance between the adjacent atoms $i$ and $j$ and $b_{ij}$ is an empirical bond-order coefficient.

The potential field used in the molecular simulations plays a crucial role in the accuracy of the results obtained. From the literature review, it was found that the Tersoff potential file is exhaustively used for simulating graphene sheets.

In this study, we modelled a pristine SLGS with 7.2nm dimension and 2040 carbon atoms using Visual molecular dynamics (VMD) [19], the data-files required for performing simulation were obtained by the topo-tool plug-in of VMD. Zhao et al. [20], confirmed that one can ignore the model size effect if the diagonal length is beyond 5 nm.

The time step for performing simulations is taken as 1 femtosecond (fs). The graphene structure is initially relaxed to the minimum energy state by the conjugate gradient (cg) energy minimization method. Then, a Nose–Hoover thermostat [21,22] is employed to simulate the graphene sheet to maintain an equilibrium temperature of 300K. Periodic boundary conditions are employed in all three directions to eliminate the finite-size effects. For studying the mechanical behaviour of a defective SLGS, we intentionally induced 1% nanopore defects at various spatial locations on the sheet by using an open-source atom manipulating software, Avogadro[23] as shown in Figure 1. The visualization of the simulation part is done in OVITO[24] (Open Visualization Tool) and snapshots are taken at a particular integration of time.

![Figure 1. Depiction of the spatial location of nanopore defects (a-h).](image)

### 3. RESULTS AND DISCUSSION

#### 3.1. Validation of the present model

MD Simulations were performed for the pristine graphene sheet at 300K and mechanical properties were obtained. The values of fracture strength, Young’s modulus and failure strain found to be in reasonable agreement with the literature (refer to table 1).
Table 1. Validation for the mechanical properties of a pristine graphene sheet

|                         | Fracture strength (GPa) | Young’s modulus (TPa) | Failure strain |
|-------------------------|-------------------------|-----------------------|----------------|
| Ni. and Z. et al. (Tersoff-Brenner) [25] | 180.0                   | 1.13                  | 0.3248         |
| Zhang and Gu (MD AIREBO) [26] | 115.9                   | 1.09                  | 0.1380         |
| Ansari et al. (MD Tersoff-Brenner) [27] | 123.0                   | 0.79                  | 0.2330         |
| Present study (MD Tersoff) | 216.2                   | 1.07                  | 0.3118         |

3.2. Mechanical properties of pristine SLGS

The SLGS was loaded in armchair and zigzag directions separately at a strain rate of 0.001/ps and mechanical behaviours such as fracture strength, Young’s modulus and failure strain were measured. It was observed that the fracture strength and failure strain in armchair direction came out to be 216.2 GPa and 31.2% respectively while it was 218.5 GPa and 34.5% in case of zigzag direction. The Young’s modulus was measured to be 1.15 and 1.27 TPa when loaded in armchair direction and zigzag direction respectively. So, overall fracture strength, failure strain and Young’s modulus were slightly higher when it was loaded in zigzag direction in contrast to that in armchair direction.

3.3. Mechanical properties of SLGS with nanopore defects in armchair direction

The stress and strain curve is represented in Figure 2. As observed from the figure it’s revealed that the fracture strength and failure strain values are quite less in a graphene sheet with nanopore defects in comparison to a pristine (perfect) one. It is also evident from the curve that the values of fracture strength and failure strain are largely dependent on the spatial location of nanopore defects.

![Figure 2. Stress-strain curve of SLGS with nanopore defects at different spatial locations (armchair direction).](image)

There is a maximum of 64.35% decrease in fraction strength and a maximum of 59.85% decrease in failure strain in a defective graphene sheet compared to a pristine one as shown by Figure 3 (a). While there is a maximum dip of 19.3% in Young’s modulus compared to a pristine sheet as evident from Figure 3 (b).
3.4. Mechanical properties of SLGS with nanopore defects in zigzag direction –
Similarly, on the lines of armchair direction, the stress and strain curve was drawn in case of load applied in zigzag direction which is represented in Figure 4. As observed from the figure it is obvious that the fracture strength and failure strain values are quite less in graphene sheet with nanopore defects in comparison to a pristine (perfect) one. It’s also evident from the curve that the values of fracture strength and failure strain are largely dependent on the spatial location of nanopore defects in case of zigzag direction too.

It is observed from Figure 5 (a) that there is a maximum of 58% decrease in fracture strength and a maximum of 51.6% decrease in failure strain in a defective graphene sheet compared to a pristine one. While there is a maximum dip of 25.6% in Young’s modulus compared to a pristine sheet as evident from Figure 5 (b).
Figure 5. Variation of mechanical properties with the different spatial location of nanopore defects (zigzag direction) (a) Fracture strength and failure strain (b) Young’s modulus.

4. CONCLUSIONS

In the present study, the effect of mechanical properties of SLGS under loading in the armchair, as well as zigzag direction with nanopore defects at various locations, is investigated. We performed a series of MD simulations on pristine and with 1% nanopores located at various spatial locations on a monolayer graphene sheet. We loaded the graphene sheet at a strain rate of 0.001/ps. The results showed that the spatial locations of defects reduce fracture strength, Young’s modulus and failure strain. In addition to that, the amount of reduction depends largely on the application of applied load and the spatial location defects. Our result suggested that spatial locations defects, as well as its loading characteristics, should be considered into account while fabricating nanodevices with graphene.

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