The size effect in mechanical properties of finite-sized graphene nanoribbon

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Size effect in mechanical behavior of finite-sized graphene nanoribbons (GNRs) under uniaxial tension is studied using Molecular Dynamics (MD) simulations. The size effect and aspect ratio effect are significant in zigzag GNRs (ZGNRs), while their influence on the mechanical behavior of armchair GNRs (AGNRs) is negligible. For square shaped ZGNRs of increasing size, the elastic modulus increases while the ultimate failure stress and strain decrease. For rectangular shaped ZGNRs, the aspect ratio effects are especially predominant in those with fixed length. Wider ZGNRs have higher elastic modulus but lower failure stress and strain. For GNRs of fixed width, neither ZGNRs nor AGNRs show significant aspect ratio effect when length increases. The results show that ZGNRs are generally stronger than AGNRs under the same loading conditions. A new concept Density of Weakness (DOW) has been proposed to explain the size effect of ZGNRs.

1. Introduction

Graphene, a single layer of carbon atoms arranged in honeycomb lattice, has promising applications in nanoelectronics \cite{1}, nano-electromechanical systems \cite{2}, and nanocomposites \cite{3}. Especially, graphene nanoribbon (GNR), tailored from the 2D graphene lattice with finite size, has been found to possess interesting electronic structures based on its width and edge shape \cite{4}. These material properties open an opportunity to construct electronic devices made completely of graphene \cite{5}.

The ultimate use of graphene will likely require an understanding of the mechanical properties that affect the device performance and reliability. The mechanical properties of bulk graphene have been extensively studied both experimentally \cite{6,7} and theoretically \cite{8,9}. For GNRs, although precise fabrication methods have been developed recently \cite{10,11}, there are still very few experimental results available in the literature. Thus, valuable exploratory studies in this field are currently done by theoretical and computational methods based on molecular dynamics (MD) \cite{9,12–14}, structural or continuum mechanics \cite{15,16}, and quantum mechanics \cite{17,18} methods.

Most computational studies concentrate on the uniaxial tensile behavior of GNRs. The edges of GNRs can be zigzag (ZGNR), armchair (AGNR), or at other chiral angles. The following literature review focuses on pristine GNRs without any functionalization.

Zhao et al. \cite{9} studied square AGNRs and ZGNRs by MD with AIREBO potential, which is the most commonly used and accurate potential for C-C bond in graphene. They reported increasing Young's modulus and decreasing Poisson's ratio as the diagonal length of GNRs becomes larger. When the diagonal length of nanoribbon is over 10 nm, both parameters converged slowly to those of bulk graphene. However, results about failure stress and failure strain are not presented. Based on Tersoff potential, Bu et al. \cite{12} report studies only for fix-length AGNRs. The results also show the increasing Young's modulus for wider AGNRs, and the size effect is appreciable only when width is smaller than 2 nm. Lu et al. \cite{13} studied infinitely long AGNRs and ZGNRs by molecular statics (i.e. no temperature presents). They use the second-generation reactive empirical bond-order (REBO) potential, which is an earlier version of AIREBO potential. As shown in their paper, both types of GNRs have a decreasing Young's modulus and decreasing failure strain as width increases, while the failure stress increases at the same time. Xu \cite{14} studied nanoribbon of the size 20 nm by 10 nm with second generation REBO potential as well, with chiral angles of 0, 15, 30. A brittle failure mechanism is observed at room temperature. Using structural mechanics based on modified Morse potential, Georganantinos et al. \cite{16} studied both AGNRs and ZGNRs of various sizes. For fixed width, longer GNRs of both types have smaller Young's modulus, and slightly smaller failure stress and failure strain. While for both type GNRs with fixed length, narrower ones have higher failure stress and higher failure strain. However, the Young's modulus of ZGNRs increase while decrease for AGNRs as the width of nanoribbon decreases. By using
quantum mechanics and quantum molecular dynamics, Gao et al. [17] reported that ZGNRs have higher failure stress than AGNRs, but the failure strain is lower. Based on first principle density functional theory, Faccio et al. [18] reported that the elastic modulus of ZGNRs is considerably higher than bulk graphene. They also reported that fewer atoms would harden the material, or small size would be stronger.

Each of the above publication discusses some aspect of GNR’s mechanical properties and gives us some insight in that direction. However, as shown above, we cannot combine them to get a consistent picture. The reason could be the usage of different potentials, different simulation methods, different loading conditions, etc.

To get a more comprehensive picture of this topic, this paper presents a systematic study of GNRs under uniaxial tension at room temperature. Besides the chirality as AGNR and ZGNR, we also focus on the size and aspect ratio effects on elastic modulus, failure stress and failure strain. In this study, molecular dynamic simulations were performed by LAMMPS [19] with AIREBO [20] potential to run extensive parametric studies in order to resolve this inconsistency. In the second section, we discuss simulation models and methods in detail. In the third section we present the parametric studies for ZGNRs and AGNRs of various sizes and aspect ratios.

2. Simulation models and methods

The size of GNR is defined by the length L (in loading direction) and the width W. The initial C–C bond length (aC–C) to start the computation is set as 1.4 Angstrom. The typical configurations of AGNR and ZGNR are shown in Fig. 1. In all simulations, a 2.5 Å wide strip at each end (the region within the yellow box shown in Fig. 1) is constrained as a boundary condition. Before loading, the system is relaxed to reach a thermodynamic equilibrium state. Then the system is deformed by displacing fixed boundary regions at each end by a strain rate of 0.001/ps. With a time step of 0.1 fs, the system is subjected to the strain increment of 0.01% and then relaxed for 1000 steps. This procedure is repeated until complete failure of GNRs. All the molecular dynamics simulations are carried out at 300 K with NVT ensemble by LAMMPS [19].

The Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) [20] potential was used for molecular interaction, as it allows for covalent bond breaking and reforming. The potential consists of three terms,

$$E = \frac{1}{2} \sum_i \sum_j E_{ij}^{REBO} + \sum_{ijkl} E_{ijkl}^{TORSION}$$

$E_{ij}^{REBO}$ stands for the hydrocarbon REBO potential; $E_{ij}^{LJ}$ includes long range interactions similar to standard Leonard–Jones potential; $E_{ijkl}^{TORSION}$ is an explicit 4-body potential that describes various dihedral angle preferences in hydrocarbon configurations. All three terms are included in our calculations.

For the REBO part of potential, a switching (cut off) function is defined to limit the interaction among the nearest neighbors,

$$f(r) = \begin{cases} 
1 & r < D_{\text{min}} \\
\frac{1}{2} & D_{\text{min}} < r < D_{\text{max}} \\
0 & r > D_{\text{max}}
\end{cases}$$

Fig. 2. Uniaxial tensile behavior of graphene.

Fig. 3. Distribution of bond length in equilibrium.

Fig. 4. Uniaxial behavior of square shaped AGNRs and ZGNRs with different size.
where \( D_{\text{max}} - D_{\text{min}} \) defines a range over which the function goes from 1 to 0, and the default values for C–C interaction are 2.0 Å and 1.7 Å [21], respectively. However, as shown in previous studies [22,23], such a cutoff function will give spuriously high bond forces around failure point without a physical basis. Following the suggestions from the developers of original REBO potential [22], larger cutoff distances were employed in literature, such as 1.9 Å in [13], 1.92 Å [24], and 2.0 Å in [9,14]. The value of 2.0 Å is used for the non-hydrogenated graphene in our study.

To study the stress–strain behavior under tension, nominal (engineering) strain and virial stress are used. And the volume of this system is calculated from the initial GNR with a thickness of 3.4 Å [25]. Then, stress is computed by averaging over all the atomistic stress of carbon atoms in the sheet, excluding those in fixed boundary regions at each end. In Zhao et al. [9], the stress is obtained by taking derivative of strain-energy over nominal strain. To validate the stress definition used here, a similar simulation is carried out for bulk graphene and the results are shown in Fig. 2. In our simulation, the failure stress and strain for zigzag graphene is 125.4 GPa and 0.2, respectively, while those for armchair graphene are 103 GPa and 0.14. In Zhao et al.’s work [9], failure strains are 0.2 and 0.13 in the zigzag and armchair cases, respectively. They also report maximum Cauchy stresses as 129 GPa and 102 GPa in the zigzag and armchair cases, respectively. The results here match very well.
In the preceding simulation, we need to relax graphene sheet with a bond length of 1.42 Å, when temperature goes from 0 K to 300 K. Similar step need to be done for GNRs. But existence of edge will introduce more difficulty to reach a stress-free state, as pointed by Bu et al. [12]. To facilitate this process, we propose to initialize the simulation with parameters of graphene at 300 K. Here, a square GNR of 10 nm is fully equilibrated by relaxing in NPT ensemble for 40 ps, with periodic boundary conditions. The bond length distribution in equilibrium state is shown in Fig. 3, with the average value of 1.408 Å. This small value of bond length can be justified by Mounet and Marzari’s first principle study on graphene [26], which shows graphene has a negative thermal expansion coefficient at room temperature.

We observed that choosing 1.4 Å as the initial bond length, rendered the sample to reach the thermodynamic equilibration faster, and reduced the initial stress at the beginning of simulation.

3. Results and discussion

3.1. Size effects of square shaped GNRs

First, we focus on the size effect on GNRs and set the aspect ratio as 1, i.e. square shaped GNRs. Five sets of square-shaped GNRs are simulated to study the size effect, with the edge lengths of 4, 6, 8, 10, and 12 nm. The stress–strain behaviors are shown in Fig. 4. ZGNRs always have higher ultimate strength compared with the armchair counterparts. The failure strain of ZGNRs is also larger than AGNRs’.

As reported by Xu [14], Fig. 5 shows that the fracture edges of both AGNRs and ZGNRs are predominately zigzag shaped. The difference of fracture strain between these two GNR types is due to two distinct fracture nucleation mechanisms that dominates their failure: interior nucleation for the ZGNRs and edge-controlled nucleation for the AGNRs [13]. We observed the similar behavior as shown in Fig. 5.

For elastic modulus, Fig. 6 shows that the elastic modulus increases as GNR becomes wider. Similar phenomenon is reported by Zhao et al. [9]. However, here we also give the size effect on failure stress and strain. Figs. 7 and 8 shows that both failure stress and failure strain of ZGNRs decrease as width increases. But, the size of effect for AGNRs is negligible.

3.2. Aspect ratio effects for GNRs of fixed length

The influence of aspect ratio on mechanical properties is studied first by increasing the width of GNRs for a fixed length of 12 nm. The widths are selected as 2.4, 4, 6, 10, 12 nm, i.e. the aspect ratio L/W are 5, 3, 2, 1.2, and 1 respectively. The stress–strain...
behaviors are shown in Fig. 9. Again, we observe that ZGNRs have higher ultimate failure stress and strain compared to AGNRs.

The results of elastic modulus are shown in Fig. 10. For AGNRs, similar phenomenon has been reported by Georgantzinos et al. [16] and Bu et al. [12]. As we can see, after the width is bigger than 4 nm, the modulus of ANGRs only has slightly increment. But according to [16], the elastic modulus of ZGNRs should decrease while width increases. However, we should point out that, the finite element method used in [16] does not have an atomic degree of freedom.

The strength of ZGNRs decreases as width increases. The difference in ultimate stress is about 20GPa between width of 2.4 nm and width of 12 nm. Therefore, wider ZNGRs have lower ultimate strength and smaller failure strain. For AGNRs, the strength slightly fluctuates within a small range, i.e. the change of width has very small influence on the failure stress of AGNRs.

Figs. 11 and 12 demonstrate that for a constant length, the strength of ZGNRs is a function of width, while the strength of AGNRs is independent of width for all practical purpose.

The different influences of width on ultimate strength of AGNRs and ZGNRs can be explained by their failure mechanisms. For AGNRs, the nucleation of failure always starts from edge. Therefore, the size of width contributes little to the onset of bonds breaking. However, the nucleation of failure in ZGNRs always starts from interior region, the initial bonds breaking probability does depend on width. This can be explained by the density of weakness (DOW) concept.

During the tensile loading, only the type B bond is stretched in ZGNRs, as shown in Fig. 13. DOW is defined as the number of potential failure sites per unit width. Those bonds on each side can be neglected. (Because they carry much less load comparing to interior bonds.) Thus, DOW can be defined as

$$DOW = \frac{4n - 2}{(3n - 1)a_{cc}}$$

where \(n\) is the column of unit cells in width direction of ZGNRs, \(a_{cc}\) is the interatomic distance of carbon atoms at equilibrium. For example, for the ZGRN shown in Fig. 14, \(n = 2\).

It is obvious that DOW of ZGNRs is a monotonically increasing function of width and converges to that of bulk graphene as it gets wider. This fact can be interpreted as wider ZGNRs are weaker, and narrower stronger.

3.3. Aspect ratio effects for GNRs with fixed width

In this final part, GNRs with fixed width of 2.5 nm are simulated to study the aspect ratio influence on mechanical behavior. The varying lengths are chosen to be 5, 7.5, 10, and 12.5 nm. Thus, corresponding aspect ratios \(L/W\) are 2, 3, 4, and 5 respectively. GNR of size 2.5 nm by 2.5 nm is neglected, because this small size will produce a too strong boundary effect on such a small sample. The stress strain behaviors are shown in Fig. 15.

Fig. 16 depicts the modulus of different GNRs. As can be seen, the modulus of ZGNRs decrease as length increases. However, length has no clear effect on elastic modulus of AGNRs. For both types, the change range is quite small compared to the average modulus value.

Figs. 17 and 18 show the length effect on the ultimate failure stress and strain of GNRs with fixed width. Compared to GNRs of varying width, the change of length has very small influence on both failure stress and failure strain of GNRs.

4. Conclusions

It is our observation that size effect studies conducted by finite element method, molecular statics and molecular dynamics simulation cannot be compared. We feel that MD simulation is the more accurate approach for this purpose. Size effects and
aspect ratio effects on mechanical failure behavior of GNRs under uniaxial tension are systematically studied, by molecular dynamics simulations with modified AIREBO [20] potential in LAMMPS [19]. For square shaped GNRs, size has significant effect on ZGNRs but has negligible effect on AGNRs. We observed that aspect ratio influence is mainly present in fixed length ZGNRs with varying width. Wider ZGNRs have higher elastic modulus and lower failure stress, strain. Again, width has negligible effect on mechanical properties of AGNRs with fixed length. For cases of fixed width GNRs, the change of length has little influence on both AGNRs and ZGNRs. It is shown that Density of Weakness (DOW) determines the size effect on mechanical properties of ZGNR.

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