Mechanical properties of graphene: effects of layer number, temperature and isotope

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Abstract

Herein the mechanical properties of graphene, including Young’s modulus, fracture stress and fracture strain has been investigated by molecular dynamics simulations. The simulation results show that the mechanical properties of graphene are sensitive to the temperature changes but insensitive to the layer numbers in the multilayer graphene. Increasing temperature exerts adverse and significant effects on the mechanical properties of graphene. However, the adverse effect produced by the increasing layer number is marginal. On the other hand, isotope substitutions in graphene play a negligible role in modifying the mechanical properties of graphene.

\textit{Keywords:} Graphene; Layer number; Isotope; Temperature; Molecular dynamics simulation
1. Introduction

The discovery of graphene in 2004 has triggered enormous research interests around the world due to its extraordinary mechanical, electronic and thermal properties. The super-strong and highly conductive graphene holds remarkable potentials in the applications in the new-generation nanoelectromechanical devices [1-3]. Lee et al. [4] measured the elastic properties of graphene experimentally. They found that the Young’s modulus of graphene is $1.0 \pm 0.1$ TPa and its breaking strength is approximately 40 N/m. Experimental works done by Ramanathan et al. [5] and Rafiee et al. [6] also found that graphene outperforms the graphite and carbon nanotubes in enhancing the Young’s modulus and tensile strength of nanocomposites. The superiority of graphene stems from its two dimensional geometry, high surface-to-volume ratio and the associated stronger interface interaction. In addition to the experimental works, atomistic simulations have also been carried out extensively to explore the mechanical properties of graphene. By using molecular dynamics (MD) simulations based on adaptive intermolecular reactive empirical bond order (AIREBO) potential [7], the research group led by Aluru [8-10] investigated the various effects on the mechanical properties of graphene under unaxial tension and shear strain. They found that size, chirality, temperature, and strain rate exert significant influences on the fracture strength of graphene. Pei et al. [11] and Zheng et al. [12] employed MD simulations to investigate the mechanical properties of the graphene functionalized with hydrogen and other chemical
groups. It is worth noting that most of the atomistic simulations focus on the mechanical characterization of monolayer graphene [8-14]. Few studies have been done on the bilayer or multilayer graphene. In the experimental works and practical application, the majority of the graphene-based nanocomposites are reinforced by multilayer graphene rather than the monolayer one [6, 15-16]. It is found from experiments and atomistic simulations that the thermal conductivity of graphene is heavily dependent of the layer number [17-19]. In view of the facts, it is crucial to understand the relationship between layer number and the mechanical properties. This is the first aim in the present paper.

It is aware that most of the studies have been conducted at the low temperature or room temperature so as to avoid the thermal fluctuation. The effect of temperature on mechanical properties is commonly neglected. In general, graphene-based nano-devices perform their functions accompanied by the heat generation [3], causing the rise of the environmental temperature. It is believed that increasing temperature can affect the performance of graphene and its composites. Therefore, it is of great significance to investigate the effect of temperature on the mechanical properties of graphene. This is the second aim of the present work.

Recently, it is experimentally confirmed that different carbon isotopes, such as $^{13}$C, can be introduced in graphene during the production and modify the thermal property of graphene significantly [20-21]. The electronic properties of isotope-doped graphene remain unchanged
due to the same number of electrons in carbon isotopes. But how does the mechanical property change with the different isotopes in graphene remain unexplored. This is the third aim in the present paper.

2. Simulation model

In this paper, MD simulations are carried out on multilayer graphene with layer number varying from one to seven to examine the effect of layer number on Young’s modulus, fracture stress and fracture strain. The isotope effect on the mechanical properties is investigated by modeling monolayer graphene with different density of carbon isotope. All the graphenes have a length of 20 nm and width of 6 nm unless otherwise stated. The software package LAMMPS [22] is used for the MD simulations. The interactions between the atoms are described by the widely used AIREBO potential [7] coupled with the Lennard-Jones 12-6 potential [23] for the long-ranged nonbonding interaction. Uniaxial tensile loading is applied along the armchair direction at a strain rate of 0.0005 ps$^{-1}$ with a time step of 0.5 fs. The environmental temperature is maintained by using the Nosé-Hoover thermostat [24,25]. Periodic boundary conditions are applied in the in-plane directions so as to eliminate the edge effects. Prior to loading, the initial configuration is optimized by using the conjugate gradient method and then the system is relaxed in NPT ensemble (i.e. constant atom, pressure and temperature) for 100 ps. In order to overcome spuriously high tensile
force when the carbon-carbon bond length is greater than 1.7 Å, the onset of the covalent interaction cutoff distance is increased to 2.0 Å [8, 11, 13, 26] in the AIREBO potential.

3. Results and discussions

3.1 Effect of layer numbers

First of all, we examine the effect of layer number on the mechanical properties of multilayer graphene under tensile loading in the armchair direction. The relationship between the tensile strain and stress for the graphenes under consideration is similar. Herein, the stress-strain curves for the monolayer, 3-layer and 7-layer graphene are depicted in Fig. 1 for the illustrative purpose. As shown in Fig. 1, the stress increases approximately linearly with increasing tensile strain at small strain level. Thereafter, it increases nonlinearly with the strain prior to the breaking. At the breaking strain, the tensile stress reaches to the peak point. Herein, the breaking strain and the peak stress are defined as the fracture strain and fracture stress.
From the stress-strain relationship, the fracture stress and fracture strain can be determined from the MD simulations for all the graphenes with different layers. For each graphene, three independent simulations have been run and the result is obtained by averaging the three results. The variation of fracture stress and strain with respect to the layer number is depicted in Figs. 2(a) and 2(b), respectively. The linear trend lines in Fig. 2(a) and 2(b) indicate that the fracture stress and strain decrease approximately with increasing layer numbers. In other words, graphene with more layers possess relatively lower fracture strength. The difference between monolayer and multilayer graphenes lies in the presence of the van der Waals interlayer interaction. The interlayer van der Waals interaction between adjacent layers is not that strong. Therefore, it cannot boost the fracture stress and strain for multilayer graphene significantly. It is shown in Fig. 2(a) and 2(b) that the fracture stresses vary from
115.9 to 114.6 GPa and the fracture strain changes from 0.138 to 0.133 when the layer number increases from one to seven. The percentage differences between the fracture stresses and strains in monolayer and seven-layer graphene are 1.08% and 3.62%, respectively. Obviously the fracture properties of few-layer graphene are insensitive to the layer number. It is expected that numerous layers in the graphite could result in considerable reduction in the fracture properties of the graphite when compared with monolayer graphene.
Next, we take a look at the effect of layer number on the Young’s modulus. Young’s modulus is the stiffness of the structure. Corresponding to the fracture stress, it is predicted that Young’s modulus is also independent of layer numbers for the multilayer graphene under consideration. The variation of Young’s modulus with respect to the layer number is shown in Fig. 3. The Young’s modulus of graphene is calculated from the stress-strain data by using the Hooke’s law $\sigma = E \varepsilon$ at small strain level ($\leq 0.02$). This is to assure that the structures are in the linear deformation region and Hooke’s law is valid for the determination of the Young’s modulus. It is shown in Fig. 3 that the Young’s modulus of graphenes is in the range of 1.09 and 1.13 TPa, which agree with the experimental result of 1.0±0.1TPa [3] and other atomistic simulation results [8,11]. Similar to the fracture stress and strain, the Young’s modulus also experiences marginal changes when the layer number varies from one to seven. The

**Figure 2.** Variation of fracture stress (a) and strain (b) with respect to layer number
maximum difference is merely 3.18%. The overall trend shown in Fig. 3 indicates that the Young’s modulus increase approximately linearly with the layer number. Therefore, the interlayer interaction in multilayer graphene plays a somewhat positive role in the Young’s modulus of graphene.

**Figure 3.** Relationship between Young’s modulus and layer number in graphene

*Effect of Temperature*

It is well-known that temperature plays a significant role in the mechanical properties of nanomaterials [27-28]. In the following, attempts are made to explore the temperature effect on the mechanical properties of graphene under uniaxial tensile loading. Herein monolayer graphene is simulated under different temperature environment to investigate its temperature-dependent mechanical properties. The fracture stress and strain decrease approximately linearly with respect to temperature up to 2000K as shown in Figs. 4(a) and
These temperature-dependent fracture properties agree with the results given by Zhao et al. [9]. With increasing temperature, the structure becomes softer and less stiff. In addition, the atoms in the graphene undergo more severe movement at higher temperature environment, leading to a reduction of its strength in resisting external tensile loading. The fracture stress drops from 125.87 to 42.93 GPa when the temperature increases from 300K to 2000K, indicating a reduction by 65.89%. Similar trend is observed for fracture strain as shown in Fig. 4(b). The fracture strains are 0.148 and 0.048 at 300K and 2000K, respectively. The reduction is up to 67.6%. The linear decreasing of fracture stress and strain with increasing temperature can also be explained from the viewpoint of energy as pointed out by Tang et al. [28]. For graphene under tensile loading, two energy terms contribute to the total energy when it breaks: strain energy and thermal energy. The thermal energy contribution increases linearly with temperature, therefore the strain energy required for breaking is reduced.
The relationship between Young’s modulus and temperature is depicted in Fig. 5. Corresponding to the fracture stress, the increasing temperature makes the graphene less stiff, as a consequence, the Young’s modulus drops. As displayed in Fig. 5, the Young’s modulus decreases monotonically with temperature, demonstrating a linear relationship. When the
temperature increases from 300K to 2000K, the Young’s modulus drops from 1.11 to 0.847TPa with a 23.7% reduction. The simulation results shown in Figs. 4 and 5 clearly reveal the pronounced effect of temperature on the mechanical properties of graphene. It is noted that there exists discrepancy in the temperature-dependent Young’s modulus of graphene in the literature [9, 29]. By simulating the thermal vibration of monolayer graphene via MD simulations, Jiang et al. [29] found that the Young’s modulus increases from 0.95 to 1.1 TPa as temperature increases from 100K to 500K. However, Zhao et al. [9] found from the MD simulations that Young’s modulus of graphene is insensitive to temperature until around 1200K, thereafter, it decreases with increasing temperatures. At the high temperature of 2400K, the Young’s modulus is reduced by merely 10% in comparison with that at 300K [9].

![Figure 5. Variation of Young’s modulus with respect to temperature](image-url)
Effect of Isotope

In nature, carbon materials are made up of two stable isotopes, $^{12}\text{C}$ (abundance $\sim 99\%$) and $^{13}\text{C}$ ($\sim 1\%$). The different composition of isotopes in carbon materials are reported to modify the thermal conductivity significantly but have no effect on electronic properties since the isotopes have the same number of electron [20-21]. In the following, we will investigate the effect of isotope-substitution on the mechanical properties of monolayer graphene. For the sake of easy manipulation in controlling the density of different isotopes, a relatively small square monolayer graphene with side length of 5nm is simulated. The total atom number in the monolayer graphene is 960. MD simulations are performed on the square monolayer graphene with different isotope density. The isotope density is defined as the number of $^{13}\text{C}$ divided by the number of $^{12}\text{C}$. For graphene with isotope density varying from 0\% (corresponding to graphene made of pure $^{12}\text{C}$) to 100\% (corresponding to graphene made of pure $^{13}\text{C}$), it is found that all the graphene possess close mechanical properties. The fracture strains are about 0.2 and 0.14 when graphene is subject to tensile loading in zigzag and armchair directions, respectively. The fracture stresses along these two directions for all the isotope-modified graphene are around 140 and 118 GPa, respectively. Young’s moduli are about 1.06 and 1.11TPa in the zigzag and armchair directions, respectively. Figure 6 displays the fracture stress and Young’s modulus in the zigzag direction with respect to $^{13}\text{C}$ density. The results in Fig. 6 exhibit minor variation with $^{13}\text{C}$ density. It is clearly shown that isotope
exerts negligible effect on the mechanical properties of graphene, opposite to thermal properties. In order to confirm this point, additional MD simulations have been carried out to graphene doped with other carbon isotopes such as $^{14}\text{C}$. Same conclusion is reached, i.e., isotope is inefficient in the modification of mechanical properties. Hence isotope-substitution is useful in manipulating the thermal properties of graphene while maintain its mechanical integrity.

Figure 6. Variation of fracture stress and Young’s modulus in zigzag direction with respect to isotope density

4. Conclusions

In this paper, the effects of layer number, temperature and isotope-substitution on the mechanical properties such as Young’s modulus, fracture stress and strain, have been investigated by MD simulations. Temperature exerts negative effect on the mechanical properties. Increasing temperature leads to a degradation of mechanical properties and this degradation is linearly dependent of temperature. However, unlike their significant effects on
the thermal properties of graphene, the layer number and isotope-substitution lead to marginal difference in mechanical properties. It is revealed from the simulation results that isotope-doped graphene and few-layer graphene can be useful in the application of thermal devices while retains their mechanical integrity. The manipulation of mechanical properties of graphene can be effectively realized via the temperature change.

References:


