



Softening Effect in Stretching Stiffness of a Rippled Graphene: Molecular Dynamics Simulation

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ABSTRACT: In this paper, the stretching stiffness of a rippled graphene is studied using the molecular dynamics simulation. The uneven surface of the rippled graphene is modeled by a random function with different amplitudes and frequencies. Two models of the rippled graphene are simulated. In the first model, it is supposed that the graphene has random wrinkles with different amplitudes and frequencies. It can be regarded as an opened crumpled graphene. In the second model, the uneven surface of the rippled graphene is modeled by the trigonometric sine shapes. The adaptive intermolecular reactive bond order potential function is utilized to model the covalence bonding of the carbon atoms and the Nose-Hoover thermostat is used to control temperature of the system. It is implemented in the software package large scale atomic/molecular massively parallel simulator in order to simulate covalent bond formation between carbon atoms in the structure of graphene layer. Results are presented for both zigzag and armchair rippled graphene sheets with different initial surfaces. It is concluded that the failure strain of a rippled graphene under uniaxial tensile loading is less than that of a flat one. It is also demonstrated that the rippled graphene has softening stretching behavior due to its uneven surface.

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1- Introduction

Strictly, two dimensional crystals are expected to be unstable due to the thermodynamic requirement for the existence of out-of-plane bending with interatomic interaction generating a mathematical paradox. The fact that free-suspended graphene is not strictly two dimensional was revealed by Transmission Electron Microscopy (TEM) experiments, where suspended graphene membranes exhibited pronounced out-of-plane deformations (ripples) with the height up to 1 nm. Graphene [1,2], a two dimensional one atom thick crystal that was discovered in the free state has unique mechanical [3] and electrical properties [4]. The properties of carbon nanostructures such as carbon nanotubes and graphene sheets led to many applications in the field of modern technologies, such as nano-composites [5,6], nano-sensors [7], ultra capacitors [8], drug deliverer [9] and biodevices [10]. This two dimensional nano-structure is not a perfectly flat sheet and there are ripples in the suspended layer of graphene [11]. Its ripples may be due to the instability of the intrinsic properties of graphene since it is a two dimensional crystal or due to the impact of external factors because of the impurities from the ubiquitous dirt in graphene. Researchers have also observed ripples in suspended layers of graphene by thermal fluctuations in graphene layers [12].

Elastic properties of graphene with various methods, such as experiments [13], continuum models [14,15] and Molecular Dynamics (MD) [16-18] have been debated for years. On the experimental part, Lee et al. [13] reported the Young's modulus of graphene to be 1 ± 0.1 TPa and the ultimate stress of 130 ± 10 GPa at a strain of 0.25 which is very close to the value obtained by Griffith [19]. Using a density functional theory with a local density approximation, Liu et

al. [20] computed the Poisson's ratio and Young's modulus of graphene as 0.186 and 1.05 TPa, respectively. They also reported the maximum Cauchy stress for a uniaxial tensile test in the zigzag and armchair direction as 121GPa and 110GPa, respectively. Molecular Dynamics simulation has also been used to compute the mechanical properties of graphene. Wang et al. [21] studied the fracture strength of graphene sheets by the MD method and reported the fracture strength (engineering stress) along the zigzag and armchair directions as 105 GPa and 90 GPa, respectively, with the corresponding fracture strain of 0.22 and 0.13.

The elastic properties of a rippled graphene is also importance. There are some debates about the stability of two dimensional layers and membranes. The long-range order of two dimensional crystals is destroyed by long-wavelength fluctuations, according to the Mermin-Wagner theorem [22]. Similarly, two dimensional membranes embedded in a three dimensional space have a tendency to become wrinkled [23], so pristine Free-Standing Graphene (FSG) has subtle intrinsic ripples that also span or fluctuate at the nanometer scale [11,24]. Fasolino et al. [23] reported that the ripples appear in graphene spontaneously with a maximum deflection of 0.07 nm. Tsoukleri et al. [25] subjected a graphene monolayer to tension and compression forces and reported its mechanical behavior based on the large-scale simulations. Jomehzadeh and Pugno [26] revealed that the rippling strongly increases the bending stiffness of graphene and affects the behavior of small length scale. Xiang and Shen [18] studied the shear buckling of rippled Single-Layered Graphene Sheets (SLGS) in thermal environments by using molecular dynamics simulation and they observed that the shear buckling capacity of a rectangular zigzag graphene sheet is higher than its armchair counterpart. It seems there are few studies on the

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mechanical properties of the rippled graphene sheets in literature and much more researches are needed because of its applications.

In the present work, the stretching stiffness of a rippled SLGS under uniaxial tensile loading is studied and its Young's modulus, fracture strength and failure strain are calculated. Also, armchair and zigzag edges in rippled graphene sheets were compared at the different temperatures. The softening behavior of stretching stiffness due to rippling can suggest the possibility of a smart tuning.

2- Modeling and Simulation

In order to study the behavior of graphene more accurate, the molecular dynamics simulation on the basis of the Adaptive Intermolecular REactive Bond Order (AIREBO) potential energy function [27] is utilized to model the covalence bonding of the carbon atoms. It is implemented in the software package Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [28] in order to simulate covalent bond formation between carbon atoms in the structure of graphene layer. The AIREBO potential consists of three potential components and is expressed as [27]

$$E^{AIREBO} = \frac{1}{2} \sum_i \sum_{i \neq j} \left[E_{ij}^{REBO} + E_{ij}^{LJ} + \sum_{K \neq i,j} \sum_{L \neq i,j,k} E_{ijkl}^{Torsion} \right] \quad (1)$$

where E_{ij}^{REBO} is the REactive Bond Order (REBO) part, which explains the bonded interaction between atoms based on the second generation reactive empirical bond order potentials of Brenner [29]; E_{ij}^{LJ} is the Lennard-Jones potential that considers the non-bonded interactions between atoms; $E_{ijkl}^{Torsion}$ includes the torsional interactions between atoms into the total energy depending on the dihedral angles of the systems. Here, the simulations are carried out in the conical ensemble at the constant room temperature ($T = 300K$) and the Nose-Hoover thermostat is employed to maintain the temperature of the system [30]. The geometrical structures

of the armchair and zigzag graphene sheets are shown in Fig. 1. In all simulations, the MD model consists of 1144 carbon atoms with the interatomic C-C distance of 0.142 nm and a total width of 52 Å and a length of 52.4 Å. Moreover, the simulation is conducted at a strain rate of 0.001 Ps⁻¹ and the Velocity-Verlet integration algorithm [31] is used for solving the equations of motion with a time step of 1 femtosecond. In the uniaxial tensile test, the engineering strain and stress are defined as

$$\varepsilon_x = \frac{l_x - l_x^0}{l_x^0} \quad \varepsilon_y = \frac{l_y - l_y^0}{l_y^0} \quad (2-a)$$

$$\sigma_x = \frac{1}{V^0} \frac{\partial U}{\partial \varepsilon_x} \quad (2-b)$$

where l_x^0 and l_y^0 are the initial lengths in x and y directions, l_x and l_y are the deformed lengths of the graphene. Also V^0 is the initial volume of the structure and U is the strain energy. Here, two models of the rippled graphene are simulated. In the first model, it is supposed that the graphene has random wrinkles with the different amplitudes and frequencies. It can be regarded as an opened crumpled graphene. In the second model, the uneven surface of the rippled graphene is modeled by the trigonometric sine shapes with 0.5 Å amplitude and unit frequency (Fig. 2). In this regard, four different samples given in Table 1 were selected for simulation.

2- 1- Result and discussion

In order to verify the accuracy of the simulation, the fracture strength of a flat graphene at 300K, under a uniaxial tensile load along both armchair and zigzag directions is evaluated. The engineering fracture stress and strain of the perfect structure at the breaking point for the current modeling is obtained about 110 GPa and 21.2%, and 92 GPa and 15.1% in zigzag and armchair directions, respectively. The maximum Cauchy stress is 129 and 101 GPa for zigzag and armchair

Table 1. Geometrical characteristics of the samples (all units are in Angstrom).

Models	Model 1			Model 2
Sample No.	1	2	3	4
Amplitude	-0.299Å < z < +0.299Å	-0.399Å < z < +0.399Å	-0.499Å < z < +0.499Å	0.5Sin(x)

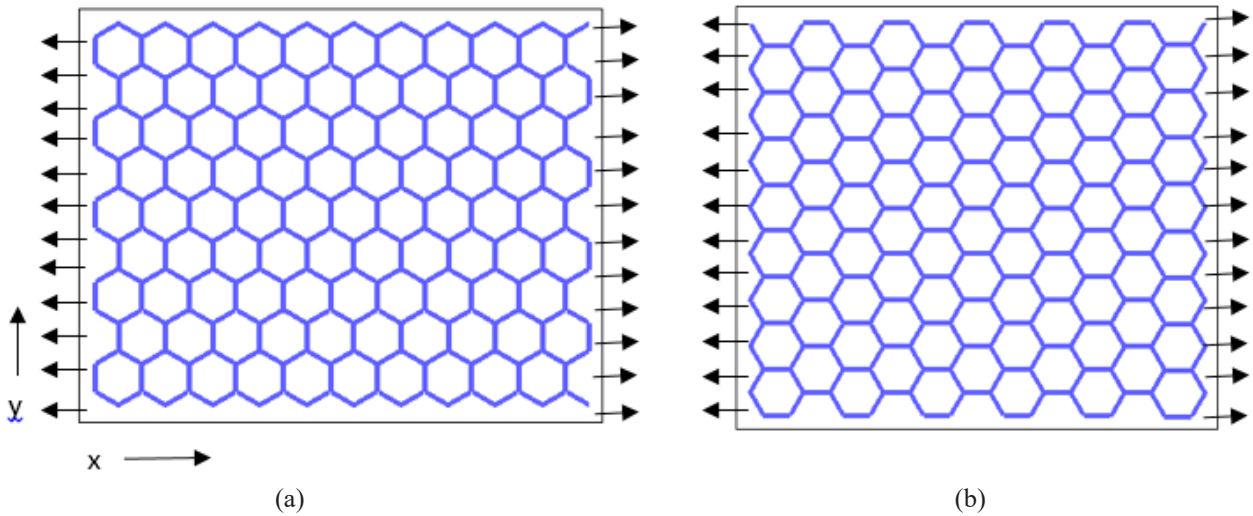


Fig. 1. Geometrical model of a graphene sheet under uniaxial tensile load along (a) zigzag direction (b) armchair direction

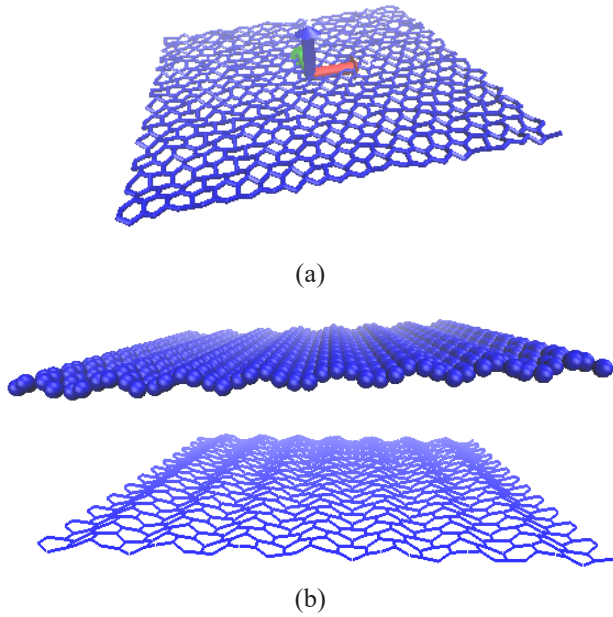


Fig. 2. a) Random wrinkles b) Trigonometric shape.

directions, respectively. These results have reasonable agreement with the experimental values (130 ± 10 GPa and 25%) [13]. Moreover, the obtained Young's modulus of the samples is compared with the available results in the literature in Table 2.

Table 2. A comparison of the computed Young's modulus of a perfect graphene

Model	Method	Young's modulus(TPa)
Present model	MD	0.834
Tsai and Tu [16]	MD	0.912
Ansari et al. [17]	MD	0.8
Lee et al. [13]	Experimental	1 ± 0.1

The stress-strain curve of a rippled graphene with a random uneven surface under the tensile loading in zigzag and armchair directions at 300K is depicted in Fig. 3. It can be seen that the rippled graphene has softening stretching behavior. As a flat surface of graphene is converted to the uneven surface, the fracture stress and strain will reduce. For sample 1, the reduction of the fracture stress and strain of the zigzag rippled graphene is approximately 3.64% and 4.72%, respectively, with respect to the flat one, while they are 9.8% and 8.7% for the armchair rippled graphene, respectively. It can be concluded that the softening behavior in armchair direction due to the rippling is more considerable than zigzag direction. Also, it can be seen that the amplitude of the wrinkles increases the reduction of the fracture stress. The stress-strain curve of the sample 1 is shown in Fig. 4 for both zigzag and armchair directions. It can be seen that the fracture stress and strain of a rippled graphene in the zigzag direction is more than the armchair direction. It can be concluded that the zigzag rippled graphene has more strength than the armchair one like the perfect graphene.

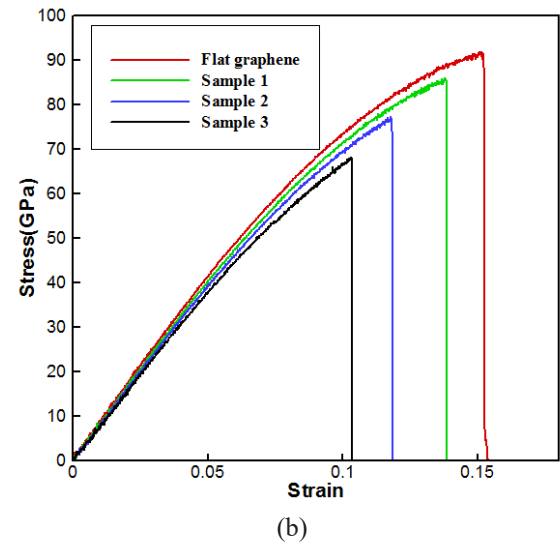
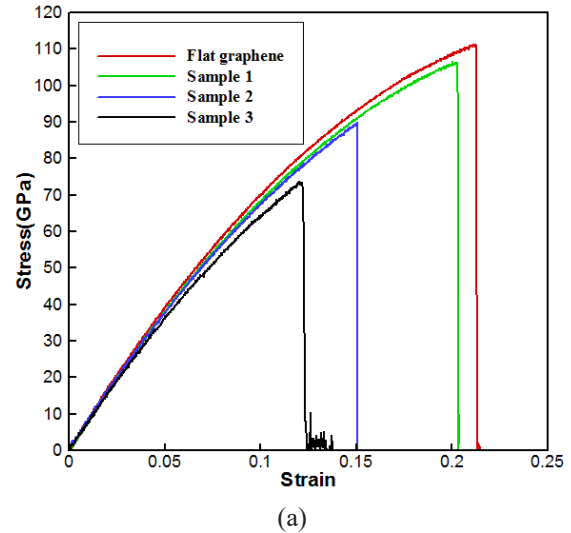


Fig. 3. Stress-Strain curve of rippled graphene: a) zigzag b) armchair

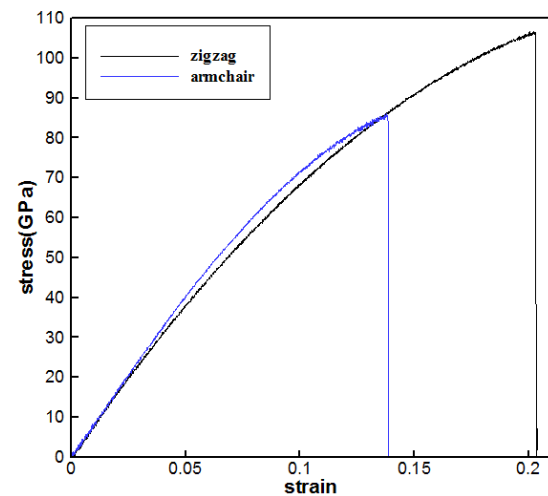


Fig. 4. Stress-strain curve in zigzag and armchair directions for sample

Also, the stress-strain curve of the rippled graphene with trigonometric surface (sample 4) in armchair direction is shown in Fig. 5 and compare with flat one. It can be seen that, for small strains the system elongates without significant stretching of the carbon bonds with negligible stress and it can be supposed as a rigid opening and then the deformation of the carbon bonds will start, and linear elastic behavior of the graphene happens. A comparison of stress-strain curve between the edges of the zigzag and armchair is shown in Fig. 6 for sample 4. It can be seen that as in previous cases the fracture stress in zigzag direction is more than the armchair direction.

The fracture stress and strain of all samples are obtained and written in Table 3. It can be seen that unlike the other samples, the fracture strain of sample 4 is more than the flat one. This is because the graphene of this sample is opened at the beginning of the stretching and then its bonds start deformation.

3- Conclusions

In this article, based on the AIREBO potential function, the molecular dynamics simulation has been developed in order to investigate the fracture strength of the rippled graphene. The Nose-Hoover thermostat has been used to control temperature of the system. Two models were simulated

for the configuration of the wrinkles and then the rippled graphene has been subjected to the tension loading in zigzag and armchair direction. It has been concluded that the rippled graphene has softening stretching behavior and the fracture stress of graphene is reduced as its surface becomes uneven. Also, the failure strain of a rippled graphene under uniaxial tensile loading is less than that of a flat one.

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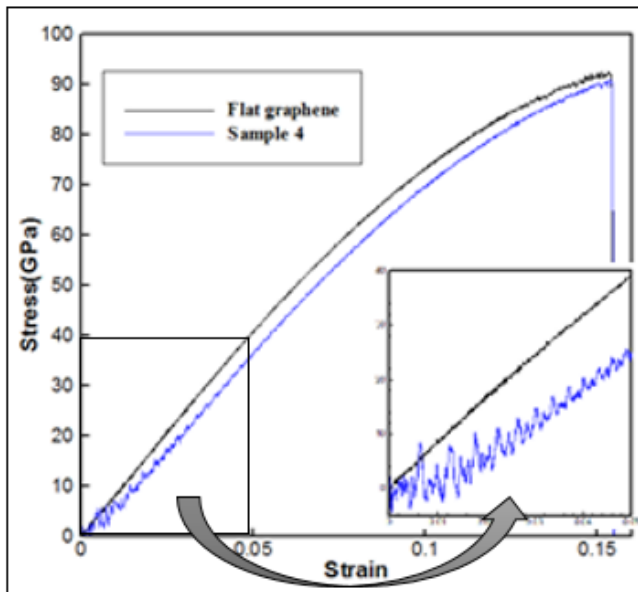


Fig. 5. Strain-stress curve in armchair direction for sample 4

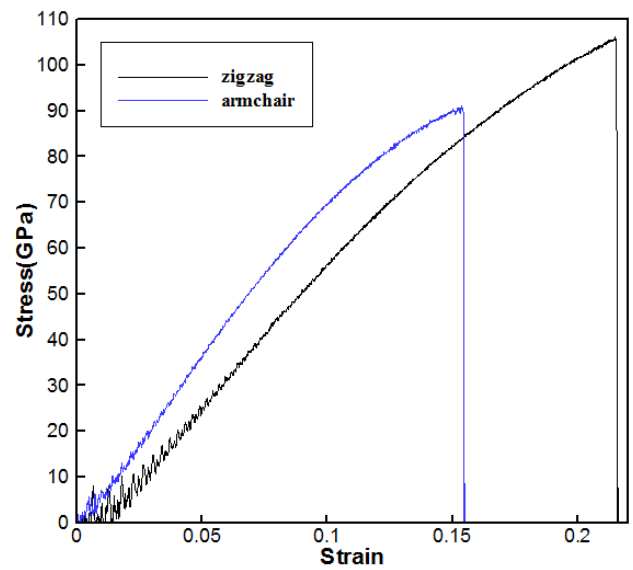


Fig. 6. Stress-Strain curve in zigzag and armchair direction for sample 4

Table 3. Fracture stress and strain of all samples

Sample No.		Flat graphene	1	2	3	4
Zigzag direction	Fracture stress	110GPa	106GPa (-3.64%)	90GPa (-18.2%)	73GPa (-33.7%)	105GPa (-4.6%)
	Strain	21.2	20.2% (-4.72%)	17.8% (-16.1%)	12.1% (-43%)	21.5% (+1.41%)
Armchair direction	Fracture stress	92GPa	83GPa (-9.8%)	77GPa (-16.4%)	68GPa (-26.1%)	91GPa (-1.6%)
	Strain	15.1	13.8% (-8.7%)	11.8% (-21.9%)	10.3% (-31.8%)	15.4% (+1.99%)

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