Young’s modulus of defective graphene sheet from intrinsic thermal vibrations

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Abstract. Classical molecular dynamics simulations have been performed to establish a relation between thermally excited ripples and Young’s modulus of defective graphene sheet within a range of temperatures. The presence of the out-of-plane intrinsic ripples stabilizes the graphene membranes and the mechanical stability is analyzed by means of thermal mean square vibration amplitude in the long wavelength regime. We observed that the presence of vacancy and Stone-Wales (SW) defects reduces the Young’s modulus of graphene sheets. Graphene sheet with vacancy defects possess superior Young’s modulus to that of a sheet with Stone-Wales defects. The obtained room temperature Young’s modulus of pristine and defective graphene sheet is $\sim 1$ TPa, which is comparable to the results of earlier experimental and atomistic simulation studies.

Keywords: Classical molecular dynamics, Young’s modulus, defects, graphene

(Some figures may appear in colour only in the online version)

1. Introduction

Graphene, the one atom thick honey-comb arrangement of carbon atoms has attracted the attention of the scientific community due to its exceptional properties. Because of its unique electronic properties, monolayer graphene has become a good candidate for various device applications [1]. Graphene shows extra ordinary mechanical properties and the Young’s modulus of graphene and its derivatives like carbon nanotubes (CNTs) are well studied using different techniques which include experiment, theory and computation [2]. Free standing graphene is the hardest known material having an elastic modulus of $\sim 1$ TPa. The highly robust nature of graphene could be useful to adjust its mechanical properties according to the demand. Lee et al measured the intrinsic breakdown strength and elastic properties of free standing monolayer graphene using atomic force microscope (AFM) and nano indentation techniques [3]. The superior strength and light weight nature of graphene is highly useful in flexible electronic devices.

The stability of two dimensional (2D) materials is a long standing topic of debate in condensed matter physics. A consequence of the famous Mermin-Wagner theorem is that a system of particles interacting with a sufficiently short range potential cannot exist in a perfectly ordered state at any nonzero temperature in two or lower dimensions [4, 5]. But, later in 2007, Fasolino et al reported that the ripples play a crucial role in the existence of graphene membranes. Due to the presence of these out-of-plane intrinsic fluctuations, graphene sheet acquires its stability [6]. The structural defects in materials have been receiving a lot of attention from the past few years. In this work, we have considered the commonly occurring vacancy and and Stone-Wales (SW) [7] defects in graphene sheet to investigate the Young’s modulus. Mono vacancy defect, which results from the missing of a carbon atom in the graphene lattice is the simplest defect that can be observed in the graphene sheet. Stone-Wales defect is a

[The rest of the content continues with the detailed discussion on the Young’s modulus and defect analysis in graphene, including simulations and results.]

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topological defect in which the adjacent four hexagons in graphene are transformed into two pentagons and two heptagons by rotating one of the C-C bonds by 90° and which forms a non-hexagonal ring in the lattice without altering the connectivity of the network. Young’s modulus is one of the most important properties in engineering design, which helps to measure of the stiffness of an elastic material. In the current study, we investigate the temperature dependence on the Young’s modulus of defective graphene by means of classical Molecular Dynamics simulation (MD) using reactive empirical bond order (REBO) potential [8].

2. Theoretical aspects to obtain the Young’s modulus of graphene

Out-of-plane height fluctuations are present in graphene even when it is in equilibrium configuration. Graphene has both optical and acoustic vibration modes present and aligned in the out-of-plane (z) direction. Here, the acoustic vibration mode is a flexural mode with low frequency and hence it will be fully excited even at very low temperatures also. The main contribution to the thermal mean-square vibration amplitude (TMSVA) of graphene is from the flexural mode in the z direction. In this work, we consider the phonon modes at temperature T, closely following Krishnan et al who experimentally investigated the stiffness of single-walled carbon nanotubes (CNTs) by observing their out-of-plane fluctuations at room temperature using transmission electron microscope and obtained the Young’s modulus as 1.25 TPa [9]. According to the plate theory of Landau and Lifshitz [10], the equation of oscillation of a graphene membrane in the z direction is given as,

$$\rho \frac{\partial^2 z}{\partial t^2} + \frac{D}{h} \Delta^2 z = 0,$$

where, $D = \frac{1}{12} Y h^3 (1 - \mu^2)$ and $\Delta$ is the two-dimensional Laplacian. $Y$ and $\mu$ are the Young’s modulus and Poisson’s ratio of the system. $\rho$ and $h$ are the density and thickness of the graphene sheet respectively. In graphene, all the modes are independent at thermal equilibrium condition, then the TMSVA at a particular temperature is given by,

$$\langle \sigma^2 \rangle = 0.31 \frac{(1 - \mu^2) S k_B T}{h^2 Y}$$

where, $Y$ is the Young’s modulus, $S$ is the area of the sheet, $k_B$ is the Boltzmann constant and $T$ is the temperature. The inter layer spacing of graphene is taken as 3.33 Å [3] and the out-of-plane height fluctuations $\langle \sigma^2 \rangle$, due to the thermal energy, is taken to be the spatial average of TMSVA over the area. Then the equation for Young’s modulus of graphene is,

$$Y = 0.3 \frac{S}{h^2} \frac{k_B T}{\langle \sigma^2 \rangle}$$

3. Details of Molecular Dynamics simulations

In this work, Classical Molecular Dynamics (MD) simulations based on the standard Velocity-Verlet time stepping algorithm has been carried out using Large scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) software package [11]. To solve the equations of motion of the pristine and defective graphene sheet, an integration time step of 0.1 fs is used. We have used 100,000 MD steps for the analysis of the effect of vacancy and Stone-Wales defects on the Young’s modulus of graphene. We used 20000 carbon atoms for the simulation and employed fixed boundary in the X direction, periodic boundary condition in the Y and Z directions and keep a vacuum separation of 15 Å in the Z direction. We also optimized the equilibrium lattice constant by minimizing the total energy of the graphene sheet using the REBO potential. This bond order potential has been shown to describe fairly well most of the structural and thermodynamic properties of different phase of carbon. The reason for the particular interest of this bond order potential is that, it correctly reproduces the best results of graphene with earlier atomistic studies [6]. Bond order potential correlate the bond length, bond strength and co-ordination, which help to changes the energetics of the conjugated bonds with desired accuracy. To control the system temperature, a Nose-Hoover type chain thermostat incorporated with canonical ensemble is used for the simulation. The mean squared height fluctuations $\langle \sigma^2 \rangle$ has been deduced from the MD simulation and investigated the values of Young’s modulus using equation (3). Figure 1 (a) and (b) shows that graphene sheets containing randomly generated mono vacancy and SW defect at room temperature.
4. Results and discussions

Study of defects is very important as they can drastically modify properties of materials. Incorporating defects for the analysis of mechanical properties helps to understand how the material behaves at different physical situations. Experimentally synthesized samples always contain different types of defects and the computational study of various types of possible defects gives a more realistic picture prior to experiment. The presence of defects may lead to reduction of, or complete loss of, symmetry of the perfect honeycomb lattice of graphene. Usually vacancies, topological defects, grain boundaries etc are the commonly occurring defects in low dimensional materials. Stone-Wales (SW) defect is one of the prominent topological defects observed in graphene in addition to vacancies. Figure 2 (a) shows the change in Young’s modulus of pristine graphene with temperature. We observed that, at high temperatures also, graphene sheet has an Young’s modulus $\sim 1$ TPa. As the temperature increases, the out-of-plane fluctuations also increases, which leads to change the Young’s modulus with temperature. Figure 2 (b) shows the change in Young’s modulus with temperature of graphene with vacancy and SW defect. The Young’s modulus of graphene with Vacancy defects is seen to be superior as compared to graphene with SW defect. At high temperature, graphene sheet with vacancy and SW defect show an Young’s modulus of $\sim 1.15$ TPa, which is comparable to the Young’s modulus of pristine graphene sheet and this result is consistent with that from earlier studies.

Figure 1. Figure shows graphene sheets containing randomly generated (a) Stone-Wales (SW) and (b) mono vacancy defects at room temperature.

Figure 2. Figure shows the variation in Young’s modulus with temperature of (a) pristine graphene sheet and (b) sheet containing randomly generated vacancy and SW defects.
The well known Mermin-Wagner theorem implies that the presence of long-wavelength fluctuations in a 2D crystal will destroy its long-range order. 2D membranes or sheets embedded in a 3D space have a tendency to show height fluctuations. These height fluctuations in membranes can be suppressed by the anharmonic coupling between bending and stretching modes. That is, the existence of a 2D membrane results in large height fluctuations on its surface [4, 6]. In our study, we also observed the height fluctuations in graphene sheet, which shows a resemblance to our earlier work of hexagonal boron nitride (h-BN), where we extracted the bending rigidity of the pristine and defective h-BN sheet in the harmonic regime [12]. Here, we found that, as the thermal energy increases, the atoms start vibrating from their mean position and the material reaches an equilibrium state after the simulation carried out a longer time. This leads to an increase of the out-of-plane height fluctuations with temperature and these fluctuations considerably change with defect concentration as shown in figure 3 (a) and (b). Krishnan et al [9] deduced the room temperature elastic modulii of CNT to be 1.25 TPa. The result obtained from our investigation on the Young’s modulus of graphene (1 ± 0.25) using the TMSV A is comparable to the recent experimental [3] as well as atomistic simulation methods [2].

Figure 3. Figure shows variation in height fluctuations with defect concentration at various temperature of graphene sheet with randomly generated (a) vacancy and (b) Stone-Wales defects.

To analyze the variation of Young’s modulus of graphene with temperature and defect concentration, we varied the temperatures from 100 K to 500 K and also the mono-vacancy and Stone-Wales defect concentration from 0.01% to 1.0%. We noticed that the Young’s modulus decreases with increase of vacancy and SW defect concentration as shown in figure 4 (a) and (b). We also observed that graphene with vacancy defect shows a superior Young’s modulus as compared to that with SW defects. We observe that the total number of atoms in graphene sheet is unaltered by the presence of SW defects, and hence preserve the sp² C-C bonding by keeping two heptagons and two pentagons corresponding to a single SW defect. On the other hand, the number of atoms reduces with addition of vacancies. Here, the missing carbon atoms breaks the perfect bonding in graphene and which results in the formation of dangling bonds, leading to a sharp decrease in the Young’s modulus. In the case of vacancy, as the defect concentration increases, the bond breaking happens and the interatomic interactions become weaker, resulting in a decrease in the Young’s modulus. It has been reported that the interaction between dangling bonds or the chemical instabilities due to the missing atoms in graphene sheet affects its mechanical properties [13]. At a higher temperature (1000 K), we noticed a significant decrease of Young’s modulus. This is due to the collective excitation of optical phonon mode along with the flexural mode at high temperature and the equation (3) cannot be valid in that condition.
Figure 4. Figure shows the variation in Young’s modulus with defect concentration at various temperature of graphene sheet with randomly generated (a) vacancy and (b) Stone-Wales defects.

5. Conclusions

Classical MD simulations have been performed to investigate the effect of defects on the Young’s modulus of free standing monolayer graphene sheet within a range of temperatures using the method of thermal mean square vibration amplitude. Our results shows that the presence of vacancy and Stone-Wales defects reduces the Young’s modulus of graphene sheet and the Young’s modulus decreases with increasing defect concentration. The calculated room temperature Young’s modulus of graphene is $\sim 1$ TPa which is comparable with the results of the earlier experimental and atomistic simulation studies. Due to the collective excitation of optical phonon mode along with the flexural mode at high temperature, the Young’s modulus shows a decrease at high temperatures. Further study and analysis is desirable to engineer the mechanical properties of graphene according to the demand.

References

[1] Geim A K and Novoselov K S. 2007. Nature Mater., 6, 183.
[2] Jiang J W, Wang J S and Li B. 2009. Phys. Rev B., 80, 113405.
[3] Lee C G, Wei X D, Kysar J W and Hone J. 2008. Science, 321, 385.
[4] Mermin N D. Crystalline order in two dimensions. 1968. Phys. Rev., 176, 250-254.
[5] Nelson D, Weinberg S and Piran T (Eds). Statistical mechanics of membranes and surfaces. World Scientific, Singapore (2004).
[6] Fasolino A, Los J H and Katsnelson M I. 2007. Intrinsic ripples in graphene. Nat. Mater., 6, 858-861.
[7] Stone A J and Wales D J. 1986. Chem. Phys. Lett., 128, 501-503.
[8] Donald W B, Olga A S, Judith A H, Steven J S, Boris N and Susan B S. 2002. J. Phys. Condens. Matter, 14, 783-802.
[9] Krishnan A, E. Dujardin, Ebbesen T W, Yianilos P N and Treat M M J. 1998. Phys. Rev. B., 58, 14013.
[10] Landau L D and Lifshitz E M. Theory of Elasticity (Pergamon, Oxford, 1995).
[11] Lien N J. 1995. Comput. Phys., 117, 1-19. (http://lammps.sandia.gov)
[12] Thomas S, Ajith K M, Chandra S and Valsakumar M C. 2015. J. Phys.: Condens. Matter, 27, 315302.
[13] Jing et al. 2012. Effect of defects on Young’s modulus of graphene sheet: A molecular dynamics simulation. RSC Advances, 2, 9124-9129.