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Thermal Transportation Behaviour Prediction of Defective Graphene Sheet at Various Temperature: A Molecular Dynamics Study

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Abstract Thermal transportation behavior and phonon-phonon scattering strongly depend on the temperature variation as well as percentage of defects in the pristine material. Non-equilibrium molecular dynamics (NEMD) simulation has been chosen as the pathway to investigate the effects of percentage of defects on phonon wave propagation and thermal transportation in single layer graphene sheet. From the simulation it is inferred that thermal conductivity of graphene sheet falls with the increase of % of defects. Optimized Tersoff potential has been employed to generate the decreasing trend of thermal conductivity of graphene sheet with the % of increase of defects. To investigate the effects of defect on the thermal conductivity, 0.2% (75 atoms), 0.5% (205 atoms), 1.05% (405 atoms), 1.32% (505 atoms), 3.13% (1200 atoms) atoms were deleted on the perpendicular of heat flow direction. To generate a more convenient outcome, Quantum correction has been applied below Debye temperature in order to include quantum effects for predicting thermal conductivity. This study concludes that up to Debye temperature, thermal conductivity shows an increasing trend with increasing temperature and then after it reaches a cliff, it starts to fall. Besides, as the percentage of defect increases, the thermal conductivity decreases. Thermal conductivity of graphene is so much high due to very strong sp^2 bonding between C atoms but when there is defects, the C atoms do not find any atom to transmit heat and consequently thermal conductivity decreases.

Keywords: *Non-equilibrium molecular dynamics (NEMD) simulation, thermal conductivity, graphene sheet, percentage of defects, Tersoff potential, Quantum correction, Debye temperature*

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1. Introduction

Graphene is basically a single layer graphite which is an allotrope of carbon. It actually exists in a two-dimensional form whereas the atoms are arranged in a hexagonal orientation. SP^2 bonds exist among the atoms of carbon [1]. This in-plane covalent sp^2 bonds between these adjacent C atoms are the strongest in nature (slightly stronger than the sp^3 bonds in diamond), with a bonding energy of approximately 5.6 eV [1]. By contrast, the adjacent graphene planes within a graphite crystal are linked by weak van der waals interactions (~ 50 meV) with a spacing of h=3.35 Angstrom. The strong and anisotropic bonding and the low mass of the carbon atoms give graphene and related materials unique thermal properties. [1]

Recently, minimization of size and high-density integration has started a new era in device technology. As a result, further development of the silicon based micro electronic device urges for the search of a new type of high thermal conductivity material. Reliable performance of a device depends on how efficiently heat is dissipated. [2] Hence the investigation of thermal properties of a material is truly needed. Graphene for its wide range of extraordinary properties has drawn attention of many researchers and engineers. Being one of the most extra ordinary materials in the present era it has a very wide range of application [2]. Thin flexible display screen, medical instrumentation, photonics circuit, chemical and process industries, solar cells, light weight are some of the applications [2]. In 2008, Exfoliation generated by graphene, is considered as one of the most expensive material in the world. Tissue engineering is blessed by graphene because of its wide use to improve different nano composites used in bone tissue application. Graphene is frequently used in Optoelectronics, different types of sensors and frequency multipliers [6].

Phonon vibration is the prime thermal energy transport mechanism for graphene or Graphene Nano Ribbon (GNR) [3,4,5]. The contribution of phonons to the thermal conductivity is about 50-100 times greater than that of electron [6]. Particularly in recent experiments, it has been found using micro-Raman spectroscopy that single layer graphene sheets show extremely large values of thermal conductivity [7]. With the use of micro-Raman spectroscopy, the room temperature thermal conductivity for a single layer graphene suspended across a trench was found in the range of 3080–5150 W/m-K by Balandin [8]. The thermal conductivity of graphene nanoribbons found in molecular dynamics simulation is of the same order of magnitude (2000 W/m-K) [9] as that of the experimental value (5300 W/m-K) [4].

While the experimental work becomes relatively difficult, several atomistic simulation techniques have been utilized to model phonon transport in nanostructured materials [14]. Two prevailing methods are Monte Carlo (MC) simulation and Molecular Dynamics (MD) simulation. The MC method has been used to solve the Boltzmann transport equation (BTE) for phonon transport under the relaxation time approximation [14]. The distribution function obtained from Boltzmann's equation can be easily related to energy and therefore to temperature. The basic principle of the MC simulation is to track the phonon energy bundles as they drift and collide through the computational domain. On the contrary Molecular Dynamics Simulation has been used to examine thermal properties in nanostructured materials where phonon-phonon scattering dominates heat transfer [14]. This method is now-a-days very popular method for calculating different transport properties. It is a very powerful toolbox in modern molecular modeling and enables us to follow and understand structure and dynamics with extreme detail-literally on scales where motion of individual atoms can be tracked. This process is simple and can deal with complex geometries [14]. In the most common version, the trajectories of atoms and molecules are determined by numerically solving Newton's equations of motion for a system of interacting particles, where forces between the particles and their potential energies are calculated using interatomic potentials or molecular mechanics force fields [15]. Molecular Dynamics Simulation can be of two approaches- Equilibrium Molecular Dynamics (EMD) Simulation and Non-Equilibrium Molecular Dynamics (NEMD) Simulation. EMD method calculates heat transfer by Green-Kubo formalism whereas NEMD is a direct approach to calculate thermal conductivity directly from heat flow [15]. In this study NEMD simulation has been used with optimized tersoff potential field. Quantum correction was also taken into account for lower temperature. 120nm × 80 nm graphene sheet was considered in this study and in-plane and out-of-plane thermal conductivity of graphene was calculated at different temperature.

2. Molecular Modeling

In this literature, non-equilibrium molecular dynamics (NEMD) simulation has been used for predicting the thermal transportation behavior of defective graphene sheet. Non-equilibrium molecular dynamics simulation works based on Fourier's law

$$\boldsymbol{J} = -\boldsymbol{k}\frac{\partial \boldsymbol{T}}{\partial \boldsymbol{x}}$$

Where J is the heat flux.

$$J = \frac{\Delta Q}{2A\Delta t}$$

Where $\frac{\Delta Q}{\Delta t}$ is the heat current, A is the cross-sectional area, and j is the effective thermal conductivity.

The dimension of both defective and pristine graphene sheet were chosen as 120 nm x 80 nm. Total 38338 atoms were created in the simulation domain. The dimension of the domain was such that it eliminates the dimensional impact on simulation results. C-12 was only considered here which actually means isotropic graphene sheet. All the simulations were performed using the LAMMPS package and visualization was done in OVITO. The codes were developed and the codes were run by LAMMPS package. The results were analyzed from the log files got after simulation. To investigate the effects of voids on the thermal conductivity, 0.2% (75 atoms), 0.5% (205 atoms), 1.05% (405 atoms), 1.32% (505 atoms), 3.13% (1200 atoms) atoms were deleted on the perpendicular of heat flow direction.

Inter-atomic potential plays the most important rule for the accuracy of MD simulation. Original Tersoff potential can be used for simulating graphene sheet but it has very poor agreement with experimental data and hence an optimization was need which gave a newly optimized Tersoff. It show a better agreement with experimental data [2]. Therefore carbon-carbon interactions were modeled by the newly optimized Tersoff potential. The velocity Varlet integration method with the timestep of 0.001 ns was used. Rectangular geometry with periodic boundary conditions in length and width directions was utilized to investigate the thermal conductivities of graphene (mimicking infinitely wide graphene).

Two most renowned NEMD schemes can be used: (1) a constant heat flux, J is imposed along one particular direction of the graphene sheet and the resulting temperature profile gradient dT/dx is measured. This is called heat flux control method. (2) The temperature difference between the heat sink and heat source is first specified during the running procedure, and the resulting heat current is calculated. This is so-called temperature control method [7]. The results of the two methods should be essentially identical within MD statistical error for graphene sheet [7]. The two methods are explained below.

2.1. Heat flux Control Method

In heat flux control method, a constant heat flux is applied through a fixed direction. As equilibrium is achieved the temperature gradient dT/dx is measured. To perform simulation, a domain is designed containing one heat source and two heat sinks. The heat source has 1.5 nm thickness which is placed at the center of the sheet and the heat sinks both having a thickness of 1.5 nm were

located at the two ends of graphene sheet (see Figure 1). A constant heat flux has been established and after sometimes the system comes to an equilibrium. When the system comes to an equilibrium, the temperature profile becomes fixed with respect to time. Temperature is averaged over 1.5 nm-wide bins. Thus, this statistically meaningful temperature profile has been used to calculate thermal conductivity.

The velocity $V_{i,new}$ of each atom in each time step is calculated according to [7]

$$V_{i,new} = V_{i,old}\left(1 \pm \frac{\Delta Q}{E_k}\right)^{\frac{1}{2}}$$

Where ΔQ is the amount of heat added or dissipated from the system. The kinetic energy E_k is given by

$$E_k = \frac{1}{2}\sum_i m v_i^2 - \frac{1}{2}\sum_i m v_G^2$$

Where V_G being the velocity of the center of mass.

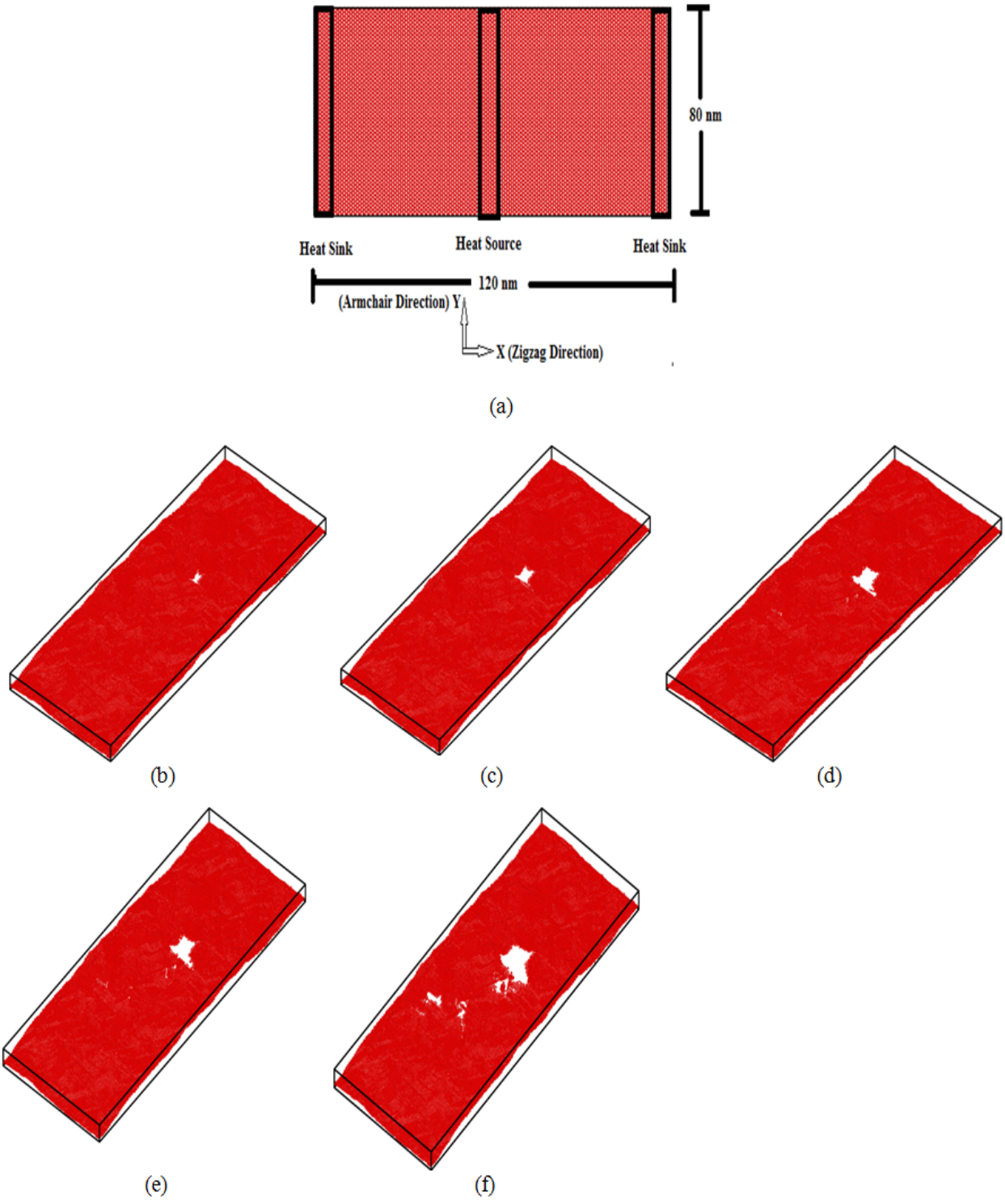

Figure 1. (a) Simulation domain of rectangular single layer graphene sheet (b) Defective graphene sheet by deleting 75 atoms (c) 205 atoms (d) 405 atoms (e) 505 atoms (f) 1200 atoms

2.2. Temperature Control Method

Another Non-Equilibrium Molecular Dynamics Simulation (NEMD) technique is temperature control method which actually depends on the idea that temperatures of two different regions of graphene (Hot and Cold region) are controlled and therefore a heat flow is established throughout the graphene [7]. Here, the Nose-Hoover thermostat is used to maintain the reservoir's temperature at a constant level. The atoms are integrated with time, basically following the Newton's equation of motion. The equation of motion of atoms in the control regions were modified with a damping parameter such that [7].

$$\frac{dr}{dt} = \frac{p_i}{m_i}$$

$$\frac{dp_i}{dt} = F_i - \zeta p_i$$

$$\frac{d\zeta}{dt} = \frac{1}{\zeta^2}\left[\frac{T(t)}{T_o} - 1\right]$$

Where r_i, p_i, F_i and m_i are atomic coordinate, momentum, inter-atomic force and mass of each atom respectively. T(t) is the instantaneous temperature of a small group (temperature reservoir) while T_0 being the desired (or target) temperature. When ς is set to zero, the NVT ensemble reduces to NVE ensemble in that small group [7].

The energy Q which is pumped through the heat reservoir can be written as [7]

$$\frac{dQ}{dt} = Nk_B T(t)(\varsigma + \frac{\varsigma^2}{2\tau^2})$$

Where N being the number of atoms in the heat reservoir, k_B being the Boltzmann constant and τ being the dynamics parameter.

2.3. Quantum Correction

Quantum correction is added to produce a better result at low temperature. The quantum corrected thermal conductivity K_{QC} can be found by multiplying the uncorrected thermal conductivity K_{MD} by dT_{MD}/dTq [16]

$$K_{QC} = \frac{dT_{MD}}{dT_Q} K_{MD}.$$

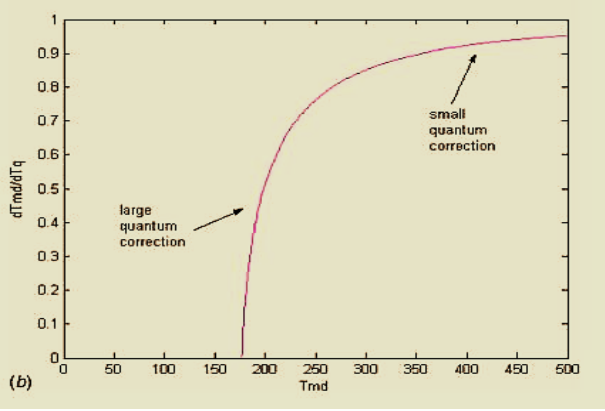

Figure 2. Ratio of MD to quantum temperature versus MD temperature [16]

From Figure 2, we can clearly see that quantum correction is dominant at low temperatures while at higher temperatures it is almost negligible [16] and hence to have a better result at low temperature quantum correction is needed.

3. Results and Discussion

Figure 3 (a) and Figure 3 (b) show the step wise temperature variation both at unstable and equilibrium phase. Figure 3(c) shows the steady state temperature profile of long graphene sheet using the heat flux control method and Figure 3 (d) shows the temperature profile of pristine graphene sheet and defective graphene sheet . The heat flux was set 0.00784 eV/(psÅ ^{2}). The system takes nearly 10 ns to reach in equilibrium. From the temperature profiles, it is evident that, at equilibrium condition the temperature profile is quite linear for both cases and it can be inferred that Fourier law can be applied here [17]. The figures shown here are used to find the thermal conductivity of defective single layer graphene sheet at room temperature 300K. From the Figure 3(b), it is evident that the temperature of the simulation domain is kept constant at 300K with a very little variation 1K.

In Figure 3(d) it is seen that the graph of defective graphene is steeper than graphene sheet with no defect. It is because, due to defects in the perpendicular to heat flow direction the temperature drops more rapidly. That is why the graph of defective graphene sheet is steeper than graphene sheet with no defect.

Figure 4 (a) shows that the thermal conductivity of both pure and defective graphene sheet decreases with the increase of temperature by using optimized tersoff potential. This phenomenon can be explained by the reduction of thermal conductivity by phonon-phonon scattering in pure lattice structures [17]. When optimized Tersoff potential is used, the thermal conductivity found in this study at room temperature is 3827.5 W/mk [18]. As temperature increases, the number of high frequency phonon increases. Hence phonon-phonon anharmonic interaction (Umklapp scattering) increases that makes the fall of thermal conductivity [2]. Again D. Nika [18] in his paper shown that heat transfer basically takes place for LA modes (in plane longitudinal modes). At lower temperature LA modes carry huge percentage of heat. As the temperature increases TA modes (in plane transverse mode) become dominant and a good percentage of heat is carried by TA mode. The percentage of heat carried by LA modes becomes lower than previous case of low temperature. This causes the fall of thermal conductivity. To incorporate the effect of defects on thermal conductivity of graphene sheet, some atoms were deleted on the perpendicular to heat flow direction. As the % of defects increases, thermal conductivity decreases which is shown at Figure 4(b). This is because when atoms are deleted, at the place of voids the particles do not find any other particle to transmit heat. So phonon-phonon anharmonic interaction increases which again acts as the reason of decreasing conductivity. Table 1 shows the effect of temperature and defects on the thermal conductivity of single layer graphene sheet. The thermal conductivity of single layer pure graphene sheet at room

temperature is highest among the known material and its value has been reported as about 2000–4000 W/mK [1]. In this work we got this value 3827.5 W/mK which surely has a very good agreement with previous records.

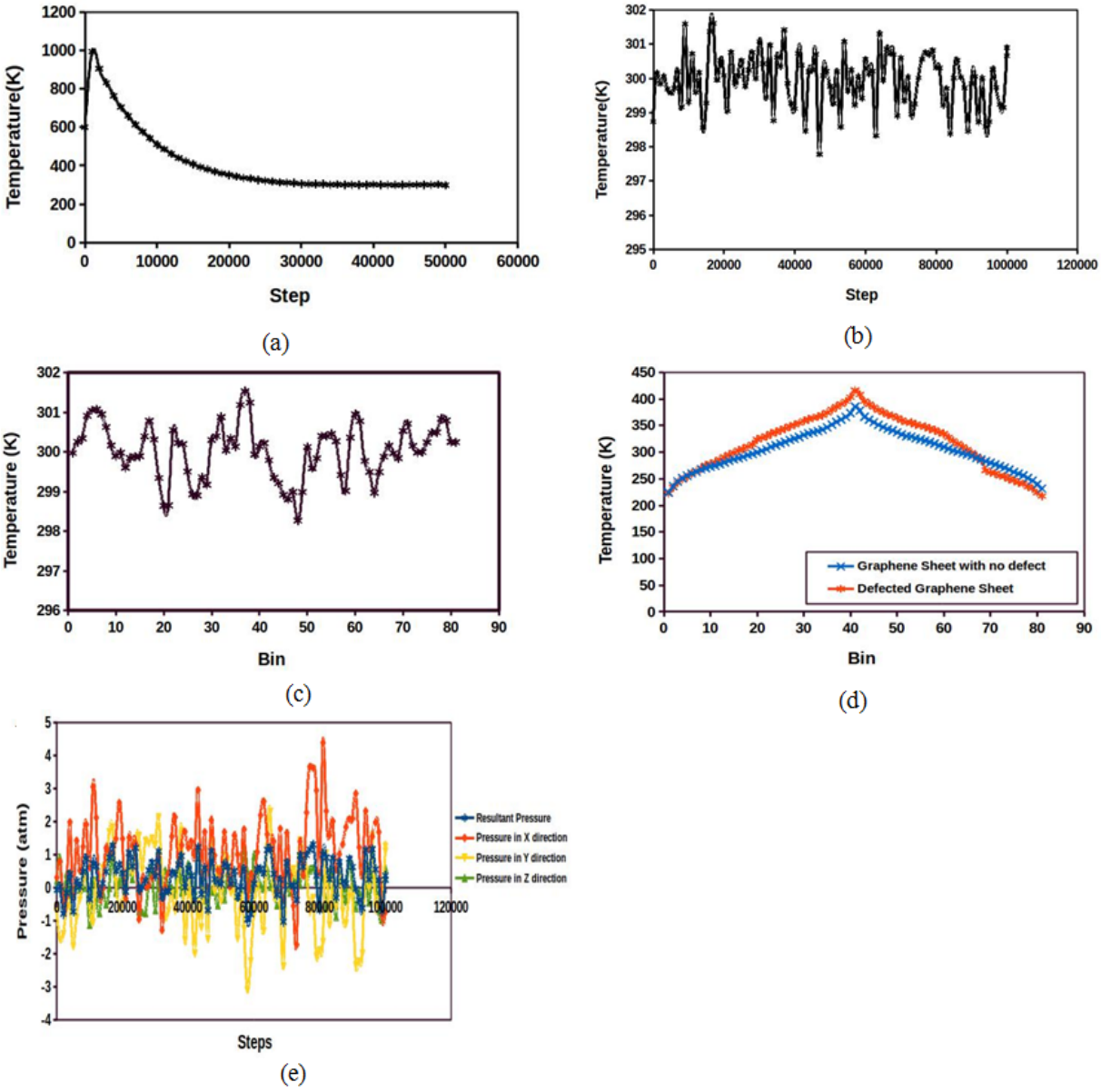

Figure 3. (a) Step-wise temperature variation all through process (b) Step wise temperature variation in equilibrium (c) Bin-wise temperature variation (d) Steady state temperature profile of pristine graphene and defected graphene sheet (e) Directional and resultant pressure distribution along 3 directions

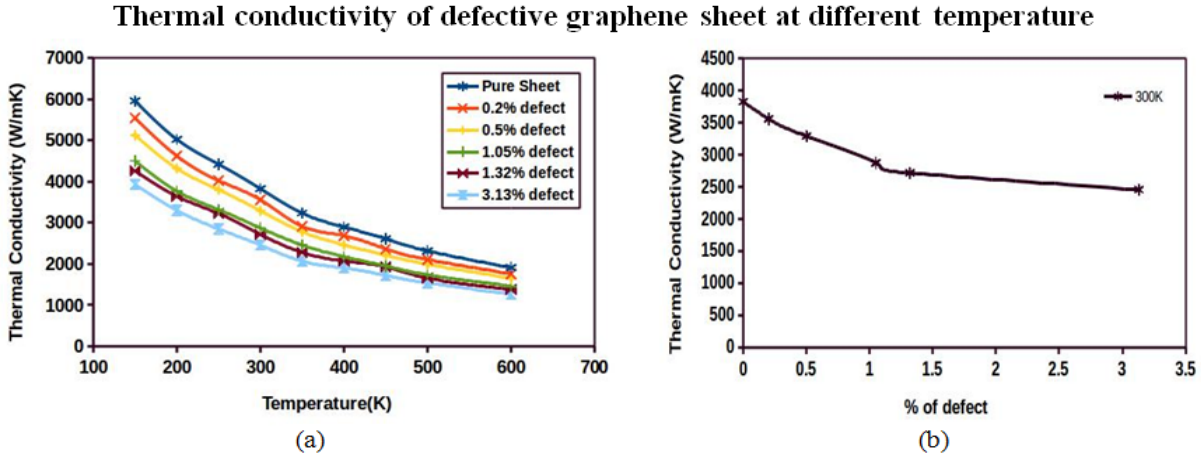

Figure 4. (a) Variation of thermal conductivity of pure and defective graphene sheet with temperature using Optimized Tersoff Potential (b) Drop of thermal conductivity with the % of defect at 300 K temperature

Table 1. Thermal conductivity of pure and defective graphene sheet with temperature using Optimized Tersoff Potential

Temperature (K)	Thermal Conductivity of Pure Sheet (W/mK)	Thermal Conductivity at 0.2% defect (W/mK)	Thermal Conductivity at 0.5 % defect (W/mK)	Thermal Conductivity at 1.05% defect (W/mK)	Thermal Conductivity at 1.32% defect (W/mK)	Thermal Conductivity at 3.13 % defect (W/mK)
150	5960.3	5543.08	5125.85	4500.02	4261.61	3933.79
200	5025.85	4623.78	4320.2	3769.38	3643.74	3301.98
250	4421.3	4023.38	3804.22	3320.39	3227.54	2851.73
300	3827.5	3559.57	3291.65	2874.45	2717.52	2457.25
350	3235.91	2912.31	2782.88	2459.29	2281.31	2067.74
400	2898.43	2689.74	2463.66	2176.72	2072.37	1904.26
450	2612.6	2362.84	2212.87	1950.56	1933.32	1724.31
500	2317.29	2108.73	1992.86	1740.28	1656.86	1540.99
600	1912.3	1759.31	1654.13	1460.99	1383.54	1266.51

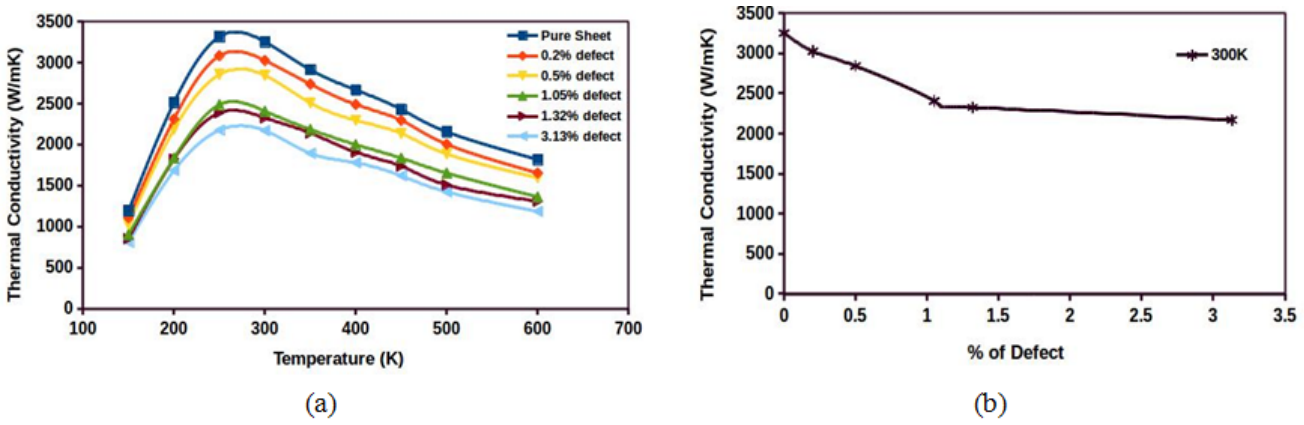

Figure 5. (a) Variation of thermal conductivity of pure and defective graphene sheet with temperature using Quantum Corrected Optimized Tersoff Potential (b) Drop of thermal conductivity with the % of defect at 300 K temperature

Table 2. Thermal conductivity of pure and defective graphene sheet with temperature using Quantum Corrected Optimized Tersoff Potential

Temperature (K)	Thermal Conductivity of Pure Sheet (W/mK)	Thermal Conductivity at 0.2% defect (W/mK)	Thermal Conductivity at 0.5 % defect (W/mK)	Thermal Conductivity at 1.05% defect (W/mK)	Thermal Conductivity at 1.32% defect (W/mK)	Thermal Conductivity at 3.13 % defect (W/mK)
150	1192.06	1108.61	1026.36	903.58	852.32	808.21
200	2512.93	2311.89	2186.24	1834.43	1824.38	1683.66
250	3315.97	3083.85	2855.05	2486.98	2387.50	2175.27
300	3253.37	3025.63	2843.44	2407.49	2326.16	2170.01
350	2912.31	2737.57	2507.50	2184.23	2140.55	1893.07
400	2666.55	2488.42	2295.89	1999.91	1906.58	1778.58
450	2429.72	2296.08	2135.72	1834.43	1737.24	1620.62
500	2155.08	2004.22	1885.69	1652.94	1508.56	1422.35
600	1816.69	1653.18	1595.05	1362.51	1308.01	1184.48

Figure 5 (a) shows that the thermal conductivity of both pure and defective graphene sheet decreases with the increase of temperature by using optimized tersoff potential. At low temperature (up to Debye temperature), quantum corrected thermal conductivity increases quite linearly with the increase of temperature, reaches a peak value and then decreases. The Umklapp process is supposed to be inactive at low temperature and therefore not available to provide thermal resistance [2] which has been considered through quantum correction. The thermal correction has been implemented by Debye phonon density of states. At room temperature and above, Umklapp scattering becomes highly significant [2] and thermally excited high energy phonons dominate the thermal conductivity. As a result, thermal conductivity decreases with the increase of temperature. To incorporate the effect of defects on thermal conductivity of graphene sheet, some atoms were deleted on the perpendicular to heat flow direction. Using quantum corrected optimized tersoff potential, as the % of defects increases, thermal conductivity decreases which is shown at Figure 5(b). This is because when atoms are deleted, at the place of voids the particles do not find any other particle to transmit heat. So phonon-phonon anharmonic interaction

increases which again acts as the reason of decreasing conductivity. Table 2 shows the effect of temperature and defects on the thermal conductivity of single layer graphene sheet by using quantum corrected optimized tersoff potential.

4. Conclusion

Theoretically an infinitely long graphene sheet was simulated and it was found that the value of thermal conductivity of graphene is extremely high compared to the other known materials. Then some of the atoms were deleted in order to find out the effect of defects on thermal transportation behavior of graphene. Both optimized Tersoff and Quantum corrected optimized Tersoff potential were employed in the study. From the simulation results, it can be inferred that:

- As the % of defects increases, thermal conductivity tends to decrease because of phonon-phonon anharmonic interactions.
- Optimized Tersoff potential predicts higher thermal conductivity at low temperature than quantum corrected optimized Tersoff potential because of not performing quantum correction. Hence optimized tersoff potential cannot predict better result under Debye temperature.
- The thermal conductivity of both pure and defective graphene sheets tends to decrease with the increase of temperature for optimized Tersoff potential because of phonon-phonon anharmonic interaction. However, when quantum correction is included in optimized Tersoff model, thermal conductivity increases up to Debye temperature quite linearly, gains the cliff and then tends to decrease with the increasing temperature.

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