

# Effect of Uniaxial Strain on Thermal Conductivity of Graphene

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**Abstract** - In this study, we investigate the effect of uniaxial strain on the thermal conductivity of zigzag graphene (ZG) and armchair graphene (AG). It is observed that the thermal conductivity reduces with strain in ZG and AG. For a given strain, the maximum reduction in thermal conductivity is observed in AG. The tensile strain causes a larger deformation of bonds in AG whereas a minor variation in bond angles is observed. This causes a high reduction of thermal conductivity in AG. DOS (Density of States) and Spectral Energy Density (SED) curves are calculated to study the phonon transport in graphene. It is found that due to strain, high frequency phonon modes undergo a red shift whereas blue shift is observed in the out-of-plane phonon modes. The phonon group velocity and lifetimes of in-plane acoustic modes get reduced because of strain and hence their contribution to the thermal conductivity reduces. But in the ZA modes, strain increases the phonon group velocities and phonon lifetimes. For unstrained graphene, in-plane acoustic modes contribute nearly 60-70% of thermal conductivity in ZG and AG. However, when graphene is strained their contribution sharply reduces and the contribution by ZA mode increases and is nearly 40-60% of the thermal conductivity. But the contribution by TA modes to the thermal conductivity is unaffected by strain. Phonon Mean Free Path (MFP) calculations indicate that MFP of phonon in strained graphene increases due to increase in the wavelength of low frequency ZA phonons. The MFP of phonons is found to be higher in AG than in ZG in both strained and unstrained conditions.

**Keywords:** Graphene, Molecular Dynamics (MD), Phonons, Strain.

## 1. Introduction

Graphene, a class of emerging two-dimensional materials, has attracted the attention of researchers in the recent past owing to its unique properties. These unique properties stem from the strong in-plane  $sp^2$  bonds, low mass of the carbon atoms and low dimensionality. The peculiar properties of graphene include high electron mobility [1], thermal conductivity [2] and superior mechanical strength [3]. Experimentally the measured thermal conductivity of single layer graphene is found to be 2000-5000 W/m-K [4]. These properties of graphene make it an ideal material in thermal management applications in nano-scale devices. However, the thermal conductivity of graphene is influenced by size [5], strain [6], defects [7], chirality [8] and so forth. Hence there is a need to understand the influence of these parameters for the effective design of graphene in nanoscale devices.

Strain is an important parameter that influences the thermal conductivity in graphene. In the conventional materials, the compressive strain augments the thermal conductivity whereas the tensile strain reduces it. The phonon modes get stiffened due to the compressive strain but the tensile strain causes softening of phonon modes [9,11]. Cuilan Ren et al. [10] studied the influence of axial tensile and compressive strain on thermal conductivity of CNT. It is observed that the thermal conductivity gets reduced when it is under compressive strain. But when it is stretched, the thermal conductivity at first increases and then decreases with further increase in the tensile strain. Radial phonon modes are found to play a dominant role in heat conduction in CNT. But in graphene, both compressive and tensile strains reduce the thermal conductivity. Under compressive strain, graphene forms corrugated structures which increases the phonon scattering [11]. The thermal conductivity of zigzag GNR (ZGNR) is found to be higher than armchair GNR (AGNR). This is due to the phonon suppressions at the edges which is observed to be higher for armchair GNR [12]. Wie et al. studied the influence of strain on AGNR and ZGNR. The tensile strain is found to have larger influence on the thermal conductivity than the compressive strain in both the GNR. For a given strain, the maximum reduction in the thermal conductivity is observed in AGNR [6]. Using Equilibrium Molecular Dynamics (EMD), Pereira et al. [13] observed that the thermal conductivity of unstrained graphene is finite and converges with size of the graphene whereas the thermal conductivity diverges beyond a uniaxial

tensile strain of 2%. ZA modes are found to be responsible for the observed divergence of thermal conductivity in graphene. Zhiyong Wei et al. [14] observed that in an unstrained graphene the in-plane acoustic modes and ZA modes contribute nearly 60 % and 25% of the thermal conductivity. The contribution by ZA modes to the thermal conductivity reduces further when it is coupled with substrates such as Silicon. Using EMD and Non-Equilibrium Dynamics (NEMD), Zheyong Fan et al. [15] observed that flexural mode is responsible for two-thirds of the thermal conductivity. They observed a logarithmic divergence of conductivity with tensile strain. Taishan Zhu et al. [16] observed that effect of tensile strain on thermal conductivity is dependent on the size of graphene system. The thermal conductivity is found to increase till a particular strain and then decrease on further straining. In spite of numerous studies on the effect of strain on thermal conductivity of graphene, a systematic analysis of phonon lifetimes, mean free path of phonons and mode-wise thermal contribution to conductivity is lacking till date. In the current study, the influence of the tensile strain on zigzag graphene (ZG) and armchair graphene (AG) is studied. Using Spectral Energy Density (SED), dispersion curves of graphene and phonon relaxation times are obtained. Furthermore, accumulation of thermal conductivity with Mean Free Path (MFP) of phonons and individual contribution of phonon modes to thermal conductivity of unstrained and strained graphene is studied.

## 2. Simulation Methods

The Molecular Dynamics (MD) simulations are performed using LAMMPS. Two different graphene structures namely zigzag graphene (ZG) and armchair graphene (AG) with length and width of 20 and 10 nm are considered. AIREBO potential is used to describe the interactions of the C-C bonds in the graphene [17]. Periodic boundary conditions are applied along the length and width of the graphene sheets and a non-periodic boundary condition is used along the z direction.

NEMD is used to calculate the thermal conductivity of the graphene. The graphene system was first equilibrated in NVT ensemble for 1.5 ns. Thereafter, the system is uniformly stretched in NVT ensemble at a strain rate of 0.01 Å/ps along the x-direction. Then the system is relaxed in NVT ensemble for another 2 ns.

The thermal conductivity of strained graphene is calculated as follows. The graphene is fixed at both of its ends and the remaining region is divided into bins of 2 Å width. Ten bins on either side of the fixed region are termed as hot and cold regions. These hot and cold regions are maintained at a temperature of 320 K and 280 K respectively using Nosé-Hoover thermostat. After the system attains the steady state, last 2.5 ns is used to obtain the temperature of bins in graphene. The heat flux is calculated by monitoring the amount of energy added or subtracted from the hot or cold regions in the graphene. Fourier's law of heat conduction is used to calculate the thermal conductivity of graphene. The thickness of the graphene sheet is taken as 3.35 Å, which represents the equilibrium distance between the graphene layers.

## 3. Results

### 3.1 Uniaxial tensile Stress-Strain Curves in Graphene

Fig 2a shows the results of the uniaxial tensile stress-strain curves in ZG and AG. The failure strains of ZG and AG are 0.21, 0.15 respectively and the corresponding failure stress is 132 and 106 GPa. Thus, the orthotropic nature of graphene is observed and Zhao et al. [18] through MD simulations have reported such similar results in their studies. The stress varies linearly with strain for the lower strain values and then increases non-linearly with strain. For a given strain, stress is observed to be higher in AG than in ZG. The higher strain in AG is observed because the elongation in bond A is higher than the elongation in bond B and the variation in angle A is small.

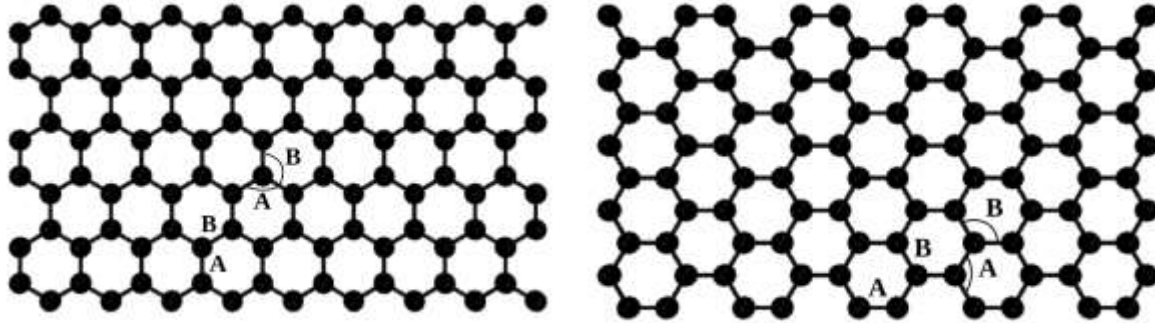


Fig. 1: (a) Zigzag Graphene (ZG) (b) Armchair Graphene (AG).

### 3.2 Effect of Strain on Thermal Conductivity of Graphene

The thermal conductivity ( $\kappa$ ) of ZG and AG is obtained as 160 and 145 W/m.K respectively. The variation of thermal conductivity with strain is given in figure 2b. However, due to strain, thermal conductivity reduces monotonically till the fracture occurs in graphene. The reduction in  $\kappa$  is observed to be higher in AG compared to ZG and for a given strain the maximum reduction is observed in AG. This variation is observed because the AG is more sensitive to the tensile strain than ZG.

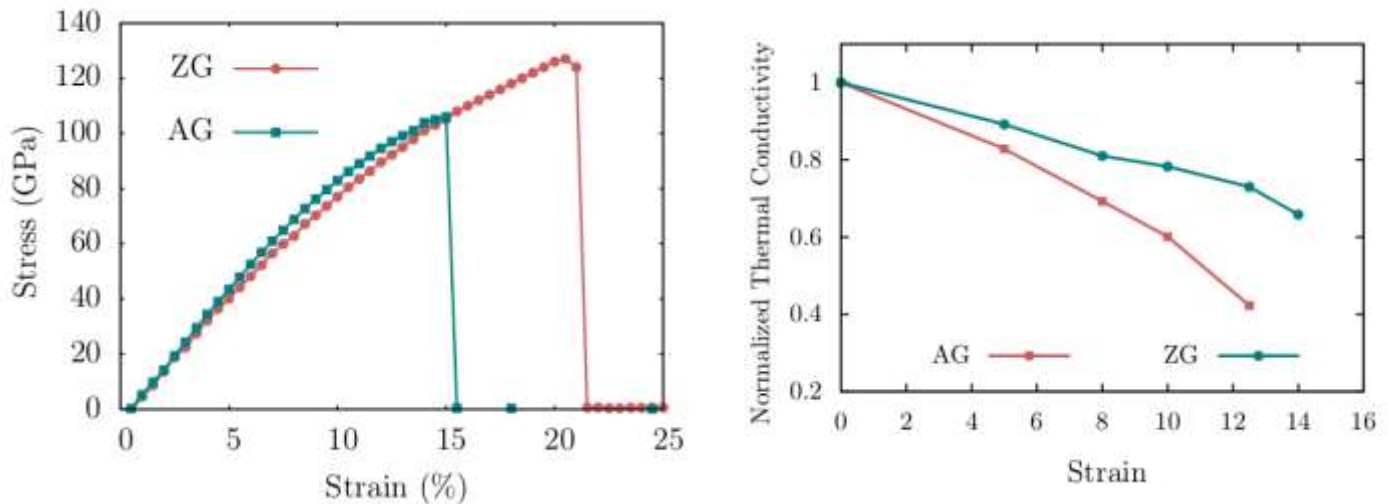


Fig. 2: (a) Stress-Strain curves of AG and ZG (b) Effect of strain on thermal conductivity of ZG and AG.

### 3.3 Density of States

Phonon density of states (DOS) are computed to understand the phonon transport in the graphene. DOS is obtained by performing Fourier transform of the velocity autocorrelation [21].

Fig 3a shows total phonon spectra in ZG. The G band peak in pristine ZG is 52.8 THz, which agrees with similar studies [4] and several points can be noted from the above spectra. Firstly, the high frequency optical modes undergo a red shift. This softens the phonon modes thereby reducing their group velocity. Secondly, broadening of the peaks is observed which reduces the phonon lifetimes and attenuate the thermal conductivity of graphene. Thirdly, the splitting of G peak into multiple peaks is observed. This is due to increase in phonon scattering in the graphene. All these factors contribute to reduction in the thermal conductivity of ZG.

Extending the analysis further, DOS is computed along the in-plane directions (both in zigzag and armchair directions) and out-plane directions. The in-plane optical and acoustic phonons contribute to the high and lower frequency modes. Comparing the spectra along the in-plane direction, it is observed that strain has severe effect on phonons along the strained direction i.e., zigzag direction. Along the transverse direction, the height of the G band with strain is found to be relatively constant. The broadening and splitting of the G band peaks with strain along the transverse direction is found to be relatively

less compared with the longitudinal direction. However, the out-of-plane modes undergo a blue shift which indicates that with strain their contribution to the thermal conductivity increase. Qualitatively similar type of phonon spectra is observed when AG is strained.

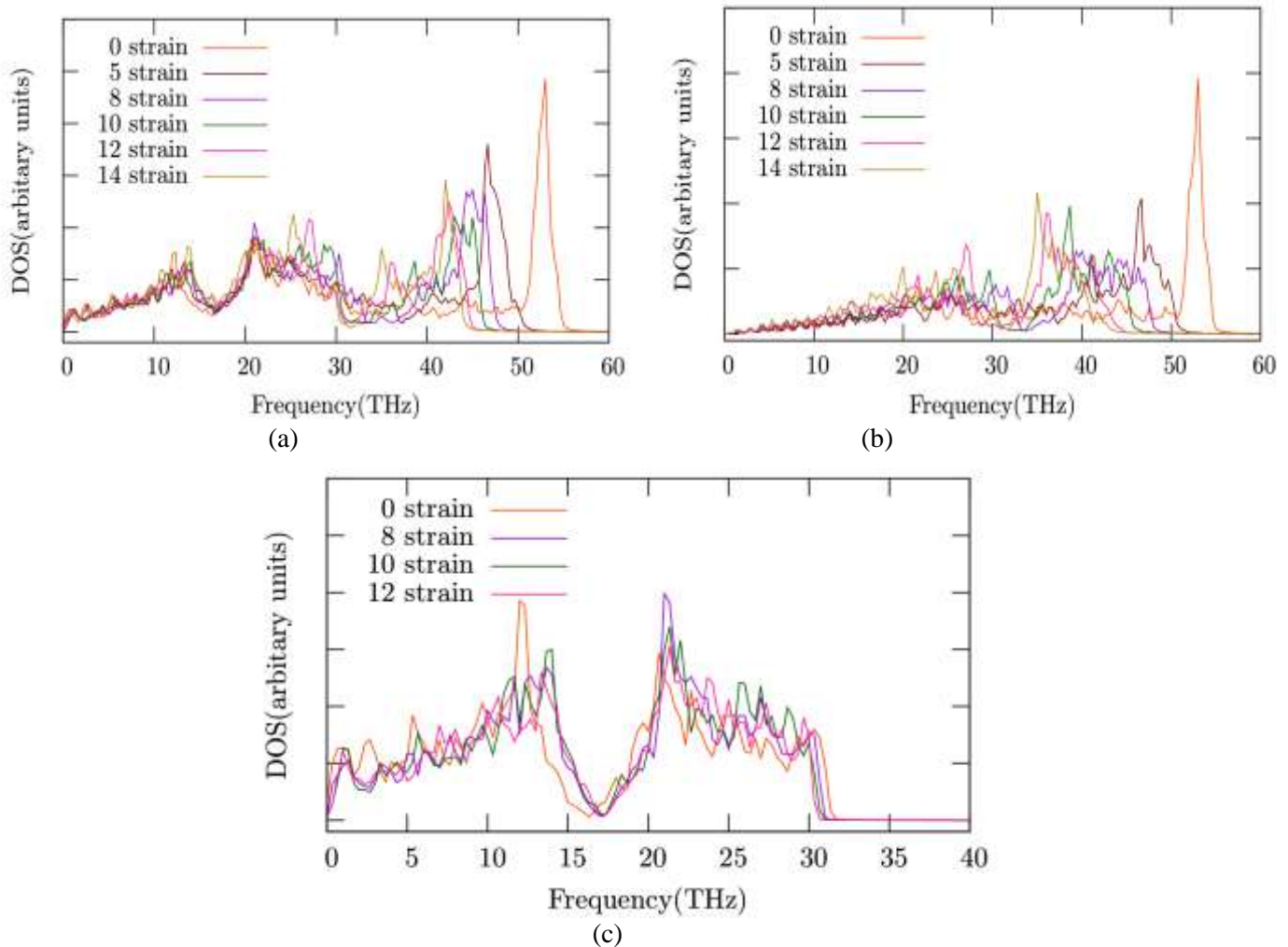


Fig. 3: DOS along ZG (a) Overall power spectrum (b) along X direction (c) along Z direction

### Spectral Energy Density (SED) Method

The phonon mode analysis is done through SED method. The phonon dispersion curves and phonon lifetimes of each mode is obtained. SED is a 2-D Fourier transform of the velocity of atoms that are obtained from molecular dynamics simulations [14]

Graphene of  $20 \times 20$  unit cell is chosen to compute the SED curves. The graphene system is equilibrated in NVT ensemble for 2 ns after which it is integrated in NVE ensemble for 6 ns. Last 4 ns are used to dump the velocity and positions of all the atoms of graphene. The dumping frequency is 5 fs

### 3.4 Phonon Dispersion Curves

Fig 4 shows the dispersion curves of pristine graphene and under tensile strain of 10%. In our system,  $\Gamma X$  and  $\Gamma Y$  represents the zigzag and armchair graphene. In an unstrained graphene, the frequency of LO and TO modes at the centre of the Brillouin Zone (BZ) is 50.7 THz. The ZA modes exhibit parabolic dispersion relations near the centre of BZ along both the  $k$ -paths. The slope of the dispersion relations gives the phonon group velocity of a particular mode. The phonon group velocity of acoustic modes is an order higher than the optical modes and the slope of acoustic modes is higher along the

zigzag direction in graphene. When graphene is strained, the phonon modes are softened. The quadratic dispersion relation of ZA curves linearizes due to the strain. Among the in-plane acoustic modes, LA modes are severely affected due to strain when compared to the TA modes. The phonon group velocities of the in-plane acoustic modes near the BZ are reduced due to strain. However, the velocity of TA modes is relatively constant under strain whereas the velocity of ZA modes are increased at the centre of BZ due to linearization of the dispersion relations.

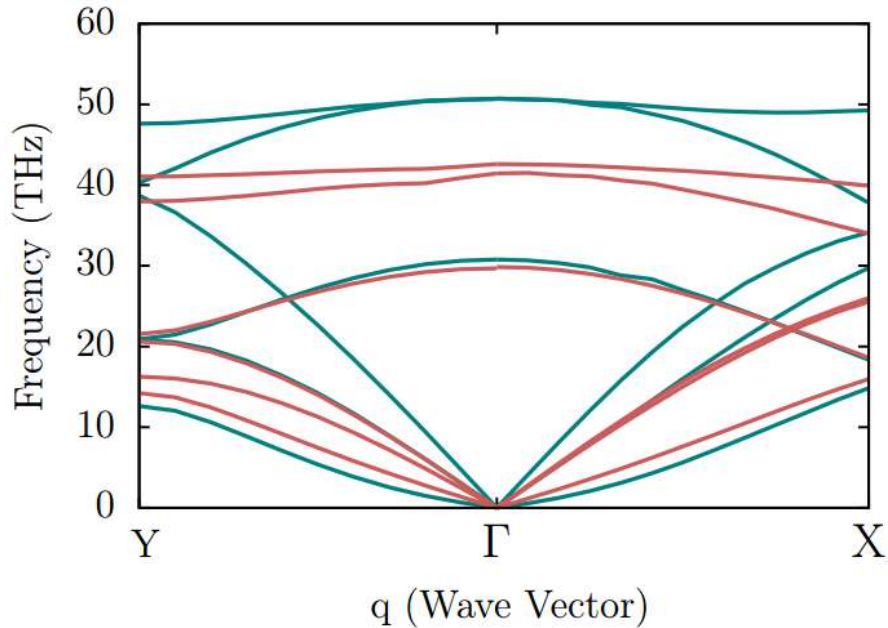


Fig. 4: Phonon Dispersion Curves of ZG and AG. Green and Red color represents zero and 10% tensile strain.

### 3.5 Phonon Lifetimes

Phonon lifetimes ( $\tau$ ) are obtained by fitting the peaks of SED curves to the Lorentzian curves. Fig 5 shows phonon lifetimes of unstrained graphene and graphene when strained by 10%. Optical mode phonons have shorter lifetimes than the acoustic modes. The lifetimes of ZA modes are higher than other acoustic modes and in general low frequency phonons near the BZ have longer lifetimes. When the graphene is strained, the phonon lifetimes of in-plane modes get reduced and greater reduction is observed in case of LA modes. However, the phonon lifetimes are increased for the ZA modes. This is due to reduction in out-of-plane fluctuations of the graphene sheet when it is strained. This reduces the scattering of ZA modes. The ZA phonon modes do not show any clear variation of  $\tau$  with the frequency in both strained and unstrained graphene. The  $\tau^{-1}$  of LA and TA modes vary with frequency as  $(0.9-1.1)$  and  $(1.1-1.3)$  in unstrained and strained conditions respectively.

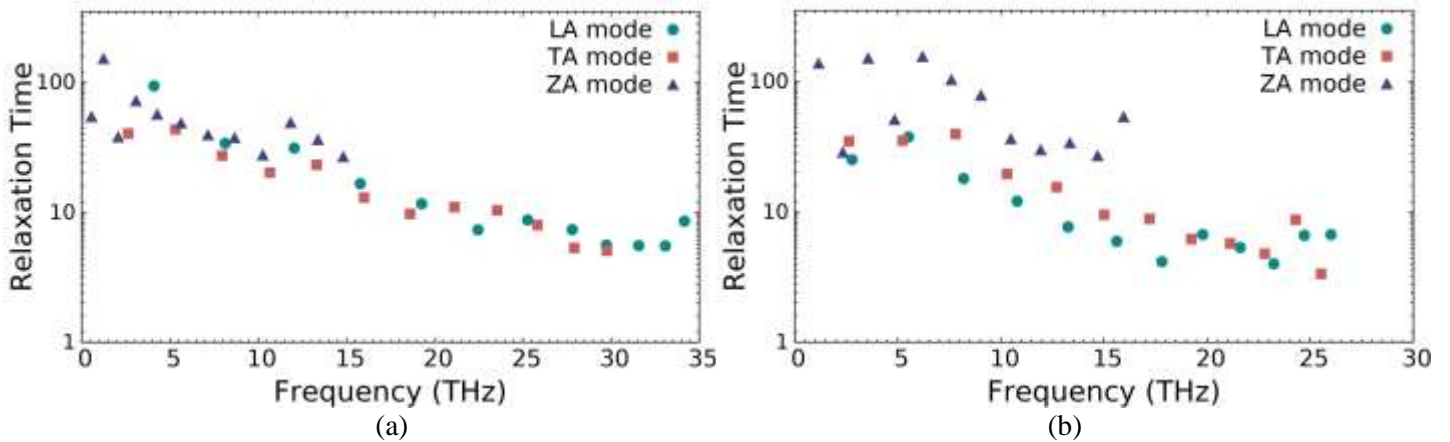


Fig. 5: Phonon Lifetimes of ZG (a) Zero strain (b) 10% tensile strain.

### 3.6 Phonon Mean Free Path

Phonon mean free path is an important parameter in the fabrication of graphene in nanoscale devices. Fig 6a shows the variation of the accumulated normalized thermal conductivity with the MFP of phonons. In the pristine graphene, LA modes have the longer MFP due to higher group velocities. Though ZA modes have higher phonon lifetimes, their group velocity is less than that of LA modes. Hence, they have smaller MFP. Phonons with MFP of 150-750 nm is found to contribute 90% of the thermal conductivity in the ZG. For AG phonons with MFP of 250-850 nm contribute 90% of thermal conductivity. When the ZG is strained we observe that the MFP phonons in graphene is increased. This is due to the increase in the phonon group velocity of the ZA modes and an increase in the phonon lifetimes. AG has higher phonon mean free path compared to ZG in both unstrained and strained conditions.

### 3.7 Mode-Wise Thermal Conductivity of graphene

Fig 6b shows the relative contribution of phonon modes to the thermal conductivity in graphene. In ZG and AG, LA modes contribute to nearly 50-55 % of thermal conductivity. Other acoustic modes contribute nearly 40-45% of the thermal conductivity. The contribution by the optical modes is less than 5% due to their lower group velocities and phonon lifetimes. However, when graphene is strained, the contribution by the ZA modes increase drastically (42% in ZG and 60% in AG). There is a great reduction in contribution by the LA modes (due to decrease in phonon group velocity and phonon lifetimes) and the relative contribution by the TA modes is unaffected by strain.

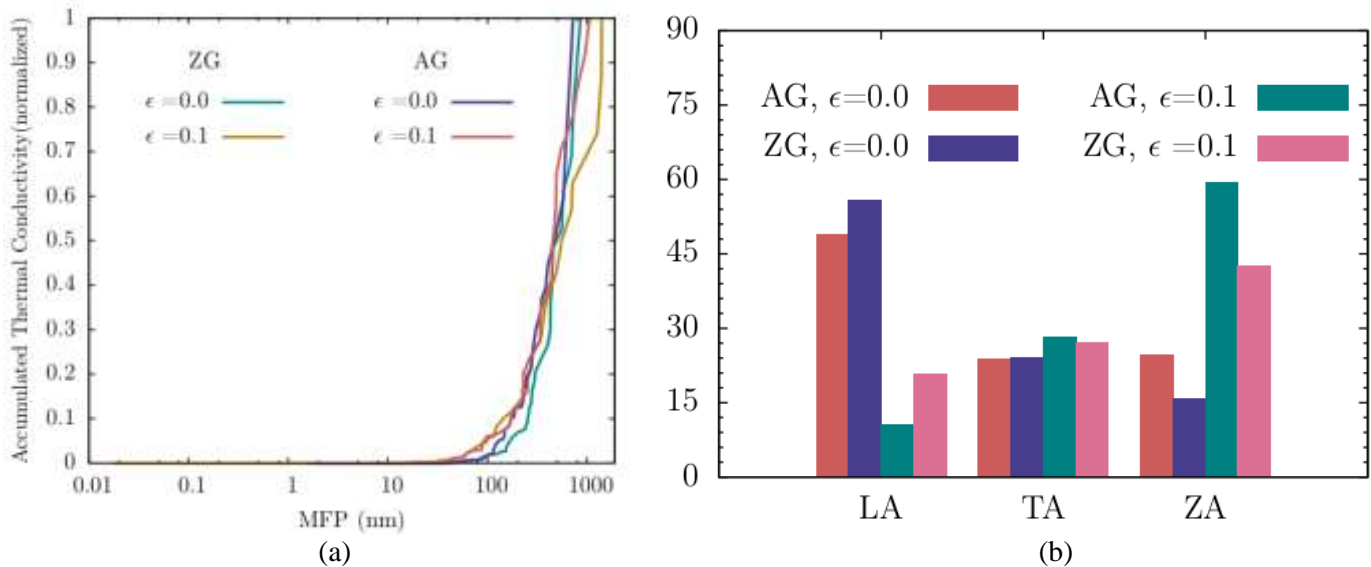


Fig. 6: (a) Accumulated thermal conductivity w.r.t MFP (b) Mode wise contribution to thermal conductivity.  $\square$  represents the value of tensile strain.

## 4. Conclusion

In the present study, the effect of strain on thermal conductivity of graphene is studied. It is observed that the strain reduces the thermal conductivity in ZG and AG and the highest reduction is found in AG. The AG have larger bond deformations and minor variation of the bond angles. This is the reason for higher stress along the AG and the greater reduction in thermal conductivity compared to ZG. DOS and SED are computed to study the effect of strain on phonon properties of graphene. It is observed that the high frequency modes undergo a red shift whereas a blue shift is observed in the out-of-plane phonon modes. The parabolic dispersion relations of the ZA modes near the BZ linearizes with strain, thus increasing their group velocities. However, softening of phonon modes is observed in the remaining acoustic modes. With strain, the phonon lifetimes of ZA modes increases whereas they reduce for LA and TA modes. This is due to reduction in the out-of-plane deformations of graphene under the strain. MFP calculations indicate that due to straining, MFP of phonon increases for the strained graphene compared to pristine graphene. The ZA mode is responsible for increase in the MFP of strained graphene. With strain, the contribution by the ZA modes to the total thermal conductivity increases drastically. These findings can be useful in design of graphene in nanoscale devices.

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