Thermal conductivity of defective graphene nanoribbons – A molecular dynamics study

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Summary The effect of dispersed Stone-Thrower-Wales defects on the thermal conductivity of both zigzag and and armchair graphene nanoribbons were determined using molecular dynamics with the AIREBO potential. Results showed the presence of defects could lead to large decreases in thermal conductivity of more than 50%, and the decrease is related to defect density. The defects also caused a significantly higher decrease in thermal conductivity in zigzag nanoribbons than in armchair nanoribbons.

INTRODUCTION

Graphene is a two-dimensional, single layer of carbon atoms arranged in a honeycomb lattice. Graphene nanoribbons (GNRs) are novel recently synthesized [1] and shown to display exceptional electronic and thermal properties. They have been found to have excellent thermal conductivity ranging from 2500 – 5300 W/(m.K). However, theoretical analyses showed that defects such as edges and point vacancies can affect the thermal conductivity of graphene nanoribbons to different extents. These defects could result from the synthesis process or through intentional application and manufacture to tailor the properties of graphene. Stone-Thrower-Wales (STW) defects are one such class of defects, and due to a lack of both theoretical and experimental evidence, it is not known how significantly STW defects could affect graphene's thermal conductivity. This study aims to fill this gap of knowledge.

SIMULATION METHODOLOGY

The MD simulation was run using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS), with the Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) potential [2]. The AIREBO potential extends the second generation Reactive Bond Order (REBO) potential, allowing for long-range atomic interactions and single bond torsional interactions. Many studies have successfully used the AIREBO potential to determine the thermal and mechanical properties of carbon-based systems.

Simulation of graphene nanoribbons

Both ZGNR and AGNR are simulated, where the samples consisted of 10-ZGNR and 19-ZGNR as determined by the number of dimer lines. Both samples are 2.1nm wide and 10.0nm long, and STW defects are introduced through a 90 degree rotation of two adjacent atoms about the midpoint of their bond.

Thermal conductivity simulation

Reverse Non-Equilibrium Molecular Dynamics (RNEMD) [3] is used to determine the thermal conductivities. In this method, heat flux is imposed to form a temperature gradient across the simulation cell. To do this, the simulation cells is divided into 50 slabs and designating the first slab as the cold slab and the middle slab as the hot slab. Hot and cold conditions are enforced through the periodic swapping of the energies of the atom with the highest kinetic energy (the "hotest" atom) in the cold slab with that of the atom of the lowest kinetic energy (the "coldest" atom) in the hot slab. After equilibrating, the temperature gradient is found through linear regression of the temperatures in each slab. Fourier's law is used to calculate the thermal conductivity, and the thickness of the sheet is assumed to be the carbon-carbon bond length of 0.142nm.

RESULTS

The variation of thermal conductivity with increasing numbers of STW defects in both ZGNR and AGNR were obtained at 300K and plotted in Fig. 1 below. It can be seen that both 19-AGNR and 10-ZGNR experienced decreasing thermal conductivities with increasing numbers of defects. Thermal conductivities are decreased sharply as number of rotated pairs of atoms increased from 2 to 6, and subsequently the decrease tapered off. This implies that the presence of STW defects caused significant phonon scattering. It can also be observed that the decrease was significantly larger in 10-ZGNR than in 19-AGNR, where the decrease was up to 54% in the former and 43% in the latter. The effect of STW defects on AGNR might have been less due the edge effects which already posed significant phonon scattering. All these

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results are in qualitative agreement with previous studies identifying decreased thermal conductivity due to other defects such as vacancies.

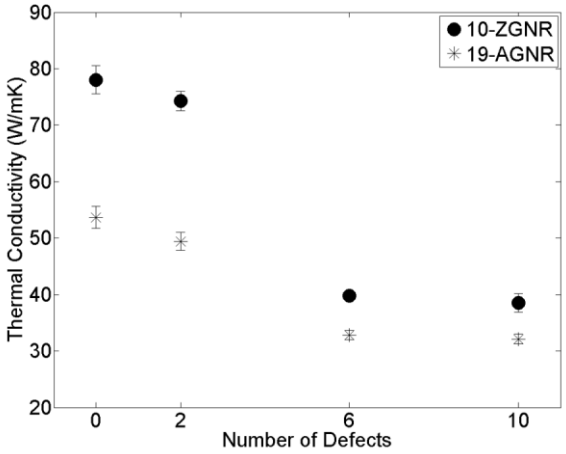

Figure 1. Variation of thermal conductivity of both 10-ZGNR and 19-AGNR at 300K with increasing number of defects.

Variation of thermal conductivity with increasing temperature was also investigated, where the temperature was increased from 100K to 600K. The results for both 10-ZGNR and 19-AGNR are plotted in Fig. 2 below.

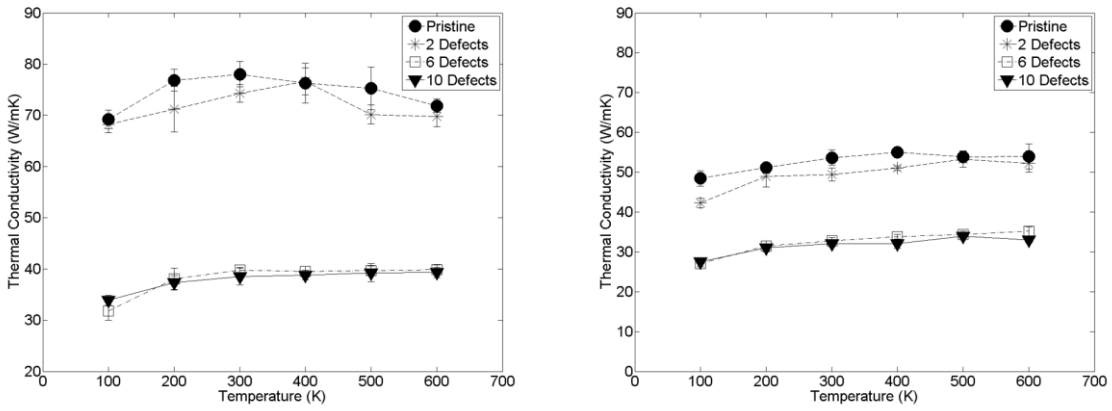

Figure 2. Dependence of thermal conductivity with temperature of 10-ZGNR (left) and 19-AGNR (right)

Variations in thermal conductivities decreased with increasing STW defects, as seen by the fact that pristine GNRs had the most fluctuations in thermal conductivities with changes in the temperature. Defective GNRs showed less variation, as shown by largely flat curves. This observation seems to imply the existence of an upper limit where further increasing STW defect densities will no longer significantly impact the thermal conductivity across the temperature range.

CONCLUSIONS

This study revealed that STW defects caused large decreases in thermal conductivity despite the invariance of total number of carbon atoms and sample. Conceivably, the direction of carbon-carbon bonds can be altered experimentally to tailor the thermal properties of GNRs. It was also established that variation of thermal conductivity with changes in temperature was less significant with larger numbers of STW defects. This implies that defective graphene could actually result in more stable thermal properties than pristine graphene in applications as thermal devices. Thermal conductivity of AGNR was always lower than that of ZGNR, regardless of number of defects. Intuitively, it may be clear that any changes to the crystalline structure of graphene will negatively impact its thermal conductivity. However, what is surprising here is the very large extent of the decrease in thermal conductivity, and that the decrease was also heavily dependent on chirality.

References

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