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Role of grain boundaries on the thermal properties of carbon nanotubes

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ABSTRACT

Carbon nanotubes (CNTs) do not exist in their pristine form naturally and they have certain types of defects. In comparison to all other types of defects, grain boundary (GB) defects may affect the thermal conductivity of CNTs significantly and the study of thermal properties of CNTs containing GB is essential. In this work, Fourier's law and Reverse Non-Equilibrium Molecular Dynamics (RNEMD) method have been applied on CNTs based on adaptive intermolecular reactive empirical bond order force field potential to calculate their thermal conductivities. The current results reveal the deviation of thermal conductivities of defective CNTs pristine ones.

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1. Introduction

Carbon is a unique element with ability to form various types of compounds and exist as allotropes in natural state such as graphite, bucky ball (C_{60}), carbon nanotubes (CNTs), Nano foams. This is due to its ability to form hybrid orbitals sp, sp^2 and sp^3. CNTs are known as rolled up graphene sheets discovered by Iijima experimentally with transmission electron microscopy [1]. CNTs have exceptional thermal, mechanical and electrical properties with many potential applications in thermal management, energy applications [2] and nanocomposite [3]. Experimental studies have shown very high values of thermal conductivity for CNTs in the range of few hundreds to thousand [4,5] which is contributed by phonons [6] rather than electrons. An experimental study by Eric et al. 2006 [7] has shown that the thermal conductivity of carbon nanotube with length 2.6 μm and diameter 1.7 nm is nearly 3500 W/mK. (See Table 1).

Molecular Dynamics (MD) method was first introduced by Alder and Wainwright in the late 1950′s to study the interactions of hard spheres [8]. Two types of methods to investigate the properties of thermal transports, equilibrium molecular dynamics (EMD) which is based on Green-Kubo relation and non-equilibrium molecular dynamics (NEMD) method based on Fourier's law. Both the methods have been used to determine the thermal conductivities of single-walled CNTs and multi-walled CNTs and the predicted values are in the range of few hundreds to thousand W/mK [9]. MD simulations were performed only for the perfect defect free CNTs known as pristine CNT. Grain boundaries (GBs) are inherent intrinsic structural impurities and are inevitable. It is caused by growth kinetics or substrate imperfections, resulting in different graphene domains with a variety of crystallographic orientations [10]. It is observed that the fracture site occurs along the grain boundary in the study of mechanical properties of graphene [11,12]. Thermal conductivity degradation of CNTs occur in presence of vacancy defects, functional groups on rings as studied in Padgett et al. [13] and Kothari et al. [5]. The study of influence of grain size orientations, and atomic structure on the mechanical properties of GBs containing CNTs using MD simulations and the failure behaviour studied [12].

The GBs will influence the heat flow and may act as a scattering site to phonons. However, the thermal properties of CNTs with GBs are not unravelled and studied. So, for the exploitation of thermal properties of CNTs, the study of the effect of GBs on thermal conductivity of CNTs is necessary for the applications in real life. This indeed provided us with the motivation for the current study.

2. Modelling

To create GBs in graphene and rolling them to form CNTs. For creating random grain distribution, Voronoi tessellation and Delaunay triangulation is performed [12,14,15]. Pentagons, heptagons, octagons and nonagons are created in different combina-

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Table 1
Shows the deviation between the values of thermal conductivities for polycrystalline CNTs with horizontal GB and pristine CNTs of same diameter.

Length (nm)	Thermal Conductivity values from [20] (W/mK)	Thermal Conductivity of pristine CNT (W/mK)	Thermal Conductivity of polycrystalline CNT (W/mK)
10	~85	80.286	43.983
25	~110	112.456	77.714
55	~140	146.228	123.038
80	~165	160.404	137.780

tions along a line to produce different types of the GBs [16]. In this work, bonds in CNT are manipulated to form pentagon-heptagon-heptagon-pentagon family (showed in the Fig. 1(a) and (b)). Quadrilaterals, octagons and nonagons are not considered in this work due to their higher formation energy and are rarely observed in experiments [17]. This is done six times along the circumference of CNT halfway through the length to obtain GBs in CNTs. After breaking and formation of bonds, these CNTs appears to be two pristine CNTs of same diameter fused together with the considered GB as shown in Fig. 1(a).

In this work, the thermal conductivity of pristine (10, 10) CNTs is found out for several lengths and for the CNTs with GBs of same length and same diameter approximately with grain boundary perpendicular to axis along the circumference at 300 K. Initial length of C–C bond is 1.42 Å. In MD simulations of this study, the adaptive inter-molecular reactive empirical bond order potential (AIREBO) is employed with a time step of 1 fs and periodic boundary conditions [5,18–20]. Velocity Verlet integration algorithm is used to calculate the velocities from the interatomic potentials based on AIREBO potential function. Thermal conductivity is found out using Reverse Non-Equilibrium Molecular Dynamics method in which a heat flux is applied along the axial direction of tube and the resulting temperature gradient is obtained. The schematic of the simulation system is showed in the Fig. 2. In Fig. 2, tube is divided into 10 layers along the axial direction. The 1st and 10th layer of length 5 nm approximately. In each sample a total of 800 atoms are considered in both the heat bath regions. The system's energy is minimized by adjusting positions of the atoms accordingly. The micro-canonical ensemble (NVE) is applied throughout the simulation to keep the system of energy constant after adjusting position of atoms, and viscosity is applied to the system for 2 ns which redistributes the energies uniformly and gives out the new positions of atoms according to AIREBO potential.

A temperature of 300 K is given to the system by re-scaling the velocities of atoms for 0.5 ns. After applying temperature, a heat flux of 0.7 eV/ps is applied every time-step for 50 ns by adding kinetic energy to the 1st layer and removing the same amount of kinetic energy from the 10th layer. The former step induces the heat flow in the axial direction which could perform a stable temperature gradient along the axial direction of the tube. The whole simulation was carried out for 52.5 ns in LAMMPS [21].

Temperatures of the hot and cold regions are calculated using the Boltzmann-Equipartition energy theorem

$$T = \frac{m\sum_{i=1}^{N_r} v_i^2}{3N_r k_B}, \quad k_B = \frac{-J}{\nabla T}$$

N_r is the total number of atoms in the hot/cold region. k_B is the Boltzmann constant. After the simulation process, statistically averaged temperature gradient is found out and the thermal conductivity of each sample can be known.

3. Results and discussion

The statistically temperature gradient of each sample is found out from simulations and Fourier's law after the temperatures of the system at each point converges to a certain value. Thickness of the ring is taken as 0.34 nm which is the inter-atomic layer distance in graphite. Diameter of every sample is same which is 1.36 ns. Fig. 3(a) shows the temperature as a function of position along the tube of CNT. The graph shows a sudden change of slope at the junctions between the heat bath regions with the layers 2–9.

The values of thermal conductivity of (10, 10) CNT for different lengths found out are consistent with the results obtained by Salaway et al. [22]. The thermal conductivity values of CNTs with GBs decreases as a result of phonon scattering at the GBs. From Fig. 3

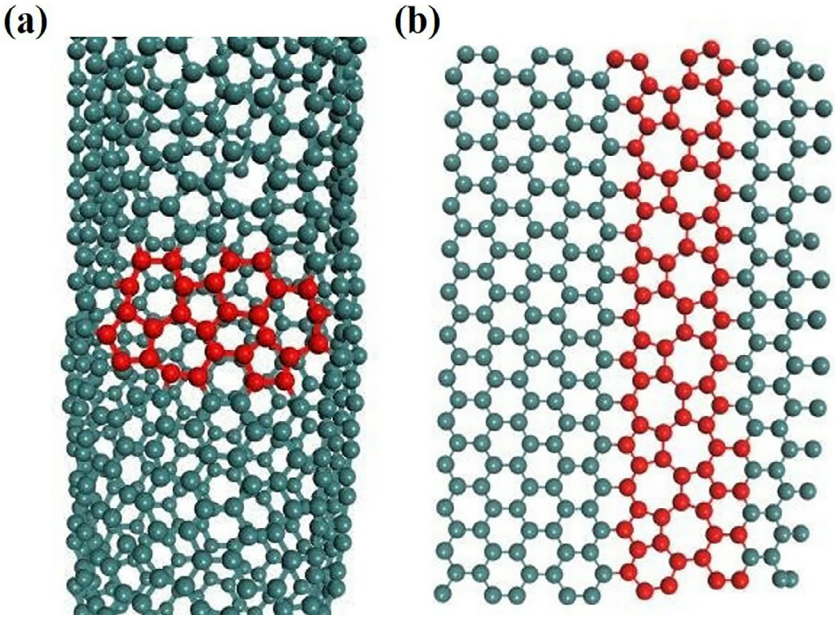

Fig. 1. (a) Shows the horizontal grain boundary along the circumference in a polycrystalline-CNT (b) Poly-Crystalline CNTs when cut along the line parallel to the axis of cylinder and spread in 2D-plane, poly-crystalline graphene with two GBs are obtained (The highlighted part is the GB which can be viewed in the coloured version of the image.)

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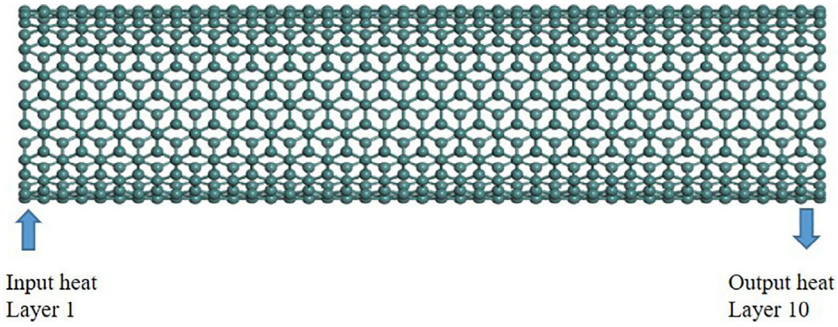

Fig. 2. Shows the schematics of the MD simulation applied.

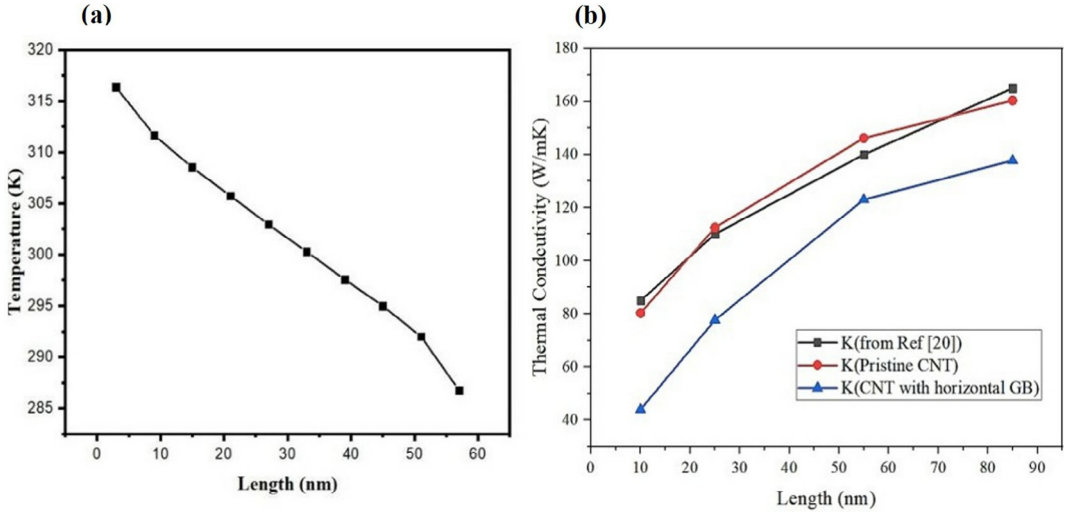

Fig. 3. (a) Shows the temperature vs length for a CNT of length 60 nm in simulations.; (b) shows the thermal conductivity variation of pristine and polycrystalline carbon nanotubes vs length with ref [20] for the considered grain boundaries.

(a), the sudden change in slope at 1st and last region is because of the heat baths. Fig. 3(b) shows that the Thermal Conductivity of CNTs is observed to increase with increasing length, which implies to the fact that more possible phonon states are available for kinetic energy transmission from hot end to the cold end. When the length of CNT approaches the phonon mean free path, phonons starts scattering which decreases the effectiveness of heat transfer but more and more phonon states will be available to contribute to thermal conductivity, as a result thermal conductivity increases with length and reaches a constant value.

4. Conclusion

In this work, thermal properties of pristine and CNTs with GBs studied using MD simulations by RNEMD method. The results show the degradation of thermal conductivity values in CNT due to the GB. The values of thermal conductivity for pristine CNT becomes steeper as the length is increased because of the transition from ballistic to diffusive regimes. The degradation of thermal conductivity values occurs because of the phonon scattering that occurs at the GB.

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