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THERMAL CONDUCTIVITY OF CARBON NANOTUBES WITH DEFECTS

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ABSTRACT

The high thermal conductivities of carbon nanotubes (CNTs) measured experimentally and predicted from theory suggest that they are good candidates for next-generation thermal management materials. The quantities of CNTs needed in applications preclude the use of pristine products. Limited work, however, has been done to study thermal transport in CNTs with defects. In this paper, the thermal conductivities of pristine CNTs and CNTs with various defect types (adatoms, single vacancies, double vacancies, and Stone-Wales) are systematically predicted using molecular dynamics simulation and a direct application of the Fourier law. We investigate the correlation between the thermal conductivity and defect energy.

INTRODUCTION

The high thermal conductivities of carbon nanotubes (CNTs) measured experimentally [1–5] and predicted from theory [6–12] suggest that they are good candidates for next-generation thermal management materials. Defects in CNTs can be generated during growth, purification, and device production [13]. Recent experiments demonstrated that electron or ion plasma can be used to tailor the structure and properties of CNTs by introducing defects with precision [14]. These naturally or artificially induced defects inevitably change the mechanical, electrical, chemical, and thermal properties of CNTs. A few molecular dynamics- and first principles-based studies have predicted that thermal conductivity decreases as the defect concentration increases [6, 15–18]. However, most of these predictions were for CNTs with length less than 100 nm. Phonon transport in such CNTs is partially ballistic and the thermal conductivities are thus length dependent. Moreover, the relative impact of various defect types on thermal transport remains unclear. Understanding how topological defects modify phonon transport in a CNT is an important step in predicting how CNT-based materials or devices will behave in heat transfer applications. In this paper, we systematically investigate the thermal conductivities of pristine CNT and CNTs with various defect types (adatoms, single vacancies, double vacancies, and Stone-Wales) using molecular dynamics simulation and a direct application of the Fourier law.

SIMULATION SETUP

Thermal conductivity, k, is defined by the Fourier Law:

$$q = -k\frac{\partial T}{\partial z}, \tag{1}$$

where $\partial T/\partial z$ is the temperature gradient along the direction of interest and q is the heat flux in that direction. We will predict the thermal conductivity of a pristine (8,8) CNT (diameter=1.10 nm) and (8,8) CNTs with various types of point defects: adatoms bonded inside the CNT (ADIN), adatoms bonded outside the CNT (ADOUT), single vacancies (SV), double vacancies (DV), and Stone-Wales (SW) at a concentration of 0.1%. The configurations of these defects on a graphene sheet are illustrated in Fig. 1. The length dependence of CNT thermal conductivity has

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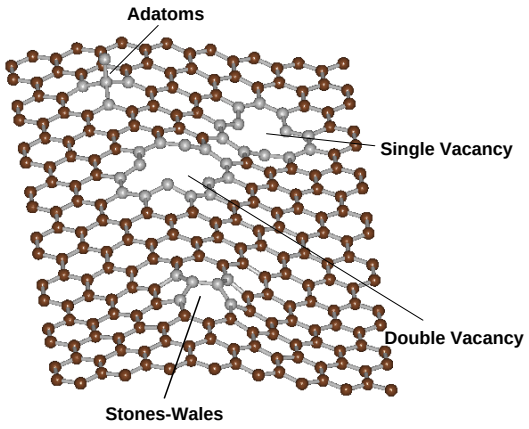

FIGURE 1. DEFECTS (ADATOMS, SINGLE VACANCY, DOUBLE VACANCY AND STONE-WALES) ON A GRAPHENE SHEET

been thoroughly discussed in the literature [19] and systematically studied by Thomas et al. [12]. Thomas et al. found that the transition of thermal conductivity from a length-dependent to a length-independent quantity occurs at 600 nm for the pristine (8,8) CNT modeled using the REBO potential [20]. This transition will occur at a shorter length for imperfect CNTs due to phonon scattering with defects [6,15,17]. Based on the results of Thomas et al. [12], in this study, we set the sample length, L, for all simulations to 600 nm, which corresponds to approximately 91000 atoms in the simulation box.

The simulation cell is shown in Fig. 2. Periodic boundary conditions are not imposed and one layer of carbon atoms at each end of the CNT is fixed to prevent atoms from sublimating. The initial pristine configuration is created using an equilibrium nearest-neighbor distance of 1.42 Å [21]. Along the CNT, defects are randomly distributed at a concentration of 0.1%. We define the cross-sectional area of the CNT to be $A_c = \pi db$, where b(=0.34 nm) is the van der Waals thickness of the CNT surface and d is the CNT diameter.

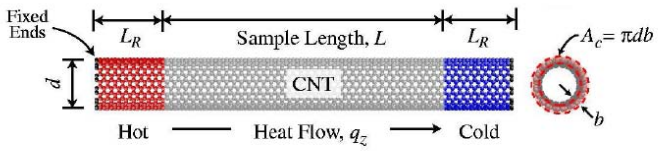

FIGURE 2. SIMULATION SET-UP TO PREDICT CNT THERMAL CONDUCTIVITY

Interactions between carbon atoms are modeled using the adaptive intermolecular reactive empirical bond-order (AIREBO) potential [22]. The AIREBO potential is derived from the-well known REBO potential [20] by modification of the bond-bond interactions and including an adaptive treatment of the non-bonded and dihedral-angle interactions. Both AIREBO and REBO are widely used in studies of chemical reactions and intermolecular interactions in condensed-phase hydrocarbon systems [20]. We use the parallel MD program LAMMPS [23] to perform the calculation. The equations of motion are integrated every 1 fs.

In a simulation, we start by relaxing the system in the canonical (NVT) ensemble (constant mass, volume, and temperature) at a temperature of 300 K for 50 ps, followed by micro-canonical (NVE) ensemble simulation (constant mass, volume, and energy). The thermal conductivity is predicted using the algorithm introduced by Jund et al. [24], which is a direct application of Eq.(1). At each time step, we introduce a heat flow by transferring a constant quantity of kinetic energy (0.1 eV for the pristine CNT and 0.05 eV for the defected CNTs) from carbon atoms in the cold reservoir to those in the hot reservoir. The reservoirs each have a length of 50 nm, which Thomas et al found sufficient to remove size effects [12]. The total energy in the simulation box is conserved and corresponds to an average temperature of 300 K. In response to the energy redistribution, however, thermal energy moves from the hot reservoir to the cold reservoir and a temperature gradient is established in the system. After turning on the heat flow, we run the simulation for 3-5 ns in order to reach steady state. The thermal conductivity is then obtained from a 5 ns data collection and averaging period. At steady state, the instantaneous thermal conductivity shows a 10% fluctuation around its average value.

RESULTS AND DISCUSSION

In Fig. 3, we present the temperature profile along the pristine CNT in the axial direction. We specify dT/dz by calculating the temperature of the carbon atoms within 60 sub-volumes (bin size=10 nm) along the sample during the data collection period. Our imposed heat flow of 0.05 eV for the defected CNTs introduces a temperature gradient that ranges from 27 K/μm (AD-OUT) to 38 K/μm (DV). The linear behavior of the temperature profile in the sample region indicates that the system is at steady state.

The variation in thermal conductivity with defect type is listed in Table 1. We predict the fully diffusive thermal conductivity of the pristine CNT to be 284 W/m-K, which is 28% lower than our previous prediction [12]. We believe that the difference comes from differences between the AIREBO and REBO potentials, specifically the contribution of non-bonded and dihedral angle interactions. The thermal conductivities follow $k_{ADOUT} \sim k_{ADIN} \sim k_{SW} > k_{SV} > k_{DV}$.

To understand the order of the thermal conductivities, we calculate the defect energy, ΔE^{def}, defined as:

$$\Delta E^{def} = E^{def} - E^{pristine}, \tag{2}$$

where E^{def} is the total energy of a CNT with one point defect and $E^{pristine}$ is the total energy of the pristine CNT with the same number of atoms as the defected CNT. The defect energy is calculated from an energy minimization algorithm provided in LAMMPS [23]. We use a CNT length of 24.6 nm with periodic boundary conditions and find that increasing this length has no detectable effect on the defect energies. In an armchair CNT, there are three possible orientations for the double vacancy or Stone-Wales defects. The E^{def} values in Table 1 correspond to an average over the orientations.

The calculated defect energies are listed in Table 1. We find that the defect energies follow $\Delta E^{ADOUT} \sim \Delta E^{ADIN} \sim \Delta E^{SW} < \Delta E^{SV} < \Delta E^{DV}$, which is consistent with the order of the thermal conductivities. This observation is consistent with the discussion in Che et al. [6] that compared to a single vacancy defect, the Stone-Wales defect is a milder form of point defect and does not change the basic form of the CNT structure. To further understand this trend, phonon-level information is required. The spectral energy density (SED) [9, 25] method could be used to obtain phonon relaxation times in pristine and defected CNTs, allowing for the frequency dependence of the phonon-defect scattering to be elucidated.

CONCLUSION

In this paper, the thermal conductivities of pristine CNTs and CNTs with various defect types (adatoms, single vacancies, double vacancies, and Stone-Wales) were systematically investigated using molecular dynamics simulation and a direct application of the Fourier law. From high to low, The thermal conductivity from high to low is in the order of $k_{ADOUT} \sim k_{ADIN} \sim k_{SW} > k_{SV} > k_{DV}$, which is the same order of their defects energies from low to high.

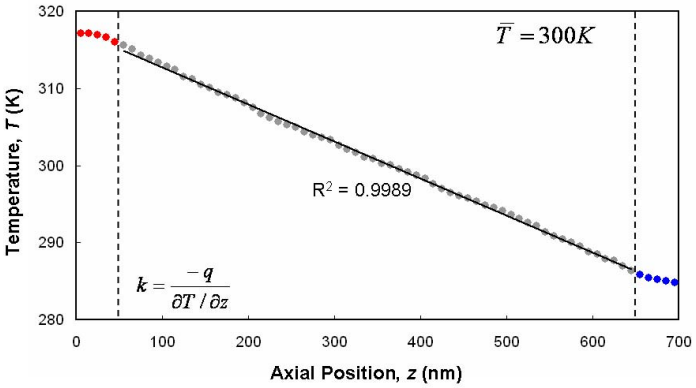

FIGURE 3. TEMPERATURE GRADIENT OBTAINED FROM MD SIMULATION OF A PRISTINE (8,8) CNT. THE DASHED LINES SEPARATE THE CNT SAMPLE AND RESERVOIRS. A LINEAR FIT TO THE TEMPERATURE PROFILE IS ALSO SHOWN.

TABLE 1. THERMAL CONDUCTIVITIES AND DEFECT ENERGIES FOR THE (8,8) CNT. THERMAL CONDUCTIVITY HAS THE UNIT OF W/m-K AND DEFECT ENERGY HAS THE UNIT OF eV. THE UNCERTAINTIES IN THE THERMAL CONDUCTIVITIES ARE 10%.

	PRISTINE	ADOUT	ADIN	SW	SV	DV
k (0%)	284	-	-	-	-	
k (0.1%)	-	238	212	203	172	153
ΔE^{def}	0.0	4.0	4.7	4.5	6.9	9.3

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