HEAT CONDUCTION OF SINGLE-WALLED CARBON NANOTUBE IN VARIOUS ENVIRONMENTS

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ABSTRACT

Some of our recent studies on the heat conduction of single-walled carbon nanotubes (SWNTs) using molecular dynamics (MD) simulations are reported. The length-dependence of pure SWNTs is investigated in a range of nanotube lengths up to 3.2μm. Non-equilibrium MD simulations were performed by minimizing the thermal boundary resistance between the thermally controlled layers and the rest of the nanotube, which was found to have a significant influence on the measured thermal conductivity. Furthermore, the heat conduction is investigated in more practical situations under the influence of inter-material interactions and intrinsic thermal resistances due to hetero-tube junctions.

Keywords: Carbon Nanotubes, Thermal Conductivity, Molecular Dynamics, Thermal Boundary Resistance.

INTRODUCTION

Single-walled carbon nanotubes (SWNTs) are expected to possess high thermal conductivity due to the quasi-one-dimensional structure and strong carbon bonds. While experimental attempts to characterize heat conduction of SWNT encounter technical difficulties, the classical molecular dynamics (MD) simulations hold an advantage as the heat conduction is phonon-dominated. MD simulations give us access to detail properties such as length dependence of thermal conductivity. Furthermore, by analyzing the spatio-temporal evolution of the lattice vibration, one can probe dynamics of individual phonon modes and their contribution to the overall heat conduction.

One of the early works on the length effect of SWNT heat conduction using non-equilibrium MD simulations by Maruyama [1, 2] showed the power-law length dependence of SWNT thermal conductivity up to sub-micrometers length. This has been discussed in relation with the one-dimensional heat conduction where theoretical models exhibit divergence of the thermal conductivity with respect to the tube-length. Among many of the works followed, Mingo and Broido [3] used linearized Boltzmann-Peierls phonon transport equations and showed that the appearance of the divergence can be related to the intensity of second order (or higher) 3-phonon scattering processes.

On computing the thermal conductivity with non-equilibrium molecular simulations, the method of temperature control plays a critical role. It was demonstrated by Maruyama [1, 2] that a straightforward application of random excitation layers at the ends of an SWNT gives rise to temperature drops i.e. thermal boundary resistances (TBRs) at the interface between the excited regimes and the bulk nanotube. In the current study, for the sake of better caparison with the theories, we compute the thermal conductivity of SWNTs with minimized TBR. Furthermore, the thermal conductivity was computed for a range of nanotube-length up to 3.2μm, considerably larger than that of Maruyama [1, 2].

While estimating thermal conductivity of an isolated pure SWNT holds significant importance, having practical situations in mind, the characterization of the heat conduction under the influence of surrounding materials would be essential. The surrounding materials are expected to influence the phonon transport along the SWNT which could result in attenuation of the heat conduction. As a simple representative case, in the current study, we take a system with interfacial interactions between SWNT and the confined ice nanotube. By measuring the effective thermal conductivity using non-equilibrium MD simulations, reduction ratio was computed for various interface areas.

Another potential cause of the heat-conduction attenuation is the intrinsic thermal boundary resistance. The heat conduction can be altered by local thermal resistance due to defects, hetero-junctions and isotope impurities. By using non-equilibrium molecular dynamics, we have previously demonstrated that the hetero-junction of different isotopes or chirality can cause the TBR even with combination of tubes with similar mass or diameter [4]. In an extensional study we simulated isotope superlattices i.e., periodically connected ^{12}C-SWNT and ^{13}C-SWNT, and investigated the dependence of thermal conductivity on the period thickness. In the present study, we probe the detail phonon dynamics of TBR at SWNT hetero-junctions with non-stationary MD simulations. The detail pictures of the phenomena can be probed by exciting local phonons and tracing their propagation [5]. This system of quasi-one-dimensional structure with absence of phonon scattering at wall boundary and with the junction roughness confined in an atomic monolayer should also serve as a fundamental model for intrinsic interfaces in general, where insight to the phonon transmission dynamics can be gained.

MOLECULAR DYNAMICS

SIMULATIONS

The carbon interactions were expressed by the Brenner potential function [6] with the simplified form [7], where the total potential energy of the system is modeled as,

$$E = \sum_i \sum_{j(i<j)} \left[V_R(r_{ij}) - B^*_{ij} V_A(r_{ij}) \right] \quad (1)$$

Here, $V_R(r)$ and $V_A(r)$ are repulsive and attractive force terms which take the Morse type form with a certain cut-off function. B^*_{ij} represents the effect of the bonding condition of the atoms. As for the potential parameters, we employ the set that was shown to reproduce the force constant better (table 2 in [6]). The velocity Verlet method was adopted to integrate the equation of motion with the time step of 0.5 fs. It has been shown that the formulation of potential function exhibits phonon dispersion with sufficient accuracy [1, 2].

Water molecules were expressed by SPC/E potential [8]. SPC/E potential is expressed as the superposition of Lennard-Jones function of oxygen-oxygen interaction and the electrostatic potential by charges on oxygen and hydrogen. The Coulombic interaction is the sum of 16 pairs of point charges. The potential function between water molecules and carbon atoms are represented by Lennard-Jones function. Here, we have ignored the quadropole interactions as they were found to have minute influence [9].

THERMAL CONDUCITIVTY MEASURMENTS

In the non-equilibrium MD simulations the thermal conductivity is calculated from the Fourier's law by measuring the quasi-steady heat flux and temperature gradient. Controlling temperature at both end-layers of a nanotube would typically give rise to temperature jumps at the boundaries between the controlled parts and the rest of the nanotube. In case of Maruyama using phantom techniques [1, 2], the temperature jumps at the interfaces account for about 50% of the total temperature difference applied at both ends. The temperature drop indicates the existence of a TBR. TBRs appear due to the mismatching of the lattice-vibrational spectra of phantom layers and the bulk nanotube. While variety of dynamics takes place in a TBR such as transmission and different scenarios of scattering, the one with the most impact to the thermal conductivity measurement would be the phonon reflection. Now, let us focus on the transport of excess phonons propagating along the temperature gradient approaching the lower temperature boundary (z=-125 nm in Fig. 1). Due to the phonon reflection at the boundary, the local temperature is enhanced and hence the temperature gradient is attenuated. This means that, to achieve certain temperature gradient, the required work at the boundary decreases i.e. the heat flux through the system increases. As a consequence, on computing the thermal conductivity through the Fourier's law, the thermal conductivity is overestimated compared with the case without TBRs. The phonon reflection also takes place on the hot boundary, however this phenomenon with fewer phonons is less influential to the overall temperature gradient.

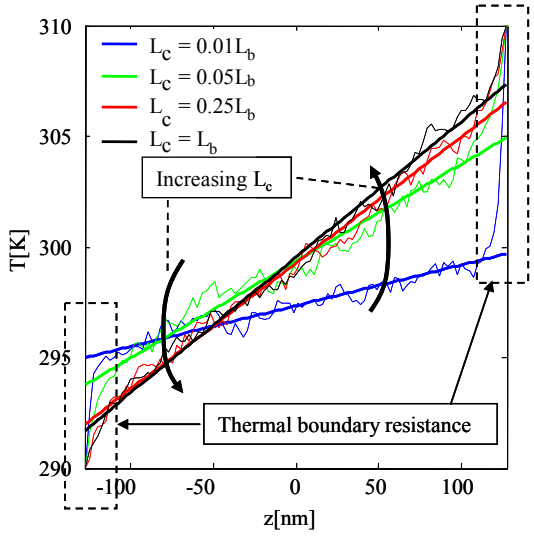

Figure 1: The influence of the thermostat length (L_c) on the thermal boundary resistance and the corresponding temperature gradient. L_b=L-2L_c is the length of the bulk SWNT.

To modify the boundary condition, we use standard Nose-Hoover thermostats [10, 11] and vary their relaxation time and length. Elongation of the thermostat length (L_c) gives rise to larger wavelength modes in the thermostat hence attenuates the discrepancy of phonon density of states with rest of the nanotube. The relaxation time (τ) gives the thermostat certain time to adjust the spectrum to that of the bulk nanotube. Figure 1 depicts the variation of the temperature profile with L_c, where the shorter L_c is, the larger the TBR is. The dependence typically saturates beyond certain value of L_c which, for τ=40 ps, is around L_c=0.25L_b where L_b is the bulk nanotube length, L_b=L-2L_c. By exploring 2d-parameter space, we take the case with minimum TBR, L_c= 0.5L_b and τ=40 ps.

As a consequence, by minimizing the effect of TBR between the temperature-controlled part and the bulk tube, we observe that the length-dependence does not follow a simple power-law for tubes shorter than 200 nm. This could be due to the contribution from diverse phonons on heat conduction in this regime. On the other hand, for (5,5)-SWNTs, in the length regime longer than 200nm, the thermal conductivity exhibits the power-law relations with the length, which suggests that the

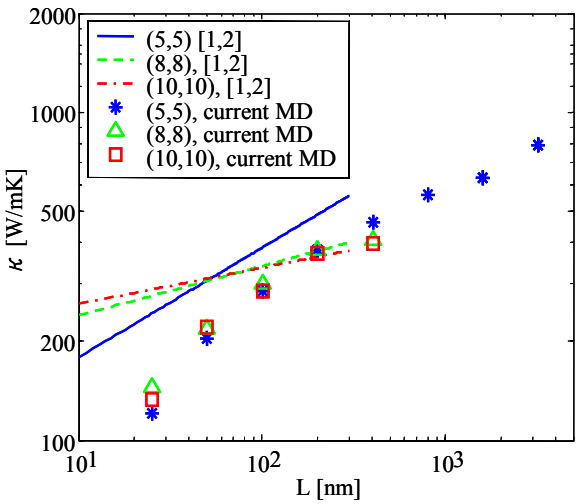

Figure 2: The length-dependence of the thermal conductivity of SWNTs with various diameters.

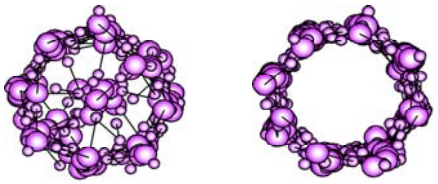

Figure 3: Structures of water confined in (10,10)-SWNTs

contribution on the thermal conductivity is limited to phonons with large ballistic lengths. In the length regime beyond the overall ballistic limit, the thermal conductivity is expected to saturate.

RESTRICTED HEAT CONDUCTION

As a representative case of reduction of axial heat conduction due to surrounding materials, we take an SWNT with a water cluster inside. Water confined in such a low dimensional geometry can exhibit anomalous phases, such as the formation of ice nanotubes whose polygonal dimensions are determined by the diameter of the surrounding nanotubes [6]. The existence of ice nanotube has been confirmed in experiments by means of X-ray diffraction analyses [7].

On freezing the water using an (10,10)-SWNT as a cast in MD simulations, depending of the simulation conditions such as cooling speed and number of water molecules N_w, different water structures are obtained. As shown in Fig. 3, one is the ice-nanotube [Fig. 3 (a)] and the other is the ice-nanotube with the hollow filled with water molecules lined along the axis [Fig. 3 (b)]. Computing the potential energies of water-water and water-carbon interactions, in a (10,10)-SWNT, ice-nanotube (a) was found to be more stable than the other (b).

In this work, we prepare a water cluster by isothermally cooling SWNT with N_w water molecules inside from T=300 K to T=200 K at relatively fast gradient so that the resulting ice takes structure (b) for all the tested cases. The water molecules are localized inside a (10,10)-SWNT which is sufficiently longer than the characteristic length of the water cluster.

The non-equilibrium MD simulations utilize the phantom control technique [1, 2] where the two ends of a 25 nm long (10,10)-SWNT were maintained at different temperatures, 190 K and 210 K. Once, the quasi-linear temperature profile was achieved, by measuring the temperature gradient and heat flux, the effective thermal conductivity κ can be computed through the Fourier's law. The data were typically sampled for about 3 ns.

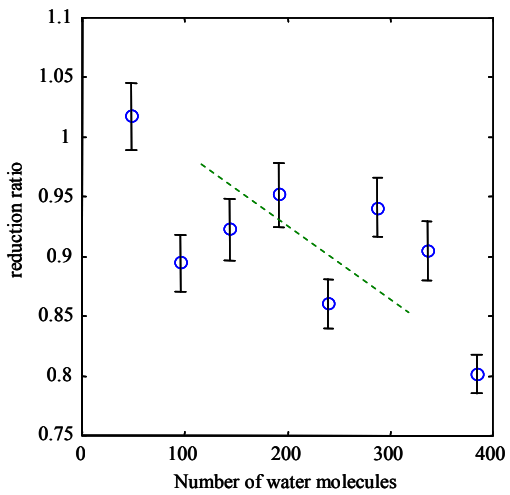

Figure 4: The reduction ratio (κ/κ_0) of an SWNT confining a cluster of N_w water molecules, where κ_0=814[W/mk] is the thermal conductivity for N_w=0.

In Fig. 4, we show the preliminary results on varying N_w up to 384. The figure exhibits attenuation of κ due to the inter-material interactions, which is enhanced with N_w. Apart from the general trend of the thermal conductivity reduction, the data are significantly scattered. This could be due to the Brownian motion of the water cluster, which becomes relatively small as temperature decreases but still non-trivial because of the small interfacial friction due to the hydrophobic surface of SWNTs. Larger samples would be necessary for better statistical values. Note that the error bars in Fig. 4 are computed based on the residual of the least square fit, and do not take the statistical errors into account.

INTRINSIC THERMAL BOUNDARY RESISTANCE

In order to gain microscopic understanding of the phonon dynamics at hetero-tube junctions, we adopt the method of probing the phonon-dependent transmission by wavepackets [5]. We present the simplest case where individual local phonon is excited in an SWNT at 0 K, i.e. phonon dynamics are at the linear limit. The mass ratio of the SWNTs is set at 2 [Fig. 5 (a)], though unrealistic, to highlight the TBR at the interface. Here, the wavepacket was generated on the side with lighter mass to travel rightwards. By recording the phonon propagation and the transmission through the junction, the energy transmission probability α can be computed.

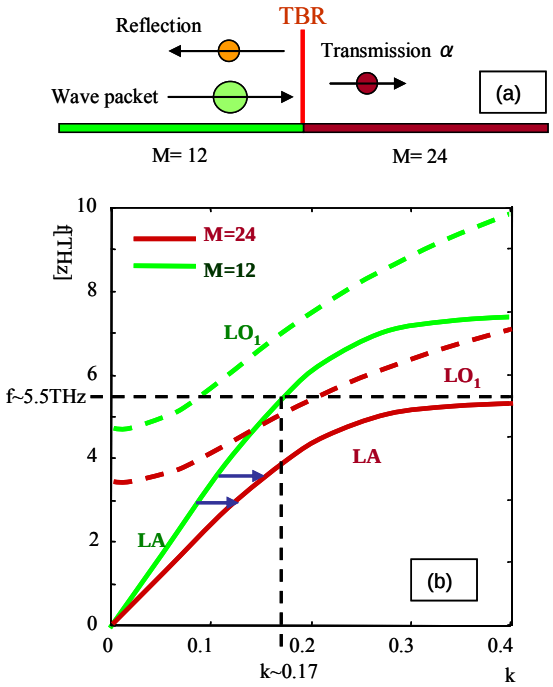

Figure 5: (a) A sketch of a generated wavepacket transmitted and reflected due to the presence of intrinsic thermal resistance. (b) Dispersion relations of ^{12}C-SWNT (M=12) and SWNT with double the mass (M=24).

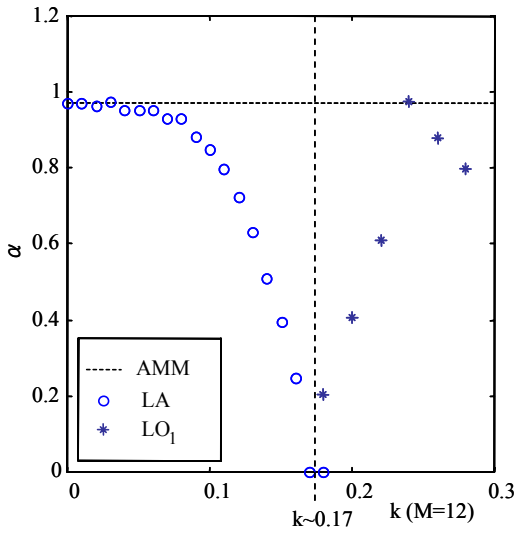

Figure 6: The energy transmission probability α of the key longitudinal phonon modes at a hetero-tube junction. The dashed line shows the value calculated by the acoustic miss-matching model.

In this report, we demonstrate the investigation of two symbolic longitudinal phonon branches, i.e. the longitudinal acoustic (LA) mode and longitudinal optical mode with unit circumferential wavenumber (LO_1). As seen in the dispersion relations [Fig. 5 (b)], these phonon branches with relatively large group velocities are expected to play significant roles in the overall heat conduction. The figure shows dispersion relations of SWNTs with two different masses, which are similar with frequency ratio equal to the square root of the mass ratio.

Fig. 6 shows α for LA and LO_1 for a range of low k_{in}, the wavenumber of incoming wavepacket. The result for LA agrees with a general trend of simple model systems where α decreases with increasing wavenumber (or frequency) [5]. Due to the energy conservation, phonons are generally transmitted maintaining the frequency hence the wavevector needs to be adjusted to satisfy the dispersion relation. The trace of phonon transmission is illustrated with arrows on the dispersion map in Fig. 5 (b). The figure depicts the critical wavenumber where the distance between the paired branches in the k-direction diverges. This explains the critical value of k_{in} where α becomes zero in Fig. 6.

As for the LO_1 branch, it was found that α takes a maximum value (~1) at k_{in}~0.24. The appearance of the maximum transmission probability in this branch can be thought in connection with the maximum of the phonon group velocity as seen in Fig. 5 (b). However, for complete understanding of the mechanism we would need further detailed investigation which will be reported elsewhere. Nevertheless, the current result indicates the contribution of diverse phonon branches on characterizing the intrinsic thermal resistance.

SUMMARIES

A few issues concerning the SWNT heat conduction were investigated. Firstly, we examined the thermal conductivity of a finite length pure SWNT. It was demonstrated that the thermal boundary resistances between the temperature controlled part and the rest of the tube has significant influence on the thermal conductivity especially for short nanotubes. By minimizing the thermal boundary resistances, the length-dependence of SWNT thermal conductivity is investigated in a range of nanotube length up to about 3.2 μm. Secondly, as a representative case of SWNTs in contact with other materials, an SWNT with ice inside was simulated. The result shows attenuation of thermal conductivity due to the restriction of phonon transport which is enhanced with increasing interaction surface. Finally, the microscopic mechanism of a thermal boundary resistance of a hetero-tube junction is investigated. In the linear limit with a frozen SWNT, the energy transmission probability is calculated for longitudinal modes and the physics is traced on the dispersion map.

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