

Temperature Dependence of the Thermal Conductivity of Single Wall Carbon Nanotubes

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(February 3, 2000)

Abstract

The thermal conductivity of several single wall carbon nanotubes (CNT) has been calculated over a temperature range of 100-500K using molecular dynamics simulations with Tersoff-Brenner potential for C-C interactions. In all cases, starting from similar values at 100K, thermal conductivities show a peaking behavior before falling off at higher temperatures. The peak position shifts to higher temperatures for nanotubes of larger diameter, and no significant dependence on the tube chirality is observed. It is shown that this phenomenon is due to onset of Umklapp scattering, which shifts to higher temperatures for nanotubes of larger diameter.

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The discovery of carbon nanotubes (CNT) by Iijima [1] and others [2,3], and subsequent observations of CNT's unique mechanical and electronic properties have initiated intensive research on these quasi-one dimensional structures. CNTs are related to both graphite and diamond, which are known for their high thermal conductivities. Consequently, CNTs or composites based on CNTs are also proposed to be attractive for heat transport management in ULSI (Ultra Large Scale Integration) chips and other miniature device components due to highly directional heat flow in CNTs. Not much has been studied about the thermal conductivities of carbon nanotubes. A single recent experiment has been reported on mats of compressed ropes of carbon nanotubes. [4] By assuming that both thermal and electrical conductivities follow the same rules for transport, values of thermal conductivity of CNTs ranging from 1750 to 5850 W/mK have been extrapolated from experimental measurement on mats of nanotube ropes. [4] The experimental results, however, are difficult to interpret due to possibly deformed nanotubes and pockets of trapped voids in the mat samples.

Using molecular dynamics (MD) simulations with Tersoff-Brenner bond order potential for C-C bonding interaction, [5] in this letter, we examine the temperature dependence of thermal conductivity of single-wall CNTs. A peaking behavior in the thermal conductivity, as a function of temperature, is observed. The peak position shifts to higher temperature for CNTs of larger diameter, while no significant dependence on tube chirality is seen. The results are explained in terms of the onset behavior of Umklapp scattering, which lowers the thermal conductivity at higher temperatures, and which is strongly dependent on the radius of the nanotube.

The MD simulations use Tersoff-Brenner bond-order potential [5] and solve Hamilton's classical equations of motion with a predictor-corrector algorithm with a fixed time step of 0.5 fs. The lengths of the single-wall nanotube (SWNT) and graphene sheet are chosen to be between 151-221 Å, with the number of atoms ranging from 1800 to 5400. Both armchair ((5,5), (8,8), (10,10), (12,12) and (15,15)) and zigzag (10,0) SWNTs are simulated. The aspect ratio (length/diameter) in all the simulations is chosen to be between 10 and 20, depending on the diameter of the nanotube, to maintain a reasonable heat flow between the

hot and cold regions of the nanotube. To simulate heat flow from a hot to a cold region, the nanotube is divided into N equal segments as shown in Fig.1a. The instantaneous temperature T_i in a segment i is determined from the kinetic energies of the atoms within the segment. The left end segment 1 is set at the temperature of a cold bath, and a hot bath is set at the middle segment at $N/2 + 1$ to allow the use of a periodic boundary condition along the axis of the nanotube. [6] The atoms in the boundary segments interact with the atoms in the rest of the tube, and at equilibrium a thermal flux is maintained via energy exchange between hot and cold regions. The heat flux in a thermally equilibrated segment is calculated as according to

$$J = \frac{\langle \frac{1}{2} \sum_{k=1}^{N_B} m_k (v_k'^2 - v_k^2) \rangle}{A \Delta t} \quad (1)$$

where A is the cross-sectional area of the SWNT taken to be an annular ring of thickness 3.4 Å, Δt is the time step taken to be 0.5 fs, and N_B is the number of atoms in the boundary layers. Figure 1b shows the final temperature distribution within a (10,10) SWNT at five different equilibrium temperatures. The thermal conductivity κ is determined from the procedure outlined in Ref. [6].

The thermal conductivities are calculated at temperatures from 100-500K. Fig. 2a shows a comparison of the thermal conductivity of a (10,10) nanotube with that of a single graphene layer having the same number of atoms with periodic boundary conditions along the surface of the layer. As expected, the temperature behavior and the magnitude of the thermal conductivity in the two cases is qualitatively and quantitatively similar. A detailed investigation for the in- and out-of-plane thermal conductivity of bulk graphite in comparison with that of a multi-wall nanotube is currently under investigation and will be published elsewhere. [7] The experimentally measured in-plane thermal conductivity of pyrolytic graphite in the temperature range 100-300K is reported to be between 500-3000 W/mK. [8,9] Most of the reported results for single-wall carbon nanotubes (SWNTs) , in this paper, are within the experimentally measured range of in-plane thermal conductivity values.

The dependence of the thermal conductivity on the radii of nanotubes of the same

chirality (armchair nanotubes) is shown in Fig. 2b for (5,5), (10,10) and (15,15) nanotubes. The temperature dependence of the thermal conductivities of (8,8) and (12,12) nanotubes were also calculated and follow the same behavior as described below. As shown in the figure, the values of the thermal conductivity at 100K for all armchair SWNTs are close to each other. As the temperature is increased, the thermal conductivity increases, by different rates for different tubes, up to a maximum value followed by a decrease to lower values at higher temperatures. Within the resolution, of the temperature dependence reported in this work, the peak values of the thermal conductivity of (5,5), (10,10), and (15,15) SWNT occur at 300K, 400K, and 450K respectively.

The dependence of thermal conductivity on the tube chirality, via a comparison of (5,5) and (10,0) nanotubes, is shown in Fig.2c. These CNTs have the same diameter, and so should not be affected by the strong diameter dependence as described above. The qualitative temperature dependence in the two cases is the same. Thermal conductivity of both peak at 300K. At lower temperatures, the thermal conductivity of the (5,5) nanotube drops faster than that of the (10,0) nanotube. This difference can be explained by the stretching strain behavior of sigma bonds as a graphene sheet is rolled up to make a nanotube. [10,11] In arm-chair nanotubes the sigma-bond along the circumference is strongly strained, while, in zigzag nanotube the sigma bond along the tube axis has the least strain. The excess strain along the circumference in armchair nanotube can limit the phonon mean free path due to scattering, and lower the thermal conductivity.

The diameter dependence of the peak positions of the armchair nanotubes in Fig.2b is explained next. The drop in the thermal conductivity beyond its peak value is generally attributed to the increased role of resistive phonon-phonon interactions known as Umklapp processes (U-processes). [4] These involve large wave vector phonons and lead to $1/T$ dependence in thermal conductivity at high temperatures. In a typical U-process, the randomization of heat flow direction [12] occurs and net heat flux along the axis is reduced. The cyclic boundary condition around a nanotube leads to the following condition,

$$n\lambda = \pi d \quad (2)$$

where n is an integer. λ is the wavelength, and d is the nanotube diameter. The maximum allowed wave length is obtained by setting $n=1$ which also determines the minimum allowed wave vector q_{min} as according to,

$$q_{min} = \frac{2\pi}{\lambda_{max}} = \frac{2}{d} \quad (3)$$

Therefore, it follows that the minimum wave vectors vary inversely with the tube diameter. In other words, the minimum wave vectors in small diameter SWNTs are larger than those in large diameter SWNTs and closer to the reciprocal lattice vector needed for a U-process. Consequently, at any given temperature, the probability of U-processes are higher in SWNT with smaller diameter as compared to that in tubes with larger diameters. Since, the U-processes cause a drop in thermal conductivity from their peak value, these peaks will occur at lower temperatures in small diameter nanotubes. This is consistent with the results in Fig. 2b where thermal conductivity peaks shift to higher temperatures for CNTs of larger diameter and there is no dependence on the tube chirality.

The above features in the thermal conductivity, explained due to the onset of U-processes, also indicate a dominant role of radial phonons as a mechanism for heat transport in SWNTs. The presence of strong radial phonons in both zigzag and armchair SWNTs have been described earlier by static lattice dynamics calculations of Charlier et. al., [13] and Rao et. al. have developed an experimentally parametrized (proportional to $1/D$) dependence of radial phonon frequency on nanotube diameters. [14] Their experimental results indicate that the frequency of radial phonons shift to lower values for CNTs of larger diameters. This allows the the thermal conductivity peaks to occur at higher temperatures for large diameter nanotubes before being suppressed by phonon-phonon scattering or U-processes.

In summary, we have investigated the temperature dependence of thermal conductivity of SWNTs near room temperature ($100 - 500K$). The electronic contribution to the thermal conductivity in graphene sheets and carbon nanotubes, at these temperatures, is expected to be negligible due to low density of free charge carriers. [4,15] The thermal conduction at

these temperatures is found to be strongly dependent on the diameter of the nanotube with no dependence on the tube chirality. The thermal conductivity for all nanotubes exhibit a peaking behavior as a function of temperature, and the peak position shifts to higher temperatures for larger diameter SWNTs. This behavior is attributed to a combination of factors; the onset behavior of Umklapp scattering, and that the heat is carried mainly through radial phonons. Both of these factors have strong tube radius dependence and weak or no chirality dependence.

Our simulation results, and the above discussion, demonstrate the possibility of developing specific materials for thermal transport management that could be optimized for applications in a particular temperature range. For example, (5,5) nanotubes provides the highest thermal conductivity at room temperature, as compared to both (10,10) and (15,15) nanotubes. A weak dependence of the temperature behavior of the CNT thermal conductivity on their chiralities, for tubes of same diameter, is probably desirable from applications' perspective, since at present it is not possible to produce nanotubes of a given chirality in a controlled manner.

A precise knowledge of CNT thermal conductivity will be useful in designing efficient thermal transport management materials and devices specially suited for micro- and nano-scale applications. Our work is a first step in that direction.

I. ACKNOWLEDGMENT

We thank Dr. T.R. Govindan, and Dr. T. Yamada of NASA Ames, and Dr. A. M. Rao of University of Kentucky for useful discussions during the development of this work. Use of computing facilities at NAS division of NASA Ames Research Center, and the Solid State Device Animation Laboratory funded by NSF's Division of Undergraduate Education through grant DUE # 9651416 is appreciated. This work was done while (MAO) was on sabbatical leave at NASA Ames, and part of this work (DS) is supported by Veridian-MRJ under NASA contract NAS2-14303.

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FIGURES

FIG. 1. (a) Simulation system of a nanotube of given length is divided in to N equal segments with a cold bath simulated at the segment 1 and a hot bath at the segment $N/2+1$. (b) Temperature profile along a (10,10) nanotube at (starting from bottom) 100-500K equilibrium temperatures.

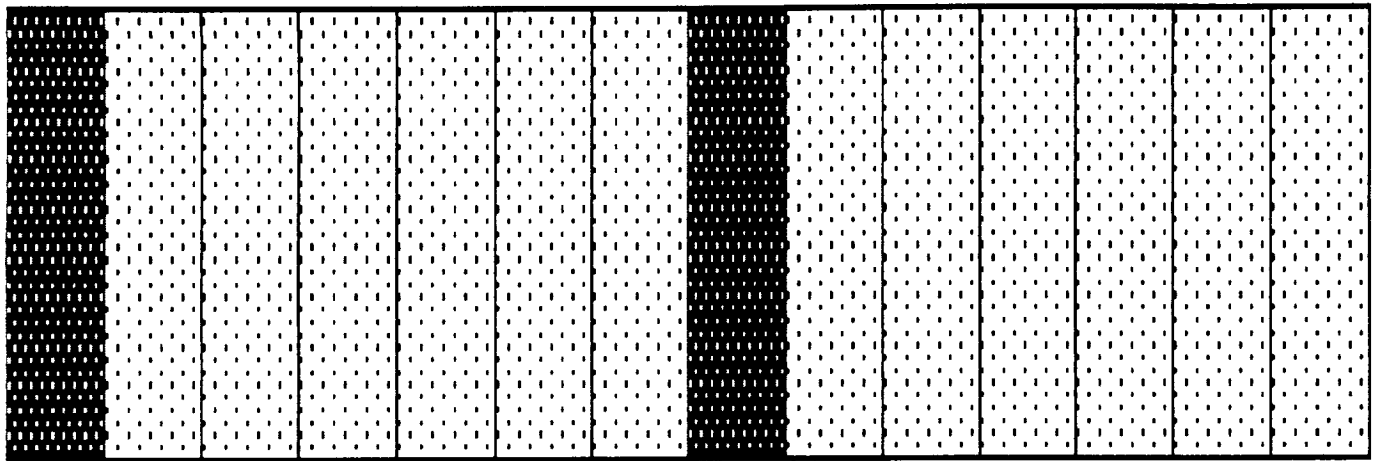
FIG. 2. (a) Thermal conductivity of a (10,10) nanotube (solid circle) as compared with that of a single graphene layer (solid square) containing the same number of atoms. (b) Same as (a) for (5,5) - solid circle; (10,10) - solid square; and (15,15) - solid triangle, nanotubes of different diameters. (c) Same as (b) but for (5,5) - solid circle, and (10,0) - open triangles, nanotubes.

(a)

1

$N/2+1$

N



(b)

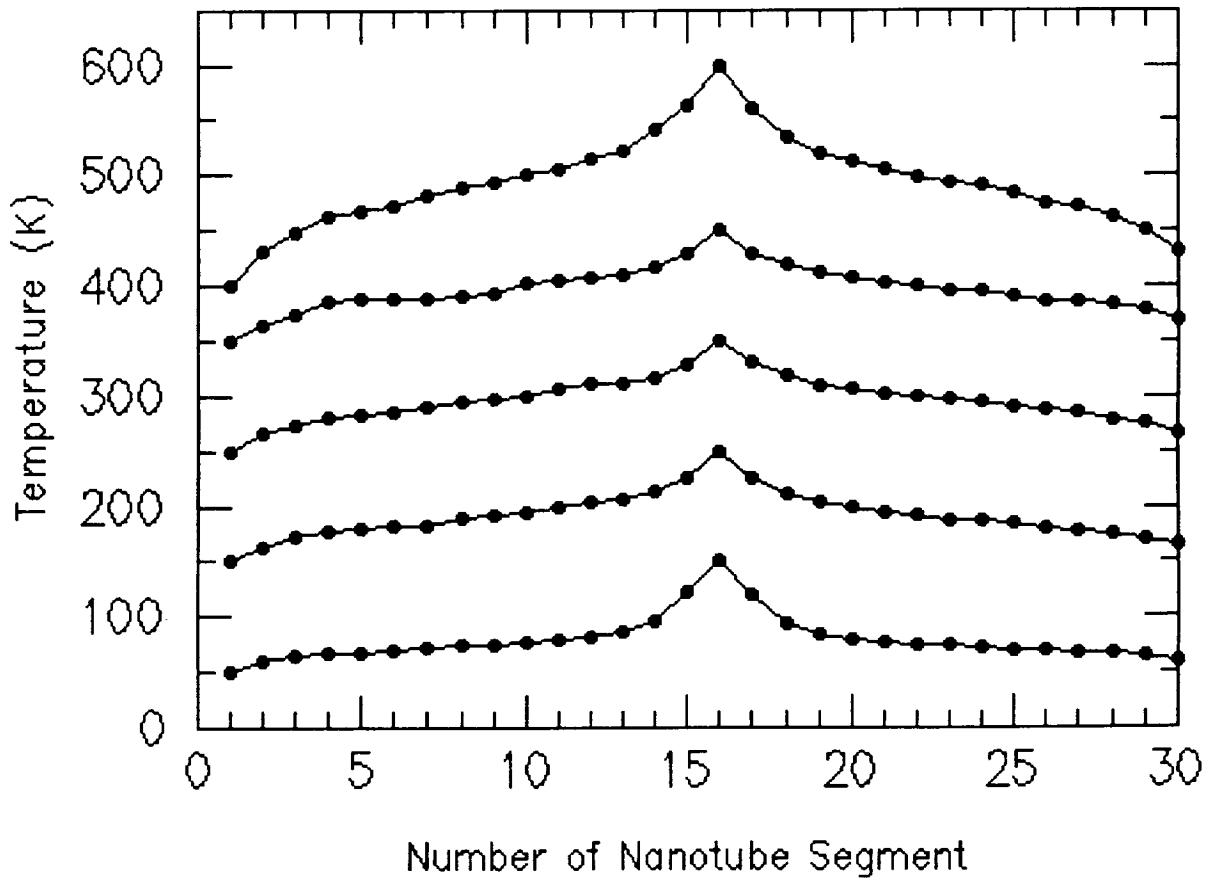


Figure 1

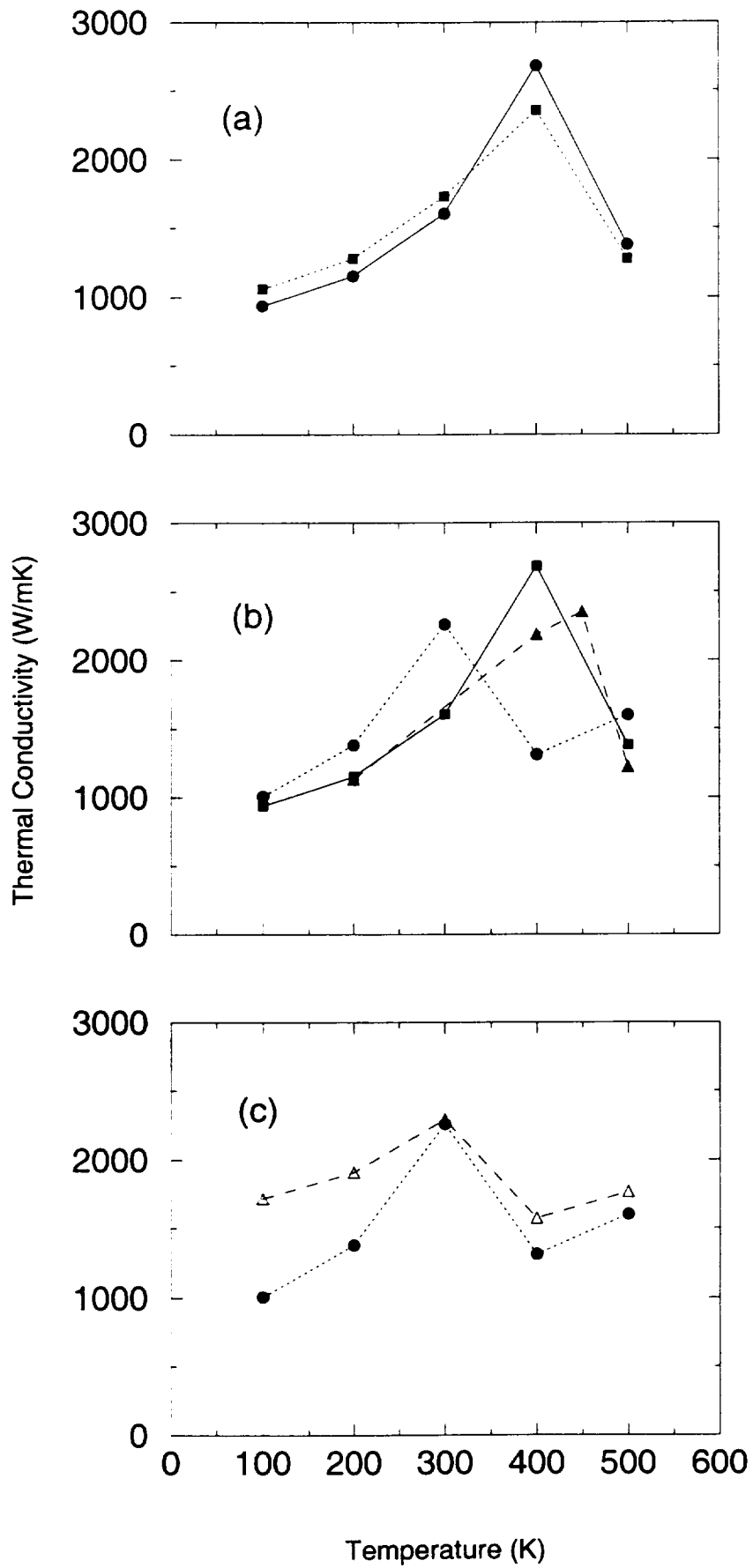


Figure 2