Thermal conductivity of carbon nanotube peapods

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Thermal conductivity of a (10,10) carbon nanotube filled with C_{60} fullerenes (or a peapod) is computed using direct molecular-dynamics simulations with the Tersoff-Brenner potential for C-C bonding interactions and the van der Waals potential for nonbonding interactions. The temperature-dependent thermal conductivity of the peapod, while showing qualitatively similar behavior to that of an unfilled carbon nanotube, is found to be higher than the nanotube at all temperatures. This is in agreement with recent experimental observations. The increase in thermal conductivity in the peapod is explained through (a) an energy transfer between fullerenes and nanotube due to low-frequency radial vibration coupling between fullerenes and nanotube, and (b) energy transfer along the peapod axis due to fullerene-fullerene collisions.

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The discovery of carbon fullerenes and nanotubes (CNT’s) (Ref. 2) coupled with successful development of techniques for their production in bulk quantities has attracted attention to many of the applications of these materials. The carbon nanotubes have been found to possess exceptionally good and unique electronic, thermal, and mechanical characteristics. CNT’s can be either metallic or semiconducting and exhibit thermal conductivity comparable to that of diamond or in-plane graphite layers. From a structural materials perspective, these are ultralight weight and very strong/stiff nanoscale fibers that can be proposed as reinforcing material in multifunctional composite materials.

A nanotube of sufficiently large diameter can be filled with spherical C_{60} fullerene molecules to build up a new hybrid structure referred to as a “peapod,” with spherical fullerenes representing peas and the CNT representing a pod as shown in Fig. 1. It is expected that the electrical and thermal characteristics of this new material would be different from those of an equivalent unfilled carbon nanotube, and several experimental and theoretical studies have confirmed this hypothesis. Using density-functional-theory (DFT) calculations based on the local-spin-density approximation (LSDA), Okada et al. have shown that the C_{60} encapsulation process is exothermic for the (10,10) nanotube, with 6.4 Å as the minimum radius for the process to be favorable. Furthermore, they found that the system is metallic with multicarriers distributed along the nanotube or on the fullerene chain. Vavro et al. measured the electrical resistivity and thermal conductivity of C_{60}-filled single-wall carbon nanotubes (SWCN) with an average tube diameter of around 1.3 nm, between 1.5 and 300 K, and compared the values with those of an unfilled equivalent CNT. According to their experiments, the presence of fullerenes reduces the electrical resistivity while the thermal conductivity is enhanced. They suggest that the C_{60} chains provide additional conduction paths for charge carriers and the increase in the thermal conductivity is perhaps due to the combined thermal and mass transport, although the chances of mass transport (via fullerenes) in a completely filled peapod are highly improbable.

The objective of the present work is to simulate the thermal conductivity of a (10,10) CNT filled with C_{60} molecules and investigate the mechanism for any observed increase in the thermal conductivity of the peapod over the corresponding nanotube in a regime where increased mass transport and charge-carrier-based effects are not feasible. This is achieved through molecular-dynamics (MD) simulations of the thermal conductivity of a peapod with C-C bonding interactions determined by the well-established Tersoff-Brenner potential and C-C nonbonding interactions via Lennard-Jones (LJ) -type van der Waals potentials. The MD simulations of the thermal conductivity via a direct approach using the same potentials in the temperature range of 100–500 K have been recently performed for a (10,10) SWCN (Refs. 6 and 7) and give a peak value of about 3000 W/mK at room temperature. Another attempt at computing thermal conductivity of single-wall nanotubes using molecular-dynamics simulations has resulted in peak values as high as 40 000 W/mK at 100 K, which is an order of magnitude larger than any simulated or experimentally observed value thus far. This may be due to the use of a very small nanotube in the simulations and the extrapolation tech-
FIG. 1. Total-energy optimized geometries of a bare (10,10) nanotube and the same (10,10) nanotube encapsulating a C₆₀ chain.

nique used for the reported results. The room-temperature heat transport is primarily driven by acoustic phonons, and mechanical and phonon behavior of SWCN (Refs. 17 and 18) have also been analyzed recently using the many-body atomistic Tersoff-Brenner potential.

The simulations involved solving Hamilton’s equations of motion with a predictor-corrector algorithm and a time step of 5 × 10⁻⁴ ps. Interactions of two different natures are present in the system, namely covalent and C-C nonbonding. This necessitates the use of two potentials. The Tersoff-Brenner potential accounts for the intramolecular forces and the van der Waals potential accounts for the nonbonded intermolecular forces. The total length of the peapod used is 196.8 Å and periodic boundary conditions are set along the nanotube axis.

To obtain the thermal conductivity in this system, we use the direct method. This technique is analogous to the way thermal conductivity is experimentally measured. A thermal gradient is applied on the system and, as a consequence, a heat flux establishes itself along the length of the tube and Fourier’s law combines both quantities to get the thermal conductivity.

\[ \mathbf{J} = -K \nabla T. \]  

The peapod is divided into segments of equal length and number of atoms. Slabs are chosen with a length of four (10,10) CNT unit cells, so that each segment contains one fullerene. It is assumed that the instantaneous temperature is a constant for each one of these slabs. To set up the gradient, in the initially uniform temperature peapod, the first slab is heated and the N/2 + 1 slab is cooled. As the amount of heat applied and removed from the system is known exactly, the thermal flux defined as the energy transferred in a given time through a surface of a given area perpendicular to the flow direction can be accurately computed through

\[ J = \frac{1}{2} \sum_{k=1}^{N_B} m_k (v'_k - v_k^2) \]

where \( N_B \) is the number of atoms in the boundary layers, \( \Delta t \) is the time step used during the simulations, and \( v_k \) and \( v'_k \) are the velocities of the atoms before and after scaling, respectively, in the hot and cold slab regions. The factor 2 in the denominator arises from the periodicity in the system (the energy can flow from the hot slab to the cold slab in two directions). The area \( A \) was considered to be of the circular cross section with radius equal to the radius of the (10,10) CNT plus half the van der Waals radius (interlayer distance in graphite \( \sim 3.4 \) Å). This corresponds to the area of cross section of a completely filled (10,10) nanotube with spherical fullerene molecules.

One main concern when using the direct method to compute the thermal conductivity is the finite-size effect, which appears when the length of the simulation cell is shorter than the phonon mean-free path. Under these conditions, the thermal conductivity is limited by the size of the system as a consequence of unreal phonon scattering at the interfaces of the heat source and sink. To study this effect, Andersen et al. have performed calculations of thermal conductivity for a much longer tube using the same method as the one described here, and they have found that (a) for a given thermal gradient (2 K/nm) the thermal conductivity of a (10,10) CNT converges to a constant value between 40 and 80 nm, and (b) thermal conductivity increases nonlinearly with decreasing thermal gradient (\( \nabla T \)) to even lower values. Based on these results, together with the fact that the main goal of the present work is not to give absolute values but to investigate the change in the thermal conductivity of a peapod with respect to that of an empty CNT, a 40 K temperature gradient for a CNT of 20 nm length is a reasonable value to use as a reference to make the comparison.

The thermal conductivity is calculated at temperatures ranging from 100 to 500 K. Figure 2 shows the final stationary-state temperature gradient profile along the tube axis at five different temperatures. The five curves display a strong nonlinear step-like temperature behavior in the vicinity of the hot and cold slabs. This is a well-known scenario, and it is corrected by not including the data points corresponding to the steplike region in the overall analysis. The thermal gradient, thus, was computed in the relatively straight steady-state region excluding the slabs adjacent to the thermostats. Another feature worth noting is that fluctua-
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FIG. 3. Temperature dependence of peapod thermal conductivity as compared with that of an empty CNT.

FIG. 4. Distribution of heat between the CNT and the C\textsubscript{60} chain at a temperature of 300 K.

...tions in the temperature are much larger than those found for an empty nanotube in a similar study by Osman \textit{et al.}\textsuperscript{7} This is because fullerenes are weakly bonded through van der Waals forces and are able to move (oscillate) about their equilibrium positions and against the wall of the nanotube with relative ease. The instantaneous kinetic temperature of fullerenes and the whole system, therefore, shows fairly large fluctuations in each segment. As will be shown below, this also is partially responsible for the observed and computed larger thermal conductivity of peapods as compared to the equivalent bare nanotube.

In Fig. 3, we show the temperature dependence of the peapod thermal conductivity and compare it with that of a bare or pristine unfilled (10,10) CNT, similar to that reported by Osman \textit{et al.}\textsuperscript{7} The qualitative behavior is the same in these two cases, both exhibiting a peak at 400 K. In the full temperature range, however, quantitatively the thermal conductivity of the peapod is more than two times larger than that of the equivalent unfilled (10,10) nanotube. This is in agreement with experimental results by Vavro \textit{et al.}\textsuperscript{11,12} They measured the thermal conductivity on buckypapers of tubes with a tube diameter of around 1.35 nm [the diameter of a (10,10) SWCN] from 1.5 to 300 K. The same temperature dependence as that of an empty nanotube was observed in this range, but with an overall increase of \approx20\% in the thermal conductivity of the peapod as compared with an equivalent nanotube. The observed experimental increase, therefore, is smaller than the increase obtained in our simulations. Vavro \textit{et al.}\textsuperscript{12} attributed their experimental finding to a mass transport due to physical motion of fullerene molecules inside the carbon nanotube. In the following, we show that this may partially be attributed to the fullerene-fullerene interactions along the length of the nanotube and partially to a phonon-based mechanism for fullerene-nanotube interactions and heat transfer. No mass transfer occurs in a completely filled peapod.

To clarify and explore the detailed mechanisms of heat transfer in the peapod, we analyzed the heat distribution (or temperature profiles), atomic vibrational amplitudes, and modes in the peapod as well as individual contributions due to C\textsubscript{60} fullerenes and the nanotube. Figure 4 shows the temperature profile along the peapod and the individual contributions due to fullerenes and the nanotube for the simulation at 300 K. As the figure shows, most of the applied heat is absorbed by the fullerenes with large temperature gradient and fluctuations in the data. The temperature gradient across the equivalent regions of the nanotube, on the other hand, remains almost flat and fluctuationless. For the same temperature difference across the peapod, the heat flux remains almost the same, but there is a dramatic reduction in the overall thermal gradient. This leads to an enhancement of the thermal conductivity of the peapod over the bare or pristine nanotube.

There are two related effects that are responsible for the above behavior in the overall peapod as compared to the individual contributions due to C\textsubscript{60} fullerenes or the nanotube. A few recent studies have identified the excitation of low-frequency (few THz) radial phonon modes as the main mechanism of heat transport in carbon nanotubes,\textsuperscript{7,18} whereas the tangential and longitudinal phonon modes typically occupy a wider spectrum from a few THz to 55 THz (limited by the simulation cell size used in typical simulations). The peak in the higher end in this frequency region (between 35 and 55 THz) typically corresponds to optical stretching modes, whereas at the lower end (1–15 THz) there is a region representing acoustic radial or out-of-plane breathing phonon modes.\textsuperscript{18} The heat transport in a pristine or bare nanotube has been shown to be mainly through the excitation of low-frequency radial phonon modes and the coupling of the radial mode with the longitudinal mode in the low-frequency region.\textsuperscript{7}

In Fig. 5, we show the computed total, radial, azimuthal, and axial spectra of the peapod at 300 K in comparison with the contributions from the C\textsubscript{60} fullerenes and the carbon nanotube part in the frequency range of 1–55 THz. This was computed by taking Fourier transform of the velocity autocorrelation function on the data at 300 K after an equilibrium was achieved. The velocity autocorrelation functions were calculated with a simulation run of over 25 ps after the initial equilibration period, and storing the velocity information at each 10th time step. The velocities were converted to a cylindrical coordinate system along the tube axis, and the radial (along the tube radius), azimuthal (tangential to the tube sur-
earlier, except for a slight enhancement of the radial modes similar to the spectra for the bare or pristine CNT published spectra of the CNT contribution is found to be qualitatively respect to that of a bare CNT peptide in the top panel show an overall enhancement with combined spectra of the CNT and fullerene contributions in a face), and axial (along the tube axis) components were used for corresponding velocity autocorrelation functions. The combined spectra of the CNT and fullerene contributions in a peapod in the top panel show an overall enhancement with respect to that of a bare CNT (not shown here but reported earlier) and the CNT contribution shown in Fig. 5. The spectra of the CNT contribution is found to be qualitatively similar to the spectra for the bare or pristine CNT published earlier, except for a slight enhancement of the radial modes at low frequencies (in the radial breathing mode region between 2 and 8 THz) and a slight attenuation in the medium-frequency region (between 10 and 30 THz). These two effects could be interpreted as due to a coupling between the radial phonon modes of the CNT and those of the fullerene chain. The observed enhancement of the radial modes in the low-frequency region means a constructive coupling, and the observed attenuation in the medium-frequency region may mean a destructive coupling. The higher-frequency region (greater than 30 THz), as shown in the purely radial component panel, is not affected at all. The axial and azimuthal phonon modes in the medium- to high-frequency region, in the bottom two panels, do not show any significant differences between the contribution of the CNT and fullerenes to the overall spectra. An examination of fullerene phonon modes in all three panels shows that the fullerene chain introduces modes along all three component directions. This was not intuitively obvious because we expected fullerene modes to be effective mostly in the radial direction. A further analysis allowed us to identify a low-frequency region (<4 THz) with intermolecular modes that arise from the movement of the fullerenes’ center of mass, and a higher-frequency region (between 6 and 7 and 50 THz) that corresponds to fullerene intramolecular modes. The radial, azimuthal, and axial intramolecular modes in an isolated fullerene (not shown here) are indistinguishable due to molecularity symmetry, and show different features as compared to when fullerenes are encapsulated in the CNT in a peapod. In particular, the main point is that the higher-frequency radial modes (between 30 and 50 THz) seem to suffer an attenuation, which is not observed in the azimuthal and axial modes. This reinforces our hypothesis of a coupling between fullerene and CNT modes in the radial direction, and the combined spectra of the CNT and fullerene contributions in a peapod, therefore, shows an overall enhancement with respect to that of an empty CNT. The radial coupling is, therefore, mainly responsible for the efficient heat-transfer mechanism between the fullerenes and CNT in the peapod.

The above explanation can be further validated by computing the mean-square vibrational amplitudes of atomic motions defined as

\[
\langle \mu_\alpha^2 \rangle = \frac{1}{2N} \sum_{i=1}^{N} \left[ \langle \mathbf{r}_{i\alpha}^2 \rangle - \langle \mathbf{r}_{i\alpha} \rangle^2 \right]
\]

along the radial, azimuthal, and axial directions in a cylindrical coordinate system (\( \alpha = (\rho, \theta, z) \)); the angular brackets denote an average over time. The mean-square vibrational amplitudes for the \( C_{60} \) fullerene and CNT contributions together with that of the overall peapod are listed in Table I. For comparison, the mean-square vibrational amplitudes of an isolated pristine CNT are also listed. The mean-square vibrational amplitudes of the fullerene atomic motion in radial and axial directions are larger by one and two orders of magnitude, respectively, than the similar mean-square vibrational amplitudes for atomic motion in the CNT. This is expected, because the fullerene absorbs heat energy mainly via the low-frequency radial breathing mode, and is free to undergo large-amplitude vibrations along the axial direction inside the peapod. The mean-square vibrational amplitudes along the azimuthal direction are of a similar order of magnitude. In the combined peapod system, therefore, there is a significant enhancement of the mean-square vibrational amplitude along the radial and axial directions over their pristine and/or unfilled CNT values. The efficient heat transfer in a peapod is due to (a) fullerene-CNT collisions in the radial direction, and (b) fullerene-fullerene collisions in the axial direction. Both of these types of events, as according to Fig. 5, have an important contribution coming from the low-frequency radial breathing mode region. There is no mass transfer involved because the simulations are for a completely filled peapod under periodic boundary conditions.
In a partially filled peapod, at room and higher temperatures, fullerenes have been experimentally observed to move within the peapod along the nanotube axis. The heat transfer in that case may have an additional component due to mass transfer as well, but the interaction or coupling between fullerenes and nanotube along the radial direction may not be as strong as observed in the present simulations of the completely filled peapod. The thermal conductivity increase in a partially filled peapod, over that of the equivalent unfilled or pristine nanotube, may not be as much as is computed for the completely filled peapod in this work.

In summary, using direct MD simulations with the Tersoff-Brenner potential for C-C bonding interactions and the van der Waals potential for nonbonding interactions, we have simulated and compared thermal conductivity of a peapod with a pristine carbon nanotube of the same radius. The temperature-dependent thermal conductivity of the peapod has the same qualitative behavior as that of a pristine nanotube of the same radius. An increase in the thermal conductivity of the peapod over the nanotube is observed at all temperature, which is in agreement with recent experimental observations. The increase is explained to be due to an efficient low-frequency fullerene-nanotube and fullerene-fullerene energy transfer in the radial and axial directions, respectively.

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