Thermal Conductivity of Nanotubes Revisited: Effects of Chirality, Isotope Impurity, Tube Length, and Temperature

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Abstract

We study the dependence of thermal conductivity of single walled nanotubes (SWNT) on chirality, isotope impurity, tube length and temperature by nonequilibrium molecular dynamics method with accurate potentials. It is found that, contrary to electronic conductivity, the thermal conductivity is insensitive to the chirality. The isotope impurity, however, can reduce the thermal conductivity up to 60% and change the temperature dependence behavior. We also found that the tube length dependence of thermal conductivity is different for nanotubes of different radius at different temperatures.

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Carbon nanotube is one of exciting nano-scale materials discovered in the last decade. It reveals many excellent mechanical, thermal and electronic properties. Depends on its chirality, the nanotube can be either metallic or semiconducting. For example, for zigzag (9,0) and (10,0) tubes, their radius are almost the same, but (9,0) tube behaves metallic and (10,0) tube semiconducting. At room temperature, the electronic resistivity is about $10^{-4} - 10^{-3}\Omega \text{cm}$ for the metallic nanotubes, while the resistivity is about $10\Omega \text{cm}$ for semiconducting tubes. The 10% difference in radius induces the change of electronic conductivity in four orders of magnitude. One may ask, whether thermal conductivity is also very sensitive to the chirality like its electronic counterpart?

On the other hand, the isotope impurity reduces thermal conductivity of most materials, such as germanium and diamond. It is surprising that 1% $^{13}\text{C}$ in diamond leads to a reduction of thermal conductivity up to 30%\(^2\). Is there same effect in carbon nanotubes?

Moreover, in electronic conductance, SWNT reveals many 1D characters. However in thermal conduction, it is still not clear whether the conduction behavior is like that one of 1D lattice or a quasi 1D (1D lattice with transverse motions) or that one in a 2D lattice.

These questions and many other relevant properties of nanotubes are very important and should be understood before the nanotubes are put into any practical application. Indeed, recent years have witnessed increasing interesting in thermal conductivity of nanotubes, the questions raised here are still open.

In this paper, we study the effects of the chirality, isotope impurity, tube length and temperature on SWNTs’ thermal conductivity by using the non-equilibrium molecular dynamics (MD) method with bond order potential. This approach is valid as it shows that at finite temperature, phonon has a dominating contribution to thermal conduction than electron does. We should pointed out that the thermal conductivity calculated in this paper is exclusively from lattice vibration. Of course, for the metallic nanotubes, the electrons may give some but limited contributions, but this is not the main concern in our paper.

The Hamiltonian of the carbon SWNT is:

$$H = \sum_i \left( \frac{p_i^2}{2m_i} + V_i \right), \quad V_i = \frac{1}{2} \sum_{j,j\neq i} V_{ij}$$

(1)

where $V_{ij} = f_c(r_{ij})[V_R(r_{ij}) + b_{ij}V_A(r_{ij})]$ is the Tersoff empirical bond order potential. $V_R(r_{ij})$, and $V_A(r_{ij})$ are the repulsive and attractive parts of the potential, and $f_c(r)$ depending on the distance between atoms. $b_{ij}$ are the so-called bond parameters depending on the bounding
environment around atoms $i$ and $j$, they implicitly contain many-body information. Tersoff potential has been used to study thermal properties of carbon nanotubes successfully.\textsuperscript{13,22} For detailed information please refer to Ref\textsuperscript{23}.

In order to establish a temperature gradient, the two end layers of nanotube are put into contact with two Nosé-Hoover heat baths\textsuperscript{24} with temperature $T_L$ and $T_R$ for the left end and the right end, respectively. Free boundary condition is used. All results given in this paper are obtained by averaging about $10^6 \sim 10^7$ femtosecond (fs) after a sufficient long transient time (usually $10^6 \sim 10^7$ fs) when a non-equilibrium stationary state is set up and the heat flux, $J$, becomes a constant. The thermal conductivity, $\kappa$, is calculated from the Fourier law,

$$J = -\kappa \nabla T,$$

where $J$ is defined as the energy transported along the tube in unit time through unit cross section area, and $\nabla T = dT/dx$ is the temperature gradient. In this paper, we chose $d = 1.44\,\text{Å}$ as the tube thickness, thus the cross section is $2\pi rd$, where $r$ is radius of the tube. In the following we shall discuss the chirality dependence, isotope impurity and tube length effect.

\textit{Chirality Dependence.} The thermal conductivity of zigzag and armchair SWNTs of same length but with different radius are calculated. Fig. 1 shows the temperature profiles of (9,0) and (10,0) nanotubes at 300K. These two temperature profiles are very close to each other, thus the temperature gradient, $dT/dx$, is almost the same. The thermal conductivity, tube radius and relative thermal conductance are listed in Table 1. The difference in thermal conductivity comes mainly from radius difference. If we use thermal conductance (defined as thermal conductivity times cross section area), the relative value (to (9,0) tube) for (9,0), (10,0) and (5,5) SWNTs with the same length is 1 : 0.97 : 1.05.

It is clear that, unlike its electronic counterpart, the thermal conductivity/conductance of SWNTs does not depend on the chirality and/or atomic geometry sensitively both at low temperature and room temperature. Our MD results are consistent with that one from Landauer transmission theory\textsuperscript{21}. The electron DOS of SWNTs depends on chirality. There is an energy gap at Fermi level in (10,0) tube, while no such a gap in (9,0) tube. However, the phonon DOS’s in different tubes do not show any significant difference\textsuperscript{25}.

\textit{Isotope impurity effect.} Isotope impurity affects many physical properties of materials, such as thermal, elastic, and vibrational properties\textsuperscript{26}. There are three isotopes of carbon
FIG. 1: The temperature profiles of (9,0) and (10,0) SWNT at 300K. The temperature is obtained by averaging over $5 \times 10^6$ fs after dropping the $10^6 \sim 10^7$ fs transient time. The tube length, $L$, is 108Å.

**TABLE I: Thermal conductivity for different tubes.**

| Tube  | $(9,0)$ | $(10,0)$ | $(5,5)$ |
|-------|---------|----------|---------|
| $\kappa$ (W/mK) | 880 | 770 | 960 |
| Radius, $r$ (Å) | 3.57 | 3.97 | 3.43 |
| Relative thermal conductance | 1.0 | 0.97 | 1.05 |

Here we study the effect of $^{14}$C impurity on thermal conductivity of SWNTs. In our calculations, $^{14}$C atoms are randomly distributed in a $^{12}$C SWNT. To suppress the possible fluctuations arising from random distribution, an average over 10 realizations is performed.
for each conductivity calculation. We also do the calculation for tube with $^{13}$C impurity and similar effect is found.

Fig. 2(a) shows the dependence of thermal conductivity on the impurity percentage. We select armchair (5,5) tube with a fixed length of about 60Å. The thermal conductivity decreases as the percentage of $^{14}$C impurity increases. With 40% – 50% $^{14}$C, the thermal conductivity is reduced to about 40% of that one in a pure $^{12}$C SWNT. This is similar to the isotope effect on thermal conductivity of diamond.

The thermal conductivity decreases more quickly at low percentage range than at high range. From this curve, we can estimate roughly that the thermal conductivity decreases about 20% with only 5% $^{14}$C isotope impurity. This decrease is not as rapid as that one in a diamond that 1% isotope impurity can reduce thermal conductivity as much as 30%.

This result tells us that one can modulate the thermal conductivity of carbon nanotubes by adding $^{14}$C or other isotope impurity as it alters only the thermal conductivity and has no effect on the electronic properties.

The thermal conductivity, $\kappa$, for (5,5) pure $^{12}$C nanotube and that one with 40% $^{14}$C impurity at different temperatures with same tube length are shown in Fig. 2(b). The difference for these two cases are obvious. The isotope impurity changes completely the temperature dependence behavior of thermal conductivity. For a pure tube (solid △), there is a maximum at about $T_M \approx 250$K. Below this temperature, $\kappa$ increases when $T$ is increased. Above $T_M$, $\kappa$ decreases with increasing $T$. However, in the case with isotope impurity, there is no maximum in the curve. The thermal conductivity monotonically decreases as the temperature increases.

These phenomena can be understood from the phonon scattering mechanism. Increasing temperature has two effects on thermal conductivity. On the one hand, the increase of temperature will excite more high frequency phonons that enhance thermal conductivity. We call this effect “positive” effect. On the other hand, the increase of temperature will also increase phonon-phonon scattering that in turn will increase the thermal resistance, thus suppress the energy transfer. We call it “negative” effect. The thermal conductivity is determined by these two effects that compete with each other.

For a pure SWNT, at low temperature regime, the phonon density is small, the “positive” effect dominates, thus the thermal conductivity increases with increasing temperature. However, at high temperature regime, as more and more (high frequency) phonons are ex-
FIG. 2: (a) Thermal conductivity, $\kappa$, versus $^{14}\text{C}$ impurity percentage for a (5,5) SWNT at 300K.

(b) Thermal conductivity, $\kappa$, versus temperature for a (5,5) pure $^{12}\text{C}$ nanotube (solid $\triangle$) and a (5,5) SWNT with 40% $^{14}\text{C}$ impurity (●). The curves are drawn to guide the eye.
ited, the “negative” effect dominates, which results in the decrease of thermal conductivity as temperature is increased. The results in Fig 2(b) is consistent the results from Savas et al.\textsuperscript{13}

However in the case with impurity, the scattering mechanism changes. In this case, most high frequency phonons are localized due to the impurity. The main contribution to heat conduction comes from the low energy phonon that has long wavelength. The “positive” effect is largely suppressed, and in the whole temperature regime, the “negative” effect dominates that leads to a decrease of thermal conductivity as the temperature is increased, as is seen in Fig 2(b).

\textit{Tube length effect.} Recent years’ study on heat conduction in low dimensional lattices shown that for a one dimensional lattice without on-site potential, thus momentum is conserved, the thermal conductivity $\kappa$ diverges with system size (length)$^{27}$, $L$, as $\kappa \sim L^\beta$, with $\beta = 2/5$. If the transverse motions are allowed, like in the quasi 1D case$^{28}$, then $\beta = 1/3$. Moreover, it has been found that this anomalous conduction is connected with the anomalous diffusion$^{29}$. For more detailed discussion on anomalous heat conduction and anomalous diffusion in different models such as lattice models, billiard gas channels, and nanotubes, see Ref$^{30}$. However, in a 2D system, it is still not known at all (both analytically and numerically) that what shall be the divergence form: power law form or logarithmic form or anything else.

As for the SWNT, Maruyama\textsuperscript{14,15} has studied the $\kappa(L)$ for tubes of different radius, and found that$^{15}$ the value of $\beta$ decreases from 0.27 for (5,5) tube, to 0.15 for (8,8) and 0.11 for (10,10).

Here we investigate this problem from different aspects, namely, we study the change of $\beta$ in different temperatures. For comparison, we also study a 1D carbon lattice model with the same interatomic potential. The carbon-carbon atom distance is also 1.44Å.

The temperature profiles for a carbon SWNT and a 1D carbon lattice are shown in Fig 3 for different temperatures. In this figure, both SWNT and 1D lattice has 100 layers of atoms. Fig 3(a) demonstrates clearly that at low temperature as low as 2K, there is no temperature gradient in both the SWNT and 1D lattice. This resembles the 1D lattice model with a harmonic interaction potential\textsuperscript{31}. This can be understood from the Taylor expansion of the Tersoff potential by keeping up to the second order term. Because at low temperature, the vibrations of atoms are very small, the potential can be approximated by a harmonic one.
FIG. 3: The temperature profile of (5,5) SWNT and 1D lattice at (a) 2K, (b) 300K, and (c) 800K. The temperature is obtained by averaging over $5 \times 10^6$ fs after dropping the $10^6 \sim 10^7$ fs transient time.
And in SWNT, the vibration displacement in transverse direction is much smaller than the one along the tube axis and can be negligible. This result means that energy transports ballistically in SWNTs at low temperature.

However at high temperature, the situation changes. As is shown in Fig. 3(b) for 300K, and Fig. 3(c) for 800K, there is still no temperature gradient in the 1D lattice, but in the SWNT, temperature gradient is set up. In 1D lattice with Tersoff potential, the increase of temperature does not change the harmonic character; while in the SWNT at room temperature and higher temperature, transverse vibration increases as temperature increases. The temperature gradient is established due to the interaction of the transverse modes and longitudinal modes.

The thermal conductivity, \( \kappa \), versus the tube length, \( L \), is shown in log-log scale in Fig. 4(a-d) for (5,5) and (10,10) SWNT at 300K and 800K, respectively. Obviously, the value of \( \beta \) depends on temperature as well as tube radius. For a SWNT, \( \beta \) decreases as temperature increases (cf. (a) and (c), (b) and (d)); and at the same temperature, \( \beta \) decreases as the tube radius increases (cf. (a) and (b), (c) and (d)). This can be qualitatively explained by the modes coupling theory. At high temperature, the transverse vibrations are much larger than that at low temperature, thus interaction between the transverse modes and longitudinal modes becomes stronger, which leads to a smaller value of \( \beta \). For (5,5) tube at \( T=300 \) K, because the small tube radius, the transverse modes can help set up the temperature gradient but the coupling with the longitudinal mode is still very weak, and the longitudinal modes dominate the heat conduction, this is why in this case the thermal conduction behaviour is very close to that one in the 1D Fermi-Pasta-Ulam type lattices, namely, the thermal conductivity, \( \kappa \), diverges with \( L \), as \( L^{0.4} \).

It is worth pointing out that the absolute values of thermal conductivities given in Fig. 4 for (5,5) and (10,10) tubes are different from that ones given in Refs.\(^{14,15}\). The reasons are that: (a) the wall thickness used in Refs.\(^{14,15}\) was 3.4\( \AA \), while in our case we use 1.44\( \AA \), this leads to our results are at least about 2.5 times larger than those ones in Refs.\(^{14,15}\); (b) the thermal state we used are different from that one in Refs.\(^{14,15}\); (c) boundary conditions are different, we use free boundary condition while Refs.\(^{14,15}\) use fixed boundary condition. If we use conductance (get rid of the effect of tube thickness and tube radius) rather than the conductivity, we believe that our results are consistent with that one from others\(^{14,15,19}\).

In summary, we have studied the effects of chirality, isotope impurity, tube length, and
FIG. 4: The thermal conductivity, $\kappa$, versus tube length, $L$, in log-log scale for (5,5) and (10,10) tubes at 300K and 800K. In all cases, $\kappa \sim L^\beta$ with $\beta$ changes from case to case. The solid line, whose slope is the value of $\beta$, is the best fit one.
tube radius on thermal conductivity in SWNTs. Our results show that the thermal conductivity is insensitive to the chirality. However, the introduction of isotope impurity suppresses thermal conductivity of carbon nanotubes up to 60% and change the temperature dependence behavior. Moreover, at low temperature the heat energy transfers ballistically like that one in a 1D harmonic lattice, while at high temperature, thermal conductivity diverges with tube length, $L$, as $L^{\beta}$. The value of $\beta$ depends on temperature and tube radius. This unique structural characteristic makes SWNT an ideal candidate for testing heat conduction theory, in particular, the mode-coupling theory$^{28}$ in low-dimensional systems.

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