Carbon Nanotube Thermal Transport: Ballistic to Diffusive

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We propose to use \( l_0/(l_0 + L) \) for the energy transmission covering both ballistic and diffusive regimes, where \( l_0 \) is mean free path and \( L \) is system length. This formula is applied to heat conduction in carbon nanotubes (CNTs). Calculations of thermal conduction show: (1) Thermal conductance at room temperature is proportional to the diameter of CNTs for single-walled CNTs (SWCNTs) and to the square of diameter for multi-walled CNTs (MWCNTs). (2) Interfaces play an important role in thermal conduction in CNTs due to the symmetry of CNTs vibrational modes. (3) When the phonon mean free path is comparable with the length \( L \) of CNTs in ballistic-diffusive regime, thermal conductivity \( \kappa \) goes as \( L^\alpha \). The effective exponent \( \alpha \) is numerically found to decrease with increasing temperature and is insensitive to the diameter of SWCNTs for Umklapp scattering process. For short SWCNTs (< 0.1 \( \mu \)m) we find \( \alpha \approx 0.8 \) at room temperature. These results are consistent with recent experimental findings.

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Carbon nanotubes (CNTs) have been reported to have remarkable electrical, mechanical, and thermal properties, making them the ideal material for various engineering applications.\(^1\)\(^2\) Of particular interest in this letter is thermal conduction of CNTs. For example, the anomalous enhancement of thermal conductivity has been experimentally observed in CNTs composites.\(^3\) However, many conflicting results of CNTs thermal conduction have been reported both theoretically and experimentally. The values of CNTs thermal conductivity ranging from 30 W/mK to 6600 W/mK have been reported at room temperature.\(^4\)\(^5\)\(^6\)\(^7\)\(^8\)\(^9\) These drastically different values make it necessary to clarify which is reliable and what are the conditions for obtaining such values. Thermal conduction in CNTs may differ from the predictions of Fourier's law based on bulk materials because the phonon mean free path (MFP) can be comparable to the length of CNTs. Ballistic phonon thermal transport behavior in CNTs has been observed in molecular dynamic (MD) simulations\(^10\)\(^11\) and recently in experiments.\(^10\)\(^11\) However, so far as we know, no satisfactory theory has been able to cover both ballistic and diffusive region. Landauer formula\(^12\)\(^13\)\(^14\) takes care of ballistic thermal transport, while Boltzmann equations\(^15\) cannot go over to purely ballistic transport.

In this letter, we propose a formula for thermal conduction covering the range from ballistic to diffusive transport. With this formula, we discuss the CNTs thermal conduction’s dependence on the tube diameter and tube length, as well as interface effect. For thermal transport in quasi-one-dimensional system, the thermal conductivity can be written as:

\[
\kappa = \frac{L}{S} \sum_{n,v,n>0} \int \frac{dq}{2\pi} \hbar \omega_n(q) v_n(q) \frac{\partial f}{\partial T} T_n(q, \omega_n),
\]

where \( L \) and \( S \) are the length and cross-section area of the system, \( T_n(q, \omega_n) \) the energy transmission for the \( n \)-th branch wave at longitudinal momentum \( q \), angular frequency \( \omega_n \), and \( f(\omega_n, T) \) is the Bose-Einstein distribution at temperature \( T \). \( v_n \) is group velocity along the direction of thermal transport given by \( v_n = \partial \omega_n / \partial q \). The integration over momentum \( q \) is within the first Brillouin zone. The central problem is to calculate the energy transmission \( T_n(q, \omega_n) \). We propose that energy transmission can be calculated for three different thermal transport regimes according to the relation between the MFP \( l_0(q) \) and the length of the system \( L \). (1) **Ballistic regime** \( l_0 \gg L \). The MFP is much larger than the length of the system. Thermal transport in this regime can be described by Landauer quantum transport formula\(^15\). There are two equivalent methods for calculating energy transmission resulting from boundary, conjunction, or defect scattering from atomistic point of view: the scattering boundary mode match method\(^16\) and the non-equilibrium Green function method\(^16\). (2) **Ballistic-diffusive regime** where \( l_0 \sim L \). The MFP is comparable with the length of the system. In this regime, the energy transmission is approximated by \( T_n(q, \omega_n) = l_0/(L + l_0) \), as has been shown in Ref.\(^17\) for electronic transport. (3) **Diffusive regime** \( l_0 \ll L \). So thermal conductivity in this limit is given by the well-known Boltzmann-Peierls formula\(^15\)

\[
\kappa = \frac{1}{S} \sum \int \frac{dq}{2\pi} \hbar \omega_n(q) v_n(q) \frac{\partial f}{\partial T} l_0(q).
\]

**Diameter dependence.** Here we assume that the thermal transport in CNTs is in the ballistic regime. To simplify the discussion and catch the essential character of ballistic thermal transport in CNTs, we assume the energy transmission \( T_n(q, \omega_n) \approx 1 \). This assumption is justified for short CNTs with few imperfections at moderate temperatures.\(^2\)\(^9\) Several different definitions for the cross section for CNTs have been used in Ref.\(^17\) because it is not well defined. To circumvent this ambiguity, we would like to use more experimentally oriented physical quantities: thermal conductance \( G_{th} = \kappa S/L \) to measure the property of thermal conduction of CNTs. In our computation, phonon dispersion for single-walled CNTs (SWCNTs) is calculated.
using the method and force constants in Ref. [1]. The group velocity is calculated from the phonon dispersion by the method in Ref. [13]. The results of thermal conduction for different chirality and diameter SWCNTs at different temperatures are illustrated in Fig. 1. It can be seen from Fig. 1 that at low temperature, for example $T = 50$ K, thermal conductance almost does not change with diameter or chirality. At the extremely low temperature limit, all CNTs give the quantized universal thermal conductance $4\pi^2k_B^2T/3h$, which corresponds to the four channels of quantum transport for acoustic phonons. When temperature increases, more optical phonon channels will contribute to thermal transport. However, it is contrary to the intuitive conclusion that thermal conductance at high temperature $T$ will be proportional to the total numbers $N_{ph}$ of phonon channels in CNTs. Thermal conductance at high temperature is proportional to the diameter $d$ of CNTs, irrespective of their chirality. For example, the ratio of channel number SWCNTs (6, 4) to (6, 0) is $N_{ph}^{(6,4)}/N_{ph}^{(6,0)} \approx 6.33$, while their diameter ratio is $d^{(6,4)}/d^{(6,0)} \approx 1.45$. It can be seen from Fig. 1 that the ratio of thermal conductance at 300 K is about 1.45, not 6.33. This proportionality to diameter is implicitly demonstrated in Ref. [14] by counting the number of phonon branches at frequency $\omega$ to calculating the transmission. This simple result can be easily understood if we approximate the integrand in Eq. (1) by a constant, obtaining the result that $G_{th}$ is proportional to the total number of modes divided by the unit cell length, which is proportional to $d$. For MWCNTs, if thermal conductance above certain temperature can be added from the contribution of each shell independently, the total thermal conductance will be $\propto \int \omega d\omega \propto d^2$. The dissipation power results in Ref. [14] have a tendency of $d^2$. It should be noted that the above results only characterize the thermal conductance in pure ballistic regime. In actual experiments, the situation is more complicated for thermal conductance in sub-micrometer lengths. For example, the contact interface and phonon scattering are inevitable in experiment. We will discuss these effects on thermal conduction in CNTs.

**Interface effect.** Interface effect on CNTs thermal transport has been studied through effective medium theory and empirical random walk simulation. However they are only rough models, not from first principles. Here we consider the interface effect from a lattice point of view. We consider an extreme case, where the semiconductor nanotube junction structure (11,0) and (8,0) is first constructed by a geometrical method as in Ref. [1]. The structure is optimized by a second-generation Brenner potential to let the atoms get their equilibrium positions. The force constants are derived numerically from the same potential. The phonon dispersion is calculated from these linearized force constants. Four acoustic branches are considered for energy transport: the longitudinal mode (LA), doubly degenerate transverse mode (TA), and the unique twist mode (TW) in nanotubes. Following the scattering boundary method we calculated the energy transmission across the CNTs junction. The details of calculation are presented in Ref. [12]. The reflected and transmitted waves across the junction for the incident LA mode waves are both only LA modes. We think that this is due to the high symmetrical properties of atomic motion for nanotubes. The LA and TA modes are common symmetrical motions for both the left and right lead. So they propagate through the conjunction. In contrast, the transmissions of the TW mode and many other optical modes are nearly zero or very small. From these results, we consider the interface between CNTs and substrate will influence the experimental measured CNTs thermal conductivity greatly, which has been indicated in experimental results.

**Length effect.** Purely ballistic thermal transport will make thermal conductivity $\kappa$ diverge linearly with the length $L$ of CNTs. Anomalous thermal transport for 1D nonlinear lattice predicts that $\kappa$ will diverge with $L$ as $\kappa \propto L^\alpha$. For 1D nonlinear lattice with transverse motion, which is similar to CNTs, it is found $\alpha = 1/3$ through MD simulation and mode-coupling theory. A few results of tube length effect on thermal transport in CNTs have been reported recently through MD simulation. A length dependence of the thermal transport in CNTs is also observed in experiment. It can be seen from Eq. (1) that thermal conductivity will depend on the length of CNTs in ballistic-diffusive regime.

The problem to calculate thermal conductivity from Eq. (1) in ballistic-diffusive regime is to compute MFP, which depends on frequency and wave length of the vibration modes, as well as temperature. Assuming that the scattering mechanisms are not coupled, MFP can be written as $1/l_i = \sum_i 1/l_i$, where the index $i$ denotes various interaction phonon processes. In CNTs, the phonon scattering process may be different from that of bulk and is not well known. Here, for simplicity, we first consider the Umklapp scattering. Umklapp phonon scattering $l_{ij}^{-1}$ in CNTs has been shown linear $T$ dependence at high temperatures through experiments and is usually given a $\omega^2$ dependency on the frequency. So
we take the form \( l_T = A/(\omega^2 T) \) for Umklapp scattering in CNTs, where \( A \) is taken to be the same as derived for graphene in Ref. 24. The phonon dispersion is calculated as in Ref. 1. The cross-section area \( S \) is defined as \( S = \pi d^2/4 \). Results are illustrated in Fig. 2 through Eq. (1) for ballistic-diffusive regime in CNTs. We should note that the exponent \( \alpha \) in Fig. 2(C,D) is an effective exponent in a limited length region, not the asymptotic one. It can be seen from Fig. 2A that thermal conductivity shows different length dependence scaling at different temperatures; we take the form \( L^\alpha \) for short CNTs (< 0.1 \( \mu \)m) and long CNTs (> 10 \( \mu \)m), denoted as \( \alpha_S \) and \( \alpha_L \) respectively, when Umklapp scattering in CNTs is considered in ballistic-diffusive regime. This is due to the relation between MFP and the length of CNTs. Average MFP \( \bar{l}_0 = \int l_0(\omega, T)D(\omega)d\omega \) is calculated from the phonon dispersion relation for CNT (6,6), where \( D(\omega) \) is normalized density of states, satisfying \( \int D(\omega)d\omega = 1 \). Figure 2B indicates that average MFP decreases rapidly from 0.25 \( \mu \)m to 0.06 \( \mu \)m, when temperature goes up from 50 K to 200 K. We also calculated average MFP for other chirality CNTs and found little difference from that of CNT (6,6). Fig. 2C shows the change of \( \alpha_S \) and \( \alpha_L \) with temperature. For example, when \( T = 50 \) K, the average MFP is as large as 0.25 \( \mu \)m and so the \( \alpha_S \) is almost equal to 1. When temperature increases, the MFP becomes shorter, so \( \alpha_S \) and \( \alpha_L \) both decrease with temperature. The dependence of \( \alpha_S \) and \( \alpha_L \) on CNTs diameter is illustrated in Fig. 2D. \( \alpha_S \) almost does not change with the chirality of CNTs and gives \( \alpha_S \sim 0.83 \) at room temperature, while \( \alpha_L \) decreases slowly with increase of the diameter of CNTs, and gives its value about \( \alpha_L \sim 0.35 \) for CNTs with diameter larger than 1 nm at room temperature. This kind of temperature dependence and chirality dependence agrees with MD simulation results.22 It is worth noting that, for CNTs with length less than 0.1 \( \mu \)m, \( \alpha = 0.32 \) and \( \alpha = 0.40 \) for CNT (5,5) at room temperature are reported by non-equilibrium MD simulation, while \( \alpha \sim 1 \) is observed using equilibrium MD simulation. For MWCNT with length less than 0.5 \( \mu \)m, roughly \( \alpha \sim 1 \) is reported. We think that the difference for non-equilibrium MD and equilibrium MD comes from the boundary condition because in short CNTs the result should be sensitive to the boundaries.

Next we discuss other phonon scattering mechanisms. If the frequency dependence of MFP is assumed as \( 1/l_0 \propto \omega^r \), then at high temperature the length dependence of thermal conductivity given by Eq. (1) can be estimated as \( \kappa \sim \int \frac{1}{l_0^{1} + 1/T}d\omega \propto L^{\frac{-1}{r}} \), that is \( \alpha = (r-1)/r \). For Umklapp scattering process, \( r = 2 \) and \( \alpha = 0.5 \), which corresponds to the effective exponent at length about 1 nm. For defect scattering mechanism, we have \( 1/l_0 \propto \omega^4 \), \( \alpha = 0.75 \). Thus, it can be argued that strong frequency dependence scattering (large \( r \)) will not have much help in eliminating thermal conductivity divergence, while weak frequency dependence scattering will contribute to eliminating this divergence. Finally, in the very long tube limit, \( \kappa \) approaches a constant within our theory.

**Conclusions.** Crossover in thermal conduction from ballistic to diffusive is illustrated. Thermal conductance at room temperature is found \( \alpha \propto d \) for SWCNTs and \( \alpha \propto d^2 \) for MWCNTs. Interfaces play an important role in thermal conduction in CNTs due to the high symmetrical property of CNTs vibration modes. Possible ways to improve thermal conduction in CNTs are suggested. In ballistic-diffusive regime, thermal conductivity \( \kappa \) behaves as \( L^\alpha \). The effective exponent \( \alpha \) is numerically found decreasing with increasing temperature and insensitive to the diameter of SWCNTs for Umklapp scattering process. The possible mechanism for the reduction of divergence for thermal conductivity is also discussed. Although the formula is still phenomenological, it does cover ballistic and diffusive regimes with a smooth crossover and gives a reasonably simple picture in the whole temperature range. This work is supported in part by a Faculty Research Grant of National University of Singapore.

FIG. 2: Length divergence in ballistic-diffusive regimes: (2A) Thermal conductivity for different chiralities SWCNTs at 300 K; (2B) Average mean free path length for nanotube (6,6) at different temperatures; (2C) Change of power law exponent for short and long CNTs with temperature; (2D) Change of power law exponent for short and long CNTs with diameter;
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