Carbon Nanotube Ballistic Thermal Conductance and Its Limits

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Calculations of the quantum-mechanical ballistic thermal conductance of single-walled carbon nanotubes, graphene, and graphite are presented, which explain previous experimental results, and directly disprove earlier theoretical calculations. The ballistic thermal conductances are smaller than had been previously thought, whereas the maximum sample lengths in which phonon transport remains ballistic are orders of magnitude larger than previously suggested. Good agreement with previous experiments is obtained, which shows that measured lower bounds to the thermal conductance of multiwalled carbon nanotubes are very close to the upper theoretical bounds for graphite. The bounds shown here draw a line between what is physical and unphysical in any measurements or calculations of carbon nanotube thermal conductance, and constitute a necessary test to their validity.

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Thermal conduction through carbon nanotubes is an important issue that has recently attracted considerable attention [1–15]. The thermal conductivity of infinitely long nanotubes has been theoretically studied, yielding high values comparable to or higher than those of graphite [5–7]. However, there are two questions that have not yet been given a satisfactory answer for carbon nanotubes: How high is the ballistic lattice thermal conductance? For how long a sample does phonon transport remain ballistic? The importance of these questions is manifest: the high thermal conductivity values predicted for infinitely long systems might be the result of either a very high ballistic thermal conductance σ_b combined with rather short ballistic lengths [16], or it might result from a not so high σ_b, but a transport that remains ballistic for very long sample lengths. These two possibilities result in radically different implications regarding the practical use of carbon nanotubes for thermal conduction. Despite this, no previous satisfactory study of carbon nanotube ballistic thermal conductance and ballistic lengths exists [17]. The possibility of short ballistic lengths and very high ballistic thermal conductance was implicitly stated in Refs. [8,9]. In this Letter we show that the actual case is precisely the opposite, with very long ballistic lengths and much smaller thermal conductances. Refs. [8–10] violate the ballistic upper bounds to thermal conductance, presumably due to the inadequacy of classical molecular dynamics to address quantum ballistic transport. Other papers have also violated the ballistic upper bounds [11,12]. The only available experimental results on individually suspended carbon nanotubes, for a multiwalled nanotube (MWNT) [2], support our findings. As we will see, the experimental conductance is below, but very close to, the theoretical ballistic conductance for graphite, being closely proportional to it in the whole 0–200 K temperature range.

The standard expression for the ballistic lattice thermal conductance is [18,19]

$$\sigma_b(T) = \int_0^\infty \mathcal{T}(\omega)\hbar\omega(df/dT)d\omega/2\pi. \qquad (1)$$

where $f(\omega, T)$ is the occupation distribution function for the heat carriers at the reservoirs, and the transmission function $\mathcal{T}(\omega)$ is defined as the number of phonon branches at frequency ω in this particular case. The thermal conductivity of a finite sample is related to its conductance by $\kappa = (L/S)\sigma$, where L is the length of the suspended segment of the nanotube, and S is its cross section. Since the cross section is not a well-defined quantity in carbon nanotubes, we will discuss results in terms of conductance. Only for convenience, we use a cross sectional conductance σ/s where we define a quantity $s = 2\pi R\delta \simeq R \times 2.105$ nm. R is the nanotube radius and $\delta = 3.35$ Å is arbitrarily chosen as the layer separation in graphite. Since R is a well-defined quantity, there is no ambiguity in doing this.

The ballistic transmission functions are calculated directly from the phonon dispersion curves. Very accurate descriptions of the phonon dispersions for graphite and graphene are, respectively, given using the 20 parameter set of Ref. [20] and the 12 parameter set of Refs. [21,22]. For consistency, the phonon dispersions of single-walled nanotubes (SWNTs) are calculated using the method of Refs. [22,23], which properly converge to the graphene limit for the large diameter nanotubes. This potential yields linear dispersions for the two lowest lying "flexural" modes, while it has been shown that those modes should have quadratic dispersions near the Γ point [24]. Nevertheless, from Eq. (1) and the definition of $\mathcal{T}$, it is apparent that, to construct the transmission function, it does not matter whether the dispersions are linear or quadratic, but only that the branch's upper and lower frequency limits should be accurately computed. We repeated all the calculations using the potential of Ref. [24] instead, and obtained very similar results to the ones presented here. The

high temperature limit of the cross sectional thermal conductance curves obtained in that case is about 10% lower than the one shown here. The ballistic thermal conductance results shown in Fig. 1 are believed to be more accurate than the ones obtained using Ref. [24]'s method for the dispersions, because the latter does not correctly reproduce the graphene phonon dispersions. We have estimated that any possible inaccuracy in the phonon dispersions we used would result in differences of only 10% or less in the computed ballistic thermal conductance.

In Fig. 1 we show the ballistic thermal conductance, scaled by $s(R)$ defined above, as a function of temperature. At low T, all nanotubes have the expected linear T dependence of the conductance, with a prefactor $4\pi^2 k_B^2/3h$, corresponding to four quanta of thermal conductance [19,25]. At higher temperatures, a T^2 dependence is achieved, as a result of higher phonon branches being active. As T increases, the curves converge to a single line, which finally saturates to a limiting high temperature value. Results for armchair tubes, not shown here, are virtually indistinguishable from the ones for zigzag tubes, when the same diameters are compared. The limiting case of a graphene sheet, given by the thick solid line, provides a lower bound for all the nanotube curves and converges with them in the high temperature limit. Unlike the nanotubes, graphene has a $T^{1.5}$ dependence at low T. This anomalous behavior also differs from the T^2 behavior expected for two-dimensional acoustic phonon gases. The reason is that one of the three acoustic branches in graphene has a quadratic rather than linear dependence with frequency. For this quadratic branch the frequency depends on the wave vector as $\omega = \alpha q^2$. For a graphene stripe of width $D \to \infty$, the contribution of this branch to the transmission function at low frequency is $\mathcal{T}(\omega) \simeq \int_{-q(\omega)}^{q(\omega)} (D/2\pi) dq = (D/\pi)\sqrt{\omega/\alpha}$. Similarly, the two linear branches contribute an amount $(D/\pi)(\omega/c^{a(b)})$, where $c^{a(b)}$ are the speeds of sound of the two linear acoustic branches. For $\omega \to 0$ their contribution is negligible compared to that of the quadratic branch. Therefore, the upper bound to the thermal conductance of graphene at low temperature goes as

$$\sigma_b/s = \eta(1/\delta) k_B^{5/2} T^{3/2}/(2\pi^2 \hbar^{3/2} \alpha^{1/2}), \qquad (2)$$

with $\eta \equiv \int_0^\infty x^{5/2} e^x/(e^x - 1)^2 dx \simeq 4.46$. Substituting the value $\alpha = 0.62 \times 10^{-6}$ m^2/s, obtained from the theoretical dispersion, and also by other calculations [26], and using $\delta = 3.35$ Å, we have $\sigma_b/s = 0.6 \times 10^6 T^{3/2}$ W/(m^2 K$^{5/2}$).

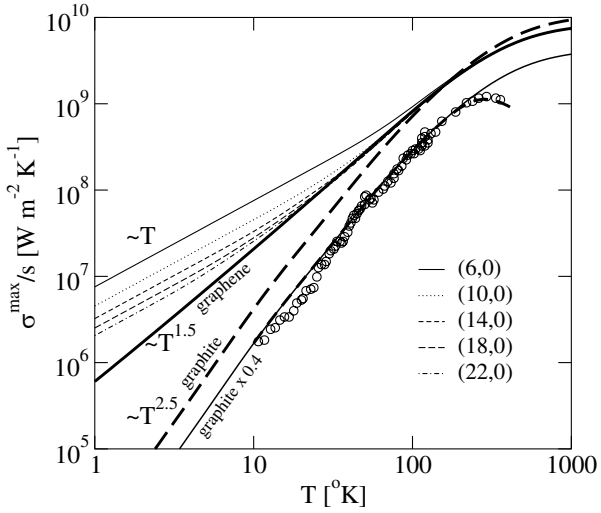

FIG. 1. Scaled maximum lattice thermal conductance (see text) for SWNTs, graphene, and graphite. Experimental results for MWNTs are proportional to the graphite curve, and only 0.4 times smaller.

The thick dashed line in Fig. 1 shows the upper bound to the thermal conductance calculated for three-dimensional graphite, in the basal plane, along the (110) direction. Accurate graphite dispersion relations were calculated following Ref. [20]. At high T, the curve for graphite goes above the graphene and SWNT curves by about 20%. To understand this, we note that the high temperature limit of σ_b is $\lim_{T\to\infty} \sigma_b(T) = (k_B/2\pi) \int_0^\infty \mathcal{T}(\omega) d\omega$, i.e., it is proportional to the area under the transmission curve. The frequency ranges of the phonon branches in graphite are generally larger than in graphene, due to the interlayer interaction. This results in a larger transmission function (at equal cross sections) for graphite, and a somewhat larger high temperature upper bound. At low temperature, the ballistic thermal conductance of graphite has a $T^{2.5}$ dependence. This limit can be obtained analytically, as for the graphene sheet. Now, there is some dispersion in the direction perpendicular to the planes, and the resulting transmission function in the low frequency limit is $\mathcal{T}_{\omega\to 0} = DW/(\pi^2\sqrt{\alpha}c)(2/3)\omega^{3/2} \times 2$, where DW is the sample's cross sectional area, and c is the lowest speed of sound in the direction perpendicular to the planes. The factor of 2 arises from the double degeneracy of this branch. Repeating the argument of the previous paragraph, one obtains the $T^{5/2}$ dependence.

The electronic contribution to the thermal conductance is negligible in the whole temperature range for the semiconducting nanotubes. For the metallic nanotubes, (6,0) and (18,0), the electronic contribution to the ballistic thermal conductance is 4 thermal conductance quanta, $4 \times T 9.465 \times 10^{-13}$ W K^{-2} throughout the whole temperature range, $T = 0$–1000 K. The contribution of electronic subbands not crossing the Fermi level is negligible, because their separation from the Fermi level is of the order of eV's. For comparison, energy differences between phonon branches are typically <0.01 eV, and so the higher phonon subbranches play an important role in the temperature behavior of the lattice thermal conductance.

The ballistic thermal conductances shown in Fig. 1 impose a stringent limit on theoretical and experimental

results: one cannot expect to measure or compute lattice thermal conductance values higher than those shown. In particular, at 300 K the lattice thermal conductance is, for all nanotubes, smaller than $\sim 8(R/\mathrm{m})$ W/K (m indicating meters). This means that all the results in Refs. [8,9] for nanotubes shorter than 10^3 Å violate the quantum upper bounds. We attribute this to the fact that those are results from a classical molecular dynamics simulation, in which the quantum limits play no role. Another paper, Ref. [12] also considers finite length nanotubes, through the inclusion of a boundary scattering term. Although the length of those nanotubes is not explicitly mentioned, the 50 ps boundary relaxation time employed there, combined with the maximum speed of sound in nanotubes of 2×10^4 m/s, implies that the maximum length of these nanotubes is ~ 1 μm. From Fig. 1, the maximum possible thermal conductivity of a 1 μm long single-walled nanotube at $T = 100$ K is in all cases less than $\sim 10^3$ W/m K, which means that at this temperature the results of Ref. [12] violate the quantum upper bound by about 1 order of magnitude.

The upper bounds shown in Fig. 1 can be attained only if phonons travel ballistically, in which case the thermal conductance does not depend on the length of the sample, L. However, beyond a critical length, which depends on temperature, scattering of phonons due to the anharmonicity of the interatomic potential begins to decrease the conductance, and the transport is no longer ballistic. We have evaluated these ballistic lengths by iterative solution [27] of the Boltzmann-Peierls transport equation for finite length nanotubes [28]. Imposing black body boundary conditions at the nanotube edges, after some algebra, an approximation for the transport equation is obtained [28],

$$v_p \hbar\omega_p/[k_B T^2] \simeq g_p 2|v_p|/L + \partial_c n_p/[n(n+1)], \quad (3)$$

where $g(x) \equiv (n_p - n)/[n(n+1)]$, with n_p the distribution function at the middle of the nanotube, $\partial_c n_p$ is the collision integral, $n \equiv (e^{\hbar\omega/k_B T} - 1)^{-1}$ being the Bose distribution, and $p = \{q, \alpha\}$ denotes the phonon's wave vector q, and branch index α. In terms of the distribution function, the thermal conductance is

$$\sigma = L \sum_\alpha \int v_p \hbar\omega_p g_p n_p (n_p + 1) dq. \quad (4)$$

Equations (3) and (4) in the $L \to 0$ limit recover the ballistic result, Eq. (1), whereas the $L \to \infty$ limit recovers the usual Boltzmann-Peierls equation for infinitely extended systems. In this ballistic length calculation we use the phonon dispersions of Ref. [24], since in this case it is essential that the quadratic character of the flexural modes be reproduced [28]. To compute the collision integral, except for the four acoustic branches, we use a relaxation time approximation with the parameters given in Ref. [29]. The four acoustic branches give an important contribution and require a special treatment [28]. For these branches we have explicitly included the three-phonon processes to first and second order in the calculation, with full observance of the particular selection rules acting between the different phonon branches of zigzag nanotubes [28]. Because of approximations in the treatment of the second order processes, the calculations for very long nanotubes, away from the ballistic regime, are expected to be accurate in their order of magnitude, but not in their actual value.

We define the ballistic length $\mathcal{L}_{-\alpha}$ as the length above which $\sigma(L)$ decreases faster than $L^{-\alpha}$, where $\alpha > 0$. Table I shows results for the ballistic lengths at different temperatures, for a (10,0) nanotube. As we see, transport below room temperature remains ballistic up to very large lengths, and it is still far from diffusive even at μm long samples. This would permit measurement of the upper bounds experimentally at these temperatures. For higher temperatures, shorter samples are needed if ballistic transport is to be achieved. The present results strongly contrast with those in Ref. [8], where $\sigma \sim L^{-0.68}$ was obtained for as short as $L > 10$ nm at room temperature.

The only available experimental results on individually suspended carbon nanotubes are for a multiwalled nanotube [2] (shown in Fig. 1 by the open circles). The experimental results are properly located below the quantum ballistic limits for single-walled nanotubes, graphene, and graphite, and interestingly, they are only about one half the graphite ballistic result and closely proportional to it over a wide range of temperatures. This suggests that the thermal conductance of MWNTs, while being far lower than that for SWNTs and graphene at low temperatures, is very similar to that of bulk graphite. For better comparison with the MWNT experiment, the graphite ballistic curve is also shown rescaled by 0.4. If, in addition, a parametrized umklapp relaxation length is included in the calculation with the commonly used form $A\omega^2 T^2 e^{-\Theta/T}$, the higher temperature part of the experimental points can be fit as well (dashed line).

The reduction of the MWNT results compared to graphite may indicate that phonon flow from the contact into the inner layers of the nanotube is limited, resulting in the outer layers carrying more heat than the inner ones, as was suggested in Ref. [2]. Another possibility is the presence of a slight diffusive boundary scattering at the surface of the nanotube. In the former case, a longer contact length might increase the conductance, which would not depend on the

TABLE I. Ballistic lengths calculated for a (10,0) SWNT at different temperatures. The ballistic length, $\mathcal{L}_{-\alpha}$, is defined as the nanotube length beyond which σ decreases with length faster than $L^{-\alpha}$.

	$T = 31.6$ K	100 K	316 K	1000 K
$\mathcal{L}_{-0.1}$	35.5 μm	0.32 μm	16.2 nm	2.0 nm
$\mathcal{L}_{-0.2}$	149 μm	1.34 μm	52.9 nm	6.6 nm
$\mathcal{L}_{-0.3}$	305 μm	9.70 μm	140 nm	17.5 nm
$\mathcal{L}_{-0.4}$	511 μm	28.9 μm	428 nm	45.3 nm
$\mathcal{L}_{-0.5}$	798 μm	53.8 μm	2.31 μm	124 nm

suspended length. In the latter case, a shorter suspended length would increase the conductance, which would not depend on the contact length. Thus, new experiments might be able to determine the origin of the reduced conductance. We have estimated the difference between the two aforementioned possibilities by solution of Eqs. (3) and (4) for a 1.5 μm (10,0) nanotube with and without an extra boundary scattering term mimicking the experimental case. For the first possibility (contact limited flow), at 400 K, we obtain a conductance reduction with respect to the ballistic limit of $\sigma/\sigma_b \simeq 0.2$, whereas for the second possibility (boundary scattering), we obtain $\sigma/\sigma_b \simeq 0.3$. The experimental MWNT reduction with respect to the theoretical ballistic conductance of graphite at this temperature is about 0.4. Although one cannot strictly compare MWNT measurements with estimates for a SWNT, this suggests that the boundary scattering possibility is a more likely case. As we see in Fig. 1, these experimental results support our finding that anharmonic effects remain weak for considerably long samples even at moderately high temperatures. We can conclude that MWNTs and graphite are very similar in their thermal conduction properties below 200 K. Above 300 K, the thermal conductivity of the MWNT is about 50% higher than that of pyrolytic graphite [30]. Since the high temperature conductivity does not depend on the sample size, this suggests that umklapp scattering in MWNTs is weaker than in graphite.

In conclusion, by computing upper bounds to the lattice thermal conductance of SWNTs, graphene, and graphite, we have shown that thermal transport through finite carbon nanotubes is profoundly different from what had previously been suggested: (1) SWNT thermal conductance is necessarily lower than previously claimed, (2) the sample lengths in which phonon transport remains ballistic are considerably longer than previously suggested, (3) these findings are supported by experimental evidence; published experimental measurements on a suspended MWNT are close to the ballistic thermal conductance for graphite, and suggest there is little difference between these two systems below 200 K. In concrete practical terms, an important message of this Letter is—some previously predicted high values of SWNT thermal conductivity, for example $\kappa_{100\ \mathrm{K}} \gtrsim 10^4$ [5], may not be achieved unless the nanotube length exceeds tens of micrometers. This may impose serious restrictions when trying to take advantage of nanotube thermal conduction properties for practical applications.

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