Theoretical description of thermal transport in graphene: The issues of phonon cut-off frequencies and polarization branches

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We discuss theoretical approaches for description of the phonon thermal transport in graphene and identify open questions and problems. Specifically, we show that due to a fundamental ambiguity in the definition of the intrinsic thermal conductivity of two-dimensional (2-D) systems the calculations that use an arbitrary low-bound cut-off for the phonon frequency in the thermal conductivity integral lead to erroneous results. The problem of the relative contributions of the longitudinal acoustic (LA), transverse acoustic (TA), and out-of-plane phonon polarization branches to thermal transport in graphene is also discussed. Theoretical thermal conductivity data for graphene, obtained by different approaches, are compared with those for carbon nanotubes.

1 Introduction

The first Raman optothermal studies [1, 2] of thermal conductivity of graphene, carried out at UC-Riverside, found that thermal conductivity $K$ can exceed that of the bulk graphite limit, which is $K \sim 2000$ W/mK at room temperature (RT). The acoustic phonon mean-free path (MFP) was estimated to be $\sim 775$ nm near RT [2]. Following independent investigations [3, 4], which utilized a similar Raman-based experimental technique determined $K$ of suspended graphene to be larger than $\sim 2500$ W/mK at 350 K, and as high as $K \approx 1400$ W/mK at 500 K [3]. The measurements of thermal properties of graphene stimulated a surge of interest to theoretical studies of heat conduction in graphene and graphene nanoribbons [5–13].

In this paper, we discuss different theoretical approaches for description of the phonon thermal transport in graphene and identify open questions and problems. Specifically, we show that using an arbitrary low-bound cut-off frequency for the thermal conductivity integral lead to erroneous results for graphene.

We start by defining the terminology and revisiting some basic facts about heat conduction in two-dimensional (2-D) systems. It is conventional to define the intrinsic thermal conductivity as the one limited by the crystal anharmonicity only, i.e., phonon–phonon interactions. The phonon interactions, which directly contribute to thermal resistance, are usually described in terms of the three-phonon Umklapp scattering. The definition of the intrinsic thermal conductivity, naturally, does not include phonon scattering on crystal defects, imperfections or rough boundaries. In three-dimensional (3-D) systems this definition allows one to obtain a finite thermal conductivity provided the crystal is anharmonic (in the harmonic approximation the intrinsic thermal conductivity will become infinite).

It is known that the similarly defined thermal conductivity limited by crystal anharmonisity only – referred to as intrinsic – has a logarithmic divergence in 2-D systems and even stronger power-law divergence in 1-D systems [14–24]. This anomalous behavior of the thermal conductivity in 1-D and 2-D systems, which leads to its infinite values, has been studied extensively both analytically and numerically for many different lattices and potentials. One needs disorder (e.g., extrinsic scattering mechanisms) in order to obtain a finite value of the thermal conductivity in 2-D systems. Alternatively, one can limit the size of the system for which the thermal conductivity is determined.
2 Thermal conductivity of graphite and graphene: Phonon cut-off frequency

In this section we address the issues of the proper low-bound cut off phonon frequency in the Klemens type models for thermal conductivity of graphene. Recently, Kong et al. [25] claimed that they calculated the intrinsic thermal conductivity of single-layer graphene (SLG) and bilayer graphene (BLG) from the first principles. Their main finding was that the RT thermal conductivity of both SLG and BLG is around 2200 W/mK, which is close to the value measured and calculated for bulk graphite. They also suggested that the number of atomic layers does not influence the value of the intrinsic thermal conductivity of few-layer graphene (FLG) [25]. Here we explain that the Kong et al. [25] calculation is erroneous, and the obtained numeric values are artifacts of the truncation procedure, which is unphysical for the case of graphene. As a result, both conclusions given by Kong et al. [25] are without merit.

Kong et al. [25] approach to calculation of the thermal conductivity of graphene is based on an approximate formula for the three-phonon Umklapp scattering processes from Klemens’ paper for bulk graphite [26]

\[ 1/\tau_u = 2\gamma^2 k_B T_o^2 / (M u^2 \omega_m). \] (1)

Here \( k_B \) is the Boltzmann constant, \( T \) is the absolute temperature, \( M \) is the mass of atoms, \( u \) is the average sound velocity, \( \omega \) is the phonon angular frequency, and \( \omega_m = 2\pi f_m \) is upper-bound cut-off frequency deduced from the phonon dispersion of the material. In order to determine the intrinsic thermal conductivity of graphene, Kong et al. [25] substituted Eq. (1) to the relaxation-time approximation (RTA) expression for thermal conductivity \( K \). As expected, the resulting integral for thermal conductivity \( K \) reveals a logarithmic divergence. In his seminal work for bulk graphite, Klemens derived an analytical expression for the Umklapp-limited thermal conductivity [26]

\[ K \propto (1/\omega_m) \int_{\omega_C}^{\omega_m} \omega^{-1} d\omega \propto (1/\omega_m) \ln(\omega_m/\omega_C). \] (2)

As one can see from Eq. (2), an attempt to integrate over the whole Brillouin zone (BZ), starting from the zone center \( (\omega q = 0) = 0 \) for acoustic phonons, requires setting the low-frequency cut-off \( \omega_C = 2\pi f_C \) to zero and leads to an infinite intrinsic thermal conductivity.

Klemens provided physical reasoning, specifically for bulk graphite, for selecting the cut-off frequency \( \omega_C \neq 0 \). The heat transport in basal planes of bulk graphite is 2-D-like only for relatively high frequencies. At very low frequencies, there appears coupling with the cross-plane phonon modes, scattering increases, and heat starts to propagate in all directions. The latter reduces the contributions of these low-energy modes to heat transport along basal planes to negligible [26]. The onset of these cross-plane coupling can be used as the low-limit of integration in Eq. (2). The presence of the ZO phonon branch with the BZ center frequency \( f_{ZO} \approx 4 \text{THz} \) in the spectrum of bulk graphite supports this argument, and provides a natural, physically meaningful, value for the cut-off frequency. Using this simple approach and the cut-off frequency of 4 THz, Klemens obtained the value of \( K \approx 1900 \text{W/mK} \), which closely matched available experimental data.

Kong et al. [25] stated that in their calculation for graphene the integration “is truncated with a cut-off frequency \( f_{ZO} \) to avoid the divergence issue at the zone center” as in Klemens’ calculation for bulk graphite [26]. This procedure leads to a wrong result because it fails to preserve the uniqueness of the phonon transport in graphene. Indeed, there is no ZO phonon branch in graphene (see Fig. 1) and no phonon flux outside the plane can be established for the low-frequency phonons either in SLG or BLG. Thus, truncating the integration at \( f_{ZO} \), Kong et al. [25] essentially obtained the thermal conductivity of bulk graphite, not of monolayer graphene or BLG. The minor difference in their value from that given by Klemens for bulk graphite is explained by the differences in the \( \gamma(q) \) values and few other material parameters (the exact values of \( \gamma \) were not known until recently and Klemens used an overestimated \( \gamma = 2 \). For this reason, the Kong et al. [25] conclusions that the intrinsic thermal conductivity of graphene is close to that of graphite and does not depend on the number of atomic layers is erroneous and does not have any physical grounds. The value obtained by Kong et al. [25] is defined by the selected low-energy cut-off \( \omega_C \) choosing it the same as in the bulk gives the intrinsic thermal conductivity of the bulk.

3 Klemens theory of thermal conductivity of graphene

It is interesting to note that Klemens calculated thermal conductivity of graphene [27, 28] even before
graphene was exfoliated. He clearly contrasted the intrinsic thermal conductivity of graphene to that of graphite. In his paper [27] he stated that in graphene “the phonon gas is two-dimensional down to zero frequency, since there are no wave vectors outside the basal plane. However, a logarithmic divergence is also prevented, because the mean free path cannot exceed a linear dimension L, determined by the size and shape of the sheet.” Klemens derived an analytical expression for the cut-off frequency in graphene replacing the bulk cut-off \( \omega_C \) with the one determined by the boundaries of the graphene sheet \( \omega_B = 2\pi f_B \sim 1/(LT)^{1/2} \) in graphene. Naturally, \( \omega_B \) has nothing to do with \( \omega_C \) at \( \Gamma_{ZGO} \). It is defined by the physical dimensions of the graphene sheet \( L \) and temperature \( T \). In his study of graphene, Klemens derived an analytical expression for its Umklapp-limited thermal conductivity [27]

\[
K = \left(2\pi \gamma^2\right)^{-1} \rho \left(\nu^4 / f_m T\right) \ln(f_m/f_B),
\]

where \( \rho \) is the mass density and

\[
f_B = \left(M \nu^3 f_m / 4\pi^2 k_B T L\right)^{1/2}
\]

is the low-bound cut-off frequency, which is an explicit function of the graphene sheet size \( L \). Thus, thermal conductivity of graphene grows with the size, and at some \( L \) exceeds that of bulk graphite along the basal planes [27, 28].

For his choice of the material parameters and large graphene sheets (\( L = 1 \) mm), Klemens obtained thermal conductivity of graphene to be \(~4400 \) W/mK, which is notably above the bulk graphite limit of \(~1900 \) W/mK. Since Klemens used an overestimated value of Gruneisen parameter, which reduced thermal conductivity, he found for thermal conductivity of a graphene flake to exceed that of bulk graphite the flake’s size should be in the range of \(~10 \) \( \mu \)m [27, 28].

We re-calculated the thermal conductivity of graphene flakes with the formula analogous to Eq. (3) but using more accurate Gruneisen parameters and maximum phonon frequencies defined separately for longitudinal acoustic (LA) and transverse acoustic (TA) phonon branches [29]. It was found that at \(~10 \) \( \mu \)m range thermal conductivity of graphene, limited by the Umklapp scattering only, is already substantially higher than that of bulk graphite. The latter is in excellent agreement with the measurements for large graphene flakes (length \(~10–20 \) \( \mu \)m, width \(~5 \) \( \mu \)m) reported by some of us [1, 2, 30–32] and in a clear contrast to Kong et al. calculations [25]. Independent experimental studies [3, 4] also support Klemens’ prediction that intrinsic thermal conductivity of graphene can exceed that of bulk graphite. To illustrate the point, in Fig. 2 we show the intrinsic thermal conductivity of graphene calculated using Klemens model for graphene with proper Gruneisen parameters, thermal conductivity of graphene calculated with Klemens model for graphite and Kong et al. [25] result for “graphene.” One can see that Kong et al. [25] calculation is pertinent to bulk graphite rather than graphene. Recent experimental studies [30] found dependence of thermal conductivity of FLG on the number of atomic planes in sharp contrast to Kong et al. [25] prediction. Thermal conductivity of suspended BLG decreases compared to that of suspended SLG [30]. Thermal conductivity of suspended graphene is closer to the intrinsic value than that of supported graphene.

It is a matter of semantics or taste how to refer to thermal conductivity calculated by Klemens [27–28] or us for graphene sheet of a given size. It can be viewed as an intrinsic thermal conductivity for a graphene sheet of a given size since it only includes Umklapp scattering and the size of the flake acts as a natural physical limit for the phonon MFP. If the size is not limited and allowed to go to infinity – so does the intrinsic thermal conductivity, as discussed in literature [5–13] and follows from Eq. (3). Alternatively, one can view it as an absence of the intrinsic thermal conductivity in 2-D systems defined via Fourier’s law. We prefer to refer to it an intrinsic 2-D thermal conductivity of a graphene flake of a given size because it does not include extrinsic effects such as the phonon scattering on defects or impurities. Despite similarity of the in-plane phonon properties of graphene (2-D systems) and graphite (3-D systems), their thermal transport is principally different. The evolution from 2-D to bulk is achieved through cross-plane coupling at the low phonon energies as was pointed out by Klemens specifically for carbon materials [26, 27] or discussed in literature in more general terms [5–13]. Such evolution for carbon systems was also confirmed through molecular dynamics (MD) simulations when an addition of coupling between graphene atomic planes led to a drastic reduction in thermal conductivity [33, 34]. One should note here that the
Umklapp-limited thermal conductivity is determined for an ideal graphene sheet without any defects. In experiments, the thermal conductivity is also limited by the external factors (point defects, polycrystalline grain boundaries, substrate coupling, bending, etc.) and it will not grow to the unphysically high values even if someone is able to produce a graphene sheet of an extremely large size. The heat conduction in graphene sandwiched between other materials can be strongly affected by the cross-plane coupling to barrier materials, disorder, and other extrinsic effects and represent a different case from that considered in this paper.

It is evident from the above discussion that the three-phonon Umklapp-limited 2-D thermal conductivity of graphene can only be determined for a graphene sheet of a finite size due to a logarithmic divergence. However, there is a possibility that higher-order phonon processes would lead to a finite value for very large ideal graphene layers when their size becomes larger than the higher-order phonon MFP. The latter still remains to be conclusively proven. Another possibility to avoid a logarithmic divergence and obtain meaningful values for the thermal conductivity of graphene is to introduce relevant extrinsic scattering mechanisms simultaneously with the intrinsic three-phonon Umklapp processes. This is equivalent to adding disorder to 2-D system in order to obtain the finite thermal conductivity without limiting system’s size [5–13]. Such calculations taking into account scattering on point defects, isotopes and rough edges of graphene flakes were reported in Ref. [5].

4 Heat conduction in graphene: Contributions of different phonon branches. An interesting open question in the theory of thermal conductivity of graphene is relative contributions to heat transport by the LA, TA, andZA phonon modes. There have been opposite view expressed to the importance of ZA phonons, from negligible [5, 26–29], to dominant [7, 35, 36]. The argument for the strong contributions of ZA modes is made on the basis of a selection rule in ideal graphene, which restricts the phase space for phonon – phonon scattering, and make graphene ZA modes long lived [7, 35, 36]. The argument against contributions states that ZA modes have large Gruneneisen parameter $\gamma$ [5, 26–29] and zero group velocity near zone center resulting in negligible contribution to heat transport. We also note that placing graphene on substrate or accounting for corrugations would break the symmetry of graphene lattice and allow for ZA modes scattering. However, a conclusive answer to the question of relative phonon mode contributions may take time, considering that after almost a century of investigations there are still debates about relative contributions of LA and TA phonons in conventional semiconductors. It is difficult to determine experimentally what phonon branches contribute the most. The measurements of temperature dependence of thermal conductivity alone cannot present an evidence in favor of one or the other dominant phonon contribution because $K(T)$ dependence in graphite is known to depend strongly on the material quality [37, 38].

One should also keep in mind that stress and strain distributions in suspended graphene as well as interactions with the substrate of supported graphene can lead to the phonon modes renormalization and corresponding changes in their contributions to thermal transport. The presence of strain is one possible factor in observed differences in experimental values for thermal conductivity of the suspended graphene membranes of different sizes and shapes.

Along with the Boltzmann transport equation and RTA models thermal conductivity of graphene was studied using MD simulations. The first equilibrium and non-equilibrium MD simulations determined $K \approx 6600 \text{ W/mK}$ for (10,10) carbon nanotube (CNT) and even a higher $K \approx 9000 \text{ W/mK}$ for graphene near RT [33]. It was noted that once graphene layers are stacked in graphite, the interlayer interactions quench $K$ of the system by an order of magnitude [33]. In the last few years, a number of MD studies, with Tersoff and Brenner potentials, addressed heat conduction in graphene nanoribbons (GNR) with various length, edge roughness, and defect concentration [6, 8–13, 35, 39]. A recent MD study found $K \approx 8000–10000 \text{ W/mK}$ at RT for square graphene sheet [6]. For the ribbons with fixed $L=10\text{ nm}$ and width $W$ varying from 1 to 10 nm, $K$ increased from ~1000 to 7000 W/mK. Thermal conductivity in GNR with rough edges can be suppressed by orders of magnitude as compared to that in GNR with perfect edges [6, 9]. In Table 1 we summarize thermal conductivity calculated for graphene and CNTs using different theoretical approaches.

Table 1 Thermal conductivity of graphene and CNTs.

<table>
<thead>
<tr>
<th>sample</th>
<th>$K$ (W/mK) at RT</th>
<th>method$^a$</th>
<th>comments</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT</td>
<td>~6600</td>
<td>MD</td>
<td>$K_{\text{CNT}} &lt; K_{\text{graphene}}$</td>
<td>[33]</td>
</tr>
<tr>
<td>CNT</td>
<td>~3000</td>
<td>MD</td>
<td>strong defect dependence</td>
<td>[39]</td>
</tr>
<tr>
<td>SW-CNT</td>
<td>~2500</td>
<td>BTE</td>
<td>$K_{\text{CNT}} &lt; K_{\text{graphene}}$</td>
<td>[35]</td>
</tr>
<tr>
<td>graphene</td>
<td>2000–5000</td>
<td>VFF, BTE, $\gamma(q)$</td>
<td>strong width dependence</td>
<td>[5]</td>
</tr>
<tr>
<td>graphene</td>
<td>1000–5000</td>
<td>RTA, $\gamma_{\text{TA}}, \gamma_{\text{LA}}$</td>
<td>strong size dependence</td>
<td>[29]</td>
</tr>
<tr>
<td>graphene</td>
<td>8000–10000</td>
<td>MD, Tersoff</td>
<td>square graphene sheet</td>
<td>[6]</td>
</tr>
<tr>
<td>graphene</td>
<td>1400–3400</td>
<td>BTE</td>
<td>length dependence</td>
<td>[7]</td>
</tr>
<tr>
<td>graphene</td>
<td>~4000</td>
<td>ballistic</td>
<td>strong width dependence</td>
<td>[8]</td>
</tr>
</tbody>
</table>

$^a$VFF—valence force field, BTE—Boltzmann transport equation, RTA—relaxation time approximation, MD—molecular dynamics, $\gamma(q)$—Gruneneisen parameter dependent on the phonon wave vector, $\gamma_{\text{LA}}$ and $\gamma_{\text{TA}}$—Gruneneisen parameter averaged separately for LA and TA phonon modes. The RT thermal conductivity of high-quality crystalline bulk graphite is ~2000 W/mK.

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Another important question in the theory of thermal conductivity of low-dimensional carbon materials is what structures – CNT or graphene – have higher intrinsic thermal conductivity. A recent theoretical study [35] found that thermal conductivity of single-wall (SW) CNTs is always below that in graphene for SW-CNT with diameters above 1 nm. The calculation included contributions from all phonon modes – TA, LA, and ZA. Thermal conductivity of SW-CNTs was found to be gradually increasing with the diameter approaching the graphene value above 1 nm [35]. The calculated thermal conductivity of CNTs is a non-monotonic function of the diameter, which gives ~2500 W/mK at RT for \( L = 3 \mu m \). The ballistic limit for thermal conductivity of graphene was found to be as high as 12 800 W/mK. It is interesting to point out that the available experimental data for multi-wall (MW) CNTs [40, 41] demonstrated a different thermal conductivity dependence on the MW-CNT diameter for the examined diameters larger than 10 nm. The differences in physics of phonon transport in SW-CNTs and MW-CNTs and comparison with thermal properties of graphene were discussed in details in Ref. [42].

In the discussion of absolute values of thermal conductivity of graphene and CNTs (see Table 1) and their comparison with graphite, one should remember about ambiguity related to a definition of the graphene thickness \( h \). Most studies used \( h = 0.34 \) nm defined by the carbon-bond length. However, this definition is not unique (a related problem in CNTs is referred to as Yakobson paradox) [43, 44]. One can introduce \( h \) from the inter-atomic potential or start from Young’s modulus and tensile strength obtaining \( h \) in the relatively large range. The latter can affect comparison of thermal conductivity of graphene with that of bulk graphite value [5]. However, consistent use of \( h = 0.34 \) nm allows for comparison of the theoretical and experimental results obtained for graphene in different groups.

5 Conclusions We have shown that the use of an arbitrary low-bound cut-off for the phonon frequency in the thermal conductivity integral for graphene leads to erroneous results. The relative contributions of the LA, TA, and ZA phonon modes to thermal transport in graphene were also discussed. Theoretical thermal conductivity data for graphene obtained by different techniques was summarized and compared with those for CNTs.

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