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Convergent and Lower-than-diamond Thermal Conductivity in Pristine Graphene

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The thermal conductivity of monolayer graphene is widely believed to surpass that of diamond even for few-micron size samples and was proposed to diverge with system size. Here, we predict the thermal conductivity from first principles by considering four-phonon scattering, phonon renormalization, an exact solution to phonon Boltzmann transport equation (BTE), and an unprecedented sampling grid. We show that at room temperature the thermal conductivity saturates at 10 μm size and above and converges to 1300 W/(m·K), which is lower than that of diamond. This indicates that four-phonon scattering overall contributes 57% to the total thermal resistance and becomes the leading phonon scattering mechanism over three-phonon scattering. On the contrary, considering three-phonon scattering only yields higher-than-diamond values and divergence with size due to the momentum-conserving normal processes of flexural phonons.

Graphene is a subject of extensive research due to its unique properties and exotic transport phenomena observed [1–6]. Among them, many experimental and theoretical studies have shown that the thermal conductivity (κ) of graphene surpasses that of diamond even for small samples of few-micron size [7–11] and some suggest that it diverges with the system size [12]. Several other experiments reported lower thermal conductivity values, which were commonly attributed to defects and impurities [13–15]. Moreover, the uncertainty of these measurement is usually too large to conclusively assess whether κ is higher than that of diamond or not. Sources of uncertainty include optical absorption [13], and strong nonequilibrium among different phonon modes [16, 17], and others.

The studies of thermal transport in graphene have yielded several new insights associated with 2D materials, supporting graphene’s high and divergent thermal conductivity. By coupling the linearized phonon Boltzmann transport equation (BTE) with empirical potential [8] or first principles [9] at three-phonon (3ph) level, it was found that the flexural phonons (ZA) [18] contribute significantly to κ and their 3ph scattering is greatly suppressed by a selection rule [8]. Due to strong momentum-conserving scattering (normal process), thermal conductivity didn’t converge for a system size of 50 μm , and the value for 10 μm size with boundary scattering at room temperature (~ 3000 W/(m·K)) are in accordance with another theoretical study at 3ph level [10] that reports ~ 2500 W/(m·K) for 10 μm sample. On the other hand, while acknowledging the out-of-plane vibrations, it has been proposed [12] that graphene resembles 2D nonlinear lattice that was extended from the Fermi-Pasta-Ulam-Tsingou (FPUT) model [19]. Therefore, the heat transport is non-Fourier [20] and κ should diverge with system size as $\kappa_{2D} \propto \log(L)$ [21, 22].

However, questions were raised recently whether these insights represent the complete physics of thermal transport in graphene. In particular, can higher-order phonon

scattering be neglected in graphene, considering that the 3ph scattering is restricted in graphene and four-phonon (4ph) scattering has been found to be important in other solids [23–26]? Also, is it sufficient to explain the behavior of graphene in terms of 2D lattice model considering that it is actually only a quasi-2D system with out-of-plane atomic vibrations? To answer these questions, Feng and Ruan [27] computed 4ph scattering rates with empirical potential and showed strong 4ph effect in ZA mode and consequently, obtained a system size-convergent and greatly reduced κ of around 800 W/(m·K). The sampling grid accessible there was relatively coarse. Gu *et al.* further incorporated phonon renormalization into this calculation with empirical potential and argued that ZA scattering rates are reduced by temperature modification [28]. However, the empirical interatomic potentials used in these studies do not accurately represent chemical bonds, and the exact role of four-phonon scattering and the value of κ remain elusive. Another mainstream approach is molecular dynamics (MD) with two different flavors in equilibrium (EMD) and nonequilibrium (NEMD) treatments. In theory, MD approach is expected to capture all orders of anharmonicity. However, the EMD simulations show size-converged κ ranging from 1000 to 2000 W/(m·K) [29–31] while the NEMD simulations show logarithm length dependence up to several microns [12, 32]. Interestingly, one MD study presents a saturation of κ when L is extended to 100 μm [33]. Besides these inconsistencies, MD simulations also suffer from the classical phonon statistics and empirical potentials, hence, the results can only be interpreted qualitatively.

Summarizing all existing studies, the thermal conductivity of pristine suspended monolayer graphene is currently widely perceived, both experimentally and theoretically, to be around 3000 W/(m·K) even for samples of few-micron size and higher than that of diamond and graphite. On the other hand, the lower values as seen in some other experiments and simulations were thought

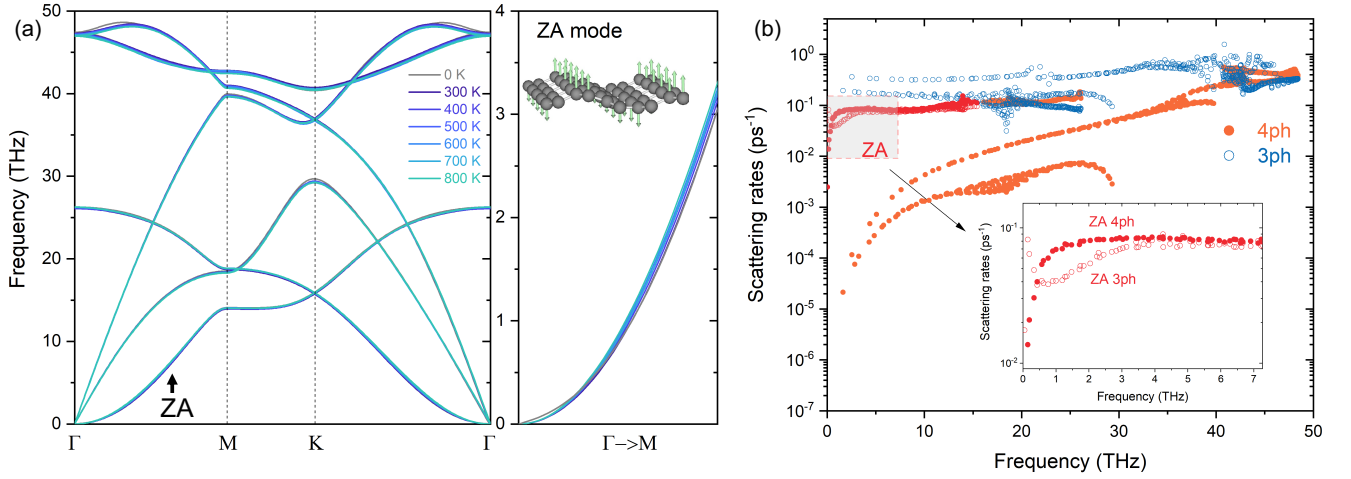


FIG. 1. Phonon self-energy in graphene. (a) Phonon dispersion at finite temperatures by TDEP method. Dispersion at 0 K is obtained by density functional perturbation theory. The right panel is a zoom-in plot of ZA mode dispersion from Γ to M in the Brillouin Zone. Schematic of ZA out-of-plane vibrations is created by an online visualization tool [34]. (b) Spectral phonon scattering rates at 300 K. The scattering rate in y -axis is presented in logarithm scale. Three-phonon ($\tau_{3\text{ph}}^{-1}$) and four-phonon scattering rates ($\tau_{4\text{ph}}^{-1}$) are shown in hollow and filled circles, respectively. The scattering rates of ZA mode are marked in red and zoomed-in in the inset.

to be due to defects or impurities, or considered as inconclusive due to large uncertainty in experiments and inaccuracies in simulations. In this Letter, we revisit the thermal conductivity of graphene with first-principles-computed four-phonon scattering, phonon renormalization, an exact solution to phonon Boltzmann transport equation (BTE), and unprecedented sampling grid. We show that the thermal conductivity, contrary to popular perception, saturates at 10 μm and converges at a room temperature value of 1300 W/(m·K), which is lower than that of diamond. This represents a factor of 2.31 reduction from 3000 W/(m·K) and indicates that four-phonon scattering becomes the leading phonon scattering mechanism. The considerations of both four-phonon scattering [23, 24] and phonon renormalization [35–38], which form the unified approach [39, 40], have successfully explained the Raman linewidth of suspended graphene in our prior work [41]. Here, we extend the methodology to all phonon modes for thermal conductivity prediction. The phonon BTE is exactly solved by an iterative scheme [42] incorporating both three-phonon and four-phonon scattering after we manage to store the iterative processes within one terabyte memory space accessible in modern supercomputer architecture. We compute from first principles that ZA mode has strong four-phonon scattering rates which are comparable to three-phonon counterpart. The sampling grid (q -mesh) is carefully checked for κ convergence of infinitely long graphene sample and we see convergence of thermal conductivity after including four-phonon scattering ($\kappa_{3\text{ph}+4\text{ph}}$) but not with three-phonon scattering ($\kappa_{3\text{ph}}$) only. Our findings challenge the perception of graphene being a better heat conductor than diamond, and will motivate future exper-

imental validation efforts.

Our first-principles calculations are based on density functional theory as implemented in the VASP package [43]. The phonon renormalization effect is included by a temperature-dependent effective potential method (TDEP) [36] to compute temperature-dependent phonon dispersions and interatomic force constants (IFCs) [38]. Phonon scattering rates summed up by Matthiessen's rule [44] $\tau_{\lambda}^{-1} = \tau_{\lambda,3\text{ph}}^{-1} + \tau_{\lambda,4\text{ph}}^{-1} + \tau_{\lambda,\text{iso}}^{-1}$ are computed by our FOURPHONON code [45], an extension module to SHENGBTE package [46]. The exact solution of BTE is implemented in the same solver by a shared-memory parallel computing strategy [47].

The computed phonon dispersion and phonon scattering rates are presented in Fig. 1(a) and 1(b), respectively. Overall, graphene is quite rigid as shown by very small change of phonon frequency at finite temperatures (see Fig. 1(a)). The frequency of in-plane optical phonons decreases with increasing temperature, a signature that has been analyzed and experimentally verified in our prior work [41]. Contrary to the decreasing trend of frequency shift for in-plane optical phonons, we find that the flexural phonons are hardened with rising temperature (see Fig. 1(a) right panel). This is a result of the coupling between flexural phonons and in-plane degrees of freedom in free-standing graphene [18]. Renormalized flexural phonons do not have a strictly quadratic dispersion. With the renormalized phonon dispersion and temperature-dependent IFCs, one can then compute the spectral phonon scattering rates τ_{λ}^{-1} using Fermi's golden rule, as shown in Fig. 1(b). Interestingly, the optical phonons and flexural phonons show comparable or even higher four-phonon scattering rates ($\tau_{4\text{ph}}^{-1}$) with

three-phonon counterpart ($\tau_{3\text{ph}}^{-1}$), while the rest of phonon modes are dominated by three-phonon scattering. Optical phonons having large $\tau_{4\text{ph}}^{-1}$ are understood as they easily satisfy the energy conservation in the recombination scattering events: $\lambda_1 + \lambda_2 \rightarrow \lambda_3 + \lambda_4$ [48]. On a different ground, the reason for the flexural phonons lies in the selection rule for general quasi-2D systems [8] that only even numbers of flexural phonons can be involved in a phonon scattering event due to reflection symmetry. As a result, the phase space for three-phonon scattering is much smaller than that of four-phonon scattering [27]. The ZA mode was considered as the major heat carrier in graphene under the 3ph scattering picture [8, 9, 49], this statement needs to be re-examined after its strong $\tau_{4\text{ph}}^{-1}$ is included.

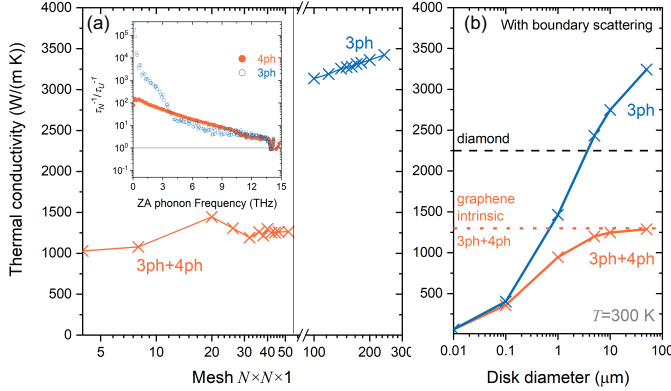


FIG. 2. Convergence of thermal conductivity of graphene at room temperature. (a) Convergence with respect to mesh size without boundary scattering. Mesh size in x -axis is presented in logarithm scale. The inset shows the ratio of ZA mode scattering rates from normal (τ_N^{-1}) and Umklapp processes (τ_U^{-1}) for both 3ph (hollow blue dots) and 4ph channels (filled orange dots). (b) Size-dependent thermal conductivity with boundary scattering under 3ph and 3ph+4ph theories.

We next solve for the intrinsic thermal conductivity by an iterative scheme [42] to account for the collective phonon excitations. This approach distinguishes the normal processes (N) that are momentum-conserving and Umklapp processes (U) that are resistive. Such a treatment is important for graphene since it has strong normal scattering process associated with its phonon hydrodynamics nature [50, 51]. The coupled equations are presented in the Supplemental Material [52]. For the BTE solution to generate meaningful results, one has to check the convergence of κ with respect to the sampling grid in the Brillouin Zone (q -mesh). A convergence being reached means that an infinitely large system has finite thermal conductivity. Figure 2 shows our test of convergence when 3ph or 3ph+4ph is included in the calculations. Mesh size $N \times N \times 1$ is uniform in-plane. In all these calculations, the energy broadening factor is unity to ensure the accuracy within our computational power. We find that with four-phonon scattering, $\kappa_{3\text{ph}+4\text{ph}}$ con-

verges around a mesh size of $N = 40$ and further increasing the mesh to $N = 52$ does not change the value of κ . In contrast, $\kappa_{3\text{ph}}$ does not reach convergence up to $N = 240$ and scales logarithmically with mesh size N . Note that the prior work [10] used $N = 128$ for 3ph. To illustrate the impact on practical samples of finite size, we plot the size-dependent thermal conductivity in Fig. 2(b) by adding a boundary scattering term [9, 10]: $\tau_{\lambda,b}^{-1} = |\mathbf{v}_\lambda|/L$, where $\mathbf{v}_\lambda$ is the group velocity of phonon mode λ and L is the disk diameter. The 3ph and 3ph+4ph results start to show considerable difference when the size is larger than $0.1 \mu\text{m}$. At 3ph+4ph level, κ would reach the intrinsic limit at around $10 \mu\text{m}$ while 3ph curve does not converge even for $50 \mu\text{m}$. To inspect the origin of this behavior, we decompose the N/U scattering for ZA mode and plot the ratio of two types of scattering events τ_N^{-1}/τ_U^{-1} in the inset of Fig. 2(a). Apart from the dominant role of normal process for both scattering channels, it is to a lesser degree for four-phonon scattering of flexural phonons at low frequencies. Given the fact that τ_N^{-1} decreases when $\omega \rightarrow 0$, we conclude that 3ph of long wavelength flexural phonons is almost entirely contributed by normal processes. The extreme case is the heat conduction in 2D nonlinear lattice where all scattering processes are momentum-conserving [22] and the thermal conductivity is logarithmic divergent. Thus, we explain the finite intrinsic thermal conductivity of graphene from two related arguments: one, four-phonon scattering provides an additional scattering channel; two, for long wavelength phonons, four-phonon scattering has considerable number of resistive U scattering events but three-phonon processes are nearly all N scattering events implying a divergence. Our numerical results share similarities with a theoretical work on carbon nanotube (CNT) [53] where the authors estimated that third-order anharmonicity leads to a divergence of thermal conductivity due to vanishing scattering of long wavelength phonons. They empirically showed that higher order process can remove such divergence. While the study on CNT is worth further investigations [54–56], we show here that four-phonon scattering converges the thermal conductivity of graphene from first principles.

The above arguments can further be seen in the spectral κ (Fig. 3(a)) where we find a singularity for near-zero frequency phonons at 3ph level but not at 4ph level. The 3ph and 3ph+4ph pictures have distinct spectral trend for low-frequency phonons. While the 3ph+4ph calculation can saturate the spectral κ when $\omega \rightarrow 0$, the 3ph only calculation shows a up-soaring spectral trend. In addition, we analyze the ZA mode contribution to κ , as shown in Fig. 3(b). At 3ph level with $N = 180$, the ZA contribution is $2833 \text{ W/(m}\cdot\text{K)}$ and 85%. After including 4ph scattering, the ZA contribution becomes $949 \text{ W/(m}\cdot\text{K)}$ and the percentage reduces to 73% for intrinsic graphene. The argument that ZA modes are the major heat carriers in graphene [8, 9] still holds. Note

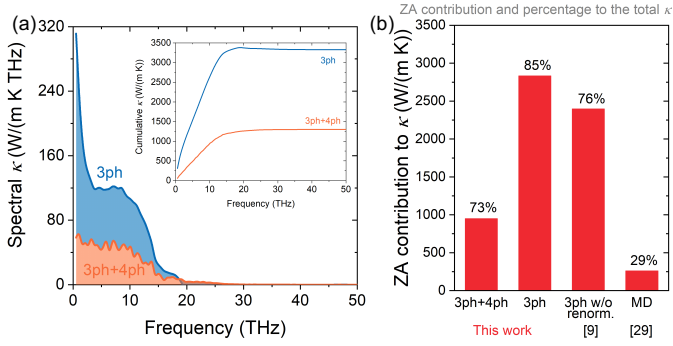


FIG. 3. Spectral and mode contribution. (a) Spectral contributions to κ of graphene at room temperature without boundary scattering. The inset shows the cumulative thermal conductivity as a function of phonon frequency. (b) ZA phonons contribution to κ and its percentage at room temperature, and comparison to first-principles at 3ph (renorm. stands for phonon renormalization that was not included before) [9] and MD work [29]. In both plots, the 3ph case presented here is calculated at $N = 180$ without boundary scattering, and note that it is not converged with N .

that our first-principles result is different from previous MD work [29]. Despite the fact that MD gives a total κ around 1000 W/(m-K), it estimates the ZA mode contribution to be only one third of total κ . This could be due to the classical statistics that overpopulates the non-ZA phonon branches.

Finally, we present the calculated thermal conductivity of graphene as a function of temperature and some comparisons to other carbon allotropes in Fig. 4. Our results κ_L at 3ph level for 10 μm size graphene with boundary scattering are consistent with prior first-principles studies [9, 10] and we see small impact from phonon renormalization (see Supplemental Material [52] for comparison without renormalization). The comparison in Fig. 4(a) shows that incorporating 4ph in the calculation significantly reduces $\kappa_{3\text{ph}}$. Nevertheless, our results of $\kappa_{3\text{ph}+4\text{ph}}$ are significantly higher than previous simulation with empirical potential at moderate mesh size [27]. This indicates that the optimized Tersoff potential probably overestimates the 4th-order anharmonicity of the ZA phonons. At room temperature and without boundary scattering, we predict that $\kappa_{3\text{ph}+4\text{ph}} = 1298$ W/(m-K). This represents a factor of 2.31 reduction from 3000 W/(m-K) and indicates that 4ph scattering overall contributes 57% to the total thermal resistance and becomes the leading phonon scattering mechanism over 3ph scattering. As a result, the thermal conductivity of graphene is lower than that of diamond from 300 K to 800 K. The first-principles results for diamond (green and black lines in Fig. 4(a)) are from Ref. [24, 39] where similar methodologies were applied including 3ph/4ph scattering, phonon renormalization and iterative solution to BTE. The comparisons show that both 4ph scatter-

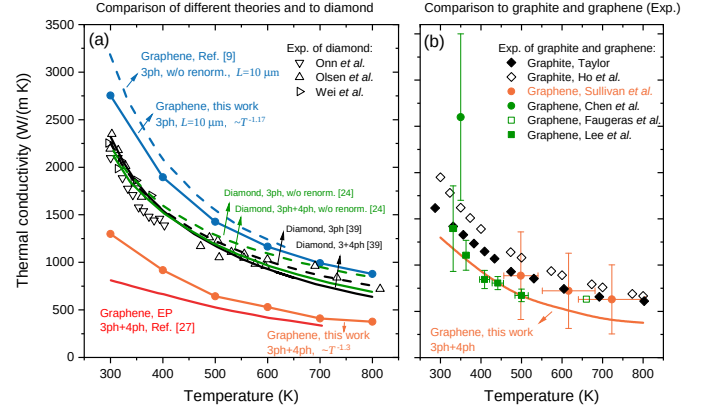


FIG. 4. Thermal conductivity of graphene as a function of temperature. (a) Prior theoretical work with empirical potential (EP) and four-phonon scattering [27] is presented in red solid line. Our results are presented in connected solid lines with orange (3ph+4ph) and blue (3ph scattering only) and a boundary scattering of $L = 10$ μm). Also, a prior first-principles 3ph work with boundary scattering [9] is shown in dashed blue line. Computational results for diamond without renormalization [24] and with renormalization [39] are presented in green and black lines, respectively (3ph results in dashed lines and 3ph+4ph results in solid lines). Several experiments on diamond are also plotted here (right-pointing triangles [57], triangles [58], inverted triangles [59]). (b) Our results compared to a recent Raman measurement on suspended graphene [17] (filled orange circles) and other previous Raman measurements (green filled circles [13], open squares [14], filled squares [15]), and experiments on graphite [60, 61] (black diamonds).

ing and phonon renormalization effect are not significant in diamond. Note that the thermal conductivity of diamond is well received, with good agreements between simulations and experiments [57–59, 62]. In contrast, the measured thermal conductivity values of graphene so far have shown a large spread. While our finding challenges a popular perception that graphene is a better heat conductor than diamond, the numerical results are self-consistent with advancements in theories and computational power. Under current computational formalism, a plausible reason for this observation is that diamond does not have strong four-phonon scattering for acoustic modes [24, 39] but flexural phonons in graphene do have large four-phonon scattering rates originated from its 2D nature. In this sense, the reduction of κ from diamond to graphene is understandable. Interestingly, the comparison between diamond and graphene singles out the effect of the dimensionality, which contributes through flexural phonons. Going from 3D (bulk) to quasi-2D case, one of the transverse acoustic vibrations shifts from a linear to a quadratic dispersion relation and its 3ph scattering is restricted by the selection rule while 4ph scattering becomes significant. Also, because of this selection rule, 5th-order term as an odd term should also be re-

stricted. Since higher-order term generally has smaller coupling matrices, we also expect 6th-order term and all other even-order terms to be negligible for the case of graphene.

In Fig. 4(b), we also cautiously compare our results to a recent Raman measurement on suspended graphene sample (in orange) [17] that is based on apparent phonon temperature, and show the estimated κ from previous Raman measurements (in green) [13–15]. Large spread and uncertainty of measured data are observed. It should be noted that some experimental data in Fig. 4(b)) appear to agree with our results in certain temperature range. However, they cannot be considered as having supported our prediction over the entire temperature range yet, because the uncertainty was too large to draw a conclusion whether κ is higher or lower than that of diamond, and/or the measurements were performed on non-pristine graphene. Future measurements on pristine graphene with significantly reduced uncertainty are needed to test our prediction. Another consequence of our results is that the predicted graphene thermal conductivity is lower than experimentally reported κ of graphite [60, 61] (Fig. 4(b)). Theoretical study on graphite considering both four-phonon scattering and phonon renormalization is not seen in literature yet. Future studies could be focusing on the layer-dependent transport behavior of multilayer graphene and graphite. We expect such comparison may motivate further experimental efforts to fully resolve the intriguing finding here. A tentative explanation might be that in bulk phase graphite the four-phonon scattering of ZA mode is suppressed by interlayer interactions. Also, the previous 4ph modeling [27] suggests that in graphite four-ZA scattering phase space is reduced by 16 times compared to graphene and one may expect 4ph scattering to be weak.

In summary, we conduct a first-principles study on the thermal conductivity of monolayer graphene. Our calculations include four-phonon scattering, phonon renormalization effect and the exact solution to BTE, all of which are state-of-the-art computational formalism. Our methods can reveal both phonon properties, their detailed scatterings and eventually the thermal conductivity of graphene over a wide range of temperature. Our results in this work provide a strong computational evidence of κ convergence to date. We expect our study to inspire further experimental efforts on graphene and theoretical understanding on general low-dimensional systems.

Detailed formalism, along with phonon mean free path and comparison to prior studies are presented in the Supplementary Material [52] (see also Refs. [63–65] therein). We are grateful to the insightful discussions with Professor Li Shi at the University of Texas at Austin. X. R. and Z. H. were supported by the U.S. National Science Foundation (No. 2015946 and No. 2321301). Simulations were performed at the Rosen Center for Advanced Computing

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