12-1-2011

On the accuracy of classical and long wavelength approximations for phonon transport in graphene

Dhruv Singh
Purdue University, singh36@purdue.edu

Jayathi Murthy
Birck Nanotechnology Center, Purdue University, jmurthy@purdue.edu

Timothy S. Fisher
Birck Nanotechnology Center, Purdue University, tsfisher@purdue.edu

Follow this and additional works at: http://docs.lib.purdue.edu/nanopub

Part of the Nanoscience and Nanotechnology Commons

http://dx.doi.org/10.1063/1.3665226

This document has been made available through Purdue e-Pubs, a service of the Purdue University Libraries. Please contact epubs@purdue.edu for additional information.
On the accuracy of classical and long wavelength approximations for phonon transport in graphene
Dhruv Singh, Jayathi Y. Murthy, and Timothy S. Fisher

Citation: J. Appl. Phys. 110, 113510 (2011); doi: 10.1063/1.3665226
View online: http://dx.doi.org/10.1063/1.3665226
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v110/i11
Published by the AIP Publishing LLC.

Additional information on J. Appl. Phys.
Journal Homepage: http://jap.aip.org/
Journal Information: http://jap.aip.org/about/about_the_journal
Top downloads: http://jap.aip.org/features/most_downloaded
Information for Authors: http://jap.aip.org/authors

ADVERTISEMENT
On the accuracy of classical and long wavelength approximations for phonon transport in graphene

Dhruv Singh, a) Jayathi Y. Murthy, and Timothy S. Fisher
School of Mechanical Engineering and Birck Nanotechnology Center, Purdue University, West Lafayette, Indiana 47907, USA

(Received 18 August 2011; accepted 29 October 2011; published online 5 December 2011)

This paper presents a critical evaluation of the approximations usually made in thermal conductivity modeling applied to graphene. The baseline for comparison is thermal conductivity computations performed using a rigorous calculation of three-phonon scattering events and accounting for the anharmonicity of interatomic forces. Three central assumptions that underlie published theories are evaluated and shown to compromise the accuracy of thermal conductivity predictions. It is shown that the use of classical phonon occupation statistics in place of the Bose-Einstein distribution causes the overprediction of specific heat and the underprediction of phonon relaxation time; for ZA phonons, the classical approximation can underpredict the relaxation time by a factor of approximately 2 at room temperature across a broad frequency band. The validity of the long wavelength (Klemens) approximation in evaluating the strength of phonon scattering events is also examined, and the findings indicate that thermal conductivity is significantly underpredicted when long-wavelength approximations are made, with the most significant discrepancy occurring for ZA phonons. The neglect of Normal processes in thermal conductivity computations is evaluated and shown to produce a diverging thermal conductivity with increasing size. © 2011 American Institute of Physics. [doi:10.1063/1.3665226]

I. INTRODUCTION

Carbon nanotubes and graphene have emerged as attractive choices for nanoelectronics due to their superior electron mobility1–5 and thermal conductivity and low levels of power dissipation.6,7 As a two-dimensional solid, graphene has enabled the study of interesting physics in truly low-dimensional systems.8,9 In recent years, several experimental measurements of the thermal conductivity of suspended10–13 and supported14,15 single- and multi-layer graphene have been reported. Notwithstanding a small spread in the measured data, all thermal conductivity measurements of free-standing graphene and carbon nanotubes (CNTs) have consistently shown significantly higher thermal conductivity than that of either diamond or graphite.

However, despite their promise, there are several bottlenecks regarding the use of graphene and carbon nanotubes for thermal applications. CNTs and graphene suffer from high thermal contact resistance with substrates16 and host materials in composites, making it challenging to retain their superior performance in practical applications. Although phonons in graphitic materials show a high group velocity and thermal conductivity,17,18 the restrictive phonon decay pathways impose a bottleneck in the transfer of energy to ZA phonons, which are the primary heat carriers,19,20 an important consideration for heat dissipation in graphene-based nanoelectronics.21,22 Therefore, the engineering of graphene devices in order to exploit graphene’s superior thermal properties requires a firm quantitative understanding of phonon transport.

Following the publication of experimental measurements, several theoretical and computational reports on phonon transport in graphene have appeared. These have primarily been divided between the use of molecular dynamics23–26 and the Boltzmann transport equation14,19,27–29 (BTE) under different approximations. Although all these studies predict room temperature thermal conductivity of graphene in the same range (and relatively close to the results of experiments), they differ significantly in their details and draw inconsistent and often conflicting conclusions.

Calculations of phonon scattering using the BTE under the relaxation time approximation28–31 have generally concluded that heat is primarily carried by LA/TA phonons in graphene at room temperature. These calculations also show a strong dependence of the thermal conductivity on the sample dimensions. Another set of calculations using the linearized BTE have questioned the applicability of the relaxation time approximation in graphene19,20,27 and conclude that heat conduction is dominated by the out-of-plane ZA phonons. These conflicts arise from a combination of approximations for the strength of phonon scattering processes, an ad hoc description of selection rules, the exclusion of N scattering processes, and the use of the relaxation time approximation.

MD calculations directly simulate phonon heat conduction accounting for atomic structure and anharmonic
interactions up to all orders. Although its use is widespread in thermal conductivity predictions, classical MD does not incorporate the quantum statistics that can be essential to the accurate computation of phonon transport and thermal conductivity. Predictions from published MD simulations show significant spread in thermal conductivity, varying from 400 W/m K to 10 000 W/m K, depending on the simulation methodology and the interatomic potential used. To the best of our knowledge, there is no published work outlining the spectral phonon transport properties of graphene from MD simulations. The prediction of thermal conductivity is mediated by size effects and the use of classical approximations. Because these effects are not separately delineated, it is difficult to make direct comparisons of MD simulations and BTE-based calculations.

Empirical expressions for scattering rates used in thermal conductivity modeling often approximate the Bose-Einstein phonon occupation statistics, \( n_0 = 1 / (\exp(h\nu/k_B T) - 1) \), by their classical limit, \( n_0 = k_B T / h\nu \). This is valid only when \( h\nu/k_B T \ll 1 \), i.e., at high temperatures (strictly speaking, temperatures greater than the Debye temperature \( \theta_D \) of the solid) or, conversely, at low frequencies. More significantly this approximation is inherent to classical molecular dynamics. Traditional molecular dynamics simulations have been relatively accurate for silicon\(^{32-34} \) because most of the thermal transport is by low frequency acoustic phonons. Because carbon is a much lighter element than Si but has a comparable bond strength, phonon frequencies are significantly higher, with \( \theta_D \sim 2000 \) K. One expects, therefore, that the use of molecular dynamics and classical approximations should be erroneous for computing the thermal properties of graphene. Traditionally, some of these issues have been circumvented via the use of quantum corrections to the system temperature. Recently Turney et al.\(^{35} \) have shown that a system-level quantum correction to the temperature is inaccurate because the quantum-corrected temperature is inherently frequency dependent. Therefore, the use of the classical approximation for graphene must be questioned, and its impact on total and polarization-specific thermal conductivity predictions quantified.

Another approximation that is frequently made in computing scattering rates is the use of simplified matrix elements and interaction rules. Scattering rates can be derived directly from considerations of crystal anharmonicity. The widely used relaxation time expressions derived by Klemens\(^{30,36} \) are based on the classical approximation to the phonon occupation statistics and an isotropic long wavelength approximation to the matrix elements. Furthermore, Klemens also makes heuristic arguments to determine the energy conservation surface. These two approximations are widely used in thermal conductivity modeling of bulk semiconductors such as Si and Ge.\(^{37} \) Recently, Balandin et al.\(^{11,28} \) relaxed some of the assumptions in modeling the thermal conductivity of graphene, i.e., they did not resort to an \textit{ad hoc} description of the energy conservation surface and included phonon occupation accurately. However, the use of Klemens-like matrix elements (with mode-wise phonon Gruneisen parameters) for three-phonon scattering was retained. This led to the conclusion that in-plane phonons dominate thermal conductivity. In Klemens’s original mono-
The aim of this paper is therefore to systematically evaluate the consequences of each approximation listed above for graphene. To test the validity of the classical approximation and Klemens matrix elements for three-phonon scattering rates, we adopt the single mode relaxation time approximation. In this case, the thermal conductivity depends only on the equilibrium occupation of the interacting phonons. Most of the results in this paper are presented for a graphene sheet in a Corbino membrane geometry with a diameter \( d = 10 \, \mu m \), except for the section on size dependence (which is used to illustrate the failure of including only \( U \) processes as resistive). We systematically analyze the effects of the following approximations on thermal conductivity computation:

1. The use of classical phonon statistics in place of Bose-Einstein statistics,
2. The use of isotropic matrix elements derived from the long wavelength approximation by Klemens,\(^{36} \) and

The results are compared to those computed from the solution of the linearized BTE with phonon scattering strengths computed using anharmonic interatomic force constants. The formulation does not approximate three-phonon scattering processes as resistive. We systematically analyze the effects of the following approximations on thermal conductivity:

II. THEORY AND MATHEMATICAL FORMULATION

From the knowledge of the phonon dispersion relationship (shown in Fig. 1 for single-layer graphene), the volumetric specific heat contribution from each phonon polarization \( C_v(p) \) can be calculated as

\[
C_v(p) = \frac{1}{V} \frac{\partial}{\partial \mathbf{P}} \sum_k h\omega_p n^0(\omega_p, T) = \frac{1}{c_0} \frac{\partial}{\partial T} \int h\omega_p \frac{dk_x dk_y}{e^{h\omega_p/k_B T} - 1} \left( \frac{2\pi}{k_0} \right)^2, \tag{1}
\]

where \( \mathbf{k} \) is the phonon wave vector, \( \omega_p \) is the phonon frequency with polarization \( p \), \( n^0 \) is the equilibrium phonon occupation at temperature \( T \), \( k_B \) is the Boltzmann constant, and \( c_0 = 3.41 \, \text{Å} \) is the interlayer spacing in graphite. The total specific heat can be calculated by summing over all polarizations. The phonon relaxation time for mode \( \mathbf{k}(p) \) can be calculated by summing over all scattering events that satisfy momentum and energy conservation as

\[
\tau_{\mathbf{k}(p)} = \frac{1}{\tau_{B}(\mathbf{k}(p)) + \frac{A}{2\pi h^2}} \times \left\{ \sum_{p',p''} \left( n^0_{\mathbf{k}(p')} - n^0_{\mathbf{k}(p'')} \right) \left| \mathcal{M}_{\mathbf{k}(p)\mathbf{k}(p')} \right|^2 \frac{dk_{\mathbf{k}'}^n}{dk_{\mathbf{k}'}^n} + \frac{1}{2} \sum_{p',p''} \left( n^0_{\mathbf{k}(p')} + n^0_{\mathbf{k}(p'')} + 1 \right) \left| \mathcal{M}_{\mathbf{k}(p)\mathbf{k}(p')} \right|^2 \frac{dk_{\mathbf{k}'}^n}{dk_{\mathbf{k}'}^n} \right\}, \tag{2}
\]

where \( \tau_{B}(\mathbf{k}(p)) \) is the relaxation time due to boundary scattering, the first sum on the right side corresponds to type 1 three phonon scattering processes \( (\omega + \omega'(p') - \omega''(p'')) = 0 \), and the second sum corresponds to type 2 three phonon scattering processes \( (\omega - \omega'(p') - \omega''(p'')) = 0 \). Here, \( k_{\mathbf{k}'}^n \) is the wave vector along line segments in the graphene Brillouin zone on which scattering events are allowed. The factor \( \mathcal{M}_{\mathbf{k}(p)\mathbf{k}(p')} \) represents the strength of the matrix element for phonon scattering and relates the crystal anharmonicity to the corresponding phonon eigenvectors. The computation of admissible phonon scattering events and their strengths is described elsewhere.\(^{19,20,38} \) The harmonic and anharmonic interatomic force constants are evaluated using the Tersoff interatomic potential\(^{46} \) with the parameterization of Lindsay and Broideo.\(^{47} \) Thermal conductivity under the SMRT approximation can be calculated from the knowledge of mode-wise specific heat, group velocity, and phonon relaxation times. In the \( x \)-direction, for example, we may write the thermal conductivity as

\[
\kappa = \frac{1}{c_0} \sum_p \int \frac{\partial}{\partial T} \frac{h\omega_p}{e^{h\omega_p/k_B T} - 1} v^2_{\mathbf{k}(p)} \tau_{\mathbf{k}(p)} \frac{dk_x dk_y}{(2\pi)^2}, \tag{3}
\]

where the summation is over all phonon polarizations. Although the SMRT approximation is widely used in thermal conductivity modeling, it is only a first-order approximate solution to the phonon BTE and has been shown to be inadequate for thermal conductivity modeling in single/few-layer graphene\(^{20,27} \) and carbon nanotubes.\(^{43} \) Alternatively, thermal conductivity can be directly calculated by solving the phonon BTE for the shift in the phonon distribution \( \left( \frac{\partial n^0_{\mathbf{k}(p)}}{\partial T} \right) \Psi_{\mathbf{k}(p)} \nabla T \) due to a temperature gradient \( \nabla T \).
\[
\kappa = \sum_p \left\{ n_0^{(p)} \left( E_{cp}^{(p)} + 1 \right) \frac{\hbar \omega}{k_B T} \Psi_{cp}^{(p),x} \Psi_{cp}^{(p),x} \right\} \frac{dk_x dk_y}{(2\pi)^2} \tag{4}
\]

The thermal conductivity obtained under the SMRT approximation [using Eq. (3)] depends only on the equilibrium occupation of the interacting phonons and their interaction strength. Results obtained using Eq. (4) incorporate, in addition, the influence of non-equilibrium phonon populations when calculating the scattering rate. Consequently, to evaluate the effect of the classical approximation (Sec. III) and Klemens-like approximations (Sec. IV) of the Einstein distribution in Eqs. (1), (2), and (3). The corresponding matrix element for each interacting phonon triad is directly calculated from the anharmonicity of the interatomic potential. A comprehensive discussion on the failure of the SMRT for graphene is presented elsewhere and is not repeated in this paper.

III. CLASSICAL APPROXIMATION

We first look at the classical approximation. This involves the substitution of \( n_0 = k_B T / \hbar \omega \) for the Bose-Einstein distribution in Eqs. (1), (2), and (3). The corresponding matrix element for each interacting phonon triad is directly calculated from the anharmonicity of the interatomic potential.

A. Specific heat

Because it represents the total energy of the crystal weighted by the respective phonon population, the volumetric specific heat of the solid gives a good indication of the errors entailed in making the classical approximation to phonon occupation statistics. The specific heat is calculated using Eq. (1). The ratio of the computed specific heat using classical statistics and Bose-Einstein (BE) statistics is plotted in Fig. 2. We also plot the corresponding ratio of the mode-wise specific heat. The classical approximation clearly overpredicts the total specific heat by more than threefold at room temperature, but the error falls significantly beyond about 1000 K or so. Under the classical approximation, the specific heat contribution due to each phonon wavevector in the system is simply \( k_B T \) (the Dulong-Petit limit). At every temperature, this value is always greater than the corresponding value obtained from BE statistics, and they converge in the high-temperature limit. From Fig. 2, this convergence temperature for graphene is greater than 1500 K for most branches. However, due to the low frequencies of the ZA branch, its specific heat contribution does not pose significant errors beyond 500 K. The largest disagreement occurs for the optical phonon modes, and their specific heat as computed from the classical distribution can be an order of magnitude higher than their corresponding Bose-Einstein values at room temperature. This artifact also implies that optical phonons would lead to an unphysically high contribution to the total thermal conductivity when using the classical approximation.

B. Phonon relaxation time

Because the phonon scattering rate is strongly tied to the occupation of the interacting modes, and because the classical approximation overpredicts phonon occupation, we expect that the relaxation time for phonons will be smaller than that calculated from Bose-Einstein statistics. The equivalent relaxation time for phonons in the classical system can be obtained by replacing the factor \( n'_0 + n''_0 + 1 \) in the quantum system with \( n'_0 + n''_0 \) for type 2 processes. The occupation factor weighing type 1 processes remains the same, i.e., \( n'_0 - n''_0 \) [Eq. (2)]. The corresponding expressions in the classical limit are obtained by replacing the quantum occupation statistics \( n_0 \) with \( (n_0 - 1/2) \). The frequency-dependent relaxation time for each polarization can then be calculated as

\[
\tau_{\omega, p} = \frac{\int \tau_{cp}^{(p)} \delta(\omega - \omega_{cp}) \frac{dk_x dk_y}{2\pi^2}}{\int \delta(\omega - \omega_{cp}) \frac{dk_x dk_y}{2\pi^2}}. \tag{5}
\]

The ratio of computed phonon relaxation times (obtained from classical and quantum statistics) as a function of frequency is shown in Fig. 3 for temperatures in the range of 200–500 K. Figure 3(a) shows this ratio for ZA phonons, and Fig. 3(b) for LA phonons. For both ZA and LA phonons, the relaxation times from the classical approximation are significantly lower than those obtained from Bose-Einstein statistics. The decrease is understandable given that the classical approximation overpredicts the occupation of interacting phonons. The difference in computed relaxation times between the classical and BE statistics also decreases at higher frequencies (and higher temperatures). This is expected because the phonon occupation under the BE statistics tends toward the classical value as the temperature increases. The dependence on frequency can be explained by the fact that the phonon relaxation time of a particular...
phonon mode $\tilde{k}(p)$ is independent of its own population and dependent only on the population of the two other phonons involved in the scattering event. Phonons at higher frequencies tend to participate in a lot more type 2 three-phonon processes in which the interacting phonons have lower frequencies. The occupation of these low frequencies is not significantly different from the corresponding value under the classical approximation because $\hbar \omega/k_B T \ll 1$. This makes the relaxation time closer to that of the quantum system at higher frequencies.

This trend is clear for LA phonons but less so for ZA phonons, with which the ratio of these relaxation times does not show a very strong frequency dependence. This arises out of the intricacies of ZA phonon scattering. It has been found that ZA phonons scatter mostly through $ZA + ZA \rightarrow LA + TA$ processes. The absence of significant type 2 scattering channels thus implies that ZA phonons will suffer from the classical-versus-quantum discrepancy over the entire frequency range. On average, the classical approximation underpredicts the relaxation time of ZA and LA phonons by a factor of 2 at room temperature.

**C. Thermal conductivity**

The ratio of classical to quantum thermal conductivity (total and polarization-wise) is plotted in Fig. 4. Most notable, the total thermal conductivity obtained from the classical approximation does not deviate significantly from the corresponding quantum calculation over the temperature range investigated here. This is because even though the specific heat is overestimated, the corresponding relaxation time is underestimated with the classical approximation, leading to total thermal conductivity values similar to those of the corresponding quantum case. However, the failure of the classical approximation is immediately obvious when one looks at the polarization-wise decomposition of thermal conductivity and its variation with temperature. In general, significant errors exist in the thermal conductivity of all branches at room temperature. However, this difference decreases with temperature, as one would expect, and the relative error is low at 800 K. Furthermore, as expected, the classical approximation ascribes a significantly higher component to the optical modes; at room temperature, the ZO mode thermal conductivity is overpredicted by a factor of 3 or more. For the LO and TO modes, the ratio is over an order of magnitude larger at room temperature and remains larger than a factor of 2 even at 800 K.
TABLE I. Comparison of the thermal conductivity in W/(m.K) contribution of each phonon branch at 300 K for quantum and classical calculations.

<table>
<thead>
<tr>
<th>Polarization</th>
<th>Quantum</th>
<th>Classical</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZA</td>
<td>820.4</td>
<td>615.37</td>
</tr>
<tr>
<td>TA</td>
<td>28.0</td>
<td>34.07</td>
</tr>
<tr>
<td>LA</td>
<td>67.9</td>
<td>91.3</td>
</tr>
<tr>
<td>ZO</td>
<td>23.8</td>
<td>69.6</td>
</tr>
<tr>
<td>TO</td>
<td>0.2</td>
<td>11.5</td>
</tr>
<tr>
<td>LO</td>
<td>2.3</td>
<td>78.6</td>
</tr>
<tr>
<td>Total</td>
<td>942.6</td>
<td>900.3</td>
</tr>
</tbody>
</table>

The values of thermal conductivity for each polarization are shown in Table I. A very large overprediction from the optical modes is seen when using the classical approximation. Whereas all other polarizations show a higher contribution than in the quantum calculations, a lower contribution from ZA modes is observed using the classical approximation. This is because at room temperature the ZA mode specific heat from the classical calculation is close to the quantum value, but the relaxation time is significantly lower. The observations made here suggest that significant quantum effects exist in phonon transport even at room temperature, and results obtained from molecular dynamics simulations must be interpreted carefully. Clearly, a discrepancy exists on all levels: the calculation of the specific heat, the relaxation time, and the polarization-wise contribution to the thermal conductivity. The use of the relaxation time approximation and the thermal conductivity obtained under this approximation can greatly change predictions of Joule heating in graphene electronics in which electrons are primarily coupled to longitudinal phonon modes. The same is expected of optical heating processes for graphene and in transport across interfaces, both of which depend strongly on the phonon frequency.

Most of the theoretical reports on graphene thermal conductivity based on non-equilibrium molecular dynamics simulations are limited to graphene nanoribbons with a width and length of a few nanometers. Because phonon mean free paths in graphene are on the order of a few hundred nanometers, these simulations are expected to suffer from significant size effects. Evans et al. used equilibrium molecular dynamics with the Tersoff interatomic potential and computed the diffusive thermal conductivity of graphene as 8000 to 10 000 W/m K at 300 K, which is significantly higher than the value predicted using BTE simulations. Because the use of the original parameterization leads to much higher phonon frequencies than those observed experimentally, the high computed thermal conductivity may be attributed to the classical nature of MD simulations; the latter result in unphysically large contributions from optical and high-frequency acoustic phonons (as discussed above). It is also interesting to note that Zhong et al. predict a decrease of almost an order of magnitude in thermal conductivity between single layer graphene nanoribbons and ultrathin graphite. This decrease is significantly larger than what is observed experimentally and in computations based on the linearized phonon BTE. This might also be an artifact of the classical approximation, which leads to reduced phonon relaxation times (due to higher occupation than in Bose-Einstein statistics).

Finally, it is noteworthy that the conclusions drawn here regarding graphene are consistent with those regarding other materials such as Si (Ref. 35) and a host of ionic materials for which it has been seen that the classical relaxation time for small to mid-range frequency phonons is always smaller than the quantum counterpart. Because ZA phonons dominate thermal conductivity in graphene, most of the contribution comes from small to mid-range frequency phonons across the spectrum, and our results show that classical thermal conductivity remains lower than quantum thermal conductivity up to 500 K, and the two values tend toward each other by 600 K (~0/3). A similar trend was observed for ionic solids such as MgO, SrTiO3, and UO2.

IV. KLEMENS MATRIX ELEMENT

Klemens approximated the matrix element for three-phonon scattering in terms of the Gruneisen parameter (to represent crystal anharmonicity) and the phonon wavevector magnitude as \( k \sim \omega / v \) (valid for small phonon wavevectors or for linear dispersion). He obtained the following expression for phonon relaxation time (corresponding to \( \Gamma \) processes):

\[
\frac{1}{\tau} = \frac{\hbar^2}{3\pi m v^2 \kappa(p)} \int \omega_0 \omega'' \left( \omega'_0 - \omega''_0 \right) \frac{dk'_j}{|\mathbf{k}'_j|} .
\]

A similar expression can be written for type 2 processes with the phonon occupation factors as \( \omega'_0 + \omega''_0 + 1 \) and a factor of \( 1/2 \) to account for the fact that \( \mathbf{k}(p) \rightarrow \mathbf{k}'(p') + \mathbf{k}''(p'') \) and \( \mathbf{k}(p) \rightarrow \mathbf{k}''(p') + \mathbf{k}'(p'') \) are identical. In order to ensure a fair comparison to the results obtained from the exact matrix element evaluated from a third-order anharmonic interatomic force constant, we use mode-dependent Gruneisen parameters calculated from the Tersoff interatomic potential to compute thermal conductivity using Eq. (6). The mode-dependent Gruneisen parameters can be calculated from the third-order anharmonic force constants as

\[
\gamma_{\mathbf{k}(p)} = \frac{1}{4\omega^2 \kappa(p)} \sum_{m,l} \sum_{n,j} \sum_{p,l} \sum_{i,j} \left( \Phi_{2p}\Phi_{1l} \right) \left. \left. e_{n,l}(\mathbf{k}(p)) e_{p,m}(\mathbf{k}(p)) \exp(i\mathbf{k} \cdot \mathbf{R}_n) \right|_{\mathbf{r}(m)} \right) .
\]
heuristic approximations employed by Klemens\textsuperscript{30,36} are not made.

Figure 5 shows the temperature variation of the thermal conductivity calculated from the Klemens approximation. The occupation statistics correspond to the BE distribution; therefore, any differences from those calculated directly from the interatomic potential (labeled “potential”) are a result of the incorrectness of the corresponding matrix elements. We also plot the variation in thermal conductivity obtained from an iterative solution of the linearized BTE for comparison.

As seen in Fig. 5(a), the Klemens approximation significantly underpredicts thermal conductivity relative to that calculated from the potential, and it displays a much weaker temperature dependence. Perhaps the biggest failure of this approximation is in describing ZA phonons. The thermal conductivity of ZA phonons as calculated from the exact matrix elements (under the SMRT) is 820.4 W/m K. In contrast, under the Klemens approximation, this contribution is a mere 5.4 W/m K. This is due to the high Gruneisen constant for ZA modes and the failure of the Klemens approximation in distinguishing the matrix elements for different scattering processes. From details of the anharmonic interatomic force constants, it has been shown that the only valid scattering processes for ZA phonons are those involving an even number of out-of-plane phonons, with $ZA + ZA \rightarrow TA$ and $ZA + ZA \rightarrow LA$ being the strongest. However, the relaxation time under the Klemens approximation [Eq. (6)] depends only on the frequency of the interacting phonons and is independent of the details of phonon eigenvectors or the anharmonic tensor. It thus ascribes an equivalent resistance to scattering processes involving an odd number of out-of-plane phonons such as $ZA + ZA \rightarrow ZA$, $ZA + LA \rightarrow LA$, etc. We have examined the behavior of thermal conductivity within the Klemens approximation by suppressing such interactions and find that although the contribution from the ZA mode increases, it still remains much smaller than that due to LA and TA phonons. This means that the scaling of the matrix element $\omega\alpha\omega''$ also entails significant errors for ZA phonons due to its flexural dispersion. A similar observation has also been made in the case of CNTs.\textsuperscript{43} The computations presented here are compared to experimental measurements of graphene sheet thermal conductivity in Fig. 5(b). A close agreement between the data and the computations is seen when both N and U processes are taken into account under the framework of full BTE in conjunction with the matrix elements derived directly from crystal anharmonicity. Figure 5(a) shows that all other sets of computations (with the exception of Klemens - U only, SMRT) are either significantly higher or lower than the measured thermal conductivity values.

V. NEGLECTING NORMAL 3-PHONON SCATTERING PROCESSES

As discussed earlier, it is also a common practice to neglect N processes in thermal conductivity modeling.\textsuperscript{28,30} The effect of this approximation is shown in Fig. 5. In general, neglecting N processes leads to thermal conductivity values that are close to an order of magnitude higher than those calculated when including them. This finding supports the assertion that N processes are very important in modeling thermal transport. It is interesting to note that making the Klemens approximation in conjunction with neglecting N processes leads to thermal conductivity values that are similar to those obtained from the linearized BTE with the exact

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{(Color online) Thermal conductivity variation with temperature. (a) The different curves are labeled in accordance with the corresponding approximation employed. The dotted lines correspond to values obtained from the solution of the phonon BTE while the solid lines denote thermal conductivity computations performed under the single mode relaxation time approximation. (b) Comparison of computed thermal conductivity with experimental data.}
\end{figure}
This peculiar behavior arises because when \( N \) processes are thermal conductivity that asymptotes beyond \( d \) as \( d \) increases. In contrast, including \( N \) processes leads to an unphysical size dependence of thermal conductivity, and that the thermal conductivity diverges with sheet size.

The consequences of not including \( N \) processes in thermal conductivity computations are best illustrated by examining the size dependence of thermal conductivity. All the simulations presented thus far have been for \( d = 10 \) \( \mu \)m. Figure 6 shows the dependence of thermal conductivity on the graphene sheet diameter \( d \). The thermal conductivity is calculated using Eq. (4) and obtained from an exact solution of the BTE (without resorting to SMRT), with the matrix elements obtained from the interatomic potential. Two cases are considered: one including all three-phonon scattering processes (both \( N \) and \( U \)), and the other considering \( U \) processes only. The results in Fig. 6 clearly show that neglecting \( N \) processes leads to an unphysical size dependence of thermal conductivity, and that the thermal conductivity diverges as \( d \) increases. In contrast, including \( N \) processes leads to a thermal conductivity that asymptotes beyond \( d = 10 \) \( \mu \)m. This peculiar behavior arises because when \( N \) processes are neglected, there are extremely few three-phonon \( U \)-processes for low wave vector phonons; indeed, some wave vectors undergo no scattering events at all. These phonons would travel ballistically, resulting in a thermal conductivity that diverges with sheet size.

The predictions of the thermal conductivity of single-layer graphene made in Refs. 11, 28, 29, and 31 do not account for selection rules specific to \( ZA \) phonons and the relationship between crystal anharmonicity and phonon eigenvectors in the relaxation time expressions. In addition, large Gruneisen parameters for \( ZA \) phonons lead to significantly lower relaxation times for \( ZA \) phonons. Consequently, these theories predict that heat is mainly carried by \( LA/TA \) phonons. For the same reason, Kong et al. also predict that there is no significant difference in thermal conductivity between monolayer and bilayer graphene because the weak interlayer coupling does not affect the inplane vibrational modes significantly.

VI. CONCLUSIONS

We have presented a detailed analysis of the errors introduced in thermal conductivity computations of graphene due to a number of commonly used approximations. It is found that the classical approximation to the phonon distribution function entails significant errors below 1000 K. However, an underprediction of phonon relaxation time and an overprediction of phonon specific heat (especially for optical phonons) often balance out in the final expression for thermal conductivity. This fortuitous situation leads to thermal conductivity values that are similar to those from quantum predictions for some conditions. However, though the thermal conductivity values predicted from the classical approximation are reasonable, the high Debye temperature of graphene suggests that spectral transport properties inferred from MD simulations might not be accurate at room temperatures.

Klemens-type approximations to scattering matrix elements fail for graphene because they do not include selection rules arising out of the out-of-plane symmetry of the graphene sheet and the restrictive anharmonic scattering rules for \( ZA/ZO \) phonons. In general, the flexural phonon dispersion of \( ZA \) phonons and the inherent anisotropy of single layer graphene render these long wavelength approximations invalid. It is also shown that neglecting \( N \) phonon scattering events can lead to a significant overprediction of thermal conductivity and a divergence in thermal conductivity with sheet size. We have shown that for graphene, these approximations and the relaxation time expressions based on them will generally produce significant errors over the entire Brillouin zone. The issues addressed in this paper might be able to reconcile the conflicting trends in published theoretical calculations of graphene thermal conductivity.

ACKNOWLEDGMENTS

D.S. would like to acknowledge the support from a Lambert graduate teaching fellowship from Purdue University. This material is based upon work partially supported by the Defense Advanced Research Projects Agency and