Length dependent lattice thermal conductivity of single & multi layered hexagonal boron nitride: A first-principles study using the Callaway-Klemens & real space super cell methods

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The phonon dispersion, density of states, Grüneisen parameters, and the lattice thermal conductivity of single- and multi-layered boron nitride were calculated using first-principles methods. For the bulk h-BN we also report the two-phonon density of states. We also present simple analytical solutions to the acoustic vibrational mode-dependent lattice thermal conductivity. Moreover, computations based on the elaborate Callaway-Klemens and the real space super cell methods are presented to calculate the sample length and temperature dependent lattice thermal conductivity of single- and multi-layered hexagonal boron nitride which shows good agreement with experimental data.

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I. INTRODUCTION

Single and multilayered boron nitride are sp² bonded boron and nitrogen atoms arranged in a hexagonal honeycomb lattice arranged in ABAB stacking in multilayered and bulk materials. In spite of the fact that they are isomorphic to the multilayered graphene and graphite with similar lattice constants, unit cell masses and Van der Waals type bonding between the layers, their phonon properties are quite different. Consequently their physical properties such as the lattice thermal conductivity derived from the phonon dispersion should shed light on the fundamental physics of phonon transport of such two-dimensional (2D) nanomaterials. These nanomaterials in the form of semiconductor multilayers and other superstructures are promising candidates of materials with enhanced thermoelectrical properties and have been a topic of intensive research in recent years¹. In contrast to a large amount of theoretical and experimental work carried out on electron transport, only few studies on phonon transport have been reported. For example, using density functional theory (DFT) with quantum transport device simulation based on non-equilibrium Green’s function (NEGF), Fiori et al² have proposed and investigated 2-D graphene transistors based on lateral heterostructures. Ab initio atomistic simulations on vertical heterobarrier graphene transistors have been analysed³,⁴. Britnell et al⁵ have modelled graphene heterostructures devices with atomically thin boron nitride as a vertical transport barrier.

Performance of any thermoelectric material is characterised by a dimensionless parameter termed as figure of merit, denoted by $ZT$, which is inversely proportional to total lattice thermal conductivity, including contributions due to electrons and phonons. However, for the materials investigated here, electron contribution is negligible compared to that of phonons owing to a considerable electronic band gap between their conduction and valence bands. Experiments to study the effects of grain-boundaries on the thermal transport properties of graphene have been carried out by a few groups⁶,⁷. These experiments show that a smaller sample length decreases the thermal conductivity, a necessity for a good thermoelectric material. Graphene has a higher thermal conductivity compared to graphite due to the long mean free path (MFP) of the phonons in the 2D lattices. The MFP can thus be reduced by creating defects in the sample. Recent studies by Malekpour et al⁸ has shown that vacancies reduces the lattice thermal conductivity in graphene. Lattice thermal conductivity of a material is highly correlated to the thickness of the sample (or number of layers). For example, graphene has a much larger thermal conductivity than bilayer graphene and graphite⁹,¹⁰. Recently reported lattice thermal conductivity for In₂Se₃ exhibits¹¹ a strong dependence on the thickness or number of layers, with a value of 4 W/mK for a thickness of 5nm which increases to 60 W/mK for the sample with thickness 35nm. These results suggest that in order to manipulate the lattice thermal conductivity $\kappa_L$, a proper understanding of its dependence on the grain size, temperature and thickness dependence is essential. However, not many experiments on grain size, temperature and thickness have been carried out so far in single and multilayered boron nitride. We believe our present work will motivate experiments in the direction of tuning $\kappa_L$ in such 2D materials.

Heat flow in single and multilayered boron nitride (SLBN and MLBN) is of great significance not only for fundamental understanding of such materials in terms of lattice thermal conductivity or thermoelectrics but also for technological applications. Single and MLBN are extremely atomically stable materials and can be easily supported between two leads. Besides, these materials exhibit a comparatively lower $\kappa_L$ in bulk than in single and multi-layered graphene. This makes SLBN and MLBN a good testing ground to study the length and temperature dependence of thermal conductivity. Manipulating the lattice thermal conductivity by varying its tempera-
ture and dimensions (through grain size engineering) will shed light on the fundamental understanding of thermoelectricity in such 2D materials and help in designing new novel materials for technological applications.

Hexagonal boron nitride (h-BN) is relatively inert as compared to graphene due to its strong, in-plane, ionic bonding of its planar lattice structure and hence is a favourable substrate dielectric to improve graphene based devices\textsuperscript{12}. Although h-BN has appealing thermal properties, most studies, both experimentally and theoretically, are confined to single and multi-layered graphene\textsuperscript{9,10,13–19}. Some experiments on lattice thermal conductivity ($\kappa_L$) have been reported by Jo et al\textsuperscript{20} for multi-layered boron nitride (MLBN). Also, theoretical studies on thermal conductivity ($\kappa_L$)\textsuperscript{21} and conductance\textsuperscript{22} on such materials have been carried out using Tersoff empirical interatomic potential. However, first principle theoretical studies of $\kappa_L$ such as using the Boltzmann transport equations (BTE) for phonons from density functional perturbation theory (DFPT) on SLBN and MLBN are apparently not available.

In this paper, we investigate numerically the sample length and temperature dependence of the thermal conductivity ($\kappa_L$) of single and multi-layer h-BN by solving the phonon BTE beyond the relaxation time approximation (RTA) using the Callaway-Klemens method and also by solving the phonon BTE in the RTA using the Callaway-Klemens approach. A long standing puzzle has been to answer phonon BTE in the RTA using the Callaway-Klemens method and a summary in the subsequent sections.

II. THEORETICAL FRAMEWORK AND METHOD OF CALCULATION

A. Electronic and phonon bandstructure calculations

First-principles DFT and DFPT calculations were carried out on a hexagonal supercell for the monolayer, bilayer and bulk boron nitride, whereas an orthorhombic supercell was used for five layers h-BN sample, using the plane wave pseudopotential method as implemented in the QUANTUM ESPRESSO code\textsuperscript{29}. We have used 2 atoms in the unit cell for SLBN, 20 atoms for five layered BN and 4 atoms in both bilayer and bulk boron nitride. To prevent interactions between the layers, a vacuum spacing of 20 Å was introduced along the perpendicular direction to the layers (z-axis) mimicking an infinite BN sheet in the $xy$ plane. For MLBN and bulk-hBN, the Van der Waals interaction as prescribed by Grimme\textsuperscript{30}, was used between the layers.

For the electronic structure calculations, Monkhorst-Pack grids of $16 \times 16 \times 1$ and $16 \times 16 \times 4$ were chosen for SLBN and MLBN, respectively, for the $k$-point sampling. Self-consistent calculations with a 40 Ry kinetic energy cut-off and a 160 Ry charge density energy cutoff were used to solve the Kohn-Sham equations with an accuracy of $10^{-9}$ Ry for the total energy. We used ultrasoft pseudopotential to describe the atomic cores with exchange-correlation potential kernel in the local density approximation\textsuperscript{31}. The electronic structure and total energy calculations were used to obtain the groundstate geometry before persuing the phonon calculations.

For the phonon bandstructure calculations, the $q$-grid used in the calculations were $6 \times 6 \times 1$ for SLBN, $6 \times 6 \times 2$ for BLBN and bulk h-BN and $4 \times 4 \times 2$ for 5-layer BN, respectively. The density functional perturbation theory (DFPT)\textsuperscript{32}, as implemented in the plane wave method\textsuperscript{29}, was used to calculate the phonon dispersion and phonon density of states (DOS) along the high-symmetric $q$-points.

B. Calculation of the lattice thermal conductivity

The calculation of lattice thermal conductivity $\kappa_L$ involves evaluation of second-order harmonic interatomic force constants (IFCs) as well as the third-order anharmonic IFCs. We have used first a real space supercell method which evaluates the third-order anharmonic IFCs in a real space grid using DFT\textsuperscript{33}, whereas the second-order IFCs are obtained from the DFPT method\textsuperscript{29,32}. Secondly, using the Callaway-Klemens method\textsuperscript{14,35}, the relaxation
times were obtained from the Grüneisen parameters. Finally, the length, thickness and temperature dependence of $\kappa_L$ were studied.

1. Real space super cell approach

In this method the third order anharmonic IFCs are calculated from a set of displaced supercell configurations depending on the size of the system, their symmetry group and the number of nearest neighbour interactions. A $4 \times 4 \times 2$ supercell including upto third nearest neighbour interactions were used to calculate the anharmonic IFCs for all the structures, generating 128 configurations for single and bulk BN, 156 for bilayer BN (BLBN) and 828 for five-layered BN (5LBN). The third order anharmonic IFCs are constructed from a set of third-order derivatives of energy, calculated from these configurations using the plane wave method. The phonon lifetimes are calculated from the phonon BTE approximation, $\Delta \tau_i = 1/(2\pi^2\hbar^2/v_s^0 \tau_0^i)\alpha^0_s$, where $\tau_0^i$ is the average of masses ($M_s$) of isotopes of the atom $i$ having a relative frequency $f_s$. $\Gamma^{\pm}$ represents the absorption (emission) processes.

In the above expression, $i, j, k$ run over the atomic indices and $\alpha, \beta, \gamma$ are the Cartesian coordinates. $M = \sum f_s(i)M_s(i)$ is the average of masses ($M_s(i)$) of isotopes $s$ of the atoms $i$ having a relative frequency $f_s$. $\Gamma^{\pm}$ represents the absorption (emission) processes. A phonon which is a result of the absorption process is a combined energy of two incident phonons, $i.e.$, $\omega_\lambda + \omega'_\lambda = \omega''_\lambda$. Similarly, the emission process depicts the energy of an incident phonon being separated among two phonons, $i.e.$, $\omega_\lambda + \omega'_\lambda = \omega''_\lambda$. Therefore in eq. 4 it is easy to see that the Dirac delta function, $\delta(\omega_\lambda \pm \omega'_\lambda + \omega''_\lambda)$, imposes the conservation of energy in the absorption and emission processes.

It should be noted that the relaxation times is calculated in the ShengBTE code using an iterative approach by solving the phononBTE starting with the zeroth-order approximation, $\Delta \tau = 0$, also known as the RTA solution. These iterations continue till two successive values of $\kappa_L$ differ by $10^{-5}$ Wm$^{-1}$K$^{-1}$. The interatomic third-order force constants (IFCs) are calculated using a real space supercell approach.

Length dependent thermal conductivity is then calculated by taking into account only phonons with a mean free path (MFP) below a certain threshold value. This is done by calculating the cumulative lattice thermal conductivity with respect to the allowed MFP. Furthermore, there have been recent advanced experimental techniques proposed to measure the cumulative $\kappa_L$ as a function of phonon mean free path.$^{36-38}$

In order to compare our calculations to the lengths corresponding to experimental measurements, we fit the cumulative thermal conductivity in the form$^{43}$

$$\kappa_L(L) = \frac{\kappa_{L,\text{max}}}{1 + \frac{L}{L_0}}.$$  

where $L_0$ is a fitting parameter. $\kappa_L$ corresponding to a given length is calculated over a temperature range using Eq. 7 and the thermodynamic limit of the thermal conductivity ($\kappa_{L,\text{max}}$) is the value of $\kappa_L$ as $L \to \infty$. 

$$\Gamma_{\lambda \lambda'}^{\pm} = \frac{\hbar}{4w_{\lambda \lambda'}^2\omega_{\lambda'}} \left[ f_0(\omega_{\lambda'}) - f_0(\omega_{\lambda'} + 1) \right] \left| \delta(\omega_\lambda \pm \omega'_\lambda + \omega''_\lambda) \right| \left( f_0(\omega_{\lambda'}) + f_0(\omega_{\lambda'} + 1) \right)$$

$$\Gamma_{\lambda \lambda'} = \frac{\pi \omega_s^2}{2} \sum_i f_s(i) \left[ 1 - \frac{M_s(i)}{M(i)} \right]^2 \left| e_\lambda \cdot e_{\lambda'} \right|^2 \delta(\omega_\lambda - \omega'_\lambda).$$

Where $V^\pm$ is the scattering matrix element and is expressed in terms of the anharmonic IFCs ($\Phi$), eigen functions ($e$) and mass ($M$) of an atom as

$$V_{\lambda \lambda'} = \sum_{i,j,k} \sum_{\alpha \beta \gamma} \Phi_{ij}^{\alpha \beta \gamma} e_i^\alpha e_j^\beta e_k^\gamma \frac{\sqrt{M_i M_j M_k}}{\sqrt{M_s}}$$
2. Callaway-Klemens approach (Analytical and numerical solutions)

In the Callaway-Klemens’s\textsuperscript{34,35} approach which has been modified by Nika et al\textsuperscript{9}, the expression for thermal conductivity along \(x\) and \(y\) directions for two-dimensional layered materials, according to the relaxation time approximation (RTA) to BTE and isotropic approximation to phonon dispersion is given by,

\[
\kappa = \frac{1}{4\pi k_B T^2 N^s} \times \sum_s \int_{q_{min}}^{q_{max}} \left( \frac{\hbar \omega_s(q)}{\hbar \omega_s(q)} \right) \frac{e^{\frac{\hbar \omega_s(q)}{k_B T}}}{\left( e^{\frac{\hbar \omega_s(q)}{k_B T}} - 1 \right)^2} dq, \tag{8}
\]

where \(k_B\) is the Boltzmann constant, \(h\) is the reduced Planck constant, \(T\) is the absolute temperature, \(N\) is the number of layers, \(\delta\) is the distance between two consecutive layers, \(\omega_s(q)\) and \(v_s(q)\) are the phonon frequency and velocity corresponding to the branch \(s\) at phonon wave vector \(q\). The wave vector corresponding to the Debye frequency and low cut-off frequency are denoted by \(q_{max}\) and \(q_{min}\), respectively. The method to calculate the low cut-off frequency will be discussed shortly. \(\tau_{U,s}\) is the three-phonon Umklapp scattering corresponding to branch \(s\) at the wave vector \(q\) expressed as,

\[
\tau_{U,s} = \frac{M v_s^2(q) \omega_{D,s}}{\gamma_s(q) k_B T \omega_s(q)^2}. \tag{9}
\]

Here, \(M\) is the total mass of the atoms in the unit cell, \(\gamma_s(q)\) is the mode and wave vector dependent Grüneisen parameter.

The validity of the form of relaxation time in the Umklapp scattering in eq. 9 for a 2D and 3D material was originally proposed by Klemens et al.\textsuperscript{39}, where phonons were treated by a two-dimensional Debye model. This sets up a mode for the thermal conductivity in terms of a 2D phonon gas. On the basis of the phonon frequency dependence of the specific heat and mean free path, the form of \(\tau_{U,s}\) in eq. 9 is valid for both 2D and 3D. Moreover, the calculations by Shen et al.\textsuperscript{40} use the same form to describe the relaxation time of the Umklapp process for graphene and their results, when \(\tau_{U,s}\) is multiplied by a factor of 3, are consistent with the paper of Lindsay et al.\textsuperscript{21} which solves the phonon BTE beyond the RTA. Since eq. 9 cannot determine whether the U-processes are forbidden or not, the factor of 3 is added due to the symmetries seen in graphene which is explained in detail later.

Grüneissen parameter \((\gamma_s(q))\) and the Debye frequency \((\omega_{D,s})\) corresponding to the branch \(s\) is calculated by solving,

\[
A \int_0^{\omega_{D,s}} dq \frac{d\omega}{d\omega} = 1, \tag{10}
\]

where \(A\) is the area of the unit cell.

The acoustic branches for in-plane modes for SLBN, BLBN, 5LBN and Bulk-IBN are linear whereas the out-of-plane acoustic mode have a quadratic behavior and hence for a simplified analytical solution we express the phonon frequencies as

\[
\omega_s(q) = v_s q \Rightarrow [s = LA, TA] \tag{11}
\]

\[
= q^2 \Rightarrow [s = ZA] \tag{12}
\]

Substituting these values in Eq. 10, we find the Debye frequency is given by

\[
\omega_{D,s} = 2v_s \sqrt{\frac{\pi}{A}} \Rightarrow [s = LA, TA] \tag{13}
\]

\[
= \frac{4\pi \alpha}{A} \Rightarrow [s = ZA] \tag{14}
\]

The mode dependent anharmonic (Grüneissen) parameters were calculated by applying a biaxial strain of \(\pm 0.5\%\) to each of the structures. Fig. 5 shows that the Grüneisen parameter for the in-plane modes have a slight deviation from its average value along the \(\Gamma\) to \(K\) direction. Therefore assuming a constant value for \(\gamma_s\) (s=LA,TA), Nika et al\textsuperscript{9} have derived the following analytical solution for \(\kappa\) associated with a particular mode \(s\).

\[
\kappa_s = \frac{M \omega_{D,s} v_s^2}{4\pi T (N^s) \gamma_s^2} \ln(e^x - 1) + \frac{x}{1 - e^x} - x \frac{\hbar \omega_{D,s}}{k_B T} \frac{\gamma_s}{\gamma_s^2} \] \tag{15}

Since there is no ZO branch in SLBN, the low bound cut-off frequency cannot be introduced in analogy to that of bulk graphite. One can however avoid the logarithmic divergence by restricting the phonon mean free path on the boundaries of the sheets\textsuperscript{27}. This is accomplished by selecting the mode dependent low cut-off frequency \((\omega_{s,\text{min}})\) from the condition that the mean free path cannot be greater in size than physical length \(L\) of the sheet, i.e.,

\[
\omega_{s,\text{min}} = v_s \gamma_s \sqrt{\frac{M v_s \omega_{D,s}}{k_B T L}} \tag{16}
\]

In the spirit of in-plane thermal conductivity study we extend our calculations to find an analytical form to the flexural phonons modes since the contribution from these branches are vital to the total thermal conductivity. Unlike for the case of in-plane modes, the Grüneisen parameters for the acoustic out-of-plane ZA modes have a strong \(q\)-dependence. From Fig. 5 it can be seen that the expression

\[
\gamma_{ZA} = \frac{\beta}{q^4}, \tag{17}
\]

is a very good fit to the actual wave vector dependent Grüneisen parameters. Substituting eq. 17 and eq. 12 into eq. 8 and making a transformation, \(x = \frac{\hbar \omega}{k_B T}\), the
analytical form for $\kappa_{ZA}$ is given by

$$\kappa_{ZA} = \frac{2M\omega_D k_B^2 T^2}{\pi N \delta^2 h^3 \alpha} \int_0^{k_B T} x^4 \frac{e^x}{(e^x - 1)^2} dx$$

$$= \frac{2M\omega_D k_B^2 T^2}{\pi N \delta^2 h^2 \alpha} G \left( \frac{\hbar \omega_D}{k_B T} \right),$$

(18)

where the function $G(z)$ is expressed as

$$G(z) = \frac{-4\pi^4}{15} + \frac{e^z}{1 - e^z} + 4e^z \ln(1 - e^z) + 12[z Li_2(e^z) - 2Li_3(e^z)] + 24Li_4(e^z).$$

(19)

Here, the polylogarithm function is defined as, $Li_n(z) = \sum_{i=1}^{\infty} \frac{z^i}{i^n}$.

III. RESULTS AND DISCUSSIONS

A. Phonon dispersion and density of states

Accurate calculations of the harmonic second order IFCs are necessary for a precise description and understanding of the thermal conductivity. Deviations due to numerical artifacts from the expected behavior of acoustic modes can lead to incorrect results especially for 2D materials. The full structural relaxation of SLBN, BLBN, 5LBN and Bulk-hBN yield a lattice constant ($a_0$) of 2.49 Å. The interlayer spacing ($c$) for MLBN is found to be 3.33 Å. The experimentally measured $a_0$ is 2.50 Å and the ratio of interlayer spacing and the lattice constant ($\frac{c}{a_0}$) is 1.332 which is in excellent agreement with our calculated value of 1.337.

The calculated phonon dispersion and phonon density of states are shown in Fig. 1 for (a) SLBN, (b) BLBN, (c) 5LBN and (d) Bulk-hBN along with experimental data (orange circles). The phonon dispersion were calculated along the high-symmetry points of the 2D Brillouin zone ($q_z = 0$) corresponding to the hexagonal cell for SLBN, BLBN, and Bulk-hBN and orthorhombic cell for 5LBN. We also plot in (d) the two-phonon DOS shown for Bulk-hBN in red dashed line. The cyan, magenta and green curves in (a,b,c,d) are the best linear and quadratic fit to the phonon dispersion referring to LA, TA and ZA modes, respectively.

The symmetries of SLBN, BLBN, 5LBN and Bulk-hBN structures at $\Gamma$ can be described using the character table shown in Table III. Using a standard group theoretical technique (see Appendix), it can be shown that for Bulk-hBN and BLBN that the 12 phonon modes are decomposed into the following irreducible representations: $2(A_{2u} + B_{1g} + E_{2g} + E_{1u})$ and $2(A_{2u} + E_g + A_{1g} + E_u)$. Similarly for SLBN, the irreducible representation is $A_{2g} + B_{1g} + E_{2g} + E_{1u}$ for the six phonon modes and 5LBN has an irreducible presentation given by $4(A'_1 + E'') + 6(A''_2 + E')$. Transitions corresponding to the basis $x, y, z$ (xy, yz, z², etc.) are Infrared (Raman) active. Those that are neither Infrared or Raman are the silent modes. Due to the momentum conservation requirement

FIG. 1. The calculated phonon dispersion (left) and phonon density of states (right) of (a) SLBN, (b) BLBN, (c) 5LBN and (d) Bulk-hBN along with experimental data (orange circles). The phonon dispersion were calculated along the high-symmetry points of the 2D Brillouin zone ($q_z = 0$) corresponding to the hexagonal cell for SLBN, BLBN, and Bulk-hBN and orthorhombic cell for 5LBN. We also plot in (d) the two-phonon DOS shown for Bulk-hBN in red dashed line. The cyan, magenta and green curves in (a,b,c,d) are the best linear and quadratic fit to the phonon dispersion referring to LA, TA and ZA modes, respectively.
(q = 0), the first-order Raman scattering process is limited to the phonons at the center of the Brillouin zone. We therefore compare our calculated frequencies at the Γ point corresponding to $A_2u$, $E_1u$, $A_1''$, $E'$, and $E_0$ to the infrared experimental data and $E_2g$, $E''_0$, $A_{1g}$, $E_g$, and $A_1''$ to the Raman experimental data as shown in Table I.

Raman spectroscopy is the most adaptable tool that offers a direct probe for multi-layered samples. Table I shows the transitions corresponding to the infrared ($E''_0$ and $A_1''$) and Raman ($E''$ and $A'$) active modes in the case of 5LBN. Further experiments for layered boron nitride would be required to verify the correctness of calculations. However, LDA with VdW interaction have shown to accurately describe the phonon dispersions for layered graphene when the geometry (i.e., interlayer distance) is represented correctly even though the local or semi-local exchange correlation functionals may not represent the interactions correctly.

Another experimental technique to analyse the modes of a system is the second-order Raman spectroscopy in which the peaks are seen over the entire frequency range. Most of these peaks are in agreement with the phonon density of states when the frequency is scaled by a factor of 2. We have hence plotted, to the right of our phonon dispersion, the frequency scaled DOS. However, as pointed out by Serrano et al., peaks which are absent in the DOS can be seen in the second-order spectroscopy because the DOS does not take both overtones, i.e., summation of modes having the same frequencies, into account. The two phonon density of states (DOS$_{2ph}$) are also essential for the understanding of phonon anharmonic decay. Experiments on the second-order Raman spectrum of h-BN has been performed by Reich et al. We show in Fig. 1(d) the two-phonon DOS

$$\text{DOS}_{2ph}(\omega) = \sum_{i,j} \delta(\omega - \omega_i - \omega_j) + \delta(\omega - \omega_i + \omega_j), \quad (20)$$

for Bulk-hBN using our calculated harmonic interactions. The peaks seen experimentally at 1639.4 cm$^{-1}$, 1809.907 cm$^{-1}$ and 2289.8068 cm$^{-1}$ are absent in the DOS. However, these large spectral features are now observed at 1680.4 cm$^{-1}$, 1821.2 cm$^{-1}$ and 2306.7 cm$^{-1}$, due to two phonon DOS (DOS$_{2ph}$).

B. Thermal conductivity calculated using real space supercell approach

In Fig. 2 (a) and (b) we show the variation of thermal conductivity as a function of temperature ($T$) and sample length, respectively. The sample length is measured along the direction of the heat flow. The theoretical computation was carried out using the interatomic force constants obtained from the real space approach and an iterative method in calculating the relaxation times as implemented in the ShengBTE code. To have a broad understanding of the thermal conductivity, we study different types of possible unit cells, i.e., MLBN considered here have even, odd and infinite number of layers since each unit cell has a different character table. Calculations were done using orthogonal cell for 5LBN and hexagonal cells for SLBN and 5LBN with bulk-hBN. The study was carried out over a wide range of sample lengths between 0.01 μm and 1000 μm with 0.1μm grid. The temperature of each sample was varied between 10 K to 1000 K with a grid of 10 K. On plotting the thermodynamic limit ($L \to \infty$) for each of the system we find that $\kappa_L$ is practically independent of length for lengths greater than 100 μm.

Our recent results of $\kappa_L$ in the thermodynamic limit ($L \to \infty$) for monolayer and bilayer graphene are in excellent agreement with the recent experimental work of Li et al., whereas the thermodynamic limit for MLBN is much larger than some recent experimental measurements. Sample lengths used by Li et al. were of the order of millimetres for the measurement of single and bilayer graphene while Jo et al. and Wang et al. have used sample lengths of 5 μm and 2 μm for 5LBN and BLBN, respectively. As mentioned earlier, $\kappa_L$ does not vary much for lengths larger than 100 μm but is extremely sensitive when the lengths are between 1 and 100 μm. Not surprising therefore, our thermodynamic limit of $\kappa_L$ are in good agreement for graphene but not for MLBN.

In order to compare our calculations to that of experiments, we calculate the cumulative lattice thermal conductivity at lengths corresponding to the sample lengths used in the experiments. The cumulative $\kappa_L$ was calculated in the temperature range 10-1000 K. Fig. 2 (b) shows the cumulative thermal conductivity at room temperature (RT).

The curves in Fig. 3, are the calculated values of $\kappa_L$ at constant lengths which are compared with the experimental results for single and bilayer BN shown as a function of (a) temperature and (b) length, using the real space approach. In (a) the curves refer to the thermodynamic limit ($L \to \infty$). In (b) the sample length is in logarithmic scale. The square and triangle data points refer to experimental measurements for BLBN and 5LBN, respectively.
TABLE I. Experimentally measured Raman and Infrared phonon frequencies for bulk-hBN and those obtained from present calculations for all the systems studied are shown at the Γ point in the BZ. Previously calculated values for bulk-hBN are also shown together with the experimental data for comparison.

| Mode | Expt. (& Prev. calculated \(^a\)) \(\omega \text{ (cm}^{-1}\) | Bulk-hBN (Sym.) | BLBN (Sym.) | SLBN (Sym.) |
|------|------------------|----------------|--------------|--------------|
| LA\(_2\) & TA\(_2\) | 51.62\(^b\) (52.43) | 58.55 \(\text{E}_{2g}\) | 25.73 \(\text{E}_g\) | - |
| ZO | Silent (120.98) | 85.01 \(\text{B}_{1g}\) | 66.54 \(\text{A}_{1g}\) | - |
| ZO | 783.16\(^c\) (746.87) | 784.05 \(\text{A}_{2u}\) | 803.01 \(\text{A}_{2u}\) | 819.37 \(\text{A}_{2u}\) |
| ZO\(_2\) | Silent (809.78) | 823.17 \(\text{B}_{1g}\) | 812.25 \(\text{A}_{1g}\) | - |
| LO | 1366.30\(^d\), 1370.33\(^d\), 1363.88\(^d\) (1379.20) | 1363.80 \(\text{E}_{2g}\) | 1364.45 \(\text{E}_g\) | 1363.88 \(\text{E}_{2g}\) |
| TO | 1367.10\(^d\) (1378.4) | 1366.95 \(\text{E}_{1u}\) | 1365.66 \(\text{E}_g\) | 1363.88 \(\text{E}_{1u}\) |
| LA & TA (cm\(^{-1}\)) | (Point Group Symmetry) | (P.G. Symmetry) | (P.G. Symmetry) | (P.G. Symmetry) |
| 14.60 \(\text{E}^\prime\) | 1409.46 \(\text{E}^\prime\) | 1405.23 \(\text{E}^\prime\) | 817.59 \(\text{A}^\prime\) |
| 31.10 \(\text{E}^\prime\) | 1408.91 \(\text{E}^\prime\) | 1404.94 \(\text{E}^\prime\) | 814.58 \(\text{A}^\prime\) |
| 38.95 \(\text{E}^\prime\) | 1408.71 \(\text{E}^\prime\) | 1404.81 \(\text{E}^\prime\) | 812.58 \(\text{A}^\prime\) |
| 47.43 \(\text{E}^\prime\) | 1408.36 \(\text{E}^\prime\) | 1404.49 \(\text{E}^\prime\) | 810.27 \(\text{A}^\prime\) |
| 5LBN | 1405.57 \(\text{E}^\prime\) | 1404.40 \(\text{E}^\prime\) | 803.27 \(\text{A}^\prime\) |

\(^a\) From \textit{ab initio} dispersion calculations, Ref.\(^{33}\).
\(^b\) Experimental Raman data, Ref.\(^{45}\).
\(^c\) Experimental Raman and Infrared data, Ref.\(^{46}\).
\(^d\) Experimental Raman data, Ref.\(^{47}\).

For the lengths used in the experiments the magnitudes of \(\kappa_L\) for Bulk-hBN and Bilayer lie in between SLBN and 5LBN with SLBN (5LBN) being the highest(lowest). The maxima of \(\kappa_L\) of \(\sim\) 500 Wm\(^{-1}\)K\(^{-1}\) for Bulk-hBN is found in the temperature range 250-300 K and tends to saturate to a value \(\sim\) 450 Wm\(^{-1}\)K\(^{-1}\). Experimentally\(^{51}\) the maxima is found between 150-200 K and tends to saturate to a value \(\sim\) 400 Wm\(^{-1}\)K\(^{-1}\). Lindsay \textit{et. al.}\(^{21}\) varies the sample length and finds an excellent fit with the experimental data for \(L = 1.4 \mu m\). It must be noted that the sample length is not mentioned in the experimental reference\(^{51}\) for Bulk-hBN. As the length of the sample increases, the maxima of \(\kappa_L(T)\) shifts towards the left, i.e. the maxima is found at a lower temperature. Therefore for BLBN and 5LBN, where the lengths used in the experiments are larger than 1.4 \(\mu m\), the maxima would be at lower temperatures, in total disagreement with the experiments\(^{20,50}\). Our calculations for BLBN and 5LBN are in excellent agreement with experiments for the same lengths. Even though our calculated values diverge from the experimental measurements by Sichel \textit{et. al.}\(^{51}\) at higher temperatures, we believe that the behavior of \(\kappa_L\) as calculated by us for bulk-hBN is correct. However, further experiments should throw more light on these discrepancies. It is our conjecture that \(\kappa_L\) of Bulk-hBN should be similar to that of BLBN since the phonon dispersions in the two cases are very similar.

In Fig. 4 we show the acoustic mode dependent contributions to the total thermal conductivity for SLBN and MLBN by solving the phonon BTE beyond the RTA. The out of plane mode is clearly seen to contribute the most to the lattice thermal conductivity for all the mentioned structures. For SLBN the contributions from the ZA, TA and LA modes to \(\kappa_L\) at room temperature are \(\sim\) 86.1 %, 7.4 % and 6.5 %. A similar trend is observed in graphene\(^{23}\). Qualitatively one can understand why the ZA mode contributes the most to \(\kappa_L\) by calculating the number of modes per frequency for each of the acoustic mode. Now the number of modes per frequency is proportional to the 2D density of phonon modes, \(D_\omega(\omega) \propto \frac{q}{2\pi} dq\), and hence the ratio of \(D_{ZA}(\omega)\) and \(D_{TA(LA)}(\omega)\) would give a measure of the contribution of the respective phonon modes. Assuming a quadratic fit to the ZA dispersion, \(\omega_{ZA} = \alpha q_{ZA}^2\), and a linear fit to the in-plane TA and LA phonon disper-

![Graph showing calculated thermal conductivity of single and multilayer BN as a function of temperature at a constant length, using the real space approach. The square, circle, triangle data points refer to experimental measurements for BLBN, Bulk-hBN and 5LBN, respectively.](image-url)
sion, \( \omega_{TA(LA)} = \frac{v_{TA(LA)} q_{TA(LA)}}{D_{TA(LA)}} \), the ratio of the density of phonon modes is \( \frac{D_{ZA}}{D_{TA(LA)}} = \frac{v_{LA(TA)}^2}{2 \alpha \omega_{LA(TA)}} \). Here \( \alpha \) and \( v_{LA(TA)} \) are fitting parameters to the phonon dispersions shown in Fig. 1 and their values are shown in Table II. Substituting these values, it is evident that \( D_{ZA} \gg 1 \) at the long wavelength limit suggesting that the major contributions to the lattice thermal conductivity are due to the out of plane modes. Representing the ZA contribution of the thermal conductivity of MLBN at room temperature with respect to SLBN, we observe that \( \kappa_{ZA}^{SLBN} = 1.28 \kappa_{ZA}^{BLBN} = 2.17 \kappa_{ZA}^{MLBN} \), suggesting that the significant decrease of the \( \kappa_L \) from SLBN to MLBN is because of the additional raised frequencies of the ZA layer breathing modes.

Kong et al.\textsuperscript{52} reported that the lattice thermal conductivity of single layer graphene and bilayer are similar, \( \kappa_{graphene}^{L} \approx \kappa_{bilayer}^{L} \), while Lindsay et al.\textsuperscript{53} reported \( \kappa_{graphene}^{L} \approx 1.3 \kappa_{bilayer}^{L} \). The difference in their methodologies is that the latter has taken graphene symmetry into account, which is discussed in detail by Seol et al.\textsuperscript{26} and Lindsay et al.\textsuperscript{53}. Besides the contribution due to the layer breathing out of plane modes, a decrease in \( \kappa_{L} \) is also due to the violation of the selection rule\textsuperscript{26,53} which is incorporated in the formalism in the super-cell real space approach. In Fig. 4 (d,e,f), we show the mode dependent \( \kappa_{L} \) at room temperature as a function of sample length. At any given length, the maximum difference in \( \kappa_{L} \) contributed from LA and TA modes for all the mentioned structure is \( \sim 47 \) and \( 65 \text{ Wm}^{-1}\text{K}^{-1} \) respectively while that from the ZA mode is \( \sim 750 \text{ Wm}^{-1}\text{K}^{-1} \), an order of magnitude larger, implying that the contribution from the in-plane thermal conductivity is almost independent of the number of layers. This characteristic has been seen using a Tersoff potential in the case of single and multilayered graphene and boron nitride\textsuperscript{53,54}. This rapid decrease in \( \kappa_{L} \) by increasing the number of layers, which is mainly due to the ZA mode, suggests that the interlayer interactions are short ranged, i.e., the BN layers only interact with neighbouring BN layers\textsuperscript{53}. In all of the structures, the contribution to \( \kappa_{L} \) from the ZA mode have a stronger \( L \) dependence as compared to the TA and LA modes, i.e., the contributions from the in-plane modes saturate to their thermodynamic limit at a lower \( L \) value as compared to the contributions from the out-of-plane modes. This is due to the larger intrinsic scattering times allowing the ZA phonons to travel ballistically and the relatively smaller scattering time which reflects the diffusive transport of the TA and LA phonons\textsuperscript{53}. Calculations based on the mode dependent contributions to \( \kappa_{L} \) as a function of mean free path and recent advanced experimental techniques\textsuperscript{36–38} should motivate further studies in these directions.

The in-plane phonon contributions having a small \( L \) dependence in comparison to the contributions from the out of plane has been calculated for graphene recently using the Tersoff potential\textsuperscript{55} and their calculated cumulative mode dependent thermal conductivity behavior is in good agreement with our calculations for SLBN.

C. Grüneisen parameter

Besides providing important information on the phonon relaxation time, the Grüneisen parameter \( (\gamma) \) also provides information on the degree of phonon scattering and anharmonic interactions between lattice waves. Therefore, an accurate calculation of the lattice thermal conductivity \( (\kappa_{L}) \) would require a precise calculation of \( \gamma \) since anharmonic lattice displacements play a vital role in calculations of \( \kappa_{L} \). Fig. 5 displays the mode dependent \( \gamma \) for SLBN, BLBN, 5LBN and Bulk-BN along the high symmetric \( q \) points. The anharmonic lattice displacements are carried out by dilating the unit cell by applying a biaxial strain of \( \pm 0.5 \% \) and is expressed as,

\[
\gamma_{s}(q) = \frac{-a_{0}}{2 \omega_{s}(q)} \frac{\delta \omega_{s}(q)}{\delta a} \\
\approx \frac{-a_{0}}{2 \omega_{s}(q)} \left[ \frac{w_{+} - w_{-}}{da} \right] 
\]

This method has been used previously for graphite\textsuperscript{56}, single and bi-layer graphene\textsuperscript{59} and MoS\textsubscript{2}\textsuperscript{17}. where \( \omega_{s}(q) \), \( \omega_{+} \) and \( \omega_{-} \) are the wave vector dependent phonon frequency of mode \( s \), phonon frequency under positive and negative biaxial strain respectively. \( a_{0} \) and \( da \) are respectively the relaxed lattice constant and difference in lattice constants when under positive and negative biaxial strain. We find that the acoustic modes correspond to the lowest Grüneisen parameters which is in-line with experimentally measured \( \gamma \).\textsuperscript{57} As in the case of graphene, the out-of-plane acoustic transverse mode has the largest negative \( \gamma \) parameters.
Positive (negative) Grüneisen parameters suggest a decrease (increase) in phonon frequencies as the lattice constant increases. Near the long-wavelength limit, $\gamma_{ZO'}$ for 5LBN is positive but becomes negative as we move along the Γ to Y direction in the BZ. $\gamma_{ZO'}$, associating with the layer breathing mode suggests that due to the additional layers the atom vibrations along the perpendicular direction between them lose their coherence and hence decreases the phonon frequencies when the system is under a biaxial strain.

As described in Table III, $E_{2g}$, $E''$, $A_{1g}$, $E_{g}$ and $A_{1''}$ are Raman active and hence in principle their Grüneisen parameter can be calculated experimentally using Raman spectroscopy. There exist experimental data for bulk h-BN but to the best of our knowledge there does not exist experimental data for single or MLBN. We therefore compare our results to that of bulk-h BN.

The lowest Grüneisen parameters along the Γ-K-M directions for the TO and LO modes were found to be 1.72 and 1.59, respectively. Our calculations for these modes are only $\sim 1.1\%$ and $\sim 1.3\%$ larger than the experiment values of Sanjurjo et al.\(^5^7\) who have obtained the Grüneisen parameters by measuring the pressure dependence of Raman lines. The slight deviation from the experimental measured value could be because the measured values are for Zinc-blende-BN and not hexagonal BN.

D. Analytical solutions to the Callaway-Klemens’s Approach

In order to compare the results obtained from the real space super cell approach (ShengBTE), we now study the mode, temperature and length dependence of single and MLBN calculated using the Callaway-Klemens’s approach as described earlier. We first obtain analytical solutions for each acoustic mode of the Phonon BTE by making some reasonable approximations to understand the basic behavior of temperature and length dependence of $\kappa_L$. In order to compare with the experimental results, we resort to exact numerical computation.

We have carried out all the length dependent calculations at a constant temperature for MLBN at RT. The corresponding length dependent curves for MLBN are plotted in Fig. 6 (e). The parameters used in our study are shown in Table II. Equations 11 and 12 are plotted in Fig. 1 and Equation 17 is plotted in Fig. 5 to compare the analytical fit to the actual phonon dispersion and Grüneisen parameters.

The individual contributions of each of the acoustic modes LA, TA, and ZA and the sum of these, i.e. $\kappa_L$, for single and multilayered h-BN are shown in Fig. 6 (a,b,c,d). The variation of $\kappa_L$ values for BLBN and Bulk-hBN are quite similar but are lower for 5LBN. This is in good agreement with experiments.\(^2^0,5^0,5^1\) In all cases it is observed that amongst the acoustic modes the TA contribution is the largest, ZA to be the least whereas LA contribution is somewhere in between. It has been quite controversial as to which acoustic mode contributes the

| System    | $v_{LA}$ (m/s) | $v_{TA}$ (m/s) | $\gamma_{LA}$ | $\gamma_{TA}$ | $\alpha \times 10^{-11}$ (m$^2$/s) | $\beta \times 10^{-20}$ (1/m$^2$) |
|-----------|----------------|----------------|---------------|---------------|-----------------------------------|-------------------------------|
| SLBN      | 17020.1        | 11599.8        | 1.546         | 0.452         | 3.99                              | -6.827                        |
| BLBN      | 16379.4        | 11474.9        | 1.585         | 0.5673        | 3.75                              | -6.086                        |
| 5LBN      | 21095          | 11420.6        | 1.48          | 0.424         | 4.2                               | -6.348                        |
| Bulk-BN   | 16379.4        | 11474.9        | 1.57          | 0.59          | 3.72                              | -7.18                         |

FIG. 6. Acoustic modes and temperature dependence of lattice thermal conductivity for (a) SLBN (b) BLBN (c) 5LBN and (d) Bulk-hBN at a constant length. The theoretical calculations are carried out by using Eq. 15 for the LA and TA modes while Eq. 18 was used for the ZA mode. The parameters used in our calculations are shown in Table II. The colour representation for each mode are shown on the right. The black dots are the experimental measurements.\(^2^0,5^0,5^1\) Length dependence is worked out by varying $L$ in Eq. 16.
most to the total lattice thermal conductivity. For example, while some reports\textsuperscript{21,24,26,53,58} show that the contributions from ZA to be the most dominant, there are many other reports\textsuperscript{19,23,40,52,59–62} that show exactly the opposite. Our analytical results concur with the latter, i.e. the contribution from the ZA mode is the least.

The thermal conductivity for two-dimensional layered materials given by Eq. 8 is derived assuming both phonon energy dispersions and phonon scattering rates are weakly dependent on the direction of the Brillouin zone\textsuperscript{19}. The calculation of $\kappa_L$ should be independent of the direction chosen resulting in an isotropic in-plane scalar $\kappa_L$. Calculation of $\kappa_L$ should therefore be independent of direction chosen. We move along the $\Gamma$ to $K$ direction for systems in which a hexagonal unit cell is used and along $\Gamma$ to $Y$ in the case of an orthorhombic unit cell. SLBN has the highest calculated $\kappa_L$, 5LBN has the least while $\kappa_L$ lies in between BLBN and Bulk-hBN. From Fig. 7 it can be easily seen that for temperatures below 100K, the contribution to the total $\kappa_L$ is mainly due to the flexural ZA modes.

As in the case of graphene, SLBN can have a total of 12 processes involving the flexural phonons. However, Seol et al\textsuperscript{60} obtained a selection rule for the three-phonon scattering. This rule states that only an even number of ZA phonons is allowed to be involved in each process. Shen et al\textsuperscript{61} have listed four flexural allowed processes. Hence, the scattering rate of the Umklapp phonon-phonon process for the acoustic flexural branch is multiplied by a factor of $\frac{4}{13}$ and the relaxation time for the ZA mode becomes 3 times of that of Eq. 9. Therefore besides having a larger velocity and a smaller averaged Gr"uneisen parameter compared to the other systems, the major contribution for an increased $\kappa_L$ is due to the symmetry of the ZA mode.

Phonon dispersions and Gr"uneisen parameters for BLBN and Bulk-hBN are very similar which explains why their calculated $\kappa_L$ have the same magnitude. In the case of 5LBN, there are additional five low frequency modes (also termed as layer-breading modes), which arise due to the interlayer moment. Due to this change in phonon dispersion, more phase-space states become available for phonon scattering and therefore decreases $\kappa_L$\textsuperscript{63}.

\section*{E. Numerical solutions to the Callaway-Klemens’s Approach}

Numerical calculations are carried out using the exact form of the phonon dispersion and Gr"uneisen parameters as displayed in Fig. 1 and Fig. 5 rather than the analytical form of the acoustic modes and averaged Gr"uneisen parameters. We numerically solve Eq. 8 for each of the modes at a constant sample length varying temperature as well as at a constant temperature varying lengths between 0.1 to 10 $\mu$m. These results are compared with experimental data\textsuperscript{20,50,51} and shown in Fig. 7. Numerically calculated values of $\kappa_L$ are in better agreement with the experimental data as compared to the analytical form. We find the contribution from the ZA modes to dominate at lower temperatures but rapidly decreases as the temperature increases making the flexural modes contribute the least at relatively higher temperatures. This is in line with previous theoretical calculations\textsuperscript{60}.

\section*{IV. SUMMARY}

Phonon dispersions using a LDA pseudopotential with vdW interactions, density of states (DOS), the Gr"uneisen parameters and the lattice thermal conductivity have been calculated by the Callaway-Klemens and Real space super cell approach for SLBN, BLBN, 5LBN and Bulk-hBN. Additionally, in the case of Bulk-hBN, we calculate the two-phonon DOS. Irreducible representation using the character table at the $\Gamma$ point in the BZ for each of the systems have been derived in order to compare the symmetry modes with those obtained from Raman and infrared spectroscopy experiments. Results from the investigations by EELS data, Raman, second-order Raman and Infrared spectroscopy are found to be in excellent agreement with the theoretical calculations based on the phonon dispersion, DOS and two-phonon DOS which rely on the harmonic second order inter atomic force constants.

Further, we have calculated the sample length and temperature dependence of lattice thermal conductivity by the real space super cell approach with the help of the second order IFCs calculated by DFPT. Lattice thermal conductivity at the thermodynamic limit for each system has a maxima between the 110-150 K. For sample sizes in
the range 1-5 $\mu$m, $\kappa_L$ does not have a maxima. However with increase in temperature it tends to saturate at a value which is an order smaller than the thermodynamic limit.

Our mode dependent calculations using the real space method suggests that the majority of the contribution to the thermal conductivity are due to the ZA phonons for all of the structures. The substantial decrease in $\kappa_L$ from single to MLBN is because of the additional layer breathing modes but mainly due to the fact that the interlayer interactions breaks the SLBN selection rule resulting in suppressing the ZA phonons contributions to $\kappa_L$ in MLBN. Contribution to $\kappa_L$ from the in-plane modes are not sensitive to the number of layers and have a lower $L$ dependence compared to the out of plane modes. This reduction in $\kappa_L$ from SLBN to MLBN which is mainly due to the ZA phonons indicate that the interlayer interactions are short ranged. The $L$ dependence of the TA and LA contributions to $\kappa_L$ saturate to their thermodynamic limit faster than that of the contribution from the ZA phonons implying that the ZA phonons travel ballistically along the sample while the TA phonons travel diffusively.

Grüneisen ($\gamma$) parameters were obtained from first principle calculation by applying a positive and negative biaxial strain. For the in-plane acoustic modes, we find that $\gamma$ does not vary much from its mean value but the out-of-plane modes have a strong q-dependence. Our calculated $\gamma$ values for Bulk-hBN at the $\Gamma$ point is $\sim 1\%$ larger than those obtained from experiments which measures the pressure dependence of Raman lines. $\gamma$ parameters for 5LBN suggest that due to the layer breathing modes, atoms along the perpendicular direction lose their coherence between each layer and decrease the phonon frequencies when under a biaxial strain.

In comparison to the real space super cell approach, lattice thermal conductivity has been calculated, both analytically and numerically, using Callaway-Klemens formalism. To obtain analytical solution of the phonon, we make a linear fit to the LA and TA modes, a quadratic fit to the ZA mode, and use an averaged value for its Grüneisen parameters for the $\gamma$ parameters corresponding to the in-plane acoustic modes and an inverse square wave-vector dependence $\gamma$ for the out-of-plane modes. Theoretical results for sample length and temperature dependence of $\kappa_L$ are in good agreement with experimental observation. The phonon BTE is then solved analytically and numerically for SLBN, BLBN, 5LBN and Bulk-h BN to calculate $\kappa_L$ for a constant length over a wide range of temperatures and $\chi$-versa again in good agreement with available experimental results.

Both the theoretical approaches, i.e. real space super cell and Callaway-Klemens, show the same magnitude for $\kappa_L$ but the temperature dependence by the two methods are different. The lattice thermal conductivity for these materials are practically length independent for sample lengths greater than 100 $\mu$m which tends to their thermodynamic limit. Calculated values for $\kappa_L$ for BLBN and 5LBN agree very well with experiments when calculated by the real space approach rather than by the Callaway-Klemens method. This may be because the experimental behavior of $\kappa_L$ for both BLBN and 5LBN tend to saturate at higher temperatures instead of having a maxima. However, the Callaway-Klemens method agrees better with available experimental data for Bulk-h BN. Further experiments could resolve this discrepancy.

Mode dependent numerical calculations using the Callaway-Klemens formalism suggest that ZA modes dominate only at very low temperatures and have the least contribution as the temperature is increased. This is in stark conflict with our calculations based on real space super cell approach. Since the velocities and Grüneisen parameters are extremely similar for single and bi layer boron nitride, one would expect $\kappa_L$ for both the systems to be similar. However, in the case of graphene, we have a significant reduction in $\kappa_L$ which is seen both experimentally$^{10}$ and theoretically$^{9,53}$. The larger $\kappa_L$ in SLBN in comparison to BLBN using the Callaway-Klemens method was due to the symmetry put by hand and not a consequence of the theory. This implies that the closed form of the relaxation time used in Callaway-Klemens method is a poor approximation having little predictive value and one must solve the BTE beyond the RTA. Our calculations suggests that for an enhanced figure of merit, $ZT$, in such materials, the sample length must be in the $\mu$m range or smaller and should be stacked on top of each other.

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Appendix: Derivation of Irreducible representations

We define the reducible representation ($\Gamma_{\text{red}}$) by placing three vectors on each atom in the unit cell which will obey the following rules when operated by a symmetry transformation.

- If a vector is not moved (reversed) by an operation, it contributes 1 (-1) to $\chi$.
- If a vector is moved to a new location by an operation, it contributes 0 to $\chi$.
where $\chi$ is the character in the reducible representation. Our reducible representations ($\Gamma_{\text{red}}$) are shown in the column before every new point group representation in table III. Using the reduction formula, $a_i = \frac{1}{g} \sum \chi_i \chi_{IR}$, where $a_i$ is the number of times an irreducible representation contributes to the reducible representation, $g$ is the total number of symmetry operations for a particular point group and $\chi_{IR}$ is the corresponding character in the reducible irreducible representation, we derive the irreducible representations.
TABLE III. The point group representation for SLBN, BLBN, 5LBN and Bulk-hBN at the Γ point in the BZ. The irreducible representation is obtained from the reducible representation $\Gamma^N_{\text{red}}$ of the system X using the reduction formula.

| $D_{6h}$ | E | 2C$_3$ | 2C$_2$ | 3C$_2$ | 3C'$_2$ | i | 2S$_6$ | 2S$_3$ | $\sigma_h$ | $\sigma_v$ | $\sigma_d$ | Basis |
|---------|---|-------|-------|-------|-------|---|-------|-------|--------|--------|--------|-------|
| $A_u$   | 1 | 1     | 1     | -1    | -1    | 1  |       |       | -1     | -1     | 1      | $z$    |
| $B_{1g}$| 1  | -1    | 1     | -1    | 1     | -1 |       |       | -1     | -1     | 1      | $yz (3x^2 - y^2)$ |
| $B_{2g}$| 1  | -1    | 1     | -1    | 1     | -1 |       |       | -1     | -1     | 1      | $xz (x^2 - 3y^2)$ |
| $E_{2g}$| 2  | -1    | -1    | 2     | 0     | 0  |       |       | -1     | -1     | 2      | 0      | $\{x^2 - y^2, xy\}$ |
| $E_{1u}$| 2  | 1     | -1    | -2    | 0     | 0  |       |       | 1      | -1     | 2      | 0      | $\{x, y\}$ |

$\Gamma^N_{\text{red}}^{\text{SLBN}}$

| $D_{3d}$ | E | 2C$_3$ | 3C'$_2$ | i | 2S$_6$ | 3$\sigma_d$ |
|---------|---|-------|--------|---|-------|-----------|
| $A_u$   | 1 | 1     | -1    | 1 |       | $z$       |
| $A_{1g}$| 1 | 1     | 1     | 1 | 1     | $z^2$     |
| $E_{2u}$| 2 | -1    | 0     | 2 | -1    | $\{xz, yz\}$ |
| $E_{1u}$| 2 | -1    | 0     | -2| 1     | $\{x, y\}$ |

$\Gamma^N_{\text{red}}^{\text{BLBN}}$

| $D_{3d}$ | E | 2C$_3$ | 3C'$_2$ | i | 2S$_6$ | 3$\sigma_d$ |
|---------|---|-------|--------|---|-------|-----------|
| $A'_1$  | 1 | 1     | 1     | 1 | 1     | $z^2$     |
| $A''_1$ | 1 | 1     | -1    | 1 | 1     | $z$       |
| $E'_{2u}$| 2 | -1    | 0     | 2 | -1    | $\{x, y\}$ |
| $E''_{2u}$| 2 | -1   | 0     | -2| 1     | $\{xz, yz\}$ |

$\Gamma^N_{\text{red}}^{\text{5LBN}}$

| $D_{3d}$ | E | 2C$_3$ | 3C'$_2$ | i | 2S$_6$ | 3$\sigma_d$ |
|---------|---|-------|--------|---|-------|-----------|
| $A_1$   | 1 | 1     | 1     | 1 | 1     | $z^2$     |
| $A_2$   | 1 | 1     | -1    | 1 | 1     | $z$       |
| $E_1$   | 2 | -1    | 0     | 2 | -1    | $\{x, y\}$ |
| $E''_{2u}$| 2 | -1   | 0     | -2| 1     | $\{xz, yz\}$ |

$\Gamma^N_{\text{red}}^{\text{Bulk-hBN}}$

| $D_{6h}$ | E | 2C$_3$ | 2C$_2$ | 3C'$_2$ | i | 2S$_6$ | 2S$_3$ | $\sigma_h$ | $\sigma_v$ |
|---------|---|-------|-------|-------|---|-------|-------|--------|--------|
| $A_u$   | 1 | 1     | 1     | -1    | -1 | 1     | -1    | -1     | -1     |
| $B_{1g}$| 1  | -1    | 1     | -1    | 1   | -1    | 1     | -1     | 1      |
| $B_{2g}$| 1  | -1    | 1     | -1    | 1   | -1    | 1     | -1     | 1      |
| $E_{2g}$| 2  | -1    | -1    | 2     | 0   | 0     | 2     | -1     | -1     |
| $E_{1u}$| 2  | 1     | -1    | -2    | 0   | 0     | 2     | -1     | -1     |

Rev. Lett. 98, 095503 (2007).

44 P. H. Tan, W. P. Han, W. J. Zhao, Z. H. Wu, K. Chang, H. Wang, Y. F. Wang, N. Bonini, N. Marzari, N. Pugno, G. Savini, A. Lombardo, and A. C. Ferrari, Nature materials 11, 294 (2012).

45 R. J. Nemanich, S. A. Solin, and R. M. Marti, Physical Review B 23, 6348 (1981).

46 R. Geick, C. H. Perry, and G. Rupprecht, Phys. Rev. 146, 543 (1966).

47 S. Reich, A. C. Ferrari, R. Arenal, A. Loiseau, I. Bello, and J. Robertson, Phys. Rev. B 71, 205201 (2005).

48 R. Cuscó, B. Gil, G. Cassabois, and L. Artús, Phys. Rev. B 94, 155435 (2016).

49 K. Esfarjani, G. Chen, and H. T. Stokes, Phys. Rev. B 84, 085204 (2011).

50 C. Wang, J. Guo, L. Dong, A. Aiyiti, X. Xu, and B. Li, Sci. Rep. 6, 25334 (2016).

51 E. K. Sichel, R. E. Miller, M. S. Abrahams, and C. J. Buiocchi, Phys. Rev. B 13, 4607 (1976).

52 B. D. Kong, S. Paul, M. B. Nardelli, and K. W. Kim, Phys. Rev. B 80, 033406 (2009).

53 L. Lindsay, D. A. Broido, and N. Mingo, Phys. Rev. B 83, 235428 (2011).

54 L. Lindsay and D. A. Broido, Phys. Rev. B 85, 035436 (2012).

55 L. Lindsay, W. Li, J. Carrete, N. Mingo, D. A. Broido, and T. L. Reinecke, Phys. Rev. B 89, 155426 (2014).

56 N. Mounet and N. Marzari, Physical Review B 71, 205214 (2005).

57 J. A. Sanjurjo, E. Lopez-Cruz, P. Vogl, and M. Cardona, Phys. Rev. B 28, 4579 (1983).

58 Y. Kuang, L. Lindsay, S. Shi, X. Wang, and B. Huang, International Journal of Heat and Mass Transfer 101, 772 (2016).

59 A. Alofi and G. P. Srivastava, Phys. Rev. B 87, 115421 (2013).

60 Z. Aksamija and I. Knezevic, Applied Physics Letters 98, 141919 (2011).

61 D. L. Nika and A. A. Balandin, J. Phys.: Condens. Matter 24, 233203 (2012).

62 Z. Wei, J. Yang, K. Bi, and Y. Chen, Journal of Applied Physics 116, 153503 (2014).

63 A. A. Balandin, Nature Materials 10, 569 (2011).